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Hinne Hettema

The Union of Chemistry and Physics

Linkages, Reduction, Theory Nets and Ontology

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Preface

This book deals with the interrelationship between theories of chemistry and theories of physics and the role played by quantum chemistry as a theory ‘in between’. Chemistry and physics exhibit a form of explanatory *unity*, where the theories in the in-between subfields – chemical physics and physical chemistry, as well as quantum chemistry – form the nexus of this unification. The aim of this book is to develop that nexus alongside a suitable formal apparatus while being true to the science and then draw some philosophical conclusions.

Traditionally, the relationship between chemistry and physics was thought to be one of *reduction*, where the reduction of chemistry to physics was seen as a simple textbook case: unproblematic and (largely) uninteresting. The existence of a smooth reduction relation was taken as a fact requiring little further comment or requiring far less comment than the problems surrounding the potential reduction of biology or the potential reduction of mental events to physical events. Even now, outside the somewhat narrow confines of philosophy of chemistry, the reduction of chemistry to physics is still usually seen as a paradigmatic but ultimately also uninteresting example of scientific reduction.

One of the early achievements of philosophy of chemistry was its insight that this reduction relationship was not so simple after all. Early philosophers of chemistry argued that the casebook on the reduction of chemistry to physics should be reopened and re-examined as a philosophical ‘cold case’ that is not only interesting in its own right but also (still) potentially paradigmatic for the reduction of other sciences.

In particular, significant problems exist around a number of core chemical ideas such as the notion of the molecular structure, the chemical bond and the nature of chemical reactions, all of which are problematic when viewed from a vantage point of austere or ‘pure’ quantum mechanics.

The early philosophers of chemistry pointed out that these problems could not just be overlooked when claiming a reduction and, moreover, that the obvious *success* of quantum theories in the explanation of chemical phenomena could not be taken as outright support for a reductive relationship. A somewhat unfortunate corollary of the early discussions in the philosophy of chemistry was however that the notion of reduction itself was seen as hopelessly flawed. This is a corollary with which I largely disagree: I will argue that this corollary is based on a straw-man version of reduction that is due for replacement. In particular, the starting point of this book is that unity of chemistry and physics is based on intertheoretical *explanation* and that it makes sense to look at *reduction* as a formal paraphrase of this explanatory unity.

The claim of reduction now stands with many questions attached. Yet the reduction of chemistry to physics is still paradigmatic for, or at least fundamental to, the notion of reduction per se: as reduction relations go, the domains of chemistry and physics are close and significantly overlapping, and there is a lot of theoretical and ontological 'borrowing' and a significant amount of continuity between the two sciences.

This book explores that interesting area in significant detail, mainly with the machinery provided by the structuralist approach to theories. This is not to claim that the structuralist approach is the only, or even the superior, approach to bring out the relevant issues. Many different approaches are possible to formally characterise the relationship between chemistry and physics, and the application of different logical schemes to characterise and investigate this relation is, I argue, an important element of a future research programme in the philosophy of chemistry.

The book will proceed as follows. In Chap. 1, I outline an approach to Nagelian reduction which is up to the task of describing the reduction relation between chemistry and physics in the necessary detail. Key to my approach to Nagel is a conception of the reduction relationship as one of *representation* and *similarity*. As would be expected, this nicely sets up the further discussion in Chap. 6, where we approach these concepts in a structuralist manner.

Part I deals with a number of practical examples from chemistry. Programmatically, these chapters lay out the land and serve to specify what exactly chemistry *is*. The examples are chosen because they provide sufficient grounds to conclude that at least a *simple* reduction relationship between chemistry and physics will fail. Chapter 2 discusses theories of the chemical bond, and Chap. 3 discusses the topic of molecular structure and quantum mechanics, while Chap. 4 discusses Eyring's theory of 'absolute' reaction rates. Chapter 5 deals with a Lakatosian reconstruction of quantum chemistry.

Part II contains formal reconstructions using the *structuralist* framework. The structuralist framework is not the only framework with which to study reduction, but it is in the present context well suited to the task. A defining feature of the structuralist framework is that it allows for a weak version of reduction based on (structural) similarity. In this part, I first discuss the notion of reduction in a structuralist framework in Chap. 6 and then proceed to a discussion of quantum mechanics and theories of chemistry in Chaps. 7 and 8.

Part III discusses the consequences for the philosophy of science in general and the philosophy of chemistry in particular. Its main focus is the ontology of atoms and elements and the nature of orbitals. I argue that 'chemical objects' have a certain explanatory depth associated with them, which makes them robust examples of how scientists might perceive objects more in general. The corollary of that fact is that ‘simple’ theories of ontology are inadequate to deal with the complexities of modern science. The reader may wish to consult only some of the parts of this book. To that end, every part is prefaced with a preface and a brief summary.

Auckland, New Zealand Hinne Hettema

Acknowledgements

This book grew out of my thesis, 'Reducing Chemistry to Physics,' and is still in large measure based on that earlier work. It is in important parts significantly rewritten. At various places, in an attempt to shorten the lengthy manuscript as well as streamline the work, chapters have been shortened, arguments tightened and unnecessary sidelines removed. Some chapters (Chaps. 4, 9 and 10) were replaced by later work to strengthen the overall argument and bolster the narrative arc of the whole.

I would like to thank my supervisors Theo Kuipers and Ria Broer and the manuscript committee members Stephan Hartmann, Igor Douven and Evert Jan Baerends for their constructive engagement with the original on which this manuscript is based.

I have to admit that I accepted this chance to write 'Release 2.0' of my thesis with some trepidation. 2.0 was certainly unplanned until the editors of EPSA came knocking at my door. My 'day job' as a security professional, largely invisible to my professional philosophy colleagues up till very recently, has become more busy, more visible and more demanding. There were, and still are, no plans to become a professional philosopher. Where I thought I could just abandon philosophy, she certainly didn't abandon me but reached out and grabbed me in the neck.

So here we are. I need to thank the members of the University of Auckland IT security team for the general flow of security banter while I spent an official holiday at the office working on this manuscript. Occasional talk about port 23, DDoS botnets, SSH keys and other security stuff provided a welcome break from the manuscript at many times, breaks from which I've generally returned refreshed. I again have to thank my family for letting me spend a large amount of time uninterrupted while working on the manuscript.

Since this is version 2.0 of an earlier work, a lot of the material was published previously. The bulk of the material is from my original PhD thesis at the University of Groningen, Hettema (2012b). No chapter has remained untouched and unrevised. Parts of Chap. 4 have been published as Hettema (2012c). That material takes the place of the original Chapter 4, Hettema (2009).

The original Chaps. 9 and 10 have been significantly rewritten in an attempt to clarify my thoughts and to take into account later work in this area. The formalisation of the periodic table was published previously as Hettema and Kuipers (1988) and was slightly revised in Hettema and Kuipers (2000). In many ways, it was this paper, originally written as a student term paper, that started it all.

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Chapter 1
Reduction: Its Prospects and Limits

Abstract In this chapter, I discuss the concept of Nagelian theory reduction. In particular, I argue that the concept of Nagelian theory reduction as consisting of identities and (strict) derivation is naive, and not in keeping with both Nagel's intention and writing on the topic. Instead, this concept of reduction seems to be given by an overly strict 'metaphysical' view on reduction in which reduction is only meaningful if and when the reduced theory is fully subsumed under the reducing theory.

Instead, in this chapter I aim to rehabilitate Nagel by arguing that reduction is heterogeneous affair based on a formal representation of inter-theoretical explanation, with not so much metaphysical, but rather methodological consequences for the reduced and reducing theory. It is this concept of reduction that is more amenable to discussing the relationship between chemistry and physics.

1.1 Introduction

The idea that chemistry stands in a reductive relationship to physics still is a somewhat unfashionable doctrine in the philosophy of chemistry. It is one that I will explore and broadly defend in what follows, though some questions and problems are obvious almost immediately.

A first question is whether 'chemistry' is actually amenable to reduction: chemistry is a *field*, whereas reduction tends to be a relation between individual theories, or between laws and theories. Then, for a chemical theory to be reduced to some physical theory, the chemical theory has to exist, be well formulated, perhaps even axiomatisable and so on. This is not necessarily the case in chemistry: chemistry as a field is best characterised as a patchwork of theories and concepts. Are typically chemical concepts such as valence, for instance, well enough formulated to allow the sort of formal treatment that a notion of reduction would entail? Do such things as 'chemical laws' even exist?

A second complication revolves around the notion of reduction itself. For reduction comes in varieties. It is sometimes unclear what version of the reductionist thesis is thought to apply or not to apply to a particular case. Reduction is too often conceived of as a straightforward derivation or deduction of the laws and concepts of the theory to be reduced to a reducing theory, notwithstanding Nagel's

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(1961) insistence that heterogeneous reduction simply does not work that way and not withstanding the ample literature that has explored non-derivational, functional, 'new wave' or 'structural' notions of reduction as alternatives to an overly simplistic notion of reductionism.

A third complication is that the fields of chemistry and physics are tightly bound. It is almost impossible to imagine a 'modern' chemistry with all physics removed. To do so, would rob chemistry of much of its tooling, such as spectrometers, atomic force microscopes, and theoretical modelling tools. In addition, it would rob chemistry of much of the framework used to make sense of the results of that tooling. But it is also hard, from this extensive use of physics, to conclude that somehow physics is more 'foundational'.

One of the main aims of this chapter is to argue that the concept of reduction is a special case of a much wider notion of 'unity of science'. The latter concept was a component of much of nineteenth century thought, and, as suggested by Bechtel and Hamilton (2007), may even go back as far as Aristotle. My approach considers the notion of the unity of science and the related notion of reduction primarily as *programmatic* statements, of which the concept of *reduction* forms a part.

There are few philosophers of chemistry (and even fewer chemists) who doubt that the theories of physics – quantum mechanics, statistical mechanics and thermodynamics – feature prominently as constructive tools in the formation of chemical theories of matter. The main problem seems to be that they do not feature very *consistently*: chemistry is made up of a patchwork of theories, often highly idealised, which do not align with a more austere notion of a 'basic' theory of quantum physics.

Hence, there is a tendency in contemporary philosophy of chemistry to assert that chemistry cannot be actually reduced: a patchwork of highly idealised theories does not lend itself well to formal treatments such as axiomatisation, which is one of the preconditions for reduction. To complicate matters further, there are doubts that the formation of laws and theories is even one of the goals of chemistry.[1]

This situation suggests a stark contrast with the optimism (or, dependent on ones point of view, hubris) presumed to be present in the famous 'Dirac quote'. Shortly after the new quantum mechanics radically altered the outlook of mechanistic explanations in chemistry Dirac wrote:

> The fundamental laws necessary for the mathematical treatment of large parts of physics and the whole of chemistry are thus fully known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved. (Dirac 1929, p. 714)

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[1] See for instance the article by Hoffmann (2007) and the collection in Kovac and Weisberg (2012) as key examples. Hoffman argues that the aim of chemists, in many if not all cases, is not theory formation, but a form of molecular engineering. In engineering we use the tools that work. Theories are among those tools, but they are not of primary interest. What counts is primarily the outcome: the new molecule or structure just created. A second example is provided by the wholesale rejection of reduction by van Brakel (2000), who, following Sellars (1963) argues that the language of chemistry is primarily a 'manifest' image which is to be contrasted to a 'scientific' image as presented by quantum chemistry.

This quote is generally taken to express the firm expectation that a 'full reduction' of chemistry[2] can one day be achieved. A closer reading of the context of the quote provides a somewhat different, and far less confident, picture. For instance,[3] consider the less often cited remainder of Dirac's comments:

> It therefore becomes desirable that approximate methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation. (Dirac 1929, p. 714)

Note the call for significant modifications and approximations in quantum theory in order to apply to complex systems. As Sutcliffe and Woolley (2005) point out, the context of this quote is in addition one in which Dirac identifies the fitting of quantum theory and relativity as the last remaining 'imperfection' of quantum theory. In this context, Dirac's remarks on chemistry are a side remark that functions more as a pointer to guide future *internal* developments in quantum theory, quite possibly *away* from chemical problems, rather than to provide detailed commentary on a possibly bleak future for chemistry.

As philosophers of science we may infer that Dirac calls for a concept of *idealisation* of quantum theories that will allow us to deal with the *qualitative* aspects of chemical theories (as in 'without too much computation') as well as a characterisation of chemistry as a *guide* programme in the sense of Zandvoort (1986).

Yet it is not difficult to multiply quotes from the early literature in quantum chemistry that seemingly echo Dirac's sentiments with regard to physics and quantum mechanics, though when these statements are made by chemists they are significantly more mellow in character. Eyring et al. (1944) write, for instance, that:

> In so far as quantum mechanics is correct, chemical questions are problems in applied mathematics. In spite of this, chemistry, because of its complexity, will not cease to be in large measure an experimental science, even as for the last three hundred years the laws governing the motions of the celestial bodies have been understood without eliminating the need for direct observation. No chemist, however, can afford to be uninformed of a theory which systematises all of chemistry even though mathematical complexity often puts exact numerical results beyond his immediate reach. (Eyring et al. 1944, p. iii)

It is in this context somewhat unfortunate that the explanatory success of quantum theory in the chemical arena has had a significant impact on the way many philosophers have conceived of the *modus operandi* of the unity of science.

To put it bluntly: the perception that the reduction of chemistry to physics was unproblematic further developed into a strongly *normative* stance on how the reduction of chemistry to physics *ought* to work, based on strict derivation and ontological identities. This normative position, perhaps best exemplified in Causey (1977), largely ignored the more complex backdrop of a longer running debate about the unity of science that has its roots in the nineteenth century, and which focused

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[2] Leaving it unresolved for the moment whether that would consist of an entire explanation of every aspect of chemistry by physics or its outright elimination.

[3] See also Hendry (2007).

on a contrast between 'unity of method',[4] versus a strongly realist interpretation of scientific theory, associated with Boltzmann and Planck. The early explanations of chemical concepts by quantum theory could be, and in some measure were, easily interpreted as providing strong support for the latter. In this heady context,[5] the problems posed by the inter-theory relationship between chemistry and physics were largely ignored.

It is hardly surprising that this austere *normative* notion of reduction does not apply in practice. The question then remains what sort of notion of reduction *would* work in practice, and what philosophical consequences might be drawn from such a revised notion. In this introductory chapter I argue that there are sound philosophical reasons why we have to drop the normative picture of reduction and adopt a notion that is more amenable to how real theories of chemistry and physics work.

Section 1.2 discusses the Nagelian notion of reduction in detail, and also focuses on many of its amendments that were proposed in the late 1960s to overcome its perceived inadequacies. Given the context of the times[6] it is perhaps little surprise that these inadequacies were mainly characterised as the Nagelian notion of reduction failing to live up to a strict derivative *cum* ontological realist interpretation of the interrelationships between scientific theories. Now, in important part due to the work of Klein (2009), Fazekas (2009), Dizadji-Bahmani et al. (2010), and van Riel (2011) this picture is due for reassessment.

There is a brief discussion of what is sometimes referred to as 'non-reductive alternatives' to the unity of science in Sect. 1.3. I focus there especially on the notion of an 'interfield theory' as introduced in Darden and Maull (1977), which will play an important role in the remainder of the book. The basic notion of interfield theories is introduced here.

In Sect. 1.4 I discuss how the liberal reading of Nagel proposed in this chapter, together with the exploration of 'non-reductive' approaches can be reconciled into an overall notion of unity of science.

Before proceeding, a small amount of disambiguation is in order. Philosophers view *reduction* as a case of a special theory 'reducing to' a more general theory, whereas in the sciences it is common to take the opposite perspective, where a more general theory 'reduces to' a less general theory under certain approximations. In the remainder, I will follow the philosophical notion of reduction.

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[4] This was primarily conceived as Machian 'economy of thought', which advocated a largely instrumentalist outlook on scientific theories.

[5] For instance, the Mach-Planck controversy, or polemics, which is covered in some detail in (Blackmore 1992, p. 127–150), shows how heated this debate got at times.

[6] Which has been explored at length in Reisch (2005) and characterised as an 'icy slope of logic'.

1.2 Nagel's Concept of Reduction

In this section I give an overview of the notion of reduction, focusing especially on its formulation in Nagel (1961), and its subsequent interpretations.[7] My main objective in this section is to argue that a close rereading of Nagel allows significantly more latitude than its interpreters, writing in the late 1960s, left it with. In the remainder it will become clear that this latitude is an essential ingredient of a revised theory of reduction.

1.2.1 Reduction of Laws and Theories

As is well known, one of the most comprehensive classical accounts of theory reduction is given in Nagel (1961). Nagel's reduction scheme is dependent on two formal conditions and a number of informal conditions. In what follows, I will propose a 'naturalised' interpretation of the Nagelian conditions, which is based on a close reading of the original text in Nagel (1961). This naturalised reading is complementary to the interpretations given in Klein (2009) and van Riel (2011).

Nagel's formal requirements are generally taken to be the requirements of connectibility and derivability, stating that a linguistic connection between the languages of the reduced and reducing theory has to exist, and that the reduced theory has to be derivable from the reducing theory *cum* 'reduction postulates'. The reduction postulates express the linguistic connection. Nagel thus conceives of a reduction essentially as a *deduction* of one theory from another with the help of a set of reduction postulates (or, as Nagel calls them 'coordinating definitions').[8] The reduction postulates do a lot of work in this scheme, but their role is often misunderstood. Nagel intends, as we shall see, the reduction postulates to be merely *facilitating* requirements (as expressed in the name 'coordinating definitions') with limited or no ontological import.

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[7] Well-known responses to the work on reduction in Nagel (1961) are the notions of reduction that are discussed by Sklar (1967), Schaffner (1967, 1969) and Wimsatt (1974). 'New wave' reductionism is discussed in the series of papers by Hooker (1981a,b,c) and references therein. An overview and critical evaluation of these reductive alternatives is given by Dizadji-Bahmani et al. (2010). The latter argue that the 'new wave' reductionism can be reconstructed as a special variety of Nagelian reductionism, and thus is less 'new wave' than its name would lead us to believe. It is also worthwhile to mention the structural notions of reduction that have been explored by Suppes (1957) and Sneed (1971).

[8] There is a significant amount of confusing and inconsistent terminology in the literature regarding reduction postulates. They are sometimes referred to as 'coordinating definitions' (Nagel), 'bridge laws', 'reduction postulates' or 'bridge principles' (Kim). In the remainder of this work we will refer to them as 'reduction postulates' except in places where this would be out of context. This is partly to be able to reserve the term 'bridge laws' for the statements that can link theories to observation in the received view.

In addition to the formal conditions Nagel also specifies a number of non-formal conditions. Nagel's non-formal conditions are much less well known. They state that (a) the reducing theory has to be well corroborated, (b) the reducing theory has to be 'mature' enough to be an effective reducing agent, and (c) ontological reduction (reduction of properties) is posterior to epistemic reduction.

It is worthwhile to initially consider Nagel's theory in a context unburdened by the requirements of an austere conception of the 'unity of science' (at least for a while) and consider it, more liberally, as a logical reconstruction of what happens when one theory explains another (law or) theory. The development of a 'close reading' and reassessment of Nagel's reduction concept will be the main aim of the next section.

1.2.1.1 The Formal Requirements

As stated before, Nagel's formal conditions for reduction are usually taken to be the condition of connectibility and the condition of derivability. A closer reading of Nagel's construction of the reduction argument, however, reveals a more complex structure to the argument.

The condition of derivability is formulated in terms of *three* formal requirements for reduction: (1) the theories involved can be explicitly stated, (2) the meanings assigned to the terms used in the formulation of the theory are fixed by local use in the theory, and (3) the statements (or theory) of the reduced theory are derivable from those of the reducing theory provided the reduced theory can be suitably modified so as to introduce and explicate the native concepts of the reduced theory. Note that the condition of connectibility more or less slips in through the backdoor at this point: for derivability to hold, additional premises are required that facilitate some connection of the terminology of the theory to be reduced to that of the reducing theory.

Specifically, Nagel formulates the three formal requirements as follows:

(1) The first formal condition is that the relevant aspects of the two sciences involved can be explicitly stated:

> It is an obvious requirement that the axioms, special hypotheses, and experimental laws of the sciences involved in a reduction must be available as explicitly formulated statements, whose various constituent terms have meanings unambiguously fixed by codified rules of usage or by established procedures appropriate to each discipline. (Nagel 1961, p. 345)

It is notable that while the 'unit' of reduction is usually taken to be a theory, Nagel does mention the axioms, special hypotheses, and experimental laws of the 'sciences' here as the proper target of what needs to be explicitly stated. This, as we shall see, potentially opens up the scope of the reduction relation to other such 'units', for which one candidate may be the notion of a 'field' as introduced in Darden and Maull (1977), or the notion of a *domain* as explored by Shapere (1977).

Another important step introduced in this requirement is that it focuses on a *formalised* reconstruction of the relevant aspects of the science. This formalisation step establishes the reduction relation as a the result of a formal regimentation or *paraphrase* of what normal practising scientists usually claim to be an explanation of one science by another. Hence, potential candidates for the formal notion of *reduction* are formed by cases in practical science where scientists claim that one particular theory *explains* another, or explains a special law or some such. Nagel does *not* claim that it is possible to immediately 'read' a reduction relation into a case of explanation without some significant formal work, in the form of formal paraphrase and formal regimentation.

(2) The second formal condition is one of sufficiently clear and fixed meanings of the terms in the theory. The condition is:

> Every statement of a science *S* can be analyzed as a linguistic structure, compounded out of more elementary expressions in accordance with tacit or explicit rules of construction. It will be assumed that, though these elementary expressions may be vague in varying degrees, they can be employed unambiguously in *S* with meanings fixed either by habitual usage or explicitly formulated rules. (Nagel 1961, p. 349)

(3) The third formal condition is the existence of both connectibility and derivability. Connectibility is here introduced more or less ad hoc. As Nagel states (p. 351–352), the reduced and reducing science usually have a number of terms in common. While the meaning of these terms is fixed by procedures *internal* to both sciences, the meanings of terms of a certain 'common vocabulary' will coincide sufficiently to pose no further problems for derivability.

On the other hand, there is also a class of terms which occur in the reduced science but not in the reducing science. Thus there needs to be a mechanism that allows the concepts native to the reduced science to be explicated in terms of the reducing science. For this mechanism, Nagel introduces, in addition to the formal requirements, the notion of *coordinating definitions* (which we will refer to as 'reduction postulates' in what follows) as an additional assumption. The reduction postulates introduce a 'modification' of the reducing theory to facilitate derivation in cases where the premise of the argument (i.e. the reducing theory) does not already contain the necessary concepts of the reduced science.

The reduction postulates stipulate:

> [...] suitable relations between whatever is signified by '*A*' and traits represented by the theoretical terms already present in the primary science. (Nagel 1961, p. 353–354)

Nagel's scheme thus hinges critically on the notion of reduction postulates. While the *role* of the reduction postulates is simple enough, the exact formulation of the reduction postulates themselves is far from simple. It is in this context important to note that the consequence relation is stated in terms of the 'reducing theory inclusive of' the reduction postulates, a text that may be open to different interpretations.

Nagel (1961) (on p. 354) explicitly discusses three possible kinds of linkages which can be expressed by reduction postulates. These can be paraphrased as follows:

(L1) The links are logical connections, such that the meaning of '*A*' as 'fixed by the rules or habits of usage' is explicable in terms of the established meanings of the theoretical primitives in the primary discipline.

(L2) The links are conventions or coordinating definitions, created by 'deliberate fiat', which assigns a meaning to the term '*A*' in terms of the primary science, subject to a criterion of consistency with other assignments.

(L3) The links are factual or material, or physical hypotheses, and assert that existence of a state '*B*' in the primary science is a sufficient (or necessary and sufficient) condition for the state of affairs designated by '*A*'. In this scenario, the meanings of '*A*' and '*B*' are not related analytically.

As Klein (2009) has argued, the reduction postulates refer to the *representational power* of the reducing theory; its ability to *introduce* the terms present in the reduced science.[9] In a similar vein, van Riel (2011) has argued that Nagel's conceptual latitude regarding the reduction postulates is capable of mitigating a significant amount of the criticism of his theory.

With all these prerequisites out of the way, the Nagelian notion of reduction as derivability then states, simply:

> [. . .] a reduction is effected when the experimental laws of the secondary science (and if it has an adequate theory, its theory as well) are shown to be the logical consequences of the theoretical assumptions (inclusive of the coordinating definitions) of the primary science. (Nagel 1961, p. 352)

Since the reduction postulates and derivability are the key *logical* components that allow the language of the theory to be reduced to be connected to the language of the reducing theory, Nagel's two conditions are generally formulated as the following two formal conditions:

1. A condition of 'connectibility' which stipulates the reduction postulates; and provides a 'modification' of the reducing theory to allow it to 'connect' to the reduced theory;
2. A condition of 'derivability' which states that the laws or theories of the reduced science are logical consequences of the theoretical premises and reduction postulates associated with the reducing science.

1.2.1.2 The Informal Requirements

In addition to the formal requirements, Nagel specifies a number of informal requirements. These introduce many qualifications and conditions that will prove to be relevant in what follows. Moreover, the informal requirements contain many qualifications to the reduction scheme that are commonly overlooked.

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[9] Note that Nagel's second formal requirement states that the terms are fixed by meanings and use *local* to the relevant theory and hence this sort of representational power is not a trivial requirement.

The main reason for introducing the informal requirements is that the formal requirements are, by themselves, incapable of distinguishing between worthwhile and worthless theory reductions. As Nagel notes, the formal conditions could in many cases be satisfied rather trivially with some ad hoc assumptions. The informal conditions are there to block this sort of trivial reductions.

(a) The first informal requirement is that of (external) corroboration of the reducing theory. As Nagel notes for the example of the reduction of thermodynamics (in fact Nagel here means the ideal gas law)[10] to the kinetic theory of gases, the reduction of the ideal gas law to the kinetic theory of gases is not trivial precisely because the kinetic theory of gases is supported by a number of other considerations, the majority of which fall *outside* the domain of thermodynamics. As examples of these Nagel mentions the support given to the atomic theory of matter by its use in chemistry, and the widespread support of the general principles of mechanics.

    This sort of external corroboration also leads to

    > [...] the intimate and frequently surprising relations of dependence that can thereby be shown to obtain between various experimental laws. An obvious type of such dependence is illustrated when laws, hitherto assessed on individual grounds, are deducible from an integrated theory as a consequence of the reduction. (Nagel 1961, p. 360)

    Overall, this informal condition of external corroboration helps in the unification of the sciences by expanding their *domains* of applicability, and strengthens the case for the corroboration of the reducing theory.

(b) The second informal requirement is that of maturity of the reducing theory. As Nagel notes, the ideal gas law could be reduced to the kinetic theory of gases only after the formulation of Boltzmann's statistical interpretation for the second law of thermodynamics, and similarly the reduction needs a sufficiently mature mechanics to be counted as a success.

    This, as Nagel notes, is sometimes a barrier to achieving a reduction that should in principle be possible; and claims of irreducibility of one science to another tend to overlook that a reducing science may in fact at some future point be capable of achieving the reduction whereas in its present state it is not.

(c) Perhaps the most important requirement for the further discussion of the reduction of chemistry to physics, and one often overlooked in this context,

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[10] This point can cause some confusion in what follows. Nagel regularly uses the term 'thermodynamics' to discuss the case of reduction, but he does so in a rather restricted sense: in the example on which the entire discussion is based, Nagel restricts the *details* of the case to 'a small part of the complicated analysis, the derivation of the Boyle-Charles law for ideal gases from the assumptions of the kinetic theory of matter' (Nagel 1961, p. 343), but he extends these details to the entire domain of thermodynamics and in the remainder uses the term 'thermodynamics' interchangeably with the ideal gas law. I believe this is not only likely to cause confusion, but is also incorrect: the reduction of other aspects of thermodynamics will involve aspects other than the identification of temperatures with mean speed, for instance. As an example, consider the formalisation of thermodynamics by Moulines (1975).

> is the third requirement of the impossibility of property reduction. Nagel claims that it is often a mistake to assume that reduction amounts to the derivation of the *properties* of one subject matter from the properties of another, and therefore denies that the reduced science can be eliminated on the basis of such property reduction. As Nagel states, 'the conception of reduction as the deduction of *properties* from other properties is potentially misleading and generates spurious problems' (Nagel 1961, p. 364).
>
> Instead, Nagel argues that the various 'properties' ascribed to chemical elements for instance, are the end result of theories about chemical elements, and if such theories are later shown to be reducible to theories of atomic physics, then this proves the existence of a *logical* relationship between *theories*, but does not provide an argument for the reduction of the essential 'natures' of the concepts that function in these theories. As Nagel argues, in true logical positivist fashion, the latter are not open to direct inspection and hence any speculation on the deeper natures of things must be classified as theory. Hence, for Nagel the presence of reduction does not provide sufficient grounds to argue for the *elimination* of properties in the form of various 'nothing but' arguments.

As a corollary, ontological reduction is not prior to epistemological reduction, but rather the other way round:

> Accordingly, whether a given set of "properties" or "behavioural traits" of macroscopic objects can be explained by, or reduced to, the "properties" or "behavioural traits" of atoms and molecules is a function of whatever theory is adopted for specifying the "natures" of these elements. The deduction of the "properties" studied by one science from the "properties" studied by another may be impossible if the latter science postulates these properties in terms of one theory, but the reduction may be quite feasible if a different set of theoretical postulates is adopted. (Nagel 1961, page 365)

Incidentally, Nagel then goes on to echo the famous Dirac quote, when he remarks that:

> The deduction of the laws of chemistry from the physical theories of the atom accepted 50 years ago was rightly held to be impossible. But what was impossible relative to one theory need not be impossible relative to another physical theory. The reduction of various parts of chemistry to the quantum theory of atomic structure now appears to be making steady if slow headway; and only the stupendous mathematical difficulties involved in making the relevant deductions from the quantum theoretical assumptions seem to stand in the way of carrying the task much further along. (Nagel 1961, p. 365)

The key point is that perceived ontological "gaps", which could provide an argument against reduction, are rather the end result of theoretical inadequacy instead of an expression of fundamental irreducibility. In fact, Nagel seems to suggest that the particular role of the reduction postulates is to *bridge* the ontological gaps. For instance:

> [...] if the "nature" of molecules is stipulated in terms of the theoretical primitives of classical statistical mechanics, the reduction of thermodynamics is possible only if an additional postulate is introduced that connects temperature and kinetic energy. However, the impossibility of the reduction without such special hypothesis follows from purely formal considerations, and not from some alleged ontological hiatus between the mechanical and the thermodynamical. (Nagel 1961, p. 365–366)

1.2.2 *Critique and Development of Nagel's Reduction Scheme*

Nagel's model for reduction was subject to a number of objections and proposals for modification. Responses to Nagel's model focused more or less equally on both the condition of connectibility and the condition of derivability.

A particular point of focus for philosophers of science has been Nagel's somewhat open formulation of reduction postulates. Reduction postulates pose a dilemma: on the one hand they do a lot of *logical* work, since they are a key part of ensuring that the laws and theories of the reduced theory are derivable from those of the reducing theory (recall that the derivability condition stipulates that the reduced theory is derivable from the principles of the reducing theory taken together with the reduction postulates); but on the other hand they also do a lot of *epistemological* work: the reduction postulates are (primarily, though perhaps not exclusively) relationships between theoretical terms of the reduced and reducing theories. Finally, it may be argued that in addition, the theoretical terms also do a lot of *ontological* work, in furnishing statements about what the theoretical terms of the reduced theory 'really' are all about.

One of the more constructive responses, and one illustrative of the more general direction in which the debate was to evolve, is that of Schaffner (1967), who not only emends Nagel's scheme, but also attempts to respond to Paul Feyerabend's (1962) critique that there is no sense of *derivability* in which we can hold that a theory T_2 is derivable from a different theory T_1. In the reconstruction of Feyerabend's argument by Schaffner (1967), 'rather T_1 is able to explain why T_2, "worked", and also to "correct" T_2 (p. 138).

Schaffner (1967) argues that a modified version of Nagel's model can meet various objections to Nagel's scheme. Schaffner's model is based on an emended model of reduction which in many ways is similar to that of Nagel, with the (important) proviso that it is possible in his model for the reducing theory to provide *corrections* to the reduced theory – as effectively a way of meeting Feyerabend's objection that the reduced theory was a false one since it is less accurate.

Schaffner (1967) also argues that some notions of reduction, notably Suppes' (1957) *structural* notion of reduction, are so weak that they do not constitute an adequate reduction paradigm (the structural notion of reduction will be discussed in more detail in Chap. 6).

Schaffner's model of reduction is based on the following requirements. The first requirement is a modified criterion of connectibility between a reducing theory T_1 and a (somewhat contrived) *corrected* secondary theory T_2^* in the following sense:

> All the primitive terms $q_1, \ldots q_n$, appearing in the *corrected* secondary theory T_2^* appear in the primary theory T_1, (in the case of homogeneous reductions) or are associated with one or more of T_1's terms such that:
>
> (a) it is possible to set up a one-to-one correspondence representing synthetic identity between individuals or groups of individuals of T_1 and T_2^* or between individuals of one theory and a subclass of the groups of the other, in such a way that a reduction function can be specified which values exhaust the universe of T_2^* for arguments in the universe of T_1;

> (b) all the primitive predicates of T_2^*, i.e., any F_i^n, are effectively associated with an open sentence of T_1, in n free variables in such a way that F_i^n is fulfilled by an n-tuple of values of the reduction function always and only when the open sentence is fulfilled by the corresponding n-tuple of arguments;
>
> (c) all reduction functions cited in (a) and (b) above be specifiable, have empirical support, and in general be interpretable as expressing referential identity. (Schaffner 1967, p. 144)

Thus Schaffner provides an alternative interpretation of the reduction postulates in which the terms of the two theories have to be connected in an *ontological* sense: the terms have to be connected extensionally. In this, Schaffner aims to follow the approach of Quine (1964), who takes co-extensivity as a hallmark of reduction. Quine argues that a reduction involves a *proxy function*, which has the interesting characteristic that its domain spans the entire range of values for the numbers in the reduced theory.

It is also interesting to note how Schaffner interprets the notion of a 'corrected' theory. Specifically, this notion has an observational, theoretical and methodological component. Schaffner requires that T_2^* should *experimentally* correct T_2 in the sense that it provides more accurate predictions than T_2 (or at least identical predictions). Moreover, T_2^* should be a *theoretical* improvement on T_2 in that it should explain why T_2 is incorrect (and why it worked in the cases where it did), and lastly, a methodological criterion specifies that T_2^* should provide a 'strong analogy' to T_2.

The other criteria are derivability and explicability. The criterion of derivability is analogous to that of Nagel: T_1, together with the reduction postulates, should be able to derive T_2^*. The criterion of explicability requires that T_2^* is (in a non-formal sense) sufficiently 'close' to T_2.

Over time, but *contra* Nagel's comments regarding property reductions, consensus seems to have grown that the 'reduction postulates' need to be *identities* in order to retain a robust sense of reduction. As Hooker (1981b) points out, there are generally three relevant 'grades of intimacy' possible in reduction postulates. These are (i) correlation, (ii) nomological connection and (iii) identity. In the decades after the publication of *The Structure of Science* the consensus converged on identities as a necessary precondition for reduction.

In particular, Causey (1977) has argued that the reduction postulates have to express identities for the reduction to be a complete reduction. Causey analyses sentences of the form

$$\forall x(\alpha x \leftrightarrow \beta x), \tag{1.1}$$

and notes that, when we have a true sentence of this form, it could be either one of three cases (i) α and β are accidentally co-extensional, (ii) α and β are nomologically correlated (and co-extensional), or (iii) α and β are identical. On Causey's analysis, (i) can be ignored, while (ii) is question begging as a reduction sentence and (iii) leads to an acceptable reduction sentence. Causey (1977) notes with regard to (ii), the concept of an ACCS (Attribute Correlation Connection Sentence):

> By now it should be fairly clear that [. . .] mere attribute-correlation law sentences, are not acceptable as connecting sentences. ACCS's are mysterious, causal law-sentences that are themselves in need of explanation. If they are used as connecting sentences . . . then we do not explain T_2 in terms of the laws of T_1 but rather in terms of T_1 plus these mysterious correlation laws. (Causey 1977, p. 86)

Causey concludes (p. 79) that adequate correlations of the form (1.1) require 'thing-identities' and 'attribute identities'.

In further detailed work on Nagel's prime example of reduction, as for instance in Kuipers (1982, 1990, 2001) it has been argued, in the spirit of Causey (1977), that reduction postulates need to be ontological identities rather than causal connections, primarily to 'close' the explanatory gap. As Kuipers (1982) points out:

> There seems to be little more than what appears at first sight to be a question-begging criterion: whereas causal connections ask for further causal explanation to bridge the gap, ontological identities do not because there is supposed to be no gap. (Kuipers 1982, p. 108)

In the same vein, Sklar (1967) gives an account of three reasons why it is preferable for reduction postulates to be identities. As Sklar notes, in the first place, the 'identities' involved in the reduction relation are more general than mere identification of individuals. In general, this is because the identities of the reduction postulates hold between *classes* of objects, and because the terms in the identities derive their meanings and sense from the wider theoretical framework of which they are part. Secondly, Sklar (1967) (like Causey 1977 and Kuipers 1982) notes that the identities differ from ordinary physical laws in that a request for further explanation is inappropriate. This is of course a required feature in a reduction which has to be self-explanatory. Thirdly, postulating that the reduction postulates are identities does not necessarily lead to ontological elimination. So if we manage for instance to identify chemical reactivity with a certain atomic structure this does not automatically lead to elimination of the term 'reactivity'. It will continue to exist and continue to be useful in chemistry. It could rather be said that we have learnt something about the nature of chemical reactivity by making the identification.

Hence, Causey (1977) argues that one of the best reasons for choosing identities as reduction postulates is precisely that they do not require any further *explanation* even though they do require some sort of empirical *confirmation*.

Hooker (1981b) gives three more reasons why it is attractive to think of reduction postulates as identities. The first one is that theoretical reduction via identities is the most powerful kind of reduction in an explanatory sense. His second reason is that this type of reduction enables ontological simplification, and the third reason is that the identities preserve metaphysical coherence.

All this still raises a number of issues. For while there now seems to be agreement with the notion that the strongest type of reduction is via identities. There is much less agreement on how these identities are instantiated, whether they hold between predicates or properties or ontologically. In this sense a famous problem in the philosophy of chemistry, whether 'water' 'really' 'is' H_2O, remains unsatisfactorily unresolved.

Another factor in play is ones particular predilection for assigning meanings to the terms featuring in scientific theories. Hempel (1966) argues that the identities in reduction postulates are *extensional* rather than *intensional*.[11] The consequence of this step is that the stated identity becomes an *empirical*, rather than an a priori (or necessary or whatever) fact. We thus seem to neatly sidestep the issue as to what the reduction postulates actually mean. As Hooker (1981b) analyses the issue, it is unlikely that an extensional interpretation of the reduction postulates manages to do this:

> Suppose one believed that the language of science was purely extensional. In this case the only logical resource for expressing empirical relations among terms is material implications. Then it seems to follow that whatever distinguishes laws from mere correlations, it cannot be any part of the logical content of the statements which express them. [...] Both two way nomic connections and identities entail correlations, so this exhausts their content. This argument may be bolstered by two further considerations: (i) Correlation suffices for extensional derivation (deduction) and hence for explanation. (ii) At the observational level no nomic relations or identities can be observed, so these things cannot be empirical features of these relations. (Hooker 1981b, p. 205)

The consequence of this view, as Hooker discusses, is that the three types of reduction postulates are often taken to be empirically indistinguishable and ones position with regard to which type of reduction postulate applies taken to be a matter of (metaphysical) taste rather than empirical fact. Hooker opposes this view, arguing specifically that in his opinion it is the end result of ‘a combination of extensionalism and bad argument’ (Hooker 1981b, p. 205).

Hooker’s argument for promoting identities over the others is that the identity may ‘materially imply a *pattern of other correlations*’ (p. 206). This is so because[12]:

> Identities place constraints on the entire patterns of explanations in which both terms are involved, nomic connections constrain only that part of the explanatory pattern matching that strictly concerns the nomic connections involved [...] while correlations constrain no more than that part of the explain*ed* pattern that contains them. [...] From whence comes then this curiously widespread misconception that identities, nomic connections and correlations are empirically indistinguishable? (Hooker 1981b, p. 205)

Kim (1990) gives the following account of both reduction and the status of the reduction postulates as follows:

---

[11] This is similar to Sklar’s (1967) first and second point given above.

[12] Hooker actually gives an example of two clocks which illustrates how the relationships are related: (i) in the first case we have two clocks which happen to strike at the same moment (correlation); (ii) in the second case we have one clock striking causing the other to strike; (iii) and in the third case we have the mirror image of the first clock as the second clock (identity). This example goes a long way to understand some of the philosophical discussions on this topic. In the first two cases (correlation and nomic connection) we could for instance change the color of the face plate on one of the clocks without changing the relationship, whereas in the third case the mirror image of the clock would change color too. Hence, the argument is that identities in this case extend their reach *beyond* the relata in the connection, whereas in the first two connections, they do not. As we will see in Part II, the distinction correlates to what we will call there a ‘loss of context’ in the reduction postulate.

> Reduction is standardly understood as a relation between theories, where a theory is understood to consist of a distinctive theoretical vocabulary and a set of laws formulated in this vocabulary. The reduction of one theory to another is thought to be accomplished when the laws of the reduced theory are shown to be derivable from the laws of the reducer theory, with the help of "bridge principles" connecting terms of the reduced theory with those of the reducer. Just what bridge laws are required obviously depends on the strength of the two theories involved, and there seems very little that is both general and informative to say about this. (Kim 1990, p. 19)

Even so, Kim (1990) formulates a minimal logical requirement on the reduction postulates that would enable them to meet the conditions imposed by Nagel's scheme in terms of a bi-conditional:

> The only requirement on the bridge laws that can be explicitly stated, independently of the particular theories involved, is the following, which I will call "the condition of strong connectibility"
>
> Each primitive predicate P of the theory being reduced is connected with a coextensive predicate Q of the reducer in a unconditional law of the form: "For all x, Px iff Qx"; and similarly for all relational predicates.
>
> If this condition is met, then no matter what the content of the two theories may be, derivational reduction is guaranteed; for these bi-conditional laws would allow the rewriting of the laws of the theory being reduced as laws of the reducer, and if any of these rewrites is not derivable from the pre-existing laws of the reducer, it can be added as an additional law (assuming both theories to be true). (Kim 1990, p. 19)

Kim's comments on Nagel's reduction have been criticised by Marras (2002) and similar arguments have been advanced by Klein (2009). Both argue that Nagelian reduction postulates are more complex and cover a wider range of cases than is subsumed under Kim's model. From the viewpoint of the present discussion, this also becomes clear once we recall Nagel's comments regarding property reductions.

I conclude at this stage that there is still room for working out in greater detail what these bi-conditionals consist of. Mere logical identities they are surely not, and at this point, at least for the reduction of physics to chemistry, the sort of metaphysical analysis we have discussed here does not really progress the matter.

My contention is that the prospects for a resolution of this problem without recourse to a set of well defined and well-understood examples from practical science is remote. This, incidentally, was exactly the point of the non-formal conditions stated by Nagel (1961), which were discussed in Sect. 1.2.1.2: the condition that reduced and reducing theories are well corroborated and mature. In this context, Klein (2009) notes that for Nagel, 'reduction is indexed to sciences-at-times' (p. 53), referring to actual scientific examples rather than to some abstract philosophical *'ism'*.

1.2.3 Nagelian Reduction: A Semi-formal Proposal

In this section, my aim is to develop a general theory of reduction in a loose formal sense, a theory that we can uses for the analyses progressed in Part I of this book. This theory is based on both a re-evaluation of the Nagel-Schaffner model as proposed by Dizadji-Bahmani et al. (2010), and the five-step model of Kuipers (1990).

1.2.3.1 A Generalised Model

Dizadji-Bahmani et al. (2010) argue that a ‘generalised Nagel-Schaffner model’ in which the reduction postulates are factual claims, is alive and well. They defend the generalised Nagel-Schaffner model against seven specific objections, concluding that none of them apply. In the terminology of Dizadji-Bahmani et al., the generalised Nagel-Schaffner model consists of a theory T_P reducing to a theory T_F through the following steps:

1. The theory T_F is applied to a system and supplied with a number of auxiliary assumptions, which are typically idealisations and boundary conditions.
2. Subsequently, the terms in the specialised theory T_F^* are replaced with their ‘correspondents’ via bridge laws, generating a theory T_P^*.
3. A successful reduction requires that the laws of theory T_P^* are *approximately* the same as the laws of the reduced theory T_P, hence between T_P and T_P^* there exists an analogy relation.

For our purposes, two features of the generalised Nagel-Schaffner model are worth noting. The first one of these is that the reduction postulates are an inherent part of the *reducing* theory, rather than some auxiliary statements that have a primarily metaphysical import. Specifically, Dizadji-Bahmani et al. argue that of the three types of linkages that may be expressed by reduction postulates (see p. 7), the first two can be discarded and reduction postulates express matters of fact.

As a result, Dizadji-Bahmani, Frigg, and Hartmann note that reductions have a high likelihood of occurring in situations where theories have an overlapping target domain:

> We are committed to the claim that if we have a situation of the kind described above (in which the two theories have an overlapping target domain), *then* one must have a reduction. (Dizadji-Bahmani et al. 2010, p. 410)

1.2.3.2 The Generalised Model Explicated: Kuipers’ Five Step Model

The generalised Nagel-Schaffner model relies on a ‘transformation’ of the theory T_F into a theory T_F^* with the help of a set of additional assumptions, as well as term replacement and ‘approximate’ similarity. Kuipers (1990, 2001) develops a five-step model of reduction which explicates these steps in more detail, and then tests this model against a number of case studies. Among the case studies he discusses are the famous case of the reduction of the ideal gas law to the kinetic theory of gases, and some cases from biology and economics.

Kuipers' model is limited to the reduction of laws and concepts, and makes no claims about other types of reduction. Its primary aim is to describe the structure of an *explanation* (by reduction). This aspect limits its applicability to general notions of reduction, but makes it more specific too; the model should not be seen as a general approach to the reduction of entire sciences.

This model is based on a study of a number of actually claimed reductions (including our original article Hettema and Kuipers (1988)[13]). Kuipers' five step reduction scheme provides a decomposition model for the reduction of laws and concepts, which involves Application, Aggregation, Identification, Correlation and Approximation steps in the following order:

$$\begin{array}{llcccccc}
(1) & \text{Application} & X & \mathrm{A}_1 & & & & \\ \cline{3-4}
(2) & \text{Aggregation} & & \mathrm{L}_1 & \mathrm{A}_2 & & & \\ \cline{4-5}
(3) & \text{Identification} & & & \mathrm{L}_2 & \mathrm{A}_2 & & \\ \cline{5-6}
(4) & \text{Correlation} & & & & \mathrm{L}_3 & \mathrm{A}_4 & \\ \cline{6-7}
(5) & \text{Approximation} & & & & & \mathrm{L}_4 & \mathrm{A}_5 \\ \cline{3-8}
 & & & & & & & \mathrm{L}_5 = L
\end{array}$$

The idea is that a Theory X will explain a law L if both a formal and an empirical condition can be met (like Schaffner's 1967 notion of reduction, this is in the spirit of Nagel 1961).

The formal condition stipulates that 'there are auxiliary mutually consistent hypotheses $A_1 \dots A_5$ such that L can be derived strictly or approximately from X using one or more times one or more of the five steps.' (Kuipers 2001, p. 86). The empirical condition that enters in this model is that there are good reasons to suppose that the theory and the auxiliary assumptions $A_1 \dots A_5$ are approximately true. The five steps are, in order:

1. Application, where a theory T is tailored to the kind of object that the law L is about;
2. Aggregation, where the total effect of 'individual laws' for many objects is calculated by suitable addition or synthesis;
3. Identification, where the aggregate law is transformed with the aid of one or more identity hypotheses, which ontologically identify object and predicate terms of the law L with terms (definable in terms) of T;
4. Correlation, where the resulting law is transformed with the aid of some causal hypothesis, correlating terms of L with terms of T;
5. Approximation, where the law is simplified by mathematical approximation.

---

[13] Note here that the reduction claim in that paper has later been criticised by Scerri (1997). While some of Scerri's arguments against our original claim are correct, even though driven by a notion of reduction as derivation (while our 1988 paper is based on the Sneedian structuralist framework and is thus closer to Suppes' notion of reduction), this does not, in my view, invalidate the model.

In what follows, we briefly explicate the model in more detail. It should first be noted that the ‘application’ step is far from trivial, and in many practical cases involves the sort of system specifications that Cartwright (1983) discusses in the context of ‘theory entry’, where the ‘phenomenon’ (in this case the phenomenon to which the theory to be reduced applies) is formulated such that the reducing theory can ‘enter’ into the explanation. Specifically, the reducing theory is modified in this step, so that it will apply to the case at hand. How these modifications work in practice can only be discussed with the help of actual examples.

This decomposition model for the reduction of laws and concepts allows one to distinguish three types of reduction. In general the collection of cases suggests that reductions involve at least one of the steps (2) Aggregation, (3) Identification or (5) Approximation. In general, the identification step forms the core of the heterogeneous reduction scheme. In Kuipers (2001) (p. 90) it is furthermore claimed that we may speak of a *reduction* of a law by a theory if in addition to the connection involving at least one of the steps (2), (3) and (5), the law has been established *prior* to the theory itself.

Dependent on the specific steps involved, reductions may be typified as micro reductions (involving at least an aggregation step), heterogeneous reductions (involving at least an identification step) and approximative reduction (reductions with an approximation step, see Nickles 1973). The five step scheme therefore captures a lot of distinctions that have been made in the literature since Nagel; a more detailed discussion of this is given in Kuipers (2001).

Steps (3) and (4) are transformation steps, for which the auxiliary hypotheses correspond to Nagel’s ‘bridge principles’ or reduction postulates. These steps, moreover, also introduce a ‘jump in language’, where new terms replace terms occurring in the previous stage, are introduced.

The first three steps in Kuipers’ five-step model can be read as a further explication of the transformation of the theory T_F into T_F^*, while the ‘correlation’ step in Kuipers’ model corresponds to the step taking us from T_F^* to T_P^*, and the final ‘approximation’ step ensures that the analogy relation holds.

In the analysis of Part I of this book, we will evaluate putative reductions primarily with the help of this scheme. It will appear that the majority of the reductive work is done through the ‘transition’ from T_F to T_F^*, usually employing various of the five steps from Kuipers’ five-step model.

1.3 Unity Without Reduction: Interfield Theories

Concepts of the unity of science that do not explicitly depend on the existence formal inter-theoretic relationships between theories have recently become more popular. Two such approaches that are relevant to what follows are a revival of the ‘encyclopaedia’ project of Neurath and the Duhemian concept of the unity of science, as well as the concept of ‘interfield theories’ proposed by Darden and Maull (1977).

The revival of a Neurathian concept of the unity of science has been proposed by Potochnik (2011). For Potochnik, the 'unity of science' is one where the sciences share a common goal of establishing 'evidential implications in the face of causal complexity' (p. 317). Thereby Potochnik focuses on a form of unity of science which allows the free transfer of *data* between the sciences, even while there is no corresponding concept of a 'unity of the world'. However, a minimal condition for this concept of the unity of science seems to be compatibility between the different sciences, otherwise the exchange of data would make little sense.

The Duhemian concept of the unity of science, which influenced Neurath to a significant degree, is based on the notion that there is no single 'foundational' theory to which all the other theories can be reduced. Rather, the idea of science is *expanded* by the addition of new theories to the existing corpus of scientific knowledge. In contrast to the unity defended by Potochnik, the Duhemian model does allow for a concept of theoretical compatibility. Specifically, Duhem (1914, 1954) argues that science is unified through incorporation. For the specific example of mechanics and thermodynamics that Duhem discusses the concept of mechanics is enriched through the addition of concepts from thermodynamics, and both mechanics and thermodynamics form part of a broader science in which neither the mechanical, nor the thermodynamical aspect of nature is 'fundamental'. The Duhemian concept has been discussed in the context of the philosophy of chemistry in a paper by Needham (2010).

Finally, the work of Darden and Maull (1977) draws attention to the nature of 'interfield theories' as a mechanism for the discussion of the unity of science. Darden and Maull argue that the unity of the sciences can be established on the basis of *fields*, which they define as follows:

> [...] a central problem, a domain consisting of items taken to be facts related to that problem, general explanatory factors and goals providing expectations as to how the problem is to be solved, techniques and methods, and, sometimes, but not always, concepts, laws and theories which are related to the problem and which attempt to realize the explanatory goals. (Darden and Maull 1977, p. 44)

The term 'domain' is here used in the sense in which the term domain was introduced by Shapere (1977), who intended 'domains' to take over the role of the 'observational' aspect of a theory. What the notion of the domain adds to the notion of a mere observational language is its ordering or structure. Beyond this description, the definition of domains is not very precise. The rough criterion for a domain given by Shapere is:

> [...] bodies of information having the following characteristics
>
> 1. The association is based on some relationship between the items.
> 2. There is something problematic about the body so related.
> 3. That problem is an important one.
> 4. Science is "ready" to deal with the problem. (Shapere 1977, p. 525)

Shapere gives the following criterion for an *ordered domain*:

> [...] domains in which types of items are classified, and those classes themselves arranged in some pattern, for example, a series, according to some rule or ordering principle. The

> series may (as in the case of the periodic table of chemical elements) or may not (as in the case of spectral classifications of stars [...]) be periodic (repeating). Orderings of domains are themselves suggestive of several different sorts of lines of further research. (Shapere 1977, p. 534–535)

Hence domains can fulfil important heuristic roles: they provide guidance as to how a problem is structured, and guidance as to what shape its likely explanation can take. Specifically, as Shapere points out, the 'items' in a domain[14] can be problematic precisely:

> [...] through being *related* to other such items in a body about which the problem exists: scientific research is in such cases generated by items in association with one another, rather than by "facts" in isolation from one another. (Shapere 1977, p. 530)

The notion of the domain allows for a distinction in two types of issues facing a scientific theory: (i) those about clarification of the structure of the domain itself and (ii) those that call for (in Shapere's terms) a "deeper" account of the domain. Shapere refers to the problems of the first kind as domain problems and to problems of the second kind as theoretical problems.

'Interfield theories' as designed by Darden and Maull are specific theories intended to deal with problems of the second kind and provide the sort of required 'deeper' account in terms of another theory. Darden and Maull further develop the notion of an 'interfield theory' as follows. The definition of an interfield theory is a theory that, in the words of Darden and Maull, does some or all of the following:

> (a) To solve (perhaps "correctly") the theoretical problem which led to its generation, that is, to introduce a new idea as to the nature of the relations between fields;
> (b) To answer questions which, although they arise within a field, cannot be answered using the concepts and techniques of that field alone;
> (c) To focus attention on previously neglected items of the domains of one or both fields;
> (d) To predict new items for the domains of one or both fields;
> (e) To generate new lines of research which may, in turn, lead to another interfield theory. (Darden and Maull 1977, p. 59)

Darden and Maull also note that the concept of interfield theory is one that stands in contrast to inter-theoretic reduction, primarily because their theory changes the primary *unit* of reduction from that of a theory to a broader concept of a *field*. In their opinion:

> The existence of such interfield theories has been obscured by analyses such as Nagel's that erroneously conflate theories and fields and see interrelations as derivational reductions. (Darden and Maull 1977, p. 43–44)

On the basis of this contrast, Darden and Maull view their concept of an interfield theory as a non-reductive concept.

However, to the extent that theories form *part* of fields, Darden and Maull's notion of an interfield theory is not incompatible with Nagelian reduction. As we have already argued on p. 6, the '*unit*' of a reduction in Nagel's original text is left

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[14] An 'item' in a domain here roughly corresponds to a 'fact' in a scientific theory.

largely undefined and Nagel talks about ‘sciences’ rather than ‘theories’. Darden and Maull’s introduction of ‘fields’ allows for a useful interpretation of the Nagelian concept of reduction in terms of localised theories which are part of broader fields. In this sense, Darden and Maull’s notion of ‘interfield’ theories may be seen as something that was closer to Nagel’s original intent than it seemed to be at first sight and compatible with a ‘naturalised’ version of Nagel’s reduction relations.

Another interesting aspect in the context of interfield theories is that the *application* step in Nagel’s scheme for actual cases of reduction leads to a ‘transformation’ of the reducing theory (see also p. 16 and p. 18 for a discussion). This application step may in some cases also take the form of Darden and Maull’s ‘introduction of a new idea’. Similarly, many of the other specifics that Darden and Maull see as important aspects of the notion of interfield theories are not incompatible with the Nagelian model of reduction, for instance the idea of prediction of new items for the domains of either field, or the idea that one theory can correct another.

An important difference between the Nagelian notion of reduction and the concept of an interfield theory is however the *dependency* of one theory on the other. In the case of Nagelian reduction, the relationship is directional – i.e. it is in general the laws of the reduced theory which are explained, it is the reduced theory which is corrected by the reducing theory, the ‘new lines of research’ are not generally generated for the reduced theory, and so on. In opposition, in Darden and Maull’s model, the relationship is more symmetric in the sense that there is a bi-directional relationship between the theories in question. It is perhaps useful to note that the strict interpretation of Nagel’s theory also has problems with directionality in this sense, i.e. as pointed out in Kuipers (1982), under a strict ‘identity’ reading of the reduction postulates, the reduced theory together with the reduction postulates may also be said to ‘derive’ the applied instance of the reducing theory.

Especially, if we take Darden and Maull’s suggestion for ‘interfield theories’ as entailing that no field of knowledge should stand on its own, and combine that with the liberal reading of Nagel advocated here, then there is scope for the view that the reductive view as advocated by Nagel is capable of accommodating some of the non-reductive views. In particular, through the reduction postulates, the reduced theory is capable of being *represented* in the language of the reducing theory, which may well come to represent the sort of *structural* connections that characterise the Neurathian concept of the unity of science. Moreover, Nagel’s informal notions of corroboration and maturity of the reducing theory associate well with the programmatic aspects of the non-reductive views of Darden and Maull, Duhem and to a lesser degree those of Potochnik.

In Chap. 6 I will work out the formal aspects and structural components of Nagelian reduction in more detail, and will clarify the relationship in terms of the formal model that I propose as the main mechanism for the technical analysis of Part II. The characterisation of the reduction relationship in these formal terms allows for a discussion of such terms as ‘data transfer’, ‘embedding’, and ‘fields’. The main mechanism in the (formal) Part II is that theory connections can be conceived in terms of inter-theoretic *links* to which ‘direction’ may be added alongside a number of other desiderata.

From that perspective, the non-reductive alternatives may not be as far removed from a Nagelian view on reduction as it would appear at first sight. As I have argued, Nagel is vague on what the unit of reduction actually is, he is moreover distinctly non-committal on the nature of 'connectibility' and requires a condition of 'logical consequence' as defining derivability. As a result, there may thus exist a degree of compatibility between a Nagelian concept of reduction and the proposed 'alternatives' which has so far been largely unexplored. The exploration of this connection requires both a logical formalism with which to analyse these relationships as well as a set of example theories which can be utilised to test the claimed relationships. One such structure will be set up and discussed in more detail in Part II.

1.4 Reconciling Reductive and Non-reductive Approaches

In all this talk of reduction of theories it is easy to forget that reduction originated as a primary glue in the unity of science. Hence reduction has a strongly programmatic aspect, which has consequences not only for the individual status of theories, but also for how theories hang together. In the remainder of this section, I will therefore discuss the programmatic aspects of reduction, focusing in particular on 'reduction' as a component in the 'unity of science'.

Nagel's notion of reduction also had a programmatic aspect, as is illustrated by the 'Dirac like' quote on p. 10, as well as by Nagel's informal requirements of corroboration and maturity of the theoryies involved. While these informal requirements were primarily intended to block trivial cases of reduction, they also constitute the kernel for a programmatic notion of reduction.

Hooker notes that some programmatic aspects of the unity of science remain unresolved in current debates on reduction. The first of these is the notion of *successor* relations between reduced and reducing theories. It is unclear, for instance, whether relativistic quantum theory is a successor to non-relativistic quantum theory and whether the latter is a successor to classical mechanics. The common notion is that reduction runs backward along the lines of succession, so that predecessor theories can be classified as (in some limit) *derivable* from successor theories. The 'derivability in some limit' in these cases may or may not be classified as a case of reduction (given that reduction generally entails a broader set of requirements than derivability).

A second one of these unresolved issues is the issue of *retention* of reduced theories. As Hooker (1981a) notes, the 'retention extreme of the retention/replacement continuum goes unoccupied, with all the implications for the empiricist tradition which that brings' (p. 45). Specifically, a reduced theory that is retained in large measure or in its entirety is more likely to 'co-evolve' with the reducing theory rather than be guided by the reducing theory. As Hooker argues, the nature of the inter-theoretic relationships changes continually and significantly as one moves towards the retention side of the continuum, and this side of the continuum has not been extensively explored in philosophical theories of reduction.

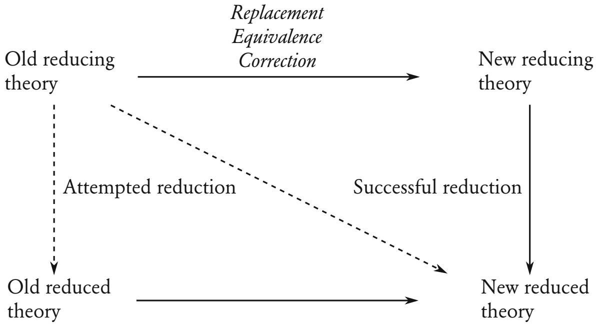

Fig. 1.1 Co-development of scientific theories as facilitated by reduction, based on Bechtel (1988). The 'attempted' (but failed) reduction gives rise to developments in both the reduced and reducing theories of such a nature that over the course of time the reduction can be achieved. The relationship between the 'old' and the 'new' theories is one of replacement, equivalence or correction.

In the remainder I will argue that the reduction of chemistry to physics is a clear case of a type of reduction that *does* occupy the retention end. Physics has not managed to 'displace' chemistry (and there is little or no prospect that it ever will). Rather, chemistry has managed to *accommodate* its potential reducing theory – quantum chemistry – as a tool in its toolkit.

In this context, Bechtel (1988) argues that a reduction *cum* retention model for reduction can facilitate a process of *co-development* of theories (see Fig. 1.1). While Bechtel focuses in particular on cognitive science, there is a *prima facie* possibility that something like this holds as well in the case of the reduction of chemistry to physics: the chemistry of say, 1800 could not be reduced to the physics of the same period, but in by now the situation is somewhat different, and the prospects for reduction would seem to be improved – of course, how far they have improved remains to be seen.

In this context, it is useful to consider the proposal made by Zandvoort (1986) for 'guide' and 'supply' programmes. A 'guide programme' provides the 'set problems' to other programmes while the 'supply programme' aims to provide solutions to these problems. Zandvoort characterises quantum chemistry as a 'supply programme' for the 'guide programme' of classical chemistry (p. 234–236) based on quantum chemical calculations performed on the problem of an 'ion pump' through an alpha-helix. It is interesting to note that in this context Zandvoort notes that the model of guide and supply programmes leaves room for what he calls 'Lakatosian competition'.

Zandvoort's proposal, in the context of the discussion on reduction, calls for peaceful coexistence with a sting. The sting is that for a programme to be useful as a supply programme a minimal translation would have to occur between chemistry and physics. At the outset, this translation would have to facilitate two things:

1. It would have to allow for the posing of chemical problems in terms of a model or situation amenable to analysis by quantum chemistry;
2. It would have to allow for quantum chemical results to be interpreted in the language of chemistry.

These two conditions would not hold in a situation of disunity (as proposed by Dupré 1993), or a situation of 'anomalous monism' as proposed by van Brakel (1999, 2000), but they seem perfectly sensible in the context of Nagel's conditions for connectibility.

I will take up a full reconstruction of quantum chemistry in terms of a Lakatosian research programme in Chap. 5, but in the meantime note that for the relationship to function as one of a 'guide' and 'supply' programme some form of connectibility would have to hold: knowledge claims generated in the context of chemical physics, physical chemistry or quantum chemistry would have to find a counterpart in chemistry proper for the relationship to work. Stated alternatively, one would expect quantum chemistry to have the correct representational power to furnish explanations for the theories of chemistry.

1.5 Conclusion: A Programme for the Philosophy of Chemistry

All this leads to an outline of my proposed approach to the reduction problem in chemistry. In brief, my proposal is that a suitable *paraphrase* of the Nagelian reduction programme – based on examples of actual scientific theories and reinforced by a modern notion of both connectibility and derivability – forms a suitable framework in which to discuss the details of a putative reduction relationship. This reframing of the relationship also has the potential to reconcile the concept of reduction with at least some 'non-reductive' approaches, and hence largely dissolve the distinction. The key operational concept will be that of theory *nets*, which have sufficient formal strength to capture the nature of inter-theory explanation, and are flexible enough to discuss matters with a significant degree of sensitivity to actual science.

It should also be clear what sort of discussion will *not* be facilitated by this approach to reduction. In particular my proposed framing of the debate severely limits the possibility of talk about various *isms*, and does not allow for any talk of 'essential properties', or a 'tutelage' of chemistry by physics. The reduction relation I propose sits on the 'theory retention' end of the scale, and sees reduction as a non-trivial, complex affair.

Ultimately, this also leads us to the question whether it is still useful to talk of reduction. Though I would happily drop the term for something better, I fear we are stuck with it. But let's agree to get rid of 'reductionism'. As a first step that would help immensely.

Part I
Networks of Theories

The aim of this part is to elucidate to what extent physics can be said to *explain* notions of chemistry. I have taken a few examples of theories that can be considered primarily 'chemical' and hence not amenable to reduction. In some cases, such as in the case of bonding and molecular structure, there are current debates over whether the phenomenon even exists. In this part I will aim for accurate rational reconstructions of these theories in order to bring out the logical aspects of their connections to physical theories in the necessary detail.

In Chap. 2 I discuss the explanation of the phenomenon of 'bonding' with quantum theory. In Chap. 3 I explore the idea, quite popular in current philosophy of chemistry, that molecular structure is not supported by quantum theory. In Chap. 4 I consider the theory of 'absolute' reaction rates, sometimes ironically referred to as the 'absolute' theory. This theory creates a complex network of interlocking theories which is ideally suited to further explain important aspects of the relationship between chemical and physical theories. In Chap. 5 I reconstruct quantum chemistry as a *research programme* of Lakatosian and other types.

In all of these examples there will be 'two sides to the story' to the extent that there are proponents of a reductive (or, in the case of scientists, one could more accurately say an 'explanatory') approach to the problem, and proponents of the opposite view. Hence all three examples form cases where the debate about reduction is more or less 'live', although instantiated in different ways and at different times. This is an advantage for the purposes of this part of the book, which is to give an overview of how these debates have expressed themselves over time.

Summary of Part I

In Part I we have discussed, with the help of a number of examples, the explanatory fabric of (quantum) chemistry in order to gain a clearer understanding of what quantum chemistry can and cannot achieve in the reduction of chemistry to physics. As a side-line, these steps were close to a process that Nancy Cartwright (1983) has referred to as 'theory entry', which involves the specification of both the conditions under which a theory can be said to *apply* to a given situation as well as a statement of its basic axioms and theorems.

Part I has defined the operative parameters for quantum chemistry quite precisely: it has specified and partially justified the non-formal conditions for theory entry in Chaps. 2 and 3. The focus of these chapters was on two areas that have been the target of recent attention in the philosophy of chemistry: the phenomenon of bonding and in particular the issue of molecular structure. Especially the latter is frequently put to the task of supporting a non-reductive view of the relationship between chemistry and physics. The arguments in these two chapters have provided support for the thesis that reduction is not a simple 'identities' *cum* 'derivation' process, but we knew that much already from a close reading of Nagel and the further developments of his scheme in Chap. 1.

What was gained in these two chapters was a more precise understanding of the conditions under which reduction *could* be said to obtain, and in this respect the situation is not as dire as the anti-reductionist literature would have us believe.

In Chap. 4 I have provided further specification for the situation as we find it in the actual science by focusing on the *networks* that make up the reductive 'substrate' for the theories of chemistry. The main lesson to learn from this chapter is that in many practical applications of the concept of reduction, there may not be *single* theory to reduce to, but there is in fact a *network* of mutually reinforcing theories providing the explanation. While this is a situation that was more or less explicitly foreseen by Nagel (1961) it is not commonly taken into account in the discussions on reduction, but, as I will argue in Part II, it has serious consequences for our view on the logic of reduction.

In Chap. 5 quantum chemistry was characterised as a 'research programme'. This characterisation allowed for a 'bracketing' of the principled problems associated with the relationship between chemistry and physics. Moreover, it allowed a specification of the relationship between chemistry, quantum chemistry and quantum theory. The relationship is one that satisfies the principal Nagelian requirements of connectibility and derivability in a loose sense: the characterisation of quantum chemistry as a 'supply programme' entails that quantum chemistry is *applicable* to chemical problems and provides partial explanations.

All of this places limits on the degree to which quantum chemistry may be classified as a 'reducing agent' for chemistry. In Part II I will develop a specific theory of reduction that is aimed to capture these limits while still adhering to a concept of reduction.

Chapter 2
Explaining the Chemical Bond: Idealisation and Concretisation

Abstract In this chapter, I focus on the 'chemical bond' – the phenomenon of bonding between two atoms – as an example of potential Nagelian reduction. There are two main competing theories, the Molecular Orbital and the Valence Bond theory, which provide a view from quantum mechanics on the phenomenon of bonding. The efficacy of both theories can be compared. It is furthermore interesting that there are systemic ways in which these theories can be improved, leading to the same computational view on the phenomenon of bonding. This means that the resulting structure is an idealisation/concretisation pair.

2.1 Introduction

The quantum theoretical explanation of the chemical bond has been the subject of renewed attention in the philosophy of chemistry recently and for good reason. The chemical bond exhibits a number of features that make it an interesting case in the philosophy of science and explanation. Among these are (i) the historical fact that the initial explanations of the chemical bond employed two distinct theories, the 'molecular orbital' and 'valence bond' theories, (ii) the introduction of the concept of 'hybridisation' in the explanation of the chemical bond, which provides its explanation in terms of 'hybrid' orbitals that are non-existent from a quantum theoretical perspective, and (iii) the fact that the introduction of electron correlation, as it is implemented in most modern quantum chemistry packages, provides explanations for the phenomenon of chemical bonding that are not easily understood in terms of the basic explanatory models. Hence the theory of the chemical bond exhibits a number of features that make it a good case study for philosophers of science to test notions of explanation, theory development, and idealisation/concretisation pairs.

The theory of the chemical bond also provides a good introduction to the issue of reduction: there is no doubt that the explanations that have been furnished by physical theories in the explanation of the chemical bond have been extraordinarily successful, yet the explanations offered for the chemical bond are 'chemical' in the sense that they involve the sort of modifications of physical theories chemists often make.

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The issues around the physical theories used in the explanation of the chemical bond have been discussed from a historical perspective by Lagowski (1966), Stranges (1982), Sutcliffe (1996), and also in two papers by Brush (1999a,b). A useful background to the issues is found in Nye (1993). More recently the issues were discussed from a philosophical perspective in papers by Hendry (2004, 2008), Harris (2008) and Healy (2011). The historically oriented study by Hendry (2004) has argued that the Valence Bond (VB) and Molecular Orbital (MO) methods for the explanation of the chemical bond correspond to two more or less divergent views on explanation. Harris (2008), based on a historically oriented study of the work of Lewis and Pauling, has argued that the chemical bond is best viewed as a theoretical synthesis or physico-chemical entity, one that expresses the interdisciplinary nature of quantum chemistry. This, incidentally, was also argued earlier by Spector (1978) on the basis of his analysis of reduction.

In a similar vein, a study by Park (2000), focusing on Slater and Pauling's discovery of hybridisation, has identified this episode in the evolution of the theory of the chemical bond as a case of 'simultaneous discovery'.

Notwithstanding the renewed interest, the study of the chemical bond has also led to a considerable amount of confusion in the philosophy of chemistry and it would appear that most of the issues of interest in the case of the chemical bond are presently unsettled.

In particular Woody (2000) and Weisberg (2008) have argued that there are systemic troubles in the explanation (or, as the case may be, reduction) of the chemical bond by physical theory, but they do so on arguments and notions of reduction and explanation that are somewhat problematic. Woody (2000) gives a useful, but flawed, analysis of the concept of explanation and her notion of diagrammatic representations of chemical bonding, while a useful tool in its own right, is by no means inconsistent with a quantum chemical explication of the chemical bond and does not provide a sufficient argument for non-reducibility. I have outlined my significantly more substantial difficulties with Weisberg's approach in Hettema (2008).

From the early days of theorising on the chemical bond, there have been two contending workable models. One, the Valence Bond (VB) theory, was pioneered by Heitler and London (1927),[1] the other, the Hund-Mulliken, or Molecular Orbital (MO) approach, was pioneered by Mulliken (1931, 1932) and inspired by Hund's treatment of molecular spectra.

The relationship between these models has sometimes been strained, incidentally mapping a somewhat similar cultural division between chemists and physicists. The Heitler-London theory can be seen as a 'chemists' theory – a theory which constructs a total molecular wavefunction from constituent atoms. On the other hand, the Mulliken-Hund approach 'extends', one could say, the methods pioneered in the study of atomic spectra to molecules. Both models supply a heuristic for further development. Moreover, the further development of both these theories eventually leads to the same end-point: an identical wavefunction is obtained if one corrects the deficiencies of both the MO and VB wavefunctions.

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[1] An English translation of Heitler and London's paper is provided in Hettema (2000).

Hence the theories of the chemical bond are good examples of an *idealisation* and *concretisation* strategy: both the MO and VB theories start with different idealisations, utilise different concretisations, and share an endpoint in the process. While the idealised wavefunctions correspond to qualitative theories of the chemical bond, the subsequently corrected wavefunctions do not directly correspond to such qualitative theories.

The concretisation step removes some conceptual clarity from the initial idealised theory. This has led Weisberg (2008) to argue that the corrected methods ‘put pressure’ on chemical theories of bonding. Similarly, it has led Woody (2000) to the conclusion that theories of the chemical bond pose a problem for inter-theory reduction: the ‘better’ models from the viewpoint of quantum theory do not directly correspond to the qualitative theories that chemists use to explain the phenomenon of bonding.

Under the reconstruction proposed here, these problems represent aspects of the idealisation/concretisation relation. I argue that the initial idealisation step corresponds to the construction of a theory specialised towards explanation in a specific domain, or a theory that is targeted in an explanatory sense. The subsequent concretisation steps join these two domains together. The idealisation steps thus correspond to the construction of specific interfield theories in the sense of Darden and Maull (1977), which were discussed on p. 20.

In this chapter I will argue that the theories of the chemical bond form a good example of how reductions of chemistry to physics are supposed to function: the existence of the idealisation/concretisation pair in the theory leaves room for both the qualitative and accurate levels of theory that are required to set up and subsequently refine reduction relationships. Far from being problematic, the theory of the chemical bond is thus reconstructed as an entity that displays many of the characteristics we would desire in a reduction relationship.

2.2 What Is a Chemical Bond?

A chemical bond is not a clear and unambiguous concept. Moreover, the concept comes in a number of confusing subtypes, such as the covalent bond, metallic bonds, ionic bonds and, with the advent of cage structure molecules such as C_{60}, even encapsulation.

Traditionally, philosophers of science have not focused on the concept of the chemical bond in any detail. For instance, there is no mention of the chemical bond in for instance Nagel (1961) or most other ‘classics’ in the philosophy of science, and it is only fairly recently that systematic studies of the historical and philosophical aspects of the chemical bond have appeared. Russell (1971) has investigated the history of the concept of valence in significant detail, and the series of articles by Brush (1999a,b) have covered some aspects of theory change in chemistry on the basis of aromaticity. The articles by Weisberg (2008) and Hendry (2004, 2008) are among the first to discuss aspects of the chemical bond from the specific viewpoint of the philosophy of chemistry.

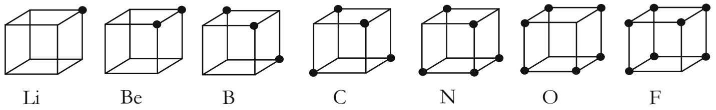

Fig. 2.1 The atomic structure diagrams from Lewis (1916), based on Abegg's law of valence and countervalence

Table 2.1 Abegg's law of valence and counter-valence as summarised in Russell (1971)

Periodic group	I	II	III	IV	V	VI	VII
Normal valencies	+1	+2	+3	+4	+5	+6	+7
Counter valencies	−7	−6	−5	−4	−3	−2	−1

Both as a story of explanation and as a historical episode in the development of science, the chemical bond has interesting aspects: it is an ambiguous notion that nevertheless lies at the heart of chemistry, and moreover, as we shall see, there exist competing explanations for one particular type of bond, the covalent bond.

As an aside, the ambiguity of the notion of a chemical bond is one of the motivations given in Bader (1990, 2009) for giving prevalence to the concept of *bonding* over the concept of a *chemical* bond, a topic which we will not discuss further here.

In a very influential paper, Lewis (1916) introduced the concept of a bonding electron pair. Lewis bases his theory of the chemical bond on a *cubical* model of the atom (which is drawn in Fig. 2.1). The model is intended as the basis for the explanation of Abegg's law of valence and countervalence (which is summarised in Table 2.1). As outlined in Russell (1971), the theory of the cubic atom is the basis for the theory of electron pair.

This model is designed to account for the laws of chemical behaviour with the help of six postulates for the theory of the chemical bond (which are worthwhile to repeat in full before continuing):

1. In every atom is an essential kernel which remains unaltered in all ordinary chemical changes and which possesses an excess of positive charges corresponding in number to the ordinal number of the group in the periodic table to which the element belongs.
2. The atom is composed of the kernel and an *outer atom* or *shell*, which, in the case of the neutral atom, contains negative electrons equal in number to the excess of 0 and 8.
3. The atom tends to hold an even number of electrons in the shell, and especially to hold eight electrons which are normally arranged symmetrically at the eight corners of a cube.
4. Two atomic shells are mutually interpenetrable.
5. Electrons may ordinarily pass with readiness from one position in the outer shell to another. Nevertheless they are held in position by more or less rigid constraints, and these positions and the magnitude of the constraints are determined by the nature of the atom and of such other atoms as are combined with it.
6. Electric forces between particles which are very close together do not obey the simple law of inverse squares which holds at greater distances. (Lewis 1916, p. 768)

Lewis comments quite extensively on these postulates, and it is not that useful to repeat the arguments here. A few points are however worth noting.

Lewis reiterates the point that the chemical valence is directional, and hence that it is difficult to see how it can be explained by something like Coulomb forces.[2] The cubical model of the atom of course supports this directionality. In the model of the chemical bond built upon this cubical model of the atom, Lewis supposes that atoms can 'share' electrons between them to fill up each position in the cube.

There is also an interesting discussion on the placement of He in the periodic table. At the time of the 1916 article, the exact number of electrons of He was not known, but it was 'almost certain' that He had either two or four electrons. Based on the fact that in the periodic table no elements between H, He and Li were known, Lewis surmises that:

> [...] it is evident from the inert character of helium, and from the resemblance of this element to the other inert gases, that here the pair of electrons plays the same role as the group of eight in the heavier atoms, and that in the row of the periodic table comprising hydrogen and helium we have in place of the rule of eight the rule of two. (Lewis 1916, p. 774)

The Lewis theory of the chemical bond is introduced almost incidentally, after considering the types of bonding in the halogens:

> In order to express this idea of chemical union in symbols I would suggest the use of a colon, or two dots arranged in some other manner, to represent the two electrons which act as the connecting links between the two atoms. Thus we may write Cl_2, as Cl : Cl. If in certain cases we wish to show that one atom in the molecule is on the average negatively charged we may bring the colon nearer to the negative element. Thus we may write Na :I, and I :Cl. Different spacings to represent different degrees of polarity can of course be more freely employed at a blackboard than in type. (Lewis 1916, p. 776–777)

The remainder of the theory is built upon this typography, with a number of examples given in Fig. 2.2.

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[2] Incidentally (or perhaps not so incidentally), Lewis at this point starts a critique of the emerging quantum mechanical models of the atom. For instance, he expresses some hesitation about the sort of theories that should form the basis of reduction with the quote we recall from Chap. 1:

> Indeed it seems hardly likely that much progress can be made in the solution of the difficult problems relating to chemical combination by assigning in advance definite laws of force between the positive and negative constituents of an atom, and then on the basis of these laws building up mechanical models of the atom. (Lewis 1916, p. 773)

A sense of how rapidly the landscape changed in early quantum chemistry is convincingly obtained by comparing Lewis' opinion on the quantum theory of the atom in 1916 and 1933. The 1933 article starts with:

> It was not long ago that the physical and the chemical pictures of the atom and the molecules seemed almost irreconcilable. Indeed, when the quantum theory was young, it could not be surmised that the development of that strange theory would bring about the reconciliation. Yet the chemist has always assumed, without being fully aware of it, a sort of quantum theory. (Lewis 1933, p. 17)

The difference between these quotes is a mere 17 years, not that long a span of time in the history of science.

Fig. 2.2 Lewis structures for H_2, H_2O, HI and I_2

Another interesting aspect of Lewis' theory is his postulate 2, in which he introduces a distinction in a *kernel* and *outer atom* or *shell*. This arrangement is based on a study of the regularities of the periodic table, but also on the idea that the *outer atom* is essentially correctly described by a cube. The idea of an 'outer atom' (or 'valence shell') has survived in significant measure in chemistry even after the advent of quantum theory, as we shall see in our discussion of the periodic table in Chap. 8.

In terms of the chemical bond, the cubical model of the atom provides an explanation for the chemical valence numbers if we assume that it is the outer atom that is responsible for the valence and that the kernel is relatively inert. Postulate 4 specifies that the atomic shells are interpenetrable, and hence that electrons can 'move' from one shell to the other when a bond is formed.

In the 1916 paper Lewis discusses a number of mechanical approaches to the inner structure of the atom (the technical details of which are of less interest here). It is interesting to note, as we did on p. 31, that Lewis' prescription for how progress in this area could be made is primarily based on chemistry rather than physics as a guiding science. Hence Lewis points to an interesting *programmatic* aspect of the relation between chemistry and physics, arguing that it is possible, or even likely, that chemical theories will provide further clues as to the constitution of the atom.

Much of Lewis' original ideas have survived in modern chemistry. The theory of valence is a key aspect of the chemical theory of bonding. As an example, Coulson (1952) (as reiterated in McWeeny 1979, which is a heavily revised version) states that the minimum requirements of a theory of valence are the following:

1. The theory of valence must show why molecules form at all;
2. The theory of valence must explain not only why molecules form in certain ratios (for instance CO_2), but must also explain the variability of such ratios (for instance the fact that CO forms as well as CO_2);
3. The theory of valence must explain the stereochemistry of molecules.

A good theory of valence should moreover give a *unified* picture of these three aspects, explaining *if* an atom has the power to attach to either itself or to other atoms, it must explain to *how many* and *what type* of atoms it may attach and finally it must explain the geometrical arrangement of the end result.2

2.3 The Quantum Theory of the Chemical Bond: A Rational Reconstruction

The aim of this section is to outline two competing theories of the chemical bond and their potential relationships, using the scheme we discussed in Sect. 1.2.3. To do so, we have to evaluate the theories relative to their respective domains.

The Molecular Orbital (MO) theory had its origin primarily in finding a correct description of the electronic structure of molecules with the purpose of explaining electronic spectra. The theory was more or less suggested first in a paper by Hund (1927), but was worked out more fully in a series of papers by Lennard-Jones (1929) and Mulliken (1928a,b, 1931, 1932), and was formulated perhaps most clearly in Mulliken (1935). However, the list of explananda summed up in Mulliken (1928a) (in the section called ‘Purposes’) hints at a somewhat broader scope, including molecular and chemical stability.

The competing ‘valence bond’ (VB) theory was based on the Heitler and London (1927) calculation for the hydrogen molecule. While the VB theory was initially better suited to explanations in chemistry, the MO theory quickly clocked up a number of successes of its own, such as a convincing explanation of the structure of benzene and aromaticity by Hückel (1931), later developed further by Goeppert-Mayer and Sklar (1938). It is incidentally somewhat doubtful that the theories were still really seen as competing by that time, given that this was three years after the publication of the review paper by Van Vleck and Sherman (1935) which makes it very clear, on p. 171, that the methods are equivalent. Nevertheless, as Brush (1999a,b) has argued, the MO theory only came into its own after the second world war.

The VB and MO approaches to the chemical bond are different, but at the next level of approximation, they lead to the same theoretical description of the chemical bond. This is a quite elementary fact of quantum chemistry that was initially not generally realised, but was well-known in the quantum chemistry community from about the 1940s onward.

Secondly, in the well-known Heitler and London (1927) paper chemical bonding is explained as the effect of electron spin, or the construction of the correct permutation symmetry for the electrons. It is this fact that leads to corresponding symmetries in the spatial wavefunction, not vice versa. In this, the Heitler-London approach (VB approach) differs from the Hund Mulliken (MO approach). Moreover, the VB theory could be extended to cover the concept of valence, as was outlined by London (1928) shortly after.

While this chapter aims to deal with the chemical bond in general, many of the concepts that we wish to illustrate are primarily exhibited in the wavefunction for the simplest molecule, the hydrogen (H_2) molecule. I will therefore restrict myself initially to the hydrogen molecule, and only take into account the lowest level H orbital, the $1s$ orbital.

2.3.1 Two Ways of Constructing the Hydrogen Molecular Wavefunction

1927 was one of those wonder years in the history of science that saw the creation of a new branch of science, in this particular case quantum chemistry. In the same year that saw the appearance of the Born and Oppenheimer paper Heitler and London published their classic paper on the chemical bond. Moreover, as indicated above, Hund also suggested the MO approach to electronic structure. In opposition to the Born and Oppenheimer paper, the Heitler-London approach to the VB wavefunction is still in use in essentially the same form in which it was first introduced, while the Hund approach was later worked out in more detail especially by Mulliken.

Both methods have a common starting point. The bond in the hydrogen molecule, in its simplest form, involves two hydrogen atoms A and B with one electron each. The wavefunctions ϕ_A and ϕ_B of the electrons are labelled (1) and (2). With regards to the effects of spin in the construction of the wavefunction, we note that the ground state wavefunctions discussed here should be combined with a singlet spin function $S(1,2) = 1/\sqrt{2}(\alpha(1)\beta(2) - \alpha(2)\beta(1))$ to give an antisymmetric wavefunction, or a with triplet spin function if the spatial wavefunction is antisymmetric under permutation of the electrons.

2.3.1.1 The VB Theory of the Chemical Bond and Valence

Heitler and London consider the creation of a molecular wavefunction from two individual hydrogen solutions ψ_1 and ϕ_1 (Heitler and London write the electronic coordinate as a subscript). They first consider a wavefunction of the form $\psi_1\phi_2$ and its equivalent $\psi_2\phi_1$ before settling on what is now known as the Heitler-London functions for the hydrogen molecule[3]:

$$\Phi_+ = \frac{1}{\sqrt{2+2S}}(\psi_1\phi_2 + \psi_2\phi_1) \tag{2.1a}$$

$$\Phi_- = \frac{1}{\sqrt{2-2S}}(\psi_1\phi_2 - \psi_2\phi_1) \tag{2.1b}$$

where S is the overlap integral $\langle\psi|\phi\rangle$. It is thus notable that Heitler and London follow what is now common practice in text books of considering both the symmetric and antisymmetric combinations of the wavefunction under permutation symmetry.

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[3] Heitler and London use α and β to designate these functions. This notation is very confusing in the context of modern quantum chemistry, and it is here altered to the more common Φ_+ and Φ_- notation.

The remainder of their paper is mainly the mechanics of working out the energetic terms of the Hamiltonian for these wavefunctions, and they arrive at the expression (which is again immediately recognisable by any recent student of quantum chemistry):

$$E_{\Phi_+} = E_{11} - \frac{E_{11}S - E_{12}}{1+S} \tag{2.2}$$

and

$$E_{\Phi_-} = E_{11} + \frac{E_{11}S - E_{12}}{1-S}. \tag{2.3}$$

They note that the energy curve E_{Φ_-} is always repulsive and corresponds to the van der Waals repulsion (elastic reflection) of the two atoms, while the E_{Φ_+} curve represents chemical bonding.

Perhaps the most interesting conclusion of the Heitler and London paper is drawn when they consider the absence of bonding between two helium atoms, and conclude that this must be due to the Pauli principle, which up to that point had been used in the explanation of atomic spectra, but not (yet) in the theory of chemical bonding. They successfully use the Pauli principle to argue that the only He_2 wavefunction that corresponds to the Pauli principle is the repulsive wavefunction.

A year later, a paper from London (1928) appeared on the homo-polar valence numbers, which provided a theory of *valence*, a chemical concept, on the basis of a theory of the atom. As London states in the introduction to this paper[4]:

> Wenn wirklich die dort berechneten Effekte die bekannten chemischen Tatsachen *ihrem Wesen nach* – und nicht nur als Resultate langerer Rechnungen – erfassen sollten, so wird man wünschen, die begrifflichen Wesenheiten, welche in der Chemie auch in komplizierten Fällen als Führer durch die Männigfaltigkeit der möglichen Verbindungen sich bewahrt haben, auch in der quantenmechanischen Beschreibung vorzufinden und sie im Zusammenhang mit der Struktur der Atome zu sehen. (London 1928, p. 31)[5]

This paper then goes on to discuss the symmetry properties of multi-atomic systems on the basis of spin symmetry and the Pauli principle. The Pauli principle states that a wavefunction Φ which describes the state of an N-electron system is antisymmetric under permutation of two electrons. London derives the following rules:

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[4] It is also worth while noting here that permutation symmetry arguments of this nature were revived in the late 1960s and early 1970s by Matsen, Pauncz and others in the so-called spin-free quantum chemistry.

[5] A translation of this quote reads:

> If the effects calculated there really grasp the known chemical facts *in their nature* – and not merely as the result of lengthy calculations – we may then wish to find the concepts of chemistry, which have been stable guides to the manifold of possible compounds even in complicated cases, in the quantum mechanical description as well and establish their connection with the structure of atoms.

The translation I provided earlier in Hettema (2000) on p. 156 (erroneously) leaves out the clause on the role of chemical principles and is hard to read.

1. A single electron that is not ‘paired’ with another electron represents an available ‘free homo-polar valence’;
2. A free valence which has been *saturated* by a corresponding free valence of another atom is no longer available for further bonding;
3. Electrons that are already in an electron pair with other electrons in an atom are not available for the formation of homo-polar bonds;
4. Valence electrons have symmetric spin functions and antisymmetric spatial functions (under permutation symmetry).

London then goes on to discuss the valence of the noble gases, halogens, oxygen, nitrogen and carbon atoms. The last section of the paper discusses a limit case between homo-polar and polar binding, or, in modern language, covalent and ionic bonds.

2.3.1.2 Molecular Spectra and MO Theory

In the same year, Friedrich Hund started a series of papers in which he attempted to interpret molecular spectra using an explanatory apparatus very similar to the interpretation of atomic spectra with quantum theory. Hund’s view of molecular spectra is based on two key elements: the first is the concept of a ‘molecular orbital’ (a molecular counterpart to the atomic orbital from atomic quantum theory) and the second are the ‘selection rules’ which govern the intensities of the transitions.

Hund and Mulliken’s theory gave rise to a competing view (the Molecular Orbital theory or MO theory) on the chemical bond. One of the key aspects of the MO theory is that it is an extension of the atomic orbital theory in which the molecular orbital spans the entire molecule. In this sense, the MO theory is primarily a theory of *electronic structure*. The orbitals for a molecule are classified as bonding or antibonding, and the chemical bond is understood in terms of an *Aufbau* of these bonding and antibonding orbitals (where bonding and antibonding orbitals are progressively populated with electrons following the Pauli principle). In the MO-LCAO approach the Molecular Orbitals are written as Linear Combinations (LC) of Atomic Orbitals (AO).

For instance, for the H_2 molecule, the molecular orbitals are constructed as the following linear combinations:

$$\phi_b = N_b(\phi_A + \phi_B) \tag{2.4a}$$

$$\phi_a = N_a(\phi_A - \phi_B) \tag{2.4b}$$

where N_a and N_b are normalisation constants and the ‘bonding’ wavefunction becomes

$$\Phi_b(1,2) = (\phi_A + \phi_B)(1)(\phi_A + \phi_B)(2), \tag{2.5}$$

which corresponds to a doubly occupied ‘bonding’ orbital ϕ_b.[6]

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[6] This should be combined with the singlet spin function $S(1,2) = 1/\sqrt{2}(\alpha(1)\beta(2) - \alpha(2)\beta(1))$ to give an antisymmetric wavefunction.

The MO approach, as was shown by Hückel (1931), was a useful model for understanding for instance the theory of aromaticity, but it was difficult to reconcile with the directional theory of the chemical bond, or with the Lewis electron pair theory.

One of the major advantages of the MO theory was its computational feasibility and scalability. Using the methods developed by Roothaan (1951) and Hall (1951) the MO approach could lend itself to a fairly straightforward computational scheme that could tackle small and large molecules with relative ease. Hence, as will be explained in more detail below, the MO theory has developed into the dominant computational approach in comparison to its rival, the VB theory.

2.3.1.3 Equivalence: Comparing the Wavefunctions

This subsection discusses some further ways of developing the VB and MO wavefunctions for the hydrogen (H_2) molecule.[7]

The Valence Bond (VB) method focuses on providing an explanation of covalent (or homo-polar) molecule formation. The specific goal of Heitler and London (1927) is a correct description of the potential energy curve for both a H-H system (which has a covalent bond) and a He-He system (which does not have a chemical bond). Their total two-electron wavefunction is distributed across two atomic centres, and made up of the linear combinations (where we have ignored normalisation of the wavefunctions, and write the electron coordinate in brackets instead of as a subscript):

$$\Phi_{VB}(1,2) = [\phi_A(1)\phi_B(2) \pm \phi_A(2)\phi_B(1)] \tag{2.6}$$

(Eq. 4a in Heitler and London 1927). Working out the equations for the energies in this model, Heitler and London find that they obtain a bonding curve which corresponds to the '$+$'-sign in the equation above and an overall repulsive curve which corresponds to the '$-$'-sign as discussed above. The bonding wavefunction corresponds to one where the electrons are in a singlet wavefunction with the singlet spin function. The *spatial* wavefunction $\Phi(1,2)$ has to be symmetric under permutation of electrons (1) and (2), or $\Phi(1,2) = \Phi(2,1)$, which is the key criterion that Heitler and London employ in their further discussion of covalent bonding.

In the MO approach, which is the basis of mainstream ab initio quantum chemistry, the 'bonding' wavefunction for the hydrogen atom is written instead as a doubly occupied 'molecular orbital' (MO) of the form $(\phi_A + \phi_B)$, as given before:

$$\Phi_b(1,2) = (\phi_A + \phi_B)(1)(\phi_A + \phi_B)(2). \tag{2.7}$$

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[7] We will not discuss the construction in terms of Hylleraas functions or other modifications to the wavefunctions. This approach pioneered by Egil A. Hylleraas (1929) is in my opinion undeservedly neglected in the philosophical literature on the chemical bond, a gap that one can only hope will be filled one day.

This expression is not equivalent to the Heitler-London wavefunction above. We see this more easily if we expand the MO wavefunction to give

$$\Phi_b(1,2) = \phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1) + \phi_A(1)\phi_A(2) + \phi_B(1)\phi_B(2). \tag{2.8}$$

The MO wavefunction contains two additional terms, which describe 'ionic' states of the system. As a result of the construction of the wavefunction, these ionic terms have equal weight in the MO wavefunction, while they are lacking entirely in the VB wavefunction.

This simple fact represents a heuristic for the improvement of both methods. What is lacking in the VB description of the hydrogen molecule is an inclusion of the 'ionic' states, even though it can be expected that these will not be present with equal weight. An improved VB wavefunction thus becomes

$$\Phi_{VB}(1,2) = \phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1) + \lambda\left[\phi_A(1)\phi_A(2) + \phi_B(1)\phi_B(2)\right]. \tag{2.9}$$

Similarly, the MO method focusing on the bonding wavefunction alone is not a complete description either. Notably, what it lacks is the interaction with an 'antibonding' wavefunction of the form

$$\Phi_a(1,2) = (\phi_A - \phi_B)(1)(\phi_A - \phi_B)(2). \tag{2.10}$$

A further refinement of the description of the chemical bond can be achieved if we consider 'configuration interaction' (CI) between this antibonding wavefunction and the bonding wavefunction:

$$\Phi_{CI} = \Phi_b + k\Phi_a. \tag{2.11}$$

We can again write out this wavefunction in terms of constituent atomic orbitals, and find that the CI and improved VB functions are equivalent if

$$\lambda = \frac{1+k}{1-k}. \tag{2.12}$$

It should be noted that this equivalence also holds for more complicated wavefunctions. If one would have to put a date on the first recognition of this fact, than the important review paper on valence and the chemical bond by Van Vleck and Sherman (1935) would be a close enough choice. They already concluded that:

> Clearly, it becomes meaningless quibbling to argue which of the two methods is better in refined forms since they ultimately merge. In fact, they may be regarded as simply two starting points of a perturbation calculation, corresponding to different choices of unperturbed wavefunction. (Van Vleck and Sherman 1935, p. 171)

Thus, by the mid 1930s the equivalence of the two theories was recognised, though how widely is a point that remains to be seen. A similar conclusion is drawn by McWeeny (1979) in his reworking of Coulson's '*Valence*':

> There is thus no real conflict between MO and VB theories; they offer somewhat different first approximations to molecular wavefunctions but converge to the same results as they are systematically refined. The importance of this conclusion can hardly be overemphasized. (McWeeny 1979 p. 126)

2.3.2 Amendments: A Sort of Quantum Theory

The chemist's idea of the chemical bond has been shaped in significant degree by the electron pair concept of Lewis (1916). Hence early in the development of the quantum theory of the chemical bond, a number of theoretical developments sought to address the issue of how the quantum theory of the chemical bond might account for localised electron pairs, which correspond better to the intuitive picture of directed bonds.

The most important ones of these were the method of *hybridisation* as developed by Pauling (1928, 1931) and Slater (1931a), and the method of *localisation* of molecular orbitals, as developed by Lennard-Jones (1949a,b).

The hybridisation approach implements a valence bond type structure on the notion of 'hybrid' orbitals for many-electron atoms where for instance *s*- and *p*-orbitals mix to give a directional 'lobe' which in turn becomes part of a VB wavefunction. The localisation approach 'localises' the molecular orbitals so as to 'read' an electron pair into a set of delocalised molecular orbitals. We discuss these methods in more detail below.

Both approaches are ways of *adapting* the quantum theoretical model of the chemical bond to adapt to the notion of 'directed valence' on which Lewis' theory of the electron pair was constructed, and so to overcome Lewis' original problems with the 'laws of force' and the development of his 'sort of quantum theory' (p. 31, footnote).

2.3.2.1 Pauling and Slater's Model of Hybridisation

Pauling and Slater's method of hybridisation was developed in Pauling (1928) and Slater (1931a). This method builds on the Heitler and London (1927) method in that it generalises the conclusions drawn for the bond in the hydrogen molecule, and use these to build up a new set of atomic orbitals that is adapted to the local symmetry of the atom.

Pauling's theory is quite easy to follow, and no detailed discussion needs to be given, except for a brief statement of the principles on which he constructs the method of hybridisation. In particular, the basis on which Pauling constructs the model of hybridisation is an 'electron pair' notion with the following properties:

1. The electron-pair bond is formed through the interaction of an unpaired electron on each of two atoms.

> 2. The spins of the electrons are opposed when the bond is formed, so that they cannot contribute to the paramagnetic susceptibility of the substance.
> 3. Two electrons which form a shared pair cannot take part in forming additional pairs. (Pauling 1931, p. 1368)

as well as the following rules (for which Pauling provides a rationale in a long footnote):

> 4. The main resonance terms for a single electron-pair bond are those involving only one eigenfunction from each atom.
> 5. Of two eigenfunctions with the same dependence on r, the one with the larger value in the bond direction will give rise to the stronger bond, and for a given eigenfunction the bond will tend to be formed in the direction with the largest value of the eigenfunction.
> 6. Of two eigenfunctions with the same dependence on θ and φ, the one with the smaller mean value of r, that is, the one corresponding to the lower energy level for the atom, will give rise to the stronger bond. (Pauling 1931, p. 1369)

This set of rules becomes a powerful tool in the explanation of the chemical bond for, for instance, atoms with s and p electrons. Pauling notes that when rules 4–6 are used in the case of water, for instance, the predicted bond angle will be 90°:

> [...] or somewhat larger because of interaction of the two hydrogen atoms. It has been long known from their large electric moment that water molecules have a kinked rather than a collinear arrangement of their atoms, and attempts have been made to explain this with rather unsatisfactory calculations based on an ionic structure with strong polarization of the oxygen anion in the field of the protons. The above simple explanation results directly from the reasonable assumption of an electronpair bond structure and the properties of tesseral harmonics. (Pauling 1931, p. 1371)

As a next step, Pauling introduces the same 'ionic' refinements that were introduced in the case of the hydrogen molecule, but probably the most well-known application of the concept of hybridisation is the explanation of the tetrahedric structure of the central carbon atom in methane, which was first given in Pauling (1928).

To construct the wavefunction for the central carbon atom, Pauling mixes the s and p wavefunctions as follows:

$$\left.\begin{aligned}\psi_1 &= a_1 s + b_1 p_x + c_1 p_y + d_1 p_z\\ \psi_2 &= a_2 s + b_2 p_x + c_2 p_y + d_2 p_z\\ \psi_3 &= a_3 s + b_3 p_x + c_3 p_y + d_3 p_z\\ \psi_4 &= a_4 s + b_4 p_x + c_4 p_y + d_4 p_z.\end{aligned}\right\} \tag{2.13}$$

Following rule 5, the best bond eigenfunction will be that which has a maximum in the direction of the bond. For instance, a bond with the maximum in the x direction is

$$\psi_1 = \frac{1}{2}s + \frac{\sqrt{3}}{2}p_x. \tag{2.14}$$

The remainder of the bonds can then be chosen, with the second bond in the xz plane, and the later expressions become increasingly fixed by the orthonormality conditions on the coefficients. The four orbitals constructed in this way have single 'lobes' that point in the directions of a tetrahedron. Similar considerations lead to constructions for double and triple bonds.

The contentious issue in this theory is the mixing of the *s*- and *p*-orbitals. Pauling's rationale for this step is that the energy gained in forming the bond will be larger than the energy required to perform the mixing of the orbitals, in particular:

> In the case of some elements of the first row the interchange energy resulting from the formation of shared electron bonds is large enough to change the quantization, destroying the two sub-shells with $l = 0$ and $l = 1$ of the *L*-shell. Whether this will or will not occur depends largely on the separation of the *s*-level ($l = 0$) and the *p*-level ($l = 1$) of the atom under consideration; this separation is very much smaller for boron, carbon, and nitrogen than for oxygen and fluorine or their ions, and as a result the quantization can be changed for the first three elements but not for the other two. (Pauling 1928, p. 361)

A large part of the success of Pauling's theory of the chemical bond was that it afforded a direct and intuitive view on molecular structure and molecular stability, and was in agreement with Lewis' (1916) concept of the atom, in which 'electron pairs' were responsible for chemical bonding.

Pauling argued that these electron pairs were the end result of pairings of electron spin (essentially in a singlet spin function). Hence the theory uses the concept of 'electron pairs' derived from the Heitler-London conception of the molecular bond, and the molecular wavefunctions are constructed on the basis of hybrid orbitals following the VB method.

The consequence of this is that Pauling's method, while guided by the findings of Heitler and London (1927) is most fruitfully classified as an extension of VB theory to complex atoms. It is also notable that the consideration of the ionic states enters into Pauling's argument where he discusses the transition between ionic and covalent bonds. The energetic refinements that have been so important in later day quantum chemistry are however absent.

These two observations suggest that Pauling's theory from the outset was intended to provide a qualitative, rather than quantitative view of the bond, in which a rationale could be provided for the explanation of the structural conception of the chemical bond.

2.3.2.2 Localisation of Molecular Orbitals

Molecular orbitals are in many cases distributed across the entire molecule. Hence the model was well suited to the explanation of aromatic systems, in which the orbitals are distributed, but there was an apparent clash with the notion of directed bonds such as are thought to occur in many organic molecules. Pauling's hybridisation model mixed the atomic orbitals at the atomic level, and then recombined them into 'bonding pair' orbitals. Thus Pauling's model does not provide an equivalent electron pair scheme for the MO method.

Lennard-Jones (1949a,b) proposed a method of 'equivalent orbitals' which were capable of providing an 'electron pair' picture from a linear combination of occupied molecular orbitals. This procedure rests on the symmetry properties of the occupied MOs, allowing linear combinations of occupied MOs so that 'localised' electron pairs are obtained. Replacing the occupied MOs with linear combinations

Table 2.2 Transformation of 'equivalent' orbitals under the symmetry group C_{2v} (From Lennard-Jones 1949a, p. 11)

C_{2v}	E	C_2	σ_v	σ_v'
χ_1	χ_1	χ_2	χ_1	χ_2
χ_2	χ_2	χ_1	χ_2	χ_1
(χ_1, χ_2)	2	0	2	0

of occupied orbitals leaves the energy expression invariant. The 'equivalent orbitals' obtained in this way are 'identical as regards their distribution and differ only in their orientation' (Lennard-Jones 1949a, p. 2).

Equivalent orbitals are equivalent from the viewpoint of the symmetry group of the molecule; Lennard-Jones discusses the case of a C_{2v} symmetry, and notes that 'equivalent' orbitals may transform as given in Table 2.2. Lennard-Jones then notes that these equivalent orbitals can be constructed from a set of occupied molecular orbitals ψ_1 and ψ_2 which transform as the irreducible representations A_1 and B_1 respectively by the following construction:

$$\chi_1 = \frac{1}{\sqrt{2}}(\psi_1 + \psi_2) \tag{2.15a}$$

$$\chi_2 = \frac{1}{\sqrt{2}}(\psi_1 - \psi_2). \tag{2.15b}$$

Of course, the orbitals χ_1 and χ_2 do not transform as the irreducible representations of C_{2v}.

The explanation of the chemical bond with quantum theory has thus given rise to a constellation of various laws and theories, which exhibits interesting properties for further study in philosophy of science. In the next section we will focus on reduction, idealisation and concretisation.

2.4 Idealisation, Concretisation and Reduction

The idea of an *idealisation* of a theory, roughly is that an approximate theory is constructed in which some terms are set to zero.[8] The idea of a *concretisation* of a theory is the opposite: terms are added to the theoretical description. The MO and VB models of the chemical bond each have refinements that allow us to conclude that a scheme of *idealisation* and *concretisation* is at work.

In terms of this model, both theories are potential idealisations in the sense that they are explicitly based on wavefunctions known to be approximate and

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[8] The idea of idealisation and concretisation has been discussed in more detail in Nowak (1980) and Kuipers (2000). The theories of the chemical bond form an interesting potential idealisation/concretisation pair.

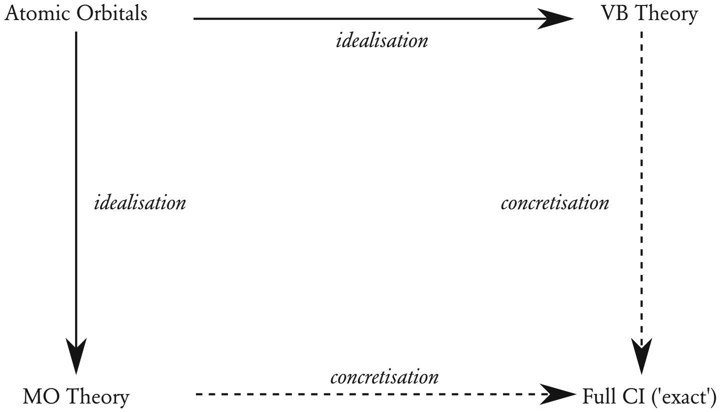

Fig. 2.3 Domain and Theory relationships for the explanation of the chemical bond. The theoretisation/concretisation relationships unify the underlying domains

incomplete. By the mid 1930s, as the article of Van Vleck and Sherman (1935) illustrates, it was well-known exactly *what* was wrong with the respective theories.[9]

Similarly, the systematic improvements of both the VB and MO theories can be seen as potential concretisations, both of which, incidentally, lead to the same theoretical description of a molecular wavefunction. In the case of the VB wavefunction this is the addition of 'ionic' states, in the case of the MO wavefunction it is the introduction of the anti-bonding wavefunction in a configuration interaction expansion. Both these refinements are not, it would seem, primarily driven by chemical (i.e. external) considerations but are integral to the conception that the VB and MO wavefunction are idealised starting points to a more comprehensive description of the chemical bond.[10]

Provided all the formal requirements can be met, the two theories have an interesting idealisation/concretisation picture, as depicted in Fig. 2.3, where the solid lines represent an idealisation step which constructs (idealised) molecular

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[9] This point is made explicitly by Van Vleck and Sherman (1935) on p. 170 and 171 of their article, where they compare the MO and VB (called the H-L-S-P – after Heitler, London, Slater and Pauling – method.).

[10] The methods are also complementary in the sense that they suggest improvements on one another. A possible improvement on the VB wavefunction is to 'add' the ionic states to the wavefunction, more or less in line with the chemical intuition that an (admittedly small) portion of the complete bond in H_2 is given by the ionic bond H^+H^-.

wavefunctions from ‘atomic orbitals’, where the subsequent concretisation steps are represented as dashed lines.[11] For the purposes of the idealisation and concretisation step, we may treat the full CI wavefunction as the ‘exact’ wavefunction.

Thus, intuitively, both the MO and VB wavefunctions are first steps towards a theory of the chemical bond in terms of an idealisation/concretisation pair of the type $\mathrm{Con}(T, T_c)$ where T_c is a concretisation of T. As Kuipers (2000) notes, it is a requirement that T and T_c have the same domain-sets.

This is the case here: the two competing notions of the chemical bond originated primarily because they were intended to ‘target’ two different explanatory domains with the help of explicit wavefunction constructions. In the case of the VB theory that was the theory of valence, while in the case of the MO theory its primary target was molecular spectroscopy. Pauling’s theory of the chemical bond was aimed at providing an explanation for the *structural* concept of the chemical bond, and was similarly tied to a specific domain.

Over time, the MO and VB theories came to be seen as different aspects of a single larger theory, and hence the domains merged into a larger entity, one which Spector (1978) has called (with a not very attractive term) ‘micro-physics-atomic theory plus quantum mechanics’ (Spector 1978, p. 99).

2.4.1 Domains of the ‘Chemical Bond’

The ‘chemical bond’ itself is an open-ended concept. One of the reasons for the confusion is the fact that there are many explanatory domains involved[12]. Some examples of ‘domains’ for the chemical bond (some trivial and some less so) follow below[13]:

1. We can think of the chemical bond as the ‘stick’ between the balls representing atoms featuring in the ball and stick models that many still associate with chemistry. At this level, the chemical bond has length and direction and the potential for torsion (rotation around the bond). Torsional motion is generally displayed in single bonds, but not in double or triple bonds.

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[11] Even while all three wavefunctions described above can describe the chemical bond, they do not do so with equal accuracy. In particular, the simplest MO-LCAO single-determinant wavefunction is not capable of describing the separation of the chemical bond correctly. In the limit where the two hydrogen atoms are very far apart the single-determinant MO-LCAO wavefunction (i.e. a wavefunction without CI) leads to an ‘overweight’ factor for the ionic states which in turn leads to a wrong prediction for the dissociation energy.

[12] In this reconstruction, the domains themselves form some sort of theory, though of an immature type: both spectroscopy and the theory of valence are useful *systematisations* of a set of phenomena, though not strong enough to form empirical laws (like the ideal gas law for instance).

[13] This scheme extends that of Hendry (2008), who argues for the existence of the ‘structural’ and ‘energetic’ view.

2. A second notion is to think of the chemical bond in term of Lewis electron pairs, thus giving a mechanistic model underpinning to the theory of valence. Typically, while Lewis bonds can be double or triple, the Lewis model does not lead to concepts of direction or distance.
3. A third notion is to think of the chemical bond in energetic terms, and of bonding as 'minimum' on a potential energy curve, which supports concepts such as dissociation energy, spectroscopy, vibrational motion and bond length.
4. A fourth notion is to think of a chemical bond as a charge distribution which is localised in a particular area of space, and has a particular topology.

All of these notions are in a sense competing but also share characteristics: for instance the idea of bond having the property of 'length' is supported both by the 'ball and stick' model as well as the 'potential energy curve', but not by the 'charge distribution' concept of the chemical bond.

My proposal is that these varied descriptions can be ordered into domains $\mathscr{D}$, where each domain captures an aspect of the chemical bond. The entire domain of the chemical bond can then be written as

$$\mathscr{D} = \bigcup \{\mathscr{D}_i\} \tag{2.16}$$

The question still remains how to partition the domain $\mathscr{D}$ in sub-domains. The only principled requirement that can be put on the total domain is the global requirement of consistency and this does not leave much to go on in deciding how to partition the domain into sub-domains.

An operational division is possible, however, based on Nagel's (1961) theory of reduction. In derivational reduction schemes, one of Nagel's requirements is that the theory to be reduced is well formulated and available as explicitly formulated statements. Concepts such as the 'chemical bond' do not, *in toto*, fulfil this requirement, while a suitably chosen domain $\mathscr{D}_i$, such as for instance a theory of valence or spectroscopy, does.

It would thus seem that there is considerable latitude in deciding how to partition a domain, and that the details of that decision are determined more by operational and explanatory requirements rather than principled arguments.

I will now turn to the question on how this model can explain some of the issues with respect to reduction that have been prevalent in the philosophy of chemistry.

2.4.2 Explaining the Chemical Bond with Multiple Domains: A Case of Reduction

We are now in a position to formulate a specific proposal for how the theories of the chemical bond are related to their domains and to each other. The proposal that I will advance hinges on the concept of multiple domains as well as on the notion of idealisation and concretisation of scientific theories and it will employ the reduction

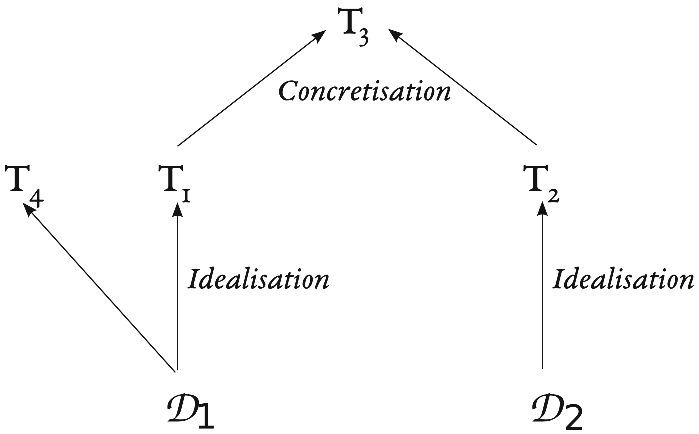

Fig. 2.4 Domain and theory relationships for the explanation of the chemical bond. The theoretisation/concretisation relationships unify the underlying domains

Table 2.3 Theories of the chemical bond and their domains

Symbol	Description
$\mathcal{D}_1$	Chemical valence and Lewis theory
$\mathcal{D}_2$	Molecular spectroscopy and electronic structure
T_1	Heitler-London or Valence Bond (VB) theory
T_2	Hund-Mulliken or Molecular Orbital (MO) theory
T_3	'Exact': Molecular Orbital and configuration interaction or Valence Bond plus 'ionic' structures
T_4	Pauling model of hybridisation

concept of Sect. 1.2.3. Specifically, I believe that this proposal has the capability to significantly clarify a relevant subset of the current debates in philosophy of chemistry, especially where non-derivability of chemical concepts from physical concepts is concerned.

The structure of the multiple domain explanation that I wish to explore is presented in Fig. 2.4, with an explanation of terms given in Table 2.3.

The first domain-set that I will consider is the domain of chemical valence and the corresponding Heitler-London theory of the chemical bond. From the viewpoint of the Heitler and London paper, the particularly relevant questions revolve around (i) chemical bonding between neutral atoms (with ionic bonding relatively well understood in electrostatic terms), and (ii) the question why chemical bonding between two hydrogen atoms was possible while at the same time such chemical bonding does not occur between two helium atoms (The statement of these problems are given in the introduction to the Heitler and London 1927 paper). In addition, London subsequently published a follow up paper in 1927 dealing with the problem of chemical valence on the basis of the calculations he undertook with Heitler earlier that year.

From the viewpoint of the MO (Hund Mulliken) approach, the primary domain-set was initially the qualitative explanation of molecular spectra (see for instance Hund 1927). This problem is primarily driven by orbital symmetries, since explanation of spectra depends on selection rules that specify which molecular electronic transitions have the right symmetry. It is little surprise, therefore, that Hund's series of papers on molecular spectra start from the concept of a 'bonding' and 'anti-bonding' orbital (even though Hund does not use those particular terms), and arrives at these two types of orbitals by considering two limit cases of atoms at infinite and infinitesimally small distance.

Hence the two competing theories of the 'chemical bond' were originally developed with two different explanatory domains in mind, and accidentally also spanning both the disciplines of chemistry and physics. As is noted in Nye (1993), for the physicist, the more natural approach was that of Hund, even though Hund's method does not lead in a natural way to the development of valence nor lent itself to a visual explanation of aromaticity, a point which is also explored in Brush (1999a,b) as an important, if not major, contributing factor to the initial popularity of the VB approach.

The need to explain 'electron pairs' also led to a separate class of theories – that of Slater and Pauling – based on a different idealisation.

The explanatory structure of the chemical bond can thus be captured in the diagram in Fig. 2.4 with the interpretation supplied in Table 2.3: the consideration of atomic valence leads primarily to the notion of an 'electron pair' and the 'valence bond' or Slater Pauling approach to the description of the molecular bond; while the consideration of spectroscopy leads in the first instance to the molecular orbital approach.

It is also clear, that on the basis of the model for reduction sketched in Sect. 1.2.3, the connections between T_3 and T_1, as well as between T_3 and T_2 are cases of reduction: by fixing certain parameters in the total molecular wavefunction expansion in T_3 we trivially obtain either T_2 or T_1. We thus have an interesting case of a complex network of theories which are connected through instances of idealisation, concretisation as well as reduction.

2.4.3 Consequences

The model outlined above can in my view provide an adequate representation of, for instance, Woody's (2000) claim that quantum chemical programs have difficulties relating to the conceptual notions of the 'bench chemist' (even though one could well argue that she overstates that case), and are capable of providing only 'token' type reductions of chemical concepts (i.e. numerically accurate representations) while there is something 'systematically, and more generally, wrong with reductive accounts of untethered relations such that they cannot capture meaningfully the connections between chemistry and quantum mechanics' (Woody 2000, p. S619). It would seem that reductive accounts *can* capture such relations, but that this is a multi-step affair: idealised models fare better than idealised/concretised models in providing a *qualitative* description of what constitutes a chemical bond in both the bonding aspect as well as qualitative discussions of the molecular spectra, while a *quantitative* treatment requires suitably concretised models.

Similarly, the model can clarify Weisberg's (2008) notion that increasingly refined models in quantum chemistry can put 'pressure' on various concepts of the chemical bond: it is indeed not clear at the outset that a theory that operates at the level of molecular orbitals can provide an 'unpressured' representation of electron pairs and localised charge densities between nuclear centres: it is not at the outset designed to do so. VB theories are however designed for that purpose, and work well in that particular sub-field.

Finally, the above description clarifies the notion of 'interdisciplinarity' that is inherent in Harris' (2008) description of the historical development of the chemical bond: the interdisciplinarity consists of a domain join, ultimately bridged by a suitable theory that glues the two domains together. This suitable theory plays the role of an 'interfield' theory in the sense of Darden and Maull (1977).

With the benefit of hindsight, both approaches have survived as valid approaches to the chemical bond in their own right, and both approaches are still actively used by quantum chemists.[14] It thus seems that neither explanation has been able to 'exclude' the other.

2.5 Conclusion

The case of the chemical bond provides an interesting example of a potential idealisation/concretisation pair, which creates a more complex theory net – a constellation of interrelated approaches. In the remainder of Part I we will see that such situations are the norm rather than the exception in chemistry.

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[14] It would be fair to say that the VB method is significantly less popular than the MO approach. The VB method works with a (non-orthogonal) set of base atomic orbitals (AOs) which significantly complicates technical implementation of the method for larger molecules. An aanalogous case could be made for Density Functional Theory, which found its origins in an as yet unexplored domain: the electronic structure of the solid state. This theory is now one of the more popular quantum chemical methods, although this case is not discussed in detail in this chapter.

Chapter 3
Molecular Structure: What Philosophers Got Wrong

Abstract The problems with the Born-Oppenheimer approximation have long been seen by the philosophy of chemistry community as indicative for the irreducibility of chemistry to physics. In this chapter I focus on this confusing discussion. The 'derivation' of molecular structure provided by the Born-Oppenheimer approximation is not 'smooth' and critically relies on a number of steps that are questionable. Yet to conclude from this that molecular structure is irreducible, as some philosophers have done, is going too far. This problem is largely unsettled in both its technical detail as well as its philosophical justification, and in this chapter I provide an overview of which questions are relevant to progress further research in this area.

3.1 Introduction

Molecular structure and molecular shape have been the topic of quite a few papers on quantum chemical explanation, reduction and emergence in the philosophy of chemistry. As topics go, this one is particularly messy. The idea of molecular structure and molecular shape are key concepts of chemistry that are difficult to reconcile with a principled form of quantum theory, whereas quantum theory itself is a theory that suffers from significant foundational problems.

The main difficulty lies in the fact that common concepts of explanation and reduction generally involve a notion of derivation and it is hard to see how molecular shape can be directly derived from quantum theory. Usually, the argument is that molecular shape cannot be reductively explained with the help of quantum theory, since the 'clamped nucleus' approximation that lies at the core of many quantum chemical calculations is not *derivable* from the Schrödinger equation but rather is *imposed* on it by use of the Born-Oppenheimer (BO) approximation from the outset.

A stronger version of the argument is that the notion of a fixed molecular shape may even be *irreconcilable* with principled quantum mechanics, since in general the clamped nucleus Hamiltonian is of lower symmetry than the full Coulomb Hamiltonian[1] and lacks a large number of its principal features. Especially, the fact

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[1] In this chapter I will follow the usual practice of referring to the 'full' (or 'all singing all dancing' as Brian Sutcliffe liked to call it at a summer school I visited a long time ago) molecular Hamiltonian with the neutral term 'Coulomb Hamiltonian'. Note that this is not a

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that nuclei are quantum mechanical particles too, and hence need wavefunctions of their own that obey the required permutation symmetries, is abandoned in the clamped nucleus approximation.

As it stands this story is a little too smooth. Too much of the literature in the philosophy of chemistry has taken the problems associated with the Born-Oppenheimer approximation as a given and too little work has been performed critically evaluating these problems. To cut a very long story very short indeed: the problem of molecular shape is currently unsettled, but (perhaps) not unsolvable. Moreover, there is a tendency in the philosophical literature on this problem to entirely ignore the more recent scientific approaches that have been developed and stick with the papers from the 1970s and 1980s instead – even though later work cannot claim to have solved the problem, progress has been made. For these reasons, as it stands, the potted critique against molecular shape is less than robust. I will contend in this chapter that its failings are manifold.

(1) Firstly, a case *can* to some degree be made for the justification of various approximations on which quantum chemists have traditionally relied, even though the argument is far from simple and to a significant degree still the subject of active research. The point is that while significant philosophical conclusions have been cashed out from the problems associated with the Born-Oppenheimer approximation, the structure and nature of these problems are often not well understood. At the flip side of this coin, a robust *philosophical* study of the potential explanations that are enabled by the Born-Oppenheimer approximation has not been undertaken, notwithstanding a copious amount of writing on the topic. Similarly, attempts to more rigorously define the mathematics of the Born-Oppenheimer approximation, such as for instance those by Combes et al. (1981), or quite detailed discussions of the issues such as for instance the discussion by Woolley and Sutcliffe (2003) or Sutcliffe (2012) have not yet influenced the philosophy of chemistry in significant measure.

(2) Secondly, and possibly more importantly, the present discussions have not at all considered more modern principled definitions of a 'molecule' such as for instance the one of Löwdin (1988). Instead they focused on the unrelated issue of molecular *shape* or geometry as a hallmark of 'molecule-ness'. Löwdin's definition of a molecule is robust from a quantum theoretical point of view, but difficult to reconcile with the notion of molecular shape.[2] Interesting new work in this area has been done by Sutcliffe (2002, 2008) and the difficulties faced by Löwdin's approach have been discussed extensively by Woolley and Sutcliffe (2003). The preliminary conclusion that can be drawn is that

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'clamped nucleus' Hamiltonian, but rather a full system Hamiltonian with only Coulomb forces as interactions between the particles. The nuclei are treated dynamically in this approach.

[2] Recalling our discussion on the possible interpretations from the previous chapter, one could argue that the 'shape' notion is based primarily on a 'structural' conception of bonding (though, as we will see in this chapter, how this is supposed to work precisely is still an interesting problem), while Löwdin's notion of a molecule is based on an energetic view of the bonding.

if one is looking for a *derivation* of molecular structure from the Coulomb Hamiltonian Löwdin's definition of a molecule is a much better starting point than the Born-Oppenheimer approximation, since it is more principled, although the difficulties are significant and perhaps insurmountable. Löwdin's notion suggests that quantum mechanics formally *may* yet yield the sort of results that quantum chemists informally ascribe to it, though how it does that exactly is a bit of a puzzle.

(3) This still leaves open the question whether molecular *shape* really ought to be one of the focal points of the reduction of chemistry to physics. In Chap. 2 we have argued that the geometrical/energetic view of the chemical bond is only one of the pictures of the bond used in chemistry. Some quantum chemists have taken the rival structural approach as a starting point. From the viewpoint of a density view of bonding, Bader (1990) proposes that we relax the notion of a molecular shape from a rigid molecular frame, and rather characterise a 'chemical' *structure* of *bonds* in terms of an open region of nuclear configuration space (see Bader 1990, p. 55 for instance), which is characterised by molecular graphs in terms of bond paths.

In this chapter, I will argue that the topology of the bonds cannot be ignored as a part of the discussion on molecular structure. The idea that *chemical structure* rather than *molecular shape* is a viable alternative reading of structure for chemists suggests that focusing on molecular *shape* may be too strong a requirement for a claimed reduction and over-determines the reduction problem. Rather than the derivation of molecular *shape* a derivation of a bond topology or chemical *structure* may be all that is required for the reduction relation to be viable. Even though the calculation of the bond topology still *does* rely on the Born-Oppenheimer Hamiltonian, it is not a unique dependence in the sense that a 'region' rather than a 'point' is associated with chemical structure.

(4) Lastly, the argument from molecular shape against inter-theoretic reduction of chemistry to physics misunderstands the notion of reduction. Usually, reduction is taken as the austere version Nagelian reduction, which reads connectibility in terms of identities and derivability as strict. This, as has been argued in Chap. 1, is a misreading of Nagel that puts the bar on reduction unachievably high.

No philosophically rigorous *rational reconstructions* have so far been available for explanations utilising the Born-Oppenheimer approximation. The focus of these reconstructions should be what quantum chemists actually *do* when they introduce the Born-Oppenheimer approximation into their calculations. This chapter will make three specific, though highly interrelated proposals for such a reconstruction.

1. One philosophical approach is suggested by Nancy Cartwright (1983) in what she terms 'theory entry'. The Born-Oppenheimer approximation functions as the first step in theory entry in the sense that it specifies 'the right kind of equation', it 'prepares' the phenomenon (chemistry) to 'enter' into quantum theory (and hence the quantum theory becomes 'quantum chemistry' in the process).
2. A second philosophical approach is suggested by a moderate theory of reduction itself: the reducing theory needs to be *applied* to the problem in question, and, as

a careful consideration of the reduction of laws and concepts shows, this involves an *application* step in the reduction which also transforms the reducing theory into a theory 'about' the phenomenon in question.

3. A third philosophical approach, to be further explored in Chap. 5 (and especially in Sect. 5.2), is the reconstruction of the Born-Oppenheimer Hamiltonian as a 'hard core' which is itself immune from criticism.

The latter two steps propose, in line with the discussion in Chap. 1 (p. 20), that the 'clamped nucleus' Hamiltonian that lies at the heart of modern electronic structure theory may be an 'intermediate' theory itself, a suggestion which I take up in more detail in Chap. 7. At least, as argued in Sutcliffe (2012), this clamped nucleus Hamiltonian is mathematically well-behaved.

These three approaches sit well with current trends in philosophy of science, and in themselves obviate many of the issues associated with the introduction of the Born-Oppenheimer approximation in quantum chemistry, though they will not support a simple reduction scheme consisting of identities *cum* strict derivation.

This chapter is structured as follows. In Sect. 3.2 I will discuss some of the recent philosophical literature with respect to the Born-Oppenheimer approximation and molecular structure. I will then outline a brief history of the Born-Oppenheimer approximation in Sect. 3.3. In Sect. 3.4 I discuss how current definitions of a molecule may be harnessed to provide a robust support for the notion of molecular structure. The last section is a conclusion.

3.2 An Overview of the Philosophical Literature on Molecular Shape

The issue of molecular shape can be summarised in the form of a common claim: molecular structure is not a feature of a molecule that can be 'derived' from quantum mechanics with the assistance of the Born-Oppenheimer approximation. Rather, the Born-Oppenheimer approximation *imposes* the shape at the outset. It is my aim in this section to outline and critically evaluate some of the key philosophical arguments. As it stands, the argument tends to focus on a small series of papers by Woolley (1976, 1977), Woolley and Sutcliffe (1977) and in smaller measure the work of Primas (1981, 1998) when discussing molecular structure.

Primas (1981) is a book length argument about the reduction of chemistry to physics and its problems. While it is generally well appreciated in current philosophy of chemistry that Primas (1981) provides a series of arguments against the idea that chemistry can be reduced to physics, there is little, if any, critical analysis of Primas' argument in the existing literature. It is therefore much less appreciated that Primas builds his argument on the basis of quite esoteric (and somewhat purist) readings of the nature of theories, logic and ontology, and that Primas argues, in important measure, that the difficulties experienced in the reduction of chemistry are important motivations for a reassessment of quantum mechanics and its interpretation.

Primas' reading of the problems associated with molecular structure is worth repeating in full here[3]:

> In pioneer quantum mechanics a molecular structure is defined via the Born-Oppenheimer approximation by a minimum energy configuration on the Born-Oppenheimer potential surface. In spite of the obvious merits of this definition, it is ad hoc. In pioneer quantum mechanics molecular structure does not represent a feature of the system since by definition features are represented by elements of the algebra of observables. According to the general use of this concept by chemists, a molecular structure is something a molecule *has*, and which can be discussed by using an unrestricted Boolean language. That is, molecular structure is a *classical* concept, and should be represented by classical observables. However, in pioneer quantum mechanics there are no classical observables. (Primas 1981, p. 335)

This passage is the key argument for Primas to argue that molecular structure is incompatible with pioneer quantum mechanics. However, in the remainder of the book Primas argues that pioneer quantum mechanics is incorrect and should be revised, partly because pioneer quantum mechanics seems incapable of rendering a robust account of concepts such as molecular shape. This leads him to devise a new argument for the appearance of molecular structure based on a robust two-level quantum system.

Primas' argument is mathematically complex and subtle. Primas' argument is based on the fact that the Born-Oppenheimer approach is based on a perturbation analysis of the Coulomb Hamiltonian in which the nuclei are treated as 'classical' from the outset, even though a molecular structure in the sense of the chemist does not exist in and is incompatible with the Coulomb Hamiltonian. The upshot of this argument is that a treatment of the nuclei that is consistent with the Coulomb Hamiltonian has to consider the nuclei as quantum particles (with an algebra of I_∞ in Primas' terminology) and that it is hard to see how molecular structure can be instantiated on such an algebraic basis. The zeroth-order of the perturbation analysis places the nuclei at fixed points in space, but the choice of these points in space is, according to Primas, ad hoc.

To flesh out the concept of molecular structure, Primas goes to significant length to set up what he calls a 'caricature' of a molecule, which exhibits molecular structure as an *asymptotic pattern* in the singular limit of infinite nuclear masses. This caricature consists of a two-level quantum mechanical system, in which the algebra of observables becomes $\mathscr{A}_{\text{ad}} = \mathscr{A}_e \otimes \mathscr{C}$, where $\mathscr{A}_e$ is the algebra of electronic coordinates, and $\mathscr{C}$ is the classical structure representing the nuclei. The key point is that in this system the nuclei have become individual entities. As Primas claims, at this point:

> There is a new pattern – the molecular structure – which is described by the classical observables in $\mathscr{A}_{\text{ad}}$. Moreover, the adiabatic caricature is a two level hierarchical quantum system. (Primas 1981, p. 339)

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[3] Primas uses the term 'pioneer quantum mechanics' for a quantum mechanics that is based on the Copenhagen interpretation of the wavefunction, as is outlined in Von Neumann (1932, 1955). He contrasts this with quantum logic or algebraic approaches to quantum mechanics.

The point that Primas makes is that it is only this two level hierarchical quantum system that exhibits the correct algebra of observables: the nuclei are considered classical particles while the electrons are considered quantum particles, which yield a potential energy curve for the motion of the nuclei.

At this point, it is worth while to investigate in more detail how Primas characterises the concept of a 'caricature' in general in relation to its explanatory powers:

> In exact science, the basic theoretical tool for creating caricatures is the study of a system in limiting approximations. As discussed by Hammer (1964, 1971): "*the result of an approximating process is the substitution of one entity for another, with the intention that the former shall play the same role in some regards as the latter.*" (Primas 1981, p. 331–332)
> The aim of a caricature is not to present the truth, the whole truth, and nothing but the truth. It is the essence of a caricature that new patterns come into evidence. "*One grievous error in interpreting approximations is to allow only good approximations. Hammer (1971)*". (Primas 1981, p. 332)

Thus the caricature of the molecule seems to play a role very similar to what Hendry (1998) has argued is a 'proxy defence' for reduction: the creation of a new set of laws that somehow 'stand in' for the original laws and exhibit the desired features. The key aspect of these laws, deriving from the asymptotic nature of the development of the pattern, is that they are not 'strictly true'. In the terminology adopted by Strevens (2012), such patterns may be 'physically undefinable'.[4] While for Hendry the 'proxy defence' fails since the features of the 'stand in' equations are not shared by the exact solutions to the 'principled' equations of the reducing science, in Primas' derivation this is not necessarily the case: the 'caricature' appears as the end result of a robust consideration of a two-level quantum system.

Philosophers of chemistry have regularly misunderstood and misreconstructed Primas' argument in the sense that they take the arguments based on the quantum nature of the nuclei too literally and disregard the derivation of the 'caricature' – for if Primas' notion of a 'caricature' of a molecule does indeed correctly predict molecular shape in a chemically relevant sense, then there is also a meaningful way in which one can claim an indirect reduction of chemistry.

Recently, Bishop and Atmanspacher (2006) have extended Primas' argument about the quantum nature of nuclei to tie it to a specific notion of *emergence*. They take the notion of *asymptotic pattern* and discuss how the concept of *asymptotic expansion* is related to the notion of emergence. For instance, Bishop and Atmanspacher (2006) write that:

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[4] One could also argue that the patterns plays the role of molecular structure in a 'corrected' sense cf. the ideas on reduction developed in Schaffner (1967, 1974) or Hooker (1981a,b,c). This would not be supported by the notion of asymptotic reduction, however. The corrections to the reduced theory discussed in Schaffner and Hooker stand apart from the issue of autonomous laws for the reduced theory. Rather, they provide corrections to the reduced theory that derive from the laws of the reducing theory. The appearance of autonomous laws at the reduced level is generally taken to be a hallmark of asymptotic reduction relationships, as is discussed in Berry (1994) and Batterman (2002).

> It is impossible to derive molecular structure from quantum mechanical first principles alone because in a complete quantum mechanical description electrons and nuclei are in entangled states. At the level of Schrödinger's equation, systems which differ by their molecular structure alone cannot be distinguished. (Bishop and Atmanspacher 2006, p. 1765)

Hence Bishop and Atmanspacher (2006) argue that the conditions imposed by quantum theory are *necessary* but not *sufficient* for the derivation of molecular structure, a condition they call contextual emergence.

From here it is only a small step towards the argument from 'downward causation' that has been forwarded by Hendry (2006, 2010), in which there is a 'configurational Hamiltonian', that adds the additional necessary steps.

Another possible response to the issue of molecular shape is that our philosophical notions of explanation and reduction need to be reconsidered in the light of the problems posed by the issues of molecular shape. Or, as Ramsey (1997)[5] holds:

> *Contra* received philosophical opinion but *with* Woolley, Primas, and the philosophers Scerri and McIntyre, I believe shape cannot be explanatorily reduced under almost any interpretation of reduction. As a result, we must revisit and revise our standard accounts of reduction and, eventually, our accounts of theoretical explanation. (Ramsey 1997, p. 233)

Specifically, the position that Ramsey wants to defend is one of reduction without levels, i.e. an ontological form of reduction.[6] Ramsey argues that the ontological notion of reduction is the only way in which it can make sense to speak of 'reduction' of molecular shape. On the basis of a fairly standard array of arguments, Ramsey analyses the claims for the reduction of molecular shape by reading the term 'reducible' in the following three senses: (i) naturally isolable within the expressions of physics, (ii) explained by the laws of physics or (iii) referring to a distinct level or view of reality (which is separate from the physical). These readings, when combined with the standard 'shape' argument subsequently imply that molecular shape is not reducible. Hence he is left with the ontological option as follows:

> If shape is conceived as a feature of some physical systems but is one which does not exist independently of measurement and time-scale considerations, then there is a sense in which shape is approximately ontologically reducible. (Ramsey 1997, p. 244)

Both Hendry and Ramsey thus shift the argument from epistemology to ontology at some point and talk about ontological reducibility. The motivation for this is that they see 'shape' as a 'property' of a molecule which, given the failure of epistemological reduction, is in need of 'ontological' reduction.

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[5] There are a number of assertions in Ramsey's paper which are somewhat irritating, such as his characterisation of the structural notion of the molecule as an instance of 'folk molecular theory' (FMT) which seems to imply that it is somehow pre-scientific. Also, his summary of the positions of Woolley, Sutcliffe and Primas does not properly distinguish between the positions of these three writers.

[6] Ramsey's paper confuses a number of issues by painting the positions of Primas, Woolley and Sutcliffe with the same brush. Specifically, Ramsey ascribes the denial of a 'separability thesis' (the idea that electronic and nuclear motions can be separated) to Woolley, Primas and Sutcliffe (which is not correct without significant qualification).

3.3 A Rational Reconstruction of Molecular Hamiltonians

The geometrical characterisation of a molecule in quantum chemistry is introduced through the well-known Born-Oppenheimer (BO) approximation (Born and Oppenheimer 1927). The currently most frequently used form of the Born-Oppenheimer approximation first appeared in the book by Born and Huang (1954). There is also a slightly earlier suggestion for a similar approximation from Slater (1927), as well as an earlier paper by Born and Heisenberg (1924) which also discusses what is now commonly called the Born-Oppenheimer approximation. Key contributions in the area of molecular structure and mechanics, such as those of Eckart (1935) and Sayvetz (1939), are generally ignored completely in the philosophical debate on molecular shape.

Philosophical discussions of this matter are therefore hampered by a lack of historical accuracy. In this section I outline the history of the Born-Oppenheimer approximation in greater detail. A quantum chemist looking up the original paper of Born and Oppenheimer (1927) expecting to find the Born-Oppenheimer approximation[7] there is going to be disappointed. What is generally considered to be the original paper on the Born-Oppenheimer approximation does not contain the derivation of the approximation as it is commonly understood.

3.3.1 Molecular Structure in Quantum Chemistry

In current practice in quantum chemistry, the BO approximation forms the foundation for a two-step approach to the computational dynamics of molecules.

The Born-Oppenheimer approximation relies on the separation of electronic and nuclear coordinates in the Coulomb Hamiltonian:

$$H = \sum_k \frac{\mathbf{p}_k^2}{2m_k} + \sum_{k<l} \frac{z_k z_l}{r_{kl}} \tag{3.1}$$

where the sums k and l runs over all particles involved. The idea of the Born-Oppenheimer approximation is that we can split this Hamiltonian into a part that contains the electronic motion (in which the nuclear coordinates appear as parameters), and a part representing nuclear motion, and then proceed to assume that the nuclei are ‘fixed’ in space, thus eliminating the kinetic energy from the nuclear motion.

Assuming that $\alpha, \beta, \ldots$ range over nuclei and $i, j, \ldots$ over electrons, the Coulomb Hamiltonian may be written

$$H = \sum_\alpha \frac{\mathbf{p}_\alpha^2}{2m_\alpha} + e^2 \sum_{\alpha<\beta} \frac{Z_\alpha Z_\beta}{r_{\alpha\beta}} + \sum_i \left(\frac{\mathbf{p}_i^2}{2m_e} - e^2 \sum_\alpha \frac{Z_\alpha}{r_{i\alpha}} \right) + \sum_{i<j} \frac{e^2}{r_{ij}}. \tag{3.2}$$

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[7] In the form in which it is commonly given in the later version by Born and Huang (1954). The paper does contain the separation of electronic and nuclear motion.

The general approach of the Born-Oppenheimer approximation is that the nuclei are ‘clamped’ in a position in space, so that the Hamiltonian simplifies to an electronic Hamiltonian which parametrically depends on the set of nuclear coordinates $\{\mathbf{x}\}$ and which reads[8]

$$H_{\mathrm{el}}(\{\mathbf{x}\}) = e^2 \sum_{\alpha<\beta} \frac{Z_\alpha Z_\beta}{r_{\alpha\beta}} + \sum_i \left(\frac{\mathbf{p}_i^2}{2m_e} - e^2 \sum_\alpha \frac{Z_\alpha}{r_{i\alpha}} \right) + \sum_{i<j} \frac{e^2}{r_{ij}}. \tag{3.3}$$

The second step consists in considering the nuclear wavefunctions with the potential energy surface calculated in the first step as a potential energy function. The calculation of nuclear wavefunctions leads to a set of interesting problems concerning the molecular rotation and vibration spectra, and the classification of nuclear motions. Generally, the work of Eckart (1935) is considered the first detailed study of the nuclear kinetic energy that derives a robust argument for the separation of the rotational and vibrational parts of the wavefunction.

For what follows, it will be interesting to evaluate this two-step procedure in the light of the actual structure of the Born-Oppenheimer approximation. We will first discuss the historical development of the Born-Oppenheimer approximation in more detail, and then focus on how the modern Born-Oppenheimer approximation supports the two step procedure above.

3.3.2 History of the Born-Oppenheimer Approximation

In this section, we discuss the history of the Born-Oppenheimer approximation in more detail.

It is relatively little known that there is an earlier paper by Born and Heisenberg (1924) with the same title as the Born and Oppenheimer (1927) paper: *‘Zur Quantentheorie der Molekeln’* (On the quantum theory of molecules).

The Born-Oppenheimer approximation proper is named after the later paper by Born and Oppenheimer (1927). The approach is to treat the nuclear motion as a perturbation on the Hamiltonian with fixed nuclei by defining an expansion parameter κ of the form

$$\kappa = \sqrt[4]{\frac{m}{M}}. \tag{3.4}$$

Here m is the mass of the electron and M some mean value of the mass of the nuclei in the molecule. Born and Oppenheimer separate the Hamiltonian in such a way that the total molecular energy corresponds to the Hamiltonian $H + \kappa^4 H_1$ where (using the same notation as Born and Oppenheimer):

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[8] In what follows, I will generally use ‘atomic units’, in which $\hbar = 1$, the electronic mass $m_e = 1$ and the electronic charge $e = -1$, which can be used to simplify the equation above accordingly.

$$\begin{cases} T_E + U = H_0\left(x, \frac{\partial}{\partial x}; X\right) \\ T_K = \kappa^4 H_1\left(\frac{\partial}{\partial X}\right) \end{cases} \tag{3.5}$$

and x refers to electronic and X to nuclear coordinates; the construction $\frac{\partial}{\partial x}$ corresponds to the momentum of x.

The full equation that Born and Oppenheimer (1927) consider is their Eq. 12:

$$\left(H + \kappa^4 H_1 - W\right)\psi = 0. \tag{3.6}$$

The zeroth order of this expansion ($\kappa = 0$) provides, as Born and Oppenheimer note, the motion of the electrons for fixed nuclei.

As in the Born and Heisenberg (1924) paper, the Born and Oppenheimer (1927) contains a treatment of the dynamics of the nuclear frame. Somewhat surprisingly, in Born and Oppenheimer (1927) there is a different choice of body-fixed frame. As is noted in Kiselev (1970) this is one of the key circumstances why the higher order equations in the Born and Oppenheimer (1927) paper become so complex.

Anyone expecting to see a relatively clear unfolding of the key aspects of both molecular structure and molecular dynamics will not find that in Born and Oppenheimer's paper. They treat the two-atomic molecule more or less exactly, but do not provide robust arguments for molecules with more than two atoms.

However, a general structure emerges in the energy equations. They assume that an electronic level E has a minimum at a certain configuration X_0 of the nuclei, which they call the equilibrium configuration. They then treat the molecular dynamics as a Taylor expansion around this minimum. As they state in their paper on p. 462, the principal aim is to show that the function $V_n(\xi)$ plays the role of a potential energy for nuclear motion. They write, in their equation (16):

$$V_n(\xi + \kappa\zeta) = V_n^0 + \kappa V_n^{(1)} + \kappa^2 V_n^{(2)}. \tag{3.7}$$

In §4 of their paper they then discuss the zeroth and first orders of the expansion. The zeroth order of the energy is the (set of) electronic energies in the field of fixed nuclei. The first order is zero. This corresponds to the notion that the configuration X_0 is a minimum on the potential energy surface, but it is at this point that Born and Oppenheimer discuss the point of molecular shape and existence of the molecule:

> Die Fortsetzbarkeit unseres Näherungsverfahrens verlangt demnach, daß die relativen Kernkoordinaten ξ_i nicht beliebig gewählt werden dürfen, sondern einem Extremwert der Elektronenenergie $V_n(\xi)$ entsprechen müssen. Die Existenz eines solchen ist also die Bedingung für die Möglichkeit der Existenz der Molekel, ein Satz, der gewöhnlich als selbstverständlich richtig angenommen wird. (Born and Oppenheimer 1927, p. 467–468[9])

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[9] A translation in English of this quote reads as follows:

> The validity of continuing our approximation procedure therefore requires that the relative nuclear coordinates ξ_i not be chosen arbitrarily, but must represent an extremum value of

The second order term becomes the energy of the harmonic approximation to the vibrational motion of the nuclei. The third order term is again zero. The fourth order term represents the energies corresponding to a number of items: the rotational motion of the frame, a part containing the anharmonic corrections to the nuclear vibrations, and finally a term containing the non-adiabatic corrections to the electronic energy.

While the equations in this paper are very complex, in general they correspond to our intuitions about molecules as balls connected by springs, a fact which has undoubtedly contributed to the later popularity of the Born-Oppenheimer approximation.

3.3.2.1 Molecular Rotations and Vibrations

The clamped nucleus approximation fixes the nuclear frame in space, and does not allow for rotations and vibrations of the nuclear frame. Hence, to make progress in molecular spectroscopy, it was necessary to separate out rotations and vibrations of the entire molecular frame.

The separation of the nuclear motions into rotation and vibration coordinates is now commonly attributed to Eckart (1935) and Sayvetz (1939).[10] The Eckart frame is a 'body fixed' frame (meaning it translates with the centre of mass of the molecule and rotates along with it too) which is defined through the two Eckart conditions. These conditions can only be defined for a molecule that has a well-defined minimum in the potential energy surface. They are summarised in Biedenharn and Louck (1977) as follows:

1. Casimir's condition: in the limit of vanishing displacements of the nuclei away from the equilibrium configuration, the term in the kinetic energy representing the Coriolis interaction between rotation and internal motions should be zero.
2. Linearity of internal coordinates. The internal degrees of freedom should be described by coordinates that are linear combinations (with fixed numerical coefficients) of the components of the displacements of the nuclei away from equilibrium, where the components are to be referred to the moving frame. This condition is imposed to assure that the normal coordinates calculated for the nonrotating molecule can be carried over, without change, to the rotating, vibrating molecule.

The two Eckart conditions come in a translational and rotational form. They are based on 'displacement vectors' $\boldsymbol{\rho}_{\mathbf{a}}$, and are generally presented in the form given

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> the electronic energy $V_n(\xi)$. The existence of such an extremum is therefore the requirement for the existence of the molecule, a theorem which is usually assumed to be self-evident.

(as translated in Hettema 2000, p. 10.)

[10] The derivation is given in a modern form in Biedenharn and Louck (1977), where the Eckart frame is derived first, and then shown to fulfil the two Eckart conditions.

by Sayvetz (1939). It should also be noted that while these conditions generally play out in a quantum mechanical universe, they are themselves not strictly speaking quantum mechanical conditions: they can hold equally well for classical systems.

The advantage of the Eckart conditions is that they allow for an easy characterisation of the remaining $3N-6$ coordinates into a vibrational and rotational part, and especially allow a precise characterisation of *normal coordinates*. They thus form a foundation on which much of later spectroscopy, as found in for instance Wilson et al. (1955), is based.

3.3.3 The Modern Born-Oppenheimer Approximation

Instead, what is now commonly understood as the modern derivation of the Born-Oppenheimer approximation is found in Born and Huang (1954). For the purposes of this chapter, I wish to be relatively brief about this derivation, even though it is in many ways more robust than the Born and Oppenheimer (1927) derivation.

The derivation starts by defining the kinetic energy of the nuclei, that of the electrons and a Hamiltonian H_0 for fixed nuclear coordinates in the following way:

$$T_N = \sum \frac{1}{2M} P^2 = -\sum \frac{\hbar^2}{2M}\left(\frac{\partial^2}{\partial X^2}\right) \tag{3.8}$$

$$T_E = \sum \frac{1}{2m} p^2 = -\sum \frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}\right) \tag{3.9}$$

$$T_E + U = H_0\left(x, \frac{\partial}{\partial x}; X\right). \tag{3.10}$$

The latter Hamiltonian does not contain the kinetic energy of the nuclei and therefore represents the Hamiltonian of the electrons for fixed nuclei.

After defining the expansion parameter $\kappa = \sqrt[4]{m/M_0}$ where M_0 is some representative nuclear mass (or the mean nuclear mass) and defining the electronic functions at some expansion point X_0:

$$(H_0 - E^0)\phi(x;X) = 0, \tag{3.11}$$

the aim is again to solve the exact equation in the neighbourhood of X_0 so that $X-X_0$ is small.

It again appears that the first order vanishes, so that X_0 has to be the equilibrium configuration where

$$\left(\frac{\partial \Phi_n(X)}{\partial X_i}\right)_{X_0} = 0. \tag{3.12}$$

The equations for the second order form the *adiabatic approximation*. This describes a situation where 'during the nuclear motion the electrons move as though the nuclei were fixed in their instantaneous positions' (Born and Huang 1954, p. 171). This is a somewhat important elucidation in the sense that the term 'adiabatic approximation' is sometimes used to refer to the 'fixed nucleus' approximation.

To conclude, it is noticeable that early and later literature on theoretical chemistry generally gives little consideration to the mathematical intricacies of the Born-Oppenheimer approximation. For instance, in the introduction to Mathematical Physics by Slater (1939) as well as in the introduction by Pauling and Wilson (1935) and the later book on molecular vibrations by Wilson et al. (1955) the separation of nuclear and electronic motion is treated as a default feature of the molecular Hamiltonian rather than as something that needs to be carefully considered and derived.[11] This has also been noted by Sutcliffe (1992), who remarks that:

> It is often supposed that the work of Born and Oppenheimer on nuclear motion published in 1927 was central to the thinking about the quantum mechanics of molecules. A survey of the literature up to about 1935 shows, however, that their paper was hardly if ever mentioned and, when it was mentioned, its arguments were used as a posteriori justification for what was being done anyway. (Sutcliffe 1992, p. 34)

3.3.4 Does Quantum Theory Support Molecular Shape?

The worries around the applicability of the Born-Oppenheimer approximation started with changes in the *experimental* situation: especially the development of high-resolution spectroscopy (which depended on the wide availability of lasers) and the capability to perform experiments on highly diluted 'beams' of molecules (leading to the capability to study *individual* molecules). These new developments were primarily responsible for the principled worries on the applicability of the Born-Oppenheimer approximation that gained momentum in the second half of the 1970s. We will focus in particular on the arguments by Woolley (1976, 1977, 1978) and Woolley and Sutcliffe (1977).

In these experiments, as Woolley (1978) argues, the molecular stationary states can be probed directly, and under these conditions *shape* is not an intrinsic property of the quantum system of nuclei and electrons that constitute the molecule. Under these conditions, argues Woolley (1978), the quantum stationary states of the molecule do not support the concept of molecular shape since the concept of size and shape has no meaning under this description.

Another way of looking at the matter is the following. The Coulomb Hamiltonian is invariant under translations and rotations. The consequence of this is that the total

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[11] This is notwithstanding the fact that the latter work devotes an entire chapter to the separation of rotation and vibration in the nuclear kinetic energy.

momentum **P** and angular momentum **L** are constants of motion; i.e. these operators will commute with the Coulomb Hamiltonian. They are defined as

$$\mathbf{P} = \sum_k \mathbf{p}_k, \qquad \mathbf{L} = \sum_k \mathbf{r}_k \times \mathbf{p}_k. \tag{3.13}$$

In the principled treatment of the molecule one has to separate the translational motion of the overall system from the Hamiltonian, and the resulting translation invariant Hamiltonian is a complex one to solve. As we will see in the next section, while it is possible for this Hamiltonian to have bound states (though even that is not easy to prove in general) it is not clear that these bound states will support the concept of molecular shape, or even have the ability to pick out individual isomers for complex molecules.

These operations do not commute with 'clamped nucleus' Hamiltonian, and hence the Born-Oppenheimer Hamiltonian is not a good Hamiltonian to use in the cases of individual molecules. As Woolley (1978) outlines, however, under normal conditions in a liquid for instance the assumption that a molecule does have a shape may be a reasonable assumption. While these arguments are valid in principle, it is still an open question how relevant they are for the *chemistry* of the liquid or solid state. Woolley (1978) is worth quoting in full here:

> The emphasis on all of these general symmetries (permutation symmetry, rotational symmetry, parity) is only relevant when the stationary states are individually resolved. In liquids and solids one is always dealing with intrinsically time-dependent quantum states of (atoms) molecules that can be represented as superpositions of the (atomic) molecular eigen-states with time-dependent coefficients; such a superposition in general will exhibit a much lower symmetry than the individual eigenstates. Furthermore we know empirically that the energy separations of adjacent stationary states in molecules containing more than, say, $\sim$10 atoms are so small that existing experimental methods cannot fully resolve the individual eigenstates; in this situation, which is equivalent to looking at a "small" molecule under low resolution, one is again concerned with a time-dependent quantum state for which a molecular structure description may be valid. (Woolley 1978, p. 1077)

Hence it may be concluded that the conditions under which molecules are studied in high-resolution spectroscopy are not the common conditions under which chemists talk of molecules. While this objection does not solve the principled problem of molecular shape, it does go some way to argue that in the *practice* of chemistry, molecules may indeed have a shape.

In the chapter on the chemical bond (Chap. 2) we have argued that there are a number of competing conceptions of the chemical bond, all of which have at various points been used in chemistry. At this point it is worth noting that the Born-Oppenheimer approach to the shape of a molecule depends on the *energetic* view of the chemical bond – the Born-Oppenheimer approximation in first order depends on an 'equilibrium' configuration which corresponds to an 'equilibrium' bond length. In opposition, the Born-Oppenheimer approximation does not utilise other aspects of the chemical bond, such as the electron density between nuclear centres.

Hence the question what features of the concept of a molecule we need to recover from its quantum chemical description is somewhat unsettled.

3.3.5 Löwdin's Notion of a Molecule

In the end section of a long paper on the mathematical definition of a molecule and molecular structure (Löwdin 1988) gives the following definition of a molecule:

> A system of electrons and atomic nuclei is said to form a *molecule* if the Coulombic Hamiltonian H'–with the centre of mass motions removed – has a discrete ground state energy E_0. (Löwdin 1988, p. 56)

The reason that the centre of mass motions have to be removed is because these lead to a continuous spectrum.

This definition of a molecule is based on the spectrum of the Coulomb Hamiltonian and extends quite complicated mathematical considerations by Kato (1951a,b) for the Helium atom, which proved that the Hamiltonian for a multi-particle Coulomb system is self-adjoint.

A lot of relevant mathematical detail and references can be found in Woolley and Sutcliffe (2003) and Sutcliffe (2008) and I will not go into the required detail here, except for a number of brief remarks.

The fact that the Coulomb Hamiltonian is self-adjoint means that the time evolution

$$\Psi(t) = \exp\left(-iHt/\hbar\right)\Psi(0) \tag{3.14}$$

conserves probability. This condition is significantly stronger than hermiticity. Kato (1951a,b) further showed that this Hamiltonian is bounded from below.

Since the work of Kato (1951a,b), more work on the spectra of Hamiltonians has been performed. It is now customary to separate the spectrum $\sigma(A)$ of an operator A into a *discrete* and an *essential* part. The discrete part of the spectrum consists of isolated eigenvalues of finite multiplicity. For the Coulomb Hamiltonian, it is generally the case that the essential portion of the spectrum contains the scattering states while the discrete portion of the spectrum contains the bound states.

Löwdin's definition of a molecule is based on the so called Hunziker, van Winter, and Zhislin (HVZ) theorem.[12] It is interesting to note that within this context, the problem of molecular shape is still an unsolved problem, as is for instance argued by Cassam-Chenaï (1998). An overview of how Löwdin's definition of a molecule may be used in the context of defining a molecular frame is given in Sutcliffe (2002). Sutcliffe's position is that the mathematical and conceptual difficulties one has to deal with when working with Löwdin's definition of a molecule are at the moment somewhat unsettled, and moreover that it is not easy to see how, even if the mathematical difficulties were settled, one could convince the chemist that a working concept of molecules does indeed appear at the end of that analysis. As Sutcliffe notes:

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[12] See Reed and Simon (1978) for an overview. The HVZ theorem states that the start of the essential part of the spectrum is the lowest two-body cluster decomposition of the N-particle system. It is not my aim to develop this argument in detail: it is based on intricate mathematical reasoning which adds little value to the philosophy of the matter.

> It seems to me that if we wish to use the word *molecule* in connection with an object in quantum mechanics, we must be able to associate with that object, in some agreed way, a reasonable number of the attributes that are accorded to the molecule in classical chemistry. Thus one might suppose at very least that one must be able to attribute a geometrical structure to it, even if a non-rigid or flexible one. Better, one might hope to offer a reasonable description of it structurally in terms of bonds, even if these are not perfectly localised. (Sutcliffe 2002, p. 71)

The article discusses a number of approaches in some mathematical detail, but ends concluding that the concept of a molecule based on Löwdin's definition so far eludes us. Thus it seems that concepts of a molecule based on the Coulomb Hamiltonian are still in need of further precision and definition.

3.4 Reevaluating Reduction

We are now in a position to evaluate the problems associated with the concept of molecular shape and molecular structure and assess their philosophical impact. Again, we may refer to the model for reduction that we discussed in Sect. 1.2.3, and from this perspective the matter seems unproblematic: we can consider the 'clamped nucleus' Hamiltonian as a candidate for a (modified) reducing theory T_F^* and proceed. This is the (pragmatic) approach that has been chosen, by and large, by the quantum chemistry community.

There are good reasons to consider this a viable approach. As argued in Sutcliffe (2012), the 'clamped nucleus' Hamiltonian is self-adjoint (which in laymens terms more or less means 'well behaved'), and thus is a good candidate for the further construction of a reducing theory.

Additionally we can argue that the explanatory domain associated with the Coulomb Hamiltonian is different in significant ways from the explanatory domain associated with the Born-Oppenheimer Hamiltonian. As outlined in Woolley (1978), the explanatory domain associated with the Coulomb Hamiltonian is the domain of the spectroscopy of diluted gases, whereas the explanatory domain more commonly associated with chemistry is the non-diluted gas phase, liquid or solid state. In terms of the Hamiltonian that is deemed most appropriate to describe the relevant features of the domain, the Born-Oppenheimer clamped nucleus Hamiltonian, which does ascribe a shape to a molecule, is more appropriate when not dealing with highly diluted gases. The fact that it does break down in this domain has led Woolley (1978) to argue that the highly diluted gases should be:

> [...] characterized as being concerned with *a novel state of matter distinct from the classical gas* since they probe the *molecular stationary states* which cannot be understood in terms of molecular structures: these experiments thus need to be distinguished from investigations of dense gases and condensed matter (or "large" molecules generally) for which the notion of structure is the key concept that essentially "solves" the macroscopic many-body problem. (Woolley 1978, p. 1073)

One could of course argue that all of this just comes down to strategically overlooking the problem, and that would indeed be the case. Although convenient, such an approach is not, however, principally wrong. Under the ‘theory entry’ model of Cartwright (1983) the specifications of the theory involve a number of unprincipled steps, and have the potential to transform the reducing theory. The Born-Oppenheimer approach to molecular shape can be seen as the first step of such theory entry, in which:

> [. . .] we prepare the description: we present the phenomenon in a way that will bring it into the theory. The most apparent need is to write down a description to which the theory matches an equation. [. . .] This first stage of theory entry is informal. There may be better and worse attempts, and a good deal of practical wisdom helps, but no principles of the theory tell us how we are to prepare the description.[. . .] The check on correctness at this stage is not how well we have represented in the theory the facts we know outside the theory, but only how successful the ultimate mathematical treatment will be. (Cartwright 1983, p. 134)

Hence, Cartwright’s model allows for adaptations in the explaining theories that are not ‘smooth’, but instead allow for significant discontinuities between the basic theory and its application. This however requires a ‘rich’ reading of the first phase of theory entry which consists not only of enumeration, but also of specific application: a detailed specification of the sort of system that the reducing theory is thought to apply to. In this sense, Cartwright’s model is often classified as a non-reductive model, but precisely such an application is the first step of Kuipers’ five step model.

Alternatively, if we view quantum chemistry as a Lakatosian research programme (a point of view we develop in Chap. 5), then the imposition of molecular shape in the form of a nuclear framework onto the Hamiltonian can become part of a ‘hard core’ of the theory and formal issues in the application can be temporarily suspended. Even stronger, Lakatos’ hard core does not actually require consistency as required by the critics of quantum chemistry, and as Lakatos points out, his key two examples of a successful research programme did not exactly have consistent cores: the Prout programme progressed in a ‘sea of anomalies’ and the Bohr programme was characterised by Lakatos as a ‘research programme progressing on inconsistent foundations’. The fact that Lakatos’ characterisations are not without its problems, is an objection beside the point: the point is that inconsistency or anomaly is not per se a reason to reject a theory as a candidate for a Lakatosian research programme.

This sort of domain restriction, bracketing, application and preparation sits well with the idea that chemists are inherently pragmatists. Ramberg (2000) traces this attitude even back to nineteenth century chemistry when he writes that chemists display:

> [. . .] a general tendency of chemists to be pragmatic, in the simple sense of being practical, in adopting the tools and concepts necessary to reach their goals. That is, chemists will adopt useful concepts and tools even if those tools and concepts raised significant physical or philosophical questions. For example, chemists adopted the principle of valence almost without question, even though it raised crucial physical questions about its nature, because it helped to explain chemical behavior of substances and the appearance of isomers. (Ramberg 2000, web edition)

A possible objection is that such a Lakatosian bracketing, 'theory entry' or application of the theory, combined with chemical pragmatism ultimately ensures the non-reducibility of chemistry to a principled form of quantum theory or some 'true' physics and hence dooms the project of reduction. For we *know* that such models are representations, or, in the words of Hendry (1998), they are a *proxy* view of idealised models which somewhere 'stand in' for intractable 'exact' models. The case for reductionism then depends on the ability to prove on a case by case basis that these idealised models correctly represent the more 'basic' but inexplicable models at least in all their relevant features. In the words of Cartwright (1983), one can go even one step further: these models are known to lie (ontologically).

Two responses are possible to this objection. The first one is that Nagelian reduction, or indeed any form of heterogenic reduction simply does not *require* this sort of continuity. The model of Nagelian reduction, as discussed in Chap. 1, requires that the conceptual apparatus of the reduced theory can be *represented*, through the reduction postulates, in the language of the reducing theory. Taking this argument seriously entails that 'raw' quantum theory – principled quantum theory without the application step – is a very poor theory to reduce to. There are a multitude of unsolved foundational problems, as well as problems with interpretation and formulation associated with quantum mechanics.

The second response is that this objection has just shifted the problem from epistemology to ontology. The objection that bracketing or theory entry make reference to imaginary objects ultimately boils down to the claim that such idealised entities do not *exist* in the manner required by the reduction. It should be noted in this context that this ontological view of theories is one of the ways, in Cartwright's terms, of 'how the laws of physics lie'. The epistemological veracity of our scientific theories in terms of such a 'proxy defence' (or 'as if' operator in Cartwright's terminology) involves various ontological lies. Thus, this ontological shift takes us into the area of 'ontological' reduction. It thus seems to be the case that there is a dilemma between epistemological or ontological veracity: we can have true theories with terms that do not 'refer',[13] or we can have a true 'ontology',[14] but with unknown theories.

In the end, the issue may come down to one of compatibility of molecular shape with the Coulomb Hamiltonian. While this question is currently unresolved, the compatibility issue seems to veer in favor of a cautiously positive response.

While a molecular shape is not a feature of the Coulomb Hamiltonian per se, the formulation of the Coulomb Hamiltonian requires a specification of (an admittedly dynamic) molecular shape in the form of a specification of the nuclear coordinates as variables. Even though, at the level of the Coulomb Hamiltonian, this is a *dynamic*

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[13] Such theories are possible, but can only be 'observationally true'. Hence the theory of molecular shape cannot be a theory in this sense.

[14] Perhaps in the sense of Primas' 'ontic' interpretation of quantum mechanics, see Primas (1975, 1981).

assignment (it is, in a sense an 'all singing, all dancing' Hamiltonian,[15]) it is an assignment of shape nonetheless. The issue with modern formulations based on the Coulomb Hamiltonian is not so much whether molecular *shape* is recoverable from the Coulomb Hamiltonian, but rather whether it is possible to redevelop the familiar aspects of a molecule in a way that is both mathematically robust and convincing for the practical chemist.

It is at this point somewhat doubtful that a feature like molecular shape, for instance, would *not* appear as the end result of a rigorous application of the molecular Hamiltonian.[16] However that may be, Sutcliffe and Woolley (2005) argue that it is unlikely that a complete concept of what chemists call a molecule, or the sort of chemistry that Dirac had in mind in his famous quote, can be obtained from the solutions of the full Hamiltonian unless 'some additions are made to the way in which the problem is formulated'. These additions, Sutcliffe and Woolley suggest, should be obtained from the currently established *practice* of quantum chemical calculations:

> To obtain chemically relevant results from the Coulomb Hamiltonian for a collection of electrons and nuclei appropriate to a given molecule:
>
> 1. nuclei should be treated as distinguishable particles even when formally indistinguishable,
> 2. calculations should start from a clamped-nuclei electronic structure point-of-view,
> 3. moving-nuclei wavefunctions should arise from clamped nuclei wavefunctions by treating the nuclear motion as a perturbation. (Sutcliffe and Woolley 2005, p. 3675)

This is of course a description that is close in most aspects to the traditional Born-Oppenheimer prescription.

I therefore believe many of the current positions in this debate to be misguided for a reason closer to home: taking molecular *shape* as the starting point for the theory to be reduced and the Coulomb Hamiltonian as the reducing theory amounts to partially barking up the wrong tree – for it is not clear to begin with that molecular shape is of significant relevance for chemistry. All that is required for reduction, indeed, all that scientists happily accept as an *explanation* in most cases, is a Born-Oppenheimer Hamiltonian and some form of bond topology as chemical structure. If one considers for instance the (strongly anti-reductionist) viewpoint expressed in Hoffmann (2007), then this is indeed all that is required to specify the necessary chemistry.

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[15] This was the term used by Brian Sutcliffe during a presentation on this topic. See Footnote 1 of this chapter.

[16] See for instance Muller-Herold (2006) where the emergence of molecular structure is investigated in a exactly solvable three-body model Hamiltonian representing Hooke's law atom. It appears that molecular structure appears beyond a critical point, where the mass of two equal particles exceeds a critical value, which in turn depends on the mass of the third particle.

3.5 Conclusion

In this chapter I have come to the conclusion that the 'foundational' problems associated with the Born-Oppenheimer, or 'clamped nucleus' Hamiltonian can be ignored in the practice of chemistry. I have aligned a number of arguments to bolster the view that the conclusion of non-reducibility of chemistry on the basis of 'molecular shape' is premature. Specifically, I have argued that worries about the non-reducibility of molecular shape in the philosophy of chemistry are generally misplaced at two levels.

In the first place, these worries get their reconstructions wrong, taking a molecule with a certain *shape* as the theory to be reduced, and a form of principled quantum mechanics as the reducing theory.

While the investigation of the reducibility of molecular shape to such a principled quantum mechanics is still an open question and the subject of active (and valuable) research, it seems to me that its importance for the matter of reducing chemical theories to physical theories is significantly overstated.

More important, however, is that these worries stem from the wrong assessment of what the reduced and reducing theories are. Specifically, the reduction of chemistry to physics is capable of proceeding on the basis of a much weaker requirement: what is to be explained is the chemical structure of molecules; i.e. the bond paths that make up the molecule. Molecules are not committed to a particular *shape* to have a chemical *structure*, and hence the problem of reducing chemistry to physics is not so much the one whether particular shapes are reducible to principled quantum mechanics, but whether chemical *structures* can be reduced to a set of properties derived from a pragmatic Born-Oppenheimer dependent, not so principled quantum calculation.

Chapter 4
Unity of Chemistry and Physics: The Theory of Absolute Reaction Rates

Abstract The reduction of Eyring's theory of absolute reaction rates is an interesting case study in chemistry. The theory reduction does not rely on a single 'reducing' theory, but on a network of multiple connected theories, each providing a piece of the answer. This situation is fairly common in chemistry, and this chapter provides an in-depth discussion of how we might think about this state of affairs as a 'reduction'.

4.1 Introduction

In this chapter I focus on the theory of chemical reaction rates, and especially Eyring's theory of absolute reaction rates[1] or 'transition state theory' (so called because it introduces a new term in chemical terminology). As an example for the philosophy of chemistry, this theory provides a number of new insights into how a network of theories is constructed in practice and how it cooperates in explanation. All the same, this theory is not widely studied in philosophy of chemistry, which is somewhat unfortunate. The theory of absolute reaction rates is in many ways a robust example of a modern chemical theory, and exhibits many of the explanatory features that characterise other theories of chemistry.

It is primarily the aim of this chapter to evaluate the theory as a realistic example of *unity of science* so that some long held theories of reduction, as well as non-reductive approaches, can be usefully compared against a realistic record. For various reasons, the theory of absolute reaction rates concerns theoretical features that are pertinent to many of the problems in philosophy of chemistry.

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[1] As the book by Nye (2011) illustrates, this theory was sometimes jokingly referred to as the 'absolute' theory of reaction rates. Many of his contemporaries found Eyring's ideas too radical, as the proceedings of the 1937 workshop at the University of Manchester illustrate. In my earlier paper (Hettema 2012c) I used the designation of 'absolute theory' throughout in absolute error. At the time I was unaware of the earlier ironic use, and thought that 'absolute theory of reaction rates' was a better stylistic choice to designate the theory than the somewhat more clumsy sounding 'theory of absolute reaction rates' on the basis that it does indeed allow for a kind of ab initio calculation of the various terms in the theory. It also made the abbreviation 'absolute theory' available. Of course, I now see the error of my ways.

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In the first place, the theory of absolute reaction rates has sufficient complexity to represent a real-life scientific theory, illustrating the problems at play in actual science.

Secondly, the theory of absolute reaction rates depends in an interesting way on a mixture of *derivation* and *comparison*. Especially the latter is not something regularly encountered in the philosophy of science and hence is of particular interest. The theory develops multiple candidates for 'reducing' theories which each add critical elements to create the final theory of absolute reaction rates, and part of the process of the development of the theory is that it allows for the *interpretation* of some of its terms in the terminology of different reducing theories. This is a situation that I believe is fairly common in chemistry, but also still underrepresented in theories of reduction.

Thirdly, the theory introduces a new type of structure in the chemical lexicon: the *transition state*. It does so with a significant degree of conceptual clarity, as well as a significant degree of precision. This new concept of the 'transition state', which gave the theory considerable explanatory power, was responsible for the continued *conceptual* success of the theory. Traditional theories of reduction do not usually foresee such introductions of new concepts, and a more detailed exploration of this concept will shed considerable light on how Nagelian reduction functions in practice.

It is thus a key real-life example of how theories of physics and theories of chemistry interact in practice to generate a theory net. Theory nets are a concept from the 'structuralist' approach which we will discuss and use in Part II of this book, but the example we discuss here – the theory of absolute reaction rates – is perhaps one of its most interesting instances. This theory is a typical 'chemical' theory in the sense that it draws on many underlying theories to synthesise a new theory. A brief overview and philosophical evaluation of the theory was given in Hettema (2012c), which I refer to for some of the details. A robust and contemporary overview of the theory is given in the book by Glasstone et al. (1941), and a later evaluation was given by Laidler and King (1983).

The theory of absolute reaction rates was independently developed by Eyring (1935) and Evans and Polanyi (1935), and was the subject of heated debate during the 1930s. In the introduction to the 1937 conference about the theory held at the University of Manchester, the president of the conference in his address remarked that the jury on the 'absolute' theory was still out:

> As to whether these methods are fundamentally sound or unsound is a question the consideration of which belongs rather to the domain of philosophy than to that of chemistry, and it may be necessary to call in an expert in that branch of science to advise us in the matter. (Travers 1938, p. 1)

Somewhat belatedly, it is my opinion that the philosophers of science are, at this point at least, likely to disappoint the scientist, and provide no such advice. However, we can pick up on the interest in this theory generated in the 1930s and give an evaluation of this theory as a prime example of a modern chemical theory: the theory of absolute reaction rates formed very much a template for later theories that combined aspects of quantum chemistry, statistical mechanics and classical theories of chemistry to develop highly insightful patterns of molecular engineering. In this sense, the theory is paradigmatic for modern theories of chemistry from the second half of the twentieth century.

I will outline the key elements of the theory in Sect. 4.2, and discuss it from the viewpoint of a philosopher of science in Sect. 4.3. Rather than providing the asked-for advice, it is the purpose of the last section of this chapter to furnish a discussion on how the theory – whether fundamentally sound or unsound – is a good illustration of how a typical chemical theory functions.

4.2 Reaction Rate Theory: Its History and Structure

The theory of absolute reaction rates was developed by Henry Eyring (1935), and has been discussed in detail in a book by Glasstone et al. (1941).[2] Eyring et al. (1944) discuss the theory in a single chapter, adding a quantum mechanical formulation of the theory. The historical development of the theory was discussed in Laidler and King (1983) as well as by Miller (1998). I follow primarily the discussion in Glasstone et al. (1941), and note that the paper by Laidler and King (1983) contains a number of useful additions to my presentation. In this section it is my aim to trace the development of the theory of absolute reaction rates from the Arrhenius equation through to the formulation in Eyring (1935) and Glasstone et al. (1941) in a limited version.

First the basics of reaction kinetics. If we consider a chemical reaction of the type

$$\mathrm{A} + \mathrm{B} + \ldots \leftrightarrow \mathrm{C} + \mathrm{D} + \ldots \tag{4.1}$$

the rate of the reaction is the rate of change of the concentrations of the reacting species and depends on the concentrations of the reactants. For instance, the rate may be defined as the decrease in the concentration of [A]:

$$-\,d[\mathrm{A}]/dt = \mathsf{k}[\mathrm{A}][\mathrm{B}][\ldots] \tag{4.2}$$

where the constant k is the reaction rate coefficient, which is a constant for each type of reaction. The consequence of this equation is that the concentration of [A] decreases exponentially, which can be proven by integrating the rate equation:

$$[\mathrm{A}]_t = [\mathrm{A}]_0 \exp(-\mathsf{k}t). \tag{4.3}$$

The purpose of the various reaction rate theories is to find a formulation of k.

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[2] In my reconstruction of reaction rate theory, I will take as a guideline the two adequacy conditions expressed by Kitcher (1993): (i) if something is attributed to a past figure than that attribution is correct, and (ii) nothing is omitted, which, if introduced into the account, would undermine the point being made (see Kitcher 1993, p. 12–13).

4.2.1 Chemical Reaction Rates

Before discussing the theory of absolute reaction rates, it is first useful to consider some examples of *non*-absolute reaction rate theory, and especially the development of the Arrhenius law. The Arrhenius law is the main explanatory target of absolute reaction rate theory.

4.2.1.1 The Arrhenius Equation

Arrhenius' law was developed 1889,[3] and describes the reaction rate of the inversion of cane sugar (sucrose) by acids. Arrhenius studied the temperature dependence of the reaction rate constant, and suggested that the reaction took place via an 'active' form of cane sugar (something Arrhenius calls a 'new hypothesis'), which is the actual reacting substance.

The active form of cane sugar in equilibrium with the inactive form of cane sugar, but the active form is continuously removed by the reaction. Hence Arrhenius' concept of 'active' cane sugar contains three important components of the theory of reaction rates, which can be reconstructed as the following set of claims:

(A1) The first claim is that there is some 'active' component of the reactants involved in the reaction, without which the reaction would not occur.
(A2) The second claim states that the 'active' and 'inactive' components are in equilibrium.
(A3) The third claim is that the 'active' form of the reactants is continuously removed by the reaction.

Conditions (A1–3) are, in generalised form, the basic assumptions of all reaction rate theories.

In Arrhenius' theory the rate constants k take the form of the Arrhenius equation

$$\mathsf{k} = A \exp(-E/RT) \tag{4.4}$$

which give the rate constant for a chemical reaction in terms of a 'frequency' factor A and an 'activation' energy E. Using condition (A3), the reaction rate constant k of the overall reaction can be written as the equilibrium constant of the chemical equilibrium between the activated state and the reactants.

Arrhenius' law posed the question of how to account for both the frequency factor and the activation energy, and, as described in Laidler and King (1983), a number of candidate theories appeared. We will now briefly sketch one of those candidate theories: the collision formulations of reaction rate theory before discussing the statistical mechanics approach due to Eyring. In all expressions, the variables relating to the transition state are indicated by the symbol ‡.

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[3] The article appears in translated form in Back and Laidler (1967).

4.2.1.2 Collision Theory

In the collision theory the ‘frequency factor’ A in Arrhenius’ equation is interpreted as equal to the frequency of collisions between the reactants. For instance for a bi-molecular (or atomic) reaction between substances A and B, we may define a collision diameter σ_{AB}, masses m_{A} and m_{B} and the collision frequency Z is given by

$$Z = \sigma_{\mathrm{AB}} \left[8\pi kT \left(\frac{m_{\mathrm{A}} + m_{\mathrm{B}}}{m_{\mathrm{A}} m_{\mathrm{B}}} \right) \right]^{1/2} \tag{4.5}$$

The collision theory assumes that all the reactants are hard spheres, and that any collision that has sufficient energy to reach the activated state will proceed to complete the reaction. This is not the complete story, however, and a modified collision theory often introduces a ‘probability factor’ P which measures the probability that a collision will lead to a completed chemical reaction. Hence, in the modified collision theory

$$\mathsf{k} = PZ \exp\left(\frac{-E}{RT} \right). \tag{4.6}$$

The ‘fudge factor’ P is introduced since the collisional cross section of a molecule bears no clear relationship to the probability for a chemical reaction. While the collision theory works well for reactions between mono-atomic gases, it breaks down for reactions between more complex molecules. In this respect, the collision theory is not capable of clarifying the internal mechanisms of chemical reactions in the necessary detail.

4.2.2 The Theory of Absolute Reaction Rates

The theory of absolute reaction rates is a theory that aims to provide explanations for both the ‘activation energy’ and the pre-exponential factor A (the ‘frequency factor’) in the rate equation from first principles. The underlying theories that it uses are quantum mechanics and statistical mechanics. The success of the theory depends on an accurate calculation of the potential energy surface of the reaction, as well as a detailed consideration of the *state* of the initial and final molecule. The theory also introduces a precise concept of a ‘transition state’ which we will discuss first.

4.2.2.1 Quantum Chemistry and Potential Energy Surfaces

In the theory of absolute reaction rates, the transition state is very like a ‘normal’ molecule. The transition state has a definite structure, definite mass, and so forth.

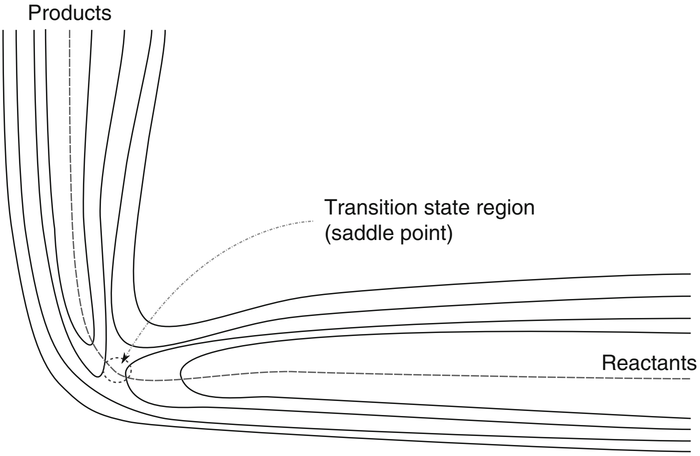

Fig. 4.1 The potential energy surface for a three-atom reaction, indicating the reaction coordinate and the transition state at the saddle point

The only exception is that there is one particular direction of motion (the ‘reaction coordinate’) which causes the molecule to ‘break up’ into the end products of the reaction.

The situation is sketched in Fig. 4.1. On the right is a ‘channel’ of reactants which transforms along a ‘reaction coordinate’ into a channel of products. At the height of the energetic barrier between the reactants and the products lies the ‘transition state’. It is thus clear that the absolute theory of reaction rates requires fairly accurate calculations of these potential energy surfaces. This is a problem that increases very rapidly in complexity for realistic chemical reactions.

Ignoring overall translations and rotations of the reacting system the dimensions of the potential energy surface scale as $3N - 6$ for non-linear structures, and $3N - 5$ for linear structures, where N is the number of nuclei. Hence for a simple 3-atomic reaction the potential energy surface is 3-dimensional and this increases rapidly with larger systems. Hence a number of simplifying assumptions are usually introduced.[4]

The accurate calculation of potential energy surfaces is one of the key prerequisites for the theory since the potential energy surface gives both a value for the activation energy as well as an indication of the spatial structure of the transition state. This is a significant problem if the calculations need to be done at scale. The problem of accurate calculations of potential energy surfaces in the 1930s led Eyring to develop the concept of *semi-empirical* quantum mechanics, which we will return to later in Chap. 10.

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[4] For instance, with the assumption that the transition state for a 3-atom reaction is linear, only two independent coordinates remain. In general, the dimensions of the potential energy surface are decomposed, through diagonalisation of the kinetic energy of the nuclear frame, into a number of ‘normal modes’ which give insight into the dynamical modes of the nuclear frame. See for instance Wilson et al. (1955).

To develop the theory, Eyring first classifies a number of theories as 'semi-empirical' when they have the following characteristics

> (a) that each electron can be assigned a separate eigenfunction which involves the co-ordinates of only this one electron. (b) Multiple exchange integrals are negligible, (c) Normalising integrals for overlapping orbitals are negligible in comparison with unity. (d) The exchange and coulombic integrals for a complicated molecular system may be estimated from a potential curve for the isolated pair of atoms. (e) For distances involved in activation energy calculations this percentage is around 20 per cent. coulombic and 80 per cent. exchange binding, and this varies but little from atom pair to atom pair. (Eyring 1938, p. 8)

Eyring then remarks that more detailed calculations, as well as principled considerations, give no support for the construction of these theories

> None of these assumptions have been rigorously derived from theory, and, as has been emphasised by Coolidge and James, if one assumes for H_3, the approximate eigenfunctions used by Heitler and London and Sugiura for H_2, the assumptions can all be shown to fail badly. (Eyring 1938, p. 8)

Hence, it can be argued that the development of semi-empirical quantum mechanics was in response to the difficulties posed by the resolution of a chemical problem, with chemistry 'guiding' the development of aspects of a quantum theory of the molecule.

4.2.2.2 Statistical Mechanics

The further development of the theory of absolute reaction rates, originating in Eyring (1935), is based on the statistical mechanics of the equilibrium between the reactants and the transition state. Eyring's introduction of statistical mechanics into the expression of the rate equation is based on the idea that the potential energy surface can be calculated with quantum mechanics, and the motion of the nuclear frame can subsequently be treated classically with statistical mechanics.

The following assumptions are made:

> The forces between atoms are due to the motion and distribution of electrons and must be calculated, therefore, using quantum mechanics. However, after this is done the nuclei themselves can be assumed to move under the influence of these forces according to classical mechanics. It must be possible, therefore, to calculate the reaction rates by the methods of statistical mechanics (or kinetic theory), if one assumes the aforementioned forces to be known. (Eyring 1935, p. 107)

At a later stage, Eyring also introduces the assumption that

> A configuration of atoms corresponding to the activated state thus has all the properties of a stable compound except in the normal mode corresponding to decomposition and this mode because of the small curvature can be treated statistically as a translational degree of freedom. (Eyring 1935, p. 109)

Hence, Eyring's formulation of the theory uses the following assumptions:

(E1) Potential energy surfaces can be calculated with quantum mechanics.

(E2) The behaviour of the nuclear frame on the potential energy surface can be described with classical mechanics.

(E3) The decomposition of the transition state into the reactants can be described as a translational motion along the reaction coordinate.

Let us reconstruct the remainder of the argument in the form in which it is given in Glasstone et al. (1941). The key element of statistical mechanics is the partition function (*Zustandsumme*) Z

$$Z = \sum_i g_i \exp\left(\frac{-\epsilon_i}{kT}\right) \tag{4.7}$$

where g_i is the degeneracy of the state corresponding to ϵ_i. The complete partition function for any system is complex to calculate, since it involves all electronic, translational, vibrational en rotational motions of the system with their degeneracies and corresponding energy levels.

Since we will be considering systems with different 'zero levels' it is necessary to correct for these different 'zero levels' in the partition functions (i.e. the usual way of expressing each partition function is to take the lowest level as zero). Specifically, since, as seen in Fig. 4.2, the energy levels of the transition state $\epsilon_{\ddagger}$ can be 'shifted' relative to the reactants by a factor $\epsilon^0_{\ddagger}$ to yield a set of levels $\epsilon'_{\ddagger}$ which is then relative to the initial state:

$$\epsilon'_{\ddagger} = \epsilon^0_{\ddagger} + \epsilon_{\ddagger} \tag{4.8}$$

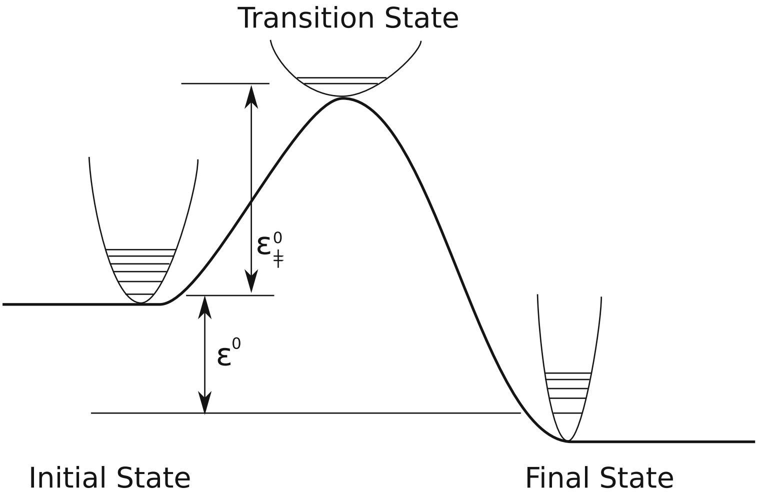

Fig. 4.2 The potential energy surface for reaction seen along the reaction coordinate. The parabolic curves with energetic levels in them should be read as being 'perpendicular' to the reaction coordinate

the partition function of the transition state when expressed in the energy levels of the reactants becomes

$$Z_{\ddagger} = \sum_i \exp\left(\frac{-\epsilon_i}{kT}\right) = \exp\left(\frac{-\epsilon^0_{\ddagger}}{kT}\right)\sum_i \exp\left(\frac{-\epsilon'_i}{kT}\right) = \exp\left(\frac{-\epsilon^0_{\ddagger}}{kT}\right)Z'_{\ddagger}. \tag{4.9}$$

This introduces a factor $\exp -\epsilon^0_{\ddagger}/kT$ per molecule or $\exp -E^0_{\ddagger}/RT$ per mole for the reaction that takes us from the reactants to the transition state, where $E^0_{\ddagger}$ is the energy difference between the ground states or lowest energy levels of the reactants and the lowest energetic states of the transition state as indicated in Fig. 4.2. $Z'_{\ddagger}$ is written starting with $\epsilon^0_{\ddagger}$ as its zero-level.

Now consider the partition function corresponding to the reaction coordinate at the transition state. The translational partition function of the activated complex along the reaction coordinate is given by

$$Z'^{t}_{\ddagger} = \frac{(2\pi m^* kT)^{1/2}}{h}\delta \tag{4.10}$$

where m^* is the reduced mass of the translation along the reaction coordinate and δ is the width of the 'transition state region' on the potential energy surface along the reaction coordinate. This is calculated by considering the translational motion along the reaction coordinate. The total partition function is written as the product of the translational component and an 'internal' component $Z''_{\ddagger}$, so that $Z'_{\ddagger} = Z'^{t}_{\ddagger}Z''_{\ddagger}$.

In the theory of reaction rates we can substitute 'concentrations' for 'partition functions' under the assumption that all modes of energy distribution are independent of each other. The partition functions express 'how much' of a quantity of matter there is in a given volume of space. Hence, we may substitute [A] by Z_A/V where V is a measure of volume.

The reaction rate is the 'speed' with which the reactant systems form the activated complex and pass over the barrier, assuming that each activated complex decomposes in the products of the reaction (assumption A3). This rate may be written as

$$\mathsf{k} = \frac{Z_{\ddagger}}{Z_A Z_B Z_{\dots}}\left(\frac{kT}{2\pi m^*}\right)^{1/2}\frac{1}{\delta} \tag{4.11}$$

We may now rewrite this equation, using both Eqs. (4.9) and (4.10), to give the rate formula of the theory of absolute reaction rates

$$\mathsf{k} = \frac{kT}{h}\frac{Z''_{\ddagger}}{Z_A Z_B Z_{\dots}}\exp\left(-E^0_{\ddagger}/RT\right) \tag{4.12}$$

This is easily seen by using expression (4.9), substituting $Z'_{\ddagger}$ by $Z'^{t}_{\ddagger}Z''_{\ddagger}$ and using the expression for $Z^{t}_{\ddagger}$. $Z''_{\ddagger}$ is the partition function for the transition state which does not include the translational motion along the degree of freedom of the reaction coordinate.

The advantage of this formulation is that the partition functions for all compounds featuring in the reaction can be calculated using statistical mechanics for vibrational and rotational motion of mechanical systems. While this is still a difficult problem, a detailed consideration of different reacting systems yields a mechanistic insight in how the reaction occurs on a molecular level. This feature distinguishes the theory of absolute reaction rates from the collision and thermodynamic theories, which can offer no such mechanistic insights into chemical reactions.

4.2.2.3 Thermodynamic Formulation

The thermodynamic formulation starts from Arrhenius' condition (A2) that the activated complex is in chemical equilibrium with the reactants, hence the equilibrium constant for the reaction

$$\mathrm{A} + \mathrm{B} + \ldots \leftrightarrow \mathrm{M}^{\ddagger} \tag{4.13}$$

is given by

$$K^{\ddagger} = \frac{[M^{\ddagger}]}{[\mathrm{A}][\mathrm{B}][\ldots]} \tag{4.14}$$

From assumption (A3), together with a set of statistical mechanical considerations derived from condition (E3), leading to Eq. (4.10), we can derive that the rate of reaction is given by

$$\mathsf{k}[\mathrm{A}][\mathrm{B}][\ldots] = [M^{\ddagger}]\frac{kT}{h} \tag{4.15}$$

and hence the reaction rate constant is

$$\mathsf{k} = \frac{kT}{h}K^{\ddagger} \tag{4.16}$$

Since the equilibrium between the activated state and the reactants is a normal chemical equilibrium it can be related to the thermodynamic theory of chemical reactions, and hence, it can be related to the normal thermodynamic entities free energy, enthalpy ('heat content'), entropy and so forth. Doing this, we get

$$\mathsf{k} = \frac{kT}{h}\exp\left(\frac{-\Delta F^{\ddagger}}{RT}\right) \tag{4.17a}$$

$$= \frac{kT}{h}\exp\left(\frac{-\Delta H^{\ddagger}}{RT}\right)\exp\left(\frac{\Delta S^{\ddagger}}{R}\right) \tag{4.17b}$$

(using the equation $F = H - TS$). We thus obtain a measure of the entropy changes associated with the reaction. The thermodynamic formulation is related to the theory of absolute reaction rates through the fact that it uses the statistical mechanical expression for the translational motion for crossing the barrier in its formulation.

4.2.2.4 Competing Formulations of the Fundamental Theories

One of the interesting aspects of the development of the theory of absolute reaction rates is that it allows for a *comparison* between several approaches to the specification of reaction rates; in particular the thermodynamic, collision and transition state approaches. While always well-formulated, these theories were not always well-founded, but they derive mutual support from the comparison feature.

The comparison feature of the net is based on identifying the mathematical and conceptual features in one fundamental theory to the mathematical and conceptual features in another fundamental theory, and then draw conclusions that in turn allow for useful expressions of thermodynamic quantities in terms of kinetic quantities or in terms of expressions based on statistical mechanics, or structural features of the transition state.

Specifically, the three formulations of the Eyring equation that are of interest are the collision theory, the thermodynamic formulation and the statistical mechanical formulation, as follows:

$$PZ \exp\left(\frac{-E_A}{RT}\right) \sim \frac{kT}{h} \exp\left(\frac{-\Delta F^{\ddagger}}{RT}\right) \sim \frac{kT}{h} \frac{Z''_{\ddagger}}{Z_A Z_B Z_{\dots}} \exp\left(-E^0_{\ddagger}/RT\right) \tag{4.18}$$

All of these three theories remain valid in the explanation. The comparison is used to illuminate various *aspects* of the mechanisms of chemical reactions. The comparison feature would allow for the further development of interesting formal work on reduction for this particular case, which we will further develop in Part II.

It is harder to read this second feature as inherent through a 'reduction postualte' even in a liberal reading of Nagel's model. Nagel's model does provide clues as to how one might go about evaluating the *reductive strength* of the three theories involved, byspecifying the amount of 'borrowing' that goes on between the fundamental theories.

These comparisons (in the form of conceptual 'borrowing') provide useful (some would say indispensable) insights into the *mechanisms* of actual chemical reactions. As an example, in Glasstone et al. (1941) the comparison with collision theory is made explicitly for a diatomic reaction on p. 17, where it is remarked that the mean of the collision diameters of the reacting substances, is instead also determined by the configuration of the activated complex. This is an important modification, which moreover generalises to cases of more complex molecules.

The key realisation is that of the various theories the collision theory is a conceptually simple theory, which allows mechanistic pictures to be developed of how the reaction proceeds. In a similar fashion, provided some simplifying assumptions are made, statistical mechanics allows for the development of partition functions for rotational and vibrational states, and hence allow for the development of mechanistic views on how the reaction proceeds.

The thermodynamic formulation then allows a recasting of these concepts in thermodynamic terms.

Taken together with the precise specification of the transition state it has allowed chemists to develop various 'reaction mechanisms', some of which step outside of the bounds allowed by the theory but are nonetheless useful explanatory vehicles.

4.2.3 *Wigner's 'three threes'*

A detailed summary of absolute reaction rate theory was given in Wigner's (1938) presentation at the 1937 Faraday conference, where he summarised the challenges, types of reactions and assumptions of the theory as a set of 'three threes'.[5] The three threes are summarised in Table 4.1, and translated into a specific set of steps (WS), groups (WG) and assumptions (WA).

Wigner's three steps are (WS1) The determination of potential energy surfaces, which gives, in the words of Wigner, 'the behaviour of all molecules present in the system during the reaction, how they will move, and which products they will

Table 4.1 Wigner's 'three threes' that characterise transition state theory. After Miller (1998). The relationship between the 'three threes' and the Arrhenius (A) and Eyring (E) conditions is also indicated. After Miller (1998)

Three steps in theory of kinetics:		
(WS1)	(=E1)	Determine potential energy surfaces
(WS2)		Determine elementary reaction rates
(WS3)		Solve rate equations for complex reaction mechanism
Three groups of elementary reactions:		
(WE1)		Vibrationally/rotationally inelastic collisions (not a chemical reaction)
(WE2)	(∼ E1)	Reactive collisions on a single potential energy surface
(WE3)		Electronically non-adiabatic reactive collisions
Three assumptions:		
(WA1)		Electronic adiabaticity: the electronic configuration is in the lowest quantum state for each configuration of the nuclei
(WA2)	(=E2)	The validity of classical mechanics for the nuclear motion
(WA3)	(∼ A3 ∼ E3)	Existence of a dividing surface that trajectories do not re-cross

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[5] Wigner refers to the theory in this paper as 'The Transition State Method'. The paper by Laidler and King (1983) contains a brief discussion of this conference and the role it played in the subsequent adoption of the theory.

yield when colliding with definite velocities, etc.' (p. 29). The solution of this problem requires the calculation of a potential energy surface, which is a quantum chemistry problem. (WS2) The next step is the calculation of 'elementary reaction rates'. (WS3) The third problem is to combine these 'elementary' reactions into a series of reactions which make up the overall chemical transformation. Of these, the 'elementary' form of reaction rate theory only considers (WS1) and (WS2) and ignores (WS3).

Wigner classifies the elementary reactions in three groups: inelastic collisions, in which the molecules exchange vibrational and / or rotational energy but do not change their chemical composition, reactions on a single potential energy surface which involve no change in electronic quantum numbers, and reactions involving multiple potential energy surfaces (non-adiabatic reactions). Only the second type of elementary reactions can be treated with transition state theory, hence, only (WE2) is considered in the theory.

Finally, Wigner discusses three assumptions (WA). The first specific assumption is the adiabatic assumption (WA1), which assumes that during the reaction the molecular system 'stays' on the lowest possible potential energy surface, and there is no change of electronic configuration. The second assumption, (WA2) is that the motion of the nuclei can be described with classical mechanics. The third assumption, (WA3), is that the reaction does not go 'backwards', i.e. all systems crossing the barrier are reacting systems. The consequence of this is that the step from the reactants to the transition state is the rate determining step for the equation. Once a set of reactants form a transition state, this transition state will fall apart to form the end products of the reaction.

The three threes form a more elaborate formulation of the Eyring conditions (E1–3) in the sense that they add precision and in this way also indicate directions for future research (e.g. reactions on non-adiabatic surfaces, quantum effects in nuclear motion etc.).

It is also interesting to note that the assumptions have been relatively stable throughout the development of the theory with the exception of (A3). Especially (WA3) can be seen as a reformulation of (A1) and (E3): the assumption that the transition state decomposes into the reaction products has developed into a 'non-crossing' criterion.

4.2.4 Summary

The structure of the theory of absolute reaction rates is given in Fig. 4.3. As stated before, the purpose of the theory was to provide exact expressions for the two constants A and E_A. From the viewpoint of *quantitative* explanations for these quantities the theory has been moderately successful, but has, in the words of Laidler and King (1983), 'its difficulties'.

It is of historical interest to note that the theory was not immediately accepted upon its appearance. As is seen in the proceedings of the 67th general discussion of

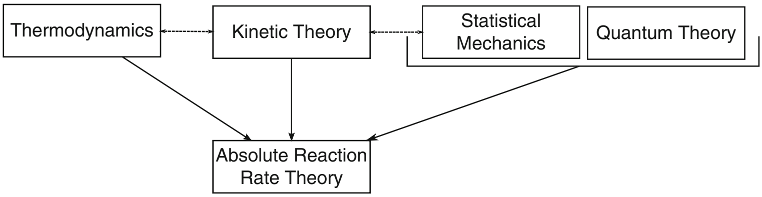

Fig. 4.3 The conceptual structure of the theory of absolute reaction rates

the Faraday Society (which was held at the University of Manchester from Monday, 13th to Wednesday, 15th September, 1937), there were some who saw the theory as somewhat speculative. These proceedings also contain a number of key papers which lay the matter out.

The theory of absolute reaction rates would not be considered a numerically adequate theory of reaction rates today. The enduring aspect of the theory of absolute reaction rates is that, again in the words of Laidler and King, it provided a

> [. . .] conceptual framework with the aid of which experimental chemists (and others) can gain some insight into how chemical processes occur. On this score the theory must receive the highest marks; for nearly half a century it has been a valuable working tool for those who are not concerned with the calculation of absolute rates but are helped by gaining some insight into chemical and physical processes. The theory provides both a statistical-mechanical and a thermodynamic insight – one can take one's choice or use both formulations. (Laidler and King 1983, p. 2664)

Thus, it was the conceptual explanatory feature of the theory of absolute reaction rates that is considered its lasting contribution. In the final analysis, the theory provided valuable insights into the *mechanisms* that drive chemical reactions at a molecular level. Hence, the theory of absolute reaction rates is a very strong example for the unity of science – it is precisely one of those examples where it is hard to imagine a chemistry with the physics removed, but at the same time it is a 'chemical' theory in that it focuses on molecules, molecular structures, and transformations.

4.3 Explanation with a Network of Theories: Reductive 'interfield' Theories

In this section, we will analyse the net in Fig. 4.3 in more detail with the theoretical machinery established in Chap. 1, specifically in terms of the model developed in Sect. 1.2.3. I will first characterise the net as a (proper) instance of an 'interfield' theory in the sense of Darden and Maull (1977). The next step in the naturalised reduction programme is to formally paraphrase the (putative) reduction of the Arrhenius equation by the various theories that constitute the net of theory of absolute reaction rates.

4.3.1 A Theory Net

One of the features that stands out in Fig. 4.3 is that the explanation of reaction rates proceeds in the context of a *net* of theories, which is depicted in Fig. 4.3. Hence in the case the theory of absolute reaction rates the explanation proceeds in terms of *multiple* underlying theories, which in turn can be evaluated and compared on the amount of *reductive strength* that they are capable of providing. In this sense, the inter-theory relationship is not between two theories, but rather in terms of a *network* of theories.

The specification in terms of a network has a number of important consequences. In particular, the specification of this network lends support to the characterisation of the theory of absolute reaction rates as an *interfield* theory in the sense of Darden and Maull (1977) (p. 20), where the theories comprising the field are in turn reductively connected. In this context, it is crucial that the reduction postulates carry a limited amount information, and that theoretical context is lost while the reductive connection is made.

First, let us consider the question of whether Darden and Maull's criteria are satisfied (for the criteria, see p. 20). The criteria are that the (network of theories) solves the (theoretical) problem by introducing a 'new idea as to the nature between fields'. The new idea that would qualify in this case is the notion of a (structural) interpretation of the 'transition state' or the 'activated complex'. It is only the combination of the field of reaction theory to quantum physics and statistical mechanics that allows that interpretation to become as specific as it does. The theory allows, as we have seen, for specific comparisons between thermodynamics, collision theory and the theory of absolute reaction rates, and this allows us to answer both 'new' questions as well as new focus.[6] As the analysis of Laidler and King (1983) illustrates, the theory has also generated new lines of research.

Thus, there seems to be no specific problem with classifying the above network of theories as an example of an 'interfield' theory in the sense of Darden and Maull.

4.3.2 Specification of the Relationships

The characterisation of this 'interfield theory' in terms of a network of specific theories also allows us to investigate whether reduction relationships between these theories exist.

As we have seen in the discussion on the structure of the absolute rate theory, the theory needs to explain the pre-exponential (or 'frequency') factor A and the activation energy E_A with the three candidate theories for T_F: collision, thermodynamics and the combination of quantum mechanics and statistical mechanics that charaterises transition state theory (or the theory of absolute reaction rates).

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[6] It would probably not be fair to say that, for instance, reaction enthalpies or collision rates were 'previously neglected' as Darden and Maull require.

In the case of the three candidate reducing theories – collision theory, thermodynamic theory and theory of absolute reaction rates – it is hard to define which theory is ‘foundational’ in the sense of a reducing theory. Good arguments can be made that all three theories are foundational in this sense, and that there is no clear delineation along Nagelian lines in terms of a ‘reduced’ and ‘reducing’ theory among these three theories themselves. What is clear, however, is that Arrhenius’ law can potentially be reduced to either of the three candidate theories in terms of our liberal Nagelian model.

It is also clear, even from a cursory analysis of the structure of Arrhenius’ law as well as the equations of the three candidate reducing theories, that the *structural* components of the three theory are identical, and hence there is no problem with the requirement that the structure of the laws and the theories are approximately the same.

Hence, under a reconstruction *qua* reduction, the case at hand is a really interesting one: rather than reducing to a single theory that can be considered ‘foundational’ the reconstruction points towards a structure in which the three theories are (reductively) related without it being obvious which theory is more foundational: as I will argue in the next section, this leads to additional conceptual strength for the theory of absolute reaction rates.

What rests here is the specification of the reductive connections. We have to consider three theories with two reductive connections per theory pair: the activation energy E_A and the structure factor A. We can do this in terms of the five steps of Kuipers’ model.

The thermodynamic theory explains the quantities involved in terms of entropy and enthalpy of the activated complex. In terms of Kuipers’ model, these are straight applications and identifications (ignorming some mathematical details). The entropy and enthalpy related to the activated complex are however still complex and abstract quantities, which can no further be accessed conceptually or empirically (apart from establishing them through a measurement of reaction rates).

In the case of the kinetic collision theory, it is easiest to conceptually connect Arrehnius’ law to a physical model: the activatio energy is equated wit the ‘saddle’ on the potential energy surface while the ‘structure’ factor A is equated with the (product) PZ: the number of collisions adjusted for the ‘chance’ that a particular collision leads to a reaction. Note that this conceptual connection is in dynamic, not in structural terms. In terms of Kuipers’ model, the relation involves an identification of E_A with the height of the ‘saddle’ on the potential energy surface and the ‘kinetic’ factor PZ with the structure factor. The collision theory thus explains that the ‘structure’ factor has a kinetic component, and hence, in addition to an identification, also involves an aggregation.

Of the three theories, the theory of absolute reaction rates is by far the most developed. The ‘activated complex’ is precisely specified as the saddle on the potential energy surface, but also as a molecule with a particular translational coordinate: the specification is precise enough that we can teach a modern quantum chemistry program to ‘search’ for a molecule with these precise properties. Similarly, the structure factor A is specified precisely as a function of the partition functions of reactants through the steps Application, Identification and Aggregation. In terms of Kuipers’ model, the connection between the structure factor and the function of partition functions. These are computable quantities, hence the name theory of ‘absolute’ reaction rates.

In Kuipers’ model, we may speak of a reduction if the connections involve a (combination of) steps (2), (3) and (5) of the five step scheme. On this count, all potential reduction relationships qualify *qua* reductions, involving at least some non-trivial steps for each.

4.3.3 Reductive Strength qua Conceptual Strength

The assessment in Laidler and King (1983) makes clear that the main contribution of the theory of absolute reaction rates is conceptual: by providing mechanisms to explain how reactions proceed (although quite often in individual instances that are difficult to generalise) the theory has had made an important contribution to our understanding of reaction rates.

In terms of the three candidate reducing theories, a significant element of explanatory power from the theory of absolute reaction rates is delivered through the comparison feature of the theory net: this allows us, for instance, to explicate the mechanisms of the reaction – which are easiest to understand in simple terms from the collision theory – in terms of a function of the partition functions of the reactants. The latter are in principle computable, and so, what was a fudge factor in the collision theory: the ‘chance’ that a particular collision would lead to a reaction, can be exactly described in terms of the properties of the molecules taking part in the reaction.

Moreover, it is only the theory of absolute reaction rates that is capable of explicating the exact properties of the ‘transition state’ in structural terms, and hence allow for its detailed analysis. One can thus conclude that the theory of absolute reaction rates has the highest conceptual strength, followed by the collision theory and then the thermodynamic theory.

But that relative evaluation tells only part of the story of how the explanation evolves in terms of the overall network of theories. The overall strength in terms of explanation and further theory development, lies in the network itself, once its constituent relations have been clarified. The reductive programme is in this sense a powerful program – even in cases where the reduction fails, the specification of the connecting relations between the constitutive theories of the field is of importance in understanding how a theory plays its explanatory role.

4.4 Conclusion: Theoretical Patchwork

Naturalised Nagelian reduction has yielded interesting perspectives on the case of theory of absolute reaction rates. The analysis of the theory of absolute reaction rates pursued in this chapter has identified a number of philosophical features that are more broadly speaking features of the putative reduction of chemistry to physics.

Specifically, the analysis of theory of absolute reaction rates in terms of the approach to Nagelian reduction developed in Chap. 1 has illuminated three salient features of the theory which are of further interest to the philosophy of science. These are:

1. The characterisation of the overall explanation in terms of a *network* of theories rather than a single theory.
2. The *specification* of the transition state as a unique sort of molecule, introducing a new theoretical concept, but pragmatically falling inside the scope of an 'interfield' theory.
3. The feature that an important element of explanation consists of an inter-theory *comparison* of several potential reducing theories in terms of their explanatory and conceptual strength.

The network that results from the analysis of the theoretical relationships is therefore pragmatically more compatible with the various non-reductive theories we have discussed than with the Nagelian model, certainly with a Nagelian model *qua* 'identities and derivation'.

This allows for the *pragmatic* classification of the theory of absolute reaction rates as an 'interfield' theory, while it also invites us to consider the detailed relationships in more (formal) detail. The case of the theory of absolute reaction rates is the first where we have encountered a network of theories that can be characterised in terms of an interfield theory, but also one where we may argue that reductive relationships exist between the different component theories, although it is hard to establish, between the three competitors, which theory is more 'foundational'.

This allows for the conclusion that moderate Nagelian reduction relationships between individual theories do not in turn amount to *tout court* reduction of a field. Nagelian reduction allows theoretical independence of a field, with theory survival, but also with meaningful interconnections between reduced and reducing theory.

An interesting aspect of the network is that theoretical concepts may be freely borrowed from other fields, and reused as theoretical 'patches' in the development of further theories. The 'loss of context' that may accompany such inter-theory reduction may formally be specified in a number of ways, for instance in terms of the 'chunk and permeate' approach to theories developed by for instance Brown and Priest (2004, 2008). Brown and Priest hold that such (paraconsistent) 'chunk and permeate' structures are even present in individual theories.

Alternatively, these concepts can also be logically developed as part of a semantic or structuralist model of theory nets and inter-theoretic *links*. For now, we will forgo these formal specifications, but will return to them in Part II.

Chapter 5
Quantum Chemistry as a Research Programme

Abstract This chapter characterises quantum chemistry, the main reducing agent in chemistry, as a Lakatosian research programme. The attraction of the concept of a research programme is that it allows us to think of quantum chemistry not as a single theory, but as a succession (or network) of co-operating theories. This in turn allows for a more balanced discussion on how quantum chemistry can be characterised as a reducing theory. It also allows us to consider a number of questions on the internal structure of quantum chemistry, such as the question whether quantum chemistry is a progressive or degenerating research programme.

5.1 Introduction

In the 1970s Imre Lakatos,[1] partly in response to the work of Kuhn (1970) and others in the history of science, introduced the notion of a *research programme*. In particular, Lakatos' concept of a research programme was aimed at reconciling Kuhn's theory of scientific paradigms with the ideas of falsification stemming from Karl Popper (1959).

Lakatos' program can be characterised as an attempt to accommodate a significant portion of the criticisms levelled at Popper's falsificationist philosophy of science. To this end, Lakatos advances a sophisticated version of falsificationism, dubbed *methodological* falsificationism, as a refinement of naive or 'dogmatic' falsificationism. Methodological falsificationism requires that scientific theories have an empirical basis. For Lakatos, that means a number of things; but most importantly, the notion of an 'empirical basis' entails the notion of a crucial experiment to compare two theories.

As is well-known, Lakatos' main contention is that a scientific research programme consists of a 'core' supported by a set of auxiliary hypotheses. The 'hard core' forms the conceptual and model basis of the research programme, while the auxiliary hypotheses form a 'protective belt' around the hard core that make

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[1] See Lakatos (1970) and Radnitzky and Andersson (1978) for an overview and critique of Lakatos' ideas, in particular the paper *Falsification and the Methodology of Scientific Research Programmes* on p. 91–196 in Lakatos (1970).

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it immune to direct falsification. Lakatos speaks only of a research programme when the auxiliary hypotheses are governed by a positive heuristic, which provides suggestions for successive improvements in the auxiliary hypotheses.

Quantum chemistry, which we will discuss in this chapter in a Lakatosian context, should provide interesting new material in a Lakatosian evaluation of science and scientific practice. Specifically, this chapter intends to address a number of issues that arise with the application of Lakatos' ideas to quantum chemistry. The first issue is whether quantum chemistry can be seen as a research programme in the sense of Lakatos and if so, whether that research programme is progressive or degenerating. The second issue, though related to the first, is whether the explanations of chemical as well as physical phenomena offered by quantum chemistry fit current philosophical notions of explanation.

The history of quantum chemistry has been of interest to historians of science for about three decades, with one of the first books appearing on the subject the work by Nye (1993). More recently, the history of quantum chemistry has been documented by Gavroglu and Simões (2011, 2012), as well as in the chapter by the same authors in Scerri and Fisher (2016).

A number of distinct questions become pertinent in the context of a Lakatosian reconstruction of quantum chemistry.

The first set of questions relates to whether quantum chemistry has made novel predictions in the sense of Lakatos, specifically in the form of new experimental facts.[2] There is also an additional, more or less theoretical 'novelty' criterion, which focuses on the generation of novel facts relative to the theories of chemistry that were available prior to quantum chemistry. In the case of quantum chemistry, this second novelty question takes on an additional urgency, since it is sometimes argued that quantum chemistry utilises chemical facts in its construction and explanation.

In this sense, the 'theoretical' novelty criterion can be used to describe the relationship between quantum and classical chemistry. While one could think that quantum chemistry is in some sense a competitor for classical chemistry my argument will not be that quantum chemistry is progressive in precisely this sense. Rather, I will argue that the relationship between quantum chemistry and classical chemistry is to be seen as the relationship between a supply programme and a guiding programme in the sense of Zandvoort (1986).

The second set of questions in this chapter focuses on explanation in quantum chemistry. In order to discuss how quantum chemistry might be successful at its business as a Lakatosian research programme we have to give a detailed account of how quantum chemistry explains. The question then arises whether the explanations of chemical and physical phenomena offered by quantum chemistry fit current philosophical notions of explanation.

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[2] In the literature, there has been some argument about what a novel prediction exactly is, notably, the original notion of Lakatos was refined by Zahar (1973a) and Worrall (1978). The novelty criterion of Lakatos is focused on whether a theory can make.

This chapter will proceed along the following lines. In the following Sect. 5.2 we will introduce the topic by outlining the methodology that quantum chemistry uses in its explanation of chemical data and discuss briefly how quantum chemistry generates ‘novel facts’ of the two kinds indicated in the light of its explanatory structure.

In the following two sections of this Sects. 5.3 and 5.4 we reconstruct quantum chemistry as a research programme. This reconstruction resolves some of the tensions between classical and ‘quantum’ chemistry in the sense that classical and quantum chemistry are seen to co-exist in the relationship of a guide and supply programme in Sect. 5.4. Moreover, we argue that quantum chemistry is indeed a research programme in the sense of Lakatos, and qualify it as a progressive supply research programme. The last section contains a conclusion.

5.2 How Quantum Chemistry Explains: A Brief Reconstruction

The goal of quantum chemistry is to explain chemical phenomena through a computational solution of the basic equations of quantum mechanics.

That quantum theory should apply to theories of chemistry is not intuitively clear. Chemistry in general, and chemical ‘laws’ in particular, deal primarily with *classes* of molecules, such as acids, salts, organic molecules and groups and the like. Computational quantum chemistry, in opposition, makes claims about *individual* molecules rather than classes of molecules. Quantum chemical methods that are suited to making claims about classes of molecules tend to be highly approximate in nature and tend to be problematic when viewed from the vantage point of more exact methods. It seems then, that quantum chemistry will allow us to have our cake of numerical accuracy, but not at the same time eat it too: highly accurate numerical wavefunctions are tailored to a single molecule, or to a molecular configuration, and do not readily ‘transfer over’ to classes of molecules. To resolve these issues, it is useful to consider the various steps that make up a calculation in quantum chemistry, and its possible connections to chemistry.

5.2.1 The Process of Quantum Chemistry

For the purposes of this section we will start by narrowing the notion of quantum chemistry down to that of ab initio ‘electronic structure theory’, which, apart from the popular Density Functional Theory (DFT) methods, is the most commonly used application of quantum chemistry today. Ab initio electronic structure theory has been implemented in a number of easy to use computer programs, and is becoming more and more a ‘black box’ chemistry tool for non-quantum chemists. In this chapter, I will not pay particular attention to DFT, though it would seem that much of the analysis of ab initio theory presented here can be extended to cover DFT.

Ab initio calculations are based on the space-fixed 'clamped nucleus' Hamiltonian. As discussed in Chap. 3, the space-fixed or 'clamped nucleus' non-relativistic theory is the most widely used implementation of quantum chemistry. I will therefore characterise this type of quantum chemistry as 'electronic structure theory' for the purposes of the Lakatosian reconstruction. An extension of the Lakatosian method is possible by investigating how the obvious restrictions in this approach can be mitigated, through introduction of both relativistic approaches to electronic structure theory, and higher orders in the Born Oppenheimer approximation, but that will not be further discussed in this chapter.

The calculations performed by quantum chemical computer programs incorporate the basic equations of quantum mechanics combined with a (significant) set of assumptions and a relevant context. It is the case that these computer programs are able to compute the properties of atoms and most small molecules with (almost arbitrarily) high precision.[3] Hettema (2009) has provided examples of how a set of 'intermediate' or 'enabling' theorems allow quantum chemists to develop the methods that are implemented in these computer programs.

The reason that these intermediate theorems are required is that the time-independent Schrödinger equation[4] for electrons

$$H\Psi = E\Psi \tag{5.1}$$

provides little guidance to its further use in modelling atoms or molecules. H is the Hamiltonian operator, which corresponds to the property of energy:

$$H = \sum_i h(i) + \sum_{i<j} g(i,j) \tag{5.2}$$

where $h(i)$ is the one particle operator (consisting of kinetic and potential energy) and $g(i,j)$ is the electrostatic interaction between electrons i and j.

In actual practice, to solve such equations for a small or large molecule, the quantum chemist relies on the following approximations, idealisations and concretisations (cf. also Woody 2000 for a slightly different enumeration[5]):

1. *Idealisation*: A geometrical structure of the molecule is chosen and the coordinates are put into the program.

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[3] There are a large number of references that I could give here, however, a good overview of the methods which we will discuss is given in McWeeny and Sutcliffe (1969), McWeeny (1989) or Helgaker et al. (2000). The DFT method, which I will not discuss, is discussed in detail in Engel and Dreizler (2011).

[4] As in previous chapters, in what follows I will use the so-called 'atomic' units, in which $\hbar = 1$, $m_e = 1$ and the charge of the electron $e = -1$.

[5] Although Woody's enumeration is somewhat different, I do in the main agree with her classification, though I believe the one presented in this chapter to be more comprehensive.

2. *Approximation*: Relativistic effects are generally ignored or treated in an approximate manner.[6]
3. *Approximation*: With each atom there is an associated 'basis set' in terms of which the wavefunction will be expanded. The quality of the basis set has a direct influence on the quality of the overall result of the calculation. Basis set selection is in fact a bit of a fine art in practical quantum chemistry.
4. *Idealisation*: Generally, the first level of solution is a 'self consistent field' solution (SCF or Hartree-Fock (HF) wavefunction) which ignores the effects of electron correlation. This wavefunction is a meaningful wavefunction which satisfies the Brillouin condition. In general, the HF wavefunction is a starting point for more complicated treatments. As discussed in Hettema (2009), it is perfectly possible, with the Hartree-Fock solution in hand, to draw pictures of the Hartree-Fock orbitals and talk about its 'orbital energies' in the sense intended by Woody (2000).
5. *Concretisation*: Electron *correlation* is introduced subsequently, either through variational methods such as Configuration Interaction (CI), Multi-Reference methods, or through perturbation theory with so-called 'Many Body' methods (either Many Body Perturbation Theory (MBPT) or the more sophisticated Coupled Cluster (CC) approach).
6. The observational properties of the wavefunction then have to be predicted with these wavefunctions – i.e. an 'operator' that corresponds with the property needs to be chosen and the 'expectation value' of this operator needs to be calculated.

These steps are of course close to Kuipers' five steps for reduction which we discussed in Chap. 1 (p. 17), and it should come as no surprise that we will conceive of (suitable) characterisations of these steps as part of a programme for liberal reduction in Chap. 7.

The computational problem for large molecules can become intractable, especially if numerically accurate wavefunctions, such as large CI expansions or higher orders of Coupled Cluster expansions, are required. However, the *practical* intractability of some of these problems does not mean that they are *principally* incapable of solution. In fact, for areas where quantum chemical solutions have been practically feasible (in general atomic calculations and small molecules) the results have been impressive, and there is little doubt that the mechanisms generally employed by quantum chemists are capable of producing these results for as yet unknown cases.

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[6] Although there is a significant research program in 'relativistic quantum chemistry', the equations to be solved tend to be an order of magnitude harder than the equations of non-relativistic quantum chemistry. The situation is not helped by the fact that relativistic effects are most pronounced for heavy atoms and molecules with heavy atoms – i.e. those areas of the Periodic Table where even non-relativistic quantum chemistry can become particularly cumbersome due to the large number of electrons and the complexity of the basis sets that need to be used. See Dyall and Faegri (2007) for a detailed discussion of relativistic quantum chemistry.

This overview presents some hints as to how quantum chemistry may be conceived as a Lakatosian Research Programme. Our basic supposition, to be further expanded later in this chapter, will be the following:

1. Its hard core consists of the basic equations of (time-independent) quantum theory applied to a molecular system consisting of (i) a nuclear framework with a particular geometric structure and (ii) a set of electrons. The core theoretical tenets are the laws of quantum mechanics. These can be conceived of as the time-independent Schrödinger equation (the laws of quantum mechanics), but, as discussed in Hettema (2009), also includes a number of lesser-known theorems (enabling theorems which are derived from the quantum theory for an 'exact' wavefunction), such as Ehrenfest's theorem, the Hellman-Feynman theorem and the creation of operators that correspond to observables. These equations are *applied* to a system of nuclei and electrons.
2. The protective belt falls apart in a set of computational methods that determine the quality of the electronic wavefunction. In practice, there is a wide range of such methods available, ranging from semi-empirical methods through to Hartree-Fock (HF) wavefunctions, and a plethora of electron correlation methods.
3. The remainder of the protective belt contains auxiliary hypotheses that correspond to some of the approximation steps above, which lead to simplified wavefunctions. These auxiliary hypotheses primarily consist of the choice of basis sets used in the expansion of the wavefunction.

5.2.2 Characterisation of Quantum Chemistry as a Research Programme

It is sometimes argued that the process of quantum chemistry does not constitute an explanation due to the various idealisations involved. These idealisations in turn provide useful guides to the initial characterisation of quantum chemistry as a research programme.

In the first place, as discussed in Chap. 3, it is sometimes argued that fixing the nuclear framework in space imposes a specific shape on the molecule from the outset, and that such a step is incompatible with the practice of quantum theory. Generally, practising quantum chemists have to start with *some* notion of molecular shape, though the starting shape of a calculation does not have to correspond to the chemical equilibrium state of a molecule. Quantum chemists regularly calculate the electronic energies and properties of molecules outside their equilibrium state, and this leads to new insights in areas such as reaction dynamics. In particular, quantum chemists are able to make predictions on the stability of molecules that do not yet exist.

Another idealisation is the already mentioned neglect of relativistic effects. This neglect is not universal. Quantum chemists are well aware that relativistic effects do have a bearing on their predictions of molecular energies and properties, and an active research programme exists in relativistic quantum chemistry. This programme is based on the Dirac equation, which is very different in its mathematical properties. Relativistic quantum chemistry is thus, on a strict interpretation of a Lakatosian research programme, best interpreted as a separate research programme since it has a different 'hard core'.

We now come to the choice of basis set. Basis set choice is something of an art in quantum chemistry in the sense that the selection of a poor basis set will have adverse results in the result of the calculation. However, basis sets are not the Achilles heel of quantum chemistry. There is research being done in improving the quality of basis sets, and there is also a solid understanding of what quality standards basis sets are required to meet in order to solve chemical problems of a certain complexity. For instance, calculation of molecular dipoles and quadrupoles requires addition of 'polarisation functions' to the basis set. These polarisation functions are not made up after the fact; we know they have to be there because a basic consideration of the symmetry of molecular integrals tells us that the calculation will be incomplete if these are not considered. It is thus the case that the *form* of the basis set can be decided a priori with reference to the molecular property we want to calculate.

There is a somewhat open question in the Lakatosian reconstruction where the quantum chemical 'methods', such as HF, CI, MBPT etc. fit into the reconstruction. On the one hand, one could argue that these form part of the theoretical core of the quantum chemistry program, on the other hand, the ready availability of a range of methods, as well as the fact that one method often builds upon another (for instance many body theories take as a starting point the Hartree-Fock wavefunction and so on) suggests that the choice of method is a more pragmatic issue, which is more properly placed in the protective belt. We have chosen the latter option, on the basis that in a Lakatosian construction, the hard core of the programme has to be stable over the lifetime of the programme.

The HF wavefunction is a common starting point for further calculations involving electron correlation. Lacking the powerful computers we have available today, quantum chemists have long lived with a situation in which these wavefunctions were the best they could do for more complicated molecules (generally the sixties, seventies and much of the eighties of the last century). At present the calculation of the HF wavefunction for small to mid-size molecules is routine.

The case of the HF wavefunction is of particular importance for our discussion and we will discuss it briefly in some more detail. A completed HF calculation specifies a set of atomic or molecular orbitals ψ_i, (of which corresponding density graphs can be plotted) and a corresponding set of eigenvalues ('orbital energies') ϵ_i. The set of orbitals consists of occupied and empty (virtual) orbitals. I have already argued in Hettema (2009) that there is an *immediate use* which can be made of quantum chemical results, and the HF wavefunction is an illustration of this. This result also aligns with the discussion on idealisation and concretisation in Chap. 2.

The particular minimal condition that has to be satisfied by the HF wavefunction is the Brillouin condition, which requires that matrix elements of the Fock operator between virtual and closed (or occupied) shell orbitals vanish. The Brillouin condition is thus a relatively weak condition, which allows for an arbitrary large number of orbital sets to satisfy the HF equation. The most often used representation is the 'canonical' HF equation, where the orbitals diagonalise the entire Fock matrix.

In partial opposition to the claim of Woody (2000)[7] it does not seem to be the case that the Hartree-Fock calculation of atomic and molecular properties yields descriptions that are irrelevant for the theories of chemistry in the sense intended by Woody. There are (see McWeeny 1989, p. 164–166, or Baerends and Gritsenko 1997) a number of chemically relevant molecular properties that may be derived from this wavefunction. (i) The HF eigenvalues ϵ_k for the occupied orbitals are reasonable approximations for the negative of the ionisation energies I_k needed to produce a positive ion by removing an electron from ψ_k through Koopman's theorem. (ii) Similarly, the eigenvalues ϵ_m represent empty places that can be taken up by an additional electron, and the difference between orbital energies provides a first approximation to the excitation energies of the system. (iii) The HF wavefunction will support the calculation of spatial electron densities. In turn, the calculation of these entities for a range of molecules allows for a systematic investigation of such properties across different molecules and the HF wavefunction will support a form of *Aufbau*.

This is not to claim that the HF method is the best possible answer to these entities (it is not), but serves as a reminder that the HF wavefunction, if desired, may provide some support for the type of diagrammatic interpretation which features in the second half of Woody's paper. It is also worthwhile to note that the HF wavefunction is not the only wavefunction that supports this type of interpretation, other types do it as well (though with more mathematical and computational effort).

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[7] Woody argues that a numerical wavefunction is best seen as a set of 'unconnected derivations' without significant relevance across molecules, a problem which grows even worse for more complicated wavefunctions. Woody's claim seems to be mostly that numerical wavefunctions such as the HF wavefunction are instances of wavefunctions for specific individual molecules and are not capable of dealing with *types* of molecules. The simpler wavefunctions that she discusses are more suited to that task. However, Woody in my view overstates this claim where she writes that:

> More important, ab initio calculations comprise a set of unconnected derivations concerning the energetic states of particular molecules. The derivations have the same starting point, the stationary state Schrödinger equation, but are otherwise distinct. As a result, there is no obvious way to capture traditional categories of chemical practice from the set of wavefunctions specified by these calculations. [...]
> With no internal relations among treatments of different systems, there also will be no significant guidance for the representation of new systems. There is no underlying *Aufbau*, no line of reasoning to aid further theory development. While chemists can think of CO_2, and SO_2, as having significantly related reactive properties, wavefunction representations do not explicitly acknowledge such facts nor is it clear how they might capture this information. (Woody 2000, p. S618)

The relatively simply HF wavefunctions do not, in my opinion, directly suffer from many of the shortcomings that Woody describes. A similar argument for the importance of DFT orbitals is made by Baerends and Gritsenko (1997).

On the other hand, the HF wavefunction also renders these diagrammatic interpretations problematic (see for instance McWeeny 1989, p. 135 and p. 200–206).

One of the first reasons for this is that the simple ‘diagrammatic’ pictures that Woody favours do not include the correct permutation symmetries of the electrons. They are based on a separation in ‘core’ and ‘valence’ electrons and treat the ‘valence’ electrons individually. This is a violation of the principal construction rule for many-electron wavefunctions.

Another, more subtle, reason is that the orbitals in the HF wavefunction are under-determined. Since the minimal condition to be satisfied for an HF wavefunction is the Brillouin condition, the occupied and virtual wavefunctions are unique up to a unitary transformation that separately mixes occupied and virtual orbitals. There is thus a large degree of arbitrariness when one applies quantum chemical wavefunctions to, say, an analysis of the number of electrons in a given chemical bond (‘population analysis’) and it is possible to come up with various spatial representations, dependent on the methods deployed to ‘localise’ these orbitals.

So far for our discussion of the HF wavefunction. Finally, we need to consider the available methods to consider electron correlation. There are generally two approaches here. The variational approach leads to Configuration Interaction (CI) or multi-reference approaches, where the wavefunction is written as an expansion of many configurations. In addition, there exist perturbation methods which view the effects of electron correlation as a perturbation on the effective one-electron Hamiltonian that governs the self-consistent field solution. There are several theories possible in this direction, for instance Many-Body Perturbation Theory (MBPT) and Coupled Cluster (CC) approaches.

These approaches generally result from quantum chemists being well aware what the limitations of the one-electron HF equation are.

We have so far sketched only a brief summary of quantum chemistry, without going into too much detail. However, we have enough to suggest that quantum chemistry can be viewed as a Lakatosian research programme, possibly even one with a positive heuristic. Improvements in the auxiliary hypotheses can be generated constructively by quantum chemists’ understanding of what the shortcomings are in previous theories (especially the limiting nature of various idealisations), and result from mitigating these problems (through various concretisations).

As successive theories are improved, their computational load tends to increase quite rapidly. Hence it is only fair to say that the practical scope of quantum chemistry is rapidly widened by improvements made in modern computer hardware and software. Hardware improvements have led to significant increases in the amount of computational power in the central processing unit (CPU), which even in a desktop computer now contains multiple computing ‘cores’, the amount of memory and the amount of available disk space. Software improvements have been made to take advantage of this increase in available power, as well as modern software development methodologies.

5.3 Quantum Chemistry: A Lakatosian Reconstruction

I now wish to turn to the discussion of how quantum chemistry could function as a Lakatosian research programme. A Lakatosian research programme is individuated by the specification of a 'hard core' and a heuristic, as well as an evaluation of whether the programme is progressive. This leads us to the consideration of two specific issues.

Firstly, there is the issue of the placement of quantum chemical 'methods' and their evaluation (the topic of Hettema 2009) in the Lakatosian scheme. I will first argue that the 'enabling theorems' form a part of the hard core of quantum chemistry, and that they should be distinguished from the methods, which are better classified as part of the protective belt.

Secondly, there is the issue of novel facts. As discussed before, this question needs to be considered at two levels: the question of whether quantum chemistry generates novel facts on its own and the question of whether quantum chemistry generates novel facts *vis a vis* the theories of chemistry. As I will argue, though not formally prove, there are good reasons to believe that the development of the heuristics of the programme consists of a case of truth approximation in the quantum chemical 'methods'. As a result we can characterise quantum chemistry as a progressively improving theory.

5.3.1 Characterisation of Quantum Chemistry as a Lakatosian Programme

In Lakatos' view of a scientific theory, the hard core of the theory can be based on views of nature that are, within the context of the programme, immune from refutation and stable over the lifetime of the programme. Lakatos argues that this is a rational view to take as long as the research programme is progressive.[8]

In the case of quantum chemistry, as we have argued in previous chapters in this part, philosophers of chemistry have raised a number of concerns about the applicability of core tenets of the quantum chemistry programme, such as its notion of molecular structure. These issues can be isolated in the hard core of the programme, and hence temporarily ignored as long as the programme itself is progressive.

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[8] In his paper on the methodology of scientific research programmes, however, Lakatos (1970) takes this a step further by arguing that in a number of practical examples, the hard cores themselves are based on a 'sea of anomalies' (as in Bohr's theory of the atom), or an inconsistent model (as in the case of Prout's theory of the elements). Lakatos thus stresses the alleged *irrationality* of the hard core to a significant degree. As Nola and Sankey (2007) point out on p. 275, the hard cores themselves do not even have to be objects of belief of the scientists working on the programme.

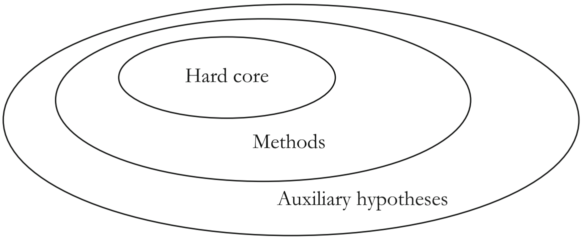

Fig. 5.1 Quantum chemistry as a Lakatosian Research Programme. The Lakatosian reconstruction distinguishes between a set of 'methods' in the 'protective belt' of the research programme and the remainder of the auxiliary hypotheses that make up the protective belt

To characterise quantum chemistry as a Lakatosian research programme, we thus have to characterise the 'hard core' and 'protective belt' of the programme, and outline how successive theories in the protective belt lead to a progressive research programme. In Hettema (2009) I have argued that the explanatory mechanism of quantum chemistry is based on a 'core' of quantum theory and a set of 'enabling theorems' which, while derived from quantum theory for an 'exact' wavefunction, are nevertheless instrumental in providing a theoretical evaluation framework for the approximate wavefunctions that are used in quantum chemical practice (Fig. 5.1).

My proposal is to make the following distinction in a 'hard core' and 'protective belt':

1. The hard core of the quantum chemistry programme consists of the *application* of quantum mechanics to atoms and molecules. This application involves both the general postulates of quantum theory and the 'enabling theorems' discussed in Hettema (2009). The latter play the role of placing theoretical bounds on the result, and also enable to *interpret* the result of the calculation in terms of the system, conceived as a mechanical model of the molecule.

   While this is not a key aspect of the Lakatosian specification of the hard core, this step can be meaningfully interpreted in the sense of creating a *model* of the atom or molecule. Specification of this application step as the 'hard core' of the programme brackets many of the general objections made in the application of quantum theory to atomic systems, such as the notion that the Schrödinger equation does not allow for the derivation of molecular structure, or the notion that the Schrödinger equation does not allow for the inclusion of relativistic effects.
2. It is fruitful in the case of quantum chemistry to split the protective belt in a group that consists of successive improvements in the approximations to the wavefunction that are used in the development of the theoretical approach and those that are truly 'auxiliary' such as basis sets and the like.

   Let us call the parts that deal with successive improvements in the theoretical approach 'quantum chemical methods' or 'methods' for short, and reserve the name 'auxiliary hypotheses' for the more straightforward aspects of quantum chemistry such as basis set selection.

Hence the proposed reconstruction distinguishes between two types of 'auxiliary hypotheses'. As suggested in the figure, the 'methods' are a special class of the protective belt. The 'methods' are closer to the actual postulates and basic equations of quantum theory in the sense that they embody specific approaches to the wavefunction which, while they are approximations, form a key part of the 'theory' that is employed in the description of the electronic structure of the molecule. The key feature that distinguishes 'methods' from the remainder of the auxiliary hypotheses is that 'methods' are open to evaluation on a theoretical level: it is possible to compare methods with each other on the basis of the degree to which they satisfy the basic equations of quantum mechanics, and the methods can be evaluated against their adherence to the enabling theorems in the manner discussed in Hettema (2009).

On the other hand, the remainder of the auxiliary hypotheses, such as basis sets, are more truly 'auxiliary' in the sense that they are logically independent from the postulates and equations of quantum mechanics. The basis sets in which the wavefunctions are expanded, while important in the determination of the overall quality of an individual calculations, are of lesser importance in conveying the *conceptual* features of a quantum chemical calculation.

In this section I will discuss the consequences of this partitioning of quantum chemistry. In particular, we will argue that the context of *application* of the basic equations amounts to the construction of an (idealised) model for atoms and molecules; and moreover that this involves idealisations that are in many cases common to other explanations through quantum mechanics. The enabling theorems form a key part of this construction, for they allow us to interpret this model in terms of a mechanical model of the molecule.

The auxiliary hypotheses will be argued to consist of a set of less problematic, but nevertheless interesting *approximations* to components of the wavefunction such as the basis sets.

5.3.2 The Hard Core: Applying Quantum Theory to Chemistry

For the purposes of this section I will discuss the non-relativistic, space-fixed nucleus approach to electronic structure theory, ignoring relativistic methods or methods that do not assume that the nuclei are fixed, such as the method of Car and Parrinello (1985).

In the hard core of electronic structure theory, the Hamiltonian is generally written in terms of an electrostatic interaction between nuclei and electrons, and contains a one-body and a two-body part. The formulation of the Hamiltonian with the Born-Oppenheimer approximation assumes in the first instance that nuclei are fixed in space, and in the second instance that the nuclei can be thought to 'move' in the potential $V(\mathbf{R})$ defined by the calculation of the nuclear energy at various points.

The dependency of the Hamiltonian on the nuclear coordinates is thus written as $H(\mathbf{r};\mathbf{R})$, where $\mathbf{R}$ is the vector of nuclear coordinates and $\mathbf{r}$ is the vector of electronic coordinates. The nuclear coordinates act as parameters, while the electronic coordinates are dynamic.

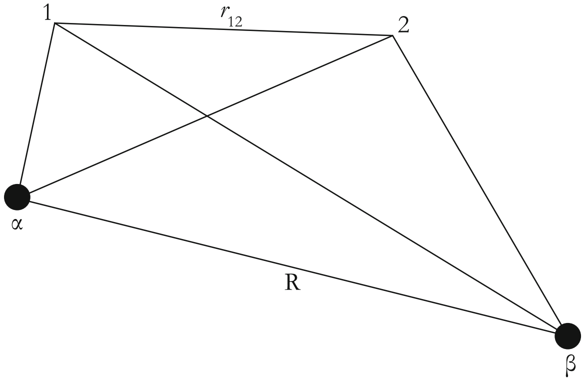

Fig. 5.2 Structure of the electronic structure Hamiltonian

A second approximation is that we consider only Coulomb interactions between the nuclei and the electrons.

With these approximations, and again using atomic units, the molecular Hamiltonian can be written as

$$H = \sum_i \left[-\frac{1}{2}\nabla^2(i) - \sum_\alpha \frac{Z_\alpha}{r_{i\alpha}} \right] + \sum_{i<j} \frac{1}{r_{ij}} + \sum_{\alpha<\beta} Z_\alpha Z_\beta \frac{1}{R_{\alpha\beta}} \tag{5.3}$$

by expanding all the terms in Eq. 5.2. The indices i, j label electrons whereas α, β label nuclei. The electronic Hamiltonian does not contain kinetic energy terms for the nuclei, and the fact that the nuclei are fixed is represented in the calculation of the $r_{i\alpha}$ and the fact that the last term is a simple additive factor for a fixed nuclear frame.

The physical model that underlies the hard core of the research programme of electronic structure theory is thus based on the following idealisations:

1. The (isolated) molecule can be characterised as having a 'frame' in the first instance, by assuming that the position of the nuclei is fixed while that of the electrons is not.
2. The interactions between the constituent parts of the molecule (nuclei and electrons) are electrostatic in nature (i.e. based on the Coulomb interaction)
3. The equation that governs the electronic structure of the molecule is the (time-independent) Schrödinger equation.

The structure of the model is outlined in Fig. 5.2. The nuclei α and β are fixed in space, while the electrons are treated dynamically (note that the figure represents some arbitrary two-electron diatomic molecule, but generalises easily to other molecules).

One of the most important aspects for what follows is that this choice of electronic Hamiltonian determines the point group symmetry of the nuclear frame. The electronic wavefunctions will also obey the same symmetry. Thus the structure of the molecular frame determines the structures of the electronic wavefunction, and this in turn determines a lot of the chemical behaviour.

The point group symmetry of the molecular frame, following the basic theorems of group theory[9] has some important consequences for the molecular electronic wavefunction.[10] Specifically, the exact wavefunctions of an electronic state belong to an irreducible representation of the molecular point group, and can be classified in terms of these irreducible representations. The symmetry properties of the exact total wavefunction are also known. For the theories of chemistry that we are interested in here, important parts of the *qualitative* information of interest are already furnished by the point group symmetry of the molecular frame.

It should also be noted that electron spin is introduced ad hoc in this model since spin is only directly a consequence of relativistic quantum mechanics. Non-relativistic quantum mechanics imposes the Fermi-Dirac statistics on fermions (such as electrons) and requires that the total electronic wavefunction changes sign under permutation of two electrons.

This hard core of quantum chemistry should be viewed primarily in terms of a *model* of the molecule. This characterisation allows us to temporarily bracket some of the principled worries that emerge from the application of quantum theory to chemistry, but the notion of a model also suggests the existence of a positive (theoretical) heuristic.

The notion that many of the key examples of Lakatosian programmes were in fact based on a Nagelian concept of a model was first explicated in Zandvoort (1984). As Zandvoort points out, many key aspects of Lakatos' methodology of research

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[9] See Weyl (1928) or Wigner (1959) for instance for the two classical references on group theory and quantum mechanics.

[10] These can be derived easily from operating with one of the symmetry operations that leave the Hamiltonian invariant (call one of these operations R) on a function ψ_i which is an eigenfunction of the Hamiltonian (so that $H\psi_i = E_i\psi_i$):

$$RH\psi_i = RE\psi_i$$

The Hamiltonian commutes with all the symmetry operations of the group. For instance, if a molecule has a rotational symmetry under a rotation of 60 deg then the molecular frame has this symmetry. Hence, if R_κ represents this operation, then $R_\kappa H = HR_\kappa$, and hence $[H, R_\kappa] = 0$.

Using this fact in the equation above, we see that $R\psi_i$ is also an eigenfunction of H with eigenvalue E_i.

Now consider two cases. (1) If E is non degenerate, then $R\psi_i = c\psi_i$, where c is some constant. (2) If E_i is degenerate, then (see Wigner 1959, Chapter 11) the operation can be written as

$$R\psi_i = \sum_{j=1}^{l} \psi_j D(R)_{ji}$$

for a set of ψ_j which belong to a set of eigenfunctions with energy ϵ_i. The $D(R)_{ji}$ form a representation of the group under which H is invariant. The dimension of this representation is the degeneracy of the energy level.

programmes can be found in some of the informal requirements of Nagel's (1961) account of reduction which we discussed in Chap. 1.[11]

But more importantly, Nagel also stresses the importance of models as an integral part of a scientific theory. For Nagel, the model is what suggests the heuristic. As Nagel writes:

> As long as experimental knowledge is incomplete and a theory continues to be fruitful as a guide to further research, there are tasks that are never finally done; and in all these tasks models continue to play important roles. [...] More generally, a model may be heuristically valuable because it suggests ways of expanding the theory embedded in it. (Nagel 1961, p. 113)

The idealisation inherent in the specification of the hard core, which limits the hard core to non-relativistic space-fixed electronic structure theory, thus suggests ways in which these idealisations might be extended with further concretisations or even replacement theories.

The hard core that specifies the current model has been the subject of a number of challenges, such as the appropriateness of for instance the Born-Oppenheimer approximation to determine molecular structure (see Chap. 3). It should also be clear that none of these objections diminish the appeal of quantum chemistry as a Lakatosian research programme.

The restrictions inherent in the model suggest that there exist systematic improvements that can be made to the model, which in this particular case consist of the consideration of relativistic effects as well as lifting the restrictions of the clamped nuclei approximation. Both of these steps lead to improved models. It is however interesting to ask how the model suggests areas for its own improvement, and thus reconstruct a *prima facie* case for truth approximation in the Lakatosian 'hard core' in a manner similar to what was argued earlier for the Bohr-Sommerfeld model of the atom in Hettema and Kuipers (1995).

It is not hard to see how this could be accomplished, even though in practice the necessary logical relationships might be much harder to prove.

First of all, the 'fixed nucleus' approximation is a first step in the Born-Oppenheimer perturbation expansion. Higher orders will necessitate the consideration of nuclear motion, even in the sense of nuclei as quantum particles having spin and the like. These higher orders of the Born-Oppenheimer approximation can be characterised as systematic improvements possible on the dynamics of a molecule.

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[11] For instance Zandvoort argues that we may recognise Popper's requirements for the growth of knowledge in Nagel's informal requirements for reduction. In Nagel's first non-formal criterion: that the reducing theory should add to our understanding of the known law, by either adding to it, or correcting it in an unforeseen way, Zandvoort recognises Popper's second criterion for the growth of knowledge. Similarly, in Nagel's second non-formal criterion: that the explaining theory reveals relations of dependence between laws that were previously unrelated (i.e. it is unifying in some way), Zandvoort recognises Popper's third criterion for the growth of knowledge, that the predictions of a new theory are confirmed.

As Car and Parrinello (1985) have argued, it is possible to integrate a dynamic molecular frame with electronic structure theory. Car and Parrinello use Density Functional Theory as their electronic structure theory.

Secondly, magnetic and relativistic terms can be added to the Hamiltonian as perturbations, and be used in this manner to calculate magnetic properties of molecules.

Finally, the approach to relativistic effects can take the form of a perturbation theory, or alternatively, it is possible to consider the relativistic Dirac equation as the core equation of quantum chemistry. Doing so involves complications that we will not discuss in detail in this thesis.[12] The issue of relativistic quantum chemistry is discussed in detail in Dyall and Faegri (2007).

5.3.3 Quantum Chemical Methods: Successions of Theories

The successive revision of the auxiliary hypotheses in the Lakatosian model are what constitutes the series of theories, and in this chapter we will be able to discuss only a few of the auxiliary hypotheses and their consequences. Quantum chemists have developed a large and varied body of approaches to the problems posed by chemistry, and have developed models with various degrees of sophistication and simplifications to respond to the challenges of chemistry.

In this section we will focus on the succession of theories that results from systematic improvement in the construction of the wavefunction and core methodologies of quantum chemistry. We will primarily limit ourselves to the so-called 'ab initio' (from first principles) approaches, and forgo a detailed discussion of contenders to this method such as the recently more popular density functional theory.

There are two approaches we can take here: a historical and a methodological approach. The historical approach focuses on the diachronics of theory development in quantum chemistry, starting with qualitative theories of quantum chemistry from the 1930s and moving through Hartree-Fock theory (also originated in the 1930s) through to the Roothaan-Hall equation and modern developments like many body perturbation theory and coupled cluster theory.

Among one of the first applications of the core of electronic structure theory were the development of the 'valence bond' approach by Heitler and London (1927) and the development of the molecular orbital approach by Hund (1927), Mulliken (1928a), Pauling (1928) and others. These developments have already been discussed in Chap. 2 and I will not extensively revisit these arguments here.

Instead, for the purposes of a Lakatosian characterisation of electronic structure theory, I focus on some later developments in approximate theories, especially Hückel theory, Hartree-Fock theory and some methods to calculate electron correlation.

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[12] The loss of the variational property of the wavefunction being one, but serious, fundamental and technical issue.

5.3.3.1 Approximate Theories

One of the first applications of electronic structure theory was the development of approximate theories for the description of the electronic structure of a molecule. The emergence of such approximate methods did not take long: already in 1931 Erich Hückel formulated an approximate theory for the description of the electronic structure of aromatic molecules. The development of such methods allowed for the application of quantum theoretical methods to large systems long before the computational machinery[13] that we currently use was developed.

Approximate theories like the Hückel theory work amazingly well in furnishing models for the behaviour of orbitals in molecules, and have given rise to a number of developments for the *qualitative* treatment of complex chemical reactions, such as in the Frontier Orbital Theory.[14] In particular, approximate models work well in the description of *classes* or *types* of molecules, such as aromatic molecules.

Yet at the same time these models are not very useful for the prediction of molecular properties such as bond lengths and angles. While the simplifications thus on the one hand enable chemists some insight into the likely behaviour and some simple properties of the electronic structure (ordering of orbital energies, symmetry properties of orbitals and the like), on the other hand these models are not successful in furnishing a description of the molecule with numerical accuracy, and thus the conceptual clarity that these models supply comes at significant cost.

The Hückel method, and the methods developed by Eyring (1931) to calculate activation energies, a series of 'semi-empirical' approaches have been developed which depend on significant oversimplifications of the wavefunction on the one hand and on the substitution of experimentally derived values for some of the integrals on the other. These semi-empirical methods have been useful in extending the 'reach' of quantum chemistry to systems that are not amenable to an 'ab initio' calculation. They have also given rise to a conundrum: on the one hand the many *qualitative* explanations for chemical phenomena that are furnished by quantum chemistry rely on features of these simplified wavefunctions; on the other hand, these wavefunctions incorporate approximations that take us far from the ideal of the approximation of the 'exact' wavefunction embodied in ab initio quantum chemistry.

5.3.3.2 Ab Initio Hartree-Fock Theory

Approximations such as Hückel can be seen as approximations to Hartree-Fock theory. In the early days of quantum chemistry such approximations were required because the available computing power was insufficient for the solution of the HF equations for anything but the simplest molecules. With the increase in available computing power, HF theory has become more available as a benchmark tool.

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[13] Where the term 'machinery' refers both to computer programs and to the computers they run on.

[14] See Fukui (1966), or Fukui and Fujimoto (1997) for a large collection of papers on this topic.

The Hartree-Fock wavefunction is built on an ‘independent particle model’, in which the two-particle interaction is modelled as an ‘effective’ one-particle potential and in which the electron moves in the average field of the other electrons. Generally, the Hartree-Fock approximation is the first step towards a more complicated wavefunction which takes the effects of electron correlation into account.

The fact that the solutions of the HF wavefunction are one-particle wavefunctions implies that many of the characteristics have an immediate conceptual use in theories of chemistry. HF theory shares this feature with some of the approximate theories like Hückel theory.

An important feature of the Hartree-Fock solutions is that the symmetry of the solutions is determined by the molecular point group symmetry of the system in question. A significant portion of Roothaan’s paper, which is now seen as one of the standard references in the derivation of HF theory, is taken up by these considerations of molecular symmetry. Computationally, the incorporation of molecular point group symmetry can give rise to a simplification of the Fock matrix, since it will ‘block out’ in distinct blocks according to the irreducible representations of the molecular point group.

Furthermore, the Hartree-Fock ground state wavefunction for a closed-shell molecule has the same symmetry characteristics as the exact wavefunction. Roothaan (1951) specifically proves the following three points for the closed shell wavefunction:

1. The closed shell antisymmetric product is a singlet wavefunction, in which each MO occurs twice,
2. The HF MOs may be grouped in sets such that each set belongs to an irreducible representation of the symmetry group,
3. The HF MOs can always be chosen real.

The Hartree-Fock solution, even though it is often numerically inadequate, thus contains a number of attractive features in its capability to connect with standard chemical intuitions about molecular behaviour, as was already discussed in Sect. 5.2.

One of these features is that the orbital energies correspond to ionisation potentials, and the ordering of the orbital energies gives us important clues as to how the diagrams featuring in Woody’s (2000) diagrammatic representation are ordered. Furthermore, the HF orbitals can, via various localisation procedures, be localised into ‘bonding’ and ‘atomic’ orbitals, thus corresponding with chemical models which rely on ‘charge transfer’ to explain bonding. HF orbitals also allow the calculation of molecular electron densities, and support Bader’s analysis of bonding (cf. Bader 1990). As a basic model of how ‘chemistry works’ at an electronic structure level, HF wavefunctions are therefore useful sources of information.

The model has also significant shortcomings, such as its inability to calculate dissociation energies correctly. In Chap. 2 we analysed this issue for the MO and VB models, and found that the MO model, on which the HF model is based, overestimates the contribution of ‘ionic’ components in the wavefunction of the dissociated molecule. Electron correlation approaches are required to overcome this difficulty, and I argued in Chap. 2 that in this sense the MO and VB methods were different idealisations, which in their concretisations led to an identical theory. The lack of electron correlation is an important drawback for both the numerical accuracy of the HF wavefunction, as well as for its conceptual usefulness in describing molecular dissociation correctly.

5.3.3.3 Electron Correlation: Some Approaches

A large part of the theoretical development of quantum chemistry has involved the development of electron correlation methods which aim to remedy the lack of electron correlation in the HF wavefunction. For the purposes of this section we will not discuss the technical details of electron correlation methods in detail. Such details are easily found in the literature, for instance in Paldus (1981, 1992), Helgaker et al. (2000), Wilson and Diercksen (1992), and many others.

Electron correlation methods can be classified (roughly) in two groups: variational (such as Configuration Interaction or Multi-Configuration approaches), or perturbational (such as Many-Body Perturbation Theory or Coupled Cluster methods). This section will deal with only a few of the possible methods.[15]

Each of these methods has its own specific advantages and disadvantages, and in this section we will aim to bring out briefly what these are.

Configuration Interaction

The Hartree-Fock wavefunction contains an important simplification: it considers only a single Slater determinant as a candidate for the electronic wavefunction. In general, electronic wavefunctions are made up of multiple Slater determinants with the same symmetry properties. Thus an improved wavefunction can be written as a linear combination of such Slater determinants:

$$\Phi = \Phi_0 + \sum_{j=1}^{n} c_j \Phi_j \tag{5.4}$$

The higher Slater determinants are obtained by 'excitations' from the ground state. Hence, they are often characterised in terms of these excitations, and enumerated as a 'single', 'double', 'triple' excitations from the ground state. A Slater determinant Φ_{ij}^{ab} for instance is one where electrons in the occupied orbitals i and j have been removed, and placed into the 'virtual' orbitals a and b. This Slater determinant thus designates a double excitation.[16] Similarly, Φ_{ijk}^{abc} is triple excitation.

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[15] We will not deal with DFT or Complete Active Space (CAS) expansions of the wavefunction in which the CI expansion is 'complete' for a limited 'active space', and both the CI coefficients for this active space and the orbitals are optimised. The methods discussed in this section have been implemented in most currently available quantum chemistry packages.

[16] In what follows, we will adhere to the usual notation of using the indices $i, j, k, \ldots$ for occupied orbitals and the indices $a, b, c, \ldots$ for virtual orbitals.

In this sense, the CI wavefunction is often written as

$$\Phi = \Phi_0 + c_i^a \Phi_i^a + c_{ij}^{ab} \Phi_{ij}^{ab} + c_{ijk}^{abc} \Phi_{ijk}^{abc} + \ldots + c_{ijk\ldots}^{abc\ldots} \Phi_{ijk\ldots}^{abc\ldots}. \tag{5.5}$$

CI calculations then use the variational principle to optimise the coefficients $c_{ijk\ldots}^{abc\ldots}$. CI calculations introduce a large number of technical complexities, which are to some degree still keeping theoretical chemists occupied. They are most often characterised by the highest level of excited Slater determinants that are considered in the CI wavefunction. Thus we have SD-CI, SDT-CI etc. The level of complexity of these calculations grows rapidly with the complexity in the wavefunction. Hence, additional simplifications are sometimes introduced, for instance in triple or quadruple excitations, which are then placed between brackets, such as, for instance, SD(T)-CI.

One of the major drawbacks of the CI method is that it does not optimise the orbitals. In most cases, CI calculations are performed with HF orbitals. As a consequence of the Brillouin theorem, the S-CI energy is in this case the same as the HF energy. At the other end of the spectrum, CI calculations exhibit another peculiarity: when we perform a full CI calculation (considering all possible combinations of all excitation levels) within a given basis set, then the orbitals no longer matter. That is, one could perform such a calculation on the basis of a set of orbitals that diagonalises the one-electron Hamiltonian instead of HF orbitals and obtain the same result. However, for truncated CI wavefunctions, for instance for SD-CI, the two choices for the orbitals would yield different energies.

A major disadvantage of the CI method is that it is not size extensive, and is hence not very well suited for comparing energies of systems composed of N molecules to the energies of N systems composed of 1 molecule each.

Many Body Perturbation Theory

MBPT is partitioning the full Hamiltonian into a (simple) zeroth-order Hamiltonian H_0 and a the ‘fluctuation potential’. It is assumed that eigenvalues and eigenfunctions for the zeroth-order Hamiltonian can be obtained relatively simply.

The partitioning in which the zeroth-order Hamiltonian H_0 is taken as the Fock operator is sometimes called the Møller-Plesset partitioning. Following Møller and Plesset (1934), we set $H_0 = F$ and partition the total Hamiltonian as

$$H = F + W \tag{5.6}$$

where F describes the independent particle operator (the sum of all one-electron Fock operators) and W describes the ‘correlation potential’. The second order energy[17] becomes

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[17] See for instance McWeeny (1989), Paldus (1981), or Paldus (1992).

$$E(\mathrm{MP2}) = \frac{1}{4} \sum_{i,j,a,b} \frac{\langle ij||ab\rangle \langle ab||ij\rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \tag{5.7}$$

where

$$\langle pq||rs\rangle \equiv \langle \varphi_p(1)\varphi_q(2)|\frac{1}{r_{12}}|\varphi_r(1)\varphi_s(2)\rangle. \tag{5.8}$$

The expressions for higher orders become more complex quite rapidly. MBPT is generally performed with the help of normal Rayleigh-Schrödinger perturbation theory on the Møller-Plesset partitioned Hamiltonian.

Coupled Cluster theories

Coupled cluster methods are based on the exponential *Ansatz* of the wavefunction in which the many electron wavefunction is written as

$$\Psi = \exp(T)\Phi. \tag{5.9}$$

The 'cluster operator' T is expanded in single, double and triple excitations as follows:

$$T = T(1) + T(2) + T(3) + \ldots \tag{5.10}$$

The coupled cluster method leads to a complex set of non-linear equations, which need to be solved in order to obtain the correlation energy.

5.3.3.4 Quality Comparison of Methods

In the Lakatosian reconstruction we have divided the protective belt in a class of 'methods' and a class of 'auxiliary' hypotheses. The reason for this distinction was that it is possible to do a *theoretical* evaluation of methods by comparing the degree to which they satisfy the basic postulates and equations of quantum mechanics, as well as chemical intuitions. We have characterised this somewhat motley collection as the 'enabling theorems' of quantum chemistry in Hettema (2009). The auxiliary hypotheses (the basis sets of quantum chemistry) do not allow such a treatment, since they are logically independent of quantum theory itself.

The enabling theorems form a framework for the evaluation of the quantum chemical methods. The main distinguishing aspect is whether methods are variational, size consistent and size extensive, as already indicated in Hettema (2009). The equations of quantum theory in our Lakatosian reconstruction refer to an (elusive) *exact* wavefunction, while the *methods* yield approximations to the exact wavefunction (in many cases truncated expansions).

Hence at the level of ‘methods’ a case can be made for a *theoretical* approximation to the truth, in which the *exact* wavefunction plays the role of the true, but in most cases unobtainable, theory, and the various approximations to the exact wavefunction play the role of candidate theories, which do some things ‘wrong’ and some things ‘right’. The evaluation criteria are the degrees to which the various approximations satisfy the basic equations of quantum theory as well as some intuitive rules – such as the notion that properties must be size extensive and size consistent (see Hettema 2009 for a discussion).

As discussed in Hettema (2009, 2012b), a *variational* method optimises the energetic value of the wavefunction, but in a truncated CI form it is usually not size extensive or size consistent. Variational CI methods have the attractive feature that they ‘approach’ the exact energy gradually as the length of the expansion increases, i.e. they have bounds. But this attractive feature comes at the cost of a loss of size extensivity (and hence consistency).

A size extensive method scales with the size of the problem (a property for a system with N particles is the same as N times 1 particle). Perturbational methods are usually size extensive, and are size consistent if their reference function is size consistent, but have no guarantee of a gradual approach to some ‘exact’ value of the energetic property associated with the expansion length of the wavefunction. Hence there is a risk that the energy of the wavefunction is subject to sudden divergences as the length of the expansion increases.

Thus there generally is a trade-off between satisfaction of the heuristic requirements of either size consistency and variational properties. As a general rule, variational methods have bounds but are not size-consistent when the CI expansion is truncated at a certain level. Size consistent methods are, again when the approximation is truncated at a certain level, non-variational and do not have bounds.

5.3.4 The Auxiliary Hypotheses: Basis Sets

The use of basis sets for the calculation an important auxiliary hypothesis, which is logically independent of quantum theory. The basis sets form an auxiliary hypothesis in quantum chemical calculation in the sense that (i) they do have the capability to determine results (up to a point), and (ii) they play the role of a ‘first suspect’ in cases where quantum chemical results do not readily align with expectations.[18] Basis set construction is discussed in, for instance, Bardo and Ruedenberg (1974), Woon and Dunning (1993) and Petersson et al. (2003), who also give further references.

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[18] Though there are no hard data available on this topic, in my personal experience ‘basis sets’ must outstrip almost any other topic as a focal point for questioning at quantum chemical seminars and conferences.

It has sometimes been suggested that basis set choice in quantum chemistry constitutes ‘use’ of chemical facts in the explanation of chemistry, and in particular, that a particular choice of basis set will allow quantum chemists to ‘hit the number’ and hence claim an explanation. Basis sets are often optimised to generate a close agreement with experiment, for instance for bond angles and distances, for a given ‘reference’ set of molecules. These basis sets in turn are then used outside the reference set to predict these properties for molecules that are not part of the reference set. This, however, does not constitute evidence that the specific choice of the particulars of basis set does indeed constitute ‘use’ of chemical facts in the construction of a quantum chemical model for a particular molecule, nor does this mean that quantum chemists have the latitude to change the parameters of the basis set to fit a particular molecule.

Moreover, not all basis sets are constructed in this manner. There are also a number of a priori considerations that guide the construction of basis sets. One of these approaches is the construction of ‘even tempered’ basis sets, which is based on a geometric sequence of coefficients, so that only a limited number of parameters have to be optimised. In general, the capability to yield the lowest energy for atoms or fragments is also used as a criterion.

For the calculation of molecular properties, it is a well known fact that any chosen basis sets need to have enough *flexibility* to describe the chemical fact in question. For instance, in the correct calculation of molecular properties such as multipole polarisabilities the basis set needs to have higher angular momentum functions in order to be able to correctly describe the molecular integrals that contribute to these properties. However, this is a theoretical criterion: the flexibility that is required in the basis set is determined by the nature of the problem, and the specification of the particular operators involved in the problem, rather than by a desire to ‘hit’ a specific number. Hence, I argue, it is the required features of the model rather than the desire to ‘hit’ a specific number that is the prime determining factor in the choice of basis set.

So while it is not the case that basis set choice is exclusively made with the aim to find agreement with some chemical fact, it is certainly the case that the flexibility required in the basis set is determined by the nature of the ‘chemical fact’, interpreted as the required features of the model.

The construction of basis sets in quantum chemistry is somewhat akin to a fine – or, some would say, black – art. Experimental data does play a role, as does a set of a priori considerations about how a well-chosen basis set should behave. The trade-off between all the possibilities is inherently pragmatic. In quantum chemical practice, many calculations are now completed with different basis sets, to eliminate, or at least understand, basis set bias in the results.

5.3.5 Novel Facts and Explanation in Quantum Chemistry

An interesting factor in the evaluation of quantum chemistry as a Lakatosian research programme is the question whether quantum chemistry generates novel facts. This evaluation needs to be considered on two levels. The first level is whether quantum chemistry generates novel facts in itself; the second level is whether quantum chemistry generates novel facts *vis a vis* the theories of chemistry. Complicating the matter is that the criterion of novelty is different in the theories of Lakatos (1970), Zahar (1973a,b) and Worrall (1978). For the latter two, the key determining criterion of 'novelty' is that the fact is not used in the process of creating the theory intended to explain it.

Quantum chemistry provides a number of easy examples for straightforward novel facts. Quantum chemistry is routinely used as a chemical tool to compute the properties of as yet unknown compounds, or as a tool in further chemical explanations, providing plausible mechanisms for chemical reactions and nanotechnological advances. The early calculations of Kolos on the H_2 molecule[19] significantly refined and extended experimentally available data up to that point, as mentioned by Herzberg (1971) in his Nobel lecture. This means that there are examples to be found of cases where quantum chemistry made predictions before measurements were complete, or cases where quantum calculations supported novel theories.

The more interesting question is whether these feats can be characterised as novel facts *vis a vis* the theories of chemistry. For it is conceivable that chemical theory is capable of predicting exactly the same things predicted by quantum chemistry – from the Lakatosian viewpoint, quantum chemistry could then still be characterised as a progressive research programme, but it would not be a comparatively better program than chemistry itself.

Historically, it might well be impossible to provide a decisive answer to this issue. As Needham (2010) has noted, quantum theory and chemistry have become so intertwined that it is almost impossible to imagine a chemistry with the quantum theory removed. From this viewpoint then, the presence of quantum theory is an inherent requirement for theories of chemistry, and there is little point in speculating on what would have happened with chemical theory in counter-factual universes in which quantum theory was discovered much later, if even at all.

Logically, this issue is related to the issue of reduction. For if chemistry can be reduced to quantum chemistry (or quantum theory) in a direct sense then there is no conceivable way in which chemistry as a science could be progressive independent from quantum theory. All chemical facts would also have to be facts of the reductive programme of quantum theory (as expressed in quantum chemistry). Similarly, an independent progressiveness of chemistry *vis a vis* quantum chemistry might assist with the argument that chemistry is not reducible in the sense of being eliminable

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[19] See for instance Kolos and Roothaan (1960) and Kolos and Wolniewicz (1964).

– even if these new ‘chemical’ facts could afterwards be explained with the help of quantum chemistry, it would then be a bad idea to eliminate chemistry in favor of quantum theory.

There is thus some evidence either way: on the one hand quantum chemistry generates novel facts (as well as novel concepts) which are used in further theories of chemistry. Examples of such facts are aromaticity, reaction coordinates, and structures of hitherto unknown molecules. On the other hand, chemists also create novel substances (or ‘facts’ about them in this context) which are amenable to further explanation with quantum chemical tools.

The detailed evaluation of this question takes us outside of Lakatos’ notion of a research programme, and will have to be solved in the context of a guide and supply programme in the sense of Zandvoort (1986), which we will turn to later in this chapter. In the context of the Lakatosian programme, we can draw the conclusion that both chemistry and quantum chemistry are independently progressive. This is an important conclusion for the theory of reduction we will discuss in Part II.

5.3.6 Putting it Together: Quantum Chemistry as a Research Programme

To conclude this section, let us summarise the conclusions so far. The ‘hard core’ of the research programme was specified as the construction of the electronic structure theory for a molecular system with a predetermined geometry (as opposed to the ‘chemical structure’ discussed in Chap. 3), based on the non-relativistic Schrödinger equation, with the enabling theorems facilitating the interpretation of this system as a mechanical model of the molecule. The protective belt was specified as consisting of two separate elements: (i) a set of ‘methods’ combined with (ii) a number of auxiliary specifications such as the basis sets.

The application of successive ‘methods’ generated a positive heuristic for the programme. As the programme progressed, the sophistication of the quantum chemical methods has increased and the (numerical) accuracy of the results has improved. Moreover, the gradually increasing understanding of the deficiencies of each method has led to improved methods over time.

We have also argued that quantum chemistry can be classified as a *progressive* research programme. Certainly, with regards to singular facts, quantum chemistry can be classified as a progressive research programme, and *vis a vis* chemistry, I have argued that both chemistry and quantum chemistry are independently progressive. The discussion on how quantum chemistry might be characterised as a ‘progressive’ research programme also illustrated the limitations of the Lakatosian scheme. These were already recognised and some emendations of the Lakatosian scheme have been proposed. In the remainder of this chapter we will discuss some emendations of Lakatos’ scheme, and investigate how quantum chemistry fits these emended schemes.

5.4 What Type of Research Programme is Quantum Chemistry?

5.4.1 Classification of Research Programmes

In Kuipers (2007) research programmes are characterised in terms of five components: (i) domain, (ii) problem, (iii) idea, (iv) heuristic and (v) model. Kuipers' characterisation is an extension of Lakatos' characterisation of a research programme, in which there only is a research programme if there is a 'hard core', or 'idea' in Kuipers' terminology, as well as a positive heuristic. As discussed in the previous section, Zandvoort (1984) has moreover argued that many examples of actual research programmes are in fact based on a *model* which generates the positive heuristic. This, as I have argued, is also the case for quantum chemistry.

Furthermore, Kuipers distinguishes four types of research programmes, even though these form ideal types and mixtures often occur:

1. *Descriptive* programmes are meant to describe a certain domain of phenomena. The 'hard core' of the programme furnishes a set of categories which direct its observation, but there is no attempt at a wider ranging explanation of the observations of the programme.
2. *Explanatory* programmes have a further aim. Explanatory programmes aim to explain the observations in their domains, to do so, they mostly employ a (quasi) deductive structure. They usually start from a descriptive research programme (together with a set of theoretical terms) to provide explanations in terms of theories or laws for observed phenomena.
3. *Design* programmes involve the design and engineering of actual products, such as new drugs or organisms, the latter by artificial selection.
4. *Explicative* programmes are directed at concept explication. This involves the 'construction of [a] simple, precise and useful concept that is similar to an informal concept' (Kuipers 2007, p. 61). As examples of explicative programmes Kuipers mentions his own programme in the area of truth-likeness, which focuses on the conditions under which scientific theories can claim to approach the truth (even though the latter may be unknowable in a strict sense).

Kuipers' characterisation of a research programme is thus more flexible than that of Lakatos in that it allows, for instance, for research programmes based on a 'problem' all the way up to an 'idea', but without a positive heuristic, let alone a model. In addition to Lakatos' synchronic characterisation of a research programme and its local development, and building upon the work of Zandvoort, Kuipers' notion includes a global developmental view of the programme. Kuipers' model claims that the development of a research programme passes through several stages, from an 'internal' phase through to an 'external' phase in which the application of a research programme in the context of research questions posed by an unrelated programme.

In the internal phase the elaboration and evaluation of the core idea are central. In the evaluation phase, the idea is elaborated for a small number of sub-domains or contexts into specific theories, and these are evaluated. If evaluation is successful, the programme may enter the external or application phase.

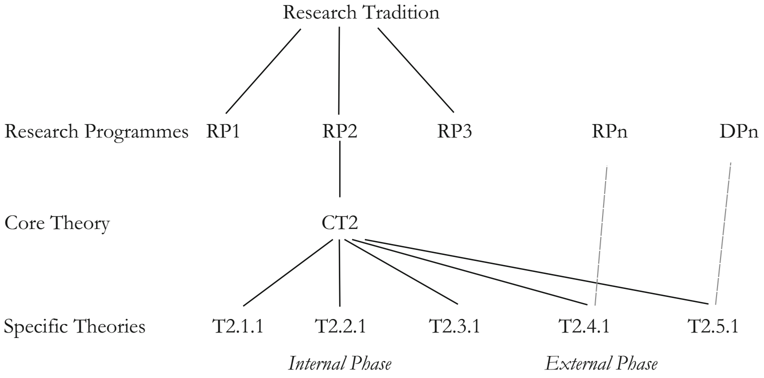

Fig. 5.3 Kuipers' model of the development of a research programme

A brief overview of how research programmes relate to phases is given in Fig. 5.3. In the remainder of this section we will give a brief sketch of how quantum chemistry might be characterised in terms of this model.

While Kuipers' model is significantly richer than Lakatos' model when it comes to the characterisation of a research programme, such flexibility comes at a cost. Specifically, for the case at hand Kuipers' finely detailed model requires further specification of the research programme of quantum chemistry.

In terms of Kuipers' model, quantum chemistry is a full research programme in the sense that it incorporates all five components of the research programme: (i) domain, (ii) problem, (iii) idea, (iv) heuristic and (v) model. The first three of these are relatively uncomplicated. The domain of quantum chemistry is clearly that of chemistry and to a somewhat smaller degree that of spectroscopy, and its aim would be explanatory. The problem is how a robust explanation of chemical phenomena may be furnished in terms of a *mechanical* model of the atom. The leading idea is that this may be done through the application of quantum mechanics.

The heuristic development of the programme takes place at two levels, which roughly correspond to the distinction between the 'theories' of quantum chemistry and what we have, in our discussion of the Lakatosian reconstruction, termed the 'methods'.

As already indicated above, the theoretical development inside the hard core is based on the notion that the Schrödinger equation provides a provisional description of the required mechanics in which relativistic effects can be ignored, which is valid only for relatively light atoms. Fortunately, there is much interesting chemistry happening at the lower atomic number end of the periodic table.

For heavier elements, the inclusion of relativistic effects is required. One way of doing this is to focus on the research programme of relativistic quantum chemistry, which is based on the Dirac equation. Relativistic quantum chemistry[20] is a subject in its own right, which has given rise to its own 'branch' of quantum chemistry.

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[20] See for instance Dyall and Faegri (2007) for a detailed exposition and discussion of relativistic quantum chemistry.

Similarly, the 'space-fixed' or 'clamped nucleus' approximation, which is one of the key approximations in the electronic structure Hamiltonian, is known to be the first step of a more comprehensive research programme that focuses on how the limitations introduced by the Born-Oppenheimer approximation may be removed. As already pointed out in Chap. 3, the science of the Born-Oppenheimer approximation is still under active research. Moreover, there are additional research programmes in quantum chemistry, such as for instance in the work of Car and Parrinello (1985) that aim to solve the electronic structure and molecular dynamical problems simultaneously.

Thus, inside the 'hard core' of quantum chemistry there is still room for theoretical improvement by extension and concretisation.

As we have argued in Sect. 5.3.3, even without these developments in its core, quantum chemistry is driven by a significant positive heuristic in the 'methods', which has led to the development of a progressively more sophisticated methods for the electronic structure of molecules.

It is also interesting to look at the phases in Kuipers' model. Is quantum chemistry currently in its internal or external phase?

It could well be argued that the internal phase started with the publication of Bohr's theory of the atom in 1912. Bohr's theory of the atom formulated an extensible model of the atom, which could be applied to, for instance the Periodic Table.[21] The theory also had further development, in Sommerfeld's subsequent specialisations in terms of elliptic orbitals (leading to the introduction of a second quantum number) and relativistic varieties of the model. In Hettema and Kuipers (1995) we have argued that the 'old' quantum theory can be described as a potential case of approaching the truth, doing so starting with a gradual introduction of both quantisation concepts through to a further refinement, in the 'Sommerfeld atom', with relativistic effects. This argument holds for the so-called 'old' quantum theory, which is based on a combination of quantisation concepts and classical mechanics.

Starting with the 'new' quantum theory in 1926, which was based on either Schrödinger or Heisenberg's formulation of quantum mechanics, a new research programme started. Shortly after the introduction of the new quantum theory, two theories of the chemical bond emerged, as is described in more detail in Chap. 2. Quantum chemistry is thus special in so far that it started to contribute to other research programmes (chemical bonding, chemical reactivity) early in its development, and in that sense perhaps never experienced an 'internal' phase. This is also reflected in Zandvoort's (1986) comment that:

> [...] the very initial success of this research programme, being responsible for the conviction that the basic theory underlying it was essentially correct, caused the sole motive for working on the programme that is considered by Lakatos' theory to disappear. For this motive, which is the aim to *test the hard core* underlying the programme, had in fact been reached through the first successful treatments of 2-electron problems: after that, nobody really doubted that more complicated problems of chemical bonding could be treated successfully as well, given of course a sufficient amount of hard work. (Zandvoort 1986, p. 217)

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[21] Even though it cannot provide a deductively rigorous explanation of the Periodic Table. See Chap. 8 for a further discussion.

This sufficient amount of hard work led to further developments in the theories of quantum chemistry, which consisted in the creation of feasible computer algorithms to perform quantum chemical calculations on molecules with increasing complexity, as well as the gradual development and refinement of the 'methods'. For instance, Many-Body methods or the Coupled Cluster approach were introduced into quantum chemistry from theories of nuclear physics in the 1960s, and created new ways of considering the structure of the electronic wavefunction.

At the moment, quantum chemistry is an important contributor to various descriptive, explanatory and design research programmes. One example is mentioned in Zandvoort (1986), who discusses quantum chemical calculations performed on the motion of a hydrogen atom through an alpha helix in a protein.

5.4.2 Quantum Chemistry as a Supply Programme

We can now return to the issue of the relationship between chemistry and quantum chemistry. In the section on novel facts I argued that both chemistry and quantum chemistry are capable of generating novel facts, and that in this sense neither theory has the better side of the bargain. Instead, I argued that chemistry and quantum chemistry are capable of fruitful cooperation.

This allows us to capture the relationship between chemistry and quantum chemistry in terms of a 'guide programme' and a 'supply programme' in the sense of Zandvoort (1986).

In this context, it is useful to return to Woody's (2000) dilemma that an increasingly more numerically accurate description of the molecular wavefunction seems to lose sight of the chemical facts. A similar point has been made by Primas (1975), where he states:

> [...] the popular attempts to "improve" the *invented* models of quantum chemistry are due to a basic misunderstanding. The role of the semi-empirical models is *not* to simplify the calculation but to describe *classes* of molecules. If we reject semi-empirical quantum chemistry as ad hoc or logically inconsistent, but nevertheless hope that a basic understanding of chemistry can be achieved by reducing it to fundamental physical laws, we have to realize that chemical systematics does not deal with particular molecules but with *classes* of structurally diverse though functionally related molecules. (Primas 1975, p. 129)

Rather than see this situation as a problem, it could be argued that there is thus a dual sense in which the facts produced by quantum chemistry are applied in a chemical context: on the one hand, quantum chemistry is capable of furnishing highly approximate approaches that are applicable to qualitative theories of bonding and, in the words of Primas, apply to *classes* of molecules, and on the other hand, quantum chemistry is simultaneously capable of following through with more robust numerical results where required.

The problem sits in the logical consistency between these two approaches: the highly approximate approaches that deliver the sort of conceptual clarity that allow us to 'transfer' properties from one molecule to another are theoretically 'further from the theoretical truth' in the sense that they violate a higher proportion of the basic equations of quantum theory (by for instance requiring an effective one-particle wavefunction and neglecting certain integrals), while at the same time having a wider empirical applicability.

Zandvoort's characterisation in terms of a 'guide' and 'supply' programme allows us to side-step this particular conundrum. In terms of Zandvoort (1986), a 'supply' programme has an external orientation, and aims not at testing its own 'hard core', but instead aims to 'supply' data and theories to some of its 'guide' programmes, which in turn supply their *problems* as interesting areas of research to various supply programmes. Hence, to act as a supply programme, a programme must have moved beyond its 'internal' phase, and aim to supply various guide programmes with its concepts, reasonable assumptions, and data. In turn, a 'guide' programme is in need of specific concepts, data, or assumptions about the elements that constitute its particular models, and is not capable of supplying these components of its scientific theories itself.

The criterion of success for quantum chemistry as a supply programme to chemistry is thus the success it enjoys in its external phase. For Zandvoort, such success has two components:

> If a research programme is to be successful in its extrinsic phase [...] then the following conditions must hold:
>
> 1. the programme must be at least explanatory successful [...]
> 2. the specific theories that are being produced must be useful elsewhere. (Zandvoort 1986, p. 226)

Zandvoort furthermore analyses the concept of 'useful elsewhere' in the specific requirement of being useful as *measurement theories*,[22] or as sources of hypotheses for other research programmes.

As I have argued, quantum chemistry supplies both sorts of data to chemical programmes. On the one hand quantum chemistry is capable of furnishing numerically accurate data for some of the parameters in chemical theories (as for instance in the discussion on activation energy in Chap. 4), and it is moreover capable of providing a rationale, where required, for the hypotheses that enter into various chemical theories. In this context, Zandvoort mentions the supply of inter-atomic potentials, both as mathematical formulae and as sets of parameters, to molecular dynamics.

Quantum chemistry has still more to offer. Quantum chemistry imparts specific concepts into the various theories of chemistry as well. Examples of this are for instance theories of aromaticity, reaction coordinates, and even the concept of 'orbital' itself, which plays such a key role in Woody's discussion of the diagrammatic view of chemical bonding. This situation has led to Needham's (2010) claim that it is hard to imagine chemistry with the physics removed. The logical untangling of that net will be part of the discussion in Part II.

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[22] This is in this context a specific technical term from the structuralist approach to scientific theories which I will discuss further in Part II. For the purposes of this section, we can read it as merely a 'measurement', dropping the 'theory'.

In terms of Zandvoort's model, quantum chemistry can stick to both ends of the bargain – it can supply a 'measurement' as well as a rationale for various hypotheses. Nevertheless, it has also given rise to the import of some of its concepts into the theories of chemistry itself. How this happened logically will be the subject of Part II. For now, we may conclude that the conundrum that is outlined by Primas (1975) and Woody (2000) is the end result of quantum chemistry living up to its expectations as a supply programme in the sense of Zandvoort. It supplies both accurate data and theoretical rationales to its guide programmes. The evaluation of the fact that these two 'channels' of quantum chemical information find themselves at opposite ends of the spectrum of quantum chemical 'methods' – one being highly instrumental but transferable between molecular systems, the other numerically accurate but lacking the sort of insight that this 'transfer' requires matters much less in this context.

5.5 Conclusion: Quantum Chemistry as a Case Study in the Philosophy of Science

In this chapter I have provided a characterisation of quantum chemistry as a scientific research programme, both in the context of a Lakatosian research programme as well as extended versions of Lakatosian programmes, notably those of Zandvoort and Kuipers.

Reconstructed as a research programme, quantum chemistry is an interesting case which has presented a number of new perspectives in the context of the 'research programme' evaluation of theories. Specifically, I have proposed that the classification of quantum chemistry as a Lakatosian research programme allows us to 'shield' a number of the pertinent issues in the philosophy of chemistry under the 'anything goes' approach that characterises the core of the Lakatosian framework. On the other hand, I have argued that in this context the Lakatosian core can be classified as a model, which also generates a positive heuristic. Hence, there are some restrictions on the notion of 'anything goes'.

Of particular interest is the role of the 'enabling theorems' which I discussed in Hettema (2009) as providing a set of success criteria for the evaluation of quantum chemical 'methods' as well as an interpretation of the molecular model system. In terms of a Lakatosian reconstruction, the gradual improvement in the methods can be characterised as both theoretical and empirical progress.

Another important result is that the Lakatosian reconstruction is capable of spanning the range of quantum chemical methods from the 'semi-empirical', or highly approximate, methods such as the Hückel method, to advanced methods which are capable of providing strong individual predictions for single chemical facts, such as bond distances and angles, or dissociation energies. Quantum chemistry, when conceived as a *programme* in this sense, thus does not suffer from the dilemma that it has to 'choose' between either furnishing highly inaccurate data with strong conceptual import, or accurate data with little or no conceptual strength to the theories of chemistry. Indeed, when conceived as a Lakatosian research programme, quantum chemistry may successfully do both, with a robust understanding of the limitations of either approach.

All this impacts on the topic of the potential reduction of chemistry to quantum chemistry. Firstly, I have characterised quantum chemistry, in agreement with the assessment made by Zandvoort, as a ‘supply’ programme, which is guided in its problem selection by a ‘guide’ programme. The relevant ‘guide’ programmes in this case are theories of chemistry. Hence while quantum chemistry can be claimed to explain a number of the core concepts and core assumptions of the theories of chemistry, this does not necessarily mean that these chemical theories are in turn *reducible* in a strict sense. I have claimed that chemistry and quantum chemistry are independently progressive, and capable of further developments on their own. This seems to mitigate against a strong notion of reduction.

How reductions between chemistry and quantum chemistry may then work is an open question, which will be discussed in Part II.

Part II
Formal Models

In this part I will focus on how a reduction of chemistry to physics might be accomplished given the limits discussed in Part I. This problem is solved through a consideration of the *structures* or *models* of the theories that make up *ab initio* quantum chemistry. The chapters in this part form in many ways the core of the argument for reduction: taking up the suggestion from Berry (1994) that reduction relationships are primarily mathematical, this part will be based on the structuralist conception of theories and relations between theories. Berry's notion of the mathematical relationship is based on *contextual emergence* whereas the method I will employ here is based on structural similarity.

I will follow common practice in the structuralist view of theories and be somewhat loose with language. Specifically, a structure will also be referred to as a *model*. This use of the word model is not to be confused with physical models, such as for instance that of a molecule as a ball and stick model, or the atom as a planetary system. The latter idea of a model is quite common in physics and chemistry, and generally denotes an idealised system, one in which annoying complexities can be temporarily ignored. Nevertheless, those are not the models intended here. When we speak of a model, we intend a model in the sense of mathematical or logical model theory.

The big advantage of the structuralist view of theories, especially over the *linguistic* view of the 'Received View' philosophers of science, is the opportunity to discuss the *formal* aspects of a scientific theory in a framework that is both rigorous where necessary and intuitively attractive. In this respect, the structural view has many implicit and explicit supporters, such as for instance Kuhn (1976), Van Fraassen (1981) and Suppe (1989). The same advantage is also a drawback: a structural notion of reduction makes a particularly weak reductive claim.

I will limit myself to discussing the structuralist framework in the sense of Sneed (1971) and Balzer et al. (1987). It is sometimes argued that this particular framework is overly complex and tends to obscure the key features of theories. Also, it sometimes appears as if the structuralist notion of theories amounts to little more than a set of angular brackets around one's convictions. As we will see in the expository chapter, some of this criticism is correct – there is a multitude of proposals for reduction relations between theories which, by augmenting the inherent weakness of the structural claim, seem to align more with philosophers' notions of what a reduction relation 'ought to be' rather than what it actually *is* in a number of representative examples.

In Chap. 6 I give an overview of the concept of reduction in a structuralist framework. We contrast a number of notions of reduction that have been proposed in the structuralist view of theories, especially those of Adams (1959) and Suppes (1957), Sneed (1971), Sneed (1984), and the 'canonical' formulation in Balzer et al. (1987). There are significant differences between all these versions, even if the leading idea – that of a structure similarity relation – remains the same. Going back to the discussion in Chap. 1, it can be seen that many of these differences are merely reflective of differences and confusions that existed in the literature on reduction anyway. I have argued there that these differences have led to a considerable confusion about the nature of the reduction relationship that may exist between chemistry and physics. I take that thread up in this chapter in a more formal fashion, arguing that the most general concept of reduction between chemistry and physics should be one built on the basis of inter-theoretic *links*. The specific proposal I will make in this chapter is that the Nagelian reduction postulates can be fruitfully reinterpreted as inter-theoretic links, and the concept of reduction taken as a set of commitments on these links.

In Chap. 7 I present the necessary formalisations – of quantum theory, quantum physics and quantum chemistry. Here, I focus in particular on the ab initio quantum chemistry of an isolated molecule. While it has been suggested that the quantum mechanics of an isolated system is a poor choice as a foundation for chemical theories (see for instance Primas 1981 and Löwdin 1998) it is a commonly used first choice and hence a good starting point for investigating the issues associated with reduction. Moreover, the proposed alternatives have not as of this point in time gained much theoretical and explanatory traction. For these reasons, in Part II I will stay with that pragmatic choice. Moreover, assessing this pragmatic choice from a formal point of view also allows us to process in more detail what sort of approximations this choice entails.

The work on inter-theory relationships is done in Chap. 8. I focus in particular on a number of 'key' reductions: the periodic table, the chemical bond and the theory of absolute reaction rates. My approach to reductive claims is largely empirical, treating reductive claims as philosophical hypotheses in need of proof rather than as *a priori synthetic* statements that are in no need of such proof. This approach allows us to classify the inter-theoretic relationships between the theories of chemistry and those of physics in terms of differing concepts of reduction, and thus helps to better characterise and understand the constellations of theories that are out to play.

Before delving into these complexities, a few remarks are in order. In general, in the structuralist approach to theories, theories are seen as structures, and therefore the nature of the reduction relation is a structural relationship. The strongest relationship between sets of structures is of course that of a subset, $\mathscr{M}_s \subset \mathscr{M}_b$.

The subset relation automatically fulfils strong criteria for reduction: the two structures are categorically identical (which satisfies the connectibility criterion trivially) and the subset relationship is the structuralist counterpart of derivability. The relationships between chemistry and physics are not of this sort.

Summary of Part II

In this part we have investigated the structuralist notion of reduction in detail, and argued that this notion can be applied to local reductions of theories and models of chemistry and physics. The structural reduction relation expresses a weak claim: it a *structural* notion of reduction, which in turn may be susceptible to a variety of Newman's objection: the fact that there is a structural relationship conveys no other information than a structural similarity.

In the structuralist approach there is a number of criteria which are usually added to the structural notion of reduction, to reflect the need to carry something *more* than just structure. We have empirically tested a number of these additions in Chap. 8.

The proposed relationship is built on the notion of *links*, which express basic structural relationships between dissimilar structures. In addition, the links are capable of featuring in what I have called 'composite' theories of quantum chemistry, which draw equally from chemistry and physics, and include the notion of *encapsulation* in their construction. More formal work on the notion of a composite theory and the characterisation of quantum chemistry as a composite theory may lead to some new insights.

This localisation of the reduction of chemistry to physics can deal with a number of objections to the notion of reduction that were raised in Part I of this work (even though we argued there that these objections were not always robust). In particular, for the reduction concept to work via reduction postulates as links, there is no need for the reduction postulate to 'carry' the entire complexity of the reducing theory, but rather, the reduction postulate represents a pragmatic choice of the minimum required to effect an explanation.

The concept of the unity of science that results from this view on reduction is, at first sight, problematic, and full of ontological issues. However, as I will argue in Part III, it is in important measure consistent with similar insights which have recently appeared in the philosophy of science, and capable of resolving its ontological difficulties in an interesting manner. My proposal advocates a basis of weak structural links combined with an *empirical* investigation of the additional relationships as they obtain in the practice of science. This approach to reduction is therefore diametrically opposed to the 'metaphysical' or 'normative' approach in which a set of somewhat ad hoc conditions for the unity of science is 'read in' into the reduction relationship.

Chapter 6
Reduction Between Structures: A Proposal

Abstract If the reduction of chemistry to physics relies on a reduction to a network of theories, the structuralist characterisation of theories might provide a fruitful departure point in considering the formal aspects of the reduction. This chapter sets up the machinery to discuss the concept of reduction in terms of the structuralist concept of theories and networks of theories. The idea is that this characterisation can give an approach that can be tested with the help for specific scenarios in Chap. 8.

6.1 Introduction

In this chapter, I introduce the majority of conceptual apparatus that will be used in this part to address the issue of the theoretical interrelation between chemistry and physics. Most of the material in this chapter will be expository in nature, following a somewhat rough historical trail of reduction concepts in the structuralist approach to scientific theories. The structuralist approach was developed, among others, by Sneed (1971, 1976), Mayr (1976), Balzer (1982) and Stegmüller (1986). The book by Balzer et al. (1987) contains the key concepts of the approach.

The complete apparatus of the structuralist conception of theories is complex, and, it should be noted, is not always conducive to an improved understanding of the issues at stake. The structuralist approach is sometimes criticised for its complexity, which, it is thought, serves to obfuscate crucial aspects of scientific theories rather than elucidate them. For a detailed understanding of the issues surrounding the reduction of chemistry, however, this criticism is largely misplaced – the actual theories that I aim to study in Chap. 8 *do* require a number of fine-grained distinctions which are hard(er) to make without a sufficient degree of precision. Something *is* gained in the development of more or less precise formal counterparts to various intuitions and approximations.

Considering reduction in the structuralist framework adds yet another layer of complexity. The development of *reduction* concepts in the structuralist approach to scientific theories is convoluted, perhaps not in the least because the *structural* characterisation of reduction originally given by Adams (1959) seems vulnerable to a variety of Newman's theorem (see Newman 1928), in which all that we can be said to gain from the recognition of a structural relationship is (not so surprisingly)

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a recognition of structural similarity. Hence the pure structural characterisation of reduction as a 'structure preserving map' does not 'carry' ontological or explanatory notions and loses out on some of the richness that we rightfully expect from the analysis of scientific theories. Halvorson (2012) has moreover argued that this weakness in the structuralist approach also leads, at points, to a mischaracterisation of inter-theoretic connections.

To retrofit this sort of richness onto the structural relationship, there are a lot of additional conditions that have been imposed on the structural notion of reduction. However, the exact conditions for a reduction in the structuralist sense are not as of yet precisely defined. In some cases it seems that extra conditions have been added with insufficient regards to both the development of a precise notion of inter-theoretic reduction as well as regard for the theories so related. Some of these augmentations are incompatible, as detailed by Mormann (1988), and as a result, a number of quite different concepts have been called 'reduction' in the structuralist approach to scientific theories. These augmented structuralist notions of reduction, moreover, are rarely tested against the record of actual theories.

In this chapter I will take up the thread from Chap. 1 and argue that the fact that reduction concepts come in a number of varieties and sizes in the structuralist approach is not too surprising and merely reflects some of the issues in the concept of reduction *tout court*.

Apart from being in significant measure expository, it is my aim in this chapter to attempt to settle a number of issues on reduction in the structuralist framework of theories in the form of a simple proposal. In its simplest form, the proposal is that I retain only the most minimalist notion of an inter-theoretic relation (here conceived as the notion of a inter-theoretic *link*) and treat the other conditions, which turn the inter-theoretic link into a reducing one, as open to empirical test. The advantage of this approach is that inter-theoretic links are the most general types of mappings that connect two structures together, and additional conditions can be placed on them based on actual practical examples of reduction between chemical and physical theories.

Inter-theoretic links were introduced originally to study the relationship between thermodynamics and the macromechanics of a system in terms of a 'corresponding principle' by Moulines (1975). Links are discussed in significant formal detail in Sneed (1984), and have also been discussed extensively in Stegmüller (1986). The key element of my contention that inter-theoretic links are sound vehicles to pursue a notion of (Nagelian) reduction is that inter-theoretic links can play precisely the sort of roles that Nagel had in mind for the reduction postulates: they can be anything from mere identities to significant theoretical statements in their own right. Then, on the basis of inter-theoretic links, a number of notions attached to inter-theory reduction may be empirically tested.

This chapter is structured as follows. In Sect. 6.2 I give a brief overview of the contrast between the structural and the linguistic approach to scientific theories, and rehash some of the pragmatic arguments in favour of the structural view. Notation and notions are introduced in Sect. 6.3. The development of the notions on reduction in the structuralist framework is sketched in Sect. 6.4 and a brief discussion on *links* is given in Sect. 6.5. My proposal is discussed in Sect. 6.6 and a conclusion is given in Sect. 6.7.

6.2 The Structuralist Approach in the Philosophy of Science

The structuralist approach is, in essence, a method for the formal analysis of empirical theories. It holds that empirical theories can be formulated in terms of set-theoretical structures. This simple approach is nevertheless a powerful tool in the philosophy of science, since it allows us to evaluate some claims with extraordinary precision and clarity.

A historical description of the development of the structuralist approach has been given in Suppe (1989). Suppe traces the origins of the structuralist approach back to the work of E.W. Beth, who, in the words of Suppe, ‘became increasingly dissatisfied with “the increasing discrepancy between science and philosophy, which is conspicuously demonstrated by the rejection, by well-known philosophers – such as H. Dingler, P. Hoenen, J. Maritain –, of fundamental conceptions quite unanimously accepted by men of science”’ (Suppe 1989, p. 6).[1]

An important next step was taken in Suppes (1957) with the development of the set-theoretic approach.[2] The set-theoretic approach views theories essentially as sets of structures. Logical relationships between theories are then captured in set-theoretic terms of inclusion, union, power sets and so forth.

The structuralist approach to scientific theories is generally contrasted with the linguistic approach that originated in the *Wiener Kreis* and later developed into what Hempel would call the ‘Standard Conception’ of scientific theories (Hempel 1970), which in turn is often referred to as the ‘Received View’.

The ‘Received View’, as formulated in Hempel (1970), consisted of a conception of a scientific theory as a formal ‘calculus’ C, augmented with a set of interpretation functions R, which contains the ‘correspondence rules’ that tie the calculus to the actual world. The view on a scientific theory is thus:

$$T = (C, R) \tag{6.1}$$

The strength of the ‘Received View’ is that its focus on the logical core of a theory is of significant assistance in the further understanding of theory, and is able to shed light on the nature of theoretical concepts, the relation of particular theories to each other, and assists in the specification of the *model* of nature that for instance Nagel (1961) argues is inherent in the theory. However, it is rare in the literature of the received view to see that kind of precision in action – as it stands, there are very few examples of such reconstructions of real-life theories that stand up to the promise.[3]

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[1] In the double quotes Suppe is quoting Beth.

[2] Suppes (1957) contains a chapter on the set-theoretic approach to theories. Another important reference, which until recently was hard to get, is the set of Lecture Notes in Suppes (2002), which makes available an earlier manuscript (unpublished in that earlier form to my knowledge) called *Set-theoretical Structures in Science* dating from 1962 or earlier. The 40 year history of the book is outlined in its Preface.

[3] Some good examples can be found in the book by Henkin et al. (1959) as well as in Kyburg (1968).

This relative clarity can come at considerable cost, however.[4] The remainder of the equation, the correspondence rules, is logically unclear. One might expect that the correspondence rules are capable of an explicit definition of theoretical concepts. In practice, the correspondence principles represent only a 'partial interpretation' of the theoretical concepts.

The structuralist approach to scientific theories is aimed at overcoming at least part of these problems. The structuralist approach does not introduce 'correspondence rules' but rather also views the experimental situation in terms of a set-theoretic structure, of which the 'intended applications' of the theory form a subset.

Hence, the structuralist approach is often deemed to be capable of yielding a more accurate description of actual scientific practice. Sneed (1976), for instance, argues that the structuralist approach to scientific theories can be seen as a *science of science*, and therefore lacks the 'normative tenor' that has characterised logical positivism up to that point:

> In much – especially the work in the logical empiricist tradition – there is a strong normative tenor. An attempt is being made to legislate what can and can not qualify as 'good' empirical science on the basis of a philosophical position held on non- empirical grounds. (Sneed 1976, p. 115)

In opposition, Sneed argues, the structuralist approach is a candidate for this science of science.

From the viewpoint of the historical approach in the philosophy of science, as developed by for instance Kuhn (1970), the structuralist approach looked appealing. Kuhn's (1976) enthusiastic endorsement of the structuralist approach was in significant measure responsible for its rapid rise in popularity. In this context, Kuhn states that:

> What has struck me from the start about the Sneed formalism is that even its elementary structural form captures significant features of scientific theory and practice notably absent from the earlier formalisms known to me. (Kuhn 1976, p. 180)

Taken together with a pretty comprehensive critical analysis of the 'Received View', which took place at a symposium in March, 1969 (the proceedings of which were subsequently published as Suppe 1977), the credentials of the structuralist approach to scientific theories started looking pretty convincing.

The core of Suppe's (1977) critique of the 'Received View' was that the latter relied on a number of distinctions, such as the observational / theoretical distinction and the analytic / synthetic distinction, that had become problematic in a number of ways. The work of for instance Quine (1961), Putnam (1962) and Feyerabend (1965) (to mention only a few) had, by the end of the 1960s, cast serious doubts on these core tenets of the 'Received View' approach. As stated already, the 'Received View' analysis of scientific theories relied on the concept of 'partial interpretation'

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[4] See for instance the extensive discussions recorded in Suppe (1977), which focus on the problems associated with the received view, as well as the first chapter in Suppe (1989).

of theoretical terms, a concept that was vague at best, and which introduced an opacity into the system that found itself at strange odds with the claims to logical rigour and clarity that originally inspired the linguistic approach.

The problems associated with the 'received view' of theories which the structuralist approach to theories claimed to be able to address were thus threefold:

1. The inability of the received view model to capture live, complicated scientific theories rather than simple 'toy' theories;
2. The issues associated with the 'partial interpretation' of scientific concepts;
3. The difficulties associated with the *historical* development of scientific theories.

With the benefit of hindsight it has become clear that the distinction between the linguistic and the structuralist approach never was quite as principled as it appeared in the middle of the 1970s. The recent paper by Halvorson (2012) also suggests that is perhaps best not to put too much focus on the principled distinction.

Kuipers (2007) argues that the choice between the linguistic or structuralist approach is a primarily a *pragmatic* question, but that there are some reasons to favor the structuralist approach above the linguistic approach. Firstly, the structuralist approach can be characterised as more of a 'bottom up' approach, which allows us to analyse a scientific theory in a form as close as possible to actual textbook representations as is formally possible. Secondly, the structuralist approach allows for a 'systemic' perspective on scientific theories that so far has not been taken up by the linguistic approach. This systemic perspective, which takes the world to consist of many interacting systems, e.g. molecular systems, is particularly useful for a fruitful discussion of the reduction relationship.

Suppes (1967) argues that another example of the advantages associated with the structuralist approach is its capability to clearly define the concept of *reduction*:

> Many of the problems formulated in connection with the question of reducing one science to another may be formulated as a series of problems using the notion of a representation theorem for the models of a theory. For instance, the thesis that psychology may be reduced to physiology would be for many people appropriately established if one could show that for any model of a psychological theory it was possible to construct an isomorphic model within physiological theory. (Suppes 1967, p. 59)

Hence, the notion of reduction in the structuralist approach can be described as one of representation and isomorphism. Before discussing the notion of reduction in detail, we first develop the necessary notions and notations.

6.3 Notions and Notations

The structuralist framework can have a daunting notational complexity, even though the main ideas expressed by the notation can be relatively simple. I will largely assume that readers are familiar with the elementary aspects of set theory. The aim of this section is to give enough detail on notation to construct the proposal for using links as reduction postulates in our theory of reduction, rather than the presentation of a complete didactical overview of the structuralist approach. In general, I will follow the notation of Balzer et al. (1987) since this is more or less the canonical formalisation of the structuralist view of theories. I will only deviate from their notation by indicating a *set* of set theoretic structures by a capital 'calligraphic' font (as in '$\mathscr{U}$') rather than the boldface type. Individual structures will be indicated by a small italic font, as in 'x'.

6.3.1 Theories as Set Theoretic Structures

In what follows, I will have to discuss relationships between theories of a different nature. Hence, it is useful to start at the highest level of classification of a model for (a set of) theories and consider a set theoretic structure as a structure species in the sense of Bourbaki as a so-called *k*-*l*-*m*-structure:

$$x = \langle D_1, \ldots, D_k; A_1, \ldots, A_l, R_1, \ldots, R_m \rangle \tag{6.2}$$

where the D_i refer to the *domains* of the theory in question, the sets A_i provide basic mathematical sets, such as the set of natural numbers $\mathbb{N}$ or the set of real numbers $\mathbb{R}$, and the R_i represent the *basic relations* of the theory. In general, I will consider the sets A_i to be 'antecedently available' and interpreted in order to avoid having to state the entire mathematical apparatus along with the theory in every instance. The R_i represent the properties and relations the laws of a theory are about.

It is sometimes also useful to denote the potential models of a theory in the following way:

$$x = \langle D_1, \ldots, D_k; A_1, \ldots, A_l; n_1 \ldots n_p, t_1, \ldots t_q \rangle \tag{6.3}$$

where the $n_1 \ldots n_p$ represent non-theoretical relations and the $t_1, \ldots, t_q$ represent the theoretical relations. Note that at this point, the distinction between non-theoretical and theoretical relations is a purely formal one, since I have not defined a theoreticity criterion.

We now need to specify the notion of a theory T on the basis of the notion of a structure.

In the Suppes / Sneed formalism, we utilise a number of structures of different type. The first type is the set of the *models* of the theory.[5] The models of the theory in turn are *extendable* to the *potential* models of the theory, and the latter set may in turn be *restricted* to the set of *partial potential* models.

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[5] Recall that these (formal) models are models in the sense of model theory, and are distinct and distinguishable from the models that form the core of a scientific theory for some scientists. Indeed, the latter models are components of the former, since not only do the *scientific* models specify the domains of the formal model, they also play a key role in specifying some of its relations.

The models are a restriction of the potential models in the sense that the models satisfy the laws of the theory, whereas the potential models encompass all structures of the required type of the theory (i.e. including the ones that do not satisfy the laws of the theory). The restriction relation between the potential models and the partial potential models is a trivial one in the sense that it removes the theoretical terms from the structure, and hence the partial potential models include only the non-theoretical, or, 'observational' terms of the theory. The latter term should of course be read in a relative sense: what is 'observational' relative to a theory T may still involve a large degree of complexity and theoretical constructs.

The insight of the structuralist approach is that the partial potential models contain things that are measurable (or can be determined) without involving the apparatus of T itself. Conversely, theoretical terms are terms whose determination does involve the apparatus of T. This leads to a theoreticity criterion, which is however still somewhat debated in the structuralist theory of science.[6]

6.3.2 Basic Notions of Theory Cores

If T is a theory, its Sneedian formulation can be summed up as follows. The first notion consists of a class $\mathscr{M}_p$ of 'potential models'. Potential models express, in a sense, the 'logical space' that is occupied by the theory proper, or they can be said to contain the 'frame axioms'.

The 'actual' theory models $\mathscr{M}$ are a subset of $\mathscr{M}_p$: $\mathscr{M} \subseteq \mathscr{M}_p$. The restriction relation r maps $\mathscr{M}_p$ onto the 'partial potential models' $\mathscr{M}_{pp}$. r transforms a potential model $x \in \mathscr{M}_p$ into an element $r(x) \in \mathscr{M}_{pp}$ by stripping $x \in \mathscr{M}_p$ of all its theoretical terms. The structure is sketched in Fig. 6.1.

The 'constraints' C express certain (second order) connections between different (potential) models to ensure that certain theoretical terms retain their values across different applications of the theory. For instance, in a model of (quantum) mechanics, constraints specify that the mass of a certain particle (let's say an electron) is the same across different models, whether those models be that of a hydrogen atom or a cathode ray. The Sneedian approach is to establish the 'constraints' on the models so that they ensure such equalities. In what follows, where we speak of a set of structures $\mathscr{M}_p$ I will assume this set to be subject to the relevant constraints. More detail on constraints is given in the Appendix.

In the structuralist framework, a theory is conceived as a 'model element' $T = \langle K, I \rangle$, where K is the theoretical core and I the set of intended applications. There are not as such formal definitions of I. I is usually seen as a set of *paradigmatic* examples, which have to be able to be extended (by addition of theoretical terms) to members of M. The common notations that will be used in this chapter (and indeed the remainder of this part) are summarised in Table 6.1.

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[6] See for instance Balzer (1985) and Gähde (1990) on theoreticity conditions in the structuralist approach.

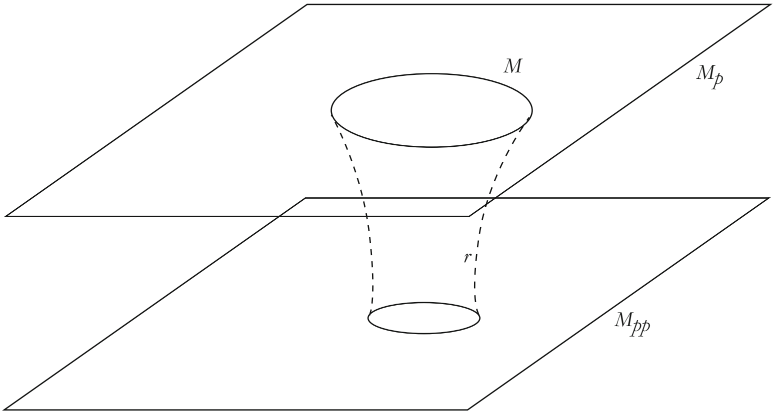

Fig. 6.1 Structuralist reconstruction of a scientific theory

Table 6.1 Specification of the components of the structuralist conception of theories, cf. Kuipers (2007)

Component	Description
$\mathscr{M}_p$	The potential models, defined as structures of the type $\langle D_1, \ldots, D_k, n_1 \ldots n_p, t_1, \ldots t_q \rangle$
$\mathscr{M}_{pp}$	The partial potential models $\langle D_1, \ldots, D_k, n_1 \ldots n_p \rangle$
$\mathscr{M} \subset \mathscr{M}_p$	The models of the theory, which satisfy all the laws of the theory
$r : \mathscr{M}_p \rightarrow \mathscr{M}_{pp}$	The 'restriction' relation which connects the potential models to the partial potential models
$C \subset \mathrm{Pot}(\mathscr{M}_p)$	The 'constraint' relation (which will be taken as implicitly present in most of what follows)
$r(\mathscr{M})$	The projected models, i.e. the restriction of the models to the level of partial potential models
K	The theory 'core', defined as $\langle M_p, M, M_{pp}, r, C \rangle$
$I \subseteq r(M)$	Weak empirical claim (note that constraints are implicitly assumed)
$I = r(M)$	Strong empirical claim (constraints are implicitly assumed)

Following Balzer et al. (1987), we generally define an isolated theory core, in which the constraints are taken as implicit, as follows:

Definition 1 $K(T)$ is a *theory-core* iff there exist (implicitly constrained) $\mathscr{M}_p(T)$, $\mathscr{M}_{pp}(T)$, $\mathscr{M}(T)$ such that:

(1) $K(T) = \langle \mathscr{M}_p(T), \mathscr{M}_{pp}(T), \mathscr{M}(T) \rangle$ is a theory core;
(2) $\mathscr{M}_p(T)$ is a class of potential models;
(3) $\mathscr{M}(T)$ is a class of models within $\mathscr{M}_p(T)$;

(4) $\mathscr{M}_{pp}(T)$ is the class of partial potential models determined by $\mathscr{M}_p(T)$ and the restriction relation r.

On this basis we can define a theory-element as follows.

Definition 2 (Theory-element) T is a theory-element iff there exist $\mathscr{M}_p(T)$, $\mathscr{M}_{pp}(T)$, $\mathscr{M}(T)$, I such that:

(1) $K(T) = \langle \mathscr{M}_p(T), \mathscr{M}_{pp}(T), \mathscr{M}(T) \rangle$ is a theory-core;
(2) $T = \langle K, I \rangle$;
(3) $I \subseteq \mathscr{M}_{pp}$.

In the structuralist framework, the *empirical claim* of the theory is that the set of 'intended applications' I, leaving constraints implicit, is a subset of the restriction of the set of models $\mathscr{M}$ to the level of partial potential models $\mathscr{M}_{pp}$. Formally: $I \subseteq r(\mathscr{M})$.

The theory-elements discussed in this section are the key building blocks in the structuralist framework. The notions of theory-nets and theory-holons are built on the basis of theory-elements.

6.4 Reductions in the Structuralist Framework

The notion of reduction in the structuralist approach to scientific theories is not in itself complex, but significant complexity arises because of the different additional conditions that are usually imposed on the concept. The aim of this section is to present a number of reduction concepts in the structuralist approach to theories and outline the critique that Mormann (1988) has levelled against existing reduction concepts.

The exposition in this section will primarily be expository and follow along with some of the key authors on the issue of reduction in the structuralist framework. The main steps in the development of the framework for the reduction relation in the structuralist framework have been set by Suppes (1957), Sneed (1971), Mayr (1976) and Pearce (1982). The different approaches to the structuralist reduction concept have been analysed and critically evaluated in significant detail in a paper by Mormann (1988). This analysis illustrates the fact that the notion of reduction is not particularly well-settled in the structuralist approach to theories.

In general we will use the following notation. 'Reduced' (or, 'reduction candidate') theories are indicated by T', and 'reducing' theories (or their candidates), by T; the reduction relation will be written $R(T', T)$. Reduction relations will be indicated with a capital letter R to denote an 'overall' reductive claim or a Greek letter ρ to denote level-specific claims.

6.4.1 A Historical Overview of Structuralist Reduction Concepts

6.4.1.1 Suppes' Notion of Reduction

The notion of reduction introduced in Suppes (1957) is based on the idea of structural automorphisms, and especially that of a representation theorem.

Suppes discusses the notion of a representation theorem in detail in the context of measurement theories, but only in passing with regard to the concept of reduction. Suppes (2002) contains an extended discussion of representation theorems, but goes into details that do not concern us here.

In brief, if $\mathscr{M}$ is the set of all models of a theory, and $\mathscr{B}$ is some subset of $\mathscr{M}$, then a representation theorem for $\mathscr{M}$ relative to $\mathscr{B}$ would consist of the claim that for any $m \in \mathscr{M}$ there exists a $b \in \mathscr{B}$ such that m is isomorphic to b (Suppes 2002, p. 57).

Suppes gives no details on the notion of reduction, except the following:

> To show in a sharp sense that thermodynamics may be reduced to statistical mechanics, we would need to axiomatise both disciplines by defining appropriate set-theoretical predicates, and then show that given any model T of thermodynamics we may find a model of statistical mechanics on the basis of which we may construct a model isomorphic to T. (Suppes 1957, p. 271)

In Suppes (2002) there is little further information on the issue of reduction.

The idea of isomorphisms is later taken up in the discussion by Mormann (1988) of reduction as a structure preserving map.

6.4.1.2 Adams' Notion of Reduction

One of the earliest examples of a specific *application* of the structuralist approach may be found in the work by Suppes' student Ernest W. Adams's (1959) reconstruction of classical particle mechanics. The theories he discusses are Particle Mechanics (PM) and Rigid Body Mechanics (RBM).

Adams' notion of reduction is akin to Nagel's in the sense that Adams states the conditions of reduction as follows:

> At first glance the usual derivation of the laws of RBM from those of PM suggests that the reduction of RBM to PM consists in the following: first, the primitive notions of RBM are defined in terms of those of PM, as indicated roughly in the intended interpretations of the primitives of RBM, and then the laws of RBM are shown to be derivable from those of PM, supplemented by the indicated definitions. (Adams 1959, p. 256).

The structuralist framework needs to be augmented with the notion of an intended application, which provides a basis for determining whether the claims of the theory are true or false. Hence, rather than conceiving of a theory as a set $\mathscr{C}$ of structures that satisfy the axioms of the theory, he argues that a theory instead should be conceived of as a tuple $\mathscr{T} = \langle C, I \rangle$, where I is the set of intended models.

An informal construction of the reduction relation then requires that for theories $\mathscr{T} = \langle C, I\rangle$ and $\mathscr{T}' = \langle C', I'\rangle$ (recall that we assume that $\mathscr{T}'$ is reduced to $\mathscr{T}$) there exists a special relation R such that every intended model $i' \in I'$ is connected to a model $i \in I$ via R. Secondly, the laws of theory $\mathscr{T}'$ must follow from those of $\mathscr{T}$. To do this without committing ourselves to a notion of *derivability* is to require that each element $c' \in C'$ which stands in the reduction relation R to an element $c \in C$ satisfies the laws of theory $\mathscr{T}'$; i.e. if C in c and $c'Rc$ then c' is in C'.

Hence, formally, a case of reduction between two theories then has to satisfy two conditions:

Adams' Condition A Let $\mathscr{T} = \langle C, I\rangle$ and $\mathscr{T}' = \langle C', I'\rangle$ be two theories such that $\mathscr{T}'$ is reduced to $\mathscr{T}$ by relation R. Then for all i' in I' there exists i in I such that $i'Ri$.

Adams' Condition B Let $\mathscr{T} = \langle C, I\rangle$ and $\mathscr{T}' = \langle C', I'\rangle$ be two theories such that $\mathscr{T}'$ is reduced to $\mathscr{T}$ by relation R. Then for all c and c', if c is in C and $c'Rc$ then c' is in C'.

Furthermore, Adams notes that these conditions do not *define* a reduction notion, but rather, that they have the consequence that for any pair of theories where $\mathscr{T}'$ is reduced to $\mathscr{T}$ by a relation R, then the correctness of $\mathscr{T}$ implies the correctness of $\mathscr{T}'$. This, as Adams notes, is all that is required in the case of reduction (and he mentions the example of the reduction of the ideal gas law to the kinetic theory of gases here): if the kinetic theory of gases is correct and the relation R is correct, then the ideal gas law is correct.

Adams' reduction conditions form the basis of almost any reduction concept in the structuralist approach to empirical theories, although, as Adams notes, they are too weak and need to be augmented with further conditions to form proper examples of reduction.

6.4.1.3 Stegmüller and Sneed on Reduction

The further development of Adams' reduction concept, in the Sneedian view on the structure of theories, is complex and convoluted.

In Sneed (1971) there is an extensive discussion of the concept of reduction. Much of this material is now only of historical interest, and adds little to a further understanding of the notion of reduction that I wish to develop in this chapter. Sneed's original notion of reduction is based on an extension of Adams' notion of reduction that will fit the structuralist framework he develops.

Stegmüller (1986) and Sneed (1976) introduce, in addition to Sneed's discussion, a number of new conditions on the reduction relation. The main one is the requirement that the reduction relation captures 'more' than just the relationships between a theory's observational matrices. We generally like to speak of the reduction of one *theory* to another, and hence, the formal reduction relation should contain components of a theory core rather than just the experimental consequences.

This modification captures some, but not all, intuitive aspects of the reduction relation. What this modification lacks, in particular, is a condition that specifies what happens at the level of ‘empirical content’ of the theory. To capture this, Sneed (1976) defines the equivalent of a weak reduction at the level of $\mathscr{M}_{pp}$, combined with a reduction at the theoretical level $\mathscr{M}_p$. This definition has potentially the feature of ‘content restriction’, where the reduced theory may be ‘corrected’ by the reducing theory.

6.4.1.4 Mayr’s Reduction Concept

One of the major new developments was initiated by Dieter Mayr (1976, 1981) who developed a first classification of the reduction concepts discussed above alongside a set of reduction concepts for the structuralist framework.[7]

Mayr’s criticism of the reduction concepts discussed above is that they do not capture a number of essential elements of the reduction relation which we would normally expect to be present in the philosophy of science. Mayr steps significantly beyond the notion of structural similarity, and investigates the *content* of the models, as well as the purpose of the theories in them, in more detail. Mayr (1976) proposes that we amend the reduction relation to read as one existing between expanded cores $T = \langle K, I \rangle$ and $T' = \langle K', I' \rangle$, and on this basis consider four different types of correspondence between the models, as in Fig. 6.2.

Of interest is the correspondence of type (iii), in which non-models of the reduced theories nevertheless correspond, through the reduction relation ρ, to

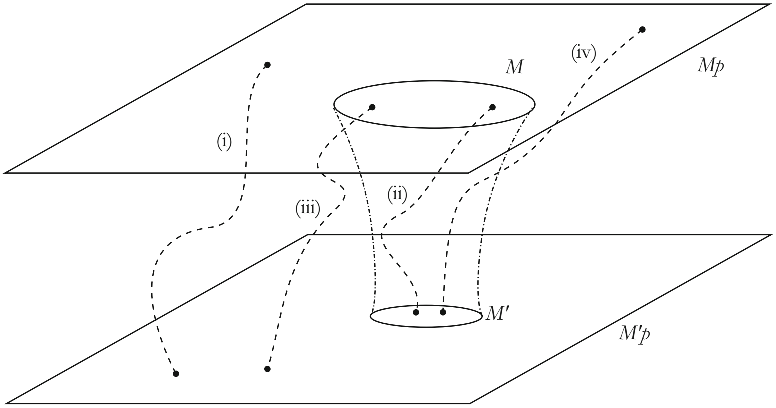

Fig. 6.2 Mayr’s four types of structure correspondence. After Mayr (1976). Note that we have indicated the reducing theory by T and the reduced theory by T'

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[7] Mayr’s comments are technical and I will only convey the most important aspects here, for full details (especially proofs), see Mayr (1976).

models of the reducing theory. As Mayr argues, this condition can be used to explicate the condition of explanation of anomalies. Mayr defines an anomaly in terms of an actual partial potential model which cannot be extended to form a model of the theory:

Definition 3 (Anomaly) An element a $a \in \mathscr{M}_{pp}$ contains an anomaly with respect to the theory $T = (K, I)$ with $K = (\mathscr{M}_p, \mathscr{M}_{pp}, \mathscr{M}, C)$ iff (i) $a \in I$; and (ii) $\mathscr{E}(a) \cap \mathscr{M} = \emptyset$.
By $\mathscr{E}(a)$ we designate the set of theoretical expansions of a in the following sense:

$$\mathscr{E}(a) = \{x | x \in \mathscr{M}_p \wedge r(x) = a\}. \tag{6.4}$$

We intuitively wish to accommodate cases of anomaly explanation by reduction; i.e. cases where a theory T' contains an anomaly a', but where T' is reduced to a theory T which does not contain this anomaly. In this case, presumably, the anomaly can be explained from the theorems of the reducing theory, or, the anomaly can be 'completed' to a model of the reducing theory T. This is captured in the following definition

Definition 4 (Anomaly explanation by reduction) A theory T explains the anomalous intended application a of the theory T' (T explains the anomaly a of T') if (i) $R(T', T)$; and (ii) $\exists m(m \in \mathscr{M} \cap D'(R) \wedge r(m) \in I \wedge (a, r(m)) \in R)$.
As Mayr (1976) explains, the Sneed / Balzer reduction concepts do not allow for anomaly explanation in this sense.

The other important criterion is the condition of preservation of specialisations. This captures the (intuitive) notion that if we have a theory T' which reduces to a theory T then the specialisations T'_σ of T' should induce similar specialisations on T such that $R(T'_\sigma, T_\sigma)$. As Mayr (1976) discusses in considerable technical detail, this is not the case in the Sneed / Balzer reduction concepts.

6.4.1.5 The 'Architectonic' on Reduction

Balzer et al. (1987) develop a general theory of reduction on the basis of the structuralist framework. This reduction relation satisfies a number of conditions.

The basic notion of a theory core in Balzer et al. (1987) is somewhat richer than the structure we have discussed up to now. One particular addition to their discussion of structures is the concept of *links*, which I have not (yet) introduced. Informally, links represent connections between structures which 'carry' information from one structure to the other. Moreover, links can be constrained in the same way that structures are, which is already suggested by the fact that we may write a constraint as a link. The specific additions include a 'global' set of constraints *GC* and a set of link constraints *GL*. Balzer, Moulines and Sneed require that these conditions are preserved across a reduction relation.

The criteria are given in Balzer et al. (1987, p. 275–277). Their most important criterion is that of derivability, which they formulate as follows:

Definition 5 (Derivability (BMS Derivability)) For all x, x': if $\langle x, x' \rangle \in \rho$ and $x \in \mathscr{M}$ then $x' \in \mathscr{M}'$.

We also require that ρ transmits constraint satisfaction, as follows:

Definition 6 (Constraint satisfaction (BMS Constraints)) For all $X \subseteq \mathrm{Dom}(\rho)$; if $X \in GC$ then $\rho^{-1}(X) \in GC'$.

In the same fashion, we require that links (which we will introduce later-on) are preserved across the reduction relation:

Definition 7 (Links (BMS Links)) For all x, x': if $X \in GL$ and $\langle x, x' \rangle \in \rho$ then $x' \in GL'$.

There are a number of additional conditions which are not strictly speaking required, but which a reduction relation could conceivably fulfil.

One of these is the condition of uniqueness, which requires that for each model of the reducing theory there is exactly *one* model of the reduced theory that is related with it.

Definition 8 (BMS Uniqueness) For all x, x', y': if $\langle x, x' \rangle \in \rho$ and $\langle x, y' \rangle \in \rho$ then $x' = y'$.

Another of the additional conditions is the requirement that the range of the reduction relation is the entire set of potential models of the reduced theory, $\mathrm{Rge}(\rho) = \mathscr{M}'$. This is equivalent to saying that all concepts of T' can be captured in T:

Definition 9 (BMS Theory capture) $\mathrm{Rge}(\rho) = \mathscr{M}'$.

We may also require that the derivation relation is independent, that is, the specification of ρ by itself is not sufficient to obtain the derivation relation, but the condition expressed in the derivation relation is independent of the specification of ρ:

Definition 10 not: $\mathrm{Rge}(\rho) \subseteq \mathscr{M}'$.

We may also require that the reduction relation ρ is compatible with the distinction between theoretical and non-theoretical terms. This is expressed as:

Definition 11 (Compatibility (BMS CT)) For all x, x', x_1, x'_1: if $\langle x, x' \rangle \in \rho_p$, $r(x) = x_1$ and $r'(x') = x'_1$ then $\langle x_1, x'_1 \rangle \in \rho_{pp}$

where the relation r and r' are the functions that remove the theoretical terms from $\mathscr{M}_p$ and $\mathscr{M}'_p$ respectively.

A final potential condition is the preservation of intended applications over the reduction relation, so that the intended applications of the reduced theory also have intended applications in the reducing theory:

Definition 12 (BMS Intended Applications) For all $y' \in I'$ there is a $y \in I$ such that $\langle y, y' \rangle \in \rho^{-1}$.

$$\begin{tikzcd}
M_p \arrow[dd, "r"] & \bar{M}_p \arrow[r, "\rho_p"] \arrow[dd, "r"] & M'_p \arrow[dd, "r'"] \\
{} \arrow[r, dashed] & {} & \\
M_{pp} & \bar{M}_{pp} \arrow[r, "\rho_{pp}"'] & M'_{pp}
\end{tikzcd}$$

Fig. 6.3 Structuralist reconstruction of the reduction concept as a structure preserving map.The picture is derived from Mormann (1988); note that we have the ‘prime’ marking the reduced theory in opposition to Mormann to remain with the rest of our notation

6.4.2 An Explication of Structuralist Reduction Concepts

Thomas Mormann (1988) has analysed the structuralist reduction concepts in great detail, and noted that there is an incompatibility between Mayr’s reduction concepts and those of Sneed and Stegmüller.[8] Mormann’s approach to reduction consists of two main steps: first the observation that the ‘reducing’ theory in a reduction relation is generally restricted in some sense, and second, the characterisation of the reduction relation in terms of a reductive map. The overall picture is presented in Fig. 6.3. Note that relative to our notation Mormann’s notation is reversed: he denotes the *reducing* theory with a prime, whereas we denote the *reduced* theory with a prime.

Firstly, Mormann notes that the reduction relationship ρ rarely involves the *complete* machinery of the reducing theory; but instead what seems to be involved in the reduction is some restriction of the reducing theory. These restricted theories are created (pragmatically) by choosing restrictions $\bar{I}$, $\bar{K}$ in a convenient way. Formally, the restriction works in the following way, by (potentially) ‘lopping off’ unnecessary terms of the reducing theory. Define $\bar{\mathscr{M}}_p \subseteq \mathscr{M}_p$; and $\bar{\mathscr{M}} := \bar{\mathscr{M}}_p \cap \mathscr{M}$, $\bar{\mathscr{M}}_{pp} := \bar{r}(\bar{\mathscr{M}}) \cap \mathscr{M}_{pp}$, and $\bar{C} := C \cap \mathrm{Pot}(\bar{\mathscr{M}}_p)$. Let $\bar{I} \subseteq \bar{\mathscr{M}}_{pp}$.

Hence we obtain suitably restricted versions of the reducing theory as key elements in the reduction relationship rather than the full theories – which is an important restriction. This restriction is indicated by the ‘bar’ over the structures, and the dashed line in Fig. 6.3.

Secondly, Mormann characterises the general reduction concept in which a theory T is reduced to a theory T' as a map $R = \langle \rho_p, \rho_{pp} \rangle$, where $\rho_p : \mathscr{M}_p \rightarrow \mathscr{M}'_p$, and $\rho_{pp} : \mathscr{M}_{pp} \rightarrow \mathscr{M}'_{pp}$ (Fig. 6.3). This mapping is able to deal with both the theoretical and observational aspects of a theory.

Mormann then distinguishes two approaches to reduction, which are in turn classified by two distinct sets of informal adequacy conditions. The two main

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[8] Mormann’s exposition is in many ways similar to that of Rott (1987), to which he refers. Both analyses seem to have been developed more or less simultaneously.

Table 6.2 Mormann's formulation of various structuralist informal adequacy requirements for reduction. In each line $R = \langle \rho_p, \rho_{pp} \rangle$

No.	Structure
M/S/B(0)	(Preservation of intended applications): R preserves the domain of intended applications if and only if $I' \subseteq \rho_{pp}(\bar{I})$
S/B(1)	(Preservation of laws): R preserves the condition of derivability if and only if the following holds: $\forall X \subseteq \mathscr{M} : (X \in \mathrm{Pot}(\bar{\mathscr{M}}) \cap C) \Rightarrow \rho_p(X) \in \mathrm{Pot}(\mathscr{M}') \cap C'$
S/B(2)	(Deductive connection of empirical claims): R preserves the deductive connection of empirical claims if and only if, when $I \in A(\bar{K})$, then $I' \in A(K')$.
S/B(3)	(Content Restriction): R satisfies the condition of content restriction if and only if $\rho_{pp}(A(\bar{K})) \subseteq A(K')$
M(1)	(Preservation of specialisations): R preserves the specialisations if and only if (i) $\forall \bar{X}(\bar{X} \in \mathrm{Pot}(\bar{\mathscr{M}}) \cap C) \Rightarrow \rho_p(\bar{X}) \in C'$ and (ii) $\mathscr{M}' \subset \rho_p(\bar{\mathscr{M}})$
M(2)	(Anomaly explaining): The condition of anomaly explanation requires that if there is an anomaly $x' \in I'$ there is an intended application $x \in \bar{I}$ so that $\rho_{pp}(x) = x'$ and x is not an anomaly for T
M(3)	(Truth preservation): $T = \langle K, I \rangle$. R is truth preserving with regard to K if and only if there exists a translation t_R for R such that for each sentence s of T the following holds: $t_R(s)$ is true in $\bar{K} \Rightarrow s$ is true in K'. Analogous for I

classes are the Sneed/Balzer/Stegmüller approach to reduction (which he denotes S/B) and the approach of Mayr (1976) (which is denoted as M). The S/B-approach is characterised by three intuitions regarding reduction: the preservation of laws ('derivability'), the reductive connection of empirical claims, and a condition of content restriction. In opposition, the M-approach is characterised by a condition of preservation of specialisations, a condition of anomaly explanation and a condition of truth preservation.

Since Mormann's approach forms the basis for my proposal to test these reduction conditions *empirically*, it is worthwhile to discuss these conditions in some detail. An overview is presented in Table 6.2.

6.4.2.1 M/S/B(0): Preservation of Intended Applications

The first condition is the preservation of intended applications. The idea of the preservation of intended applications is that for each intended application of the reduced theory there is at least one intended application of the reducing theory that corresponds to it via the reduction relation. Formally, R preserves the domain of intended applications if and only if $I' \subseteq \rho_{pp}(\bar{I})$.

An issue may be that the reduced theory T' is not successful in all its intended applications, and we may wish the reduction relation to correct that (or, alternatively, specify some limits of validity on the reduced theory). Mormann (1988) proposes that we could restrict this condition on I' to *confirmed* (or successful) intended applications instead.

6.4.2.2 S/B(1) Preservation of Laws

The next condition is a structuralist counterpart to Nagel's well-known derivability condition: a reduction relation satisfies the condition of law preservation if and only if it is possible to deduce the fundamental laws of the reduced theory T' from the fundamental laws of the reducing theory T and the reduction relation. In structuralist terms the derivability condition becomes a containment relation. For a reduction relation R one can claim that R preserves the condition of derivability if and only if the following holds: $\forall X \subseteq \mathscr{M} : (X \in \mathrm{Pot}(\bar{\mathscr{M}}) \cap C) \Rightarrow \rho_p(X) \in \mathrm{Pot}(\mathscr{M}') \cap C'$.

This is a purely structural connection, which Mormann (1988) proposes to enrich in the following way. The condition entails $\rho(\mathscr{M}) \subseteq \mathscr{M}'$. If we assume that these models are restricted to some appropriate language and denote the corresponding sets of sentences by Σ and Σ', then these sentences can be interpreted as the sets of laws of the reducing and reduced theory. The entailment means that we obtain a 'derivability' condition:

$$\Sigma \vdash \Sigma'. \tag{6.5}$$

6.4.2.3 S/B(2) Deductive Connection of Empirical Claims

Intuitively, one would require that a reduced and reducing theory have at least (partially) the same empirical claims.

A reduction relation satisfies the condition of deductive connection of empirical claims if and only if the empirical claim of T' can be deduced from the empirical claim of T and the reduction relation R. Formally, a relation R preserves the deductive connection of empirical claims if and only if, when $I \in A(\bar{K})$, then $I' \in A(K')$, where $A(K)$ is defined as the set of models that are 'permitted' by the theory at the level of $\mathscr{M}_{pp}$. It is defined as follows:

Definition 13 $\mathscr{A}(K) = \{X | X \subseteq \mathscr{M}_{pp}$ and there exists $Y \subseteq \mathscr{M}$ such that $r(Y) = X\}$.

6.4.2.4 S/B(3) Content Restriction

The condition of content restriction captures the notion that the reducing theory could have a corrective influence on the reduced theory, or, the reducing theory allows us to correct the reduced theory. Formally, in these cases, R satisfies the condition of content restriction if and only if:

$$\rho_{pp}(A(\bar{K})) \subseteq A(K'). \tag{6.6}$$

Mormann furthermore notes that this condition is in some sense complementary to the condition of preservation of intended applications.

6.4.2.5 M(1) Preservation of Specialisations

The condition of preservation of specialisations holds that if T' is a (reduced) theory which has a specialisation T'_s, then there is a specialisation T_s of T so that R reduces T'_s to T_s.

Formally, $R = \langle \rho_p, \rho_{pp} \rangle$. R preserves the specialisations if and only if (i) $\forall \bar{X}(\bar{X} \in \mathrm{Pot}(\bar{\mathscr{M}}) \cap C) \Rightarrow \rho_p(\bar{X}) \in C'$ and (ii) $\mathscr{M}' \in \rho_p(\bar{\mathscr{M}})$.

Mormann notes, following Mayr (1976, 1981), that S/B reductions are not in general specialisation preserving.

6.4.2.6 M(2) Anomaly Explaining

The condition of explanation of anomalies states that if T' is reduced to T then (some of) the anomalies of T' are explained by the reducing theory T. Formally, the condition of anomaly explanation requires that if there is an anomaly $x' \in I'$ there is an intended application $x \in \bar{I}$ so that $\rho_{pp}(x) = x'$ and x is not an anomaly for T.

6.4.2.7 M(3) Truth Preservation

A final condition discussed by Mormann (1988) is that of truth preservation. In brief, there exists a translation t_R for R. In this context, a translation for R is an assignment $t_R(s)$ for each sentence s of T such that $\rho_p(m) \models s \Leftrightarrow m \models t_R(s)$.

Formally, for $T = \langle K, I \rangle$, R is truth preserving with regard to K if and only if there exists a translation t_R for R such that for each sentence s of K the following holds: $t_R(s)$ is true in $\bar{K} \Rightarrow s$ is true in K'. Analogous for I.

6.4.2.8 Mormann's Analysis of These Conditions

Mormann logically analyses these conditions and draws the conclusion that these conditions are inconsistent in the sense that a reduction relation cannot fulfil all of these conditions simultaneously.

Specifically, fulfilment of S/B(1) ('derivability') precludes M(1). As Mormann notes, this has significant implications for the reductions of theory nets, where we would generally require a preservation of specialisation relations in order to be able to say that one theory net reduces to another.

Mormann compares the condition of truth preservation to the reduction concept of Spector (1975), which is based on the idea of reduction as concept replacement. As Mormann argues, the notion of concept replacement, while too strong to apply in many practical cases, is nevertheless a useful addition even to the S/B-approach to reduction. Mormann furthermore proves that the S/B condition of derivability implies a weaker condition of concept replacement.

It is now interesting to compare this structural analysis of reduction concepts to the informal analysis of reduction set out in Chap. 1. Two remarks are in order.

First of all, while Mormann does not discuss whether an analysis of M(3) would be equally feasible for Nagel's formulation of reduction postulates. Nagel's reduction postulates similarly capture a weaker sense of 'truth preservation' between the reduced and reducing theories. Specifically, Nagel's three variant specifications of the reduction postulates might be reinterpreted from a formal perspective in this way. This approach could shed interesting new light on what the formal consequences of each of these reduction postulates might be.

Secondly, it is worth noting that the structure of the reduction relationship $R = \langle \rho_p, \rho_{pp} \rangle$ is somewhat similar to the distinction in the reduction concepts by Nagel (1961) and Kemeny and Oppenheim (1956). Nagel's notion of reduction works at the level of entire theories, including the theoretical apparatus, and thus corresponds to the 'full' relation R, whereas the Kemeny-Oppenheim notion of reduction seems restricted to the relation ρ_{pp}.

Before going on to discuss my specific proposals for characterising reduction relations, one more structuralist concept is needed: that of inter-theoretic links.

6.5 The Structuralist View Emended: Links

In this section we will present the notion of theory nets and inter-theoretic links, with the ultimate aim to reconstitute the latter as key elements in a reduction relation. The notion of theory nets was introduced in Balzer and Sneed (1977, 1978), and is discussed in detail in Balzer et al. (1987). Theory nets are now the standard way of conceiving of complex scientific theories in the structuralist approach. Links were introduced by Sneed (1984), and are also discussed in detail in Balzer et al. (1987).

6.5.1 Theory-Nets

Theories of realistic complexity cannot in general be expressed as single elements. To allow for a more flexible formal apparatus in theory reconstruction as well as the development of an apparatus in which successive theories can be usefully evaluated, Balzer and Sneed (1977, 1978) developed the notion of 'theory nets'. Theory nets capture, in addition to the theory itself, some of its most immediate environment, either in the form of specialised or approximative theories, or less frequently, in the form of theoretisations of existing theories.

The scope of a theory-net is broader than the scope of a single theory, but smaller than the entire field of science. Intuitively, the scope is perhaps best seen as spanning a multi-branched Lakatosian research programme: within the theory net, there is generally a stable theory core (with only the notion of a theoretisation adding terms to the core in a limited fashion), while there is room to develop specialised theories that are all closely related to each other.

Theory nets can be built on at least three specific relations that exist between theory cores: (i) specialisation, denoted as σ, (ii) theoretisation, denoted as τ and (iii) reduction, denoted as ρ. The specialisation relation is of special interest:

Definition 14 (Specialisation) If $\mathscr{T}$ and $\mathscr{T}'$ are theory-elements, specified by $\langle K(T), I\rangle$ and $\langle K'(T), I'\rangle$ in the definitions above, then $\mathscr{T}'$ is a specialisation of $\mathscr{T}$ (denoted by $\mathscr{T}'\sigma\mathscr{T}$) iff:

(1) $\mathscr{M}'_p = \mathscr{M}_p$;
$\mathscr{M}'_{pp} = \mathscr{M}_{pp}$;
(2) $\mathscr{M}' \subseteq \mathscr{M}$;
$C' \subseteq C$;
$I' \subseteq I$.

The definitions of the remaining two relations are not of interest here, because they are not concerned with theories with different vocabularies.

We can now turn to a definition of theory nets. In the original formulation, theory-nets allowed only for specialisation inter-theory relations between theory elements. With this limitation, the definition of a theory-net based on specialisation is now as follows:

Definition 15 (Specialisation theory-net) $\mathscr{N}$ is a specialisation theory net iff there exist $\mathscr{T}$ and σ such that:

1. $\mathscr{N} = \langle \mathscr{T}, \sigma\rangle$;
2. $\mathscr{T}$ is a finite, non empty set of theory-elements;
3. $\sigma \subseteq \mathscr{T} \times \mathscr{T}$ is the specialisation relation.

On the basis of this definition, we can consider types of theory nets, such as connected nets or trees. This is done in some detail in Balzer et al. (1987) and there is no need to repeat these definitions here.

It is of interest to consider the empirical claim of a theory net. Intuitively, the empirical claim of the entire net would be the claim that $I \subseteq \mathscr{A}(K)$ for every theory-element in the net. Hence:

Definition 16 (Empirical claim of a theory net) If $N = \langle \mathscr{T}, \sigma\rangle$ is a theory net, then we define the empirical claim of the net as follows: For all $\langle K, I\rangle \in \mathscr{T} : I \in \mathscr{A}(K)$.

6.5.2 Theory-Holons and Inter-Theory Links

Intuitively, the notion of a 'theory net' seems rather restricted for our purposes, and hence, it seems likely at the outset that the notion of a theory net needs to be widened to include inter-theory relationships other than specialisation. Theory nets, as specified in the subsection above, are designed to capture the *local* (i.e. between theories of the same type related through specialisation relations) surroundings of a particular theory, but they will not be sufficient for the specification of *global* surroundings of a theory (i.e. capture relationships between theories of different type, which is a typical requirement for heterogeneous reduction).

In the relationship between chemistry and physics we consider the confrontation of two different branches of science, and the somewhat narrow classification of inter-theory links in specialisation, theoretisation and the like is unlikely to be sufficient for specifying the complexities of this relationship.

To describe this particular confrontation in the structuralist framework we have to consider the notion of inter-theoretic 'links' L. Links in this sense are actually related to constraints in the sense that constraints operate between models that are part of the same set of potential models and links operate between models that are members of different sets of potential models.

These links between two theories T and T' can, but need not be, reductive. *Reductive* links have a set of specific requirements, which are discussed in more detail in Sneed (1984), whereas the concept of *links* is a more general formal condition. There is nothing a priori that commits us to specific additional conditions on the links.

Abstract links are simply relationships between two sets of potential models of two theories. An abstract link is defined as (Balzer et al. 1987, p. 61):

Definition 17 (Abstract link) L is an *abstract* link from $\mathscr{M}_p$ to $\mathscr{M}'_p$ iff $L \subseteq \mathscr{M}_p \times \mathscr{M}'_p$.
So the leading idea of the abstract link is that it provides a relationship between two different types of potential models, but does little else.

Concrete links refer explicitly to the functions that play a role in the link and do not link structures *tout court*. To define a *concrete* link, first define a 'picking' function π as follows:

Definition 18 ('Picking' function) For any theory T and given natural numbers $i_1, \ldots, i_n$, let the 'picking function' $\pi(T, i_1, \ldots, i_n)$ denote the class of all tuples $\langle R_{i_1}, \ldots, R_{i_n} \rangle$ for which there is some $x \in \mathscr{M}_p(T)$ such that for $j = 1, \ldots, n : R_{i_j} = R^x_{i_j}$.

In the latter formulation the notation $R^x_{i_j}$ indicates the i_j-th component of structure $x \in \mathscr{M}_p$. Thus the π function 'picks' from the set of potential models for T all those terms for which we wish to define a link. On the basis of this function, we can define a concrete link as one that is relative to a choice of 'picking' function π in the following way:

Definition 19 (Concrete link) L is a *concrete* link from $\mathscr{M}_p$ to $\mathscr{M}'_p$ iff:

1. L is an abstract link;
2. $\mathscr{M}_p$ and $\mathscr{M}'_p$ have m and m' members, respectively;
3. there are $i_1, \ldots, i_s \in \{1, \ldots, m\}$ and $j_1, \ldots, j_t \in \{1, \ldots, m'\}$ such that:
    (a) $L \subseteq \mathscr{M}_p \times \pi(T, i_1, \ldots, i_s) \times \mathscr{M}'_p \times \pi(T', j_1, \ldots, j_t)$;

(b) if $\langle x, \langle r_1, \ldots, r_s\rangle, y, \langle s_1, \ldots, s_t\rangle\rangle \in L$ then for all $k \leq s$ and $l \leq t$: $r_k = R^x_{i_k}$ and $s_l = R^y_{j_t}$.

Example 1 As an example, consider two models of two theories T and T', which are of different type:

$$x = \langle D_1, D_2, n_1, n_2, n_3, t_1, t_2\rangle$$

and

$$x' = \langle D_1', D_2', D_3', n_1', n_2', n_3', n_4', t_1', t_2', t_3'\rangle$$

that is, $x \in \mathscr{M}(T)$ and $x' \in \mathscr{M}(T')$. For instance, the function $\pi(T, 3, 5, 7)$ then picks the terms $\langle n_1, n_3, t_2\rangle$. An instance of an abstract link is a structure:

$$\langle\langle D_1, D_2, n_1, n_2, n_3, t_1, t_2\rangle, \langle D_1', D_2', D_3', n_1', n_2', n_3', n_4' t_1', t_2', t_3'\rangle\rangle.$$

An instance of a concrete link is a tuple that depends in addition on one's choice of the 'picking' functions π. For instance,

$$\langle x, \langle D_1, t_2\rangle, x', \langle D_3', t_3'\rangle\rangle$$

would be a tuple that relates D_1 and t_2 in x and D_3' and t_3' in x'.

Let us briefly discuss this informally. An instance of a concrete link between the potential models of a theory T (with potential models $x \in \mathscr{M}_p$) and T' (with potential models $x' \in \mathscr{M}_p'$) is a tuple of the type:

$$\langle x, \langle r_1, \ldots, r_s\rangle, x', \langle s_1, \ldots, s_t\rangle\rangle$$

which connects (some) terms of the potential models of the two theories. The groups of terms that are picked are collected in the tuples $\mathscr{R} = \langle r_1, \ldots, r_s\rangle$ and $\mathscr{S} = \langle s_1, \ldots, s_t\rangle$. Of course, links can be defined at the level of the potential models of the theory as well as at the level of the partial potential models of the theory. Moreover, the *nature* of the connection is not specified; thus concrete links need additional machinery to describe possible inter-theory relationships.

There are some further considerations that are sometimes useful in the consideration of inter-theoretic links (see Sneed 1984, p. 101). Let us denote the value of some components in some sub-structure $x = \langle r_1, \ldots, r_s\rangle$ by:

$$|\{x\} : r_1, \ldots r_s|, \tag{6.7}$$

and by $|X : r_1, \ldots r_s|$ all possible numerical values that the value of the components $r_1, \ldots r_s$ of (sub-)structure x can take in the link.

The domains of a link L for T and T' are defined as $D(L)$ (the domain with respect to $\mathscr{M}_p$) and $D'(L)$ (the domain with respect to $\mathscr{M}_p'$). These domains are restrictions on the full set of potential models in the following sense: there are some possible values for the r and s components in the structures $\mathscr{M}_p(T)$ and $\mathscr{M}_p(T')$ which do not appear in structures that are related by the link.

Formally, let us designate by $D(L) : \{r_1, \ldots, r_s\}$ the domain of the link restricted to components $r_1 \ldots, r_s$, and by $|A : \{a_1, \ldots, a_k\}|$ the values of the components of $\{a_1, \ldots, a_k\}$ in the structure $\mathscr{A}$. Then this condition becomes:

$$|D(L) : \{r_1, \ldots, r_s\}| \subseteq |M_p(T) : \{r_1, \ldots, r_s\}| \tag{6.8}$$

$$|D'(L) : \{s_1, \ldots, s_t\}| \subseteq |M'_p(T') : \{s_1, \ldots, s_t\}|. \tag{6.9}$$

Another condition is one regarding the uncorrelated components (i.e. the components which do not take part in the link). Generally, all values that these components can take in either $\mathscr{M}_p(T)$ or $\mathscr{M}_p(T')$ are present in the link. If we denote these components by $\{u_1, \ldots, u_m\}$ and $\{v_1, \ldots, v_n\}$, respectively, then:

$$|D(L) : \quad \{u_1, \ldots, u_m\}| \times |D'(L) : \{v_1, \ldots, v_n\}| = \tag{6.10}$$

$$|M_p(T) : \{u_1, \ldots, u_m\}| \times |M_p(T') : \{v_1, \ldots, v_n\}|. \tag{6.11}$$

The idea of this is that the link has the capacity to somehow restrict only the range of numerical values that can be taken by the linked variables of the theory, but places no restrictions on the unlinked variables.

The concept of an inter-theoretic link is the most general concept that allows us to connect the framework of two theories together. Links allow for relationships between structures of different type, and links allow us to 'pick' the information that we wish to share. An interesting question is what sort of conditions may turn a link into a reduction. In what follows we will deal with interpreting and reducing links as the most relevant examples of inter-theoretic links.

But first we introduce one new concept, based on a combination of both a theory net and a link. The 'link based' extension of the theory-net is the theory holon. A theory holon is an element of the 'global' structure of science, which is discussed briefly in Balzer et al. (1987) in the last chapter, where no specific examples are given.

The leading concept of a theory-holon is the concept of an inter-theoretical link L. On this basis, a holon is defined as follows (Balzer et al. 1987, Def VIII-1, p. 389):

Definition 20 (Theory-holons) $\mathscr{H}$ is a theory-holon iff there exist $\mathscr{N}$ and L such that $\mathscr{H} = \langle \mathscr{N}, L \rangle$ and:

1. $\mathscr{N}$ is a non-empty set of theory-elements;
2. $L : \mathscr{N} \times \mathscr{N} \to \cup\{\mathrm{Pot}(\mathscr{M}_p(T) \times \mathscr{M}_p(T')) | T, T' \in \mathscr{N}\}$ is a partial function;
3. for all T, T': if $\langle T, T' \rangle \in \mathrm{Dom}\,(L)$ then $L(T, T') \subseteq \mathscr{M}_p(T) \times \mathscr{M}_p(T')$ hence L is an abstract link;
4. If $\mathscr{N}$ contains more than one element, then, for all $T \in \mathscr{N}$, there exists $T' \in \mathscr{N}$ such that $\langle T, T' \rangle \in \mathrm{Dom}\,(L)$ or $\langle T', T \rangle \in \mathrm{Dom}\,(L)$;
5. for all T, T', T'': if $\langle T, T' \rangle \in \mathrm{Dom}\,(L)$ and $\langle T', T'' \rangle \in \mathrm{Dom}\,(L)$ then $\langle T, T'' \rangle \in \mathrm{Dom}\,(L)$.

Theory holons can contain concrete links with some adaption of these definitions. To the degree that links are general characterisations of the specialisation, theoretisation and reduction relation that feature in the theory nets of Balzer and Sneed (1977, 1978), holons are generalisations of theory nets.

6.5.3 Interpreting Links

It is not possible to give an exact formulation of interpreting links, though, as Sneed (1984) notices, a number of necessary conditions for an interpreting link can be formulated.

In this section, I define some properties of an interpreting link using the concept of an abstract link. Intuitively, interpreting links provide an interpretation of a concept from one theory in terms of another and thus constrain the values that are admissible in the concept that is interpreted through the link (this also indicates a potential strengthening of the concept of constraint that we will turn to later).

The concept of an interpreting link can be contrasted with that of a reducing link. A reducing link is a stronger notion than an interpreting link. In addition to carrying information between the two theories it contains the notion that the reduced theory is isomorphic to some (systematically described) subset of models of the reducing theory, which is also the interpreting theory.

In this sense, the idea of the interpreting link is that the linked terms are interpreted but not reduced. The idea of interpretation is that the 'interpreting' theory provides an interpretation for terms that appear in another theory. We indicate the structures of the interpreting theory by $\mathscr{M}(T_i)$ and the structures of the theory which' terms are interpreted by the interpreting theory by $\mathscr{M}(T)$.

Consider a link L which provides the interpretation for (some) terms of a theory T with the help of an interpreting theory T_i (where the notation is chosen to make the relationships clear). It then seems reasonable to require the following conditions to be satisfied.

A first requirement is that some models of T_i must be linked:

$$D(L) \cap \mathscr{M}(T_i) \neq \emptyset. \tag{6.12}$$

A second requirement determines the 'admissible range' of values determined by the link. The strongest requirement is that if $\langle x_i, x\rangle$ and $\langle y_i, y\rangle$ are both L-linked, then the values for $\langle r_1, \ldots, r_s\rangle$ in both links must be the same. This condition may be too strong, however, and Sneed (1984) proposes to weaken it to a condition that stipulates that a range of values is admissible.

The exact specification of this is a little cumbersome, but not conceptually difficult. We again denote the value of the components of some structure $x = \langle r_1, \ldots, r_s\rangle$ by $|\{x\} : r_1, \ldots r_s|$. The statement that the values must be the same reads

$$|\{x\} : u_1, \ldots u_s| = |\{y\} : v_1, \ldots v_s|. \tag{6.13}$$

As Sneed (1984) points out, in many cases the condition is not strictly required for interpretation, all that is required for an interpreting link is a condition that if two sets of potential models $\mathscr{M}_p$ and $\mathscr{M}_p'$ are linked and the values are determined in $\mathscr{M}_p$ than the corresponding values in $\mathscr{M}_p'$ are restricted in some sense.

One condition on the link is that the interpretation holds independent of the laws of the theory with the interpreted terms, or more precisely, there exist $\langle x', x\rangle \in L$ such that $x' \in \mathscr{M}(T')$ and $x \notin \mathscr{M}(T)$. The converse holds as well, i.e. there exist $\langle x', x\rangle \in L$ such that $x \in \mathscr{M}(T)$ and $x' \notin \mathscr{M}(T')$. The first condition reflects the criterion that the laws of the theory which' terms are interpreted, $\mathscr{M}(T)$, has nothing to do with the values these interpreted terms can take, that task is performed by the interpreting theory together with the link. The second condition reflects the criterion that there may be some "bad data" which just satisfies the laws of T but which is not open to interpretation. Both of these criteria are violated for a reducing link. The reason for this is that the interpreting link does not make any (meaningful) claims about the relation between the *laws* of the reduced and reducing theory, whereas a reducing link does make such claims.

With this, we obtain the following definition for the minimum formal conditions for an interpreting link.

Definition 21 (Interpreting link) L is an *interpreting* link from $\mathscr{M}_p(T)$ to $\mathscr{M}_p'(T)$ iff:

1. L is an abstract or concrete link;
2. $D(L) \cap \mathscr{M}(T_i) \neq \emptyset$;
3. There exist $\langle x_i, x\rangle$, $\langle y_i, y\rangle \in L$ such that:
   (i) $x_i \in \mathscr{M}(T_i)$ and $x \notin \mathscr{M}(T)$; and
   (ii) $y \in \mathscr{M}(T)$ and $y_i \notin \mathscr{M}(T_i)$.

6.5.4 Reducing Links

We now turn to the concept of a reducing link. There are of course some differences between the structuralist conception of *reduction* and *reducing links*. Simply put, the difference is that a full structuralist reduction specifies a global relationship between entire structures (and hence is based on what we have called an *abstract* link above), whereas a link potentially specifies only a *partial* relationship between structures (and is potentially based on the notion of a *concrete* link). Designate the relevant subset of models by $\mathscr{M}_r$. $\mathscr{M}_r$ is a restriction on the full reducing theory.

Hence, we need a notion of reduction based on the idea of a concrete link. This can be achieved by suitably adapting the concept of the restricted theory $\mathscr{M}_r$.

In cases where the reducing link is based on an abstract link, the structure $\mathscr{M}_r$ can be defined as a subset of $\mathscr{M}_p$. In the cases where it is based on a concrete link, the members of $\mathscr{M}_r$ are 'stripped' of those terms that do not participate in the concrete link.

The requirements for a reducing abstract link are:

Definition 22 (Reducing abstract link) L is an *reducing* link from $\mathscr{M}_p$ to $\mathscr{M}'_p$ iff:

1. There exists some subset $\mathscr{M}_r$ of $\mathscr{M}_p$ such that:
    (i) $\mathscr{M}_r \subseteq \mathscr{M}_p$;
    (ii) $\mathscr{M}_r \cap \mathscr{M} \neq \emptyset$;
    (iii) $L^{-1} : \mathscr{M}_r \rightarrow \mathscr{M}'_p$ (surjective);
    (iv) If $x' \in \mathscr{M}'_p$ is linked (through L) to a model for the reducing theory then x' must be a model for the reduced theory.

In the next section I will propose that we consider the concept of links as the basis for reduction relations. The concept of a reducing link will not be used further there: it will appear that it is more useful (and in line with a Nagelian set of connectivity requirements) to specify explicit conditions on top of concrete links.

6.6 A Pragmatic Proposal: Links Qua Reduction Postulates

It would seem that a straightforward application of the currently proposed reduction relations in the structuralist framework has little chance of carrying our project further: there are many different conditions corresponding to different notions of reduction, these conditions are not all compatible, and moreover, it would seem that there is little *practical* justification for imposing such a framework on the reduction of chemistry to physics.

In this section I develop a proposal for a robust structuralist reduction relation that can be *empirically* tested against the reduction of chemistry to physics. In the remainder of this chapter I will set out the proposal in more detail. In the next two chapters I will focus on how this proposal may be used in the reduction in question.

Specifically, the proposal for a structuralist reduction relation revolves around two separate issues. The first one is how the reduced and reducing theories can be connected. The connections in Nagel's theory of reduction are facilitated primarily by reduction postulates. The structuralist approach to scientific theories provides connection criteria for theoretical frameworks most generally in the language of inter-theoretical links. The second issue is how links might relate to Mormann's (1988) 'adequacy conditions', especially the 'truth preservation' condition M(3). It is at this level that the structuralist approaches disagree, though they do not disagree in a fashion dissimilar from the disagreement of the specific theories of reduction that we discussed in Chap. 1.

Before arguing these aspects in more detail, let us turn them into a proposal. In brief, there seems to be sufficient ground for proceeding with the formal investigation of reduction relationships in the following manner:

1. Reconstitute the concept of reduction postulates in terms of an inter-theoretical link. As we will see below, there is significant overlap between the notion of an inter-theoretical link and the concept of a reduction postulate.
2. Investigate further reductive claims empirically. Specifically, I propose to focus on the conditions of law preservation, preservation of specialisations, reductive connection of empirical claims, preservation of intended applications and the condition of content restriction.

This is a pragmatically oriented approach to the problem of reduction, which will be developed further in the remainder of this section.

6.6.1 How Links May Function as Reduction Postulates

My proposal is to consider inter-theory links as key constituting aspects of the reduction postulates for a theory of reduction, and to this end, start with the weakest condition of a concrete link. This leads to a relatively austere definition of the reduction relation, which is likely to be stronger in many practical cases. My claim is that this proposal satisfies the requirements for *reduction* though it may not satisfy the more stringent (metaphysical) requirements for *reductionism* (which requires that the reduction postulates express identities of some sort). The proposal is sketched, in simple form, in Fig. 6.4.

Formally, we will indicate links existing between *potential* models of the theory by L_p and links existing between the *partial potential* models of the theory by L_{pp}. The advantage of this notation is that we can specify the checklist of reductive claims in terms of claims at the *theoretical* or *empirical* level of the theory.

It should be noted that this scheme is similar to that of Mormann (1988) except for the (somewhat vague) modifications that are made to the reducing theory in the latter scheme. The work done by these modifications is more easily performed by the links. This has the added advantage that these modifications become explicit in the reduction relation. The domain of the links is capable of 'picking out' both the required terms and the range of applicability of these terms in the reduction relation.

Thus links seem to be an excellent form for reduction postulates. To make this claim intelligible, note that links fulfil the informal criteria for Nagelian reduction postulates (which were given on p. 7), and that formally they are very similar to the

$$\begin{tikzcd}
M_p \arrow[r, "L_p"] \arrow[d, "r"] & M'_p \arrow[d, "r'"] \\
M_{pp} \arrow[r, "L_{pp}"'] & M'_{pp}
\end{tikzcd}$$

Fig. 6.4 Links as reduction postulates: the links contain the selection of terms that are linked so that the development of special versions of the reducing theory is no longer required type of reduction postulates as proposed by Schaffner (1967), (which were given on p. 12). Links can also fulfil, at least at a superficial level, Neurath's condition of 'structural similarity' (Neurath (1983), cf. Sect. 1.3).

The issue of whether inter-theoretical links can reproduce reduction postulates is a matter first of function and second of logical form. Let us turn to these requirements in more detail and see how the concept of inter-theoretic links may fulfil the conditions that both Nagel (1961) and Schaffner (1967) place on links.

First the Nagelian requirements. As discussed, for Nagel (1961), the reduction postulates are either (i) logical connections, (ii) conventions or coordinating definitions, or (iii) factual, material, or physical hypotheses, where the meanings of the terms involved in the link are not related analytically (but perhaps open to empirical verification). Inter-theoretical links fulfil these functions by linking theories together in such a manner that the sort of additional conditions we might want to place on the links are left open. In contrast, Schaffner's formulation of the reduction criteria are based on the logical form that reduction postulates have to assume if they are taken to be *identities*. Schaffner proposes a set of extensional criteria, which were enumerated on p. 12 of this thesis.

Colin Klein (2009) has argued that Nagel's criteria for reduction postulates are more liberal than any metaphysical account could be.[9] Specifically, Klein argues that when it comes to connectibility, a reducing science should be capable of *introducing* a term that the reduced science lacks:

> Connectibility is thus determined primarily by the representational power of the reducing science: if it possesses the resources to refer to the same properties as the reduced science, then it is on its way to reducing the latter. If not, then not. (Klein 2009, p. 39–40)

The concepts of inter-theoretical links capture precisely the required sort of flexibility: they are capable of establishing a relationship between terms of the reduced science and terms of the reducing science in a general form.

In a somewhat similar vein, Rafael van Riel (2011) has classified Nagelian reduction in the following terms[10]:

1. Reduction is a relation holding among a great variety of scientific representational devices, among which theories play an important epistemological role.
2. Interesting reductions are explanations that consist in deductions that are carried out with the help of bridge laws, and they have to obey (some of) the relevant nonformal criteria (unification, appropriateness of reducing theory and bridge laws, and, if possible, correction should be involved in reduction).

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[9] Thus, Klein also distinguishes between the two possible accounts of reduction we have outlined in the preface: the 'top down' approach in which we first stipulate what sort of relationships reduction relations *have to be* to support the unity of science, and the naturalistic approach in which we give primacy to what these reduction relationships *actually are*.

[10] The $*$ signs from van Riel's enumeration in the quote below may be confusing, but are redundant in the present context. Van Riel distinguishes a traditional analysis of Nagel's criteria as a set *a*) - *e*), and contrasts this with a new set a^*) - e^*). Only van Riel's re-analysis of Nagel's criteria in terms of his 'starred' set is of interest here and this is the one in the quote below. In my discussion of van Riel's criteria I will drop the stars.

> 3. Bridge laws are to be regarded as stating ontological links (identities or relations among extensions) a posteriori.
> 4. Reduction is not direct (in the sense that it just is not a case of theory explanation) – it goes together with explanations of the phenomena of the reduced theory by the reducing theory.
> 5. The Nagel model is not an epistemological model of reduction. (van Riel 2011, p. 371–372)

Of these, item (a) draws attention again to the 'representational power' of the devices that stand in the putative reduction relationships, which may be captured by links. Some of the remainder of van Riel's re-interpretation of Nagel corresponds to what my current proposal aims to test empirically (items (b) and (d)). Items (c) and (e) will be the focus of Part III.

The second issue is one of logical form. Schaffner (1967), in his conditions on reduction postulates from p. 12 borrows from Quine (1964), who defines reduction postulates in extensional terms as follows:

> The standard of reduction of a theory θ to a theory θ' can now be put as follows. We specify a function, not necessarily in the notation of θ or θ', whose values exhaust the universe of θ for arguments in the universe of θ'. This is the proxy function. Then to each n-place primitive predicate of θ, for each n, we effectively associate an open sentence of θ' in n free variables, in such a way that the predicate is fulfilled by an n-tuple of values of the proxy function always and only when the open sentence is fulfilled by the corresponding n-tuple of arguments. (Quine 1964, p. 215)

This is what inter-theoretical links do: the general logical structure of an inter-theoretical link is one that relates an n-tuple of one theory to an m-tuple of another. Quine's condition of exhaustion entails, in the language of links, that the link is a reducing link.

6.6.2 Possible Alternative Classifications

As an important aside, we can also classify links on the basis of the model for inter-theoretic reduction proposed by Kuipers (1990). Recall from Chap. 1, (and especially p. 17) that Kuipers' model is based on some combination of the following argumentative steps in an explanatory argument: Application, Aggregation, Identification, Correlation and Approximation. A reduction requires the presence of either Aggregation, Identification and Approximation. The links that make up the core of the reduction can also be classified accordingly into aggregation links, identification links, correlation links and approximation links. While I will not work out this discussion in formal detail, it would provide an interesting alternative point of view on the reduction relation.

Usually the application of a theory involves some sort of specialisation relation, in which a more general theory is specialised to account for a particular situation to which it will be applied. The specialisation of the theory may involve the specification of its entities, as well as a number of additional laws which apply only in the particular situation to which the theory will be applied. Alternatively, the ‘restriction’ of the reducing theory discussed on p. 137 can similarly be seen as an application step.

Another interesting aspect of the structuralist approach is that it is capable of explicating in more formal detail the concept of a ‘structural’ relationship between theories which forms the core of the analysis of the quantum-classical relation developed by Alisa Bokulich (2008) and which she calls ‘interstructuralism’. Bokulich analyses the structural relationship not in semantic terms, as in this chapter, but notes that:

> Interstructuralism is an approach to intertheory relations that emphasises the importance of structural continuities and correspondences in giving an adequate account of the relation between two theories. It recognises a richer diversity of correspondence relations than does any form of reductionism or pluralism. (Bokulich 2008, p. 173)

To the degree that Bokulich identifies ‘reductionism’ with the strict interpretation of Nagelian reduction as ‘identities’ *cum* ‘strict derivation’ (and her book suggests that she does) the approach I am advocating to Nagelian reduction is to a significant degree compatible with interstructuralism.

There is thus a degree to which the ‘naturalised’ Nagelian reductive connections, as advocated here as well as by Klein (2009) and van Riel (2011) are conducive to a unification of reductive and non-reductive approaches, and can contribute to an overall ‘structural’ view on the unity of science. Bokulich explicitly advocates her approach as one that takes us ‘beyond reductionism and pluralism’, and as one that has a non-reductive thrust, but there is little in her book to suggest that the liberal and structural reading of the Nagelian connections is incompatible with her proposals.

Similarly, the structural approach to the Nagelian connections, and the semantic approach to theories, is capable of reconciling the concept of Nagelian reductions with the ‘interfield’ approach advocated by Darden and Maull (1977) which we discussed on p. 20. The notion of a ‘field’, which forms the core of their analysis, is approachable from the viewpoint of the structuralist conception of theories, as a ‘set of phenomena’, or a set of empirical claims, to which different theories may apply.

Hence, apart from the prospect of explicating the ‘naturalised’ reduction relationships, the structural approach also seems capable of *reconciling* the reductive views with a number of non-reductive views.

6.6.3 A Checklist of Reductive Claims

The second leg of my proposal is that any additional requirements or adequacy conditions can be empirically tested against *actual* theories. To this end, we will define a number of reductive conditions that have been advanced in the structuralist literature, and consider the extent to which they obtain in the actual reduction of chemistry to physics in Chap. 8.

Table 6.3 The additional conditions on the reductions that we propose to test. Recall that $\bar{I}$ and $\bar{K}$ refer to the intended applications and the theory core of the reducing theory. $R = \langle L_p, L_{pp} \rangle$ in each line

	Condition	Structure
IA	Preservation of intended applications	R preserves the domain of intended applications if and only if $I' \subseteq L_{pp}(I)$
L	Law preservation	R preserves the condition of derivability if and only if the following holds: $\forall X \in \mathscr{M} : (X \in \text{Pot}(\mathscr{M}) \cap C) \Rightarrow L_p(X) \in \text{Pot}(\mathscr{M}') \cap C'$
D	Preservation of specialisations	R preserves the specialisations if and only if (i) $\forall X (X \in \text{Pot}(\mathscr{M}) \cap C) \Rightarrow L_p(X) \in C'$ and (ii) $\mathscr{M}' \in L_p(\mathscr{M})$
E	Deductive connection of empirical claims	R preserves the deductive connection of empirical claims if and only if, when $\bar{I} \in A(\bar{K})$, then $I' \in A(K')$
CR	Content restriction	R satisfies the condition of content restriction if and only if $L_{pp}(A(\bar{K})) \subseteq A(K')$

This proposal is a further development from the observation, made independently by Mormann (1988) and Rott (1987), that the various adequacy conditions imposed on the structuralist notion of reduction are mutually incompatible.

Table 6.3 summarises the additional conditions (informal adequacy conditions in the terminology of Mormann 1988) on the reduction relation that we propose to test.

We now discuss the adequacy conditions in turn.

1. The preservation of intended applications is one of the core claims of the reduction: it states that the reducing theory aims to explain, among other things, the same facts as the reduced theory.
2. The condition of law preservation requires that any fundamental laws of the reduced theory T' are derivable from the laws of the reducing theory and the reduction relation. The structuralist counterpart is a purely structural connection which states that $L_p(\mathscr{M}') \subseteq \mathscr{M}$.

   This condition has been discussed by Mormann (1988) who has argued (see above) that from this condition one may under certain conditions derive $\Sigma \vdash \Sigma'$.
3. The deductive connection of empirical claims is the requirement that the empirical claims of the reduced theory follow from those of the reducing theory *cum* the reduction postulates.
4. The condition of content restriction captures the intuition that the reducing theory may *refine* the reduced theory in non-trivial ways.

5. The condition of preservation of specialisations is required to allow a reduction of theory nets.

It should be noted that these five conditions are not a complete representation of all reduction claims that have been made in the structuralist approach to theories. Nevertheless in my view they represent the most important ones.

6.7 Conclusion

Our overview of the structuralist reduction concept has suggested that there is a large number of reduction concepts that are applicable to the structuralist conception of theories. However, most of these stem primarily from an attempt to 'read in' the requirements of reductionism into a structural relationship. Hence, it should come as no surprise that some of the reduction concepts that have been proposed in the structuralist literature are incompatible.

This chapter has argued that rather than a straightforward specification of a connectibility and derivability criterion, the structuralist conception of reduction is better placed to explicate concepts of *explanation* in terms of how the structures are inter-related. The introduction of *links* in the structural approach allows for a characterisation of the Nagelian connections of connectibility and derivability as primarily *structural* connections, which can be empirically tested against actual scientific theories.

Reading the structural connections in this manner also opens up significant scope to reconcile a 'naturalised' Nagelian reduction with various non-reductive approaches, and hence gain new insights into the unity of science. In this sense, the structural approach fulfils the promise of Sneed's 'science of science'.

In the following two chapters it is my aim to put this proposal to the test. To that end, in the next chapter, Chap. 7, I propose a structuralist characterisation of quantum chemistry, which is structurally connected to the theories of chemistry in Chap. 8.

Chapter 7
Models for Quantum Chemistry

Abstract This chapter provides the basic concepts for the characterisation of quantum chemistry as a research programme. I start with the characterisation of a quantum mechanics, and then gradually add the components that turn a generic quantum mechanics into quantum chemistry. This approach allows two specific philosophical outcomes: it allows us to make explicit what type of further characterisations are necessary to turn quantum mechanics into quantum chemistry and it allows us to specify in sufficient detail what the structure of quantum chemistry qua explanatory theory is.

7.1 Introduction

The Sneedian or structuralist approach to scientific theories has never, to my knowledge, offered convincing structural characterisations of quantum theory (as opposed to Newtonian and relativistic mechanics).[1] The reason for this may well be that the axiomatic foundations of quantum mechanics are relatively unsettled, or, as Muller (1998) has argued, that there is in fact a *family* of structures to consider. The formalisation of quantum chemistry that we will present in this chapter shows, in formal detail though without many of the Sneedian embellishments, something that philosophers of chemistry have suspected for longer: quantum mechanics is not a particularly tidy theory to reduce to.

It also shows that these problems can be overcome, at least as far as the reduction of chemistry to physics is concerned. The structures that characterise ab initio quantum *chemistry* can be shown to be primarily (but not exclusively) of a 'simple' form of quantum mechanics, one in which a state function and a probability play a lesser role. In opposition, the concerns expressed especially by Primas (1981) about the reducibility of chemistry instead relate to a 'complex' form of quantum mechanics, in which the matters of a state function and acceptable probability distribution play a major role.

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[1] The only attempt to formalise quantum theory in a Sneedian framework that I am aware of is an unpublished attempt by Gerhard Zoubek from 1997, see Zoubek (1997), which deals with the spinless case for wave mechanics, and the work of Muller (1998), who does not strictly speaking use the Sneedian framework.

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In this chapter, I will present structuralist characterisations of quantum mechanics and define its relation to quantum chemistry. This chapter forms the first half of two chapters that deal formally with quantum chemistry, chemistry and the matter of reduction. Of those two chapters, this chapter deals with the structural characterisation of quantum mechanics and quantum chemistry, and defers the discussion of many chemical and reduction matters to the next chapter. The main philosophical point of this chapter is that the manner in which quantum chemistry can be characterised as a 'chemistry' forms part of the 'application' or 'transformation' step of the basic theory.

The ultimate aim of this chapter is twofold. The first aim is to characterise quantum chemistry as a theory in a structuralist sense and to answer a few pertinent questions on its specification – in particular whether quantum chemistry can be properly characterised as a quantum mechanics on the one hand and as a theory of chemistry on the other. The second aim of this chapter is to flesh out the actual structures of quantum chemistry in more detail. To answer this question, we focus on the sort of relationships that may exist between various theories of quantum chemistry, and how these relations can be structurally characterised.

The characterisation of quantum chemistry as a member of the family of quantum mechanical theories is of course of the utmost importance for the nature of the reduction relation; if quantum chemistry cannot be properly characterised as a quantum mechanics then the matter of reduction ends there.

Similarly, the question on reduction would end if quantum chemistry would prove to be incapable of maintaining the required sort of relationships to the theories of chemistry. This question will be partially answered by investigating how the 'core' of quantum chemistry can be expanded into theory nets, which, as was argued in the previous chapter, are a special case of linking commitments between theories. The relation on a theory net is that of specialisation, in which 'special case' theories are constructed to deal with a subset of phenomena or a model system. Such theory nets correspond to a loose web of theories about matter that in their combination form chemistry.

To sum up, the issues to be addressed in this chapter are the following:

1. What are the relationships between quantum chemistry and quantum theories?
2. How can quantum chemistry be classified as quantum mechanics?
3. Can quantum chemistry also be classified as a chemical theory?
4. What is the relationship between the structures of chemistry and those of quantum chemistry?
5. How is quantum chemistry specified as a theory net?

I will argue that quantum chemistry is classified somewhat more properly as *chemistry* rather than as *physics*: quantum chemistry as a reducing theory already contains a number of key chemical assumptions in its *application* to chemical problems. There are some pragmatic reasons for this classification as well: not only is the attitude to foundational problems more pragmatic in quantum chemistry than in quantum physics, but also the explanatory structure of chemistry is less unified, in a sense, than in physics.

Logically, this chapter proceeds as follows. The first issue we consider is that of the structuralist formalisation of quantum theory itself. The axiomatisation of quantum mechanics is a complex topic, which, in contrast to the various axiomatisations of classical mechanics (see Adams 1959; Sneed 1971; Balzer et al. 1987), does not seem to have been completely solved. Notwithstanding the fact that a full Sneedian characterisation of quantum mechanics may well prove to be difficult, all that is required for the current project is the specification of the structure *species*, a much simpler project that can be successfully completed.

In Sect. 7.2 I present the proposed model for quantum mechanics, deriving a set-theoretic formulation of quantum mechanics from the work of Muller (1998, 2003). I introduce some members of the family of quantum mechanical structures that will be required for the discussion of quantum chemistry later on, focusing on a 'simple' and 'complex' quantum mechanics. The 'complex' quantum mechanics augments the simple quantum mechanics with a state operator and a probability function.

The determination of formalisations that are usable in quantum *chemistry* as opposed to quantum *physics*, is one that has a longer standing in chemistry. Specifically, it has been argued by for instance Primas and Müller-Herold (1978) and Primas (1981) that chemistry is in need of a more general framework for quantum mechanics, which allows for a more seamless integration between quantum mechanical and classical systems – something that Primas argues lies at the heart of a chemical theory of matter.

These sentiments are certainly reflected by other chemists too. For instance, part of the rationale that Löwdin (1982) presents for presenting a formulation of the theorems of quantum mechanics as a trace algebra is the following:

> Even if the main reason for this work was purely pedagogical, it was still hoped that, since the "trace algebra" renders a unification of quantum mechanics, quantum statistics, classical thermodynamics, and – to a certain extent – classical mechanics, it may turn out to be of value in the study of temperature-dependent chemical reactions and in quantum biology. (Löwdin 1982, p. 275)

Thus there is a line of argument in chemistry where chemists have argued for an 'extended' view of quantum mechanics, a quantum mechanical formalism that is rich enough to capture the wider range of physical theories that feature so prominently in chemical explanation.

I will argue in this chapter that while these concerns are valid,[2] it can be argued that quantum chemistry can be reconstructed in terms of a much simpler form of quantum structure that largely bypasses these problems. Moreover, such a step may be classified, from the viewpoint of a theory of scientific reduction, as an 'application' or 'modification' step of the reducing theory. Specifically,

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[2] Part of the problem lies in the fact that the foundations of quantum mechanics can be based on a number of formalisms. Among these are (i) an algebraic approach, (ii) a quantum-logic approach, and (iii) the convex state approach. For the purposes of the models in this thesis we will consider primarily the algebraic approach based on Hilbert spaces and consider those subsets of quantum theory that are most directly applicable to quantum chemistry.

quantum chemistry can be characterised as a quantum mechanical structure without a probability measure.

The key goal of this chapter is to determine a structuralist formulation of quantum *chemistry*. In Sect. 7.2 I define a number of structural aspects of the theory of quantum mechanics. Then, in Sect. 7.3 I present a Sneedian reconstruction of quantum chemistry *qua* ab initio electronic structure theory. This reconstruction will allow us to address the question whether quantum chemistry can be seen as a quantum mechanics, and it will also form the foundation of the remainder of this chapter and the material in Chap. 8. I then consider the matter of the characterisation of quantum chemistry as a quantum mechanics in more detail in Sect. 7.4. The next section, Sect. 7.5, is concerned with the extension of the 'core' of quantum chemistry into a collection of theory 'nets'. The last section is an interim conclusion, which sums up the degree to which quantum *chemistry* is a modified theory *vis a vis* quantum mechanics, and hence part of an 'application' step that initiates reduction.

7.2 Architecture of a Quantum Mechanics and Its Structure Species

In order to classify quantum chemistry as a species of quantum mechanics we first have to define what sort of structure species makes up quantum mechanics. There are no 'single' structures that define quantum mechanics. As the detailed set-theoretic considerations of Muller (1998) have indicated, there is rather a 'family' of such structures.

In this section I will discuss some (simple) structural characterisations of quantum mechanics, without invoking the entire machinery of the structuralist formalism (potential models, models and partial potential models). This is possible because our aim in this section is primarily directed at *characterisation*: we wish to answer the question whether quantum chemistry can be characterised as a quantum mechanics, and if so, what sort of quantum mechanics. The restriction is also necessary in the sense that a uniform characterisation of quantum physics in structuralist terms is unlikely.

In the formulation of structure species for quantum mechanics, I will take my cue from Muller (1998), who has discussed the 'equivalence myth' of Heisenberg's matrix mechanics and Schrödinger's wave mechanics.[3] Contrary to common opinion, Muller argues, these two early formulations of quantum theory were not initially theoretically and empirically equivalent, though the 'final' versions of these theories were. The debate of the equivalency myth is not in itself useful for our further discussion, but the formal, especially the structural characterisations of quantum physics that it produced are.

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[3] The relevant chapters in Muller (1998) were also published separately in Muller (1997a,b). Muller (1998) contains additional material and some corrections.

Muller discusses a number of formalisations of both wave mechanics and matrix mechanics and formulates a number of possible structure species for a quantum mechanics to discuss these claims. Those structuralist characterisations are of interest here. Muller (1998) analyses the architecture for quantum mechanics as it is given in Von Neumann (1932) with the help of ten potential structures. The exact choice is dependent on whether one considers simple or composite systems, pure or mixed states, and dependent on whether one accepts some or all of the postulates of quantum mechanics. In our presentation, we follow the simplified approach presented in Muller (2003).

7.2.1 *Components of a Quantum Physics*

Let us first generally develop the structure species that are necessary in the further specification. Quantum mechanics is based on a number of components. These are at a minimum a system specification $\mathscr{S}$, a Hilbert space $\mathscr{H}$, and a set of operators (and their associated spectra), which we will designate by $\hat{A}$ and $\sigma(\hat{A})$. Furthermore one can define specific state operators and a probability measure.

We briefly describe these components, first building up the model for a *simple* quantum mechanics, which is a quantum mechanics without a state operator and probability measure. Then we go on to formally define a *complex* quantum mechanics with a state operator and probability measure. I will argue that much of today's quantum chemistry can be classified as a 'simple' quantum mechanics and hence is capable of bracketing some of the more fundamental problems associated with the interpretation of quantum mechanics.

The (formal) structure of a quantum physics is built upon the physical representations of a *system*, *state* and *operator*. We first explicate and relate these representations.

Quantum mechanics is about a *system*. A system is a specification of a set of particles, such as, for instance, the specification of a proton and an electron with a Coulomb interaction. The specification of this system is primarily a task of *enumeration*. Hence from the specification of the system we can derive the number of dimensions of its configuration space, and in most cases write down the Hamiltonian.

Formally we will indicate a system with the letter $\mathscr{S}$, and characterise it as a collection of particles $\mathscr{P}$. The cardinality of $\mathscr{P}$ (the number of particles) is indicated by N. Somewhat arbitrarily we will define $n = 3N$. On $\mathscr{S}$ it is useful to define a sortal function Π.[4] Π sorts the members of $\mathscr{P}$ into types $\mathscr{T}$, such that a type is associated with each particle;

$$\Pi : \mathscr{P} \to \mathscr{T} \tag{7.1}$$

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[4] See for instance Zoubek (1997), where a very similar description of a system is given.

Furthermore, we can define functions m and z which assign masses and charges to the types (and hence to the particles $p \in \mathscr{P}$);

$$m : \mathscr{T} \to \mathbb{R} \tag{7.2}$$

and

$$z : \mathscr{T} \to \mathbb{R}. \tag{7.3}$$

These definitions (formally) allow for charge-less and mass-less particles, such as photons, to be counted as members of the set. In the practice of ab initio quantum chemistry, which is our target, the practical restrictions are however that mass-less and charge-less particles are not part of the system under consideration, and hence we may restrict the above formulas to $m : \mathscr{T} \to \mathbb{R}^+$ and $z : \mathscr{T} \to \mathbb{R}^+$.

With these definitions, m and z are transported into $\mathscr{P}$ as follows: $m(p) = m(\Pi(p))$ and $z(p) = z(\Pi(p))$. This allows us to consider the simple $m(p)$ and $z(p)$ in what follows.

We can thus formally define a 'system' as a tuple $\langle \mathscr{P}, \mathscr{T}, \Pi, m, z \rangle$ as follows

Definition 1 $\mathscr{S} = \langle \mathscr{P}, \mathscr{T}, \Pi, m, z \rangle$ characterises a system of quantum theory if and only if

(1) $\mathscr{P}$ is a system of particles;
(2) $\mathscr{T}$ is a collection of types;
(3) Π is a sortal operator which assigns types to particles: $\Pi : \mathscr{P} \to \mathscr{T}$;
(4) $m : \mathscr{T} \to \mathbb{R}^+$ assigns mass to the types
(5) $z : \mathscr{T} \to \mathbb{R}$ is an electric charge function.

The constraints on the representation of a system are that types, mass and charge are constrained between models. Formally the constraints are of the form C, where $C \subseteq \text{Pot}(\mathscr{S})$. Following the practice of Chap. 6 we ignore the constraints most of the time.

The mass and charge constraints specify that 'electrons' for instance have the same mass and charge in each system that we consider. Hence in cases where we have two classes of particles $\mathscr{P}$ and $\mathscr{P}'$ (with members p and p' respectively), if it is the case that $\Pi(p) = \Pi(p')$ (the particles in the two systems are of the same type), then also $m(p) = m(p')$ and $z(p) = z(p')$.

The constraint on types specifies that the same particle cannot belong to different types. It is again of the form $C \subseteq \text{Pot}(\mathscr{S})$, and specifies that if we have two classes of particles $\mathscr{P}$ and $\mathscr{P}'$, and corresponding type assignments Π and Π', that for a particle p which appears in either class $\Pi(p) = \Pi'(p)$ (a particle is assigned the same type in different systems).

While on the surface this looks like a complex machinery, in practice the *enumeration* step of the application of quantum theory works through these elements as follows. For instance, consider a system which consists of an atomic nucleus N with mass $m(N)$ and charge $Z = +2$ and two electrons with masses $m(e) = 1$

and charges $Z(e) = -1$ (in atomic units).[5] Hence there are 3 particles of two sorts to consider ($N = 3$). There are nine spatial coordinates ($n = 3$; $N = 9$) of which three are of further interest: the distance of each electron to the nucleus and the distance between the electrons. The remainder of the coordinates relate to the overall rotation and translation of the system. The corresponding system Hamiltonian is the Hamiltonian of two electrons in the Coulomb field of the nucleus with additional terms for translation and rotation of the overall system. Hence the Hamiltonian contains the kinetic energy terms for the three particles[6] and the Coulomb interactions.

Systems need to be distinguished from *states*.[7] In classical mechanics a state is obtained from a system by specifying numerical values for the positions and momenta; in quantum mechanics a state is obtained from a system by assigning a wavefunction ψ to the system. Hence, classically, states are characterised by determinate combinations of properties of a system, such as position and momentum. In quantum theory, a *state* is associated with a system in the sense that the state is a specification of the wavefunction $\psi(x_1, \ldots, x_n, t)$ of a system.

The wavefunction ψ depends on both coordinates x and time t and specifies a function from $\mathbb{R}^{3N} \times \mathbb{R}$ into the complex numbers $\mathbb{C}$:

$$\psi : \mathbb{R}^{3N} \times \mathbb{R} \to \mathbb{C}. \tag{7.4}$$

The formal requirements on the wavefunction ψ are that it is twice differentiable, and that the derivative functions are again members of $\mathscr{H}$.

We may also define a multiplicative operator by the symbol $\hat{O}$, and require $\hat{O}\psi = o\psi$ with $o \in \mathbb{R}$.

In many textbooks the mathematical representatives of states are vectors in *Hilbert* space, which is how Von Neumann (1932, 1955) treats states in the early chapters of his discussion on the mathematical foundations of quantum mechanics.[8] From Chap. III onwards, von Neumann considers ensembles and hence has to define a specific 'state operator' on Hilbert space.[9]

Furthermore, the (formal) structure of quantum physics is characterised in terms of Hilbert (or Fock)[10] spaces. We will not discuss these in large detail, but make the following brief remarks.[11]

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[5] One of the links we specify in Chap. 8 will go one step further and call this system a Helium atom.

[6] Note that these become complicated once the translation and rotation are split off from the total.

[7] See footnote 155 in Von Neumann (1955) on p. 297.

[8] This can potentially lead to confusions, as Muller (1998) (p. 377) points out. Also Primas and Müller-Herold (1978) draw attention to this fact on p. 32.

[9] Band (1964) refers to it as the 'von Neumann operator'.

[10] A Fock space is a multi-particle extension of the Hilbert space which consists of the direct product of N 1-particle Hilbert spaces.

[11] We refer for instance to Akhiezer and Glazman (1961), Lengyel (1968) and Muller (1998) for further relevant details and further references to the literature.

The defining characteristics of a Hilbert space are that a Hilbert space is a linear space with a norm. The requirements for vectors in Hilbert space are that they satisfy the properties

$$\langle f|g_1 + g_2\rangle = \langle f|g_1\rangle + \langle f|g_2\rangle \tag{7.5}$$

$$\langle f|g\alpha\rangle = \langle f|g\rangle\alpha \tag{7.6}$$

$$\langle f|g\rangle = \langle g|f\rangle^* \tag{7.7}$$

$$\|f\|^2 \equiv \langle f|f\rangle \tag{7.8}$$

In the last line, note that $\langle f|f\rangle = 0$ if and only if $f = 0$, otherwise $\langle f|f\rangle > 0$.

For quantum chemistry, we can consider the (relatively unproblematic) Hilbert space of the set of square integrable functions in L^2 (or $\psi \in L^2$). A member of L^2 satisfies the condition that the functions are square integrable

$$\langle g|f\rangle = \int f(x)g^*(x)dx < \infty. \tag{7.9}$$

(i.e. the integral is finite). The norm is $\langle f|f\rangle$. Indicating a differentiation to a function $|g\rangle$ with respect to its j-th variable by D_j we also require that $D_j|g\rangle \in L^2$.

Observables are generally associated with operators. Operators project the Hilbert space onto itself: $\hat{A} : \mathscr{H} \to \mathscr{H}$ in the sense that $\hat{A}|f\rangle = |\hat{A}f\rangle$ where $|\hat{A}f\rangle \in \mathscr{H}$. Operators correspond to physical magnitudes such as position, momentum and energy.

Associated with the operators is a *spectrum*, which we will denote by $\sigma(\hat{A})$ for an operator $\hat{A}$. Informally, σ contains the possible outcomes on experiments on the quantum system. In quantum chemistry, we can usually work with Hermitian operators and a finite dimensional space. With these restrictions, the associated functional theory is as follows.

An operator $\hat{A}$ is associated with a set of eigenfunctions $|a\rangle$ where $|a\rangle$ is an eigenfunction of the operator $\hat{A}$, or $A|a\rangle = a|a\rangle$. If $F_a = \{|a\rangle : A|a\rangle = a|a\rangle\}$ is the space of functions with eigenvalue a, then a *projector* on this space of functions F_a will be indicated by P_a or its index i if $a = a_i$.

The spectral decomposition of $\hat{A}$ in terms of these projectors becomes

$$\hat{A} = a_1P_1 + a_2P_2 + a_3P_2 + \dots \tag{7.10}$$

The set of $\sigma(\hat{A})$ is the *spectrum* of operator $\hat{A}$.

The probability measure associated with quantum mechanics is the Born measure.

The traditional von Neumann interpretation of quantum mechanics is based on the consideration of a system $\mathscr{S}$ characterised by a set of basis vectors $\{|\psi_i\rangle\}$, spanning a Hilbert space $\mathscr{H}_{\mathscr{S}}$, which interact with a measurement system $\mathscr{A}$ which in turn is characterised by $\hat{A}$ and eigenfunctions $|a\rangle$ and span a Hilbert space $\mathscr{H}_{\mathscr{A}}$. The totality of the system and measurement apparatus (the total system $\mathscr{S}$ combined with $\mathscr{A}$) is then in a superposition state which is a member of the direct product of the two Hilbert spaces $\mathscr{H}_{\mathscr{S}} \otimes \mathscr{H}_{\mathscr{A}}$.

In actual measurements we measure outcomes a_i but not superpositions of outcomes. How to extract definite outcomes a_i from the superposition of states in $\mathscr{H}_{\mathscr{S}} \otimes \mathscr{H}_{\mathscr{A}}$ is usually referred to as the *measurement* problem in quantum mechanics. Much has been written about this measurement problem. However, we will not need to consider this problem further for our purpose.

7.2.2 A Structure for a Simple Quantum Physics

We now use these concepts to define a 'simple' quantum physics. A simple quantum physics is based on the concept of a system, a Hilbert space, operators and a spectrum.

A Hilbert space and a set of operators form the minimal requirements for a quantum mechanics, so that a minimal structure for a quantum mechanics becomes a structure $\mathscr{Q}_s$

Definition 2 (QM-S) x is a characterisation of a simple quantum mechanics, ($x \in \mathscr{Q}_s$) iff

1. $x = \langle \mathscr{S}, \mathscr{H}, \hat{A}, \sigma(\hat{A}) \rangle$;
2. $\mathscr{S}$ is a system of particles;
3. $\mathscr{H}$ is a separable Hilbert space;
4. $\hat{A}$ is an operator on $\mathscr{H}$;
5. $\sigma(\hat{A})$ is the spectrum of $\hat{A}$.

The simple quantum physics thus specifies a structure with a wavefunction, an operator and associated spectrum. It does not use the concepts of 'state' or 'probability'. In many cases in quantum chemistry the simple quantum physics will be sufficient for our task. In practice in these cases, the operator $\hat{A}$ will be the Hamiltonian operator $\hat{H}$.

The (time-dependent) Schrödinger equation may be written (where $\hbar = 1$):

$$iD_{n+1}\psi = H\psi \tag{7.11}$$

where the differentiation D_{n+1} is with respect to the time coordinate of the wavefunction, i.e. for a wavefunction $\psi(x_1, \ldots x_n, t)$, $D_{n+1} = d/dt$.

Models of the simple quantum mechanics are the potential models that satisfy the Schrödinger equation.

7.2.3 Structures for a Complex Quantum Physics

To complete our discussion we give a brief formulation of a complex quantum physics. In all formulations of the structures for a complex quantum physics, we start from the structure of the simple quantum physics.

There are two more components that 'complete' the simple quantum mechanics into a 'full' version of quantum mechanics. These concern the state operator and the probability measure. The state operator assigns a specific physical *state* to a function in Hilbert space (and functions as the operator counterpart of von Neumann's view that a system turns into a state by assigning a wavefunction to it). The final component is the probability measure P. As Muller (2003) notes, a probability measure is not a prerequisite for a structure of quantum mechanics, and for the discussion of ab initio quantum chemistry it is safe to drop this.

A complex quantum mechanics is now characterised as a structure $\mathscr{Q}_c$:

Definition 3 (QM-H) x is a characterisation of a complex quantum mechanics ($x \in \mathscr{Q}_c$) iff

1. $x = \langle \mathscr{S}, \mathscr{H}, \hat{A}, \sigma(\hat{A}), W, P \rangle$;
2. $\mathscr{S}$, $\mathscr{H}$, $\hat{A}$ and $\sigma(\hat{A})$ are defined as in the definition for a simple quantum physics;
3. W is a state operator;
4. P is the probability measure.

The potential models for a complex quantum physics therefore add machinery to aid in its interpretation: the state operator and the probability measure. It will turn out that a large part of quantum chemistry can be characterised as a simple quantum mechanics which does not depend on this additional machinery. Some quantum chemical problems do, however. Among these are chiefly the calculation of spectral line intensities, which depends on a probability mechanism, and the direct calculation of chemical reaction rates through scattering theory.

Models of the complex quantum theory similarly satisfy the Schrödinger equation.

This definition forms a broad characterisation of a 'quantum physics'. The general idea of this characterisation is

> [...] that in every branch of physics where phenomena are 'modelled quantum-mechanically', such as atomic physics, solid state physics, quantum chemistry, quantum optics and quantum transport theory, the concept of a 'quantum-mechanical model' can be construed as a set-structure of some type such as defined above [...] or of some sibling type. (Muller 2003, p. 196)

It now needs to be shown that quantum chemistry can be established as a set-theoretic structure of quantum mechanical type.

7.3 A Structuralist Reconstruction of Quantum Chemistry

In this section we present a structuralist reconstruction of quantum chemistry, adhering to the correct ‘family’ relationships so that quantum chemistry can also be seen as a ‘branch’ of quantum physics.

The idea is to reconstruct quantum chemistry primarily as a science of its own, and then establish the necessary connections with the quantum theory on the one hand and chemical theories on the other. The degree to which this characterises quantum chemistry as an ‘interfield theory’ in the sense of Darden and Maull (1977) will be discussed in Chap. 8. In addition, this chapter will not focus on all of quantum chemistry, but will focus on the most prevalent version of it: ab initio electronic structure theory.

Ab initio electronic structure theory is one of the more often used approaches in quantum chemistry, and has developed into a chemists’ desktop tool. Using the computer programmes developed as part of the development of ab initio quantum chemistry, chemists’ now regularly investigate molecules ‘theoretically’ in addition to experimentally. The framework constructed in this chapter is moreover general enough to be extended to semi-empirical or density functional methods. Since extending the framework to these latter two would add a lot of complexity without much benefit, these extensions will not be discussed further. For the purposes of this chapter, ab initio quantum chemistry can be taken as paradigmatic.

7.3.1 Prerequisites

The structure of quantum chemistry consists of a number of components that taken together make up the entire fabric of the reconstruction of quantum chemistry. The components are the representation of a nuclear frame, the representation of atomic and molecular orbitals, and the representation of various laws and principles of quantum mechanics.

We will begin by defining a number of substructures that make up the key elements of ab initio quantum chemistry. These substructures define the representation of an atomic nucleus, a collection of electrons, a molecular frame and the representation of an orbital. In this sense, the representation of a ‘molecule’ in ab initio quantum chemistry is a specialised kind of ‘system’, which has specific links (in the technical sense of Chap. 6) to the representation of a system from the previous section, and, in the case of quantum chemistry, replaces the system by a combination of a molecular frame and an electronic structure.

To this combination of a frame and an electronic structure we will then apply the machinery of quantum mechanics. This application step is characterised as another link between the potential models of quantum chemistry and the structural characterisations of quantum mechanics from the previous section.

7.3.1.1 Molecular Frames

The nuclei in ab initio electronic structure theory are viewed as point masses fixed in space, defining a molecular 'frame'. The concept of a frame is related to and builds on the concept of 'system' from the previous section.

The aim of this section is to build up the representation of a 'molecular frame'. A *frame* is a collection of N nuclei fixed in space. Hence the representation of a frame is best characterised in terms of a representation of an 'atomic nucleus'. The main specification that enters into the representation of the nucleus is a position vector $\mathbf{R}$ and a nuclear charge $z = Ze$, where Z is the atomic number and e is the unit charge.[12] We define the structure for a nucleus as $\langle \mathbf{R}, Z \rangle$, where $\mathbf{R}$ is the position vector and Z is the (positive) nuclear charge in unit charges. Of course, $Z \in \mathbb{N}^+$.

In what follows, I will focus on that portion of the system that can be classified as the *nuclear* portion. In the characterisation of the frame, we ignore the electronic portion. Without loss of generality, we can subdivide the 'system' into an *electronic* part, represented by a collection of electrons $\mathscr{P}_e$, where $\mathscr{P}_e = \{p|\Pi(p) = e\}$ (in which 'e', denotes electronic type) and a 'nuclear' part $\mathscr{P}_\text{N}$ where $\mathscr{P}_\text{N} = \{p|\Pi(p) \neq e\}$. Note that for electrons $m(p) = 1$ (in atomic units) and $z(p) = -1$ (in atomic units).

This model for the frame of atomic nuclei is of course an idealisation. It represents the nuclei as point charges, and ignores any internal structure of the nucleus. In terms of the terminology of the previous chapter, however, the model for the atomic nucleus is linked to an (undefined) fuller model of the atomic nucleus which takes the internal structure into account. We have not identified this set of models here, but surmise that some link L must exist which connects this model of the nucleus to a more complete model of the nucleus in the following (informal) way: (i) the position vector $\mathbf{R}$ corresponds to the centre of mass of the nucleons that make up the atomic nucleus, and (ii) the atomic number Z is identical to the overall positive charge of the nucleus. It would seem that a (complete) structuralist treatment of science which includes nuclear physics would have to have such a link as a consequence. For the present purposes we state its existence without further proof.

In general, quantum chemistry is not concerned with the internal structure of nuclei as far as the mass is concerned. There are some applications of electronic structure theory, however, where some sort of charge distribution of the nucleus

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[12] We will throughout the remainder of this chapter work in 'atomic units' in which $\hbar = 1, e = -1$, and the unit of mass is the mass of the electron $m_e = 1$.

Table 7.1 Mapping of the first twenty chemical elements to the enumerated models of the atomic nuclei in ab initio quantum chemistry

Element	Z	Element	Z
H	1	Na	11
He	2	Mg	12
Li	3	Al	13
Be	4	Si	14
B	5	P	15
C	6	S	16
N	7	Cl	17
O	8	Ar	18
F	9	K	19
Ne	10	Ca	20

is assumed. This charge distribution may be uniform or Gaussian. Examples of such applications are found in relativistic quantum chemistry and Mössbauer spectroscopy.

We define an 'atomic nucleus' as a structure:

Definition 4 $x \in \mathscr{N}$ is a (quantum chemical) model of an 'atomic nucleus' iff

(1) $x = \langle \mathbf{R}, Z \rangle$;
(2) $\mathbf{R} \in \mathbb{R}^3$ is a position vector;
(3) $Z \in \mathbb{N}^+$ is the nuclear charge.

These basic elements map to chemical elements in the following way. For the hydrogen atom, we assign $Z = 1$, for the helium atom, $Z = 2$ and so on. For the first 20 elements, the mapping is given in Table 7.1. In fact, many ab initio computer programs allow the user to specify the chemical element rather than the nuclear charge.

Restricting ourselves to the nuclear portion of the frame, we take into account that in a molecule there are generally multiple nuclei, so that a 'molecule' in quantum chemistry is characterised as a 'collection of structures' $\{\langle \mathbf{R}_1, Z_1 \rangle, \ldots, \langle, \mathbf{R}_N, Z_N \rangle\} \in \operatorname{Pot} \mathscr{N}$.

Such a collection represents a chemical formula by using the translation table; for instance a collection of three nuclei with 2 nuclei of type $Z = 1$ and one of type $Z = 8$ represents the chemical formula H_2O. However, it does not necessarily represent the chemical compound 'water'. The formula H_2O *may* represent a 'water' molecule, but may also represent a system H + OH for instance. Similarly, if we consider a system with 4 'C' atoms and 10 'H' atoms, there would still be multiple compounds relating to the 'formula' C_4H_{10}, representing the chemical compounds butane and isobutane respectively.

What is still lacking in the 'collection', of course, is the notion of molecular *shape*. To impose a geometrical shape on the frame, the nuclear coordinates have to be read as *parameters* in the overall Hamiltonian, cf. Eq. (3.3) or Eq. (5.3). The difficulties experienced with molecular shape were discussed in detail in Chap. 3, and in the context of the present discussion correspond to taking the molecular positions as *parameters* in the frame, rather than as a dynamic variable. We will indicate this by a change in notation from $\mathbf{R} \to \mathsf{R}$, and (formally) use the term 'collection' for the former and 'frame' for the latter. This is in accordance with the practice of ab initio quantum chemistry, in which nuclear coordinates are taken as parameters and a *geometrical structure* is imposed on the collection to turn it into a frame. This geometrical structure distinguishes between a 'collection' and a 'frame', and also disambiguates, although a posteriori, the chemical structures.

We will define a molecular *collection* with N nuclei ($\mathscr{C}(N)$) as a structure $\langle \mathbf{R}_1, \ldots, \mathbf{R}_N; Z_1, \ldots Z_N \rangle$. Similarly, we define a molecular *frame* with N nuclei ($\mathscr{F}(N)$) as a structure $\langle \mathsf{R}_1, \ldots, \mathsf{R}_N; Z_1, \ldots Z_N \rangle$, where the set $\{\mathsf{R}\}$ is the parameter set of nuclear coordinates and the set $\{Z\}$ the corresponding set of atomic numbers. There are minimal formal differences between frames and collections, and we will primarily work with frames from this point onwards.

We will denote the position vector for all nuclei in the frame by R, and the vector of nuclear charges by $\mathbf{Z}$.

Hence we can define the structure of the nuclear frame as follows:

Definition 5 $x \in \mathscr{F}$ is a molecular frame iff

(1) $x = \langle \mathsf{R}, \mathbf{Z} \rangle$;

(2) R is a nuclear position vector (containing all parametrised positions of the nuclei);

$\mathbf{Z}$ is a nuclear charge vector (containing all nuclear charges);

(3) For all translation vectors $\mathbf{r}_t$: $\langle (\mathsf{R}_1 + \mathbf{r}_t), \ldots, (\mathsf{R}_N + \mathbf{r}_t); Z_1, \ldots Z_N \rangle$ is isomorphic to a frame $\langle \mathsf{R}_1, \ldots, \mathsf{R}_N; Z_1, \ldots Z_N \rangle$ for any $\mathbf{r}_t$;

(4) For all rotations R around the centre of mass of the nuclear frame $\langle R(\mathsf{R}_1), \ldots, R(\mathsf{R}_N); Z_1, \ldots Z_N \rangle$ is isomorphic to a frame $\langle \mathsf{R}_1, \ldots, \mathsf{R}_N; Z_1, \ldots Z_N \rangle$.

In some instances it will be useful to add a parameter N to the frame indicating the number of nuclei in the frame, i.e. $\mathscr{F}(N)$. The formal definition for collections is of course identical to the above with the substitution $\mathbf{R}$ for R in all relevant positions.

The isomorphism conditions of clauses (4) and (5) are analogous to the transformation procedure which reduces the total number of free coordinates in the nuclear collection from $3N$ to $3N-6$ (or $3N-5$ for a linear molecule). These transformations lead to complex forms for the Hamiltonian in the case of collections.

Clause (4) The first represents the fact that we may translate the entire frame in space by some (arbitrary) translation $\mathbf{r}_t$. This will leave the frame invariant. That is, a frame $\langle (\mathsf{R}_1 + \mathbf{r}_t), \ldots, (\mathsf{R}_N + \mathbf{r}_t); Z_1, \ldots Z_N \rangle$ is isomorphic to a frame $\langle \mathsf{R}_1, \ldots, \mathsf{R}_N; Z_1, \ldots Z_N \rangle$ for any $\mathbf{r}_t$.

Formally the constraint can be defined as a relation $C \in \mathrm{Pot}(\mathscr{F}) \times \mathrm{Pot}(\mathscr{F})$ such that a frame $\mathscr{F}$ is isomorphic to a frame $\mathscr{F}'$ if $\langle \mathsf{R}'_1, \ldots, \mathsf{R}'_N; Z_1, \ldots Z_N \rangle$ can be written as $\langle (\mathsf{R}_1 + \mathbf{r}_t), \ldots, (\mathsf{R}_N + \mathbf{r}_t); Z_1, \ldots Z_N \rangle$ for fixed $\mathbf{r}_t$.

Clause (5) represents the fact that the frame may be rotated by an arbitrary amount around its centre of mass. A rotation R transforms the (parametrised) position vector R into its image $R(\mathsf{R})$. This will again leave the frame invariant. That is, a frame $\langle R(\mathsf{R}_1), \ldots, R(\mathsf{R}_N); Z_1, \ldots Z_N \rangle$ is isomorphic to a frame

$\langle \mathsf{R}_1, \ldots, \mathsf{R}_N; Z_1, \ldots Z_N \rangle$ for any R. The constraint formulation is similar to the one for the translation.

Frames also have to fulfil the constraints on mass, charge and type assignments of the system.

A concrete link (in the technical sense of Chap. 6) between the frame $\mathscr{F}$ and the system $\mathscr{S}$ will be referred to as $L_{sf}(\mathscr{S}, \mathscr{F})$ and has the following form.

$L_{sf}(\mathscr{S}, \mathscr{F})$ 'imports' (or transports) the types and charges from the system into the frame. The masses are not transported for the nuclei that make up the frame (though they are for a collection). Recall that for electrons, we have defined a set $\mathscr{P}_e$ and we have defined a set of nuclei by $\mathscr{P}_{\mathrm{N}}$ such that $\mathscr{P}_{\mathrm{N}} = \{p | \Pi(p) \neq e\}$. The link will ignore electrons and be restricted to systems of $\mathscr{P}_{\mathrm{N}}$.

Hence, the definition of the link becomes:

Definition 6 $L_{sf}(\mathscr{S}, \mathscr{F})$ is a link between a system and a frame iff $\forall xy$ if$\langle x, y \rangle \in L_{sf}(\mathscr{S}, \mathscr{F})$, then $\exists \mathscr{P}, \mathscr{T}, \Pi, m, z$ and $\exists$ $\mathsf{R}, \mathbf{Z}$ such that

(1) $x = \langle \mathscr{P}, \mathscr{T}, \Pi, m, z \rangle$ is a system and $y = \langle \mathsf{R}, \mathbf{Z} \rangle$ is a frame;
(2) $\exists$ l_r and l_z such that

1. l_r is a 1 to 1 function $\mathscr{P}_{\mathrm{N}} \rightarrow \mathsf{R}$, where l_r indicates the position (parameters) of nucleus p;
2. l_z is a 1 to 1 function $\mathscr{P}_{\mathrm{N}} \rightarrow Z$ such that $l_z(p) = z(p)$; i.e. the charge in atomic units.

The link is thus responsible for 'importing' some of the physical characteristics of a system into the frame. Also note that the link is unidirectional. The *structural* characterisation of the frame, as well as the division in nuclei and electrons is added to the notion of a 'system'.

Furthermore it should be noted that the frame does not ascribe the correct masses to each particle – there is only room for a dual assignment in which electrons are assigned mass $m_e = 1$ and the mass of all other types is infinite.

The specification of a frame thus extends the representation of a system by the introduction of *structure* into the problem, and goes beyond the mere *enumeration* that characterises the system in quantum theory. Hence, some aspects of the 'full' quantum theory, which would apply to collections do not apply to frames: there is an infinite mass and fixed position for the nuclei, as well as a loss of permutation symmetry for the nuclei. In this sense, the transition is not 'smooth'. Formally, the important aspect is that the above link captures this transition.

The pragmatic reasons for this step and the philosophical problems associated with these reasons, were discussed in Chap. 3.

7.3.1.2 Electronic Structure

The next step is the definition of the total number of electrons in the system. For a neutral system, the total number of electrons is identical to the sum of all nuclear charges Z_i (where i runs from $i = 1$ to $i = N$). An *ion* is a molecule (or atom) that has either a positive or negative charge. An ion with a *negative* charge has an 'oversupply' of electrons, whereas an ion with a positive charge has an undersupply.

The total number of electrons, denoted by N_e is the sum of all the nuclear charges in the frame with the ionic charge of the system subtracted. Denoting the system charge by z, the total number of electrons in the system is

$$N_e = \sum_{i=1}^{N} Z_i - z \tag{7.12}$$

The electrons have a set of electron coordinates associated with them, which is denoted $\{\mathbf{r}\}$.

We define an electronic 'structure' $\mathscr{E}$ as follows. The particles taken from the collection of electrons $\mathscr{P}_e$ (where $\mathscr{P}_e = \{p | \Pi(p) = e\}$ in which 'e', denotes electronic type), denoted by p_i, the electronic coordinates by $\mathbf{r}_i$, and the set has cardinality N_e (it has N_e members). The set of electrons is translationally and rotationally invariant in the same way as the molecular frame. Hence $\mathbf{r} : P \rightarrow \mathbb{R}^3$ is a function from P into the 3-dimensional space of real numbers.

In addition, we add a spin function $\sigma(p)$ to the set, denoting the value of the electron spin; hence $\boldsymbol{\sigma} : P \rightarrow \boldsymbol{\Theta}$ where $\boldsymbol{\Theta}$ are the spin functions.

We also define the many-electron wavefunction Ψ as a function from $\mathbb{R}^{3N_e} \times \mathbb{R}$ into the complex numbers, specifically, $\Psi : \mathbb{R}^{3N_e} \times \mathbb{R} \rightarrow \mathbb{C}$.

From the specification of a quantum system we retain the structure of the operator set $\{\hat{A}\}$, with spectrum $\sigma(\hat{A})$, which is a set of operators that corresponds to the properties of interest of the system. We then define a magnitude set $\mathsf{M}(\hat{A}, \Psi)$ which maps the expectation value of operators $\hat{A}$ and the wavefunction Ψ onto a set of SI units U,

$$\mathsf{M} : \hat{A} \times \Psi \rightarrow \mathbb{R} \times \mathsf{U}$$

Roughly speaking, M collects the set of measurable magnitudes of the electronic system. For instance, the operators could represent the electronic coordinates, magnetic operators or operators representing other areas of interest of the molecule. It should be noted that the expectation value, represented by the 'measure set' M is a 'weighted sum' of eigenstates of $\hat{A}$, and hence there is a correspondence between $\sigma(\hat{A})$ and M.

The structure is then characterised as follows:

Definition 7 $x \in \mathscr{E}$ is an electronic structure iff

(1) $x = \langle \mathscr{P}_e, \mathbf{r}, \boldsymbol{\sigma}, \Psi, \hat{A}, \mathsf{M} \rangle$;
(2) $\mathscr{P}_e$ is a set of electrons;
(3) $\mathbf{r} : \mathscr{P}_e \rightarrow \mathbb{R}^3$ assigns a position to each electron;
(4) N_e (the cardinality of $\mathscr{P}$) is the number of electrons;
(5) $\boldsymbol{\sigma} : \mathscr{P}_e \rightarrow \boldsymbol{\Theta}$ assigns the spin function to each electron;

$\Psi : \mathbb{R}^{3N_e} \times \mathbb{R} \rightarrow \mathbb{C}$ is the electronic wavefunction;

(6) $\mathsf{M} : \hat{A} \times \Psi \rightarrow \mathbb{R} \times \mathsf{U}$ is the 'measure' set.

We may define a link between the electronic structure $\mathscr{E}$ and a system $\mathscr{S}$ in terms of a number of *identity* assignments, in which the electrons are assigned a mass and charge (non-electrons are dropped from the link). Similar to the link between the system and the frame, the existence of a coordinate which is assigned to the electron is stated. Formally:

Definition 8 $L_{se}(\mathscr{S}, \mathscr{E})$ is a link between a system and an electronic structure iff $\forall xy : \langle x, y\rangle \in L_{se}(\mathscr{S}, \mathscr{E})$, then $\exists \mathscr{P}_e, \mathscr{T}, \Pi, m, z$ and $\exists\ \mathscr{P}, \mathbf{r}, \boldsymbol{\sigma}, \Psi, \hat{A}, \mathsf{M}$ such that

(1) $x = \langle \mathscr{P}, \mathscr{T}, \Pi, m, z\rangle$ is a system and $y = \langle \mathscr{P}_e, \mathbf{r}, \boldsymbol{\sigma}, \Psi, \hat{A}, \mathsf{M}\rangle$ is an electronic structure;
(2) $\forall p \in \mathscr{P}_e$: $m(p) = 1$ (in atomic units) and $z(p) = -1$ (in atomic units).

7.3.1.3 Wavefunctions and Symmetry

The members of the set of electrons $\mathscr{P}_e$ are described by an N_e-electron wavefunction of distinct spatial and spin symmetry. The spatial symmetry is determined by the point group symmetry of the molecular frame, whereas the spin symmetry is determined by the spin function. This wavefunction will be denoted $\Psi(N_e)$, and will be from the position vectors (which are transported into $\mathscr{E}$) and the time coordinate into the complex numbers:

$$\Psi(N_e) : \mathscr{E} \times \mathbb{R}^+ \to \mathbb{C}. \tag{7.13}$$

The specific form of the wavefunction will be dependent on the models of the actual theories. In general, the wavefunction is a linear combination of products of one-electron wavefunctions, following Slater (1931b). The one-electron wavefunctions are the (spin-)orbitals. In what follows, spin-orbitals are written $\psi_I(\mathbf{r}_i)$, and spatial orbitals $\phi_I(\mathbf{r}_i)$. The spin-orbital is a product of the spatial orbital with a spin function $\psi_I(\mathbf{r}_j) = \phi_I(\mathbf{r}_j)\sigma(\mathbf{r}_j)$. The labeling is lowercase (i.e. 'j') for electron coordinates and uppercase for orbitals (i.e. 'I'). There are generally more possible orbitals than electrons, so that the N_e electrons 'occupy' some subset $A, B, \ldots, X$. We assume the set of spin-orbitals to be complete and orthonormal.

Following McWeeny and Sutcliffe (1969) or McWeeny (1989), the most general form of the wavefunction is

$$\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_{N_e}) = \sum_{A,B,\ldots,X} c_{A,B,\ldots,X}\psi_A(\mathbf{r}_1)\psi_B(\mathbf{r}_2)\ldots\psi_X(\mathbf{r}_{N_e}) \tag{7.14}$$

where the coefficients are defined as

$$c_{A,B,\ldots,X} = \langle \psi_A(\mathbf{r}_1)\psi_B(\mathbf{r}_2)\ldots\psi_X(\mathbf{r}_{N_e})|\Psi(\mathbf{r}_1, \ldots \mathbf{r}_{N_e})\rangle. \tag{7.15}$$

Applying the permutation operator, it appears that we can write the wavefunction as a linear combination of anti-symmetrised spin-orbital products (or 'Slater determinants'), where κ is an abbreviation for the so-called 'dictionary order' of the $A, B, \ldots, X$:

$$\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_{N_e}) = \sum_{\kappa} c_\kappa \Phi_\kappa(\mathbf{r}_1, \ldots, \mathbf{r}_{N_e}) \tag{7.16}$$

where (we now write $\psi(1)$ for $\psi(\mathbf{r}_1)$ and so on)

$$\Phi_\kappa(\mathbf{r}_1, \ldots, \mathbf{r}_{N_e}) = \begin{vmatrix} \psi_A(1) & \psi_B(1) & \ldots & \psi_X(1) \\ \psi_A(2) & \psi_B(2) & \ldots & \psi_X(2) \\ \ldots & \ldots & \ldots & \ldots \\ \psi_A(N) & \psi_B(N) & \ldots & \psi_X(N) \end{vmatrix}. \tag{7.17}$$

The overall electronic (or N_e-electron) wavefunction satisfies (usually, although there are exceptions) the symmetry restrictions. This means that the overall wavefunction is an eigenfunction of the total spin operator S^2, and it transforms according to the irreducible representations of the molecular point group.

In non-relativistic quantum chemistry, the addition of the spin functions is somewhat ad hoc. The spin symmetry is imposed on the total wavefunction rather than a consequence of the formalism.

In terms of the electronic wavefunction, the magnitude set M is defined as an expectation value associated with some operator $\hat{A}$:

$$\mathsf{M}(\hat{\mathsf{A}}, \Psi) = \left\{ M(\hat{A}) | M(\hat{A}) \right\} = \frac{\langle \Psi | \hat{A} | \Psi \rangle}{\langle \Psi | \Psi \rangle}. \tag{7.18}$$

The quantities that we measure in general depend on the spatial distribution of the electrons as well as the overall spin. In the expression above, the dependency on r and σ is through Ψ, which is a function of both r and σ.

7.3.1.4 Basis Sets

The last topic to consider is that of basis sets. Generally, the N_e-electron functions are expanded in so-called 'basis sets' of either Slater Type Orbitals (STOs) or Gaussian Type Orbitals (GTOs). A basis set is characterised by a set of functions χ which are usually (though not necessarily) centered on the nuclear coordinates.

There are many choices of basis sets available, and both the initial choice and parametrisation is usually debated extensively in quantum chemistry literature. For our purposes, there is no need to consider the choice of basis set in detail, apart from the fact that its choice generally determines the outcome.

For the purposes of the structuralist formulation of quantum chemistry all that is required is that we define a set $\{\chi\}$ as the chosen basis set for the molecular frame. We choose a composite index running from 1 to some value α to indicate the parametrisation and degree. Even though in practice the number of basis functions is not hard to determine, it is hard to give precise formulae that cover all cases.

Again we collect the all position vectors $\mathsf{R}_1, \ldots, \mathsf{R}_M$ into an 'overall' or 'composite' position vector R_B and the entire basis set into a vector $\boldsymbol{\chi}$.

Hence we define a basis set for ab initio quantum chemistry as a set $\{\chi\}$ in the following way:

Definition 9 $x \in \mathscr{B}$ is a molecular basis set iff $\exists \mathsf{R}_B, \boldsymbol{\chi}, \alpha$ so that

(1) $x = \langle \mathsf{R}_B, \boldsymbol{\chi}, \alpha \rangle$;
(2) R_B is a composite of (potentially nuclear) position vectors;
(3) $\chi : \mathbb{R}^3 \to \mathbb{R}$ is a real valued function;
(4) $\alpha \in \mathbb{N}^+$ is a (complicated) index determined by the type of molecule and type of basis set.

The position vectors that form the origins for the basis sets may coincide with the molecular frame (as is mostly the case), but there is no strict requirement that they do. Basis functions can be placed anywhere in the molecule, and there are occasions where it is useful to have a basis set without an atom. Basis sets without a corresponding atom are usually called 'ghost orbitals'.[13]

In most practical cases, however, the 'frame' of the basis set will coincide with that of the molecular frame, and moreover, all atoms of a certain type will have identical basis sets (again, this is not a strict requirement, but is done in most cases).

Another point worth noting is that basis sets are not strictly required: for a small subset of systems of chemical interest (atoms and diatomic molecules) numerical solutions that do not require a basis set are possible. We will encounter such a situation in our discussion of the chemical bond, where we deal with orbitals directly and are not concerned with their expansion in basis sets.

7.3.2 Potential Models for Quantum Chemistry

We can now proceed with the definition of the potential models of quantum chemistry in terms of these prerequisites.

We are in general looking for the following. A potential model for a theory of ab initio quantum chemistry is constructed of (a set of) nuclei, conceived as charged points fixed in space and a basis set, which is used to expand the wavefunction. The total constellation satisfies a number of laws of quantum mechanics, and the wavefunction satisfies the symmetry requirements of both the molecular point group symmetry and the spin symmetry.

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[13] A case where the use of 'ghost orbitals' is common is the calculation of intermolecular interaction energies with the 'super-molecule' method. In this case, the ghost orbitals are required to deal with the basis set superposition effect.

With this, we can define a potential model for *an initio* quantum mechanics in the following:

Definition 10 x is a potential model for ab initio quantum chemistry ($x \in \mathscr{M}_p$(QCAI)) iff there are (sub)structures $\mathscr{F}$, $\mathscr{E}$ and $\mathscr{B}$, such that

(1) $x = \langle \mathscr{F}, \mathscr{E}, \mathscr{B}, \rangle$;
(2) $\mathscr{F}$ represents the molecular frame of the form $\langle \mathsf{R}, \mathbf{Z} \rangle$;
(3) $\mathscr{E}$ represents the electronic structure of the form $\langle \mathscr{P}_e, \mathbf{r}, \boldsymbol{\sigma}, \Psi, \hat{A}, \mathsf{M} \rangle$;
(4) $\mathscr{B}$ represents an atomic basis set of the form $\langle \mathsf{R}_B, \boldsymbol{\chi}, \alpha \rangle$;

It is worthwhile expanding this definition in its full complexity for future reference:

Definition 11 x is a potential model for ab initio quantum chemistry ($x \in \mathscr{M}_p$(QCAI)) iff $x = \langle \mathsf{R}, \mathbf{Z}, \mathscr{P}_e, \mathbf{r}, \boldsymbol{\sigma}, \Psi, \hat{A}, \mathsf{M}, \mathsf{R}_B, \boldsymbol{\chi}, \alpha \rangle$; with all the definitions as above.

For reasons that will become apparent, this definition is loose in the sense that it allows for considerable freedom in the choice of N_e-electron wavefunctions. This is deliberate, since many of the 'methods' that we discussed in Hettema (2009) make a particular choice for this wavefunction and hence in this particular characterisation count as 'theories' for which we can construct specific models. We now turn to a more precise specification of the models of quantum chemistry, focusing particular attention on a distinction between *theories* of quantum chemistry and quantum chemical *methods*. As theories we take the structures that satisfy the requirements for an 'exact' wavefunction (as specified in Hettema 2009) and as *methods* we take the special theories which, in the language of Chap. 5, make up the 'hard core' of quantum chemistry.

Then, in the next section, we consider the question whether quantum chemistry is a quantum mechanics.

7.3.3 Theories and Methods of ab initio Quantum Chemistry

We now need to further specify the theories of quantum chemistry. In the structuralist approach, the specification of the theory places additional restrictions on the potential models and define a particular subset of the potential models which is then said to be a model of the theory in question.

There are no 'general' theories of quantum chemistry, apart from a restriction to wavefunctions that satisfy the Schrödinger equation. As outlined in Hettema (2009), the 'exact' wavefunction of quantum chemistry plays a key role as a theoretical ideal. In Hettema (2009) we discussed a number of 'enabling theorems' that are valid for such exact wavefunctions, and which play a key role in the evaluation of the approximate wavefunctions of quantum chemistry. Among such 'enabling theorems' were the variational theorem, the Hylleraas-Undheim theorem, the virial theorem, the Hellman-Feynman theorem and the Ehrenfest theorem. As further outlined in Hettema (2009) and Chap. 5, these theorems provide the further framework to evaluate the quality of approximate wavefunction *vis a vis* the chemical problem in question. As examples of such problems we discussed energetic bounds, dissociation energies, atomic and molecular force frameworks and time evolution of properties.

We will generally admit as *models* of quantum chemistry those structures in $\mathscr{M}_p$(QCAI) which satisfy the enabling theorems.

As also discussed in Chap. 5, there are a number of quantum chemical 'methods' which amount to approximations to the 'exact' wavefunction. If we were to treat these as models of quantum chemistry, the plethora of methods in quantum chemistry would then lead to a similar plethora of models to consider in our formalisation. Discussing each model in detail would become quite cumbersome, and my focus here will be on a limited subset of methods such as the Hartree-Fock method, the CI method, and many body methods such as the Coupled Cluster method. All of these methods can be characterised as *specialisations* of the general theory of quantum chemistry.

7.3.3.1 Methods of Quantum Chemistry

Quantum chemistry uses much of the normal machinery of quantum mechanics, as outlined in Chap. 5 of this thesis. The main aspects are the time-*in*dependent Schrödinger equation

$$H\Psi = E\Psi \tag{7.19}$$

which holds for an isolated system if H contains no time-dependent potential. It is obtained from the time-*de*pendent Schrödinger equation by writing the total time-dependent wavefunction as a product of a spatial and time dependent function $T(t)$

$$\psi(\mathbf{R}, t) = \Psi(\mathbf{R})T(t) \tag{7.20}$$

and using the time-dependent Schrödinger equation. In what follows, we will consider the time-independent Schrödinger equation.

The time-independent Schrödinger equation is commonly solved either variationally or via perturbation theory to form an 'approximate' wavefunction. A model of quantum chemistry is simply a potential model in which the wavefunction satisfies the Schrödinger equation. For an 'exact' wavefunction (see Chap. 5 and Hettema 2009) this means that the wavefunction also satisfies the 'enabling' theorems.

Hence a *model* for quantum chemistry is simply a potential model with a wavefunction that fulfils these additional criteria. Specifically:

Definition 12 (Models of quantum chemistry) x is a model for ab initio quantum chemistry ($x \in \mathscr{M}$(QCAI)) iff ($x \in \mathscr{M}$(QCAI)) iff $x = \langle \mathsf{R}, \mathbf{Z}, \mathscr{P}_e, \mathbf{r}, \boldsymbol{\sigma}, \Psi, \hat{A}, \mathsf{M}, \mathsf{R}_B, \boldsymbol{\chi}, \alpha \rangle$; with all the definitions as specified for the potential models and where x fulfils the Schrödinger equation and the 'enabling' theorems of Hettema (2009).

What we have specified as a theory in the sense of quantum chemistry is thus an ‘ideal’ quantum chemistry, based on an elusive ‘exact’ wavefunction. ‘Exact’ wavefunctions only exist for highly idealised systems and cannot generally be computed for systems of chemical interest. Hence at the business end of quantum chemistry, there has been a lively interest in the development of approximations to these exact wavefunctions that have a number of the desired features such as size extensivity, variational properties (which guarantee a ‘smooth’ approach to the calculated quantity) and so on.

These approximations will be discussed in the next section. To distinguish the ‘exact’ wavefunction from the approximations, we will introduce the convention that Φ represents the approximations to the exact wavefunction, or $\Psi \rightsquigarrow \Phi$.

7.3.4 Quantum Mechanical Methods

The aim of this section will be to present some further details on the quantum mechanical *methods*. We will classify the methods based on these approximate wavefunctions in terms of a specialisation theory net in the last section of this chapter. This section contains a brief sketch of the form of the wavefunction, and some of the relevant details on the characteristics of a specific approximate wavefunction. For detailed technical discussions of the approaches discussed in this section, the reader may consult the works by McWeeny (1989) or Helgaker et al. (2000), and, to a much lesser extent, the section on wavefunction construction in the technical appendix of Hettema (2012b).

As an interesting aside, the developmental history of many of these approaches is now beginning to be collected as well. For further details on the historical development of these approaches I refer the reader to the work by Dykstra et al. (2005), which contains a collection of first-person accounts of the creation of these methods.

The approaches are most easily classified if we consider the general many electron wavefunction as an expansion of Slater determinants (see also Chap. 5):

$$\Phi(x_1, x_2, \ldots, x_N) = \sum_{\kappa} c_\kappa \phi_\kappa(x_1, x_2, \ldots, x_N) \tag{7.21}$$

where the κ enumerates some standard order of labeling the Slater determinants. Successive approximations in the models of quantum chemistry now differ in how they construct this wavefunction.

A second classification is in whether the methods are based on variational or perturbation theory. Variational methods employ the variational principle whereas perturbational methods are based on perturbation theory. We focus on the methods first and give a recapitulation and comparison at the end of this section.

In what follows, I will first discuss a general framework to discuss these various theories of the molecular wavefunction, and then proceed to a discussion of the specific wavefunctions.

The general principle is that the canonical order of the wavefunction is a ‘leading’ Slater determinant with successive ‘excitations’ that take electrons out of ‘occupied’ orbitals into ‘excited’ orbitals. This canonical scheme, *inter alia*, does not commit us to a specific version of chemistry: all that is specified is the symmetry of the state under investigation.

Several methods are possible to construct wavefunctions and calculate energy expressions from them. This section will take up the criteria developed in Hettema (2009) to evaluate the various methods. Later on in this chapter we will argue that these methods give rise to *specialisations* of the core theory of quantum chemistry in their own right.

7.3.4.1 The Hartree-Fock Method

The Hartree-Fock method for closed shell systems limits the general form of the ground state wavefunction Φ to a single Slater determinant:

$$\Phi \leadsto \Psi_{\mathrm{HF}} = \Phi_0 \tag{7.22}$$

and then optimises the parameters that define the molecular orbitals ϕ in terms of a basis set. Most commonly, the molecular orbitals are written as a linear combination of atomic orbitals (LCAO). The latter in turn are written in terms of the basis functions χ. Hence this HF method amounts to the choice, in Eq. (7.21), of $c_0 = 1$, $c_\kappa = 0$ for $\kappa > 0$.

This leads to the well known Hartree-Fock equations or self-consistent field (SCF) wavefunctions. The key Hartree-Fock criterion is that the matrix elements of the Hamiltonian between the ‘occupied’ and ‘virtual’ orbitals vanish (Brillouin’s theorem):

$$\langle \Phi_0 | H | \Phi_i^a \rangle = 0. \tag{7.23}$$

Often the calculations produce *canonical* HF orbitals. The canonical HF orbitals are the orbitals that diagonalise the Fock matrix:

$$\mathbf{F}\boldsymbol{\phi} = \boldsymbol{\epsilon}\boldsymbol{\phi}. \tag{7.24}$$

The Hartree-Fock model is an effective one-particle model, in which each electron ‘moves’ in the field of the nuclei and the ‘average’ field of the other electrons. The Hartree-Fock equations are solved by iteration, and are often referred to as Self-Consistent Field (SCF) equations.

The Hartree-Fock model is the starting point for most more advanced methods in quantum chemistry and the canonical HF orbitals are the most commonly used orbitals for methods that study electron correlation.

7.3.4.2 Configuration Interaction

In the configuration interaction method we restrict the wavefunction Ψ but to a 'reference' configuration and a number of 'excited' configurations, which are obtained from 'moving' a number of electrons from the 'reference' configuration to unoccupied orbitals. The general index κ is thus more conveniently written in terms of 'excitations', and the general expansion of the wavefunction is

$$\Phi \rightsquigarrow \Psi_{\mathrm{CI}} = \Phi_0 + \sum_{i,a} c_i^a \Phi_i^a + \sum_{ij,ab} c_{ij}^{ab} \Phi_{ij}^{ab} + \ldots + \sum_{ij\ldots,ab\ldots} c_{ij\ldots}^{ab\ldots} \Phi_{ij\ldots}^{ab\ldots} + \ldots \tag{7.25}$$

The coefficients are determined with the variational principle. The *orbitals* that make up the $\Phi_{ij\ldots}^{ab\ldots}$ are not varied, but are kept at some set of orbitals (usually the canonical HF orbitals).

The expansion coefficients of the Slater determinants are optimised by variational theory. Most commonly, the orbitals are fixed at the HF level, since in that case the single excitations vanish (due to the Brillouin theorem).

Nonetheless, the CI expansion may be very large, and hence the computational effort involved in a CI calculation is usually considerable.[14]

The CI optimisation problem consists of finding the lowest eigenvalue of the very large matrix equation

$$\mathbf{Hc} = \mathbf{EMc} \tag{7.26}$$

where (McWeeny 1989, p. 347) **M** is usually the unit matrix. A variety of techniques have been designed to find restrictions of this problem that focus on the lowest eigenvalue only. The best known of these is the Davidson technique (see Langhoff and Davidson 1974).

7.3.4.3 Multi-configurational Hartree-Fock Methods

In the multi-configurational methods both the expansion coefficients of the Slater determinants as well as the orbitals that make up the Slater determinants are optimised variationally. Due to its computational complexity, the multi-configurational Self Consistent Field (MCSCF) method is usually limited to smaller wavefunction expansions than the CI method. MCSCF methods became more prominent only after quadratically convergent techniques were developed and successfully implemented.

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[14] The milestone of a billion Slater determinants was reached around 1992.

The general form of the MCSCF wavefunction is similar to the CI equation:

$$\varPhi \rightsquigarrow \varPsi_{\mathrm{MCSCF}} = \varPhi_0 + \sum_{i,a} c_i^a \varPhi_i^a + \sum_{ij,ab} c_{ij}^{ab} \varPhi_{ij}^{ab} + \ldots + \sum_{ij\ldots,ab\ldots} c_{ij\ldots}^{ab\ldots} \varPhi_{ij\ldots}^{ab\ldots} + \ldots \qquad (7.27)$$

but the variational principle for the energy also includes orbital variations in addition to the variations of the CI coefficients. The details of the derivation of the MCSCF equation are given in McWeeny (1989) and Helgaker et al. (2000), for instance.

7.3.4.4 Many Body Methods: Many Body Perturbation Theory

In many-body perturbation theory the expansion of the wavefunction is the same as in the CI method, but the coefficients are determined through perturbation theory rather than variational theory.

The original form of the perturbation theory was developed by Møller and Plesset (1934), and the partitioning of the Hamiltonian into a Hartree-Fock potential and 'fluctuation' potential is commonly referred to as the Møller-Plesset partitioning. A detailed discussion of these methods is found for instance in the (unpublished) Paldus (1981) or Paldus (1992). While the MP2 energy expression is easily evaluated, the complexity of the Møller-Plesset expansion grows rapidly with higher orders.

7.3.4.5 Many Body Methods: Coupled Cluster Methods

The coupled cluster method starts with an exponential *Ansatz* for the wavefunction and solves the coupled cluster equations. The cluster *Ansatz* is usually written in the form

$$\varPhi \rightsquigarrow |\varPsi\rangle = \exp(T)|\varPhi_0\rangle \qquad (7.28)$$

where $|\varPhi_0\rangle$ is the reference state. The cluster operator is then decomposed in terms of single, double etc operators where

$$T = T_1 + T_2 + T_3 + \ldots \qquad (7.29)$$

The energy is determined by projecting the energy equation:

$$(H - E)\exp(T)|\varPhi_0\rangle = 0 \qquad (7.30)$$

against the 'excited' cluster configurations. In this way one can develop an algorithm for the solution of the CC equations and the determination of the coefficients of the cluster expansion. The coupled cluster method gives rise to very complex non-linear equations that determine the expansion coefficients.

Table 7.2 Overview of the quantum chemical methods discussed in this chapter

Method	Determination of expansion coefficients	Determination of orbitals
HF	$c_0 = 1, c_\kappa = 0 (\kappa > 0)$	Variational
MCSCF	Variational	Variational
CI	Variational	Fixed orbitals
MBPT	Perturbation equations	Fixed orbitals
CC	CC equations	Fixed orbitals

CC theory usually gives excellent results in cases where the HF approximation forms a good starting point, even for (relatively) simple expansions that are restricted to T_2 with an estimation for T_3, leading to the well-known CCSD(T) method.

7.3.4.6 Summary: Methods for Quantum Chemistry

We can now summarise the models discussed for quantum chemistry so far. Table 7.2 presents an overview of some of the most common methods in the calculation of the wavefunction.

There is a common trade-off in the methods of quantum chemistry, as outlined in Hettema (2009), that variational methods in general are not size-consistent, and size consistent methods have the drawback that they do not provide bounds on the energetic values calculated by them. Hence there is an optimal method dependent on the application: for instance if we want to calculate in detail the separation energy of a molecule it is usually best to use a size consistent method.

Usually, in the structuralist approach to scientific theories, what method to apply in a given situation will depend to some degree on the 'intended application'. We will return to this idea more fully once we have discussed the specialisation relations of quantum chemistry. In the meantime, we turn to the question of how the proposed potential models of quantum chemistry relate to both chemistry and physics.

7.3.5 Semi-empirical Methods

The set of models for quantum chemistry we have discussed so far is not capable of capturing all cases of chemical interest completely. Specifically, it leaves out the large class of 'semi-empirical' models such as the Hückel model.

Formally, one might thing that this class of models can be constructed as a specialisation, in the sense of Chap. 6, of the models of quantum chemistry, but this is not the case. These models are classified more appropriately as idealisations of the models of quantum chemistry. Hence, formally, the transitions between the models of quantum chemistry and the semi-empirical model is not smooth.

In the practice of chemistry, these models are of interest because they capture a sense in which 'electronic structure' is *transferable* between molecules and atoms. For instance, popular explanations of the periodicity of the Periodic Table draw on semi-empirical methods when they discuss 'outer electron configuration'. In Hettema (2016) I have discussed another example: the case of 'frontier orbital' theory in which the electronic structure and a subset of the electronic orbitals feature prominently in the construction of a chemical theory. Hence it is also useful to consider a 'richer' set of models in which 'orbitals' and aspects of electronic structure can be considered.

The specific steps to obtain models for semi-empirical quantum chemistry from quantum chemistry consist in specifying 'semi-empirical' varieties of the frame, the electronic structure and the basis set. Usually no change are made in the frame.

The restricted class for the 'electronic structure' can be created as follows. First consider the sets of 'core' and 'valence' electrons, where $\mathscr{P}_c \cup \mathscr{P}_v = \mathscr{P}_e$. The set of valence electrons is thus a subset of $\mathscr{P}_e$, $\mathscr{P}_v \subseteq \mathscr{P}_e$ (equivalence usually obtains for instance for first row atoms). There is no principled way in which the set of electrons can be split in a set of 'core' and 'valence' electrons, this is often a matter of deciding the relevant 'chemistry'.

Furthermore, in the semi-empirical method, we usually approximate the total wavefunction Ψ by a single Slater determinant of the valence electrons only, neglecting the 'core' electrons explicitly. Mathematically, this step changes the Hamiltonian to one that is properly parametrised to take the neglect of the core electrons into account. These approximations are usually made in either a set of parameters introduced in the operators, or specific approximations that are made in the integrals. In both cases therefore, the measure set M of the 'full' problem is restricted to a 'restricted' measure set M_r, which may also contain values obtained from experiment.

We therefore define a restricted electronic valence structure in this sense:

Definition 13 (Valence Structures for $\mathscr{E}$) x_v is a restricted (valence) electronic structure iff there are $x \in \mathscr{E}$ such that

1. $x_v = \langle \mathscr{P}_v, \boldsymbol{\sigma}, \Psi, \hat{A}, \mathsf{M} \rangle$;
2. $\mathscr{P}_v$ is the set of valence electrons;
3. $\mathbf{r}_v : \mathscr{P}_v \to \mathbb{R}^3$ assigns a position to each valence electron;
4. N_v (the cardinality of $\mathscr{P}_v$) is the number of valence electrons;
5. $\boldsymbol{\sigma} : \mathscr{P}_v \to \boldsymbol{\Theta}$ assigns the spin function to each valence electron;
6. $\Psi : \mathbb{R}^{3N_e} \times \mathbb{R} \to \mathbb{C}$ is the electronic wavefunction;
7. $\mathsf{M}_r : \mathbf{r} \times \boldsymbol{\sigma} \to \mathbb{R} \times \mathsf{U}$ is the semi-empirical 'measure' set.

Finally, the basis sets are similarly restricted to the valence electrons only, which we formally indicate by the symbols $\boldsymbol{\chi}_v, \alpha_v$.

The potential models of the semi-empirical method in this case may be defined as:

Definition 14 x is a potential model for ab initio quantum chemistry ($x \in \mathscr{M}_p$(QCAI)) iff there are (sub)structures $\mathscr{F}$, $\mathscr{E}$ and $\mathscr{B}$, such that

(1) $x = \langle \mathscr{F}, \mathscr{E}, \mathscr{B}, \rangle$;
(2) $\mathscr{F}$ represents the molecular frame of the form $\langle \mathsf{R}, \mathbf{Z} \rangle$;
(3) $\mathscr{E}$ represents the electronic structure of the form $\langle \mathscr{P}_e, \mathbf{r}, \boldsymbol{\sigma}, \Psi, \hat{A}, \mathsf{M} \rangle$;
(4) $\mathscr{B}_v$ represents an atomic 'valence' basis set of the form $\langle \mathsf{R}_B, \boldsymbol{\chi}_v, \alpha \rangle_v$.

On the basis of these potential models, similarly a set of 'methods' might be defined that represent the specific theoretical commitments of the semi-empirical methods.

7.3.6 Partial Potential Models

We now complete our formalisation of quantum chemistry by defining the partial potential models.

In this section my approach to the issue will be that at the level of partial potential models, quantum chemistry has to be a 'chemical' theory[15] of matter. The partial potential models formally 'strip' the theoretical terms from the potential models through the 'restriction relation' (see Chap. 6) in order to specify this chemical theory.

Formally, in the structuralist approach, a 'theoretical term' is any term in the structure that presupposes the (truth of) the full theory for its measurement. This approach to theoreticity in the structuralist method, which largely stems from Sneed (1971), is open to discussion. Specific different approaches have been suggested by Balzer (1985) and Gähde (1990). My proposal for the determination of the theoretical terms is informal: start by specifying a partial potential model as a theory of chemistry, and in a second step enumerate the theoretical terms to determine if their measurement will involve the theory of quantum mechanics.

To follow this approach, it is necessary to re-use some elements from the model – the restriction relation between $\mathscr{M}_p$ and $\mathscr{M}_{pp}$ is to all intents and purposes a relation which 'strips' the theoretical terms off the model and thereby restricts the full potential models of the theory to its partial potential models. Hence, the specification of chemistry as a partial potential model of quantum chemistry in this way involves a restriction of the science of chemistry to those aspects that can be considered, either formally or intuitively (of course, preferably both) as 'observational' for quantum chemistry. The point is that in this sense the application of quantum chemistry to chemical problems involves a limitation on the chemical problem.

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[15] This is similar to the formalisation of for instance mechanical theories, which are a kinetic theory at the level of the partial potential models. It is also a pragmatic choice which allows us to overcome (or at least temporarily bracket until Part III) the issues related to the *applicability* of quantum mechanical theories to the theories of chemistry: we surmise that these issues hide somewhere in the Ramsey sentence.

Specifically, in order to specify a ‘chemical theory’ in this sense I propose that in the first instance we specify a ‘chemical’ theory of matter as a model[16] of a molecule which consists of ‘balls’ representing the atoms and ‘sticks’ representing the supposed connections between them. This therefore represents a *mechanical* model of a molecule. This may not be as much of a restriction as it would appear at first sight. For example, this sense of a chemical theory is well-aligned with the diagrams that Hoffmann (2007) characterises as typical for a chemists’ way of looking at the world. The representation of this ball and stick model is captured in the representation of the molecular frame. In addition to this, we need to define a ‘magnitude set’ of chemical properties in order to be able to speak of the properties of molecules.

This leaves almost the entire apparatus of quantum theory as ‘theoretical’, and it primarily connects quantum theory to the ‘real’ world through expectation values. The expectation values behave as their classical counterparts (through Ehrenfest’s theorem) on the potential energy surface calculated through the electronic structure calculation. We will refer to this class of partial potential models as ‘mechanical’ partial potential models.

Formally, a mechanical partial potential model for quantum chemistry is thus the following structure:

Definition 15 x is a mechanical partial potential model for ab initio quantum chemistry ($x \in \mathscr{M}_{pp}$(QCAI)) iff there are (sub)structures $\mathscr{F}$, and M such that

(1) $x = \langle \mathscr{F}, \mathsf{M} \rangle$;
(2) $\mathscr{F}$ represents the molecular frame;
(3) M is a magnitude set.

Let us now consider what partial potential models in this sense count as ‘observational’. The short answer is molecular structure and molecular properties. Hence everything ‘quantum mechanical’ in this approach counts as ‘theoretical’, which aligns with our intuitions. The measure set M contains the measurable quantities of the chemical system that are associated with operators by calculation of their expectation value as in Eq. (7.18).

In the next chapter we will investigate how we can classify some typical ‘chemical’ theories in structuralist terms and then connect them to the models and partial potential models of quantum chemistry. In the remainder of this chapter we discuss the extent to which quantum chemistry can be seen as a quantum theory.

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[16] In the sense of a real ‘physical’ model and not the set theoretic variety.

7.4 Is Quantum Chemistry a Quantum Physics as well as a Chemistry?

At a surface level, quantum chemistry is a version of 'applied' quantum physics. In this section we will investigate this claim in further detail, and argue specifically that quantum chemistry can be classified as a 'modified' reducing theory in the sense of Mormann (1988) or in the sense of the *application* step from Kuipers (1990, 2001). We first discuss the prospects of the 'pure' subset relation, which corresponds to a 'direct' form of derivation of quantum chemistry from the general formalism of quantum theory. Not surprisingly, we will conclude that the prospects of the pure subset relation are not impressive. We then continue to discuss some proposed modifications to the interpretation of quantum theory, especially modifications that have the prospect of being compatible with the emergence of a 'classical' structure from the Coulomb Hamiltonian. Finally, we consider a 'context free' proposal based on the specification of inter-theoretic links between quantum chemistry and quantum theory.

7.4.1 The Subset Relation

A straightforward deductive relation in structuralist terms would require that the models of quantum chemistry can be classified as a *subset* of a set of structures that classify quantum mechanics. The (im)possibility of this is the main topic of Primas (1981).

In order to argue that ab initio quantum chemistry classifies as a quantum physics it needs to be shown that the potential models of quantum chemistry classify as a subset of a more general theory of quantum mechanics. As discussed in Sect. 7.2 the general theory of quantum mechanics was based on a Hilbert space $\mathscr{H}$, a set of operators $\hat{A}$ with a spectrum $\sigma(\hat{A})$, a state operator set W and a probability P.

Following the theme from the last section, for quantum chemistry to be a quantum mechanics, it has to have the broad structure:

$$\mathscr{M}(QM) = \langle \mathscr{H}, W, \hat{A}, \sigma(\hat{A}), P \rangle \tag{7.31}$$

or, more precisely, that $\mathscr{M}(\text{QCAI}) \subset \mathscr{M}(QM)$. The subset relation cannot be easily proved. Specifically, the construction of a number of items in the models of quantum chemistry relied on transitions from the structures of quantum mechanics that are not structurally 'smooth', but instead rely on somewhat arbitrary 'cuts' of the system into portions that are then subsequently treated entirely differently. As an example, the transition from the 'system' to the 'frame' and 'electronic structure' provided a such a non-smooth transition, which specifically treated the nuclei as classical particles and the electrons as quantum particles. The various approaches discussed in the semi-empirical model introduce further varieties of these cuts, for instance in the distinction between ‘core’ and ‘valence’ electrons.

Moreover, it is not clear what family member of QM should be the ‘enveloping’ theory: as was discussed in Sect. 7.2, there are a number of possible formalisations of quantum mechanics, each of which is better suited to a particular (set of) possible applications, and hence, in the words of Muller (2003), quantum mechanical structures can be said to ‘float in a sea of stories’ (p. 198).

That still leaves aside the fact that quantum chemistry is itself not much of a single theory; as we will see later in this chapter, quantum chemistry is best characterised as a theory *net* with the various ‘methods’ taking over the role of specialised theories that are members of the net.

7.4.2 Altered Interpretations

These problems have given rise to a strand in the philosophy of chemistry which argues for a new interpretation of quantum mechanics that would make it more amenable to the approximations commonly used in quantum chemistry.

The problems posed by the interpretation of quantum mechanics in the context of the reduction of chemistry formed the basis of a book-length argument by Primas (1981). Primas’ argument, in a nutshell, is that quantum mechanics is not a sound theory to reduce to, since it involves a basic structure in its robust interpretation which is not mirrored in the more classical science of chemistry. Hence the structures of chemistry are not ‘embeddable’ without further ado in the structure of quantum mechanics. Note that Primas also argues that this should in all probability lead to modifications in the interpretation of quantum mechanics, as is for instance exemplified in Primas (1975) and Primas and Müller-Herold (1978). Primas (1998) instead argues for a relationship along the lines of an asymptotic relationship, which is also argued for in Batterman (2002).

Primas’ argument deserves more unpacking than it has up to now received in the literature on the philosophy of chemistry, where so far the common attitude has been to accept this work rather uncritically. This is unfortunate, because Primas is an author who has both much to say and an author who says many controversial things.

Primas’ argument hinges on the notion of a ‘cut’ between the classical and quantum worlds. The phenomena studied by quantum chemistry, argues Primas (primarily in his Primas 1975), depend crucially on that cut in the sense that a particular choice of cut creates a *model* of the system under study. However, there are no unique cuts, so that the model is usually chosen to focus on the phenomena we want to study, or ‘One man’s reality is another man’s “stuff as dreams are made of”’ (Primas 1975, p. 146).

The upshot is that for reduction to hold,

> [...] we have to require that the phenomenological theories of biology and chemistry are *interpretatively connected* with molecular quantum mechanics. That is, the regulative principles used in the phenomenological theories have to follow from the regulative principles adopted in molecular quantum mechanics. Regulative principles are of normative nature, they must be compatible with but are not implied by empirical facts and the mathematical formalism of the theory. (Primas 1975, p. 127–128)

Hence it would seem that Primas' view is that an interpretive connection also involves some form of derivation.

Primas (1975) proposes that the 'cut' between the quantum chemical description and the rest of the world can be described in terms of a Schmidt decomposition of a total 'world' state Φ (effectively an idealisation), so that the quantum chemical system becomes a 'reduced state' in comparison to the world. Specifically, for instance, in the case of the H_2 molecule described by a wavefunction $\Psi(R_e)$, Primas notes that $\Psi(R_e) \otimes \Xi$ is a reasonable approximation of the world state Φ for the H_2 molecule at or close to the equilibrium internuclear distance. However, at infinite distance, assuming that $\Psi(R_e)$ is written in the VB approximation, the superposition

$$\Phi \approx \frac{1}{\sqrt{2}}[\varphi_A(1)\varphi_B(2) + \varphi_A(2)\varphi_B(1)] \otimes \Xi$$

is *not* a reasonable approximation to Φ; instead, a 'reasonable' approximation becomes then either

$$\Phi \approx \varphi_A(1)\varphi_B(2) \otimes \Xi$$

or

$$\Phi \approx \varphi_A(2)\varphi_B(1) \otimes \Xi.$$

Primas takes these arguments to indicate that the core theory in the reduction, quantum mechanics, is in need of modification and re-interpretation so as to be able to *derive* the classical patterns in the world.

It is not the purpose of the present work to discuss Primas' construction of 'ontic' quantum theory in detail, though the effort would certainly be worthwhile and should be undertaken as part of the programme of work in the philosophy of chemistry. A recent evaluation of Primas' theories may be found in the recent volume edited by Primas et al. (1999).

Another approach that has so far not been used in this programme is the currently fashionable 'decoherence' approach to the interpretation of quantum mechanics (see e.g. Zurek 2003; Schlosshauer 2005, 2007).[17] The application of a decoherence

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[17] There are to my knowledge no discussions of the possible applications of the decoherence approach to the problem of 'teasing out' a molecular structure from the Coulomb Hamiltonian. Given the nature of decoherence, this might also be a difficult project to undertake.

approach to the problems posed by molecular structure holds out a hope that the 'classical' molecular structure may be recovered as a 'pilot state' in the sense of the decoherence interpretation of quantum mechanics.

7.4.3 A Reconnection to Reduction

For the present purposes, showing that chemical theories do indeed reduce to a suitable set of quantum mechanical theories adapted to the task at hand, will suffice. Hence, the view we will develop in the remainder of this chapter is that a structuralist view, or a Nagelian reduction, at least, does not require such a strict embedding relation. The saving grace is the *transformation* of the reducing theory in the light of the reduced theory. Hence, rather than a principled, *direct* derivation relation, what obtains instead is an *indirect* reduction relation, which involves an 'intermediate' theory.

That such a step might be necessary is also suggested in the approach to Nagelian reduction discussed in Dizadji-Bahmani et al. (2010), and to a lesser extent in Klein (2009) and van Riel (2011). As discussed in Chap. 1 (p. 16), Dizadji-Bahmani et al. (2010) discuss a 'generalised Nagel-Schaffner' model for reduction, in which the reductive steps involve a specification of a general theory T_F, which is, with the help of boundary conditions, restricted to a special theory T_F^*. This theory T_F^* is connected, via bridge laws, to a theory T_P^*, which stands in a 'strong analogy' to the reduction candidate T_P. The generalised Nagel-Schaffner model thus forms a formal characterisation of such an indirect reduction relationship, though it is not characterised in structural terms. In terms of the transformations required in the reducing theory, quantum chemistry does indeed contain the system specifications, idealisations, and reduction postulates qua factual claims that are required by the generalised Nagel-Schaffner model.

7.4.4 A Pragmatic Proposal

For the existence of a heterogeneous reduction relationship, the proof of a direct embedding relation is not strictly speaking required. The reason for this is that the reducing theory is *transformed* to partake in the reduction relationship. This transformation is well known, but not often explicitly stated, especially in the structuralist approach. As we saw in Chap. 6, the argument of Mormann (1988) is that the reduced theory undergoes a transformation into a 'specially restricted' theory to enable it to partake as a reducing agent in the reduction relationship. In Chap. 6 we also argued that these non-smooth transitions could be captured as instances of specific linking commitments.

Two specific non-smooth transformations are part of the informal construction of quantum chemistry as a special case of quantum theory in this chapter.

The first one is the creation of the molecular ‘frame’, which also introduces a form of the ‘cut’ between the classical and quantum worlds, and which forms, from the viewpoint of explanation, an example of *idealisation*. The key aspect of this ‘cut’ is that the atomic nuclei are treated as fixed in space. The philosophical aspects of this step were discussed in more detail in Chap. 3. It is important to note that the ‘transformation’ of the basic theory of quantum mechanics brackets this step in the sense that the use of the Born-Oppenheimer approximation is already presupposed in the reducing theory, rather than a consequence of the reduction itself. Hence this shape determining application step is far from trivial, though it is easy to overstate its importance for the potential of quantum chemistry to *explain* the behaviour of molecules. As we have argued in Chap. 3, molecular *shape* is much less a determining factor for chemistry than the bonding *structure*. The use of the Born-Oppenheimer approximation in no way presupposes the latter.

The second key transformation is the construction of a many-electron wavefunction for the electronic structure in terms of *orbitals* and the various simplifications of the wavefunction which limit it to, for instance, a single determinant, or even a product function. As discussed in the section on semi-empirical quantum chemistry, one specific issue that needs to be addressed in the context of this second specialisation is that there is a direct relationship between a wavefunctions’ capability to describe *classes* of molecules, which depend on the ‘transferability’ of the orbital structure between molecules (and hence is more capable of explaining chemical *laws* across multiple molecules) and the severity of the approximation implied in its construction. That is, *classes* of molecules are usually described in terms of the most ‘simple’ wavefunctions that neglect significant amount of numerical detail. Conversely, ‘better’ wavefunctions (i.e. ones that approach the ‘exact’ wavefunction more closely) have a much lessened capability to describe classes of molecules, because more complex, especially correlated, wavefunctions are not transferable in this way. This fact was also pointed out by Primas (1975) (who ascribes it to a 1964 paper by Harald), and is responsible for a significant amount of confusion in the literature in the philosophy of chemistry, as exemplified by the papers by Woody (2000) and Weisberg (2008). We will return to this issue in the next Chapter, especially in the sections on the reduction of chemical bonding and the periodic table.

The key aspect of the reduction is thus that quantum chemistry, as ‘applied quantum theory’ makes a number of presuppositions that are by no means trivial, and which transform the theory of quantum mechanics into a quantum theory of molecular systems. It is the latter idealised specific theory, not the former, which is the proper reducing theory in the reduction of chemistry to physics. In the next section we formalise this relationship in terms of a link.

7.4.5 Linking Molecular Quantum Mechanics to Quantum Mechanics

The molecular quantum mechanical system is a combination of an element of the set of models of the frame $\mathscr{F}$ and an element of the set of models of the electronic $\mathscr{E}$. The set of such combinations will be indicated by $\mathscr{F} \otimes \mathscr{E}$, and the 'application' of the simple quantum mechanics can hence be described as two links between the system and the 'frame' and 'electronic' structure components of this set of combinations, $L_{sf}(\mathscr{S}, \mathscr{F} \otimes \mathscr{E})$ and $L_{se}(\mathscr{S}, \mathscr{F} \otimes \mathscr{E})$.

The effect of the two links between the system and the frame and electronic structure is to 'reassemble' the system into a frame with a surrounding cloud of electrons. These links are not approximations in a traditional sense, they are more properly characterised as *idealisations*. The most important idealisation is that the definition of a 'frame' includes the stipulation that the nuclear coordinates are fixed in space (up to translations and rotations of the entire coordinate system).

The electronic wavefunction $\Psi(N_e)$ is a member of the group of square integrable functions L^2: $\Psi(N_e) \in L^2$ (cf. Eq. (7.9)). The Hamiltonian maps the coordinates of the electrons and the parameters of the nuclear frame onto an operator H, which has the molecular energy as an eigenvalue.

For completeness and in order to allow for the calculation of molecular properties such as energies, dipole and multipole moments, we also define a set of (quantum mechanical) operators $\hat{A}$ (with a spectrum $\sigma(\hat{A})$) operating on this wavefunction.

This establishes the important links between the 'electronic structure' and the characterisation of quantum mechanics:

Definition 16 $L_{qe}(\mathscr{Q}_s, \mathscr{F} \otimes \mathscr{E})$ is a link between a simple quantum mechanics and a molecular quantum mechanics iff $\forall xy : \langle x, y\rangle \in L_{qe}(\mathscr{Q}_s, \mathscr{F} \otimes \mathscr{E})$, then $\exists \mathscr{S}, \mathscr{H}, \hat{A}, \sigma(\hat{A})$ and $\exists\ \mathscr{P}, \mathbf{r}, \boldsymbol{\sigma}, \Psi, \hat{A}, \mathsf{M}$ such that

(1) $x = \langle \mathscr{S}, \mathscr{H}, \hat{A}, \sigma(\hat{A}\rangle$ is a simple quantum mechanics;
(2) $y = \langle \mathscr{P}, \mathbf{r}, \boldsymbol{\sigma}, \Psi, \hat{A}, \mathsf{M}\rangle$ is a molecular quantum mechanics;
(3) $\mathscr{S} = \mathscr{P}_e \otimes \mathscr{P}_\mathrm{N}$ (the system is the idealised frame and electronic structure);
(4) $\hat{H}$: $\mathbf{r} \otimes \mathsf{R} \to \{\hat{A}\}$ is the Hamiltonian operator $\hat{H} \in \{\hat{A}\}$;
(5) $\Psi, \boldsymbol{\sigma}$ are elements of the Hilbert space $\Psi, \boldsymbol{\sigma} \in \mathscr{H}$;
(6) The structure $\langle \hat{A}, \sigma(\hat{A})\rangle$ corresponds to M as defined in Eq. (7.18).

Figure 7.1 gives an overview of how the various components relate together. To sum up the various conclusions from this section, we have argued that quantum chemistry cannot be structurally identified with quantum theory, in the sense that quantum chemistry is a subset of a quantum mechanical structure. Broadly speaking, this was also the conclusion that Hans Primas (1981) reached in his book-length discussion of this issue, though based on a different set of considerations.

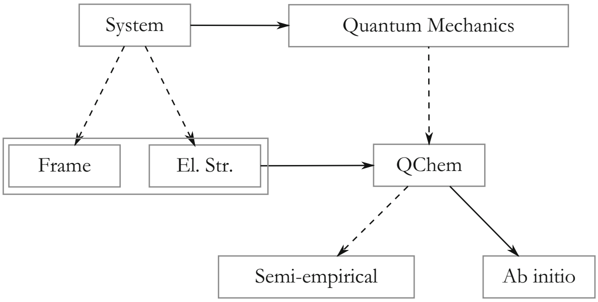

Fig. 7.1 Structuralist reconstruction of the reduction relationship between 'quantum mechanics', quantum chemistry and the theories of chemistry. 'Smooth' transitions are drawn in *solid lines*, and 'idealisations' are drawn as *dotted lines*

The strict 'embedding' relationship fails because the transformation steps that lead us from quantum mechanics to quantum chemistry, conceived as ab initio electronic structure theory, are not structurally 'smooth', but instead involve various 'cuts' that not only partition the chemical system but also impose a molecular *shape* onto the quantum system. From the viewpoint of the modern analyses of the Nagelian reduction theory, however, such steps are not only relatively unproblematic, but perhaps even expected.

7.5 Specialisation Theory Nets for Quantum Chemistry

So far, we have sketched quantum chemistry with a rather broad formal brush; the characterisation we have presented up to now will not suffice to discuss the reduction relation to chemistry in sufficient detail. The reduction relations, as we will see in Chap. 8, involve *specific* theories of chemistry which are commonly explained by *specific* quantum theories. Hence to be amenable to act as a reducing theory in the proposed reduction, we have to consider specific *specialisations* and *approximations* of the basic theory. This all builds on top of the specific *idealisations* which were discussed in Sect. 7.4.4.

Recall from Chap. 6 that the characterisation of a specialisation theory net is based on restricting to a subclass of *models* of the same type as the overall theory. In this sense, the various approximations to the ab initio wavefunction may be reconstructed in terms of a specialisation net. The various approximations reflected in the methods of ab initio quantum chemistry rely on specific restrictions in the form of the 'exact' expansion of the wavefunction. This reconstruction of the various methods as specialisations does account, to some degree, for the experience of quantum chemistry that some methods are not performing well in particular situations.

Furthermore, specialisations of the theory are possibly by restricting the ‘frame’ to specific classes of molecules, or the cardinality of the set of electrons to a certain number. Interestingly, considering these two ‘dimensions’ of the specialisation relation, we may obtain something like a ‘Two-Dimensional Chart of Quantum Chemistry’, as proposed by Pople (1965).

What this classification does not allow, however, is a specification of models, such as semi-empirical quantum chemistry, where the transition is not ‘smooth’, and further ‘cuts’, for instance between ‘core’ and ‘valence’, are made in the electronic structure. To classify semi-empirical theories as part of the net, we have to introduce an *idealisation* relation into the net structure. The relationship between the various idealised structures is formed by a collection of interpreting links in the sense of Chap. 6. While it would be hard to specify the content of such an idealisation relation generally in structuralist terms, since the idealisations rely on various restrictions in sets and relations in the structures that are made for pragmatic reasons, it is in principle possible to specify the emergence of semi-empirical quantum chemistry as a case of idealisation accompanied by approximation in this sense, and so characterise quantum chemistry properly as a theory *holon*. In the next chapter, after the discussion of the various structural reduction relations, we can specify this characterisation formally.

This discontinuity in practice was recognised by Coulson (1960) where he talked of ‘two groups’ of quantum chemists. The division ran between ‘Group I’, Coulson calls them the ‘electronic computors’, who perform numerical calculations though for a limited number of electrons and ‘Group II’ (nonelectronic computors) who were more interested in something akin to *mechanism*. On the advice of a friend, however, Coulson quips that the two groups might also be called the ab initio-ists and the a posteriori-ists.

The structure that emerges from the consideration of the specialisation relations is thus similar to what Park (2003) has called ‘the hyperbola’ of quantum chemistry – referring to Pople’s chart. The ‘hyperbola’ of quantum chemistry is a curve on our two directions of specialisation – taking into account both the methods and the number of electrons.

The next question is how the structures thus specified in the net are applied to the theories of chemistry, which is a question we will consider in the next chapter.

7.6 Conclusion

In this chapter I have formalised the theories of quantum chemistry, and argued that quantum chemistry is properly characterised as an applied quantum mechanics, though the structural *links* that perform the ‘application’ are not structurally ‘smooth’ and introduce various idealisations.

Mormann (1988) has discussed the theory transformations that usually accompany reductions in the context of the structuralist framework (as discussed in Chap. 6, p. 137). The transformations in this chapter do something similar: they restrict the reducing theory to specific cases where the reducing theory *applies* to the situation that is of interest to the reduced theory.[18]

As we have seen, the nature of the application involves a number of 'transformations' of the theory that *idealise* it to a theory of quantum mechanics applied to problems of chemical interest. Hence, the way in which quantum chemistry can be classified as a quantum mechanics is at various points *guided* by chemistry.

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[18] This would be covered in Kuipers' application step discussed in Chap. 1, but note that the specialisations discussed in this section are more specific.

Chapter 8
Networks of Structures in Chemistry

Abstract In this chapter the focus is on the practical implications of the formal reconstructions in the previous two chapters. I specifically focus on the formal structures involved in reductions three examples: the periodic table of the elements, bonding, and the absolute theory of reaction rates. In all these three cases it will prove to be the case that formal connections exists between the reduced and reducing theories in the form of inter-theoretic links. Practically, the form of these links is situational and adapted to the specific case at hand. This implementation of reduction shows us that reduction is primarily an affair of practical science, and one that can only be said to have limited consequences in terms of an overarching 'grand' architecture of science: science is best conceived as a complex network of theories, where the links between these theories do enough work to be reductive in the liberal Nagelian sense discussed in Chap. 1, but no more.

8.1 Introduction: An Experiment in Reduction

In this chapter we introduce our main formal reconstructions of some of the key theories of chemistry and connect these to the formalised picture of quantum chemistry given in Chap. 7. We then proceed to discuss their connections to the models of quantum chemistry we also discussed in the previous chapter, and more importantly, discuss how these relations can be classified as *reductions* in the sense of Chap. 6.

Specifically, in this chapter I will consider the reduction of the periodic table and the chemical bond as representative theories of chemistry. These topics when taken together do not form a complete 'theory' of chemistry and as a result of this limitation it is not possible to claim that we discuss a 'branch' reduction here. Rather, the discussion in this chapter focuses on partial, or 'local', reductions of individual theories. However, the present discussion forms a template for the reduction of other chemical theories, such as the theory of frontier orbitals and reaction rate theory.

My strategy in this chapter will be the following: first construct a number of constitutive elements of chemical theories of matter, and then investigate the sort of relationships that exist between these theories and the underlying theory of quantum

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mechanics. Hence my proposed approach to reductive claims is pragmatic and based on the 'experimental' assessment of reduction proposed in Chap. 6.

The links can be called 'reductions' in a pragmatic sense of the word – after all, the sort of links that we will encounter should count as prime examples of the sort of things philosophers want to classify as reductions. Following the thread from Chap. 6, we can then investigate which of the claimed *additional* properties of reductions obtain in actual cases of reduction, and hence, clarify our notion of reduction. A sufficient subset of such links should provide us with a number of examples, worked in sufficient logical detail, of actual inter-theory reductions, and assist in fleshing out a notion of reduction. Of course, we then still need to determine whether the notion of reduction that survives has any philosophical import. My contention is that they do: the partial reductions that we discuss in this chapter, rather than discrediting the notion of a possible reduction of chemistry to physics, shed new and interesting light on the nature of chemical theory.

This empirical approach to reduction that I propose to follow here is of course quite the opposite of the one more generally followed in philosophical approaches to reduction, where philosophical notions of what reduction *should* be tend to predetermine whether we are prepared to call an actually existing relation a 'reduction'.

I discuss reduction relations for two main theories: the periodic table of the elements and atomic theory, and the theory of the (chemical) bond, bonding and valence. Increasingly, as will become apparent, the reduction postulates that feature in these reductions become complex, or, as I will call them later, 'composite' theories in their own right, and cannot be identified with something as simple as 'identities', or causal connections. Instead, they may be said to feature more in the role in 'interfield theories' in the sense of Darden and Maull (1977), though the details of how they might fit that bill have to be determined through further formal analysis. Hence there is, in the structuralist reconstruction that we are developing here, significant scope to view the interrelationships between theories in terms of a non-reductive model, and to some degree the distinction between reduction and non-reductive models is collapsed. The (ontological) consequences of these moves will be further discussed in Part III.

In all cases of reduction, I will consider three specific aspects of the reduction relation in more detail. The first one is the issue of inter-theoretic links or reduction postulates. The structuralist conception of scientific theories will allow us to quite specifically discuss the form and content of the relevant reduction postulates. It will turn out that this latitude is required as well – none of the reduction postulates are particularly simple. Secondly, I will consider the issue of derivability, and discuss whether the 'laws' of the reduced theory can be derived from the reducing theory.

Finally, we take up a thread from Chap. 6 and consider which of the reductive requirements can be fulfilled in the practical examples we have discussed. In all cases the reducing theory will be the theories of quantum chemistry we have formalised in Chap. 7. Thus we do not work with 'corrected' reduc*ing* theories in each case. The main reason for this, as outlined in Chap. 7, is that the formalisation of quantum chemistry can in itself already be considered a correction, or theory-entry step, of a more general quantum theory, using the enabling theorems discussed in Hettema (2009) as well as the specification of a system. The matter of the correction of the reduc*ed* theories is to be decided through the 'test' of the criterion of content restriction in each case.

This chapter is structured as follows. In Sect. 8.2 I take up the issue of 'transferability' of orbitals so that they may feature in theories of chemistry. In Sect. 8.3 I discuss the reduction of the Periodic Table, and in Sect. 8.4 I focus on the reduction of the chemical bond. The links that enable the characterisation of the theory of absolute reaction rates are discussed in Sect. 8.5. Finally, I draw a number of conclusions in Sect. 8.6.

8.2 A Chemical Conundrum: The Role of Simple Theories of Quantum Chemistry

The formalisation of the structure of quantum chemistry, which was discussed in the previous chapter may be seen as first step towards the 'transformation' of the reducing theory that is to be effected by the reduction postulates. These specialisations of the general quantum theory involve various non-trivial deviations from quantum theory which amount to an *application* of quantum theory to the chemical situation at hand. Especially of interest is the distinction between semi-empirical and ab initio quantum chemistry, where the former is a further *idealisation* on quantum chemistry itself.

The distinction between ab initio and *semi-empirical* is useful in addressing the conundrum, sketched by Woody (2000), that quantum chemistry is incapable of dealing with a *range* of molecules in terms of a 'single' theory. Individual quantum chemical calculations appear disconnected, and cannot provide, on the surface, a 'pen and paper' theoretical framework that correctly captures a range of molecules, or, even stronger, certain 'classes' of molecules. Semi-empirical methods *do* have superior strengths in this regard, but in turn rely on idealisations that are not always robust from the viewpoint of basic quantum chemistry. This conundrum has led Woody to conclude that quantum chemistry as such is incapable of 'type' reductions, since the results of quantum chemical calculations are 'tokens' that have no obvious generalisations. While the conundrum is real, I believe Woody's conclusion to be mistaken. Let us first sketch the conundrum in more detail.

First of all, the conundrum is well known. Gavroglu and Simões (2011) describe one of the early responses to the Heitler and London paper as follows:

> [...] it was to the credit of the physicist that he can now calculate the energy of formation of the hydrogen molecule by using the Schrödinger equation. But the difficulty in a theory of valence was [...] to predict the existence and absence of various compounds and the unitary nature of valence that can be expressed by a series of small whole numbers leading to the law of multiple proportions. (Gavroglu and Simões 2011, p. 19)

At this stage of the development of quantum chemistry, there was still hope that such a unified theory might be found without introducing too severe approximations in the underlying formalism.

That hope did not last, however. In the context of the discussion of potential energy surfaces for reaction rates Eyring (1938) has given a clear definition of the conundrum. For the purposes of calculating the potential energy surface for a chemical reaction, he first classifies a number of theories as ‘semi-empirical’ when they have the following characteristics:

> (a) that each electron can be assigned a separate eigenfunction which involves the co-ordinates of only this one electron. (b) Multiple exchange integrals are negligible, (c) Normalising integrals for overlapping orbitals are negligible in comparison with unity. (d) The exchange and coulombic integrals for a complicated molecular system may be estimated from a potential curve for the isolated pair of atoms. (e) For distances involved in activation energy calculations this percentage is around 20 per cent. coulombic and 80 per cent. exchange binding, and this varies but little from atom pair to atom pair. (Eyring 1938, p. 8)

Eyring then remarks that more detailed calculations, as well as principled considerations, give no support for the construction of these theories:

> None of these assumptions have been rigorously derived from theory, and, as has been emphasised by Coolidge and James, if one assumes for H_3, the approximate eigenfunctions used by Heitler and London and Sugiura for H_2, the assumptions can all be shown to fail badly. (Eyring 1938, p. 8)

Thus stated, the conundrum seems fatal to the project of reduction: it seems that the sort of reduction that derives chemical ‘laws’ directly from basic quantum theory can only be achieved on the basis of theoretical assumptions that are unjustified from the viewpoint of basic theory and which can moreover be shown up as factually wrong in a large number of practical cases.

The conundrum is also formulated by Primas (1975) as follows:

> The failure of non-empirical quantum chemistry to explain the richness of chemical systematics is related to the non-robustness of the usual models of quantum chemistry. In contrast to the ab initio methods, the semi-empirical methods are occasionally more powerful because they accept the autochthony of chemistry. (Primas 1975, p. 129)[1]

but, according to Primas, this should prompt us to rethink the way quantum mechanics is applied to the theories of chemistry, as opposed to a mere acceptance of its fatality for the case of reduction:

> The role of the semiempirical models is *not* to simplify the calculation but to describe *classes* of molecules. If we reject semiempirical quantum chemistry as ad hoc or logically inconsistent, but nevertheless hope that a basic understanding of chemistry can be achieved by reducing it to fundamental physicals laws, we have to realize that chemical systematics does not deal with particular molecules but with *classes* of structurally diverse though functionally related molecules. *If we are to understand chemical taxonomy at all, then we have to develop a quantum mechanical theory of classes of molecules.* (Primas 1975, p. 129)

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[1] The word ‘autochthony’ seems to be out of place here. The word refers to the ‘place where [something] is found’, and hence one could argue that semi-empirical methods are autochtonous *to* chemistry, but not that they ‘accept’ the autochtony *of* chemistry.

Primas' observation does not answer the question whether such a transferability of the wavefunction is a required feature of explanation, even as one might perhaps argue that it is a *desirable* feature. The attempt to solve this problem is in large measure the motivation for the project of Primas (1981).

One of the features that enables chemists to think of classes of molecules quantum mechanically, is what Primas calls the 'transferability' of the wavefunction. This feature refers to Eyring's point (a) above ('each electron can be assigned a separate eigenfunction which involves the co-ordinates of only this one electron'), and thereby enables a description of the atomic wavefunction in which specific closed and open shells are gradually filled as one moves through the periodic table, where we have the property of *Aufbau*, and where one can talk meaningfully about the 'spatial' properties of individual orbitals. Eyring's condition (a) thus allows us to create a 'general' many-electron wavefunction that can be 'transferred' from molecule to molecule by changing both the nuclei in the frame and the occupations of the various orbitals that make up the wavefunction (the additional conditions (b) and (c) simplify the calculation of the energies).

One could take this one step further, and argue, with Paul van der Vet (1987), for the existence of a 'chemical' theory of the atom. The concept of a 'chemical theory of the atom' (CTA) was introduced by van der Vet to capture this highly approximate quantum notion of the atom in which:

> (a) The chemical properties of an (unbonded) atom are determined by the electron arrangement of the atom in a state which will be called the atom's *basic state* [...];
> (b) The chemical properties of molecules are determined by their electron arrangements [...];
> (c) The electron arrangement of a molecule depends on the constituent atoms and is determined: (i) by the basic configurations of the constituent atoms directly; and (ii) by the molecule's structure, which is partly determined by the basic configurations of the constituent atoms. (van der Vet 1987, p. 170–171)

In Chap. 10 I will discuss this theory further as a starting point towards a 'chemical atom': an example of one of the multi-faceted objects that populate the chemical ontology.

It seems that the case for reduction has arrived at a dilemma. The derivation of the 'laws' of chemistry seems possible only on the basis of approximations in the wavefunction and energy equations that are unjustified on both principled and practical grounds. On the other hand, wavefunctions that are closer to the 'exact' wavefunction do not exhibit properties that are easily generalised to different molecules of the same class in terms of a 'pen and paper' theory.

A number of responses to the conundrum are possible. In the line of Park (2009) one might argue that the continual refinement of the *numerical* methods represents a theoretical advance in its own right. The idea that a 'pen and paper' theory would have to be used in reduction as opposed to a computational tool might well be outdated in an era of rapid advanced in computer technology.

Secondly, one could argue that ab initio calculations do indeed provide some support for the many assumptions and idealisations on which the semi-empirical models are based. That is, in many cases semi-empirical models are capable of capturing *essences* of mechanisms and the like in an appealing form, and while ab initio methods add a certain measure of numerical accuracy to these models, they do not, in fact, alter the proposed mechanisms in a meaningful way.

Thirdly, ab initio calculations could be used to provide clues to new sorts of semi-empirical models, either through calculation of some of their parameters, or by suggesting new approximations and approaches which simplify quantum chemical models to a ‘pen and paper’ version. In a similar vein, the results of ab initio calculations can be meaningfully *compared* across a range of atoms or molecules, to provide a new sort of ‘chemical law’ based on their results.

A more principled objection to the conundrum is that the ‘token’ view of ab initio quantum chemistry assumes that it is the *wavefunction* rather than molecular *properties* that is the end result of a calculation. This, as we will see in what follows, is not the case. The wavefunction is instrumental in calculating a set of properties which subsequently are interpreted in the context of chemistry, but from the viewpoint of the structuralist reconstruction we develop in this chapter it is more properly characterised as a ‘theoretical term’ – a systematising feature of the system that does not itself appear in measurable results.

Lastly, there is also a practical objection to the conundrum which rests on the observation that fairly advanced ab initio quantum chemical methods are increasingly used in the chemical laboratory as *bench-top* tools. These consist of visualisation of the structure of molecules and transition states, calculation of energy differences between conformations and the like. Quantum chemists have been able to furnish the software to perform such calculations fairly routinely even for non-experts in the field. Hence at a practical level the principled wavefunctions of quantum chemistry can’t be all that useless.

Quantum chemistry can thus respond to the conundrum not with an either-or of semi-empirical or ab initio approaches, but rather with a range of options that can be meaningfully compared with each other in the context of what I will call a ‘composite’ theory. In what follows, I will evaluate some of these alternatives in the form of a reduction to a ‘principled’ and ‘unprincipled’ form of quantum theory, where the latter refers to semi-empirical theories. As we shall see, the explanatory features of these two theories are different in interesting ways.

In the next two sections I will discuss these explanations in the context of inter-theory reduction of the periodic table and the chemical bond.

8.3 Example 1: The Periodic Table of the Elements

The first example concerns the reduction of the periodic table of the elements. The periodic table of the elements is one of the key theories in chemistry, and is widely studied in the philosophy of science. My approach will be to first recapitulate the formalisation of the periodic table from Hettema and Kuipers (1988, 2000), and then discuss a critique of this paper by Eric Scerri (1997). I will then continue to place this discussion in the context of more recent work on the periodic table, such as that from Scerri (2007) and Cahn (2002) and discuss the claimed reduction of the period table in the context of the specific structuralist proposal from Chap. 6.

8.3.1 Prerequisites

The history and the structural changes of the periodic table are discussed extensively in van Spronsen (1969) and Scerri (2007) (only a very, or even irresponsibly, brief historical introduction was presented in Hettema and Kuipers 1988, 2000). Since then a significant amount of new historical work has been done on the periodic table, as well as a significant amount on work on the optimal form of the periodic table. Of especial interest in this context are the work by Cahn (2002) and Scerri (2007), both book length arguments that have added significantly to our understanding of the periodic table.

In addition to new historical work, a significant amount of chemistry oriented work has been performed as well (see especially Schwarz (2007), Scerri (2003, 2008, 2009, 2010)). The focus of this work has been on clarifications on the nature of chemical elements, properties that make up the notion of 'chemical similarity' that underpins the periodic table, and has implications for what one might propose as the optimal *form* of the periodic table, as well as the explanation of the periodic table by a theory of the atom.

One of the most interesting aspects of the history of the periodic table was its radical changes in form. Indeed, there have been a large number of different periodic tables in the literature. Even now, the discussion on the most appropriate form of the periodic table is still continuing.[2] One interesting aspect of this situation is that there is still a lively debate about the (re)organisation of the periodic table.

Another aspect that is important for our discussion is the disambiguation of the notion of 'chemical element' found in Paneth (1962a,b)[3] in a 'basic' and 'simple' substance. Scerri (2000b, 2009) has suggested that adhering to this distinction and constructing the periodic table in terms of basic rather than simple substances was one of the key elements of Mendeleev's success in developing the periodic table.

A long and thorough overview, suggesting a number of new pertinent questions in the current state of the periodic table, was given by Schwarz (2007). Schwarz notes that the questions around the periodic table are currently far from settled. Specifically, Schwarz notes that:

> There are three fields of open questions concerning the relation between [Periodic Tables] PTs and physics: (i) the relation between the chemical facts and the concept of a periodic system (PS) of chemical elements (CEs) as represented by PTs; (ii) the internal structure of the PS; (iii) The relation between the PS and atomistic quantum chemistry. The main open questions refer to (i). (Schwarz 2007 p. 139)

Hence a complicating factor in the discussion on the reduction of the periodic table, as for instance the book of van Spronsen (1969) or Scerri (2007) shows, is that there are many formulations of the periodic table.

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[2] See for instance Scerri (2008, 2010) and Marks and Marks (2010) for an example of these discussions.

[3] See Chap. 10 for a detailed discussion.

It will turn out that the reduction of the periodic table to a theory of the atom is far from clear-cut. While this conclusion may seem to differ significantly from the one drawn in earlier work (see Hettema and Kuipers 1988, 2000), this difference is only apparent: our reduction claim has always been moderate, and our conclusions regarding the nature of the connecting relationships still stand, though the exact nature of *how* they stand can be explicated in terms of the notion of reduction relations in Chap. 6.

8.3.2 Formalisation of the Periodic Table

In this section I will present a recapitulation of our earlier formalisation of the Periodic Table, which was published as Hettema and Kuipers (1988, 2000) and compare this recapitulation to the criticism levelled against this by Scerri (1997). Specifically, with the formalisations presented in the previous chapter, the (claimed) reduction relation can be made more precise (and hence the problems more acute).

I will follow the usual approach by first defining the potential models, and then defining restrictions on them in the form of a law leading to the models. After that, I will discuss the reduction relation.

8.3.2.1 Potential Models

In order to construct a potential model for the periodic table we first postulate a non-empty finite set E, representing the set of chemical elements. Here, we assume naively that there exists in some sense a fixed and complete set of elements. Let e, e' denote elements of E.

Next we postulate the atomic mass function m from E into the positive real numbers $\mathbb{R}^+$, which ascribes an 'atomic mass' to each element of E.

Further we assume the binary chemical similarity relation $\sim \subset E \times E$, which denotes the relationship of 'exhibiting the same chemical behaviour', or belonging to the same chemical group. This term suggests already that $\sim$ is an equivalence relation, which will be assumed throughout. The group to which an element e belongs is the equivalence class $\{e' | e \sim e'\}$.

Finally we assume the 'atomic number function' z from E into the positive natural numbers $\mathbb{N}^+$. In order to exclude non-essential, isomorphic varieties, we assume that there is a 'first element' with the value 1, or $1 \in \mathrm{R}ange(z)$.

We propose the following potential model of the periodic table:

Definition 1 (M(PT)) x is a potential model for the periodic table if and only if

(1) $x = \langle E, m, \sim, z \rangle$;
(2) E is a non-empty, finite set (the set of chemical elements);
(3) $m : E \rightarrow \mathbb{R}^+$ (the atomic mass function);
(4) $\sim \subset E \times E$ is the chemical similarity equivalence relation;
(5) $z : E \rightarrow \mathbb{N}^+$ is the atomic number function.

Broadly speaking, the potential models of the periodic table rely on a characterisation of chemical elements that ascribes a similarity relation as well as a mass function to the element. z is in this potential model the only theoretical term.

8.3.2.2 Models

There is only one model of the periodic table and that is the table itself.

The following three conditions apply. The first one is a condition of (loose) order preservation, which is not exceptionless:

$$m(e) < m(e') \qquad \text{iff} \qquad z(e) < z(e') \tag{8.1}$$

There are a number of well-known exceptions to this rule, due to isotope mixtures. Examples are for instance the placement of Ar at position 18 and K at position 19; while $m(\mathrm{Ar}) = 40$ and $m(\mathrm{K}) = 39.1$.

The second condition is the surjection requirement:

$$\mathrm{Rge}(z) = 1, 2, \ldots, \max(z) \tag{8.2}$$

Exceptions to this rule (which we call existential exceptions) have played an important role in the periodic table. These sort of exceptions have allowed chemists to predict the existence of new elements occupying certain positions in the table.

Moreover, the third condition on z is that it is a one-one function:

$$z(e) = z(e') \Rightarrow e = e' \tag{8.3}$$

On the basis of these principles, in our earlier paper we formulated a *naive* and *sophisticated* periodic law, with the naive law as a special case of the sophisticated law. The naive law was roughly based on Mendeleyev's 1871 'short form' periodic table, which is not exceptionless. The number '8' was introduced to indicate the 8 different groups that this table distinguishes. The naive law claims that all chemically similar elements differ with a period of 8:

$$\text{(NPL)} \quad e \sim e' \quad \text{iff} \quad |z(e) - z(e')| = n \times 8 \qquad (n = 1, 2, \ldots)$$

Of course, the naive periodic table has a number of problems associated with it, especially the placement of rare earths and the fact that some groups have multiple elements in one row.

The sophisticated law allows for varying periods, but limits these to periods of length $2n^2$. As such, the sophisticated form of the law allows for various shapes of the periodic table, such as the 'medium-long form' periodic table and the 'left step' periodic table.

The sophisticated law is formulated in two clauses, the latter with a forward clause and a backward clause.

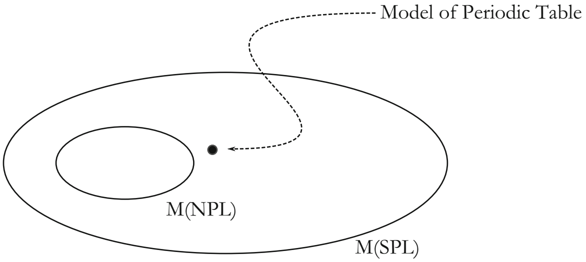

Fig. 8.1 Structuralist reconstruction of the periodic table. Note that the naive periodic law NPL is more restrictive than SPL, and furthermore that the 'true' periodic table is a single element of the set allowed by SPL

(SPL(i)) If $e \sim e'$ and $z(e) < z(e')$ then there exists an n $(= 1, 2, 3, \ldots)$ such that $z(e) - z(e') = 2n^2$ or there exists an e'' such that $e \sim e''$ (and hence $e \sim e'$) and $z(e) < z(e'') < z(e')$.

(SPL(iia)) *Forward:* For all e there exist an e' and an n $(= 1, 2, 3, \ldots)$ such that $z(e) - z(e') = 2n^2$ or there is no similar element after e (i.e. or there is no e' such that $e \sim e'$ and $z(e') > z(e)$).

(SPL(iib)) *Backward:* For all e there exist an e' and an n $(= 1, 2, 3, \ldots)$ such that $z(e') - z(e) = 2n^2$ or there is no similar element before e (i.e. or there is no e' such that $e \sim e'$ and $z(e) > z(e')$).

It would appear that the sophisticated periodic law is much too generous, for in practice there is only one periodic table and the admissible numbers n are determined quite precisely. As it stands at present, the proposed formulation of the periodic law still admits a number of 'periodic tables'. The formulation, however, seems to be the best that can be said if the periodic table is formulated as a law. The situation (at the level of $\mathscr{M}_p$) is thus as depicted in Fig. 8.1.

It is interesting to note that Eric Scerri (2008, 2009) has suggested that the notion of 'triads' could be used in a meaningful way as descriptive devices for the periodic table. The notion of similarity relations between three elements, which is captured in the concept of a triad, is exactly what is described in SPL. Scerri's focus on triads also leads him to consider alternative forms of the table.

8.3.3 *Explaining the Periodic Law*

One of the requirements of Nagelian reduction is that of explanation. In this section we will give an overview of how attempts to explain the periodic law on the basis of atomic theory have fared. Generally, the success of the explanation hinges on two separate aspects:

1. The explanation of the regularities in the periodicity on the basis of the structure of the atom;
2. The explanation of the chemical similarity relation on the basis of the inner structure of the atom.

While these two questions are related (since the regularities in the periodicity are based on the similarity relation) it is preferable to treat these as somewhat separate questions.

As described by Kragh (2001), the attempts at explanation of the properties of the periodic table as a result of subatomic regularities of matter are almost as old as the periodic table itself. The tendency to develop ‘atomic’ models based on the periodic table precedes the development of quantum mechanics. Kragh gives examples from both Thompson and Bohr’s early atomic models, and argues that the structure of the periodic table formed an important *guiding* principle in the construction of these models; hence, as Kragh (2001) concludes:

> The historical roots of the modern theory of atomic structure are to be found not only in the development of physics, but also in the development of chemistry. Among the chemical phenomena that have influenced atomic theory, the periodic system of the elements is perhaps the most important. The existence of regularities in the properties of the elements, such as summarised in the periodic table, was a source of puzzle as well as inspiration to many scientists who wanted to know the underlying mechanisms and causes they assumed to exist. (Kragh 2001, p. 139)

Kragh also notes that the *guiding* role of the periodic table imposed the condition that good models of the atom were expected to *explain* the structure of the periodic table, or at least be consistent with it.

As the above quote already suggests, the structure of the explanation is far from direct. An important difficulty is that the formulation of the periodic law itself[4] is not exactly straightforward, but rather open to a degree of predilection and interpretation. As Scerri (2007) notes, a large number of ‘candidate’ periodic tables have been proposed, and currently the number of possible periodic tables runs into the thousands.

Moreover, the theoretical basis on which the periodic law should be based is far from fixed, and several approaches, representing more or less the ‘range’ op quantum chemical responses to the chemical conundrum from the previous section, have been proposed in the literature.[5]

The common textbook interpretation of the explanation of the periodic law is in terms of a simple (‘unprincipled’) one-electron model, in which shells are filled with electrons in increasing order (usually referred to as *Aufbau*, see Sect. 8.2). In addition, the periodic law has been discussed in terms of a statistical model of the electron gas by Fermi (1928). A number of ab initio calculations have been performed (see Froese Fischer 1977). In addition there are group theoretical approaches (see for instance Kibler 2007) to the explanation of the periodic law. It has been claimed that our most sophisticated theories of the atom (even including

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[4] Witness the very large number of ‘periodic tables’ as well as Schwarz’ remark, quoted on p. 199, that ‘the relation between the chemical facts and the concept of a periodic system (PS) of chemical elements’ is still a key issue.

[5] The paper by Ostrovsky (2001) contains an overview of the literature on the explanation of the periodic table.

the Hartree-Fock approximation) are in fact too complicated to assist much in the interpretation of the periodic table (see Ostrovsky 2001), primarily because they do not recover simple law-like schemes directly. To overcome this difficulty, recently Borgoo et al. (2004) have undertaken a number of numerical calculations and have defined a ‘similarity’ criterion based on the calculated densities.

The replay of the chemical conundrum in this context is that the best guidance to the ‘derivation’ of the periodic table is given by simple atomic models, such as for instance hydrogenic models, which are known *not* to present the ‘true’ state of affairs from the viewpoint of the quantum theory of multi-electron systems. Hence we may call these classes of models ‘unprincipled’. An additional complication is that for heavier systems relativistic effects play an important role, and the quantum theory of relativistic systems is even more complex, and less conceptually transparent, than the quantum theory of non-relativistic systems.[6]

We now discuss a few approaches in more detail to get a better sense of the issues they present.

The ‘textbook’ explanation for the chemical similarity relation is based on the idea of an *Aufbau* rule, and the periodicity is established on the basis of the properties of the outermost occupied orbitals, or the valence orbitals. In this model the electronic configuration is thought to be constructed by consecutive ‘filling’ of the shells, so that the periodic table is ‘built up’ according to the scheme in Table 8.1.

The method starts by assigning the single electron of the H atom to the $(1s)$ ground state. The He atom has an additional electron, and based on the Pauli principle can still occupy the ‘free’ spot in the $(1s)$ orbital to give a ground state configuration $(1s)^2$. Since this fills up the $(1s)$ shell, the next element, which has 3 electrons, will start filling the $(2s)$ shell and so on.

An important property of a system with a single-particle spherical potential is that the one-electron wavefunctions can be described as products of a radial and angular momentum function as follows:

$$\psi_{klm}(r) = R_k(r) Y_l^m(\vartheta, \varphi)\sigma_s \tag{8.4}$$

where $R_k(r)$ is the radial function, the Y_l^m are the angular momentum functions and the σ_s is the spin function. The main, or ‘shell’ quantum number n is defined as $n = k + l + 1$; k counts the number of ‘nodes’ in the radial function.

For the *Aufbau* view, this fact is combined with the Pauli principle to explain the $2n^2$ periodicity obtained in the sophisticated periodic law. The wavefunction is characterised by three quantum numbers n, l and m, where $n = 0, 1, 2, 3, \ldots$ is the principal quantum number, l can take on the values $0, 1, \ldots, n-1$ and $-l \leq m \leq l$, hence a total of $(2l + 1)$ m-values for a given l. The spin function adds a degeneracy of 2.

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[6] In this respect it is useful to remark that Pyykkö (2011) has predicted elements up to $Z = 172$ based on Dirac-Fock calculations.

Table 8.1 The Aufbau result for the periodic table as it is usually found in textbooks. This table only covers the first 20 elements. This particular table is from Gasiorowicz (1974), and the same information is found in the 'long form' periodic table format in Eyring et al. (1944). IP is the ionisation potential, a measure for the strength with which the weakest bound electron is bound

Z	Element	Configuration	Term	IP(eV)
1	H	$(1s)$	$^2S_{1/2}$	13.6
2	He	$(1s)^2$	$^1S_0$	24.6
3	Li	$(\mathrm{He})(2s)$	$^2S_{1/2}$	5.4
4	Be	$(\mathrm{He})(2s)^2$	$^1S_0$	9.3
5	B	$(\mathrm{He})(2s)^2(2p)$	$^2P_{1/2}$	8.3
6	C	$(\mathrm{He})(2s)^2(2p)^2$	$^3P_0$	11.3
7	N	$(\mathrm{He})(2s)^2(2p)^3$	$^4S_{1/2}$	14.5
8	O	$(\mathrm{He})(2s)^2(2p)^4$	$^2P_2$	13.6
9	F	$(\mathrm{He})(2s)^2(2p)^5$	$^2P_{3/2}$	17.4
10	Ne	$(\mathrm{He})(2s)^2(2p)^6$	$^1S_0$	21.6
11	Na	$(\mathrm{Ne})(3s)$	$^2S_{1/2}$	5.1
12	Mg	$(\mathrm{Ne})(3s)^2$	$^1S_0$	7.6
13	Al	$(\mathrm{Ne})(3s)^2(3p)$	$^2P_{1/2}$	6.0
14	Si	$(\mathrm{Ne})(3s)^2(3p)^2$	$^3P_0$	8.1
15	P	$(\mathrm{Ne})(3s)^2(3p)^3$	$^4S_{3/2}$	11.0
16	S	$(\mathrm{Ne})(3s)^2(3p)^4$	$^3P_2$	10.4
17	Cl	$(\mathrm{Ne})(3s)^2(3p)^5$	$^2P_{3/2}$	13.0
18	Ar	$(\mathrm{Ne})(3s)^2(3p)^6$	$^1S_0$	15.8
19	K	$(\mathrm{Ar})(4s)$	$^2S_{1/2}$	4.3
20	Ca	$(\mathrm{Ar})(4s)^2$	$^1S_0$	6.1

Hence, for each n, we have

$$2\sum_{i=1}^{n}(2i-1) = 2[(2n-1)+\ldots+1] = 2n^2 \tag{8.5}$$

possibilities in the row of the periodic table.[7]

Dependent on the shape of the central potential $U_a(r)$ we can define different 'shell filling' rules (see Ostrovsky 2001). For $U_a(r)$ equal to the Coulomb potential one arrives at the (n,l) *Aufbau* scheme, where the orbitals are filled in the order of increasing quantum number n and for equal n they are filled in the order of increasing l, hence

$$1s < 2s \approx 2p < 3s \approx 3p \approx 3d < 4s \approx 4p \approx 4d \approx 4f \ldots \tag{8.6}$$

In this notation $<$ indicates 'will be filled prior to' and $\approx$ means 'will be filled at about the same time as'.

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[7] Recall the 'sum of odd numbers rule' $1+3+\ldots(2n-1) = n^2$.

Table 8.2 Prediction of the period lengths in the periodic table from the Madelung rule following Ostrovsky (2001)

$n + l$	Shells	Period length
1	$1s$	2
2	$2s$	2
3	$3s, 2p$	8
4	$4s, 3p$	8
5	$5s, 4p, 3d$	18
6	$6s, 5p, 4d$	18

Following this *Aufbau* scheme, we get period lengths of $2, 8, 18, 32, \ldots$. While it has been shown that highly ionised atoms do behave in this manner it is not a correct representation of the periodic table.

The periodic law is however most closely approached, with some exceptions, by the Madelung $(n + l, n)$ rule, which states that shells are filled in order of increasing $n + l$ and in order of increasing l for equal $n + l$.[8] The explanation of this rule from first principles is now sometimes referred to as Löwdin's challenge. This rule for instance correctly describes why in the transition metals the $4s$-shell is filled prior to the $3d$ shell (the $n + l$ value of the $4s$-shell is $(4 + 0) = 4$ and the $n + l$ value of the $3d$-shell is $(3 + 2) = 5$). Nevertheless, the Madelung rule is not as a whole exceptionless, and it has never been derived from first principles. The Madelung rule predicts the following *Aufbau*:

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s \ldots \tag{8.7}$$

but still suggests the wrong lengths of the periods (see Table 8.2)

$$2, 2, 8, 8, 18, 18, 32, 32, \ldots \tag{8.8}$$

There have been a limited number of attempts to derive the Madelung rule from first principles, none successful. The lack of attempts prior to 1969 led Löwdin (1969) to formulate what is now sometimes referred to as 'Löwdin's challenge':

> It is perhaps remarkable that, in axiomatic quantum theory, the simple energy rule $[(n+l, n)]$ has not yet been derived from first principles. (p. 332) [...] It would certainly be worth while to study the energy rule $[(n+l, n)]$ from first principles, i.e. on the basis of the many-electron Schrödinger equation. (Löwdin 1969, p. 334)

as well as its corollary:

> If the orbitals in the neutral atoms are arranged after $(n + l, n)$, and the orbitals in the hydrogen-like ions are arranged after n, one may also ask the question at what degree of ionization the energy rule has become changed. (Löwdin 1969, p. 334)

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[8] As Löwdin (1969) points out, it is also referred to as the Goudsmit rule or the Bose rule. In his paper discussing this rule and laying down the 'Löwdin challenge, Löwdin does not refer to the rule as the Madelung rule.

This challenge is still largely unsolved, though a resolution has been claimed by Allen and Knight (2002), which was later criticised by Scerri (2006). The approach of Allen and Knight is based on a ‘perturbation operator’, which they write as

$$[(n-1)+(l+1)]nl = (n-1)(l+1) \tag{8.9}$$

which, in the words of Allen and Knight, ‘acts on [an orbital] *nl* and changes it into a close lying, more stable one with a higher *l* value’ (p. 85).

Other approaches to the calculation of the periodic table are possible. For instance, in the paper by Fermi (1928), which is also one of the core papers of the Density Functional Approach, the central potential is approximated by

$$U_a^{\mathrm{TF}}(r) = \frac{Z}{r}\chi(kr); \qquad k = \left(\frac{8\sqrt{2}}{3\pi}\right)^{2/3} Z^{1/3} \tag{8.10}$$

where there is no known analytic expression for the function χ and various approximations have appeared in the literature. In the original approach by Fermi (1928) the potential is determined numerically from a differential equation for the potential which is solved subject to the boundary conditions for a neutral atom, i.e.

$$\lim_{r\to 0} U = \frac{Ze}{r} \tag{8.11}$$

and

$$\int n d\tau = Z. \tag{8.12}$$

The first condition expresses the fact that at the nucleus the potential becomes the ‘unshielded’ Coulomb potential; the second condition expresses the fact that the integration of the electron density over all space is equal to the nuclear charge Z (hence the theory applies to a neutral atom).

In later work, such as that of Latter (1955) or Ostrovsky (2001), the function χ is approximated by some mathematical expression, for instance, (as in Ostrovsky 2001 and the technical references therein) by

$$\chi = \frac{1}{(1+\alpha x)^2}. \tag{8.13}$$

It is still open to discussion, however, what these theoretical developments imply for the Nagelian notion of derivation. The two salient features of this explanation are that there is a large number of formulations of the theory to be reduced, many of which are not strictly speaking exceptionless, and a large number of candidates for a reducing theory, none of them perfect.

My proposal is that the reduction proceeds via a ‘composite’ theory, which combines principled and unprincipled aspects of the reducing theory. To specify that concept, we first investigate the links between the periodic table and atomic theory formally.

8.3.4 Linking (Some) Atomic Theory and the Periodic Table

Generally, we claim that the periodic table can be reduced to ‘atomic theory’, which is a quantum theory of the atom. Following the proposal for reduction relationships developed in Chap. 6, we need to define the links between the notion of ‘chemical element’ and the models of quantum chemistry. Hence in order to discuss the necessary relationships between the structures, we need to consider two separate links:

1. A link L_1 between the chemical element and some restricted structure of ab initio quantum chemistry which replicates the ‘internal structure’ of an element;
2. A link L_2 that instantiates the ‘chemical similarity’ relation.

As we will see, the link L_2 comes in two varieties.

8.3.4.1 L_1: The Definition of an ‘Element’

The first link seems relatively straightforward, but, as we shall see, is fraught with some difficulties of its own. In terms of the models of the previous chapter, a quantum theory of the atom would seem to be a subset of the quantum mechanics in which there is only a single nucleus. Subsequently, we can still apply all the theories to this particular subsystem and achieve a measure of reduction.

The issue of the identification of the notion of ‘chemical element’ in relation to the reduction of the periodic table was recently discussed by Schwarz (2007) and this paper was commented on quite extensively by Scerri (2009). The issue is one of how the ‘reducing’ structure should be conceived. The standard ‘textbook’ interpretation is based on the theory of a neutral atom, with a shell structure derived from the solutions of the hydrogen atom. The *Aufbau* principle is then subsequently employed to ‘fill’ these shells with electrons.

Hence for this simple situation we claim that all models of atomic theory are specialisations of quantum mechanics in the sense that they have a single atomic nucleus (have a frame $\mathscr{F}(1)$ with $N = 1$). It is unclear however what the electrical *charge* of such systems should be, as well as what sort of quantum theory would be best suited to ‘derive’ a form of the periodic law: as the previous section on the explanation argued, there are a number of potential solutions here. Hence we will specify the link at the simplest level, claiming that a ‘chemical’ element e corresponds to a ‘system’ of a nucleus with charge Z given by $z(e)$ (the atomic number of e) and at least one electron.

We first define a restriction of the general structure of ab initio quantum chemistry $(M)_p(\text{QCAI})$, Definition 10, which consists of limiting the system to a single atom. Formally, such a restriction can be described as $\langle R = \mathbf{0}, Z, P, \mathbf{r}, \boldsymbol{\sigma}, R_M = \mathbf{0}, \boldsymbol{\chi}, \Psi, \rangle$. This structure is simplified in the sense that there is a single nuclear position vector, which is chosen as the origin $\mathbf{0}$, a single nuclear charge Z ($\mathbf{Z}$ in the full structure simplifies to Z) and the origin of the basis set is the origin. We call this specialisation an *atomic* structure, and indicate it by $\mathscr{M}_p(\text{QCAI}(a))$. The specialisation is defined as follows:

Definition 2 (The QCAI(a) restriction (to atomic theory)) The structure $\mathscr{M}_p(\text{QCAI}(a))$ is a specialisation of QCAI iff for all $x \in \mathscr{M}_p(\text{QCAI}(a))$ x is a potential model of QCAI ($x \in \mathscr{M}_p(\text{QCAI})$) and hence of the form $x = \langle \mathsf{R}, \mathbf{Z}, \mathscr{P}_e, \mathbf{r}, \boldsymbol{\sigma}, \Psi, \hat{A}, \mathsf{M}, \mathsf{R}_B, \boldsymbol{\chi}, \alpha \rangle$ (see p. 174) with the following restrictions

1. $\mathsf{R} = \mathbf{0}$; (the nucleus is at the origin);
2. $\mathbf{Z} = \{Z\}$ (a single element);
3. $\mathsf{R}_M = \mathbf{0}$ (the origin of the basis set is the 0-vector).

Hence $\mathscr{M}_p(\text{QCAI}(a))$ is a specialisation of $\mathscr{M}_p(\text{QCAI})$ in the sense that the potential models are restricted to a single nucleus on the origin. The basis set requirement is less strict, since in principle the wavefunction of a single atom could be computed in any basis, but in practice the restriction holds for most cases.

These structures connect to chemical elements through the usual relations given in Table 7.1, but does not explicitly specify the number of electrons in the atomic structure. This is to reflect the fact that it is in fact *unclear* what the correct atomic structure for the reduction of the periodic table should be, though the most natural choice would be the use of an electrically neutral structure.

It is relatively straightforward to define a link between the models of the periodic table and the models of QCAI(a) as follows:

$$L_1 = \langle \mathscr{M}_p(\text{QCAI}(a)), \langle Z \rangle, \mathscr{M}_p(PT), \langle E, z \rangle \rangle \text{ where } Z = z(e)). \tag{8.14}$$

The link is instantiated by equating Z in $\mathscr{M}_p(\text{QCAI})$ to $z(e)$ in $\mathscr{M}_p(PT)$ and utilising the mapping in Table 7.1. It is of course an interesting question to what degree the utilisation of this mapping already presupposes the periodic table. This is a question that we will return to later.

The relation is a many to one relation, which links many structures of the type $\mathscr{M}_p(\text{QCAI}(a))$ to a single element e.

8.3.4.2 L_2: Chemical Similarity

It is harder to define a link to the chemical equivalence relation $\sim$. Firstly, as Cahn (2002) and Schwarz (2007) (see Schwarz' quote on p. 199) point out, the $\sim$ relation is somewhat problematic even at the level of chemistry. According to Cahn, the term itself is ambiguous: similarity may mean that two objects are similar in some or all of their properties, while similarity may also mean that two objects are similar in terms of some specified property Cahn 2002, p. 43. Both meanings of similarity are used in the construction of the periodic table. A complicating factor is that quantum mechanical calculations yield a number of results, from atomic energies to atomic properties, wavefunctions and the like which all combine in some complex way to make up the similarity relation $\sim$.

In the discussion on reduction in our 1988 paper, we employed the second notion of similarity for 'atomic theory', and linked the chemical similarity relation to similarities in outer electron configuration, based on a generic *Aufbau* model, and furthermore described this relationship as a causal *correlation*, in which similarities in the 'outer electron configuration' were causing the chemical similarity. This is a rather weak reductive claim. As has been illustrated by Scerri (1997), this correlation is not strictly speaking exceptionless.

We now argue that the links may be specified in two particular ways: one correlating to an 'unprincipled' atomic theory and the other to a 'principled' atomic theory.

'Unprincipled' Atomic Theory

The 'unprincipled' notion of atomic theory is based on the simplifications that arise from a specific tailoring of the basic theory to support various notions of chemical atoms, *Aufbau* and transferable wavefunctions. The key explanatory feature of the unprincipled approach is that it supports a qualitative consideration of the chemical issues at stake. The 'unprincipled' version of Atomic Theory is thus, in the manner discussed in Chap. 7, based on further idealisations from quantum chemistry, and, in the terminology of Coulson (1960), part of a 'Group II' approach.

This successful qualitative reduction of the periodic table depends on a number of factors, which we captured in our original Hettema and Kuipers (1988, 2000) in the term 'chemical' and 'physical' theory of the atom. An approximate theory like the chemical theory of the atom is key to the 'pen and paper' derivation of the periodic table. The specific feature required from such a theory is the use of a 'transferable' wavefunction in order to support *Aufbau*.

Such wavefunctions can be progressively 'filled' with electrons in the manner of Table 8.1, and in this case it can also be argued that chemical similarity can be correlated with 'outer electron configuration'.

We can now enhance this characterisation with the assistance of the more detailed characterisation that we have given of quantum chemistry. In the simple *Aufbau* model discussed earlier the link appears as it did largely in our original approach in Hettema and Kuipers (1988, 2000). That is, since each electron occupies a single orbital, one is justified to speak of a 'core and valence electron' approach, and base the chemical similarity relation on the 'outer electron configuration'. Hence, a simple *Aufbau* model formulates the link as a correlation between 'chemical similarity' and 'having the same valence electron configuration'.

This particular explanation of the similarity has a use in chemistry as an explanatory tool: it allows us to talk of 'classes' of elements and turn these classes into the specific 'groups' of the periodic table. It also forms the basis for the simple 'bonding' diagrams that Woody (2000) argues are important parts of chemical theorising.

Hence there is room for an 'unprincipled' variety of the link, which may be specified as follows. We start defining a restricted version of $\mathscr{M}_p(\text{QCAI}(a))$ in which the wavefunction Ψ is a simple product function Φ_p of $1s$, $2s$, $2p$, ... orbitals. The measure set M is a set of orbital energies $\{\epsilon\}$. For simplicity, we also drop the set of electronic coordinates $\mathbf{r}$ and the basis set structure $\mathscr{B} = \langle \mathsf{R}_B, \boldsymbol{\chi}, \alpha \rangle$ from the definition. Let us call this structure $\mathscr{M}_p^u(\text{QC})$, where the superscript u denotes an 'unprincipled' version of atomic theory and we furthermore drop the 'Ab Initio' (AI) designation, since this version of the theory is not an ab initio theory anymore.

The spin function $\boldsymbol{\sigma}$ is also simplified, and assigns an 'up' or 'down' spin to each individual electron. We also add an *Aufbau* rule which orders the (individual) electrons into the orbitals, $A : P \to \{\epsilon\}$.

Hence, the 'unprincipled' atomic theory may be specified as a set of structures:

Definition 3 (Unprincipled Atomic Theory) The set of structures $\mathscr{M}_p^u(\text{QC}(a))$ is an unprincipled atomic theory iff $x = \langle \mathsf{R}, \mathbf{Z}, \mathscr{P}_e, \boldsymbol{\sigma}, \Phi_p, \{\epsilon\}, A \rangle$ such that

1. $\mathsf{R} = \mathbf{0}$; (the nucleus is at the origin);
2. $\mathbf{Z} = \{Z\}$ (a single element);
3. $\mathscr{P}_e$ is the electronic structure;
4. $\boldsymbol{\sigma}$ is a spin function;
5. Φ_p is a product function of electronic orbitals;
6. $\{\epsilon\}$ is a set of orbital energies;
7. $A : P \to \{\epsilon\}$ is the *Aufbau* function which assigns orbital energies to electrons.

The *models* of unprincipled atomic theory then obey a number of simple rules. Specifically, the orbitals are filled in order of the lowest orbital first and no orbital can be occupied more than twice. It is not necessary to give further formal definitions of these rules.

The link specifies 'chemical' similarity in terms of a correlation to a specific *Aufbau*. We may therefore define a relation $a_\sim$ which captures this notion of *Aufbau* similarity. $a_\sim$ is defined as a relation on $\mathscr{M}_p^u(\text{QC}(a)) \times \mathscr{M}_p^u(\text{QC}(a))$ which specifies that the electron configurations are similar. In terms of Cahn's distinction between the different meanings of similarity, $a_\sim$ expresses a similarity between two elements on a well-defined property, namely the *Aufbau*.

To further specify this similarity relation, we may introduce an (artificial) separation between 'inner' and 'outer' electron where an 'inner' electron is part of a filled 'shell' and an 'outer' electron is part of an 'open' shell. This further distinction allows us to specify the 'similarity' relation with some more precision, but is not (formally) necessary.

The ‘unprincipled’ link is then specified by

$$L_2^u = \langle \mathscr{M}_p^u(\mathrm{QC}(a)), \{\epsilon\}, a_\sim, \mathscr{M}_p(PT), \sim \rangle. \tag{8.15}$$

The approach based on the *Aufbau* model has been criticised by Scerri (1997) on various grounds which we will discuss later on; one of those was that the *Aufbau* model relies on a number of assumptions that do not obtain in quantum theory. Our formalisation of the link has made that clear: the big difference between the set of structures $\mathscr{M}_p(\mathrm{QCAI}(a))$ and $\mathscr{M}_p^u(\mathrm{QC}(a))$ is that the wavefunction in the latter structure is a simple product function of atomic orbitals, and in this sense, the electrons have become individual particles.

‘Principled’ Atomic Theory

It is valid to ask if it is possible to base the similarity relation on a wavefunction that does *not* rely on some form of *Aufbau*, and which does not rely on the spurious distinction between ‘inner’ and ‘outer’ electron and in this way form a ‘principled’ version of the same link.

The original work of Fermi (1928), and the more recent work by Borgoo et al. (2004) illustrate that such a specification of the chemical similarity relation of the periodic table on the basis of a more principled theory of the atom is indeed possible. For instance, the work on chemical similarity undertaken by Borgoo et al. (2004) concluded that

> [. . .] numerical Hartree-Fock densities for atoms H – Xe combined in a similarity index with a Dirac delta function separation operator yield a nearest neighbour dominated similarity, masking periodicity. Introduction of the information discrimination concept with reference to the noble gas atom of the previous row leads to periodicity, with more pronounced results when densities are replaced by shape functions throughout. (Borgoo et al. 2004, p. 366)

which indeed indicates that periodicity may be defined in a principled sense, and, perhaps somewhat surprisingly, is also is related to some sort of function of ‘outer electron’ configuration. If this were not the case, the introduction of the density of the noble gas atom of the previous row would not be necessary.

In the stronger construction, the similarity relation is related to the measure set M on the atomic structure. Again, we can only argue for a causal correlation and nothing stronger.

A link between a system of atomic quantum mechanics and the chemical similarity relation links $\mathscr{M}_p(\mathrm{QCAI}) \times \mathscr{M}_p(\mathrm{QCAI})$ to $\mathscr{M}_p(PT) \times \mathscr{M}_p(PT)$ in the following way.

At the level of $\mathscr{M}_p(\mathrm{QCAI})$ we define a set of properties $\mathsf{M}_s \subseteq \mathsf{M}$ which are suitable for instantiating the periodicity. For instance, such properties can be (computed) densities and orbital occupations, but also predictions of spectra, for instance, provided the latter are accompanied by a suitable *characterisation* on which to base chemical similarity.

Chemical similarity can be expressed as a 'nearest neighbor' relationship on the subset of properties M_s. If we consider two atomic quantum structures with different Z the nearest neighbor relation on the properties M_s is defined as the point of lowest 'distance' between the values of the sets M_s. We indicate the distance between a set M_s^1 and M_s^2 by $d(\mathsf{M}_s^1, \mathsf{M}_s^2)$. Since we have no further specifications of the contents of this set (we want to keep the set general for now) this function may take a number of mathematical forms.

The 'nearest neighbor' can be defined on the basis of this distance if we define an ordering relation $<$ on the distances so that we can express statements such as M_s^1 is 'closer to' M_s^2 than to M_s^3, or $d(\mathsf{M}_s^1, \mathsf{M}_s^2) < d(\mathsf{M}_s^1, \mathsf{M}_s^3)$. The 'nearest neighbor' relation is now defined in terms of the 'closest' element as follows:

Definition 4 (Nearest neighbor) For any $x \in \mathscr{M}_p(\mathrm{QCAI}(a)$ there is an $x_n \in \mathscr{M}_p(\mathrm{QCAI}(a)$ such that for any $x_j \in \mathscr{M}_p(\mathrm{QCAI}(a))$, $d(\mathsf{M}_s, \mathsf{M}_s^n) < d(\mathsf{M}_s, \mathsf{M}_s^j)$. x_n then is the nearest neighbor of x.
One could expect a difference between a 'lower' and 'higher' nearest neighbor, but at the level of properties this is not the case.

Note that the relationship is reflexive and symmetric but not transitive. Hence it would seem that the relationship of a nearest neighbor relation is not fully explanatory in the sense that a 'gap' may exist where a structure a is the nearest neighbor of b and b in turn the nearest neighbor of c, but a is not the nearest neighbor of c. Nevertheless, at the level of chemical similarity a and c would be considered chemically similar. In the formulation of the periodic law this is solved by positing an 'existence' claim for an element 'in between'.

More generally, a relation $p_{\sim}$ may be defined on $\mathscr{M}_p(\mathrm{QCAI}(a))$ as follows:

$$p_{\sim} \subseteq \mathscr{M}_p(\mathrm{QCAI}(a) \times \mathscr{M}_p(\mathrm{QCAI}(a). \tag{8.16}$$

Hence, $p_{\sim}$ is the counterpart of $\sim$ at the level of $\mathscr{M}_p(PT)$. The 'principled' version of the link can thus be characterised as:

$$L_2^p = \langle \mathscr{M}_p(\mathrm{QCAI}(a)), \mathsf{M}_s, p_{\sim}, \mathscr{M}_p(PT), \sim \rangle. \tag{8.17}$$

It is hard to give a precise interpretation of the link. Even in the simple *Aufbau* model the link is a causal correlation, and there is no direct relationship between chemical similarity and the 'outer electron configuration'. At the levels of more intricate models of quantum chemistry, this does not get clearer, and giving precise formal definitions gets harder with the improvement in the level of quantum chemical treatment. Part of the problem is that chemical similarity itself is not clearly defined and is based on a number of atomic characteristics or characteristics of chemical elements such as chemical valence, spectroscopic information, or a periodicity in various properties such as atomic volume, melting and boiling points and the like. None of these regularities are moreover strictly speaking exceptionless.

For many specific properties that regulate chemical similarity it is however possible to find a correlate in the atomic theory. The problem is that these correlates are not universal. Hence while it is fairly straightforward to formally construct a link between the *Aufbau* model and a model of chemical valence (something we will discuss in the next section) the nature of this link is best characterised as a theory in its own right, drawing equally from both chemistry and physics.

8.3.5 Reducing the Periodic Table

We now consider the relationship of the periodic table and quantum chemistry *qua* instance of reduction. We will first discuss the issue of *Aufbau* and the chemical theory of the atom, and then consider the reduction relationship from the perspective of the substance of the reduction relation, the issue of derivability and the issue of theory correction.

The links functioning as the reduction postulates have already been specified as the two links that identify the physical system of a nucleus with an electron cloud as the quantum chemical notion of an element and the link specifying the concept of ‘chemical similarity’ on the basis of either a highly approximate notion of the wavefunction, or in terms of a more nebulous ‘similarity index’ as discussed by Borgoo et al. (2004).

The reduction thus seems possible in terms of an ‘unprincipled’ atomic theory in which we have *Aufbau* and hence a fairly *direct* interpretation of chemical similarity, as well as in terms of a ‘principled’ version of atomic theory in which we cannot specify chemical similarity in terms of such notions as ‘valence’ or ‘electron configurations’.

We can now investigate which of the reductive claims of Chap. 6 obtain in the present reduction, in both the principled and unprincipled form of the theory.

8.3.5.1 Unprincipled Atomic Theory

The key elements of unprincipled atomic theory are the separation into a ‘core’ and ‘valence’ set of electrons, and the distinguishability of the electrons. The ‘unprincipled’ version of atomic theory is the main one we discussed in Hettema and Kuipers (1988, 2000). In this section, I briefly discuss how successful unprincipled atomic theory is as a potential reducing theory of the periodic table.

IA (Preservation of intended applications) The intended application of the periodic table is the periodicity in chemical behaviour, which is captured in the periodic table itself. The class of intended applications of unprincipled atomic theory is much wider, and includes, among other things, also theories of chemical bonding (see next section). So while the reduced theory (the periodic table) still has the same intended application, the reducing theory has a wider range of intended applications.

L (Law preservation) In a simple sense, the periodic law is preserved in the sense that it can be derived from unprincipled atomic theory. The periodic law, as we formulated it in SPL is preserved in the sense that period lengths are indeed multiples of $2n^2$ for some n.

Unprincipled atomic theory *explains* why this is so. However, stronger versions of the periodic law, such as the Madelung rule, can be *formulated* in terms of atomic theory, but not *explained*. As was pointed out in the formulation of SPL, SPL may also be fruitfully considered a regulation of 'triads', which can be used in elaborating specific aspects of the table and the placement of particular individual elements.

The partial explanation of the table with the assistance of atomic theory has led to an ontological change. As Scerri (2009) points out, the development of atomic theory shifted attention from the periodicity of the *macroscopic* properties of elements to the properties of neutral atoms.

D (Preservation of specialisations) The only specialisation of interest is the case of 'triads'. Generally, in the case of unprincipled theory, triads are preserved, though it has been suggested by Scerri (2008, 2009) that triads could be used in a meaningful way to alter the shape of the periodic table.

E (Deductive connection of empirical claims) The empirical claims of the periodic table are about periodicity in the properties and valence of the chemical elements, and unprincipled atomic theory does provide a partial and local rationalisation for valence. However, unprincipled atomic theory does not provide a rationalisation for the periodicity of the *macroscopic* properties of the elements (such as melting points for instance), and therefore only fulfils this condition partially.

CR (Content Restriction) Content restriction refers to the capability of a theory to 'correct' the reduced theory. Since the form and shape of the periodic table is still to some extent open and changing, partly under the influence of attempts to explain the periodic table in terms of quantum theory, the criterion of content restriction is satisfied.

8.3.5.2 Principled Atomic Theory

Somewhat surprisingly, principled atomic theory is a weaker theory of reduction on the criteria: specifically, principled atomic theory does not support the criteria of law preservation, deductive connection of empirical claims and content restriction as strongly as unprincipled atomic theory.

The support for the condition of *L (Law preservation)* is weakened. As the work of Borgoo et al. (2004) illustrates, there are no strong indications for periodicity in terms of a similarity of the electronic structure unless we consider a '*differential*' electronic structure in which the density of the preceding noble gas is subtracted from the density before the similarity is calculated. Principled atomic theory does not allow for a *correlation* between a particular *Aufbau* structure and the placing in the periodic table. Hence the claim that the periodic table can be *derived* from principled atomic theory is somewhat tenuous. Similarly, stronger versions of the periodic law, such as the Madelung rule, have so far not been derived from principled atomic theory.

E (Deductive connection of empirical claims) Principled atomic theory does not allow for the separation of 'valence' and 'core' electrons and does not support *Aufbau*. However, principled atomic theory does allow for the calculation of bonding, and a subsequent *interpretation* of its results in terms of an *Aufbau* model. This step however requires the re-insertion of a variety of unprincipled atomic theory 'in between' the calculation and the explanation.

CR (Content Restriction) Content restriction is similarly weakly satisfied. Principled atomic theory does not influence refinements of the periodic table without the intervention of some form of unprincipled atomic theory. The latter serves as a model which provides the interpretation of the periodic table in terms of a model of the theory of the atom.

Hence we have arrived at an interesting conundrum: on the one hand the 'unprincipled' theories of the atom are relatively successful in providing explanations of the regularities observed in the periodic table, while on the other hand more 'principled' theories struggle to provide that kind of conceptual clarity, and need the intervention of 'unprincipled' theories of the atom to provide the required explanatory power. My suggestion, to be fully developed in Sect. 9.3, is that the explanation proceeds via a 'composite' theory, in which aspects of both theories interact to form an explanatory basis for the periodic law.

8.4 Example 2: The Chemical Bond, Bonding and its Physical Basis

A second example of interest is the theory of the chemical bond. The example of the chemical bond is similar in that it involves both a highly specialised form of quantum chemistry to explain chemical laws and phenomena, as well as various identifications and links similar to those made in the reduction of the periodic table.

To discuss this theory, we focus on quantum systems with two nuclei ($N = 2$), which, as in the previous case, are specialisations of the general theory, and specialise this further to discuss in detail the models of H_2. This is a simple system that displays most of the complexities of the relation, and which can be generalised for more complex cases.

8.4.1 Prerequisites

We discussed some aspects of the philosophy of chemistry and the explanation of the chemical bond, focusing especially on the simple H_2 bond in Chap. 2, and discussed the example of aromaticity in Chap. 5. For the present discussion, we will focus on bonds between diatomic molecules. In Chap. 2 we discussed the MO and VB construction of the bonds, and noted that successive improvements on these models eventually yielded the 'exact' solution (in terms of either full CI or a mix of valence bond and ionic structures). We refer to that chapter for further details.

One problem with the formalisation of the chemical bond is that it is poorly understood what makes a particular type of bond a 'chemical' bond (as opposed to for instance a van der Waals interaction). For Bader (1990, 2009) there is something suspect about the concept of a chemical bond altogether: there are bonds and bond-paths, but no special category of 'chemical' bonds. For Bader's theory, the density is the foundational aspect of the bond.

The chemical bond is another one of the examples where the simpler theories of quantum chemistry (i.e. those with the more severe approximations) seem better suited to discuss classes of bonds and types of molecules.

Our discussion of the chemical bond ignores the effects of the basis set (cf. Sect. 7.3.1.4 on p. 172). Specifically, we deal with orbitals centered on the nuclear positions directly. The reason for this is that a consideration of the basis set in this discussion would add complication without much benefit: the reductive relation that we wish to show can be argued on the basis of the concept of an 'orbital'.

In Chap. 2 we discussed the chemical bond as an idealisation concretisation pair with a domain join, arguing that the MO and VB models of the chemical bond initially represented two different idealisations of the bond which were each representative of a specific domain of phenomena. Respective concretisations of these theories, consisting of adding additional refinements, yields the same theory for both the MO and VB approach.

In this section, we will investigate this situation formally and focus on the H_2 bond. While this is a significant restriction in terms of the molecular systems we consider, the (formal) aspects of this situation are general, and the theory we discuss for the special case of the H_2 bond can be generalised.

8.4.2 Molecules and Models

In order to specify the explanatory structure of bonding in more detail, we first have to specify the set of models for a molecule. To simplify, we will take as a molecule a substance of known chemical composition with a determinate spatial structure, which we specify as $\mathscr{M}_p(M)$ in the following manner.

E is a set of chemical elements that form part of the composition of the molecule M. A function n specifies the number of atoms of a particular element in the molecule: $n : \mathbf{E} \rightarrow \mathbb{N}^+$. We then define an expanded set **X** in which each element from **E** occurs $n(e)$ times. **X** is therefore a labeled set of the 'atoms' that occur in the molecule. For instance, for the water molecule H_2O, $\mathbf{E} = \{H, O\}$ and $\mathbf{X} = \{H^1, H^2, O^1\}$. It is also useful, though redundant, to assign a *type* to elements of **X** such that $T : \mathbf{X} \rightarrow \mathbf{E}$.

An obvious constraint on this type assignment is that two identical elements are of the same type. We may take the 'type' as a mapping between an atomic symbol and a number, similar to Table 7.1.

A location function L assigns a position $\mathsf{r}(x) = \mathsf{x}(x), \mathsf{y}(x), \mathsf{z}(x)$ to each element of $\mathbf{X}$, or $L : \mathbf{X} \to \mathbb{R}^3$. We furthermore define a set of molecular properties P which contains the measurable properties of the molecule.

With these definitions, the structural definition for a molecule becomes:

Definition 5 (Definition of a molecule) The structure $x \in \mathscr{M}_p(\mathrm{M})$ is a structural definition of a molecule iff $x = \langle \mathbf{E}, \mathbf{X}, n, T, L, \mathsf{P} \rangle$ such that

1. $\mathbf{E}$ is a set of chemical elements;
2. $\mathbf{X}$ is an 'expanded' (atomic) set of chemical elements which contains all the atoms that constitute the molecule;
3. $n : \mathbf{E} \to \mathbb{N}^+$ is the number of 'occurrences' of a chemical element in a molecule;
4. $T : \mathbf{X} \to \mathbf{E}$ is the type of the atom (i.e. a specification of its chemical element);
5. $L : \mathbf{X} \to \mathbb{R}^3$ assigns a location to each atom;
6. P contains the measurable properties of the molecule.

From this general definition we may define a special case of the H_2 molecule as follows. We specify the molecule $m = H_2$. Then $\mathbf{E}$ is $\{H\}$ and $n(m) = 2$. The expanded set $\mathbf{X} = \{H^1, H^2\}$ and the type is assigned through $\forall a \in \mathbf{X} : T(a) =$ 'H'. The location function can be defined as $\mathsf{r}(x_1) = (0, 0, z)$ and $\mathsf{r}(x_2) = (0, 0, -z)$.

Of course, as part of the specification of the links, there is a link between this concept of a molecule and a frame.

8.4.3 Formalisation of the Chemical Bond

The frame we will consider in this section is the diatomic frame, which is characterised by the specification of the two atomic nuclei as well as the inter-atomic distance R. Thus, in the construction of our reconstruction of the chemical bond we immediately have to consider a *specialisation* of the general structure to discuss a particular case.

This is a general situation in the formalisation of quantum chemistry, since each individual frame can be constructed as a specialisation 'theory' of the more general theory.

8.4.3.1 Potential Models of the Hydrogen Bond

To construct the specialisation for the hydrogen bond, we consider a specialisation structure $\mathscr{F} = \langle \{\mathsf{R}_A, \mathsf{R}_B\}, \{Z_A, Z_B\} \rangle$ where we place the origin on the centre of mass of the frame and the inter-atomic bond along the z-axis. The coordinates of the two nuclei are $\mathsf{R}_A = (0, 0, z)$ and $\mathsf{R}_B = (0, 0, -z)$ so that $R = 2z$ is the intermolecular bond distance. The bond vector is indicated by R. The nuclei are both hydrogen ($Z = 1$) nuclei, so the 'charge vector' is $\binom{1}{1}$. We can treat this as implicit in the remainder.

The specialisation of the electronic structure is a set $P(2)$ of 2 electrons with an associated wavefunction Ψ with electronic coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$ and spin coordinates σ_1 and σ_2. We define a wavefunction and measure set in the usual fashion as in Chap. 7.

While we will not consider the effects of a basis set in detail, we need a set of orbitals to do the future construction of the wavefunction. We define a set of orbitals ϕ_A and ϕ_B centered on nucleus A and B respectively. We will furthermore provide a simplification in the assumption that both ϕ_A and ϕ_B are the ground state $1s$ orbitals of the hydrogen atom. We define a set $B = \{\phi_A, \phi_B\}$ as a set of orbitals corresponding to the ground state orbitals of the hydrogen atom for atoms A and B. This is again a simplification without loss of generality.

The wavefunction Ψ of the overall molecule is a two-electron function formed from functions in the set B and a set of spin functions following the usual rules of quantum mechanics for fermions. In usual fashion, the function is written as a product function of a spatial function Φ and a spin function Θ, $\Psi = \Phi(\mathbf{r})\Theta$.

The spatial wavefunction is defined as a sum of product functions of elements of B, let us label them b_i and b_j:

$$\Phi(r_1, r_2) = \sum_{i,j} c_{ij} b_i(r_1) b_j(r_2). \tag{8.18}$$

The spin functions of interest are the two-electron spin functions $\Theta_2^{(S,S_M)}$ where S is the total spin with possible values $S = \{0, 1\}$ and M_S has possible values $-1, 0, 1$. The restriction is due to the fact that we only consider two particles with spin $\frac{1}{2}$. As we will see in the section on models, specific choices for the wavefunction then in turn correspond to choices in the parameters c_{ij}.

We can define a potential model of the chemical H_2 bond simply as follows:

Definition 6 x is a potential model for the bond in the hydrogen molecule ($x \in \mathscr{M}_p(H_2)$) iff $x = \langle \mathsf{R}, P(2), \mathbf{r}_1, \mathbf{r}_2, \Theta_2^{(S,M_S)}, \Psi(1,2), B, \mathsf{M}\rangle$ such that

(1) R is the position vector of the nuclei;
(2) $P(2)$ is a set of two electrons;
(3) $\mathbf{r}_1, \mathbf{r}_2$ are the position vectors of the two electrons;
(4) $\Theta_2^{(S,M_S)}$ is the overall spin function (restricted to $S = \{0, 1\}$ and possible values for $M_S = -1, 0, 1$);
(5) $\Psi(1, 2)$ is the overall wavefunction, restricted to two electrons $(1, 2)$;
(6) $B = \{\phi_A, \phi_B\}$ is a set of orbitals corresponding to the ground state orbitals of the hydrogen atom for atoms A and B.

M is the set of observables associated with the wavefunction.

8.4.3.2 Models of the Hydrogen Bond

The detailed specification of the models is limited to H_2. The wavefunction we consider will be both the MO and VB wavefunctions discussed in Chap. 2. Hence we create an 'MO' model and a 'VB' model. The distinction between the models is the construction of the wavefunction. We will specify an MO and VB wavefunction as in Chap. 2.

Neglecting normalisation, we define the VB function as

$$\Phi_{VB}(1,2) \propto [\phi_A(1)\phi_B(2) \pm \phi_A(2)\phi_B(1)] \tag{8.19}$$

and the MO function in terms of a bonding

$$\Phi_b(1,2) \propto (\phi_A + \phi_B)(1)(\phi_A + \phi_B)(2) \tag{8.20}$$

and an anti-bonding function

$$\Phi_a(1,2) \propto (\phi_A - \phi_B)(1)(\phi_A - \phi_B)(2). \tag{8.21}$$

The functions Φ_a and Φ_b can be expanded in terms of the basic functions which are elements of B. The two choices of wavefunction thus consist of specific choices in the coefficients c_{ij} in Eq. (8.18). These functions have to be combined with the spin functions so that the total wavefunction Ψ is anti-symmetric under permutation: $\Psi(1,2) = -\Psi(2,1)$.

This choice in coefficients in turn 'generates' two classes of models, one for each theory: $\mathscr{M}_{\mathrm{VB}}(\mathrm{H}_2)$ and $\mathscr{M}_{\mathrm{MO}}(\mathrm{H}_2)$.

The 'measure sets' defining the properties M are in turn 'generated' by the wavefunctions, and contain, for instance, the binding energy, spectra, densities and the like.

It should be noted that this method of constructing the models can be generalised in the sense that it is equally possible to define CI, CC and the like functions in terms of this structuralist characterisation of the chemical bond, since these functions correspond to a different choice of parameters c_{ij}, with the constraint that the overall wavefunction remains antisymmetric. The latter condition places a restriction on the relative signs of the coefficients c_{ij}. These cases are not very interesting for the simple case we consider here, but become complex very rapidly with more complex basis sets and molecules.

Molecules different from H_2 can be treated by introducing more functions into the set B and constructing more complex wavefunctions. While this leads to more complex equations and models, the H_2 molecule is capable of illustrating the relevant relations and links.

8.4.3.3 Partial Potential Models and Intended Applications

We can define a partial potential model of the chemical H_2 bond as follows:

Definition 7 x is a partial potential model for the hydrogen bond ($x \in \mathscr{M}_{pp}(\mathrm{H}_2)$) iff there are $x = \langle \mathsf{R}, \mathsf{M} \rangle$ such that

(1) R corresponds to the inter-atomic distance parameter;
(2) M is the set of observables associated with the wavefunction.

This seems (and is) a thin definition. The empirical claim is that the intended applications of quantum chemistry are a subset of the (restricted) models: $I \subseteq r(\mathscr{M})$.

While this empirical claim is fulfilled, it only allows for a set of crude characterisations of the intended applications. As already discussed in Chap. 2, in some of these aspects the MO and VB theory were radically different. Initially the theories were developed to provide a clear and direct interpretation in terms of 'intended applications'. For instance in London (1928) the VB theory was extended to provide an account of chemical valence, which was seen as a somewhat surprising byproduct of the description of the H_2 bond in Heitler and London (1927), while the MO theory, as in Hund (1927), provides an explanation for the phenomenon of molecular spectra with MO theory. But then both these theories were developed further. As described in Chap. 2 eventually the further concretisation of the models of the MO and VB theory in terms of configuration interaction and 'ionic structures' led to the same model for the H_2 molecule.

Interestingly, in addition to the *direct* intended applications, there is also a considerable set of *inferred* observables of the theory, such as equilibrium bond length, molecular diameter and the like, which correspond to a theory about a set of sets $\{\mathsf{M}\}$. This notion of 'inferred' observables is interesting in its own right: it implies that for a set of models calculated at different electronic distances other measurable factors may be *inferred* with the help of theorems or notions that are not strictly part of quantum theory itself, but rather form part of a 'composite' theory, consisting of a *physical model* of a molecule to which quantum theory provides a set of necessary parameters. Specifically, using such external notions, a form of deductive connection of empirical claims is possible.

This can be represented as follows. A set of observables may be defined on the basis of a *set* of (partial potential) models $\{x_i | x_i = \langle \mathsf{R}_i, \mathsf{M}_i \rangle\}$. A further theory is constructed on the basis of this set $\{x\}$ with the help of a set of external (theoretical) notions $\{t_e\}$, drawing on mechanical concepts of the molecule which are part neither of 'pure' quantum theory nor chemistry, and are applied to a physical 'model' of the molecule. The idea is thus that the individual results of quantum chemistry, the $\{x_i | x_i = \langle \mathsf{R}_i, \mathsf{M}_i \rangle\}$, form a 'theoretical basis' upon which further models of the molecule may be constructed. The development of such further models may take a number of forms, of course, and the formulation of the composite theory, as well as the source of the theoretical notions $\{t_e\}$ is a problem in its own right, which we will discuss in more detail in Sect. 9.3.

Two examples are of particular interest. The first example is that of an 'equilibrium' bond length. With the help of the Born-Oppenheimer approximation this can be derived as the point where the first derivative of the intermolecular bond energy is zero (Cf. Eq. (3.12)). Born and Oppenheimer describe this criterion as an *existence* criterion for the molecule, and it is a requirement for the validity of the approach.

To calculate the equilibrium bond length in practice one calculates a set of partial potential models $x_i \in \text{Pot}(\mathscr{M}_{pp})$ and finds the point where the energy of the system is a minimum. This point is designated as the equilibrium distance.

The second example is that of bonding. In the case of the MO theory the MO diagrams calculated at various inter-atomic distances allow, via the concept of *Aufbau*, for the calculation of MO correlation diagrams, which can be used in a theory of chemical bonding. The construction and use of such diagrams is described in, for instance, Van Vleck and Sherman (1935), or Eyring et al. (1944, Ch. XI) and has been discussed from the viewpoint of a 'token' versus 'type' reduction by Woody (2000).

A third class of inferred properties is formed by the 'atoms in molecules' approach of Bader (1990). This approach takes the properties of the density as the key property from which molecular properties may be inferred.

The classification of these properties as 'inferred' allows us to make sense of Woody's conundrum. The 'inferred' properties are derived with the help of models and theorems which are *outside* the theory itself, such as for instance the notion of an 'equilibrium distance' or an orbital correlation diagram. The resulting models are specific models built on *top* of the set of partial potential models of the theory.

These inferred models allow for a chemistry that is concerned with more than measurements, and can introduce concepts such as equilibrium distance, molecular symmetries and spectra, and the occurrence and nature of a bond between compounds (as opposed to atoms). Rather than featuring as individual tokens, quantum chemical theories are most useful in terms of a theoretical 'basis' upon which such further models may be constructed.

The situation is depicted in Fig. 8.2. The consequence of this for the issue of reduction is that reduction becomes a *local*, rather than *global* affair. While the necessary links do exist between the various levels of theory, they exist between versions of theory and observation that have a somewhat limited local range of application. When it comes to explanation, chemists have a somewhat promiscuous attitude, taking advantage of a range of theoretical and experimental solutions on offer.

In the next section we will discuss some of these local reduction relations in more detail.

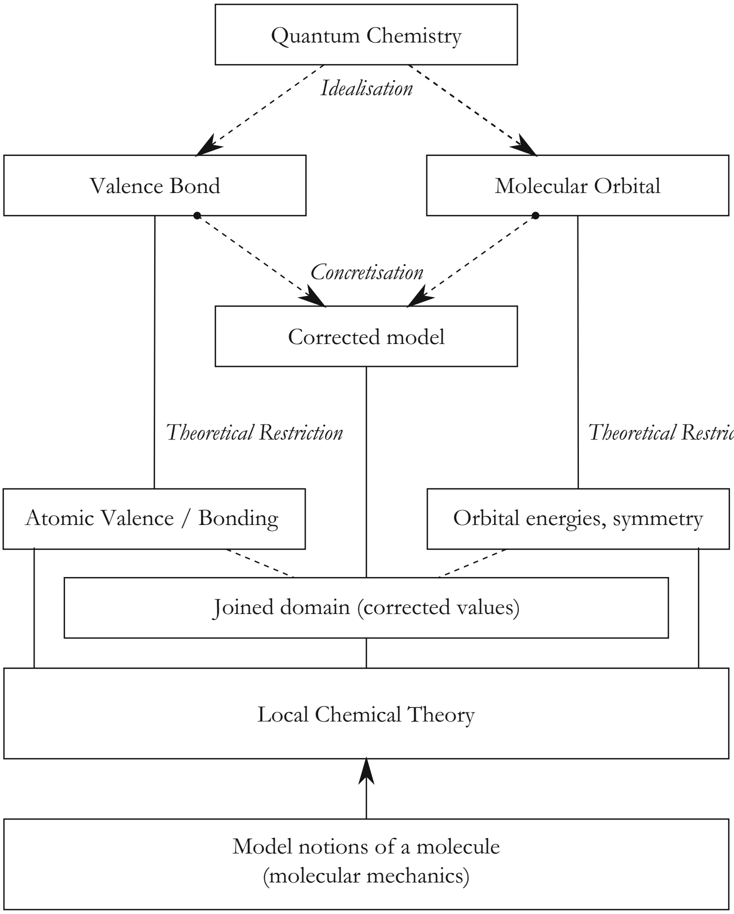

Fig. 8.2 Explanation of bond formation with quantum chemistry: apart from the various models introduced in quantum chemistry, and the domain joins discussed in Chap. 2, a number of mechanical models of the molecule are introduced to go from individual quantum chemical calculations to a 'model' of the molecule

8.4.4 Reduction of the Chemical Bond

We now turn to the topic of the reduction of the chemical bond. The specification of this reduction relation will consist of a number of *local* claims with regard to the reduction, whereas the issue of the unity of science (or global / branch reduction) can only be discussed after the local reduction relations have been sufficiently specified. The first aspect of the reduction is the specification of the necessary links, the second aspect is the discussion of the reduction itself.

8.4.4.1 Links

We first specify the link between a molecular frame and a molecule:

$$L_1 = \langle \mathscr{F}, \langle \mathbf{Z} \rangle, \mathscr{M}_p(\mathrm{M}), \langle \mathbf{X}, T \rangle \rangle \quad \text{where} \quad T(\mathbf{X}) = \mathbf{Z}. \tag{8.22}$$

The link specifies an identification of the type of element with an atomic number, which is interpreted in terms of the (positive) charge of the nucleus. This link therefore forms part of the application step of the reductive scheme.

Furthermore, one might expect that his link should state that a 'molecule' is linked to a molecular frame through the specification of a molecular *shape* R. A frame is generally a wider concept than a molecule, and a general connection between a molecular geometry and a frame is not possible: the frame may specify any geometric structure without this necessarily having to be a 'molecule'. For some cases, where for (local) reasons we want to make an identification between a shape and a specific molecule, it could be useful to consider an amended link which does include a connection between shape and location:

$$L_1' = \langle \mathscr{F}, \langle \mathsf{R}, \mathbf{Z} \rangle, \mathscr{M}_p(\mathrm{M}), \langle \mathbf{X}, L, T \rangle \rangle \quad \text{where} \quad L(\mathbf{X}) = \mathsf{R} \quad \text{and} \quad T(\mathbf{X}) = \mathbf{Z}. \tag{8.23}$$

One special case is the geometric 'equilibrium' shape R_e; another one, to be discussed in the next section, is the 'transition state' $\mathsf{R}^{\ddagger}$. As discussed, this equilibrium configuration is an inferred property on the set M, and is different for each level of approximation (formal specialisation) of quantum chemistry, and hence the equilibrium configuration is captured in the property link specified below.

The remainder of the links are specified in terms of the relation between the measure set M of quantum theory and the set P of molecular properties in terms of a function f which relates observables from the quantum theory to the properties of the molecule:

$$L_2 = \langle \mathscr{M}_p(\mathrm{M}), \langle \mathsf{M} \rangle, \mathscr{M}_p(\mathrm{M}), \langle \mathsf{P} \rangle \rangle \quad \text{where} \quad f : \mathsf{M} \to \mathsf{P}. \tag{8.24}$$

The first part of the link is a straightforward identification. Here f is in general a complex function, which is given here only in its simplest form. More complex formulations of f may involve combinations of measurables leading to a property $\mathsf{p} \in \mathsf{P}$, for example

$$f : \mathsf{M} \times \mathsf{M} \to \mathsf{P}.$$

This definition leaves room for the 'inferred' molecular properties that are not directly representable as measurements from quantum theory.

The differences in explanatory aim of the two approaches to the chemical bond manifest themselves in the links. The MO theory captures the concept of chemical bonding in terms of orbitals and orbital correlation diagrams, the VB theory captures the notion of chemical bonding in terms of valence. We now briefly discuss the 'direct' links to MO theory and VB theory (the links that do not include inferred properties).

Links to MO Theory

The link to MO theory is based on the following structural connections. MO theory considers the structure of the wavefunction expressed in molecular orbitals, which (spatially) extend over the entire molecule. Associated with this set of molecular orbitals is a set of orbital energies and orbital symmetries. Electronic spectroscopy can be explained with the help of these two quantities. This link in addition enables a theory of bonding in which orbitals of increasing energy are gradually filled with electrons, supporting an *Aufbau* model of the chemical bond.

It is thus useful to define a set M_o which defines the set of measures from MO theory as a set of orbital energies $\{\varepsilon_i\}$ and a set of symmetry properties $\{s_i\}$; usually for an orbital i these appear in a pair $\langle \varepsilon_i, s_i \rangle$. We then define

$$\mathsf{M}_o = \{\langle \varepsilon_i, s_i \rangle\}. \tag{8.25}$$

Note that this set M_o cannot be linked directly to a set P of observable properties of molecules. While the set P remained largely unspecified in Sect. 8.4.2, P was defined as a set of 'measurable' properties and both orbital energies and orbital symmetries are not directly measurable. Instead they feature in a further theory about the appearance of molecular spectra.

The empirical claim of MO theory is that the set of intended applications is a subset of the partial potential models of the theory, which is certainly the case. The set of intended applications is a pragmatic concept, and can (somewhat crudely) be represented by M_o in the present context. As discussed, the set M_o can in turn be used in a further model of the molecule, in which measurable properties such as equilibrium bond lengths and bonding can be discussed with the *Aufbau* model.

Links to VB Theory

The specification of the link in the case of VB theory has a highly localised character, and in many ways involves specific theories of chemistry. The following aspects are important.

The VB theory requires a link between the phenomenon of chemical bonding to the 'valence' of the elements that constitute the molecule. In turn, valence is interpreted in terms of the atomic wavefunction as the number of 'unpaired' electrons, but is determined an ad hoc and local version, with the placement of an element in the periodic table also playing a role. It is thus hard to precisely connect the type of an element to its valence. In the case of the hydrogen atom, the valence is (somewhat trivially) 1.

A formal specification of the link for general cases is the following. Consider a subset M_b of M which contains the 'bonding' properties calculated with a VB wavefunction. This subset is then related, in an unspecified fashion, to the 'valence' associated with the type of element that constitutes the bond, and thereby to the type. Formally:

$$L_2^{\mathrm{VB}} = \langle \mathscr{M}_p(M), \langle \mathsf{M}_b \rangle, \mathscr{M}_p(\mathrm{M}), \langle \mathbf{X}, T \rangle \rangle \quad \text{where} \quad f_v : \mathsf{M}_b \rightarrow T(X) \times T(X). \tag{8.26}$$

This definition, however, adds formal complexity without much enlightenment. In general we would be interested in its inverse, leading from 'types' of molecules to the 'bonding types'.

In the general case of VB theory, the link furthermore has a principled and unprincipled version. The unprincipled version makes certain assertions about the number of 'unpaired' electrons in the element, hence, it imposes a different restriction in some M of an 'atomic' system to a 'number of unpaired electrons'. The number of unpaired electrons is determined based on guidance from the periodic table and its interpretation in terms of the *Aufbau* model.

Further modifications of the link may also include Pauling's notion of 'hybridisation', which can be formalised as an equivalence relation on the level of the formal model of the chemical element.

8.4.4.2 Reduction

I now consider the reduction relationship from the perspective of the substance of the reduction relation, the issue of derivability and the issue of theory correction.

A first conclusion is that reduction relations exist in a local, as opposed to a global, fashion. We have introduced a difference between 'direct' and 'inferred' properties, and have noted that the latter have an interdisciplinary character. Hence, as also argued by Harris (2008), the explanation has an interdisciplinary structure, in which the results of quantum calculations are used in the further construction of molecular models. These interdisciplinary models will be discussed in the next section.

The detailed consideration of the local reductions does allow us to specify the structure of this interdisciplinary relationship in greater detail. Some brief remarks follow.

IA (Preservation of intended applications) The explanations in terms of both VB and MO theory are not capable of entirely preserving the intended applications of the theory of the molecule. Instead, these theories focus on aspects of the molecule, for instance spectra or the valence / bonding structure, as opposed to a theory of the molecule as a whole. The remainder of intended applications is generated via the *inferred* properties, and these do indeed preserve the intended applications, though with the assistance of an intermediate or interfield theory (see below).

L (Law preservation) As an extension of the points made above, law preservation (derivability) holds only in a local sense, and comes in a qualitative and quantitative variety. MO and VB theory are capable of deriving *aspects* of the theory of the molecule, whereas the derivation of *inferred* properties makes the argument partially circular: some of the 'molecular mechanics' steps that are introduced in the derivation of the 'inferred' properties are in turn based on the theory of the molecule itself.

D (Preservation of specialisations) There are no specialisations of interest in the theory of the molecule, and this criterion remains for the present case undecided.

E (Deductive connection of empirical claims) Deductive connection of empirical claims does not hold: there are a number of empirical claims in the quantum theory of the molecule which do not have a counterpart in the theory of the molecule, for instance the explanation of molecular spectra. This was an explicit aim of the MO theory of the molecule, which is unique to this theory.

CR (Content Restriction) The condition of content restriction applies in the sense that progressively advanced quantum theories 'correct' the models of the molecule progressively, though in important measure through 'inferred' properties. As illustrated in Chap. 2 and Sect. 8.4.3.3, the construction and refinement of a model of the molecule is an indirect affair.

8.5 Example 3: Reaction Rates

The structure of the network for the theory of absolute reaction rates was sketched in Chap. 4. In the remainder of this chapter, I wish to be brief about the establishment of links for reaction rates, and outline the two key salient points. In the discussion of the structure of reaction rate theory we can draw on the work done in the previous section on chemical bonding to a large extent.

The first key notion to draw out is the approximate nature of the model of chemical bonding that underlies the potential energy surface and with it the idea of an 'activated complex'. Eyring's notion of 'semi-empirical' quantum chemistry (p. 75) adds further revisions onto ab initio quantum chemistry by specifying a distinction between 'core' and 'valence' electrons which is unprincipled from the viewpoint of ab initio quantum mechanics, but necessary from the viewpoint of practically implementing the theory without the help of a computer.

This step is a further restriction on the links we discussed for the chemical bond above, primarily in the sense that the quantum *system* is further restricted to a set of 'active' valence electrons, and the substitution of emprical values for some elements of the (usually computed) set $\{\langle \varepsilon_i, s_i \rangle\}$ to facilitate easier overall calculation of the potential energy surface.

The connection between statistical mechanics and transition state theory is made by calculating the partition functions of the reactants. The definition of the 'transition state' is obtained by eliminating, from the partition function of the activated complex, the translational component due to the motion along the reaction coordinate (see Glasstone et al. 1941, p. 189).[9] This separation step is made through

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[9] A detailed discussion of why this is so falls outside the scope of this paper, but can easily be determined by stepping through the mathematics.

the addition of a 'special law' on statistical mechanics. Moreover, this 'special law' characterises the 'transition state' precisely in terms of its degrees of freedom.

The 'transition complex' as defined here is a combination of a *structural* notion of a type of molecule together with a modified sum of states which captures its thermodynamic state. This structural notion of a transition state that is amenable to investigation in terms of its potential energy surface topology. Through this specification, the notion of 'transition state', the 'saddle' point on the reactive potential energy surface, can be specified as a 'special law' on top of 'ab initio' quantum chemistry.

In what follows I will outline the special 'law' in terms of a structural restriction on the link (very similar to the 'equilibrium' structure discussed in Eq. 8.23) in the sense that the 'transition state' is a particular type of structure:

$$L_1'^{\ddagger} = \langle \mathscr{F}, \langle \mathsf{R}, \mathbf{Z} \rangle, \mathscr{M}_p(\mathrm{M}), \langle \mathbf{X}, L, T \rangle \rangle \quad \text{where} \quad L(\mathbf{X}) = \mathsf{R}^{\ddagger} \quad \text{and} \quad T(\mathbf{X}) = \mathbf{Z}. \tag{8.27}$$

What turns a particular structure into an 'activated complex' or 'transition structure' is however a matter that is not decided at the level of the quantum theory of the atom – the designation is a structural characterisation on the possible set of geometries $\{\mathsf{R}\}$ determined by the local geometry of the (energetic) potential energy surface. It should be easy to see that $L_1'^{\ddagger} \subset L_1'$. The specific structure $\mathsf{R}^{\ddagger}$ is specified as the 'transition structure'; i.e. the point where the potential energy surface of the complex has one 'free' translational motion. The potential energy surface itself is a function of the molecular energy for different geometrical arrangements of the nuclear frame, i.e. in terms of a link L_2 between a 'molecule', its 'energy' and geometrical arrangement, which is again similar to their counterpart in the problem of bonding:

$$L_2 = \langle \mathscr{M}_p(M), \langle \mathsf{M}_b \rangle, \mathscr{M}_p(\mathrm{M}), \langle \mathbf{X}, T \rangle \rangle \quad \text{where} \quad v : \mathsf{M} \to V(\mathsf{R}). \tag{8.28}$$

i.e. the function v plays the role of a 'potential energy' function which maps the system onto a potential energy surface.

The second key feature of the theory of absolute reaction rates is that it facilitates *interpretations* of thermodynamic and molecular mechanics concepts in terms of micro-physics, and hence illustrates how especially a mechanical, but dynamic, picture of a molecular reaction can emerge in terms of the movements in a molecular frame. This aspect is harder to model. The comparisons between the thermodynamic, collision and 'absolute' theories are at this stage difficult to determine, since detailed structuralist characterisations of these theories are not readily available. However, one would expect that these characterisations will yield similar insights.

This section has not provided a full characterisation of the (formal) aspects of the theory of absolute reaction rates, but has indicated some directions for future research.

8.5.1 Reduction Postulates

In this secton, I will again focus on how the links discussed above may be evauated *qua* reduction postulates for the early version of the theory of absolute reaction rates, in which the potential energy surface was calculated with the assistance of semi-empirical methods. Nowadays, it is of course possible to calculate potential energy surfaces with high precision *ab initio* methods and forego many of the approximations that are part of semi-emprical theory.

IA (Preservation of intended applications) The explanations for chemical reactions in terms of the various theories do preserve the intended applications of the originating theories, although in some cases with a loss of numerical precision.

L (Law preservation) The steps that are taken in order to make the theory work do not always quarantee the preservation of laws in the originating theories. A good example is for instance the specification of 'valence' electrons in the semi-empirical theory of bonding which breaks a number of fundamental laws of the theory of the atom, notable the law of indistinguishability of electrons.

D (Preservation of specialisations) Similarly, the steps that are taken in order to make the theory work do not always quarantee the preservation of specialisations of the originating theories. A good example is for instance the semi-empirical theory of the atmo which underpins the calculation of the potential energy surface, in which the ab initio calculation of emprical properties, for instance with MO theory, is given up for empirical substitution.

E (Deductive connection of empirical claims) Deductive connection of empirical claims applies in a limited sense: the derivations are strict only on the basis of highly approximate formulations of the reducing theory that themselves introduce inconsistencies the laws of the approximate theory and the laws of the reducing theory. Deduction thus carries a heavy price.

An interesting addition furnished by the theory of absolute reaction rates is that identification / comparison of quantities, e.g. between the thermodynamic theory, the kinetic theory and the theory based on quantum and statistical mechanics play a key role in the understanding of chemical reactions. Rather than a deductive relationship, we have a theoretical identification of quantities from three different theories that effect the explanation.

CR (Content Restriction) Content restriction applies in this case, especially in the sense of conceptual models that assist in the explanation of chemical reaction rates. As an example one can consider the explication of the 'reactive complex' in *structural* terms, which is still in use in quantum chemistry today.

8.6 Conclusion: Reductive Claims in the Structuralist Framework

With these practical examples of reduction in hand, it is now possible to revisit the conundrum mentioned at the beginning of this chapter and place the explanatory structure of quantum chemistry in context. The reduction relation has been reconstructed as a bundle of *local* reduction relationships between specific theories with links that can be specified in detail.

For practical examples in quantum chemistry, the links come in a great number of varieties, and as the section on the properties of the links have explored, there is no single picture that emerges for what happens when we can say that a theory *explains* another law or theory. Thus, when we view putative reductions as (formal) representations of scientific explanation of laws and theories by another theory, there is no clear picture that emerges for what actually constitutes these relationships.

The second conclusion is that we have now detailed information on two cases of inter-theory explanation and have specified, in considerable detail, the inter-theoretic links between these two theories. Our considerations in Chap. 6 can now be evaluated in the light of these three inter-theory relations.

The picture that has emerged from the reduction of these specific scientific theories is that the reduction relations that do obtain are far removed from the simple 'identities' *cum* 'derivation' picture that philosophers of chemistry sometimes associate with Nagelian reduction.

There is room, however, to argue that the relations may fit a suitably relaxed picture of Nagelian reduction, especially one where reduction postulates can take the form of individual theories. This conclusion fits with the view, developed by Dizadji-Bahmani et al. (2010), that the reduction postulates represent matters of fact, and form constitutive elements of the reducing theory. The characterisation of the reduction relationships as links has allowed us to develop a wide range of logical forms for the reduction postulates which reflect this conclusion in formal terms.

In many cases the relations hold only partially or in a local sense. This reflects both the intermediate nature of the 'composite' theory (which will reduce the strength of the reduction from 'full reduction' to 'partial reduction'), as well as the fact that at various points, ad hoc criteria are required to facilitate the reduction. My conclusion is that reductions in chemistry are partial, but that a formal investigation of how these reductions work exactly – using the model supplied in essence by Nagel – is bound to yield interesting insights into the actual workings of scientific theories.

Part III
Ontological Consequences

In Part III I focus on how the structure of chemistry as a network of theories connected by links has a bearing on the ontology of chemistry. The guiding principle in this part of the book is that – perhaps due to my history as a practicing scientist – I find it impossible to see how we can sensibly talk about realism and ontology without an explicit understanding of the science that lies in front of it. Much of the writing on the 'metaphysics side' of philosophy strikes me as expensive grandstanding on the basis of folk-science. As you sometimes hear at conferences: 'but surely it must be the case that ... ' From my perspective, whether something really is the case or not is a matter of science rather than intuition.

So I lay some explicit cards on the table first: 'ontology' in my view is best seen as the end-result of extensional quantification over suitably formalised mature theories, and not as something that one can 'a priori' determine and then impose. In this view, the idea that there is some 'ontology' that is 'prior' to theories is really tantamount to choosing intuitive theories of nature over scientifically robust ones. As a matter of taste and ethics, it is 'not done' to for philosophers of science to lecture or critique scientists on this basis. My overall approach is that I argue for a strongly 'naturalised' epistemology for the philosophy of chemistry in the sense that ontological arguments follow, generally through a process of ontological commitment and ontological grounding, *from* epistemic arguments rather than being *prior* to them.

This finally touches on a topic that in my view needlessly confuses many otherwise fine philosophers of chemistry: ontological reduction. My proposal is that the problems around ontological reduction are best solved in the context of ontological commitment in combination with a notion of 'grounding'. On the view that theories are ontologically committed to their theoretical entities and have a grounding relation to other entities, ontological reduction becomes a function of epistemological reduction. This somewhat austere view on ontology allows us to critically evaluate the notion of 'ontological reduction'.

Summary of Part III

In this part, I have explored the *ontological* consequences of the formal models developed in Part II. I have thereby adhered to a rather strict operational interpretation of ontology: the quantification over suitable formal paraphrases of actual theories. This is a scientists' approach, and alternative approaches are possible. From my point of view, however, these still amount to the same thing: building a chemical ontology on top of, for instance, a mereological framework still entails a subscription to a theory about what is part of what. while such theories are often seen as self-evident or not in need of further defence, in my opinion in practice they may vary rather a lot in how well they are empirically supported. While it might certainly be possible to come to some results this way, I far prefer the road that leads from actual, empirically supported theories to ontological entities.

The problem, which I have merely outlined in this part, is that when it comes to theories of chemistry not only the actual existence of such theories might be in doubt, but moreover, in cases where such theories can specified with sufficient precision, they are highly complex networks of theories, joined by links that are in turn highly selective in the amount and nature of information they convey from one part to the other.

I have argued that such a situation is problematic for some highly simplified theories of ontology, but should be welcomed by those philosophers who argue for more refined models of ontology, such as rainforest realism, 'depth' or engineering. And these may not be the only alternatives. There may be more philosophy to be had.

I firmly believe that the future of philosophy of chemistry lies not in rehashing the old arguments around reference, hard realism or complex arguments based on the quantification of intuitively attractive but ultimately weakly supported notions of what 'surely must be the case'. The future, if it is to be fruitful, will have to consider empirically supported theories of chemistry in their full complexity and pair this with a suitable notion of what a chemical object looks like. In the end, ontologists will just have to learn to put up with that.

Chapter 9
Promiscuous, Interesting and Unsettled: Ontology in the Philosophy of Chemistry

Abstract In this chapter I focus on what the ontological consequences of the reductive framework discussed in Chap. 8 might be. The view from the examples discussed in Chap. 8 is that while formal connections between reduced and reducing theories exist, the matter of 'reduction postulates' in the sense of Nagel is best left to individual scientific cases as a case of scientific theorising rather than stating metaphysical truth. Specifically, the view that these reduction postulates express aspects of interfield theories in the sense of Darden and Maull has some support. This raises questions about the ontology of science as a whole. I argue that ontologies for specific theories are local, but not internal (in the sense of Putnam) affairs. Rather, the formal unity expressed by reduction allows us to speak of one ontology, while the local and specific expressions given to this formal reduction relationship allow us to think of 'objects' featuring in these relations as having 'depth' or 'computational complexity'. In this sense, we can build up a complex view on scientific theories that is both empirically adequate (in the sense of conforming to our best scientific understanding of what such theories look like) and philosophically meaningful (in the sense of specifying what exactly happens when we speak of unity of science or reduction).

9.1 Introduction

Chemistry as a science raises a number of interesting ontological issues, which have led to numerous discussions in the literature.[1] Quite often these ontological discussions are initiated because of a perceived failure of epistemological reduction, especially of the 'austere' type in which reduction postulates are identities. As a result, it is no longer quite clear what chemical entities exactly *are*.

As is apparent from the analysis in Parts I and II, chemical theories are best perceived as networks of theories, which are loosely connected through a variety of means in the form of reduction postulates. This, however, has consequences for the conception of chemistry as a *field*, and, in particular, for the concept of 'chemical' ontology. It is this epistemic situation that creates the ontological

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[1] As examples, see for instance the work by Hendry (2010) and Lombardi and Labarca (2005).

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confusion: chemical ‘theories’, as we have seen, often are a patchwork of disparate theories with various approximations and reformulations along the way. On this epistemic constellation, however interesting it may be, it is hard to evaluate claims of exactly what chemists say there *is*.

Ontologists like their theories simple, and, come to think of it, prefer to not call their ‘theories’ at all. They prefer statements such as ‘the cat is on the mat’ or ‘there is beer in the fridge’ to more complex theoretical statements such as ‘two atoms of hydrogen combine to form a bond’, or ‘the $sp)^3$ hybridisation of the cabon atom gives rise to the tetrahedron shape of CH_4’, believing the first class of statements to be simpler and more easily evaluated. I believe this is a mistake when it comes to evaluating the ontologies for large and complex sciences (such as chemistry). The ‘simple’ statements of apparent empirical fact on which many ontologists base their assessements are in fact better conceived as ‘toy theories’, which in turn rapidly and easily translate into informal, untested, intuitive and quite often plain wrong theories when considering more complex sciences.

My contention is that there is value in starting at the other end by taking the empirical structure of a real science as an input to developing further theories about the ontologies of the sciences through Ramsey sentences. Of all available alternatives, this seems the only way to me in which one can derive a meaningful ontology for a science that is true to that science. I am well aware that this sentiment is not shared universally, and that there are approaches in the philosophy of chemistry that take ontology as prior to epistemology. From the perspective of a practicing scientist, however, I find it hard to defend such approaches. Withhout wanting to pick on specific examples more than is necessary, it seems to me that ontological arguments based on, for instance mereology (see Harré 2009) or combinatorics (see LePoidevin 2005) take *theories* of mereology of combinatorics as their starting point *qua* chemical theories, and then attempt to draw ontological conclusions on that basis. While these theories seem trivially true for a science like chemistry, in practice they are empirically untested, and, from my perspective as a chemist, contestable to a significant degree.

This chapter proceeds as follows. In Sect. 9.2 I discuss my proposed approach to ontologies and realisms taking into account the actual situation in chemistry. In the next section, Sect. 9.3 I evaluate the formal characterisation of theories of chemistry developed in Part II. Section 9.4 discusses some of the more formal aspects of my proposal, especially focusing on Hempel’s ‘Theoretician’s Dilemma’ and the role of unobservables and theoretical terms.

9.2 Ontology and Realisms

From the perspective I am defending here, there is no fruitful ontology without a theory. Hence the development of a scientific theory is prior to the establishment of an ontology – it is the theory that postulates ‘what there is’ in the world, that endows that ‘mere existence’ with properties, purpose and agency, and ultimately it is also a scientific theory, when combined with a set of suitable experiments, that makes these entities existing in the world accessible.

The approach I take towards ‘metaphysics’ is very close to that discussed in Ladyman et al. (2007), who argue that metaphysics needs to be intimately connected to the sciences, and especially to physics.

9.2.1 Motivation: The Problem with ‘Ontological Reduction’

Ontological reduction has been a relatively popular term in the philosophy of chemistry, but not one that is particularly clear[2]. Moreover, ontological reduction is a concept that is somewhat peculiar to the philosophy of chemistry. It was introduced by LePoidevin (2005) with the comment that:

> The thesis of ontological reduction is that properties we would recognize as paradigmatically falling within the domain of chemistry are determined by more fundamental properties. Ontological reduction is not committed to the view that we are already acquainted with these more fundamental properties, nor even that, once acquainted with them, we could successfully derive the chemical properties from the fundamental ones. (LePoidevin 2005, p. 120)

One could parse this comment in multiple ways. Reading LePoidevin as a Nagelian reductionist, ontological reduction may be read as a failure of *derivability* while a form of *connectibility* – which stipulates that the ‘determination by more fundamental properties’ still remains. Alternatively, we might read the statement as a programme, an exhortation to practicing scientists to further elaborate on these ‘fundamental properties’.

The vaguess of the concept, however, suggests that the idea of a prior ‘ontological reduction’ in chemistry is unattractive. The idea of ontological reduction is rooted in the conviction that there are somehow, somewhere, some basic entities where ultimately chemistry and physics are ‘the same’ (even if we seem to be unable to connect the theories themselves). My contention is that this metaphysical project is doomed to fail without the corollary that there must also be a way in which we can

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[2] As pointed out by Needham (2010) the use of the term ‘ontological reduction’ in the philosophy of chemistry was unfortunate. As Needham argues:

> In the philosophy of chemistry literature an unhappy distinction is often made between epistemological and ontological reduction [. . .]. This is unfortunate because although a distinction can be drawn between what the relation itself involves and knowing whether these conditions obtain, the possession of such knowledge does not amount to a kind of reduction. (Needham 2010, p. 169)

The precise meaning of this statement is not entirely clear to me: the statement seems to be somewhat ambiguous in its use of the word ‘relation’, and its precise meaning depends on whether a reduction relation or ontological relation is meant in its discussion of ‘what the relation itself involves’.

relate chemical and physical theories – i.e. some form of inter-theory connection. The notion of 'ontological' reduction is incoherent if there is no epistemological counterpart.

As a starting point, I would suggest that chemistry is in need of an ontology which enables its connection to physics, and which 'reaches out' of its silo with the help of deterrminable (logical and factual) connections. My proposal for such a method to 'reach out' is based on a notion of objects, where various disciplines form 'windows' into objects without each holding the entire and complete true picture of objects. In this sense, objects are opaque and their properties are inferred from the various 'windows' we have into them.

While that is the end-point, it is still necessary to develop the argument. I start with a discussion of various forms of realism, and how these realisms fare in the context of networks of theories.

9.2.2 Realisms

Philosophers being what they are, there are many varieties of realism. In this section I will pick out a representative sample of some of the common varieties of realism – varieties that have a chance of being applicable to chemistry for various reasons. I will focus on scientific realism, internal realism and structural realism.

9.2.2.1 Scientific Realism

Since chemistry is a science, one might expect to see qa form of 'scientific realism' as the best approach to an ontology for chemistry. Michael Devitt (2007) has characterised scientific realism as the realisation that science is committed to the existence of a variety of unobservable entities, in terms of the following theses:

> (SR) Most of the essential unobservables of well-established current scientific theories exist mind-independently.

SR is a thesis about entities, but not about the properties of these entities. Hence, a stronger version of SR is possible, which also includes a 'fact' realism claiming that not only do the unobservable entities exist, they also have the properties attributed to them by our scientific theories. The 'fact' realism then runs as follows:

> (SSR) Most of the essential unobservables of well-established current scientific theories exist mind-independently and mostly have the properties attributed to them by science.

Devitt argues that these theses can in turn come in epistemic and semantic varieties. The epistemic variety claims that a belief in the unobservables of science is justified, the semantic variety claims that (i) the theoretical terms of theories refer to the sort of mind-independent entities featuring in SR and (ii) the theories' statements about its theoretical entities are approximately true.

It is hard to see how we can adhere to a form of scientific realism for chemistry. As we have discussed in earlier parts of this book, chemical theorires are more properly characterised as *networks* of (smaller) theories. As a result, our perspective on the 'essential unobservables' of such theories becomes a composite notion, to which the qualifier 'approximate' applies only with some difficulty. One counter example to a 'hard' realism for chemistry is Paneth's well-known and influential historical disambiguation of the notion of chemical element found in Paneth (1962a,b) which we will discuss in more detail in Chap. 10.

9.2.2.2 Internal Realism

Some authors have suggested that we can conceive of the ontology of chemistry as a form of internal realism. Internal realism was introduced by Putnam (1981). Internal realism is the idea that ontologies are private to the sciences they co-develop with.

Internal realism is, as Lombardi (2014) notes in a critical review on my original thesis, closely related to a Kantian view of objects. On the face of it, internal realism would seem a perfect fit for chemistry: it allows for theoretical discontinuity, which can be translated into ontological discontinuity through the mechanism of ontological commitment. It does allow for a highly pluralistic view on scientific theories, and can match many of the scientific facts well.

My main problem with internal realism as a solution to the conundrum of how chemistry and physics connect is that it places chemistry and physics in respective silo's – each with their own set of theories and ontologies. As a result, for the internal realist, chemistry and physics do not connect at all. My problem with this solution – however neat from the viewpoint of a philosopher of chemistry concerned only with chemistry and nothing else – is two-fold.

In the first place it seems empirically inadequate. Methods of physics are widely used as tools in chemistry and vice-versa. As an entirely 'internal' point of view internal realism has difficulty accounting for that fact. The corollary of this is that using existing disciplinary boundaries as boundaries for realisms seems to me a strange choice – the sciences are divided in disciplines for all kinds of reasons, but the construction and maintenance of a special internal realism doesn't seem to be one of them and probably shouldn't be.

The second reason is that internal realism is incapable of making sense of the unity of science. As I say in the introduction to the book, science without unity is an unappealing prospect. My reasons for finding this prospect unappealing are again two-fold: in the first place it seems to me that in that case we have problems demarcating science from non-science. That, in an age of shrinking funding and increased competition for it is no longer entirely an 'academic' (in the sense of largely non-consequential) problem. Secondly, it also brings into question the validity of longer held beliefs such as scientific progress and scientific method.

While I think that on a per-discipline basis internal realism is a neat starting point, it clearly needs to be enabled to 'reach out' of its silo and form part of a greater whole if we wish to move from ‘philosophy of chemistry’ to the greater project of ‘philosophy of science’.

9.2.2.3 Structural Realism

The last type of realism I will discuss is structural realism. Structural realism holds that what is real in science is the *structure* that emerges from a structural reconstruction of the theory. In a form close to this, it was first formulated by Worrall (1989) as a form of realism that had the potential to reconcile both the Pessimistic Induction and the No Miracles Argument.[3] Structural realism argues that the focus of realism needs to shift: in particular it is the structure of the theories that is maintained through theory change rather than its entities.

Worrall’s argument does not make clear what exactly is meant by structure: the examples he provides focus on mathematical structure or logical structure of the theory, but not in great detail. As a result, there has been some debate about what aspects of structure are endorsed by structural realists.

It is furthermore well known that structural realism suffers from Newman’s objection: the claim that structural realism is trivially true. Newman’s objection has generated a vast amount of discussion in the literature[4] which it is not my aim to add to or evaluate.

Rather, I focus on the empricial adequacy of structural realism for the theories of chemistry and physics we are focusing on here. In the case of theories of chemistry and physics, it is somewhat unclear how structural realism might apply. There is no clearly identifiable structure in these theories that gets preserved: instead, as the (informal) analysis in Part I shows, theories are created ‘on the fly’ – entities, structures and all – to fit the particular needs of the day.

While the intention of structural realism gets something right – we can use the No Miracles Argument in favour of our current theories even *vis a vis* a historical situation in which past theories have postulated the wrong entities – *structure* does not seem to be the main feature of what is preserved. In what follows, I will argue for a view of theories in which key features of entities and structures are revised rather than replaced.

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[3] The No Miracles Argument (NMA) claims that the empricial success of our current theories entails that our current theories get something right about the world – in particular, the NMA is often posited as a defence of scientfic entity realism. Pessimistic Induction (PI) is a counter argument against this line of reasoning. PI holds that (empricially) many of our past theories have proven to be false, with the entities they postulate non-existing. However, at a time in the past, the NMA would equally have argued for realism with regard to these theories – hence, we have no good reason to believe that our current theories get the nature of reality right.

[4] See for instance Muller (1998), Psillos (2000a), Ketland (2004), Ainsworth (2009), Smithson (2016) and references therein.

9.3 Composite, Intermediate and Interfield Theories

In the previous section, we concluded that none of the ‘standard’ realisms is capable of dealing with the challenges posed by theories in chemistry. In this section,, it is my aim to outline in more detail what theories of chemistry exactly are, what their structure is and how they function, and then develop a method that allows us to build an ontology.

From the analysis of Parts I and II we can conclude that chemical theories are shaped like networks with (partial) information links. In the case of the reduction of the periodic table, we have seen that neither ‘principled’ nor ‘unprincipled’ atomic theories are capable of providing a satisfactory reduction of the periodic law. For the chemical bond, the situation is similar. Moreover, in the latter case, the reduction is based on both the direct and inferred properties and hence, as suggested by Harris (2008), seems to be based on intermediate theories, or, in terms of Darden and Maull (1977), ‘interfield theories’.

It will be the aim of this section to flesh out the aptness of such chemical theories to description as an ‘interfield theory’ and also to develop a related concept – that of a composite theory – in more detail. I will propose the name ‘composite’ theories for theories that draw on aspects of composing theories (in the present case these are (quantum) physics, chemistry, and mathematics), and features of models in a principled, unprincipled, or pragmatic way. Moreover, composite theories have a particular structure: they *encapsulate* some of the abstract concepts of their source theories. It is through that mechanism that they give up strict requirements of consistency, and also allow for a measure of *revision* of their ontological claims.

Moreover, I will argue that for the reductions discussed in this book, the reduction postulates in the Nagelian reduction can be classified as composite theories in this sense, and hence feature as both coordinating theories and as (admittedly highly liberal versions of) reductive theories.

9.3.1 Interfield Theories

Let us start by considering the criteria for an ‘interfield’ theory as discussed by Darden and Maull (see Chap. 1, p. 20 for a discussion), which expresses, in the words of Angela Potochnik (2011, p. 306), a ‘coordinate sense of unity’. Recall that by a ‘field’ Darden and Maull do not signify individual theories, rather, they signify areas of research.

For our purposes, we may take the disciplines of ‘chemistry’ and ‘physics’ as the relevant fields. Darden and Maull sharply distinguish between ‘fields’ and ‘theories’, and we also note that Nagelian reduction is primarily concerned with laws and theories. Hence the classification of the physics inspired theories of chemistry which we discussed before as something akin to an ‘interfield theory’ in the sense of Darden and Maull does therefore not a priori preclude their role as a reductive agent for theories of chemistry in the sense of Nagel (even though it would preclude ‘field’ reduction for chemistry as a whole. But field reduction is not what we’re after).

Let us first see to what degree physics inspired theories of chemistry may be classified as an interfield theory, and then focus on its activity as a reductive agent.

Darden and Maull’s first criterion is that the interfield theory is capable of solving the theoretical problem which led to its generation. As we have discussed in the section on the explanation of both the periodic table and the chemical bond, this is true to the extent that physics inspired theories of chemistry take significant latitude in the selection and use of the various concepts of the composing theories, with significant ontological consequences.

The second criterion is that the theory ‘answers questions which cannot be answered using the concepts and techniques’ of each of the composing fields alone. As we have seen, physics-based theories of chemistry have led to a considerable introduction of quantum concepts in the theories of chemistry, and would seem to satisfy this criterion. It is in this vein, that Gavroglu and Simões (2011) have argued that quantum chemistry introduced ‘theory’ into chemistry.

Thirdly, the theory is required to ‘focus attention on previously neglected items of the domains’. This criterion, as it stands, is somewhat vague, though in the case of physics inspired theories of chemistry we can take it to mean the various domain joins introduced by the quantum theory of the atom: the combination of theories of bonding and molecular spectroscopy, and the formulation of a theory for chemical reaction rates and so forth.

Next, the requirement for the theory is to ‘predict new items for the domains of one or both fields’. One can read this as a requirement to generate new observational facts, facts which would not have been discovered without the specific interfield theory in play. This was certainly achieved with these theories, which predicted, through the introduction of quantum concepts in the theories of chemistry, the existence of new types of compounds and introduced new explanations for various chemical phenomena, which each had observational consequences.

Finally, the theory is required to ‘generate new lines of research which may, in turn, lead to another interfield theory’. As Gavroglu and Simões (2011) argue, the development of quantum chemistry through this original set of physics inspired theories of chemistry went through various phases. The latest phase they describe is computational chemistry. New phases may yet be on the horizon. As Gavroglu and Simões argue, quantum chemistry has opened discussions on the status of *theory* in chemistry (p. 247). The status of theory in chemistry, through the intervention of quantum chemistry, turned into a ‘theoretical particularity’ of chemistry, in which quantum chemists were actively involved in establishing a theoretical *autonomy* for chemistry with respect to physical theories in the same domain. Specifically, Gavroglu and Simões argue that quantum chemistry introduced new concepts into chemistry:

> Throughout the history of quantum chemistry, it appears that in almost all the cases, the reasons for proposing new concepts or engaging in discussions about the validity of the various approaches were

> 1. To circumvent the impossibility to do analytical calculations.
> 2. To create a discourse with which chemists would have an affinity.
> 3. To make compatible two languages, the language of classical structure theory and that of quantum mechanics.
>
> Perhaps it may be argued that the involvement in such discussions of almost all who did pioneering work in quantum chemistry [. . .] had to do with *legitimizing the epistemological status of various concepts in order to be able to articulate the characteristic discourse of quantum chemistry*. (Gavroglu and Simões 2011, p. 255)

So it seems that quantum chemistry, and the various qualitative physics-inspired theories that preceded it, can be aptly described as an interfield theory.

But how does this set of theories function as a reductive agent? There is something peculiar about them in that it, as a final theory, mixes concepts from the ‘unprincipled’ theory with the possibility of accurate calculation of the ‘principled’, or ab initio theory and sometimes also draws on a number of ad hoc, simplifying assumptions and mechanical concepts of the molecule which are part neither of quantum physics or chemistry. As we have now discussed on a number of occasions, even ab initio quantum chemistry is not smoothly continuous with quantum theory. From this perspective, quantum chemistry is difficult to classify as an interfield theory, and in the case of quantum chemistry, a more apt description is perhaps ‘composite theory’. It functions pragmatically as an interfield theory, but at the same time has a number of unique features.

9.3.2 Composite Theories

In this section it is my aim to develop the notion of a composite theory in more detail and discuss the characterisation of quantum chemistry as a composite theory. The key to the development of the concept of ‘composite theory’ is both the notion of an ‘interfield’ theory as well as the realisation, deriving from the examples of reduction discussed above, that reductions happen in a ‘local’, rather than ‘global’ manner. Specifically, aspects of the reduction relationship can be clarified with either ‘principled’ or ‘unprincipled’ theories, and these specific ‘local’ reductions gradually build up a map of the overall inter-theory relationship between chemical and physical theories.

9.3.2.1 Characterisation

A composite theory is defined as a theory that draws concepts and observations from a larger body of other theories and fields in a usually pragmatic fashion. A key element is that the concepts are drawn in as intertheoretic links, as specified in Chaps. 6 and 8. There are no formal criteria, apart from the general criteria in Chap. 6, on how these interpreting links are to be constructed precisely, though they are usually easily determined on a case by case basis. Conceptually, we can see these links as ‘information channels’, which convey (partial) concepts and structures into the composite theory. The partiality of the links implies that composite theories may be logically inconsistent with their parent theories.

The term composite reflects a certain structural and ontological discontinuity between theoretical constructs, without breaking a sense of unity. There are a number of tensions between the source fields and the composite theory. Specifically, composite theories may draw concepts out of context, and re-use the concept in a manner not admissible to the theory in which the concept was first introduced. Hence there is both an epistemological and ontological tension between composite theories and their composing theories: the loss of context may threaten global consistency constraints between the composite and composing theories, and as a result, objects posited by the composite theories may not exist, or at least not exist in the way the composite theory says they do.

Composite theories function in practice very similar to interfield theories. What distinguishes a composite theory from an interfield theory is their grab bag nature. This sounds somewhat informal but there are a number of candidate formal specifications of composite theories which will be discussed in Sect. 9.3.3. As an example, in the language of structuralism, one might classify quantum chemistry as a theory *holon*, a term introduced in Balzer et al. (1987) without specific examples. They consider the holon to be part of the ‘global’ structure of science. In the next subsection I address one potential example: the phenomenon of chemical bonding, before moving on to discuss the various ways in which the concept of a composite theory might be *formally* implemented.

9.3.2.2 Example: Models of the Chemical Bond as a Composite Theory

In Chap. 5 I have classified quantum chemistry not as a single theory, but rather as a collection of theories. Furthermore, in Chap. 7 I argued that this collection of theories was best described as combination of a specialisation and an ‘idealisation net’, where the latter was more aptly characterised as a ‘theory holon’, with the formal properties ascribed to it. Hence, quantum chemistry satisfies the criteria for a composite theory in the following sense.

The various theories of ab initio quantum chemistry have been classified as belonging to a specialisation *net*. In opposition, the divide between ab initio and *semi-empirical* quantum chemistry, as argued in Chap. 7, cannot be captured in terms of a specialisation link, but is rather captured in terms of interpreting links. Furthermore, the interpreting links can only be specified on a case by case basis.

As an example, consider the formalised theory of the H_2 bond, in which the *models* specify properly antisymmetrised wavefunctions as a choice in the parameters b_i. The ‘semi-empirical’ or CTA type wavefunctions (see p. 197) are not of this sort; the requirement that ‘each electron can be assigned a separate eigenfunction which involves the co-ordinates of only this one electron’, as required in Eyring (1938), requires instead that the wavefunction be written as a simple product function, e.g. $|\phi_a(1)\phi_b(2)\ldots|$. Hence, this product function is not part of a proper model of the chemical bond, but stands in the relation of an interpreting link to such a model. The context that is lost is the requirement of a proper anti-symmetric wavefunction with indistinguishable electrons.

The end result of this analysis is a network of theories that is connected through conceptual and data links of various sorts.

9.3.3 Formal Specifications of a Composite Theory

The concept of a composite theory can be developed following multiple formal mechanisms. While in this book I focus on the structuralist method, and primarily conceive of composite theories as connected by inter-theoretic links, there are a number of competing formal methods which can assist in the formal characterisation of a composite theory. In this section I discuss a structural characterisation, a 'chunk and permeate' characterisation and a characterisation in terms of belief revision.

9.3.3.1 Structural Characterisation

In the structural characterisation, *links*, especially interpreting links, are the key formal elements of a composite theory. As we have seen in Chap. 6, links allow for a pragmatic 'picking' of concepts *qua* partial structures from composing theories to constitute a new theoretical framework. Links do not (formally) specify *how* concepts should be picked, they only specify *that* concepts are picked. Moreover, recall from our discussion of interpreting links in Sect. 6.5.3 that interpreting links can be constructed independent of the laws of the theory involved. They are, so to say, 'partial concept carriers'.

Conceptually one might say that the composite theory is based on a concept of 'encapsulation', a term that indicates that some of the originating theoretical complexity is hidden from sight in the composite theory. Encapsulation is intended to capture this 'loss of context'. The terms in the theories that are linked 'encapsulate' these terms in the link and transfer the notion to another context, but, as we have seen in a number of instances, the links transfer only the information useful in the formulation of the composite theory and ignore in many cases not only the detail, but in more notorious cases also the principle of the composing theory. It is thus that a concept of 'orbital' can be 'carried' between quantum theory, via quantum chemistry, directly into a theory of chemistry, a situation which was dsicussed previously (Hettema (2012a) and Hettema (2016)). In a similar manner, the results of ab initio calculations are amenable to interpretation in terms of a much simpler theory, as discussed in Sect. 8.4.3.3.

From the viewpoint of reduction, composite theories are theories that retain the Nagelian condition of derivability at the cost of a form of connectibility that 'transports' data and concepts from one theoretical context into another. Hence the notion of a composite theory introduces one worry. The range of theories that constitutes quantum chemistry, from the ab initio on the one hand to the various semi-empirical models on the other, are connected via links, which each may introduce a loss of context. With the loss of context may also come a loss in consistency, and hence with the concept of a composite theory we may lose the unity of science if we conceive of this unity as a requirement of global consistency of scientific theories.

Links have a similar sort of feature: concepts from one theory, say, the concept of a model of the chemical element as a nucleus with an electron cloud which has certain computable properties is allowed to 'permeate' into the periodic table of the element, *en passant* ignoring many of the fine points of quantum theory or even, at points, being at odds with the basic requirement of many-electron wavefunctions.

9.3.3.2 Chunk and Permeate

In the structural characerisation we hinted at the possibility that the loss of context – or the 'pick and mix' attitude to selection of key elements of a composite theory could lead to an overall loss of global concistency. While it is possible to argue that this fatally flaws the concept of a composite theory, it is equally possible to argue that there are ways in which the inconsistency may be controlled and the loss of context may not be vicious.

As has been argued in the context of para-consistent approaches to scientific theories (see for instance Brown and Priest 2004, 2008), such cases may even be the norm rather than the exception in science. Specifically, Brown and Priest show that many scientific theories employ what they call a 'chunk and permeate' approach, in which concepts are constructed as a logical process in 'chunks' (which are internally consistent) and are then allowed to 'permeate' in a limited form – i.e. with loss of context – into other chunks.

The idea is that many concepts in science can be reconstructed in the framework of para-consistent logic (i.e. a logic in which contradictions do not entail everything).

The idea of 'chunk and permeate' is that a field can be subdivided first in consistent parts (the 'chunking' procedure), and information be allowed to flow from part to part ('permeation').

They formally define the 'chunk and permeate' approach as follows[5]: let L be some classical language and let $\vdash$ represent the classical consequence relation. If Σ represents a set of sentences in the language, then $\Sigma^{\vdash}$ is the closure of Σ under $\vdash$.

A *covering* of Σ is a set I such that $\{\Sigma_i \mid i \in I\}$, such that $\Sigma \cup_{i \in I} \Sigma_i$, and for all $i \in I$, Σ_i is classically consistent. If $C = \{\Sigma_i \mid i \in I\}$ is a covering of Σ, call ρ a

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[5] The next paragraphs follow Brown and Priest (2004) closely.

permeability relation on C if ρ is a map from $I \times I$ to subsets of the formulas of L (e.g., those of some particular syntactic form). If $i_0 \in I$, we will call any structure $\langle C, \rho, i_0 \rangle$ a C&P structure on Σ.

If we now define $\mathfrak{p}$ as a chunk and permeate structure on Σ, then we can define the 'chunk and permeate' consequences recursively as follows

$$\Sigma_i^0 = \Sigma_i^{\vdash} \tag{9.1}$$

$$\Sigma_i^{n+1} = \left(\Sigma_i^n \cup \bigcup_{j \in I} \left(\Sigma_j^n \cap \rho(j,i) \right) \right)^{\vdash} \tag{9.2}$$

The consequences for a finite set are

$$\Sigma_i^{\omega} = \cup_{n<\omega} \Sigma_i^n \tag{9.3}$$

The idea is thus that the set of 'chunk and permeate' consequences of $\mathfrak{p}$, $\vdash_{\mathfrak{p}}$, consists of the set of consequences of Σ_i plus whatever 'flows' into Σ_i through the permeation relation ρ from other chunks j.

An interesting feature of the chunk and permeate approach is that it allows us to work with paraconsistent theories – theories that are inconsistent but where the inference relation $\vdash$ does not lead to trivial results, and hence the inconsistent information is still informative. Brown and Priest (2004) claim that this sort of situation obtains in the derivation of the infinitesimal calculus. In a subsequent paper (as yet unpublished), they claim this sort of relationship for Bohr's model of the atom and the old quantum theory.

The chunk and permeate approach has a number of interesting consequences for the relationship. Specifically, if the only information that is allowed to flow is identities of some kind, in which one 'chunk' calculates a number of values that are then passed on to the next chunk, then we may say that the relation ρ takes the form $f(x_1, \ldots, x_n) = c$. In this case, Brown and Priest (2004) argue that we can prove that some axiomatic Σ_T augmented with the permeated information has a model and hence is consistent (we assume that there are no axioms governing f in Σ_T, so that we can interpret f in Σ_T in any way we like).

Might the chunk and permeate approach be interpreted in terms of inter-theoretic links? It seems that it might if we identify the permeability relation ρ as an inter-theoretic link. Specifically, for the lemma to hold, the inter-theoretic links must be of the form $f(x_1, \ldots, x_n) = c$.

9.3.3.3 Belief Revision

Another way om which we can conceive of composite theories logically is the method of belief revision. The basic idea was discussed in Gärdenfors (1988) in terms of an epistemic dynamic, in which conceptual states are revised by expansions, revisions or contractions of sets of beliefs, and the rationality criteria under which it is admissible to do so. The idea of a composite theory *qua* belief revision is that the networks of theories that characterise chemistry are seen as dynamic networks of knowledge, where dependent on the context or application certain beliefs from a basic theory, such as for instance quantum mechanics, are revised to provide a better fit to the context in which the theory is to be applied.

In order to reconstruct the notion of a composite theory in terms of 'belief revision' I will focus on the relationship between AGM theory and the development of 'conceptual spaces' as discussed by Gärdenfors and Zenker (2011).[6] While this would not be a 'standard' characterisation of belief revision, it is nevertheless a robust connection to the structuralist framework I have developed in this book.

Gärdenfors and Zenker note that the framework of conceptual spaces allows for four types of theory change:

1. addition and deletion of special laws (e.g. the creation different models of the theory or the creation of specialisation theory nets);
2. change of scale or metrics as well as the salience of dimensions;
3. change in the separability of dimensions;
4. addition and deletion of dimensions which make up the space

In this context, 'dimensions' refers to the terms in the general structure $\langle D_1, \ldots, D_k, x_1 \ldots x_{p+q} \rangle$ rather than to physical dimensions. In other words, the belief-revision strategies for theory change may involve limited changes of the theoretical cores as modelled in the structures $\mathscr{M}$.

In Chap. 8 I proposed that we view reduction relationships as an instance of an interstructural *link*, sufficient to establish a global unity of science, but also capable of dropping local 'context'. Belief revision is a stronger theory in the sense that it provides additional specification of how such a link might work.

Abstract links are simply relationships between two sets of potential models (or the 'conceptual spaces') of two theories. The leading idea of the abstract link is that it provides a relationship between two different types of potential models, but does little else. In practice, links are instantiated as connection pairs between terms of the 'conceptual space' of one theory to those of another; e.g. $\langle \langle x'_i, x'_j, \ldots \rangle, \langle x_p, x_q, \ldots \rangle \rangle$ that may have some additional restrictions in terms of either values that the quantities can take in the link, or a (law-like) relation between these concepts. The machinery for links can become cumbersome, but the concept

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[6] In addition, belief revision has been introduced into the structuralist model by Enqvist (2011). Enqvist develops a highly specific alternative to the notion of 'reduction postulates' qua 'linking commitments' which I developed in Hettema (2012b). Enqvist's construction relies on a construction of specialisation theory nets, to which he applies the AGM belief revision strategies. Enqvist does not fully develop the AGM theory in a structuralist model, and ignores the stratification between theoretical / non-theoretical levels of the theory. In general, developing complex notions in the stratified model adds complications which are usually ignored in the first 'step' of the development of such models, see for instance the development of truthlikeness developed by Kuipers (1992).

is not conceptually complex: it expresses that some terms in one 'conceptual' space can be connected to (a number of) terms in the other conceptual space.

It is possible to define additional properties on links, and in this way develop a concept of interpreting links, reducing links, and so on. Of particular interest is that in the structuralist approach, the unity of science is formulated in terms of theory *holons*, which are large-scale global structures connected by inter-theoretic links. In Chap. 8 I have argued that reduction postulates can fruitfully be interpreted in terms of links, and the concept of links can be made to fit the three criteria for reduction postulates that were originally developed by Nagel.

The analysis by Gärdenfors and Zenker adds structural precision to the generative strategies that are available to establish links. The main import of treating conceptual disconnects in this way, as Gärdenfors and Zenker argue, is that the scope of *incommensurability* between a predecessor and successor theory, or between a reduced and reducing theory, is limited significantly.

From the viewpoint of reduction, this approach is capable of formalising, and subsequently de-fanging, the discontinuity between concepts in the theories of chemistry and the theories of physics.

9.4 The Theoretician's Dilemma

If theories of chemistry are indeed loose, but linked collections of various sub-theories, then a question about chemical *ontology* must be asked: what sort of objects are 'chemical objects'? In this section, I will approach this problem from the viewpoint of Hempel's 'Theoretician's Dilemma'. The Theoretician's Dilemma is a question about the meaning of theoretical terms, raised as a dilemma. As such, there are a number of ways in which Hempel's 1958 paper *The Theoretician's Dilemma* can be seen as both a template and a problem for the philosophy of chemistry.

The paper can be characterised as a template in the sense that it forms one of the core papers of modern philosophy of science, and states, in the form of a dilemma, some key questions on the nature of theories and theoretical terms. The paper moreover relates these issues back to a more fundamental question on the role of scientific theories as either inductive generalisations or explanatory frameworks. On the other hand, Hempel's paper can be characterised as a significant problem for the philosophy of chemistry. The specific solution it proposes to resolve the dilemma, the idea that theoretical terms do *more* than just act as connective tissue between empirical observations, poses particular problems for the philosophy of chemistry. The problems arise for several reasons. Whereas in the theories of physics it could be maintained that terms once deemed 'theoretical' such as the term electron, could over time migrate into an 'observational' category by further scientific advances, this notion is much harder to sustain for the theories of chemistry.

In this section I will briefly discuss some of the key aspects of Hempel's paper. I will then propose a way in which Hempel's notion of realism can be reconstructed so that its potential applicability to the theories of chemistry can be understood.

9.4.1 The Theoretician's Dilemma

Before publishing *The Theoretician's Dilemma*, Hempel had worked on the problem of theoretical terms for some years. In 1952 he published, as part of the *International Encyclopedia* project, the small book *Fundamentals of Concept Formation in the Physical Sciences* (Hempel 1952). In 1958 he published the *Theoretician's Dilemma*, around the same time that he wrote the contribution on Carnap's philosophy for the Schilpp volume on Rudolf Carnap (Hempel 1963). As was pointed out by Psillos (2000b) Carnap's later work on the Ramsey sentence was influenced significantly by Hempel's work on theoretical terms. Thus, the *Theoretician's dilemma* forms a pivotal point in the conception of theoretical terms in logical positivist philosophy of science. Its views on theoretical terms straddle what Craig (1953, 1956) has called the 'replacement programme', which argues that theoretical terms are somehow definable, and the Ramsey (1960) view on theoretical terms, which maintains that observational languages are meaningfully extendable. It also (arguably) led Carnap to the Ramsey sentence.

The Theoretician's Dilemma is subtitled 'A study in the logic of theory construction' and focuses on the role and function of theoretical terms. As a starting point, Hempel views theories largely as bodies of systematised knowledge, which connect observations to each other through theoretical machinery. Specifically, Hempel states that

> [...] the assumption of non-observable entities serves the purposes of systematisation: it provides connections among observables in the form of laws containing theoretical terms, and this detour via the domain of hypothetical entities offers certain advantages [...] (Hempel 1958, p. 45)

Thus, the role and function of theoretical terms in scientific theories allow (Hempel quotes Feigl here), 'a nomologically coherent formulation on the level of hypothetical construction' (p. 68).

Hempel distinguishes between empirical generalisation (which generally proceeds without the use of theoretical terms) and theory formation, which does use theoretical terms. His statement of the theoretician's dilemma is a direct consequence of how he conceives the role and function of a scientific theory. Thus (on page 43), we find the (somewhat rhetorical) question

> Why should science resort to the assumption of hypothetical entities when it is interested in establishing predictive and explanatory connections among observables? Would it not be sufficient for the purpose, and much less extravagant at that, to search for a system of general laws mentioning only observables, and thus expressed in term of observational vocabulary alone?

This leads Hempel to formulate the theoretician's dilemma as follows:

> If the terms and principles of a theory serve their purpose they are unnecessary [...] and if they don't serve their purpose they are surely unnecessary. But given any theory, its terms and principles either serve their purpose or they don't. Hence, the terms and principles of any theory are unnecessary (Hempel 1958, page 49–50).

Hempel then goes on to investigate the ways in which the theoretical vocabulary can be avoided (or is *eliminable*) in more formal terms. Specifically, Hempel discusses the suggestions by Craig (1953) and Ramsey (1960) for the treatment of theoretical terms in a formalised system as two approaches to this problem. In the first case, it can be maintained that theoretical terms are *definable* in terms of observational concepts (even if this definability is only partial). This approach relates to the notion of reduction sentences as introduced by Carnap (1936, 1937), and what Craig (1953, 1956) has called the 'replacement programme'.

Secondly, theoretical terms can be seen as useful (in a sense still to be specified) extensions to our observational language. This approach depends on the concept of a 'Ramsey sentence'. The Ramsey view on theoretical terms is based on F.P. Ramsey's notion of theoretical terms as it was introduced in Ramsey's well known paper '*Theories*' (reprinted in Ramsey 1960).[7] Ramsey's proposal relies on a two step approach to the introduction of theoretical terms. In the first step, we consider a sentence of the form $T(o_1, \ldots, o_m; t_1, \ldots, t_n)$, which contains both observational terms o and theoretical terms t, and we replace all theoretical entities t_i by variables x_i. Then, in the second step, we introduce existential quantifiers for the variables x_i, so that we obtain a *Ramsey sentence* of the form

$$\exists x_1 \ldots \exists x_n T(o_1, \ldots, o_m; x_1, \ldots, x_n) \tag{9.4}$$

The Ramsey sentence thus introduces an element of ontology, or, more precisely, 'ontological commitment'[8] into its construction: it makes specific existence claims for entities x_i that satisfy the theoretical constructs of the theory, but at the same time is also careful to extensionally restrict the scope of that existence claim.

Under Hempel's reconstruction, the theoretician's dilemma asks whether it is not possible to avoid these ontological commitments altogether. Thus, the*Theoretician's Dilemma* ultimately poses a question about the *purpose* of scientific theories and theoretical terms. If theoretical terms actually fulfil their function as the connective tissue between observations, they *can* be dispensed with, and if they do *not* fulfil this function, they *should* be dispensed with. In response to this, Hempel argues that theoretical terms do *more* than fulfil a role as a connective glue between observational terms: following Ramsey's ontological suggestion, they actually describe, or refer to, 'essential constituents or aspects of the world we live in' (p. 87), a contention which is supported by the fact that theories with such theoretical terms lend themselves to inductive systematisation.

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[7] Psillos (1999, 2000a) gives an interesting account of how the Ramsey view on theories came to be introduced in the philosophy of science. Ramsey sentences are also discussed by Carnap (1966) and Lewis (1967).

[8] Hempel uses this term on p. 86.

9.4.2 From the Theoretician's Dilemma to Realism

The road from the *Theoretician's Dilemma* to scientific realism is not a direct one. Hempel lays out the theoretician's dilemma in great detail, but resolves it rather hastily. Hempel's principled realist way out of the dilemma is to argue that is premise is misconstrued: theoretical terms do *more* than serve as mere instrumental devices in derivational chains linking observables: following the Ramsey view of theoretical terms they have an *ontological* import and are thus 'truth tracking' (in the terminology of Psillos (1999)). As Hempel sees it, asserting that partially interpreted theoretical terms actually have factual reference, is tantamount to saying that the theoretical statements concerning them are true:

> To assert that the terms of a given theory have factual reference, that the entities they purport to refer to actually exist, is tantamount to asserting that what the theory tells us is true, and this in turn is tantamount to asserting the theory. (Hempel 1958, p. 84)

Thus, in the words of Suppe (1989), Hempel's theoretician's dilemma could evolve into the 'classic positivistic statement of scientific realism' (p. 21).[9]

Hempel's purported realist resolution of the dilemma leads to a number of questions. First of all, the statement is somewhat difficult to unpack. Hempel does not specify in detail the sort of 'factual reference' and 'truth-making' that he is after. Furthermore, it is not clear entirely that Hempel is committed to an overly hard realism for the resolution of the dilemma. Hempel's argument is more subtle, and relies on ontological commitment of the Ramsey type, as well as on the feature of inductive generalisations allowed by the theoretical entities. In this sense, Hempel's rejection of the theoretician's dilemma is not an unconstrained acceptance of scientific realism, but something rather more modest.

It would seem that a simple solution to the *Theoretician's Dilemma* along these realist lines is not available to philosophers of chemistry. For this, there are several reasons. The first one is that many chemists take the entities of their theories with varying degrees of commitment, and it is unclear whether the sort of hard realism that Hempel seems to require to avoid the consequences of the *Theoretician's Dilemma* can be put to work in chemical theories. Secondly, the hard-realist way out of the dilemma drives us headlong into the ontological discontinuity of many chemical concepts and physical concepts: it should be clear that a hard-realist line of the sort needed by Hempel is not possible in cases of such strong discontinuities unless the theories themselves are competitors. In the case of physics and chemistry the two sciences are clearly not competitors, but rather cooperators: as Needham

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[9] As an aside it might be noted that in his contribution to the Carnap volume, Hempel (1963) mounts a slightly different argument against the avoidability of theoretical terms, arguing that statements in which theoretical terms are avoided are not capable of featuring in statements of an inductive character. As Hempel argues there, these inductive steps are key to the use of scientific theories, and hence scientific theories are *more* than just deductive inferences between sets of observations. However, in the remainder of this contribution I will focus on Hempel's realist resolution of the dilemma.

(2010) has remarked, the two sciences cooperate to the degree that it is hard to image chemistry with the physics removed. Lastly, for sciences like chemistry that are theoretical foragers (and have a somewhat promiscuous attitude to theoretical concepts as a result), a hard realism of the sort ascribed to Hempel seems out of the question.

Hence, it is an open question how Hempel's solution to the Theoretician's Dilemma applies to composite theories as they are in use in chemistry.

9.5 Quantification on Restricted Channels: The Chemical Object

In this section I will develop the outline for an ontology for chemistry that is capable of dealing with the ontological issues presented by chemical theories. In brief, the steps leading to this concept of a 'chemical object' are the following. The suggestion of Hempel's *Theoretician's Dilemma* is that theoretical terms do *more* than just organise observations, while the considerations from ontology suggest that this *more* consists of some combination of existence claims and grounding. Chemical theories reflect this complex interplay, and also illustrate that there can be issues of priority.

I will first illustrate what chemical objects are not, specifically arguing that chemical objects are not 'models' or 'proxies' that just 'stand in' for more complex underlying structures. Secondly, in Chap. 10. I will reconstruct Paneth's disambiguation of the notion of chemical element as a step in a Kantian framework of thinking about matter. This metaphysical reconstruction will be careful. My starting point is found in more recent Kant scholarship, especially that of draw inspiration from the debate between Allison (2004) and Langton (1998), Ruthenberg (2009, 2010) which is instructive in this reconstruction.

Finally, I will develop my proposal. My specific proposal is based on a loose analogy with the notions of 'objects' as they appear in object oriented programming, though I will drop a lot of the technicalities and will, in some cases, use the language suggestively. Object oriented programming is a specific method of engineering large software programs, and my use of the lingo should not suggest that I believe at some level chemical objects really *are* computational. Instead, my claim is that the specific slicing and dicing of complex computational objects that underlies object oriented programming has an application in the particular context of chemical objects as well. Hence the relationship to object oriented programming is one of analogy rather than identity.

The aim of this section will be to propose an answer to Hempel's *Theoretician's Dilemma* by specifying what, in the theories of chemistry, theoretical terms *do* in addition to serving as the theoretical machinery to tie observations together, and elucidating the interplay between existence claims and grounding. In brief, my answer is that they export and import various concepts from other scientific theories, and hence tie chemistry as a science to other sciences. The other science that I will consider in the most detail is physics, but there is reason to believe that the same mechanisms operate in the direction of biology or materials science as well. Finally, I connect the notion of a chemical object that I develop to some recent work in the philosophy of science which points in the same direction, and outline some agreements and differences with this work.

9.5.1 What Chemical Objects Are Not

Let me first outline what chemical objects are not. In brief, chemical objects are not *models* or proxies for more complex realities. The idea that chemical objects might be such proxies was introduced by Hendry (1998) in his idea of the 'proxy defence' (which he does not endorse). The proxy defence has been characterised by Hendry (1998) as follows:

> One attractive defence of realism is that although idealised models *themselves* falsely represent their subjects, they *stand in* for intractable exact treatments in theoretical deduction from true premises that constitute explanations and predictions. (Hendry 1998, p. 123)

Hendry is, justifiably in my view, critical of the proxy defence in theories of chemistry. Based on the example of molecular structure[10] he argues one would normally expect certain relationships to hold between model and 'exact' treatment that *fail* to hold in the theories of chemistry. Similar objections can be raised against Paul van der Vet's (1987) notion of the 'chemical theory of the atom' (see p. 197), or our notion (see Hettema and Kuipers 1988, 2000) of a 'physical' and 'chemical' picture of the atom.

The reason these relationships fail to hold is the fact that the idealised models exhibit features that are not shared by the 'exact' treatment. Moreover, these extraneous features are in many cases key features of the explanatory power of the idealised model. Hence it becomes impossible to ensure that an 'exact' treatment of the problem, if it were possible, would exhibit the same explanatory features as the idealised model.

In this sense, these 'model' objects fail to do the work required by Hempel's *Theoretician's Dilemma* because on the one hand they serve their purpose in organising observations of a particular sub-field (like chemistry), but on the other hand they cannot be further grounded. Hence, these 'model' objects are subject to the claim that they can be eliminated, and, in the light of the ontological (grounding) difficulties they invite, it might be argued that they should be eliminated.

Another, loosely related, issue with the 'proxy' defence is that it rather heavily relies on *models* and thus has little to say about *theories* and theoretical terms. The

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[10] The discussion in Chap. 3 differs however in significant repects from Hendry's exposition in the technical details. The example of molecular structure is notoriously difficult, and though often used in philosophy of chemistry as an example of non-reducibility in principle, it still remains to be seen whether a principled treatment of molecular structure might not after all be possible. See for instance Sutcliffe and Woolley (2005) as one of the more recent discussions of this problem.

relationship between theories and models is indirect at best (see Frigg and Hartmann (2009) for an overview). In this way, extensive use of the proxy defence limits the scope of philosophy of chemistry to such models, and leaves no or only limited room for a detailed consideration of theories.

It is not clear that philosophy of science is able to function without a notion of theories. For instance, the concept of 'unity of science' depends on the measure in which it is possible to connect various *theories* to each other, a feature that is more difficult to satisfy for models. For this reason, it would be unwise to build a philosophy of chemistry that limits itself to models that, at the end of analysis, are fictional entities. In the remainder of this section I will develop my alternative.

9.5.2 Chemical Objects

To conclude this argument, it is my aim to outline a theory of chemical objects that is based on the dual conception of objects as they exist and objects as they are grounded. The notion of chemical object that I will introduce is the ontological counterpart of the notion of a 'composite' theory, which was identified as the main locus of the reduction relationship in Part II. The model itself is a further development of Paneth's dual conception of the term element and its Kantian interpretation by Ruthenberg, as well as a further development of the notion of a 'composite' theory developed in Chap. 8, this time focusing on the ontological commitments of such a theory. As defined there, composite theories are theories that are inter-field theories with a twist: they connect to theories of their respective fields through links which encapsulate (i.e. hide from view) some of the internal complexities of the concepts and data that they consume. Then, to put it bluntly: 'composite' theories are ontologically committed to composite objects.

This theory of objects could potentially be situated in a context of similar work in the philosophy of science, such as the 'rainforest realism' of Ladyman (2007), the 'engineering' discussed in Wimsatt (2007), or the account of 'depth' presented by Strevens (2008), which will be discussed after the main outlines have been laid out.

To develop my point of view, I will take Kant as a creative, but perhaps not entirely coherent philosopher (in the sense in which Derek Parfit (2011) engages with Kant's ethical concerns), and develop a notion of a chemical object as a multi-perspectival notion. What the debate between Langton and Allison illustrates is that there is an open question about the *relationship* between the noumenon ('thing in itself') and the 'phenomenon'. My aim is to elucidate how this works in the philosophy of chemistry, and how 'chemical objects' result as ontological commitments of composite theories.

An example, discussing the chemical element as a 'simple' and 'basic' substance is given in Fig. 9.1. My proposal is to separate the 'dottted line' into a series of specific *links*, in the sense of 'interpreting links' of Chap. 6, between the objects. The links are specific reductive commitments which establish the various 'grounding'

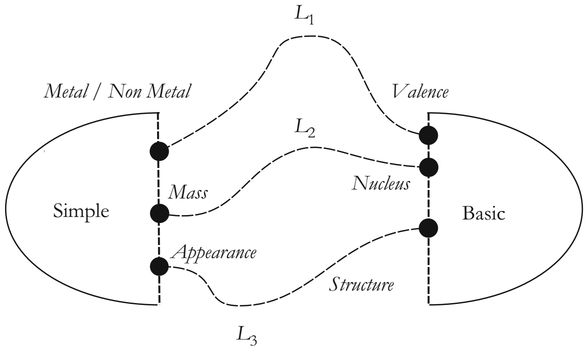

Fig. 9.1 Proposal for the 'chemical object' as applied to the notion of element, disambiguated between a 'simple' and 'basic' object. The links between the objects are structural links in the sense of Part II, though the objects themselves are not structure theoretical objects

relations in terms of which we can say that the concept of a chemical element as a 'simple substance' is grounded in a concept of a chemical element as a 'basic substance'.

Three examples are given in the figure. The links L_1, L_2 and L_3 are examples of the sort of *interpreting* links that may be expected to connect the descriptions of the two notions of chemical element together. The links express reductive commitments and hence also form part of the grounding relations.

This notion of object has a number of interesting consequences. Some concepts from object oriented programming will assist in further developing the necessary conceptual framework.

The first notion I wish to develop is the notion of *encapsulation*. In object oriented programming a large complex program is split up into 'objects', say, transactions in a banking system, or personal records, which perform certain functions and which function as 'black boxes' for the remainder of the program. The object 'person' in the computer program may 'expose' certain methods, such as 'age', 'address', 'sex', 'income' (if the program in question is run by the tax department) and so on. Other parts of the program can 'consume' these methods, but do not have to know how they are implemented, the 'method' itself is 'encapsulated'. The internal definition is hidden from view, but the results are accessible to the component that wants to use the method.

My proposal is that chemical objects work in a similar manner: both chemistry and physics populate their relevant concepts – say, atom or chemical element – with encapsulated methods. To develop a quantum theory of atoms and molecules, the early quantum physicists and quantum chemists developed a number of concepts such as 'orbitals', 'atomic nucleus', 'electron' etc., which were later, in abstracted form and with significant loss of context, *imported* into the science of chemistry. Similarly, chemists developed the concept of 'valency', 'directed bonding', and so on which were in turn imported into the early theories of quantum chemistry as explanatory questions. Inside the field of either chemistry or physics, these concepts are necessary elements of theorising, but ultimately, some of these concepts get 'imported' to somewhere else in encapsulated state, and relevant context is lost in the process.

In short, my suggestion is that the objects and theoretical terms that feature in the theories of chemistry are more or less amenable to the criteria of encapsulation, and the general term ‘importing’ and ‘exporting’ of objects from one theory into another may cover this multitude of activities. From the ontological perspective, such objects can exist in a dual sense, dependent on the context of their grounding.

An example may help here. Chemical elements, conceived as ‘simple’ substances are grounded in how they appear to our senses, even though this grounding is somewhat trivial. ‘Basic’ substances were initially grounded in the observation that certain types of ‘stuff’ cannot be decomposed by chemical means. Chemical elements as ‘basic’ substances function as the ‘principles’ behind this observation, but at the same time they pose a question of how these principles can be explained. In the process of explanation, various concepts of the theory of the atom, such as ‘nucleus’, ‘orbital’ and ‘electron’ are packaged up and shipped into a structure like CTA, which is explanatory efficacious, but lacks much of the context of its original. Over time, these models are further developed and the links are re-engineered into a more advanced theory, say, ab initio quantum chemistry. The development of the necessary ‘grounding’ can be described in the terminology of philosophy of science – focusing on theory development, approximations, limit cases, and reduction.

This theory of chemical objects fits the bill both a resolution of Hempel’s *Theoretician’s Dilemma* and as an ontology for chemistry. As a resolution of the *Theoretician’s Dilemma* it is capable of outlining how theoretical terms ‘do more’ than just connect observations to each other: it suggests that theoretical terms that are particularly efficacious in an explanatory sense are capable of the sort of import and export that the model suggests. Similarly, the model allows for simple existence claims for the theoretical terms, but again fleshes out the notion of grounding in terms of import and export. A ‘grounded’ concept, in this sense, is one that satisfies the criterion that it is capable of being ‘imported’ from a neighboring science.

One particularly important issue is how this model of ‘loosely coupled’ objects preserves the unity of science. The loss of context that accompanies these processes may (in the case of orbitals, even does) lead to inconsistencies in the overall unity of science, which may well be fatal to the concept. The answer to that objection is that depends: recent logical work in the area of para-consistency (see Brown and Priest 2004, 2008) suggests that these sort of issues are more common in scientific theories than is usually assumed. In a similar vein, Alisa Bokulich (2008) has argued that the relationship between classical and quantum mechanics can be classified as one of ‘inter-structuralism’, in which there exist close analogies between two different theories, and an adequate account of how the two theories relate can be given (p. 173).

Philosophy of chemistry has much to gain by reexamining the relationship between physics and chemistry in this light.

The hope for a reduction relation which consists of ‘correspondence qua identity’ and strict derivation (a particularly austere interpretation, due to Causey (1977), of the reduction conditions given by Nagel (1961)) has now vanished, and the prospects of disunity are unattractive. However, the suggestion that the ontological relationship of grounding, through a process of importing and exporting concepts in and out of theories, may just create the necessary middle way.

9.5.3 Relating 'Chemical Objects' to Philosophy of Science

In this section I will connect this idea of the 'chemical object' to some recent work in philosophy of science, and argue that there is a significant overlap, as well as a number of differences, between this work and the concept of a 'chemical object' developed above. In the following chapter, we will discuss this linkage in more detail with regards to orbitals and the 'chemical' theory of the atom.

Specifically, I will discuss the notion of 'rainforest realism' stemming from Ladyman et al. (2007), the notion of 'depth' developed by Michael Strevens (2008) and the 'engineering' approach developed by William Wimsatt (2007) as examples that illustrate how a philosophy of science sensitive to science has reached conclusions very similar to the ones we have drawn regarding chemistry.

9.5.3.1 Ladyman and Ross: PNC and PPC

Ladyman et al. (2007) develop what they call a 'rainforest realism' based on two principles. The first principle is the Principle of Naturalistic Closure:

> (PNC) Principle of Naturalistic Closure: Any new metaphysical claim that is to be taken seriously at time *t* should be motivated by, and only by, the service it would perform, if true, in showing how two or more specific scientific hypotheses, at least one of which is drawn from fundamental physics, jointly explain more than the sum of what is explained by the two hypotheses taken separately[11] (Ladyman et al. 2007, p. 37).

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[11] In the interest of completeness, note that Ladyman et al. 2007 interpret these principles in terms of the following terminological stipulations:

> Stipulation: A 'scientific hypothesis' is understood as an hypothesis that is taken seriously by institutionally bona fide science at *t*.
> Stipulation: A 'specific scientific hypothesis' is one that has been directly investigated and confirmed by institutionally bona fide scientific activity prior to *t* or is one that might be investigated at or after *t*, in the absence of constraints resulting from engineering, physiological, or economic restrictions or their combination, as the primary object of attempted verification, falsification, or quantitative refinement, where this activity is part of an objective research project fundable by a bona fide scientific research funding body.
> Stipulation: An 'objective research project' has the primary purpose of establishing objective facts about nature that would, if accepted on the basis of the project, be expected to continue to be accepted by inquirers aiming to maximize their stock of true beliefs, notwithstanding shifts in the inquirers' practical, commercial, or ideological preferences. (Ladyman et al. 2007, p. 38)

The second principle is the Primacy of Physics Constraint, which is stated as follows:

> (PPC) PPC articulates the sense in which evidence acceptable to naturalists confers epistemic priority on physics over other sciences (Ladyman et al. 2007, p. 38)

In terms of these two principles, the notion of 'composite theories' may be read as a metaphysical notion that satisfies the PNC. In contrast, PPC would at first blush meet with objection: under the construction of quantum chemistry as an 'interfield theory' there is no specific epistemic priority of physics, but rather epistemic *equality*, as would be expected from the classification of a composite theory as a (variety of) an interfield theory. In opposition, PPC introduces an explicit asymmetry, and gives physics epistemic priority over the special sciences.

At second sight, however, for the philosophy of chemistry this condition may be less of a problem: as the 'stipulations' of the PNC show, Ladyman and Ross are at pains to limit their notions to 'respectable' theories in some sense and chemistry certainly is a theory that fits the conditions of these stipulations. At the same time, the field of chemistry may, for the purposes of Ladyman and Ross, be close enough to physics to make satisfaction of the PPC trivial.

The 'rainforest realism' that results is a theory of ontology that is based on the existence of 'information channels' between theories – carrying *data* from one theory to the other in the sense of the Shannon theory of communication – and that at the 'receiver' end are algorithmically compressed, to, so to say, 'rediscover' the pattern that existed in the initial data. At this point Ladyman and Ross discuss a number of technical notions from the theory of information, namely projectability and depth.

For the purposes of our discussion, we do not need to delve in the logic of this in detail, but it will suffice to remark that 'projectability' refers to any pattern $x \rightarrow y$ in which y is obtained from a computation with x as input. The notion of 'depth' results from the pattern being 'compressible' in some useful way.

Rainforest realism is defined as:

> To be is to be a real pattern; and a pattern $x \rightarrow y$ is real iff
>
> 1. it is projectible; and
> 2. it has a model that carries information about at least one pattern P in an encoding that has logical depth less than the bit-map encoding of P, and where P is not projectible by a physically possible device computing information about another real pattern of lower logical depth than $x \rightarrow y$. (Ladyman et al. 2007, p. 233)

Our notion of a 'composite' theory is not restricted to carrying only information as data, instead, the concept of interpreting links on which the notion of a composite theory is constructed can carry concepts as well as data, and is in that sense thus a richer structure. This capacity to carry concepts marks a sharp divergence from rainforest realism: rainforest realism relies on a 'recomputation' of the pattern at the receiving end to develop the necessary ontological commitments, whereas recomputation is not required in the case of composite theories.

While the notion of ‘composite theory’ thus satisfies much of the requirements of ‘rainforest realism’, it is in some aspects a richer theory (especially in its capacity to carry theoretical concepts *tout court*) and in some aspects poorer: composite theories do not share a strict adherence to PPC, even as in the case of chemistry it is an open question whether PPC might be satisfied after all.

9.5.3.2 Senses of Depth

Another area where the notion of a composite object is linked to a similar recent position in the philosophy of science is another notion of depth than the one before. The notion of depth which is developed as part of ‘rainforest realism’ ontology is reconstructed as a *computational* property of the receiver. Depth in this sense is related to redundancy.

In opposition to this entirely computational approach, the recent work by Strevens (2008) focuses attention on depth as a causal quality of explanations. Strevens refers to his approach as a kairetic account of explanation, which is based on ‘difference making’ causal entailments. In addition, Strevens quantifies this difference making as the loss of accuracy that would result as a result of absence of this causal factor.

What makes Streven’s model interesting in the context of quantum chemistry is that it allows us to see how models may trade accuracy for generality – as we saw in Chap. 8, this is a significant issue in quantum chemistry, which we referred to as the ‘conundrum’ of quantum chemistry.

Depth is an important part of composite theories, since it provides a plausible interpretation of the ontological notion of ‘grounding’, but it is not a causal concept in the sense of Strevens. Rather, in a composite theory, *causality* is the ontological counterpart, through ontological commitment and grounding, of a law-like relation.

In other words, at the epistemic level of composite theories ‘depth’ is an epistemic, structural aspect of the overall theoretical structure. As a result, the way depth operates in the context of a composite theory is conceptual and data driven. It shares the data driven aspect of depth with rainforest realism, but does not rely on the ‘recomputation’ of rainforest realism.

9.5.3.3 Wimsatt’s Engineering

I wish to be brief about the notion of ‘re-engineering’ developed in Wimsatt (2007). Wimsatt introduces a number of new terms and concepts in the philosophy of science which result from his work in the philosophy of biology. Of the three positions which could be interpreted as ‘related’ to the notion of a composite theory, Wimsatt’s is perhaps the most remote. Wimsatt’s position develops through a series of papers on specific topics, and is perhaps most coherently formulated in Appendix C of his book. Taking this appendix as a guide, we can briefly discuss some properties of theories in Wimsatt’s terminology and outline how our notion of a ‘composite’ theory fits with that notion.

Engineering perspective: Wimsatt characterises the engineering perspective as a ‘cluster of theses derived from the assumption that theory has much to learn from practice and application’ (p. 354). Composite theories embody this engineering perspective heuristically: there are no a priori positions on how to set up the relevant links between theories of disparate fields without a clear understanding of what is needed.

Kludge[12]: ‘an unpretty but conditionally effective fix for a program or design failure or “bug” ’ (p. 356). Composite theories do rely on kludges, as for instance in ‘semi-empirical’ quantum chemistry. Where the term ‘kludge’ in Wimsatt’s description carries a subjective connotation – indicating a level of ‘ugliness’ associated with its introduction. In composite theories kludges are sometimes also called ‘approximations’. In these approximations, uncomputable aspects of the model are substituted, often ad hoc, for simpler expressions that ‘just work’.

Levels: Levels in Wimsatt’s theory refer to ‘compositional levels of organisation’, and in this fashion reappear in the notion of composite theories. The notion of ‘encapsulation’ was introduced in the composite theories to capture the need for abstraction introduced by the different compositional levels. In this sense, the notion of a composite theory decontextualises.

Multi-perspectival realism: by this, Wimsatt means that there is no single theory that claims to be exhaustive. As we saw in the discussion of rainforest realism, the composite theory, at least the composite theory of quantum chemistry, is not committed in a strong sense to the Primacy of Physics Constraint, but is committed to a dual, or perspectival notion, of objects.

Perspectives: ‘give organised approaches to a cluster of problems and techniques, often span levels, cross-cutting levels and each other, and give knowingly incomplete descriptions of the systems to which they are applied’ (p. 358). From this definition of perspectives, the concept seems applicable to composite theories: composite theories draw on various composing theories, and abstract both concepts and data from these theories, to sometimes (as in the case of semi-empirical quantum chemistry) give a knowingly incomplete description of the system.

Robustness: ‘is the existence of multiple means of determination or access to an entity, property process result or theorem that are at least partially independent’ (p. 359). Composite theories in this sense may or may not be robust. In some cases, there are only single means to determine an entity, on others, there may be such multiple ways.

While composite theories such as quantum chemistry have a significant area of agreement with at least the conceptual apparatus of Wimsatt’s view on science, Wimsatt’s view is deliberately piecemeal. Composite theories do not share this piecemeal approach and deliberately make stronger claims: they do adhere to overall structure based on well defined links between theories. That is, composite theories are committed to a unity of the sciences beyond Wimsatt’s engineering.

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[12] In Wimsatt’s book this is referred to as a ‘Kluge’, which is probably a typo. The term ‘kluge’ is unknown to me. However, the interpretation given by Wimsatt is usually referred to as a ‘kludge’ in software engineering.

9.6 Conclusion

Theories of chemistry form an interesting challenge for philosophers of science, and have the tendency to re-open some longer standing debates, such as the debate on the ontological status of theoretical terms. Moreover, I have illustrated that chemical theories – conceived as composite theories – form an excellent playground to test philosophical intuitions about theories, and look at the problem of reduction with a logical that allows controlled inconsistency (e.g. belief revision or a 'chunk and permeate' approach to paraconsistent logics). In this sense, the characterisation of chemical theories as composite theories outlines a programme of research in the philosophy of science of which chemistry could form a core component.

In specifics, this chapter has argued that robust philosophical engagement with the theories of chemistry might lead to new insights on theoretical terms and the ontological solution to Hempel's *Theoretician's Dilemma*. The standard ('realist') ontological resolution of the *Theoretician's Dilemma* is not available for composite theories. An analysis of ontology in terms of ontological commitment as well as grounding gives rise to a multi-perspectival notion of a chemical object.

The project of constructing chemical ontologies from the ontological commitments of 'composite theories' is part of a larger reassessment of these concepts that is currently still ongoing in the philosophy of science. The recent books by Ladyman et al. (2007), Wimsatt (2007), and Strevens (2008) all contain first steps in a similar direction, notwithstanding the significant differences between their positions. The programme seems to be one of advocating a philosophy of science that takes science, as opposed to metaphysical dogma, as primary in the evaluation of scientific theories.

There are some important differences in the concept of 'composite theories' that I advance here and these other approaches. In contrast to rainforest realism, composite theories do not need to 'recalculate' the depth carried in the data, and overall composite theories do not share the strong computational aspects of rainforest realism. Also, in opposition to Strevens' causal notion of depth, composite theories are primarily epistemological. In contrast to Wimsatt, composite theories are better organised: they do adhere to an overall structure of science.

Composite theories are based on the idea of inter-theoretic, often *interpreting* links, which have the capability to carry both concepts and information. In this sense, they may be seen as part of a non-reductive relation between the sciences of chemistry and physics. Yet the links that exist inside the object carry reductive commitments. These reductive commitments are not in the form of Nagelian identities and derivations, but are rather of assistance in the interpretation of the object, and the specification of the ontological commitments of the respective theories. These type of linkages are still in the spirit of Nagel, but less in the spirit of Causey (1977) (and to some degree, for instance Kim (1993)).

Chapter 10

Atoms, Chemical Atoms and Orbitals as Chemical Objects

Abstract In this chapter I develop the view on 'chemical objects' theoretically laid out in the previous chapter with the help of two specific examples: the notion of 'orbital' and the notion of 'chemical element'.

10.1 Introduction

In this brief chapter, it will be my aim to illustrate the concept of the ontological commitments of a composite theory with the help of the concepts 'orbitals', atoms, chemical atoms, and eventually a 'chemical theory of the atom' (CTA). A lot of the ontological and conceptual problems that are prominent in the philosophy of chemistry are the result of the problems of ontological quantification of composite theories.

Let us start with the notion of 'orbitals. The ontological problem with orbitals is briefly this. In quantum theory, an orbital is a part of a many-electron wavefunction. As such, the notion of an orbital is a key component in the understanding of the structure of many-electron wavefunctions and the energetic properties of molecules. But the way in which the concept of 'orbital' is used in many theories of chemistry can take matters much further than that. For instance, in the textbooks of organic chemists, an orbital can easily reappear as a structural component of a molecule, somewhat comparable to the struts that hold the ball and stick models of molecules together; hence, there is a somewhat unsettling identification of an orbital and a bond. Needless to say, such an identification is not at all supported by quantum theory.

The realisation that there is a dichotomy of the concept of orbital between the theory of physics and the theories of chemistry is not new. For instance, Richard Bader (1990) argues that:

> The orbital model has, however, been extended beyond its intended use of predicting and providing an understanding of the electronic structure of a system, by associating the forms of individual orbitals with the assumed spatially localized pairs of bonded or non-bonded electrons, and by attempting to define atomic properties in terms of coefficients of atomic-centred basis functions appearing in the expansion of molecular orbitals. These steps are admittedly arbitrary, as are attempts to define atoms through a partitioning of the Hamiltonian operator. This latter step violates the indistinguishability of the electrons from the outset. (Bader 1990, p. 131)

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There appears to be an ontological discontinuity between the term ‘orbital’ as it is used in many theories of chemistry, and the term ‘orbital’ as it is used in quantum theory: while chemistry has been successful in acquiring the term ‘orbital’ from physics, it has put this term to a use that is inconsistent with the use of the term in quantum theory. Hence, one could argue that epistemic inconsistency translates into an incoherent ontology. These two are the source of much confusion in the philosophy of chemistry.

A similar problem happens with the theory of the atom. In theories of chemistry, ‘atoms’ are multi-varied objects, which are described with various levels of detail, approximations, functions and roles, dependent on what a theory in question ‘needs’ an atom to be. For instance, in structural chemistry, atoms can be coloed balls, which have a certain geometrical valence allowing connections to other atoms with the purpose of creating spatial structures. This familiar picture – well-known from chemistry high school classes – underpins a significant amount of chemistry. For the spectroscopist, ‘atoms’ may be complex systems with a lot of internal structure leading to electronic spectra.

The problem of the ‘chemical theory of the atom’ is that it does not exist. The chemical theory of the atom is a philosophers’ conception of what an atom is in chemistry, and to my knowledge the term was first coined by Paul van der Vet (1987). It was used in our original article discussing the formalisation of the periodic table (Hettema and Kuipers 1988, 2000) in the context of a reductive theory. In his critique of our paper, Eric Scerri (1997) pointed out that the term ‘chemical theory of the atom’ did not, as such, exist. With Scerri (2016) he has revised his positions on reduction, but there are no further discussions on the existence of the ‘chemcial theory of the atom’ as an explantory structure that can act as a reductive substrate for the periodic table. It is my aim in this chapter to address that lacuna.

Thus, the ontology of chemistry is the ontology of a network of theories, each of which has different aims and objects, and a different view on ‘what there is’. This role and function of theories translates to the ontologies that they can support. Firstly, the ontology of a network of theories leads to objects that have depth and multivarious interpretations. Secondly, this view of chemistry sets out a programme in the philosophy of chemistry, which allows for a rich interpretation of its theories and objects. In this chapter, I will argue that rather than a mushy ‘anything goes’, a robust specification of the theories involved is necessary to shed light on these complex structures.

This is an important lesson for philosophers of science. The traditional view on theoretical terms is that they start out as theoretical postulates. which are specified with increasing precision as time goes by, and which in some cases the become amenable to experimental observation (see e.g. Nola 2007). The case of chemistry suggests that matters may not be quite so simple.

In the remainder of this chapter, I discuss the case of orbitals in Sect. 10.2 and the case of the ‘chemical’ theory of the atom in Sect. 10.3. I draw some conclusions relevant to the philosophy of science in the last section.

10.2 Orbitals as ‘Chemical Objects’

The matter of the actual existence of orbitals has been a recurring debate in the philosophy of chemistry since the publication of a paper in (and a photo on the cover of) *Nature* which claimed to depict actual orbitals (see Zuo et al. 1999).

In this section, it is my main aim to argue that the claim of physical observation of orbiitals misses the point in several important ways.

For the reasons described in Scerri (2000a), the claims of actual observation of orbitals should be treated with the utmost care. In the theory of quantum physics, ‘orbitals’ are mathematical constructs that are not in themselves observable. Instead, the theory of quantum mechanics treats orbitals as mathematical constructs that assist in the construction of the molecular many-electron wavefunction, and the wavefunction itself is treated as a probability amplitude. Scerri’s main argument, laid out in two papers, Scerri (2000a) and Scerri (2001), is that orbitals are in principle non-observable. Scerri underpins his caution about the claimed observation of orbitals by pointing out that orbitals are mathematical constructs and that ‘they do not pick out any entity which may be said to physically exist in the same sense that a planetary orbit exists’ (Scerri 2001, p. S84). Indeed, as Scerri concludes:

> [. . .] it is surely essential to be more discerning in attributing physical reality to entities that are defined theoretically and that the theory itself informs us do not exist physically. (Scerri 2000a, p. 1494)

In a recent paper, Labarca and Lombardi (2010) take issue with Scerri’s rebuttal of the claimed observations of orbitals and argue that the notion that orbitals do not exist relies on a ‘metaphysical reductionism’, which clashes with the practice of chemistry. The issue is also discussed in a paper by Mulder (2011), who argues that the ‘observability’ issue suffers from a somewhat ill-defined notion of ‘observation’. Following Scerri’s approach, Labarca and Lombardi (2010) address the issue from both a mathematical and a conceptual angle and in what follows we will discuss these in turn.

In the remainder of this section, I will argue that the focus on the existence or the observation of orbitals, deriving from the claims of Zuo et al. (1999), is likely to lead us up the wrong track in understanding the role and function of the concept of ‘orbital’ in actual theories of chemistry and physics, and hence will end up in giving us the wrong philosophy. It is not the physical observation of orbitals that matters most, it is the role and function of the concept of orbital qua tooling in the construction of chemical theory that is the most important.

10.2.1 The Mathematical Angle: The Role of Orbitals

The mathematical argument proceeds from the notion that orbitals are approximations (somewhat analogous to the ‘orbit’ approximations of planets in a solar system). Labarca and Lombardi (2010) take issue with Scerri (2000a) who argues that 'orbitals' are in fact not analogous to approximate orbits. Scerri argues that orbitals form a 'basis set'[1] for the expansion of a many-electron wavefunction:

> The continuing value of orbitals lies in their serving as basis sets, or a form of coordinate system, with which the wavefunction of an atom, ion, or molecule can be expanded mathematically to any degree of accuracy dictated by the available computational power. (Scerri 2001, p. 79)

Scerri then goes on to note that modern quantum chemistry has taken the easily envisaged concept of an 'orbit' and gradually turned it into an abstract entity, where not even the individual assignment of electrons to orbitals is consistent with quantum mechanics. Hence:

> Orbitals have not only lost their former pictorial aspect which they possessed at the beginning of the century when they were still called orbits, but now even the mere assignment of electrons to specific orbitals, or electronic configurations, as regularly carried out in chemistry and physics has lost its physical significance. (Scerri 2001, p. 79)

Labarca and Lombardi (2010) take issue with this characterisation. They argue that Scerri turns a mathematical limitation into an ontological fact. For, so argue Labarca and Lombardi (2010), the situation is analogous to planetary orbitals in the sense that the non-separability of both the planetary equations and the Hamiltonian of a many-electron system implies that these orbits/orbitals just have more complex shapes than originally envisaged – the non-separability leads to a more complex shape of the orbital, but leaves the essential concept untouched:

> But, as the fact that the planetary orbits around the Sun have complex shapes due to the interactions between planets does not imply the inexistence of planetary orbits, the complex shape of the electronic orbitals due to the interactions between electrons neither implies that orbitals – the spatial regions where the location of the electrons is more probable – do not exist. (Labarca and Lombardi 2010, p. 151–152)

Labarca and Lombardi get, in my opinion, a number of things wrong here. First note that Labarca and Lombardi perform a significant sleight of hand where they interpret orbitals as 'the spatial regions where the location of the electrons is more probable', since in the expansion of the wavefunction the orbitals are more accurately described as a basis, and, as I will argue in the next section, the 'spatial regions' that they consider to be orbitals are, at best, in the sense of Schwarz (2006), 'inferred orbitals'.

They are right to state that all mechanical three- (or more) particle systems are inseparable, and this is not a feature that is introduced in quantum mechanics. But they confuse the concept of 'orbital' per se (the concept of orbital as a 'basis') with the concept of the electron density resulting from an *occupied* orbital by interpreting the orbitals as a spatial region of 'more probable' electron density. Therefore,

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[1] I am somewhat unhappy with Scerri's terminology of a 'basis set' in this context, since it easily leads to confusion with the 'basis sets' used in quantum chemistry. I believe that the correct term to be used is that of a 'basis'. The term 'basis' is best seen as a 'coordinate system' for the expansion of the wavefunction.

for Labarca and Lombardi the refinements to the wavefunction[2] that are made by considering electron correlation, amount to refinements to the density resulting from the occupied orbitals – this is how they maintain the analogy between a planetary orbit and an orbital.

10.2.2 The Conceptual Angle: The Reference of Orbitals

Lombardi and Labarca also take issue with the argument, developed in Scerri (2001), that the term 'orbital' does not refer apart where it concerns the one-electron orbitals of the hydrogen-like atoms.

Specifically, Labarca and Lombardi argue, the non-referring character of orbitals does not imply non-existence. Rather, the non-reference of the term orbital depends on a 'deep conceptual breakdown' between the notion of orbital as it exists in quantum mechanics and as it is used in chemical theories. They argue that chemistry is the science not of atoms, but of molecules, and then discuss a number of issues around molecular shape, similar to the ones we discussed in Chap. 3, to illustrate another example of the deep conceptual breakdown that they are after.

At this point, the argument seems to be that if molecules can be real despite the theoretical problems with the concept stemming from quantum theory, then orbitals can be too, since once:

> [. . .] the two theories involved in the discussion about orbitals are clearly identified, it is easy to see that the problem of the reference of the term 'orbital' is rooted on a deep conceptual breakdown. Whereas in quantum mechanics 'orbital' is a non-referring term, in molecular chemistry orbitals exist as spatial regions on the basis of which the shape of the local and individual molecules can be explained. (Labarca and Lombardi 2010, p. 155)

Labarca and Lombardi conclude that the idea that orbitals do not exist can only be sustained on the basis of commitment to a deep 'metaphysical reductionism' which gives primacy to quantum mechanics in deciding such matters, and which disregards the legitimacy of chemistry as a science a priori.[3] They recommend that

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[2] As we have seen in Chap. 5, a many-electron wavefunction, when it is expanded as a single Slater determinant is separable, since in this case, the wavefunction is written as an antisymmetrised product of one-electron functions (which is sometimes referred to as an 'independent particle model' (IPM)). In this approximation, the Slater determinant still expresses the correct permutation symmetry between the electrons, but the inseparability resulting from the fact that a many-electron atom usually has three particles or more is, for single Slater determinants, disregarded. Further refinements to the wavefunction use either configuration interaction or perturbation theory, in which 'occupied' and 'unoccupied' orbitals are used to construct a more accurate wavefunction.

[3] The argument that they use to argue for this is somewhat curious: they argue as follows:

> Let us consider two theories T_1 and T_2, both containing a term 'C', which is non-referring in T_1, but refers to the entity C in T_2. Moreover, T_2 cannot be epistemologically reduced to T_1. For what reason can we say that the entity C does not exist *simpliciter*? Since epistemological reduction fails, the entity C described in T_2 does not exist only under the

we give up this commitment to metaphysical reductionism. This conclusion aligns with the idea that the ontological relationship between chemistry and physics is one of ontological plurality, with no reduction or priority relationships between the various concepts. Upon closer examination, these arguments are quite imprecise and in need of further clarification.

As a brief aside, Peter Mulder (2011) has recently argued, in a well written and concise paper, that the 'observability' claim of orbitals depends on one's notion of observability. Mulder distinguishes two notions of observability: the 'strict' notion of observability as used in quantum mechanics, and a looser notion of 'observability' relating to observations of (variations in) electronic density. Orbitals are observable when interpreted as the 'corresponding' regions of high electron density, and observability is constructed in a loose sense.

From this perspective Mulder argues that the use of the term 'orbital' in chemistry and physics is continuous, and that Lombardi and Labarca's argument for the discontinuity between chemistry and physics is incoherent. For Mulder, the incoherence is already present in quantum theory itself, and equally affects both the quantum mechanical and chemical meaning of the concept of orbital.

10.2.3 A Tooling Perspective

As an example of a theory of chemistry with sufficient complexity and sufficient specifiability, I considered the problem of stereo-selection which may be solved using specific roles of the orbital on the basis of the work of Kenichi Fukui (1966), which in turn is based on Hückel orbitals, in Hettema (2016). I concluded there that the discussion on the 'observability' of orbitals misses the mark in important ways: not only does it confuse the notion of an orbital with the notion of electron density (which is an observable associated with the overall wavefunction), it also ignores the *explanatory* role of orbitals. The concept of orbital has an existential and an explanatory role. Moreover, its existential role is not particularly interesting, while its explanatory role is.

This is a conclusion that generalises. In the approach to philosophy of chemistry advocated by Hoffmann (2007) and Kovac and Weisberg (2012), chemists are

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> assumption that T_1 is the "true" theory or, at least, the theory most appropriate to describe reality. (Labarca and Lombardi 2010, p. 155)

A lot seems to ride here on the notion that 'epistemological reduction' fails, although the sense in which it fails is unspecified. If we read 'epistemological reduction' as a variety of Nagelian reduction, then the failure can be a failure of either connectibility or derivability. Of the two, connectibility is primarily an ontological criterion, it says what terms of the reduced theory 'are' under the reduction, whereas it would seem that a failure of only derivability does not allow for the sort of ontological discontinuity inferred in the above statement. However, it seems to me that the failure of the connectibility criterion is what the debate on the existence of orbitals is all about.

predominantly molecular *engineers*, not theory builders. As such, chemists are apt to work with theoretical concepts that get the job done, as opposed to worrying about the theoretical robustness and empirical observability of such objects.

My theory of a chemical object is to some degree compatible with this engineering view. I disagree with Hoffmann that chemists are not interested in theories at all – in fact, the diagrams that he presents in support of his view themselves are ‘theoretical’ in important measure – but I agree that the use of theoretical concepts is pragmatic and limited to suitability for purpose.

This opens up the possibility of a ‘tooling’ perspective on theoretical concepts. This tooling perspective can be reconciled with the notion of ‘chemical objects’ that I developed in my previous chapter with relative ease. At the same time, this concept will pose difficulties for ‘hard’ ontologists and metaphysicians.

10.3 Multi-faceted Objects: Chemical Atoms

The second example of a ‘chemical object’ that I want to discuss is the notion of a ‘chemical theory of the atom’. In the previous chapter I outlined a theory of a chemical object loosely based on the concept of atoms. It is now necessary to provide some brief further context and connection with other research.

In the original paper on the formalisation of the periodic table we introduced, and subsequently used, the term ‘chemical theory of the atom’ in the following context:

> First, we will define what is meant by the term ’chemical’ conception of the atom. The ’chemical’ conception of the atom pictures the atom as a basic entity, with certain chemical characteristics, in particular the ability to form molecules with other atoms. On these chemical characteristics the chemical equivalence relation is based. [. . .] In chemistry [. . .] there exists a tendency to base qualitative discussions on a highly approximate level of the physical picture of the atom. (In fact, the level of approximation can become so high, that this kind of picture cannot be called ’physical’ any longer.) (Hettema and Kuipers 1988, p. 400)

In a follow-on sentence, this distinction is also characterised as ‘crude and intuitive’. In his criticism of our paper, Eric Scerri (1997) notes that

> [. . .] the authors express the view that physicists and chemists have a different conception of the atom. It is not clear whether they intend this as a historical claim, which would be correct at a certain epoch of the development of chemistry and physics, or whether they imply, incorrectly, that this is the current view. Later in paper it becomes clear that they do in fact intend this distinction to hold for contemporary chemistry and physics. (Scerri 1997, p. 233)

In this section it is my aim to clarify and discuss these different conceptions of the atom as a reductive basis for theory. I will start with a discussion of Paneth’s disambiguation of the notion of a chemical element, and then move on to van der Vet’s ‘chemical theory of the atom’ (CTA).

As a first step to a 'dual' notion of an element we might Paneth's well-known and influential historical disambiguation of the notion of chemical element found in Paneth (1962a,b).[4] The core of the disambiguation is formed by a distinction between the notion of chemical element into that of a *simple substance* and that of a *basic substance*. For Paneth, the difference between the two is the following:

> I have referred throughout to *'basic substance'* whenever *the indestructible substance present in compounds and simple substances was to be denoted*, and to *'simple substance'* whenever *that form of occurrence was meant in which an isolated basic substance uncombined with any other appears to our senses.* (Paneth 1962b, p. 150)

Paneth moreover distinguishes the practical definition of a chemical element stemming from Lavoisier, in which a chemical element is considered as a non-decomposable substance, from the more, if one must, 'metaphysical' considerations of the philosophers (which for instance sometimes limited the number of available elements to some predetermined number). Thus, as a simple substance, gold is a yellow metal, while as a basic substance it denotes the element 'gold'.

Although much has been made of Paneth's distinction in these two notions of chemical element, my contention is that the key to the story lies rather in Paneth's notion that chemistry was born of the *identification* of these two notions of element; the realisation that 'basic substances' manifest themselves as 'simple substances' to our senses. The fact that thet identification of the two notions of an element lead to the science of chemistry provides strong support for the notion that 'chemical objects' – objects which result from ontological quantification over the composite theories that make up the science of chemistry – are indeed multifaceted.

The multi-faceted nature of chemical objects leads to the insight that the properties of chemical objects may only persist in some theories, not in all theories. In this vein, Paneth writes that:

> [...] the great *significance* of elements for the whole body of chemical theory lies in the assumption that the same substances which produce the phenomenon of 'simple substances' serve in the quality-less, objectively real sphere of nature as 'basic substances' for the construction not only of simple but also of composite substances. *The fundamental principle of chemistry that elements persist in their compounds refers to the quality-less basic substances only.* (Paneth 1962b, p. 151)

Paneth argues that chemists employ a certain 'naive realism' with respect to simple substances, but that this naive realism cannot be carried over into the realm of basic substances, which are abstract entities in themselves devoid of properties. Thus, the notion that 'basic substances' somehow persist in chemical compounds requires a leap into a 'transcendental world devoid of qualities' (p. 150). The notion of a chemical element as it is commonly understood today refers primarily to the 'basic

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[4] The detailed historical studies by Ruthenberg (2009, 2010) have illustrated that Paneth's disambiguation of the notion of chemical element has strong Kantian roots. It is not my aim to settle any of these controversies in the context of Kant scholarship. Usually, this disambiguation is discussed in the context of the causal theory of reference. See for instance Scerri (2005) and Hendry (2005).

substance', whereas the 'simple substance' is a left-over from a more naive realist period in chemistry, in which, for instance:

> [...] the properties of sulphur are just those properties which it exhibits to us in the special case when it is not combined with any other basic substance. (Paneth 1962b, p. 151)

In what remains, we can flesh out some of the philosophical consequences of this approach.

A first observation is that for the notion of 'chemical element' as a theoretical term the realist way out of the theoretician's dilemma is not directly available. More precisely, it is not entirely clear, in the light of Paneth's disambiguation what a chemical element exactly *is*. It could be argued that simple substances refer to observables while basic substances are 'theoretical' in the sense that they do provide the sort of organisational characteristics that Hempel requires from theoretical terms. This reading of Paneth's disambiguation might suggest that the notion of a chemical element as a 'simple' substance has gradually disappeared from our vocabulary, in a manner similar to how Sellars (1963) has suggested that a 'manifest' image of nature is over time gradually replaced by a 'scientific' image.

This suggestion is erroneous. The replacement model has been criticised in the philosophy of chemistry, most notably by Jaap van Brakel (2000) and, from a different viewpoint, by Hoffmann (2007). From the viewpoint of classical philosophy of science, this replacement model also seems to get its direction wrong: it replaces, over time, an 'observational' term (i.e. the chemical element as a simple substance) with a 'theoretical' term (i.e. the chemical element as a basic substance). The standard route for the realist view on science, as for instance argued in Nola (2007), runs however in the other direction: science usually *postulates* the existence of particular abstract objects which over time can be observed.

Paneth's disambiguation rather suggests that both views of the chemical element have a role to play. A detailed reconstruction of Paneth's argument, drawing from Paneth's philosophical as well as his chemical work, is given in Scerri (2000b). Scerri argues that the tension between these two views of the elements[5] can be resolved by adopting an 'intermediate position', which is:

> [...] a form of realism, [...] tempered by an understanding of the viewpoint of the reducing science but which does not adopt every conclusion from that science. (Scerri 2000b, p. 52)

The sort of scientific realism suggested by Devitt (2007) is not in this sense available, and scientific realism, however attractive as a starting point, is a poor type of realism for theories of chemistry.

The way forward is suggested by taking Paneth's approach seriously, and further developing the angle that the science of chemistry originated in the realisation that both pictures of the element are accurate in chemical theorising.

In this context it is useful to recall the discussion about *semi-empirical* quantum chemistry which we discussed in the context of the calculation of potential energy

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[5] Scerri discusses orbitals as well, but his 'intermediate position' is developed primarily on the basis of the chemical elements and the periodic table.

surfaces on page 75. One of the defining problems of the theory of absolute reaction rates was the calculation of the (reactive) potential energy surface, a complex multi-dimensional entity that required significant simplifications in the quantum mechanical view of an atom. As was noted there, these simpplifications were incompatible with a fundamental view on the atom as it derived from quantum mechanics. While Eyring was not the first to make these particular approximations, which 'are shown to fail badly' (Eyring 1938 p. 8) from a fundamental point of view, Eyring's formulation is one of the first clear and comprehensive formulations of what the construction of a 'chemical' theory of the atom actually entails. From the viewpoint of the philosopher of science, it is interesting and relevant that this formulation took place in the context of what we may, with the benefit of hindsight, characterise as a 'guide programme' in the terminology of Zandvoort (1986).

We can build on this notion of a 'complex' ontological entity if we reconsider the notion of a 'chemical theory of the atom'. As discussed in Chap. 8 (p. 197) Paul van der Vet (1987) has similarly argued for the existence of a 'chemical' theory of the atom (CTA). The CTA concept was introduced as an approximate quantum theory of the atom in which:

> (a) The chemical properties of an (unbonded) atom are determined by the electron arrangement of the atom in a state which will be called the atom's *basic state* [. . .];
> (b) The chemical properties of molecules are determined by their electron arrangements [. . .];
> (c) The electron arrangement of a molecule depends on the constituent atoms and is determined: (i) by the basic configurations of the constituent atoms directly; and (ii) by the molecule's structure, which is partly determined by the basic configurations of the constituent atoms. (van der Vet 1987, p. 170–171)

This theory can be further developed, using additional approximations into the Slater/Pauling model or a variety of Eyring's semi-emprirical notion of an atom. It can also be seen as an interpretation of Paneth's 'basic substance' notion of a chemical element.

While these models are incompatible with the fundamental notions of quantum mechanics, and also ab initio quantum chemistry, they play keys roles, again in important measure *qua* tools, in the development of theoretical views on compounds, reaction mechanisms and the periodic table. In brief, they form the building blocks of molecular design[6] and thereby, with all their limitations, and adaptations to different contexts, the basic building blocks of chemistry.

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[6] As alludedd to in an earlier section of this chapter, one might take this idea to subscribe to a view of chemistry as a form of 'molecular engineering'. This view is defended passionately, and with some justification, by Hoffmann (2007) and Kovac and Weisberg (2012). While I do not agree with some of its conclusions, notably the one that chemists do not have any interest in theory building, the main line of the argument: that chemistry is different from physics in many important respects, is correct.

10.4 Conclusion

In this chapter I have further developed two particular notions of a chemical object – the notion of an 'orbital' and the'chemical theory of the atom' – as examples of how objects function in chemistry. In particular, I have focused on the notion of an 'orbital' and the notion of a 'chemical theory of the atom'.

The chemical theory of the atom is *related* to quantum theoretical notions of the atom, but at the same time *incompatible* with them. The chemical theory of the atom is a key example of the pragmatic borrowing that goes on in the development of chemical ontologies. I have also argued that this 'pragmatic borrowing' gives rise in important measure to a view of chemical theories as tools rather than as theoretical entities which purport to answer the 'big' questions such as 'how the world really is'. Chemists usually do not have a lot of time for such questions, and little patience with overbearing answers.

The tooling perspective, however, does commit us to a form of realism – we would like our tools to be real in a general sense after all – but it is realism of a complex sort. As a realism, it commits us to viewing objects as having depth and structure, and not necessarily as 'hard' 'simple' objects that completely constitute a world. Chemical objects are, in an important sense, provisional and malleable.

How we exactly specify these chemical objects is kept deliberately somewhat vague. It is my opinion that the exact specification can form a proving ground for refined models of ontology and theoretical interconnections, and that it is quite possible that a variety of philosophical and logical approaches could work in specifying more precisely what chemical objects are. It is a somewhat tired cliché, but this should be left as an exercise for the reader.

Postscript

Postscripts are about what has been gained, and about the positioning of one's efforts into the broader context of things. The purpose of this postscript is to give a sampling of these broader contexts and provide a number of 'take home' points that may inform further research in both the philosophy of chemistry and the philosophy of science. In doing so, I will primarily focus on the role of reduction as a mechanism to draw out the necessary inter-theory connections.

Some perennial issues in the philosophy of science – about the nature of reduction, the nature of scientific observation, and the nature of theoretical entities – take on extra poignancy in chemistry. A detailed study of the science of chemistry thus holds out considerable promise that the wider philosophical sensibilities on these issues can be significantly sharpened. Philosophy of chemistry is not only a recent, but also a small field, and its practitioners are in general not very well known in wider philosophy circles. That is a pity, because philosophy of science has much to gain, I believe, not only from a closer consideration of chemistry as a science, but also from taking on board some of the specific issues and concerns of philosophy of chemistry.

My specific aim in this postscript is threefold. I first address the question of how the model of reduction between chemistry and physics that we have developed here impacts on the relative *status* of chemistry and physics. Partly, this is to allay some fears that the consequence of a successful 'reduction' might be elimination of chemistry as a discipline. How the descent from 'reduction' to elimination might actually work in practice is not always clearly stated, nor well understood. Once the steps that lie between reduction and elimination are made clear, I believe that the concept of reduction that I have advocated holds out no prospects for the elimination of chemistry in favor of physics.

I also investigate the extent to which our conclusions about reduction might generalise. The concept of reduction that I have advocated here is very liberal, and is in some interesting sense not that far removed from non-reductive views on the unity of science, such as those of Duhem (1914) or the views discussed by Potochnik

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(2011). Much of the recent work on the reinterpretation of the Nagelian theme of reduction is arguing for a similar sort of unity, and thus there is a sense in which it might be said that a *unification* of reductive and non-reductive approaches might be in the wings. In this postscript I only scratch the surface of that project.

Finally, I discuss in more detail what the consequences of the present discussions might be for the developing field of philosophy of chemistry. Chemistry as a science is interesting beyond reduction, and much work still remains to be done in the area of chemical explanation, chemical theory formation, and the metaphysics of chemistry as a science. This work can be related, in important measure I believe, to similar work in the philosophy of science that focuses on sciences other than chemistry and physics.

Reduction and Disciplinary Elimination

One of the original motivators for philosophers of chemistry to be critical of reduction, I believe, was the fear that a successful reduction might lead to a 'takeover' of chemistry by physics – or a situation in which chemistry was placed under the tutelage of physics. The title of the thesis of Paul van der Vet (1987), '*The aborted takeover of Chemistry by Physics*', suggests that quantum chemistry attempted a 'takeover' of chemistry at some stage. As the title furthermore suggests, this takeover was, at some point, aborted. It seems reasonable to surmise that the fear that some day chemistry may be 'reduced' to quantum chemistry (and thereby eliminated to some degree) formed a partial inspiration for the critique of a reductionist programme in chemistry and physics.

A 'takeover' may be classified as one extreme of a range of inter-disciplinary and policy options which form part of a 'sociological' component of reduction. The danger usually associated with the sociological component of reduction is some sort of *tutelage*: the idea that the reduced science can be placed under the supervision of the reducing science.

It should by now be obvious that chemistry is in no such danger: if chemistry ever was in any danger of being 'taken over' by physics, that would have happened long ago. Instead, all that has happened is that quantum chemistry has been imported as a bench-top 'tool' alongside many devices from physics lab practice. As an experimental thesis, it would therefore seem that the 'takeover' thesis has been thoroughly falsified – not only has chemistry not been eliminated during about 80 years of developments in quantum chemistry, the current practice suggests that chemistry has successfully *accommodated* quantum chemistry.

The model of reduction that was developed here is capable of capturing this sort of relationship fruitfully: the links that form the basis of the reduction relationship match to a considerable degree with the 'logical structure matching' (p. 18), which formed the (formal) basis of Neurath's unity of science programme. In our model of reduction, any sort of dependency relation that could be imposed on this relationship should be empirically tested, and holds only in a contingent, not in a necessary manner.

It is in this context particularly useful to trace the steps that would need to be taken to achieve a 'takeover' from a successful 'explanation' to clarify where the attempted takeover of chemistry by quantum theory or quantum chemistry – if there ever was such a thing – went off the rails.

The view that successful reductions may lead to disciplinary elimination was perhaps first elucidated in Kallen's criticism of the concept of reduction discussed in Reisch (2005).[1] As the response to Kallen's paper shows, philosophers have had an uneasy time with the concept of disciplinary elimination (though perhaps less so with its reduction).

The reason for this is that disciplinary elimination proceeds through a number of progressive steps which obtain rarely in practice, such as strict identity of reduction postulates and robust derivability. A preliminary list of these steps would run more or less as follows:

1. The first step would be *explanation*, in which one science can be said to successfully *explain* (aspects of) another science.
2. The next necessary step would be one for (formal) reduction in a strong sense – especially it would need to be shown that the reduced science adds nothing 'new' to the explanation provided by the reducing science.
3. The third step would be that the reduction postulates assume the form of identities – that is, the theoretical entities and properties of the reduced science can be shown to be 'nothing but' entities and properties of the reducing science.
4. The fourth step would be theoretical elimination, assuming it is easier to speak of the phenomena of the reduced science in terms of phenomena of the reducing science.
5. The final step would be social elimination, where the reduced science is subsumed under the reducing science.

In the reduction of chemistry to physics, it would seem that the first step is relatively unproblematic, albeit local – quantum chemistry *can* explain many aspects of chemistry, and has moreover fruitfully contributed to concept formation in chemical theories. The second step is more problematic. The reduction that obtains is not always reduction in a strict sense, and theories of chemistry do in many cases have something 'new' to add to quantum chemical explanations. As we saw in Chap. 8, in many instances the explanations are only partial.

The remainder of the steps do not obtain at all. In many cases the reduction postulates are not identities, but are of weaker 'correlating' or 'aggregating' forms or express experimental facts. This means that it is not possible to hold that chemical

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[1] See the discussion in Reisch (2005) on Horace Kallen's critique of reduction. Kallen's work is nowadays not influential, but it can perhaps be argued that this sort of critique formed the nucleus of the many critiques of logical positivism in the 1960s; if not in substance, then at least in motivation.

entities are ‘nothing but’ entities of quantum theory in general. Similarly, the last two steps do not obtain in this case.

Hence the view on reduction I have developed here holds that we have a case of fruitful explanation, partial reduction, and partial ontological independence, though, as illustrated in Part III, interesting ‘grounding’ linkages exist, leading to ‘dual’ objects that feature in a type of theory we have classified as ‘composite’ theories. These are all contributing factors to quantum chemistry’s important accommodation into chemistry as a useful tool. In this sense, reduction is not a threat for chemistry, but rather an enabler.

The view on the reduction of laws and theories that I have defended is Nagelian in the sense that it accommodates the autonomy of the special sciences, and does not defend elimination. The reason for this, and this should be clear from the discussion in Chap. 8, is that the prevailing reduction relationships are not identities, but rather come in a large number of varieties. The scientific explanations on which the reductions are based therefore amount to (some form of) Nagelian reduction, but escape the straitjacket of ontological ‘nothing but’ arguments which eventually lead to the elimination of a discipline.

To a metaphysically oriented philosopher of science, especially metaphysicians of the sort excoriated in the first chapter of Ladyman et al. (2007), such a conclusion might be somewhat disappointing. If reduction relationships are not based on identities, in the spirit of Causey (1977), some old thinking about the unity of science must be discarded, and some new thinking developed.

Reduction and the Unity of Science

The view on reduction that I have used up to this point is very much a view of *theories*, in which quantum chemistry has developed into a useful *tool* in chemical theorising and model building. In Chaps. 9 and 10 I have furthermore argued that the ‘ontological’ forms of reduction that have become popular in the philosophy of chemistry can only be understood as special features of the reduction of laws and theories, and especially cannot be understood in the sense of a ‘prior’ type of reduction that somehow precedes ‘epistemological’ reduction.

The ‘unity of science’ in this context can therefore not be viewed in terms of Neurath’s ‘pyramidical’ structures. Rather, the sort of unity of science that is supported by the reductive claims of this thesis amounts to logical *accommodation* of one science by another, together with a significant amount of subject autonomy.

As was discussed in Chap. 8, the reduction postulates are in this work represented as ‘information channels’ which carry a limited amount of information from one theory to the other on an ‘as required’ basis. What they do not carry is *context*, a situation which led to the proposal of ‘composite’ theories. Hence it is possible that concepts of one science are used ‘out of context’ in another science. The best example of this in the philosophy of chemistry is perhaps the notion of atomic and molecular orbital, which was discussed in Chap. 10. As discussed there, orbitals

Table 1 Classification scheme for the unity of science derived from consistency and reduction requirements as given in Needham (2010)

	Reductionist (derivation)	Non-reductionist
Consistent	(i) No autonomous regions	(ii) No Autonomous regions (interconnections)
	(a) Autonomous regions	(iii) Autonomous regions
Inconsistent	(b) Para-consistency (Chunk and permeate)	(iv) Disunity

are used in the quantum theory of atoms and molecules as components of a wavefunction, while in some chemical theories they develop a life of their own.

The moderate reduction relationship on which my argument is based therefore support a 'unity of science' in which different sciences have a significant autonomy.

Needham (2010) has summarised the various positions on reduction and the unity of science, leading to the fact that:

> [. . .] several general positions can be initially distinguished: (i) unity in virtue of reduction, with no autonomous areas, (ii) unity in virtue of consistency and not reduction, but still no autonomy because of interconnections, (iii) unity in virtue of consistency and not reduction, with autonomous areas, and (iv) disunity. (Needham 2010, p. 163–164)

Needham's argument may be conveniently represented as in Table 1, where it is extended with two (new) positions (a) and (b). The two main dimensions are between 'reductionist' (involving a notion of derivation and Neurath's 'pyramidical' structure) and non-reductionist on the one hand, and a notion of *consistency* on the other. The matter is then whether a notion of *autonomy* may be supported and what the nature of this autonomy would be. It should be clear that the present work argues for notion (a) with allowance to be made to accomodate notion (b) at times, but it is useful to investigate what the other positions would entail to contrast (a) properly from its alternatives.

Position (i) argues for a strict 'metaphysical' reductionism in which derivation is strict and reduction postulates are identities. This sort of reductionism does not apply in the reduction of chemistry to physics, and, as argued before, recent work on the Nagelian theory of reduction also indicates that this sort of reduction is not what Nagel had in mind.

Position (ii) is usually not discussed in the philosophy of science, and describes a situation in which two or more theories are (empirically) equivalent, and are furthermore dependent on each other, but there is no relation of derivation. Following Needham's text, which in turn relies on Duhem (1954), examples would be the comparison between Keplerian mechanics and classical mechanics. However, this position does not well describe the relationship between chemistry and physics since, despite the domain overlap, both sciences inhabit different empirical realities and are in this sense autonomous. The nature of the 'interconnections' is moreover not well specified in Needham's scheme. Finally, the theories of chemistry and physics are not as strongly dependent on each other as implied (though not stated) in position (ii) in the scheme.

Position (iii) describes a conception of cooperation, in which several autonomous sciences cooperate to describe empirical reality. This conception is closest to Neurath's conception of the unity of science. In comparison to position (a), what is lost in position (iii) is the idea that one science may fruitfully *explain* aspects of another. In brief, it is hard to see what a non-reductive relationship between theories amounts to, and, in comparison to position (a), (iii) seems to underestimate the amount of explanation that does go on. Position (iv) is described by Dupré (1993), and is the 'silo' approach favored in post-modernism.

I have argued for position (a) with perhaps an occasional spill-over in position (b). The main attraction of position (a) over position (iii) is that position (a) allows us to specify what a theory relationship amounts to. The formal conditions for explanation and derivation in the Nagelian framework are suitably loose to allow for theoretical and empirical autonomy, while at the same time allowing *accommodation* of one theory into another.

The box labeled para-consistency is interesting in its own right. The issue of context in logical environments is currently an active area of research. What may be especially important for the philosophy of science is a recent series of papers by Brown and Priest (2004, 2008), who develop a 'chunk and permeate' approach that they claim holds even inside a single theory. It is my personal belief that this is in important measure where the future of philosophy of chemistry lies: we can argue for a Nagelian reduction scheme *qua* paraphrase and then impose a para-consistent scheme of deduction. This approach would allow for significant formal rigour, which, this time around, has a chance of doing justice to the complexity of chemistry as a science.

Needham does not provide an option in the case where the two fields are inconsistent, but where a reductionist relation still holds. While this might at first sight also seem an impossibility, it is nevertheless possible that the notion of 'chunk and permeate' provides exactly such a case. Brown and Priest argue that the structure of many sciences hinge on such 'chunk and permeate' structures, in which the encapsulated information deriving from consistent 'chunks' are is allowed to logically 'permeate', but with a loss of (logical) context. If Brown and Priest are right, it is not only possible, but even likely, that such an approach would similarly work for the unity of science.

Reduction and the Philosophy of Chemistry

The moderate form of a reduction relation that I have advocated here also has a number of interesting consequences for the philosophy of chemistry.

In the first place, the reduction relation leaves the *autonomy* of chemistry intact. At the same time, the specific form of the reduction relation also incorporates the possibility that reducing theories may be used as elements in the formulation of chemical theories or as chemical lab-bench *tools* on the other. This sort of accommodation of a reducing theory in chemical practice may lead to interesting further work on concept formation, tool formation and chemical practice. Chemistry is sufficiently different from physics to lead to some new interesting insights which may impact on the wider philosophy of science.

The reduction relations exhibited between chemistry and physics show an unexpected variety and richness. The investigation of these relationships, and the translation of the results to reduction relationships that may obtain in other sciences will guarantee the intellectual health of philosophy of chemistry for a long time to come. The proposed model of *accommodation* of the reducing theory by the reduced theory is close to the Duhemian model of science, in which, as Needham (2010) formulates it, the putative reduced theory is *extended* by the putative reducing theory, though, as I argued in the previous section, the Duhemian approach is not my preferred one.

I have also argued that philosophers of chemistry better rid themselves of the concept of 'ontological reduction'. Apart from all the reasons given in Chap. 9, the concept of ontological reduction is representative of a drive to specify that the concepts of one science are 'nothing but' concepts of another, and in the relationship between chemistry and physics such attempts are doomed to fail.

The re-establishment of a reduction relation could also spark some interesting new insights into *how* quantum theory is so successful in explaining a *classical* science like chemistry.

There is some work being done in the emergence of a classical world out of quantum theory which could assist in settling these fundamental issues, with the book by Bokulich (2008) as an interesting example. However, since at the moment some of the *science* regarding these issues is unsettled, philosophers had perhaps better stand aside till the scientific questions are settled, unless they are particularly sure of their own scientific footing. As some of the early attempts of philosophers of chemistry to intervene in the debate on molecular shape, as well as the current debate on the existence of orbitals have shown, unless they have a deep understanding of the scientific issues involved, philosophers may have little to contribute.

Even so, these debates are unlikely to settle the issue of why particular composite theories, which we have defined here as theories (of chemistry) which import 'quantum concepts' from physics are such key explanatory tools in the science of chemistry. The notion of a 'field' plays a role (given the provenance of composite theories in the model of Darden and Maull (1977)).

Consequences

Philosophy of science has recently rethought the notion of the Nagelian reduction relationship significantly, and as a consequence has largely moved away from the strict derivation *cum* identities which characterised the interpretation of the Nagelian scheme until recently. The consequence of this rethink is that new formal and practical work needs to be done to investigate whether such more moderate reduction relationships obtain in real life examples.

This development will have interesting spin-offs in the areas of epistemology, theory formation, and ontology.

In the area of epistemology the incorporation of concepts and methods from other sciences as practical *tools* adds a new dimension which has not been extensively explored. The notion of knowledge as 'justified true belief' may gain considerable complexity and depth once the idea of justification includes tool-making from underlying sciences and notions of justification draw on multiple bodies of knowledge. Epistemology has suddenly become a lot more interesting if we have to consider *networks* of beliefs, with limited channels of information.

Theory formation has always been a somewhat unsatisfactorily unresolved issue in the philosophy of science, with much of the work undertaken by the *Received View* philosophers abruptly abandoned once the Kuhnian paradigm appeared on the scene. The Kuhnian paradigm postulates what the *Received View* philosophers sought to explain – the emergence of theories from facts, and the logical framework which allowed the sort of imaginative creative leaps and bounds that enter into the construction of a scientific theory. The idea that there is a fruitful *exchange* of concepts and explanations between the sciences could perhaps put new impetus into this flagging area of research.

Lastly, the science of chemistry presents multiple ontological issues, of which I have barely managed to scrape the surface. I believe that a consideration of ontology prior to a thorough consideration of epistemology is bound to fail, and that the approach that takes us from 'theory' to 'ontological commitment' *cum* 'grounding' more or less gets things right. That means that the sort of epistemological depth present in our theories has profound consequences for how we construct chemical ontologies. As I have argued, chemical objects are strange objects, but not outside the scope of what might be fruitfully studied by philosophers.

The reduction of chemistry to physics is in this sense indeed a paradigm case for the notion of reduction.

Appendix A
Acronyms and Notational Conventions

A.1 Acronyms

Quantum chemical acronyms	
BO	Born-Oppenheimer (approximation)
CAS	Complete active space
CC	Coupled cluster (theory)
CI	Configuration interaction (theory)
GTO	Gaussian type orbital
HF	Hartree-Fock (theory)
LCAO	Linear combination of atomic orbitals
MBPT	Many body perturbation theory
MCSCF	Multi configurational self consistent field (theory)
PES	Potential energy surface
QTAIM	Quantum theory of atoms in molecules
RHF	Restricted Hartree-Fock (theory) (the wavefunction is an eigenfunction of the spin operator S^2)
SCF	Self consistent field
STO	Slater type orbital
UHF	Unrestricted Hartree-Fock (theory) (the wavefunction need not be an eigenfunction of the spin operator S^2)
Philosophical acronyms	
GTC	General test conditional
GTI	General test implication
HD	Hypothetico-deductive (method)
SIS	Sufficient isolation (of S)

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A.2 Notational Conventions

In this thesis we follow the following notational conventions.

Operators are indicated as $\hat{A}$. Vectors and matrices are generally indicated in boldface, as in $\mathbf{R}$. In the discussion of molecular shape, we also need a concept of vectors of parameters, which are indicated in sans-serif font, as R. Dirac notation will be used throughout, as in $\langle x|A|z\rangle$ to denote quantum chemical quantities.

The structuralist conception of theories employs a complex notation, which is gradually introduced in Chap. 6. Set theoretic structures are indicated by capital 'calligraphic' font, as in $\mathscr{U}$ rather than the boldface type used for structures in Balzer et al. (1987). Again, to expand structures into their relevant elements, angular notation will be used, as in $\langle x_1, x_2, \ldots\rangle$. The difference between this and Dirac notation is generally clear from the context.

'Reduced' (or, 'reduction candidate') theories are indicated by T', and 'reducing' theories (or their candidates), by T; the reduction relation will be written $R(T', T)$. Note that this notation is the opposite from that used in the key paper by Mormann (1988), where the primed and unprimed versions are switched. Reduction relations will be indicated with a capital letter R to denote an 'overall' reductive claim or a Greek letter ρ to denote level-specific claims.

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