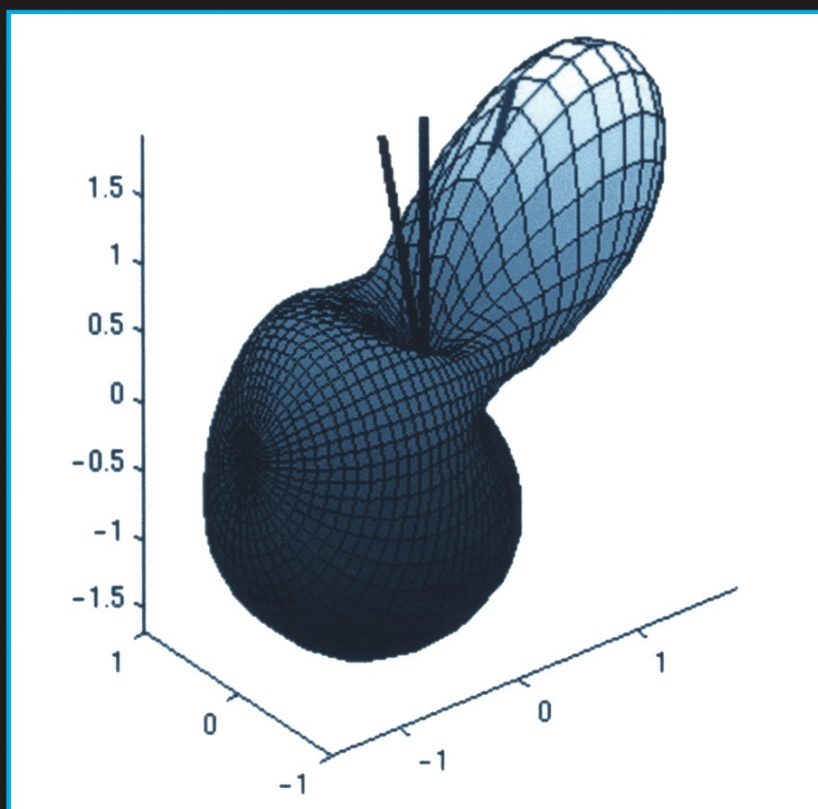


PHYSICS OF ATOMS AND MOLECULES

ELECTRON SCATTERING

From Atoms, Molecules,
Nuclei and Bulk Matter



Edited by
Colm T. Whelan and Nigel J. Mason

Electron Scattering

From Atoms, Molecules, Nuclei, and Bulk Matter

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Electron Scattering

**From Atoms, Molecules, Nuclei,
and Bulk Matter**

PHYSICS OF ATOMS AND MOLECULES

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Preface

There is a unity to physics; it is a discipline which provides the most fundamental understanding of the dynamics of matter and energy. To understand anything about a physical system you have to interact with it and one of the best ways to learn something is to use electrons as probes. This book is the result of a meeting, which took place in Magdalene College Cambridge in December 2001. Atomic, nuclear, cluster, solid state, chemical and even bio- physicists got together to consider scattering electrons to explore matter in all its forms. Theory and experiment were represented in about equal measure. It was meeting marked by the most lively of discussions and the free exchange of ideas. We all learnt a lot.

The Editors are grateful to EPSRC through its Collaborative Computational Project program (CCP2), IOPP, the Division of Atomic, Molecular, Optical and Plasma Physics (DAMOPP) and the Atomic Molecular Interactions group (AMIG) of the Institute of Physics for financial support. The smooth running of the meeting was enormously facilitated by the efficiency and helpfulness of the staff of Magdalene College, for which we are extremely grateful. This meeting marked the end for one of us (CTW) of a ten-year period as a fellow of the College and he would like to take this opportunity to thank the fellows and staff for the privilege of working with them.

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ATOMIC CONFINEMENT

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Abstract We review the recent revival of interest in the subject of confined atoms, motivated by experimental developments in a number of areas, e.g. atoms under extreme pressure, atoms confined in zeolites, in bubbles, in solids, in quantum dots or trapped in molecular cages, as occurs in metallofullerenes. The subject originated very early in the development of quantum mechanics, and even provided a theme for Arnold Sommerfeld in a birthday celebration in honour of Wolfgang Pauli. After this high point, it languished relatively unnoticed, except by a few practitioners who mostly used wavefunctions of confined atoms as a starting approximation to describe atoms in solids. The recent discovery of new forms of confinement demonstrates that concepts must be refined to bring out the rich diversity of effects expected in the spectroscopy of confined atoms. They allow atomic behaviour to be explored under novel circumstances, and provide a new bridge (alternative to cluster physics) from the atom to the solid. At present, metallofullerene targets are still difficult to manufacture with sufficient number density for ultraviolet and soft X-ray spectra to be probed. It is likely that this experimental problem will soon be resolved. Thus, the motivation already exists to predict what novel effects may occur and what their likely spectral manifestations will be. This should turn into a thriving new area.. Some current theoretical problems in the treatment of confined atoms will be described. A discussion of the recent classification of resonances in confined atoms into three different types will be presented. The influence of confinement on correlations will be indicated. Possible connections to the theory of EXAFS will be outlined.

Keywords: confined atoms, clusters, quantum dots, fullerenes, metallofullerenes

Introduction

In addition to the fact that they involve new objects – for example, the metallofullerenes, quantum bubbles or quantum dots – whose existence had not previously been supposed, confined atoms are of interest for a variety of reasons. First, they offer prospects of a new path in the practical application of atomic physics. Second, they complete our understanding of classical problems in atomic physics, such as the self-consistent field or quantum defect theory, where new boundary conditions can be applied. Third, they offer the possibility of allowing correlations to be actively probed, both experimentally and theoretically.

Thus, the confined atom emerges as a new and distinctive topic in atomic physics. Like any new problem it has its own history, and this must first be described, to dispell the impression that it has suddenly come out of the blue. In this sense, it is similar to the subject of cluster physics, which also emerged in recent times as an apparently new development, but actually has its roots in early experiments, especially the study of atomic beams for Stern-Gerlach measurements. The parallel with cluster physics is an interesting one. As we shall bring out, there are also interesting differences between these two subjects, which have in some ways developed along opposite lines.

In the present paper, we review some of the early history of confined atoms, then present some more recent work, culminating in actual experimental realisations. In conclusion, we present our own view as to the importance of this area of atomic physics, and the reasons why it deserves to be pursued.

1. Some Early History

In contrast to cluster physics, which has a long history of having been missed by the early investigators of the Stern-Gerlach effect who considered clusters as some kind of molecular nuisance, confined atoms were discovered early, and, for a long time, investigated only as theoretical objects, with some esoteric applications. The earliest relevant paper seems to be the one of Michels et al. [1], who were concerned about the effects of very high pressures. They suggested to replace the interaction of the atoms with surrounding atoms by a uniform pressure on a sphere within which the atom is considered to be enclosed. This led them to consider the problem of hydrogen with modified external boundary conditions. This paper was soon followed by a very remarkable contribution to the subject, due to Sommerfeld and Welker [2]. These authors realised that one could actually solve the confined hydrogen problem exactly, because the existing excited state solutions for higher ns functions of the free

hydrogen atom satisfy the modified boundary conditions exactly for certain combinations of n and the cavity radius, when a node occurs at the cavity wall.

From the early studies of Sommerfeld and Welker [2], the general law of energy variation with of the ground state binding energy with cavity radius for hydrogen was obtained, and certain rules were established concerning the degree of binding which turn out to be general for all atoms in cavities. In particular, they showed that there exists a cavity radius below which the optical electron is no longer bound. Sometimes (following [2], this is described as 'ionisation' but a better word is perhaps delocalisation, since the electron is no longer bound to the atom, but is still confined within the cavity). They applied their analysis to the new situation of an atom confined within the Wigner-Seitz cell in a solid, and argued that, below this critical radius, the situation resembles the formation of the conduction band.

Although it is not usually thought of in this way, one can also regard the Thomas-Fermi model of the atom as an example of quantum confinement, since it imposes a finite radius, outside which there is no electronic charge density. Thus, in a sense, all the more refined methods which stem from Density Functional theory, such as the LDA, are examples of atomic confinement, which may also explain why they are so effective to describe the behaviour of atoms in solids.

Thus, spherical confinement emerged essentially as a theoretical problem, brought about by the desire to transfer separability and the conventional structure of atomic physics to confined species, rather than as an experimental discovery. This is the opposite situation to the discovery of clusters, where studies of optical absorption in metallic vapours or of the Stern-Gerlach effect in atomic beams both indicated the presence of new types of molecules. In the case of metallic clusters, the assumption of spherical symmetry was also introduced in, say, the jellium model, but this came in later, to aid in the interpretation of the results.

2. Modern Developments

The more recent papers on confined atoms relate rather to the excitement generated by the discovery of new objects such as metallofullerenes, in which an atom is trapped within what is an almost spherical molecular 'cage'. This has led to a revival in the physics of confined atoms, and to widespread interest in the spectroscopy of such species.

Again, the predominant theoretical approach is to assume that spherical symmetry applies, and to modify the external boundary conditions appropriately. Note that, even for C_{60} the true boundary conditions are

not spherical. In quantum mechanics, a perfect sphere cannot rotate, so there are features of the true physical problem which disappear under the assumption of spherical symmetry, most notably rotation and vibration of the confining cavity. Nonetheless, a variety of simple models have been developed and applied, to represent not only hydrogen, but also many-electron atoms in cavities. Regarding the boundary conditions, the scope has also widened. It now extends to penetrable as well as impenetrable spheres, and to potentials which can be attractive as well as repulsive, with soft or hard edges.

Symptomatic of the more modern approach is the work of Boeyens [3], who modelled atomic compression in Hartree-Fock-Slater numerical calculations by changing the outer boundary conditions, and calculated the critical radius r_0 for many-electron atoms. These 'ionisation radii' (to use his term) were found to exhibit a remarkable periodicity, commensurate with the known chemistry of the elements, and could therefore be regarded as a new fundamental theoretical index chemical activity.

In the work of Boeyens [3], it was assumed that the chemical response of an atom is somehow governed by the ease with which it can be ionised by compression, but chemical activity is often an elusive concept, and the physics of this 'chemical pressure' was not explored. In fact, the behaviour of compressed many-electron atoms is highly non-linear [4]. In a series of papers [5, 6, 7] Connerade argued that atomic compressibility is intimately linked to the theory of orbital collapse [8, 9] and is indeed related to the idea of controlled collapse [10, 11]. Thus, the most interesting cases for study (the 'softest' atoms) are those in which the order of filling of the shell structure can be altered under pressure [12] so that the Periodic Table under pressure (and, by implication: the chemistry) becomes different from that for free atoms.

3. Dimensionless Plots of Compressibility

The property of non-linearity rendered the representation of the data and the comparison between different atoms somewhat unclear until a method of dimensionless representation applicable to all atoms was proposed [13]. It was then found that the atomic compressibility (an essentially coulombic property), when reduced to these dimensionless variables, becomes nearly the same for all atoms, essentially because of the scalability of coulomb forces. Once this nonlinear part is accounted for, what remains is an atomic factor independent of pressure, which is a hardness characteristic of each atom in the ground state.

Let the mean volume occupied by the free atom $V^f = 4\pi \langle r^3 \rangle / 3$, where $\langle r^3 \rangle$ is the expectation value of r^3 , calculated from the

outermost wavefunction of the atom. Then, the corresponding quantity V^p can again be defined for the atom under a pressure p , arising from any kind of spherical potential, as explained above. We introduce the dimensionless shrinkage parameter

$$\xi \equiv V^p/V^f \quad (1)$$

From the definitions, we can deduce that the quantum pressure

$$p = \frac{\Delta E}{\Delta V} = \frac{E_B^f}{V^f} \left(\frac{\varepsilon - 1}{\xi - 1} \right) = \frac{E_B^f}{V^f} \bar{p} = \eta \bar{p} \quad (2)$$

where $\bar{p}$ is a *reduced pressure*. What our definitions of ε and ξ achieve is to scale all the variables systematically by the appropriate factor for each atom, yielding a *reduced compressibility*. The important point, as we will show, is that most of the variation of compressibility from atom to atom is removed by this method of scaling, so that, for all atoms, the actual variation in ε as a function of ξ turns out to be almost the same.

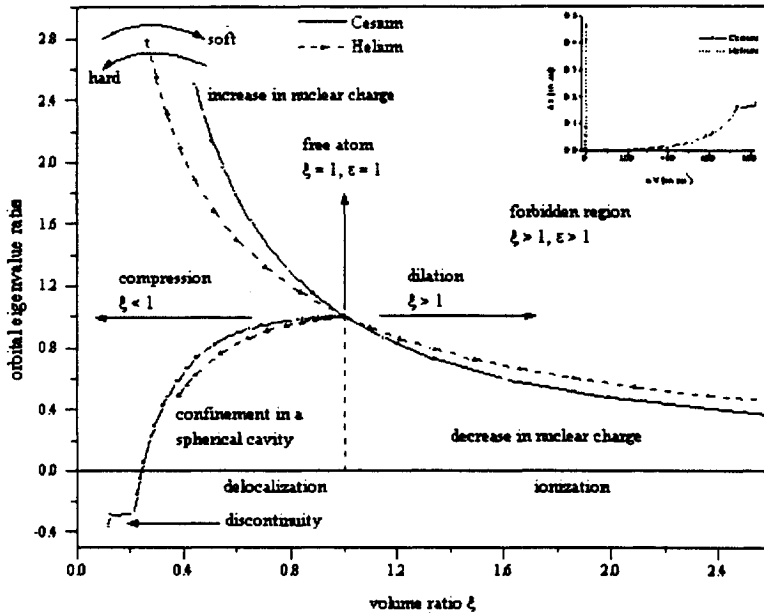


Figure 1. Dimensionless plot of compressibility (see text)

Some indication of how this occurs comes from magnitudes obtained for free atoms. From multiconfigurational Dirac-Fock calculations, we find, for caesium:

$$\eta_{Cs} = \frac{3}{4} E_{6s} / \pi \langle r_{6s} \rangle^3 = 1.3591 \times 10^{-4} \text{ a.u.}^{-2}$$

while, for helium:

$$\eta_{He} = \frac{3}{4} E_{1s} / \pi < r_{1s} >^3 = 0.27491 \text{ a.u.}^{-2},$$

which implies that Cs (one of the largest atoms in the Periodic Table) is roughly 2000 times more compressible than He (the smallest atom), provided ε and ξ exhibit similar variations.

Since both ε and ξ are dimensionless, we can now plot the reduced compressibility, or (ε, ξ) curves for all atoms onto a single graph.

From the data used to plot the confined atom curves, we can also deduce the reduced quantum pressure $\bar{p}$ by using equation (3) above. This can be plotted against the volume ratio ξ . The interesting feature of such a plot is that, again, there is a marked similarity between the curves, despite an enormous difference of hardness between the two atoms. With appropriate scaling, even the functional variations turn out to be nearly the same over a wide range.

We now enumerate some general features of (ε, ξ) curves:

(i) As the spherical perturbation tends to zero (for example the height of the confining step $V \ll 0$, or the nuclear charge tends to that of the neutral atom) then both $\varepsilon = 1$ and $\xi = 1$, so that all the (ε, ξ) curves go through a universal point (1,1).

(ii) Since a free neutral atom exists only at zero pressure, and since zero pressure corresponds to $\partial\varepsilon/\partial\xi = 0$, it follows that the slope of the (ε, ξ) for the neutral atom confined by a sphere tends to zero as $(\varepsilon, \xi) \rightarrow (1,1)$.

(iii) For atoms compressed by an impenetrable repulsive sphere, there is a confining radius within which E_B^p , and therefore also ε , changes sign, i.e. the (ε, ξ) curve crosses the $\varepsilon = 0$ abscissa. This corresponds to delocalisation,

(iv) For atoms compressed by an increase in nuclear charge, the ionisation potential increases with charge, i.e. as the atom becomes smaller, its binding energy also increases, so the (ε, ξ) curves veer upwards rather than downwards.

(v) Atoms can be dilated as well as compressed by a spherical perturbation, either by a reduction of nuclear charge or by an attractive spherical shell. In this case, the binding energy is reduced, until eventually ionisation occurs. Since an increase in ionisation potential never occurs on dilation, there is a forbidden region for $\xi > 1$, $\varepsilon > 1$ in the (ε, ξ) plane.

(vi) The real physical pressure is given by $p = \eta[(\varepsilon - 1)/(\xi - 1)]$. The first factor undergoes a very large variation from atom to atom, from the smallest atom in the Periodic Table with the highest binding energy, which is He, to the largest atom with the smallest binding energy, i.e. a heavy alkali (Cs or Fr), which define the hardest and softest atoms respectively.

(vi) Slightly different curves are obtained if compression is applied to the atom by using an external cavity, or else by the device of a fractional increase in nuclear charge, which is sometimes used to generate starting functions in applications to solid state physics (internal compression).

The reason for the difference is that increasing the nuclear charge cannot ionise the atom, whereas external compression eventually results in delocalisation, as explained above

Of course, to describe the filling of shells in transition elements and lanthanides really requires a relativistic model for consistency. Since the most interesting cases are the heavy atoms, it became important to develop a fully relativistic model of the confined atom. This poses some specific and non-trivial problems as regards the implementation of boundary conditions [14] but at least within reasonable approximations such a theory can now be formulated, and has been applied with success to a parameter-free calculation of the isomorphic phase transition in Cs metal [15], with results in quite good agreement with experiment.

4. Boundary Conditions and External Potentials

Developments have also taken place in the manner of treating the boundary conditions and the externally applied potentials. In the work of Sommerfeld and Welker [2], the boundary condition was an infinitely high wall at the radius of the confining cavity, corresponding to an impenetrable sphere. This is convenient when dealing with hydrogen, since the radius of the cavity then corresponds exactly to a node in the wavefunction. For other atoms, however, it is not such a useful approximation since several nodes very rarely coincide. Arguments against it are as follows:

(i) For all cases which must be solved numerically, the infinitely high wall poses computational problems, because a discontinuity is created at the radius of the cavity. It is numerically more stable to pick a fairly high value for the height of a finite step, and to verify that the wavefunction decays exponentially at radii larger than the radius of the cavity, falling to a low value within a few points of the mesh. One must also check that the binding energy is essentially unchanged by small changes in the magnitude of the step. There are many subtle tricks to achieve reliable convergence, especially as cavity radii become small.

(ii) An infinitely high step is an unrealistic assumption, because it effectively isolates the atom from the rest of the universe by placing it in a totally impenetrable sphere. To model a real situation, one needs to introduce a potential of finite depth as the confining cavity, and perhaps also to consider how abrupt its edges can be.

(iii) Many of the real confinement problems involve specific forms of potential barrier. For example, an atom in a solid is usually modeled [16] by confining it within a Watson sphere [17] which gives a more suitable form to the wavefunction at large distances. In metallofullerenes, the potential is a thin hollow shell, and is attractive. Luckily, making reasonable assumptions about its geometry, one can deduce its depth from the observed binding energies of fullerene negative ions.

(iv) If one considers the fully relativistic problem, then an infinitely high potential step at a given value r_0 is, it turns out, an inconsistent boundary condition. The symptom which reveals that it violates the laws of relativity is that, if imposed, it would lead to what is known as Klein's paradox, i.e. the spontaneous creation of electron positron pairs, which is clearly unphysical [18].

For all these reasons, a good deal of effort has been expended in improving and refining the boundary conditions and obtaining suitable potentials. It is now understood how to select suitable potentials for most problems, and the differences between the relativistic and non-relativistic conditions are also understood.

5. Beyond the Spherical Cavity and Centred Atom

The simplest model problem concerns the atom at the centre of a spherical confining cavity, because that is the easiest situation to calculate. However, it does not correspond to any real physical situation, and one must therefore see it as the starting point in a series of simple models or approximations which allow us to understand the behaviour either of real systems or of much more complex and unwieldy numerical treatments whose physical content is hard to understand without reference to such models.

Several situations arise which can be regarded as a straightforward step beyond the simple spherical model, viz:

- (i) The atom is not necessarily at the centre of the sphere, but may be off-centre. In practice, this depends to a large extent on whether the cavity has attractive or repulsive walls. With repulsive walls, the atom tends to be forced to the centre of the cavity [19]. With attractive walls (as in a fullerene) the atom tends to be off-centre, on an orbit within the cavity. This problem can be treated perturbatively, by expanding as a sum of spherical harmonics, as a number of authors have shown [20]
- (ii) The cavity is not necessarily spherical, but can be a oblate or a prolate spheroid. This tends to happen for some of the fullerenes, which are closed shells but are not spherical (for example C_{82}). This situation can be modeled by introducing a more elaborate set of coordinates, which allows the cavity to be distorted progressively from its spherical shape [21]. It is also possible to consider other problems such a spherical clusters becoming attached to a surface in terms of such coordinates.
- (iii) The atom can be inside a cavity which is not a complete sphere, but is made up of scattering points distributed symmetrically over its surface. This problem has been tackled by Baltenkov et al [22] who introduced a factorisation to represent these scattering centres, provided the amplitudes of the atomic functions are small in the vicinity of the confining 'sphere'. This problem is clearly very similar to the treatment

of scattering by a 'coordination sphere' which occurs in the analysis of EXAFS.

6. Cavity Resonances, and the Excitation Spectra of Confined Atoms

The confined atom has a clear spectral signature, which can be deduced from simple calculations, and is confirmed by more elaborate calculations. Essentially, it is the excitation spectrum of the atom dressed by the cavity. The cavity itself exhibits characteristic resonances, which are essentially those of the spherical square well [23]. They can occur in amongst the bound states, in which case they appear as 'anticrossings' or may lie in the continuum, in which case they appear as 'cavity resonances' which will be seen in the photoionisation spectrum [24]. The extent to which these cavity resonances persist to high energies depends on how completely the surface of the confining shell is covered with electrical charge.

Thus, the spectrum of a confined atom is a combination of features which would arise for the free atom, but are modified by the presence of the cavity, of features which would arise for a cavity, but are modified by the presence of an atom inside, and of features which are new, i.e. would not be displayed either by the atom or the cavity in isolation. As an example of the latter, one can take the fact that the true cavity is not perfectly spherical even for C_{60} . It therefore breaks the atomic symmetry, allowing different angular momentum states to mix. As a result, new excitation channels appear [25] for the confined atom which would not be present in the free atom limit. Resonances of this nature are termed 'molecular' because they arise in the same manner as the molecular shape resonances in photoionisation [26].

One can thus achieve a classification of resonances in confined atoms into three basic types [27]:

- (i) Atomic resonances
- (ii) Cavity resonances
- (iii) Molecular resonances.

Usually, these three types of resonances are well-separated in energy. However, it is also possible that they come together in energy, and exhibit features which denote mutual interactions. We have already mentioned the avoided crossings in the bound state region of the spectrum. In the continuum, autoionising features are found [?] which can exhibit all the properties associated with interacting resonances in conventional atomic physics [29]. Furthermore, by modifying the properties of the confining shell, which can be achieved by exciting or removing an elec-

tron, one can ‘tune’ cavity resonances in and out of coincidence with atomic structure, which opens up completely new possibilities

7. Correlations

There remains an interesting question, namely the way in which electron correlations are modified by confinement of the atom inside a cavity. Naively, one might expect that correlations would increase, simply because the electrons are brought closer together. However, this turns out not to be the case. In fact, correlations may be either increased or decreased by confinement. In some cases, the energy spacing between shells increases on confinement, so that correlations are actually reduced, while in other cases (especially in the presence of orbital collapse) energy different configurations move closer together when the atom is compressed.

Since the issue is a complex one, attempts have been made [28] to develop general models such as the RPAE and apply them to the confined atom. At the moment, there exist very few calculations of this type, the cases studied being the smallest atoms in which orbital collapse occurs. However, this is clearly an interesting area for future investigations.

Conclusion

As we have stressed all along, there are a number of new experimental situations which relate closely to the theory of confined atoms, and which either exist already, or are on the point of being realised. For example, the ultraviolet spectroscopy of endohedrally confined atoms (metallofullerenes) is not yet achieved, essentially because it is difficult to create the material in sufficient number density to be probed, but new methods are being developed for this purpose [30]. Also, bubbles in solids have been discovered in the walls of nuclear reactors, which are due to ageing, and the pressure inside them can be deduced from the spectroscopy of the atoms they contain [31]. Similarly, the theory of quantum dots employs a Hamiltonian which is essentially the same as that of a confined atom [32]. More speculatively, one can also consider atoms confined within nanotubes or nanowires, in which the external symmetry will be cylindrical rather than spherical, and the consequences this might have for both shell filling and chemistry.

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CORRELATION STUDIES OF TWO ACTIVE-ATOMIC-ELECTRON IONIZATION PROCESSES IN FREE ATOMS

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Abstract During the last decade major advances have been made in the modelling of low energy inelastic scattering processes involving a single atomic electron. Experimental correlation studies of these processes have exposed the inadequacies of earlier calculations and played a key role in providing sensitive tests of the new theoretical approaches. Interest, both experimental and theoretical, is now turning to the more difficult problems involving two active atomic electron processes. The latest developments in this area are discussed with emphasis on double excitation-autoionization and simultaneous excitation-ionization.

Keywords: ionization, autoionization, ionization-excitation

Introduction

The experimental study of the dynamics of inelastic electron scattering from atoms was greatly enhanced by the application of coincidence/correlation techniques to these processes. Two pioneering experiments were those of Ehrhardt et al¹ for ionization and Eminyán et al² for excitation. The ionization results from these (e,2e) experiments, expressed as triple differential cross sections (TDCS), showed that the ejected electrons were preferentially ejected into two angular regions, referred to as the binary and recoil peaks. The excitation data from electron-photon correlation measurements allowed a complete descrip-

tion of the excitation process, including both the magnitudes and phases of excitation amplitudes. Much progress has been made since then and this has been summarised by, for example, Lahmam-Bennani³ for ionization and Andersen and Bartschat⁴ (and references therein) for excitation.

Parallel theoretical studies have also been made. Indeed the recent work of Rescigno et al⁵, claiming a complete solution of the Coulomb 3-body problem, has sparked intense debate with respect to ionization of atomic hydrogen.

In this article we concentrate on recent developments using both experimental techniques to study ionization processes other than those which lead directly to production of the ground state ion. The main examples are double excitation-autoionization and simultaneous ionization-excitation. These processes, involving two active atomic electrons, have been the subject of relatively little experimental study using these techniques and theoretical approaches have met with only limited success so far.

1. Double excitation-autoionization

A simple example of this type is:

$$e(k_0) + He(1s^2)^1S \Rightarrow He(2l, 2l')^{1,3}L + e(k_s), \quad (1)$$

the doubly excited state decaying to the ground state ion,

$$He(2l, 2l')^{1,3}L \Rightarrow He^+(1s)^2S + e(k_e). \quad (2)$$

These doubly excited states are degenerate in energy with continuum states from the direct ionization process,

$$e(k_0) + He(1s^2)^1S \Rightarrow He^+(1s)^2S + e(k_s) + e(k_e). \quad (3)$$

Interference between the two processes occurs, dependent on both the magnitudes and relative phases of the competing direct and resonant amplitudes. These in turn depend on the scattered and ejected electron momenta and the resonant state symmetry.

The first (e,2e) studies of these autoionizing states were performed by Weigold et al⁶ and then by Pochat et al⁷. However, the more recent higher energy resolution experiments⁸⁻¹⁴ are of greater value as a test of theoretical models¹⁵⁻¹⁸.

Figure 1 shows the measured¹¹ ejected electron energy dependence of the normalised coincidence signal in the region of the $(2p^2)^1D$ (35.42 eV) and $(2s2p)^1P$ (35.56 eV) autoionizing states of helium at an incident electron energy of 200 eV and an electron scattering angle $\theta_1 = 12^\circ$. The

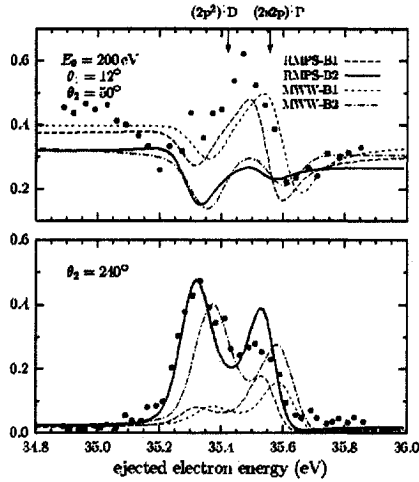


Figure 1. (e,2e) spectra as a function of ejected electron energy in the vicinity of the $(2p^2)^1D$ and $(2s2p)^1P$ autoionizing states of helium at an incident electron energy of 200 eV and an electron scattering angle $\theta_1 = 12^\circ$. •, experiment of Crowe and McDonald¹¹; RMPS-B1/B2, Fang and Bartschat¹⁸; MWW-B1/B2, Marchalant et al¹⁷. (from Fang and Bartschat¹⁸)

bottom spectrum, showing data at an ejected electron angle $\theta_2 = 240^\circ$ is dominated by the autoionizing states with little or no evidence of interference. On the other hand, the upper spectrum at an ejected electron angle of 50° shows strong interference between the direct ionization and autoionizing channels.

Also shown in figure 1 are the recent calculations of Marchalant et al¹⁷ and of Fang and Bartschat¹⁸. Both groups used first- and second-order models to predict the spectra. It is clear that for $\theta_2 = 240^\circ$, both first-order calculations fail to predict the relative intensities of the two states, while the second-order calculations show a major improvement, supporting the view that a two-step mechanism^{19,20} must be included in any realistic description of the process. At $\theta_2 = 50^\circ$, the agreement between theory and experiment is less good. Indeed, the first-order theories seem to do better in this case.

From figure 2, which shows the rapid variation of the TDCS as a function of ejected electron energy, calculated using the second-order approach of Fang and Bartschat, it is clear that care has to be taken in comparing theoretical and experimental results. Experimental resolution must be accurately accounted for in making comparisons¹⁰. This may be most important when extracting resonance parameters^{21,22} from the data and may explain why consistent parameters could not be ex-

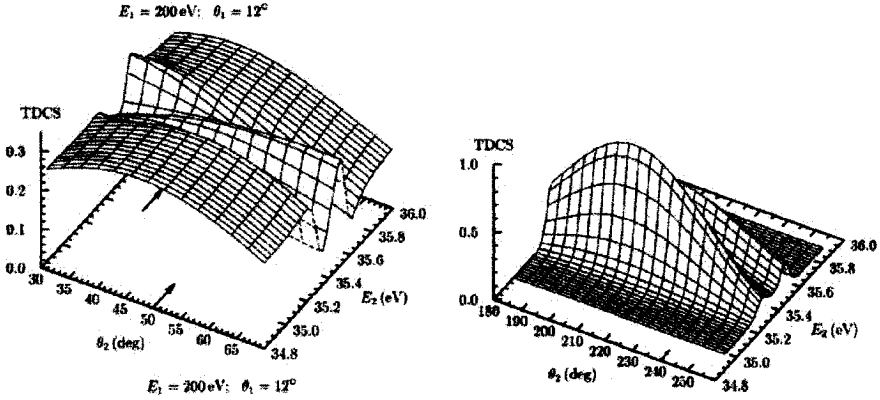


Figure 2. TDCS as a function of ejected electron energy E_2 and angle θ_2 in the vicinity of the $(2p^2)^1D$ and $(2s2p)^1P$ autoionizing states of helium at an incident electron energy of 200 eV and an electron scattering angle $\theta_1 = 12^\circ$, calculated using the RMPS-B2 approach of Fang and Bartschat¹⁸. (from Fang and Bartschat¹⁸)

tracted from the data of and McDonald and Crowe¹⁰ for resolutions ≥ 80 meV. Although good agreement is obtained between the resonance parameters for the $(2s^2)^1S$, $(2p^2)^1D$ and $(2s2p)^1P$ states measured by Lower and Weigold⁸ and McDonald and Crowe^{9,10}, especially in the forward direction, it is clear that more experimental and theoretical work is required to provide a better understanding of these processes.

2. Simultaneous ionization-excitation

As an example we consider the process:

$$e(k_0) + He(1s^2)^1S \Rightarrow He^+(n=2) + e(k_s) + e(k_e). \quad (4)$$

A number of experimental (e,2e) studies of the dynamics of this process have been carried out at incident electron energies ranging from under twice the threshold energy E_{th} to $85 E_{th}^{23-28}$. Recent examples of corresponding theoretical studies include those of Marchalant et al²⁹⁻³¹, Kheifets et al³² and Fang and Bartschat³³. Figure 3 shows a comparison between data at incident electron energies of 5.5 keV and scattering angles $\leq 1^\circ$ and at 645 eV and a scattering angle of 4° for different ejected electron energies, and two recent theoretical calculations.

It is clear that unlike ionization of helium where the ion is left in its ground state, the TDCS for the $n=2$ states, particularly at lower ejected electron energies, no longer show the two well defined 'binary' and 'recoil' peaks. The additional complexity in this case can be shown²⁹ to

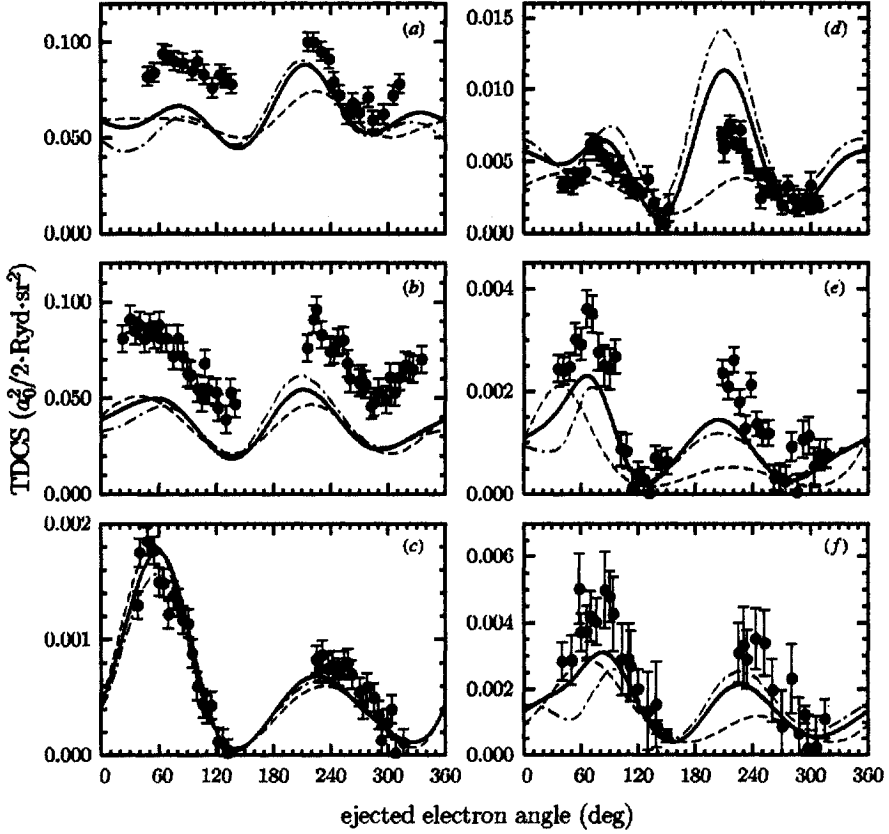


Figure 3. TDCS for ionization-excitation to the $n = 2$ states of He^+ . Experiment: Dupre et al²⁵, $E_0 \approx 5500\text{keV}$ and ejected electron energies of 5 eV (a), 10 eV (b), 75 eV (c), for scattered electron angles $\leq 1^\circ$; Avaldi et al²⁴, $E_0 = 645\text{ eV}$ and ejected electron energies of 10 eV (a), 40 eV (b), 20 eV (c), for a scattered electron angle of 4° . Theory: Marchalant et al³¹, second-order two-step (dash-dot); Fang and Bartschat³³, second-order RMPS (full curve); first-order RMPS (broken curve). (from Fang and Bartschat³³)

arise from the different angular contributions of the unresolved $2s$, $2p_{0,1}$ states. Good qualitative agreement is seen between the two second-order calculations and the experiments, the level of agreement being generally worse at the lower ejected electron energies. The very recent RMPS-B2 calculations of Fang and Bartschat³⁴ show that both the $(4\ell, 4\ell')$ autoionizing states and the experimental resolution can significantly affect comparisons with these experiments and that of Rouvellou²⁸ when the ejected electron energy is close to the energy separation between these states and the $\text{He}^+(n = 2)$ states ($\approx 10\text{ eV}$).

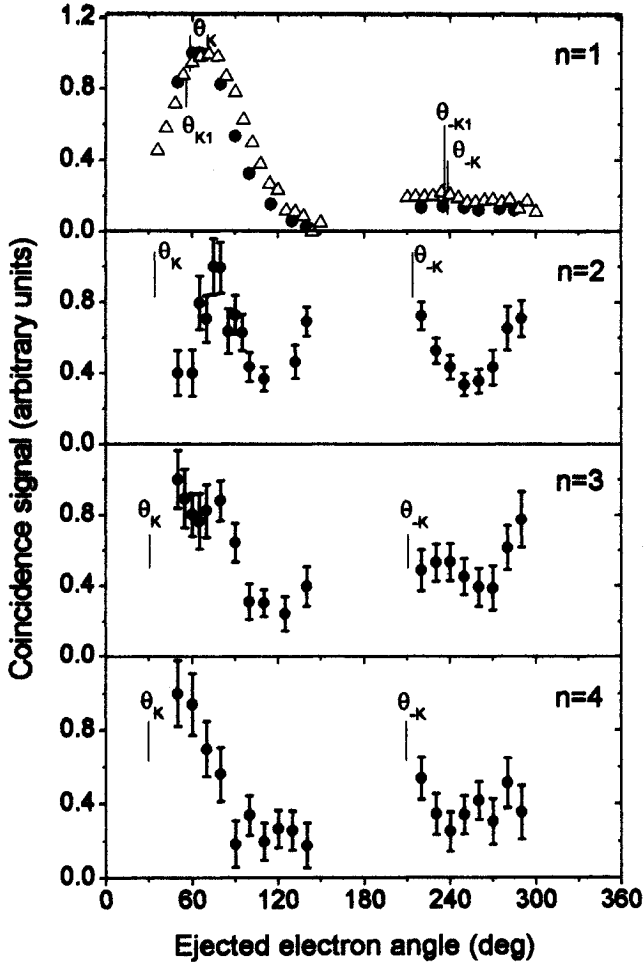


Figure 4. Measured (e,2e) cross sections for the $n = 1 - 4$ states of He^+ for 200 eV electron scattering through 11° . •, Dogan and Crowe²⁷; Δ , Schlemmer et al³⁵ for $n = 1$ at 250 eV and a scattering angle of 12° . θ_K is the momentum transfer direction in the experiment of Dogan and Crowe and θ_{K1} in that of Schlemmer et al.

A recent extension of this work in this laboratory²⁷ to the $n = 3, 4$ states of He^+ is shown in figure 4. The higher angular momentum states excited for $n = 3, 4$ obviously present a major theoretical challenge. No calculations are available for the $n = 2 - 4$ states at 200 eV.

The (e,2e) method has disadvantages, both inherent and in practice, when applied to $\text{He}^+(n = 2)$. The inability to separate the 2s and 2p

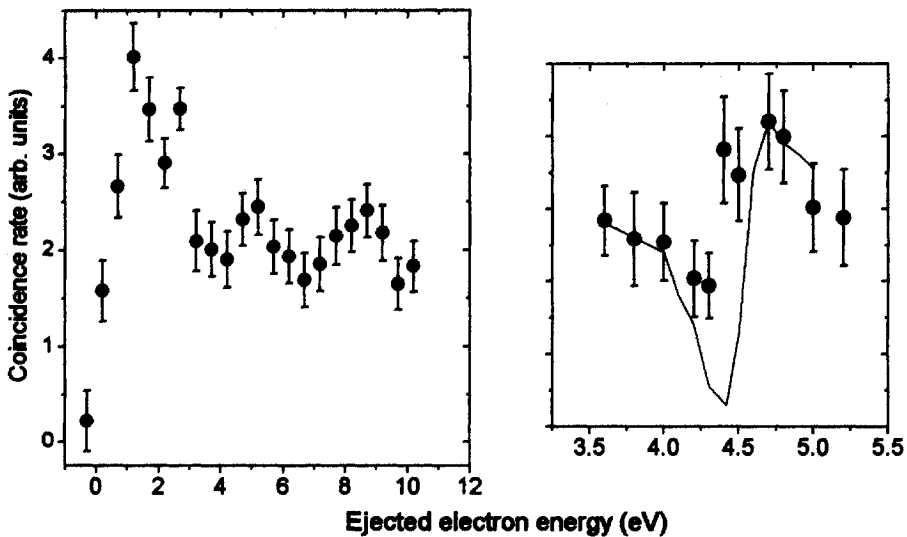
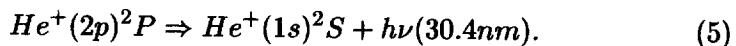


Figure 5. Measured DDCS of Dogan et al.³⁷ for the $\text{He}^+(2p)$ state as a function of ejected electron energy. The incident electron energy is 200 eV, the scattering angle 5° and the photon detection angle is 130° . The energy resolution is ≈ 1 eV (FWHM). On the right are data at a higher resolution ≈ 0.5 eV (FWHM) in the autoionization region compared with a calculation of Balashov (private communication).

ion states has already been mentioned. The TDCS for most kinematics is more than two orders of magnitude lower than for ground state ionization. This not only reduces the $n = 2$ true coincidence signal relative to $n = 1$, but in addition a large random coincidence signal is observed due to the high number of indistinguishable $n = 1$ electrons detected.

The electron-photon correlation method enables the $2p$ ion state to be isolated and studied in more detail. The decay process is:



Two groups^{36,37} have observed this photon in coincidence with a fast scattered electron. The coincidence signal as a function of the energy of one of the outgoing electrons gives the double differential cross section (DDCS) (slightly distorted due to the different electron-photon angular correlations for different outgoing electron energies) for the $\text{He}^+(2p)$ state.

Figure 5 shows the experimental data of Dogan et al.³⁷ at an incident electron energy of 200 eV and for the fixed electron and photon detector angles shown. The characteristic peak at zero ejected electron

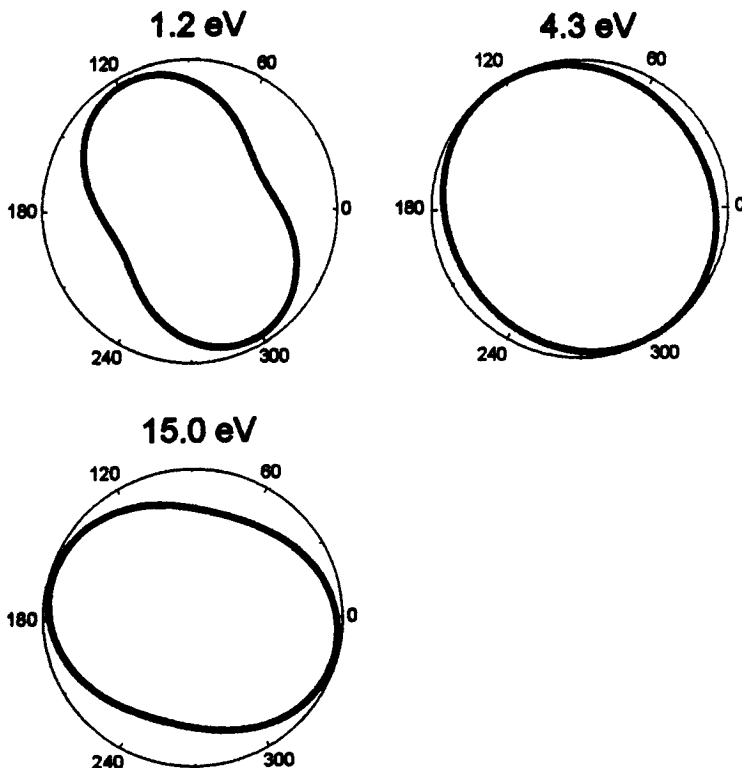


Figure 6. Measured electron-photon angular correlations of Dogan and Crowe³⁸ for the $\text{He}^+(2p)$ state for the three ejected electron energies shown. The incident electron energy is 200 eV and the scattering angle 5° . The solid lines shown are fits to the experimental data. The incident electron beam is in the zero direction.

energy, followed by a decrease to higher energies is observed. However, there is also clear structure in the DDCS. The structure at ejected energies around 4.3 eV can be associated with interference between direct $\text{He}^+(2p)$ production and indirect production through the $(3\ell, 3\ell')$ autoionizing states. The maximum around 8 eV may be due to the influence of higher autoionizing states. Alternatively it lies close to the energy corresponding to the $\text{He}^+(n = 3)$ states which cannot be isolated from the $\text{He}^+(2p)$ signal in these experiments. A kinematically complete $(e, 2e\gamma)$ experiment^{39,40} is required to remove this ambiguity.

Figure 6 shows electron-photon angular correlations measured in this laboratory at an incident electron energy of 200 eV and a scattering

angle of 5° . The amplitude of the correlation is greatest for the lowest ejected electron energy of 1.2 eV and is well reproduced by various Born-R-matrix calculations³⁷. When the ejected electron energy corresponds to the autoionization feature at 4.3 eV, an almost isotropic distribution is observed. However, at an energy of 15.0 eV, the correlation has become more anisotropic again, perhaps indicating that indirect processes are less important at this energy. There is also a substantial change in the angular position of the correlation maximum compared with the lower ejected electron energies.

3. Summary

Recent developments, both experimental and theoretical, in the study of ionization processes involving two active atomic electron processes in the simplest atom supporting these, helium, are discussed. Considerable progress has been made in the last few years but further work is required before the level of agreement between theory and experiment is similar to that for one active electron processes. For ionization-excitation, no calculations of the TDCS are available for incident electron energies below 366 eV, where some of the most interesting aspects are likely to be found and experimental data are available.

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COHERENT ELECTRON IMPACT EXCITATION OF ATOMS

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Abstract

Experimental studies of electron impact excitation of atoms with closed ns shells are discussed in terms of electron impact coherence parameters, EICPs. Experimental and theoretical data leading to full determination of complex scattering amplitudes for the S-D excitation in helium and S-P in alkaline earth atoms are presented. Similarities and differences in the angular behaviour of EICPs within the alkaline earth group are discussed and compared with helium.

1. Introduction

Electron impact excitation of atoms has been traditionally characterized by measurement of differential cross sections, DCS, which are specific for scattering kinematics. More recently, electron impact excitation is characterized in a very detailed way by measurement of Electron Impact Coherence Parameters, EICPs. Compared to DCS, EICPs contain additional information on the excitation of magnetic sublevels correlated to a particular momentum transfer. Measurement of a sufficient number of EICPs can provide complete information on complex scattering amplitudes, their magnitudes and relative phases. In this sense, such experiments are known as "perfect" or "complete" scattering experiments and parameter sets as complete sets (Bederson, 1969a; Bederson, 1969b).

Generally accepted nowadays is a frame independent set of EICPs, known as Andersen or charge cloud parameters. These present the most transparent description of the shape and dynamics of the excited state charge cloud. However, the charge cloud parameters are not the best set when complete information on excitation of higher angular momentum states is to be achieved. This is the case in the well studied S-D excitation in helium where a new parameterization has been recently introduced (Andersen and Bartschat, 1996; Andersen and Bartschat, 1997).

Being relative, EICPs present an ideal ground for comparison of experimental and theoretical data. In addition, they present the most stringent test on theoretical modelling. This is especially the case when optically forbidden transitions are studied, i.e. transitions where two or more units of angular momentum are transferred in the collision or when transitions involving change of spin are studied. An example is excitation of the 3D states in helium, where good agreement with experiments has been observed only after the development of a new generation of theories, Convergent Close Coupling, CCC, (Fursa and Bray, 1995) and R-matrix with Pseudo States, RMPS (Bartschat, 1999).

In view of the success and significance which a co-ordinated experimental and theoretical effort has had in the description of the 3D excitation in helium, it seems appropriate that similar studies on excitation of alkaline earth atoms should be a logical continuation. Like helium, alkaline earth atoms have two electrons in a full s shell. The existence of a closed shell core and electron correlation effects, different from the helium case, result in additional complexities in theoretical modelling of alkaline earth atoms. These differences should be reflected on modelling of the collision dynamics but with increasing atomic mass along the group, the structure calculation part as well.

2. Experimental methods

Data on excitation of helium are obtained from electron photon coincidence experiments, the majority of them by application of the polarization correlation method. Excitation of the alkaline earth atoms has been studied by the polarization correlation method and by superelastic scattering, both of which have been described previously. For examples of experimental arrangements used for some of the data presented here, i.e. polarization studies on helium and magnesium in Newcastle, see Fursa et al., 1997 and for superelastic scattering on barium, see Li and Zetner, 1994 and references therein.

Both methods are based on electron spectrometers with a crossed beam geometry. The essential geometry in both types of experiment is

the same, but the order of events is reversed so they can be considered, to a first approximation, as time reversed. In a polarization correlation experiment, the incident electron beam with well defined energy and momentum incoming along x-axis intersects an atomic beam. After exciting the atom, electrons identified by their specific energy loss and scattering angle θ , are detected in coincidence with photons emitted in the subsequent decay of the excited atom. Direct measurement of coincidence intensities for particular states of polarization of emitted radiation leads to determination of differential Stokes parameters and represents the population and relative phases of the magnetic substates. The momenta of the incident and scattered electrons define a plane of symmetry, called the scattering plane. The detection geometry ensures that a subset of identically prepared states are selected for observation. In the superelastic scattering experiment, polarized laser radiation excites the atom and particular magnetic substates are created. Electrons incoming at an angle θ with respect to the x-axis are scattered from these identically prepared atoms. Those scattered superelastically in the x-direction are detected as a function of laser polarization. The pseudo-Stokes parameters are obtained from simple intensity measurements of superelastic features in the energy loss spectrum and expressed in a way similar to the usual expressions for Stokes parameters. The relationship between pseudo-Stokes parameters obtained from superelastic scattering and Stokes parameters from the polarization correlation method involves coefficients dependent on the conditions of optical pumping in every given experiment.

The two methods each have their strong and weak points and limitations. A major advantage of coincidence studies is that optically forbidden transitions can be easily excited. Experiments based on superelastic scattering are much faster and better resolution can be achieved. This is due to the combined advantages of directional nature and large intensity in the laser beam and the fact that the superelastic signal is generally the only signal at the negative energy loss side of elastic peak, opposite from all inelastic processes.

3. Excitation of higher angular momentum states in helium

The polarization correlation method has been predominantly used in the study of helium 3D state excitation. A comprehensive experimental and theoretical study for both the 3³D and the 3¹D state exists. The major new challenge presented to experiment was the achievement of complete determination of scattering amplitudes. Magnitudes of these

are readily obtained from the traditional set of charge cloud parameters

$$(P_l, \gamma, L_\perp, \rho_{00}). \quad (1)$$

These correspond to linear polarization and alignment angle of the excited state charge cloud in the scattering plane, angular momentum transferred in the collision and the relative height of the charge cloud, respectively. A problem arises because the $m = \pm 2$ phases, relative to the $m = 0$, cannot be uniquely determined. This is a consequence of the fact that the polarization pattern is not uniquely related to the excited D state wave function. Two wave functions, one a mirror image of the other, will give the same set of Stokes parameters. The situation has been analysed in detail and a new parameterisation for the D state excitation was introduced by Andersen and Bartschat, 1996 and Andersen and Bartschat, 1997. The new parameters

$$(L^\pm, \gamma^\pm) \quad (2)$$

do not relate to the charge cloud but to the two possible decay routes, one through the $m = 1$ and the other through the $m = -1$ magnetic sublevel of the intermediate 2P state. They do not represent angular momentum and alignment angle. However, together with an absolute differential cross section the parameter set (2) leads to a complete description of the S-D excitation. To measure the phase difference, a complete experiment has to look at a coherent superposition of the two decay channels by following the decay down to the ground 1^1S state. This involves detection of the D-P and P-S cascade photons in coincidence with the scattered electron. Detection of the D-P photons, as is done in polarization correlation experiments, leads to a weighted but incoherent sum of the two channels resulting in non unique values for both the γ^+ and γ^- parameters, related directly to relative phases, $\beta_{\pm 2} = -2\gamma^\pm \pm \pi$. The two values differ in a choice of $\pm$ sign and apart from this, the two sets (2) and (1) can be directly related.

One pioneering complete, triple coincidence experiment was performed by Mikosza et al., 1997, at a scattering angle of 40° and 60 eV. However, the counting rate in such experiments is low and statistical accuracy does not permit its wide use over a large range of kinematics. In view of this, an alternative approach, leading to complete information by distinguishing between the two possible solutions for $\gamma^\pm$ by comparison with a reliable theory was adopted in Newcastle (Fursa et al., 1997). Both the CCC and RMPS theories can be used, as an overall good agreement is observed between the two theories and experiment right from the excitation threshold. This contrasts with the previous situation where theoretical predictions did not agree either with experiments or between

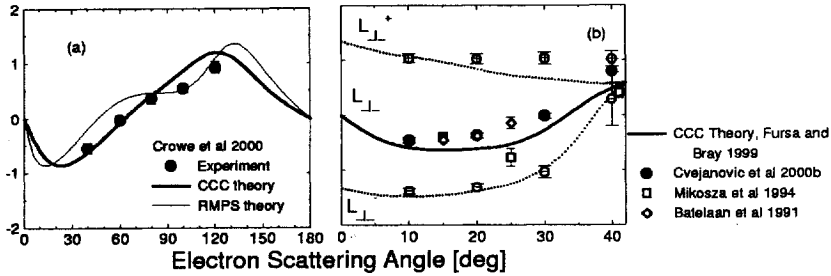


Figure 1. Negative $L_{\perp}$ values observed at small scattering angles in excitation of the 3D states of He: a) 3^3D at 23.45 eV; and b) 3^1D at 60 eV.

themselves. In this sense study of the 3D states in helium has highlighted the complexity involved in theoretical modelling when optically forbidden transitions are excited by electron impact and has presented a rigorous test on different theories.

Positive values of $L_{\perp}$ were observed in an overwhelming number of excitation processes, not only for different transitions, but different atoms. For a recent discussion see Bartschat et al., 1999. However, recent results on excitation of the D states in He, for example excitation of the 3^3D state at 23.45 eV (Crowe et al., 2000) where excitation is strongly dominated by a negative ion resonance (Cvejanovic et al., 2000a), and excitation of the 3^1D state at small scattering angles, show negative values of $L_{\perp}$ violating the Andersen-Hertel propensity rule. Negative values of $L_{\perp}$ observed in excitation of the 3^3D state at 23.45 eV (Crowe et al., 2000) and 3^1D state at 60 eV (Cvejanovic et al., 2000b; Batelaan et al., 1991; Mikosza et al., 1994; Fursa and Bray, 1999a) are shown in figure 1. In excitation of the 3^3D state the negative values at small scattering angles, figure 1a, may be a consequence of temporary electron attachment in the negative ion, but could be a more general threshold phenomenon. The negative values in excitation of the 3^1D state at 60 eV, figure 1b, must have a different origin.

The first experiment to measure Stokes parameters for an even higher angular momentum state, i.e. the mixed 4F states in helium, has been reported by Cvejanović and Crowe, 1998 using the polarization correlation method. These authors gave a detailed discussion of problems involved in the measurement, mainly originating from the nature of the excitation and decay of the excited state, resulting in a low counting rate of true as opposed to random coincidences and consequently low statistical accuracy of the data. In view of this experience, it does not look possible to expect a complete experiment for excited states with higher

angular momentum, i.e. $\Delta l \geq 3$ by the method of multiple coincidence detection and in the same sense of completeness as achieved for the 3D states.

4. Excitation of resonant transitions in alkaline earth atoms

Compared with helium, experimental studies in alkaline earth atoms are more difficult as these materials need first to be vaporised. On the other side, excitation energies are considerably lower, permitting both electron photon coincidence based methods and superelastic scattering from laser excited atoms to be used. The application of the superelastic scattering method is limited by the wavelength range of available lasers and consequently magnesium, having the resonant transition in the UV region of the spectrum, was studied only by electron photon coincidence detection, calcium by both methods, while barium was studied only using superelastic scattering. An overview of existing data for alkaline earth atoms was recently given by Crowe et al., 2002.

With few exceptions, the majority of experiments investigated the first resonant $^1S\text{-}^1P$ transitions. The three Stokes parameters, P_1, P_2 and P_3 , were measured, and from these a complete set of charge cloud parameters, P_l, γ and $L_\perp$ is determined. The Stokes parameters measured around an incident electron energy of 40 eV for Mg (Brunger et al., 1989; Brown et al., 2002), Ca (Dyl et al., 1999; Law and Teubner, 1995), Sr (Hamdy et al., 1993) and Ba (Zetner et al., 1993; Li and Zetner, 1994) are shown in figure 2.

Relativistic distorted wave calculations, RDW, (Kaur et al., 1997; Srivastava et al., 1992) exist for all the alkaline earth atoms at the experimental energies shown in figure 2 and are in good agreement with experimental data. Besides the RDW, CCC for Mg (Fursa and Bray, 2001) and Ba (Fursa and Bray, 1999b), and RMPS for Mg (Bartschat, 2001) data are shown as well. For magnesium all theories show good agreement with experiment. Similar agreement is observed for barium, except that there, the RDW theory seems to be closer to the experimental data of Li and Zetner, 1994.

The conclusion which can be made from a comparison of the different theories and experimental data is that similar to the situation in helium, modelling of the optically allowed $^1S\text{-}^1P$ excitation is more straightforward. Even in the heaviest atom, barium, all the theories agree reasonably well indicating that relativistic effects do not seem to be important at least for the strongest $^1S\text{-}^1P$ excitation. Furthermore, an analysis of Fursa and Bray, 2002 shows that for this particular excitation EICPs are

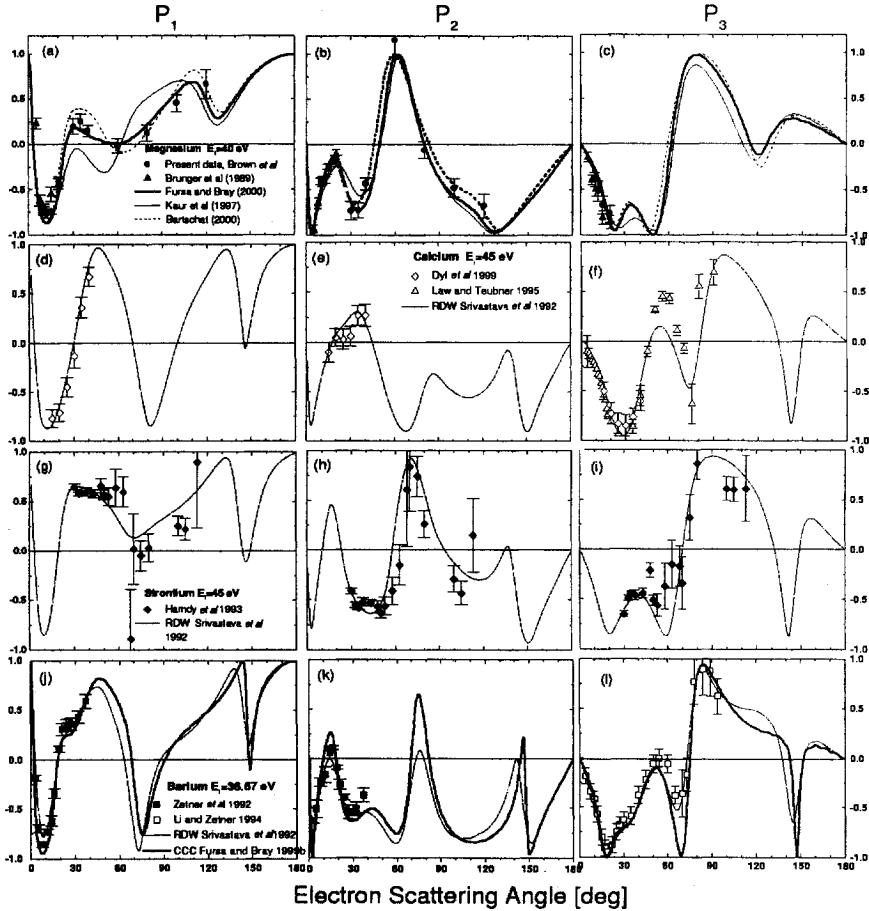


Figure 2. Stokes parameters P_1 , P_2 and P_3 for the alkaline earth atoms .

not very sensitive to channel coupling or to the electron correlations in the target wave functions. As in helium, excitations involving transfer of two units of angular momentum and/or change of spin need to be experimentally studied as a more stringent test for modelling.

The behaviour of the Stokes parameters in figure 2 illustrates some trends along the alkaline earth group, similarities between different atoms as well as the differences with respect to helium. Note, however, that in the case of the alkaline earth atoms, the energy of 40 eV is rather high, around 10 times excitation energy, and it is the high energy behaviour that is demonstrated in figure 2. Except for barium, there are no experimental data for an adequate comparison at low energies, although this is a desirable range to test theoretical modelling.

The angular behaviour of the Stokes parameters is more structured than was the case in helium leading to a more structured angular dependence of the coherence parameters. In figure 3 the behaviour of $L_{\perp}$ is shown along with the differential cross sections for He, Mg and Ba. For the sake of clarity only CCC calculations and experimental data for $L_{\perp}$ and only CCC calculations for the DCS are shown. Compared to helium, the alkaline earth data for $L_{\perp}$ show additional and very pronounced structures. Figure 3 indicates a direct correspondence between the structures observed in $L_{\perp}$ and in the DCS. A similar relationship between the first zero crossing in $L_{\perp}$ and the DCS minimum has been discussed for sodium by Teubner and Scholten, 1992.

The occurrence of additional structures compared to helium is characteristic for all the alkaline earth atoms and all the energies studied. An analysis has been done recently by Fursa and Bray, 2002. Their comparison for Mg at 40 eV (9.3 threshold energies), Ba at 20 eV (9.1 threshold energies) and He at 200 eV (9.5 threshold energies) illustrates the situation under similar excitation regimes. The evidence, also in Ca and Sr, at energies around 40 eV is illustrated by the behaviour of the Stokes parameter P_3 in figure 2. Differences exist between different atoms in the shape and angular position of these structures. Figure 3 illustrates the difference between the lightest atom in the group, magnesium and the heaviest, barium.

A strong energy dependence is illustrated by the data for barium at electron impact energies of 20 and 36.67 eV in figure 3. At the higher energy, the observed structures are narrower and a more dramatic angular shape is observed. A significantly different behaviour of the 'non-helium' structures in $L_{\perp}$ and in relation to the two DCS minima are observed. At the forward scattering angles zero values of $L_{\perp}$ correspond to the first DCS minimum, while for the second minimum CCC predicts a dramatic change of shape in a fashion characteristic of interference phenomena. A joint effort both on the experimental and theoretical side, to clarify the origin of these structures in alkaline earth atoms, is very desirable. Experimental results are especially needed at large scattering angles and low impact energies.

5. Summary

A comprehensive set of experimental and theoretical data in good mutual agreement now exists on excitation of the $3^3,^1D$ states in helium. Negative values of $L_{\perp}$ observed at small scattering angles in excitation of the 3^3D state at 23.45 eV and 3^1D state above 40 eV need physical explanation. The angular behaviour of EICPs for the n^1S - n^1P resonant

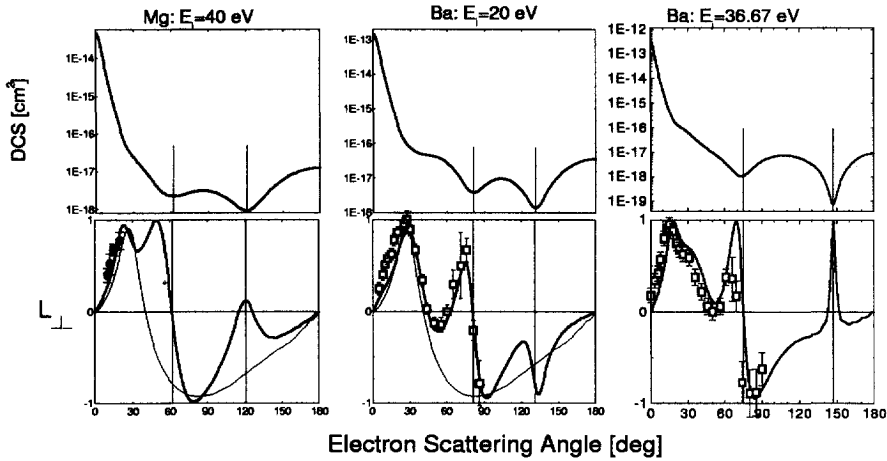


Figure 3. Comparison of the angular behaviour of $L_{\perp}$ and the DCS for excitation of the first $1P$ state of Mg, Ba and He in similar excitation regimes and in a different regime for Ba. Experiments and bold line same as in figure 2. Full thin line is CCC theory in He at 200 eV (Fursa and Bray, 1995)

excitation in alkaline earth atoms is more structured and significantly different from the helium case. As in helium, a number of theoretical models agree well with experiments for this simple S-P excitation. In view of the situation in helium, it is desirable to extend investigations in alkaline earth to lower energies and to S-D excitation as well as to transitions involving change of spin. It is expected that these transitions would be more sensitive to details involved in theoretical modelling.

Acknowledgments

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ELECTRON AND PHOTON IMPACT STUDIES OF CF₃I

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Abstract: Differential cross sections (DCS) for elastic scattering and electronic and vibrational excitation of CF₃I by electron impact have been measured using electron energy loss spectroscopy (EELS). Differential oscillator strengths are derived from EELS measurements and compared with photo-absorption cross sections. Assignments have been suggested for each of the observed absorption bands incorporating both valence and Rydberg transitions. Vibrational structure in each of these bands is observed for the first time.

Key words: Plasma etching, photo-absorption, electron energy loss spectroscopy (EELS), resonance enhanced multi-photon ionization (REMPI).

1. INTRODUCTION

Silicon dry etching is traditionally performed using perfluoro-compounds (PFCs), most importantly CF_4 , C_2F_6 , C_3F_8 , CHF_3 , and $\text{c-C}_4\text{F}_8$. These species have very high global warming potentials (GWP) as they absorb strongly in the infrared and have very long residence times in the Earth's atmosphere. CF_4 , for example, remains for up 50000 years [1]. The current generation of plasma reactors release a high proportion of unreacted etch gas into the atmosphere. Polymerization on the reactor walls requires that cells are regularly cleaned, a process which involves further release of environmentally damaging gases.

One possible alternative to PFCs is CF_3I since, due the weak C-I bond, it should be possible to produce high yields of the etching radical CF_3 in a plasma by direct electron impact dissociation. Furthermore, by using a combination of CF_3I and C_2F_4 in a reactor, polymerization and etching can be independently controlled through the selective generation of CF_2 and CF_3 radicals [2]. Due to their high photolysis rates, both gases are expected to have very short lifetimes in the atmosphere and thus low GWP. At present, the optimum relative concentrations appear to be 20% CF_3I to 80% C_2F_4 .

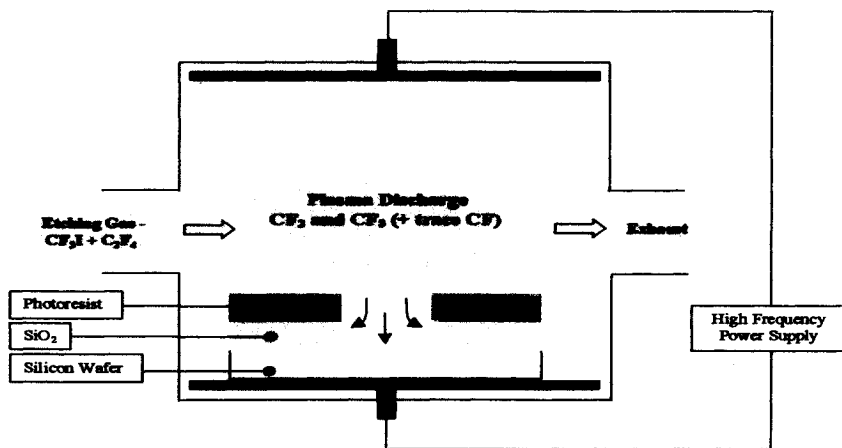


Figure 1. A capacitive plasma processing cell using a mixture of CF_3I and C_2F_4 to etch

The need for progress in this line of research was highlighted in the 1996 US DOE Report with the following statement; 'The main roadblock to the development of plasma models is the lack of fundamental data on collisional, reactive processes occurring in the plasma. Among the most

important missing data are the identities of key chemical species and the dominant kinetic pathways that determine the concentrations and reactivities of these key species, especially for the complex gas mixtures commonly used in industry."

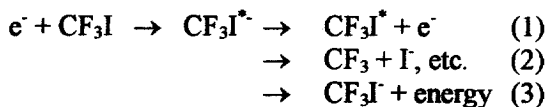
The results given in this paper provide important new quantitative data which will be used to model the behaviour of CF_3I in the atmosphere and in future $\text{CF}_3\text{I} / \text{C}_2\text{F}_4$ reactors.

2. REVIEW OF THE STRUCTURE, GEOMETRY AND PROPERTIES OF CF_3I

CF_3I is a symmetrical top of symmetry C_{3v} . It is considered a pseudo-triatomic molecule. This means that the three fluorine atoms can be considered to act as one F_3 atom at their centre of mass. The six vibrational normal modes are classified in the symmetry types $\Gamma_{\text{vib}} = 3A_1 + 3E$, where, according to Herzberg's [3] notation, $\nu_1 = 0.133$ eV, $\nu_2 = 0.092$ eV, $\nu_3 = 0.036$ eV, $\nu_4 = 0.147$ eV, $\nu_5 = 0.067$ eV, and $\nu_6 = 0.033$ eV.

The ground electronic state is totally symmetric A_1 . The highest occupied orbital in CF_3I was found to be the iodide lone pair (n) orbital which is highly spin-orbit split (calculated $\Delta_{\text{SO}} = 5300 \text{ cm}^{-1}$, experimentally about 5030 cm^{-1}), followed by the C-I bonding orbital (σ) [4]. The C-F bonding orbitals and the fluorine lone pairs are at much lower energies. The lowest unoccupied orbital has mainly C-I antibonding character (σ^*), while the next unoccupied orbital is a diffuse one of mostly iodine 6s character. The lowest-energy excitations arise from a promotion of a single electron from the two highest occupied orbitals to these two empty orbitals.

Negative ions produced in the collision of a molecule with an electron are usually via a temporary negative ion (TNI) state [5]. In the case of CF_3I , the TNI may subsequently decay through one of several pathways, as shown below.



Where (1) represents electron autodetachment, (2) the dissociation into a stable anion and a neutral fragment (i.e. dissociative electron attachment (DEA)), and (3) the stabilization to ground state CF_3I . The last may occur only if the initial excitation energy of a non-dissociative, intermediate CF_3I^*

can be transferred to a third body, a process requiring high gas pressures and will not be studied in the present experiment.

3. PHOTO-ABSORPTION STUDIES

3.1 Experimental

Photo-absorption spectra for CF_3I were recorded at the Rutherford Appleton Laboratories (RAL) and at the Institute for Storage Ring Facilities, University of Aarhus, Denmark [6]. The light source at RAL is a UV lamp used in combination with a high resolution Fourier transform spectrometer to select the irradiation wavelength. The beam passes through calcium fluoride windows into two connected stainless steel chambers housing the gas cell, optical components and a photo-diode detector. The interaction region can be cooled using liquid nitrogen. At the University of Aarhus, measurements were made using synchrotron radiation. The lithium fluoride window of the gas cell limits the minimum wavelength to 110nm

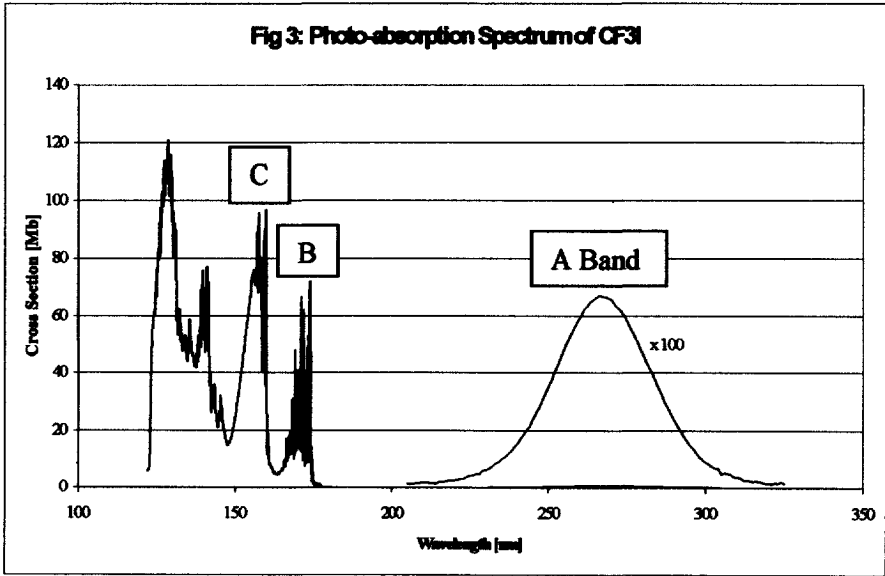
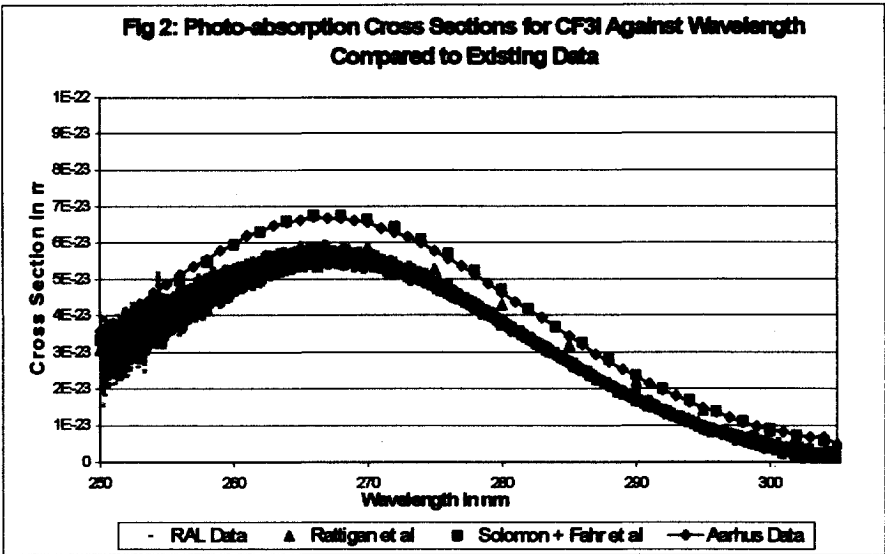
3.2 Results and Discussion

At RAL, photo-absorption cross sections were measured in the range 250 to 300nm. The results are shown in Fig 2. The continuum centred around 266nm, 4.7eV is known to correspond to transitions from the ground (X) to the 1st excited (A) states caused by excitation and de-excitation of an anti-bonding orbital along the CI bond [7]. Therefore, this energy region is of great interest due to its relevance in the dissociation of CF_3I to CF_3 . RAL spectra were compared at gas temperatures of 296K, 272K and 259K. In accord with previous measurements [8] no obvious variation with temperature was observed.

The measured photo-absorption cross sections for the A band recorded at RAL are some 10% lower than the averaged results of Solomon et al [9] and Fahr et al [8] but agree with those of Rattigan et al [10]. As shown in Fig 2, the results taken using synchrotron radiation in Aarhus support Solomon and Fahr et al. Further work is clearly necessary to determine the cause of these differences.

The full range of the spectrum measured using synchrotron radiation is shown in Fig 3. In addition to the weak A band transition, four prominent structures are observed between around 125 and 175nm. The smaller of the

two labelled peaks is attributed to B band excitation centred at 174.0nm, 7.126eV, the larger to C band excitation centred at 159.8nm, 7.757eV. The fine structure superposed on the B band peak is dominated by a vibrational progression in the C-I stretching mode [6]. The greater part of the lower wavelength peaks are interpreted as Rydberg series converging on CF_3I^+ ground state doublet. Work to assign all transitions shown in the plot is ongoing.



4. ELECTRON ENERGY LOSS SPECTROSCOPY (EELS)

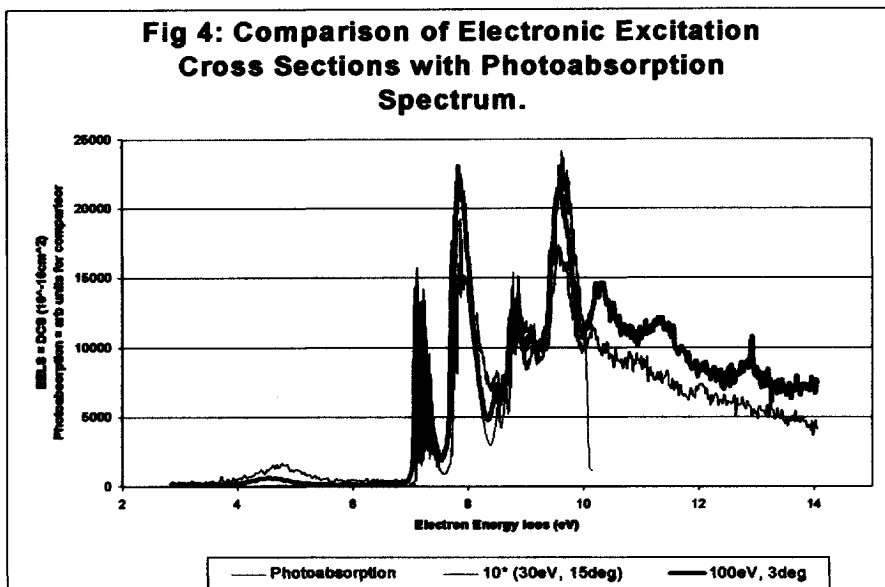
4.1 Experimental

EEL Spectra were recorded at UCL and at Sofia University, Tokyo. The experimental arrangement and procedure used in the present DCS measurements are similar to that used in previous studies [11]. Monochromatic electrons are passed through a gas beam and analyzed post-interaction. The analyzer can be rotated around the scattering center covering an angular range from -10° to 130° with respect to the incident electron beam. A key spectroscopic advantage of this technique is that electrons can lose any amount of kinetic energy in a collision, exciting a molecule to any level. EELS can probe photon forbidden collisions. Photo-absorption and REMPI occur only when the (multi-) photon energy is resonant with the excited energy level. Resonance effects remain significant in EELS as a low-energy electron can be attach itself to a molecular target to form a TNI. This causes much more efficient energy transfer than by direct nuclear scattering.

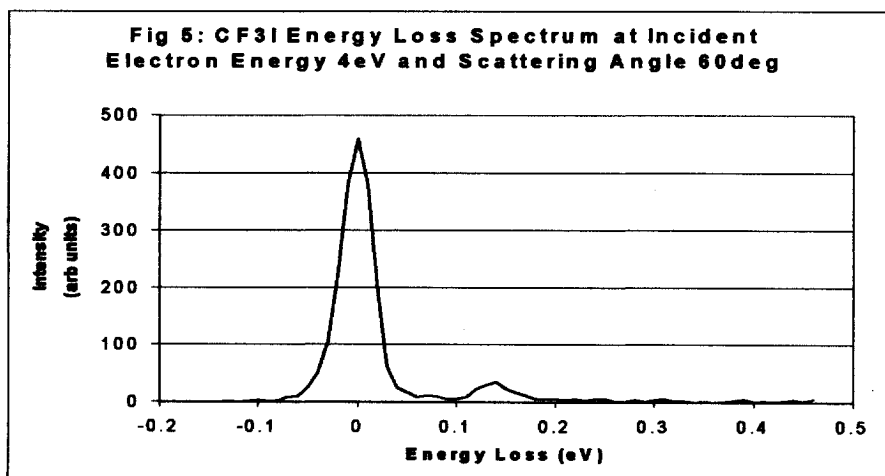
The scattering spectrometer is operated in two ways. For the measurements of the angular dependence of the excitation processes, the intensity of the scattered electron signal is monitored as a function of energy loss at a fixed impact energy and scattering angle. To study resonances, the analyzer is set to transmit only signals corresponding to a specific energy-loss channel and transmission measured as a function of impact energy.

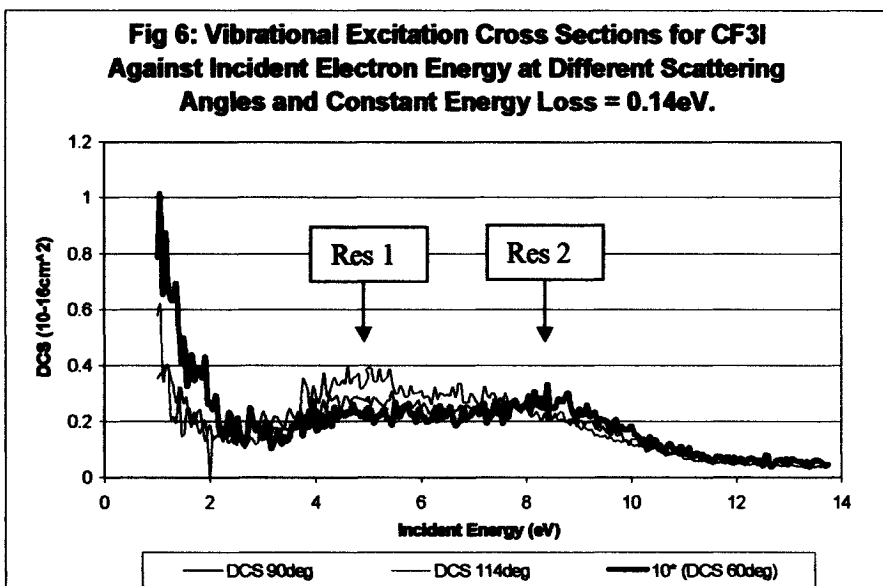
4.2 Results and Discussion

An EEL spectrum taken at constant electron impact energy is compared to the photo-absorption spectrum in Fig 4 [6]. At large scattering angles and low incident energies forbidden transitions dominate while at small scattering angles and high incident energies optically allowed transitions are most important. The four prominent bands show larger differential cross sections at higher incident energies, a trend characteristic of optically allowed transitions. The slightly shifted centre of the lowest energy peak at lower incident energy and greater scattering angle suggests that this peak may be a superposition of two or more electronic states.



In general, negative ion resonances will be more clearly visible in inelastic scattering than in elastic. Figure 5 shows an energy loss spectrum measured at an impact energy of 4 eV and scattering angle of 60° [12]. The energy resolution (30–40 meV) of the result shown is not sufficient to resolve individual modes. The main peak represents elastic interactions. The other peak corresponds to vibrational inelastic interactions. To probe the vibrational excitation due to composite C-F₃ stretching and deformation modes (the *umbrella* vibration), incident energy was varied at fixed energy loss, as shown in Fig 6.





Below 2 eV there is a steep increase in cross section. Above this energy there are some overlapping structures including a peak at 5.5eV, a shoulder at 8eV, and a long tail up to 12 eV, their respective strength varying with scattering angle. These features provide evidence for the presence of shape resonances. From total electron scattering cross section measurements, these resonances can be interpreted as being associated with the composed symmetry of a_1 ($C-F\sigma^*$) and e ($C-I\pi^*$) MO's. This assignment is based on ab initio self-consistent-field calculations of the electron attachment energies [13].

Figure 7 shows the elastic excitational differential cross sections for CF₃I over the impact energy region from 1.5 to 60eV for scattering angles between 20° and 130° [12]. At low incident energies (< 6eV) the steep increase in the cross section at forward angles may be attributed to the large permanent dipole-moment of CF₃I. The DCS also show a shallow minimum near 30° and a clear hump around 70° followed by a sharp dip near 120°. The 30° feature is found to move towards smaller angles with rising impact energy, becoming a monotonic increase at 4eV.

As the energy increases from 6 to 8 eV, a new minimum emerges around 70°. Resonant enhancements in the total electron scattering cross section of CF₃I have also been observed at 4.9 and 8.0 eV [13]. This energy region corresponds to the position of a shape resonance commonly observed in alkanes and fluoroalkanes. For energies above 10 eV, a steep increase in DCS is observed near the zero scattering angle. The 90° structure observed

at 6 eV begins to shift toward smaller angles as the scattering energy increases. It becomes conspicuous at 60 eV, where also observed are a small shoulder at 50°, a deep minimum at 90°, and a sharp increase toward backward scattering angles. No directly comparable experimental or theoretical data is available in the literature.

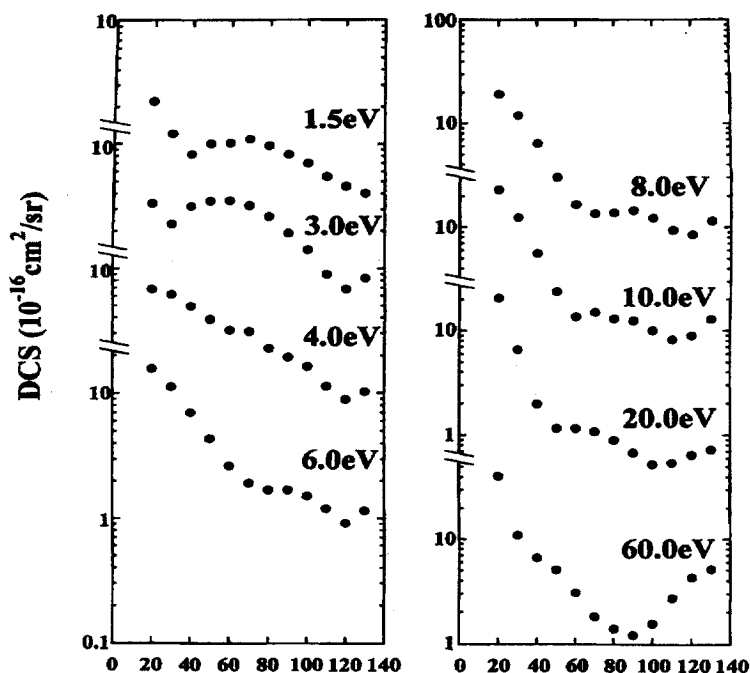


Figure 7. Electron impact elastic scattering differential cross sections for CF_3I

5. STUDY OF INDUCED DISSOCIATION USING RESONANCE ENHANCED MULTI-PHOTON IONIZATION (REMPI)

To perform REMPI, an intense ionizing LASER beam is passed through a gas. The most favorable (1+1) form of multi-photon ionization occurs when an incident photon excites an electron to a new state [14]. This excited state acts as an intermediate step from which a second photon can raise the electron to the ionization level. Excitation to the intermediate state is subject

to the sharp resonance conditions related to the molecule's gas phase UV spectrum. Only when these resonance conditions are met can the second photon be absorbed efficiently. Thus, REMPI applied to a mixture of gases in a potential can be used to isolate one of the constituent species.

The technique is very well suited to the detection of neutral radicals in the ground state. Such species are very difficult to detect by conventional spectroscopic techniques due to their typically short lifetimes and similar mass-spectrometric signature to that of their parent. An alternative technique is to use the radicals' propensity to react with tellurium at a surface to produce volatile tellurides which can easily be distinguished from the parent compound [15].

An experiment is under development at UCL to perform REMPI on the short-lived neutral fragments responsible for the etching process. In the case of CF_3I , most interest lies in the production cross sections of CF , CF_2 and CF_3 within reactors. The gas will be dissociated by a continuous electron beam, simulating the plasma conditions at which processing takes place. Simultaneously, the sample will be probed with the laser beam. An example of the reactions expected is as follows:

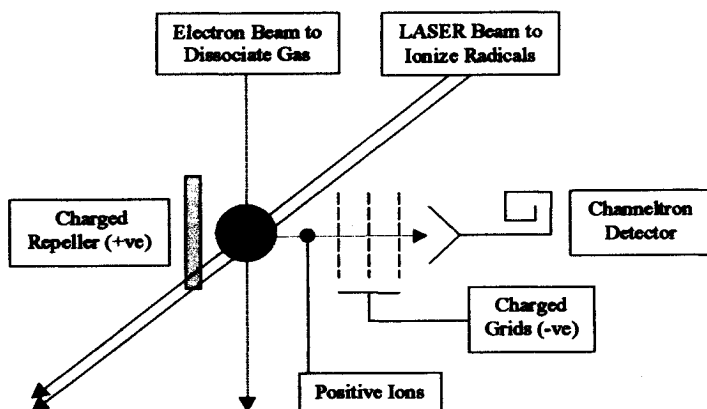
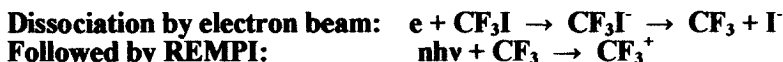


Figure 8. The REMPI system

6. CONCLUSION

The work presented in this paper is part of a global effort to introduce environmentally friendly alternatives to the PFCs used in the plasma processing industry. The electron impact results are the first of their kind on CF_3I and give important new information to help understand the behavior of this potentially key industrial gas. Photo-absorption results help to provide clarity where some contradictory measurements have been recorded in the past. Further results including those from experiments on CF_3I and C_2F_4 using REMPI to probe for radical products of electron interactions will be reported in the near future.

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TIME DELAYS AND COLD COLLISIONS

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Abstract. A brief description is given of how low energy electron beam scattering experiments may be conducted in the energy range down to a few meV. Experimental data demonstrating virtual state scattering in CO₂ are shown. Expressions are given for the time delays (or lifetimes) of low energy electron molecule encounters and these expressions are used to give insight into the nature of virtual state scattering. These ideas are extended to include cold atom collisions and it is shown that there is a universal maximum collision lifetime, for an ultracold collision energy E , given by $(2E)^{-1}$.

1. INTRODUCTION

When low energy electrons encounter molecules, remarkable quantum scattering events have been found to take place (Field et al. 2001a). Elastic scattering may occur with very large cross-section, as in CO₂ (Field et al. 2001b) and benzene (Field et al. 2001c) and vibrationally and rotationally inelastic scattering may also be encountered. For pure rotationally inelastic events, cross-sections may exceed 1000 Å². In this chapter, discussion is however limited to elastic scattering with special reference to the lifetimes of collision complexes which form in cold encounters. Special attention is given to the mechanism of virtual state scattering, which greatly enhances very low energy elastic scattering cross-sections.

Low energy electrons, of energies between a few meV and a few eV, may temporarily enter, or attempt to enter, the lowest unoccupied molecular orbital (LUMO) of target species. In doing so, they form a temporary

negative ion (TNI). In general the nuclear framework of the fully relaxed negative ion is substantially different, both in symmetry and in terms of bond lengths, from the neutral target. Thus scattering phenomena are influenced by coupling between the electronic and nuclear motion. The extent of this coupling has a fundamental impact on the outcome of electron-molecule collisions. The degree to which the nuclear framework may relax towards that of the most stable configuration is a determining feature of many systems. An example is an encounter in which the target dissociates into a stable negative ion and a neutral, e.g. electrons and carbon tetrachloride yield CCl_3 and Cl^- . If no relaxation, or very little, is possible, the collision is said to proceed non-adiabatically. For full relaxation, the encounter is adiabatic. Since nuclear relaxation requires time to take place, the lifetime of the encounter is one of the most illuminating parameters for insight into the nature of these collisions. For example, if the time is long, then the TNI may relax more fully and the collision is partially adiabatic. In this chapter we report expressions for calculating the time delays in collisions, which may also be regarded as collision lifetimes, for elastic encounters between electrons and molecules. Analysis is also extended to include cold collisions between atoms which share many properties with low energy electron collisions. We define cold collisions as those in which the de Broglie wavelength of one or both projectiles is very much greater than the typical size of a molecule (Weiner et al. 1999, Field et al. 2001a). For example, the de Broglie wavelength of a 10 meV electron (or a Rb atom at 5×10^{-4} K) is 122 Å, an order of magnitude larger than the dimensions of a simple molecular species.

The concept of time delay in scattering has been applied largely to resonances (Bosanac 1990, Gauyacq 1990, Newton 1982). The concept has entered rather little into the discussion of cold atom collisions. The greatest time delays, which may extend beyond 100 μs , are found in collisions involving an interaction potential that supports one or more bound states, such as in attachment of electrons to SF_6 (Chutjian and Alajajian 1985, Gauyacq and Herzenberg 1984). However in the present work we restrict our discussion specifically to encounters in which bound states are not found and concentrate on virtual state scattering, with a short section devoted to cold atom collisions.

2. EXPERIMENTAL DATA

Estimates of time delays are based on experimental data, for example the measurement of the variation of absolute scattering cross-sections with collision energy in electron scattering, or experimental estimates of the

scattering length for cold atom collisions. Below, we review briefly how we obtain cold electron scattering data in the energy range of a few meV to a few hundred meV.

The experimental requirement is for a beam of electrons tunable to low energy, with the accompanying requirement of an energy resolution of a few meV or better. Electrons are formed by a synchrotron radiation photoionization technique involving the threshold photoionization of Ar, using the ASTRID storage ring at the University of Aarhus. Figure 1 shows a scale diagram of the apparatus, sited on the undulator beamline on ASTRID. Synchrotron radiation is focussed into a strip of light of thickness of the order of less than ten microns. Electrons are formed, using Ar at a pressure of a few tens of mPa, with monochromatized radiation tuned to 78.65 nm, ~ 3 meV above the threshold for photoionization. The energy resolution of the electrons is determined by the energy resolution of the photon beam and is typically 1 meV to 1.5 meV, full-width half-maximum. An electric field of 0.2 to 0.4 V per cm across the region of photoionization draws electrons out of the source region. Electrons are formed into a focussed beam using electron optical elements, including a 4-element electrostatic lens (see Figure 1).

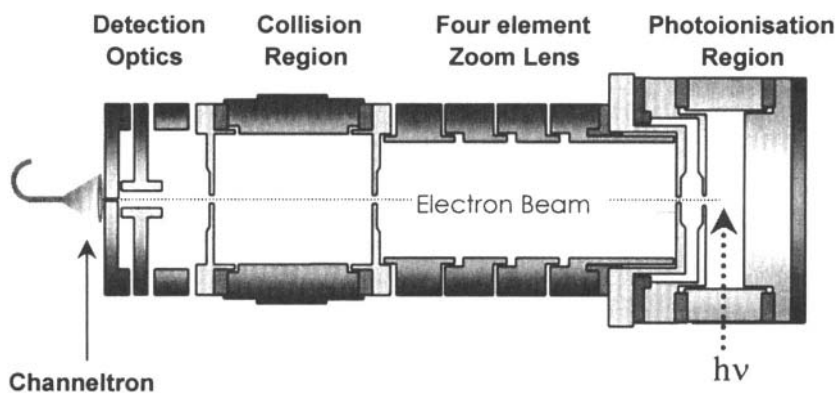


Figure 1. Schematic diagram of the apparatus. Using the undulator and spherical grating monochromator beam-line at ASTRID, monochromatic synchrotron radiation ($h\nu$) at 78.65 nm is focussed into a cell containing argon, yielding photoelectrons of ~ 3 meV energy and energy resolution of ~ 1 meV. Electrons are accelerated and focussed into the target gas using a 4-element zoom lens (Martinez et al 1983).

The electron beam passes through a cell containing the target gas, where its attenuation as a function of electron energy is measured by recording the electron current on a channel electron multiplier detector (Galileo channeltron 7010M) situated beyond various further optical elements. The electron energy is controlled by varying the potential in the photoionization

source. The whole apparatus can be immersed in an axial magnetic field, which is typically set to 20 Gauss (Gulley et al. 1998).

Absolute cross-sections are measured through attenuation of the incident beam using

$$I_t = I_0 \exp(-\sigma NL)$$

where I_0 and I_t are the unattenuated and attenuated electron currents respectively, σ is the scattering cross-section (see below), N is the target gas number density, measured with a Leybold Viscovac VM212 rotating ball gauge, and L is the effective electron path length in the target gas. Detailed tests using He and N_2 show that the geometrical length of the collision path (30mm) is the true effective length, within experimental error.

In the absence of an axial magnetic field, the measured cross-section is the total integral scattering cross-section, where 'total' refers to all elastic and inelastic events (so far as the geometry and potentials in the system allow) and integral refers to integration over the full 4π solid angle. When electrons are scattered by the target gas in the presence of the axial magnetic field, those that are directed into the forward hemisphere are picked up by the magnetic field and continue along an axial path. These electrons exit the scattering cell and are recorded at the detector (see Figure 1). Electrons which are scattered into the backward hemisphere are again picked up by the magnetic field, in this case retracing their paths backwards through the apparatus. These electrons are lost in the vicinity of the source region. Thus in the presence of the magnetic field, the measured cross-section is a total backward scattering cross-section, that is, a cross-section integrated over the 2π solid angle associated with the backward hemisphere. Energy calibrated scattering spectra for N_2 (Kennerly 1980) and O_2 (Randell et al. 1994 and references therein) provide a calibration of the absolute electron kinetic energy, which can be specified with an uncertainty at higher energies of ± 5 meV and better than ± 1.5 meV at the lowest energies.

Figure 2 shows data for integral and backward scattering for CO_2 . In a recent paper (Field et al. 2001b) we have described in detail how the data in Figure 2 may be analyzed to yield a set of s-wave phase shifts as a function of electron collision energy and to give the s-wave scattering length, A_0 , for CO_2 . At the low energies shown in Figure 2, only s- and p- waves contribute significantly to scattering, with s-waves strongly dominant, especially at the lowest energies. For example at 10 meV, the s-wave contributes $118\text{\AA}^2$ and the p-wave $\sim 10\text{\AA}^2$ to the integral scattering cross-section. The corresponding s-wave phase shift at 10 meV, η_0 , is +0.158 radians. The value of A_0 is -6.28 ± 0.12 au. The negative sign of A_0 signifies that there are no bound states of the electron in the electron- CO_2 potential. This is a critical

feature of virtual state scattering, as opposed to scattering involving attachment through a bound state in the potential - characterized by a positive A_0 , as for example in SF_6 . The data in figure 2 are the first experimental demonstration in an atomic or molecular system of virtual state scattering, a phenomenon which has attracted very considerable theoretical interest for many years, especially recently. Detailed comparison with calculations may be found in (Field et al 2001a) but suffice it to say that the latest calculations of the integral scattering cross-section in Mazevet et al. 2001 agree closely with our experimental results for integral scattering.

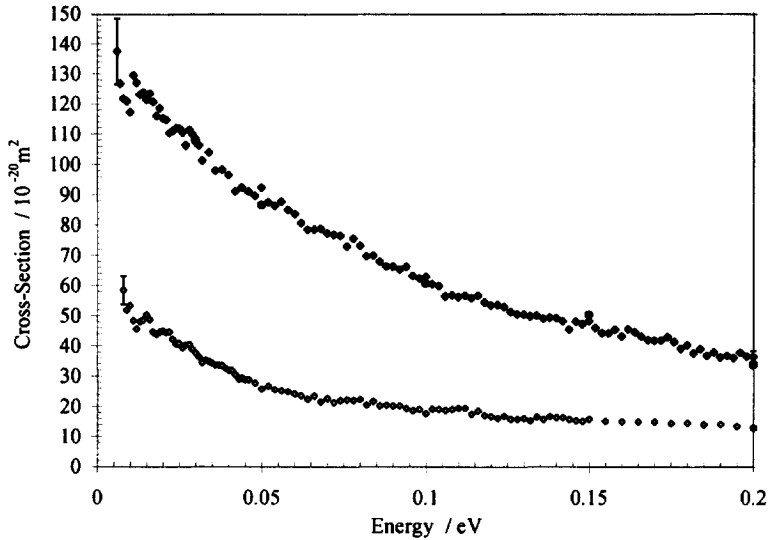


Figure 2. The variation of the integral (upper set) and backward (lower set) scattering cross-sections for low energy electrons and CO_2 as a function of electron kinetic energy between a few meV and 200 meV

3. TIME DELAYS: THEORY AND RESULTS FOR ELECTRON SCATTERING

It is well-known that a wave packet analysis (Eisenbud 1948, Bohm 1951, Wigner 1955) yields the result that a partial wave ℓ , when scattered, undergoes a time delay of

$$\tau_\ell = 2 \frac{d\eta_\ell}{dE} \quad (1)$$

where here and subsequently atomic units are used. Matter wavepackets in cold collisions are narrow in energy and correspondingly broad in time. For example an energy resolution of 1 meV in an electron scattering experiment, as here, corresponds to an electron wave train of coherence length 19 nm or duration 660 fs. The equivalence between a wavepacket description, for a wavepacket narrow in energy and broad in time, with a time-independent description, is illustrated by calculations presented in Gauyacq 1990. A time-independent formalism is used in the present work. Smith 1960 has shown that a rigorous time-independent analysis of time delay yielded an expression for time delay identical to that of equation 1, where time delay was defined as follows. Smith 1960 considered the difference in the density of particles in a region of space in the presence and absence of a scattering centre. This difference was obtained by integrating over a region which formally extends to an arbitrarily large distance from the scattering centre, such that the interaction becomes negligible. The resulting excess or deficiency of particles in the vicinity of the scattering centre, divided by the total flux through an arbitrarily distant closed surface, gives the delay or advance in time associated with the interaction. The time delay in equation 1 is in the centre of mass frame and represents a time of interaction, or a collisional lifetime, in which events such as rearrangement of the molecular nuclear framework or photon emission may take place.

We now consider the specific case of electron-CO₂ scattering as a generic example of the interaction of a cold electron with a non-polar molecule. The electron-CO₂ interaction is strongly dominated by a charge-induced dipole interaction in the energy range of interest, that is, down to a few meV (Field et al. 2001b). It follows from modified effective range theory (O' Malley 1963), for pure elastic scattering in a r^{-4} potential, that η_0 and η_1 , respectively the s- and p-wave phase shifts, may be written

$$\tan \eta_0 = -A_0 k [1 + (4\alpha/3)k^2 \ln(k)] - (\pi\alpha/3)k^2 \quad (2a)$$

$$\tan \eta_1 = (\pi\alpha/15)k^2 \quad (2b)$$

where α is the polarizability of CO₂, $k = (2E)^{1/2}$ is the magnitude of the electron wave vector, E is the electron impact energy in au (1 au = 27.2114 eV). Empirical correction terms in k^3 and k^4 will be included subsequently.

Using equation 1 in conjunction with equation 2a, we obtain for the s-wave time delay τ_0

$$\tau_0 = -2 \frac{\cos^2 \eta_0}{k} \left[A_0 (1 + 4\alpha k^2 \ln k + \frac{4\alpha}{3} k^2) + \frac{2\pi\alpha k}{3} \right] \quad (3a)$$

and for the p-wave, τ_1

$$\tau_1 = \frac{4\pi\alpha}{15 + \frac{(\pi\alpha k^2)^2}{15}} \quad (3b)$$

In equation 3a, the $\cos^2 \eta_0$ term may be evaluated explicitly, if A_0 is known, or it may be incorporated into a rather more cumbersome expression for τ_0 , using equation 2a. Inserting values of s-wave phase shifts vs electron impact energy, and using $A_0 = -6.28$ au (see back), the variation of τ_0 with electron impact energy may be calculated. This is shown in figure 3.

The p-wave time delay for electron scattering by CO_2 at 10 meV is 248 attoseconds, evaluated using equation 3b, but including an empirical correction term in k^3 . This illustrates the general result that time delays in cold collisions may be represented to a good approximation by the time delay of the s-wave.

When the s-wave scattering length is a positive quantity, equation 3a shows that the s-wave time delay can be negative, that is, there is a time advance rather than a delay, with the incoming electron accelerated past the scattering centre. An example is electron scattering by N_2 (Randell et al. 1994), which shows a time advance of 408 attoseconds for an impact energy of 10 meV, accompanied by a p-wave delay of ~ 40 attoseconds.

The time delays shown in Figure 3 provide useful insight into the nature of virtual state scattering. For virtual state scattering, the incipiently forming TNI must be unbound to spontaneous electron loss ("autodetachment") in the equilibrium geometry of the neutral (Gauyacq & Herzenberg 1984), which in the case of CO_2 is linear geometry. The TNI must however be able to form a quasi-bound state in some other geometry, where quasi-bound implies that the TNI should be non-adiabatically metastable to autodetachment.

Recent calculations on the CO_2 anion illustrate very nicely that CO_2 fits these requirements (Gutsev et al. 1998). The linear CO_2 anion sits on a energy saddle point with respect to the OCO angle. The anion becomes stable to autodetachment when the species bends to an angle of less than $\sim 150^\circ$. However CO_2 has a negative electron affinity and even the most stable configuration is unstable to autodetachment to form the neutral.

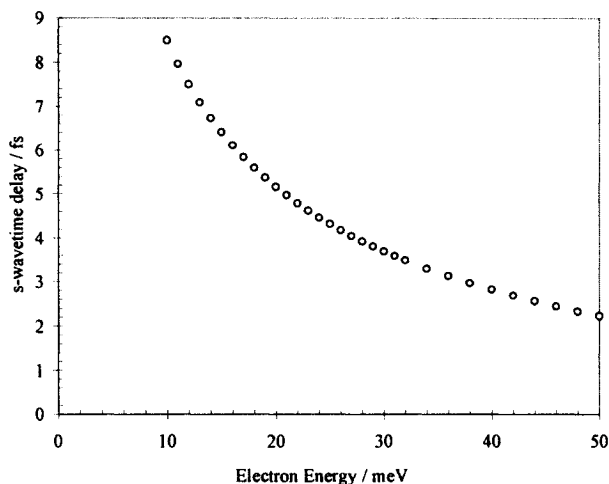


Figure 3. Variation of the s-wave time delay as a function of electron impact energy for electron collisions with CO_2 . Values are calculated using equation 3a, but including empirical correction terms involving k^3 and k^4 .

Thus the negative ion is never more than non-adiabatically stable. In an encounter of ~ 5 fs duration, see Figure 3, there is insufficient time for the species to bend and to explore the non-adiabatically stable regime. However the system may be viewed as borrowing time through $\Delta t \cdot \Delta E \geq \hbar/2\pi$. In this borrowed time, the nuclei may move virtually. Most of the borrowed time is given back after the interaction is complete. The time delay of femtosecond(s) may be seen as a relic of the borrowed time. A virtual state is therefore a quasi-stationary state of the system which is accessed through borrowed time. In more conventional terms, the virtual state represents a superposition, or sampling, of all trajectories, including those involving nuclear motions in the target leading to quasi-bound bent configurations. The longer the lifetime of the electron- CO_2 transition state, the greater the sampling of trajectories associated with bent configurations and the greater the cross-section.

An important point in this connection is that bending of the molecular ion splits the degeneracy of the lowest unoccupied molecular orbital from $^2\Pi_u$ into orbitals of A_1 and B_1 symmetry, with A_1 lying lower. The LUMO of the linear species will not accept an s-wave and therefore bending of the species is an inherent part of the mechanism, since the resulting A_1 orbital can accept the s-wave. This provides additional strength to the argument that the lifetime of the intermediate is a determining feature of the interaction.

4. TIME DELAYS IN COLD ATOM SCATTERING

To adapt the famous phrase of Eddington in the *Internal Constitution of the Stars*, let us go and find a colder place. We now consider the fully asymptotic situation, in which only the longest range contribution to the potential dictates the scattering phase shifts. In this limit, relevant only to very low energy, the leading term in equation 3a dominates and yields the general result

$$\tau_0 \approx -\frac{2A_0\mu}{k} \frac{1}{1 + A_0^2 k^2} \quad (4)$$

where μ is the reduced mass of the collision partners, included since we are now dealing with heavy particles. Equation (4) holds for all potentials of the form r^{-n} for $n \geq 2$. Equation 4 is thus quite general and applies to all ultra-cold elastic collisions save those between two charged particles. Ultra-cold collisions involving ${}^6\text{Li}$ illustrate the lifetimes of collision complexes that may be encountered in cold atom scattering. For ${}^6\text{Li}$ self-collisions, A_0 has been measured to be -2100 ± 250 , on the triplet interaction surface (Abraham et al. 1997). For illustration, we estimate the value of k from the rms speed of the particles, that is, we assume an impact energy of $(3/2)k_B T$. Thus if $T = 1\mu\text{K}$, then Equation 4 yields a lifetime of the collision complex of $1.99 \pm 0.23\mu\text{s}$. On the singlet surface, $A_0 = 45.4 \pm 2.5$ (Abraham et al. 1997), and at $T = 1\mu\text{K}$, a time advance of $52.9 \pm 2.8\text{ ns}$ may be estimated.

An interesting prediction of Equation 4 is that for any scattering length there is an energy for which the maximum collision lifetime will be found and that this maximum is a universal quantity. Equation 4 shows that τ_0 reaches a maximum when $k = |A_0|^{-1}$, that is to say when the matter wave fits snugly inside the target, interpreting the scattering length as some measure of the target size. Since it is possible to tune the scattering length by applying a magnetic field to cold atom systems (Tiesinga et al. 1992, 1993), one may, at least in principle, tune A_0 to satisfy the condition for maximum lifetime. This lifetime is given very simply by $\tau_{\text{MAX}} = (2E)^{-1}$, where E is the collision energy of the encounter. For example at $1\mu\text{K}$, $\tau_{\text{MAX}} = 3.88\mu\text{s}$ for all systems. Naturally, the magnetic field necessary to tune the condition that $k = |A_0|^{-1}$, remains special to any system.

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RELATIVISTIC BASIS SET METHODS

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Introduction

Relativity, like gravitation, cannot be switched off. Whilst relativistic effects on the physics of light elements are often tiny, they grow rapidly with nuclear charge and become progressively harder to ignore as we go down the Periodic Table. We have seen in this meeting, for example, that at energies of several hundred keV, which is comparable with the rest energy of the electron, relativistic effects in electron impact ionization are significant and need a full-blooded relativistic treatment [1]. This is partly because of the relativistic character of the dynamics of fast electrons, but also because the many-electron target – atom, molecule, atomic cluster or solid – may also reveal relativistic effects.

Relativistic theories of many-electron systems can be regarded as a branch of quantum electrodynamics (QED) (see any good text, for example, [2]). The geometry of space-time is described by the group of inhomogeneous Lorentz transformations. The corresponding Lie algebra is built from the infinitesimal generators for space and time displacements, rotations and boosts (which relate 4-vectors in inertial frames moving with different velocities). These generators can be identified with quantum mechanical operators: linear 4-momentum, angular momentum and so on. The irreducible representations can be labelled by the particle's rest mass, m and its angular momentum in the rest frame of the particle, s , the intrinsic spin : $1/2$ for electrons, 1 for photons (which have zero mass). The time-like component of linear 4-momentum is the particle energy which, unlike nonrelativistic mechanics, can be either positive or negative. The infinitesimal generators of rotations about coordinate directions are operators describing the *total* angular momentum, $\mathbf{j} = \mathbf{l} + \mathbf{s}$ where, as usual the orbital angular momentum $\mathbf{l} = \mathbf{r} \times \mathbf{p}$, where $\mathbf{r}$ is the (3-)vector of position and $\mathbf{p}$ is the linear momentum operator, $-i\hbar\nabla$.

This *spin-orbit coupling* implies that neither l nor s are separately conserved in spherically symmetric systems although j is conserved.

The presence of negative energy states means, as pointed out by Dirac, that even the hydrogen atom must be considered as a many-electron system. He supposed that the ground state of the hydrogen atom could be stabilized by saying that all negative energy electron states are occupied in accordance with the Pauli principle. Vacancies in the negative energy states behave like positively charged electrons, and today we interpret these vacancies as positrons. QED describes the physics of interacting quantized fields: the electron-positron field (whose quanta are electrons and positrons) and the electromagnetic field (whose quanta are photons). The numbers of electrons and positrons are not separately conserved in this theory although the *total charge* is a constant of the motion: this implies that a state which has nominally N_e (non-interacting) electrons and no positrons can interact with real or virtual states of the same total charge having $N_p > 0$ positrons and $N_e + N_p$ electrons. As it requires energies of order $2mc^2 \approx 1$ MeV to create a physical electron-positron pair the positron states only occur as intermediate virtual states in the theory of low energy processes. Thus it is often enough to consider negative energy states as inert (just like non-relativistic deep core states); this is known as the *no-pair approximation*.

It is hardly surprising that relativistic atomic and molecular structure has remained the preserve of specialists, and the literature exhibits much confusion about how to implement the principles of QED. Although relativistic quantum mechanics was formulated at the same time as nonrelativistic quantum mechanics in the late 1920s, it was necessary at the time to treat the former by perturbation methods starting from the Schrödinger equation, and textbooks still reflect this primitive approach. Most people still think of perturbation theories of “relativistic corrections” as the standard way to visualize the physics of atomic and molecular structure. In fact, after some 70 years, we now possess the mathematical tools to handle relativistic problems as well as the computational tools to perform the numerical calculations. The purpose of this talk is to highlight some of the principles in an effort to demystify the subject.

Processes involving one-electron systems have usually been treated by analytical methods as described in textbooks [2]. Many-electron atoms require more elaborate algorithms which traditionally depend on finite difference methods to generate Dirac spinor wavefunctions, either for one-body model potentials or for self-consistent fields [3, 4, 5, 6]. Electron correlation is described by superposition of configurations, either as part of a CI calculation or using the multi-configuration Dirac-Hartree-

Fock (MCDHF) procedure¹. However, this approach is useless when we come to deal with molecules, atomic clusters or solids and it is best to adapt ideas from nonrelativistic quantum chemistry to treat such systems. Early experiments by quantum chemists assumed implicitly that it was only necessary to expand each of the four components of a Dirac spinor independently in a basis set (see [7] for a review of the position in 1984), but this was doomed to failure as it failed to take into account the strong coupling of the components, especially near the nucleus. Many quantum chemists therefore lost interest in methods based on the Dirac operator, and opted instead for 2-component (Pauli-type) approximations based on *relativistic effective core potentials* (RECP) or *pseudo-potentials* (PP) [8] or on effective Hamiltonians [9] which could be grafted on to existing quantum chemistry packages without much difficulty. The main difficulty with all such schemes is that the errors of approximation are hard to quantify and that spin-dependent effects are treated in an *ad hoc* fashion.

We now know how to construct 4-component spinor basis sets which make it possible to implement a matrix realization of QED for atoms, molecules, atomic clusters and so on. Whilst this scheme has not yet been exploited in scattering problems, an understanding of its principles may well be important for future work.

1. Central field Dirac spinors

The central field approximation plays a major role in modelling atomic and molecular electronic structure as it does in nonrelativistic physics. We use the notation and units of [6, §22.5] in the following. The central field Dirac equation can be written

$$\hat{H} \Psi(t, \mathbf{x}) = i\hbar \frac{\partial}{\partial t} \Psi(t, \mathbf{x}), \quad \hat{H} = c \boldsymbol{\alpha} \cdot \mathbf{p} + \beta mc^2 + U(r) \quad (1)$$

where $\boldsymbol{\alpha}$, β are 4×4 matrices in the Dirac representation and $U(r)$ is a central field potential function such as $U(r) = -Z/r$ (in atomic units) for a hydrogenic atom of charge Z . Equation (1) has stationary states with energy E of the form

$$\Psi(t, \mathbf{x}) = \psi_{E\kappa m}(\mathbf{x}) e^{-iEt}, \quad (2)$$

where

$$\psi_{E\kappa m}(\mathbf{x}) = \frac{1}{r} \begin{bmatrix} P_{E\kappa}(r) \chi_{\kappa, m}(\theta, \varphi) \\ iQ_{E\kappa}(r) \chi_{-\kappa, m}(\theta, \varphi) \end{bmatrix}.$$

This 4-component spinor has radial amplitudes $P_{E\kappa}(r), Q_{E\kappa}(r)$, whilst

$$\chi_{\kappa,m}(\theta, \varphi) = \sum_{\sigma=\pm 1/2} \langle l, m - \sigma, 1/2, \sigma | l, 1/2, j, m \rangle Y_l^{m-\sigma}(\theta, \varphi) \phi_\sigma$$

is a 2-component spin-orbital, a simultaneous eigenfunction of $\mathbf{j}^2, \mathbf{l}^2, \mathbf{s}^2$ and j_z with eigenvalues $j(j+1), l(l+1), s(s+1) = 3/4$ and m respectively. Here $\langle l, m - \sigma, 1/2, \sigma | l, 1/2, j, m \rangle$ is a Clebsch-Gordan coefficient, $Y_l^{m-\sigma}(\theta, \varphi)$ is a spherical harmonic and $\phi_\sigma = (\delta_{\sigma, 1/2}, \delta_{\sigma, -1/2})^t$ (t denotes vector transposition) are spin eigenfunctions. The $\chi_{\kappa,m}$ are eigenfunctions of the operator

$$K = \mathbf{l}^2 + \mathbf{s}^2 - \mathbf{j}^2 - 1 = -1 - \boldsymbol{\sigma} \cdot \mathbf{l}. \quad (3)$$

so that

$$K\chi_{\kappa m}(\theta, \varphi) = \kappa\chi_{\kappa m}(\theta, \varphi), \quad \kappa = \pm(j + \frac{1}{2}) \text{ if } l = j \pm \frac{1}{2} \quad (4)$$

Inserting numerical values for the Clebsch-Gordon coefficients we find that

$$\chi_{\kappa m}(\theta, \varphi) = \begin{pmatrix} -\eta C_{lm}(-\eta) Y_l^{m-1/2}(\theta, \varphi) \\ C_{lm}(\eta) Y_l^{m+1/2}(\theta, \varphi) \end{pmatrix} \quad (5)$$

where $C_{lm}(\eta) = +\sqrt{(l + \frac{1}{2} + m\eta)/(2l+1)}$, with $\eta = \text{sgn } \kappa$, $l = j + \frac{1}{2}\eta$, $j = |\kappa| - \frac{1}{2}$. In terms of the old vector coupling model, the value of η determines whether the spin and orbital angular momenta are coupled in parallel or anti-parallel, whilst $\kappa = (j + 1/2)\eta$ also serves to define the magnitude of the resultant. In the formal non-relativistic limit $c \rightarrow \infty$ it is well-known that $P_{E,\kappa}(r)$ becomes the nonrelativistic Schrödinger radial amplitude, whilst $Q_{E,\kappa}(r)$ is $O(1/c)$, and hence vanishes.² For this reason $P_{E,\kappa}(r)$ is usually designated the *large* component and $Q_{E,\kappa}(r)$ the *small* component, though these descriptions must not be taken too literally. The result is that the angular character of the state in the nonrelativistic limit is the value of l for the *large* component, whether $j = l \pm 1/2$. Dirac central field states are therefore often given *spectroscopic labels*, $s_{1/2}, p_{1/2,3/2}, d_{3/2,5/2}, \dots$, for $l = 0, 1, 2, \dots$ respectively, where the subscripts denote the possible j values.

We can partition $\hat{H}$ to reflect this structure

$$\hat{H} = c\boldsymbol{\alpha} \cdot \mathbf{p} + \beta mc^2 + U(r) = \begin{pmatrix} mc^2 + U(r) & c\boldsymbol{\sigma} \cdot \mathbf{p} \\ c\boldsymbol{\sigma} \cdot \mathbf{p} & -mc^2 + U(r) \end{pmatrix}. \quad (6)$$

where if $\mathbf{e}_r = \mathbf{x}/r$

$$c\boldsymbol{\sigma} \cdot \mathbf{p} = -i\hbar c \sigma_r \left(\partial_r + \frac{K+1}{r} \right), \quad \sigma_r = \boldsymbol{\sigma} \cdot \mathbf{e}_r. \quad (7)$$

Note the important relation

$$\sigma_r \chi_{\kappa m}(\theta, \varphi) = -\chi_{-\kappa m}(\theta, \varphi). \quad (8)$$

This implies, in particular, that the upper and lower components have the same angular density, so that the total particle density factorizes

$$\|\psi_{E\kappa m}(\mathbf{x})\|^2 = \rho_{E\kappa m}(\mathbf{x}) = \frac{D_{E\kappa}(r)}{r^2} A_{|\kappa|m}(\theta) \quad (9)$$

where $D(r) = P(r)^2 + Q(r)^2$, and $A_{|\kappa|m}(\theta) = \|\chi_{\pm\kappa m}(\theta, \varphi)\|^2$.

2. Central spinor properties

The 4-component spinors $\psi_{E\kappa m}(\mathbf{x})$, $m = -j, \dots, +j$ span a $(2j+1)$ -dimensional representation of the rotation group $\text{SO}(3)$. This means also that they can be taken as basis functions for the relativistic double point groups [10, 11]. A package (TSYM) for constructing double group molecular symmetry orbitals with this structure can be downloaded from the CPC Program Library [12].

The Hamiltonian $\hat{H}$ commutes with operators for both space and time reflection. The spatial reflection operator for Dirac 4-spinors is $\hat{P} = \beta \hat{P}_0$, where $\hat{P}_0 \Psi(\mathbf{r}) = \Psi(-\mathbf{r})$ is the ordinary parity operator. Then $\hat{P} \psi_{E\kappa m}(\mathbf{x}) = (-1)^l \psi_{E\kappa m}(\mathbf{x})$, where $l = j + \eta/2$ is the value of orbital angular momentum associated with the *large* component of the 4-spinor. Time reversal maps $\Psi(t, \mathbf{r})$ into $\Psi(-t, \mathbf{r})$; for a Dirac 4-spinor this is accomplished by the operator $\hat{T}_0 = -\sigma_y \hat{K}$ applied to both 2-spinors, where $\hat{K}$ denotes complex conjugation and σ_y is a Pauli matrix:

$$\hat{T}_0 \frac{F(r)}{r} \chi_{\kappa, m}(\theta, \varphi) = (-1)^{l-j+m} \frac{(\hat{K}F)(r)}{r} \chi_{\kappa, -m}(\theta, \varphi). \quad (10)$$

The Dirac spinors $\psi, \hat{T}\psi$, where $\hat{T} = \text{diag}(\hat{T}_0, \hat{T}_0)$, are said to constitute a *Kramers' pair*. If ψ is an eigensolution of Dirac's equation belonging to the energy eigenvalue E , then so is $\hat{T}\psi$ in the absence of an interaction that violates time reversal symmetry. The identification of Kramers' pairs is a valuable check on the accuracy of numerical solutions of molecular Dirac equations.

The Hamiltonian $\hat{H}$ couples the radial components so that, in particular, the asymptotic behaviour of $P(r)$ and $Q(r)$ is linked as $r \rightarrow 0$ and

also as $r \rightarrow \infty$. The former is particularly important because electrons move fastest in the high field region of the origin. We must take this into account when approximating radial wavefunctions, whether using finite differences or analytical functions.

3. The matrix Dirac equation

The Rayleigh-Ritz method constructs energy levels and wavefunctions by a variational procedure applied to a functional of the wavefunction ψ , which as approximated by a linear combination of suitable functions - the *basis set*. In the notation we use for the molecular calculations, we assume such trial wavefunctions are given by

$$\psi_a(\mathbf{x}) := \begin{bmatrix} \sum_{\mu=1}^N c_{\mu a}^L M[L, \mu, \mathbf{x}] \\ i \sum_{\mu=1}^N c_{\mu a}^S M[S, \mu, \mathbf{x}] \end{bmatrix}, \quad (11)$$

where a labels the atomic or molecular spinor and the expansion coefficients $c_{\mu a}^T$ (in general complex numbers) are to be determined. The multi-index μ has the form $\mu := \{\mathbf{A}_\mu, \kappa_\mu, j_\mu, m_\mu, \dots\}$ where $\mathbf{A}_\mu$ is an atom centre and the dots signify other parameters. We shall often indicate explicitly that $M[T, \mu, \mathbf{x}]$ is a function of $\mathbf{x}_{\mathbf{A}_\mu} = \mathbf{x} - \mathbf{A}_\mu$ when there is more than one atom centre. Using the notation of (2),

$$M[L, \mu, \mathbf{x}] = \frac{1}{r} f_\mu^L(r) \chi_{\kappa m}(\theta, \varphi), \quad M[S, \mu, \mathbf{x}] = \frac{1}{r} f_\mu^S(r) \chi_{-\kappa m}(\theta, \varphi), \quad (12)$$

where $\{f_\mu^T(r), \mu = 1, \dots, N\}$ are a family of suitable square integrable functions on $(0, \infty)$.

The Rayleigh quotient $R[\psi_a] = \langle \psi_a | \hat{H} - c^2 | \psi_a \rangle / \langle \psi_a | \psi_a \rangle$, is a ratio of quadratic forms in the coefficients. We make $R[\psi_a]$ be stationary with respect to independent variation of the coefficients $c_{\mu a}^L$ and $c_{\mu a}^S$ giving matrix eigenvalue equations of the form

$$\begin{bmatrix} \mathbf{U}^{LL} & c \mathbf{\Pi}^{LS} \\ c \mathbf{\Pi}^{SL} & -2c^2 \mathbf{S}^{SS} + \mathbf{U}^{SS} \end{bmatrix} \begin{bmatrix} \mathbf{c}^L \\ \mathbf{c}^S \end{bmatrix} = \epsilon \begin{bmatrix} \mathbf{S}^{LL} & \mathbf{0} \\ \mathbf{0} & \mathbf{S}^{SS} \end{bmatrix} \begin{bmatrix} \mathbf{c}^L \\ \mathbf{c}^S \end{bmatrix} \quad (13)$$

in which all the submatrices are of dimension $N \times N$. The Gram (overlap) matrices are denoted by $\mathbf{S}^{TT}$ and matrices of the central field potential U by $\mathbf{U}^{TT}$. The kinetic matrices $\mathbf{\Pi}^{T\bar{T}} = \mathbf{\Pi}^{\bar{T}T\dagger}$ (where $\bar{T} = S$ when $T = L$ and *vice versa*) are given by

$$\begin{aligned} \Pi_{\mu\nu}^{LS} &:= \int M^\dagger[L, \mu, \mathbf{x}] \boldsymbol{\sigma} \cdot \mathbf{p} M[S, \nu, \mathbf{x}] d\mathbf{x}, \\ \Pi_{\mu\nu}^{SL} &:= \int M^\dagger[S, \mu, \mathbf{x}] \boldsymbol{\sigma} \cdot \mathbf{p} M[L, \nu, \mathbf{x}] d\mathbf{x}. \end{aligned} \quad (14)$$

and the energy, $\epsilon = E - c^2$, has been shifted to correspond to the nonrelativistic energy zero. The system is Hermitian and has real eigenvalues.

There has been a long-running acrimonious debate, which I shall not review here, on whether this formalism has any value. Sucher persuasively promulgated the view that no stable bound state solutions of Dirac variational problems exist [14], and papers such as [7] assume the truth of this assertion. We now know that this is wrong. The free particle Dirac operator has a spectrum with two disjoint continua $-\infty < E \leq -mc^2$, $mc^2 \leq E < \infty$ so that, unlike the Schrödinger operator, the spectrum is not bounded below. As demonstrated in quantum mechanics textbooks [13, Chap. 13], there is also a point spectrum in the gap $(-2mc^2, 0)$ in the presence of a binding atomic potential such as $-Z/r$, of bound eigenvalues $\epsilon_{n\kappa}$, $n \geq l_\kappa$ such that $\epsilon_{n\kappa} \rightarrow 0$ as $n \rightarrow \infty$. The absence of a global lower bound to the spectrum lies at the heart of Sucher's analysis. However, it has recently been realized that for any admissible negative definite atomic potential such as $-Z/r$, there will exist a finite U_{min} such that $0 > \langle \psi_a | \hat{U} | \psi_a \rangle \geq U_{min}$ for any sensible *normalized square integrable* trial function ψ_a . If also $\langle \psi_a | \hat{H} | \psi_a \rangle \geq mc^2$, then $\langle \psi_a | \hat{H} + \hat{U} | \psi_a \rangle > \langle \psi_a | \hat{U} | \psi_a \rangle \geq U_{min}$ so that the point spectrum is bounded below after all! By the same token, if $\langle \psi_a | \hat{H} | \psi_a \rangle \leq -mc^2$, then also $\langle \psi_a | \hat{H} + \hat{U} | \psi_a \rangle < -mc^2$. These two disjoint sets of trial functions remain disjoint as long as $U_{min} > -2mc^2$, and this is easily satisfied in practice. An account of the basis set method is given in [6] and the mathematical details and numerical demonstration of the Rayleigh-Ritz procedure for Dirac operators in [15]. As in nonrelativistic equivalents, there is no difficulty of principle in extending these results to many-electron problems.

Matrix Dirac equations with sensible mean field atomic potentials have a discrete spectrum having two disjoint sets of simple eigenvalues. If the shifted eigenvalues are numbered in order of increasing energy, $\epsilon_1, \dots, \epsilon_{2N}$, then $\epsilon_1 < \dots < \epsilon_N < -2mc^2$, whilst $-2mc^2 < U_{min} < \epsilon_{N+1} < \dots < \epsilon_{2N}$. The eigenvalues in the two continua are square integrable approximations to scattering states of the appropriate energy, and those in the bound state gap approximate bound eigenvalues of $\hat{H}$.

4. Relativistic electron-electron interaction

The covariant interaction Hamiltonian for coupling a 4-current densities $j^\mu(x)$ and $j^\mu(y)$ has the general form

$$\hat{H}^{(2)} = -i \sum_{\alpha\beta\gamma\delta} c_{\alpha\beta\gamma\delta} \int d^4x \int d^4y j^\mu_{\alpha\beta}(x) D_F(x-y)_{\mu\nu} j^\nu_{\gamma\delta}(y) \quad (15)$$

where $\psi_\alpha(x)$ is a 4-spinor, $j_{\alpha\beta}^\mu(x) = \bar{\psi}_\alpha(x) \gamma^\mu \psi_\beta(x)$ is an overlap 4-current density between spinors α and β , c is the speed of light (≈ 137 Hartree units), γ^μ a Dirac matrix, $D_F(x-y)_{\mu\nu}$ is the causal propagator for light to travel from y to x and $c_{\alpha\beta\gamma\delta}$ are coefficients. It is common to pick the Coulomb gauge, in which case $-ie^2 D_F(x-y)_{00}$ reduces to the *instantaneous* Coulomb interaction $(e^2/4\pi\epsilon_0)/R$ where $\mathbf{R} = \mathbf{x} - \mathbf{y}$, $D_F(x-y)_{0i} = D_F(x-y)_{i0} = 0$, $i = 1, 2, 3$ and $D_F(x-y)_{ij}$, $i, j = 1, 2, 3$ generates a retarded interaction between the space currents at $\mathbf{x}$ and $\mathbf{y}$. In general this gives the Möller interaction which at low energy can be approximated by the Breit interaction; the latter can be used in structure calculations unless we need very high accuracy but the Möller interaction must be used for high energy scattering calculations [1].

Thus in closed shell atoms, the Coulomb repulsion energy (in Hartree units) derived from (15) reduces to the familiar

$$E_C^{(2)} = \frac{1}{2} e^2 \sum_{\alpha\beta} \iint d^3x d^3y \frac{\rho_{\alpha\alpha}(\mathbf{x}) \cdot \rho_{\beta\beta}(\mathbf{y}) - \rho_{\alpha\beta}(\mathbf{x}) \cdot \rho_{\beta\alpha}(\mathbf{y})}{R}, \quad (16)$$

where $\rho_{\alpha\beta}(\mathbf{x}) = \phi_\alpha^\dagger(\mathbf{x}) \phi_\beta(\mathbf{x})$ summed over all occupied orbitals α, β , whilst the Breit energy is

$$E_B^{(2)} = -\frac{e^2}{2c^2} \sum_{\alpha\beta} \iint d^3x d^3y \sum_{i,j=1}^3 \left(\delta_{ij} + \frac{R_i R_j}{R^2} \right) \frac{J_{\alpha\alpha}^i(\mathbf{x}) J_{\beta\beta}^j(\mathbf{y}) - J_{\alpha\beta}^i(\mathbf{x}) J_{\beta\alpha}^j(\mathbf{y})}{2R} \quad (17)$$

where $\mathbf{J}_{\alpha\beta}(\mathbf{x}) = c \phi_\alpha^\dagger(\mathbf{x}) \boldsymbol{\alpha} \phi_\beta(\mathbf{x})$ is the overlap current density. This can be written in terms of the more familiar Breit interaction [16, Equation (38.7)] $\hat{b}_{ij} = \boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j / 2R_{ij} + (\boldsymbol{\alpha}_i \cdot \mathbf{R}_{ij})(\boldsymbol{\alpha}_j \cdot \mathbf{R}_{ij}) / 2R_{ij}^3$ by rearranging the integrand. The Dirac $\boldsymbol{\alpha}$ matrices couple the large and small components, whilst there is no such mixing for the Coulomb interaction.

5. DHFB equations

The matrix Dirac-Hartree-Fock-Breit (DHFB) equations are a popular starting point for relativistic many-electron calculations. They can be derived from the energy expression for a state represented by a single determinantal wavefunction,

$$E = \sum_a (a | \hat{H} | a) + \frac{1}{2} \sum_{ab} [(aa | \hat{g} + \hat{b} | bb) - (ab | \hat{g} + \hat{b} | ba)], \quad (18)$$

where the sum runs over all occupied orbitals a, b . A systematic reduction of the atomic relativistic DHF energy was first given in [3] and extended to the MCDHFB case and to CI calculations in [4, 5]. The reduction assumed that finite difference methods would be used for computing radial wavefunction amplitudes, so that the formalism is intended only to be used for atoms, though some parts of the reduction are still useful in molecular calculations.

The matrix approach is more appropriate for molecules, atomic clusters and other systems. The closed shell matrix DHFB equations can be written

$$\mathbf{FC} = \epsilon \mathbf{SC}, \quad \mathbf{F} = \mathbf{H} + \mathbf{G} + \mathbf{B}. \quad (19)$$

where $\mathbf{H}$ has the structure of (13), $\mathbf{G}$ and $\mathbf{B}$ come from the two parts of the electron-electron interaction, and have no non-zero blocks. In the construction of the two-electron matrix elements, it is convenient to define the density matrix elements $D_{\mu\nu}^{TT'} = \sum_a c_{a\mu}^T c_{a\nu}^{T'}$ where the $\{c_{a\nu}^T\}$ is the set of expansion coefficients of a molecular spinor, ψ_a , the sum over a includes only *occupied* positive-energy states, and $TT' = LL, LS, SL$, and SS . Then, if N is the basis set dimension,

$$G_{\mu\nu}^{TT} = \sum_{\sigma\tau}^N \left[\{(\mu^T \nu^T | \hat{g} | \sigma^T \tau^T) - (\mu^T \tau^T | \hat{g} | \sigma^T \nu^T)\} D_{\sigma\tau}^{TT} + (\mu^T \nu^T | \hat{g} | \sigma^{\bar{T}} \tau^{\bar{T}}) D_{\sigma\tau}^{\bar{T}\bar{T}} \right] \quad (20)$$

$$G_{\mu\nu}^{T\bar{T}} = \sum_{\sigma\tau}^N -(\mu^T \tau^T | \hat{g} | \sigma^{\bar{T}} \nu^{\bar{T}}) D_{\sigma\tau}^{\bar{T}T}, \quad T\bar{T} = LS, SL.$$

where $(\mu^T \nu^T | \hat{g} | \sigma^T \tau^T)$ involves only basis set components. Similarly

$$B_{\mu\nu}^{T\bar{T}} = \sum_{\sigma\tau}^N \left[\{(\mu^T \nu^{\bar{T}} | \hat{b} | \sigma^T \tau^{\bar{T}}) - (\mu^T \tau^{\bar{T}} | \hat{b} | \sigma^T \nu^{\bar{T}})\} D_{\sigma\tau}^{T\bar{T}} + (\mu^T \nu^{\bar{T}} | \hat{b} | \sigma^{\bar{T}} \tau^T) D_{\sigma\tau}^{\bar{T}T} \right] \quad (21)$$

$$B_{\mu\nu}^{TT} = \sum_{\sigma\tau}^N -(\mu^T \tau^{\bar{T}} | \hat{b} | \sigma^{\bar{T}} \nu^T) D_{\sigma\tau}^{\bar{T}T}.$$

Only exchange terms appear in $\mathbf{B}$ for closed-shell systems. The more complicated open shell cases can be written down following arguments similar to nonrelativistic theory.

6. Relativistic basis sets

6.1 L-spinors

L-spinors [17, 15] stand in the same relation to hydrogenic Coulomb bound state eigenfunctions as do the nonrelativistic Coulomb Sturmians [18] to the Schrödinger hydrogenic eigenfunctions. The L-spinors have useful properties of completeness and linear independence on appropriate function spaces and reduce to the Coulomb Sturmians in the nonrelativistic limit. These enable demonstration of convergence of Rayleigh-Ritz approximations to Dirac bound eigenvalues, eigenspinors and matrix elements as the basis is systematically enlarged [15]. Perturbation calculations require summing contributions from virtual states in the continuum; this is a matter of simple matrix algebra in this formalism. In this way, we can demonstrate the non-negligible contribution of negative energy states to changes in the effective nuclear charge of relativistic hydrogenic atoms expected because of basis set completeness. This contribution demolishes the popular notion (e.g. [14, 7]) that one can simply project out negative energy state contributions in low energy processes; ignoring these contributions introduces unquantified errors which may not be as small as is often supposed.

The main problem with L-spinors, as with Coulomb Sturmians, is the difficulty of calculating electron-electron interaction integrals, especially if there is more than one nuclear centre. The Coulomb Sturmians underpin the successful CCC method for electron-atom collisions [19]. I am not aware of any attempt to use L-spinors in a similar fashion so far.

6.2 S-spinors

A more amenable set for atomic many-electron calculations are S-spinors, which can be viewed as relativistic analogues of Slater-type functions. The radial amplitudes $f^{(T)}(r)$ in (12) are constructed from the L-spinors with minimal nodes, giving

$$f^{(T)}(r) = \{A^T + rB^T\} r^\gamma e^{-\lambda r}, \quad T = L, S, \quad (22)$$

where $A^L = A^S = 1$, $B^L = B^S = 0$ for $\kappa < 0$ and

$$A^L = \frac{(\kappa + 1 - N_{1,\kappa})(2\gamma + 1)}{2(N_{1,\kappa} - \kappa)}, \quad A^S = \frac{(\kappa - 1 - N_{1,\kappa})(2\gamma + 1)}{2(N_{1,\kappa} - \kappa)}$$

and $B^L = B^S = 1$ for $\kappa > 0$. The *Dirac hydrogen cusp exponent* is $\gamma = \sqrt{\kappa^2 - Z^2/c^2}$ and $N_{1,\kappa} = \sqrt{\kappa^2 + 2\gamma + 1}$ is the *effective principal quantum number*.

An S-spinor basis set consists of functions given by (19) with a suitably distributed set of positive real exponents $\{\lambda_m, m = 1, 2, \dots, d_\kappa\}$ (details

in [20, pp. 235–253]). They have been used for a variety of atomic structure calculations; technical details of the implementation and some applications are in [21, pp. 159–183, 185–199].

Notice that $A^L \rightarrow 0$ for $\kappa > 0$ ($p_{1/2}, d_{3/2}, \dots$ symmetries), so that the leading power of $f^{(L)}(r)$ is $l+1$ in the nonrelativistic limit. Were A^L not to vanish, as in many calculations reported in the literature, the leading power would be l giving a nonrelativistic amplitude with the wrong cusp behaviour at $r = 0$.

S-spinors inherit from L-spinors the important matrix property

$$\lim_{c \rightarrow \infty} \Pi^{LS} (\mathbf{S}^{SS})^{-1} \Pi^{SL} = \mathbf{T}^{LL}, \quad (23)$$

where $T_{\mu\nu}^{LL} = \int M^\dagger[L, \mu, \mathbf{x}] (-\nabla^2) M[L, \nu, \mathbf{x}] d\mathbf{x}$, which ensures that the operator equivalence $(\boldsymbol{\sigma} \cdot \mathbf{p})^2 = \mathbf{p}^2$ holds also at the matrix level [20, 6, pp. 235–253]. Basis sets that do not have this property generally give spurious low relativistic energy because the resolution of the identity operator in (23) is then incomplete.

6.3 G-spinors

G-spinors were developed to permit a relativistic generalization of the Roothaan approach to electronic structure of atoms, molecules and solids [22, 23, 24]. In this case the large components of (11) are (spherical Gaussian-type) SGTO 2-component spin-orbitals and, in analogy to (23) the small components are constructed from

$$M[S, \mu, \mathbf{x}] = \text{constant} \times \boldsymbol{\sigma} \cdot \mathbf{p} M[L, \mu, \mathbf{x}], \quad (24)$$

which gives radial amplitudes $f_\mu^{(T)}(r) = N_\mu^{(T)} g_\mu^{(T)}(r)$, where

$$g^{(L)}(r) = r^{l+1} e^{-\lambda r^2}, \quad g^{(S)}(r) = [(\kappa + l + 1) - 2\lambda r^2] r^l e^{-\lambda r^2}, \quad (25)$$

so that the small component has leading power $l+2$ when $\eta = -1$, $(\kappa + l + 1) = 0$, and l when $\eta = +1$, $(\kappa + l + 1) = 2l + 1$. Molecular integrals over SGTF, surveyed recently by Kuang and Lin [25], rest on the Gaussian product relation

$$e^{-\lambda_\mu \mathbf{r}_A^2 - \lambda_\nu \mathbf{r}_B^2} = e^{-\lambda_\mu \lambda_\nu (\mathbf{A} - \mathbf{B})^2 / (\lambda_\mu + \lambda_\nu)} e^{-(\lambda_\mu + \lambda_\nu) \mathbf{r}_{A\mu\nu}^2} \quad (26)$$

where $\mathbf{r}_{A\mu} = \mathbf{r} - \mathbf{A}_\mu$, $\mathbf{r}_{\mu\nu} = \mathbf{r} - \mathbf{A}_{\mu\nu}$, $\mathbf{A}_{\mu\nu} = (\lambda_\mu \mathbf{A}_\mu + \lambda_\nu \mathbf{A}_\nu) / (\lambda_\mu + \lambda_\nu)$ expresses products of GTF centred on $\mathbf{A}_\mu$ and $\mathbf{A}_\nu$ as a GTF centred on a third point $\mathbf{A}_{\mu\nu}$. Products of polynomials in $\mathbf{r}_{A\mu}$ and $\mathbf{r}_{A\nu}$ can similarly be expressed as a polynomial in $\mathbf{r}_{A\mu\nu}$ so that the overlap charge-current

density $j_{\mu\nu}^q(x)$ can be written as a sum of terms

$$M^\dagger[T, \mu, \mathbf{r}_{A_\mu}] \sigma_q M[T', \nu, \mathbf{r}_{A_\nu}] = N_\mu^T N_\nu^{T'} e^{-\lambda_\mu \lambda_\nu (\mathbf{A}-\mathbf{B})^2 / (\lambda_\mu + \lambda_\nu)} \quad (27)$$

$$\times \sum_{\alpha\beta\gamma} E_q[\mu, T; \nu, T'; \alpha, \beta, \gamma] H(\lambda_\mu + \lambda_\nu, \mathbf{r}_{A_{\mu\nu}}; \alpha, \beta, \gamma).$$

where σ^q , $q = 1, 2, 3$, is a Pauli matrix generating the components of the (3-)current density $\mathbf{j}_{\mu\nu}$ and $q = 0$ labels the charge density $\rho_{\mu\nu}$. The numerical coefficients $E_q[\mu, T; \nu, T'; \alpha, \beta, \gamma]$ absorb the 2-spinor structures and the molecular geometry and $H(\lambda_\mu + \lambda_\nu, \mathbf{r}_{A_{\mu\nu}}; \alpha, \beta, \gamma)$ is an Hermite Gaussian function. The structure (27) is central to the powerful and widely used McMurchie-Davidson algorithm [26] for electron-electron interaction integrals. A relativistic generalization [27] is used in our BERTHA relativistic molecular structure package. Thus BERTHA, which has so far been used for a limited number of studies of atoms, molecules and atomic clusters, has a simple structure which is much the same as in conventional quantum chemistry codes and can exploit many of the same tricks to improve efficiency, which is vital if BERTHA is to be used, as intended, to study large molecules containing heavy metal atoms.

7. Current outlook

A survey of progress is given in [28, 29]. In addition to trial DHF calculations on small molecules, [30], verifying that BERTHA generates the appropriate molecular symmetry orbitals for relativistic double groups in such cases as N_2 , CO , H_2O , NH_3 and benzene, the code has also been used for relativistic second-order many-body perturbation theory of water [31] and hydrogen halides HX ($\text{X}=\text{F}, \text{Cl}$), Zeeman effect in atoms and molecules [28, 29, 30], magnetic hyperfine shielding in water [31] and ammonia (in which the negative energy states provide the dominant shielding effect). DHFB calculations have been done for a number of molecules including water [31] and AgCl . We have also made an extensive study of YbF in connection with parity-violating effects [32] as well as of other molecules such as TlF (unpublished).

It is clearly important to analyse how to go to larger molecules, and a pilot study of germanocene (21 atoms) is reported in [28]. One-centre atomic integrals are cheap, even if the full Breit interaction is included, and this can be exploited in molecular calculations. The J-matrix technique due to Almlöf *et al.* [33] can be generalized to the relativistic problem, and reduces the time of calculation of the direct (J-matrix) part of the $\mathbf{G}$ matrix relative to the generalized McMurchie-Davidson algorithm by a factor of about 5 for p functions and 50–100 for f functions.

This has been exploited in a relativistic density functional module in BERTHA (Quiney, unpublished). The exchange contribution to $\mathbf{G}$ is less tractable, but a new scheme based on transforming the electron-electron interaction matrix into an equivalent expression involving an integral over local electrostatic fields has the potential to make similar economies[34]. This has direct application to relativistic density functional calculations for large systems with heavy atom constituents, which should make the study of electromagnetic and spin-dependent effects in molecules and other systems easier. It should also be possible to extract information on scattering processes from BERTHA wavefunctions, but this is still in the future.

Acknowledgments

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Notes

1. The name Hartree has often been omitted in much of the literature. We include it here to emphasize his contribution.
2. It is important to realize that the roles of the two components are reversed when $E < 0$.

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INNER SHELL ELECTRON IMPACT IONIZATION OF MULTI-CHARGED IONS

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Abstract The ionization mechanism for (e,2e) processes on multi charged ions is investigated. Theoretical calculations of three dimensional cross sections are presented.

1. Introduction

In an (e,2e) experiment, an incoming electron ionizes a target atom and both the scattered and ejected outgoing electrons are detected with their energy and position in space resolved. The probability of such an event is expressed by the triple differential cross section (TDCS). In a series of experiments, Nakel and collaborators (Schüle and Nakel, 1982; Ruoff and Nakel, 1987; Bonfert et al., 1991; Prinz et al., 1995) explored the inner shell ionization of heavy metal targets using relativistic electrons. These experiments were kinematically complete, absolute and even extended to spin asymmetry measurements. As a result of this work a number of theoretical models were developed the most successful of which was the relativistic distorted wave Born approximation (rD-WBA) (Keller et al., 1994). Both theory and experiment for relativistic (e,2e) processes are reviewed in (Nakel and Whelan, 1999).

A common restraint of all these experiments has been the limitation to coplanar geometry, in which the momenta of all the three unbound electrons form a common plane. Recently, there have been great advances in the design and implementation of (e,2e) experiments, where one is able to circumvent this restriction and detect one of the outgoing electrons at

an (almost) arbitrary position in three dimensional space; for example the COLTRIMS technique (Dörner et al., 1999) and the multi-electron detector approach of (Viefhaus et al., 1996; Pinkás et al., 1999) for low and intermediate energies. For energies involving a relativistic description there are now accelerator experiments being constructed, designed to simulate electron impact ionization processes using multi-charged ions (Kollmus et al., 1999). Again, these experiments will be able to deal with a broad range of geometries but will almost certainly be purely relative.

In this paper we will apply the rDWBA approximation to develop the theory for these experiments. We will consider a high energy case and predict that the triple differential cross section will be highly sensitive to relativistic and distortion effects. We will present cross sections in the full three-dimensional space.

It is our view that at intermediate energies, i.e. high but not relativistic, the same type of experiments could be usefully employed to study collisions where there are two active target electrons, e.g. excitation-ionization or double ionization. This will be discussed elsewhere (Marchalant et al., *ress*). In this paper, however, we will only consider problems with a single active target electron.

2. Theory

At low energies, the non-relativistic distorted wave Born approximation (DWBA) is the simplest possible approach that can be used to include multiple scattering in both the incident and final channels. Having seen that the DWBA works very well for a range of geometries for incident electrons of low momenta (Whelan, 1999), the equivalent relativistic method, the relativistic distorted wave Born approximation (rDWBA) is therefore a serious candidate to describe (e,2e) processes at relativistic energies. For a fully relativistic problem, we have to solve Dirac equations to obtain the wavefunctions for both the bound and the continuum electrons. Furthermore the interactions involving the latter must be described by using the full QED photon propagator. It turns out, that the propagator plays a significant role at high energies, i. e. retardation and magnetic effects are not negligible, but exchange in the elastic channel and final state e^- and e^- -repulsion are likely to be unimportant.

We will adopt the same conventions as previously (Keller et al., 1994), i.e. atomic units ($\hbar = m_e = e = 1$) are used and the numerical value of the vacuum velocity is $c = 137.03604$, the metric tensor is

$$\text{diag}(g_{\mu\nu}) = (1, -1, -1, -1),$$

contravariant four vectors are written $x^\mu = (ct, \mathbf{x})$ and the summation convention is understood. We assume that the incident electron has an

energy E_0 and momentum $\mathbf{k}_0$ and that two outgoing electrons having energies E_1, E_2 , momenta $\mathbf{k}_1, \mathbf{k}_2$ are emitted into solid angles Ω_1, Ω_2 . Without loss of generality we will assume that $E_1 \geq E_2$.

The triple differential cross section (TDCS) for the relativistic (e,2e) process where the spins are not resolved is given (Keller et al., 1994) by

$$\frac{d^3 \sigma}{d\Omega_1 d\Omega_2 dE} = \frac{(2\pi)^2}{c^6} \frac{k_1 k_2}{k_0} E_0 E_1 E_2 \frac{N_\kappa}{2N_m} \times \sum_{\epsilon_1 \epsilon_0 \epsilon_2 \epsilon_b} |\langle k_1 \epsilon_1, k_2 \epsilon_2 | \hat{S} | k_0 \epsilon_0, \kappa \epsilon_b \rangle|^2 \quad (1)$$

where $\hat{S}$ is the S matrix operator. The symbols 0,1,2 and b refer to the incoming, the two outgoing and the initially bound electron, respectively. We are using κ to denote the quantum numbers of the atomic bound state and ϵ_i are the spin projection operators with respect to the quantization axis, which we take in the beam direction. In the form (1) the TDCS is insensitive to spin polarization, because we have averaged over the initial spins (ϵ_b, ϵ_0), and summed over the final spins (ϵ_1, ϵ_2). Hence the factor $N_\kappa/2N_m$. The quantity N_κ is the occupation number of state κ and N_m the number of degenerate states with this set of quantum numbers.

Since we describe the electrons as eigenstates of the Dirac equation with the inclusion of a potential, this first-order evaluation corresponds to the relativistic distorted-wave Born approximation (rDWBA). Perturbation theory is being applied to the electron-electron ionizing interaction, which is retained to first order. However, the elastic electron-atom interaction on the incident and final channels is implicitly included to all orders in the distorted waves. A detailed description of the methods used to evaluate (1) has been given elsewhere (Keller et al., 1994). We will therefore focus on the results and identify the physical effects in the character of the cross section.

In the Tübingen experiments (Schüle and Nakel, 1982; Ruoff and Nakel, 1987; Bonfert et al., 1991) all measurements were carried out in coplanar geometries, where all the momentum vectors lay in the same plane (Fig. 1). All these experiments were performed in one of the following three geometrical arrangements:

- 1 In the *coplanar symmetric geometry* the two outgoing electrons are detected with equal energies. Their momenta lie in the same plane as the momentum of the incident particle and make the same angle with the beam direction. This can be described as a "hard" collision, since the incident electron loses more than half of its initial momentum. One would reasonably expect that the

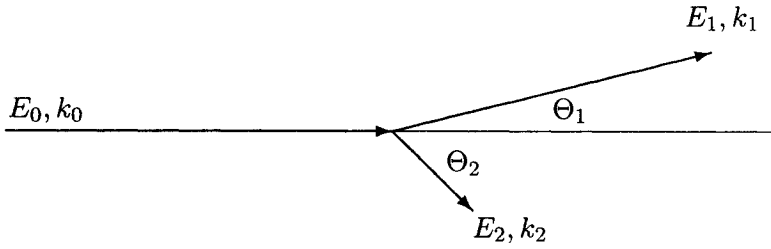


Figure 1. Schematic diagram of a coplanar (e,2e) experiment showing the energies, momenta and angles of the incoming and the two outgoing electrons, respectively. These are denoted with the symbols 0, 1 and 2.

nucleus could well play a major role in such a geometry and indeed this has been established at non relativistic energies (Zhang et al., 1990). At relativistic energies one sees a very pronounced large angle peak. The TDCS in this arrangement is extremely sensitive to 'spin flip' channels. (Ast et al., 1996)

- 2 In the *coplanar asymmetric geometry* a fast outgoing electron, which has a small angle with respect to the primary beam, is detected at a fixed angle and the angular distribution of the slow outgoing electron is measured. In this arrangement, the two outgoing electrons have greatly different energies. For the outer shells of atoms this geometry is an ideal one for a perturbative treatment (Ehrhardt et al., 1986). However, as shown by Zhang et al. (Zhang et al., 1992) even at non relativistic energies inner shell ionization remains sensitive to distortion effects. In the case of relativistic (e,2e) processes, the effect of the strong nucleus is seen in a significant reduction of the binary peak and a large enhancement of the recoil. The more greatly charged the target nucleus the larger the enhancement of the recoil relative to the binary peak, (Prinz et al., 1995; Keller et al., 1996). In this geometry the spin asymmetry due to Mott scattering is most pronounced in the recoil direction and for the heavier elements. Further, there is a definite sensitivity to fine structure in the target in the spin asymmetry for L shell ionisation (Keller et al., 1996; Besch et al., 1998).
- 3 In the *coplanar constant θ_{12} geometry* the angle between the exiting electrons is held fixed, θ_{12} , and both rotated around the beam direction. This geometry was first considered by (Whelan et al., 1994) while studying Coulomb three body effects in low energy (e,2e) and then at relativistic energies (Whelan et al., 1996). At

the higher energies it proved very useful for studying distortion effects and Pauli blocking.

Until now, experiments and theoretical calculations have been mostly limited to some well defined geometries. However, one can gain further insight into the scattering process by lifting the strong limitation to a certain geometry and considering the TDCS in three space. We can always choose our coordinate system such that the momentum vectors of the incoming and fast scattered electron form a plane, which we will denote by the xz -plane. The slow outgoing electron can then be detected at any position in space defined by the spherical angles θ_s and ϕ_s . The TDCS as a function of these scattering angles can then be parametrised as

$$\frac{d^3 \sigma}{d\Omega_1 d\Omega_2 dE}(\theta_s, \phi_s) = \rho(\theta_s, \phi_s), \quad (2)$$

where the (x, y, z) coordinates are the cartesian coordinates of our coordinate system. These are given by

$$x = \rho \sin(\theta_s) \cos(\phi_s) \quad (3a)$$

$$y = \rho \sin(\theta_s) \sin(\phi_s) \quad (3b)$$

$$z = \rho \cos(\theta_s) \quad (3c)$$

Using this transformation, the distance from any point on the surface described by the cartesian coordinates (x, y, z) to the origin of the coordinate system represents the probability of finding the slow outgoing electron at this position in space. Using this transformation, we are then able to visualize the cross section in three space.

2.1 Calculations

Cross sections are given in figure 2 and 3. We consider the electron impact ionization of hydrogen-like uranium, where all but one electron have been removed. The energy of the impacting electron was chosen to be $E_0 = 500\text{keV}$. The fast scattered electron is detected under a fixed angle $\theta_f = 18^\circ$ and the slow ejected electron is measured at an energy of $E_2 = 100\text{keV}$. Even in the simple semi-relativistic first Born model used to calculate the graph of figure 2, the cross section is no longer symmetric about the direction of momentum transfer. This break of symmetry is due to using the full QED photon propagator in the mathematical description, rather than using the Coulomb interaction as in the non-relativistic case. Proceeding to the rDWBA approach represented in figure 3, we used fully relativistic wavefunctions and again the full QED photon propagator to describe the electron-electron interaction. The

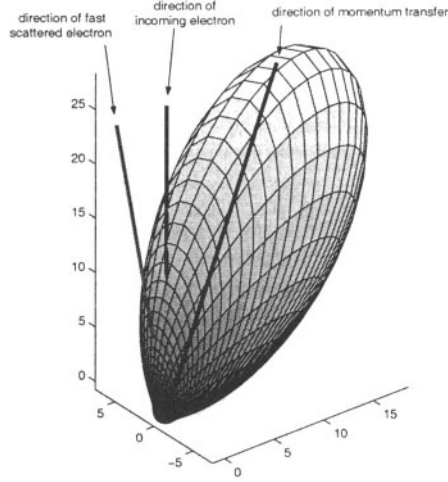


Figure 2. The TDCS for the electron impact ionization of hydrogen-like uranium in a semi relativistic mode. The incoming electron has an energy of $E_0 = 500\text{keV}$, the fast scattered electron has an energy of $E_1 = 285\text{keV}$ and is scattered under a fixed angle $\theta_f = 18^\circ$. The slow ejected electron is detected with an energy of $E_2 = 100\text{keV}$.

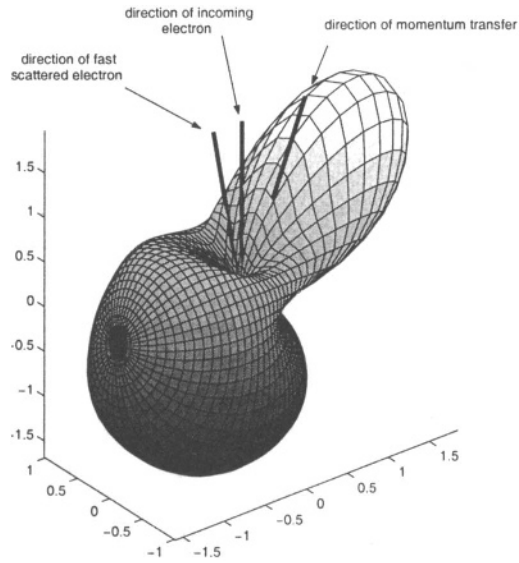


Figure 3. The TDCS for the same kinematical and geometrical arrangement as in figure 2, but in the rDWBA model.

symmetry about the direction of momentum transfer is again broken, both due to the propagator and the effect of the nucleus and the recoil peak is largely enhanced. This clearly represents the strong effect of the nucleus. The effect of the interactions with the nucleus is immediately apparent. The rDWBA has an entirely different shape and is roughly an order of magnitude smaller. The symmetry breaking is again visible and due to both the propagator and the distortion effect of the nucleus.

3. Conclusion

In conclusion, we have isolated the observable key points for impact ionization from multi charged ions at relativistic energies. In our calculation, we have lifted the limitation to a certain geometry and presented cross sections in three space. Using this approach, direct comparison between theoretical calculations and experiments should be possible, once experimental facilities become online.

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A STUDY OF ITERATIVE METHODS FOR INTEGRO-DIFFERENTIAL EQUATIONS OF ELECTRON-ATOM SCATTERING

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Abstract We describe a novel iterative method for numerically solving the integro-differential equation used in electron-hydrogen scattering. An adaptive approach to the iteration is introduced. Converged solutions can be efficiently obtained for a wide range of initial conditions. We confirm the reliability of the present method by comparing the numerical data of elastic phase-shifts with previous calculations.

Keywords: electron-atom collisions, integro-differential equations, iterative methods

1. Introduction

At the heart of almost all effective methods for solving the electron scattering problem is the partial wave decomposition and if one makes such a decomposition one is inevitably lead to looking for numerical solutions of sets of coupled integro-differential equations. In this paper we will consider the simplest possible case corresponding to a single integro-differential equation. This equation needs to be solved in many cases for example in the case of electron-hydrogen scattering in the Distorted Wave Born Approximation (DWBA) (Rasch, 1996). In most if not all applications of this method (Rasch, 1996; Jones and Madison, 1994; Dorn et al., 1998) a further simplification is made where the non-local exchange potential is approximated by an effective local potential (Furness and McCarthy, 1973). This is a case for concern particularly in low energy scattering problems where one could reasonably expect exchange effects to be strong (Röder et al., 1996).

As a first step towards replacing local by exact exchange in the DWBA we have begun an investigation of the optimum method for solving integro-differential equations using an iterative method. This method is conceptionally simple and we will show that it can be used to give reliable results for the electron-hydrogen scattering problem.

As a test case considered elastic scattering of electrons from hydrogen with incident energies between 0.05 and 12.5 a. u. and angular momentum between 0 and 2. This corresponds to a fairly typical setup where exchange is likely to be important. The ordinary differential equation is solved by a range of methods in particular Numerov method, 4th-order Runge-Kutta method and EXPFIT4 (?; Ixaru et al., 1997b). We compare for the different methods the CPU time, convergence properties and number of iterations used.

2. Mathematical basis

The mathematical theory for the distorted wave Born approximation is developed in Ref. (Rasch, 1996). Here we only give a brief summary.

The partial differential equation in distorted wave to solve is

$$\begin{aligned}
 (T_1 + V_1 - E_k) | \chi^{s,t}(\mathbf{k}, \mathbf{r}_1) \rangle &+ \langle \phi(\mathbf{r}_2) | V_{12} | \phi(\mathbf{r}_2) \rangle | \chi^{s,t}(\mathbf{k}, \mathbf{r}_1) \rangle \\
 &\pm \delta_{l_0} E_{bk} | \phi(\mathbf{r}_1) \rangle \langle \phi(\mathbf{r}_2) | \chi^{s,t}(\mathbf{k}, \mathbf{r}_2) \rangle \\
 &\pm \langle \phi(\mathbf{r}_2) | V_{12} | \chi^{s,t}(\mathbf{k}, \mathbf{r}_2) \rangle | \phi(\mathbf{r}_1) \rangle \\
 &= 0,
 \end{aligned} \tag{1}$$

where

$$V_1 = -\frac{1}{r_1}, \quad V_{12} = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}, \quad T_1 = -\frac{1}{2}\nabla_{\mathbf{r}_1}^2, \quad (2)$$

$\chi^{s,t}$ denotes the unknown outgoing distorted wave functions, ϕ the wave function for the bound state hydrogen, $E_{bk} = E_b - E_k$, $E_k = \frac{1}{2}k^2$ the energy of the incident electron, $E_b = -\frac{1}{2n^2}$ the energy of the bound state electron for hydrogen atom, n the quantum number, $\mathbf{k}$ the wave number, V the potential, δ the Kronecker delta, and l the angular momentum quantum number. Subscript 1 and 2 denote the incident electron and outgoing electron, respectively.

Because of the nature of the approximation we get different differential equations depending on whether we have singlet or triplet scattering. In Eq. (1) above the + sign corresponds to the singlet and - sign corresponds to the triplet wave function, which are denoted by the superscripts s and t , respectively. We develop the following partial wave expansion for the distorted and bound state wave function:

$$|\chi^{s,t}(\mathbf{k}, \mathbf{r}_1)\rangle = \sqrt{\frac{2}{\pi}} \frac{1}{k} \sum_{l,m} i^l e^{i\Delta_l} \frac{u_l^{s,t}(kr_1)}{r_1} Y_{l,m}^*(\hat{\mathbf{k}}) Y_{l,m}(\hat{\mathbf{r}}_1) \quad (3)$$

and

$$|\phi(\mathbf{r}_2)\rangle = i^{l_b} \frac{w_{l_b}(r_2)}{r_2} Y_{l_b, m_b}(\hat{\mathbf{r}}_2), \quad (4)$$

where $u_l^{s,t}(kr_1)$ and $w_{l_b}(r_2)$ denote the radial component of the scattered and bound state wave functions respectively. Δ_l denotes the phase shift, $Y_{l,m}(\hat{\mathbf{r}})$ the spherical harmonics, m the magnetic quantum number, and the subscript b the bound state.

We can obtain the integro-differential equation for $u_l^{s,t}$ as

$$\mathbf{L}u_l^{s,t} = \pm \mathbf{M}u_l^{s,t}, \quad (5)$$

$$\begin{aligned} \mathbf{L}u_l^{s,t} = & \left[\frac{d^2}{dr_1^2} - \frac{l(l+1)}{r_1^2} + k^2 \right. \\ & \left. - 2 \int_{r_1}^{\infty} \left(\frac{2}{r_2} - \frac{2}{r_1} \right) r_2^2 w^2(r_2) dr_2 \right] u_l^{s,t} \end{aligned} \quad (6)$$

and

$$\mathbf{M}u_l^{s,t} = \delta_{l0} \left(-\frac{1}{n^2} - k^2 \right) r_1 w(r_1) \int_0^{\infty} r_2 w(r_2) u_l^{s,t}(r_2) dr_2$$

$$\begin{aligned}
& +2r_1 w(r_1) \int_0^\infty r_2 w(r_2) u_l^{s,t}(r_2) \sum_{\lambda} \frac{r_{>}^\lambda}{r_{>}^{\lambda+1}} \\
& \times \epsilon(l_b, \lambda, l) \begin{pmatrix} l_b & \lambda & l \\ 0 & 0 & 0 \end{pmatrix}^2 dr_2, \quad (7)
\end{aligned}$$

where $r_{>}$ indicates the larger and $r_{<}$ indicates the smaller of r_1 and r_2 , and where $\begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$ denotes the Wigner $3j$ symbol (Edmonds, 1957). $\epsilon(j_1, j_2, j_3)$ is equal to 1 whenever three arguments satisfy the triangular condition otherwise it is equal to zero. In this paper, we consider the cases of $n = 1$ and $l_b = 0$.

3. Numerical methods

We consider the iterative procedure for $u_l^{(j),s,t}$, where

$$\mathbf{L}u_l^{(0),s,t} = 0 \quad (8)$$

and

$$\mathbf{L}u_l^{(j),s,t} = \pm \mathbf{M}u_l^{(j-1),s,t} \quad j \geq 1, \quad (9)$$

where the superscript j denotes the number of iterations. $u_l^{(0),s,t}$ is the static state.

The non-local nature of the exchange term is the major difficulty in achieving numerical convergence and some really quite complex techniques have been suggested to deal with it. In this paper we apply a much simpler iterative procedure where the solution $u_l^{(j-1),s,t}$ enters the kernel $\mathbf{M}$ and we then solve for $u_l^{(j),s,t}$.

In doing so we found that the convergence depended crucially on how one deals with the initial conditions that start off the ODE-solvers. The basic idea for the treatment of the initial condition of the calculations is shown in Figure 1. The value dr denotes the radial step size of the equidistant grid on which we want to store the solution. In the case of $l = 0$ we use Scheme I in Figure 1. The value of ϵ_r , which should be much smaller than dr , denotes the small constant to avoid the divergence of the $1/r$ and $1/r^2$ terms in the calculations. In Scheme I we set

$$\begin{aligned}
u_l^{(j),s,t}(\epsilon_r) &= 0 & j &= 0, 1, \dots \\
u_l^{(j),s,t}(\epsilon_r) &= u_l^{(j-1),s,t}(\epsilon_r) & j &\geq 1
\end{aligned} \quad (10)$$

as the initial values to start off the numerical integration where any numerical derivative method for obtaining $u_l^{(j-1),s,t}(\epsilon_r)$ could be used.

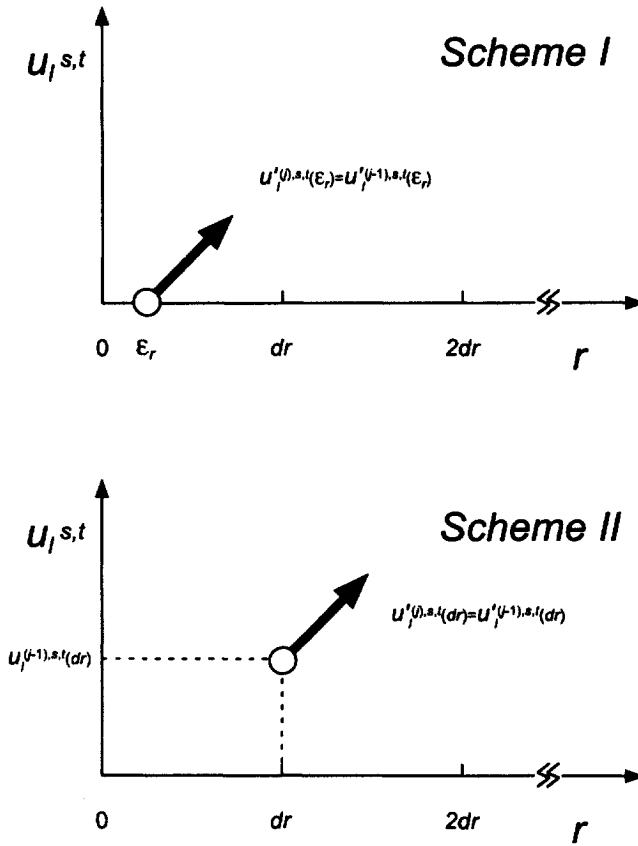


Figure 1. Basic idea of treatments of initial conditions for iteration.

$u_l^{(0),s,t}$ can initially be set to any non-zero value. We have checked that the converged answer is indeed independent of this initial value.

For $l > 0$, we start the calculation by the use of Scheme I. $u_l^{(0),s,t}(\epsilon_r) = 0$ and an arbitrary non-zero value for $u_l^{(0),s,t}(\epsilon_r)$ are used. After that, the following Scheme II is applied for $j \geq 1$

$$\begin{aligned} u_l^{(j),s,t}(dr) &= u_l^{(j-1),s,t}(dr) & j \geq 1 \\ u_l'^{(j),s,t}(dr) &= u_l'^{(j-1),s,t}(dr) & j \geq 1 \end{aligned} \quad (11)$$

In these cases, the initial values of $u_l^{s,t}$ and the first derivative $u_l'^{s,t}$ must be updated at every iteration in contrast to Eq. (10) where only $u_l'^{s,t}$ is updated. It should be noted that the intermediate values of $u_l^{s,t}$ must be normalised at every iteration.

In all the cases considered here converged solutions were easily obtained. We present results using the Numerov method, 4th-order Runge-Kutta method and EXPFIT4 for the comparison. We used the standard program COULFG to generate the asymptotic form of the wave function which we used to obtain the boundary conditions and the normalisation (Barnett, 1982). We used Gauss-Legendre quadrature for the numerical integration of the exchange kernel.

4. Results and discussion

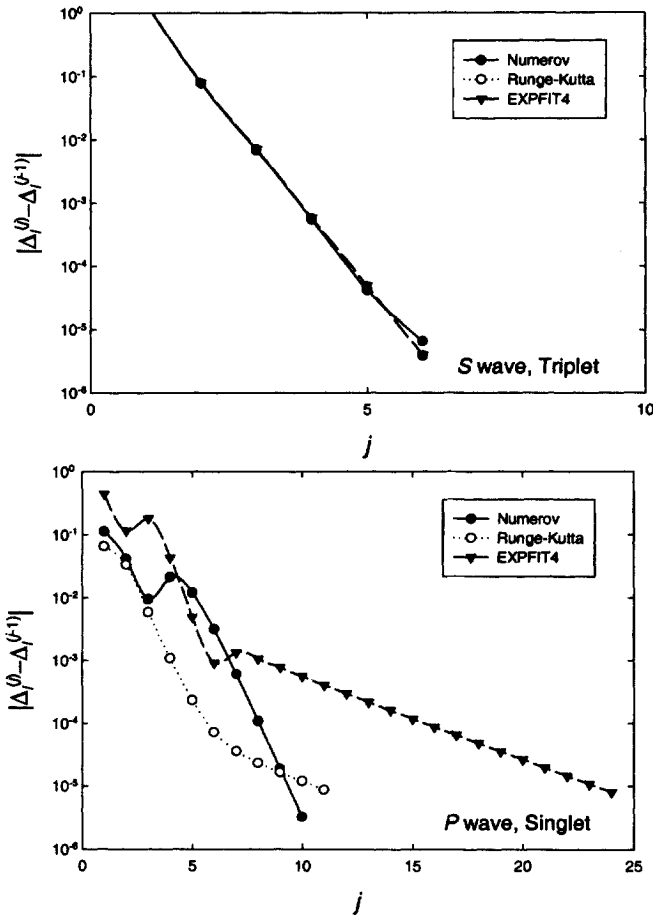
Tables 1, 2 and 3 show the samples of the numerical results of phase shift for various k and l values using the methods discussed above. These results are compared with those given in the review article of Riley and Truhlar (1976)

The one local exchange calculation by us is marked with *. In our calculation we used 1000 grid points with a maximum r of 20 a. u. The constant GIVTOR in EXPFIT4 was equal to 1×10^{-12} . For the integration of the exchange term from 0 to the maximum r , we used a grid of 200. The small constant ϵ_r discussed above was set to 1×10^{-13} . We continued iterating until the following relation was satisfied.

$$|\Delta_l^{(j)} - \Delta_l^{(j-1)}| \leq 1 \times 10^{-5} \quad (12)$$

For better agreement, the one case needs to increase the number of grid points to 4000 for the Numerov method, which is denoted by superscript #.

Without the iterative scheme outlined above the numerical solutions to the phase shifts either did not converge or converged to the wrong answer. EXPFIT4 is an adaptive solver and gave the best accuracy. The Numerov method was the least accurate. In terms of timing we found that EXPFIT4 used considerably more CPU time than the other two methods. We benchmarked the approaches by using a DEC Alpha-21164 533 MHz. For example, in the case of triplet S wave and $k^2=1$, the CPU times were 32.92 sec in Numerov, 33.71 sec in Runge-Kutta and 37.80 sec in EXPFIT4 while for the singlet P wave and the same energy they were 51.28 sec, 58.87 sec and 141.97 sec in Numerov, Runge-Kutta and EXPFIT4, respectively. In Figure 2 we have plotted the value $|\Delta_l^{(j)} - \Delta_l^{(j-1)}|$. Very similar patterns of convergence are seen for all three methods for the S wave while in the P wave case EXPFIT4 converges much more slowly and both it and the Numerov method exhibit initial oscillations. The Runge-Kutta method is fast and needs a small number of iterations, however, there seems to be a tendency to saturate. In order to improve the accuracy one would need to decrease dr .


 Figure 2. Iteration processes in $k^2=1$

5. Concluding remarks

By means of a simple iterative method we have developed a technique for solving the integro-differential equations characteristic of electron-atom scattering. We shall shortly present results for electron impact ionisation on hydrogen using the DWBA approximation with exact rather than local exchange.

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Table 1. Data of phase shift for S wave

$k^2=0.1$	<i>Static</i>	<i>Singlet</i>	<i>Triplet</i>
Numerov	1.049362	1.456420	-0.697502
Runge–Kutta	1.050218	1.458396	-0.708480
EXPFIT4	1.050218	1.459492	-0.715160
Previous	1.050	1.461	-0.7146
$k^2=1$	<i>Static</i>	<i>Singlet</i>	<i>Triplet</i>
Numerov	0.905495 [#]	0.544211 [#]	1.388188 [#]
Runge–Kutta	0.905523	0.544689	1.387326
EXPFIT4	0.905523	0.542699	1.390764
Previous	0.906	0.543	1.390
$k^2=16$	<i>Static</i>	<i>Singlet</i>	<i>Triplet</i>
Numerov	0.491423	0.467507	0.514775
Runge–Kutta	0.491892	0.467670	0.515536
EXPFIT4	0.491921	0.467530	0.515724
Previous	0.4919	0.4673	0.5156
$k^2=25$	<i>Static</i>	<i>Singlet</i>	<i>Triplet</i>
Numerov	0.433270	0.420381	0.446016
Runge–Kutta	0.433724	0.420664	0.446639
EXPFIT4	0.433810	0.420660	0.446813
Previous	0.4338	0.4202	0.4465

Table 2. Data of phase shift for P wave

$k^2=0.1$	Static	Singlet	Triplet
Numerov	0.007681	-0.027266	0.058666
Runge-Kutta	0.007681	-0.027254	0.058652
EXPFIT4	0.007681	-0.027242	0.058637
Previous	0.0077	-0.0272	0.0586
$k^2=1$	Static	Singlet	Triplet
Numerov	0.111474	-0.105802	0.357933
Runge-Kutta	0.111474	-0.105782	0.357896
EXPFIT4	0.111474	-0.105783	0.357890
Previous	0.1115	-0.1057	0.3581
$k^2=16$	Static	Singlet	Triplet
Numerov	0.246095	0.224357	0.268134
Runge-Kutta	0.246053	0.223989	0.267713
EXPFIT4	0.246073	0.224015	0.267732
Previous	0.2461	0.22539*	0.26646*

Table 3. Data of phase shift for D wave

$k^2=0.1$	Static	Singlet	Triplet
Numerov	0.000179	-0.000648	0.001037
Runge-Kutta	0.000179	-0.000650	0.001040
EXPFIT4	0.000179	-0.000635	0.001031
Previous	0.0002	-0.0006	0.0010
$k^2=1$	Static	Singlet	Triplet
Numerov	0.017813	-0.017540	0.055457
Runge-Kutta	0.017813	-0.017553	0.055469
EXPFIT4	0.017813	-0.017525	0.055443
Previous	0.0178	-0.0175	0.0554
$k^2=16$	Static	Singlet	Triplet
Numerov	0.139575	0.123582	0.155436
Runge-Kutta	0.139545	0.123542	0.155415
EXPFIT4	0.139569	0.123587	0.155419
Previous	0.1396	0.12420*	0.15482*

RELAXATION BY COLLISIONS WITH HYDROGEN ATOMS: POLARIZATION OF SPECTRAL LINES

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16 – 19 DECEMBER 2001.

Abstract

New technological improvements have made possible in recent times the development of telescopes and post-focus instrumentation for solar research capable of pushing the polarimetric accuracy of spectroscopic observations to unprecedented limits. The operation of these instruments has revealed a wealth of new phenomena, especially in the detection of puzzling signals of linear polarisation in the solar spectrum observed at small angular distances from the limb. Through its interpretation it is indeed possible to diagnose several important aspects of the physics of the higher layers of the solar atmosphere, such as the degree of anisotropy of the radiation field, and, probably the most important item, the presence and quantitative measurement of weak magnetic fields.

However, it is important to remark that weak magnetic fields act, on resonance polarization, with a general depolarization mechanism and, from this point of view, they are quite similar to depolarizing collisions. A diagnostic of weak magnetic fields in the higher layers of the solar atmosphere is thus possible, from the analysis of the linear polarization solar spectrum, only if the role of depolarizing collisions is fairly understood.

A detailed treatment of collisional relaxation rates due to collisions with hydrogen atoms is presented; a particularly striking example is the sodium doublet which shows an intriguing profile in the linear polarisation solar spectrum observed very close to the solar limb (in particular with the solar telescope THEMIS). This profile has been tentatively interpreted as due to the presence of ground level atomic polarisation in the sodium atoms of the solar atmosphere but this hypothesis has

1 Introduction

Recent observations [2, 3, 4, 5, 6, 7, 8] very close to the solar limb show a number of unexpected phenomena and, in particular, the existence of a very complex polarization profile in the D1 (right hand-side) and D2 (left hand-side) lines (figure 1). The polarization spectrum exhibits a structure that is not easy to understand and interpret: Landi Degl’Innocenti E. [9] shows that such a structure is mainly due to the lower levels atomic polarization (with hyperfine structure), coupled to coherent scattering. For a quantitative interpretation of this spectrum, the depolarizing effect of collisions with neutral hydrogen atoms must be taken into account.

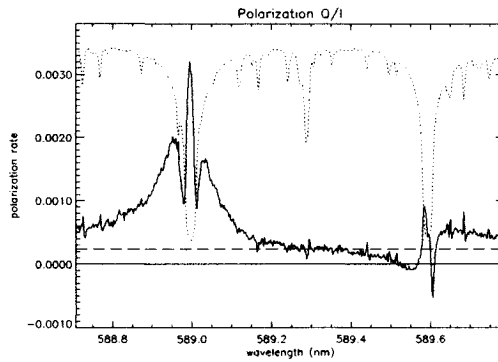


Figure 1: Polarization of the D1 5896Å and D2 5890Å lines, as observed on 2000 August 29, at 4.1 arcsec from the solar limb [5, 6].

The D lines are due to transitions between the to terms $3s\ ^2S$ (the fundamental term) and $3p\ ^2P$ of the Na atom.

2 *ab initio* interatomic potentials

The results concern the $X^1\Sigma^+$ and $a^3\Sigma^+$ states correlated to the $Na(3s\ ^2S) + H(^2S)$ asymptote and the $A^1\Sigma^+$, $B^1\Pi$, $b^3\Pi$ and $c^3\Sigma$ states correlated to the $Na(3p\ ^2P) + H(^2S)$ asymptote. The Gaussian basis sets employed for their calculation are general contractions based on atomic natural orbitals and include for hydrogen and sodium the primitive basis set $[6s, 4p]$ [11] and $[13s, 10p, 4d]$ [12] contracted to $[3s, 2p]$ and $[7s, 5p, 2d]$ respectively. The total number of contracted Gaussian functions was 41. Adiabatic potentials for NaH have been determined using multireference

configuration interaction (MRCI) wave functions constructed using multiconfiguration self-consistent field (MCSCF) active space [10] with core and valence orbitals ($1\sigma - 7\sigma, 1\pi - 2\pi$). The MRCI wave functions accounted for more than 4 millions of configurations which were internally contracted to 250 thousands. All the calculations have been performed with the MOLPRO code.¹

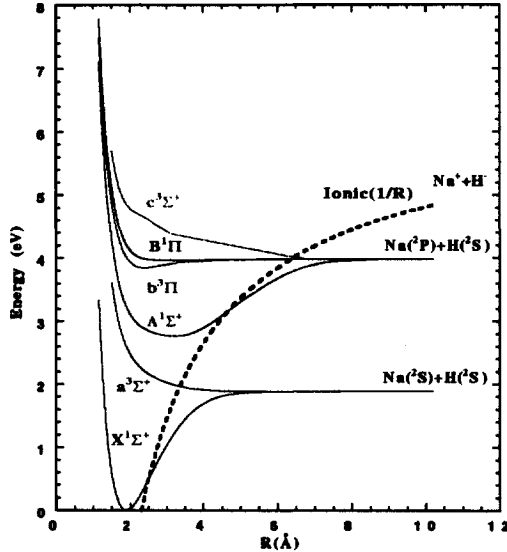


Figure 2: Potential curves from the present calculations.

3 Dynamics of the collision

The potentials described above were used to compute relaxation and transfer cross sections. Fully quantal close-coupling studies of the neutral system was performed using the formulation given by Mies [13] and generalized by Launay and Roueff [14]. The radiating atom with angular momentum J collides an H atom with angular momentum j_2 . We couple J and j_2 to obtain the total angular momentum j of the two atoms. Owing to the invariance of the interaction potential V under rotations of the

¹MOLPRO is a package of *ab initio* programs written by H. -J. Werner and P. J. Knowles, with contributions from J. Almlöf, R. D. Amos, A. Berning, M. J. O. Deegan, F. Eckert, S. T. Elbert, C. Hampel, R. Lindh, W. Meyer, A. Nicklass, K. Peterson, R. Pitzer, A. J. Stone, P. R. Taylor, M. E. Mura, P. Pulay, M. Schuetz, H. Stoll, T. Thorsteinsson, and D. L. Cooper.

total system, the total angular momentum $J^T = j + \ell$ and its space fixed projection M^T are conserved during the collision. It is convenient to use scattering channel states $|Jj_2j\ell J^T\rangle$ which describe the asymptotic fragments with relative angular momentum ℓ . The total wave function is expanded in terms of these channel states, the expansion coefficients are the radial amplitudes $F_{j'j_2j'\ell',Jj_2j\ell}^{JT}$ which satisfy the usual coupled radial equations [16]. This set of equations is always decoupled into two blocks as a result of parity conservation. In the calculations, we have assumed that the H atom remains in its ground ^2S state ($L_2 = 0, j_2 = 1/2$) and we have neglected collision-induced quenching to the other L states of the radiating atom. The scattering equations were solved subject to boundary conditions which define the T -matrix elements [16].

$$\left(\frac{d^2}{dR^2} - \frac{\ell(\ell+1)}{R^2} + k_j^2\right)F_{Jj_2j\ell,Jj_2j\ell}^{JT}(R) - 2\mu \sum_{j'\ell'} V_{Jj\ell,J'j'\ell'}^{JT}(R)F_{Jj_2j\ell,J'j_2j'\ell'}^{JT}(R) = 0 \quad (1)$$

μ is the reduced mass of the colliding system, k_j is the wave number defined by $k_j^2 = 2\mu(E - \epsilon)$ where E is the kinetic energy and ϵ is the fine structure splitting. The numerical method used was the Log Derivative Method [17].

The ground state of the Na atom corresponds to an electronic angular momentum $L = 0$ and an electronic spin $S = 1/2$ so that the total electronic angular momentum is $J = 1/2$. The excited state of the Na atom corresponds to an electronic angular momentum $L = 1$ and an electronic spin $S = 1/2$ so that the total electronic angular momentum are $J = 1/2, 3/2$. For each energy two sets of 2 (6) uncoupled (coupled) equations were solved for the ground state (excited state).

4 Collisional rates

A similar approach in terms of the irreducible tensor T_q^κ as in reference [15] was followed here. The impact approximation expressions of Nienhuis [18] and Reid [19] were used. Due to the isotropy of the collisional relaxation, only the multipole components with the same values of κ and q are coupled and the relaxation rate constants are q -independent. Hence the relaxation equations may be written as:

$$\left(\frac{d\rho_q^\kappa(\lambda J)}{dt}\right)_{rel} = - \sum_{\lambda'J'} g^\kappa(\lambda J, \lambda' J') \rho_q^\kappa(\lambda' J') \quad (2)$$

For $J = J'$:

$$g^\kappa(J) = n_H \int_0^\infty v f(v) dv \sigma_\kappa^\kappa(J) \quad (3)$$

For $J \neq J'$ $g^\kappa(\lambda J, \lambda' J')$ corresponds to collisional transfer of population ($\kappa = 0$), orientation ($\kappa = 1$) and alignment ($\kappa = 2$) from state J' to state J :

$$g^\kappa(\lambda J, \lambda' J') = -n_H \int_0^\infty v f(v) dv \sigma^\kappa(J' \rightarrow J) \quad (4)$$

The cross sections σ^κ , $\Lambda^\kappa(J)$ and $\sigma(J \rightarrow J')$ have the following expressions:

$$\sigma^\kappa(J) = \Lambda^\kappa(J) + \sum_{J' \neq J} \sigma(J \rightarrow J') \quad (5)$$

$$\Lambda^\kappa(J) = \sum_m \frac{2m+1}{2J+1} [1 - (-1)^{2J+\kappa+m} (2J+1) \left\{ \begin{matrix} m & J & J \\ \kappa & J & J \end{matrix} \right\}] B(JJ; m) \quad (6)$$

$$\sigma(J \rightarrow J') = \frac{\pi}{k^2} \sum_{J^T j j' \ell \ell'} \frac{2J^T + 1}{(2J+1)(2j_2+1)} |\langle J' j_2 j' \ell' J^T | T | J j_2 j' \ell' J^T \rangle|^2 \quad (7)$$

$$\sigma^\kappa(J' \rightarrow J) \equiv \sum_m (-1)^{J+J'+\kappa+g} (2m+1) \left\{ \begin{matrix} J' & J' & \kappa \\ J & J & m \end{matrix} \right\} B(JJ', m) \quad (8)$$

with:

$$\begin{aligned} B(JJ'; m) &= \frac{\pi}{(2j_2+1)k_j^2} \sum_{j_b j_{b'} \ell \ell'} (j_b+1)(j_{b'}+1) \\ &| \sum_{J^T j j'} \sqrt{(2j+1)(2j'+1)} (-1)^{J+j_2+J^T} \left\{ \begin{matrix} J & j_2 & j \\ \ell & J^T & j_b \end{matrix} \right\} \\ &\left\{ \begin{matrix} J' & j_2 & j' \\ \ell' & J^T & j_{b'} \end{matrix} \right\} \left\{ \begin{matrix} J & J' & m \\ j_b & j_{b'} & J^T \end{matrix} \right\} \\ &\langle J' j_2 j' \ell' J^T | T | J j_2 j' \ell' J^T \rangle|^2 \end{aligned} \quad (9)$$

where n_H is the perturber (H atom) density, $f(v)$ is the Maxwellian distribution of relative velocities v at temperature T and coefficients B are generalization of Grawert factors [19]. The first contribution to σ^κ , Λ^κ is due to transitions into the same multiplet J . The term in (4) describes the transfer to $\rho_q^\kappa(\lambda J)$ from $\rho_q^\kappa(\lambda' J')$. All cross sections were calculated for a range of energies spanning from 200K to 80000K. Convergence as function of J^T was carefully checked.

4.1 Relaxation constants G_K and Q_K of the hyperfine states

The generalization of (2) with $J = J'$ to include the effects of nuclear spin has been studied by Omont [20]. We consider the case of a single hyperfine multiplet, with electronic angular momentum J and with nuclear spin I . The total angular momentum F takes the values $F = |J - I|, |J - I| + 1, \dots, J + I$ and we may consider possible off diagonal elements of the corresponding density matrix. The density matrix $\hat{\rho}$ can be expanded as:

$$\hat{\rho} = \sum_{FF'} \sum_{KQ} \rho_Q^K(FF') T_Q^K(FF')^\dagger \quad (10)$$

The density matrix for the electronic states can be expanded in terms of the tensors $T_{q_J}^{\kappa_J}$ ($0 \leq \kappa_J \leq 2J$) and the density matrix for the nuclear states have the tensors $T_{q_I}^{\kappa_I}$ ($0 \leq \kappa_I \leq 2I$) as a basis. The unitary transformation from the basis $T_Q^K(FF')$ to the basis $T_{q_J}^{\kappa_J} \otimes T_{q_I}^{\kappa_I}$ is given by:

$$\begin{aligned} T_Q^K(FF') &= \sum_{\kappa_J q_J} \sum_{\kappa_I q_I} [(2F+1)(2F'+1)]^{1/2} \\ &\quad [(2\kappa_J+1)(2\kappa_I+1)]^{1/2} \left\{ \begin{matrix} J & I & F \\ J & I & F' \\ \kappa_J & \kappa_I & K \end{matrix} \right\} \\ &\quad \langle KQ | \kappa_J q_J \kappa_I q_I \rangle T_{q_J}^{\kappa_J} T_{q_I}^{\kappa_I} \end{aligned} \quad (11)$$

where $\{ \}$ denotes a Wigner 9j-coefficient [21].

It is well known that internal energy differences which corresponds to frequency separations that are small compared to the inverse duration of a collision do not affect the scattering process. Then the collision S-matrix is just the direct product of the identity in the nuclear spin space and the collision matrix relative to the electronic coordinates computed in the absence of nuclear spin.

As the relaxation matrix is known in the “uncoupled” basis $T_{q_J}^{\kappa_J}(JJ)T_{q_I}^{\kappa_I}(II)$, in the case of an electronic multiplet $\{\lambda J\}$:

$$\begin{aligned} \frac{d}{dt} \rho_{q_J}^{\kappa_J} \rho_{q_I}^{\kappa_I} &= -g^{\kappa_J}(\lambda J) \rho_{q_J}^{\kappa_J} \rho_{q_I}^{\kappa_I}(\lambda J) \\ &- \sum_{\lambda' J' \neq \lambda J} g^{\kappa_J'=\kappa_J}(\lambda J, \lambda' J') \rho_{q_J}^{\kappa_J'} \rho_{q_I}^{\kappa_I}(\lambda' J') \end{aligned} \quad (12)$$

we obtain the new matrix in the “coupled” basis $T_Q^{(K)}((JI)F, (JI)F')$ from the following unitary transformations:

$$\begin{aligned}
\rho_Q^K(\lambda(JI)F, \lambda(JI)F') &= \sqrt{(2F+1)(2F'+1)} \\
&\sum_{\kappa_J q_J} \sum_{\kappa_I q_I} \sqrt{(2\kappa_J+1)(2\kappa_I+1)} \\
&\langle \kappa_J \kappa_I q_J q_I | KQ \rangle \left\{ \begin{matrix} J & I & F \\ J & I & F' \\ \kappa_J & \kappa_I & K \end{matrix} \right\} \rho_{q_J}^{\kappa_J} \rho_{q_I}^{\kappa_I}
\end{aligned} \tag{13}$$

$$\begin{aligned}
\rho_{q_J}^{\kappa_J} \rho_{q_I}^{\kappa_I} &= \sum_{FF'} \sum_{KQ} \sqrt{(2F+1)(2F'+1)} \sqrt{(2\kappa_J+1)(2\kappa_I+1)} \\
&\langle \kappa_J \kappa_I q_J q_I | KQ \rangle \left\{ \begin{matrix} J & I & F \\ J & I & F' \\ \kappa_J & \kappa_I & K \end{matrix} \right\} \rho_Q^K(\lambda(JI)F, \lambda(JI)F')
\end{aligned} \tag{14}$$

If the hyperfine Zeeman levels F of the multiplet are well defined, the time variation due to collisional relaxation of the element $\rho_Q^K(FF')$ is given by:

$$\begin{aligned}
\frac{d^{(\lambda J)} \rho_Q^K(FF')}{dt} &= - \sum_{F''F'''} G_K(FF', F''F''')^{(\lambda J)} \rho_Q^K(F''F''') \\
&- \sum_{F''F'''} \sum_{J' \neq J} Q_K(FF', F''F''')^{(\lambda' J')} \rho_Q^K(F''F''')
\end{aligned} \tag{15}$$

where the relaxation rates G_K are related to the electronic relaxation rate $g^{\kappa_J}(\lambda J)$ [20]:

$$\begin{aligned}
G_K(FF', F''F''') &= [(2F+1)(2F'+1)]^{1/2} \\
&[(2F''+1)(2F''' + 1)]^{1/2} \sum_{\kappa_J \kappa_I} (2\kappa_J+1)(2\kappa_I+1) \\
&\left\{ \begin{matrix} J & I & F \\ J & I & F' \\ \kappa_J & \kappa_I & K \end{matrix} \right\} \left\{ \begin{matrix} J & I & F'' \\ J & I & F''' \\ \kappa_J & \kappa_I & K \end{matrix} \right\} g^{\kappa_J}(\lambda J)
\end{aligned} \tag{16}$$

we obtain transfer hyperfine rates [22] pertaining to the electronic transfer rate $g^{\kappa_J}(\lambda J, \lambda' J')$:

$$\begin{aligned}
Q_K(FF', F''F''') &= [(2F+1)(2F'+1)]^{1/2} \\
&[(2F''+1)(2F''' + 1)]^{1/2} \sum_{\kappa_I \kappa'_I} \sum_{J' \neq J}
\end{aligned}$$

$$(2\kappa'_J + 1)(2\kappa_I + 1)g^{\kappa'_J}(\lambda J, \lambda' J') \left\{ \begin{matrix} J & I & F \\ J & I & F' \\ \kappa'_J & \kappa_I & K \end{matrix} \right\} \left\{ \begin{matrix} J' & I & F'' \\ J' & I & F''' \\ \kappa'_J & \kappa_I & K \end{matrix} \right\} \quad (17)$$

The nuclear spin of the Na atom is $I = 3/2$, which leads to two hyperfine levels in the ground state, $F = 1$ and $F = 2$. The energy difference between those two levels is $\nu = 1771.6 \text{ MHz}$. In the $^2P_{1/2}$ state, $F = 1$ and $F = 2$, we obtain four hyperfine levels in the $^2P_{3/2}$ state, $F = 0$, $F = 1$, $F = 2$ and $F = 3$. The energy differences between those levels are respectively $\nu = 192 \text{ MHz}$, $\nu = 17.1 \text{ MHz}$, $\nu = 36.6 \text{ MHz}$ and $\nu = 60.9 \text{ MHz}$. The time duration τ of the collision Na+H can be estimated as follows: for a temperature of 5000 K, the relative velocity is $v \simeq 1.3 \cdot 10^6 \text{ cm s}^{-1}$. Thus the frequency splitting is very small compared to the inverse of τ and the hyperfine splitting of the levels is negligible during the collision. We can apply equations (3,4) to obtain the relaxation rates of the Zeeman multiplet and then deduce from (16,17) all the relaxation rates between the hyperfine levels.

For $J = 1/2$, the only non-zero relaxation rate is $g^1(J = 1/2)$, whereas for $J = 3/2$ we consider g^1 , g^2 and g^3 and the transfer rates between the structure fine components: $g^0(1/2, 3/2)$ and $g^1(1/2, 3/2)$. The relaxation rates between the hyperfine levels, relevant for radiation polarization correspond to $K = 0, 1, 2$, $K = 0, 1$ being useful for circular polarization studies and $K = 0, 2$ being of interest for linear polarization.

5 Radiative processes

In order to obtain Stokes parameter of the emitted radiation by the sodium atom in the presence of: perturbers (H atoms) and incident anisotropic radiation which can be supposed unpolarized and cylindrically symmetric around the solar radius, we solved the multilevel statistical equilibrium coupled equations in the presence of collisional and radiative rates. Radiative processes are given by the following equations in the tensorial scheme where fine structure is neglected for simplicity [24]:

$$\frac{d}{dt} \rho_{q_1}^{\lambda_1 J_1} = -i\omega_{\lambda_1 J_1} q_1^{\lambda_1 J_1} \rho_{q_1}^{\lambda_1 J_1} + \sum_{\lambda_2 J_2 \kappa_2 q_2} \Gamma_{\lambda_1 J_1 \kappa_1 q_1 \leftarrow \lambda_2 J_2 \kappa_2 q_2}^{\lambda_2 J_2} \rho_{q_2}^{\lambda_2 J_2} - \sum_{\kappa'_1 q'_1} \Gamma_{\lambda_1 J_1 \kappa_1 q_1 \leftarrow \lambda_1 J_1 \kappa'_1 q'_1}^{\lambda_1 J_1} \rho_{q'_1}^{\lambda_1 J_1} \quad (18)$$

The explicit calculations of the tensorial components of the incident radiative field, which appear in the statistical equilibrium equations, is given by the measure of center to limb darkening coefficient [23]. Anisotropic incident radiation (at least one of its Φ_Q^K elements (with $K \neq 0$ is non zero) is responsible from the alignment

of the levels and thus from the line-polarization at 90° scattering.

The density matrix Ψ_Q^K of the emitted radiation at 90° scattering is related to the Stokes parameters [24]:

$$\begin{cases} I = \frac{3}{8\pi} \left(\frac{2}{\sqrt{3}} \Psi_0^0 + \frac{2}{\sqrt{6}} \Psi_0^2 \right) \\ Q = -\frac{3}{8\pi} (\Psi_2^2 + \Psi_{-2}^2) = -\frac{3}{8\pi} 2\text{Re}\Psi_2^2 \\ U = \frac{3}{8\pi} i(\Psi_{-2}^2 - \Psi_2^2) = \frac{3}{8\pi} 2\text{Im}\Psi_2^2 \\ V = \frac{3}{8\pi} \sqrt{2} \Psi_0^1 \end{cases}$$

(19)

An axis rotation was accomplished to bring the quantification axis with respect to the line of sight.

6 Polarization of the D2 line

We calculate the linear polarization rate P_L in the center of the D2 line as function of the density n_H see (figure 3). We also put forward the competitive processes of transfer and relaxation of the alignment in the hyperfine levels of $^2P_{1/2}$, $^2P_{3/2}$ and $^2S_{1/2}$ states. Calculations were performed at a temperature $T \simeq 4500K$ (region of formation of the D lines [25]).

6.1 Relaxation in the $^2S_{1/2}$ state

The analysis of the polarization under the effect of relaxation in the ground state hyperfine levels presents a variation between two limits: the upper one corresponds to a situation where collisions are absent ($n_H = 0$), the other corresponds to the case where all hyperfine levels are depolarized (infinity of collisions). P_L decreases between these two limits respectively: $P_L = 0.549\%$, and $P_L = 0.404\%$. From this result we conclude that atomic polarization is completely destroyed at $n_H \simeq 2.0 \times 10^{15} \text{cm}^{-3}$.

6.2 Relaxation in the $^2P_{1/2}$ and $^2P_{3/2}$ states

The hyperfine collisional rates pertaining to these levels were included for the resolution of the coupled equations, the polarization rate was found to decrease more rapidly toward zero. Three regimes were involved:

- 1) $n_H \leq 2.0 \times 10^{13} \text{cm}^{-3}$: highest polarization $P_L = 0.404\%$.

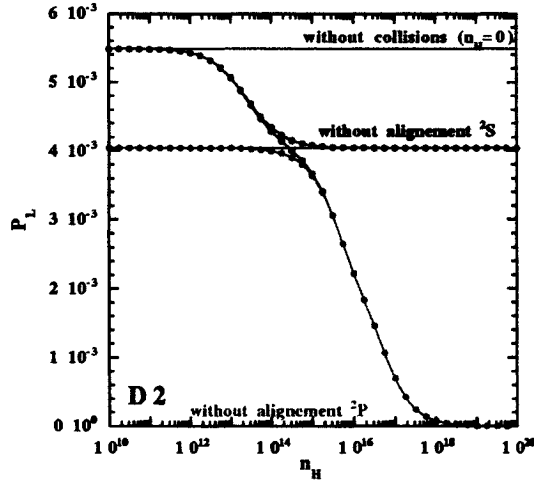


Figure 3: Polarization in the center of D2 line versus hydrogen density in cm^{-3} .

- 2) $2.0 \times 10^{13} \text{cm}^{-3} \leq n_H \leq 2.0 \times 10^{18} \text{cm}^{-3}$: intermediate polarization. Existence of an inflexion point when $g^{\kappa}(^2P) = A_{21}$ where $A_{21} = 6.29 \times 10^7 \text{s}^{-1}$ is the Einstein spontaneous emission coefficient.
- 3) $n_H > 2.0 \times 10^{18} \text{cm}^{-3}$: polarization completely destroyed.

The polarization rate calculated taking into account depolarizing parameters related to hyperfine levels of the ground and excited states follows exactly the two precedent curves, this implies that the collisional depolarization occurs firstly into the ^2S state, and secondly in the ^2P states for much higher densities n_H .

7 Conclusion

These results show that the collisions of the sodium atom with the surrounding hydrogen atoms could destroy the lower level atomic polarization. In order to progress in the understanding and interpretation of this spectrum and of the magnetic field effects, it would then be necessary to achieve a better modelization of the line polarization formation, by solving the coupled equations of polarized radiative transfer and statistical equilibrium of the multilevel atom, taking into account coherent scattering, which has never been completely achieved for the moment.

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ELECTRON ENERGY LOSS SPECTROSCOPY OF TRIFLUOROMETHYL SULPHUR PENTAFLUORIDE

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Abstract: Electron Energy Loss Spectroscopy (EELS) has been used to study the UV/VUV photoabsorption spectrum of trifluoromethyl sulphur pentafluoride (SF_5CF_3) for the first time. Comparison is made with the EEL spectrum of sulphur hexafluoride (SF_6). The photolysis of the compound has also been investigated to give an estimate of the lifetime in the atmosphere. It is estimated that the lifetime of SF_5CF_3 is of the order of 1000 years. The lifetimes are then used to calculate the Global Warming Potential (GWP). The calculated GWP value of SF_5CF_3 is found to be between 17,000 and 18,100.

Key words: Electron Energy Loss Spectroscopy; Photolysis; Greenhouse gases

1. INTRODUCTION

Global Warming is a topic of much concern in modern science with the recent International Panel on Climate Change (IPCC) report [1] indicating that mean global temperatures may rise by as much as 5.8°C by the end of the 21st century. The major contributions to the anthropogenic global warming budget come from bulk atmospheric species such as carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O). There are also contributions from atmospheric species present in far smaller quantities, which are effective global warming gases by virtue of their extremely high infrared absorbances. An example of this type of molecule is sulphur hexafluoride (SF_6), but the recently discovered molecule trifluoromethyl sulphur pentafluoride (SF_5CF_3) also falls into this category.

2. INITIAL MEASUREMENTS

SF_5CF_3 was detected in the atmosphere in 1999 as an unidentified peak in a stratospheric air sample using mass spectrometry, and was only later identified by Sturges et al [2]. Trifluoromethyl sulphur pentafluoride is a molecule for which there is little information in the literature. It is, however, known that the molecule is of purely anthropogenic origin with no known natural sources. One possible source is from SF_6 used as a gas phase dielectric in high voltage electrical equipment. During high voltage electrical discharges, molecules of SF_6 may be dissociated and the SF_5 products formed can then react with fluoropolymers present inside the equipment casing to form SF_5CF_3 . The resultant SF_5CF_3 can then be released to the atmosphere via leakages or during servicing of the equipment. A second possible source is as a byproduct of certain fluorochemical processes. Indeed, the paper of Sturges prompted the company 3M to release a reply indicating that a source of SF_5CF_3 is from one of their processes and that they have subsequently acted to reduce emissions of this and other greenhouse gases [3]. Whether or not these two potential sources can account for the concentration rates of SF_5CF_3 seen in the atmosphere is open to conjecture and the identification of the sources of this molecule must remain a high priority.

Despite the uncertainty surrounding source identification, the concentration levels of SF_5CF_3 in the atmosphere are known to a high degree of accuracy. Sturges used two separate techniques to measure the concentration levels. The first was to extract air trapped inside the Antarctic firn at different depths. As the snow falls onto the surface, air is trapped under the layers which eventually are converted to glacial ice. The air can take many decades to diffuse away and hence the depth of the trapped air will correspond to its age. The second method was to obtain air samples from various altitudes in the stratosphere. The samples from higher altitudes correspond to older air and can once again give a concentration profile over a time period. Combining the two techniques gives the concentration profile as shown in figure 1 [after Sturges [2]]. The present level is seen to be approximately 0.13 ppt by volume and growing at 6 % per annum. In mass terms, the total burden is 3900 tonnes increasing at 210 tonnes per year.

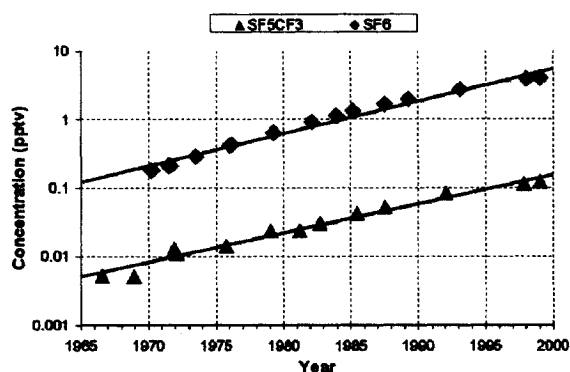


Figure 1. Trifluoromethyl sulphur pentafluoride atmospheric concentrations

It was also found that the concentration levels of SF_5CF_3 parallel those of SF_6 and so it would seem that in the atmosphere, SF_5CF_3 is intimately linked with SF_6 . If we therefore assume the two molecules are closely related we can make some initial guesses about how SF_5CF_3 may behave based on SF_6 . SF_6 has a very long atmospheric lifetime, given by Ravishankara et al [4] as 3200 years, and it also is a very effective infrared absorber. These two facts combined make the molecule a highly potent greenhouse gas and by association, would also make SF_5CF_3 a strong greenhouse gas. In order to study the infrared properties of SF_5CF_3 , Sturges also measured the infrared absorption cross sections. We have also performed measurements of these cross sections, our results are shown in figure 2.

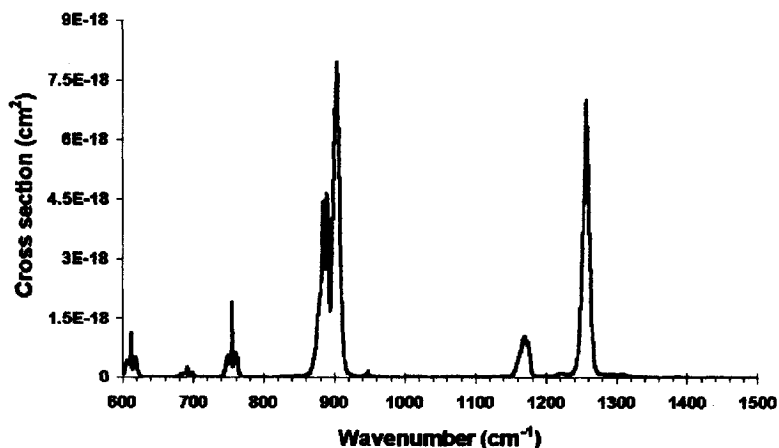


Figure 2. Infrared photoabsorption cross sections at 298K

Compared with the work of Sturges, our IR measurements have been performed with a far greater resolution and at several different temperatures. The measurements were performed on the highest resolution FTIR instrument in the UK at the Rutherford Appleton Laboratory [5]. Our 298 K measurements are in good agreement with the values that Sturges obtained. Sturges then used the infrared cross section values to calculate the radiative forcing of SF_5CF_3 . The radiative forcing is defined as being a change in the balance between incoming solar radiation and outgoing infrared radiation [6]. A greenhouse gas has a positive value for the change in ratio as it traps infrared and thus causes warming. In the case of SF_5CF_3 the radiative forcing value is $+0.57 \text{ W m}^{-2} \text{ ppb}^{-1}$. This is the highest value on a per molecule basis for any gas found in the atmosphere (even higher than SF_6 which has $0.52 \text{ W m}^{-2} \text{ ppb}^{-1}$). We have confidence in this value given that our infrared measurements match those used in this calculation by Sturges. Hence, in common with SF_6 , this molecule has a highly effective infrared absorbance and the overall global warming potential is therefore dependent on the lifetime in the atmosphere. As with much about SF_5CF_3 , no experiments had been performed to look at the lifetime of the molecule. We therefore decided that we would try to determine this value and proceeded to use the techniques of electron energy loss spectroscopy (EELS) [7] and VUV photoabsorption spectroscopy to do so.

3. ELECTRON ENERGY LOSS SPECTROSCOPY (EELS)

EELS is a very adaptable technique that has been used over a large number of years to measure the spectroscopy of atomic and molecular targets in both gas and solid phases. The configuration used in this gas phase work uses electrons with an impact energy of 150 eV. The electrons that are detected are constrained to only those that have travelled undeflected from their pre-collision trajectory. These particular criteria are selected as the electron impact excitations then closely follow optically allowed selection rules. This occurs as an electron with sufficiently high energy ($>100 \text{ eV}$) scattered at small angles (~ 0 degrees) will induce an electric field at the molecule very similar to that of a photon pulse. The electric field interacts with the transition dipole of the molecule with electric dipole transitions being predominantly excited [8]. Hence, in this configuration, the EELS experiment will closely approximate a photoabsorption experiment. This is useful as it means that results obtained in the EELS experiment will have direct relevance in modelling the molecule's behaviour in a sunlit atmosphere.

The EELS experiment also has certain advantages over photoabsorption experiments, namely that a wide energy range from visible to VUV wavelengths is easily accessible without the need to change optical lamps or filters. A cutaway diagram of the apparatus is shown in figure 3. The apparatus is encased in a stainless steel vacuum chamber and is shielded by mu-metal casing to minimise magnetic fields.

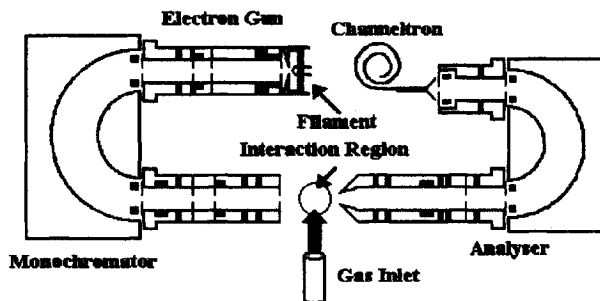


Figure 3. Schematic of the EELS apparatus

Briefly, the mode of operation is as follows. A current of around 2.3 Amperes is passed through the filament to generate the electrons. The electron gun is then used to accelerate the electron beam into the monochromator. The monochromator is of a hemispherical electrostatic design and reduces the energy spread of the beam from around 0.5 eV to 50 meV. The quasi-monochromatic energy beam is then accelerated to an energy of 150 eV and is collided with a perpendicularly travelling gas beam in the interaction region. The gas leaving the interaction region flows directly into a diffusion pump thus eliminating multiple scattering from recycling molecules. Electrons whose path is undeflected after the interaction region then pass through the aperture in the front of the analyser section and are decelerated into the second hemisphere. This hemisphere acts as an energy loss selector and the voltage is set according to the energy loss required. The energy loss is determined by the incident energy minus the pass energy of the analyser section. Thus setting the analyser voltage to 140 Volts will let through only electrons with an energy loss of $150 - 140 = 10$ eV. Thus the only electrons to reach the channeltron detector will fulfil the criteria specified to simulate photoabsorption. By varying the analyser voltage by up to ± 5 Volts it is possible to detect electrons with an energy range of up to 10 eV. A Multi Channel Analyser (MCA) cumulatively adds the electron counts over a number of sweeps over the voltage range and hence builds up an EEL spectrum. The energy loss scale is calibrated by

measuring the well-known spectrum of nitrogen before we introduce the target gas of interest.

The EELS spectrum is not directly comparable with photoabsorption data. In order to relate the two quantities it is necessary to use the following equation [8] to convert the EELS data to differential oscillator strengths (DOS):

$$\frac{df}{dE} \propto \frac{E\Delta\theta}{R} \frac{I(E)}{\ln[1+(\Delta\theta/\gamma)^2]} \quad \text{where } \gamma^2 = \frac{E^2}{4T(T-E)}$$

Where df/dE is the DOS, T is the incident electron energy, E is the energy loss, $\Delta\theta$ is the acceptance angle, R is the Rydberg constant and $I(E)$ is the intensity of the scattered electron beam. The DOS values are directly proportional to the photoabsorption cross sections but are relative values as they are only proportional to the intensity losses of the electron beam. The EELS and DOS spectra obtained for SF_5CF_3 are shown in figure 4.

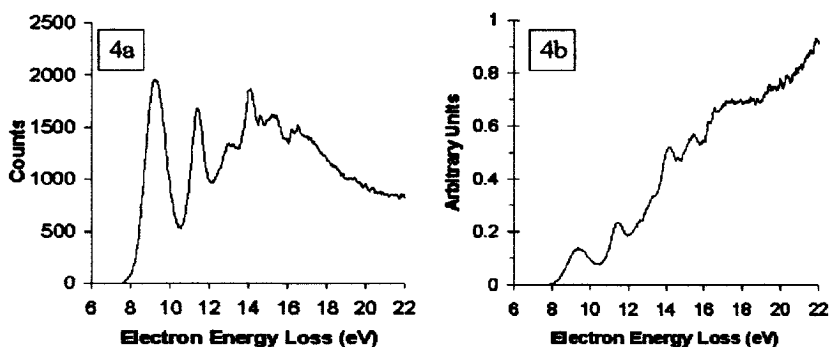


Figure 4. a) Raw EEL spectrum of SF_5CF_3 , b) DOS spectrum of SF_5CF_3

In order to scale the DOS values to obtain the cross section, a source of absolute data was required. We therefore measured the absolute photoabsorption cross sections at the Daresbury Synchrotron Facility. These values were then used to normalise our electron generated DOS data.

4. RESULTS

4.1 Atmospheric Lifetime and Breakdown

Our results are shown in figure 5.

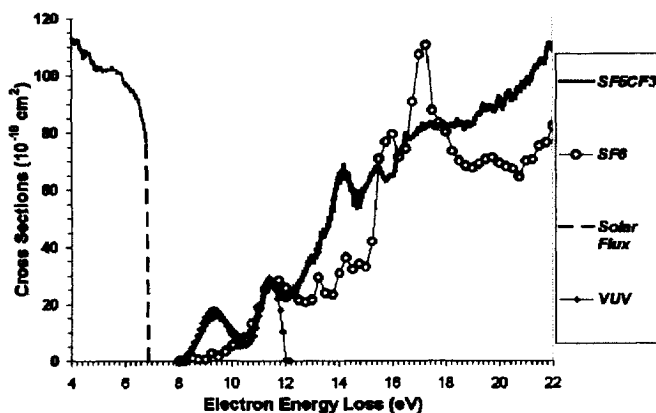


Figure 5. SF₅CF₃ UV/VUV photoabsorption cross sections

The solid curve is the DOS of SF₅CF₃, now scaled to the absolute cross section values from the VUV photoabsorption experiment. The VUV photoabsorption data is shown as black diamonds in the range of 8 to 12 eV. The 12 eV cutoff occurs due to the LiF windows used in the apparatus. The shapes of the two curves in this region are in good agreement and suggest that the scaling in this region can be correctly used to scale the whole of the EELS data. The open circles are an EELS spectrum of SF₆ measured for comparison and scaled to a previous study by members of this group. The dashed line to the left is the shape of the solar actinic flux (in arbitrary units) at 50 km altitude in the Stratosphere [9]. Two important facts relating to the lifetime of SF₅CF₃ can be obtained from this graph. Firstly, SF₅CF₃ has a peak at around 9 eV that is not seen in SF₆. This peak will mean that SF₅CF₃ will be better at absorbing photons at lower energies. This implies that the molecule will be more easily dissociated and will hence have a shorter lifetime in the atmosphere than SF₆. The second important piece of information is that there is no structure in SF₅CF₃ below this peak so the molecule is unable to absorb photons with energies less than 8 eV. At the very top of the stratosphere, however, the highest energy solar photons available are only around 7 eV. In order for photodissociation to occur there must be overlap between the photon flux available and the absorption

spectrum. The lack of overlap indicates that the lifetime in the atmosphere will be long and hence the global warming potential will be correspondingly large.

4.2 Breakdown Methods

There appear to be two potential breakdown methods, both of which occur in the upper levels of the atmosphere. The first is photodissociation, not now in the stratosphere but in the ionosphere/mesosphere regions of the atmosphere. In the upper regions of the atmosphere there are higher energy photons available [9] and considerable overlap between the solar flux and SF_5CF_3 absorption bands is observed (figure 6).

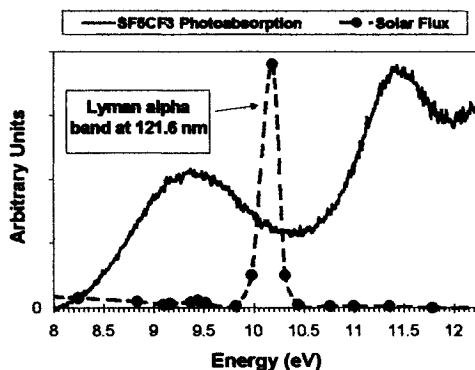


Figure 6. Solar flux and photoabsorption overlap

The second method of breakdown is through ion-molecule reactions. Kennedy and Mayhew [10] used an electron swarm experiment and studied the products formed. They found that only one channel was observed:



This was subsequently confirmed by Sailer et al [11]. Kennedy and Mayhew placed an estimated lifetime for SF_5CF_3 using this destruction method on the order of 1000 years. Using these two methods and our knowledge of the lifetime of SF_6 (3200 years) and acknowledging that the lifetime of SF_5CF_3 looks to be shorter than that of SF_6 we can place an estimated atmospheric lifetime on the molecule. We thus estimate that the lifetime of SF_5CF_3 in a sunlit atmosphere will be between several hundred and a few thousand years.

4.3 Global Warming Potential Calculations

The calculated lifetime of SF_5CF_3 can now be used to calculate its Global Warming Potential (GWP). GWP values are used to calculate the global warming effectiveness of gases compared to a reference gas (CO_2). The underlying equation [12] follows from the International Panel on Climate Change (IPCC) 1990 [13] definition of GWP.

$$\text{GWP}_x = \left(\frac{m_{\text{CO}_2}}{m_x} \right) \cdot \left(\frac{a_x}{a_{\text{CO}_2}} \right) \cdot \left(\frac{\tau_x}{\tau_{\text{CO}_2}} \right) \cdot \left(\frac{(1 - \exp(-t/\tau_x))}{(1 - \exp(-t/\tau_{\text{CO}_2}))} \right) \cdot \text{GWP}_{\text{CO}_2}$$

Figure 7. GWP equation

where m is the mass of the molecule, a is the radiative forcing, τ the lifetime in the atmosphere, t the timescale over which the GWP is to be considered and GWP the global warming potential. The subscript x refers to the molecule of interest and CO_2 to carbon dioxide, which is the reference gas used. A spreadsheet may then be set up so that the user inputs the molecules radiative forcing, lifetime and mass and the timescale over which the GWP is to be measured. The spreadsheet then automatically calculates the GWP value of the molecule relative to CO_2 and a number of other greenhouse gases including SF_6 . In the present work, the Sturges value for the radiative forcing ($0.57 \text{ W m}^{-2} \text{ ppb}^{-1}$) was used as it agreed with our IR measurements. The results, all over 100 year timescale relative to carbon dioxide, are given in tabular form in table 1 for a variety of lifetimes (LT). Also given are the GWP values as a percentage of the GWP value for SF_6 (22,200).

Table 1. GWP values of SF_5CF_3 calculated by lifetime

LT (yr)	GWP	% SF_6	LT (yr)	GWP	% SF_6	LT (yr)	GWP	% SF_6
600	17000	76.4	1100	17600	79.3	1750	17900	80.5
700	17150	77.6	1200	17660	79.6	2000	17960	80.8
800	17300	77.9	1300	17720	79.8	2500	18050	81.3
900	17420	78.5	1400	17770	80.1	3000	18100	81.5
1000	17520	78.9	1500	17810	80.2	3200	18125	81.6

From table 1 it can be seen that the GWP value for SF_5CF_3 lies between 17,000 and 18,100. This means that if 1 kilogram of carbon dioxide and 1 kilogram of SF_5CF_3 are released into the atmosphere then, after 100 years have passed, the kilogram of SF_5CF_3 will have caused 17,000 to 18,100 times more global warming than the kilogram of carbon dioxide. An alternative way to look at this is that current emission levels (270 tonnes per year) are in GWP terms equivalent to around one percent of the annual UK carbon

dioxide emission [2]. For comparison, the 100 year GWP values of a number of other greenhouse gases are; carbon dioxide (1), methane (21), nitrous oxide (310) and CFC – 12 (8,100). Indeed, the only higher recorded value of GWP for an atmospheric molecule is that of SF_6 (22,200). This value is higher than that of SF_5CF_3 because although the radiative forcing is smaller per molecule ($0.52 \text{ W m}^{-2} \text{ ppb}^{-1}$, c.f. $0.57 \text{ W m}^{-2} \text{ ppb}^{-1}$), SF_6 is less massive and hence there are a larger number of molecules per kilogram. Given the very small amounts present in the atmosphere, SF_5CF_3 has only a very minor contribution to overall radiative forcing at $\sim 0.000075 \text{ W m}^{-2}$. However, the high GWP of SF_5CF_3 when combined with the current growth rate mean that unchecked it is a potentially powerful contributor to the anthropogenic greenhouse effect. Indeed, given the long lifetime in the atmosphere it is possible to imagine that if sources remain uncontrolled levels could reach a point where the accumulation is sufficient to cause serious levels of global warming. At this point, even if sources of SF_5CF_3 are shut down completely, it will take on the order of ~ 1000 years to empty the atmosphere of the molecule and in the intervening period the global warming effects will be inescapable.

5. SUMMARY AND CONCLUDING REMARKS

SF_5CF_3 is a new greenhouse gas discovered in the atmosphere in 1999. In order to determine the lifetime of this molecule we have used the technique of electron energy loss spectroscopy (EELS) to study the UV/VUV spectrum of SF_5CF_3 for the first time. Our results indicate that SF_5CF_3 has larger absorbance at lower energies than SF_6 and so will probably be shorter lived in the atmosphere. There is also no overlap of the photoabsorption bands and the solar flux present at 50 km altitude. This indicates that photodissociation will not be possible in the troposphere/stratosphere regions and implies that SF_5CF_3 will have a long lifetime. The possible destruction methods for SF_5CF_3 will probably be via ion-molecule reactions or photodissociation, in both cases only in the upper atmosphere regions of the ionosphere or mesosphere. The lifetime involved is expected to be shorter than the 3,200 years for SF_6 and given the above destruction methods will probably be between several hundred and a few thousand years. The Global Warming Potential (GWP) values for SF_5CF_3 have been evaluated for a number of prospective lifetimes between 600 and 3200 years. The results range from 17,000 (600 years) to 18,100 (3,200 years) giving SF_5CF_3 the second highest GWP value recorded for any atmospheric molecule. A GWP value of 18,000 indicates that one kilogram of SF_5CF_3 will cause 18,000 times more global warming over 100 years than one kilogram of carbon dioxide.

The levels of SF_5CF_3 currently present in the atmosphere are small at approximately 0.13 pptv so the overall effect of SF_5CF_3 on global warming is correspondingly small. However, levels are rising at a significant rate of 6 % per year. If this growth rate remains constant the levels in the atmosphere would double in 12 years, increase tenfold by 2040 and grow to 340 times present levels by 2100. Thus what is presently not a problem could become one in the future. This is especially true given that the long lifetime of SF_5CF_3 means that even complete cessation of emissions would be followed by a very long period (hundreds to thousands of years) where the global warming of this highly effective greenhouse is still felt.

In order to prevent such a scenario a number of things can be done. The first and most important is to identify the sources of this molecule. Given that SF_5CF_3 is purely anthropogenic, if the sources can be correctly identified, there is a possibility of considerable control or even complete cessation of emissions. Secondly, there is a dearth of information in the literature about SF_5CF_3 and so more studies, both theoretical and experimental, must be performed in order to understand this molecule better. This is especially important since, given the 100 % anthropogenic nature of this molecule, SF_5CF_3 is a perfect testbed for studies into greenhouse gases free of any natural background.

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THE USE OF THE MAGNETIC ANGLE CHANGER IN ELECTRON SPECTROSCOPY

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Abstract A new magnetic angle-changing technique is described together with its use in electron spectroscopy. The technique opens up new ranges of angular observation, particularly for scattering in the backward hemisphere. Measurements of elastic and inelastic electron scattering in atoms and molecules using the technique are described together with observations of resonance excitation. New experimental opportunities presented by the technique are also discussed.

1. Introduction

The scattering of electrons by atoms and molecules continues to be an active area of both experimental (e.g. Trajmar and McConkey 1994) and theoretical (e.g. McCarthy and Weigold 1995) study. One of the significant limitations of experimental measurements of differential cross sections (DCS) has been that the observable range of scattering angle was limited to typically 10° to 130° . The upper limit occurs because, in conventional electron spectrometers, the energy selector gets in the way of the energy analyser at larger scattering angles. Obviously, this limitation does not apply to theoretical calculations. Methods have been devised to determine DCS for elastic and inelastic scattering at 180° (e.g. Amis and Allen 1997) or to measure cross sections integrated over the backward hemisphere (Greenwood et al 1995). It appears, however, that there were no previous differential measurements for scattering angles covering the whole of the backward hemisphere. This experimental limitation has recently been overcome by the development of the magnetic angle-changing technique (Zubek et al 1996, Read and Channing 1996). This is based on a localised magnetic field placed at the interaction region of a conventional electron spectrometer. This can change

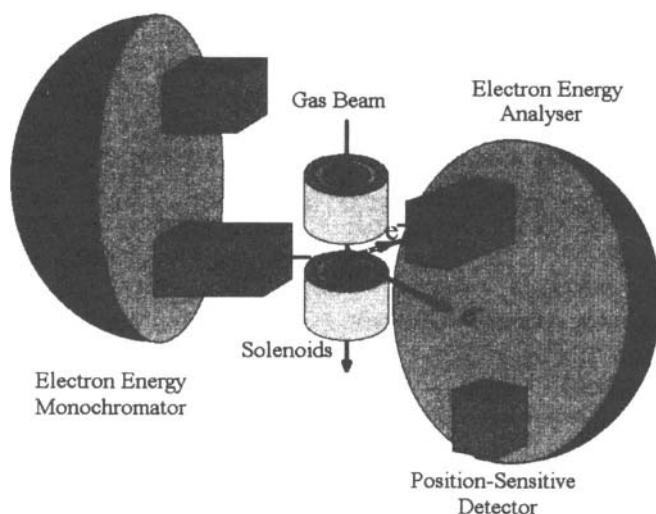


Figure 1. Schematic diagram of the electron spectrometer with the magnetic angle changer placed at the interaction region.

the directions of the electrons without changing the operation of the electron energy selector or analyser. Looking in the backward direction provides important new information. The DCS may be determined over the whole scattering range from 0° to 180° without recourse to extrapolation techniques, and full comparison with theoretical predictions may be made. This article describes the principles of operation of the magnetic angle-changing technique and its use in studying elastic and inelastic electron scattering in atoms and molecules. New opportunities in electron spectroscopy presented by the technique are also discussed.

2. Principles of operation of the magnetic angle changer

The magnetic angle changer consists of a set of two (or more) pairs of coaxial solenoids as illustrated in figure 1. The device is placed at the interaction region of the spectrometer with the axial magnetic field perpendicular to the scattering plane. Each pair of solenoids is separated to allow passage of the electron beams. There are two main principles of operation of the device. Firstly, the magnetic field produced by the solenoids is highly localised in order not to disturb the operation of the electron energy selector or analyser. This is achieved by making the overall magnetic dipole moment of the system equal to zero using the

condition

$$\sum_i I_i \cdot R_i^2 = 0 \quad (1)$$

where i labels the windings of the solenoids, I_i is the current and R_i is the radius of the layer. The magnetic field then falls off rapidly at large distances as r^{-5} . Secondly, the system of solenoids is axially symmetric, so that the axial component of the generalised momentum of an electron in this field becomes a conserved quantity. This component is zero at the axis of the system as well as in the field-free region away from the axis for electrons initially directed towards the axis. Consequently any such electrons change direction in the magnetic field but still pass through the centre of the interaction region. Similarly electrons which originate from the interaction region move radially away from it once they reach the field free region.

The magnetic angle-changing device has been realised in several versions. In one version (e.g. Zubek et al, 1996) the solenoid currents are held constant and give a fixed angular deflection to all the electrons of a specific energy. The analyser then rotates about the interaction region in the conventional way. A second version has been developed for angular studies in photoelectron spectroscopy (Cubrić et al, 1997). Here, the analyser is held fixed in position and the currents in the solenoids are varied to change the direction of the photoelectrons.

3. Measurements of elastic electron scattering.

Measurements of elastic DCS over the complete scattering sphere can yield integral cross sections without recourse to extrapolation techniques. Similarly, they also yield momentum transfer cross sections and here it is noteworthy that the DCS contribution to this has a greater weighting factor in the backward direction than in the forward direction. Measurements of elastic scattering in the backward direction are also of interest in the wave description of scattering and for the determination of the phase shifts. The first use of the magnetic angle-changing technique was to measure elastic DCS in argon (Zubek et al 1996). Since then the studies have been extended to molecules (e.g. Cho et al 2000). Experimental and theoretical studies of low-energy electron scattering in molecules are essential to develop an accurate description of the electron-molecule interactions. Comparison between experiment and theory is especially important to adequately account for the short- and long-range correlation (polarisation) and exchange interactions.

Zubek et al (2000) have recently presented absolute differential cross sections for elastic electron scattering and vibrational ($v = 0$ to 1) excitation in nitrogen at an energy of 5 eV, over the range from 120° to

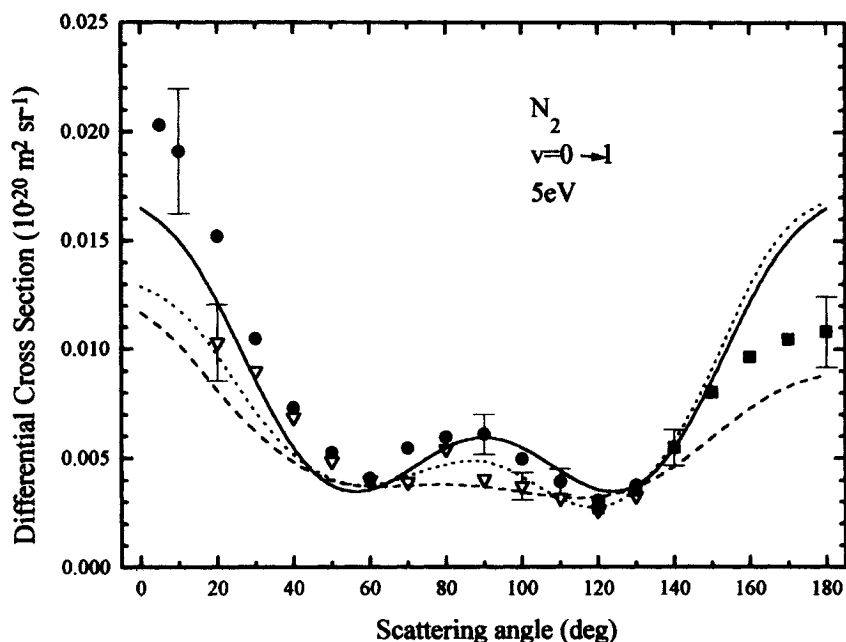


Figure 2. Absolute DCS for elastic electron scattering in nitrogen at an incident energy of 5 eV: experimental and theoretical results. From Zubek et al (2000).

180°. This energy is close to the region that is dominated by the $^2\Pi_g$ resonance and so the measurements give an estimate of the resonance contribution to the cross section. The absolute DCS measurements of Zubek et al are shown in figure 2. These high-angle scattering data obtained using the magnetic-angle changing technique agree well with the low scattering angle results in the overlap region and combine to give elastic cross sections from 20° to 180°.

The hybrid theory calculations of Chandra and Temkin (1976) (shown as the full line in figure 2, show the best agreement with the experimental cross section although they are about 20 to 30 percent higher in magnitude. This theory combines vibrational, close-coupling with the adiabatic nuclei approximation. The R-matrix calculations (Gillan et al 1987, shown as the dotted line) overestimate the DCS in the forward direction below 5° and the Schwinger multichannel results (Huo et al 1987, shown as dashed dotted line), deviate from the experimental DCS in the region above 100°. These discrepancies have been attributed to inadequate representation of the long-range and short-range correlation interactions for low- and high- angle scattering respectively.

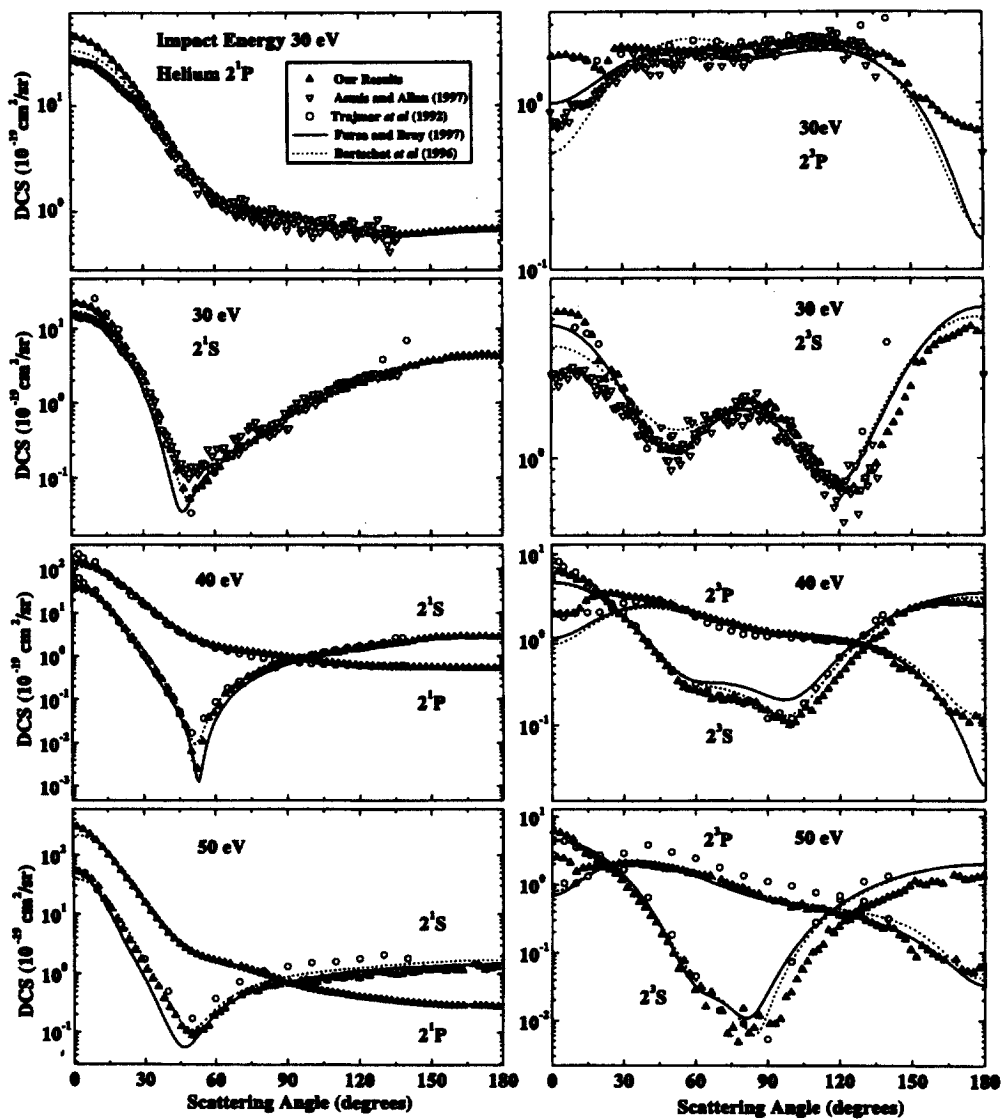


Figure 3. Measured and calculated DCS for for the 2^3S , 2^1S , 2^3P and 2^1P states of helium, (Cubrić et al, 1999)

4. Measurements of inelastic electron scattering.

The magnetic angle-changing technique has an additional advantage in the study of inelastic electron scattering, for the observation of elec-

trons that are inelastically scattered at 0° . In conventional spectrometers, those electrons inelastically scattered in the forward direction follow the same path as the unscattered electrons in the incident beam. They are, however, typically 10^6 times smaller in number and so are difficult to detect in the presence of the incident beam. This has often limited differential cross section measurements to a minimum angle of about 20° . The magnetic angle-changing technique, however, physically separates these two beams: they have different energies and therefore are deflected by different amounts.

Figure 3 shows inelastic DCS measurements for the 2^3S , 2^1S , 2^3P and 2^1P states of helium (Cubrić et al, 1999) obtained using the magnetic-angle changing technique. These measurements appear to be the first over the full angular range for any target system. Figure 3 also shows measurements made at lower scattering angles and various theoretical results. Helium was chosen because of the central role it plays in theoretical studies and because it is widely used to normalise and calibrate experimental results obtained for more complex targets. The measurements have been put on an absolute scale using the accurate measurements of Trajmar et al (1992) and the CCC calculations of Fursa and Bray (1997). In general, agreement between theory and experiment for the DCS of the other states is good. There remain, however, substantial discrepancies, particularly at the angles that were previously inaccessible to experiment. The largest disagreements, by factors of 2-7, between experiment and theory occur at the lower impact energies and the highest scattering angles. Serious disagreement becomes apparent for the 2^3P results. For example, at 0° and 30eV the measured value is a factor of approximately 2 higher than the CCC results (Fursa and Bray) and a factor of 4 than the R-matrix results (Bartchat et al 1996), while at 180° and 30 eV the measured values are a factor of 4 higher than the calculated ones. This emphasises the importance of extending the experiments to higher angles to fully test the various theories.

5. Resonance studies

The formation of negative-ion states in electron scattering by atoms and molecules produces resonance structure in scattering cross sections. Their appearance at various scattering angles is determined by the contribution from potential, non-resonant scattering. The shapes give information about the symmetries of the states, while the analysis of the structures again gives important information about the partial waves involved and the phase shifts. Indeed, they give complementary information to that provided by the DCS measurements. Mielewska et al

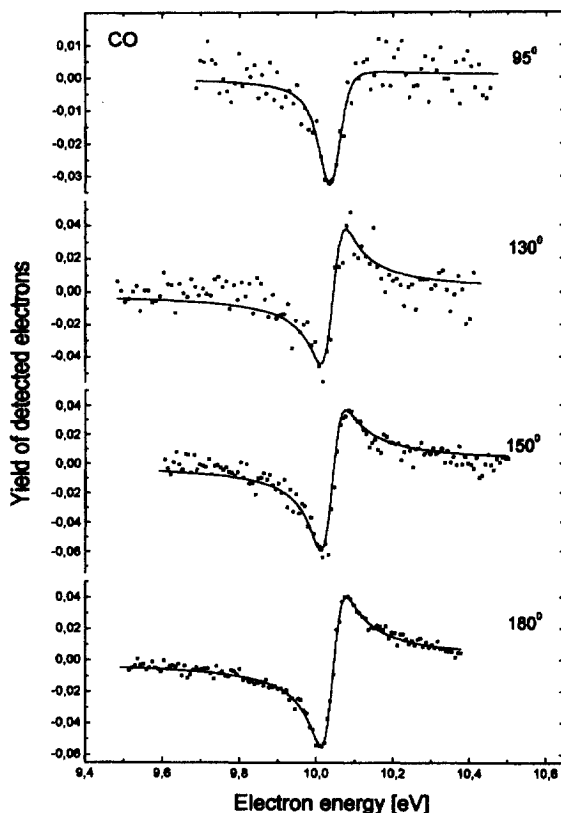


Figure 4. Resonance structures corresponding to the $(3s\sigma)^2\ ^2\Sigma^+$ state in carbon monoxide for various scattering angles. (Mielewska et al 1998)

(1998) have recently reported measurements for the $(3s\sigma)^2\ ^2\Sigma^+$ state in carbon monoxide at 10.044 eV and the $(3s\sigma_g)^2\ \Sigma$ state in nitrogen at 11.49 eV. These were made in the elastic scattering channel over the range 95° to 180° and were the first observations of the structures above 130°. The authors used the magnetic angle changing technique: electrons scattered at the interaction region over the angular range from 95° to 180° were observed when the analyser was rotated over the range from 25° to 118° with respect to the direction of the incident electron beam. A three-coil system was used to obtain a zero magnetic field at the interaction region. This minimised any degradation of the angular resolution of the measurements due to a finite magnetic field in the interaction region. Figure 4 shows the measured resonance structure for the $(3s\sigma)^2\ ^2\Sigma^+$ state in carbon monoxide. The underlying backgrounds to

these structures have been subtracted and the scale of the detected yield shows the size of the structure with respect to that of the (non-resonant) background. The observed structures were analysed to give a resonance width of 42 meV, in agreement with earlier estimates. In the lower-angle measurements the $^2\Sigma^+$ resonance appeared as a dip. The new measurements show that above 130° the peak develops on the high-energy side of the resonance structure to form a slightly asymmetric dip-peak feature. The shape and angular behaviour of the resonance support the $^2\Sigma^+$ symmetry of the resonance and also indicate the dominance of the s-wave in the potential scattering. As might be expected the behaviour is similar to that seen for the $2s^2\ ^2S$ resonance in helium where again the s-partial wave dominates (Brunt et al 1977). The width of the resonance has also been deduced from calculations of the resonance into two main channels, namely the $a^3\Pi$ and $A^1\Pi$ excited states (Pearson et al 1976) and a value comparable to the experimental one has been obtained.

6. Towards higher electron energies.

The curvature of the trajectory of a charged particle of kinetic energy, E , depends on the magnetic field as $B/E^{1/2}$. In its first applications, the angle changer used coils of wire to produce the localised magnetic field. However, the strength of the magnetic field that could be produced was constrained by overheating in the vacuum environment and this limited the maximum electron energy to about 50 eV. In many applications much higher energies are required, e.g. for doubly-excited states or for inner-shell excitation. For the higher magnetic field strengths required it is necessary to use magnetic materials in conjunction with the wire coils. This was done by Cubrić et al (2000) who used soft iron with a magnetic permeability of about 1000. The use of the iron cores multiplied the magnetic field by a factor of 5 while preserving field localisation. This enables electron energies 25 times larger to be handled.

The iron-cored system has been used to make electron energy loss studies of studies of the $n = 2$ states of helium and to obtain excitation functions for the 2^3S and 2^1S states of helium in the backward direction (Cubrić et al, 2000). Prominent structures in the excitation function spectra were observed between 56 and 59 eV at angles of 0° , 90° and 180° . These correspond to the triply excited negative-ion resonances $2s^22p\ ^2P$ and $2s2p^2\ ^2D$. These are the first measurements of these resonances at 180° .

7. Conclusions and suggestions for future applications of the magnetic angle changer.

In electron scattering, the magnetic angle changer opens up angular regions that were previously inaccessible. In general, in these newly exposed angular regions, i.e. at very large and very small angles, there are significant discrepancies between theory and experiment, typically by factors of 3 - 10. The technique opens up a new chapter in the interplay between experiment and theory that should improve our understanding of electron-atom/molecule interactions. The use of magnetic materials is increasing the available magnetic field strength of the technique so that higher electron energies are becoming accessible. These larger fields should also make it possible to handle heavier charged particles such as positive ions. Measurements of DCS test the magnitudes of the scattering amplitudes summed over magnetic sub-levels. Information about the individual scattering amplitudes including their relative phases can be obtained if the scattered electrons are measured in coincidence with dipole radiation arising from the excited atoms. Such experiments have already provided a wealth of information yielding electron-impact coherence parameters as described elsewhere in this volume. Again, however, the angle of observation of the scattered electron has been confined to angles below about 120° . The extension of the magnetic angle technique to electron-photon coincidence studies promises a wealth of new information and new physics.

Acknowledgments

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MECHANISMS OF PHOTO DOUBLE IONIZATION OF HELIUM BY 530 EV PHOTONS

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Abstract We have measured fully differential cross sections for photo double ionization of helium 450 eV above the threshold using the COLTRIMS technique. We have found an extremely asymmetric energy sharing between the two electrons and an angular asymmetry parameter $\beta \simeq 2$ for the fast electrons and $\beta \simeq 0$ for the slow electrons. The asymmetric energy sharing together with the asymmetry parameter $\beta \simeq 2$ for the fast electron indicate that the fast electron absorbs not only most of the photon energy but also its angular momentum. The electron angular distributions show that the very slow electrons (about 2 eV) are emitted isotropically with a slight backward emission to the momentum of the fast electron which is expected from the shake-off mechanism. At the same time, the slow electrons at higher energies are mostly emitted at 90 degree to the fast electron indicating an (e,2e) like collision between the two electrons. All our data are in good agreement to CCC calculations.

How does a single photon lead to emission of two electrons from an atom? This problem has been intensely discussed in the literature. Most of this discussion has been concentrated on the photo double ionization (PDI) of the helium atom which is the simplest single-photon-two-

electrons process (see [Mcguire95] and [Briggs00jpb] for reviews). Two mechanisms seem to be responsible for the PDI: The shake-off is a relaxation of the correlated initial state onto the new He^+ eigenstates after a sudden removal of one electron. It is generally believed that the shake-off mechanism makes the largest contribution to PDI at high photon energies, because the shake-off requires a certain excess energy which enables the first atomic electron to leave the atom quickly enough to produce the sudden change in the effective nuclear charge. In contrast, close to the threshold, the PDI is dominated by the process which is called two-step-one (TS1): one electron absorbs the photon and knocks out the second electron in an (e,2e) like collision. The dominance of the TS1 mechanism near the threshold is supported by the experimental observation of [Samson90] that the ratio of the total double to total single ionization cross-sections is proportional to the cross section for electron impact ionization of the He^+ ion from the threshold up to an excess energy of about 200 eV. In the high photon energy limit, however, the ratio of the total double to total single ionization of helium converges to a constant $R = 1.67\%$. This limit R is theoretically expected for the shake-off mechanism, see [Levin91,Spielberger95prl].

Fully resolved triple differential cross sections (TDCS) are necessary for detailed experimental and theoretical studies of the angular and energy correlation between the two photoelectrons or, equivalently, one photoelectron and the recoiling ion [Briggs00jpb]. The PDI-studies which were reported so far, however, are limited to relatively low photon energies where the shake-off mechanism is believed to be not significant. Additionally, in this low energy regime the angular distributions and the energy sharing are determined almost entirely by the long range Coulomb repulsion of the photoelectrons and the dipole selection rules, which completely hide the signatures of particular ionization mechanisms.

We present experimental data and theoretical calculations of PDI of helium at 529 eV photon energy where the shake-off yields a significant contribution. We show later that characteristics of the shake-off and TS1 can be clearly seen in the TDCS: very slow electrons with an energy of about 2 eV are mainly produced by the shake-off while 30 eV electrons get into the continuum through the TS1. This confirms a theoretical prediction of [Teng94] who found that at high photon energies the ionization mechanism would leave clear signatures in the angular distribution of the two electrons.

The experiment has been performed using the COLTRIMS technique (see [Doerner00pr] for a general review and [Doerner96fullydiff, Doerner98pra] for application to synchrotron radiation). The photon beam

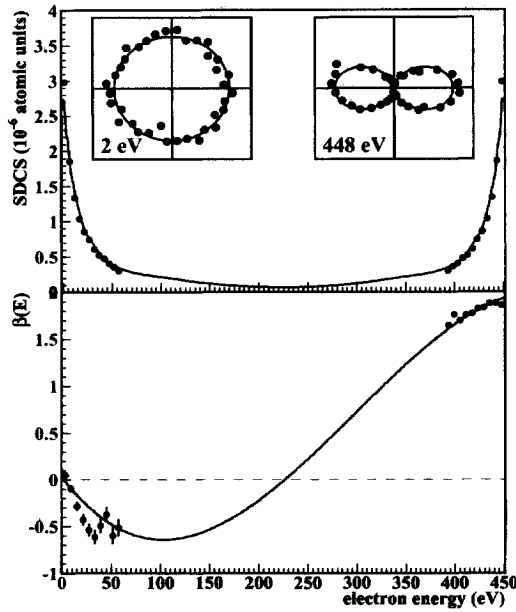


Figure 1. PDI of He at $\hbar\omega = 529$ eV. a) Presented is the single differential cross section $d\sigma/dE$. The dots are the experimental data, the line is the CCC calculation. The insets show the DDCS $d\sigma^2/(d\Omega dE)$ at $E = 2$ eV and 448 eV (the vertical axis is the light propagation). The experimental data are normalized to the CCC calculation. b) The asymmetry parameter β is plotted versus the electron energy. The line is a polynomial fit through the CCC calculated β parameters.

($\hbar\omega = 529$ eV) from beamline 4 of the Advanced Light Source (ALS) at the Lawrence Berkeley National Laboratory is focussed into a supersonic helium gas jet. Electrons of an energy below 60 eV are collected with 4π by a combination of electric and magnetic fields onto a large area position sensitive channel plate detector [Roentdek]. Also, the electric field guides the ions with 4π solid angle for all momenta onto a second position sensitive detector. From the time-of-flight and the position of impact the momentum vector and the charge state of the charged particle is deduced [Moshhammer95nim]. The momentum vector of the fast electron is calculated from the measured slow electron and the recoiling ion using momentum conservation.

In the following paragraphs we present the experimental evidence for a two-step picture in which one electron absorbs the photon energy and also its angular momentum and, subsequently, the second electron is ei-

ther shaken off or knocked out. We find an extremely asymmetric energy sharing and an angular asymmetry parameter $\beta \simeq 2$ for the fast electron and $\beta \simeq 0$ for the slow electron. We investigate the angular correlation between the photoelectrons and find that the angular distributions of the very slow electrons show a slight backward emission relative to the fast electron as expected from the shake-off. At the same time, the slow electrons at higher energy ($E_2 = 20$ eV and above) are mostly emitted at 90° to the momentum of the fast electron indicating that a binary electron-electron collision is necessary to transfer the energy.

Our experimental findings are supported by a series of convergent close coupling (CCC) calculations (see [KB98b] for details). In our model the fast photoelectron of energy E_1 is described by a Coulomb wave whereas the slow photoelectron of energy E_2 is represented by a positive energy pseudostate of the He^+ ion. We can identify the shake-off mechanism by calculating the dipole matrix element between a highly correlated ground state wave function and a product of the Coulomb wave E_1 and the pseudostate E_2 . In contrast, the TS1 mechanism requires the inelastic scattering of the fast electron on an eigen- or pseudostate of the ion. The amplitude of this process is given by a non-diagonal element of the scattering T -matrix. On the other hand, the diagonal part of the T -matrix describes the elastic electron scattering in which the quantum state of the slow electron does not change. The only result of this elastic scattering can be seen in the distortion of the Coulomb wave representing the fast electron, and so has to be attributed to the shake-off mechanism [Kheifets01jpb].

We calculate a series of cross-sections starting from the most detailed TDCS $d^3\sigma/(d\Omega_1 d\Omega_2 dE_1)$. Integrating the TDCS over $d\Omega_2$ leads to the double differential cross-section (DDCS) which gives the energy and angular distribution of one photoelectron integrated over all the angles of the second electron. By assuming the dipole approximation the DDCS can be written as [A90]

$$\frac{d^2\sigma}{d\Omega dE} = \frac{d\sigma}{dE} \frac{1}{4\pi} \left[1 + \beta(E) \left(\frac{3}{2} \cos^2 \vartheta - \frac{1}{2} \right) \right]. \quad (1)$$

$d\sigma/dE$ is the single differential cross-section (SDCS) which describes the energy sharing distribution between the two photoelectrons, β is the angular asymmetry parameter and ϑ is the polar angle of the electron with respect to the polarization axis of light.

The upper image of Figure 1 shows the measured and calculated SDCS. The measured data resented by the dots are well reproduced by the calculated CCC curve which has a characteristic U-shape and peaks sharply at 0 eV and 450 eV. This extreme asymmetric energy sharing

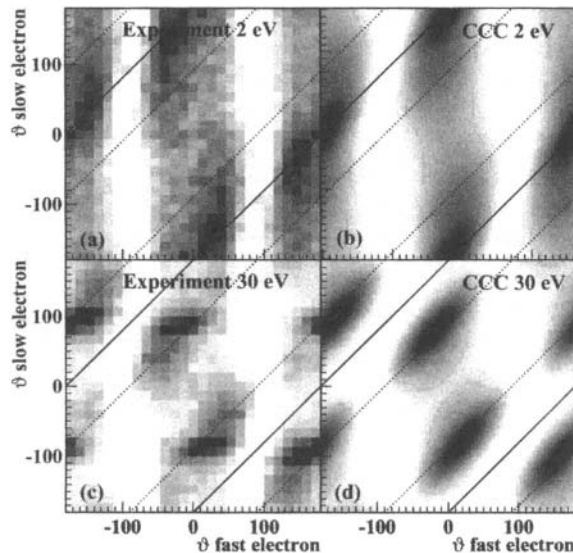


Figure 2. Overview of the TDCS of the PDI of Helium at 450 eV excess energy [(a) and (c) experiment, (b) and (d) CCC calculation] and coplanar emission for electron energies between 0 - 3 eV for the slow electrons (this means 447 - 450 eV for the fast electron) (a,b) and 20 - 40 eV (410 - 430 eV for the fast electron, respectively) (c,d). The horizontal axis shows the angle ϑ_1 of the fast electron with respect to the polarization vector, the vertical axis displays the angle ϑ_2 of the slow electron to the polarization vector. The full lines indicate the back-to-back emission $\vartheta_{12} = 180^\circ$ (the shake-off), the dashed line defines emission of the two electrons of an angle $\vartheta_{12} = 90^\circ$ as expected from the TS1 mechanism. Experimental data and theory are integrated over the same energy and angular range.

is in contrast to the SDCS near the threshold, where there are mostly symmetric sharing of the energy of the two electrons.

The bottom panel of Figure 1 shows the measured and calculated β parameter versus the electron energy. We find an angular asymmetry parameter $\beta \simeq 2$ for the very fast electrons (450 eV) and $\beta \simeq 0$ for the very slow electrons (0 eV). A very asymmetric energy sharing together with an angular asymmetry parameter $\beta \simeq 2$ indicate that the fast electron absorbs not only most of the photon energy but also its angular momentum. This suggests an interpretation of the PDI as a two-step process with the fast electron being the primary photoelectron. Two examples of the experimental DDCS at $E = 2$ eV and 448 eV are shown in the insets together with the line obtained from Eq. (1), using CCC calculations of the SDCS and β .

To learn more about the mechanism by which the second electron is emitted an overview of the TDCS of both electrons is given in Figure 2. The horizontal axis shows the polar angle ϑ_1 of the fast electron with respect to the polarization, the vertical axis displays the angle of the slow electron to the light polarization ϑ_2 . Both electrons are chosen to be coplanar, i.e. the slow electron is within $\pm 35^\circ$ in the plane defined by the fast electron and the polarization axis. The fast electron has almost no intensity at $\vartheta_1 = 90^\circ$ reflecting a β parameter of close to 2, see Eq. (1). The two left panels show the experimental data whereas the corresponding right panels exhibit the TDCS from the CCC calculations. Good agreement between theory and experiment can be found for all angles at both energy spreadings.

In these two-dimensional plots the typical characteristics of the shake-off and TS1 mechanisms can be clearly identified. For the shake-off one would expect that the slow electron is emitted isotropically or slightly backwards to the fast primary electron. The locus of such events is indicated by the full line $\vartheta_{12} \equiv |\vartheta_1 - \vartheta_2| = 180^\circ$. The TS1 is, in contrast, a binary encounter between two electrons, i.e. two particles of equal mass, hence one expects it to peak at $\vartheta_{12} = 90^\circ$. This is indicated by the dashed line also in Figure 2. At an electron energy $E_2 = 2$ eV of the slow electron the maximum of the TDCS follows closely the $\vartheta_{12} = 180^\circ$ lines supporting that such slow electrons are produced predominantly via shake-off. At an electron energy of $E_2 = 30$ eV the maxima are clearly along the lines with $\vartheta_{12} = 90^\circ$, indicating that higher energy electrons are produced predominantly via a binary encounter between the two electrons. This means we have a switch from the shake-off to a binary collision with higher energies of the slow electron. A significant energy transfer from the primary to the secondary electron seems to require a binary collision and does not likely occur via the shake-off mechanism. It can be noted from the U-shaped SDCS (figure 1) that the contribution of the slow shake-off electrons to the total cross section is by far dominant over the electrons of 30 eV and higher. Thus the total PDI cross section is dominated by the shake-off process [Kheifets01jpb].

For a closer inspection and a detailed comparison with theory we have plotted a small subset of the experimental data shown in Figure 2 as polar plots (figure 3). In all cases one of the two electrons has been fixed into the direction within 10° of the linear polarization. The energy and direction of this electron is indicated by the number (energy) at the arrow (direction); the TDCS of the complementary electron is plotted. Thus data from figure 2 within the range $-10^\circ < \vartheta_1 < 10^\circ$ appear in Figure 2 (b) and (d), and in the range $-10^\circ < \vartheta_2 < 10^\circ$ are shown in Figure 2 (a) and (c). The TDCS for electrons $E_2 < 3$ eV (figure 3b) has a pear-like

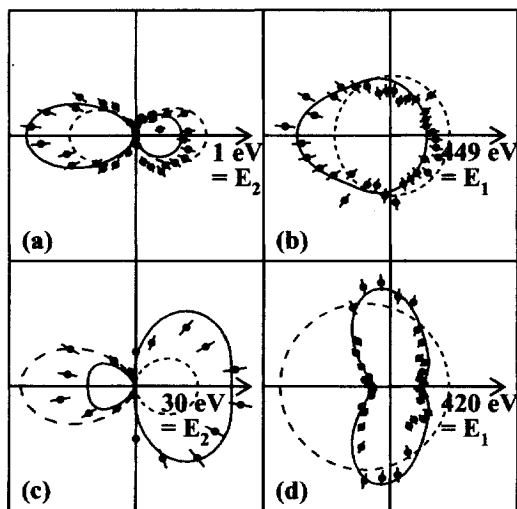


Figure 3. TDCS of the He PDI at 529 eV photon energy are presented. In all panels the electrons are coplanar within $\pm 25^\circ$, the polarization axis is horizontal. The direction and the energy of one of the two electrons is fixed as indicated by the number and the arrow, i.e. the slow electron is fixed in panels (a) and (c) and the fast electron is fixed in (b) and (d). The polar plots show the angular distribution of the complementary electron. The upper panels (a) and (b) are for the case $E_2 \simeq 2$ eV; the lower panels have $E_2 \simeq 30$ eV. The solid line is a full CCC calculation, the dashed line is a shake-off only CCC calculation. The measurements are normalized to the full CCC calculation. The shake-off calculation on the left side in (c) is multiplied by 0.4. The measurements and calculations are integrated over the same angular and energy ranges. a) $447 < E_1 < 450$ eV, $-10^\circ < \vartheta_1 < 10^\circ$, b) $0 < E_2 < 3$ eV, $-10^\circ < \vartheta_2 < 10^\circ$, c) $410 < E_1 < 430$ eV, $-10^\circ < \vartheta_1 < 10^\circ$, d) $20 < E_2 < 40$ eV, $-10^\circ < \vartheta_2 < 10^\circ$.

shape peaked at 180° to the fast electron. Contrary to all TDCS reported at lower photon energies so far, these slow electrons show a significant intensity for parallel emission into the same direction. This is possible because of the very asymmetric energy sharing of the two electrons. The solid line is a full CCC calculation which is in excellent agreement with the measurements. The dashed line is the CCC calculation representing the shake-off in which only the diagonal part of the T -matrix is retained. For the TDCS of the fast electron ($E_1 > 447$ eV) we see a dipolar shape (Figure 3a) with the lobe for parallel emission into the same direction of the electrons being slightly suppressed.

The TDCS for slightly faster electrons which have an energy of $E_2 \simeq 30$ eV (figure 3 c,d) are completely different from the low energetic ones. We find emission of the slower electrons into a narrow cone at 90° to the faster electron (figure 3 d), which is expected from a binary collision between the two electrons. Again the full CCC calculation is in very good agreement with the measurements. Since the fast electron peaks parallel to the polarization, the 90° angle between the electrons also leads to a slightly negative β at these electron energies (see Figure 1b).

In conclusion, we have presented experimental and theoretical TDCS of the PDI of helium at the photon energy $\hbar\omega = 529$ eV (excess energy of 450 eV above the double ionization threshold). At such a high excess energy, with highly asymmetric energy sharing of the two electrons we may think of the fast and slow electrons as being distinguishable. The angular distributions of the two electrons indicate that the very low energy secondary electrons are mostly emitted via the shake-off process while higher energy transfer requires a hard binary collision and leads to an angle of 90° between the momenta of the two electrons.

Acknowledgments

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EXCHANGE EFFECTS IN THE OUTER SHELL IONISATION OF XENON

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1. INTRODUCTION

In $(e, 2e)$ experiments an electron is scattered by a target, which could be an atom, an ion, a molecule, a cluster or even a solid, ionises it and both electrons are then detected in coincidence.

The central observable in $(e, 2e)$ experiments is the triple differential cross section (TDCS)

$$\frac{d^3\sigma}{d\Omega_1 d\Omega_2 dE_2},$$

which is a measure of the probability that an incident electron of momentum $\mathbf{k}_0$ and energy E_0 produces two electrons of energy and momenta E_1, E_2 and $\mathbf{k}_1, \mathbf{k}_2$ in the solid angles $d\Omega_1(\theta_1, \phi_1)$ and $d\Omega_2(\theta_2, \phi_2)$ respectively. These *kinematically complete* experiments are almost at the limit of what is quantum mechanically knowable. For reviews about this field see e.g. Ehrhardt *et al.* (1986), Byron and Joachain (1989), Whelan *et al.* (1993, 1997, 1998) and Nakel and Whelan (1999).

If one would be able to perform $(e, 2e)$ measurements where the spin of the projectile and the angular momentum state of the target were prepared and the spin quantum numbers of both final state electrons were measured (which is not yet possible), the experiment would be *quantum mechanically complete*. By using polarised electrons, one makes a first step towards a quantum mechanically complete experiment and gains an additional observable, the spin-up/spin-down asymmetry A

$$A = \frac{d^3\sigma(\uparrow) - d^3\sigma(\downarrow)}{d^3\sigma(\uparrow) + d^3\sigma(\downarrow)}.$$

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Conventionally, one would expect a non-vanishing spin asymmetry to be caused either by relativistic spin-orbit coupling in the continuum (as in elastic electron scattering), or by exchange between projectile and target electrons. In recent years, a number of ($e, 2e$) measurements with polarised beams have been performed in the middle energy range (40 - 200 eV) for the outer shells of xenon in Canberra (Jones *et al.* (1994), Guo *et al.* (1996), Dorn *et al.* (1997)) and Münster (Mette *et al.* (1998)). These xenon experiments were motivated by the idea of searching for a possible third reason for a non-vanishing spin asymmetry, the so called fine structure effect, an effect well known from inelastic scattering (Hanne (1983)). Xenon was particularly attractive as target because the $5p_{1/2}$, $E_b = 13.44$ eV and $5p_{3/2}$, $E_b = 12.13$ eV orbitals fulfil one important prerequisite for the fine structure effect, namely that the fine structure splitting be experimentally observable.

Comparison of the experimental data with semirelativistic distorted wave Born (SRDWBA) (Mazevet *et al.* (1998)) and nonrelativistic DWBA (DWBA) (Madison *et al.* (1998)) calculations showed quite good agreement for a major part of the experimental data. However, there remained some discrepancies between experiment and theory and the question was raised if these differences could be attributed to relativistic effects not included in the SRDWBA, like continuum spin-orbit coupling of the electrons moving in the field of the rather heavy xenon nucleus ($Z = 54$).

Another open question concerned the influence of the distorting potentials on the TDCS and the spin asymmetries. Both, the DWBA and the SRDWBA, found that the inclusion of the Furness-McCarthy (FM) (Furness and McCarthy (1973)) potential in their calculations was of crucial importance for the understanding of most of the measured data. The FM potential is an energy-dependent effective potential, aiming at the description of exchange effects between the projectile and the target electrons, the projectile target exchange (PTX).

In this contribution we present a fully relativistic DWBA (RDWBA) study (see Keller *et al.* (1994), Ancarani *et al.* (1998), Nakel and Whelan (1999) and Lechner *et al.* (2001)) including the exact exchange between the target electrons, the intra target exchange (ITX), and neglecting the PTX. We can give a definite answer concerning the importance of relativistic effects and we are able to study the influence of the exact ITX on the measured quantities.

2. THEORY

The main task in the computation of an $(e, 2e)$ cross section lies in the evaluation of the (squared) T -matrix element

$$\frac{d^3\sigma_{(e,2e)}}{d\Omega_1 d\Omega_2 dE_2} = (2\pi)^4 \frac{k_1 k_2}{k_0} \frac{E_0 E_1 E_2}{c^6} \frac{1}{2} \sum_{\epsilon_0 \epsilon_1 \epsilon_2 \epsilon_b} |T(k_1 \epsilon_1, k_2 \epsilon_2; k_0 \epsilon_0, \kappa_b \epsilon_b)|^2. \quad (1)$$

where the quantum numbers $\epsilon_{i,b}$ denote the spin and angular momentum projections of continuum and bound electron states.

As the RDWBA has originally been designed for the description of $(e, 2e)$ ionisation events by relativistic electrons on the inner shells of heavy atoms it is founded on Quantum Electrodynamics (QED) in the Furry picture. Within this formalism one retains the influence of the external potential (nucleus plus target electrons) to all orders while the electron-electron interaction of the two active electrons is treated in first order perturbation theory.

Written out explicitly, the direct and the exchange T -matrix elements of the RDWBA approach are given by (with the notation conventions of Itzykson and Zuber (1980))

$$\begin{aligned} T &= T^{\text{dir}} - T^{\text{ex}} \\ &= \int d^3r \bar{\psi}_{\mathbf{k}_1, \epsilon_1}^{(-)}(\mathbf{r}) \gamma^\mu \psi_{\mathbf{k}_0, \epsilon_0}(\mathbf{r}) \\ &\quad \times \int d^3r' D_{\mu\nu}^0(\mathbf{r} - \mathbf{r}') \bar{\psi}_{\mathbf{k}_2, \epsilon_2}(\mathbf{r}') \gamma^\nu \psi_{\kappa, \epsilon_b}(\mathbf{r}') \\ &\quad - \int d^3r \bar{\psi}_{\mathbf{k}_2, \epsilon_2}(\mathbf{r}) \gamma^\mu \psi_{\mathbf{k}_0, \epsilon_0}(\mathbf{r}) \\ &\quad \times \int d^3r' D_{\mu\nu}^0(\mathbf{r} - \mathbf{r}') \bar{\psi}_{\mathbf{k}_1, \epsilon_1}(\mathbf{r}') \gamma^\nu \psi_{\kappa, \epsilon_b}(\mathbf{r}') \end{aligned} \quad (2)$$

The wave function for the bound electron $\Psi_{\kappa, \epsilon_b}$ is an exact solution of the Dirac equation with an atomic OPM-potential (see subsection 2.1), while the continuum or distorted waves $\Psi_{\mathbf{k}, \epsilon}^{(\pm)}$ are elastic scattering eigenfunctions of the Dirac equation also with the same atomic OPM potential for the incoming and outgoing electrons.

One might argue that a long range potential like the OPM potential is not the adequate choice for the description of the incoming electron, i.e. the projectile in the field of a neutral atom. However, it is clear that using different potentials in the entrance and exit channels could introduce spurious contributions due to the nonorthogonality (caused by the different Hamiltonians) of the in- and outgoing electrons. To avoid

such spurious contributions we decided to apply the long range potential to the calculation of all three continuum electrons.

The above T -matrix elements are evaluated numerically by using the partial wave decomposition of the continuum electrons, exploiting that the Dirac equation separates in spherical coordinates. Furthermore, we make use of a multipole expansion of the photon propagator, for details see Keller *et al.* (1994).

A density matrix formalism to deal with the polarised electrons has been developed by Keller *et al.* (1996).

2.1 Distorting Potentials - Density Functional Theory

In our approach, the effective potentials applied to the calculation of the distorted waves and the bound state are calculated in the framework of density functional theory (DFT), see Dreizler and Gross (1990), which allows the mapping of the interacting N -electron problem onto an effective one particle problem .

We are especially interested in the relativistic (Engel *et al.* (1995)) version of implicit density functionals (Engel and Dreizler (1999)), which allow an exact treatment of exchange and relativistic effects via the relativistic optimised potential method (OPM), Engel *et al.* (1998).

The self-consistent solution of the relativistic Kohn Sham (KS) equations

$$\{-i\alpha \cdot \nabla + \beta mc^2 + \alpha_\mu v_{KS}^\mu(\mathbf{r})\} \phi_k(\mathbf{r}) = \epsilon_k \phi_k(\mathbf{r})$$

yields the Kohn Sham spinors ϕ_k from which the four current (or, in the nonrelativistic limit, the density) is constructed:

$$j^\mu(\mathbf{r}) = \frac{1}{2} \left[\sum_{\epsilon_k \leq \epsilon_F} \bar{\phi}_k(\mathbf{r}) \gamma^\mu \phi_k(\mathbf{r}) - \sum_{\epsilon_F < \epsilon_k} \bar{\phi}_k(\mathbf{r}) \gamma^\mu \phi_k(\mathbf{r}) \right] .$$

A closer inspection of the Kohn Sham potential $v_{KS}^\mu(\mathbf{r})$ shows that all the complicated many body effects are hidden in the exchange-correlation (xc) potential, which is the crucial quantity in DFT:

$$v_{KS}^\mu(\mathbf{r}) = v_{\text{nuc}}^\mu(\mathbf{r}) + v_{\text{H}}^\mu(\mathbf{r}) + v_{\text{xc}}^\mu(\mathbf{r}).$$

The xc potential itself is given by the functional derivative of the xc energy $E_{xc}[j]$ with respect to the four current $j^\mu(\mathbf{r})$

$$v_{\text{xc}}^\mu(\mathbf{r}) = \frac{\delta E_{\text{xc}}[j]}{\delta j_\mu(\mathbf{r})}$$

In the x-only limit, E_x is given by the Fock term, replacing the Hartree Fock orbitals by their KS counterparts,

$$E_x = -\frac{e^2}{2} \int d^3r \int d^3r' \sum_{\epsilon_k, \epsilon_l \leq \epsilon_F} \frac{\phi_k^*(\mathbf{r})\phi_l(\mathbf{r})\phi_l^*(\mathbf{r}')\phi_k(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

Expressing the functional derivative of E_x via KS orbitals rather than the four current and solving the resulting OPM equations self-consistently together with the KS equations yields a multiplicative (in contrast to Hartree Fock) v_x^μ which for large r behaves like $-\frac{e^2}{r}$. This asymptotic behaviour just reflects the exact cancellation of the self-interaction arising in the Hartree term.

In the standard DFT approach, i.e. the local density approximation (LDA) (Vosko *et al.* (1980)), a model relying on the homogeneous electron gas, cancellation of the self-interaction is incomplete and the potentials show the wrong asymptotic behaviour.

To illustrate these statements, we show two (semi-logarithmic) plots of the various components of the potential times the radial coordinate r as a function of r .

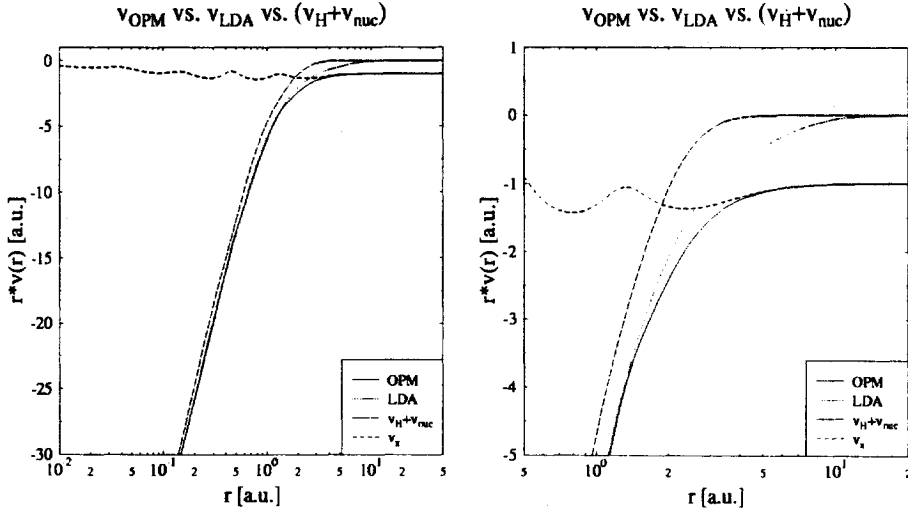


Figure 1. Semilogarithmic plots of different effective potentials times the radial coordinate. Note the different x-range.

While OPM and LDA potential look rather similar in the core region, the asymptotic behaviour is clearly different. But it is primarily the asymptotic form of the potential that determines the description of the outgoing electrons, as has been demonstrated in the case of ion-atom

collisions by Kirchner *et al.* (1997).

To highlight the difference between our approach to the distorting potentials and the effective potential methods usually applied in DWBA models like the SRDWBA, we briefly describe the main features of those standard (non-DFT) effective potentials.

2.2 Non-DFT Approach

The potential describing the target electrons and the nucleus is calculated by taking the atomic wavefunction from a Hartree- or Dirac Fock calculation. Calculating the corresponding density and solving the Poisson equation yields a local potential $v_H + v_{nuc}$. It is thus not obvious to which extent the ITX is included (or if it is included at all) in the resulting potential.

The usual way of incorporating exchange effects between the target electrons and the projectile (PTX) is the energy-dependent Furness-McCarthy potential, often applied in the following form:

$$U_{ex} = -\frac{1}{2} \left\{ (\epsilon_i - U_i) - \sqrt{(\epsilon_i - U_i)^2 - (-)^S 2\rho(r)} \right\}.$$

ϵ_i is the energy of incoming/outgoing electron, $U_i = v_H + v_{nuc}$ the scattering potential calculated via solution of the Poisson equation and ρ denotes the radial density of the bound orbitals. S stands for the total spin of the two electrons. This potential works quite well for high energies but it is well known that it breaks down for low energies (Winkler *et al.*, (1999)). It should be emphasised that this local exchange approximation is by no means exact.

We would like to emphasise again that PTX effects as modelled by the Furness-McCarthy potential are in no way included in our calculations.

3. Results

Although there have been measurements not only by the Weigold group in Canberra but also by the Münster group, we restrict ourselves to the experiments in coplanar asymmetric geometry from Canberra.

A discussion of the Münster experiments and the corresponding nonrelativistic and relativistic DWBA calculations can be found in Lechner *et al.* (2001) and Mette *et al.* (1998). To investigate the importance of relativistic effects for the measured quantities, we look at the relative relativistic correction,

$$R = \frac{d^3\sigma(rel) - d^3\sigma(nonrel)}{d^3\sigma(nonrel)}. \quad (3)$$

We calculated this quantity for all geometries considered with the fully relativistic RDWBA code and its nonrelativistic limit ($c \rightarrow \infty$) (but retaining a relativistic description of the bound state) and found that relativistic effects can be completely neglected for the continuum electrons. To illustrate this statement, we show R for the TDCS at an observation angle of $\theta_1 = 15^\circ$.

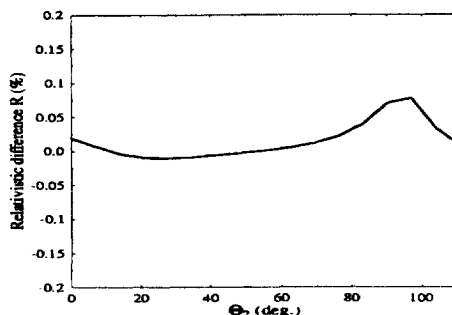


Figure 2. Relative relativistic correction for TDCS at $\theta_1 = 15^\circ$.

A short glimpse at fig. 2 makes already clear that all further investigations must concentrate on the choice of the effective potentials. However, we performed all our calculations presented here with the fully relativistic RDWBA code to treat continuum and bound electrons on equal footing.

Fig. 3 shows the triple differential cross sections and the branching ratio for the $J = \frac{1}{2}$ and $J = \frac{3}{2}$ transitions for $\theta_1 = 15^\circ$.

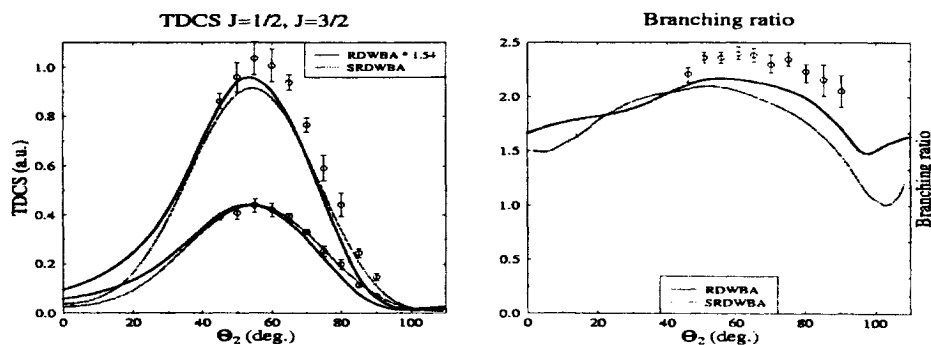


Figure 3. Triple differential cross sections and branching ratio for $\theta_1 = 15^\circ$. The experimental TDCS-data is normalised on the semirelativistic theory for $J = \frac{1}{2}$ and $\theta_2 = 55^\circ$. Solid line : RDWBA, dotted line: SRDWBA.

Both theories yield a good description of the experimental data. As the experimental results are normalised with respect to the semirelativistic DWBA, the comparison of the two DWBA models is difficult and one might wonder about the difference (a factor of 1.54) in the absolute size of the calculations.

So it is very instructive to have a look at the branching ratio B , which, defined as the ratio of the two cross sections, does not depend on any normalisation procedure

$$B = \frac{d^3\sigma(J = \frac{3}{2})}{d^3\sigma(J = \frac{1}{2})}.$$

The OPM-based RDWBA calculation is a little bit closer to the experimental data than the SRDWBA, although the difference is not very large.

For the spin asymmetries (fig. 4), both theories are again in good agreement with the experiment, the RDWBA again being superior to the SRDWBA.

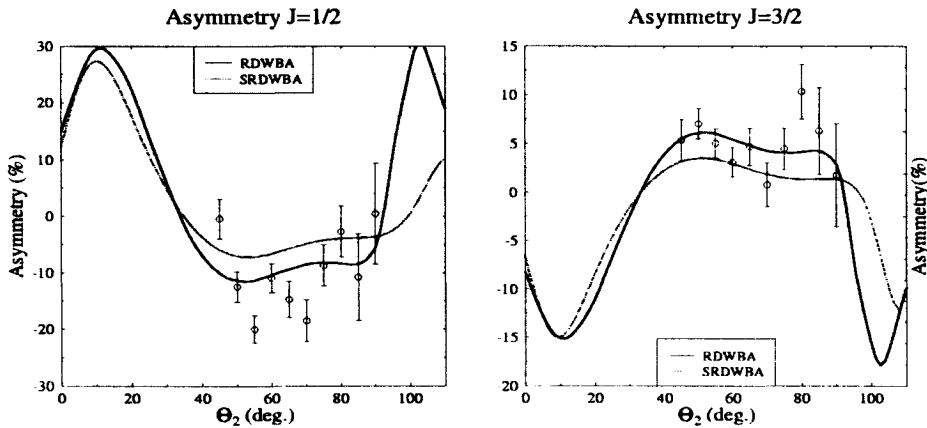


Figure 4. The asymmetry functions for transitions to the $J = \frac{1}{2}$ and $J = \frac{3}{2}$ final ion states. The fast electron angle is 15° .

To get an idea of the importance of the correct asymptotics, we replaced the OPM potential in the entrance and exit channels by a pure electrostatic potential, i.e. the sum of the nuclear potential and the electronic Hartree potential. So we neglected all quantum mechanical exchange effects (except for the description of the bound state before the ionisation process takes place) which is in a way the appropriate description of the incoming electron but clearly yields the wrong asymptotic behaviour in the outgoing channel. The spin asymmetries for the $J = \frac{1}{2}$ and $J = \frac{3}{2}$

transitions change dramatically by applying the electrostatic potentials to the calculation of the continuum electrons, the description of the experimental data clearly gets worse, see fig. 5. So it is obvious that the correct asymptotic behaviour of the distorting potential is very important for the description of the spin asymmetries.

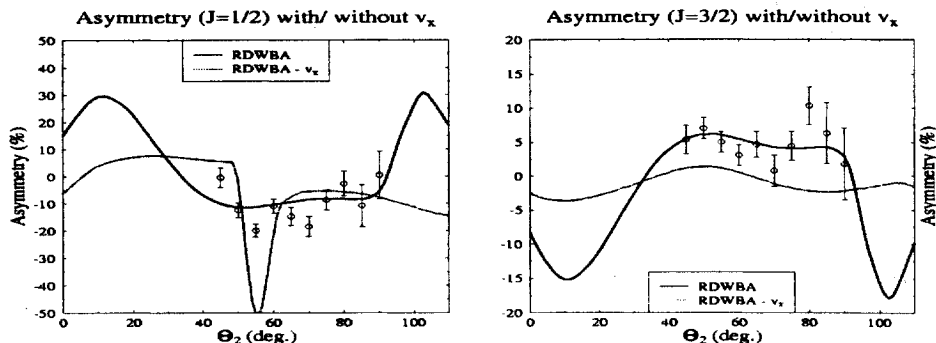


Figure 5. The spin asymmetries for the $\theta_1 = 15^\circ$ data, calculated with (solid line) and without (dotted line) the exact exchange potential v_x .

In fig. 6 we show the differential cross sections and the branching ratio for Bethe ridge conditions.

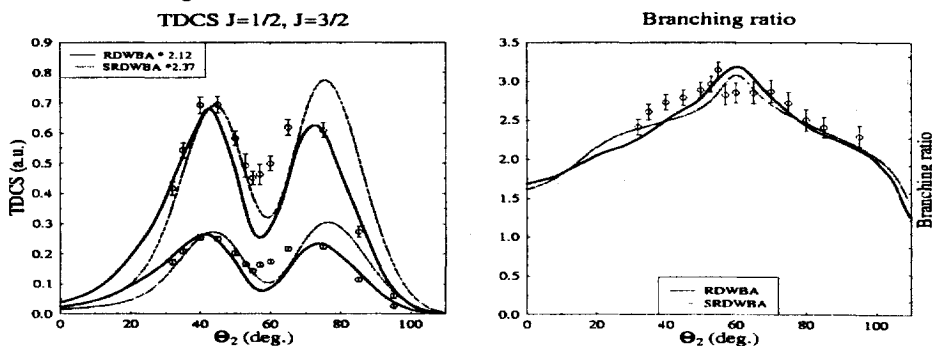


Figure 6. The unpolarised TDCS and the corresponding branching ratio for the $J = \frac{1}{2}$ and $J = \frac{3}{2}$ final states of the ion. Both theories are scaled by a multiplicative constant for $\theta_2 = 40^\circ$ at the $J = \frac{1}{2}$ transition for the TDCS.

The triple differential cross section, or more precisely, the split binary peak, shows the typical structure of a p -orbital, as should be expected for Bethe ridge conditions. Agreement between experiment and the calculations is rather good, but the ratio of the two maxima is better reproduced by the RDWBA. Whilst the experiment and the RDWBA have

the larger maximum for smaller θ_2 , the SRDWBA predicts the larger maximum for larger θ_2 .

We attribute this feature to the use of the different effective potentials. As already for the 15° data, the branching ratio is slightly better reproduced by the RDWBA including an OPM potential. The structure of the spin asymmetries (see fig. 7) is again satisfactorily reproduced by both calculations, although the agreement is worse than for 15° .

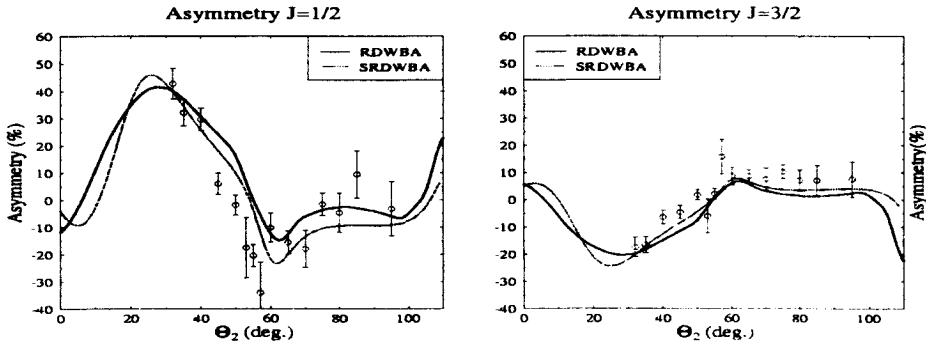


Figure 7. Spin asymmetries for $\theta_1 = 28^\circ$ for the $J = \frac{1}{2}$ and $J = \frac{3}{2}$ final ion states.

4. CONCLUSIONS AND OUTLOOK

The comparison of the fully relativistic RDWBA calculations with RDWBA calculations in the nonrelativistic ($c \rightarrow \infty$) limit unambiguously demonstrates that relativistic effects in the electronic continuum can be completely neglected for the experiments considered.

The dominant effect for the understanding of the triple differential cross sections, branching ratios and spin asymmetries is the correct asymptotic behaviour of the distorting potentials in the outgoing channels.

Neglecting the exact exchange potential, which ensures the right asymptotics, causes significant changes in the description of the spin asymmetries for an observation angle $\theta_1 = 15^\circ$.

A modelling of the projectile target exchange via the Furness-McCarthy potential is not necessary for an understanding of the experimental results.

Further investigations concerning the influence of the exact exchange would help to further clarify the situation.

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IONIZATION OF ATOMS BY ANTIPROTON IMPACT

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Abstract The theory of the ionization of atoms by antiproton impact is superficially similar to that for ionization by electron impact, indeed one of the possible time reversed processes is the ionization of protonium by electron impact. The large mass of the antiproton relative to the electron introduces key differences which have emerged in quantitative calculations. We have employed the advanced adiabatic approximation to compute ionization and protonium formation. Results are compared with classical trajectory Monte Carlo calculations.

Keywords: antiproton, protonium

Introduction

When antiprotons are trapped they undergo atomic reactions with background gases which remove them from the trap. They may lose energy by ionizing collisions with or without capture into bound states and subsequent annihilation by nuclear interactions. An understanding of these processes requires reliable cross sections for low-energy collisions of antiprotons with atoms.

At present ionization cross sections have been reported^{1,2,3} that are based on the semiclassical method that is essentially exact for energies above a few hundred eV when the projectile's mass is comparable to the proton mass. In this range, there are a wide variety of techniques that can be reliably employed to compute ionization cross sections. Im-

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portant for experiment, however, are energies in the 0-50 eV range. In this range one typically uses some sort of adiabatic representation for the electron motion and a wave treatment for the relative motion of the nuclei. This approach becomes problematical for antiprotons owing to protonium formation which is not represented in standard adiabatic bases. Only the hyperspherical representation is readily adapted to this region, however, the hyperspherical adiabatic method is impractical owing to the need for a large number of basis states that are difficult to compute. For that reason, the only protonium formation cross sections that are available at the present time employ some variant of the classical trajectory Monte Carlo method, since bound protonium orbits can evolve from collisions of antiprotons with atoms where the much lighter electrons are initially also in bound orbits.

In this manuscript we report calculations that directly employ the conventional adiabatic picture for electron motion in the collisions of antiprotons with hydrogen atoms. Of course, it is not possible to simply use an expansion in adiabatic eigenstates since there are no adiabatic eigenstates representing protonium channels. The advanced adiabatic theory, however, is able to represent such channels, as we will demonstrate. Essentially, the advanced adiabatic method derives from an exact Sturmian representation, given by Macek and Ovchinnikov⁴, of the full wave function for three particles interacting via electrostatic interactions. For that reason it must include all reaction channels, including protonium channels even though no protonium wave functions are included in the basis set. Even in the one-Sturmian approximation, which is crucial to the advanced adiabatic theory, all physical channels are included. Using this method we compute ionization and protonium formation in the energy region $0 < E < 25 \text{ keV}$. Atomic units are employed throughout this manuscript unless otherwise indicated.

1. Advanced adiabatic theory

The conventional adiabatic electron energies for an electron in the field of $p + \bar{p}$ in the separated atom limit are the Stark energy levels of the H-atom in the field of the antiproton. At some finite distance, called the Fermi-Teller radius $r_{\text{FT}} = 0.693\dots$, the electron just becomes bound in the finite dipole field of the $p, \bar{p}$ system. At the united atom limit, where the antiproton coincides with the proton, the electron nuclei potentials cancel and the electron is completely free. The ground state potential curve $\varepsilon(R)$ therefore moves into the continuum with decreasing internuclear separation.

The advanced adiabatic theory of Solov'ev⁵ employs the quantity $R(\varepsilon)$ inverse to $\varepsilon(R)$. This quantity is the solution of the equation $\varepsilon(R) = \varepsilon$. The complete three particle wave functions takes the form

$$\Psi(\mathbf{r}, \mathbf{R}) = \int_c A(\varepsilon) S(\varepsilon, \mathbf{r}/R) F_\varepsilon(\mathbf{R}) d\varepsilon \quad (1)$$

where the Sturmian function $S(\varepsilon, \mathbf{r}/R)$ relates to the adiabatic eigenfunction $\phi(R(\varepsilon), \mathbf{r}/R(\varepsilon))$ according to

$$S(\varepsilon, \mathbf{r}/R) = N(\varepsilon) \phi(R(\varepsilon), \mathbf{r}/R(\varepsilon)), \quad (2)$$

where $N(\varepsilon)$ is a normalization constant. Note that the physical radius $R = |\mathbf{R}|$ differs from the function $R(\varepsilon)$. Here the single adiabatic function is understood in the sense articulated by Demkov⁶. The coefficient $A(\varepsilon)$ is the solution of an ordinary differential equation and is known in closed form. The function $F_\varepsilon(\mathbf{R})$ describes the relative motion of the the proton and antiproton. Usually it will be computed in the WKB approximation as will be done here.

One feature of the inverse function $R(\varepsilon)$ is that the associated basis functions represents bound and continuum electrons. The relative motion in the coordinate R represented by $F_\varepsilon(\mathbf{R})$ can also describe bound or continuum states. In the final state the classical action for the heavy particle motion is

$$K_f(R) = \sqrt{2\mu \left(E - \varepsilon_{\mathbf{k}} - \frac{(L+1/2)^2}{2\mu R^2} + \frac{1}{R} \right)} \quad (3)$$

where $\varepsilon_{\mathbf{k}}$ is the energy of the ionized electron. If the quantity $E - \varepsilon_{\mathbf{k}}$ is negative, then the wavefunction in R satisfies acceptable asymptotic conditions only when the action takes on half integral multiples of π , i. e. the R motion is quantized according to

$$E - \varepsilon_{\mathbf{k}} = -\frac{1}{2} \frac{\mu}{n^2} + \varepsilon_{\mathbf{k}} \quad (4)$$

where $-\mu/(2n^2)$ is the binding energy of the n 'th state of protonium.

The advanced adiabatic theory emerges when the integral representation for Ψ is evaluated in for large r in the stationary phase approximation. For ionization processes, the coefficient of the product of outgoing waves for the electron and the $\bar{p}, p$ pair $\exp(ikr + iKR)$, where $K = \sqrt{2\mu E}$, is computed. When $E - \varepsilon_{\mathbf{k}}$ is negative this same coefficient becomes the amplitude for the rearrangement process

$$\bar{p} + H \rightarrow (\bar{p}, p)_n + e^- \quad (5)$$

up to a normalization constant. In this way one extracts the rearrangement amplitude even though no protonium states are included in the basis set.

There is little difference theoretically between ionization with and without protonium formation as is apparent from the continuity of ionization cross sections across the protonium threshold seen in classical trajectory Monte Carlo calculations^{1,3}. This allows a simple way to compute protonium formation in the advanced adiabatic theory, namely, we compute ionization without reference to the quantization of the protonium energies and then identify the cross section for negative values of $E - \varepsilon_{\mathbf{k}}$ with protonium formation. This is convenient for computations of total protonium formation cross sections, but by using the $\frac{dE}{dn}$ energy interval weighting, n -distributions can also be obtained. In this manuscript we report only total ionization and protonium formation cross sections.

The advanced adiabatic theory gives the probability for ionization $P(E, \varepsilon_{\mathbf{k}})$ as

$$P(E, \varepsilon_{\mathbf{k}}) = \left| \frac{dK(R_M)}{dE} C(\varepsilon_{\mathbf{k}}) \exp \left(i \int_{R_i}^{R_M} K(R) dR + i \int_{R_M}^{R_T} K_f(R) dR \right) \right|^2, \quad (6)$$

where

$$K(R) = \sqrt{2\mu \left(E - \varepsilon(R) - \frac{(L + 1/2)^2}{2\mu R^2} - 1/R \right)}, \quad (7)$$

and where R_i is a large value of R on the initial branch of $\varepsilon(R)$, R_T is the turning point in final channel, and R_M is the complex value of R where $\varepsilon(R) = \varepsilon_{\mathbf{k}}$, and $C(\varepsilon_{\mathbf{k}})$ is the coefficient of the outgoing electron wave $\exp(ikr)$ in the asymptotic Sturmian wave function. The quantities $\varepsilon(R)$ and $C(\varepsilon_{\mathbf{k}})$ are computed for complex values of R using the program of Ovchinnikov and Solov'ev⁷. These numerical values are used to compute the matching radius R_M and classical actions in Eq. (6).

At very low energies, antiprotons may be temporarily trapped in the combined polarization and centrifugal potentials

$$V_{\text{eff}} = \frac{L(L+1)}{2\mu R^2} - \frac{\alpha_p}{2R^4},$$

where $\alpha_p = 9/2$ is the polarizability of the hydrogen atom. The associated orbiting resonances can decay by electron emission thereby leading to protonium formation via a process similar to associative ionization in negative ion collisions. If one assumes unit probability for decay

via electron emission then one obtains an upper bound cross section σ_p for protonium formation given by $\sigma_p = \pi \sqrt{2\alpha_p/E}$, an estimate that is thought to exact for vanishingly small E .

2. Results

Our computed ionization cross sections are shown in Fig. (1) for energies between 10 eV and 100 keV. Also shown are the results of essentially exact solutions of the time-dependent Schrödinger equation in the straight line approximation³.

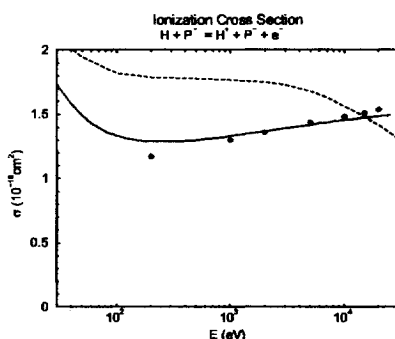


Figure 1 Computed cross sections for the ionization of hydrogen atoms by antiproton impact. Solid circles-exact TDSE and dashed curve-CTMC from Schultz *et al.*³, solid curve-advanced adiabatic.

The agreement between the advanced adiabatic theory and the "exact" results is very good over the energy range where the straight line approximation is expected to apply. Only at the lowest energy point (200 eV) do departures, of the order of 15%, between the theories appear. This good agreement gives us confidence in the application of the advanced adiabatic theory for the study of antiproton interactions.

The advanced adiabatic theory should be more reliable at the lower energies where the relative velocities of the heavy particles become much smaller than the electron velocities. In this region ionization occurs only by protonium formation. Figure 2 shows our protonium formation cross in the region below the protonium formation threshold at 27.21 eV. Also shown is the "upper limit" cross section σ_p . Our computed cross section is below this limit, as it must be.

Also shown are CTMC results of Schultz *et al.*³. The agreement of these results with the advanced adiabatic cross sections is very good for $5\text{eV} < E < 25\text{eV}$. Both results are larger than would be obtained by extrapolating the TDSE calculations into this region, indicating that orbiting probably plays an important role even though both calculations are below the "upper limit" orbiting cross section σ_p . The orbiting effect

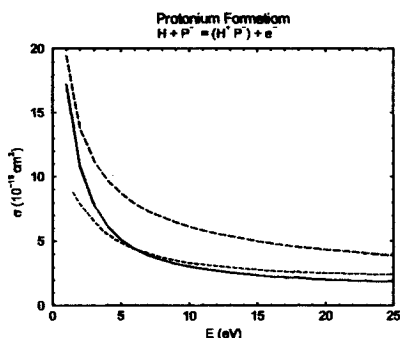


Figure 2 Cross sections for protonium formation. Short dash curve-CTMC from Schultz *et al*³, long dash curve-upper limit orbiting cross section, solid curve-advanced adiabatic.

is expected to become important as $E \rightarrow 0$. This trend is apparent in the advanced adiabatic calculations, but not in the CTMC results.

3. Summary and Conclusions

We have used the advanced adiabatic theory to compute ionization and protonium formation for low energy impact of antiprotons on atomic hydrogen. Our results agree with the TDSE calculations of ionization at energies above 300 eV, and with CTMC calculations of protonium formation in the energy range $5\text{eV} < E < 25\text{eV}$. Below 5 eV our cross sections rise above the CTMC results and approach a value indicative of capture via orbiting resonances.

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High resolution electron interaction studies with atoms, molecules, biomolecules and clusters

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Abstract: Ionisation and attachment by electrons are two of the most fundamental inelastic electron collision processes. Electron-impact ionisation/attachment processes are also important in many practical applications such as low-temperature plasma processing, fusion edge plasmas, planetary atmospheres, radiation chemistry and chemical analysis. Considerable progress in the experimental and theoretical description of electron-driven ionisation and attachment processes involving atomic and molecular targets has been achieved in the past decade, for instance concerning the quantitative determination of total and partial electron impact ionisation cross sections. Nevertheless, with respect to information about the finer details of this interaction, which has to come primarily from experimental studies, little is known due to the fact that experiments require the availability of electron beams of high quality in terms of electron energy resolution and accuracy.

The very recent development, refinement and application of new experimental techniques in our laboratories (novel types of molecular beam sources and high

resolution electron beam and mass spectrometry techniques, e.g., HEM-QM and TEM-QM allowing us to achieve in both routinely electron energy resolutions of about 30 to 50 meV at electron currents in the nA range, which are still high enough to carry out statistically relevant measurements for systems with low interaction cross sections) made this the ideal time for carrying out a coordinated series of experiments planned to attack the many open questions in this field. In this review we will first discuss the experimental set-up and techniques and then present some prototypical examples including (i) the determination of appearance energies and Wannier exponents for multiple ionisation of rare gases, (ii) isotope effects in the electron impact ionisation of H_2/D_2 and $\text{H}_2\text{O}/\text{D}_2\text{O}$, (iii) appearance energy, binding energy and structure of the ozone dimer and finally (iv) vibrational structure in the dissociative electron attachment to formic acid.

Key words: electron monochromator, appearance energy, binding energy, ionisation cross section law, electron attachment spectrum, molecules, dimers,

1. INTRODUCTION

Ionisation and attachment by electrons are two of the most fundamental inelastic electron collision processes. Electron-impact ionisation/attachment processes are also important in many practical applications, such as low-temperature plasma processing, fusion edge plasmas, planetary atmospheres, radiation chemistry and chemical analysis [1-3]. Considerable progress in the experimental and theoretical description of electron-driven ionisation and attachment processes involving atomic and molecular targets has been achieved in the past decade, for instance concerning the quantitative determination of total and partial electron impact ionisation cross sections [4]. Nevertheless, with respect to information about the finer details of this interaction, which has to come primarily from experimental studies, little is known due to the fact that experiments require the availability of electron beams of high quality in terms of electron energy resolution and accuracy.

The past few years we have constructed [5,6] and constantly improved (e.g., see [7,8]) two high-resolution crossed beams machines each including various molecular beam gas inlet sources, a high resolution electron gun and a quadrupole mass spectrometer (QM). One of these electron guns consists of a hemispherical electron monochromator (HEM) [5,7] and the other of a trochoidal electron monochromator (TEM) [6,8] allowing us to achieve in both routinely electron energy resolutions of about 30 to 50 meV (in special cases even a much higher resolution [9,10]) at electron currents (in the nA range), which are still large enough to carry out statistically relevant measurements for systems with low interaction cross sections.

This has enabled us to measure details of electron impact ionisation cross section functions and electron attachment spectra with high resolution,

high accuracy and high sensitivity. Results thus obtained and to be discussed here in an illustrative manner include

- (i) threshold laws and appearance energies for multiply charged rare gas ions,
- (ii) isotopic dependence of appearance energies for molecules,
- (iii) size dependence of appearance energies for atomic and molecular clusters; binding energy, and
- (iv) new resonances and structures in electron attachment spectra of molecules and clusters

In addition to a recently growing theoretical interest in the basics of the electron/atom and electron/molecule inelastic collisions (see as an example a recent solution to the problem of collisional break up in a quantum system of three charged particles – one ion, two electrons in the outgoing channel – by Rescigno et al.[11]), there are a number of areas of application where data for these basic ionisation processes are of utmost interest.

For instance, recent studies in the field of thermonuclear fusion based on the magnetic confinement of high temperature plasmas have demonstrated that the conditions at the plasma periphery („plasma edge“) play an important role for achieving, sustaining and controlling the thermonuclear fusion plasma [2,12]. In order to understand and elucidate the role of the radiative and collisional processes in this plasma edge region (in particular their influence on the plasma properties and dynamics and their use for controlling the plasma conditions) it is essential to have available a detailed and quantitative knowledge for these elementary processes such as cross sections, reaction rate coefficients etc. Because of the relatively low temperature in the plasma edge the plasma contains -besides electrons and atomic ions- also a significant number of neutral atoms and molecules, low-charged atomic and molecular impurities (produced and introduced for instance via plasma/wall interactions, via diagnostics or via cooling). The most important collision processes (from a standpoint of their effects on plasma edge properties and behaviour such as ionisation balance, plasma energy, plasma transport etc.) are electron impact excitation/ionisation reactions with plasma edge atoms, ions and molecules [2]. The impurities present in such an edge plasma obviously will depend on the materials used for the plasma facing components (first wall, protective tiles, divertor plates, antennas for rf heating etc.) and on the gases introduced for cooling and diagnostic purposes, nevertheless Janev [2] has given a list of atomic and molecular impurities to be considered in such studies including the rare gases, Li, Be, B, C, Al, Si, Mg, Ti, Cr, Fe, Ni, Cu, Mo, Nb, Ta, W, and CO, CO₂, CH₄, C₂H₂, C_nH_m, H₂O. Some of these impurities may reach levels of about 1 to several percent of the plasma density. The most important impurity generating processes are according to Janev [2] thermal and particle-induced desorption and chemical sputtering from the walls. Carbon

based materials (such as graphite, carbon-carbon composites) are currently being used in most of the operating magnetic fusion devices as plasma facing materials. The reason for this is the low radiation power capacity and the capability to withstand high heat fluxes for these materials. These materials have also been included as one of the plasma facing materials in the divertor design of the International Thermonuclear Experimental Reactor (ITER) [13]. The interaction of hydrogenic plasma with carbon materials, however, results in production of a variety of hydrocarbon molecules C_xH_y (and also others) by for instance "chemical erosion" [14] which enter the plasma as molecular impurities. The composition of the erosion flux depends on a number of parameters such as the mass and energy of the bombarding species, the surface temperature, etc. At higher impact energies (appr. 30-500 eV) lighter hydrocarbon molecules are being produced and are the dominant species (up to CH_4 and C_2H_2), whereas at lower energies and in particular at hyperthermal energies at around 1 eV the heavier hydrocarbons (up to about C_3H_8) are being produced and become dominant (see [15]). Today's tokamaks tend to operate with divertor plasma temperatures of around and below 5 eV, thus lying in the range where also heavier hydrocarbon molecules are released from the surface. Once present in the plasma volume, a multitude of collision processes involving plasma electrons and plasma protons can proceed with these molecules [16]. Some of these processes lead to the dissociation of molecules and as a result of this hydrocarbon molecules will be present initially not produced by the erosion. As documented in several reviews (see [17]) the various collision processes of hydrocarbon molecules have been studied in the past only for a limited number of C_xH_y species and a limited number of processes. In particular differential characteristics are rather scarce. So even for well characterized conditions certain cross sections are missing, even more so for more complicated type of situations such as internally excited targets etc. This necessitates for modelling purposes the use of crude approximations or extrapolations.

Recently, formic acid has been identified as being present in the interstellar medium (ISM) [18,19] and been identified in the coma of the Hale-Bopp comet [20,21]. It has, therefore, been suggested that it may be a key compound in the formation of biomolecules such as acetic acid (CH_3COOH) and glycine (CH_3COONH_2) in the ISM. Glycine is the simplest biologically important amino acid, since all that is needed to form glycine is to combine acetic acid and ammonia. Amino acids are the building blocks of proteins and DNA. Thus, should it be possible to understand the formation mechanisms of amino acids in space, it may be possible to identify those regions in space where more complex, biologically important molecules might be located and hence where the conditions for the development of life exist. Interstellar dust grains are also thought to play a crucial role in

synthesizing complex molecular species like formic acid, acetic acid and glycine on the early Earth to help start prebiotic organic chemistry. However, we know remarkably little about the stability of these molecules to either UV radiation or electron bombardment, both prevalent in the interstellar medium and the Earth's atmosphere.

It is now generally assumed that the types of primary damage induced in DNA by ionising radiation leading to the most significant biological effects are double-strand breaks (DSB) and clustered lesions. Clustering of strand breaks and base damages formed where radiation tracks cross the DNA molecule are believed to have the greatest significance, a view is supported by experimental evidence coupled with information from modelling studies. The genotoxic effects of ionising radiation (α , β , γ , ions) in living cells are produced not only by the direct impact of the primary high energy projectiles, but, as demonstrated very recently by Sanche and co-workers [22], mutagenic, recombinogenic and other potentially lethal DNA lesions (double strand breaks) are also induced by *secondary species* generated by the primary ionising radiation, e.g., free electrons with low energies, typically below about 20 eV. Therefore, it is recognized that radiation action in bio-molecules cannot be described solely by the interaction of the primary encounter between radiation and the molecule involved, but that the simultaneous and consecutive action of the primary, secondary and tertiary species must be included in any quantitative consideration of radiation damage.

Therefore, we have initiated an experimental programme that will probe the effects of these (secondary low energy) electrons with atoms, molecules and clusters under isolated conditions prevalent in the single collisions that exist in the crossed molecular beam geometry adopted in the current experiments. These studies have been performed using several selected prototypical targets, including in the past two years besides rare gas atoms [23-26], molecules of atmospheric relevance (e.g., H_2 [27], H_2O [28], N_2O [29,30], O_3 [10,31], $OCIO$ [32], Cl_2O [32,33], C_3H_6 [34], C_3H_8 [35], SF_5CF_3 [36,37]), simple organic acids (e.g. formic acid [38,39], acetic acid [40], propionic acid [41]), simple nitrogen containing hydrocarbons (e.g. nitromethane [42], nitroethane [43], nitrobenzene [40], acetonitrile [40]) and the nucleic acid bases such as uracil [44,45] and chlorouracil [46]. The very recent development, refinement and application of new experimental techniques in our laboratories (e.g., novel types of molecular beam sources, high resolution electron beam and mass spectrometry techniques HEM-QM and TEM-QM [5-10]) made this the ideal time for carrying out a coordinated series of experiments planned to attack the many open questions in this field. In this review we will first discuss the experimental set-up and techniques (section 2) and then present some prototypical examples including (i) the determination of appearance energies and Wannier exponents for multiple

ionisation of rare gases (section 3.1), (ii) isotope effects in the electron impact ionisation of H_2/D_2 and $\text{H}_2\text{O}/\text{D}_2\text{O}$ (section 3.2), (iii) appearance energy, binding energy and structure of the ozone dimer (section 3.3) and finally (iv) vibrational structure in the dissociative electron attachment to formic acid (section 3.4).

2. EXPERIMENTAL

2.1 HEM-QM Apparatus

The HEM-QM apparatus developed and used in Innsbruck (Figure 1) has been described in detail in previous publications [5,7] so only the most salient details will be given here. The electron spectrometer consists of an electron gun, a collision chamber and an electron collector. The electrons are monochromatised using a standard 180° hemispherical analyser such that the spread of the electron energy distribution is decreased from about 500 meV to a final energy resolution of about 30 meV FWHM with an electron current of approximately 1 nA. In some of the reported experiments, however, due to the small quantities of sample and hence the low ion fluxes and due to the sometimes small cross sections it was necessary to select a higher electron current with a slightly poorer resolution of up to 100 meV. Ions formed in the collision region were extracted by a weak penetrating electrostatic field and subsequently analysed by a quadrupole mass spectrometer with a nominal mass range of 2000 amu. The ions were detected by a channel electron multiplier operated in pulse counting mode. Data acquisition during the experiments was controlled by a PC. The apparatus was configured such that it was easy to transfer between collection of anions (produced by dissociative electron impact) and cations. The incident electron beam resolution was therefore calibrated using the well known s-wave attachment cross section for the Cl^- anion formation from CCl_4 , while the energy scale in the low energy region was calibrated in addition (i) using the vertical high energy onsets for the production of O^- from CO and NO [47] and (ii) against the appearance energies of cations from the rare gases with an estimated accuracy of <10 meV. At higher impact energies the calibration was carried out using at around 60 eV the well known position and features of two triply excited $n = 2$ intrashell He^- resonances $(2s^2 2p)^2\text{P}$ and $(2s^2 2p)^2\text{D}$ in the electron impact He^+ cross section function at 57.06 and 58.15 eV (for details see [48]).

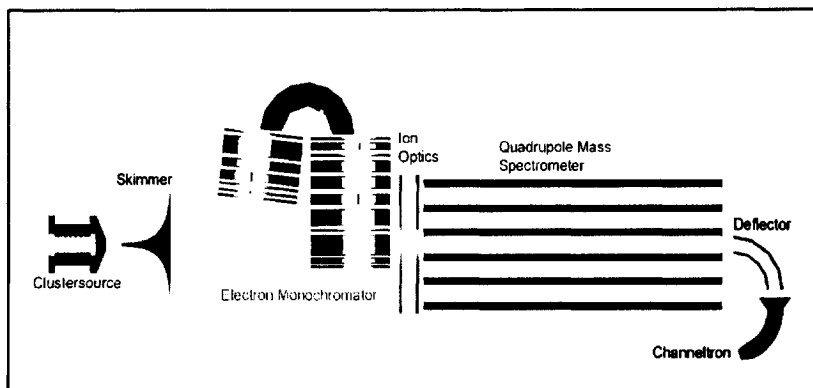


Figure 1. Schematic diagram of the crossed beams instrument HEM-QM. Electrons are emitted from a hot filament and focused into a beam. They pass the hemispherical energy monochromator (HEM) at a constant energy of about 2 eV and are focused and brought to a final collision energy before they interact perpendicular with the neutral beam produced in the neutral beam source. Ions produced are extracted and mass analyzed by a quadrupole mass (QM) spectrometer.

The appearance energies of the product cations were derived using a novel data handling procedure described in detail in a recent publication [49,50]. The data analysis is based on a Wannier-type power law function

$$\sigma(E) = \text{const.} (E - AE)^p \quad (1)$$

for the near-threshold behaviour of the cross section for multiple ionization of atoms. Appearance energies and the corresponding exponents p in the Wannier-type law were determined from a fit of the measured data sets to either a 2-function or a 3-function trial function using the Marquart-Levenberg Algorithm (MLA) and appropriately selected initial conditions for each ion. In cases where the background signal was constant, we used a 2-function fit to the experimental data of the form

$$\begin{aligned} f(E) &= b & \text{for } E < AE \\ f(E) &= b + c (E - AE)^p & \text{for } E > AE \end{aligned} \quad (2)$$

where “ b ” represents the constant background. The constant “ c ” denotes the slope of the ion signal above the appearance energy AE and is thus a measure for the intensity of a given ion signal. The exponent “ p ” expresses the curvature of the function in the near-threshold region. However, many appearance energies were quite high (above 100 eV) and it was found that

the background was no longer a constant in that energy regime. A sloping background may be caused by small contributions to the recorded ion signal from residual gas molecules such as hydrocarbons and water vapor. In those cases (and as long as the background signal was small and essentially a linear function of the electron energy) we used a modified 3-function fit of the form

$$\begin{aligned} f(E) &= b && \text{for } E < E_B \\ f(E) &= b + c(E - E_B) && \text{for } E_B < E < AE \\ f(e) &= b + c(E - E_B) + d(E - AE)^p && \text{for } E > AE \end{aligned} \quad (3)$$

to extract the desired quantities “AE” and “p”. Here E_B denotes the appearance energy of the sloping background signal. We also note that we applied a weighting factor w of the form

$$w = 1/(1 + N) \quad (4)$$

to the measured ion counts in an effort to increase the statistical weight of the data points right near the ionization threshold (here N refers to the number of recorded ion counts). The fitting procedure was performed using the SIGMAPLOT programme providing the optimised fitting parameters and the corresponding standard deviations. The data was fitted for singly charged ions over an energy range from below the AE (where the only signal is background) to some 3eV above AE.

Recently, we refined our data fitting technique further [7,44,48] by allowing for the finite electron distribution to be treated as a free parameter. This enables us also to deduce the actual electron energy distribution at the energy position of the appearance energy. For this purpose, we assume that the electron energy distribution is approximately a Gaussian distribution centered around AE with a full width at half maximum (FWHM) of ΔE . The fit function (1b) is then numerically convoluted with the electron distribution

$$P(E) = \int_{-\infty}^{+\infty} e^{-\frac{(E-AE)^2}{2\Delta E^2}} (b + c(E - AE)^p) dE \quad (5)$$

and compared with the experimental data. This comparison yields information about the experimental FWHM of the electron energy resolution (see Fig. 1 in Ref. [7] which shows the corresponding curves for the ionization of He). The results obtained by this method are similar to results obtained by measuring the s-wave attachment cross section to CCl_4 and thus

demonstrate that the FWHM of the electron energy distribution of the present experimental set-up does not depend on electron energy.

2.2 TEM-QM Apparatus

You will The high resolution electron attachment spectrometer TEM-QM (Figure 2) consists of a molecular beam system, a high resolution trochoidal electron monochromator and a quadrupole mass filter with a pulse counting system for analysing and detecting the ionic products. The modified TEM used here has recently been described in detail [8]. In summary we use a hairpin filament to produce a high electron current with an electron distribution of about 700 meV. Electrons emitted thermally from the filament tip are extracted by an electric field of several V/mm and guided by an axial magnetic field of up to 50 Gauss. The magnetic field is produced by two 100 mm solenoids, which are about 250 mm apart. Typical electron emission currents are in the order of several μA . After passing two electrostatic lenses with orifices of 1 mm diameter the beam enters the dispersive element where a weak electrostatic deflection field of about 100 V/m perpendicular to the magnetic field is applied. According to the trochoidal principle the electrons are deflected depending on their kinetic energy in forward direction. Subsequently, at the exit of the dispersive element part of the electron distribution ($<150\text{meV}$) is allowed to pass through the orifice in the exit electrode. These electrons are then accelerated to the desired energy and enter the collision chamber, where the monochromatic electron beam is crossed by a molecular beam. The anions produced by the electron attachment processes are weakly extracted into a quadrupole mass filter where they can be analyzed and detected. After crossing the collision region the remaining electrons are collected and the electron current is monitored online during the experiment using a picoammeter.

It has been demonstrated in [8] that the very high energy resolution ($< 10\text{ meV}$) obtained at energies close to zero eV in the original instrument [6,9,10] quickly deteriorates to 100 meV with increasing electron energy. An improved instrument has been designed, on the basis of trajectory calculations, that overcomes these deficiencies, with the new monochromator, an energy resolution of 40 meV or better (independent of the electron energy) can routinely be achieved. For the present experiments, the instrument was operated at an FWHM of about 100 meV which was a reasonable compromise between product ion intensity and incident electron resolution. The energy scale may be calibrated by recording either SF_6^- from SF_6 or Cl^- from CCl_4 which both show very narrow features close to zero eV energy.

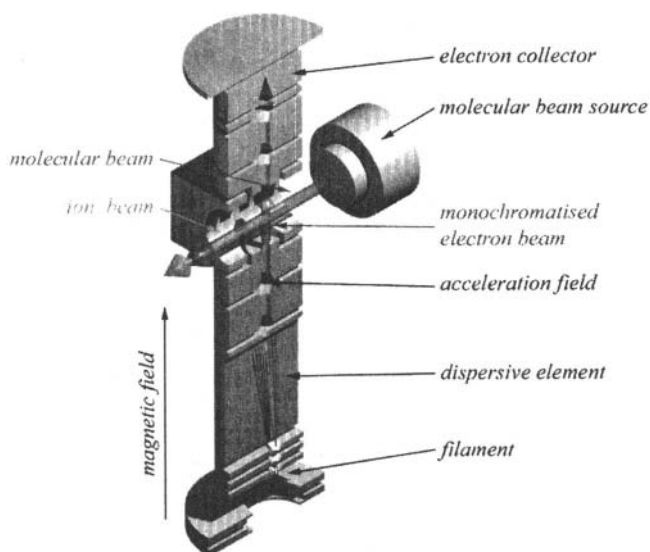


Figure 2. Schematic diagram of the crossed beams instrument TEM-QM. Electrons emitted thermally from the filament tip are extracted by an electric field of several V/mm and guided by an axial magnetic field of up to 50 Gauss. After passing two electrostatic lenses with orifices of 1 mm diameter the beam enters the dispersive element where a weak electrostatic deflection field of about 100 V/m perpendicular to the magnetic field is applied. According to the trochoidal principle the electrons are deflected depending on their kinetic energy in forward direction. Subsequently, at the exit of the dispersive element part of the electron distribution is allowed to pass through the orifice in the exit electrode. These electrons are then accelerated to the desired energy and enter the collision chamber, where the monochromatic electron beam is crossed by a molecular beam. The anions produced by the electron attachment processes are weakly extracted into a quadrupole mass filter where they can be analyzed and detected. After crossing the collision region the remaining electrons are collected and the electron current is monitored online during the experiment using a picoammeter.

3. RESULTS

3.1 Appearance energies and Wannier exponents for multiply charged rare gas ions (argon)

The experimental determination of multiple ionisation cross sections of the rare gases, particularly the determination of appearance energies (AEs) and the functional dependence of the cross sections in the near-threshold region is a challenging task because of the low ion signal rates involved. In addition, there is an inherent difficulty (see discussion in [7]) of determining

the AEs from the intersection of a gradually rising, low, and often smeared-out ion signal as a function of electron energy with a background signal that may or may not be constant in this energy range. Several theoretical models describing the low-energy behaviour of atomic single and multiple ionisation cross sections have been discussed in the literature. Perhaps the most widely referenced model is that of Wannier [51] based on arguments from classical physics which yields the well-known Wannier threshold law

$$\sigma(E) = \sigma_0 (E - E_T)^{1.127} \quad (6)$$

for the case of single ionisation of a neutral atom by an electron (three charged particle system in the exit $A + e \rightarrow A^+ + e + e$). Since this classical work of Wannier many authors formulated quantum mechanical theories of near threshold ionisation involving various degrees of classical or semi-classical assumptions (see recent reference [52] summarizing also earlier work) all of them with some exceptions [53] essentially confirming the validity of this early prediction (see also some experimental studies [54] and also [55]) on the near threshold ionisation of atoms by electron or photon impact). This Wannier model was originally derived for the formation of singly charged (hydrogen) ions only, but several attempts have been made to extend the validity of the Wannier model to the formation of more highly charged ions.

As early as 1955, Wannier [56] suggested that n -fold electron impact ionisation of atoms should follow an approximate threshold law of the form given in equ. (1) where the Wannier exponent $p = n$ based on a simple classical phase space argument. The same behaviour was independently predicted by Geltman [57] using a quantum theoretical treatment of inelastic scattering. In the following years a number of theoretical studies using classical, semi-classical and quantum-mechanical methods addressed the multiple-electron escape process including electron correlation effects (see [58]). In general, the validity of equation (1) (sometimes called the n -th power Wannier-Geltman threshold law) was confirmed by these calculations. However, in all of these studies p values slightly larger than n were predicted when the Coulomb interaction between the electrons in the exit channel was taken into account (similar to the case of single ionisation). In particular, p values of 2.270, 3.525 and 4.78 were deduced for double, triple, and quadruple ionisation of neutral atoms by electron impact (this is sometimes referred to as the "generalized Wannier law").

Despite the interest from the theoretical point of view most high resolution experiments were concerned primarily with the threshold law for single ionisation. There is only one, rather recent, serious effort by Wiesemann and co-workers [59-62] to generate reliable experimental data for the threshold law and the appearance energies for rare gas atoms. The

exponents obtained for a power law from a least squares fit to their data did, however, not confirm the predictions of the generalized Wannier law or the simple n -th power law. In order to shed more light onto the discrepancy between experimental data and theoretical predictions we carried out experiments on all five rare gases [25,26] which extended the previous studies in several respects. We have extended the range of ionisation charge state up to $n = 8$ (e.g., for Xe) and employed a recently constructed high resolution electron impact ionisation apparatus HEM-QM (see above) which has a much higher energy resolution (up to a factor of ten in the best case compared to the 500 meV energy resolution used by Wiesemann and co-workers [59-62]). We also developed new ways to calibrate the electron energy scale and verify its linearity over a wide range of impact energies (see above). Lastly, we applied a recently developed improved data analysis procedure to deduce reliable and accurate appearance energies and corresponding threshold power law exponents (see above). As an example we report here the results of the experimental determination of the appearance energies and the exponents p in the Wannier law for the formation of multiply charged Ar up to a charge state $n = 6$ following controlled electron impact on the neutral Ar atoms.

The appearance energies extracted from our measured data sets for the formation of Ar^{n+} ($n = 1-6$) ions are summarized in Table I and are compared to other available data including spectroscopically obtained AE's and experimentally determined values obtained from a variety of other methods. Where error margins are given for data from other authors, these errors refer to the error margins quoted in the original publications. As noted above, no other group carried out the kind of detailed data analysis and error estimation that has described here. There is a very good agreement between the present AE values and the spectroscopic values [63] for Ar^{n+} up to $n = 5$. For charge state $n = 6$, we find that the present value is somewhat higher than the spectroscopic value. For reasons discussed in detail in Ref. [25], the values of Stuber [64] are significantly higher than our values for $n > 3$ (which is not unexpected since they used a linear extrapolation method) and the values of Redhead [65] are significantly lower than the present (and spectroscopic) values which may be attributable to problems with his method of using step-wise ionisation processes (e.g., low signal rates for high stages of ionisation). The state-selected data of Gerdorf et al. [62] are in excellent agreement with the present values. The AE value for Ar^{3+} determined recently by Syage [66] using a power-law function to fit their cross section data is in good agreement with our result and with the spectroscopic value, whereas his AE's for Ar^{4+} and Ar^{5+} are slightly larger than our data and the spectroscopic values. AE results obtained by Syage [66] when fitting the data to a linearised function of $\sigma^{1/n}$ gave even lower values, i.e., 81 instead of 84 eV for Ar^{3+} and 135 instead of 148 eV for Ar^{4+} . The single value of 83.7

± 0.5 eV for Ar^{3+} formation (not given in Table 1) given by Dorman et al. [67] using n -th root extrapolation is in agreement with our value and with the spectroscopic data.

Ion	Spectroscopic value [63]	Stuber [64]	Gerdorf et al. [62]	Red-head [65]	Syage [66]	This work
Ar^+	15.759	---	---	---	---	15.76 ± 0.01
Ar^{2+}	43.388	43.0	43.95 ± 0.67	42.8	---	43.36 ± 0.02 (43.20)
Ar^{3+}	83.14	85.0	84.50 ± 0.88	80.8	84	84.3 ± 0.4 (84.5)
Ar^{4+}	143.94	147.0	---	135.8	148	144.0 ± 1.5
Ar^{5+}	218.96	285.0	---	208.8	225	222.5 ± 3.7
Ar^{6+}	309.97	430.0	---	297.8	---	328.0 ± 3.7

Table 1. AEs in eV for the formation of Ar^{n+} ions ($n = 1 - 6$) in comparison with other measured or calculated AE's. The present data in brackets have been measured values using the trochoidal monochromator instead of the hemispherical monochromator.

The exponents "p" extracted from our measured data sets for the formation of Ar^{n+} ($n = 1-6$) ions are summarized in Table 2. We find that our exponent "p" for $n=1$ is slightly larger than the Wannier prediction of 1.127 which might be due to interference from the second spin orbit state. In the case of $n=2$, our exponent is in satisfactory agreement with the generalized Wannier prediction and both values are somewhat lower than the exponent reported by Koslowski et al. [59]. Nevertheless, within the error bar our value is also consistent with the prediction of the Wannier-Geltman n -th power law. We note that the value derived by Wiesemann and co-workers [59,60] for the state-selected ground-state ion curve (given in brackets) is somewhat lower than the value for the all-inclusive ion curve and is thus in better agreement with the present value. For $n=3$, our exponent is in reasonable agreement with the exponent reported by Koslowski et al. [59] in view of our error margin and both values are lower than the prediction of the generalized Wannier model, but agree with the predictions of the Wannier-Geltman n -th power law. For $n=4$ we find a value of 3.15 with a rather large error bar, which is in reasonable agreement with the value of Koslowski et al. [59] and with the Wannier-Geltman prediction, but lies below the generalized Wannier law limit. For $n=5$ and 6, we find an essentially constant exponent of about 4 with an error margin of 1.4, which is far below both theoretical predictions. This might indicate that the extension of these threshold laws to the formation of highly charged ions, for which it was not originally derived, may be questionable.

Ion	Wannier-Geltman	Generalized Wannier	Koslowski et al. [59]	This work
Ar ⁺	1	1.127	---	1.27±0.05
Ar ²⁺	2	2.27	2.6 (2.0)	2.11±0.2 (2.38)
Ar ³⁺	3	3.5	3.0 (1.7)	2.75±0.5 (2.58)
Ar ⁴⁺	4	> 4.7	2.5	3.15±0.9
Ar ⁵⁺	5	> 4.7	---	4.01±1.4
Ar ⁶⁺	6	> 4.7	---	3.89±1.4

Table 2. Exponent “p” for the formation of Arⁿ⁺ ions (n = 1 – 6) in comparison with other measured or predicted values of “p”. The values of Koslowski et al. [59] given in the brackets refer to the state-selected ground state ions Ar²⁺(³P) and Ar³⁺(⁴S°), respectively. In a later paper these authors [62] have revised these ground state values upwards to 2.23 ± 0.2 and 2.41 ± 0.41. The present data in brackets have been measured using the trochoidal monochromator instead of the hemispherical monochromator.

3.2 Isotope Effects in the Electron Impact Ionisation of H₂/D₂ and H₂O/D₂O

Recently, Snegursky and Zavilopulo [68] reported shifts in the measured appearance energies (AEs) of parent and fragment ions produced by electron impact ionisation and dissociative ionisation of H₂O/D₂O from a few tenths of an electronvolt (eV) to about 3 eV (albeit with an energy resolution of about 0.5 eV) which these authors attributed to isotope effects. Isotope effects in the electron impact ionisation of atoms and molecules manifest themselves primarily in slightly different appearance energies for the parent ions and - in case of a molecular target – also the fragment ions. These shifts are caused by small differences in the atomic ionisation energies for the various isotopes of a given atom or by the different molecular potential energy curves and the different molecular constants of the various isotopes of a given molecule. The only accurately known AE values for an isotope system are those for atomic hydrogen where the ionisation energy of H, IE(H⁺/H) = 13.59844 eV is lower by approximately 5 meV than the ionisation energy of D, IE(D⁺/D) = 13.603 eV according to the NIST tables [69]. Also, the electron affinity EA(H) = 0.75419 eV is slightly lower (by approximately 0.4 meV) than EA(D) = 0.754580 eV), whereas molecular hydrogen shows a somewhat larger isotope shift of approximately of 41 meV, i.e., IE(H₂⁺/H₂) = 15.42593 eV vs. IE(D₂⁺/D₂) = 15.46658 eV. For most atoms and molecules, isotope effects in the appearance energies of the various ions can be calculated to a very high precision and in almost all

cases, one would expect shifts in the appearance energies due to isotope effects to be in the order of about 200 meV or less (see below). We used our high-resolution crossed beams apparatus HEM-QM to determine the appearance energies of all parent and several fragment ions produced by electron impact ionisation of the isotope systems H_2/D_2 and $\text{H}_2\text{O}/\text{D}_2\text{O}$ with high precision [28]. We compare the experimentally determined appearance energies with calculated values that we derived from calculations using standard quantum chemistry codes (for details see [28]) and, to the extent available, also with appearance energies listed in standard reference data tables [69].

Table 3 summarizes the measured and calculated appearance energies for the formation of the H_2^+ (see also Fig.3) and D_2^+ parent ions from H_2 and D_2 and for the formation of the respective H^+ and D^+ fragment ions. H_2/D_2 is the only isotope system where reliable data for the adiabatic ionisation energies for the parent ions are available for both isotopes. Thus, it served as a benchmark system for the experimental and theoretical methods employed here. Very good agreement exists between the present experimental results, an earlier experimental determination from this laboratory using xenon as a reference gas, and the NIST data. Moreover, there is very good agreement between the present results obtained with a stagnant gas target and measurements carried out using the supersonic molecular beam inlet. The experimental results are supported by our B3LYP/6-311G* computations, although the calculated absolute values for both isotopes are consistently larger by approximately 40 to 60 meV than the experimental values. Nevertheless, the calculated isotope effect Δ_c of 49 meV is in very good agreement with the presently and earlier measured isotope shift of 35 meV and 45 meV, respectively, and with the tabulated shift Δ_m of 41 meV (NIST tables).

For the fragment ions produced by electron impact ionisation of H_2 and D_2 , accurate tabulated appearance energies are only available for H_2 . Both our measured and calculated appearance energies are in excellent agreement with the most accurate value given in the NIST table, 18.078 ± 0.003 eV reported by Weitzel et al. [70] using the PIPECO technique. Unfortunately, the only entry in the NIST tables for D^+ from D_2 of 25.3 ± 0.2 eV corresponds to the appearance energy of fragment ions measured by Olmsted et al. [72] who selected ions with a significant amount of excess kinetic energy. Thus, their value cannot serve as a reliable reference. The present measurement was further complicated by the fact that the D^+ ion signal coincides with the H_2^+ signal from H_2 in the background gas in the vacuum chamber. Nevertheless, within the present margin of error, our experimental value of 18.41 ± 0.2 eV agrees reasonably well with the calculated value of 18.17 eV. The isotope effect Δ_c for the fragment ions obtained from our

calculations of 87 meV is almost a factor of two larger than the isotope effect that was found for the parent ions.

Ion	IE [69] (eV)	AE _m (eV)	AE _c (eV)	Δ _m (meV)	Δ _c (meV)
H ₂ ⁺ /H ₂	15.42593±0.00005	15.428±0.025	15.47	35	49
---	---	---	---		
D ₂ ⁺ /D ₂	15.46660±0.00010	15.463±0.025	15.52	320	87
H ⁺ /H ₂	18.078±0.003	18.09±0.08	18.08		
---	---	---	---		
D ⁺ /D ₂	(25.3±2) [*]	18.41±0.2	18.17		

Table 3. Comparison of the measured AE_m values (using a stagnant target) and calculated AE_c values (using the B3LYP/6-311G* procedure) for ions produced by electron impact on H₂ and D₂ with data from the NIST tables [69]. Also listed are the respective measured Δ_m and calculated Δ_c differences (Δ = AE(D₂⁺) – AE(H₂⁺) etc.) in the appearance energies for each isotope pair. * This value corresponds to ions with a certain amount of excess kinetic energy (see text for further details).

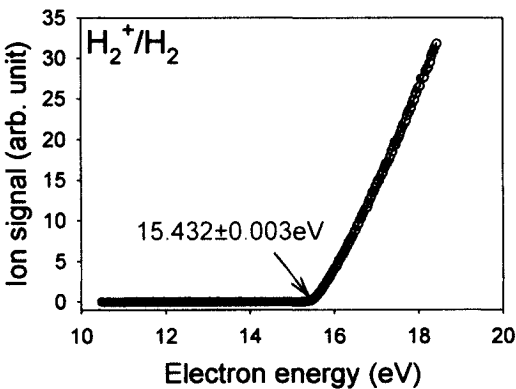


Figure 3. H₂⁺ ion signal produced by electron impact on H₂ as a function of the electron energy from 10 eV to 18 eV measured with an energy resolution of about 110 meV (20nA electron current). The open circles correspond to the raw data and the full line is a fit to the data to extract the corresponding appearance energies as described in the text. The energy scale has been calibrated with helium measured under identical conditions. The error bars given for the appearance energies deduced in this figure is derived from the fitting procedure alone, thus giving solely the statistical error of this single data run. The actual uncertainties derived by averaging over a larger number of experimental runs are much larger and given in the table.

Table 4 summarizes the measured and calculated appearance energies for the $\text{H}_2\text{O}^+/\text{D}_2\text{O}^+$ parent ions from H_2O and D_2O and for the formation of the respective OH^+/OD^+ , H^+/D^+ , and O^+ fragment ions. As it was the case for the H_2/D_2 system, the appearance energies for the ions resulting from the deuterated target are consistently higher than the appearance energies for the ions from the hydrogenated targets. The differences range from a minimum of 45 meV for the parent ions to a maximum of 190 meV for the H^+ and D^+ fragment ions. This trend that the fragment ions have a larger isotope shift than the parent ion is also supported qualitatively and to some extent even quantitatively by the quantum chemistry calculations that we carried out. This is apparent from Table 4 which lists calculated values for the appearance energies and appearance energy differences obtained by using the B3LYP/6-311G* method and the *ab initio* MP4/6-311G* treatment. There appears to be an average discrepancy of about 30% between the calculated and the measured appearance energy differences Δ throughout. Nonetheless, two observations are noteworthy: (1) the fact that the measured AE of the deuterated species consistently exceeds the measured AE of the hydrogenated species is reproduced by both calculations and (2) a comparison of our B3LYP calculations with the *ab initio* MP4 approach using the same 6-311G* basis set yields only insignificant differences for the quantity Δ_c . Thus, both methods are essentially equally suitable for the calculation of isotope effects for the $\text{H}_2\text{O}/\text{D}_2\text{O}$ system. However, the B3LYP appearance energies are generally in better agreement with the experimental values than those based on the MP4 method.

A comparison of our measured appearance energies with ionisation energy values listed in the NIST data tables [69] (to the extent that those tabulated values are available) leads to the following conclusions. Within their margin of error, the measured parent ion appearance energies are in agreement with the respective high accuracy adiabatic ionisation energies determined from photo-ionisation studies with IE ($\text{H}_2\text{O}^+/\text{H}_2\text{O}$) values ranging from 12.59 eV to 12.62 eV and IE ($\text{D}_2\text{O}^+/\text{D}_2\text{O}$) values ranging from 12.62 eV to 12.64 eV. An isotope shift of 17 meV deduced from a recent molecular beam photoelectron spectroscopic studies of both isotope systems by Reutt et al. [72] is in rather good agreement with our calculated values of 21 and 22 meV and in fair agreement with our measured value of 40 meV given the respective error bars of our AE values. In general, isotope shifts deduced from simultaneous studies of both isotopes range from a few meV up to about 30 meV (see [69]). In the case of the fragment ions, a meaningful comparison with the results of other authors is more difficult due to the small number of studies reported in the literature, which were also all carried out before 1978. Nevertheless, it is instructive to compare the present results with those of two earlier studies where the AEs of fragment ions of both isotopes were investigated. We find very good agreement with the

results from the photo-ionisation studies by Mc Cullough [73], who reported appearance energies $AE(OH^+/H_2O) = 18.115 \pm 0.008$ eV and $AE(OD^+/D_2O) = 18.219 \pm 0.008$ eV, as well as with their isotope shift of 104 meV (see Table 4). On the other hand, the electron impact data of Appell and Durup [74] yielding $AE(H^+/H_2O) = 18.7 \pm 0.5$ eV and $AE(D^+/D_2O) = 18.7 \pm 0.5$ eV are slightly lower than the present values and do not show an isotope shift within their comparatively larger error margin.

Ion	AE_m (eV)	AE_c [B3LYP] (eV)	AE_c [MP4] (eV)	Δ_m (meV)	Δ_c [B3LYP] (meV)	Δ_c [MP4] (meV)
H_2O^+/H_2O	12.56 ± 0.03	12.29	11.88	40	21	22
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D_2O^+/D_2O	12.60 ± 0.03	12.31	11.86	110	117	148
OH^+/H_2O	18.13 ± 0.09	17.66	16.69			
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OD^+/D_2O	18.24 ± 0.14	17.77	16.83	190	106	125
H^+/H_2O	18.75 ± 0.05	18.33	17.96			
---	---	---	---			
D^+/D_2O	18.94 ± 0.05	18.43	18.08	140	88	106
O^+/H_2O	18.38 ± 0.15	18.41	17.01			
---	---	---	---			
O^+/D_2O	18.52 ± 0.15	18.50	17.12			

Table 4. Comparison of measured AE_m values (using a stagnant target) and calculated AE_c values (using the B3LYP and MP4 procedure with the 6-311G* basis set, respectively) for ions produced by electron impact on H_2O and D_2O . Also listed are the respective measured Δ_m and calculated Δ_c differences ($\Delta = AE(D_2O^+) - AE(H_2O^+)$ etc.) in the appearance energies for each isotope pair.

Our measured shift in the AE values for the O^+ ion from both isotopes of 140 meV is about a factor of 5 smaller than the 0.7 eV shift reported by Snegursky and co-workers [68]. A further comparison of our results with those of Snegursky and co-workers [68] for this isotope system is not possible, since low signal rates for the formation of H_2^+ and D_2^+ ions from respectively H_2O and D_2O in our experiment prevented an accurate appearance energy measurements for these two ions in the present work. However, the 3 eV difference in the AE values for these two ions reported in [68] is significantly larger than any isotope shift that we measured for this isotope system in the course of the present work. We further note that Snegursky and Zavilopulo [68] find a lower appearance energy for the deuterated system, a fact that is not supported by quantum chemistry calculations.

3.3 Appearance energy, binding energy and structure of the ozone dimer

Recently, there has been renewed interest in ozone (O_3), chlorine dioxide (OCIO) and dichlorine monoxide (Cl_2O) as they are intricately linked in the stratospheric ozone cycle [75]. Gas phase reactions were unable to explain the most dramatic observations of ozone loss in the terrestrial atmosphere, the Antarctic 'ozone hole'. Within a few days of the onset of the polar spring the ozone layer over the Antarctic continent is observed to decrease by upwards of 80% of its normal winter levels [76], a process now ascribed to the presence of atmospheric aerosols within the Antarctic polar vortex. The chemical reactions upon such particulates (in polar stratospheric clouds, PSC's) are complex but introduce the possibility of small molecular aggregates (clusters) being formed on the surfaces and being involved in the ozone destruction. To date there have been only a few studies of the properties of clusters of the three molecules mentioned (including ionisation studies of OCIO aggregates by electron impact [77], by photodissociation and *ab initio* calculations [78], photo-ionisation of the chlorine oxides [79] and electron attachment to ozone clusters [80]), no appearance energies for these aggregates have been reported in the literature. Here we report the appearance energies for product cations obtained by electron impact ionisation from the monomers and dimers of ozone measured using a recently developed high resolution electron impact spectrometer HEM-QM. Measured ionisation energies are compared with earlier experimental values where available and thermochemical data (binding energies) are derived [31]. In order to elucidate the rather low ionisation energy for the ozone dimer and the concomitant rather large binding energy for the 'dimer' ion relevant binding energies and ionisation energies were calculated for the ozone system by quantum mechanical methods.

Figure 4 shows experimental data for the present determination of the appearance energy value for $(O_3)_2^+$. The appearance energy for the $(O_3)_2^+$ dimer was derived from these data to be 10.02 ± 0.32 eV with a p-value of 1.21 (a repeat determination with slightly better statistics gave a value of 10.10 ± 0.3 eV). This value should be contrasted with the appearance energy for the monomer of 12.70 ± 0.02 eV, the greater statistical error for the dimer arising from the much smaller ion signal and the poorer resolution of the incident electron beam. To the present authors' knowledge no previous determination of this dimer appearance energy is available for comparison. In contrast, the present monomer value is in agreement with two earlier electron impact determinations for the appearance energy of 12.84 ± 0.10 eV [81] and 12.80 ± 0.05 eV [82], in particular when taking into account the somewhat larger error bars of the two previous studies. Moreover, two photoelectron spectra (PES) give an adiabatic ionization energy (referring to

the first vibration of the first ionised state consisting altogether of seven peaks) of 12.44 ± 0.01 eV [83] and 12.43 ± 0.025 eV [84], whereas the most recent photo-ionisation mass spectrometer (PIMS) value for the adiabatic ionisation energy is 12.519 ± 0.004 [85]. All of these adiabatic ionisation energy values derived from photon ionisation experiments are somewhat below the present value (outside of the combined errors bars). Conversely the present electron impact value for the appearance energy of 12.70 ± 0.02 eV, however, is close to the values for the vertical ionisation energy reported in these photo-ionisation studies, e.g., of 12.75 eV [86], 12.75 ± 0.01 [83], 12.73 ± 0.025 eV by [84] and 12.755 ± 0.004 eV by [85].

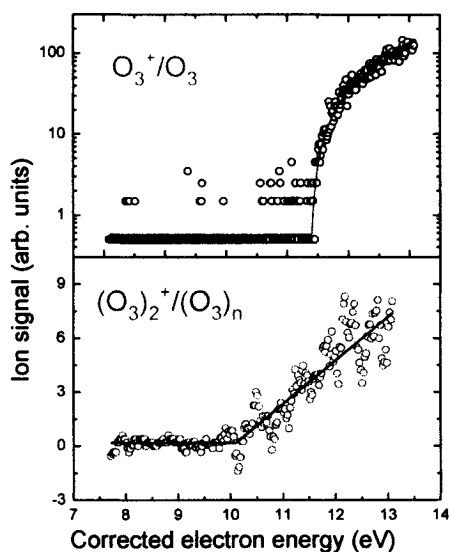


Figure 4. Upper panel: Ionisation efficiency curve (logarithmic z-axis) for the production of O_3^+ by electron ionisation of neutral O_3 . Lower panel: Ionisation efficiency curve (linear z-axis) for the production of $(\text{O}_3)_2^+$ by electron ionisation of a neutral ozone cluster beam which consists predominantly of ozone monomers and ozone dimmers (interference from larger clusters is negligible). The full lines are fits to the data to extract the corresponding appearance energies as described in the text. Both curves have been measured with an electron energy resolution of about 300 meV and an electron current of about 30 nA. The energy scale has been calibrated with argon measured under identical conditions. The negative values for the dimer ion result from a background signal subtraction procedure.

Having measured the appearance energies of $(\text{O}_3)_2^+$ it is now possible to deduce an estimate for the bond energy $D(\text{O}_3 - \text{O}_3^+)$ of the $(\text{O}_3)_2^+$ ion from the known data. Since in general if two neutral O_3 molecules form a cluster binding energy is released, the O_3 dimer lies energetically below the neutral O_3 monomer by an energy equivalent to the binding energy of the dimer $D(\text{O}_3 - \text{O}_3)$. The bond energy of the $(\text{O}_3)_2^+$ ion is then given by:

$$D(O_3 - O_3^+) = IE(O_3) + D(O_3 - O_3) - IE((O_3)_2^+) \quad (7)$$

In order to derive this bond energy we use the best values available for the quantities given on the right hand side of equ. (7), i.e., for $IE(O_3^+)$ we use the measured adiabatic ionisation energy 12.519 ± 0.004 [85], for the neutral dimer binding energy a calculated $D(O_3-O_3) = 0.13$ eV [87], and for $IE((O_3)_2^+)$ we use the presently determined appearance energy 10.10 ± 0.3 eV. This gives for the bond energy of the $(O_3)_2^+$ ion a value of 2.55 eV. Moreover, it should be noted that this value is a lower limit in so far as we have used instead of the adiabatic ionisation energy of the dimer the experimental value determined in the present study which corresponds –as has been discussed above – to a value somewhat above the adiabatic ionisation energy. In order to account for this uncertainty we add an error of + 0.15 eV (difference between the adiabatic and vertical ionization energy of the monomer) and thus arrive at an estimate for this dimer ion binding energy of $(2.55 - 0.5 + 0.65)$ eV.

This is a very high value compared to the bond energy of rare gas atomic clusters or other molecular clusters [88,89], including OCIO [31] and Cl₂O [33] studied also in our laboratory for comparison with ozone. Such a large value is, however, not without precedent. Mähnert et al [88] studied the formation of the $(CO)_2^+$ ion by the dissociation of $Ar(CO)_2$ clusters in a threshold photoelectron photoion coincidence experiment and determined a binding energy of the $(CO)_2^+$ dimer ion of 1.80 eV from which they suggested that the CO dimer has a trans planar structure. In order to shed more light on this we have performed systematic quantum chemical calculations on the O₃, OCIO, and Cl₂O system described in detail in Ref. [31,33].

Based on these quantum chemical calculations on various levels we are led to the conclusion that the ion produced by ionisation of the ozone dimer is no longer a conventional dimer ion where the two monomer units are still present (as is the case for e.g. the OCIO system and the Cl₂O), but rather an ion of the form $O_2...O_4^+$. Evidence for the stabilization of this ion has been recently reported by Lugez et al. [90]. Moreover, when optimising the geometry of the $O_2...O_4^+$ complex by means of CAS-SCF calculations using the 6-311G(2d) basis set (O_2 in the triplett and O_4^+ in the dublett state; the active space consisted of three occupied and three empty molecular orbitals), a stable complex was found. The adiabatic ionisation energy of the planar O_4 unit in this complex (planar O_4 by itself is a saddle point on the O_4 energy surface with only slightly higher energy than O_4 in its optimal geometry) is 10.47 eV – already agreeing to the measured value 10.10 ± 0.3 eV within the combined limits of accuracy. This value was also checked by calculations up

to the QCISQ(T) level with the aug-cc-pVTZ basis set where a virtually identical result (10.44 eV) was obtained.

3.4 Electron attachment to formic acid: magnitude and shape of cross section

Formic acid (H_2CO_2 structured as HCOOH) is the simplest organic acid. It occurs naturally for example in ants and in the fruit of the soap tree and is also formed as a byproduct in the atmospheric oxidation of terpentine. The principal commercial source is sodium formate, which is prepared by the reaction of carbon monoxide and sodium hydroxide under pressure and heat. Formic acid is used in leather manufacture to control pH, as well as in the acid dyeing of some leathers; in the latter case, causing the dye to fix on the leather. Moreover it is interesting to note that the formic acid /formate anion moiety, e. g. together with a bound water molecule is considered to represent the catalytic centre for enzymatic activity [91,92]. In the present report we will present the first results (see also [38,39] for more details) on low energy electron impact obtained from the simplest of the organic acids formic acid (HCOOH).

Electron impact with HCOOH in the electron energy range 0-10 eV generates three anionic fragments HCOO^- , OH^- and O^- with intensity ratios (as monitored by the count rate at the highest peak of the respective cross section curves) of 240 : 10 : 1. The present relative cross section data of HCOO^- have been calibrated (see Fig.5) by using the absolute data for the total cross section for CCl_4 reported in Ref. [9]. The low energy feature peaking at 1.25 eV arise from different closely spaced single particle shape resonances (see the *ab initio* calculations discussed in [39]) while the structures at higher energy are most likely due to excited anion states where the extra electron is bound to an electronically excited formic acid (core excited resonances).

The electron transmission (ET) spectrum reported earlier [93] exhibits a nearly symmetric resonance in the energy range between ≈ 0.9 eV and ≈ 3 eV with a maximum located at 1.8 eV. The HCOO^- ion yield associated with the low energy resonance (Fig. 5), on the other hand, is clearly *asymmetric* with an onset at 1.15 ± 0.05 eV (obtained by a linear extrapolation of the experimental onset curve and in accordance with the calculated $\Delta H_0 = 1.37 \pm 0.23$ eV from data in the NIST [69]) and a peak at 1.25 ± 0.05 eV. In the picture of potential energy surfaces the pronounced asymmetry of the DEA ion yield curve is the result of the particular disposition of the potential energy surfaces (Franck-Condon area) in relation to level of the exit channel. While in ET the entire Franck-Condon region is probed, DEA is operative only above the threshold. The onset of the experimental curve is then a convolution of the step at the low energy tail of the resonance (opening of

the DEA channel) and the monochromator function. The peak of the DEA resonance (1.25 eV) is located appreciably *below* that obtained in ET (1.8 eV). While the ET spectrum reflects the initial Franck-Condon transition, DEA contains additional information on the decomposition dynamics. Dissociation of the (TNI) transient negative ion $\text{HCOOH}^\#$ is principally affected by the competing decay channel of autodetachment (AD) which is operative until the crossing between the potential surfaces. The autodetachment rate usually strongly increases with the electron energy with the consequence that DEA reactions at lower energy become more probable. This results in a shift of the maximum of the DEA resonance to lower energy (survival probability shift [94]) by 0.55 eV with respect to that of the initial transition.

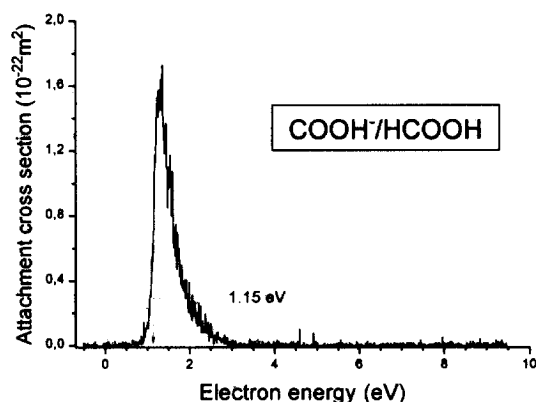


Figure 5. Formation of negative ions HCOO^- by dissociative electron attachment to formic acid. The pressure in the apparatus was 10^{-6} mbar and electron energy spread was about 140 meV.

A closer inspection of the HCOO^- ion yield (see Fig.6) curve exhibits weak but distinct and clearly reproducible structures on the high energy tale of the resonance. The solid line is a Gaussian curve fitted to the experimental data. A Gaussian peak shape is expected for a situation when the reflection principle [94] can be applied, i. e. when the fragment ion yield curve can be represented by the reflection of the (square of the) vibrational wave function of the ground state of the neutral at the repulsive part of the anionic potential energy surface. Such a situation holds, e.g., for diatomic molecules when internal excitation of the atomic fragments can be neglected. In a polyatomic system the dissociation of the TNI does usually not proceed directly along the repulsive part of the potential surface and excitation of internal degrees of freedom in the transient anion can take place. For the present system the ETS [93] in fact reveals a series of more than 12 peaks separated by about

65 meV and assigned to the population of the OCO -bending levels in the anion (in neutral formic acid excitation of the corresponding vibrational level requires 77 meV [69]).

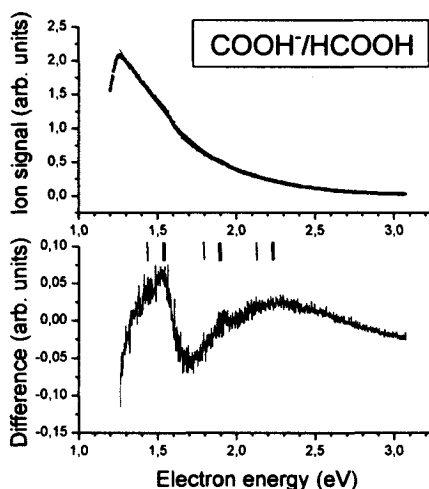
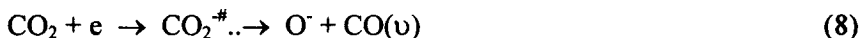


Figure 6. COOH^- ion yield (accumulated data from several experimental runs) recorded at an energy resolution of 60 meV to show the structures. The solid line is a Gaussian fit to the experimental data (top). Difference between the Gaussian curve and the experimental data (bottom).

It has been demonstrated recently on the simpler system CO_2 [95,96]



that structures due to quasi vibrations in the transient negative anion TNI can besides in ETS also be seen on the fragment ion yield channel. The condition is that the detection efficiency is independent on the translational energy of the ion. Conversely, successive population of vibrational levels in the final CO channel produces structure in the ion yield curve when the instrument is set to detect only fragment ions with zero kinetic energy. This has clearly been demonstrated by Dressler and Allan [95] by switching their instrument between the two modes. In the zero kinetic energy mode, the O^- ion yield curve exhibits a series of 5 strong peaks separated by 0.27 eV due to population of the vibrational levels $\nu = 0 - 4$ in CO. Conversely, when the instrument is operated with constant detection efficiency (for ions in the energy range up to 0.5 eV) the O^- yield exhibits a series of peaks separated by 0.1 ± 0.01 eV, related to the symmetric stretch vibration in the transient ion.

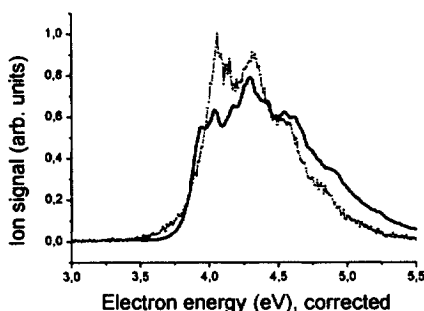


Figure 7. Formation of O^- by electron attachment to CO_2 measured with the present TEM-QM set-up (stars connected by a line) as compared to the results obtained by Dressler and Allan [95] (designated by full line).

A comparison of the O^- curve from CO_2 obtained by the presently used instrument with the data of Dressler and Allan (see Fig.7 where we demonstrate the capability of the present instrument in comparison to the results of [95] for seeing both vibrational progression at once) indicates that it strongly discriminates (although not quantitatively) against translational energies of the ions. Thus the structure in Fig.6 in the $HCOO^-$ ion yield should focus on the population of vibrations in $HCOO^-$ and thus constitute the first experimental evidence for vibrational structure of the fragment anion channel. The structures have been reproduced several times resulting in a prominent maximum followed by two further weak maxima at a separation of 340 ± 30 meV (solid bars in Fig. 6). It is interesting to note that in addition we can see in Fig.6 further less prominent structures indicated by broken lines. Following the above argument these structures could be a fingerprint of vibrations in the formate anion.

4. ACKNOWLEDGEMENTS

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Electron Driven Processes

Scientific Challenges and Technological Opportunities

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Abstract: Electron scattering is a mature area of scientific research and one that plays a key role in many disparate areas of science and technology. Recent advances in both experimental techniques and computational methodology have led to a renaissance in the study of electron interactions with atomic and molecular targets in both gaseous and condensed phases of matter. Many of these new studies are at the forefront of modern interdisciplinary research. In this article a brief review of the current state of knowledge in electron scattering will be discussed and a few examples of the new and exciting areas of electron research presented.

Key words: Electron scattering; Energy-loss spectroscopy; Biomolecules; Ozone; Optical grating; Electron diffraction.

1. INTRODUCTION

Electron induced reactions in both gaseous and condensed phases initiate and drive the basic physical-chemical processes in many different areas of science and technology from industrial plasmas to living tissues. For example, in contrast to previous hypotheses, radiation damage in the DNA of living systems has now been shown to arise primarily from collisions of very low energy (sub-ionization) secondary electrons through dissociative attachment to the components of DNA molecules or to the water around them (Boudaïffa et al (2000)). A collaborative project probing electron induced fragmentation of ozone has revealed the possibility of a direct coupling mechanism between the lower ionosphere and the Earth's ozone layer and thus predicted that alterations in global ozone concentrations may

directly affect terrestrial radio transmissions, providing a new methodology for probing upper atmosphere ozone loss and mesospheric chemistry (Senn et al (1999)). In the technological field electron induced reactions underpin most of the multibillion dollar modern semiconductor industry since it is those reactive fragments produced by electron impact of etchant gases that react directly with the silicon substrate (Tanaka et al (2000)). Electron induced processes are also of extraordinary importance for determination of structure and chemical reactivity of species adsorbed on surfaces indeed recently it has been demonstrated that discrete electron reactions may be performed at the individual molecular level using STM based technology thus introducing the prospect of designer synthesis on the nanoscale (Hla et al (2000)).

The energy region below 3 eV is of particular interest since here the cross section for electron induced processes are often dominated by the formation of temporary negative ions (anions) These quasi bound states are provided by the short range polarization interaction induced when an electron approaches a target molecule the subsequent decay of which may lead leave the target molecule excited or even lead to dissociation. In the case of dissociative electron attachment (DEA) in many systems a 100 % selectivity with respect to the cleavage of a particular bond can be obtained ! This opens interesting prospects for a selective chemistry induced by electrons. It should also be noted that electron induced processes are often directly linked to photon induced processes since photons of sufficient energy excite or liberate electrons from targets which may then drive the local chemistry for example such processes lead to the formation of molecules in the interstellar medium, molecules that may be the precursors of life itself (see Dawes et al in this volume).

However at present only the rudiments of such electron induced reactions are understood such that the paucity of our knowledge of such processes is limiting further development in many of other areas of science and technology. We therefore urgently require an in depth understanding of the basic dynamics of electron induced reactions in both the gaseous and condensed phases of matter. This paper will review current areas of research in electron induced reactions and highlight a few exciting new areas of applied research in atmospheric physics, astronomy and biophysics.

2. ELECTRON SCATTERING FROM ATOMS AND MOLECULES

2.1 The State-of-the Art

The interaction of electrons with atoms and molecules has been studied experimentally for almost a century, since the pioneering work of Franck and Hertz (1914) and Ramsauer (1921). Franck and Hertz provided a validation of the Bohr theory on the discrete nature of atomic energy levels, while Ramsauer and Kollath provided the first evidence of the polarisation of the target charge cloud by an incident charged particle, hence demonstrating the need for a quantum mechanical representation of the scattering of discrete particles. The first quantum mechanical calculations of Massey and Mohr (1931) established the now traditional interactive development of theoretical and experimental techniques in this research field. A good example of such experimental/theoretical interactive development was the experimental discovery of short lived negative ion 'resonances' by Schulz (1963) that led to the development of time dependent calculations incorporating nuclear motion. The intricacy of theoretical calculations also led to the development of coincidence experiments to test the theoretical treatments of electron-atom excitation processes.

The field of electron-atom/molecule scattering is therefore well established and as is shown in many of the papers in this volume, we have a good understanding of the major mechanisms and dynamics involved in electron collision processes.

However, the demand for accurate scattering cross sections and knowledge of the final quantum mechanical states of the collisional 'reactants' has grown rapidly in the last decade. Therefore there remains a crucial need to provide extensive data on electron-atom, electron-molecule and electron-ion collision cross sections, yet after eighty years of experimental study we have 'complete' information on only a few target systems (the rare gases) while several targets (e.g. radioactive atoms and free radical molecules) have yet to be studied. Even if it were feasible to collect all the data presently required by the applied science community, it would require the attention of the whole of the world's atomic and molecular research teams for over fifty years! Hence in the past twenty years great emphasis has been placed upon the development of reliable theoretical techniques that, once validated experimentally, will be able to produce the

data required to an acceptable level of accuracy. Great advances have been made by the theoretical community e.g. the development of the R-Matrix method by Burke and co-workers and the adoption of parallel computational techniques, particularly in the understanding of electron-atom scattering (see papers by Whelan and co-workers in this volume) but theory alone is not yet capable of producing the volume and accuracy required for all the many systems of interest. Therefore experimentalists are continuously developing techniques to provide stringent tests of the developing theoretical treatments of electron collision processes, for example:

- The development of novel methods of laser and collision spectroscopy to prepare molecules in specific target states now provides the opportunity for the investigation of state-to-state collision processes.
- The utilization of chemical synthesis techniques to produce beams of transient (radical) molecular targets has opened the possibility of probing electron/positron energy transfer processes in highly reactive systems pertinent to both industry and biochemistry.
- The prospect of trapping molecules in optical traps will provide an opportunity to study well isolated cooled (no internal energy) molecules (possibly biological) under controlled experimental conditions.
- The ability to prepare and analyse the effect of charged particle irradiation of bio-molecules such as DNA.
- The development of new instrumental techniques e.g. highly efficient position-sensitive detectors, angle-changing electron spectrometers and the use of STM technology.

In the remainder of this article examples of such experimental advances and their impact on the field will be given.

3. ELECTRON INTERACTIONS WITH BIOMOLECULES

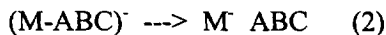
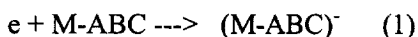
3.1 Degradation of DNA and its nucleotide bases by irradiation with subionization electrons

Many of the mutagenic or lethal effects of ionizing radiation can be traced to structural and chemical modification of cellular DNA. The mechanisms by which such degradation occurs have been the subject of considerable research effort with genotoxic effects of ionizing radiation in living cells

being commonly attributed to direct impact of high-energy quanta or by complex radical chemistry (triggered by production of OH species by primary ionizing radiation). However recently this explanation has recently been questioned by the pioneering work of Sanche and co-workers who suggest that DNA lesions are induced by the *lower energy, secondary electrons* generated by the primary ionizing radiation. Sanche and co-workers revealed that

- low energy electron irradiation directly induces both single and double strand breaks at energies well below the ionization limit of DNA (7.5eV) and
- that the probability of strand breaks are one to two orders of magnitude larger for electrons than for corresponding energy photons.

The typical energy distribution of secondary electrons created in ionizing radiation impact of mammalian tissue is shown in the upper portion of figure 1. The majority of the copious secondary electrons ($\sim 5 \times 10^4$ per MeV) created within 10^{-15} s along the radiation track have energies below 20eV. These low-energy electrons must undergo multiple inelastic scattering events as they thermalise. The primary energy-loss channels for electrons with energies typical of the secondary distribution are ionization, direct electronic excitation and most important (but until recently little studied) **resonance scattering**. The latter results in the formation of Temporary Negative Ions (TNIs), which decay via electron autodetachment and dissociative electron attachment (DEA) the latter process leading to direct dissociation of the parent molecule. This process may be summarised in the two step 'reaction';



where $(M-ABC)^{\cdot -}$ is the temporary negative ion which decays to a residual anion ($M^{\cdot -}$) and a (reactive) molecular fragment ABC.

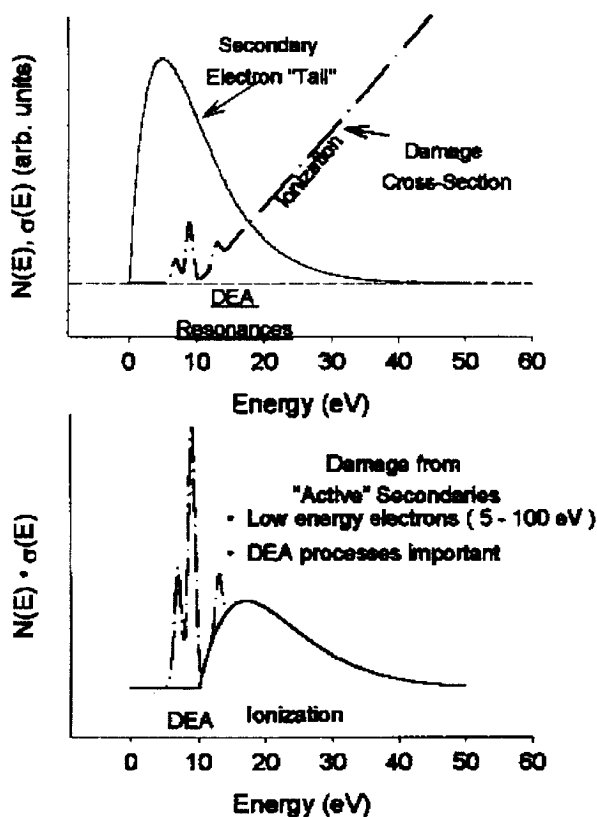


Figure 1. Top Frame: Typical energy distribution of secondary electrons emitted during a primary ionizing event. Also shown are the estimated relative cross-sections for some of the main inelastic electron energy-loss channels that the secondaries undergo as they traverse the interface. Lower Frame: Estimate of the effective "damage" probability obtained by convoluting the energy-loss cross sections with the secondary electron energy distribution.

Hence the process of DEA provides a direct low energy process for the degradation of DNA (and other key cellular material) by resonant electron attachment to basic molecular components (base, deoxyribose, phosphate, or hydration H_2O) suggesting that single strand damage is *site specific* and

proceeds through *discrete molecular bond rupture*. This in turn suggests that double strand breakage is simply induced through local chemical reactivity. The DEA fragments produced within the cellular DNA subsequently reacting with adjacent bases (at 3.4Å), or the phosphate-sugar backbone (at < 5Å) leading to clustered damage within the DNA strand. Further studies on electron interactions with the molecular components of DNA and DNA itself are on going as part of a European Network programme involving over a dozen research groups.

4. ELECTRON SCATTERING FROM TRAPPED ATOMS

The ability to cool trap and manipulate atoms, culminating in the successful formation of Bose-Einstein Condensates (BEC), is one of the most exciting advances in the field of atomic and molecular physics in the late 20th century. Such experimental advances are pioneering the construction of new instrumentation at both the atomic and nanoscale (e.g. the development of atomic interferometers) and has led to orders of magnitude improvement in our ability to measure time while opening the possibility of developing the new technologies of atom lasers, quantum computing, quantum cryptography and teleportation.

To date the role of collisions in atom traps has been viewed mainly as detrimental- leading to trap loss - but recent experiments and new theoretical formalisms suggest that collisions between trapped atoms, between trapped atoms and external stimulation phenomena (e.g. photons) and between cold atoms and external surface media may lead to new physico-chemical phenomena that may, in turn, allow new exciting fields of atomic, molecular and optical and condensed matter physics to be developed. For example in photo-association spectroscopy excited bound molecular states are created from free atoms by using laser photons to form alkali dimers. Such sources of cold molecules will allow high resolution spectroscopic measurements to be performed to test modern QED theory.

A source of cold trapped atoms in a well defined quantum state provides an ideal target for electron collisions. Preliminary experiments (Shappe et al (1995)) using electrons as a projectile have shown that trapped atoms may be used to measure *absolute* total scattering cross sections and ionisation cross sections from both ground and excited atomic states with *very high*

accuracy. Traditionally such values are derived from crossed electron-atom/molecule beam experiments but the accuracy of such measurements are currently limited by inherent problems in determining collisional geometry's and both the target and projectile number densities. Many of these problems are absent when the target is a well defined cold atom source, since absolute cross sections may be derived by measurement of only *ONE* number density and by the simple measurement of the ratio of trapped atom flux before and after electron irradiation. Hence cross sections may be measured with an accuracy of 1-2% for both ground state and excited state atoms, producing data that will provide the most stringent test of modern theoretical formalisms of electron scattering from the heavier (i.e. not H or He) atomic targets, calculations that require the incorporation of relativistic effects within the scattering problem.

Experiments that can, and should, now be developed include:

- (i) the study electron collisions with unstable/radioactive nuclei (capable of being held in a trap e.g. Fr^{17}),
- (ii) the use positrons to study antimatter - atom collisions,
- (iii) the use ultracold electrons (energies < 100 meV) to study electron cold atom collisions where the interaction time between the two particles is significantly lengthened and pure quantum interference phenomena may be revealed (Field et al (2002) this volume)
- (iv) the study of electron interactions with cold *molecules* formed by photo-association in a dense atom trap,
- (v) to probe the effect of electron injection on the structure, cohesion and formation of cold atom clouds (including BECs) hence introducing the prospect of using condensed matter techniques i.e. electron diffraction to study cold atom physics.

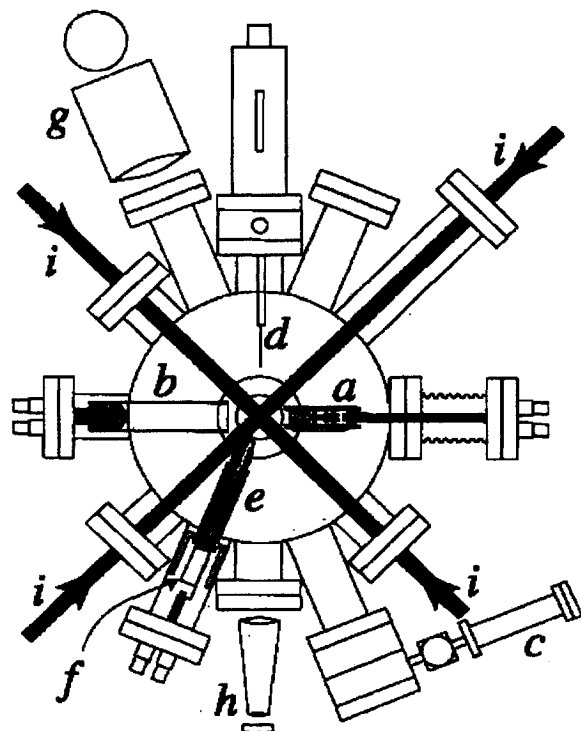


Figure 2. Experimental apparatus used to study electron collisions with trapped atoms.

5. ELECTRON SCATTERING FROM AN OPTICAL GRATING

The demonstration of wave-particle duality was fundamental to the development of quantum mechanics with the classic Davisson and Germer (1927) experiment revealing that electrons could show wave like properties being one of the pivotal experiments of the early 20th century. Shortly afterwards P L Kapitza and Paul Dirac wrote a farsighted paper predicting that in a manner analogous to the diffraction of light by a mechanical grating electrons would be diffracted by light if the light particles (photons) were arranged in a periodic manner similar to that found in a crystal! Indeed such a process is the reverse of common undergraduate laboratory experiments in which the light (e.g. X-ray) is the wave and the electrons (through their periodicity in the surface/crystal) the matter.

Such an experiment requires the formation of a regular lattice for optical radiation coupled to a well collimated electron beam. Kapitza and Dirac suggested that such an optical lattice could be produced by an optical standing wave formed using two counter propagating and overlapping light beams however since electrons will only interact very weakly with the optical grating, via the so called ponderomotive potential it was not possible to attempt to measure such an effect until the development of lasers. However early attempts to observe what is now known as the Kapitza-Dirac effect in the 1960s were inconclusive in part due to the lack of stability in early laser systems, their short coherence lengths and modest intensity. However it was soon recognised that the effect will be resonantly enhanced if the electrons are within an atom and hence experiments performed in the 1980s revealed the diffraction of atoms by an optical grating (the so called atomic Kapitza-Dirac effect). This has led to important advances in atom optics through for example the use of the effect to form atomic beam splitters.

However only in 2001 was the Kapitza-Dirac effect demonstrated for *free electrons*. Freimund et al reporting the diffraction of 380 eV electrons by an optical grating formed from a standing wave of 532 nm radiation (Figure 3). This pioneering experiment opens the possibility of developing a new range of electron optical devices in a way similar to those using atoms, e.g. Since the diffracted electron beams are coherent the Kapitza-Dirac effect forms a coherent beam splitter for electrons which may be used to construct a sensitive electron interferometer. The development of a super-sensitive electron interferometer has been suggested as capable of revealing electron-

atom scattering phase shifts, the quantum state of the electromagnetic field and even may be capable of detection of gravity waves.

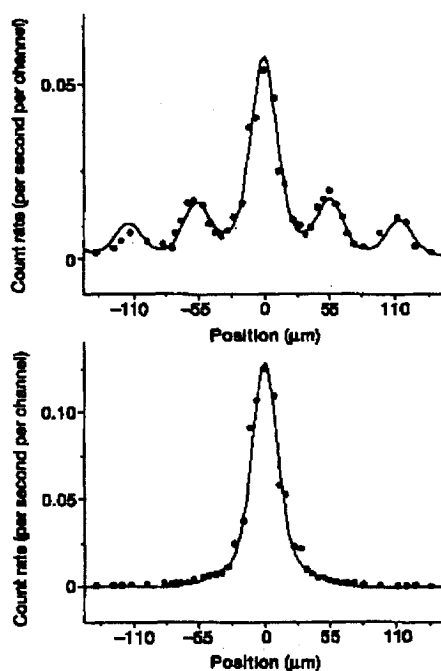


Figure 3. Observation of the Kapitza-Dirac effect for free electrons diffracting from an optical grating. Dots experimental data, solid line numerical solution of the Schrodinger equation.

6. CONCLUSIONS

Electron-atom/molecule scattering has been the subject of intense research activity, both experimentally and theoretically, for nearly a century, yet particularly for electron-molecule scattering our understanding of the dynamics of such processes remains limited. Due to their importance in a myriad of industrial, astrophysical, atmospheric and biological processes absolute electron scattering cross sections are required for most atomic and molecular systems yet the current database is limited to a few easily prepared systems. Only recently have experimental studies been extended to

unstable reactive and free radical species while new experimental techniques incorporating advances in atom trapping and laser spectroscopy are being adapted to provide new insight into electron collision dynamics. The combination of traditional gas phase electron spectroscopy with condensed matter techniques is allowing collective effects to be probed, while electron scattering studies from clusters provide a useful intermediate between free atom/molecules in the gas phase and collective effects in the condensed phases. Experimental electron scattering is therefore undergoing something of a renaissance, and as we approach the centenary of the first electron scattering experiments we may at last, be able, to understand *and exploit* the intricacies of electron scattering interactions from atoms and molecules.

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QUANTUM TIME ENTANGLEMENT OF ELECTRONS

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Abstract Correlation is often significant in electron scattering from atoms, nuclei and bulk matter. Mathematically, as well as conceptually, correlation and entanglement are defined in the same way. Both correlation and entanglement connote mixing. Both are described as a deviation from a product (uncorrelated) form. In quantum optics the term entanglement is used to describe the spatial mixing of states of a system by external electromagnetic fields. In static systems correlation arises from inter-particle fields that mix wavefunctions. Correlation dynamics, intrinsic in scattering from few and many body systems, adds the dimension of time to the basic conceptual framework. Time correlation, described here, mixes the time evolution of the particles. This time entanglement, which is non-local, requires both spatial correlation and quantum time ordering.

Introduction

Time and space are dialectic. On the one hand time is commonly regarded as a fourth dimension, where ict is treated on an equal basis with the three x, y, z spatial dimensions. This isomorphism of time and space occurs in both the wave equation and in relativity. From this point of view correlation in time should be similar to correlation in space. On the other hand physical systems can be moved back and forth in space, but not in time. There is a direction to time. Moreover, N -body systems

are conventionally described in terms of $3N$ spatial coordinates, but only one time coordinate.

The direction of time is made explicit by time ordering of interactions. Without the constraint of time ordering the interactions of each particle may be grouped together, and the overall time evolution may be factored into a product of single particle time evolution operators. Entanglement in time then disappears. Our description of time entanglement is guided by previous studies of spatial electron correlation dynamics [1, 2, 3], and we use the words "time entanglement" and "time correlation" interchangeably.

Time entanglement of electrons, the question of how electrons communicate about time, has been addressed in a series of recent papers [4, 5, 6, 7]. Time ordering places a pairwise constraint on the sequencing of time dependent external interactions that determine the time evolution of a multi-electron system. This constraint provides interconnections of the electrons in time, i.e., time correlation. Time ordering, time correlation, time entanglement, sequencing of interactions, the direction of time propagation, non-commutivity of interaction operators, off-energy-shell effects, and the asymptotic macroscopic condition needed to specify the solution to the Schrödinger equation, are all interconnected [4], as we shall discuss. Recently experimental evidence has been found for time entanglement of electrons in observations of polarized light emitted following ionization with excitation into the first excited state of helium in collisions with both electrons and protons [8].

1. Formulation

1.1 Time entanglement

Time ordering occurs in the equation for the time evolution operator, $U(t_2, t_1)$, which describes how the system changes between time t_1 and time t_2 , namely [3, 7, 9],

$$\begin{aligned} U(t_2, t_1) &= \sum_{n=0}^{\infty} (-i/\hbar)^n \int_{t_1}^{t_2} dt^{n'} V(t^{n'}) \cdots \int_{t_1}^{t'''} dt'' V(t'') \int_{t_1}^{t''} dt' V(t') \quad (1) \\ &\equiv \sum_{n=0}^{\infty} \frac{(-i/\hbar)^n}{n!} \int_{t_1}^{t_2} dt^{n'} \cdots \int_{t_1}^{t_2} dt'' \int_{t_1}^{t_2} dt' T V(t^{n'}) \cdots V(t'') V(t'). \end{aligned}$$

Here $V(t)$ is the interaction (or sum of interactions) of an atomic or nuclear system with light or matter, and T is the Dyson time ordering operator [9], which imposes the causality-like constraint that $V(t')V(t) = 0$ if any $t' < t$. We note that all of the time dependence of the system is carried by $T V(t^{n'})V(t^{n'-1}) \cdots V(t'')V(t') = \sum_p V(t^{n'})\Theta(t^{n'} -$

$t^{n'-1})V(t^{n'-1})\dots V(t'')\Theta(t''-t')V(t')$, where $\sum_p$ denotes a sum over all $n!$ permutations of time sequences, and $\Theta(t'-t) = 1$ (or 0) for $t' > t$ (or $t' < t$) is the Heavyside step function.

The time ordering operator, T , may be generally decomposed into two terms [7], namely, $T = \bar{T} + \Delta T$. The term $\bar{T}$ is the time independent part of T , which does not connect the various interactions $V(t)$ in time. Without ΔT the sequence of the $V(t^{n'})\dots V(t'')V(t')$ interactions is unimportant, and there is no time ordering. In this case the evolution operator for the system may be expressed as a product of evolution operators for each electron [5]. The enforcement of time ordering by ΔT on the sequence of interactions, $V(t^{n'})\dots V(t'')V(t')$, gives rise to pairwise time connections between external interactions $V(t)$ between the various electrons [7]. These connections provide correlation in time, i.e., time entanglement.

1.2 Time entanglement in second order

The effect of time entanglement first occurs in the second order contribution in V , where it may be expressed as a non-zero commutator of $V(t)$ with $V(t')$. To illustrate this point in the context of the calculation presented below, let us a two-electron transition occurring via $V(t) = V_1(t) + V_2(t)$. In this case there are four second order terms, namely, V_1V_1 , V_1V_2 , V_2V_1 and V_2V_2 . The V_1V_1 and V_2V_2 terms do not contribute to correlation between different electrons. While they are included in our calculations below, we ignore them here and consider the cross correlation terms in V_1 and V_2 that may connect the time evolution of different electrons. One may write $T V_1(t'')V_2(t') = \frac{1}{2}[\Theta(t''-t')V_1(t'')V_2(t') + \Theta(t''-t')V_2(t'')V_1(t')]$. Using $\bar{T} = 1$, which corresponds to replacing $\Theta(t)$ by its time average value of $\frac{1}{2}$, it is evident that,

$$\bar{T} V_2(t'') V_1(t') = \frac{1}{2}(V_2(t'')V_1(t') + V_2(t')V_1(t'')) \quad , \quad (2)$$

so that,

$$\Delta T V_2(t'') V_1(t') = \frac{1}{2}\text{sign}(t''-t')[V_2(t''), V_1(t')] \quad . \quad (3)$$

The commutator $[V_2(t''), V_1(t')]$ provides an explicit time connection between interactions at different times, t' and t'' . The origin of such commutators is discussed briefly below. Including ΔT corresponds to a Magnus-like expansion [10, 11, 12] of the evolution operator in commutators. The operator ΔT produces non-local time entanglement between electrons, as illustrated in figure 1. In previous papers [4, 5, 6, 7] we

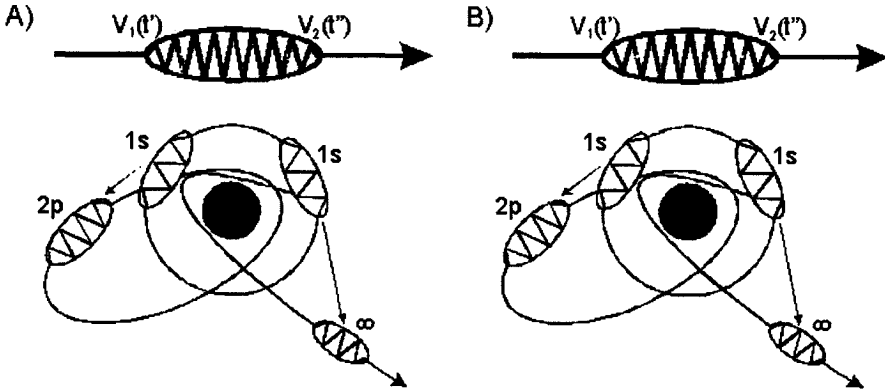


Figure 1. Entanglement of two electrons changing from a $(1s, 1s)$ initial state to a $(2p, \infty)$ final state via interactions $V_1(t')$ and $V_2(t'')$. Time correlation occurs when $V_2(t'')$ is connected to $V_1(t')$. With quantum time ordering $V_2(t'')V_1(t')$ may differ from $V_1(t')V_2(t'')$. Then the evolution of the two electrons become entangled in time.

have referred to ΔT as the time correlation operator, T_{cor} , and $\bar{T}$ as the uncorrelated term, T_{unc} . We note that $\Delta T \sim \text{sign}(t'' - t')$ is antisymmetric in $t'' - t'$, while $\Delta TV(t'')V(t')$ is symmetric in $t'' - t'$. Thus, both $\bar{T}V(t'')V(t')$ and $\Delta TV(t'')V(t')$ are invariant when either the direction of time is reversed between the two interactions, or the overall direction of time is reversed, e.g. by reversing the sign of η in Eq(3) below.

1.3 The direction of time

To understand the influence of $\bar{T}$ and ΔT , it is instructive to look at their contributions in energy space. The Fourier transform $\Theta(t' - t)$, which occurs in the time propagation between interactions $V(t')$ and $V(t'')$ in Eq(1), corresponds to [13],

$$\begin{aligned} -i \int d(t' - t) \Theta(t' - t) e^{-i(E_0 - E)(t' - t)} &= \lim_{\eta \rightarrow 0^+} \frac{1}{E_0 - E + i\eta} \\ &= i\pi \delta(E_0 - E) - \frac{P_v}{E_0 - E} \quad (4) \end{aligned}$$

In the formulation of stationary scattering theory [14], $\eta \rightarrow 0^+$ corresponds to the asymptotic condition for incoming plane waves and outgoing scattered waves [14], and P_v is the principal value contribution that excludes the singularity at $E = E_0$. Since $\int d(t - t') e^{i(E_0 - E)(t - t')} =$

$2\pi\delta(E_0 - E)$, it follows from Eq(3) that,

$$\frac{i}{2} \int d(t' - t) \text{sign}(t' - t) e^{-i(E_0 - E)(t' - t)} = \frac{P_v}{E_0 - E} . \quad (5)$$

The Fourier transform of ΔT is the principal value part of the energy propagator, which corresponds to the η asymptotic condition. Thus ΔT , time ordering, the direction of time propagation, time correlation and the sequencing of interactions all correspond to the η asymptotic condition. The direction of time propagation may be reversed by reversing the sign of η , where outgoing scattered waves are replaced by incoming scattered waves.

Note that even though $\eta \rightarrow 0^+$, the influence of this term is usually finite. An elementary example is an isolated resonance whose amplitude is proportional to $\frac{1}{E_0 - E + i\Gamma}$, i.e. a simple pole in the complex plane [15] where Γ corresponds to $\eta \rightarrow 0^+$. In a well isolated resonance, without interference with other competing amplitudes, the contribution from $\eta \rightarrow 0^+$ accounts for half of the total scattering cross section [15]. We emphasize that omitting the η term, which gives the direction of the time propagation of the system, is different than taking the limit $\eta \rightarrow 0^\pm$.

1.4 Correlation in space and in time

1.4.1 The spatial independent electron approximation.

Obtaining the eigenstates of an unperturbed Hamiltonian, such as,

$$H_0 = \sum_{j,k \neq j} (H_{0j} + 1/r_{jk}) , \quad (6)$$

is often a non-trivial task in itself for a many-electron system. Coupling these multi-electron eigenstates to interactions with a time dependent external interaction, denoted in the interaction representation by, $V(t) = \sum_j V_j(t) = \sum_j e^{iH_0 t} \tilde{V}_j(t) e^{-iH_0 t}$ is even more difficult. Therefore approximating the electron correlation term, $1/r_{jk}$, by an average effective one electron term simplifies the dynamic many-body problem considerably. Without correlation the Hamiltonian for the N -electron system reduces to a sum of N uncoupled Hamiltonians. This is the key step in the independent electron approximation. Without spatial correlation the single particle Hamiltonians then commute with each other; $[H_{0j}, H_{0k}] = 0$. As a result the target's electrons can be considered independently of one another. In the fully correlated system, however, the operators $V_j(t) = e^{iH_0 t} \tilde{V}_j(t) e^{-iH_0 t}$ are multi-electron operators due to the $1/r_{jk}$ correlation interactions, which interconnect the various electrons in H_0 . As a consequence it is only in the independent electron

approximation [3] that $[H_{0j}, V_k(t)] = \delta_{jk}[H_{0j}, V_j(t)]$, so that the external interaction, reduces to a sum of single particles operators, namely, $V(t) = \sum_j e^{iH_0 t} \tilde{V}_j(t) e^{-iH_0 t} = \sum_j e^{iH_{0j} t} \tilde{V}_j(t) e^{-iH_{0j} t}$.

Only when spatial electron correlation is removed, do the $V_j(t')$ commute with the $V_k(t')$. When these various $V_j(t')$ terms commute the evolution operator reduces to a product of evolution operators for individual electrons,

$$\begin{aligned} U(t, t_0) &= T e^{-i \int_{t_0}^t \sum_j V_j(t') dt'} = \prod_j T e^{-i \int_{t_0}^t V_j(t') dt'} \\ &= \prod_j U_j(t, t_0) \equiv U_{\text{IEA}}(t, t_0). \end{aligned} \quad (7)$$

Now the electrons evolve independently during the collision. This problem may now be easily solved by the method of separation of variables so that the solution is a simple product of single electron terms. The transition probability is then also a product of independent single-electron probabilities [3].

All phase information between electrons is lost in the independent electron approximation. In the independent electron approximation there is no time ordering between electrons, although time ordering for each individual electron remains.

We note here that it is convenient to use the interaction representation to track the influence of non-commuting operators. This representation is often used when V is an explicit function of the time. Nevertheless time entanglement occurs in various representations.

1.4.2 The independent time approximation. The time evolution of different target electrons becomes interdependent (correlated) if the Hamiltonian H_0 cannot be split into a sum of single electron terms. The operators $V_j(t)$ and $V_k(t')$ do not commute, and the evolution operator is not separable. This means that the presence of spatial correlation results in correlated time evolution of the electron amplitudes. The interaction of the projectile with one of the electrons influences all the other electrons, and the target reacts as a whole.

One may associate with each external interaction a transition between virtual target states. In this picture, one may ask whether the result of interaction first with a state j and then a state k is different from interacting first with k , and then with j . If the two interactions cannot be commuted, the system is temporally aligned. Then the time evolution for each individual interaction time is no longer translationally invariant, and the associated energy is not conserved. Only on the macroscopic level is energy conservation restored.

In analogy with independent electron approximation, we can introduce the independent time approximation assuming that time evolution of a target electron occur independently on other electrons in some time averaged field [6]. Formally, we assume that, under certain conditions, one may rewrite Eq. (1) as

$$\begin{aligned} U(t, t_0) &= T e^{-i \sum_j \int_{t_0}^t V_j(t') dt'} \approx \bar{T} e^{-i \sum_j \int_{t_0}^t V_j(t') dt'} \\ &= \prod_{j=1}^N \bar{T} e^{-i \int_{t_0}^t V_j(t') dt'} = \prod_{j=1}^N \bar{U}_j(t, t_0) = U_{\text{ITA}}(t, t_0). \end{aligned} \quad (8)$$

The operator $\bar{T}$ gives uncorrelated temporal propagation, yet may include a time averaged contribution from time ordering. Temporal correlation is defined as the difference between an exact result and an uncorrelated limit, e.g. $T_{\text{cor}} = T - \bar{T} = \Delta T$. This also corresponds to the statistical notion of correlation as a fluctuation about some mean value [16]. The correlation or entanglement term, ΔT , regulates sequencing and gives time correlation or time entanglement of the interactions $V(t)$. In dynamic systems [7] time correlation is provided by enforcement of time ordering on the sequence of interactions, $V(t_n) \dots V(t_2)V(t_1)$, which cause the quantum system to change.

Time correlation (or entanglement) between electrons corresponds to cross correlation [17] between the time propagation of amplitudes for different electrons, and describes how electrons communicate about time. Autocorrelation, arising from entanglement of interactions, i.e., $[V_1(t''), V_1(t')]$ and $[V_2(t''), V_2(t')]$, is also an observable effect [18].

1.4.3 Comparison of spatial and temporal correlation.

There are similarities between the temporal independent time approximation and the spatial independent electron approximation, as seen in table 1. Both time and space correlation can be defined as a deviation from an uncorrelated limit. The uncorrelated limit may be defined by a product form. Particle identity, which has been ignored for conceptual simplicity, may be restored by antisymmetrizing the uncorrelated single particle wavefunctions, as done in our calculations below. The uncorrelated limit may also be described by an average of the appropriate correlation operator, given in table 1. Then correlation may be defined in terms of the fluctuation from the average term, as done in statistical mechanics [16]. In both the spatial and temporal cases the average term can form the basis for useful approximate calculations.

There are also notable differences between temporal and spacial correlation, detailed in table 1. While correlation in space arises in the asymptotic target Hamiltonian, H_0 , and affects both the asymptotic

Table 1. Comparison of correlation in space and time.

	Spatial correlation	Temporal correlation
Cause:	$v_{ij} = 1/r_{ij}$ internal Coulomb interactions	$T V(t'')V(t')$ time ordering of external interactions
Origin:	$H_0 = \sum_j H_{0j} + v_{ij}$	$i\hbar \partial U(t)/\partial t = U(t)$
Uncorrelated limit:	IEA	ITA
product form	$\psi(x'', x') = \prod_j \psi_j(x^{j'})$	$\psi(t'', t') = \prod_j \psi_j(t^{j'})$
no fluctuations	$v_{cor} = v_{ij} - v_{av} = 0$	$T_{cor} = \Delta T = T - T_{av} = 0$
average value	$v_{ij} \simeq v_{av} = v_{mean \ field}$	$T \simeq T_{av} = \Delta T$

wavefunction, $|i\rangle$, and the evolution operator, U , correlation in time occurs only in the time evolution operator $U(t, t_0)$. Correlation in space comes from $1/r_{ij}$ inter-electron interactions within the target. In the independent electron approximation (IEA) phase coherence and time correlation between electrons are both lost, as is evident from equation (7). Time correlation arises from the time ordering of the external $V(t)$. This time ordering in U corresponds to an asymptotic condition that is enforced when $\Delta T \neq 0$. When $\Delta T = 0$, then T is replaced by a constant average value of T , namely $\bar{T}$. In this uncorrelated limit all time sequences of the $V(t)$ are equally weighted, leading to a single time averaging over each $V(t)$ in Eq (1). Removing some or all of the sequencing terms is straightforward in practice since the ΔT terms are easily identified since the ΔT terms are a factor of i out of phase from the $\bar{T}$ terms, evident from Eq(3).

2. Results

2.1 Calculations

The calculations which we present below are done by including the external interaction, V , through second order and the internal electron-electron interactions to all orders[19, 20]. Our technique is standard,

so that our method for including time ordering may be used in other calculations [21, 22, 23, 24]. The most challenging part of these calculations is evaluation of the second order amplitude with fully correlated intermediate states, namely [20],

$$\lim_{\eta \rightarrow 0^+} \sum_{\alpha} \int d^3k \frac{\langle \phi_f | V(\vec{k} - \vec{k}_f) | \phi_{\alpha} \rangle \langle \phi_{\alpha} | V(\vec{k}_i - \vec{k}) | \phi_i \rangle}{(\vec{k} - \vec{k}_f)^2 [k_i^2 - k^2 - 2m_p E_{\alpha} + i\eta] (\vec{k}_i - \vec{k})^2} . \quad (9)$$

Here $\vec{k}_i$ ($\vec{k}_f$) and m_p denote the initial (final) momentum and mass of the projectile, and α denotes an intermediate state. There is a sum over bound and an integral over continuum intermediate states, $|\phi_{\alpha}\rangle$. In the calculations presented here, V is the Coulomb interaction between the projectile and a target electron. Since in most cases $V(t)$ changes slowly compared to the period of oscillation of the carrier wave, $\hbar/E_{inc}$, where E_{inc} is the energy of the incident projectile, the use of stationary scattering is usually well justified. Including only the dipole contribution of this interaction can be used to evaluate the amplitude for scattering of atoms in strong photon fields.

In our calculations the energy propagator is separated into two terms,

$$\frac{1}{k_i^2 - k^2 - 2m_p E_{\alpha} + i\eta} = i\pi \delta(k_i^2 - k^2 - 2m_p E_{\alpha}) - \frac{P_v}{k_i^2 - k^2 - 2m_p E_{\alpha}} \quad (10)$$

This corresponds to Eq(3) above. The principal value contribution is the most difficult to evaluate. We evaluate this contribution by numerical integration, which is time consuming. The principal value contribution may be easily omitted. Then there is no time ordering of the $V(t)$ interactions (as is evident from the discussion below Eq(3)), the asymptotic condition corresponding to outgoing scattering waves is not enforced, and there is no time correlation between the time evolution of different electrons. Eliminating this principal value contribution gives what we have previously described [6] as the independent time approximation. Without the principal value integral, the calculation in figure 2 took less than one hour on a 900 MHz computer. When the principal value integrals were included, the calculation required several days on the same computer.

2.2 Comparison with experiment

In figure 2 we present total cross sections for ionization-excitation by electron impact as a function of the velocity of the projectile. It is clear in this figure that the first Born calculation is not accurate at the lower projectile velocities shown, but does converge to the full second Born calculation (which includes first Born contributions) at the higher velocities

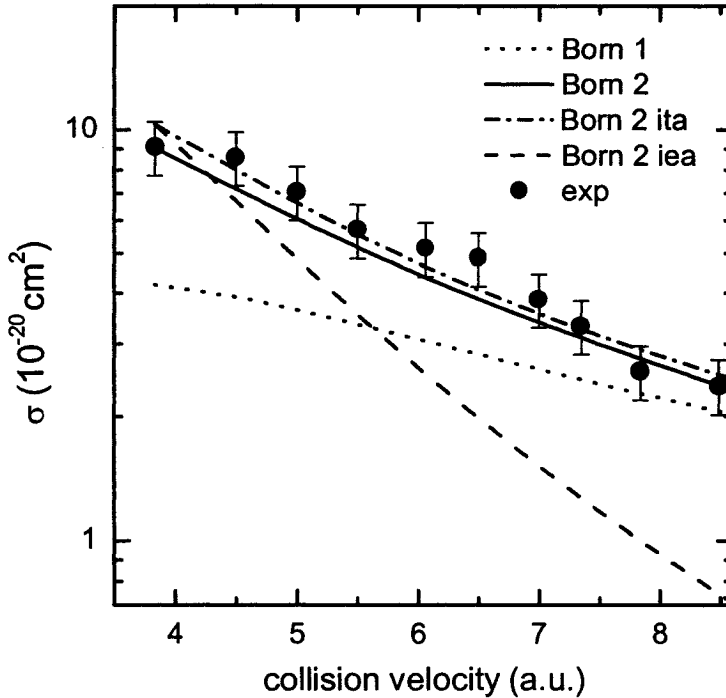


Figure 2. Cross section for the ionization-excitation of helium to $\text{He}^+(2p)^1\text{P}$ state by electron impact. Theoretical results: full line, full second-order calculations including time entanglement; chain line, calculations in the independent time approximation with time entanglement removed from our full calculations; broken line, independent electron approximation with spatial correlation removed; dotted line, first Born approximation where time entanglement is not possible. Experimental results[8]: full circles.

as expected. At high velocities the independent electron approximation fails. The failure is due to the absence of first Born contributions, which arise due to spatial correlation between electrons. In figure 2 the effect of time correlation results in increasing the total cross section. We note that the experimental cross sections have been normalized to our full second Born calculation at high velocity [8]. Similar results for proton impact have been reported elsewhere [5]. In the case of proton impact there is a 35% effect due to time entanglement between the two electrons in the polarization of the emitted light. This effect has been confirmed by experiment [8]. Other calculations have been done [5, 7]. In numer-

ous cases the effect of time correlation is small. But there are cases in which the effects are large [7].

3. Discussion

The description of scattering dynamics in quantum systems used in this paper relies on three principal features, namely, i) an asymptotic condition imposed on a differential equation, ii) the use of dual frequency-time representations, and iii) an energy-frequency relation. In our case the asymptotic condition carried by $\eta \rightarrow 0^+$, which is imposed on the solution to the Schrödinger equation, gives a unique wavefunction with outgoing scattered waves. This corresponds to a forward direction of time propagation, imposed on the time evolution operator. The effect of this $\eta \rightarrow 0^+$ contribution can be significant, as we have shown above. This property may be associated with causality [5]. By use of dual representations we mean that interrelated conjugate spaces are defined by integral transforms so that amplitudes may be analyzed using alternate representations. For example, the propagator $G(\omega', \omega)$ is the Fourier transform of the propagator $U(t', t)$, as is used in Eq(3). Such transforms between conjugate spaces provide a convenient way to deal with physically realistic wavepackets that are neither infinite, e.g. e^{iEt} , nor infinitesimal, e.g. $\delta(t)$, in their temporal (or spatial) extent. Amplitudes related by Fourier transforms are constrained by the band width theorem, $\Delta\omega\Delta t \geq 1/2$. The operator that generates ω in ω -space may be represented as id/dt in the dual t -space. The energy-frequency relation commonly used in quantum mechanics is linear, namely, $E = \hbar\omega$. One example is the Einstein photo-effect. In the general time dependent Schrödinger wave equation, the linear energy-frequency relation corresponds to an energy operator, $E_{op} = i\hbar\partial/\partial t$, which leads to non-commutivity, namely, $[E_{op}, t] = \hbar$. We have found these basic features useful in tracing the nature of various properties of time dependent quantum wavefunctions, in understanding the origin and role of commutators, in distinguishing quantum effects from classical effects, and in understanding the meaning of an asymptotic condition in both an energy and a time representation.

3.1 Arrow of time

In the introduction we noted the similarity of space and time. Space and time also differ. Space has no preferred direction. However, both causality and entropy give time a preferred direction. For example in the expression for ΔT in Eq.(3), $\text{sign}(t - t') = (t - t')/|t - t'|$ may be regarded as a unit vector in the direction of increasing time. However, on the atomic scale observables such as cross sections are usually invariant

under a reversal of time. Thus these microscopic properties may indicate the presence of an arrow of time as described above, but do not indicate the direction of the arrow of time. The direction of the arrow of time usually involves irreversibility. In practice most experiments are not irreversible. Performing the experiment for ionization with excitation of an atom interacting with an incoming beam of electrons described in section 3.2 with outgoing scattered waves (corresponding to $\eta \rightarrow 0^+$) is considerably easier than performing the time reversed experiment with multiple incoming ($\eta \rightarrow 0^-$) electrons. The issue of symmetry (or lack of symmetry) of the arrow of time often involves issues of coherence, phase space, statistics and entropy in practical experiments. Entropy is usually defined in terms of a temperature, which requires statistical equilibrium. In nuclear physics [25] the entropy of a many body system (say 30 or so nucleons) may be identified after a collision when the system has reached thermal equilibrium. This equilibrium is characterized by a Maxwellian distribution of velocities of the nucleons. Particles that come out of the interaction quickly do not have such a distribution and are not in thermal equilibrium. Slower particles, which have interacted with one another, are thermalized. This can be tested experimentally. One may also calculate how long it takes for the system to reach equilibrium. For many electron systems the equilibrium time may in some cases be the correlation time required for a correlated system to adjust. Calculations of this correlation time could be compared to experiment that observe whether or not the electrons have reached thermal equilibrium. This line of analysis also suggests that time ordering (i.e., causality) may be more fundamental in defining the arrow of time than entropy.

3.2 Energy non-conservation

In this paper and other recent papers [5, 6, 7] we have described the interconnection of various concepts associated with time ordering. This includes the term ‘off-shell’, which connotes a non-conservation of energy. As Madison has pointed out [21, 26], the use of ‘off-shell’ is potentially confusing because energy is conserved on a macroscopic time scale in most calculations, including those presented in this paper, where energy conservation is enforced by taking $\eta \rightarrow 0$. However, as discussed at the end of section II above, this limit is not unique: for example, taking $\eta \rightarrow 0^\pm$ differs from omitting η all together. Madison has demonstrated [21, 26] that the Green’s function may be generally found without separation into off-shell and on-shell parts. He has also presented a possibly general case, in which omitting η altogether gives standing waves, while applying $\eta \rightarrow 0^+$ (or 0^-) yields outgoing (or incoming)

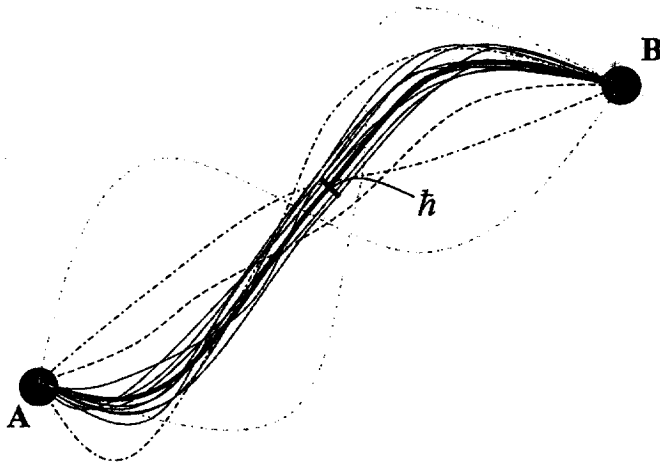


Figure 3. Competition between classical and quantum action. Classical action determines on true path between A and B. In quantum mechanics the action, $\int E dt$, is quantized. Within this limit of uncertainty, the system is free to follow any path. Pathways outside a quantum envelope of $\hbar$ are unlikely.

scattered waves. In any case energy non-conservation is permitted by the uncertainty principle in quantum systems for short times. We label the contributions arising from the principal value integral in Eq(3) as ‘off shell’ since the principal value contribution specifically excludes the on-shell contribution at $E = E_0$. It is this off-shell ($\eta \rightarrow 0^\pm$), principal value contribution that corresponds to ΔT , as discussed in Eq(5), which corresponds to time ordering, time correlation, sequencing, a direction to time and non-commutivity of the interaction operators. We view this macroscopically connected $\eta \rightarrow 0^\pm$ contribution as a sum over energy non-conserving quantum fluctuations in intermediate states, which correspond to non-local time entanglement of electrons [27].

3.3 Classical versus quantum action

One may also regard time ordering as the result of a competition between the classical and the quantum constraints on the action of the system. Action [28] is an integral of the energy of the system over time. In classical physics the trajectory of a particle is constrained by Fermat’s principle [29]: that nature seeks the most (or possibly the least) efficient way to go from A to B. The particle’s unique path is determined by minimizing the action. On the other hand quantum mechanics may be obtained from classical mechanics [30] by constraining the action to be

an integer multiple of $\hbar$. This leads, for example, to the uncertainty principle, $\Delta E \Delta t \geq \hbar$. In quantum mechanics all paths from A to B are possible, although those outside of an envelope of trajectories, whose width is proportional to $\hbar$, are statistically improbable [31]. Within this envelope of quantum uncertainty, time and energy may not be simultaneously localized. The non-locality in energy means that there are quantum fluctuations in energy, not present in solutions to classical equations, which violate conservation of energy for a short time. These non-local energy terms correspond to quantum time correlation arising from the constraint of time ordering corresponding to Eq(5). Time correlation between electrons occurs directly only when electrons interact with one another [6]. Then the effects of time ordering of external interactions for different electrons become coupled, and the evolution operators for different electrons with independent initial wavefunctions become interconnected in time. This correlation insures that the electrons cooperate in seeking the most efficient way to get from A to B, subject to both the constraint of time ordering and the freedom of quantum uncertainty. This is illustrated in figure 3. We expect that our time entanglement is a quantum phenomenon not present in classical descriptions of Newton or Maxwell.

3.4 Multiple times in the N -body problem

It is conventional to use N spatial coordinates to describe a system of N particles, e.g. $\psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_{N-1}, \vec{r}_N)$. In the uncorrelated limit $\psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_{N-1}, \vec{r}_N)$ reduces to $\prod_j^N \psi_j(\vec{r}_j)$. Mathematically it is possible, in principle, to describe the time dependence similarly, namely $\psi(t_1, t_2, \dots, t_{N-1}, t_N)$. The time dependence of an uncorrelated N particle system with N different times could be described by $\prod_j^N \psi(t_j) = \prod_j^N e^{iE_j t_j}$ for N free particles. Each time, t_j , would have its own conjugate energy, E_j . In the uncorrelated limit the total energy would be the sum of the independent single particle energies. If inter-particle correlation were turned on [32], after some time a correlated state could be formed with a unique eigen-energy, E , and a unique time, t . This is the form of $\psi(t)$ that is conventionally used with a single time. The correlated particles are now coherent. One may picture the reverse process, where a correlated target is taken apart so that the correlation interactions go to zero. Eventually random fluctuations in the environment disrupt, often irreversibly, the phase relations between the N particles, so that $e^{i \sum_j^N E_j t} \rightarrow \prod_j^N e^{iE_j t_j}$.

3.5 Complex systems

There is a need to bridge from understanding of simple static atomic systems to more complex dynamic systems, especially in those that may be of practical value. The N -body problem is, however, difficult. Kohn [33] estimated that a minimum number of parameters needed in a computer calculation to characterize the N -body problem varies as e^{3N} for large N . Fortunately computer capacity is doubling approximately every 1.5 years. Combining these two exponential rates one finds that it takes about 7 years to develop computer capacity to increase N by one. Thus to extend our understanding, for example, from a strong field interacting with helium to a strong field interacting with carbon, which has 4 more interacting electrons, requires about 28 years. To complete the periodic table at this level would take about 700 years, and DNA would require a thousand times the age of the universe. Thus it makes sense to consider faster, but approximate methods for dealing with complex, dynamic N -body systems. As noted above, omitting time entanglement speeds up our calculations by over two orders of magnitude, even in our second order calculations. The savings in time are greater, possibly exponentially greater, as the number of particles in the system increases.

3.6 Applications

The effects of time entanglement may be large, especially in systems where multiple electron transitions are important, e.g. for strong external fields [34, 35]. Correlation between electrons may be useful in characterizing quantum transmission of information and sequencing in complex electronic systems. In applications from molecular dynamics [36] to quantum computing [37], connections between electrons increase the number of possible reaction pathways. Electronic mixing can redistribute energy and facilitate transitions that would otherwise be forbidden. Both the external and internal interactions can be used to shape and dynamically control nanostructures [38]. In these applications it would be of interest to be able to estimate where effects of space and time are significant. Spatial correlation will be strong when the action of the correlation interaction, $\int v dt$, is not small compared with $\hbar$. It is not yet clear to us in general where entanglement in time is large, however.

4. Summary

We have discussed quantum time entanglement, which arises from time ordering of interactions. In principle such entanglement occurs

in any quantum system interacting with a macroscopic environment, including incident beams of electrons and photons, as well as various external fields. Time entanglement corresponds to energy-non-conserving quantum fluctuations occurring for short times in intermediate states of a system. These terms might be used to understand and control quantum transmission of information in complex multi-particle systems.

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ANALYTIC CONTINUATION: CONTINUUM DISTORTED WAVES

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Abstract The continuum distorted-wave eikonal initial-state (CDW-EIS) approximation is reviewed and two-centre effects such as the saddle-point mechanism discussed. The continuum distorted-wave theory is then generalized such that the azimuthal angle dependence is factored into the final state. This is achieved by the analytic continuation of hydrogenic-state wave functions from below to above threshold, using parabolic coordinates and magnetic quantum numbers, thus providing a more complete set of states. Double differential cross sections are considered for the single ionization of a H atom and molecule, ejected in the forward direction at a collision impact energy of 40 keV and 100 keV respectively.

Keywords: Electron scattering, ion-atom collisions, continuum distorted-waves, saddle-point mechanism, ionization.

Introduction

Over recent years an intense effort and significant progress has been made in understanding the process of single ionization in ion-atom collisions. However despite this progress, the theory of ionization remains incomplete. From a theoretical point of view the main problem is the representation of the final electronic state, where the ionized electron travels in the presence of two Coulomb potentials due to the target and the projectile. Due to the long ranged nature of the Coulomb potential the 'free particle' cannot be truly represented by a plane wave. This in turn implies that the Schrödinger equation for the three body system cannot be solved exactly, though an exact asymptotic form can be obtained¹.

In this article we review an approximation that satisfies the exact asymptotic states in the initial and final states, namely the continuum distorted-wave eikonal

initial-state (CDW-EIS) approximation¹. The CDW-EIS model in essence is based on the assumption that the final continuum wave function is taken as a product of a plane wave and two continuum factors corresponding to the projectile and the target, whereas the initial state is represented by a projectile eikonal state. This approximation which treats the influence of both the target and the projectile on the ejected electron on an equal footing should be able to describe two-centre effects well. However we find that this is not the case which has prompted us to re-examine the treatment and generalize it in the final state.

The CDW-EIS approximation

Let us consider the single ionization of a hydrogenic target by charged particle impact in the keV energy range. Our analysis is within the semi-classical rectilinear impact parameter ρ time-dependent formalism. This is depicted in figure 1 where an ion of nuclear charge M_P is shown to impinge with collision velocity v on a neutral target atom of charge Z_T and mass M_T .

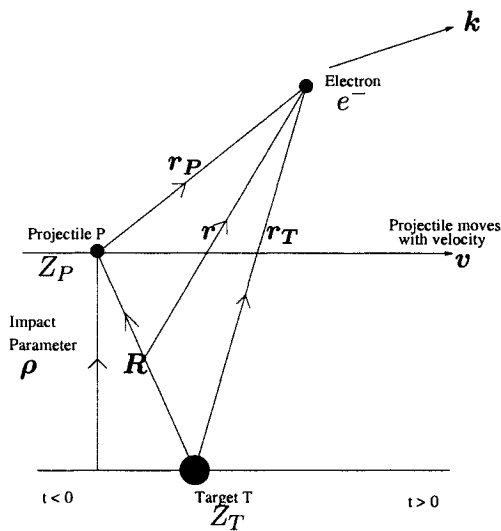


Figure 1. The coordinate system for the three body problem. Here a projectile travelling with velocity v impinges upon the electron-target subsystem. $\mathbf{R}$ is the internuclear separation and ρ is the impact parameter. In general the vectors $\mathbf{r}_T$, $\mathbf{r}_P$ and $\mathbf{r}$ do not lie in the same plane as ρ , $\mathbf{R}$ and $\mathbf{v}$.

As $M_{T,P} \gg 1$, the motion of the nuclei can be uncoupled from that of the electron², hence the trajectory of the projectile is characterized by two

parameters ρ and v , where $\rho \cdot v = 0$. The internuclear coordinate is defined by

$$\mathbf{R} = \mathbf{r}_T - \mathbf{r}_P = \rho + vt \quad (1)$$

and

$$\mathbf{r} = \frac{1}{2}(\mathbf{r}_T + \mathbf{r}_P) \quad (2)$$

where $\mathbf{r}_T$, $\mathbf{r}_P$ and $\mathbf{r}$ are the position vectors of the electron relative to the target nucleus, projectile nucleus and their midpoint respectively.

Using generalized non-orthogonal coordinates, the time-dependent Schrödinger equation may be written as $(H - i\frac{d}{dt})\Psi = 0$ where

$$\begin{aligned} H - i\frac{d}{dt} &= -\frac{1}{2}\partial_{\mathbf{r}_P}^2 - \partial_{\mathbf{r}_P} \cdot \partial_{\mathbf{r}_T} - \frac{1}{2}\partial_{\mathbf{r}_T}^2 + V - i\partial_t - \frac{1}{2}i\mathbf{v} \cdot \partial_{\mathbf{r}_T} + \frac{1}{2}i\mathbf{v} \cdot \partial_{\mathbf{r}_P} \\ V &= -\frac{Z_T}{r_T} - \frac{Z_P}{r_P} \end{aligned} \quad (3)$$

the internuclear potential having been removed by a phase transformation³. The essence of the continuum distorted wave approximation is that it treats the non-orthogonal kinetic energy term $-\partial_{\mathbf{r}_P} \cdot \partial_{\mathbf{r}_T}$, as the perturbation^{4,5}. The approximation is particularly suitable in this energy regime and has had much success mainly due to the fact that the long range boundary conditions are satisfied with both the initial and final states normalised.

Following Crothers and McCann¹, the initial and final states in the CDW-EIS wave treatment are respectively given by

$$\begin{aligned} \psi_i^+ &= \phi_i(\mathbf{r}_T) \exp\left(-\frac{1}{2}i\mathbf{v} \cdot \mathbf{r} + i\mathbf{K}_i \cdot \mathbf{R}\right) D_v^+(\mathbf{r}_P, Z_P) \\ &\quad \exp\left(\frac{iZ_P Z_T}{v} \ln(vR - \mathbf{v} \cdot \mathbf{R})\right) \end{aligned} \quad (4)$$

$$\begin{aligned} \psi_f^- &= (2\pi)^{-\frac{3}{2}} \exp\left(-\frac{1}{2}i\mathbf{v} \cdot \mathbf{r} + i\mathbf{K}_f \cdot \mathbf{R} + i\mathbf{k} \cdot \mathbf{r}_T\right) D_{\mathbf{k}}^-(\mathbf{r}_T, Z_T) \\ &\quad D_{\mathbf{k}-\mathbf{v}}^-(\mathbf{r}_P, Z_P) \exp\left(-\frac{iZ_P Z_T}{v} \ln(vR + \mathbf{v} \cdot \mathbf{R})\right) \end{aligned} \quad (5)$$

where

$$D_v^+(\mathbf{r}; Z) = \Gamma\left(1 - \frac{Z}{v}\right) \exp\left(\frac{\pi Z}{2v}\right) M\left(\frac{Z}{v}, 1, i\mathbf{v}r - i\mathbf{v} \cdot \mathbf{r}\right) \quad (6)$$

and

$$D_v^-(\mathbf{r}; Z) = [D_{-\mathbf{v}}^+(\mathbf{r}; Z)]^* \quad (7)$$

except that for the eikonal initial-state in equation (4) we have the asymptotic approximation, which nevertheless satisfies the long range (though not the short range) boundary condition:

$$D_v^+(\mathbf{r}_P, Z_P) \sim (vr_P - \mathbf{v} \cdot \mathbf{r}_P)^{-i\frac{Z_P}{v}}. \quad (8)$$

In the above, the $\exp(-\frac{1}{2}i\mathbf{v} \cdot \mathbf{r})$ term is the electron translation factor and the relative momentum of the heavy particles initially and finally are given by $\mathbf{K}_i$ and $\mathbf{K}_f$ respectively.

As previously mentioned in this paper we are interested in examining two-centre effects which because of the treatment of the projectile and the target in the final state should be described well by the CDW-EIS approximation. In particular we are interested in the 'saddle-point mechanism' which is when the ejected electron is stranded on the saddle-point of the two-centred potential between the residual target and the receding ion. Feeling no net force the ejected electron is promoted into the continuum.

Olson⁶ was the first to predict the existence of such mechanisms by examining the single ionization of H by H^+ impact at energies greater than 25 keV. Olson⁶ argued that when the electron is ejected with velocity k relative to the target, k is given by

$$k = \frac{v}{1 + (Z_P/Z_T)^{1/2}} \quad (9)$$

and using CTMC predictions he later concluded that saddle-point ionization was an important mechanism for H^+ +He collisions for energies around 100 keV⁷.

In figure 2 we compare the experimental and CDW-EIS results (Nesbitt et al⁸) for 40 keV H^+ projectiles incident on He for electron emission at zero degrees.

Both the experimental and theoretical results are shown to be in good accord, with the entire spectrum dominated by the asymmetric ECC peak. The existence of saddle-point electrons can not be confirmed by the CDW-EIS calculations or experimentally.

However turning then to 100 keV H^+ projectiles in collision with He for electron emission at zero degrees the situation is slightly different. Again the entire spectrum is dominated by the ECC peak with the experimental results predicting no saddle points. However the theoretical calculations predict a broad ridge with its maximum at $k/v \approx 0.25$. This is consistent with the findings of Olson et al⁷, though we found this rather puzzling since saddle-point electrons are normally expected to be associated with lower impact energies.

The same impact energy of 100 keV is shown in figure 4 with the He target replaced by a H_2 .

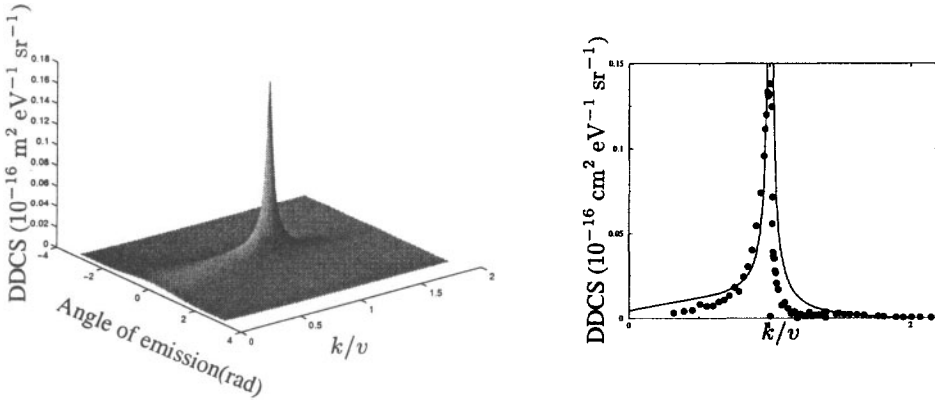


Figure 2. Measured double differential cross sections for electron emission at zero degrees in collisions of 40keV H^+ with He compared with CDW-EIS predictions (Nesbitt et al⁸).

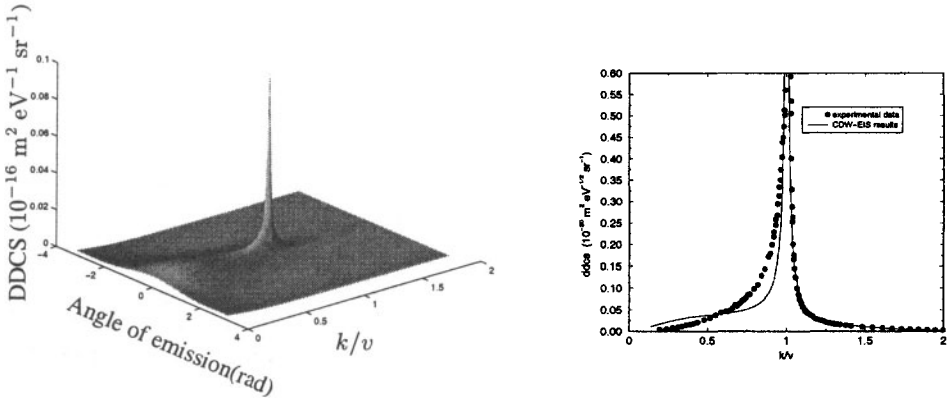


Figure 3. Measured double differential cross sections (McGrath et al⁹) for electron emission at zero degrees in collisions of 100keV H^+ with He compared with CDW-EIS predictions (O'Rourke et al¹⁰).

Again the same behaviour is exhibited with the asymmetric ECC peak dominating the spectrum and the experimental results showing no evidence of saddle-point emission. Also similar to figure 3 there is a pronounced ridge situated at $k/v \approx 0.25$ implying the saddle-point mechanism.

Generalized CDW-EIS

Following the incongruous behaviour of our calculations we were moved to reconsider the very basis of the CDW-EIS model, in particular the final state. In the CDW-EIS approximation the final state is described by a continuum wave

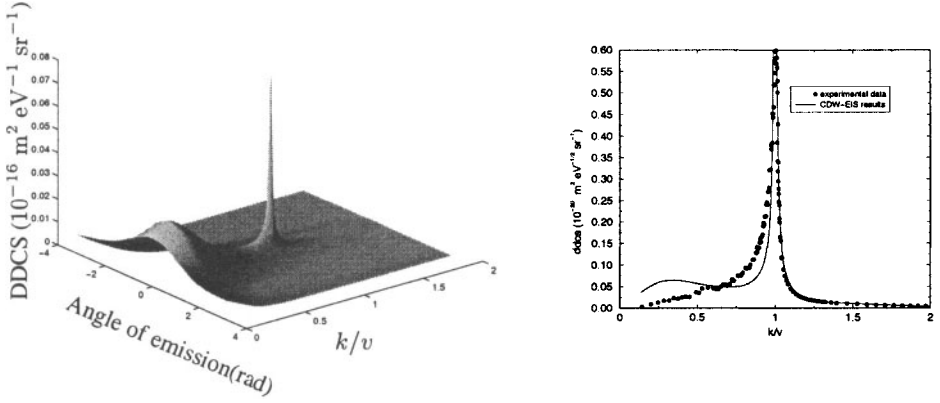


Figure 4. Measured double differential cross sections (McGrath et al⁹) for electron emission at zero degrees in collisions of 100keV H^+ with H_2 compared with CDW-EIS predictions (O'Rourke et al¹⁰).

function taken to be the product of a plane wave and two continuum factors corresponding to the projectile and the target Coulomb interactions. It is in fact a two-centre zero magnetic quantum number analytic continuation of the well known exact hydrogenic bound states with parabolic quantum numbers and co-ordinates.

This treatment is now generalized(G) in the GCDW-EIS theory, to non-zero magnetic quantum numbers giving a more complete set of states. It is hoped that by including non-zero magnetic quantum numbers contributions the theory should be improved. In the GCDW-EIS model the initial and final states are respectively given by

$$\begin{aligned} \psi_i^+ &= \phi_i(\mathbf{r}_T) \exp\left(-\frac{1}{2} i\mathbf{v} \cdot \mathbf{r} + i\mathbf{K}_i \cdot \mathbf{R}\right) \exp\left(-\frac{iZ_P}{v} \ln(vr_P + \mathbf{v} \cdot \mathbf{r}_P)\right) \\ &\quad \exp\left(\frac{iZ_P Z_T}{v} \ln(vR - \mathbf{v} \cdot \mathbf{R})\right) \end{aligned} \quad (10)$$

$$\begin{aligned} \psi_f^- &= (2\pi)^{-\frac{3}{2}} \exp\left(-\frac{1}{2} i\mathbf{v} \cdot \mathbf{r} + i\mathbf{K}_f \cdot \mathbf{R} + i\mathbf{k} \cdot \mathbf{r}_T\right) m_T D_{\mathbf{k}}^-(\mathbf{r}_T, Z_T) \\ &\quad m_P D_{\mathbf{k}-\mathbf{v}}^-(\mathbf{r}_P, Z_P) \exp\left(-\frac{iZ_P Z_T}{v} \ln(vR + \mathbf{v} \cdot \mathbf{R})\right) \end{aligned} \quad (11)$$

where

$$\begin{aligned}
 {}^m D_{\mathbf{v}}^{-}(\mathbf{r}, Z) = & \exp(-im\phi + \frac{\pi\zeta}{2}) M(-i\zeta + \frac{1}{2}|m|, 1 + |m|, -iv\mathbf{r} - i\mathbf{v}\cdot\mathbf{r}) \\
 & M(\frac{1}{2}|m|, 1 + |m|, iv\mathbf{r} - i\mathbf{v}\cdot\mathbf{r}) (v\mathbf{r} + \mathbf{v}\cdot\mathbf{r})^{|m|/2} (v\mathbf{r} - \mathbf{v}\cdot\mathbf{r})^{|m|/2} \\
 & \frac{\Gamma(1 + \frac{1}{2}|m| + i\zeta)\Gamma(1 + \frac{1}{2}|m|)}{\Gamma^2(1 + |m|)}
 \end{aligned} \tag{12}$$

In equation (12) we note $\zeta = \frac{Z}{v}$ and m_T , m_P represent the magnetic quantum numbers for the target and the projectile CDWs. Also ϕ_P is the angle between $(\mathbf{r}_P, \mathbf{p})$ and $(\mathbf{v}, \mathbf{p})$ and ϕ_T is the angle between $(\mathbf{r}_T, \mathbf{k})$ and $(\mathbf{v}, \mathbf{k})$.

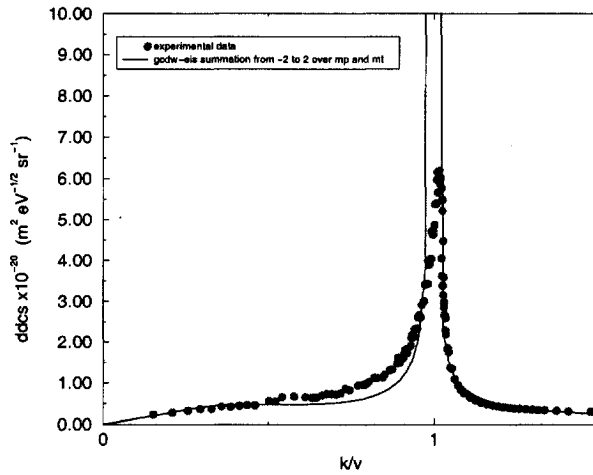


Figure 5. The double differential cross sections (ddcs) for the collision of 100 keV H^+ with H_2 at an electron emission angle of 0 degrees. Solid line - GCDW-EIS with double summation over m_P and m_T from -2 to +2. Circles - experimental results of McGrath et al⁹.

In figure 5 we present the double differential cross sections (summed over m_P and m_T each from -2 to +2) for the collision of 100 keV H^+ with H_2 at an electron emission angle of zero degrees. The agreement between the suitably scaled experimental results (McGrath et al⁹) and the theoretical predictions seems much improved compared to our basic CDW-EIS ($m_P = 0 = m_T$) theory. We note that all of the cross sections are increased compared to the CDW-EIS predictions and the peak is significantly broader. This would make physical sense as the slower electrons will have more time to experience rotational coupling out of their azimuthal plane. It is also noted that the saddle point effect is absent in figure 5, however upon further examination we conclude there is a shelf effect rather than a saddle.

Conclusion

To conclude we have reviewed the CDW-EIS approximation and discussed the experimental and theoretical evidence of saddle-point electrons. These findings led us to re-examine the approximation and generalize it in the final state to achieve the GCDW-EIS model. This approximation has resulted in better agreement with experiment and the conclusion that for the collision $H^+ + H_2$ there is a shelf rather than a saddle.

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Electron Impact Ionization of Atoms with Two Active Target Electrons

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Abstract: The ionisation of atoms with two target electrons is reviewed. The use of perturbative and non-perturbative methods is discussed

keywords: (e,2e), excitation ionisation, excitation-auto-ionization

Introduction

The only way we can learn about an atomic system is to interact with it. It is from the interaction of a system of charged particles with an electromagnetic field that we extract the most basic information about such systems. An (e,2e) process is one where an electron is fired at a target, ionizes it and the two ejected electrons are detected in coincidence, with their energies and angles resolved. The resulting triple differential cross section (TDCS) represents all most all that we can know about a scattering process. [1] Experiment is now driving the subject into exciting new areas: the study of highly correlated systems, (in particular systems involving 2 active electrons) and ionization in extreme kinematical conditions. In order to understand the former one needs to consider double excitation processes such as (γ ,2e), (e,3e), (e,2e),excitation-ionization and (e,e'Auger) ,[2], for the latter coincidence studies of inner shell ionization has yielded profound

insights,[3]. In this paper we will be concerned exclusively with the problem of two active target electrons.

TWO ACTIVE TARGET ELECTRONS

Excitation-Ionization & Excitation-Autoionization

Because the Hydrogen atom problem-essentially two charged particles interacting via an electrostatic interactions can be solved analytically, it has become the paradigm for atomic structure calculations. Until relatively recently all quantitative calculations of atomic processes were essentially based on the independent particle model with collective effects being treated as small corrections. A major area of concern for modern Atomic Physics is the study of those situations where such an approach is clearly inappropriate.

Ionization with two active electrons is an example of such an interesting quintessential quantum problem. The features that made conventional simple ionization worth studying are there, only much more strongly felt. The cross section will be sensitive to correlation in the target, that is to a description of the target beyond the Hartree Fock and the collective interactions of the particles will provide the most stringent test on our scattering models. The first thing to do, of course is study Helium and the first experimental studies have begun.

Suppose the projectile is an electron and let us assume that it is moving fast enough so that one could hope to develop a perturbative approach. Here, since we have lots of interactions we need to be careful in specify what we mean by the last statement. We mean that the projectile acts on the target once in the first Born term, e.g. for electron impact in the first Born approximation, the fast incident and scattered electrons are represented by plane waves and the initial and final states of the atom are the undistorted atomic wave functions. The scattering amplitude in the first Born approximation, for helium target, is then given by

$$f^{b1} = -\frac{1}{2\pi} \langle e^{ik_f \cdot r_1} \Psi_f(r_2, r_3) | V | e^{ik_i \cdot r_1} \Psi_0(r_2, r_3) \rangle \quad (1)$$

where

$$V = \frac{-2}{r_1} + \frac{1}{r_{12}} + \frac{1}{r_{13}} \quad (2)$$

is the interaction potential between the incident electron and the target, $\Psi_0(r_2, r_3)$ is the initial state of the atom, and $\Psi_f(r_2, r_3)$ is the final doubly excited state of the atom. Now therefore even to describe the first Born term we have got to have a wave function that accurately describes the Helium ground and excited states Ψ_0, Ψ_f . Indeed there is not much else in the 1st Born term, i.e. apply the Bethe relation to equation (2) we have

$$\stackrel{=>}{f}^{b1} = -4/q^2 \langle \Psi_f(r_2, r_3) | -1 + e^{iq \cdot r_2} | \Psi_0(r_2, r_3) \rangle$$

where $q = k_0 - k_f$ is the momentum transfer.

It is instructive to follow the simple argument given in Marchalant *et al* [4,5].

Let $\Psi_0(r_2, r_3) = \varphi_0(r_2) \varphi_0(r_3)$,

$$\Psi_f(r_2, r_3) = N_{fg} (\varphi_f(r_2) \varphi_g(r_3) + \varphi_g(r_2) \varphi_f(r_3))$$

where

$$\langle \varphi_f(r_2) | \varphi_g(r_3) \rangle = \delta_{fg}$$

i.e. we are treating the spin singlet initial state and the spin singlet final state in a completely uncorrelated model. Then we see that the first Born term is exactly zero.

If however we were to go to second order in the projectile target interaction then the 2nd Born term would not be zero, i.e. in one collision we take one electron to state $\varphi_f(r_2)$ and in a second we take the other to a state $\varphi_g(r_3)$.

The Marchalant *et al* analysis gives us two basic insights

- a) we can not ignore correlation in the target
- b) the second Born approximation is in a privileged position in this type of double excitation process.

Marchalant *et al* [4] looked at excitation-ionization and excitation-autoionization. The first Born element was evaluated with a close coupled wave function on the left hand side and a highly correlated target wave functions on the right hand side. The second Born term was evaluated using

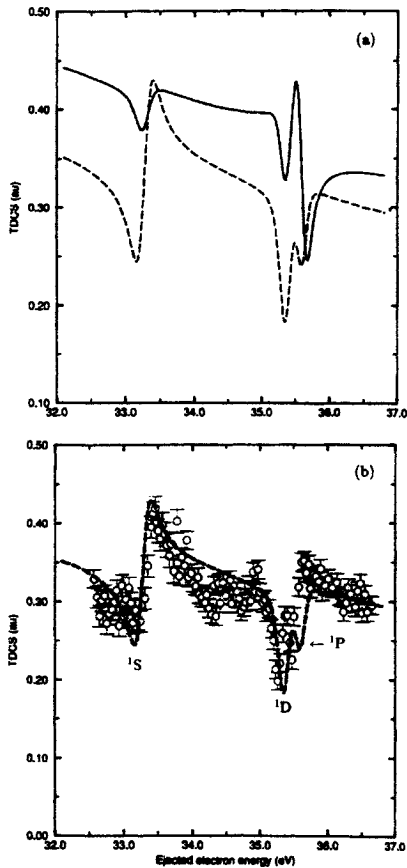
closure. In these early papers the simplest possible realistic choice was made for the close-coupling and target functions. For excitation-ionization a 3 state close coupling and a Tweed Langlois, [7] radially correlated function were employed. It was demonstrated that the 2nd Born term remains important even up to quite high energies. In the case of excitation-autoionization calculations were performed to compare with Experiments on Helium using 200eV electrons with an ejected electron energy region which encompasses the $(2s^2) \ ^1S$, $(2s2p) \ ^1P$, $(2p^2) \ ^1D$ resonances. Marchalant Whelan and Walters considered this problem by going to second order in the electron-electron interaction, using a close coupling wavefunction $(1s,2s,2p,3s,3p,3d)$ for the final state, and the Tweed Langlois for the initial. Again, this was the simplest possible approximation consistent with the Physics. Agreement with both the experiments of Crowe and McDonald [8] and those of Lower and Weigold [9] are satisfactory, with the 2nd Born term giving a very major contribution. In Marchalant *et al* [6] the excitation-ionization problem was revisited the close coupling wave function was extended to include a large number of pseudo-states and a series of different target wave functions containing both radial and angular correlation were studied,[10]. It is clear that the 1st Born term is now fully converged and that the original conclusion about the strength of the 2nd Born has been vindicated. The experimental data presently available is patchy and there is an urgent need to cover a much wider range. The second Born calculations of Marchalant *et al*, [6], give encouraging agreement with the Orsay experiments at high impact energies but in at least one case striking disagreement with the Rome experimental data at 570 eV. The most likely explanation for this is that the perturbative approach has broken down at this low energy.

$(\gamma,2e)$, $(e,3e)$

For $(e,3e)$ or $(\gamma,2e)$ the construction of the final state Ψ_f is not so easy.

If we use the close coupling approach as used by Marchalant *et al* for excitation ionization then we in essence require that the coupled pseudo states approximation to the $e^+ \text{He}^+$ should contain the ionized He^+ channels, This is the approach adopted by Rasch *et al*, [11] and independently by Bray and Khefitets [12] when calculating the photo-double ionization of Helium- this is the equivalent zero momentum transfer limit of the $(e,3e)$. An alternative approach is the analytic ansatz approach where a solution satisfying the 'correct 3 body' boundary conditions is guessed,[13] and then the cross section calculated.

An interesting observation from our earlier work was the significance of gauge invariance. Now as is well known if we had the exact wave functions Ψ_0, Ψ_f the first Born amplitude could be expressed in a number of equivalent forms- length, velocity, acceleration. Now if Ψ_0 and Ψ_f are not eigenfunctions of the same Hamiltonian this equivalence no longer holds. In the calculations we are discussing the initial and final state Helium wave functions are generated entirely separately. In [11] [14] an extensive study was presented of this gauge problem for the photo-double ionization of Helium. These papers considered varying not only over different Ψ_0 but also the Ψ_f . We used the very best available analytic ansatz wave functions as well as coupled pseudo-state for the final state and a range of target wave functions. All the analytic final state functions behaved only poorly and produced wild gauge discrepancies. Agreement between the gauges being only achieved with the best of the highly correlated target functions and the large pseudo-state calculations. It is worth noting one point that when the final state electrons had equal energy all the calculations gave more or less good shape agreement with the available experimental data-even though one found extreme variations in absolute size. The reason for this is, we believe, simply that for the photon-case you have some elementary symmetries due to conservation of parity, electron repulsion and the like which forces zeros in the cross-section, [14]. The cross section is a positive quantity and all it can do is increase away from the zeros. Clearly relative measurements with equal energy electrons offer a good test if the apparatus is working or the code is stable but next to no information on the value of different theoretical approximations. Non-equal energy sharing is much better-we can at least see when the theory is not working the ansatz approach clearly fails for example. However we can reach a point where the available experimental data is not good enough to distinguish between different high quality target wave functions even though we still see a gauge discrepancy in all but the very best. However the pseudo-state calculations suffer from a serious defect when compared with the absolute size of the triple differential cross section. For equal or near equal energies close to threshold it has difficulty reproducing the absolute size of the cross section. The ansatz approach is difficult to improve since each attempt to include more physics forces one to generate a new trial wave function. The convergent close coupling approach or 1 electron R-matrix has the advantage that one may continuously add more pseudo states, but its asymmetric character and the nature of three-body interactions in the final channel means that it will not be possible to simply extend this procedure to convergence.



TDCS for the ionization to He⁺(1s) at E₀=200 eV, θ_f=13° and direction of momentum transfer, θ_q=50°. Curves are theoretical convoluted with the experimental energy resolution of 150 meV. In (a): solid curve, 1st Born approximation; dashed curve second Born approximation.

Figure (b) shows the experimental of Lower and Weigold [9] normalized to give best visual fit to the second Born curve (from [4])

What we need is a theory which

- Treats the electrons symmetrically
- Is non-perturbative
- Is not restricted to two electron atoms
- Can work in any geometries and kinematics
- Is computationally very efficient

In Roche et al[15] an outline of a general way of calculating atomic collision processes is presented. The goal is an *ab initio* calculation of electron impact ionization and double photo-ionization, which is applicable

to a variety of target systems. This new method has all the characteristics needed now the “only thing” is to do is to calculate with it.

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ELECTRON COLLISIONS WITH AGGREGATED MATTER

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Physique des Atomes, Lasers, Molecules et Surfaces

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Abstract A recent synchrotron radiation experiment in which the absorption of high energy x-rays by soot particles in an ethylene flame has revealed what seems to be a complex interaction mechanism involving collisions between Auger electrons, and secondary electrons with nano-particles in an aggregated structure. The overall electron loss thus generated, produces local charging of the particles resulting in a Coulomb explosion. The implications for astrophysics and combustion physics will be discussed and a brief commentary on aggregate matter physics and chemistry will be presented.

Keywords: Aggregate, nanoparticle, electron collisions, x-ray, synchrotron radiation

Introduction

In a recent article, *diStasio* [1] refers to aggregates as being a fifth form of matter. Indeed there is some truth to this statement for aggregated structures do respond in different physical ways to outside influences compared to gases, liquids, solids or plasmas. Aggregates are free to move like molecules in the gas phase but can undergo collective motions as do liquids. They can condense to form larger structures through processes of coalescence and agglomeration. They can carry electrical charges and respond to electromagnetic fields. Their physical nature is typically solid though the forces involved in their individual and collective behaviour differ from those controlling bulk matter properties. One way in which aggregates differ from the other four states of matter is in response to electronic collisions. In this article, an example is given where the interaction of electrons with a nanoparticle has a character that is peculiar to the aggregated state. In the following discussions the

term aggregate is given to mean a structure made up of an assembly of particles having dimensions of the order of nanometres.

Aggregated structures are found in many different physical situations. Soot particles, formed in hydrocarbon flames, are comprised of small nanometre sized spherical particles that are connected together to form a chain-of-pearls, fractal like structure [2]. How such particles are formed is a subject of ongoing research and debate [3],[4]. The generally accepted mechanism includes particle inception from the gas phase followed by coalescence, surface growth, agglomeration and finally destruction via oxidation. Recent studies [4] have attacked this scientific edifice however, suggesting that in fact soot particulates originate from liquid globules of Polycyclic Aromatic Hydrocarbon (PAH) mixtures, formed early in the flame, whose chemical composition undergoes constant change due to radical molecule reactions. As these structures age in the flame, they lose hydrogen and undergo a process known as graphitisation yielding structures such as those identified using particle sampling and electron microscopy [5]. Knowledge of these processes is vital for soot formation and subsequent smoke emission is a universal problem in combustion.

Small soot-like particles are believed to be formed in interstellar space. Gas phase molecular species condense out onto these cold grains and thus are depleted from the gas phase. The surfaces of the grains can act as catalytic sites for molecule formation and one of the important questions in astrochemistry is how molecules, once formed, can be returned to the gas phase where they are identified by radioastronomy observations [7], [6]. In addition to carbon particles, there are silicate grains in space that contain metals such as magnesium and iron. Silicate particles are also formed in terrestrial plasmas during the processing of semiconductor materials. These particles, being electrically charged, hang in suspension in electrostatic potential wells, thus giving them time to grow. When they drop onto semiconductor surfaces, they interfere with the production of microstructures and thus are a serious nuisance to the electronics industry. Dust particles act as nucleation sites for cloud formation in the earth's atmosphere and play a critical role in atmospheric processes such as rain formation, lightning and ozone depletion. Lastly, one can note that viruses of have structures that resemble aggregates and so their response to physical influences must be similar to that found in these other areas. In all of these examples just mentioned, the aggregates interact with electrons and this has a critical effect on their life cycles and general behaviour. Particles acquire negative charges via electron attachment though hot soot particles also lose electrons via thermionic emission. Interstellar grains can be positively charged by photoionisation by energetic photons [8]. Such charging has an important effect on ag-

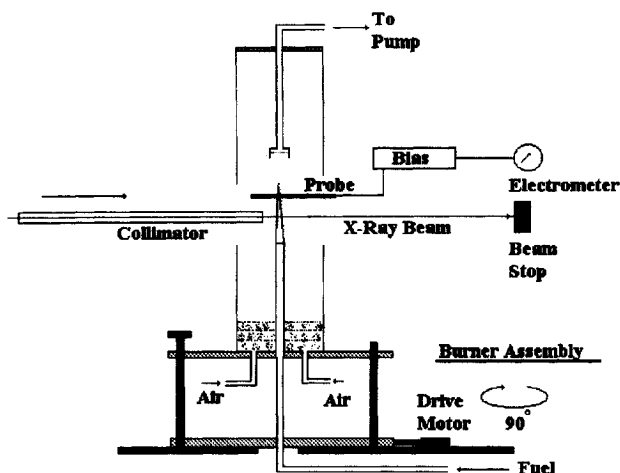


Figure 1. Schematic of the x-ray absorption experiment showing the burner assembly that can be moved horizontally and vertically so that the soot density in the flame can be mapped. The electrically biased probe is used to collect the ionisation products formed naturally in the flame and due to ionisation of soot particles and background air molecules by x-ray absorption.

glomeration and growth of aggregated structures and as discussed below can lead to their physical disruption.

1. X-ray Ionisation Experiment

In an experiment, performed recently at the European Synchrotron Radiation Facility (ESRF) in Grenoble, [9],[10] a high energy x-ray beam was directed through a cylindrically symmetric ethylene diffusion flame and ionisation produced by x-ray absorption by soot particles, was detected using an electrically biased wire probe, located just above where the beam passed through the flame (Figure 1). Ethylene diffusion flames have been very well characterised and it is known that typical soot particle densities within particle rich zones in such flames are of the order of 10^{11} cm^{-3} and that their diameters range from 10 – 200 nm [5],[11]. They represent therefore a very inexpensive system for the production and study of nano-particles.

The photon flux used was 3×10^{11} photons/sec and the beam dimensions at the flame were $50\mu\text{m} \times 50\mu\text{m}$. The x-rays in the beam ranged in energy from 10 to 30 keV. The flame had a visible height of 40 mm

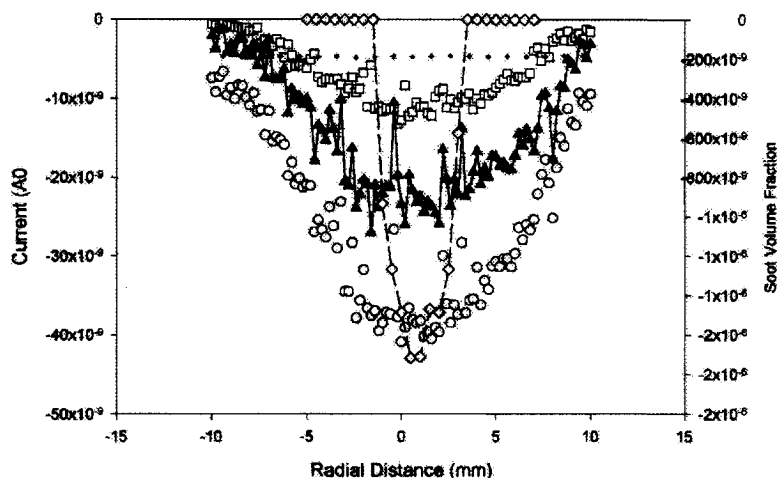


Figure 2. Measured ionisation current to a positive probe at height of 32mm above the burner. Open circles and open squares are ionisation current with and without the x-ray beam respectively. The solid triangles represent the difference in these two measurements with the contribution due to air absorption subtracted. The ionisation signal due to background air ionisation is shown as crosses. The dashed line shows the soot volume fraction as a function of radius, measured using a laser absorption method.

and was scanned horizontally and vertically by the x-ray beam in order to map out the location of soot particles formed during the combustion process. Prior to performing measurements on the actual flame, ionisation produced by passage through the background air and while ethylene gas flowed through the burner was measured in order to determine the baseline signal.

Figure 2 shows the negative ionisation current measured across the flame when the x-ray beam intersected the flame at a height of 32 mm above the burner throat. It can be seen that the x-ray induced signal is about a factor of five larger than the background gas ionisation rate. Absorption of high energy x-rays in molecules and solids is in fact atomic-like for energies greater than 50 eV [12]. This means that one can take the cross section for absorption by individual elemental atoms and sum over the number of such atoms in the target. For 20 keV x-rays, the absorption cross section in air is $1.95 \times 10^{-23} \text{ cm}^2$. At room temperature and atmospheric pressure, the density of molecules is $2.4 \times 10^{19} \text{ cm}^{-3}$ and the distance over which the ionisation signal was collected was ap-

proximately 5 cm. Using the Beer-Lambert absorption law:

$$I = I_0 \exp(-nl\sigma)$$

where I_0 is the incident beam intensity, I is the beam intensity after a distance l , σ is the ionisation cross section, one finds a ratio of the number of absorption events to the incident beam intensity: $(I_0 - I)/I_0 = 2.4 \times 10^{-3}$ for absorption in the background air. In a separate measurement of optical absorption by soot particles in the flame it was shown that the volume of the flame occupied by soot particles, (the soot volume fraction f_v) is of the order of 10^{-5} in regions where the soot concentration is highest. Taking the density of soot particles to be similar to graphite ($\rho = 2.2 \text{ g.cm}^{-3}$) and using Avogadro's number one finds that the number density of carbon atoms in the flame is $1.1 \times 10^{18} \text{ cm}^{-3}$. The path length of the beam through the flame is roughly equivalent to the diameter of the burner (1.1 cm) and so again using the Beer-Lambert law, but with the ionisation cross section for carbon atoms ($4.1 \times 10^{-24} \text{ cm}^2$), one obtains a value of $(I_0 - I)/I_0 = 4.5 \times 10^{-6}$, i.e. a factor of 532 times less than the number of absorption events occurring in the background air. Given the observed large x-ray induced signal, it would appear that absorption by the soot particles results in an intense release of electrons.

Similar plots were obtained for the collection of positive species though the measured currents were smaller over most of the flame height. The current measured by a probe in an atmospheric flame [13] is proportional to the one fourth power of the particle mobility, $(\mu)^{1/4}$. Thus highly mobile free electrons, released from soot particles will yield larger measured currents than the heavy positive species left behind. It was found that the electron current peaked at around 20 mm above the burner and then declined between 20 and 35 mm, eventually reaching a value similar to that of the positive current, (that had been constantly rising over the same height range). The reason for this decline in the measured negative current is that free electrons attach to neutral heavy soot particles, whose number density rises with height-above-burner and thus the mobility of the negative charge carriers drops sharply. The equality in the positive and negative currents indicates that at this stage of the combustion, the electrical charge is carried by solid particles rather than by free electrons and ions.

2. Discussion

High energy X-ray photons are absorbed primarily by atomic inner-shell electrons (rather than outer-shell valence electrons as is the case for

ultra-violet absorption). The electrons are ejected from the atom and thus a primary ionisation event occurs that leaves an inner-shell vacancy in the target atom. This vacancy is then filled by an electron from a higher level either of the target atom or of a neighbouring atom. In this event a high energy photon can be emitted (fluorescence) or the energy release can lead to the ejection of another electron from the atom (the Auger effect). If a lower lying electron is ejected then a second such Auger process can occur etc. This is known as an Auger cascade though in fact for carbon only one 262.4 eV Auger electron is released [14]. Since the target atom is located within a solid matrix, the departing primary photoelectron and the Auger electron must traverse this material in order to escape. The mean free path of a 20 keV electron in carbon is of the order of 4000 nm so it will most likely simply escape the particle without further interaction. That for a 260 eV electron is of the order of 5 nm however, and so it will undergo inelastic collisions with other atoms in the solid, resulting in secondary electron emission. Thus the primary x-ray absorption can lead to the ejection of a number of electrons. If such a process occurs in an electrically unbiased bulk solid, the electrons will probably return to the surface thus re-neutralising it. In the case of a small particle, it is quite likely that the electrons will escape if the size of the particles is small compared to the electron mean free path in the surrounding gas and this will leave the particle with a net positive charge. (Natural soot particles usually are electrically charged, whether positively due to thermionic emission or negatively due to electron or negative ion attachment. Flames also contain ions formed via chemical processes [13]. These phenomena are responsible for the current measured with the flame but without the x-ray beam). This series of processes is illustrated schematically in figure 3. The positive charge built up on the particle will give rise to an electric potential and given the small dimensions within the aggregate, the resulting electric field generated can be enormous. ($Few \times 10^8$ V/m!). Studies [15], [16], [17] have shown that fields of the order of $10^6 - 10^7$ V/m induce field emission of electrons from carbon nanotubes. It is very likely therefore that strong electric fields can be induced within such aggregated particles that would lead to electron emission and subsequent disruption. This phenomenon can be a runaway process and it has been predicted [18], [19],[20] that this can lead to the actual disruption of the particle that will break up into positively charged fragments. Thus this is in essence a Coulomb explosion phenomenon.

There is other experimental information that shows that small particles can give rise to anomalous electron emission effects. In a series of experiments, Schmidt-Ott and co-workers [21], [22], [23], [24] observed

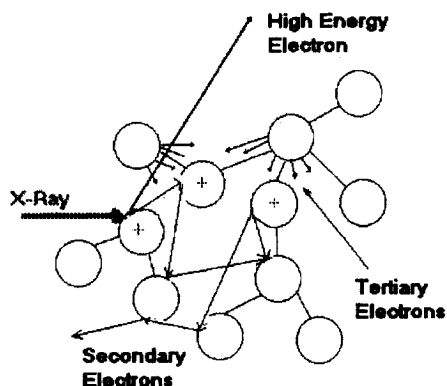


Figure 3. Schematic of the release of electrons following x-ray absorption by an aggregated structure.

a large enhancement of photoemission yields from 5 nm diameter silver particles, irradiated by 10 eV photons. This enhancement could not be explained by photoemission theory [25]. Anomalous electron emission has also been seen when magnesium is burned in air [26], [27] and when granular deposits of magnesium oxide are irradiated by ultra-violet light [28]. It seems reasonable to suppose that these observations can also be interpreted in terms of a field emission phenomenon though in none of these experiments was the resulting state of the emitting particle studied. A new apparatus is under construction that will address this point. Experiments are planned where time-of-flight mass spectrometry will be used to determine the masses of the positive particles produced during the absorption process. It is also planned to study the process as a function of incident photon energy, extending the measurements into the vacuum ultra-violet (VUV) region of the spectrum.

3. Speculations

One can perhaps ask the question if aggregated structures can act as quasi-molecules having complementary chemical and physical properties. While atoms in molecules are held together via ionic and co-valent bonds, the underlying force coming from direct interaction between charged particles, aggregates are held together by adhesion forces. The nature of

these forces is not well defined but they can involve polarisation forces such as Van der Waals, ion enhanced polarisation, and even chemical forces. The surfaces of aggregates can have chemisorbed or physisorbed species adhering to them. Generally however, one can say that adhesion between aggregated particles is much weaker than the binding between atoms in a molecule. Our knowledge of the binding forces of molecules allows us to calculate the properties such as binding energy, vibrational frequencies etc. It should be possible to calculate similar properties for aggregates and indeed to predict their emission spectra. Aggregates do give rise to infra-red and indeed visible emissions when heated. A recent astronomical observation of the radio emissions due to the rapid rotation of dust particles having a dipole moment has confirmed earlier predictions of this phenomenon [29].

One can go further and speculate about the chemical properties of aggregates. Let us consider electron capture. If a molecular ion captures an electron, it can undergo dissociation thus allowing the conversion of potential energy into kinetic energy in a process known as dissociative recombination. This results in the stabilisation of the recombination for the recombination energy is released as the fragments separate. Will a similar process occur when an ionised aggregate captures an electron? This is a subject that we have little understanding of, though we believe that for a sufficiently large molecule, recombination energy can be absorbed as vibrational energy, negating the need for dissociation. In aggregate consisting of small molecules, can the recombination energy be absorbed as vibrational motion of the primary particulates? This is a subject deserving of study. One might think that a comparison with cluster ion recombination would provide us with some guidance here but unfortunately this is also a poorly understood subject.

Acknowledgments

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ROTATIONAL AND VIBRATIONAL EXCITATION IN ELECTRON-MOLECULE SCATTERING

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Abstract This article reviews recent progress with the problem of incorporating vibrational and rotational coupling and excitation into the quantitative theory of electron-molecule scattering.

Keywords: Electron-molecule scattering, rovibronic, vibrational excitation, dissociative attachment

Introduction

A computationally practicable treatment of rovibrational (rotational and vibrational) excitation in electron-molecule scattering requires a significant and historically challenging extension of bound-state theory. Born and Oppenheimer[7] showed for bound states that the small electron-nuclear mass ratio m/M justifies the qualitative physical principle that transfer of kinetic energy between electrons and nuclei can be neglected in the lowest order of a perturbation expansion. Far from neglecting these Born-Oppenheimer corrections, a valid theory of electron-impact rovibrational excitation must compute the scattering effects of such terms with quantitative accuracy. The phenomenon of interest is precisely the energy transfer between electronic and nuclear motion. Electron-molecule scattering data, observed experimentally or computed with methodology available as of 1980, were reviewed in detail by Lane [31]. Since that time, bound-state molecular computational methods have been extended to fixed-nuclei electron scattering[9, 29], but the theory of rovibrational excitation is still evolving.

Rotational level spacing is small for most molecules and can be resolved only by precise spectroscopic techniques. Typical electron scattering data is rotationally averaged. Special methods based on adiabatic theory are valid under these circumstances, except for interpreting com-

plex scattering phenomena due to dynamical long-range potentials near scattering thresholds. The present discussion of computational methodology will concentrate on vibrational excitation and on threshold effects. Dissociative attachment, capture of an electron by a target molecule, which then dissociates, is a striking example of kinetic energy transfer from electron to nuclei. It will be considered here as an application of rovibrational theory.

An electron scattering resonance is characterized by a singularity of the scattering matrix when analytically continued to a complex energy value $\epsilon_{res} - \frac{i}{2}\gamma$ [44], defining a width parameter $\gamma > 0$. The simplest example is a *shape* resonance, when a scattered electron can be temporarily trapped in a potential well behind a finite potential barrier. An electron initially bound in the potential well leaks out through the potential barrier with a time constant $\hbar/\gamma$. Poles of the analytically-continued scattering matrix cause energy-dependent Wigner cusp or rounded step structures[64, 8] in scattering cross sections at energy thresholds where a new continuum becomes accessible. This behavior does not require a potential barrier[44]. A typical phenomenon is a *virtual state*, which occurs in simple potential models at $\ell = 0$ thresholds, with no centrifugal barrier.

Resonance and threshold structures in fixed-nuclei electron-scattering cross sections are replicated, with characteristic energy shifts, in rovibrational excitation cross sections. One of the most striking examples is provided by the prominent multiple peaks observed in the electronically elastic and vibrational excitation cross sections for electron scattering by the N_2 molecule[53, 26, 21, 31]. These peaks are associated with a fixed-nuclei resonance at approximately 2eV, but their width arises from electron-vibrational coupling and their spacing does not correspond precisely to the vibrational level structure of either the neutral target molecule or of a vibrating transient negative ion. A quantitative theory of these excitation structures has been developed through several advances in both formalism and computational technique, ultimately based on variational theory of the interacting electron-vibrational system. Another striking example is the observation of excitation peaks associated with each successive vibrational excitation threshold in electron scattering by dipolar molecules such as HF , HCl , and HBr [52]. Because of the electric dipole moment of such target molecules, if low-energy scattering theory is to be relevant it must provide a detailed analysis of rotational screening of the long-range dipole potential.

1. The local complex-potential (LCP) model

A fixed-nuclei electronic resonance defines a complex-valued effective internuclear potential function. The vibrational levels of the real part of this complex potential are a first approximation to resonance energies such as those observed in N_2 . The "boomerang" model of Herzberg [30] considers a transient vibrational state in such a local complex potential (LCP) that survives only a single vibration out and back before decaying into vibrational states of the neutral molecule. With appropriate parametrization, this model gives a convincing explanation of the observed vibrational resonance peak shapes and separations in $e - N_2$ scattering [6, 20]. The complex-potential model originated as a qualitative explanation of dissociative attachment [4]. A fixed-nuclei electronic resonance is described by an LCP that crosses below the ground-state vibrational potential and then continues as a bound state of the negative molecular ion out to dissociation. Applied to the dissociative attachment of H_2 [3, 5, 63], this parametrized model accurately reproduces available experimental data.

The LCP model has the significant practical problem that there is no a unique theory of the resonance state when its decay width becomes large. For the LCP model of H_2^- , serious discrepancies between various parametrized and computed values of the energy and width of the $^2\Sigma_u^+$ shape resonance indicate that a more fundamental, first-principles theory is needed to give fully convincing results. As the decay width becomes large, the concept of a well-defined LCP model becomes questionable, since the scattering resonance fades into the background scattering continuum [45]. Analytic theory implies an energy shift which may qualitatively change the character of the assumed resonance potential curve [11, 17].

1.1 The projection-operator method

The semiclassical picture of nuclear motion inherent in the LCP model has a quantum-mechanical foundation that is most directly developed in the projection-operator formalism of Feshbach [23, 24, 44]. Domcke [17] reviews the application of this formalism to resonant effects in electron-molecule scattering. Neglecting the kinetic energy of nuclear motion, $\hat{T}_n$, an electronic resonance at nuclear coordinate(s) q is characterized by a pole of the analytically-continued scattering matrix $S(q, \epsilon)$ at complex energy $\epsilon = \epsilon_{res}(q) - \frac{1}{2}i\gamma(q)$, where γ is the decay width of the resonance. The set of values $\epsilon_{res}(q)$ defines the real part of the LCP effective potential curve. The Feshbach formalism in electron-molecule scattering is ordinarily applied to the static-exchange model of fixed-nuclei scat-

tering, coupled to the Hamiltonian H_n for nuclear motion[16, 50, 51, 2]. The electronic wave function is represented by a model state Φ (Slater determinant), whose orbital functions are orthogonalized to a normalized, localized orbital function $\phi_d(q; \mathbf{x})$ that interacts with a continuum orbital wave function ψ_k to produce the scattering resonance. For fixed nuclei, this formalism is exactly the same as resonance theory for atoms, resulting in a complex-valued nonlocal optical potential. It is most directly described by a Green function that is formally orthogonalized to the postulated localized function ϕ_d [44, 17].

In the LCP model of vibrational excitation, parametrized functions $\epsilon_{res}(q)$ and $\gamma(q)$, together with the ground-state potential curve, $V_0(q)$, suffice to determine cross sections averaged over rotational substructure. The full Feshbach formalism requires parametrized transition matrix elements between ϕ_d and orthogonalized background continuum orbitals $\hat{\phi}_k$, as well as $V_0(q)$ and the mean electronic energy $V_d(q)$ of a postulated discrete state ϕ_d . In a one-electron model[17], the Feshbach optical potential is added to the effective electronic Hamiltonian for static exchange. This formalism is readily extended to an orbital-functional theory that includes electronic correlation[47]. The transition element V_{dk} , parametrized as a function of both q and the electronic continuum energy ϵ , models the $(N+1)$ -electron matrix element $(\Psi_d|H|\mathcal{A}\Theta_0\psi_k)$, where Ψ_d is a postulated discrete $(N+1)$ -electron state, Θ_0 is the target electronic ground state, and ψ_k is a continuum orbital function at energy $\epsilon = \frac{1}{2}k^2$. The full function $\mathcal{A}\Theta_0\psi_k$ must be orthogonal to Ψ_d . Thus the formalism defined by such matrix elements applies to the original case considered by Feshbach, where Ψ_d is a core-excited state such as $He : (1s3s^2)^2S$ at 22.45eV excitation energy, as well as to the explicitly modeled one-electron attached state.

The vibronic Hamiltonian in the one-electron model is $H = H_0 + V$. The kernels of these operators are

$$\begin{aligned} h_0 &= \phi_d[\hat{T}_n + V_d(q)]\phi_d^* + \int k dk d\Omega_k \hat{\phi}_k[\hat{T}_n + V_0(q) + \frac{1}{2}k^2]\hat{\phi}_k^* ; \\ v &= \int k dk d\Omega_k \phi_d V_{dk}(q)\hat{\phi}_k^* + hc. \end{aligned}$$

The coupled Schrödinger equations can be projected onto the $\phi_d \cdots \phi_d^*$ subspace by Feshbach partitioning, giving an equation for the coefficient function $\chi_d(q)$ in the component $\phi_d \chi_d(q)$ of the total wave function. The effective Hamiltonian in this equation is $\hat{T}_n + V_d(q) + \hat{V}_{opt}$, which contains an optical potential that is nonlocal in the q -space. This operator is

defined by its kernel in the $\phi_d \cdots \phi_d^*$ subspace,

$$v_{opt}(q, q'; E) = \int k dk d\Omega_k V_{dk}(q) (E - \frac{1}{2}k^2 - \hat{T}_n - V_0(q) + i\eta)^{-1} V_{dk}^*(q').$$

This defines a nonlocal complex energy shift $v_{opt} = \Delta - \frac{1}{2}i\Gamma$ such that

$$\Delta(q, q'; E) = \sum_v \int k dk V_{dk}(q) \chi_v(q) [E - \frac{1}{2}k^2 - E_v]^{-1} \chi_v^*(q') V_{dk}^*(q'),$$

$$\Gamma(q, q'; E) = 2\pi \sum_v V_{dk_v}(q) \chi_v(q) \chi_v^*(q') V_{dk_v}^*(q').$$

Here $k_v^2 = 2(E - E_v)$ for the bound or continuum vibrational state indexed by v . Thus the Feshbach formalism implies energy-dependent, nonlocal energy-shift and width functions for a resonance.

Neglecting nonresonant scattering, the resonant contribution to the transition matrix is [17]

$$T(\mathbf{k}_f, v_f; \mathbf{k}_i, v_i) = (v_f | V_{d\mathbf{k}_f}^* G(E) V_{d\mathbf{k}_i} | v_i),$$

deduced from the Lippmann-Schwinger equation. Here $G(E)$ is the resolvent operator in the $\phi_d \cdots \phi_d^*$ space,

$$G(E) = (E - \hat{T}_n - V_d(q) - \hat{V}_{opt} + i\eta)^{-1},$$

evaluated in the limit $\eta \rightarrow 0+$ for outgoing-wave boundary conditions. The transition matrix can be computed as

$$T(\mathbf{k}_f, v_f; \mathbf{k}_i, v_i) = (v_f | V_{d\mathbf{k}_f}^* | \chi_d),$$

since the projected equation for the coefficient function $\chi_d(q)$ implies $\chi_d(q) = G(E) V_{d\mathbf{k}_i} \chi_{v_i}$. This projected equation is

$$\{\hat{T}_n + V_d(q) + \hat{V}_{opt} - H\} \chi_d(q) = -V_{d\mathbf{k}_i} \chi_{v_i}(q), \quad (1)$$

which is nonlocal in the nuclear coordinates [2].

Although in earlier applications $V_d(q) + \hat{V}_{opt}$ was approximated by an empirical local complex potential (LCP), more recent work has solved this nonlocal equation directly [17], obtaining detailed resonance excitation and near-threshold cross sections in excellent agreement with experimental data. Model calculations, using the nonlocal formalism, indicate that a local approximation can yield accurate results for vibrational excitations [11, 42]. The local model is inadequate for very broad resonances [41] and for near-threshold singularities [18, 19]. The neglect of nonresonant scattering implies significant discrepancies for elastic scattering.

Despite the practical success of the projection-operator formalism for resonant scattering, the underlying electronic theory is still restricted to a static-exchange model, augmented by an optical potential derived from empirical functions $V_d(q)$ and $\Gamma_d(q)$ or $V_{dk}(q)$.

2. Adiabatic approximations

In the semiclassical LCP model, the small mass ratio m/M justifies an assumption that the electronic wave function adjusts essentially instantaneously to displacements of the nuclei, because electronic velocities are much greater than nuclear velocities in a time-dependent semiclassical model. Thus nuclear motion is described in an adiabatic picture. This suggests various levels of adiabatic approximation based fundamentally on the inherently small kinetic energy of nuclear motion $\hat{T}_n$. A complete quantitative theory must use the full variational theory of interacting electrons, but can take advantage of significant simplifications in the treatment of nuclear motion.

Because molecular rotational kinetic energy and rotational level spacings are small in all cases, a rotationally adiabatic model has been widely and successfully used for electron-molecule scattering[31]. The essence of this *adiabatic nuclei* (ADN) approximation[49, 14, 15, 59] is that a scattering amplitude or matrix computed for fixed nuclei is treated as an operator in the nuclear coordinates. The rotational state-to-state scattering amplitude or matrix is estimated by matrix elements of this operator in the basis of rotational states. The basic assumption is that of the Born-Oppenheimer separation: the commutator between the fixed-nuclei scattering operator and the operator $\hat{T}_n$ is neglected. This approximation becomes difficult to justify only when the precise energy of individual rotational levels is important, near thresholds or in the presence of long-range potentials. Fixed-nuclei scattering matrices are computed in a body-fixed reference frame. In contrast, rotational scattering structure is observed in a fixed laboratory frame. Unless an explicit rotational frame transformation is carried out, strong rotational coupling occurs as a computational artifact[31]. For this reason, applications of the rotational ADN model require such a frame transformation[13].

The ADN approximation has been much less successful for vibrational excitation, as might be expected from the much larger vibrational level spacings and the strong variation of fixed-nuclei resonance parameters with nuclear displacements. This motivated the proposal[12] of a *hybrid* close-coupling model. As applied to $e - N_2$ vibrational excitation, this model combines fixed-nuclei electronic close-coupling calculations for nonresonant body-frame molecular symmetry states with extended

vibronic close-coupling calculations in the $^2\Pi_g$ resonant symmetry of N_2^- . Although multi peaked vibrational excitation and vibrationally elastic cross sections are obtained in qualitative agreement with experiment, the peak shapes and spacings are not in good agreement. This can be attributed to truncation of the electronic partial-wave expansion and of the limited number of vibrational states included in the close-coupling basis. A deeper problem is that any complete set of vibrational states, such as the eigenfunctions of a parametrized Morse potential, must include the vibrational continuum. No practical way has been found to do this in the close-coupling formalism.

2.1 The energy-modified adiabatic approximation (EMA)

In many scattering processes, energy levels of the target system are split by a perturbation that is weak relative to the interaction responsible for the scattering. The adiabatic approximation neglects the effect on threshold scattering structures and on resonances of the energy-level splitting and energy shifts of the perturbed target states. Especially for threshold structures, this can lead to qualitatively incorrect results. For example, transition matrix elements computed below a rovibrational excitation threshold do not vanish if only the fixed-nuclei target energy is taken into account. This qualitatively incorrect behavior of adiabatic cross sections near rotational excitation thresholds can be compensated simply by modifying electron momenta in the adiabatic cross-section formula[15]. With these corrections, the ADN theory appears to be adequate for rotational excitation[27].

Much larger anomalous effects occur in vibrational excitation because the energy shifts are larger. The energy-modified adiabatic approximation (EMA)[43] was introduced in order to provide a systematic treatment of such effects, while retaining the computational efficiency of the adiabatic approximation. The usual adiabatic approximation is modified by allowing for the dependence of unperturbed scattering matrices on the kinetic energy of the perturbed target state, using formulas that are qualitatively correct for threshold and resonance structures. For molecules, this means that for target geometry determined by a generalized coordinate q the energy $\epsilon(q) = E - V(q)$ of a continuum electron must be replaced in principle by $\epsilon_{op}(q) = E - H_n(q)$, an operator in the nuclear coordinates. Fixed-nuclei calculations produce scattering matrices that are functions of numerical parameters q, ϵ . In the EMA, the integrals that project these matrices onto rovibrational states are evaluated by approximations that replace the parameter ϵ by the operator ϵ_{op} .

The simplest such approximation, for diagonal matrix elements in a rovibronic state indexed by μ , is to replace ϵ by $\epsilon_\mu = E - E_\mu$. If nondiagonal matrix elements between states indexed by μ and ν are evaluated for the geometric mean energy $\epsilon_{\mu\nu} = [(E - E_\mu)(E - E_\nu)]^{\frac{1}{2}}$, this implies correct threshold behavior for general short-range potentials. When applied to the energy-denominator characteristic of a fixed-nuclei molecular resonance, this state-dependent modification of ϵ to ϵ_{op} was shown to give qualitatively correct results for the multi peaked vibrational excitation structures observed in $e - N_2$ scattering[43]. Because the EMA formalism replaces fixed-nuclei scattering matrices by operators that are represented by vibronic scattering matrices, a single fixed-nuclei or threshold structure becomes a set of overlapping scattering structures, displaced with possibly irregular energy shifts by the discrete vibronic energy level structure of the target molecule[43]. This repetition and displacement of underlying structures is characteristic of observed electron scattering cross sections for molecular targets. A more recent extension of the EMA formalism to the context of variational R-matrix theory is discussed below.

3. Vibronic R-matrix theory

Recognizing that exact quantum electron-molecule scattering theory for interacting nuclei and electrons is and will remain computationally intractable, except for the simplest diatomic molecules, Schneider[54] initiated reconsideration of the Born-Oppenheimer approximation as a logical foundation for the adiabatic-nuclei (ADN) formalism. For a long-lived (narrow) resonance, neglect of vibrational derivatives of the fixed-nuclei electronic wave function should be no less valid for electron scattering at low energies than it is for molecular bound states. This argument is the basis of an electronic R-matrix methodology in which eigenstates, defined by eigenvalues of the Bloch-modified electronic Hamiltonian from which the R-matrix is constructed, are used to define effective molecular potential functions, parametrized by nuclear coordinates[56]. The small mass ratio m/M justifies neglecting derivatives of the electronic eigenfunctions of this fixed-nuclei Bloch-modified Hamiltonian with respect to the nuclear coordinates.

This work introduced the concept of a vibronic R-matrix, defined on a hypersurface in the joint coordinate space of electrons and internuclear coordinates. In considering the vibronic problem, it is assumed that a matrix representation of the Schrödinger equation for $N+1$ electrons has been partitioned to produce an equivalent set of multichannel one-electron equations coupled by a matrix array of nonlocal optical potential

operators[44]. In the body-fixed reference frame, partial wave functions in the separate channels have the form $\Theta_p(q; \mathbf{x}^N) Y_L(\theta, \phi) \chi_v(q)$, multiplied by a radial channel orbital function $\psi(q; r)$ and antisymmetrized in the electronic coordinates. Here Θ is a fixed-nuclei N-electron target state or pseudostate and Y_L is a spherical harmonic function. Both Θ and ψ are parametric functions of the internuclear coordinate q . It is assumed that the target states Θ for each value of q diagonalize the N-electron Hamiltonian matrix and are orthonormal.

An electronic R-matrix radius a is chosen such that exchange can be neglected for $r > a$. An upper limit q_d for the internuclear coordinate q is chosen so that a dissociating electronic state Φ_d is bound for $q \geq q_d$. This defines a vibronic hypercylinder[46] with two distinct surface regions: an electronic wall with $r = a$ for $0 \leq q \leq q_d$ and a dissociation cap defined by the enclosed volume of the electronic sphere for $q = q_d$. For nondissociating molecules, q_d should be large enough to enclose the highest vibrational state to be considered. The R-matrix is defined by matrix elements of the variational operator $\mathcal{R}$ in a complete basis of surface functions[46], such as the spherical harmonics on the wall surface.

A matrix of operators $\mathcal{R}_{pp'}$ is defined by projection of $\mathcal{R}$ into the multichannel representation indexed by N-electron target states Θ_p . This defines the vibrational excitation submatrix of the R-matrix as

$$(pLv|R|p'L'v') = \int dq \int dq' \int d\Omega \int d\Omega' \\ \chi_v^*(q) Y_L^*(\theta\phi) \mathcal{R}_{pp'}(q\theta\phi; q'\theta'\phi') Y_{L'}(\theta'\phi') \chi_{v'}(q').$$

This matrix can be computed from a general variational formula, using a complete set of vibronic basis functions

$$\Psi_\alpha(\mathbf{x}^{N+1}, q) = \mathcal{A} \Theta_p(q; \mathbf{x}^N) Y_L(\theta, \phi) \psi_\alpha(q; r) \chi_\alpha(q).$$

It is assumed that target states Θ_p are indexed for each value of q such that a smooth diabatic energy function $E_p(q)$ is defined. This requires careful analysis of avoided crossings. The functions χ_α should be a complete set of vibrational functions for the target potential $V_p = E_p$, including functions that represent the vibrational continuum. All vibrational basis functions are truncated at $q = q_d$, without restricting their boundary values. The radial functions ψ_α should be complete for $r \leq a$.

Free boundary conditions are not allowed in the formulation of the theory by Schneider *et al*[56], based on the nonvariational theory of Wigner and Eisenbud[65]. Specific boundary conditions are imposed using a Bloch operator. This determines boundary conditions correctly at energy poles of the R-matrix determinant, but requires a Buttler correction [10] for energy values between such poles[56]. This becomes problematic

for the internuclear coordinate, because the physical model of the dissociating state is a complex potential function for $q \leq q_d$, so that fixed boundary conditions imply complex energy eigenvalues. Nevertheless, in the usual case that R-matrix poles are associated with homogeneous Neumann boundary conditions on the R-matrix boundary, the Wigner-Eisenbud theory and variational R-matrix theory derive the same equations for the vibronic R-matrix.

The projection integrals on the electronic wall are

$$(pLv|\alpha) = (A\Theta_p\chi_v|\Psi_\alpha)_{r=a} = \int_0^{q_d} \chi_v^*(q)\psi_\alpha(q;a)\chi_\alpha(q)dq.$$

In agreement with[56], the R-matrix for vibrational excitation is

$$(pLv|R|p'L'v') = \frac{1}{2} \sum_{\alpha,\beta} (pLv|\alpha)(H_B - E)_{\alpha\beta}^{-1}(\beta|p'L'v'),$$

where H_B is the Bloch-modified vibronic Hamiltonian. This requires vibrational kinetic energy matrix elements to be evaluated as the Hermitian form $\frac{1}{2\mu} \int dq \frac{d\chi_v}{dq} \frac{d\chi_{v'}}{dq}$.

The derivation up to this point involves no approximations if the vibronic basis set is complete in the closed hypervolume, including its surface. If a dissociation channel exists, it can be approximated by projection onto a single diabatic state $\Phi_d(q; \mathbf{x}^{N+1})$, assumed to be well-defined as a discrete state on the cap surface $q = q_d$. The projection integrals on this surface are

$$(d|\alpha) = (\Phi_d|\Psi_\alpha)_{q=q_d}.$$

The R-matrix connecting wall and cap surfaces, obtained by projecting the $\mathcal{R}$ operator onto both surfaces, is

$$(d|R|pLv) = \frac{1}{2} \sum_{\alpha,\beta} (d|\alpha)(H_B - E)_{\alpha\beta}^{-1}(\beta|pLv),$$

which determines excitation-dissociation transitions. The R-matrix in the cap surface is

$$(d|R|d) = \frac{1}{2} \sum_{\alpha,\beta} (d|\alpha)(H_B - E)_{\alpha\beta}^{-1}(\beta|d).$$

This is the reciprocal of the logarithmic derivative of the wave function $\chi_d(q)$ in the dissociation channel, for $q = q_d$. At given total energy E these R-matrix elements are matched to external scattering wave functions by linear equations that determine the full scattering matrix for

all direct and inverse processes involving nuclear motion and vibrational excitation. Because the vibronic R-matrix is Hermitian by construction (real and symmetric by appropriate choice of basis functions), the vibronic S-matrix is unitary.

Schneider *et al*[56] use Born-Oppenheimer vibronic basis functions as indicated above, and neglect Born-Oppenheimer corrections determined by the internuclear momentum operator acting on the electronic wave function. Radial basis functions $\psi_k(q; r)$ correspond to R-matrix pole states, whose energy values $E_k(q)$ define an indexed vibrational potential. Vibrational basis functions $\chi_{k\mu}(q)$ are computed as eigenfunctions of the corresponding Hamiltonian. Since resonance states are not treated by projection, the method depends on effective completeness of the double expansion in electronic and vibrational eigenfunctions. The first application of this method, to the multipeaked vibrational excitation structure observed in $e - N_2$ scattering, was remarkably successful[57], in much closer agreement with experiment than were comparable calculations using the hybrid ADN close-coupling formalism[12]. Electronic wave functions with fixed boundary conditions at $r = a$ were used for the four lowest R-matrix pole states, and vibrational wave functions were computed without considering the vibrational continuum. Boundary values on the cap surface are not relevant since dissociation is not involved. A Buttle correction for the electronic basis was computed using adiabatic theory.

These calculations were later extended up to 30eV[25] scattering energy, including differential cross sections for elastic scattering and vibrational excitation. The original method was modified to use a fixed electronic basis set for all internuclear distances, in order to mitigate problems arising from avoided crossings of R-matrix pole state potential curves. Vibrational wave functions were represented in a basis of shifted Legendre polynomials. These procedures were used for calculations of integral and differential cross sections in $e - HF$ scattering[37] and for similar calculations on HCl [38], both examples of threshold excitation peaks due to the molecular dipole moment. Because results computed with this method, based on a fixed boundary condition at $q = q_d$, depend strongly on the choice of q_d , a modified theory has been proposed in which the evidently successful R-matrix theory of vibrational excitation is combined with resonance-state theory for nuclear motion[22]. The approximation of neglecting derivatives of electronic wave functions with respect to internuclear coordinates appears to be satisfactory in all of these applications[55].

3.1 Phase-matrix theory

The success of projection-operator methods indicates that quantitative calculations can be based on the strategy of separating singularities of scattering matrices from a smoothly varying background[17]. The R-matrix is a real symmetric matrix with isolated real energy poles, analogous to the K-matrix in scattering theory. These poles have no special physical significance, simply indicating that the sum of eigenphases of the corresponding unitary S-matrix passes through an odd multiple of $\pi/2$ radians. The choice of pole states of the R-matrix to define "vibrational" potential functions in the method of Schneider *et al*[56] is an arbitrary construction whose principal effect is to produce linearly independent vibronic basis states.

To establish a better-motivated connection to resonance theory, the fixed-nuclei R-matrix can be converted to a phase matrix Φ , defined such that $\tan \Phi = k(q)R$. The corresponding unitary matrix is

$$U = (I + ik(q)R)/(I - ik(q)R),$$

the analog of the scattering S-matrix, whose complex energy poles define scattering resonances and bound states. The factor $k(q) = [2(E - V_0(q))]^{\frac{1}{2}}$ makes Φ dimensionless. A resonance is characterized for real energies by a point of most rapid increase of the eigenphase sum[58, 44], which is the trace of the matrix $\tan^{-1} K$. Evaluated at specified $r = a$, the phase matrix Φ of the R-matrix has analogous properties. For real energies, Φ has a monotonically increasing trace, which can be made continuous by suitable choice of the branch of each multivalued eigenphase function, adding or subtracting integral multiples of π at each energy value. A point of maximum slope defines a "precursor resonance" [46], which corresponds to a pole of the analytically continued S-matrix as the R-matrix boundary is increased. The proposed methodology uses time-delay analysis[58] to separate a given fixed-nuclei phase matrix into a rapidly varying resonant part and a slowly varying background part. The rovibronic phase matrix is constructed by applying resonance theory to the resonant phase matrix only, treating the nonresonant background part by energy-modified adiabatic theory. By separating out rapid variations of Φ this methodology reduces the completeness requirement from the double expansion inherent in the method of Schneider *et al*[56] to a single expansion for a well-defined precursor resonance state. Vibrational completeness is obtained by using a special basis of "spline-delta" functions that make no distinction between bound and continuum vibrational wave functions[48].

3.2 Separation of the phase matrix

With current computational methods, accurate fixed-nuclei R-matrices R^{FN} can be obtained that interpolate smoothly in a vibrational coordinate q and in the electronic continuum energy ϵ . The fixed-nuclei phase matrix Φ^{FN} is defined such that

$$\tan \Phi^{FN}(q; \epsilon) = k(q)R^{FN}(q; \epsilon),$$

where eigenphases are adjusted by multiples of π to make matrix elements continuous in both ϵ and q . For the vibronic phase matrix,

$$\tan \Phi_{vv'} = k_v^{\frac{1}{2}} R k_{v'}^{\frac{1}{2}},$$

where $k_v = [2(E - E_v)]^{\frac{1}{2}}$. A precursor resonance corresponds to rapid variation of the trace of the phase matrix. Single-pole parameters for a resonance can be determined from the energy derivative of the phase matrix[58]. Analysis of a single-channel resonance[44] shows that an S-matrix pole at complex energy $\epsilon_{res} - \frac{1}{2}i\gamma$ implies that the energy derivative of the phase shift $\eta(\epsilon)$ has a maximum value at ϵ_{res} . Assuming constant background phase variation, $\epsilon_{res}(q) = E_{res}(q) - V_0(q)$ is defined by a local maximum of $\frac{d}{d\epsilon} T r \Phi$. The maximum eigenvalue of the matrix $\frac{d}{d\epsilon} \Phi$ at ϵ_{res} is $2/\gamma$ [58]. The eigenvector y defines a resonance eigenchannel. This analysis determines the parameters in the Breit-Wigner formula for an isolated multichannel resonance[44], consistent with a single pole of the analytically-continued U-matrix as defined above. This implies an analytic formula for the resonant phase matrix Φ_1 , which will be considered in more detail below. Given the phase matrix Φ , this construction of Φ_1 defines a background matrix Φ_0 by subtraction, such that $\Phi = \Phi_0 + \Phi_1$. This procedure can be repeated for several neighboring precursor resonances if necessary. Since Φ is unchanged, no information is lost.

3.3 Phase matrix formalism:EMAP

After separation into resonant and background parts, the nonresonant fixed-nuclei phase matrix Φ_0 is converted to a vibronic or rovibronic phase matrix by the energy-modified adiabatic phase matrix method (EMAP)[60]. This is simply an adaptation of the EMA formalism to the phase matrix Φ_0 . The implied vibronic background phase matrix is

$$(pLv|\Phi_0|p'L'v') = \int \chi_v^*(q)(pL|\Phi_0^{FN}(q; \epsilon_{vv'})|p'L')\chi_{v'}(q)dq,$$

where $\epsilon_{vv'} = [(E - E_v)(E - E_{v'})]^{1/2}$. The geometric mean is appropriate to the dimensionless vibronic phase matrix for general short-range potentials[35], as in the earlier EMA theory[43].

The EMAP method has been used in *ab initio* calculations of near-threshold rotational and vibrational excitation in electron scattering by polar molecules[60, 61]. Computed differential cross sections are in quantitative agreement with available experimental data for $e - HF$ scattering. This methodology was able to obtain results equivalent to converged close-coupling calculations including both vibrational and rotational degrees of freedom. Specific treatment of rotational structure is essential for such molecules because of rotational screening of the long-range dipole potential. These calculations provide a detailed analysis of the striking threshold peak structures observed for such dipolar molecules. For $e - H_2$ vibrational excitation, in a direct comparison with the FONDA (first-order nondegenerate adiabatic) approximation [39, 1, 40], and with benchmark vibrational close-coupling results[62], the EMAP method was found to be computationally efficient and reasonably accurate at energies somewhat above threshold and away from a scattering resonance[33].

The EMAP method has been used to compute elastic scattering and symmetric-stretch vibrational excitation cross sections for electron scattering by CO_2 [34]. This is one of the first *ab initio* calculations of vibrational excitation for a polyatomic molecule. The results are in good agreement with experiment, which shows unusually large low-energy cross sections. The theory identifies a near-threshold singularity in the fixed-nuclei scattering matrix, changing from a virtual state to a bound state as the vibrational coordinate varies[36, 34].

3.4 Nonadiabatic theory:NADP

For low collision energies, especially when electronic resonances occur, and for processes such as dissociative attachment, adiabatic theory is not adequate for vibrational excitation and energy transfer. The strategy of separating the fixed-nuclei phase-matrix into resonant and nonresonant parts makes it possible to apply resonance analysis, analogous to the projection-operator method[17], to the rapidly varying part of the phase matrix. This nonadiabatic phase-matrix (NADP) formalism is derived here. The discussion here is limited to the model considered above, specifically for a diatomic molecule in the body-frame, with only one internuclear coordinate q .

Time-delay analysis[58] of the energy derivative of the phase matrix Φ determines parametric functions that characterize the Breit-Wigner for-

mula for the fixed-nuclei resonant R-matrix $R_1^{FN}(q; \epsilon)$. The resonance energy $\epsilon_{res}(q)$, the decay width $\gamma(q)$, and the channel-projection vector $y(q)$ define R_1^{FN} and its associated phase matrix Φ_1^{FN} , such that $\tan \Phi_1^{FN} = k(q)R_1^{FN}$, where

$$R_1^{FN}(q; \epsilon) = \frac{1}{2} y(q) \gamma^{\frac{1}{2}}(q) [\epsilon_{res}(q) - \epsilon(q)]^{-1} \gamma^{\frac{1}{2}}(q) y^\dagger(q). \quad (2)$$

Using the basic rationale of EMA theory[43], the parametric function $\epsilon(q)$ becomes $\epsilon_{op}(q) = E - H_n$ when the kinetic energy of nuclear motion cannot be neglected. However, the operator $(\epsilon_{res}(q) - \epsilon_{op}(q))$ has a well-defined c-number value in vibrational eigenstates determined by the eigenvalue equation

$$(\hat{T}_n + E_{res}(q))\chi_s(q) = \chi_s(q)E_s. \quad (3)$$

Defining $\epsilon_s(q) = E_s - V_0(q)$, this implies

$$(\epsilon_{res}(q) - \epsilon_{op}(q))\chi_s(q) = \chi_s(q)(\epsilon_s(q) - \epsilon(q)).$$

Here $\epsilon_s(q) - \epsilon(q) = E_s - E$, independent of q . Thus the energy denominator in Eq.(2) can be replaced by $E_s - E$ in the vibrational eigenstate χ_s . In the NADP method, Eq.(3) is solved in a basis of spline-delta functions[48], which determines bound and continuum vibrational eigenfunctions to graphical accuracy (a cubic spline fit) in the coordinate range $0 \leq q \leq q_d$. Substituting this c-number energy denominator into Eq.(2), and evaluating matrix elements of the resulting operator in the vibrational coordinate q , the NADP resonant vibronic R-matrix for vibrational excitation is

$$(pLv|R_1|p'L'v') = \frac{1}{2} \sum_s (v|y_{pL}\gamma^{\frac{1}{2}}|s)(E_s - E)^{-1}(s|\gamma^{\frac{1}{2}}y_{p'L'}^\dagger|v'). \quad (4)$$

For comparison with projection-operator theory, this corresponds to a Born-Oppenheimer precursor resonance state

$$\Psi_s(\mathbf{x}^{N+1}, q) = \Phi_d(q; \mathbf{x}^{N+1})\chi_s(q),$$

where Φ_d is a postulated discrete state, defined for $q \leq q_d$, that interacts with the background electronic continuum. For this precursor state, the projection integrals on the electronic wall of the vibronic hypercylinder are $(pLv|s) = (\mathcal{A}\Theta_p Y_L \chi_v | \Psi_s)_{r=a}$, and the corresponding projection integral on the dissociation cap is $(d|s) = (\Phi_d | \Psi_s)_{q=q_d} = \chi_s(q_d)$, a normalized eigenfunction of Eq.(3). The vibronic R-matrix for this precursor resonance state is

$$(pLv|R_{res}|p'L'v') = \frac{1}{2} \sum_s (pLv|s)(E_s - E)^{-1}(s|p'L'v'), \quad (5)$$

the R-matrix connecting wall and cap surfaces is

$$(d|R_{res}|pLv) = \frac{1}{2} \sum_s \chi_s(q_d)(E_s - E)^{-1}(s|pLv),$$

and the R-matrix on the cap surface is

$$(d|R_{res}|d) = \frac{1}{2} \sum_s \chi_s(q_d)(E_s - E)^{-1} \chi_s^*(q_d).$$

As a consistency check, if a Green function is defined by

$$G(q, q') = \frac{1}{2} \sum_s \chi_s(q)(E_s - E)^{-1} \chi_s^*(q'),$$

all formulas agree with Schneider *et al*[56].

Comparing Eqs.(5) and (4), they would be identical if the "magic formula"

$$(pLv|s) \cong (v|y_{pL}\gamma^{\frac{1}{2}}|s)$$

were valid. The NADP formalism postulates this to be true, implying that the R-matrix connecting wall and cap surfaces is

$$(d|R_1|pLv) = \frac{1}{2} \sum_s \chi_s(q_d)(E_s - E)^{-1}(s|\gamma^{\frac{1}{2}}y_{pL}^\dagger|v),$$

and the R-matrix on the cap surface is

$$(d|R_1|d) = \frac{1}{2} \sum_s \chi_s(q_d)(E_s - E)^{-1} \chi_s^*(q_d).$$

Because the postulated diabatic state Φ_d is never computed explicitly, the NADP formalism avoids the conceptual difficulties associated with this state in the LCP and projection operator methods. Reduction of the vibrational computation to solution of Eq.(3) removes the difficult issue of vibrational completeness inherent in vibrational close-coupling theory and in the method of Schneider *et al*.

The NADP method was first tested in calculations of $e - N_2$ rovibrational excitation. The efficiency of this formalism was demonstrated by carrying the calculations to effective completeness for combined rotational and vibrational close-coupling. The multi peaked vibrational excitation structure was computed to an accuracy that appears to agree more closely with experiment than does any previous theoretical work [28]. Computed differential vibrational excitation cross sections are in close agreement with experiment. More recently, the NADP method has

been used in a series of calculations of $e - H_2$ scattering intended to calibrate the method against earlier work that was designed to give definitive results for low-energy vibrational excitation cross sections. The $^2\Pi_u$ shape resonance of H_2^- , which dominates electron scattering for energies below 10eV, has traditionally been very difficult to characterize, because the indicated decay width becomes very large at internuclear distances near the the ground-state equilibrium q_0 . It was found in NADP calculations [35, 32] that the precursor resonance considered in this methodology is in fact very well defined, and the resulting resonance vibrational excitation cross sections are in close agreement with the best available prior calculations.

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INTERACTIONS BETWEEN ELECTRONS AND HIGHLY CHARGED IRON IONS

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Abstract This paper is a summary of recent work our group has carried out on cross section measurements of highly charged iron ions. Electron impact ionization cross sections for hydrogen-like iron [1] and dielectronic recombination resonant strengths for the KLM, KLN and KLO processes in helium-like iron were determined [2]. These experiments were performed using an electron beam ion trap.

Keywords: highly charged ions, EBIT, electron impact ionization, dielectronic recombination

1. Introduction

The study of the interactions between highly charged ions and electrons is an important branch of atomic physics. Highly charged ions (HCIs) occur throughout the universe. Fusion plasmas also operate at temperatures sufficient to generate highly charged ions which can be a source of contamination in these devices. The properties of highly charged ions differ quite markedly from those of neutral atoms or singly charged ions. Scaling laws allow us to develop a feel for these properties. For example the 'size' of the ions reduces with increasing charge state. For one electron atoms the radius scales as $R \propto 1/Z$ so Fe^{25+} has a wavefunction which is 25 times more spatially compact than that of a hydrogen atom. The ionization energy also increases rapidly with increasing charge state, scaling as $U(Z) \propto Z^2$. A simple estimate of the ionization energy (U) of hydrogen-like iron gives $U = 13.6 \times (26)^2 = 9.2 \text{ keV}$. Similarly the separation of energy levels also changes dramatically. The strong coulomb attraction of the nucleus pulls the low lying levels down causing the energy levels to become more separated. For

transitions that produce photons in the visible region in neutral atoms, x-ray photons may be produced in isoelectronic highly charged ions. In the Bohr model the orbital velocity of the bound electron is $v = Z\alpha c$, where α is the fine structure constant, $\alpha \approx 1/137$, and c is the speed of light. For HCl's this orbital velocity can therefore approach a large fraction of the speed of light, indicating relativistic treatment. Finally the electric fields inside highly charged ions are perhaps among the strongest in the universe. The electric field scales as Z^3 which gives a field of approximately 9×10^{15} V/m in hydrogen-like iron. For a comprehensive recent review of the physics of highly charged ions, see Gillaspay [3].

This paper describes how an electron beam ion trap (EBIT) has been used to investigate several charge changing interactions in highly charged iron ions.

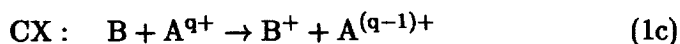
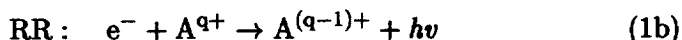
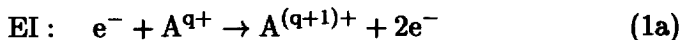
2. The electron beam ion trap (EBIT)

A detailed description of the principles and construction of an EBIT has been given elsewhere [4], so only a brief summary will be given here. The EBIT is a device for producing and confining HCl's. The Tokyo EBIT [5, 6] consists of three main components, an electron gun, a trap region and a collector. Electrons are emitted from a high perveance electron gun and are accelerated to a trap region which is positively biased with respect to the cathode. A large axial magnetic field simultaneously compresses the electron beam. The magnetic field is generated by a super-conducting electromagnet and produces a field of a few Teslas in the trap region. After passing through the trap region the electrons are decelerated before entering the collector. The magnetic field decreases and the electron beam re-expands in this region.

Inside the trap the compressed electron beam interacts with atoms and ions introduced into the trap region. Ions are produced by successive electron impact ionization (EI) of neutrals or low charge state ions. Radial trapping of the ions is due to the space charge of the electron beam. The trap is composed of three cylindrical electrodes and axial trapping is produced by applying appropriate voltages to these electrodes.

A variety of atomic processes compete to determine the final charge state balance of the ions inside the trap. Successive electron impact ionization by the electron beam tends to increase the charge state of the ions. A limit is reached when the electron beam energy is lower than the ionization potential of the ion concerned. On the other hand both radiative recombination and charge exchange act to reduce the charge state of the ions. Radiative recombination (RR) is the process by which an electron is captured by an ion with the emission of a photon. Charge

exchange (CX) occurs when a HCI interacts with a neutral atom. HCIs are the most chemically reactive species known and can pull one or more electrons from a neutral atom before the coulomb repulsion of the newly created ion repels the highly charged ion. These processes are summarized in the following equations.



3. Electron impact ionization of hydrogen-like iron ions

3.1 Introduction

Electron impact ionization cross sections were determined for hydrogen-like iron ions [1]. Ionization of hydrogen-like ions occurs by a direct mechanism only, there are no resonant effects contributing to the cross section. This makes these process of fundamental interest and somewhat more straightforward to calculate.

For less highly charged ions, cross sections have been measured by a crossed beams technique. The difficulty of these measurements is demonstrated by the fact that the first results for the ionization of hydrogen were not published until 1958 [7]. A further thirty years passed before the next ion in the sequence Li^{2+} was reported [8]. Recently the same group published results for the hydrogen-like ions B^{4+} - O^{7+} [9], the state of the art for absolute measurements.

For more highly charged ions it becomes very difficult to measure cross sections using this technique. Donets and Ovsyannikov [10] determined electron impact cross section by modelling the measured charge state evolution of ions in an electron beam ion source (EBIS). Using this technique they reported qualitative results for ions as highly charged as K^{33+} and Xe^{47+} . The electron impact ionization cross section of hydrogen-like uranium, U^{91+} was measured by Marrs *et al* [11] using an EBIT. They subsequently reported results for Mo^{41+} , Dy^{65+} , Au^{78+} and Bi^{82+} [12].

3.2 Method

The method used is an extension of the one reported previously by Marrs *et al* [11, 12]. Essentially a comparison of the number of hydrogen-like and bare ions at equilibrium, together with a correction for charge

exchange, is used to determine the cross section. This equilibrium ionization balance is obtained from x-ray measurements of radiative recombination into the K-shell of hydrogen-like and bare ions.

Low charge state iron ions were injected into the trap along the beam axis using a metal vapor vacuum source (MEVVA). The ions were trapped and rapidly ionized by the electron beam. Neutral neon was injected into the trap at 90°. Neon atoms become ionized and can escape from the trap with the removal of energy. This decreases the temperature and increases the trapping time of the highly charged iron ions. X-rays were detected at 90° to the beam axis using a solid state detector. After a trapping period of 4 s the trap was emptied and the MEVVA triggered again. Both x-ray energy and the time during the cycle were recorded using a multiparameter system [13].

At equilibrium the electron impact ionization cross section, σ_H^{EI} , is given by,

$$\sigma_H^{EI} = \frac{N_{hvB}}{N_{hvH}} \frac{\sigma_B^{\Sigma RR} (d\sigma_H^{RR=1}/d\Omega)}{(d\sigma_B^{RR=1}/d\Omega)} \left(1 + \frac{N_0}{I} \langle \sigma_B^{CX} \rangle_{eff} \right) \quad (2)$$

where N_{hvB} and N_{hvH} are the measured photon yields from RR into bare and H-like ions respectively. $\sigma_B^{\Sigma RR}$ is the total RR cross section into bare ions and $d\sigma_H^{RR=1}/d\Omega$ is the differential RR cross section into the K-shell of H-like ions. $\langle \sigma_B^{CX} \rangle_{eff}$ is an effective charge exchange cross section, N_0 is the pressure at the neutral gas inlet which we assume is proportional the background neutral density and I is the electron beam current. Radiative recombination cross sections were calculated to high accuracy by applying detailed balance to the photoionization cross sections. Total photoionization cross sections and angular distribution coefficients were calculated for a given effective potential by the independent particle approximation (IPA). Total RR cross sections $\sigma^{\Sigma RR}$, were obtained by summing over the cross sections to any excited state.

The x-ray spectra were fitted to determine the ratio N_{hvB}/N_{hvH} . Since the analysis is only valid at equilibrium the spectra were fitted at various times throughout the cycle. The range of times over which the ratio of bare and H-like ions was constant was extracted and used for further analysis. One unknown factor in eq. 2 is the effective charge exchange cross section $\langle \sigma_B^{CX} \rangle_{eff}$. This was accounted for by performing the experiment over a range of neutral densities, N_0 and beam currents I . At a beam energy of 15 keV both of these parameters were varied independently and the results fitted simultaneously with N_0 and I as

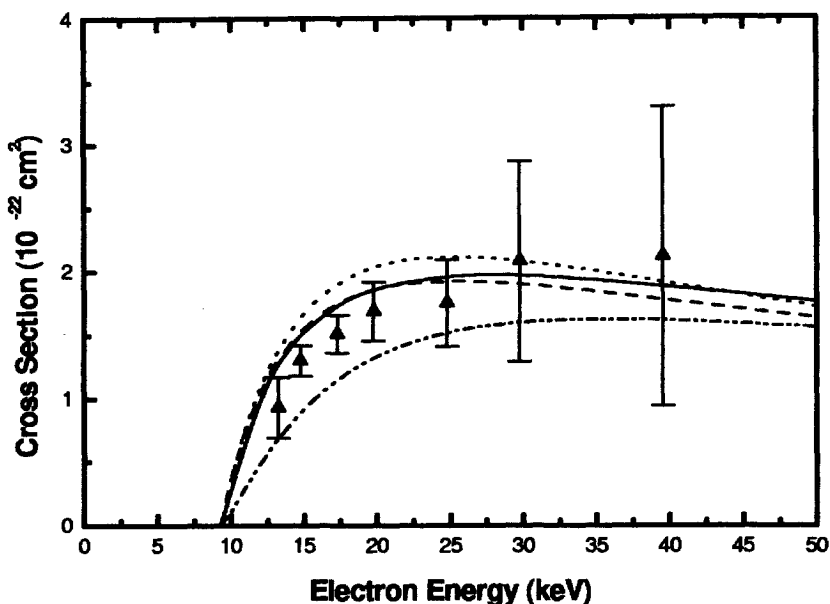


Figure 1. Measurements of the electron impact ionization of hydrogen-like iron ions. Our distorted wave calculation (—), the Lotz formula (---), the Rost-Pattard parameterization (···) and the Deutsch-Mark formulation (- · - ·).

variables. Using this procedure the effective charge exchange contribution was determined.

3.3 Results and discussion

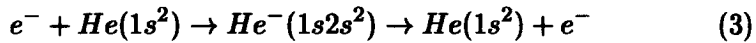
The measurements of the electron impact ionization cross section of hydrogen-like iron are shown in figure 1. The experiment was performed at 7 different energies from 1.45 to 4.3 times the threshold energy. Our group's distorted wave calculation is shown as a solid line in the figure. Several other theoretical formulations are also plotted including the semiempirical Lotz formula [14], the parameterization of Rost and Pattard [15, 9] and the Deutsch-Märk theory [16, 17].

The measured values agree well with theoretical calculations. The Lotz formula is non-relativistic and agrees well with the data and the distorted wave calculation at low energies, indicating that relativistic effects are not very important in this process. The experimental uncertainties, although large, represent some of the most accurate cross section measurements in an highly charged hydrogen-like ion.

4. Dielectronic recombination of helium-like iron ions

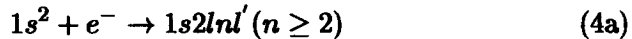
4.1 Introduction

The discovery of the $1s2s^2$ resonance by Schulz in 1963 [18, 19] in atomic helium marked the dawn of electron impact resonance spectroscopy. A doubly excited state is formed which decays by emission of an electron.

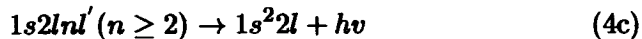
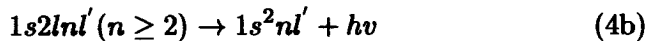


As indicated earlier, many processes in atomic physics have characteristic scaling laws as a function of nuclear charge, so new physics can be revealed when comparing neutral and highly charged isoelectronic counterparts. For example, the radiative transition rate A^r scales as Z^4 whereas the Auger decay rate is independent of charge to a good approximation. Hence as the nuclear charge increases, the $1s2s^2$ resonance predominantly stabilizes radiatively, giving rise to a process known as dielectronic recombination (DR). This process was first proposed by Massey and Bates in 1942 [20]. It was not until 1983 that the first DR cross section measurements were performed, with results for C^+ and Mg^+ reported using crossed beams experiments [21, 22]. In the same year Dittner *et al* [23] published DR cross sections for the Li-like ions B^{2+} and C^{3+} using a merged beams apparatus. The importance of DR can be appreciated by considering hot plasmas, where it generally proceeds at a much higher rate than RR, and therefore plays an important role in determining the charge state balance in astrophysical and fusion plasmas [24].

For He-like ions the formation of the intermediate state can be written as



This state decays by photon emission through either of two decay channels;



Ali *et al* [25, 26] reported DR cross sections for He-like Ar ions by measuring the charge state balance of extracted ions as a function of the beam energy in an EBIS. He-like cross sections were also measured in

the ions Ar, Fe, Ni, Kr, Mo and Ba using an EBIT [27, 28, 29, 30, 31]. In our experiment the dielectronic recombination (DR) resonant strengths of the KLn ($3 \leq n \leq 5$) resonances were measured for helium-like iron ions [2]. These measurements were performed by measuring the x-ray spectra while scanning the electron beam energy of the EBIT.

4.2 Method

The iron ions were introduced to the EBIT using a MEVVA. The potential of the trap was set to be 4 kV and the electron gun to -4.5 kV with respect to laboratory earth. The interaction energy was therefore 8.5 keV just below the He-like ionization potential. By holding this energy for 150 ms the ions are rapidly ionized and He-like ions become by far the most dominant species present. At this point the beam energy was ramped linearly from 8.5 to 4.3 keV, lower than the KLL resonant energy, and then back to 8.5 keV again. This sweep lasted 3 ms, fast enough to preserve the charge balance during the observation. During the scan the x-ray spectra and the beam energy were recorded simultaneously by the multiparameter system.

4.3 Results and discussion

A plot of the DR spectrum is shown in figure 2. The sharp peaks are the resonances denoted by the labels KLL, KLM etc. KLM signifies that a free electron has been captured to the M shell (or L shell) and a bound electron is promoted from the K shell to the L shell (or M shell). X-rays arising from transitions $n = 2 \rightarrow 1$ are indicated as the $K\alpha$ cut. The RR cut denotes x-rays with energy equal to that for RR into the $n = 2$ level of He-like ions. This energy increases linearly with the beam energy and so this cut is at an angle to the $K\alpha$ cut. These cuts were extracted and compared with theoretical calculations. In these calculations the electron beam width is convoluted with the calculated cross sections to obtain a spectrum. The agreement between theory and experiment was found to be good [32].

By normalizing the spectra to the KLL resonant strength measured by Beiersdorfer *et al* [29] the resonant strengths were determined. The total resonant strengths obtained were $5.0 \pm 0.4 \times 10^{-19}$, $2.1 \pm 0.2 \times 10^{-19}$ and $1.1 \pm 0.1 \times 10^{-19}$ cm²eV for KLM, KLN and KLO respectively.

Since the width of the resonances are narrow the resonant strengths are commonly used instead of the cross sections. These are obtained by integrating the cross section over the energy. Defining the initial state as i , the intermediate doubly-excited state as d and the final state as f , the resonant strength is written in atomic units as,

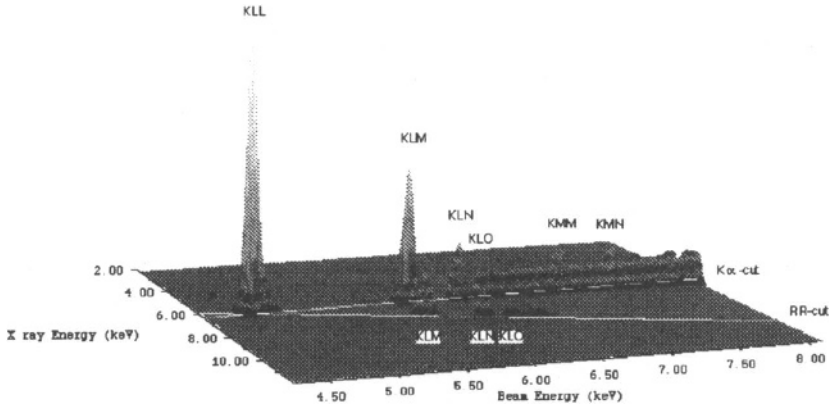


Figure 2. A surface plot of the spectrum with dielectronic recombination resonances labelled.

$$S_{idf} = \int_0^{\infty} \sigma_{idf}^{DR}(E) dE = \frac{\pi^2}{E_{di}} \frac{g_d}{2g_i} \frac{A_{di}^a A_{df}^r}{\Sigma A^a + \Sigma A^r} \quad (5)$$

where $\sigma^{DR}(E)$ is the DR cross section, g_i and g_d are the statistical weights of i and d , A_{df}^r is the rate of radiative transition from d to f , A_{di}^a is the autoionization rate from d to i and E_{di} is the resonant energy. These parameters scale as $A^r(Z) = Z^4 A^r(H)$, $A^a(Z) = A^a(H)$ and $E(Z) = Z^2 E(H)$ respectively [33] where H is the non-relativistic hydrogenic value. The resonant strength may then be written as,

$$S = \frac{1}{m_1 Z^2 + m_2 Z^{-2}} \quad (6)$$

where m_1 and m_2 are parameters which can be calculated from non-relativistic hydrogenic wavefunctions. Further experiments are needed over a wide range of atomic numbers to investigate the validity of eq. 6. Its derivation is only valid for a single resonance while it is applied to an unresolved manifold of resonances.

5. Conclusion

Interactions between electrons and highly charged iron ions have been investigated using an EBIT. Cross sections for electron impact ionization of hydrogen-like ions have been measured. Determining cross sections is a difficult task and our uncertainties were barely able to discern between the several theories considered. Although the experimental uncertainties

are large, these measurements include some of the most accurate EI cross sections available for highly charged ions.

Dielectronic recombination into helium-like iron ions was also investigated. Resonant strengths were measured for the KLM, KLN and KLO processes. Theoretical calculations were found to be in good agreement with the measured spectra. A scaling law for the resonant strengths has also been developed and is consistent with results measured previously.

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AN INVESTIGATION OF THE TWO OUTERMOST ORBITALS OF GLYOXAL AND BIACETYL BY ELECTRON MOMENTUM SPECTROSCOPY

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Abstract: Electron momentum spectroscopy is applied to study the two outermost orbitals of glyoxal and biacetyl. From the experimental momentum profiles, it has been unambiguously concluded that through-bond interaction dominates in these molecules. The results are compared with associated theoretical profiles, illuminating the importance of electron correlation effects for quantitative predictions of electron densities of the orbitals.

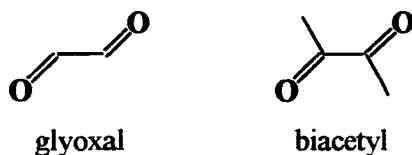
Key words: Electron momentum spectroscopy, Orbital imaging, Electron density, (e,2e)

1. INTRODUCTION

It is well known that the wavefunction is the most compact and perfect way to represent all information of atomic and molecular systems. While quantum mechanical calculations have given insight into various fields, approximate wavefunctions that minimize the variational energies sometimes fail to predict other properties such as dipole moment and polarizability. In fact, quantitative descriptions of electronic states of molecules have long been a challenging subject in quantum theory, and really accurate calculations are still only possible for systems containing few electrons. Thus it is of fundamental significance to experimentally examine the wavefunction itself. Once the reliable wavefunction is determined, it can be used to predict all sorts of properties accurately. Binary (e,2e), also

known as electron momentum spectroscopy (EMS)¹⁻³, is particularly well suited for the purpose.

EMS has been developed as a powerful tool to study electronic structure and electron correlation effects in matters. Especially, the ability to measure momentum density distribution of the target electron, the square modulus of the momentum-space representation of the ionized orbital, is a remarkable feature of this technique. Since electron momentum density is very sensitive to diffuse parts of the position-space wavefunction, EMS has been applied to a large body of molecules for acquiring direct information on density distributions of chemically reactive valence electrons.

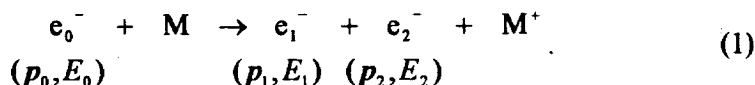


The molecules studied here are glyoxal and biacetyl, both of which have identical functional groups, oxygen lone-pair orbitals. These molecules are among the first systems to be studied with respect to the concept of through-space (TS) and through-bond (TB) interactions, which has been proposed originally by Hoffmann et al.^{4,5} TS interaction arises from the direct overlap between the semi-localized orbitals of the functional groups and places their symmetric linear combination ($n+$) below the anti-symmetric one ($n-$). In contrast, TB interaction, which occurs with participation of intervening bonds, may force the orbital ordering to be the reverse. These TS and TB interactions are usually competitive and hence the orbital ordering depends on the molecule in question. In the target systems, the $n+$ and $n-$ orbitals constitute the two outermost orbitals. It is, therefore, very important to know which interaction dominates, since reactivity and other properties of a molecule largely depend on the symmetry and electron density distribution of the highest occupied molecular orbital (HOMO).

In the present work, a newly constructed EMS spectrometer⁶ has been applied to the two outermost orbitals of glyoxal and biacetyl. Significantly improved electron momentum profiles over the previous study⁷ are presented, giving direct and unambiguous experimental evidence of the TS and TB interactions for the molecules. The results are also employed to compare with associated theoretical profiles generated by the Hartree-Fock (HF) and density functional theory (DFT).

2. THEORETICAL BACKGROUNDS AND CALCULATIONS

EMS is a high-energy electron-impact ionization experiment in which kinematics of all the electrons are fully determined, with coincident detection of the two outgoing electrons.¹⁻³ The collision process can be described by



Here p_0 , p_1 , and p_2 are the momenta and E_0 , E_1 , and E_2 are energies of the incident and two outgoing electrons, respectively. Conservation of energy and momentum requires that

$$E_0 = E_1 + E_2 + E_{\text{bind}} \quad (2)$$

and

$$p_0 = p_1 + p_2 - p, \quad (3)$$

where E_{bind} and p is the binding energy and momentum of the target electron.

Within the plane-wave impulse approximation (PWIA), the EMS cross section can be written as

$$\sigma_{\text{EMS}} \propto \int \left| \langle P \Psi_f^{N-1} | \Psi_i^N \rangle \right|^2 d\Omega_p. \quad (4)$$

Here Ψ_i^N and Ψ_f^{N-1} are the total electronic wavefunction for the N -electron target species and the $(N-1)$ -electron product ion, respectively, and P is a plane wave representing the target electron at the collision instant. If the many-body wavefunctions Ψ_i^N and Ψ_f^{N-1} are replaced by the independent-particle determinants of target HF orbitals, then Eq. (4) simplifies to

$$\sigma_{\text{EMS}} \propto \int |\psi_j^{\text{HF}}(p)|^2 d\Omega_p, \quad (5)$$

where $\psi_j^{\text{HF}}(p)$ is the momentum-space wavefunction of the ejected j -th electron.

Recently, Duffy et al.^{8,9} have proposed an alternative approximation to the EMS cross section, which replaces the HF orbital by the Kohn-Sham orbital as expressed by Eq. (6).

$$\sigma_{\text{EMS}} \propto \int |\psi_j^{\text{KS}}(p)|^2 d\Omega_p \quad (6)$$

They have shown that for atoms and small molecules the calculations can give superior description of electron momentum profiles to HF and provide results very similar to those by a full neutral-target/final-ion overlap according to Eq. (4).

Theoretical momentum profiles of glyoxal and biacetyl have been calculated by HF and DFT using the Slater exchange and VWN5 correlation functional¹⁰. Briefly, the position-space wavefunctions were generated with the Gaussian98 program¹¹ by using several standard basis sets. In the calculations optimized geometry was used for each molecule. The calculated wavefunctions were subsequently converted to momentum profiles with the help of the HEMS program developed by Brion and his co-workers. To compare with experiments, all the profiles were folded with the instrumental momentum resolution according to Migdall et al.¹²

3. EXPERIMENTAL

A schematic of the symmetric non-coplanar scattering geometry employed is shown in Figure 1. In this kinematics two outgoing electrons with equal energies ($E_1=E_2$) and equal scattering polar angles ($\theta_1=\theta_2=45^\circ$) are detected in coincidence. Then magnitude of the target electron momentum p is expressed by

$$p = \sqrt{\left[\sqrt{2}p_1 - p_0\right]^2 + \left[\sqrt{2}p_1 \sin\left(\frac{\phi}{2}\right)\right]^2}, \quad (7)$$

where ϕ is the out-of-plane azimuthal angle difference between the two outgoing electrons. If energy and momentum of the incident electron are fixed, a given ionization transition (E_{bind}) can be selected simply by detection energies ($E_1=E_2$) and the target electron momentum p becomes a function of only ϕ .

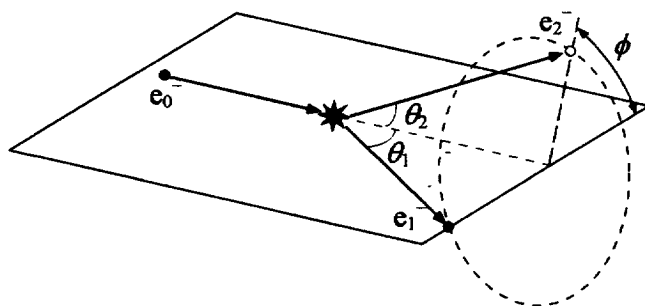


Figure 1. Schematic of the symmetric non-coplanar kinematics for the binary $(e,2e)$ reaction.

Details of the spectrometer have been described elsewhere⁶. Briefly, it consists of an electron gun, conical decelerating lenses, a spherical analyzer, and a pair of position-sensitive detectors (PSDs)¹³. The spectrometer is schematically shown in Figure 2. By taking advantage of cylindrical symmetry for the scattering process, as is evident from Eq. (7), it is possible to sample the EMS cross sections over a wide range of energies and azimuthal angle differences simultaneously. This extensively improves coincidence count rates and statistical precision, compared with those achieved by the previous spectrometer¹⁴ employing an array of channel-electron-multipliers instead of the PSDs.

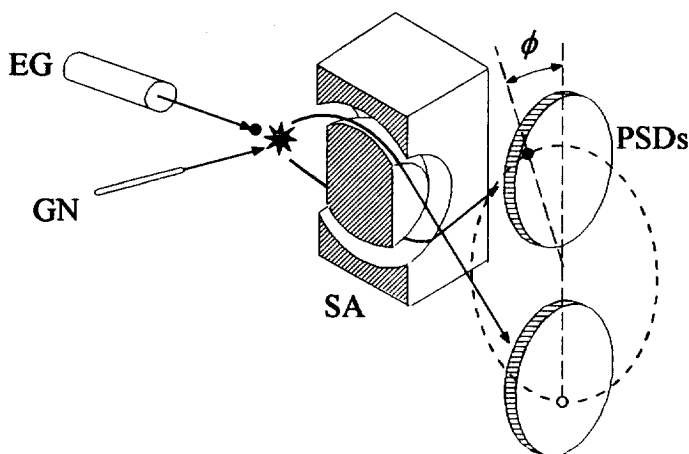


Figure 2. Schematic of a multichannel EMS spectrometer. EG; electron gun, GN; gas nozzle, SA; spherical analyzer, PSDs; position-sensitive detectors.

Throughout the course of the present measurements, an impact energy of 1205 eV was used. Outgoing electrons having energies from 590 eV to 600 eV were detected. Under these conditions, a binding-energy range from 5 eV to 25 eV and a ϕ range up to 40° were covered at the same time. The energy resolution was measured to be 1.4 eV (FWHM). The angular spreads of $\Delta\theta=\pm 0.75^\circ$ and $\Delta\phi=\pm 2.6^\circ$ estimated by trajectory simulations correspond to a momentum resolution of about 0.23 au for the impact energy.

Glyoxal was synthesized from trimer dihydrate (Aldrich) according to the procedure by Butz et al.¹⁵ Commercially available biacetyl (Kanto Chemicals) was degassed by repeating freeze-pump-thaw cycles before use. No detectable impurities were observed in the binding energy spectra shown below.

4. RESULTS AND DISCUSSION

4.1 Binding energy spectra

Figures 3(a) and (b) show binding energy spectra of glyoxal and biacetyl, both of which have been obtained by summing all the coincident signals over the entire ϕ range. Vertical bars indicate ionization energies of the molecules reported by HeI photoelectron spectroscopy study¹⁶. Although the resolution does not allow a complete separation of the bands, it is possible to extract contributions from the HOMO and the next HOMO (NHOMO) by deconvolution. Assuming a Gaussian shape for each transition, the deconvoluted curves are shown by broken lines and their sum by a solid line. A similar fitting procedure was employed for a series of binding energy spectra at each ϕ in order to produce experimental momentum profiles (XMPs).

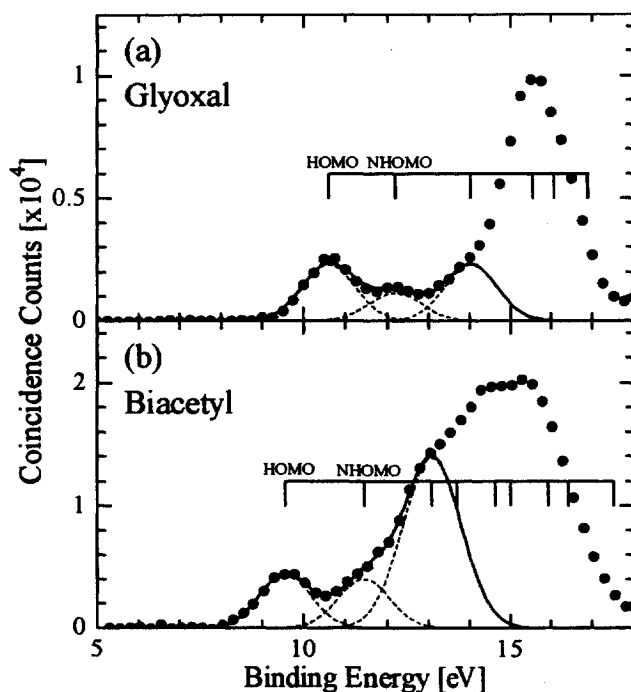


Figure 3. Binding energy spectra for (a) glyoxal and (b) biacetyl. Vertical bars indicate the ionization energies by HeI photoelectron spectroscopy. The dotted lines are the Gaussian deconvolution functions of the data and the solid line is their sum.

4.2 Through-space and through-bond interactions

Figures 4(a) and (b) show XMPs of the HOMO and NHOMO for glyoxal and biacetyl, respectively. It is evident that in both the molecules the XMPs of the two orbitals are quite distinct from each other, the most significant difference lying in intensity near the momentum origin $p=0$. For example, in glyoxal, while the XMP of the NHOMO shows almost zero intensity at $p=0$, that of the HOMO exhibits a maximum.

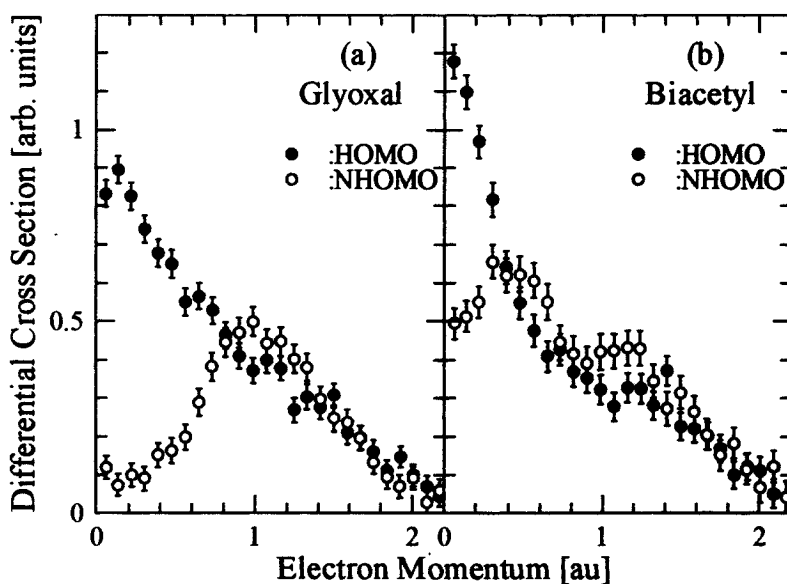


Figure 4. Comparison of experimental momentum profiles of the two outermost orbitals for (a) glyoxal and (b) biacetyl.

The intensity of momentum profile at the momentum origin $\rho(p=0)$ is explicitly expressed by

$$\rho(p=0) = \left| (2\pi)^{-3/2} \int \psi(r) dr \right|^2, \quad (8)$$

where $\psi(r)$ is the position-space wavefunction for the ionized orbital. This equation means that only totally symmetric orbitals can have non-zero intensity at the momentum origin. Hence the observed profiles are expected to tell us which of the two outermost orbitals is totally symmetric. For glyoxal the HOMO with a maximum at $p=0$ is thus clearly totally symmetric $n+$. Accordingly, the NHOMO with almost zero intensity can be attributed to the counterpart orbital $n-$. By contrast, for biacetyl both the XMPs show appreciable intensities at the momentum origin. However, by considering the finite angular spreads, one can reach a conclusion that the HOMO is $n+$ and NHOMO is $n-$; associated theoretical profiles for the latter, which do not have any intensity at $p=0$, reproduce well the characteristics of the experimental result when folded with the momentum resolution, as will be seen later. Thus, it can be unambiguously concluded that TB interaction dominates in both the molecules.

Other interesting trends are also apparent from the results in Figure 4. Comparing the XMPs of the two orbitals for each molecule, we find that the maximum of the profile for the NHOMO lies at higher momentum region than that for the HOMO. This is consistent with expected rapid curvature of

the $n-$ orbital at around its nodal surfaces produced by the anti-bonding nature, since momentum p is related to the gradient of the position-space wavefunction. On the other hand, it can be found that the XMPs of biacetyl exhibit, by contrast with those of glyoxal, prominent secondary maxima at about $p=1.2$ au. This observation is ascribed to substituent effects, as discussed later.

4.3 Comparison between experiment and theory

Figures 5-8 compare associated theoretical profiles generated by the HF and DFT calculations for the HOMO and NHOMO of glyoxal and biacetyl, respectively, together with the XMPs. In each figure the upper and lower right panels show position and momentum density contour maps of the orbital for an oriented target molecule calculated by DFT using the aug-cc-pVTZ basis set.

While simple valence bond descriptions predict that the two outermost orbitals of the molecules are symmetric and anti-symmetric linear combinations of oxygen lone-pairs, it is clear from the position density maps that these orbitals are not composed of oxygen p atomic orbitals only. First, for the HOMOs there are considerable densities on the carbon atoms and participation of the carbon-carbon σ bond into the orbitals is seen, as expected. Second, the two outermost orbitals are slightly delocalized over the hydrogen atoms for glyoxal and strongly diffused by the methyl groups of biacetyl. Delocalization of these orbitals is evident also in the momentum density maps that show "wrinkled" contours. It reflects the interference effects, often called bond oscillations^{17,18}, due to multiple atomic centers participating in the bonding or anti-bonding interaction.

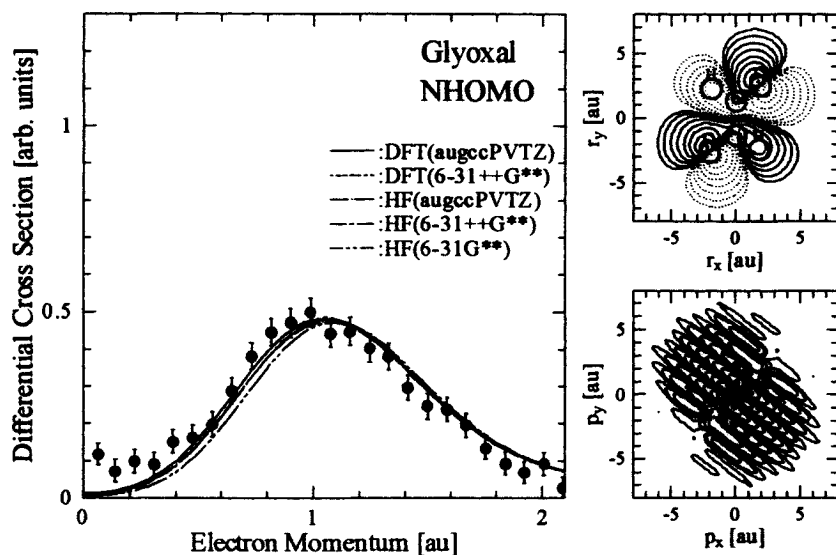


Figure 5. Comparison of experimental and theoretical momentum profiles for the HOMO of glyoxal. Right panels show position and momentum density contour maps.

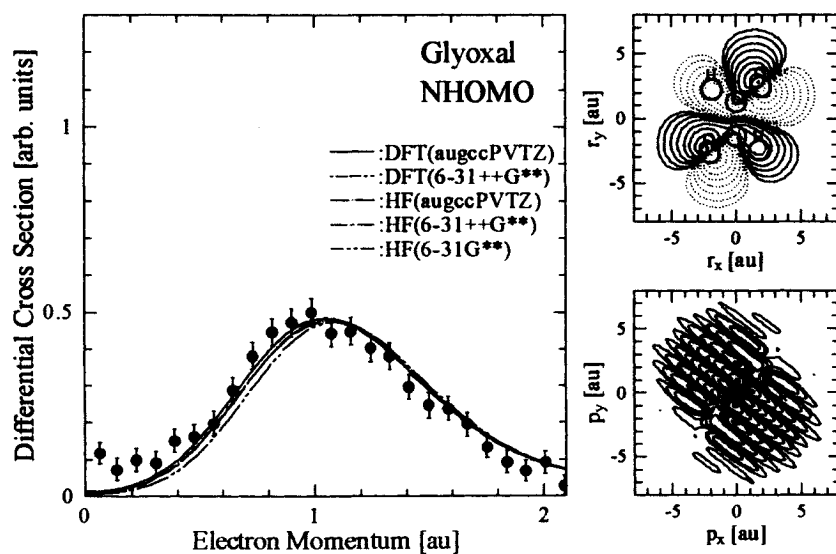


Figure 6. Comparison of experimental and theoretical momentum profiles for the NHOMO of glyoxal. Right panels show position and momentum density contour maps.

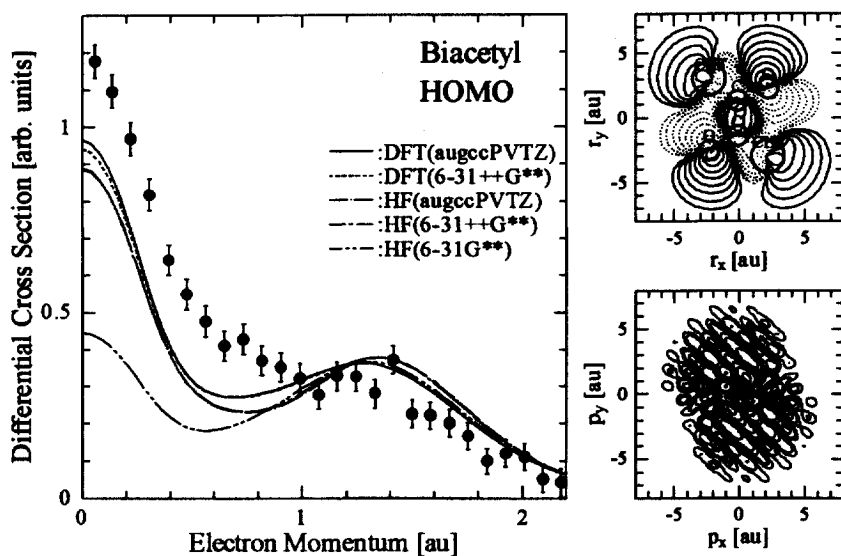


Figure 7. Comparison of experimental and theoretical momentum profiles for the HOMO of biacetyl. Right panels show position and momentum density contour maps.

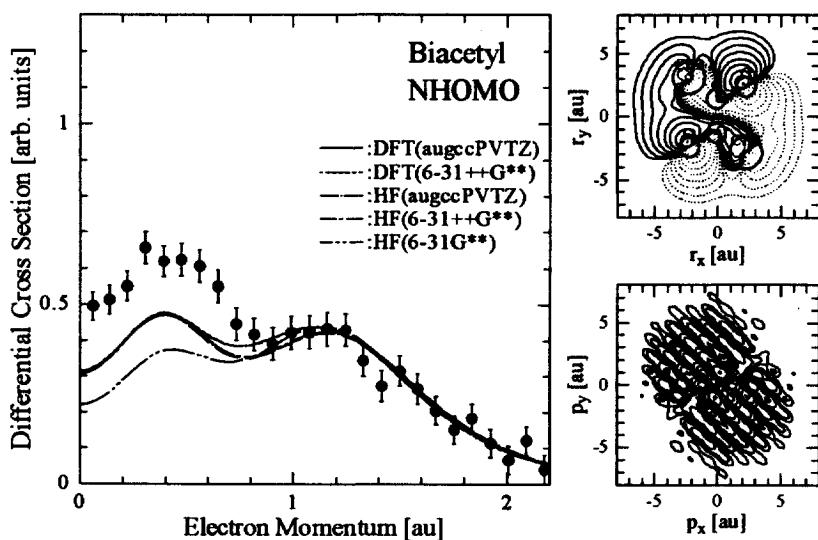


Figure 8. Comparison of experimental and theoretical momentum profiles for the NHOMO of biacetyl. Right panels show position and momentum density contour maps.

As can be seen from the position density maps, substitution of methyl groups for hydrogen atoms gives rise to additional nodal surfaces. An increase in the number of nodal surfaces in the position-space and the resultant bond oscillations in the momentum-space contribute to an increase in high momentum components of momentum profiles. Moreover, it has been suggested for methyl- and ethyl-substituted amines that formation of subsidiary maxima at higher p region in momentum profiles is due to introduction of additional nodal surfaces when compared with the simplest system ammonia.¹⁸⁻²⁰ Clearly, a similar effect has been found in dicarbonyls studied here.

It is noticed from Figures 5-8 that all the theoretical profiles reproduce the essential characteristics of the corresponding XMPs. However, different degrees of agreement between experiment and theory are observed, depending on the basis set and theoretical method employed.

HF calculations using the 6-31G** basis set (HF(6-31G**)) significantly underestimate the intensities in the low momentum region. Inclusion of the diffuse functions (HF(6-31++G**)) drastically reduces the marked discrepancies between experiment and theory, while total energy of the system remains almost unchanged. Larger basis set aug-cc-pVTZ (HF(augccPVTZ)) gives almost the same results as HF(6-31++G**), and this suggests that the HF limit has been closely approached at least for momentum profiles of glyoxal and biacetyl. Importance of the diffuse functions in describing low momentum components has already been pointed out in the earlier EMS study by Bawagan and Brion²². It should be remarked that EMS is very sensitive to low momentum parts (diffuse parts in the position-space) of valence electrons, which plays an important role in chemical reactions²³ and molecular recognition²⁴.

It can be found also that DFT calculations, (DFT(6-31++G**) and DFT(augccPVTZ)), substantially reduce the discrepancies between experiment and the HF calculations for the HOMO of glyoxal and noticeably do for other three orbitals. For the NHOMO of glyoxal satisfactory agreement is seen at this level of calculations. These observations indicate that electron correlation effects must be included for quantitatively describing outer valence electron densities of the molecules. It may be worthwhile to note that for the HOMO of glyoxal DFT(6-31++G**) provides slightly better description of momentum profile than DFT(augccPVTZ), while the former is always regarded as less accurate calculations in terms of total energy.

In spite of the considerable improvements by the DFT calculations, apparent discrepancies between experiment and theory still remain in the p region below about 0.5 au for the HOMO of glyoxal, and below 1 au and in the entire p region for the NHOMO and HOMO of biacetyl, respectively. In

every case the theoretical calculations underestimate the intensities of the low momentum components. Furthermore, it seems that degree of the disagreement becomes larger as the target electron is more loosely bound and more delocalized.

This is not the first observation of such unpredictably large electron densities in the low momentum region. Interestingly, similar observations have been restricted to molecules²⁵⁻²⁹, except for Xe4d electron that is much more tightly bound³⁰. Possible causes for the discrepancies between experiment and theory involve a failure of the PWIA description for EMS process at the impact energy of 1205 eV employed and lack of orbital relaxation and electron correlation effects in the final ion-state for the calculations. Experiments at lower and higher impact energies are now in progress.

In summary, the present work has demonstrated the remarkable ability of EMS for symmetry determination of molecular orbitals. The results not only elucidate importance of electron correlation effects in describing outer valence electron densities of glyoxal and biacetyl, but also suggest the need of higher levels of experiments and theoretical calculations to quantitatively interpret the momentum profiles.

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ELECTRON SCATTERING FROM NUCLEI

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Abstract The description of nuclei at distances on the order of a fermi or less poses a difficult challenge for theoretical physicists. At larger distances the traditional description of the nucleus as a collection of interacting nucleons has been quite successful and substantial progress has been made in recent years in describing few-nucleon systems using this approach. However, it has been known for several decades that the nucleons themselves are composite objects which are believed to be described by Quantum Chromodynamics (QCD). QCD is a complicated nonlinear strongly interacting field theory which can only be used for calculation in special circumstances. Due to the property of asymptotic freedom exhibited by QCD, perturbative calculations of QCD can be made at large momentum transfers and have achieved substantial success for a variety of processes. Understanding the transition from traditional pictures of nuclei to QCD is a substantial challenge. As an example of this problem, this paper describes recent calculations of elastic electron-deuteron scattering based on a relativistic extension of the traditional nuclear physics approach. The results of this work are compared to new data obtained at the Thomas Jefferson National Accelerator Laboratory and to the predictions of perturbative QCD.

1. Introduction

One of the outstanding challenges in nuclear physics is to understand the problem of the appropriate effective degrees of freedom at different distance scales.

The traditional view of the nucleus as a collection of nucleons interacting by means of potentials dates from 1932[1]. This approach has

had considerable success in describing various nuclear properties and reactions at low energies. Indeed this approach when combined with modern computational techniques has been used to obtain wave functions and spectra for light nuclei which are exact within this context[2]. The two-nucleon potentials used in this approach are obtained by fitting the scattering matrix to data using a general form for the potential and modern versions provide a fit to data with $\chi^2 \sim 1$ per degree of freedom [3, 4, 5]. These potentials contain terms proportional to $\boldsymbol{\tau} \cdot \boldsymbol{\tau}$, where $\boldsymbol{\tau}$ is a vector of the usual Pauli matrices operating in the isospin space of the nucleons. These terms allow for the exchange of charge between proton-neutron pairs. This is usually associated with the exchange of charged mesons between nucleons as part of the nucleon force. Reactions involving electromagnetic probes of the nucleus, such as electron scattering, can be sensitive to this flow of charge and models must include two-body meson-exchange currents to account for it. Effectively this extension of the traditional approach describes the nucleus as being composed of nucleons and mesons as the effective degrees of freedom.

We now understand that nucleons and mesons are themselves composite particles of quarks and gluons as described by the theory of quantum-chromodynamics (QCD). The difficulty with describing nuclei in terms of these underlying degrees of freedom is the result of the inherent complexity of QCD. QCD is a strong-coupling nonabelian gauge theory with nonlinear interaction terms. At present there are only two techniques for exploring the consequences of this theory. The most comprehensive of these is Lattice QCD where the field theory is discretized on a four-dimensional lattice and then the corresponding Feynman path integrals associated with observables are integrated using Monte Carlo techniques [6]. This is an extremely computationally intensive problem and current efforts in this direction are limited by the capabilities of computers. At present, these calculations are limited to describing the properties of single mesons and nucleons. With the rapid increase in the capabilities of computers for a given cost, it is likely that some limited attempts to describe light nuclei may be possible in the future.

The other technique for exploring QCD is perturbative QCD (PQCD) [7]. This approach takes advantage of the unusual properties of QCD. The interactions in field theories lead to the dressing of the “bare” particles of the lagrangian. For example in quantum electrodynamics (QED) a bare charge is dressed by polarizing the vacuum through the creation of virtual electrons and positrons from the vacuum. This dressing results of a screening of the charge of the electron. At low energies (long distances) a probe of the electron charge will see the usual physical charge e . As the energy is increased and the distance probed decreases, the probe sees

less of the screening charge and the charge of the electron increases. For QED this changing of the magnitude of the charge with distance is very slow and is of no practical importance for most physical processes. The nonabelian character of QCD results in an opposite trend. The color charge decreases with decreasing distance as the result of anti-screening. This property is called asymptotic freedom. As a result, if processes can be found where all of the momenta are sufficiently large, then QCD can be calculated using perturbation theory just as for QED. PQCD has been used to study a large number of high energy processes in particle physics with considerable success. The main drawback to PQCD is that all physical process contain some contributions where some quarks and gluons are not of sufficiently high energy for this approximation to be applied. These “soft” contributions tend to determine the overall size of cross sections while the perturbative contributions tend to give the functional form of the change with momentum. Since the soft contributions are inherently nonperturbative, PQCD generally leads to information about trends in processes as a function of four-momentum transfers and models of the soft contributions are necessary to describe the size of processes.

We are then left with the following problem: While we know that the underlying degrees of freedom are quarks and gluons, we also know that at low energies we have had considerable success with a traditional nuclear physics of mesons and nucleons as effective degrees of freedom, whereas at high energies PQCD with explicit quark and gluon degrees of freedom is needed to describe data. It now becomes necessary to establish how we make the transition from the low energy model of mesons and nucleons to the high energy theory of quarks and gluons. That is, where does it become necessary to deal explicitly with the underlying degrees of freedom? Answering this question was one of the primary reasons for the building of the Continuous Electron Beam Facility (CEBAF) at the Thomas Jefferson National Accelerator Facility (Jefferson Lab.) As an example of how this search is progressing, this paper will concentrate on one process: elastic electron-deuteron scattering[8, 9, 10].

2. Elastic Electron-Deuteron Scattering

The Feynman diagram in Fig. 1 represents electron scattering from a nucleus in the one-photon-exchange approximation where k and k' are the initial and final electron four-momenta, $q = k - k'$ is the four-momentum of the virtual photon, and P and P' are the initial and final four-momenta of the nucleus. For electron scattering, the four-momentum of the virtual photon must be spacelike and it is traditional

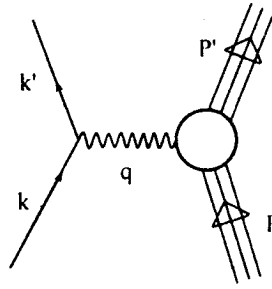


Figure 1. Feynman diagram representing electron-nucleus scattering.

to define a positive quantity

$$Q^2 = -q^2 = \mathbf{q}^2 - \nu^2 \quad (1)$$

where $\mathbf{q}$ is the photon three-momentum and ν is the photon energy.

For elastic electron-deuteron scattering Lorentz covariance, parity conservation and gauge invariance require that the current matrix element can depend on only three scalar form factor dependent upon Q^2 . It is conventional to choose these three form factors to be the monopole charge form factor $G_C(Q^2)$, the dipole magnetic form factor $G_M(Q^2)$ and the quadrupole charge form factor $G_Q(Q^2)$ which are constrained such that

$$G_C(0) = 1 \quad (2)$$

$$G_M(0) = \frac{M_d}{m} \mu_d \quad (3)$$

$$G_Q(0) = M_d^2 Q_d \quad (4)$$

where m is the nucleon mass, M_d is the deuteron mass, $\mu_d = 0.857406(1)$ is the deuteron magnetic moment in nuclear magnetons and the deuteron quadrupole moment is $Q_d = 0.2859(3) \text{ fm}^2$.

The cross section for elastic electron-deuteron scattering in the one-photon-exchange approximation is the Rosenbluth formula

$$\frac{d\sigma}{d\Omega} = \sigma_{\text{Mott}} f \left[A(Q^2) + B(Q^2) \tan^2 \frac{\theta}{2} \right] \quad (5)$$

where θ is the electron scattering angle, the Mott cross section σ_{Mott} is the scattering cross section of an electron from an infinitely heavy unit charge,

$$f = \frac{1}{1 + \frac{2E}{M_d} \sin^2(\theta/2)} \quad (6)$$

is a recoil factor, and $A(Q^2)$ and $B(Q^2)$ are structure functions that contain all of the information about the deuteron electromagnetic currents. These structure functions can be represented in terms of the three form factors as

$$A(Q^2) \equiv G_C^2(Q^2) + \frac{2}{3}\eta G_M^2(Q^2) + \frac{8}{9}\eta^2 G_Q^2(Q^2) \quad (7)$$

and

$$B(Q^2) \equiv \frac{4}{3}\eta(1+\eta)G_M^2(Q^2) \quad (8)$$

where

$$\eta = \frac{Q^2}{4M_d^2}. \quad (9)$$

Although $B(Q^2)$ can be used to determine the magnetic factor, the charge monopole and quadrupole form factors can not be separated by using this in $A(Q^2)$. The total separation of the form factors requires that the cross section be measured for a polarized deuteron in either the initial or final state. Since the deuteron has a total angular momentum of 1, the deuteron is subject to both vector and tensor polarizations. The response which is typically chosen to effect the total separation of the form factors is tensor response $t_{20}(Q^2)$. This is defined as:

$$\begin{aligned} t_{20}(Q^2) = & - \left\{ \frac{8}{3}\eta G_C(Q^2)G_Q(Q^2) + \frac{8}{9}\eta^2 G_Q^2(Q^2) \right. \\ & \left. + \frac{1}{3}\eta \left[1 + 2(1+\eta)\tan^2 \frac{\theta}{2} \right] G_M^2(Q^2) \right\} \\ & \times \left[\sqrt{2} \left(A(Q^2) + B(Q^2)\tan^2 \frac{\theta}{2} \right) \right]^{-1} \end{aligned} \quad (10)$$

3. Relativistic Meson-Nucleon Model of the Deuteron

Understanding this transition in effective degrees of freedom requires that the consequences of both pictures be examined in the transition region. Since this region is expected to be typified by Q^2 values of a few GeV^2 , it is necessary that the conventional picture of nuclear physics be extended to accommodate these large four-momentum transfers. In particular, since the nucleon mass is on the order of 1 GeV , it is necessary to construct nuclear models that are consistent with the special theory of relativity.

One approach to construction of relativistic models of the deuteron is to start with some effective Lorentz invariant lagrangian constructed

from nucleon and meson fields. The sum of all possible Feynman diagrams contribution to nucleon-nucleon scattering and the formation of the deuteron bound state can be formally expressed in terms of the Bethe-Salpeter equation[11]. This equation is constructed by separating the Feynman diagrams into two classes: all diagrams that cannot be separated into two pieces by simply cutting two nucleon lines are said to be two-particle irreducible while the remainder are said to be two-particle reducible. The sum of all possible diagrams can be produced by summing the infinite set of irreducible diagrams into the kernel of a four-dimensional integral equation (the Bethe-Salpeter equation) which then generates the sum of all reducible and irreducible diagrams.

In practice, however, it is impossible to evaluate all of the infinite number of irreducible diagrams so the kernel is approximated by only a few low-order diagrams. Most applications of this approach to two-nucleon systems approximate the kernel with single meson exchanges for some collection of mesons.

An additional problem with this approach is that it is an integral equation in the four-dimensional Minkowski space. This causes considerable complications in the solution of the integral equation due to the analytic structure of the scattering matrix. This problem can be addressed by analytic continuation to complex time although this imposes the additional complication of analytic continuation of the solution to the Bethe-Salpeter equation to real time.

A variant of the Bethe-Salpeter approach is the quasipotential approach. Quasipotential equations can be obtained by constraining the relative energy or time in the Bethe-Salpeter equation in such a manner that the equation is reduced to a three-dimensional integral equation that is more amenable to solution by traditional techniques common in nuclear physics. There are a large number of possible ways to accomplish this reduction resulting in a corresponding number of different quasipotential equations. Although this may appear to be a severe approximation to the Bethe-Salpeter equation it has been shown that quasipotential reductions may actually improve the convergence of the scattering matrix to the exact result with respect to approximations to the kernel[12].

In order to calculate the elastic scattering amplitude, it is necessary to know the current operator. Since the exchanged mesons can be charged, there will be currents associated with this flow of charge in addition to the currents of the individual constituent nucleons. These exchange or interaction currents can be determined in the Bethe-Salpeter and quasipotential approaches by identifying the two-particle irreducible diagrams associated with two nucleons absorbing a photon. Care must be taken

to ensure that the approximations of kernels and interaction currents are consistent in order to guarantee current conservation.

An additional complication with these models is that the nucleons and mesons are themselves composite objects of approximately 1 fm in size. It is therefore necessary to include this phenomenologically by including form factors at all interaction vertices. This can also interfere with current conservation if not imposed with care.

Figure 2 shows several relativistic calculations of $A(Q^2)$, $B(Q^2)$ and $t_{20}(Q^2)$ in comparison to data. The curves labelled “Van Orden and Gross” are produced in the context of a quasipotential equation called the Spectator or Gross equation[13, 14, 16, 17, 18]. This approach is manifestly covariant and current conserving. A one-boson-exchange interaction with six mesons is fit to NN scattering data up to 300 MeV. Electromagnetic form factors for the nucleon are taken as parameterizations of nucleon electromagnetic form factor data[19] and according to a prescription that guarantees current conservation[20, 21]. The curves labelled “Hummel and Tjon” are the result of another quasipotential approach[22, 23] and the curves labelled “Forrest and Schiavilla” are for a semirelativistic potential model[24].

Clearly, “traditional” nuclear physics can account for the available data remarkably well up to $Q^2 = 6 \text{ GeV}^2$. Some caution is required, however, in making this statement since the results shown in the figure reflect choices concerning the ingredients of the calculation some of which are not constrained by external data. In particular, the single-nucleon electromagnetic current operator used in this calculation has a piece that only contributes off mass shell. This contribution has a form factor that is constrained only at $Q^2 = 0$. It can not be fixed by other data for other values of Q^2 . The curve labelled “Van Orden and Gross” uses the arbitrary choice that this form factor have a form similar to the on-shell form factors. This freedom to choose the form factor can be exploited to improve the description of the data. This has been done in the curve labelled “Van Orden and Gross, Offshell Fit.” Unfortunately, this freedom severely limits the predictive power of these models.

4. Perturbative Quantum Chromodynamics

Perturbative QCD can be used to calculate the rate of fall of the the deuteron form factors for large values of Q^2 . This follows from examination of diagrams such as that in Fig. 3 which shows six quarks interacting by exchanging gluons. If the photon transfers a large amount of momentum to the deuteron, this momentum must be distributed evenly among the quarks in order that the quarks can then be reconstituted

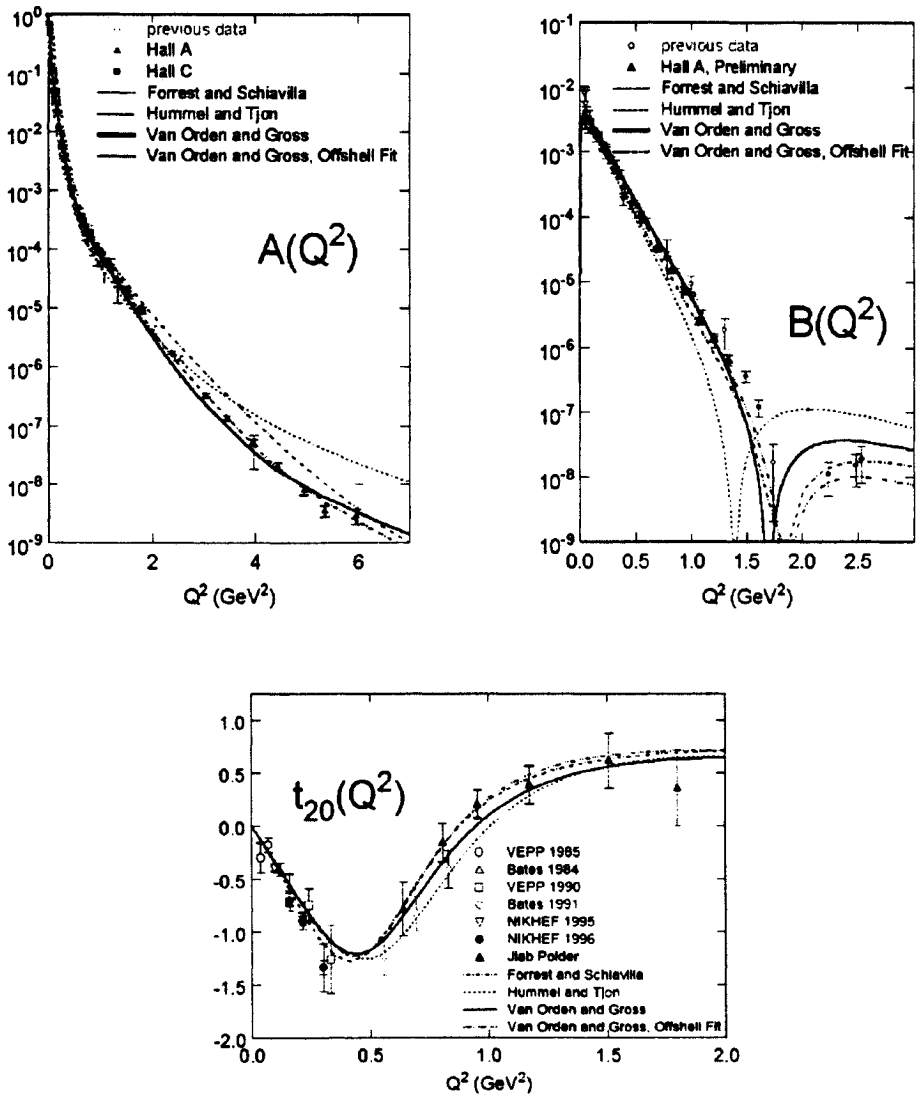


Figure 2. The structure functions $A(Q^2)$, $B(Q^2)$ and $t_{20}(Q^2)$ for several relativistic models.

as a deuteron in the final state. This requires that all of the quark and gluon propagators from the absorption of the photon and the final gluon exchange must also carry large four-momenta. Examination of the forms of the quark and gluon propagators then lead to a set of quark counting

rules that determine the rate of fall of the form factors at large Q^2 . For

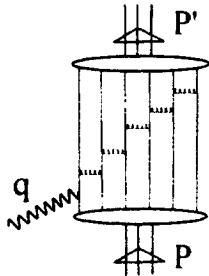


Figure 3. A typical diagram used in obtaining the PQCD quark counting rules for elastic electron deuteron scattering.

$A(Q^2)$ these rules predict that this structure function must fall as

$$A(Q^2) \sim \frac{c_0}{Q^{20}} \tag{11}$$

Figure 4 shows the data for $A(Q^2)$ for $3.0 \text{ GeV}^2 < Q^2 < 6.0 \text{ GeV}^2$ compared to Q^{2n} for three values of n with the curves normalized such

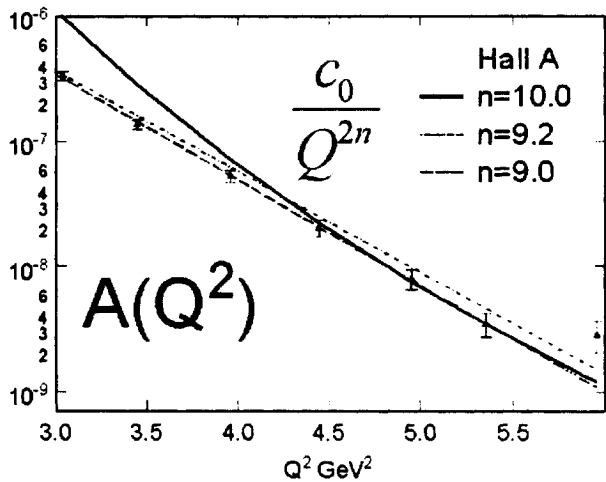


Figure 4. The structure function $A(Q^2)$ for several relativistic models.

they pass through the center of the penultimate data point. This semilog plot shows that all of the data with the exception of the last point appear

to be along a straight line consistent with power law fall of the structure function. However, while the PQCD prediction of $n = 10$ is consistent with the higher Q^2 points, the best fit to all of the data (with the exception of the last point) is for $n = 9.0$. The evidence for the onset of PQCD in this data would appear to be ambiguous at best.

5. Conclusions

The current status of the search for the quark degrees of freedom in elastic electron-deuteron scattering is unclear. Traditional nuclear physics model provide a reasonable description of elastic electron-deuteron scattering up to $Q^2 = 6 \text{ GeV}^2$ but are subject to ambiguities that at present can not be eliminated phenomenologically. This limits their predictive power.

From the QCD side, nonperturbative calculations using lattice QCD for this process are not currently practical due to present capabilities of computers. While PQCD can predict the rate of fall of the form factors, it can not predict the normalization. The current data for $A(Q^2)$ are not unambiguously consistent with the predicted rate of fall.

The current situation suggests that it may be difficult to find evidence of an abrupt transition from the regime of traditional nuclear physics to the regime of QCD.

Acknowledgments

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ELECTRON SCATTERING AND HYDRONAMIC EFFECTS IN IONIZED GASES

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Abstract Intensive effort to understand the complex phenomenology of propagation and dispersion of shock wave in weakly ionized medium has been initiated recently, in view of the prospect for wide range of applications that could follow. Underlying mechanisms for the observed effects could be attributed to various electron collision processes. Although most applications involve molecular gases, the dispersion effects with a comparable intensity are observed in noble gases. Interaction of shock wave with ionized gas generates rapidly moving multiple electric layers, which form regions of increased electron density. Transient electric field in the electric layers enables new channels of communication between upstream and downstream regions. Time scale of collective interactions is comparable to the electron collision time and lifetime of excited states. In this environment electron scattering with excited atoms affects the macroscopic phenomenology as much as the transient field affects the collision itself. This results in an intricate ionization and recombination dynamics where the electron scattering with excited states is among the most important processes.

1. Introduction

Hydrodynamic effects in ionized gas have generally been a neglected object of investigation until a complex phenomenology of "anomalous" dispersion and propagation of acoustic shock waves was revealed in a series of laboratory experiments (Klimov *et al*, 1982; Mishin, Serov and Yavor, 1991; Bletzinger and Ganguly, 1999; Popović and Vušković, 1999a;

Bletzinger, Ganguly and Garscadden, 2000). These results generated a renewed interest in this subject. The anomaly was found in the fact that the effects were observed in weakly ionized gases (WIG), at degree of ionization as low as 10^{-7} , but the neutral particles were involved in the modification of shock waves. With the experiments still inconclusive on the matter, thermal (reducible to electron-neutral elastic and superelastic scattering) and non-thermal (reducible to inelastic scattering) arguments were posted. While the thermal argument leads to the interpretation based on heat transfer specifics, the non-thermal argument leads to less trivial assumptions. There are still no systematic spectroscopic measurements of local excited-state populations in leader, precursor and relaxation regions of weak shocks in WIG. However, there is some circumstantial evidence for the link between the excessive excited-state population and the observed anomaly (Popović and Vušković, 1999a). Also, there are partially explained experimental results of (McIntyre *et al.*, 1991) on strong, ionizing shock waves in neon. These results show the population of excited states in precursor region that could not be accounted for using the standard ionization-recombination model.

Weakly ionized gas is generated in electric discharges at elevated pressure, typically from several hundred Pa to atmospheric conditions. While their radiative properties have been utilized in numerous applications related to new lasers and non-coherent light sources, their electromagnetic, aerodynamic, and reactive properties are only now starting to draw attention. These discharges are always partially ionized, with electron energy distribution quite away from the local thermodynamic equilibrium. Excited-particle densities can exceed the charged-particle density sometimes even by an order of magnitude.

Our primary motivation in this study is to underline the importance of electron impact ionization on the hydrodynamic properties of weakly ionized gas. In this case the ionization-recombination process departs from the usual presentation of ionization rate based on the rate-controlling excitation to the first excited state (Horn, Wong and Bershader, 1967). Rather, one has to adopt a non-equilibrium presentation of ionization, where the ionization rate contains at least three terms: direct ionization from the ground state, ionization from an excited state, and ionization in the collision of two excited states (Ferreira, Louriero and Ricard, 1985).

This paper is organized as follows. After brief description of the shock dispersion phenomenology in Section 2, we proceed with concise outline of the non-equilibrium ionization-recombination model of shock interaction with weakly ionized gas in Section 3. In Section 4 we discuss present situation on the availability of electron-impact ionization data, illustrating the problem on one of few available examples. We conclude

this paper with the statement that much more data on electron scattering are needed in order to obtain an adequate interpretation of the observed effects that govern hydrodynamics of weakly ionized gas.

2. Shock Dispersion Phenomenology

Dispersion of shock wave is probably the most obvious effect in its interaction with glow discharge. An example is shown in Fig. 1, presented in the form of a photoacoustic signal taken from a microwave cavity discharge in nitrogen. Shock wave in the absence of discharge has the usual abrupt form, but the shock wave through discharge has an elongated structure extended over a finite, much longer distance.

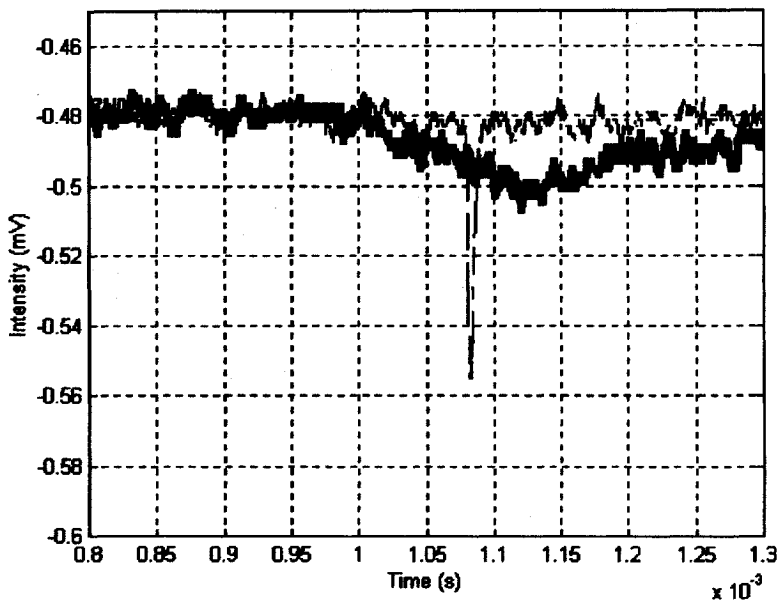


Figure 1. Laser deflection signal due to shock wave ($M=1.4$) propagating through weakly ionized argon (thick solid line) and through neutral argon gas (dashed line) illustrating the dispersion of shock wave in interaction with WIG.

Floating probe signals and current waveforms from two observation points (Bletzinger and Ganguly, 1999) were used to evaluate the profile of electron density across the shock structure. It is obvious from both waveforms that the influence of shock wave on space charge is felt on a much larger distance than the width of the dispersed shock structure. In Fig. 2 is given the result of reconstructed electron density profile along

the axis of the discharge during shock propagation by combining current waveform and drift velocity profile. The structure observed in the electron density profile indicates the presence of multiple electric layers in the discharge. This indicates the complex interaction of charged particle fluxes with the space charge and background gas. Shock propagation

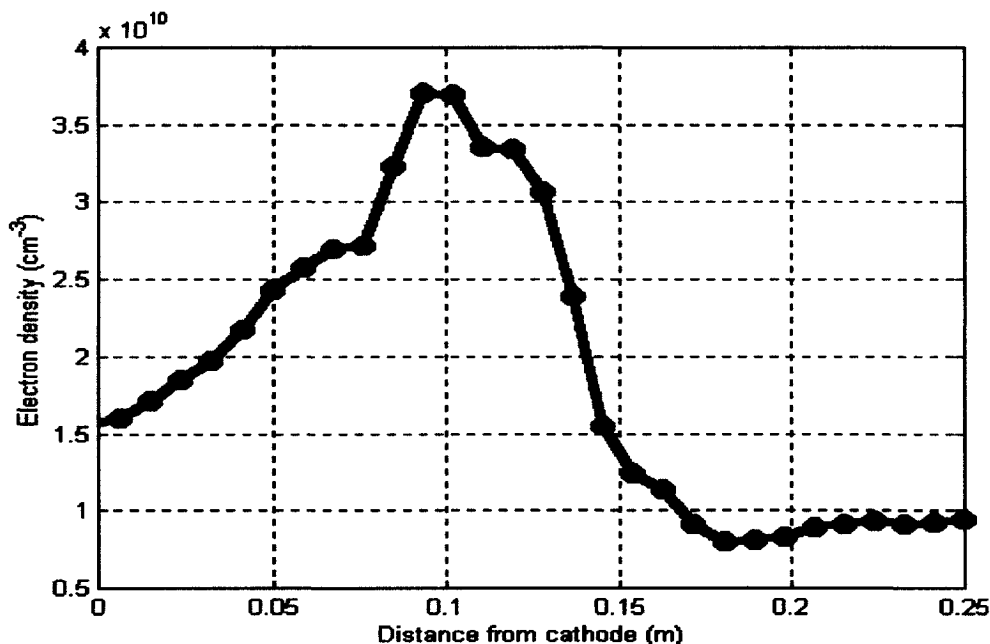


Figure 2. Electron density distribution along d.c. glow discharge with shock wave "frozen" at 0.1 m from cathode. Primary double electric layer is located in the region of strong negative gradient. Secondary layers are indicated by the minor structural features of the electron density distribution.

velocity along the axis of the glow discharge in argon had to be much higher in the cathode region than in the positive column in order to account for the registered time of flight between spark location to the first and second monitoring positions. After including the time of flight of the shock through the neutral gas in front of the discharge we obtained much larger velocity in the cathode region than in the positive column (Popović and Vušković, 1999a).

In order to achieve shock dispersion effects (Exton *et al.*, 2001) in wind tunnel experiments, it is important to generate ionized gas in the near flow field ahead of a supersonic model. The "precursor" plasma has to modify the oblique shock and exhibit dispersion and detachment effects. The successful projection of such a precursor plasma would also

have some similarity to an aerodynamic "spike" that was shown to improve effective aerodynamic shape of the model, but without the cooling requirement. In present experiments seed electrons for the projection are provided by a radioactive source or by a laser excited optical breakdown. In addition to ionization processes in the double electric layer at oblique shock, there is interest for electron-atom (molecule) attachment processes near the aperture of microwave source. This is because the electron attachment processes reduce the number density of free electrons that leads to decrease of reflections from secondary plasma formations near the aperture of microwave source. Therefore, electron attachment processes directly affect the efficiency of microwave transmission into the region in front of the oblique shock.

Various types of discharges have been used in the experimental studies and applications of shock wave dispersion, although the full understanding of the phenomenon has not been established yet. The understanding usually requires complete information on atomic collisions involved in ionization/recombination process across the shock structure. This knowledge requires complete set of data on electron impact ionization of ground and excited states as well as other processes that contribute to the generation of free electrons and fluctuation of electron number density in the shock-WIG interaction region.

3. Ionization-Recombination Model in Shock-WIG Interaction

Model for shock interaction with weakly ionized gas is composed of the gas-dynamic model based on the governing equations for shock wave propagation, charge-separation model incorporating gas-electrodynamics equations describing the double electric layer associated with the shock wave, and the ionization-recombination model. Non-equilibrium ionization and recombination balance is of importance for present discussion. Thus, it will be outlined briefly in subsequent paragraphs, while the integrated model is described elsewhere (Popović and Vušković, 1999b).

Present ionization-recombination model starts from the expressions for the net rates of ion and electron production. For the sake of simplicity, this presentation applies to ionized gas involving the monatomic neutral species with the absence of impurities. In the one-dimensional case, the one-dimensional atomic model has the following form

$$\dot{N}_i = \dot{N}_{i(ion)} - k_{Re} N_i N_e^2 - D \frac{d^2 N_i}{dx^2} \quad (1)$$

$$\dot{N}_e = \dot{N}_{e(ion)} - \dot{N}_{e(rec)} \quad (2)$$

where $\dot{N}_i$ and $\dot{N}_e$ are the net ion and electron production rates; k_{Re} is the recombination rate coefficient; D is the effective diffusion coefficient; N_i and N_e are the ion and electron densities; $\dot{N}_{e(ion)}$ is electron production rate due to ionization; and $\dot{N}_{e(rec)}$ is the rate of electron loss due to recombination.

Net ion production rate contains the ionization rate, recombination rate and the rate of ion loss due to diffusion, the term that effectively describes ion inertia, which is one of the main causes of charge separation along the shock structure.

The electron production rate due to ionization is expressed in the following form

$$\dot{N}_{e(ion)} = k_{di}N_aN_e + \sum_i k_{ie}N_iN_e + \sum_{i,j} k_{pij}n_in_j \quad (3)$$

where first term presents the direct ionization from the ground state, second term is the ionization from an excited state and the third is total ionization in pair collisions of excited states. Here k_{di} , k_{ie} and k_{pij} are the ionization rate coefficients for ionization from the ground state, ionization from the excited states, and ionization through energy pooling processes. Direct ionization from ground state is important at very low pressure, usually below the pressure range of practical interest here. Ionization from an excited state is the dominating process at high pressure. There is a wide intermediary range of pressures where ionization by excited pair collision is important. In the case of gas mixtures or in the presence of impurities the last mechanism is responsible for the Penning ionization. In order to treat quantitatively the ionization processes involving excited states a separate model was introduced. Transient population of a number of aggregated representative excited states was obtained by solving simultaneously a set of equations of the temporary balance of excited states by combining gains by excitation, deexcitation from upper levels, and recombination with the losses by ionization or deexcitation to lower levels.

Steady-state recombination term is defined by

$$\left(\frac{dN_e}{dt}\right)_{rec} = \alpha N_e N_i. \quad (4)$$

The formula for recombination rate coefficient that we adopt here was derived by (Stevefelt, Boulmer and Delpech, 1975).

The accuracy of the ionization-recombination model depends strongly on precision and availability of the electron impact ionization data, and the data on the ionization in collision between two excited atoms. In addition, the complete electron impact excitation data are required in

order to describe accurately the temporary balance of excited states during shock-WIG interaction. The effect of energy pooling processes is the least known. In the present model two aspects of this ionization process are important. Besides the obvious need for accurate cross-section data, the dynamics of these collisions is also important, since they produce highly energetic, non-thermal electrons. In addition, production of molecular ions through associative attachment that is important at near-atmospheric pressures and low gas temperatures, increase the complexity of the ionization-recombination process. In most cases all these data are available from calculations using a very crude approximations. Therefore, the model is far from being complete, even in the simplest case of weakly ionized noble gases.

4. Electron Impact Ionization of Excited Atoms

Experimental work on ionization of excited atoms was reviewed by (Trajmar and Nickel, 1992). So far there are no measurements of differential cross sections for ionization of an excited atom by electron impact. All experimental data refer to integral ionization cross section. Further, most measurements have involved metastable targets. We will not list here all available data on ionization from excited atoms, even though they are far from abundant, since the information given in (Trajmar and Nickel, 1992) cannot be modified substantially due to the lack of new experiments. On the other hand, the calculations of cross sections have still not achieved the desired level of accuracy. The Convergent Close-Coupling (CCC) calculations (Bray, 1994) of ionization cross section describe correctly the threshold behavior. However, CCC method tends to underestimate absolute values of ionization cross section at higher energies. In the modelling of gas discharge conditions, the most frequently used data are based on simplified empirical or semi-empirical formulae, such as the formula derived by (Vriens, 1969 and 1973). This formula tends to overestimate cross sections close to the threshold but agrees better with experimental data at higher energies. Work on the refinement of experimental and theoretical data still remains to be done.

In the previous section we stated that the electron impact ionization from excited states are the most important ionization processes during the shock-WIG interaction. We note that the structure of excited states of noble gases shows many similarities with the electronic structure of alkali atoms. Hence the interest for sodium become obvious. However, in order to make the data on the electron scattering from alkali atoms applicable to the scattering from the excited noble gas atoms, more theoretical justification has to be done.

Our measurements of electron impact ionization of laser-excited 3P state of sodium (Tan *et al.* (1996) and the experiment on barium (Trajmar, Nickel and Antoni, 1986), still remain the only ionization measurements on a short-lived system. We have measured the absolute cross sections in the incident electron energy range from threshold to 30 eV both for excited and ground state. The results for the ground-state cross-section are consistent with other experimental data (Johnson and Burrow, 1995). However, the results of CCC calculation (Bray, 1994) tend to agree with experiment near threshold, but remain below experimental data at higher energies. On the other hand, the calculations employing generalized oscillator strength (GOC) based on the Born approximation (McGuire, 1977) tend to underestimate cross sections near the threshold, but agree better with experimental data at higher energies. The same trend is amplified in the case of the excited state that is shown on Fig. 3. Position of the maximum is close to the one pre-

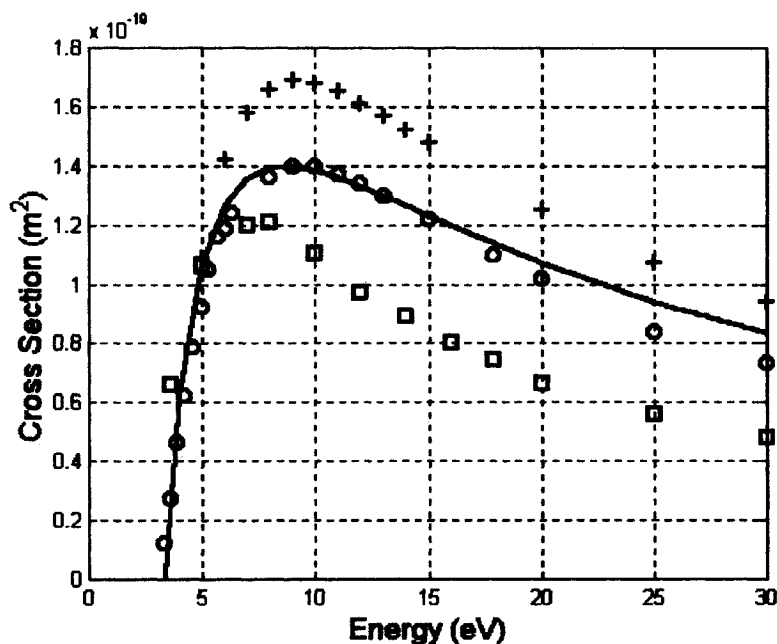


Figure 3. Electron Impact Ionization of Excited (3P) Sodium: circle, Tan *et al.* (1996); full line, Vriens (1973); cross, McGuire (1977); square, Bray (1994).

dicted by GOS calculation, while the CCC underestimates the energy at the maximum by 3 eV. In the same time, the semi-empirical equation

(Vriens, 1969 and 1973) agrees surprisingly well with the experiment, much better than the two, more elaborate calculations.

There are reported ionization cross section of metastable helium, neon and argon (Dixon, Harrison and Smith, 1976). The results on He 2^1S are also reasonable well reproduced by Vriens formulae. The calculation overestimates the cross section around threshold and maximum, and agrees rather well with the experimental results at higher energies.

5. Conclusion

Hydrodynamic effects in weakly ionized gas are strongly affected by electron scattering processes. Generally, weakly ionized gas is far from thermodynamic equilibrium and the shock interaction region is adding to the complexity of this medium by forming fast moving multiple electric layers, by inducing the separation of space charges and by generating radiation trapping effects. Therefore, collective expressions of transport phenomena based on equilibrium assumptions are not valid, and detailed knowledge of electron scattering processes is necessary to generate a plausible description of shock-plasma interaction phenomenology.

Electron impact ionization of an excited atom is the dominant ionization process at most conditions involving interaction between shock wave and weakly ionized gas.

Interpretation of hydrodynamic effects in weakly ionized gas is further complicated by underdeveloped diagnostics of the transient shock-plasma interaction region, which also suffers from insufficiency of electron collision data, especially for the description of electron dynamics that is important, however, mostly unknown. With a complete set of the collision data for at least one atom, the nature of dispersion phenomenon could be resolved in more detail.

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TESTING THE LIMITS OF THE SINGLE PARTICLE MODEL IN $^{16}\text{O}(\text{E},\text{E}'\text{P})$

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Abstract This paper describes measurements of electron scattering proton knockout from Oxygen, $^{16}\text{O}(\text{e},\text{e}'\text{p})$, performed at Jefferson Lab. The first experiment measured the energy and momentum distributions of protons in oxygen (within a sophisticated model) and determined that a relativistic description of the proton was required. A follow-up experiment at more extreme kinematics is testing the limits of validity of single proton knockout models.

Introduction

Coincidence electron scattering from nuclei, detecting the ejected proton ($\text{e},\text{e}'\text{p}$), has been used for many purposes: to measure the proton's energy and momentum distribution in the nucleus (within a model); to test models of nucleon (proton or neutron) knockout; to understand the effects of nucleon-nucleon correlations, meson exchange currents, and relativity; and to look for more exotic QCD effects such as color transparency (very small, non-interacting configurations of the nucleon).

At nuclear physics energies, $E_{\text{beam}} > 200$ MeV, electron scattering from light nuclei proceeds via exchange of a single virtual photon (first Born approximation). This single virtual photon exchange allows us to separate the problem into an electron scattering part and a nuclear physics part. The electron scattering part is easy.

The nuclear physics part of the problem is much more difficult. It turns out that the simple mean-field shell model works surprisingly well. In atomic physics, mean field theory works because we have a central attractor (the nucleus), a weak well-understood interaction (QED), and point particles (electrons). In nuclear physics, we have none of these.

Despite this, a tremendous amount of nuclear structure is described by the shell model, including magnetic moments, binding energies, etc.

By varying the beam energy, scattered energy and scattering angle of the electron, we can vary the energy transfer $\omega = E_{\text{beam}} - E_{\text{scat}}$ and momentum transfer $\vec{q} = \vec{k} - \vec{k}'$ independently (where $\vec{k}$ and $\vec{k}'$ are the momenta of the incident and scattered electron, respectively). q sets the spatial scale and ω selects the nuclear excitation.

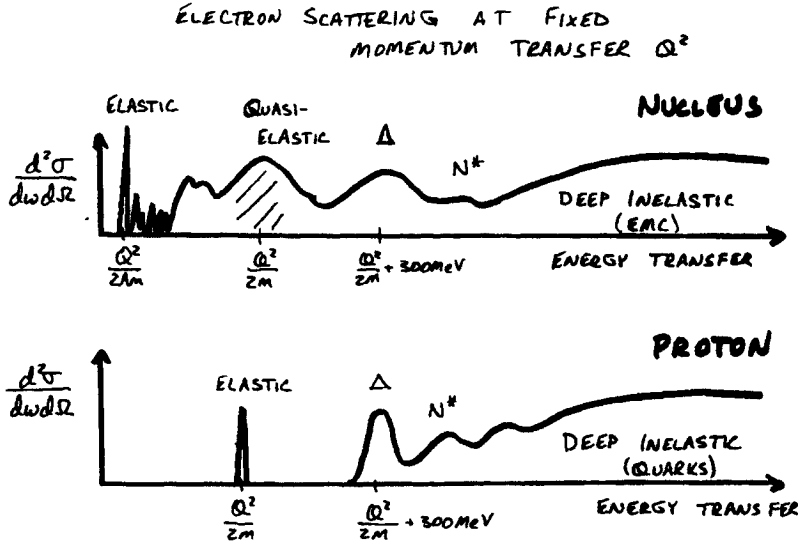


Figure 1. Generic (e,e') electron scattering spectrum. Cross section versus energy transfer at fixed momentum transfer (note that $Q^2 = \vec{q}^2 - \omega^2$).

If we study scattering events where $\omega \approx q^2/2m_p$ (where m_p is the proton mass), then we are choosing events where one proton can absorb the virtual photon without having to share the energy or momentum with other nucleons. This is the condition for 'quasielastic' scattering, elastic scattering from a bound nucleon. A plot of the electron scattering (e,e') cross section versus energy transfer at fixed momentum transfer shows a peak at $\omega \approx q^2/2m_p$ with a width proportional to the nucleon momentum distribution (see Figure 1).

The next step is to detect the ejected proton with kinetic energy T_p and momentum $\vec{p}_p$. Then we can characterize the reaction by the missing energy $E_m = \omega - T_p$ and the missing momentum $\vec{p}_m = \vec{q} - \vec{p}_p$. The missing energy and momentum are related to the binding energy and initial momentum of the struck nucleon in the nucleus. When we quasielasti-

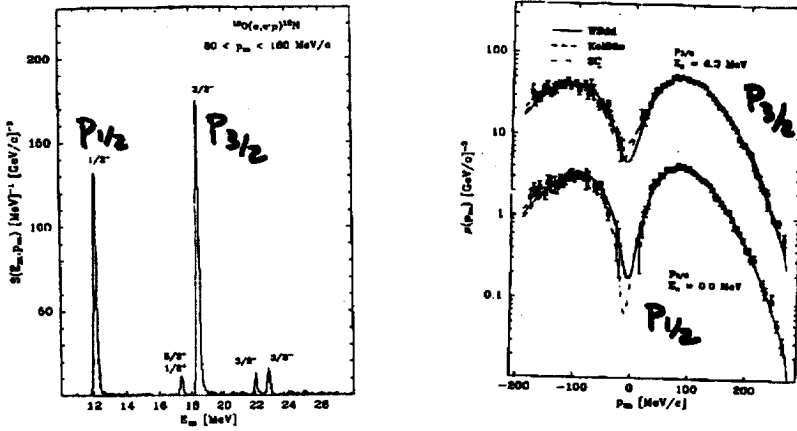


Figure 2. $^{16}\text{O}(e,e'p)$ cross sections for $E_{beam} = 400$ MeV. a) Reduced cross section versus missing energy. Note the large peaks due to proton knockout from the $1p_{1/2}$ and $1p_{3/2}$ states of ^{16}O and smaller peaks due to proton knockout from other states. (Knockout from the $1s_{1/2}$ state begins at larger missing energies than measured here.) b) Reduced cross section versus missing momentum for the $1p_{1/2}$ and $1p_{3/2}$ states. Note the characteristic $l = 1$ momentum distribution. The curves are distorted wave impulse approximation calculations using different optical potentials. The data are from Leuschner et al. and the calculations are described therein.

cally knock out protons from the nucleus, we see characteristic missing energy and momentum distributions for $1s$, $1p$, $1d$, $2s$, $2p$, ... shells. Typical missing energy and missing momentum plots for $^{16}\text{O}(e,e'p)$ can be seen in Figure 2. These experiments allow us to determine the energy and momentum distributions of nucleons in the nucleus (within a model) and the reaction mechanisms by which they are knocked out. (Two good reviews of this field are by Frullani and Mougey and by Kelly.)

Since these models work well, we naturally try to determine the regimes where they break down. This means extending the experiments to higher values of momentum transfer and missing momentum.

1. Electron Scattering Theory

In the first Born approximation for ultra-relativistic electrons (where helicity is conserved, unlike at lower energies), we can write the unpolarized cross section for $(e,e'p)$ as

$$\frac{d^6\sigma}{d\omega d\Omega_e dE_m d\Omega_p} = \frac{E_p p_p}{(2\pi)^3} \sigma_{Mott} (V_L R_L + V_T R_T + V_{LT} R_{LT} \cos \phi_{pq} + V_{TT} R_{TT} \cos 2\phi_{pq})$$

where Ω is the solid angle, ϕ_{pq} is the angle between the electron scattering plane (containing the incident and scattered electrons and the virtual photon) and the reaction plane (containing the virtual photon and the outgoing proton), $V_i = V_i(q, \omega, \theta_e)$ are known kinematic factors and $R_i = R_i(q, \omega, E_m, p_m)$ are the response functions containing all of the nuclear information. (In the case where the incident electron is polarized and we measure the polarization of the outgoing proton, there are 18 response functions. Only a few of them have been measured so far.)

R_L , the longitudinal response function (so called because it comes from the part of the virtual photon that is longitudinally polarized [and is thus absent for real photons which are entirely transverse]), measures the charge distribution; R_T , the transverse response function, measures the current and magnetic distributions; R_{LT} , the longitudinal-transverse interference response function, measures the interference of the longitudinal and transverse currents; and R_{TT} is the transverse-transverse interference response function. The interference response functions, R_{LT} and R_{TT} , are much more sensitive to small changes in the model and hence measuring these response functions provides a much more stringent test of models.

1.1 Plane Wave Impulse Approximation

In the simplest model, Plane Wave Impulse Approximation (PWIA), we assume that a) the virtual photon is absorbed on a single nucleon, b) the struck nucleon is detected, and c) the struck nucleon leaves the nucleus without further interaction (i.e.: as a plane wave). In this approximation, the missing momentum is exactly equal to and opposite the initial momentum of the struck nucleon. Then we can write the cross section as

$$\frac{d^6\sigma}{d\omega d\Omega_e dE_m d\Omega_p} = \frac{E_p p_p}{(2\pi)^3} \sigma_{ep} S(p_m, E_m)$$

where E_p is the energy of the outgoing proton, σ_{ep} is the electron-proton cross section (for bound protons), and $S(p_m, E_m)$ is the spectral function, the probability of finding a proton in the nucleus with binding energy E_m and initial momentum p_m . In the independent particle shell model

$$S(E_m, p_m) = \sum_{\alpha} n_{\alpha} |\psi_{\alpha}(p_m)|^2 \delta(E_m - E_{\alpha})$$

where α refers to all the quantum numbers of the bound state, n_{α} is the occupation number, $\psi_{\alpha}(p_m)$ is the wave function, and E_{α} is the binding energy of the state. σ_{ep} has L, T, LT , and TT components.

1.2 Distorted Wave Impulse Approximation

Since we cannot ignore the interaction of the outgoing nucleon, we generally use the Distorted Wave Impulse Approximation (DWIA) where the outgoing nucleon interacts with the residual nucleus via an optical potential typically derived from elastic nucleon-nucleus scattering. The DWIA cross section is typically 30 to 50% lower than the PWIA (for missing momenta less than 200 MeV/c). The cross section as a function of missing momentum is also shifted as the ejected nucleon leaves the nuclear potential. Typical cross sections for $^{16}\text{O}(e,e'p)$ measured by Leuschner et al. are shown in Figure 2. Note the sharp peaks in the missing energy distribution corresponding to proton knockout from the $1p_{1/2}$ and $1p_{3/2}$ states of ^{16}O . Note the smaller peaks from fragmented $1p_{3/2}$ states and from a $2s/1d$ state (due to configuration mixing in the oxygen ground state). The missing momentum spectrum shows typical $l = 1$ momentum distributions for the $1p_{1/2}$ and $1p_{3/2}$ states, shifted due to the effect of the final state interactions. Note that the DWIA calculations describe the data remarkably well at these moderate momentum transfers ($q \approx 350$ MeV/c) and missing momenta ($p_m < 200$ MeV/c).

1.3 Beyond the Impulse Approximation

It is possible to knock out nucleons with more exotic mechanisms. These fall into two categories, two nucleon correlations and two-body currents. When two nucleons are at very short range, they have a very large relative momentum and are considered correlated. In that case, if the virtual photon is absorbed by one of the nucleons, then the other nucleon has enough momentum that it will also exit the nucleus. Since we only detect one of these two nucleons, the event has a lot of missing energy (energy carried away by the undetected nucleon). These effects should become more important as the missing momentum increases beyond the fermi momentum ($p_{\text{fermi}} \approx 250$ MeV/c).

In a two-body current, the virtual photon is effectively absorbed by two nucleons which share the energy and momentum transfer. This can happen if the photon strikes a meson being exchanged by the two nucleons (a Meson Exchange Current or MEC) or if the photon excites one nucleon to a delta (the first excited state of the proton at $m_\Delta = 1232$ MeV) and the delta then de-excites by emitting a pion which is absorbed by a second nucleon. If the second nucleon is also ejected from the nucleus, then the event will appear at high missing energy (ie: not in one of the $1p$ shell peaks). If the second nucleon is not ejected from the nucleus, then the two-body current can interfere with the one body

current to affect the 1p shell knockout cross section. These effects are expected to decrease as the momentum transfer increases.

These effects are typically more complicated and hence more difficult to calculate and to study.

1.4 The Experiment

In order to test the validity of the DWIA approximation at more extreme kinematics, we measured the $^{16}\text{O}(e,e'p)$ cross section at $q = 1000$ MeV/c and $p_m \leq 350$ MeV/c. We measured the cross section at fixed (ω, q) for the same range of (p_m, E_m) for several values of θ_e (by varying the beam energy) and ϕ_{pq} in order to separate the response functions R_L, R_T , and R_{LT} . (See Bertozzi et al for the experimental proposal. Also see www.jlab.org/~fissum/e89003.html for more information on the experiment.)

This was the first experiment performed in the newly commissioned experimental Hall A at the Thomas Jefferson National Accelerator Facility (Jefferson Lab) located in Newport News, Virginia. See www.jlab.org and hallaweb.jlab.org for descriptions of the laboratory and the experimental hall. The 70 μA 100% duty-factor beam of beam energies $E_{beam} = 845, 1645$ and 2445 MeV was incident on a three-foil waterfall target with total thickness of about 400 mg/cm². We used the two High Resolution Spectrometers (HRS) to detect the scattered electron and the outgoing proton. Each HRS has three quadrupole magnets to focus the scattered particles and a dipole magnet to momentum analyze them. They are approximately 25 m long and have an angular acceptance $\Delta\Omega = 4.6$ msr and a momentum acceptance $\Delta p/p = 7\%$. The in-plane angular resolution is 2 mrad and the momentum resolution is $\delta p/p = 2.5 \cdot 10^{-4}$. We varied the missing momentum by moving the proton spectrometer from $\theta_{pq} = -20^\circ$ to $+20^\circ$. (Since the spectrometers weigh on the order of 1000 tons, they must remain on the floor of the experimental hall and thus the electron scattering plane and the reaction plane must be parallel. $\theta_{pq} > 0$ corresponds to $\phi_{pq} = 180^\circ$, $p_m > 0$, and $\theta_p > \theta_q$. $\theta_{pq} < 0$ corresponds to $\phi_{pq} = 0^\circ$.)

Since our waterfall target contained both hydrogen and oxygen, we could simultaneously measure the $^{16}\text{O}(e,e'p)$ cross sections and normalize them to the known $\text{H}(e,e'p)$ cross sections. These simultaneous measurements also allowed us to constrain our kinematics, making sure that we were measuring the same range of missing momentum at the different incident beam energies.

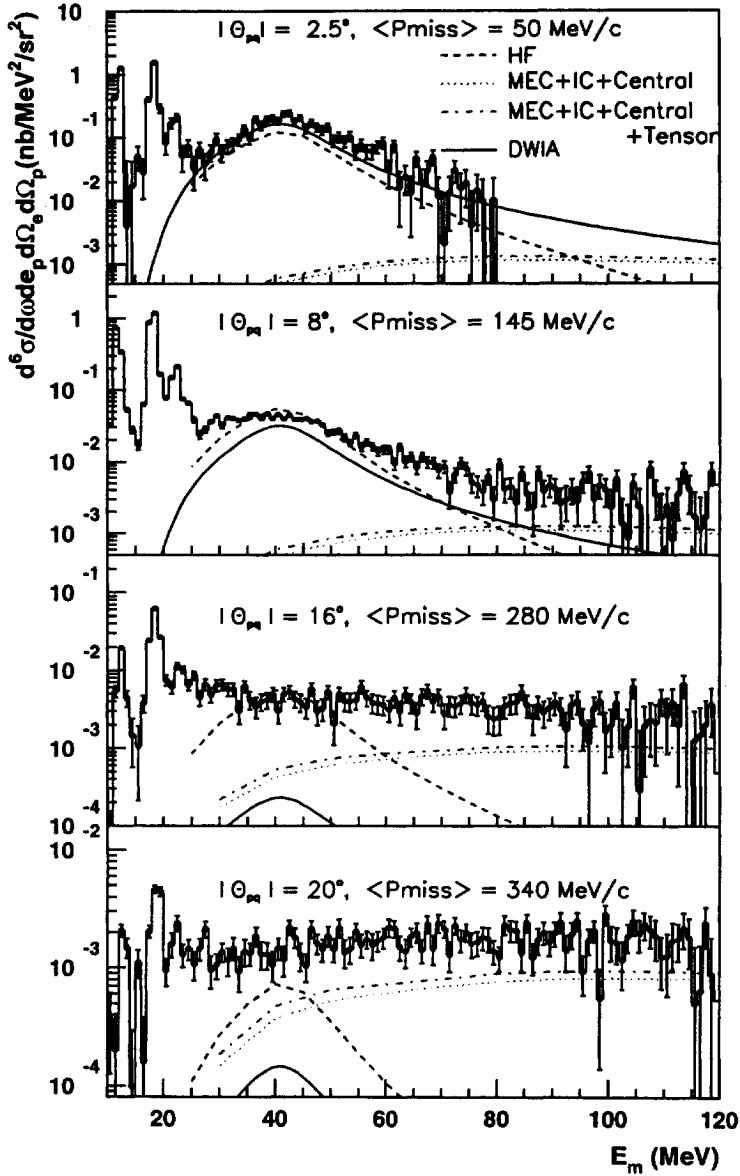


Figure 3. $^{16}\text{O}(e,e'p)$ cross section versus missing energy at $E_{\text{beam}} = 2.4$ GeV, $q = 1000$ MeV/c and $\omega = 440$ MeV for four different proton-virtual photon angles. The solid curve is the DWIA calculation by Kelly, the dotted and dot-dashed curves are calculations of two nucleon knockout by Janssen and Ryckebusch. (Data from Liyanage et al. Calculations described therein.)

2. Results

The cross section as a function of missing energy (excitation energy of the residual nucleus) is shown in Figure 3. The four panels correspond to four different angles of the proton spectrometer: $\theta_{pq} = 2.5^\circ, 8^\circ, 16^\circ$ and 20° . The larger angles correspond to larger average missing momenta. In the top panel, you can clearly see two peaks at $E_m = 12$ and 16 MeV corresponding to knocking a proton out of the $1p_{1/2}$ and $1p_{3/2}$ states of ^{16}O , a smaller peak at about $E_m = 20$ MeV (probably a $1p_{3/2}$ fragment state), and a broad bump from about 25 to 60 MeV corresponding to knockout of protons from the $1s_{1/2}$ shell. Since the threshold for two nucleon knockout is at about 25 MeV, ^{15}N with a $1s_{1/2}$ hole is unstable and hence the $1s_{1/2}$ peak has a width corresponding to its brief lifetime.

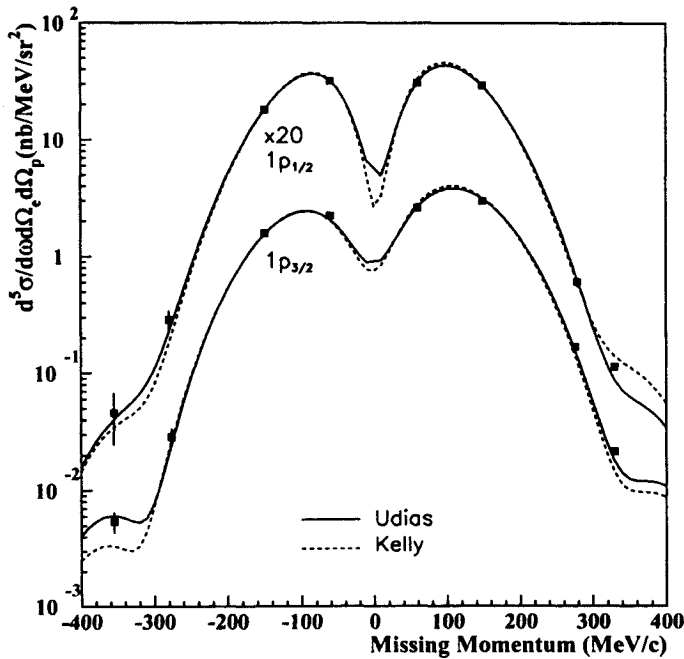


Figure 4. $^{16}\text{O}(e,e'p)$ cross section versus missing momentum for the $1p_{1/2}$ and $1p_{3/2}$ shells at $q = 1000$ MeV/c and $\omega = 440$ MeV. (Data from Gao et al. Calculations described therein.)

As the missing momentum increases, the cross section for the $1p$ states decreases, although the states are still clearly visible, even at $p_m = 340$

MeV/c. The cross section for the 1s state also decreases and the state vanishes below a flat 'continuum' cross section. The more rapid decrease of the 1s state cross section with missing momentum is consistent with an $l = 0$ momentum distribution. The continuum cross section is due to the knockout of two (or more) nucleons.

At low missing momenta, the 1s cross section is well described by the DWIA calculation (solid line). At higher missing momenta, the continuum cross section is qualitatively described by a calculation including NN correlations and two-body currents. This indicates that for $E_m > 25\text{ MeV}$, single nucleon knockout dominates at $p_m < 100\text{ MeV/c}$ and that two nucleon correlations and two-body currents dominate at $p_m > 200\text{ MeV/c}$. These correlations and currents are not yet quantitatively understood.

2.1 1p shell cross sections

The cross sections for 1p shell knockout are shown in Figure 4. The points are the experimental data with uncertainties. The curves are DWIA calculations by Udias et al. and by Kelly. Note that the DWIA calculations describe the data accurately as the cross section decreases by a factor of 1000. The cross sections for negative and positive missing momenta are not equal; this is due to a nonzero value of the longitudinal-transverse interference term, R_{LT} .

We calculated the longitudinal-transverse asymmetry (effectively the longitudinal-transverse response function scaled by the cross section)

$$A_{LT} = \frac{\sigma^0 - \sigma^{180}}{\sigma^0 + \sigma^{180}} = \frac{V_{LT}R_{LT}}{V_LR_L + V_TR_T + V_{TT}R_{TT}}$$

where σ^0 and σ^{180} are the cross sections for $\phi_{pq} = 0$ and 180° , respectively. A_{LT} is shown in Figure 5. Note the decrease of A_{LT} from $p_m = 0$ to $p_m = 280\text{ MeV/c}$ followed by a significant increase from 280 to 340 MeV/c. See Gao et al. for more information about the data and the calculations. The fully relativistic DWIA calculations predicted the rapid change of slope. These calculations used Dirac spinors for the protons and modified ('distorted') the lower components of the spinors to reflect the effects of the proton-nucleus potential. The calculation without spinor modification did not describe the data.

Thus, the fully relativistic DWIA ($e,e'p$) calculation works for 1p shell knockout. The protons must be described properly using Dirac spinors. Two nucleon correlations and two-body currents are apparently not needed. There is only one free parameter in this calculation, the overall magnitude.

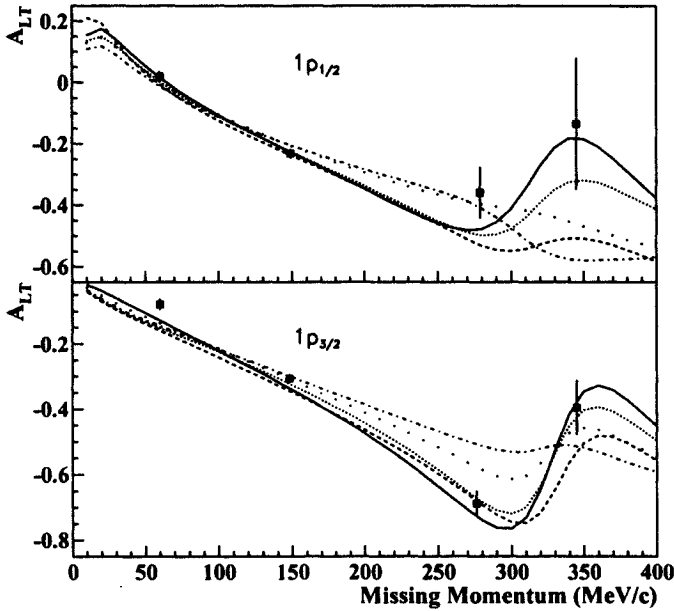


Figure 5. $^{16}\text{O}(e,e'p)$ longitudinal-transverse asymmetry, A_{LT} , versus missing momentum for the $1p_{1/2}$ and $1p_{3/2}$ shells at $q = 1000$ MeV/c and $\omega = 440$ MeV. The dashed line is the Kelly calculation, the others are by Udias et al. The solid line is the fully relativistic calculation and the dot-dashed curve is a non-relativistic calculation. The densely dotted and loosely dotted lines are semirelativistic. (Data from Gao et al. Calculations described therein.)

3. The Future

The extraordinary (and unexpected) success of the relativistic DWIA calculations in describing $1p$ shell knockout from $p_m = 0$ to $p_m = 340$ MeV/c, led us to propose a follow-up experiment at Jefferson Lab, E00-102. (See <http://www.jlab.org/~fissum/e89003.html> for the proposal itself and <http://www.jlab.org/~fissum/e00102/e00102.html> for information on the experiment.) This experiment took data in Fall 2001, extending the previous measurement out to a missing momentum of 750 MeV/c in order to more stringently test the theoretical models. We expect preliminary results within a year.

4. Summary

We measured proton knockout from the $1p_{1/2}$ and $1p_{3/2}$ shells of ^{16}O out to a missing momentum of 350 MeV/c at a momentum transfer of $q = 1000$ MeV/c and $\omega = 440$ MeV.

The data is described surprisingly well by distorted wave impulse approximation calculations with a correlated bound state wave function, relativistic (Dirac equation) dynamics, and optical potential rescattering.

We have taken new data out to $p_m = 750$ MeV/c to **really** test the model.

Acknowledgments

The author wishes to thank the Jefferson Lab accelerator staff, Hall A staff, and Hall A Collaboration for making these measurements possible. The author also gratefully acknowledges the support of the US Department of Energy. The Southeastern Universities Research Association (SURA) operates the Thomas Jefferson National Accelerator Facility for the United States Department of Energy under contract DE-AC05-84ER40150.

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$(\gamma, 2E)$ AND $(E, 2E)$ USING A 2-ELECTRON $\mathcal{R}$ -OPERATOR FORMALISM

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Abstract Here we present a new variational approach for calculating atomic ionisation processes. In particular we outline the method for calculating the photo-doubleionisation of H^- and He and the electron impact ionisation of atomic hydrogen. We present elastic scattering phase shifts results for electrons scattering from atomic hydrogen as an intermediary calculation to indicate of the effectiveness of this approach. One of the main features of the approach is that, by construction, the two ionised electrons are treated in a totally symmetrical way. In the 2-electron problems we consider configuration space to be divided into two regions, separated by a 5-dimensional hypersurface Σ . The approach is based on the variational determination of a 2-electron $\mathcal{R}$ -operator, a linear operator that relates function values to normal derivatives on the bounding hypersurface inside which the function satisfy the Schrödinger equation. We calculate the S-matrix on a particular subsurface of Σ , from our knowledge of the $\mathcal{R}$ -operator, and use it to remove incoming flux. The channel wave functions are propagated out to some asymptotic distance, determined by convergence. Cross-sections will be evaluated by calculating the ratio of incoming to outgoing flux through the hypersurface at large hyperradii.

1. Introduction

Spectacular strides have been made in the past few years in experimental atomic collision physics. Accurate absolute experimental data has recently become available for a range of targets. These measurements are kinematically complete, that is, the fragments of the collisions are detected with their energies and angles resolved. Much of the work in the field has been directed to the study of electron impact ionisation and of photo-doubleionisation (Walters et al., 1993) (Marchalant et al., 1997). The *ab initio* calculation of these reliable experiment results now presents a substantial challenge to theory.

The benchmark problem of electron-impact ionisation of atomic hydrogen has very recently been resolved experimentally. Considerable effort is currently being focused on experimentally producing the analogous benchmark data for helium photo-doubleionisation (King and Avaldi, 2000). While there have been a number of significant theoretical contributions there is, as yet, no universal theory which can describe the full range of data for atomic targets. Recent experimental studies of the ionisation of molecules and solid surfaces lie still further beyond current theoretical capabilities (Stefani, 1999). These are the main motivational factors for developing the approach presented here. The advantages of the variational $\mathcal{R}$ -operator approach outlined here over other methods, like the Convergent Close-Coupling (CCC) (Bray and Stelbovics, 1992), conventional R-matrix calculations (Burke and Robb, 1975), Complex Exterior Scaling (CES) (Rescigno et al., 1999a) and Hyperspherical R-matrix Method with Semi-classical Outgoing waves (HRMSOW) (Malegat et al., 1999) is firstly, it is applicable to a wider variety of experiments than any one of the above methods, secondly, by its very construction it is totally symmetric in how it treats the two electrons in, for example, an ionisation problem and hence will not suffer in the same way as close-coupling calculations like the CCC and the conventional R-matrix do in highly symmetric geometries, and thirdly it is computationally very efficient, not requiring vast computer resources like the, for example, the CES method. What we present here is an outline of a generalised way of calculating atomic collision processes. Our goal is an *ab initio* calculation of electron impact ionisation and photo-doubleionisation, which is applicable to a variety of target systems. We consider our approach outlined here to be readily generalisable to much more complex systems than atomic hydrogen or helium. The application of this new approach will extend to complex atoms, ions, molecules and even surfaces. This generalisation will be the focus of future work.

2. The $\mathcal{R}$ -operator

R-matrix techniques have been widely used in scattering theory calculations, both in nuclear and atomic physics. The technique was originally developed by Wigner and Eisenbud (Wigner and Eisenbud, 1947) in the context of nuclear physics and later developed by Burke and Robb (Burke and Robb, 1975) and their collaborators for electron scattering in atomic physics. The conventional R-matrix method has been successfully applied to many different atomic scattering processes, including electron collisions with atoms, ions and molecules over a wide energy range. The method in essence divides configuration space into two regions, an 'inner' and an 'outer'. In the inner region, which effectively contains the target, all interactions including exchange are taken into effect. In the outer region exchange effects between the scattered or ionised electrons and the target electrons may be neglected. This splitting of configuration space allows one to employ different computational, or even different physical models, in the two regions. It is because of this partitioning of configuration space that the approach outlined here will be able to treat such a wide variety of systems. If one can suitably formulate the problem in the inner region then one can use the $\mathcal{R}$ -operator approach given here.

In order to appreciate the $\mathcal{R}$ -operator let us consider the somewhat simpler idea behind a typical R-matrix calculation. Essentially, the R-matrix relates the value of the first derivative of a function to the function values at the boundary between the two regions. In atomic scattering theory the functions encountered are the channel functions of the scattered electrons, which are functions of the a single radial variable. The problem with R-matrix calculations, and also CCC calculations, when considering ionisation problems is that the close-coupling expansion results in an asymmetric treatment of the two electrons. This is not problematic when considering elastic, inelastic scattering and ionisation processes in asymmetric geometries but does encounter difficulties when considering ionisation processes in very symmetric geometries (Bray, 1997) (Rescigno et al., 1999b). The reason for this problem stems from considering one of the electrons to be in some positive energy pseudostate, whose positive energy corresponds to that of one of the ionised electrons. Treating the electrons in this manner is inappropriate, especially in symmetric, equal energy sharing geometries.

The concept of an R-matrix has been extended to a general coordinate hyperspace by the introduction of an $\mathcal{R}$ -operator (Nesbet, 1984), a linear operator that produces function values on the hypersurface Σ , which encloses the hypervolume Ω , when acting on the normal derivative of

the function at this surface. In the calculations presented here this hyperspace is a 6-dimensional space, 3 position coordinates for each of the two electrons. For solutions of the Schrödinger equation at a given energy E that are regular within the closed volume Ω , but whose boundary values on the enclosing surface are unspecified, the $\mathcal{R}$ -operator is defined (Nesbet, 1984) such that

$$\psi(\sigma_1) = \int_{\Sigma} \mathcal{R}(E, \sigma_1, \sigma_2) \nabla_n \psi(\sigma_2) \cdot d\sigma_2 \quad (1)$$

where σ denotes the coordinates of some point on the hypersurface Σ . Hence, if we know $\mathcal{R}$ for some specified energy E , and specify the outward normal gradient $\nabla_n \psi = \xi$ we can obtain the value of the wavefunction ψ on the bounding surface Σ for the specified normal gradient. This is an example of the classical Neumann boundary problem.

It can be shown that there exists a variational functional for the $\mathcal{R}$ -operator which is stationary if and only if the trial wavefunction satisfies the Schrödinger equation throughout the enclosed volume. Crucially this provides us with a way of calculating the $\mathcal{R}$ -operator. Since we are considering atomic scattering processes the defining differential equation is the Schrödinger equation.

An explicit formula for the stationary value of the $\mathcal{R}$ -operator is obtained by expanding the trial wave function, $\Psi \approx \Psi_t = \sum_i c_i \Psi_i$, inside Ω in a set of linearly independent basis functions, $\Psi_i(\mathbf{r}_1, \mathbf{r}_2)$, which are regular functions in Ω . One very important point to note it that the only requirement of the basis functions is that they regular and linear independent. The $\mathcal{R}$ -operator (Nesbet, 1984) is given explicitly as

$$\mathcal{R}(E, \sigma_1, \sigma_2) = \frac{1}{2} \sum_{\alpha} \sum_{\beta} \Psi_{\alpha}(\sigma_1) (H_B - E)_{\alpha\beta}^{-1} \Psi_{\beta}^*(\sigma_2) \quad (2)$$

where $(H_B - E)^{-1}$ denotes the inverse of the matrix $(H_B - E) = \langle \Psi_{\alpha} | H_B - E | \Psi_{\beta} \rangle$ and H_B include a Bloch operator term (Bloch, 1957). The Bloch modification is a natural feature of this method and is not simply added *ad hoc*. A Bloch-modified Hamiltonian ensures that the kinetic energy operator is Hermitian over the finite inner region. E is the total energy of the system.

The relation between the $\mathcal{R}$ -operator and the R-matrix is straightforward. The R-matrix is the projection of the $\mathcal{R}$ -operator onto a complete set of functions on each distinct subsurface of bounding the hypersurface Σ . For example, in our calculations presented here, the $\mathcal{R}$ -operator is

a function of the position coordinates of the two electrons in the system. A point in the 6-dimensional hypervolume is therefore given by stating the value of the coordinates $(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2)$. To obtain the $\mathcal{R}$ -matrix, relating a function of r_1 and the derivative of the function at some boundary $r_1 = \rho$, we simply project out the functional dependence on the other variables.

When the angular variables are projected out one is left with a reduced $\mathcal{R}$ -operator, which acts only on the radial variables r_1 and r_2 . This is depicted in Figure 1. In Figure 1 the various regions are labeled according to the following scheme, in AA ($r_1, r_2 \leq \rho$) both electrons are considered to be close to the nucleus, in XX ($r_1, r_2 \geq \rho$) both electrons are considered to be far from the nucleus - ionisation region. The regions XA ($r_1 \leq \rho \leq r_2$) and AX ($r_2 \leq \rho \leq r_1$) are physically equivalent and one of the two electrons interacts strongly with the nucleus - elastic and inelastic scattering region. Also shown in Figure 1 are the subsurfaces σ_I and σ_{II} , which are defined by fixing one of the radial coordinates, $\sigma_I(r_1 = \rho)$ and $\sigma_{II}(r_2 = \rho)$. An important point to note is that when the $\mathcal{R}$ -operator acts on properly symmetrised basis functions, which are used in our calculations and will be outlined in the next section, we can confine our attention to a single subsurface, say σ_I , as the effect on σ_{II} can easily be calculated by symmetry considerations. In the subsequent discussion we will mainly focus on the subsurface σ_I , since we know calculations carried out on it are related to the solutions of the whole problem.

3. Solving the interior problem

It was earlier stated that the configuration space is divided into an inner and outer region. We now wish to consider in more detail the inner region, where all interactions are considered, and see how one obtains and uses the $\mathcal{R}$ -operator to relate solutions across the bounding surface, which separates the two regions. As is well known the Schrödinger equation can be expanded in any complete set of basis functions. We use spherical polar coordinates to define the position of the electrons in our system. The basis functions will therefore be composed of angular and radial components. The particular set of one-electron radial basis functions we employ in our 2-electron $\mathcal{R}$ -operator calculations is the set of Sturmian functions. One advantage of the Sturmian functions is that the calculation of required matrix elements is very easy to evaluate and are given by simple algebraic expressions, which can be numerically evaluated in terms of simple recurrence relations. The form of the Stur-

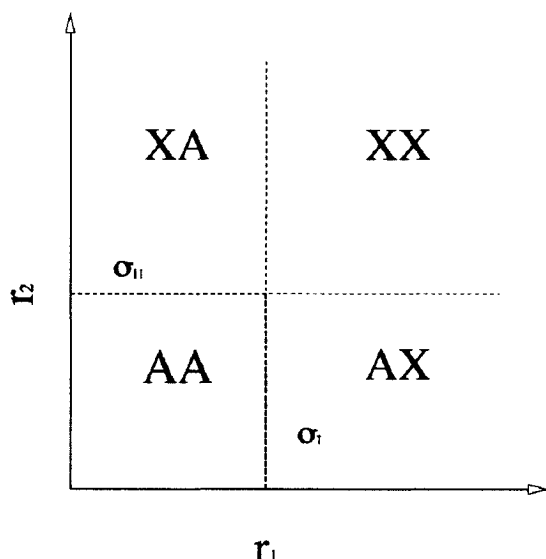


Figure 1. r_1 - r_2 plane with each of the four regions, AA, XX, AX, XA shown. The subsurface σ_I and σ_{II} are also shown.

mian functions used is $\chi_a(r) = r^{n_a-1} \exp(-\alpha r)$, where α is a parameter that characterises a particular basis.

3.1 Basis functions

The 2-electron basis functions, $\Psi_{ab}^{LSP}(\mathbf{r}_1, \mathbf{r}_2)$, where L denotes the total angular momentum, S the total spin angular momentum and P the parity, are constructed from 1-electron basis orbitals, ϕ_a ,

$$\phi_a(\mathbf{r}) = N_a \chi_n(r) Y_{lm_l}(\hat{\mathbf{r}}) \quad (3)$$

where N_a is a normalisation coefficient. The subscript a denotes a particular set of the quantum numbers $a = \{n, l, m_l\}$. Coupled angular functions are given by

$$\Xi_{l_a l_b}^L(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) = \sum_{m_a, m_b} C(l_a l_b m_a m_b; LM) Y_{l_a m_a}(\hat{\mathbf{r}}_1) Y_{l_b m_b}(\hat{\mathbf{r}}_2) \quad (4)$$

where $C(l_a l_b m_a m_b; LM)$ denotes the Clebsch-Gordan coefficient. The complete 2-electron basis wavefunctions, for a given LSP symmetry, can be written as

$$\Psi_{ab}^{LSP}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2} N_a N_b \left\{ \chi_a(r_1) \chi_b(r_2) \Xi_{l_a l_b}^L(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) + (-1)^{P+L+S} \chi_b(r_1) \chi_a(r_2) \Xi_{l_b l_a}^L(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) \right\} \quad (5)$$

The total wavefunction is expanded in terms of these 2-electron LSP basis functions, and they are used in equation (2) to obtain an explicit expression for the $\mathcal{R}$ -operator. When one uses the 2-electron basis functions defined in equation (5) the resulting integrations for the matrix elements are of a very simple form, expressible in terms of 1-electron integrals, which in turn can be numerically evaluated in terms of simple recurrence relations.

3.2 Close-coupling expansion and channel wavefunctions

Once we have constructed the $\mathcal{R}$ -operator, valid for the interior region and the bounding surface, we next consider how to use this to relate information about the total wavefunction to the exterior region. Exchange effects are assumed to be negligible outside the bounding hypersurface. This approximation can be made arbitrarily accurate provided the bounding hypersurface is chosen to be sufficiently large. Neglecting the exchange part one can expand the total wavefunction in the set of 2-electron basis functions given in equation (5),

$$\Psi_j^{LSP}(\mathbf{r}_1, \mathbf{r}_2, E) = \sum_{l_1, l_2} \sum_{n_1, n_2} \chi_{n_1}(r_1) \chi_{n_2}(r_2) \Xi_{l_1, l_2}^L(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) c_j^{l_1, l_2, n_1, n_2} \quad (6)$$

where the subscript j denotes a set of quantum numbers for a particular incident channel, $j = \{k_1, l_1, n_2, l_2\}$. The $c_j^{l_1, l_2, n_1, n_2}$ are expansion coefficients. Given a particular set of the quantum numbers L, l_1, l_2 the resulting 2-electron radial equation can be expressed in terms of a close-coupling expansion as

$$\sum_{n_1, n_2} \chi_{n_1}(r_1) \chi_{n_2}(r_2) c_j^{n_1, n_2}(l_1, l_2) = \sum_i \frac{u_{ij}(r_1)}{r_1} \hat{\phi}_i(r_2) \quad (7)$$

where i denotes the set of the quantum numbers of the i^{th} channel, corresponding to the 1-electron pseudostate $\hat{\phi}_i$.

The pseudostates $\hat{\phi}_{i=\{n, l\}}(\mathbf{r})$ are constructed by diagonalising the target Hamiltonian in a particular basis. One particular choice of basis is a set of orthogonal Laguerre functions, $\zeta_{kl}(r)$. The pseudostates

are expressed as a linear combination of the basis functions, $\hat{\phi}_{nl}(\mathbf{r}) = \sum_k C_{nk}^l \zeta_{kl}$. The C_{nk}^l coefficients are obtained after diagonalisation.

By using the reduced $\mathcal{R}$ -operator projected onto the surface σ_I one can calculate independent channel wavefunctions $u_{ij}(r_1)|_{r_1=\rho}$ by setting the normal gradient $(r^{-1}u_{ij}(r))'|_{r=\rho} = \delta_{ij}$. This then enables us to calculate the R -matrix, from the relation $u_{ij}(\rho) = \sum_k R_{ik} u'_{kj}(\rho)$. Further this enables the independent channel functions to be indexed by a single index i .

4. Calculating elastic and inelastic scattering processes

Having calculated the R -matrix, which relates the value of the channel wavefunction $u_i(r = \rho)$ and its derivative $u'_i(r = \rho)$, we next proceed to calculate the S (scattering)-matrix, which follows from standard scattering theory, and produce cross-sections for various scattering processes.

Asymptotically the channel functions and their derivatives are expressed as a superposition of ingoing and outgoing waves,

$$u_i(r) \underset{r \rightarrow \infty}{\sim} k_i^{-1/2} \{-A_i \exp(-i\theta_i) + B_i \exp(i\theta_i)\} \quad (8)$$

$$u'_i(r) \underset{r \rightarrow \infty}{\sim} k_i^{-1/2} \{-A_i \exp(-i\theta_i)' + B_i \exp(i\theta_i)'\} \quad (9)$$

where, for neutral targets, $\theta_i = k_i r - l_i \pi/2$. The $\exp(\pm i\theta_i)$ are asymptotic spherical Bessel functions. For charged targets the Bessel functions are replaced by Coulomb functions.

The S -matrix (scattering matrix) is defined from the asymptotic behaviour of the solutions of the radial Schrödinger equation. Note that the coefficients A_i and B_i are not independent but rather that if the amplitudes of the ingoing waves, A_i , are known then the amplitudes of the outgoing waves, B_i , are determined uniquely by equation (8) or (9). The relation between the coefficients A_i and B_i defines the scattering matrix, S ,

$$B_i = \sum_{i'} S_{ii'} A_{i'} \quad (10)$$

If the R -matrix boundary is sufficiently large then the channel wavefunctions, u_i , and their derivatives, u'_i , can be matched to the asymptotic functions in order to determine the S -matrix. One can directly relate the R -matrix and the S -matrix by using equations (8) and (9) in the R -matrix expression $u_i = \sum_k R_{ik} u'_k$. Using equation (10) to relate the A and B coefficients results in the relation

$$\sum_k (\delta_{ik} f_k^{\text{out}} - R_{ik} g_k^{\text{out}}) S_{ki} = -(\delta_{ij} f_j^{\text{in}} - R_{ij} g_j^{\text{in}}) \quad (11)$$

where

$$f_i^{\text{in}} = -k^{-1/2} \exp(-i\theta_i), \quad g_i^{\text{in}} = \frac{df_i^{\text{in}}}{dr} \Big|_{r=\rho} \quad (12)$$

$$f_i^{\text{out}} = k^{-1/2} \exp(i\theta_i), \quad g_i^{\text{out}} = \frac{df_i^{\text{out}}}{dr} \Big|_{r=\rho} \quad (13)$$

The relation between the S -matrix and the K -matrix is given by

$$K_{ii'} = \{\delta_{ii'} - S_{ii'}\} \{-i\delta_{ii'} - iS_{ii'}\} \quad (14)$$

The S -matrix can be written in terms of the K -matrix as

$$S = (I + iK)/(I - iK) \quad (15)$$

and in turn the T -matrix is defined by

$$S = I + 2iT \quad (16)$$

With knowledge of the T -matrix one can obtain values for elastic and inelastic scattering processes, see (Nesbet, 1980), (Blatt and Biedenharn, 1952).

It is worth pointing out here that what we are presenting is not just a novel variational way of calculating an R -matrix. As will be explained in more detail later, when we consider explicitly ionisation events, one of the main advantages of the formalism presented here is the way it deals with the two active electrons in the system. The choice of symmetrised basis functions and the way the $\mathcal{R}$ -operator acts on these functions ensures that the electrons are treated in a totally symmetrical way. This ensures that our system is highly symmetric and will not suffer from the same problems encountered by other scattering theories in very symmetric geometries, most notably the Convergent Close-Coupling.

5. Calculating ionisation processes

For ionisation processes we adopt a different approach to that taken for elastic and inelastic scattering. The residual charged ion and the ejected electron interact with the scattered electron via the long range Coulomb interaction. It is for this reason that we must propagate the

total wavefunction out to some large asymptotic distance before extracting ionisation cross-sections. The ratio of incoming to outgoing flux through the far asymptotic, enclosing hypersurface defines the ionisation cross-section. It is the individual channel wavefunctions that are in fact propagated out to some large distance, the total wavefunction being the sum of products of channel functions and pseudostates.

5.1 The Schrödinger equation for the channel functions

The method of propagation simply involves propagating the radial Schrödinger equation, where the boundary conditions required to initiate the propagation are the value of the channel wavefunction $u_i(\rho)$ and its derivative $u'_i(\rho)$, which we have already evaluated from our $\mathcal{R}$ -operator.

In the outer region, $r > \rho$, exchange effects can be neglected and the general form for the Schrödinger equation is

$$\left\{ \frac{d^2}{dr_1^2} + k_i^2 - 2v_i(r_1) \right\} u_i(r_1) = 2 \sum_{i'} v_{ii'}(r_1) u_{i'}(r_1),$$

where,

$$v_i(r_1) = \frac{\ell_i(\ell_i + 1)}{2r_1^2} - \frac{Z - 1}{r_1},$$

and

$$v_{ii'}(r_1) = (\hat{\phi}_i(r_2) | \frac{1}{r_{12}} | \hat{\phi}_{i'}(r_2)) - \frac{1}{r_1} \delta_{ii'}. \quad (17)$$

This equation and the two boundary conditions for $u_i(\rho)$ and $u'_i(\rho)$ are sufficient to initiate propagation of the solution out to some asymptotic distance, which is determined by convergence of the resulting cross-sections.

5.2 Numerical method for solving coupled differential equations

An efficient method for solving coupled equations of this form is to represent the solution by modulations of known functions.

$$u_i(r) = c_i(r)w_{0i}(r) + s_i(r)w_{1i}(r) \quad (18)$$

$$u'_i(r) = c_i(r)w'_{0i}(r) + s_i(r)w'_{1i}(r) \quad (19)$$

where w_{0i}/w_{1i} is an outgoing/ingoing Coulomb wave. As we propagate outwards the slowly varying $c_i(r)$ and $s_i(r)$ functions tend to constant values. In our ionisation calculations the $s_i(r)$ function is expected to be very small as it is associated with an incoming wave. Convergence of c_i and s_i implies convergence of the cross section.

5.3 Obtaining ionisation cross-section

Consider a scattering process where asymptotically the scattered wavefunction Ψ_{sc}^+ decomposes into a sum of discrete (elastic and inelastic/excitation) two-body channels and a term Ψ_{ion}^+ that describes the ionisation continuum. It can be shown (Peterkop, 1977) and (Rudge, 1968) that in the far asymptotic region where all interparticle distances are large, the ionisation term behaves as

$$\Psi_{ion}^+(\mathbf{r}_1, \mathbf{r}_2) \underset{\rho \rightarrow \infty}{\sim} -\sqrt{\frac{i\kappa^3}{\rho^5}} \exp i \left(\kappa\rho + \frac{\eta(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \alpha)}{\kappa} \ln(2\kappa\rho) \right) f(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \alpha) \quad (20)$$

where $f(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \alpha)$ is the ionisation amplitude, the hyperspherical coordinates ρ and α are defined by $\rho = (r_1^2 + r_2^2)^{1/2}$, $\alpha = \arctan(r_1/r_2)$ and κ is related to the total energy by $\kappa = \sqrt{2E}$. The current density vector $\mathbf{j}$ for a wavefunction Ψ is defined as the

$$\mathbf{j} = 1/2i [\Psi^* \nabla \Psi - \Psi \nabla \Psi^*] \quad (21)$$

In hyperspherical coordinates the gradient operator ∇ is

$$\nabla = \frac{\partial}{\partial \rho} \hat{\rho} + O(1/\rho) \quad (22)$$

and a surface element is given by

$$d\Sigma = \rho^5 \sin^2 \alpha \cos^2 \alpha \, d\alpha \, d\hat{\mathbf{r}}_1 d\hat{\mathbf{r}}_2 \quad (23)$$

$$= \rho^5 \sin 2\alpha \, dE_1 \, d\hat{\mathbf{r}}_1 d\hat{\mathbf{r}}_2 / 4E \quad (24)$$

where $\hat{\mathbf{r}} = \{\theta, \phi\}$. Using equation (22) in equation (21) and calculating the asymptotic current density associated with the wavefunction Ψ_{ion}^+ , as given in equation (20), gives to leading order

$$\mathbf{j} = \frac{\kappa^4}{\rho^5} |f(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \alpha)|^2 \hat{\rho}. \quad (25)$$

Again with reference to equation (20) it follows that

$$\mathbf{j} = \kappa |\Psi_{ion}^+|^2 \quad (26)$$

The asymptotic flux $\mathcal{F}_{out} = \int_{\Sigma_\infty} \mathbf{j} \cdot \mathbf{n} d\Sigma$ of $\mathbf{j}$ through a hypersurface Σ , where $\mathbf{n}$ is a unit vector in the direction of the outward normal to the hypersurface, of infinite hyperradius is given by

$$\mathcal{F}_{out} = \kappa \lim_{\rho \rightarrow \infty} \int_{\Sigma_\rho} \rho^5 |\Psi_{ion}^+|^2 \sin^2 \alpha \cos^2 \alpha d\alpha d\hat{\mathbf{r}}_1 d\hat{\mathbf{r}}_2 \quad (27)$$

The cross-section is the ratio of the outgoing flux $\mathcal{F}_{out}$ out to the incoming flux $\mathcal{F}_{in}$.

$$\sigma = \lim_{\rho \rightarrow \infty} \frac{\kappa \int_{\Sigma_\rho} \rho^5 |\Psi_{ion}^+|^2 \sin^2 \alpha \cos^2 \alpha d\alpha d\hat{\mathbf{r}}_1 d\hat{\mathbf{r}}_2}{\mathcal{F}_{in}} \quad (28)$$

We assume that the incident photon or electron can be represented by a plane wave, which has a current density $\mathbf{j} = k_0 \hat{\mathbf{z}}$. The incident flux is therefore $\mathcal{F}_{in} = k_0$.

$$\sigma = \frac{\kappa}{k_0} \lim_{\rho \rightarrow \infty} \int_{\Sigma_\rho} \rho^5 |\Psi_{ion}^+|^2 \sin^2 \alpha \cos^2 \alpha d\alpha d\hat{\mathbf{r}}_1 d\hat{\mathbf{r}}_2 \quad (29)$$

$$= \frac{\kappa}{k_0} \lim_{\rho \rightarrow \infty} \int_0^{\pi/2} \sin^2 \alpha \cos^2 \alpha d\alpha \int \rho^5 |\Psi_{ion}^+|^2 d\hat{\mathbf{r}}_1 d\hat{\mathbf{r}}_2 \quad (30)$$

and using equation (24) gives

$$\sigma = \frac{\kappa}{4k_0 E} \lim_{\rho \rightarrow \infty} \int_0^E \sin 2\alpha dE_1 \int \rho^5 |\Psi_{ion}^+|^2 d\hat{\mathbf{r}}_1 d\hat{\mathbf{r}}_2 \quad (31)$$

Furthermore the triple differential cross-section is given by

$$\frac{d^3 \sigma}{dE_1 d\hat{\mathbf{r}}_1 d\hat{\mathbf{r}}_2} = \frac{\kappa}{4k_0 E} \lim_{\rho \rightarrow \infty} \rho^5 |\Psi_{ion}^+|^2 \sin 2\alpha \quad (32)$$

6. Applications

6.1 Elastic scattering

The only complete application of our method to date has been the calculation of elastic scattering phase shifts, which are comparable to

definitive variational calculations in the standard literature, (Schwartz, 1961), (Armstead, 1968). One should bear in mind that our calculations were carried out with a relatively small basis set, a boundary of only $8a.u$ and took only approximately two seconds to calculate on a standard PC. This was a first test of the method which is greatly encouraging as it indicates that correlation and polarisation effects are being well accounted for by the formalism even with a box size of $8a.u$.

6.2 Ionisation

Currently work is focused on calculating the photo-doubleionisation of H^- , as a prototype to the photo-doubleionisation of helium. We calculate a particular solution ($^1P^o$) of the inhomogeneous equation for photo-doubleionisation using a Green's function approach. The Green's function is expanded in the set of 2-electron basis functions, equation (5), and is related to the $\mathcal{R}$ -operator. So from our knowledge of the $\mathcal{R}$ -operator we can calculate the appropriate Green's function. The channel wavefunctions and their derivatives are matched to ingoing and outgoing waves which define the two sets of coefficients $\mathbf{a} = A_i$ and $\mathbf{b} = B_i$. Only outgoing flux can contribute to ionisation and the removal of incoming waves is achieved by using the ($^1P^o$) S-matrix calculated for the electron-hydrogen problem (homogeneous solution) and subtracting this from the inhomogeneous solution. For the resulting wavefunction, the coefficients of the ingoing waves are equal to zero and the coefficients of the outgoing waves replaced by $\mathbf{b} - \mathbf{S}\mathbf{a}$. This procedure for the removal of incoming flux works very well in our calculations. The channel wavefunctions are then propagated to some large distance before extracting the cross section using the procedure outlined above in section (5.3).

For the ionisation of atomic hydrogen we propose a similar scheme to that used to calculate the photo-doubleionisation cross sections, the main difference being that the number of possible angular momentum states in the partial wave expansion is now much greater, due to the infinite range of angular momentum states of incoming electron. For each of these states we can use our knowledge of the S-matrix to remove any incoming wave components from the channel wavefunctions. We will consider treating the higher partial waves by using the method of Born closure, see for example (Whelan, 1986)

7. Summary

In this article we have outlined a new formalism for the calculation of atomic scattering processes with a particular emphasis on ionisation. One of the most important features of this formalism is that it treats the

two electrons in a symmetric manner. Another important feature is that the calculations are very computational efficient, due to the integrals involved in the evaluation of the basis functions being analytic. Results have been shown for elastic scattering of hydrogen but the next step is to calculate differential cross-sections for the photo-doubleionisation of He , H^- and the electron impact ionisation of atomic hydrogen. The formalism can be further applied to other systems provided the target is sufficiently described within the bounding hypersurface. All the necessary information required for propagation of the wavefunction can then be related, at the hypersurface, by the R -operator. Cross-sections can then be calculated from the propagated wavefunction.

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Table 1. Comparison of elastic scattering phase shift. The subscript a denotes the phase shifts calculated using the $\mathcal{R}$ -operator approach outlined here and the subscript b denotes calculations of (Schwartz, 1961) (Armstead, 1968)

k	1_a^S	1_b^S	3_a^S	3_b^S	$1P_a^O$	$1P_b^O$	$3P_a^O$	$3P_b^O$
0.1	2.5512	2.553	2.9175	2.938	0.0004	0.0070	0.0050	0.0114
0.2	2.0661	2.0673	2.6945	2.7171	0.0143	0.0147	0.0329	0.0450
0.3	1.6948	1.6964	2.4835	2.4996	-0.0096	0.0170	0.0905	0.1063
0.4	1.4142	1.4146	2.2944	2.2938	-0.0318	0.0100	0.1814	0.1872
0.5	1.2083	1.202	2.1120	2.1046	-0.0089	-0.0007	0.2733	0.2705
0.6	1.0523	1.041	1.9123	1.9329	-0.0312	-0.009	0.3277	0.3412
0.7	0.9242	0.930	1.7584	1.7797	-0.1149	-0.013	0.3889	0.3927

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Laboratory Synthesis of Astrophysical Molecules

A new UCL apparatus

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Abstract: A prototype apparatus has been constructed to study the synthesis of molecules on or within thin icy mantles under simulated interstellar, planetary and atmospheric environments. Molecular synthesis is stimulated by photon (4 - 13 eV lamp or synchrotron radiation), electron (< 20 eV) and ion (keV-MeV) irradiation. Products are probed by a combination of UV-Vis, FTIR and VUV spectroscopy. The first results of photoabsorption experiments of VUV irradiated water ice have shown evidence of photolysis and possible luminescence effects. These results are discussed and proposals for future experiments made

Key words: Astrobiology; Molecular Synthesis; Dust Grains; Interstellar Medium; Dissociative Electron Attachment; Photolysis

1. INTRODUCTION

To date over a hundred molecular species have been reported in the interstellar medium (ISM), in cometary tails, in planetary atmospheres, and on the surfaces of icy satellites within our Solar System. These molecules range in complexity from the simplest diatomics like H₂ and CO to larger molecules consisting of up to thirteen atoms. Interestingly, most of the molecules that have been observed are organic, many of which are found on earth and play an important role as constituents in biological processes. Some of the notable examples of organic molecules observed in the ISM are Formaldehyde, Acetic Acid (vinegar), Formic Acid (produced by ants), Glycolaldehyde, the simplest monosaccharide (Hollis 2000), and various alcohols including methanol and ethanol. There has also been a report of a

tentative discovery of Glycine, the simplest amino acid (Sorrell 2000). The discovery of Benzene last year is also very important in the study of interstellar PAHs (polycyclic aromatic hydrocarbons).

Molecular synthesis and destruction in the ISM is a never-ending cycle, driven by a large variety of processes ranging from highly energetic ionising events due to cosmic rays and stellar radiation, to the chemical reactions that occur at very low temperatures ($<20\text{K}$) in dense molecular clouds. The latter have become the subject of much recent research since the discovery of interstellar ices through the detection of infrared absorption spectra of deeply embedded protostellar objects. One such object that has provided substantial evidence and an inventory of interstellar ices is W33A (Allamandola 1987). However, as the fundamental vibrational modes of the molecules that constitute the astrophysical ices are in the mid-IR region, the observation of species is limited to those that have IR active vibrational transitions: i.e. transitions that undergo a change in the dipole moment during excitation.

In the 1980's a number of groups began laboratory research programmes to produce ice analogues that may be used in the interpretation of astrophysical spectra and in the understanding the processes involved in molecular synthesis within such environments (Allamandola 1987, Allamandola 1998, Gerakines 1996, d'Hendecourt 1985, Charnley 2001, and references therein). Despite this, there is still insufficient laboratory data to fully understand the processes involved in the formation of the observed species and their abundances.

Recent observations of organic molecules and ozone on icy bodies in the outer Solar System suggest heterogeneous processes that may be responsible for their formation. This is particularly interesting as until recently it was believed that the simultaneous discovery of Ozone and water on an exoplanet would provide a signature for biological processes. However this is not the case as possible mechanisms for abiotic formation of ozone have been shown following the discovery of ozone, through the detection of the Hartley band (255nm) on Rhea and Dione, two icy satellites of Saturn (Borget 2001).

Due to the universal nature of organic chemistry, it is now increasingly believed that the chemical building blocks of terrestrial life were synthesised in the dense molecular clouds, which are coincidently regions of star formation, and have provided the ingredients for the formation of the Earth and other planets within the protostellar environment. Comets and meteorites are believed to have provided the fundamental organic ingredients to the primitive Earth during the early bombardment era (Sorrell 1999, Charnley 2001). Thus, observation and interpretation of molecular formation in interstellar and circumstellar environments beyond our solar system may

provide clues about the chemical history of our own solar system. Furthermore, understanding the chemistry of our solar system during its formation and that of the primitive Earth, is of important astrobiological significance in terms of the identification of the source of biological precursors, and hence the chemical origin of terrestrial life.

This year, at University College London, we have developed an experimental apparatus to study various heterogeneous and bulk processes, on or within astrophysical ice analogues, as well as terrestrial atmospheric particles, by employing novel experimental techniques. We intend to investigate chemical processing of known ice mixtures under various sources of irradiation (electron, photon and ion) in different simulated cosmic environments which include both interstellar and solar system environments. The mechanisms that require investigation and current models will be outlined in § 3, and § 4 contains some of our preliminary results of photoabsorption experiments and proposed future experiments using this apparatus.

2. SURFACE CHEMISTRY IN SPACE

2.1 The Interstellar Medium

Solid phase chemistry in the ISM occurs in dense molecular clouds on surfaces of dust grains. These are small, micron-sized carbonaceous or silicate particles with temperatures of ~ 10 K. A proportion of the dust grains are covered in thin icy mantles (~ 0.02 μm thick) formed by accretion of gas phase atoms, molecules and radicals onto the cold grain surfaces. The dominant constituents of such ices have been identified, through mid-IR astrophysical absorption spectra, to be H_2O , CO , CO_2 , CH_3OH , H_2CO , CH_4 and NH_3 (Gerakines 1996, Charnley 2001, and references therein). The mantle composition depends on a number of factors such as dust grain surface structure, temperature and charge, as well as the local H/H_2 ratio; hydrogen being about 10^4 times more abundant than the next most abundant elements: O, C and N. With a higher proportion of atomic hydrogen, hydrogenation processes dominate where the light hydrogen atoms tunnel or diffuse across the surface and react with O, N, C and CO to form H_2O , NH_3 , CH_4 and CH_3OH respectively. In the case where molecular hydrogen dominates atoms react with one another forming molecules such as O_2 , N_2 ,

CO and CO₂. Thus ices on dust grains can roughly be classified into polar and non-polar types.

As grain mantles form they undergo chemical processing stimulated by photon, electron and ion impact which arise from stellar radiation, photoelectrons or secondary/tertiary electrons and cosmic rays. Thus more complex molecules are formed, via the formation of radicals and ions by dissociation. The radical-radical reactions require almost no activation energy, but the radicals may remain trapped within the icy matrix until external energy is provided to release them. This may be provided via collisions between grains or from a shock in the cloud, which may be due to a nearby supernova explosion. Radical-molecule and ion-molecule reactions may occur if sufficient energy is supplied to overcome the activation barriers.

The ice mantles evolve with time, as more atoms or molecules adsorb and are processed either on the surface or within the bulk of the mantle, to form a quasi-layered structure, where the more complex organic molecules form an inner mantle, which is shielded from destructive radiation by an outer mantle consisting of volatile ices. Some of the molecules may return to the gas phase by desorption or grain explosions where sufficient chemical energy is stored within the mantle and its sudden release may be triggered by grain collisions. Thus the gas phase molecular composition may be enriched by molecules originally formed in the solid phase on grain surfaces.

2.2 The Solar System

Within our own solar system surfaces for heterogeneous chemistry are found on the icy satellites of the outer planets, on asteroids, on interplanetary dust and planetary rings. The chemistry within our solar system is driven by ion, photon and electron collisions. Ion collisions with the surfaces of icy satellites in the outer solar system play an important role in molecular synthesis. The surfaces of comets, which are thought to be comprised of interstellar ices and dust (Allamandola 1988), are heavily processed in the Kuiper belt or the Oort cloud by cosmic rays, a high proportion of which are protons. Unlike other cosmic ices, cometary composition is interpreted from spectroscopy of gas-phase molecules in the cometary tails that form as a comet approaches the sun. A high proportion of the identified molecules is thought to reflect the composition of the cometary nucleus, although other species may be formed by gas-phase collisions between species within the cometary tail, or UV processing (Strazulla 2001).

2.3 Mechanisms

Within the scope of investigations at this stage we will only consider chemistry on ice layers that have already been formed and neglect for instance the bare interstellar grain-surface structure, and hence, the substrate structure. As molecules continue to adsorb to ice surfaces, reactions may occur on the surface, at the solid-gas interface, or within the bulk of the ice mantles. The dominant constituent of cosmic ices is H_2O which has been observed in both amorphous and crystalline form in the ISM. The nature of water ice is directly related to the temperature (Seiger 2000). Amorphous ice is formed at temperatures below 100-130 K, depending on the deposition rate. Crystalline ice is formed at higher temperatures and amorphous ice crystallises upon heating. This is important in determining the nature of the surface upon which reactions take place.

The important parameters associated with adsorption are binding energies, surface mobility of molecules/ions/electrons on the surface and sticking coefficients of molecular species.

2.3.1 Photon irradiation of ices

The icy mantles of dust grains in the outer regions of molecular clouds are continuously irradiated by stellar UV, with a mean interstellar flux of $\sim 10^8$ photons $\text{cm}^{-2}\text{s}^{-1}$ (Hagen 1879). However, within the centre of some dense molecular clouds, where stellar UV cannot penetrate, the main source of photons is from cosmic ray induced luminescence of H_2 . The UV flux in these cold dark clouds is estimated to be 10^3 - 10^4 photons $\text{cm}^{-2}\text{s}^{-1}$ (Sorrell 2000). The UV radiation photolyses the molecules within the mantles forming highly reactive species such as: H, OH, NH_2 , CH_3 and CHO radicals. The energy range required for photolysis is 4-13.6 eV. These radicals remain frozen in the icy matrix until they are released following a heating episode which may occur as a result of a grain-grain collision, a shock wave within the cloud or cosmic ray bombardment.

Molecular synthesis within photon irradiated ices has been studied extensively by a number of groups (for example Allamandola 1987, Gerakines 1996, and references therein).

2.3.2 Electron irradiation of ices

Low energy electron impact with ice layers plays an important role in molecular synthesis under high vacuum conditions, by opening up reaction channels that are otherwise not possible with photon induced reactions.

These may arise from transitions that are otherwise optically forbidden and via the formation of anions.

The following reaction scheme becomes possible via the capture of a low energy electron (<20 eV), which may be a photoelectron or a secondary electron:



This is then followed either by:

- a) Electron autodetachment,
- b) Dissociation into a stable anion and a neutral fragment, known as Dissociative Electron Attachment (DEA), or
- c) Stabilisation of the transient molecular anion to ground state forming a stable molecular anion.

The products may remain within the bulk of the mantle or desorb off the surface. Some of the products that remain on the surface may subsequently photodesorb. Desorption rates may be measured experimentally by measuring the gas phase concentration of species.

DEA is known to play an important role in terrestrial atmospheric chemistry on polar stratospheric cloud particles in the formation and destruction of Ozone.

2.3.3 Ion-irradiation of ices

Ion processing of ices dominates surfaces of the satellites of the outer planets in our solar system where the UV flux is comparably low and the ion source is magnetospheric rather than from a galactic cosmic ray source (Moore 2001). The inner satellites of Jupiter (Europa, Ganymede and Callisto), as they orbit within the planet's magnetosphere, are constantly bombarded with ions. Results from the International Ultraviolet Explorer have shown a change in albedo of the surfaces of these satellites as a function of longitude (Noll 1996). This variation in albedo can be explained in terms of the variation of ion flux, in the Jovian magnetosphere, between the leading and trailing hemispheres of the satellites as they orbit the planet. The ion collisions with the ice surfaces chemically alter the composition of ice and thus their reflectance properties.

There is also evidence (Dumas 2001) that Pluto's satellite Charon, which is mostly covered with water ice, contains other species due to ion-surface reactions with ions that escape Pluto's atmosphere.

3. THE UCL APPARATUS

The apparatus has been designed to employ a wide range of spectroscopic techniques, including UV-Vis, FTIR, VUV and mass spectrometry, and utilise a variety of different sources of irradiation. Most of the electron and photon irradiation experiments are performed on site at UCL. Synchrotron experiments are conducted either at the Daresbury Synchrotron Facility, UK, or the Storage Ring Facility at Aarhus University, Denmark. Ion irradiation experiments will be performed at the research accelerator facilities at Queen's University Belfast.

3.1 Experimental Design

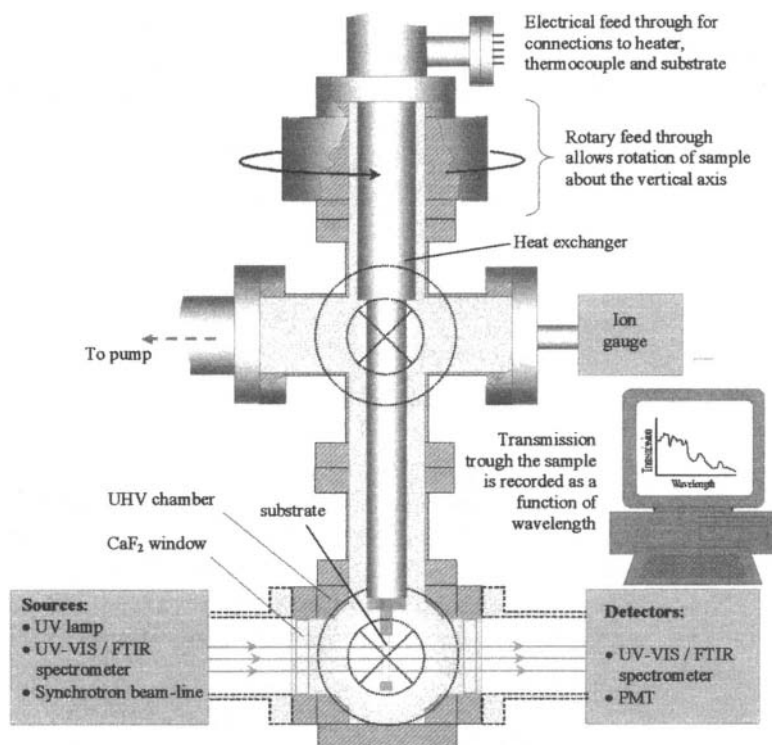


Figure 1. The Experimental Set-up

The apparatus, shown in Figure 1, consists of a very simple UHV system. A pressure of $\sim 10^{-8} - 10^{-10}$ mbar is maintained by means of a turbo-

molecular pump, which is backed by a rotary pump. However this is still a million times denser than the densest regions of interstellar space! The ice layers will be created by vapour deposition directly onto either a UV or IR transmitting substrate.

At this stage in our investigations, the structure of the substrate (grain surface) is ignored, provided that the layers of ice deposited are thick enough to ignore any structural effects influenced by the substrate structure. This is a good approximation for experiments involving the investigation of synthesis within the bulk or upon the surface of a pre-formed mantle.

The substrate is in physical contact with a continuous flow liquid Nitrogen/Helium cryostat. The choice of cryogen, along with a variable resistive heater, allows for any desired sample temperature to be attained between 10K and 300K. The sample temperature is monitored with a Copper-Constantan thermocouple which is in contact with the substrate.

The substrate window is situated in the centre of a cubical chamber and can be rotated through 360°, about the vertical axis, to one of four desired ports. The ports are used to mount transmitting windows (for spectroscopy and UV irradiation), the electron gun, the gas inlet system and other analytical instruments such as a mass spectrometer. The set-up can easily be adapted for use in a synchrotron beamline or an ion accelerator.

3.2 Experimental Procedure

3.2.1 Sample preparation and deposition

The ice samples will be prepared by vapour deposition directly onto a pre-cooled substrate. The temperature of the substrate and rate of gas deposition will determine the nature of the ices formed. The thickness of ice samples may be determined in two ways: by measuring the deposition rate of vapour of known concentration onto a known surface area, and determining the path-length during deposition by transmission spectroscopy, using the Beer-Lambert Law.

3.2.2 Sample irradiation

Once the ice samples are deposited they will be irradiated either by photons, electrons or ions. A photon source can be either a lamp or synchrotron radiation. In the former case the lamp is mounted onto one of the viewports during irradiation and removed during spectroscopy

measurements. In the latter case the entire apparatus is bolted onto a synchrotron beamline system with a monochromator, and the same source is used both for irradiation and spectroscopy. The advantage of using a synchrotron source to a UV lamp is that it is continuously tuneable and closely matches stellar radiation. Additionally, using a grating monochromator allows flexibility in selecting a particular wavelength for irradiation, e.g. to break a particular bond within an ice mixture, or zero order light which includes all wavelength of synchrotron radiation. In the laboratory frame, an hour of irradiation is equivalent to 1000 years of irradiation in the ISM!

Low energy electrons (<20eV) are produced by a mini-electron gun, designed and built at UCL. The electron gun is mounted within the experimental chamber ~2cm from the surface. For these experiments a silver coated substrate is used. The surface is electrically isolated from the rest of the apparatus and surface current can be measured via conduction wires that are mounted in contact with the silver layer.

Ion irradiation experiments will be conducted at Queen's University Belfast where the chamber will be mounted directly onto a beamline of an ion accelerator.

3.2.3 Spectroscopy

Once a sample has been irradiated, photoabsorption studies are used as an analytical tool, both to monitor sample thickness and probe for products. At present we use a combination of UV-vis, FTIR and VUV transmission spectroscopy. The product yield may be determined by measuring changes in the relative cross-sections of parent and product molecules, following fixed periods of successive irradiation, using the Beer-Lambert Law.

Measurement of ice surface albedo will be performed using reflection techniques, where the UV source and detector will be placed at 90° to each other and the reflected intensities compared before and after irradiation.

4. RESULTS AND DISCUSSION

4.1 Photoabsorption of UV irradiated H₂O ice

First experimental results were taken at the Daresbury Synchrotron Facility. Liquid nitrogen cooled water ice samples were irradiated with zero-order synchrotron radiation for several hours. Absorption spectra, recorded

at various time intervals during continuous sample irradiation, are shown in Figure 2.

Three features became apparent as successive spectra were taken in the 150–450 nm range: a 200 nm peak, which grew as a function of the irradiation time, a shoulder at 240 nm, which also became more prominent the longer the sample was irradiated, and a ‘negative absorbance’ feature at 370 nm. The 200 nm peak and the shoulder at 240 nm may be attributed to the described characteristic features of the H and the OH radical formation following photolysis of water ice (Langford 2000).

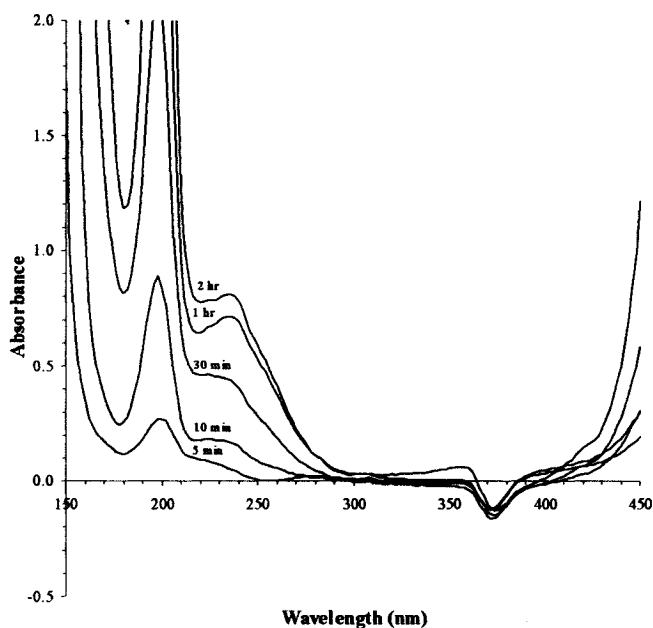


Figure 2. First results of photon irradiated ice.

The negative absorbance feature at 370 nm in the absorption spectrum translates to an emission feature. The origin of this reproducible feature is not understood, but may be attributed to luminescence from the photoproducts in UV the photolysed ice (Langford 2000). It is speculated that a luminescence feature in this region may be due to the recombination of O atoms in the ice to form an excited state of O₂ (Langford 2000, Trotman 1986). Luminescence in this region has also been reported in electron-irradiated ice. We will be investigating this feature in greater detail for both photon and electron irradiated ices for different ice phases, under different

simulated cosmic environments. Luminescence has also been reported from mixtures of UV irradiated ice samples during warm up (10–45K) (Hagen 1979). Luminescence from irradiated ices may prove to be a useful astrophysical tool if such effects can be ‘seen’ in interstellar ices.

4.2 Future Experiments

Preliminary test experiments are currently being undertaken and the apparatus is being tested to support various desired conditions. As a first experiment of molecular synthesis, water ice with co-adsorbed oxygen will be irradiated with electrons to form ozone, which can easily be identified by the characteristic Hartley band (254 nm). Also, the possibility of ozone formation from irradiated CO₂ ice will be investigated, with relevance to Martian polar ice caps.

A similar experiment will be performed at Queen’s University Belfast using an ion irradiation source. In these experiments ice samples will be irradiated with H⁺, He⁺ ions in the MeV range. The intensity of reflected UV light in the Hartley band range will be measured and thus ozone production may be monitored, measurements of albedo of the surface will also be undertaken.

Future experiments will involve irradiation of mixtures of ices or molecules adsorbed on water or other ice, under various temperatures, to probe for molecular products. Measurements of adsorption and desorption rates, and of sticking coefficients will be made for various species. Attempts will be made to determine activation barriers and product yield for a number of reactions.

5. CONCLUDING REMARKS

The new apparatus has been built to study the formation of molecules on or within ice layers, under environments that are analogous to those of the interstellar medium, cometary tails, surfaces of satellites or planetary and terrestrial atmospheres. Results of photoabsorption and albedo measurements of ion, electron and photon irradiated ices will be of great astrobiological and atmospheric/environmental significance. New results will be interpreted to better understand the mechanisms involved and to calculate important parameters pertinent to surface chemistry under cold temperature, low pressure environments.

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