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Slobodan Danko Bosanac

Electromagnetic Interactions

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Preface

Electromagnetic field carries the bulk of information about the structure of matter, atoms and molecules, nuclei or even elementary particles. Theory in this respect has the basic task: to retrieve this information from the available data that are obtained from experiments. The task is, therefore, finding a connection between the density of charges and the intensity of emitted radiation that they produce when subjected to external agitation; in short the task is solving the inverse intensity problem. However, the task as described is not that simple, although the problem of direct inverse intensity problem is immensely difficult one to solve. Charges that one discusses are basically electrons and protons, or their conglomerates, but they are quantum objects for which the concept of charge density must be fundamentally modified from that for classical charges. Electrons and protons are individually, as classical objects, point-like charges but as quantum objects they must be treated as delocalized particles and therefore treated as charge densities. The problem, however, is more difficult than that, because being treated as delocalized particles they are described essentially by probability densities and therefore by assuming that as charge densities must be taken with great caution. There are circumstances when probability density could be treated as charge density but there are when this is not a correct assumption. The choice when and how to distinguish between these two concepts, probability density versus charge density, depends on the problem to analyze, which is also sometimes not a simple task.

There are essentially four problems to analyze in electromagnetic interactions. One is dynamics of charges under the impact of electromagnetic force, another is radiation that is produced by moving charges, the third is structure of conglomerates of charges, and the fourth is the problem of field interaction, essentially unification of electromagnetic force and the force that results from radiation. All of these problems have been thoroughly studied, perhaps with exception of the last one, however, extreme states under which charges are placed, extreme states of electromagnetic field that interact with charges and fine details of this interaction have room for further investigations. Placing the field and charges under extreme conditions requires theoretical tool that adequately could describe these situations.

Relativistic classical and quantum theory are the foremost tools, description of electromagnetic field of finite extent in all dimensions, and also having accurate description in nonrelativistic theoretical tools.

Electromagnetic field itself is also essential to be understood because this has direct impact on how from experiments one interprets structure of matter. The basic principles of electrodynamics are well established, but with the development of quantum principles and applied on the scale of atoms and smaller another of its feature emerged, which is universally accepted: electromagnetic interaction is mediated by photons, manifestation of particle-like interaction on charges. Origins of the idea for the particle nature of electromagnetic field go back to explaining black body radiation, photoelectric effect, and finally the Compton effect. Success of the model is undisputable but there are limitations on how far it could be applied, for example in the case of very strong electromagnetic fields. There is an obvious question and this is what is the true nature of the photon model, because despite successful in explaining many features of matter there are some limitations of it, for example in interpretation of the Coulomb law as exchange of photons among charges. The answer to this question is not yet clear, and it should be found with in-depth understanding of solutions of the basic equations of dynamics: Dirac and Maxwell equations, coupled with the relativistic classical equation for particles.

Those four mentioned problems are investigated in this book, by giving qualitative description to get their essence before applying exact tools and these are equations for electromagnetic field and both classical and quantum dynamics, and relativistic and nonrelativistic, for charges. Separate discussion is on equations for relativistic dynamics, Maxwell and Dirac equations, as the essential tools for investigating the charges under extreme confinements and their interaction with the electromagnetic field. The basic tool for describing photon interaction with matter, quantum electrodynamics, is not used; however, it is mentioned in the context when the particle-like exchange of electromagnetic interaction is encountered.

Zagreb, Croatia Slobodan Danko Bosanac

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About the Author

Prof. Slobodan Danko Bosanac graduated in Theoretical Physics from the University of Zagreb in 1968 and received Ph.D. from the University of Sussex, UK, in Molecular Sciences in 1972. After postdoctoral research at the University of Bristol, UK, in 1974, he obtained a research position at the R. Boskovic Institute, Zagreb, which had been since then his permanent domicile institution. During his research carrier, he published around 100 papers, three books and was principal investigator in several international science projects. Professor Bosanac was visiting professor at a number of universities: University of Florida, University of Kaiserslautern, MPI fur Stromungsforschung in Gottingen, University of Sussex, Harvard University, MIT, Universidade Federal de Minas Gerais, to mention a few. For his research, he received two state prices in science, in 1997 and 2013.

His field of research is atomic and molecular physics, electromagnetic interaction with charges, astrophysics. In 1986, he initiated interdisciplinary conferences under a general title, Brijuni Conferences, that since then has run continuously on a biannual basis. Professor Bosanac is the President of the Croatian branch of the US-based organization Center for Inquiry whose primary aim is promotion of science. He was also recently appointed Head of the Swiss Space Systems branch for Croatia, with a general aim of setting up Space Center Croatia with the central object, the Space Port.

Chapter 1
Introduction

Abstract Properties of electrons and protons, as the basic charged elements of matter, are briefly reviewed. The concept of charge and the quantum probability densities is examined and discussed under what circumstances the two are identical. Charge density and resulting properties of molecules is reviewed, together with describing adiabatic expansion for calculating their structure. Particular emphases is to derive non adiabatic coupling among the electron states of molecules.

1.1 Properties of Elementary Charges

Elementary particles of importance are the electron, proton and neutron. The electron and proton are carriers of electric charge,[1]

$$e = 1.60217733 \times 10^{-19}\,\mathrm{C}$$

whilst neutron is neutral. However, in addition to charge these particles are also carriers of magnetic dipole but their values differ from one particle to the other. Their values are

$$m_e = 9.2847701 \times 10^{-24}\,\mathrm{JT}^{-1}$$
$$m_p = 1.41060761 \times 10^{-26}\,\mathrm{JT}^{-1}$$
$$m_n = 9.6623707 \times 10^{-27}\,\mathrm{JT}^{-1}$$

The theory predicts that neutron, based on the evidence that it has internal structure, should have a small electric dipole moment, but so far there is no strong experimental evidence for it. Therefore for any practical purpose one could assume (for the electron and proton predicted moment is even smaller) that the particles do not have this dipole moment, although from the conceptual point, and also for the consequences, yes or no is very important. However, neutron and proton might have internal distribution of charge density [20], about which there will be here more discussion.

[1] SI units are used in this section.

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A charge at rest produces static *electric component* of the *electromagnetic field*, the Coulomb electric field

$$\overrightarrow{E} = \frac{e}{4\pi\varepsilon_0 r^2}\widehat{r} \tag{1.1}$$

where $\varepsilon_0 = 8.854187817 \times 10^{-12}\,\mathrm{Fm}^{-1}$ is permittivity of the vacuum, and the sign $\widehat{}$ indicates the unit vector. On the other hand *magnetic dipole* $\vec{m}$ at rest produces a static *magnetic component* of the electromagnetic field

$$\overrightarrow{B} = \frac{\mu_0}{4\pi r^3}\left[3\left(\overrightarrow{m}\cdot\widehat{r}\right)\widehat{r} - \overrightarrow{m}\right] = -\frac{\mu_0}{4\pi}\nabla\times\left(\overrightarrow{m}\times\nabla\frac{1}{r}\right) = \nabla\times\vec{A} \tag{1.2}$$

where

$$\vec{A} = \frac{\mu_0}{4\pi}\overrightarrow{m}\times\frac{\widehat{r}}{r^2}$$

and $\mu_0 = 1.2566370614 \times 10^{-6}\,\mathrm{NA}^{-2}$ is permeability of the vacuum.[2] The *force* that the two components of the electromagnetic field produces on another particle with charge q and magnetic dipole moment $\vec{n}$ could be written as

$$\overrightarrow{F}_{eb} = -\nabla\, V_{eb} \tag{1.3}$$

where the *potential energy* is

$$V_{eb} = V_c + V_d$$

The first term is the *Coulomb potential*

$$V_c = \frac{qe}{4\pi\varepsilon_0 r}$$

whilst the second is the *magnetic dipole potential*

$$V_d = -\frac{\mu_0}{4\pi}\,\vec{n}\cdot\nabla\frac{\left(\overrightarrow{m}\cdot\widehat{r}\right)}{r^2}$$

The magnetic dipole potential energy is in general much smaller than the Coulomb potential energy, however, at short distances the former increases more rapidly due to its r^{-3}dependence. For the electrons one can make an estimate of the relative importance of the two forces by writing the total potential energy as

$$V_{eb} = \frac{e^2}{4\pi\varepsilon_0 r} + \frac{\mu_0}{4\pi r^3}\left(\frac{e\hbar}{2M}\right)^2\eta$$

[2]Magnetic induction $\overrightarrow{B}$ (Tesla) and the magnetic field $\overrightarrow{H}$ (Ampere/Meter) are related by $\mu_0\overrightarrow{H} = \overrightarrow{B}$.

where η is of the order 1, and $\frac{e\hbar}{2M}$ is approximate magnetic dipole of the electron (Bohr magneton). The potential energy can be written in another form

$$V_{eb} = \frac{e^2}{4\pi\varepsilon_0 r}\left(1 + \frac{1}{4r^2}\frac{\hbar^2}{c^2 m_e^2}\right)$$

where the relationship

$$\mu_0\varepsilon_0 = \frac{1}{c^2}$$

was used. The contribution from the magnetic dipole becomes significant when

$$\frac{1}{4r^2}\frac{\hbar^2}{c^2 m_e^2} \approx 1$$

or

$$r = \frac{\hbar}{2cm_e}$$

The Coulomb energy at this distance is

$$W_c = \frac{1}{2\pi}\frac{cm_e e^2}{\hbar\varepsilon_0} \approx 7500 \text{ eV}$$

which means that in the collisions above this energy one should consider also the contribution of the magnetic dipoles of the particles to the cross sections.

Classical equations of motion that are based on the force (1.3) are not complete without equation that couples rotation of the magnetic dipole due to the *torque* that magnetic field exerts on it. The additional equation is

$$d_t\vec{m} = \gamma\vec{m} \times \overrightarrow{B}$$

where γ is a factor that relates spin to the magnetic dipole. For the three elementary particles this factor is derived from the fact that they have spin $\hbar/2$ and from the Bohr magneton one obtains

$$\gamma_{electron} = 1.001\,2\frac{e}{M_{electron}}$$
$$\gamma_{proton} = 2.792\,8\frac{e}{M_{proton}}$$
$$\gamma_{neutron} = 1.915\,7\frac{e}{M_{neutron}}$$

The additional factors indicate that the Bohr magneton is only approximate value for the magnetic dipole of the elementary particles with the half spin, except for the electron for which it is given relatively accurately.

1.2 Charge Density in Molecules

Although the constituents of a molecule are protons, electrons and neutrons it is only the former two that play the essential role in the interaction with the electromagnetic field. The neutrons change the overall magnetic dipole of the nuclei and as such they are important when this type of interaction is investigated. The protons are localized in the nuclei, which, for all practical purpose, could be regarded as the point like objects with the well defined position (this statement must be taken with a caution and is only relevant for the calculation of the density of charges in molecules). The electrons, on the other hand, are delocalized over a molecule, and their position can only be satisfactory defined through the probability density

$$P(\vec{r}_1, \vec{r}_2, \vec{r}_3, \ldots, \vec{r}_n) = |f(\vec{r}_1, \vec{r}_2, \vec{r}_3, \ldots, \vec{r}_n)|^2$$

where $f(\ldots)$ is the probability amplitude (wave function) for the system of n electrons. It gives the probability density of finding electron 1 at the position $\vec{r}_1$, electron 2 at $\vec{r}_2$ etc. However, the probability density of finding electron j at $\vec{r}_j$, irrespective of the whereabouts of the other electrons, is given by

$$P(\vec{r}_j) = \int |f(\vec{r}_1, \vec{r}_2, \vec{r}_3, \ldots, \vec{r}_n)|^2 \; d^3r_1 d^3r_2 \ldots d^3r_{j-1} d^3r_{j+1} \ldots d^3r_n$$

which could be associated with the charge density for this electron, meaning that it could not be treated as a true charge density. Contribution of this electron to the overall Coulomb potential at $\vec{r}$ that comes from the other electrons and the nuclei is then given by

$$V_c^j = -e \int \frac{P(\vec{r}_j)}{|\vec{r} - \vec{r}_j|} d^3r_j$$

which, strictly speaking, should be interpreted as the average potential from the j-th electron. However, this expression is identical with the potential when $P(\vec{r}_j)$ is a charge density and therefore the probability density could be also associated with a charge density of the j-th electron. The difference between the true charge density and the probability density that plays the role of it is in the self repulsion term. The true charge density has a self repelling term that tends to make it unstable, whilst the probability density has no such term.

1.2.1 Self Energy of Hydrogen Atom

Hydrogen atom is a system of proton and the electron, and in the simplest approximation is that proton is at a precise position whilst the electron is delocalized. Electric potential of the proton is given by Coulomb law for a point charge, whilst that of the

electron should be calculated from the assumption that the probability density is also charge density. Therefore, the overall potential of the hydrogen atom at the distance r from the proton, for the electron in the ground state, is given by

$$V(r) = \int d^3r' \frac{P(r')}{|\vec{r} - \vec{r}\,'|} = \frac{\alpha^3}{2\pi^3} \int d^3r' \int d^3k \, \frac{e^{i\,\vec{k}\cdot(\vec{r}-\vec{r}\,')}}{k^2 + i\,\eta} e^{-2\alpha\,r'}$$

where α is the fine structure constant, and the identity

$$\frac{1}{|\vec{r} - \vec{r}\,'|} = \frac{1}{2\pi^2} \int d^3k \, \frac{e^{i\,\vec{k}\cdot(\vec{r}-\vec{r}\,')}}{k^2 + i\,\eta} \tag{1.4}$$

is used. The potential is finally

$$V(r) = \frac{1}{r} - \frac{1 + \alpha r}{r} e^{-2\alpha r}$$

If the probability density is the charge density then this potential could be used to calculate self repulsion energy for the electron, and add it as the correction to the basic equation for Hydrogen atom. This energy is

$$V_{self} = \frac{\alpha}{2} \int d^3r' \, d^3r \, \frac{P(r)P(r')}{|\vec{r} - \vec{r}\,'|}$$

and by using (1.4) the final expression is

$$V_{self} = 4\alpha\pi^2 \int dr' \int dr \; r \; r' \left(r + r' - \left|r - r'\right|\right) P(r) P(r')$$

The ground state of Hydrogen atom is then solution of the radial equation

$$e\; g(r) = -\frac{1}{2} g''(r) - \frac{\alpha}{r} g(r) + \frac{1}{4} \alpha \int dr' \, dr'' \, \frac{\left(r'' + r' - \left|r'' - r'\right|\right)}{r''\, r'} g^2(r'') g^2(r')\, g(r)$$

which is an integro-differential equation. One way of solving it is by iteration, where in the first step the uncorrected probability density is used to calculate the self repelling term and in the next iteration calculate new ground state probability amplitude. The iteration is repeated until the ground state eigenenergy e converges. For Hydrogen atom this eigenenergy is $e = -0.187\ \alpha^2$, which should be compared with $e = -0.5\ \alpha^2$ when the correction is not included. The difference is sufficient to dismiss the assumption that the probability density is the charge density. However, if another charge is placed in the field of this Hydrogen atom then its potential energy agrees very well with the observations.

1.2.2 Charge Density in Molecules

Molecules are neutral species but in most of them certain sites around atoms have slight excess of positive or negative charge. For example proton in a water molecule are slightly positively charged whilst oxygen atom is negatively charged, or Hydrogen atom in the HF molecule is slightly negatively charged whilst Fluorine is positively charged. Determining the amount of charge at the sites of a molecule is of importance in various circumstances (for example in calculating radiation by a rotating molecule Sect. 7.3.2) and therefore it is necessary to define what is meant by it. However, there is a problem with this task because positive charges are well localized in atoms whilst negative are essentially delocalized all around a molecule. The problem is well described if one asks a question what is charge density within Hydrogen atom? (here the assumption is that proton is localized at a fixed point whilst when it is not shall be discussed in Sect. 1.2.3). The answer appears simple, away from proton (nucleus) charge density is that of the probability density for the electron, which is formally correct and hence the question for a molecule seems solved. This, however, is not what is meant by charge density for a molecule, because it is defined as an effective amount of charge that a test charge experiences when approaching it. Another aspect of the concept of effective charge density is a nonuniform moving molecule, for example a rotating one. Resulting radiation comes as superposition of the individual motion of charges, nuclei and the electrons, however, it could be approximately treated by assuming that each atom is a charged particle having some effective charge. The overall charge density of a molecule is deduced from the calculation of the total potential due to all charges, and it is given by

$$V = -e\sum_{j=1}^{n}\int \frac{P(\vec{r}_j)}{|\vec{r}-\vec{r}_j|}d^3r_j + \sum_{i=1}^{N}\frac{e_i}{\left|\vec{r}-\vec{R}_i\right|}$$

where $\vec{R}_i$ is position of the i-th nuclei (e.g. with respect to the centre of mass of molecule), and the number of electrons n is equal to the number of protons, i.e. $ne = e_1 + \cdots + e_N$. Because of the symmetry between electrons one has the identity

$$P(\vec{r}_j) = P(\vec{r}_k)$$

for any pair, then

$$V = -ne\int \frac{P(\vec{r}_1)}{|\vec{r}-\vec{r}_1|}d^3r_j + \sum_{i=1}^{N}\frac{e_i}{\left|\vec{r}-\vec{R}_i\right|} \tag{1.5}$$

and therefore the charge density in a molecule due to the electrons is

$$\rho(\vec{r}) = -neP(\vec{r}) = -ne\int |f(\vec{r},\vec{r}_2,\vec{r}_3,\ldots,\vec{r}_n)|^2\ d^3r_2\ldots d^3r_n$$

In a number of circumstance it is useful to define effective charge that one associates with an atom in a molecule, in particular atoms that are on its surface. One starts by noting that the excess of electron charge density is localized around a particular atom, and its extent is smaller than the distance of this atom to the centre of mass of a molecule. Therefore one expands potential (1.5) as

$$V \approx -e\sum_{j=1}^{n}\int \frac{P(\vec{r}_j)}{r}\left(1+\frac{\vec{r}\cdot\vec{r}_j}{r^2}\right)d^3r_j + \sum_{i=1}^{N}\frac{e_i}{\left|\vec{r}-\vec{R}_i\right|}$$
$$= \frac{\vec{r}\cdot}{r^3}\left[\sum_{i=1}^{N} e_i\vec{R}_i - ne\int P(\vec{r}_j)\vec{r}_j d^3r_j\right]$$

which has a form of potential for an electric dipole, where the dipole has the value

$$\overrightarrow{p} = \sum_{i=1}^{N} e_i\vec{R}_i - ne\int P(\vec{r}_j)\vec{r}_j d^3r_j = \sum_{i=1}^{N} q_i\vec{R}_i$$

The parameter q_i is associated with the effective charge on atom i, and its value is calculated by the least square fit, in which case they are solutions of the set of equations

$$\sum_{i=1}^{N} q_i\vec{R}_k\cdot\vec{R}_i = \sum_{i=1}^{N} e_i\vec{R}_k\cdot\vec{R}_i - ne\int P(\vec{r}_j)\vec{R}_k\cdot\vec{r}_j d^3r_j$$

In an external electric field, which is represented by the potential $V_{ext}(\vec{r})$, a molecule has potential energy

$$W = -ne\int \rho(\vec{r})V_{ext}(\vec{r})\,d^3r + \sum_{i=1}^{N} e_i V_{ext}(\vec{R}_i)$$

In those circumstances when variation of the external field over the size of a molecule is small one can write approximately

$$V_{ext}(\vec{r}) \approx V_{ext}(\vec{R}_c) + \left(\vec{r}-\vec{R}_c\right)\cdot\nabla\, V_{ext}(\vec{R}_c)$$

where $\vec{R}_c$ is position of a point within the molecule, for example it is its centre of mass. The first term in the expansion, for a neutral molecule, gives

$$W_0 = -ne\int \rho(\vec{r})V_{ext}(\vec{R}_c)\,d^3r + \sum_{i=1}^{N} e_i V_{ext}(\vec{R}_c)$$
$$= -neV_{ext}(\vec{R}_c)\int \rho(\vec{r})d^3r + V_{ext}(\vec{R}_c)\sum_{i=1}^{N} e_i = 0$$

where the condition

$$\int \rho(\vec{r}) d^3 r = 1$$

was used.

The next term gives

$$W_1 = -ne \int \rho(\vec{r}) \left(\vec{r} - \vec{R}_c\right) \cdot \nabla \, V_{ext}(\vec{R}_c) \, d^3 r + \sum_{i=1}^{N} e_i \left(\vec{r} - \vec{R}_c\right) \cdot \nabla \, V_{ext}(\vec{R}_c)$$

$$= \left[-ne \int \rho(\vec{r}) \left(\vec{r} - \vec{R}_c\right) \, d^3 r + \sum_{i=1}^{N} e_i \left(\vec{r} - \vec{R}_c\right) \right] \cdot \nabla \, V_{ext}(\vec{R}_c)$$

which can be written as

$$W_1 = \vec{d} \cdot \nabla \, V_{ext}(\vec{R}_c)$$

The vector $\vec{d}$ is the *permanent dipole moment* of the molecule.

There are several objections with the previous derivation: (a) variation of the external field over a molecule may not small, (b) whilst definition of a permanent dipole is well defined for small, say a diatomic, molecule, for large ones may not have meaning, and (c) definition of a permanent dipole moment assumes that the probability amplitude (wave function) for the electrons is unaffected by the external field. This is never true, but in many circumstances this effect is negligible.

1.2.3 Charge Density in Hydrogen-Like Atom

Delocalization of two oppositely charged particles, one having mass m_1 and the other mass m_2, that are bound by a force produce charge density. The stationary bound state problem is solved in the centre of mass system, and for the relevant coordinates, which are defined as

$$\vec{r} = \vec{r}_1 - \vec{r}_2; \quad \vec{R} = \frac{m_1 \vec{r}_1 + m_2 \vec{r}_2}{m_1 + m_2}$$

the probability amplitude for the system is

$$\psi\left(\vec{r}, \vec{R}\right) = f\left(\vec{r}\right) g\left(\vec{R}\right)$$

The charge density is then defined as (particle 1 has positive charge $e = 1$)

$$\rho\left(\vec{s}\right) = \int d^3 r_2 \left| f\left(\vec{s} - \vec{r}_2\right) g\left(\frac{m_1 \vec{s} + m_2 \vec{r}_2}{m_1 + m_2}\right) \right|^2$$

$$- \int d^3 r_1 \left| f\left(\vec{r}_1 - \vec{s}\right) g\left(\frac{m_1 \vec{r}_1 + m_2 \vec{s}}{m_1 + m_2}\right) \right|^2$$

and it is a function of the coordinates $\vec{s}$.

The coordinates are scaled with the Compton wave number $\kappa = mc/\hbar$, where m is reduced mass

$$m = \frac{m_1 m_2}{m_1 + m_2}$$

of the two particles, in which case they are dimensionless, and for a Hydrogen-like atom particle 1 is proton and particle 2 is a negatively charged particle. The ground state probability amplitude is

$$f(\vec{r}) = Ne^{-\alpha r}$$

but for the probability density for the centre of mass one takes delta function[3]

$$\left|g\left(\vec{R}\right)\right|^2 = \delta\left(\vec{R}\right)$$

The last choice means that the charge density is defined for a system that is localized at the origin as a point-like particle. The radial charge density is now

$$\rho(s) = \left(1 + \frac{m_1}{m_2}\right)^3 s^2 \left| f\left[\left(1 + \frac{m_1}{m_2}\right)\vec{s}\right]\right|^2 - \left(1 + \frac{m_2}{m_1}\right)^3 s^2 \left| f\left[\left(1 + \frac{m_2}{m_1}\right)\vec{s}\right]\right|^2$$

and for the Hydrogen-like atom it is

$$\rho(s) = \frac{\alpha^3 s^2}{\pi}\left(1 + \frac{m_1}{m_2}\right)^3 e^{-2\alpha\left(1+\frac{m_1}{m_2}\right)s} - \frac{\alpha^3 s^2}{\pi}\left(1 + \frac{m_2}{m_1}\right)^3 e^{-2\alpha\left(1+\frac{m_2}{m_1}\right)s}$$

Typical charge densities are shown in Fig. 1.1 for two examples (in the appropriately scaled coordinates). If negatively charged particle is muon, which has comparable mass with the proton, the charge density has two pronounced extremes, one for the positive charge and the other for the negative (lower graph). On the other hand, if mass of negatively charged particle is that of the electron then positive charge density is concentrated in close proximity of the origin (upper graph). More realistic analysis that involves relativistic dynamics is discussed in Sect. 5.4.3.

1.2.4 Electric Dipole of Molecules

Electric dipole moment of a molecule changes when external field on a molecule is applied, and it is called induced electric dipole moment. This is manifested either as a dipole moment for molecule that has zero permanent dipole moment, or variation of the latter with the external field. The induced dipole moment is calculated from

[3] It should be pointed out that the delta function choice is not physical, because the size of the system as the whole cannot be smaller than the with of the binding potential. In this case this choice is only for the modelling purpose.

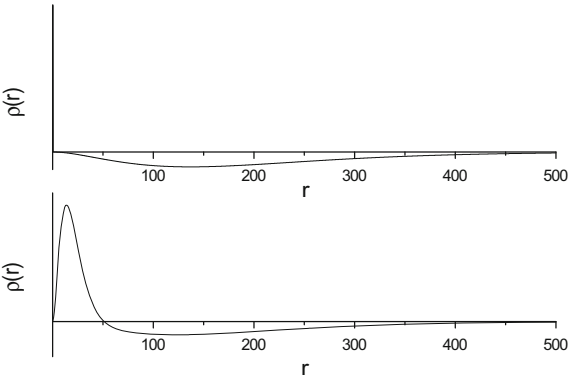

Fig. 1.1 Radial charge density for hydrogen atom (*upper graph*), where the positive component from proton is very close to the origin. Radial charge density for a hydrogen-like atom for muon as negatively charged particle is shown by the *lower graph*

the probability amplitude of a molecule in the presence of external field, and for a weak field one uses perturbation theory. If Hamiltonian of a molecule is H_0 and its eigenfunction is f_0, with the eigenenergy E_0, then in the external field the new eigenfunction f satisfies equation

$$(H_0 + V_{ext})\ f = E\ f$$

By replacing solution with

$$f = f_0 + g$$

and likewise the eigenenergy with

$$E = E_0 + \epsilon$$

The equation for correcting term g, in the first order of perturbation, is

$$H_0 g + f_0 V_{ext} = f_0 \epsilon + g E_0$$

and by expanding it in the eigenfunctions f_j of the Hamiltonian H_0

$$g = \sum_j \varepsilon_j f_j$$

the expansion coefficients are

$$\varepsilon_m = \frac{1}{E_0 - E_m} \int f_0 V_{ext} f_m \, dV; \quad m \neq 0$$

Within this correction the charge density is

$$\rho(\vec{r}) = \rho_0(\vec{r}) - 2ne \int f_0(\vec{r}, \vec{r}_2, \vec{r}_3, \ldots, \vec{r}_n) g(\vec{r}, \vec{r}_2, \vec{r}_3, \ldots, \vec{r}_n)\, d^3r_2 \ldots d^3r_n$$

where the second term is the induced dipole moment, and it is explicitly given by

$$\begin{aligned} \vec{d}_{ind} &= -2ne \int \left(\vec{r} - \vec{R}_c\right) \sum_{m \neq 0} \varepsilon_m \rho_m(\vec{r}) \\ &= -2ne \sum_{m \neq 0} \frac{\int f_0 V_{ext} f_m \, dV}{E_0 - E_m} \int \left(\vec{r} - \vec{R}_c\right) \rho_m(\vec{r})\, d^3r \end{aligned} \tag{1.6}$$

where

$$\rho_m(\vec{r}) = \int f_0(\vec{r}, \vec{r}_2, \vec{r}_3, \ldots, \vec{r}_n) f_m(\vec{r}, \vec{r}_2, \vec{r}_3, \ldots, \vec{r}_n)\, d^3r_2 \ldots d^3r_n$$

Permanent and induced dipole moments always go together, and the magnitude of the latter is primarily determined by the differences in the eigenenergies of a molecule. In general the larger the molecule the greater the impact of the external field on the dipole moment, however, even for smaller molecules the same may hold true if the energy level spacing is small. In particular the induced dipole moment may play significant role for the time dependent external field having an impact on the spectrum a molecule.

It should be noted that the series for the induced dipole moment is not convergent, it is so called asymptotically convergent, which for the strong external fields manifests itself as the tunneling ionization.

Dipole moment for molecules is measured in the units of *debey*, and its unit value is

$$1\,\text{debey (D)} = 3.336 \times 10^{-30}\,\text{Cm}$$

To understand the meaning of this unit one takes charge of the electron that is at the distance $r = 10^{-10}\,\text{m}$ (typical dimension of a diatom molecule) from its opposite charge, and this dipole moment has the value

$$d = 4.8\,\text{D}$$

Atoms do not have dipole moments, they acquire it only when they are subjected to the external field. The simplest is Hydrogen atom, for which the probability amplitude of the electron, if subjected to the electromagnetic wave of the resonance frequency for $1S \to 2P$ transition, is a linear combination

$$f = \frac{a}{\sqrt{\pi a_0^3}} e^{-\frac{r}{a_0}} + \frac{b}{4\sqrt{2\pi a_0^5}} r e^{-\frac{r}{2a_0}} Y_{1,0}(\theta, \phi)$$

where $a_0 = 0.5292 \times 10^{-10}$ m is the Bohr radius. The coefficients a and b are in general complex time dependent coefficients, but without loss of generality they could be assumed real, with the property[4]

$$a^2 + b^2 = 1$$

The dipole moment is then

$$\vec{d} = -e \int d^3r \; f^{\,2} \, \vec{r} = -e \frac{256\sqrt{2}}{243} a\sqrt{1-a^2} a_0 \, \hat{z}$$

which is indeed zero if either the electron is in the ground state ($a = 1$) or the excited state ($a = 0$). Its maximal value is attained for $a = 2^{-1/2}$, when the dipole moment has the value

$$d = 1.89 \text{ D}$$

The induced dipole moment of Hydrogen atom in this electromagnetic wave therefore oscillates with this amplitude.[5]

Hydrogen atom could be permanently polarized in a constant electrostatic field. If Hydrogen atom is in the ground state, and only the $2P$ state is taken into account, then from the perturbation expression (1.6) for the dipole moment one gets

$$d = \frac{524288}{177147} \frac{e^2 a_0^4 m_e}{\hbar^2} E$$

where m_e is mass of the electron and E is the strength of the electric field. If the dipole moment should equal its amplitude when the atom is subject to the oscillating electromagnetic field then E is

$$E = \frac{729}{2048} \frac{\hbar^2}{\sqrt{2} e m_e a_0^3} = 1.29 \times 10^{11} \text{ V/m}$$

which is in practice virtually unobtainable.

Molecules, in general, may have *permanent dipole moment*, and few typical ones are given in Table 1.1 [1]. As the result molecule 1 with a dipole moment produces electrostatic field

$$\vec{E}_1 = \frac{1}{4\pi\varepsilon_0 r^3} \left[3 \left(\vec{d}_1 \cdot \hat{r} \right) \hat{r} - \vec{d}_1 \right]$$

[4] Their exact time dependence is the subject of separate analysis in later discussions.

[5] It should be noted, though, that the frequency of oscillations with this amplitude is not that of the electromagnetic wave, it is a function of the strength of the field (see Rabbi oscillations).

Table 1.1 Dipole moments of molecules

Molecule	d/D
CO	0.112
O_3	0.53
H_2O	1.85
CN_2H_2	4.27
KBr	10.41

and another molecule with a dipole $\vec{d}_2$ in this field has potential energy

$$V_{dip-dip} = -\frac{1}{4\pi\varepsilon_0 r^3}\left[3\left(\vec{d}_2\cdot\widehat{r}\right)\left(\vec{d}_1\cdot\widehat{r}\right) - \overrightarrow{d}_1\cdot\vec{d}_2\right]$$

where r is separation between the dipoles and $\widehat{r}$ points from one to the other molecule. Potential energy depends on the relative orientation of the two dipoles: the interaction could be attractive (parallel configuration) or repulsive (antiparallel configuration). This feature of interaction between the two dipoles results in the *torque* that the field of one molecule exerts on the other, which has the form

$$I_2\, d_t\vec{\omega}_2 = \vec{d}_2 \times \vec{E}_1$$

where I_2 is momentum of inertia and $\vec{\omega}_2$ is the angular velocity of the molecule 2 (for the equation of the molecule 1 the indices are interchanged) given by (the index is omitted)

$$\vec{\omega} = -d_t\theta\sin\phi\,\hat{x} + d_t\theta\cos\phi\,\hat{y} + d_t\phi\,\hat{z}$$

In terms of the spherical angles the dipole $\vec{d}$ is

$$\vec{d} = d\left(\sin\theta\cos\phi\,\hat{x} + \sin\theta\sin\phi\,\hat{y} + \cos\theta\,\hat{z}\right)$$

Dipole-dipole interaction is dominant when the molecules are separated, and its absolute magnitude is better expressed in the scaled units, being

$$V_{dip-dip} = -\frac{0.6242}{r^3}\left[3\left(\vec{d}\,'\cdot\widehat{r}\right)\left(\vec{d}\cdot\widehat{r}\right) - \overrightarrow{d}\cdot\vec{d}\,'\right]$$

where the separation between them is now measured in the units of 10^{-10} m (Angstroms) and the dipole moments are given in debeys. Depending on the molecules but in general dipole-dipole interaction dominates until the distances of the order 10 A. A simpler system is atom-molecule system the potential is

$$V_{dip-atom} = -\frac{2.998q}{r^2}\vec{d}\cdot\widehat{r}$$

where the charge of atom q is in the units of elementary charge. On the other hand if atom is neutral then the dipole field induces charge separation in it, which is of the order r^{-2}, and the interaction decays more rapidly, as $V_{dip-atom} \sim r^{-4}$.

1.2.5 Van der Waals Potential

Neutral atoms or molecules, without polarization of charge density still exerts a force on another species with the same characteristics. The force is responsible for formation of clusters, which is manifested, for example, as formation of liquids from gas phase, adhesion and it is essentially the explanation of the Casimir effect [2]. The theory that explains the force is very well documented [2,3] and here we give a brief overview of its essentials.

Relatively few molecules do not have electric dipole moment, but atoms and the molecules without it exert a force on the like species by attractive force that arises from the finite extent of the charge density of the electrons. The force is expected to be weak but significant at large separations of the species, where the chemical forces are negligible. Therefore at these separations the electron densities of these species do not overlap appreciable, the assumption that will be used in the following analysis. For simplicity this force is derived for two Hydrogen atoms, the derivation that has straightforward generalization to more complex situations.

Based on the assumption that the two Hydrogen atoms are well separated the potential energy of the system is

$$\begin{aligned} V_W &= \frac{q^2}{r} - \frac{q^2}{\left|\overrightarrow{r} + \overrightarrow{r}_2\right|} - \frac{q^2}{\left|\overrightarrow{r} - \overrightarrow{r}_1\right|} + \frac{q^2}{\left|\overrightarrow{r} + \overrightarrow{r}_2 - \overrightarrow{r}_1\right|} \\ &\approx q^2 \left[\frac{\overrightarrow{r}_2 . \overrightarrow{r}_1}{r^3} - 3\frac{\left(\overrightarrow{r} . \overrightarrow{r}_2\right)\left(\overrightarrow{r} . \overrightarrow{r}_1\right)}{r^5} \right] \end{aligned}$$

where $\overrightarrow{r}$ is separation of atom 2 from atom 1, which is placed at the origin. The vectors $\overrightarrow{r}_2$ and $\overrightarrow{r}_1$ are positions of the the electrons 2 and 1 relative to their respective nuclei. In the last step expansion is made in the ratio of r_n/r, and the leading term retained. This interaction perturbs electronic states, and the (nearly) complete set of the unperturbed ones are (the continuum states are not included)

$$F^{(0)}_{n_1,n_2}\left(\overrightarrow{r}_1, \overrightarrow{r}_2\right) = f^{(0)}_{n_1}\left(\overrightarrow{r}_1\right) f^{(0)}_{n_2}\left(\overrightarrow{r}_2\right) \tag{1.7}$$

where the assumption of the non overlapping electronic probability amplitudes was implemented. Impact of interaction potential V_W on the state (n_1, n_2) is calculated from the perturbation expansion, and the probability amplitude with the leading correction is[6]

[6]The convenient $\langle||\rangle$ abbreviates integral over all variables that are involved.

$$F^{(1)}_{n_1,n_2} = F^{(0)}_{n_1,n_2} + \sum_{m_1,m_2} \frac{\left\langle F^{(0)}_{n_1,n_2} \left| V_W \right| F^{(0)}_{m_1,m_2} \right\rangle}{E^{(0)}_{n_1,n_2} - E^{(0)}_{m_1,m_2}} F^{(0)}_{m_1,m_2}$$

Correction to the unperturbed eigenergies is then

$$\left\langle F^{(0)}_{n_1,n_2} \left| V_W \right| \sum_{m_1,m_2} a_{n_1,n_2;m_1,m_2} F^{(0)}_{m_1,m_2} \right\rangle \tag{1.8}$$
$$= \left\langle F^{(0)}_{n_1,n_2} \left| V_W \right| F^{(0)}_{n_1,n_2} \right\rangle + \sum_{m_1,m_2} \frac{\left| \left\langle F^{(0)}_{n_1,n_2} \left| V_W \right| F^{(0)}_{m_1,m_2} \right\rangle \right|^2}{E^{(0)}_{n_1,n_2} - E^{(0)}_{m_1,m_2}}$$

which is r dependent and is associated with the long range atom-atom interaction, known as the Van der Waals potential.

Potential V_W represents essentially electric dipole-dipole interaction, which means that induces also correlation between the two of them. This correlation effect is calculated from

$$\langle \widehat{r}_1 \cdot \widehat{r}_2 \rangle = \int d^3 r_1 d^3 r_2 F^*_{n_1,n_2} \left(\widehat{r}_1 \cdot \widehat{r}_2 \right) F_{n_1,n_2} \tag{1.9}$$

and by using approximation for the probability amplitude

$$\langle \widehat{r}_1 \cdot \widehat{r}_2 \rangle \approx 2 \, \mathrm{Re} \left[\sum_{m_1,m_2} \frac{\left\langle F^{(0)}_{n_1,n_2} \left| V_W \right| F^{(0)}_{m_1,m_2} \right\rangle}{E^{(0)}_{n_1,n_2} - E^{(0)}_{m_1,m_2}} \left\langle F^{(0)*}_{n_1,n_2} \left| \widehat{r}_1 \cdot \widehat{r}_2 \right| F^{(0)}_{m_1,m_2} \right\rangle \right]$$

Previous derivation is valid under the assumption of no degeneracy, meaning that no two pair of energies $E^{(0)}_{n_1,n_2}$ and $E^{(0)}_{m_1,m_2}$ are equal for any set of quantum numbers unless $(n_1, n_2) = (m_1, m_2)$. The problem arises because for Hydrogen atom, as an example, the probability amplitude is specified by three quantum numbers (n, l, m) whilst the appropriate eigenenergy is a function of only the principal quantum number n and independent of the angular momentum ones l and m. Therefore for the quantum number n the eigenergies are n^2 degenerate. Degeneracy also arises when two atoms are identical, in which case by interchanging the pair (n_1, n_2) with (n_2, n_1) the eigenergies are the same. Previous analysis that is based on the non-degenerate perturbation expansion must therefore be replaced by the theory that takes into account degeneracy.

In the degenerate perturbation expansion one isolates a set of degenerate states, say there are d degenerate ones. If f_n are eigenstates of unperturbed Hamiltonian then the first d states (for convenience the set of eigenstates are ordered in this way) have the same eigenenergy e_d. One defines a new basis set h_n, which is a linear combination of f_n but only for the indices smaller or equal to d whilst the rest are unaltered. The first d states are g_n for $n \leq d$ are defined so that they diagonalize perturbing potential V_W, i.e.

$$\left(\widetilde{U}\right)_{n,i}\left\langle f_i\left|V_W\right|f_j\right\rangle U_{j,m}=\left\langle h_n\left|V_W\right|h_m\right\rangle=e_n^{(1)}\delta_{n,m} \tag{1.10}$$

which means that

$$h_m=f_jU_{j,m}$$

In the new basis set one uses the rules of the non-degenerate perturbation theory, thus the first order corrected eigenergies, for all n, are

$$e_n^{(1)}=e_n+\left\langle h_n\left|V_W\right|h_n\right\rangle$$

and the first order corrected probability amplitudes are

$$h_n^{(1)}=h_n+\sum_m\frac{\left\langle h_n\left|V_W\right|h_m\right\rangle}{e_n-e_m}h_m$$

The second order corrected eigenergies are therefore

$$e_n^{(2)}=e_n+\left\langle h_n\left|V_W\right|h_n^{(1)}\right\rangle=e_n+\left\langle h_n\left|V_W\right|h_n\right\rangle+\sum_m\frac{\left|\left\langle h_n\left|V_W\right|h_m\right\rangle\right|^2}{e_n-e_m} \tag{1.11}$$

Degenerate perturbation expansion is the most demanding when two atoms are identical. The two indices that specify the state of each atom (each index should be understood as a set of quantum numbers, 3 in the case of Hydrogen atom) do not only individually represent degenerate states but also upon the exchange of them one gets also another set that is degenerate with the previous one. For example, if one seeks Van der Waals potential between two Hydrogen atoms where one is in $n=1$ state and the other in $n=2$, $l=1$ and $m=0$ state one cannot but not to include the other l and m states in this atom. In general one combination has 4 states and upon interchange of the states there are another 4 states. There are, therefore, altogether 8 states are degenerate and should be considered for calculating the potential. However, within these states some are not coupled by the matrix element in (1.10) and their eigenergies are not affected by transformation, but their probability amplitudes are. Furthermore, the diagonal elements in this coupling matrix are zero therefore the sum of the eigenvalues in (1.10) are zero. This means that for this system the states whose eigenergies are affected by the transformation come in pairs, one for which the shift from their unperturbed values is positive and the other that is negative. Upon the exchange of atoms the two affected states are of the opposite sign, being result of the symmetry of V_W with respect to this exchange.

Correlation of the two electric dipoles (1.9), in the case of degeneracy is approximately

$$\left\langle\widehat{r}_1\cdot\widehat{r}_2\right\rangle_n\approx\left\langle h_n\left|\widehat{r}_1\cdot\widehat{r}_2\right|h_n\right\rangle \tag{1.12}$$

and it is not in general zero.

In the previous analysis the states for which the Van der Waals potential was defined are fixed, however, in most applications regarding dynamics of atoms one works with a general expansion

$$G = \sum_{m_1,m_2} c_{m_1,m_2} F^{(0)}_{m_1,m_2}$$

where the coefficients are, in general, time dependent, therefore the Van der Waals force is also time dependent. Straightforward generalization of the previous. non degenerate, perturbation analysis gives for the Van der Waals potential

$$\begin{aligned}&\left\langle G\,|V_W|\,G^{(1)}\right\rangle \\ &= \sum_{m_1,m_2}\sum_{n_1,n_2} c^*_{m_1,m_2} c_{n_1,n_2} \left[\begin{array}{c} \left\langle F^{(0)}_{m_1,m_2}\,|V_W|\,F^{(0)}_{n_1,n_2}\right\rangle + \\ \sum_{i_1,i_2} \frac{\left\langle F^{(0)}_{n_1,n_2}|V_W|F^{(0)}_{i_1,i_2}\right\rangle}{E^{(0)}_{n_1,n_2}-E^{(0)}_{i_1,i_2}} \left\langle F^{(0)}_{m_1,m_2}\,|V_W|\,F(^{(0)}_{i_1,i_2}\right\rangle \end{array}\right]\end{aligned}$$

In the case of degeneracy one defines a new basis set based on the recipe that was given earlier. The degenerate states form a subset of the complete set, and for each one of them one performs transformation that was described earlier. After the transformation the unitary matrix that transforms the entire basis set is a block matrix, where each one transforms a particular degenerate subset. This unitary matrix is used to define a new basis set which used in the perturbation expansion.

1.2.5.1 Two Hydrogen Atoms

Two Hydrogen atoms is the simplest system where to describe calculation of the Van der Waals potential, and if both of them are in their ground state there is no degeneracy and it is calculated from (1.8). The ground state probability amplitude is $F\,[1, 0, 0; 1, 0, 0]$ (the indices n, l and m are written in the brackets for better visualization, where r_1 is associated with the first set whilst r_2 with the second) and in the simplest approximation it is in general coupled to $F\,[2, l, m; 1, 0, 0]$, $F\,[1, 0, 0; 2, l, m]$ and $F\,[2, l, m; 2, l, m]$. However, by the symmetry considerations it is only coupled to $F\,[2, 1, -1; 2, 1, 1]$, $F\,[2, 1, 1; 2, 1, -1]$ and $F\,[2, 1, 0; 2, 1, 0]$ in which case one gets for the Van der Waals potential[7]

$$V_W \approx -\frac{2.46\,q^2}{\alpha^6 r^6}$$

where q is electric charge and α is fine structure constant (appropriate units are used).

One is tempted to assume that the same reasoning applies for the potential when both atoms are in $2S$ state. Although this state is degenerate with $2P$ states that would not be a problem if the coupling between them is zero. However, this is not the case

[7] In the calculations it is assumed that the two atoms are along the z axes.

because $F\,[2,0,0;2,0,0]$ is coupled to $F\,[2,1,-1;2,1,1]$, $F\,[2,1,1;2,1,-1]$ and $F\,[2,1,0;2,1,0]$, and therefore one must use degenerate perturbation expansion. The complete set of degenerate probability amplitudes for $n=2$ when both both atoms are included has 16 terms, and out of 136 coupling terms only 12 are are coupled. The list of those coupled states is in (1.14), but there are 8 states that are not coupled to any other. In practice one forms the coupling matrix (1.10) with the entire set, and combination of basis set functions that have zero eigenvalue correspond to the uncoupled set. 8 eigenvalues that are not zero are $\{\pm 22.05, \pm 18, \pm 9, \pm 9\}$. Therefore Van der Waals potential between two atoms in $2S$ state has no meaning because these states come in a linear combination with the states from $2P$. However, among the linear combinations those with the largest absolute eigenvalue have the largest weight and the two are given by

$$F_{2S} = \frac{1}{\sqrt{2}} F\,[2,0,0;2,0,0] \mp \frac{1}{\sqrt{3}} F\,[2,1,0;2,1,0] \mp \frac{1}{\sqrt{12}} F\,[2,1,1;2,1,-1] \mp \frac{1}{\sqrt{12}} F\,[2,1,-1;2,1,1] \tag{1.13}$$

which are symmetric with respect to the interchange of two atoms. For each of the two linear combinations one associates a potential, one is attractive, corresponding to the negative eigenenergy, and the other is repulsive, corresponding to the positive one. Important feature of these potentials is their rate of decay is r^{-3}, which is much slower than r^{-6} for a typical Van der Waals interaction. The two potentials have also different sign, one describes attraction of the two atoms and the describe repulsion. The states (1.13) describe interaction of two atoms in predominantly $2S$ states and to show this one calculates correlation (1.12), which is shown to be zero. The result supports this conjecture because correlation is zero if the two atoms are in a spherically symmetric states.

$\langle 2,0,0;2,0,0\,\vert 2,1,-1;2,1,1\rangle$	$\langle 2,0,0;2,0,0\,\vert 2,1,0;2,1,0\rangle$
$\langle 2,0,0;2,0,0\,\vert 2,1,1;2,1,-1\rangle$	$\langle 2,0,0;2,1,-1\,\vert 2,1,-1;2,0,0\rangle$
$\langle 2,0,0;2,1,0\,\vert 2,1,0;2,0,0\rangle$	$\langle 2,0,0;2,1,1\,\vert 2,1,1;2,0,0\rangle$
$\langle 2,1,-1;2,0,0\,\vert 2,0,0;2,1,-1\rangle$	$\langle 2,1,-1;2,1,1\,\vert 2,0,0;2,0,0\rangle$
$\langle 2,1,0;2,0,0\,\vert 2,0,0;2,1,0\rangle$	$\langle 2,1,0;2,1,0\,\vert 2,0,0;2,0,0\rangle$
$\langle 2,1,1;2,0,0\,\vert 2,0,0;2,1,1\rangle$	$\langle 2,1,1;2,1,-1\,\vert 2,0,0;2,0,0\rangle$

(1.14)

The other linear combinations involve states $2S$ and $2P$, for example the two that correspond to the second largest in magnitude eigenergies are

$$F_{2S} = \frac{1}{\sqrt{2}} F\,[2,1,0;2,0,0] \mp \frac{1}{\sqrt{2}} F\,[2,0,0;2,1,0]$$

and they produce the Van der Waals potential when the P state has quantum numbers $l = 1$ and $m = 0$. One state is antisymmetric with respect to the interchange of atoms and the potential is repulsive. The other is symmetric and the potential is attractive. Correlation (1.12) is not zero, and in the former case it is $\langle \widehat{r}_1 \cdot \widehat{r}_2 \rangle = -1/4$, thus indicating that on average the two dipoles are antiparallel, which means repulsion.[8] For the symmetric state the correlation is $\langle \widehat{r}_1 \cdot \widehat{r}_2 \rangle = 1/4$, and represents attraction. The other two linear combinations represent similar interactions.

1.3 Structure of Molecules

Constituents of molecules are electrons and nuclei, but when it comes to determining their structure and dynamics the two sets of particles play different role. The key parameter that distinguishes them is their mass, the nuclei having much larger than the electrons. However, this statement should be taken with some caution, depending on how it is applied. The intuition tells that if the nuclei of a mass M and the electrons of the mass m have nearly equal energy E then the ratio of their velocities is proportional to $\sqrt{m/M}$. This means that nuclei move more slowly than the electrons, for example kinetic energy of the protons in the ground state of Hydrogen molecule is of the order 0.1 eV whilst that of the electrons is 10 eV and so the ratio of the two velocities is $v_{prot}/v_{elec} \approx \sqrt{0.1/10 \times 1/2000} \approx 10^{-3}$. Furthermore the momentum exchange between the electrons and the nuclei is small, again due to the ratio of their masses, and based on the two arguments one assumes a similar concept as in thermodynamics, the adiabatic approximation. The approximation applies to a system with two groups of degrees of freedom[9] where each one has independent dynamics of the other. In the case of molecules, therefore, the adiabaticity, the Born-Oppenheimer approximation as it is also called, means that the motion of nuclei is independent of the motion of the electrons. Validity of the Born-Oppenheimer approximation has been discussed on various occasions [5–8], whilst here in Sect. 1.3.2 its limitations are discussed more explicitly on example of Hydrogen atom in harmonic oscillator.

In practice the adiabatic approximation is formally implemented in the following way. For a fixed configuration of nuclei one calculates eigenstates of the electrons, and the relevant probability amplitudes are $f_n(r, R)$, where n refers to a set of indices that characterize a particular electronic state. r is the set of coordinates for the electrons, in the form $r = \{x_1, y_1, z_1, x_2, y_2, \ldots\}$ whilst R is similar set for the nuclei. Energy of the electronic states depend parametrically on the coordinates R and it is written as $e_n(R)$, meaning that if E is the overall energy of molecule then energy of the nuclei is $E - e_n(R)$. In equation for the nuclei, therefore, the energy $e_n(R)$ plays

[8] It should be noted that the two dipoles are defined with respect to the line that connects two atoms, thus antiparallel means electron-proton-proton-electron configuration.

[9] In thermodynamics the parameters that determine a system are pressure, volume, temperature and the heath bath with which the system has energy exchange. The adiabatic approximation means that the temperature always changes in unison with that of the heath bath and it is not affected by the changes in pressure and volume.

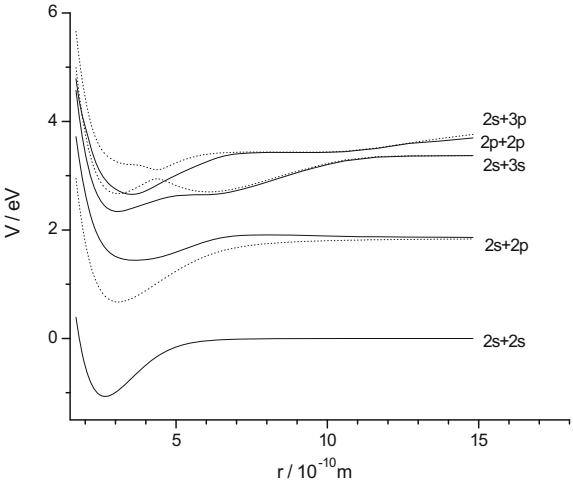

Fig. 1.2 Electronic energies of Li_2 molecule [4] as a function of their internuclear separation. The energies are labeled by the dissociation states of the molecule

the role of potential in which they move due to, roughly speaking, averaging over the electronic degrees of freedom. Typical potentials for $Li–Li$ molecule are shown in Fig. 1.2, which are characterized by the asymptotic states of individual atoms when they are pulled apart. Although the procedure is straightforward the question is when one expects the adiabatic approximation to fail?

The answer to this question will be given on a general level but a simpler one derives from an order of magnitude argument. The adiabatic approximation is valid provided the electrons move much faster than nuclei, and so its failure is expected when the two velocities are nearly equal. This, however, means that kinetic energy of the nuclei should be greater than the same for the electrons by the ration of the mass of the former to the mass of the latter. This ratio is typically of the order 10^4 and so if binding energy of the electrons (valence electrons) is of the order 1 eV then energy of the nuclei should be roughly 10^4 eV, which is indeed very large. However, there may be circumstances when the adiabatic approximation fails for much smaller kinetic energy of the nuclei, e.g. when atoms are in highly excited states (Rydberg states) and their binding energy is much smaller. For example, the electron in Hydrogen atom in the state with the principal quantum number $n = 100$ has energy of the order 10^{-3} eV and so it is expected that adiabatic approximation would fail when nuclei have few eV.

The essence of breakdown of the adiabatic approximation could be demonstrated on a simple classical model. In this model the electron is coupled to the motion of the nucleus whilst the latter is coupled to an external potential. The simplest is to assume Hydrogen atom on which the force $\overrightarrow{F}\left(\overrightarrow{R}\right)$ is applied and analyze how the motion of the electron is affected by it. Adiabatic approximation assumes that motion of the electron is independent of motion of the proton, or to be more precise, energy of the electron is affected but its change is smaller than some predetermined value. There are two sets of classical equations that describe this system. One for the proton, and

if it has the mass M and the position vector $\overrightarrow{R}$ it is given by

$$M \ddot{\overrightarrow{R}} = \overrightarrow{F}\left(\overrightarrow{R}\right) + \overrightarrow{G}\left(\overrightarrow{R} - \overrightarrow{r}\right)$$

On the other hand, equation for the electron is

$$m \ddot{\overrightarrow{r}} = -\overrightarrow{G}\left(\overrightarrow{R} - \overrightarrow{r}\right)$$

where $\overrightarrow{G}\left(\overrightarrow{R} - \overrightarrow{r}\right)$ is force between the electron and proton, the Coulomb force

$$\overrightarrow{G}\left(\overrightarrow{R} - \overrightarrow{r}\right) = -\nabla V_{Coul}\left(\left|\overrightarrow{R} - \overrightarrow{r}\right|\right) = -\frac{e^2}{4\pi\varepsilon_0}\frac{\overrightarrow{R} - \overrightarrow{r}}{\left|\overrightarrow{R} - \overrightarrow{r}\right|^3}$$

By defining

$$\overrightarrow{u} = \overrightarrow{R} - \overrightarrow{r}$$

then equation for the electron is

$$m \ddot{\overrightarrow{u}} = \overrightarrow{G}\left(\overrightarrow{u}\right) + \frac{m}{M}\overrightarrow{F}\left(\overrightarrow{R}\right) + \frac{m}{M}\overrightarrow{G}\left(\overrightarrow{u}\right)$$

The adiabatic approximation is to neglect the last two terms, which are of the order mM^{-1}, when trajectory for the electron is

$$\overrightarrow{r} = \overrightarrow{R} - \overrightarrow{u}(t)$$

which depends parametrically on the coordinates of proton. By definition this is adiabatic solution for the electron. Motion of the proton is then derived from equation

$$M \ddot{\overrightarrow{R}} = \overrightarrow{F}\left(\overrightarrow{R}\right) + \overrightarrow{G}\left(\overrightarrow{u}\right)$$

where $\overrightarrow{u}$ is solution of adiabatic equation for the electron. Measure of this approximation is energy of proton, whose change in time is given by

$$\Delta E_{pr} = \int dt \, \dot{\overrightarrow{R}} \cdot \overrightarrow{G}\left[\overrightarrow{u}(t)\right]$$

and motion is adiabatic if ΔE_{pr} is smaller than some predetermined value.

1.3.1 Adiabatic Approximation

Deriving rigorous adiabatic approximation for the system of N_{el} electrons and N_{nu} nuclei one starts from equation

$$[T_{el}(r) + T_{nu}(R) + V(r, R)] f(r, R) = E f(r, R) \tag{1.15}$$

where $T_{el}(r)$ is kinetic energy operator for the electrons, $T_{nu}(R)$ is the same for the nuclei and $V(r, R)$ is the potential energy of the whole system. Few words about the coordinates and the symbolic way how they are represented. The symbol r represents the Cartesian coordinates set $r = \{x_1, y_1, z_1, x_2, y_2, \ldots\}$ of the individual electrons whilst R stands for the set of nuclear coordinates in the centre of mass coordinates system, which is obtained by neglecting the mass of the electrons. Therefore the components $R = \{X_1, Y_1, Z_1, X_2, Y_2, \ldots\}$ are obtained from the coordinates of individual nuclei by removing the centre of mass coordinate and the remaining are chosen so that the kinetic energy operator is in the form

$$T_{nu}(R) = -\frac{\hbar^2}{2} \sum_{n}^{3N_{nu}-3} M_n^{-1} \Delta_{R_n} = -\frac{\hbar^2}{2} M^{-1/2} \nabla \cdot M^{-1/2} \nabla \equiv T_{nu}^{1/2}(R)\, T_{nu}^{1/2}(R) \tag{1.16}$$

where M is a $3N_{nu} - 3$ (the centre of mass coordinates are removed) diagonal matrix of the masses that are related to those of the nuclei (see Appendix D), which on the diagonal has the values $M_{j,j} = \{M_1, M_1, M_1, M_2, M_2, \ldots\}$. The operator ∇ is a single column matrix having the elements

$$\nabla = \left\{\nabla_{X_1}, \nabla_{Y_1}, \nabla_{Z_1}, \nabla_{X_2}, \nabla_{Y_2}, \ldots\right\}.$$

In contrast to the nuclear kinetic energy the operator $T_{el}(r)$ is the sum of contributions from individual electrons. The parameter E is the total energy of the system.

Overall motion of a molecule appears as a nonessential information and could be removed from the solution of equation (1.15). The removal is indeed justified in many circumstances but there are processes when it is important to know motion of the centre of mass of a molecule. For example, when the electromagnetic field interacts with a molecule then the result is also its translational motion, which means that there is coupling between all the coordinates involved. In this case it is imperative to including the centre of mass coordinates into the dynamics equations. These processes are not analyzed here, in Chap. 6 they are analyzed in details for atoms, the interest is focused on investigating how to implement the adiabatic approximation for an isolated molecule and under what circumstances it is applicable.

Adiabatic, or Born-Oppenheimer, approximation is briefly or in more details reviewed in almost any textbook where molecular structure is analyzed. Nowadays the methods of calculating molecular structures has grown to be a very sophisticated tool, but always in the background is this approximation. However, the problem still

remains corrections to this approximation, the non adiabatic processes, which is the emphases in this section.

The adiabatic approximation is derived by writing solution of equation (1.15) in the form of expansion

$$f\,(r,\,R) = \sum_n g_n\,(r,\,R)\,w_n\,(R) \tag{1.17}$$

where $g_n\,(r,\,R)$ are eigenfunctions of the electronic Hamiltonian for a fixed configuration of a molecule, i.e.

$$H_{el}\,(r,\,R)\,g_n\,(r,\,R) = W_n\,(R)\,g_n\,(r,\,R)$$

However, here another approach is adopted that will prove to be useful in later analysis. One starts by the diabatic expansion, which essentially means that for a fixed configuration of nuclei R_0 one defines a complete set of eigenfunctions of the electronic Hamiltonian (for simplicity it is assumed that all electronic states are bound.) by solving equation

$$[T_{el}\,(r) + V\,(r,\,R_0)]\,g_n\,(r) = W_n\,(R_0)\,g_n\,(r) \tag{1.18}$$

For any other nuclear configuration one then writes expansion for the solution of equation (1.15) as

$$f\,(r,\,R) = \sum_n g_n\,(r)\,w_n\,(R)$$

This expansion is expected to be poorly convergent for all R but in a small vicinity of R_0 it may have advantages over the adiabatic expansion. By replacing expansion in (1.15) one gets a set of equations for the "coefficients" $w_n\,(R)$, which are in a matrix form given by

$$T_{nu}\,(R)\,w\,(R) = \left[E - O^{di}(R)\right]w\,(R) \tag{1.19}$$

where $O^{di}\,(R)$ is a matrix with the elements

$$\begin{aligned} O^{di}_{i,j}(R) = & \int d^{3N_{el}}r\ \left[V\,(r,\,R) - V\,(r,\,R_0)\right]g_i\,(r)\,g_j\,(r) + W_i\,(R_0)\,\delta_{i,j} \\ \equiv & \ \langle g\,(r)\,|\,O(r,\,R)|\,g\,(r)\rangle_{i,j} \\ = & \ \langle i\,|\,V(r,\,R) - V\,(r,\,R_0)|\,j\rangle^{di} + W_i\,(R_0)\,\delta_{i,j} \end{aligned} \tag{1.20}$$

where the superscript indicates the diabatic basis. One now defines a unitary matrix U that diagonalizes O^{di}, i.e.

$$\widetilde{U}(R)O^{di}(R)U(R) = \lambda(R) \equiv O^{ad}(R) \tag{1.21}$$

where $\lambda(R)$ is a diagonal matrix. The role of the matrix U is deduced from this property, it changes the basis set of the electronic functions, from those fixed at R_0 to those at R. Explicitly

$$\widetilde{U}(R)g(r) = g(r, R) \tag{1.22}$$

which is changing from diabatic basis set in expansion (1.19) into the adiabatic in expansion (1.17). Therefore, study of the matrix $U(R)$ is bridging the gap between the two expansions.

The diabatic set of equations (1.19) is transformed by using the relationship (1.22), when one gets

$$T_{nu}(R)\, w(R) = \left[E - U(R)O^{ad}(R)\widetilde{U}(R)\right] w(R)$$

where now the matrix elements are in the adiabatic basis. In accordance with the transformation of the electronic basis functions the nuclear ones must also be modified by writing

$$W(R) = \widetilde{U}(R)w(R)$$

and so they satisfy the set of equations

$$\widetilde{U}(R)T_{nu}(R)\left[U(R)W(R)\right] = \left[E - O^{ad}(R)\right] W(R) = \left[E - \lambda(R)\right] W(R)$$

By using nuclear kinetic energy operator (1.16) the left side is transformed, where one has to calculate derivatives $\nabla_{R_n} U(R) \equiv U_n'(R)$. By making parametrization

$$U_n'(R) = U(R)\eta_n(R)$$

and from the definition of the matrix $U(R)$ it is deduced

$$\eta_{n;i,j}(R) = \begin{cases} \frac{\langle i | V_n'(r,R) | j \rangle^{ad}}{\lambda_j(R) - \lambda_i(R)} & ; \quad i \neq j \\ 0 & ; \quad i = j \end{cases} \tag{1.23}$$

where the superscript indicates the adiabatic electronic basis. Further derivatives are similarly deduced, and given by

$$\nabla_{R_n}\eta_{i,j}(R) = \frac{\langle i | V_n''(r,R) | j \rangle^{ad}}{\lambda_j(R) - \lambda_i(R)} + \frac{2\lambda_k(R) - \lambda_i(R) - \lambda_j(R)}{\lambda_j(R) - \lambda_i(R)}\eta_{n;i,k}(R)\eta_{n;k,j}(R) - \frac{\lambda'_{n;j}(R) - \lambda'_{n;i}(R)}{\lambda_j(R) - \lambda_i(R)}\eta_{n;i,j}(R)$$

and

$$\lambda'_{n;i}(R) = \langle i | V_n'(r,R) | i \rangle^{ad}$$

so that the final set of equations is

$$-\frac{\hbar^2}{2}\sum_{n}^{3N_{nu}-3} M_n^{-1}\left[\nabla_{R_n}+\eta_n(R)\right]^2 W(R) = [E-\lambda(R)]\,W(R) \tag{1.24}$$

where one distinguishes two terms of different order in powers of mass M. The term $\nabla_{R_n} W(R)$ is of the order $M^{1/2}$ whilst the matrix η is independent of mass and therefore by the criterion that the nuclear mass is large one neglects this term and the set simplifies

$$T_{nu}(R)\,W(R) = [E-\lambda(R)]\,W(R)$$

which is the adiabatic approximation, or the Born-Oppenheimer approximation.

In general η is small and the mass of the nuclei is large which means that the adiabatic approximation is quite accurate. However, the matrix elements of η depend on the separation between the eigenvalues $\lambda_i(R)$, as shown in their definition (1.23), and their proximity is a measure of the failure of the adiabatic approximation. In order to understand that better it is worth investigating the source of encounter of the electronic energies $\lambda(R)$, and for that one should recall how in practice they are calculated. Direct solution of equations (1.18) is not feasible, instead one resorts to the variational principle, and the simplest of the methods is the Hartree-Fock.[10] It essentially assumes a fixed electronic configuration, being a product (properly antisymmetrized though) of functions that describe independent electronic states, and then the parameters in these functions are optimized to minimize the lowest eigenvalue of the integral

$$W(R_0) = \min\left\{\int d^{3N_{el}}r\; g_{tr}(r)\,[T_{el}(r)+V(r,R_0)]\,g_{tr}(r)\right\} \tag{1.25}$$

where $g_{tr}(r)$ is a trial multi-electron function with some free parameters. The trial functions may be chosen to correspond to a certain dissociation limit, and hence if two of these are decide upon (in the simplest case) then for another configuration of the nuclei the related electronic energies are independent of each other. In principle they could cross, i.e. become degenerate, for a particular configuration. More accurate trial function, however, is a combination of the Hartree-Fock ones, so called configuration interaction functions. In this case the minimization procedure of the kind (1.25) becomes the minimization of the eigenvalues of the matrix that is obtained from these configurations, say for two of these $g_{tr}^{(1)}(r)$ and $g_{tr}^{(2)}(r)$ it is given by

$$H = \begin{vmatrix} H_{1,1} & H_{1,2} \\ H_{2,1} & H_{2,2} \end{vmatrix}$$

[10]The Hartree-Fock method is far from being accurate for calculating energies of the electronic states, however, in here it is not used for this purpose but to demonstrate why these do not become degenerate. In short, to demonstrate the source of the avoided crossing of the electronic energies.

where

$$H_{i,j}(R) = \int d^{3N_{el}} r \; g_{tr}^{(i)}(r) \left[T_{el}(r) + V(r, R) \right] g_{tr}^{(j)}(r)$$

If the diagonal elements are degenerate at R_{deg} then in their vicinity one can write

$$H \approx \begin{vmatrix} H^{(0)} + (R - R_0) \cdot H_{1,1}^{(1)} & H_{1,2}^{(0)} \\ H_{2,1}^{(0)} & H^{(0)} + (R - R_0) \cdot H_{2,2}^{(1)} \end{vmatrix}$$

where

$$H_{i,j}^{(0)} = \int d^{3N_{el}} r \; g_{tr}^{(i)}(r) \left[T_{el}(r) + V(r, R_0) \right] g_{tr}^{(j)}(r),$$

$$(R - R_0) \cdot H_{1,1}^{(1)} = \sum_{n}^{3N_{nu}-3} \left(R_n - R_{n;0} \right) \int d^{3N_{el}} r \; g_{tr}^{(i)}(r) \nabla_{R_n} V(r, R_0) \, g_{tr}^{(j)}(r)$$

The eigenvalues are therefore

$$\lambda_{1,2} = \frac{1}{2} \left[2H^{(0)} + (R - R_0) \cdot \left(H_{1,1}^{(1)} + H_{2,2}^{(1)} \right) \right] \pm \frac{1}{2} \sqrt{\left[(R - R_0) \cdot \left(H_{1,1}^{(1)} - H_{2,2}^{(1)} \right) \right]^2 + (\Delta H)^2} \tag{1.26}$$

where

$$\Delta H = 2 \left| H_{1,2}^{(0)} \right|$$

and the electronic energies do not cross. The splitting is due to the "coupling" between the configuration interaction basis functions, and this effect on its own cannot be the sign of the breakdown of the adiabatic approximation. The breakdown is entirely due to the coupling that causes nuclei to change motion from one electronic energy state into another. Example of the avoided crossing of the electronic energies is shown in Fig. 1.3, where the diabatic electronic energies are indicated by H_1 and H_2.

From the previous remarks one traces the cause of the breakdown of the adiabatic approximation to the matrix η because in the set of equations (1.24) it mixes the channels of different electronic states. This matrix, the coupling matrix among the electronic states, appears in the form of the first power and the second power. The latter could be neglected in the qualitative analysis, because η has only the off diagonal elements whilst η^2 has the diagonal ones as well, but especially in a two state problem when its off diagonal elements are zero. Therefore, the quadratic term does not contribute towards mixing of the electronic states, at least not in an essential way. This, however, is not always true as it will be shown later.

From the explicit expression (1.23) of the matrix elements of η mixing of the states starts when the eigenvalues $\lambda(R)$ are not well separated, i.e. when they are in the regime of the avoided crossing. The source of the avoided crossing was discussed, and as argued this happens in a relatively small interval around some isolated

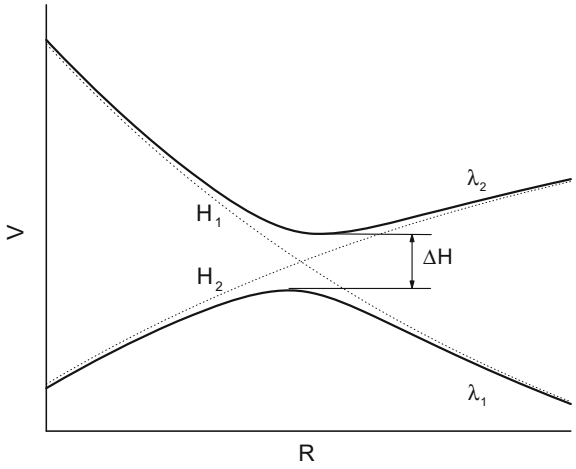

Fig. 1.3 Electronic energies of two states in the regime of avoided crossing

configurations of the nuclei. Based on this finding it could be assumed that for the purpose of estimating the extent of mixing of the electronic states it is sufficient to analyze a two state problem. In this case the only non-zero elements of η are

$$\eta_{n;1,2}(R) = -\eta_{n;2,1}(R) = \frac{1}{\lambda_2(R) - \lambda_1(R)} \sum_{i,j=1}^{2} U_{i,1} \left\langle i \left| V'_n(r, R) \right| j \right\rangle^{di} U_{j,2}$$

and in the vicinity of the avoided crossing the diabatic elements are (nearly) constant whilst the denominator has a functional dependence based on the estimate (1.26). The unitary matrix U parametrizes as

$$U = \begin{vmatrix} \cos\phi & \sin\phi \\ -\sin\phi & \cos\phi \end{vmatrix}$$

in which case one derives

$$\eta_{n;1,2}(R) = \nabla_{R_n}\phi = \frac{1}{\lambda_2(R) - \lambda_1(R)} \left(\frac{V'_{n;1,1} - V'_{n;2,2}}{2} \sin 2\phi + V'_{n;1,2} \cos 2\phi \right)$$

where

$$V'_{n;i,j}(R) = \left\langle i \left| V'_n(r, R) \right| j \right\rangle^{di}$$

In the vicinity of crossing of the diabatic electronic states the matrix elements $V'_{n;i,j}(R)$ are nearly constant and could be fixed to have value the $V'_{n;i,j}(R_0)$. It follows from this, and the definition of the diabatic states, that $V'_{n;1,2} \approx 0$ and

$$V'_{n;1,1} - V'_{n;2,2} \approx H^{(1)}_{1,1} - H^{(1)}_{2,2}$$

hence the equation for the phase ϕ has a solution

$$\tan\phi = (R - R_0)\cdot Q + \sqrt{[(R - R_0)\cdot Q]^2 + 1}$$

where

$$Q_n = \frac{H^{(1)}_{n;1,1} - H^{(1)}_{n;2,2}}{\Delta H}$$

and the coupling matrix is

$$\eta_n = \begin{vmatrix} 0 & 1 \\ -1 & 0 \end{vmatrix} \nabla_{R_n}\phi = \frac{|Q_n|}{2}\frac{1}{[(R - R_0)\cdot Q]^2 + 1}\begin{vmatrix} 0 & 1 \\ -1 & 0 \end{vmatrix}$$

There are two limits to consider depending on the value of $|Q_n|$, the "coupling constants" among the electronic states, but in fact depending on ΔH. In one limit ΔH is very small in which case the coupling constants $|Q_n|$ are very large. The matrix η is in this case nearly a delta function and the set of equations (1.24), without the quadratic term in the same matrix, have a straightforward solution. The unitary matrix has a step-like property, on one side of the turning points R_0 it is, say, (nearly) a unit matrix and on the other side it is a matrix with the zero elements on the diagonal. This means, for example, that if on one side solution in a particular channel corresponds to the electron energy 1 on the other side it corresponds to the electron energy 2. This behavior is precisely that of a diabatic solution. However, obtaining this solution from the set (1.24) is not possible because the quadratic term in η is of the order of the square of a delta function, the singularity that is not integrable. In this case the adiabatic expansion fails, and hence the adiabatic approximation, the Born-Oppenheimer approximation, has no meaning. The way out is to transform the set (1.24) into the diabatic form when it could be solved by a perturbation method, say the distorted channel method. In this case one could define, by analogy, the diabatic approximation.

The other limit is when the coupling constants are small, i.e. when ΔH is large. In this case the matrix η is small and hence its quadratic form is smaller, and also $\nabla_{R_n}\eta_n(R)$ is negligible. The adiabatic approximation has meaning in this case and its corrections are calculated from the set (1.24) by a perturbation method.

In between these two extremes there is a transition region where one could say that the adiabatic approximation has meaning but it is not accurate. The details of how to analyze solution in this case is not elaborated here, this is a topic on its own.

1.3.2 Hydrogen Atom in Harmonic Oscillator

1.3.2.1 Classical Theory

Adiabatic approximation in a classical system is demonstrated on example of a proton being subject to a harmonic force and the electron is coupled to the proton by

Coulomb force. For simplicity the problem is treated in two dimensions. Equations to be solved are

$$\begin{aligned} \ddot{\vec{R}} &= -\omega^2 \vec{R} - \alpha \frac{m}{M} \frac{\vec{u}}{u^3} \\ \ddot{\vec{u}} &= -\alpha \left(1 + \frac{m}{M}\right) \frac{\vec{u}}{u^3} - \omega^2 \vec{R} \end{aligned} \tag{1.27}$$

where $\vec{R}$ is coordinate of the proton and $\vec{u}$ is connected with the coordinate of the electron $\vec{r}$ by $\vec{u} = \vec{R} - \vec{r}$. The coordinates and time are dimensionless, $\vec{R}$ and $\vec{u}$ stand for $\vec{R}\,\kappa$ and $\vec{u}\,\kappa$, respectively, whilst time t stands for $tc\kappa$, where

$$\kappa = \frac{mc}{\hbar} = 2.58961 \times 10^{12}\,\mathrm{m}^{-1}$$

is Compton wave number for the electron. In the adiabatic approximation one neglects the terms of the order M^{-1}, which also includes ω^2 because it is of the same order of magnitude. The set of equations to solve is now

$$\begin{aligned} \ddot{\vec{R}}_{ad} &= -\omega^2 \vec{R}_{ad} \\ \ddot{\vec{u}}_{ad} &= -\alpha \frac{\vec{u}_{ad}(t)}{u_{ad}^3(t)} - \omega^2 \vec{R}_{ad} \end{aligned}$$

where α is the fine structure constant, which is defined as

$$\alpha = \frac{e^2}{4\pi\varepsilon_0 \hbar c} = \frac{1}{137.036}$$

Motion of proton is independent from that of the electron, whilst trajectory of the electron is parametrically dependent on the coordinates of the proton.

Solution for the adiabatic trajectory of the proton is

$$\vec{R}_{ad} = \vec{R}_0 \cos(\omega t + \delta) + \frac{1}{\omega} \vec{V}_0 \sin(\omega t + \delta)$$

and by assuming the simplest case, that the electron is in a circular orbit of the radius $1/\alpha$ (ground state Bohr orbit) around the proton, then its adiabatic trajectory is

$$\vec{u}_{ad}(t) = \vec{u}_0(t) - \frac{\omega^2}{\omega_{el}} \int_0^t d\tau \sin\left[\omega_{el}\,(t - \tau)\right] \vec{R}_{ad}(\tau) \tag{1.28}$$

where

$$\vec{u}_0(t) = \frac{1}{\alpha} \left[\hat{x} \cos(\omega_{el} t + \delta_{el}) + \hat{y} \sin(\omega_{el} t + \delta_{el})\right]$$

From the adiabatic solutions one calculates corrections, and of particular interest is correction to the trajectory of the proton. Solution for this trajectory is in direct relationship to what is the purpose of the Born-Oppenheimer approximation. Trajectory for the proton is solution of equation

$$\ddot{\vec{R}} = -\omega^2 \vec{R} - \alpha \frac{m}{M} \frac{\vec{u}_{ad}}{u_{ad}^3}$$

or in approximate form

$$\ddot{\vec{R}} \approx -\omega^2 \vec{R} - \alpha^4 \frac{m}{M} \vec{u}_{ad}(t)$$

where it is assumed that $u_{ad}^3 \approx u_0^3$. The equation has solution

$$\vec{R} = \vec{R}_{ad} - \frac{1}{\omega} \alpha^4 \frac{m}{M} \int_0^t d\tau \sin\left[\omega (t-\tau)\right] \vec{u}_{ad}(\tau)$$

and by replacing $\vec{u}_{ad}(t)$ with (1.28) one gets two integrals in the time variable. The integral that involves $\vec{u}_0(t)$ is straightforward to solve and solution is oscillatory, with the bounded amplitude. On the other hand the integral with the second term in (1.28) is

$$\vec{R} \approx \alpha^4 \frac{m\omega}{M\omega_{el}} \int_0^t d\tau \int_0^\tau ds \sin\left[\omega (t-\tau)\right] \sin\left[\omega_{el} (\tau - s)\right] \vec{R}_{ad}(s)$$

and its amplitude increases linearly in time. This result is of particular interest because it shows that expansion in the powers of $\frac{m}{M}$, at least in classical mechanics, may not be convergent.

1.3.2.2 Quantum Theory

Hydrogen atom that is subject to an external harmonic force is a good example where one could study interdependence of the electron and the proton motion. Classical study was done in Sect. 1.3.2 and here it will be shown how the problem is solved in quantum dynamics. Equation for this system, in the same scaling as in Sect. 1.3.2, is

$$\left(-\frac{q}{2}\Delta_R - \frac{1}{2}\Delta_r + \frac{1}{2q} w^2 R^2 - \frac{\alpha}{\left| \vec{r} - \vec{R} \right|} \right) f\left(\vec{R}, \vec{r}\right) = E\, f\left(\vec{R}, \vec{r}\right) \tag{1.29}$$

which is solved by writing solution as expansion

$$f\left(\overrightarrow{R}, \overrightarrow{r}\right) = \sum_n g_n\left(\overrightarrow{R}\right) h_n\left(\overrightarrow{r} - \overrightarrow{R}\right)$$

where $h_n\left(\overrightarrow{r}\right)$ is solution of equation

$$\left(-\frac{1}{2}\Delta_r - \frac{\alpha}{\left|\overrightarrow{r} - \overrightarrow{R}\right|}\right) h_n(\overrightarrow{r} - \overrightarrow{R}) = e_n h_n(\overrightarrow{r} - \overrightarrow{R}) \tag{1.30}$$

As before one chooses the parameter $q = m/M$ as the measures of quality for adiabatic expansion. When the expansion is replaced in (1.29) one obtains a set of equations for the functions $g_n\left(\overrightarrow{R}\right)$, which is in a matrix form given by

$$-\frac{q}{2}\left(\nabla_R - \langle h|\nabla h\rangle\right)^2 g + \frac{1}{2q} w^2 R^2 g + \frac{q}{2}\left(\langle h|\nabla h\rangle^2 - \langle h\,|\Delta|\,h\rangle\right) g \tag{1.31}$$
$$= (E - e)\, g$$

where in derivation equation (1.30) was used. The matrix elements are defined as

$$\left[\langle h|\nabla h\rangle\right]_{i,j} = \int d^3 r\; h_i\left(\overrightarrow{r}\right) \nabla h_j\left(\overrightarrow{r}\right)$$

and e is diagonal matrix.

Ratio of the two masses q appears in the part of the set (1.31) that refers to the motion of the centre of mass of Hydrogen (proton) and also in the term that couples it to the motion of the electron (the last term on the left). It would appear that by neglecting this ratio the two motions would be decoupled, which would indeed be the case if it is not that the coupling also appears in the kinetic energy of the Hydrogen. Therefore, in addition to neglecting the ratio of the two masses it should be assumed that momentum of the heavier mass, the average of ∇_R, is much larger than the average of momentum of the lighter one $\langle h|\nabla h\rangle$. This approximation, however, may not be the sole criterion, if the energy difference in e is very large then by replacing g with

$$g = e^{\overrightarrow{R}\cdot\langle h|\nabla h\rangle} f$$

then (1.31) is approximately

$$-\frac{q}{2}\nabla_R^2 f + \frac{1}{2q} w^2 R^2 f = (E - e)\, f$$

The equation describes entirely de-coupled motion of the atom from that of the electron.

Chapter 2
Relativistic Wave Equations

Abstract There are three sets of equations that are relativistic invariant, equations for vector and scalar potentials, Klein-Gordon equation and Dirac equation, and they could be derived from a single equation. Solutions are analyzed and with special emphases on applying various Green functions. Particular emphases is devoted to analyzing Dirac equation, being representative of relativistic quantum dynamics for spin half particles.

For discussion of particles, and in particular charges, that are confined within a small space it is imperative to use relativistic classical and quantum theory. The former is often a very good substitute for quantum theory, whether one wants only estimates or getting understanding of the essential dynamics for these circumstances. It is not only that particles are necessarily confined in the small space that relativistic theory should be used, they could also move at nearly the speed of light. There is also the problem of understanding very fine corrections in interaction of these particles with the electromagnetic field, when in particular one needs to know the meaning of solutions of the equations that describe relativistic particles. There are three equations that would be used for relativistic treatment of dynamics of particles, classical dynamics excluded. One describes dynamics of the electromagnetic field (in fact a set of equations) and the other two describe quantum dynamics of particles. All of them could be derived from an all encompassing equation, the approach that gives better insight into the nature of relativistic dynamics.

2.1 Unifying Equation

Three equations are used when relativistic dynamics is implemented for description of wave phenomena: one is for the electromagnetic field and the other two are Klein-Gordon and Dirac equations. These equations, however, have single basic, unifying, form

$$\Delta f(\vec{r},t)-\frac{1}{c^2}\partial_t^2 f(\vec{r},t)-\frac{m^2c^2}{\hbar^2}f(\vec{r},t)=\rho(\vec{r},t) \tag{2.1}$$

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for example, if $m = 0$ and $\rho(\vec{r}, t)$ is charge density then $f(\vec{r}, t)$ is scalar potential for the electromagnetic field. On the other hand if $\rho(\vec{r}, t)$ is replaced by the charge current then solution is for the vector potential. Klein-Gordon equation is when $m \neq 0$ where $\rho(\vec{r}, t)$ is collection of all terms from the equation for a particle with the charge q that interacts with the electromagnetic field

$$\left(\nabla - i\frac{q\overrightarrow{A}}{\hbar c}\right)^2 f(\vec{r}, t) - \left(\frac{1}{c}\partial_t + i\frac{qV}{\hbar c}\right)^2 f(\vec{r}, t) - \frac{m^2c^2}{\hbar^2} f(\vec{r}, t) = 0 \tag{2.2}$$

and when it is put into the form (2.1).

Similarly Dirac equation for interacting charged particle with the electromagnetic field is

$$\left(\frac{1}{c}\gamma_0\partial_t + \overrightarrow{\gamma} \cdot \nabla + i\frac{mc}{\hbar}\right) f(\vec{r}, t) = -\rho(\vec{r}, t) \tag{2.3}$$

where $\rho(\vec{r}, t)$ is obtained from

$$\left(\frac{1}{c}\gamma_0\partial_t + i\frac{qV}{\hbar c}\gamma_0 + \overrightarrow{\gamma} \cdot \nabla - \frac{iq}{\hbar c}\overrightarrow{\gamma} \cdot \overrightarrow{A} + i\frac{mc}{\hbar}\right) f(\vec{r}, t) = 0 \tag{2.4}$$

by collecting the appropriate terms. The symbols that are used are defined as

$$\overrightarrow{\gamma} = \begin{vmatrix} 0 & \vec{S} \\ -\vec{S} & 0 \end{vmatrix}, \quad \gamma_0 = \begin{vmatrix} I & 0 \\ 0 & -I \end{vmatrix} \tag{2.5}$$

and

$$S_x = \begin{vmatrix} 0 & 1 \\ 1 & 0 \end{vmatrix}, \quad S_y = \begin{vmatrix} 0 & -i \\ i & 0 \end{vmatrix}, \quad S_z = \begin{vmatrix} 1 & 0 \\ 0 & -1 \end{vmatrix}$$

and I is the unit matrix. In the spherical coordinates

$$S_r = \begin{vmatrix} \cos\theta & e^{-i\phi}\sin\theta \\ e^{i\phi}\sin\theta & -\cos\theta \end{vmatrix}, \quad S_\theta = \begin{vmatrix} -\sin\theta & e^{-i\phi}\cos\theta \\ e^{i\phi}\cos\theta & \sin\theta \end{vmatrix},$$
$$S_\phi = \begin{vmatrix} 0 & -ie^{-i\phi} \\ ie^{i\phi} & 0 \end{vmatrix}$$

By parametrizing solution as

$$f(\vec{r}, t) = \left(\frac{1}{c}\gamma_0\partial_t + \overrightarrow{\gamma} \cdot \nabla - i\frac{mc}{\hbar}\right) g(\vec{r}, t) \tag{2.6}$$

one obtains equation

$$\Delta g(\vec{r}, t) - \frac{1}{c^2}\partial_t^2 g(\vec{r}, t) - \frac{m^2c^2}{\hbar^2} g(\vec{r}, t) = \rho(\vec{r}, t)$$

which is formally the same as the previous two inhomogeneous wave equations, the only difference being that $g(\vec{r}, t)$ has four components.

Equation (2.1) is transformed into the integral equation form

$$f(\vec{r}, t) = f_0(\vec{r}, t) + \int ds\, d^3u\, K\left(\vec{r} - \overrightarrow{u}, t - s\right) \rho(\overrightarrow{u}, s) \tag{2.7}$$

for the sake of finding solution by iteration with the advantage that at each step the boundary conditions are preserved. $f_0(\vec{r}, t)$ is solution of homogeneous equation and the remaining term is solution of (2.1) if

$$\left(\Delta - \frac{1}{c^2}\partial_t^2 - \frac{m^2c^2}{\hbar^2}\right) K\left(\vec{r} - \overrightarrow{u}, t - s\right) = \delta\left(\vec{r} - \overrightarrow{u}\right) \delta(t - s) \tag{2.8}$$

2.2 Homogeneous Equation

Homogeneous form of the wave equation (2.1) is

$$\Delta f(\vec{r}, t) - \frac{1}{c^2}\partial_t^2 f(\vec{r}, t) - \frac{m^2c^2}{\hbar^2} f(\vec{r}, t) = 0$$

with the simplest solution in the form of two plane waves

$$f(\vec{r}, t) = e^{i\overrightarrow{k}\cdot\overrightarrow{r} \pm i\epsilon t/\hbar}$$

where $\epsilon = c\sqrt{\hbar^2k^2 + m^2c^2}$. The plane wave solutions have only mathematical significance because they extend over the whole space and in that sense they do not represent physical state of a particle. Particle is normally localized within a certain space region when solutions of the homogeneous equation are more complex.

Solving homogeneous equation requires defining initial and boundary conditions for its solution, which in turn are defined by physical circumstances. Two initial conditions are required at $t = 0$

$$f(\vec{r}, 0) = F_0(\vec{r}), \quad \partial_t f(\vec{r}, 0) = G_0(\vec{r})$$

whilst no particular boundary conditions on these are assumed. Solution of the homogeneous equation is now

$$f(\vec{r}, t) = \int d^3u \left[K_1\left(\vec{r} - \overrightarrow{u}, t\right) F_0(\overrightarrow{u}) + K_2\left(\vec{r} - \overrightarrow{u}, t\right) G_0(\overrightarrow{u})\right] \tag{2.9}$$

with the requirement that

$$K_2\left(\vec{r}-\overrightarrow{u},0\right)=0,\quad K_1\left(\vec{r}-\overrightarrow{u},0\right)=\delta\left(\vec{r}-\overrightarrow{u}\right)$$

and

$$\partial_t K_2\left(\vec{r}-\overrightarrow{u},0\right)=\delta\left(\vec{r}-\overrightarrow{u}\right),\quad \partial_t K_1\left(\vec{r}-\overrightarrow{u},0\right)=0$$

One shows that

$$K_2\left(\vec{r},t\right)=\frac{\hbar}{(2\pi)^3}\int d^3k\ \frac{\sin\left(\epsilon t/\hbar\right)}{\epsilon}e^{i\overrightarrow{k}\cdot\overrightarrow{r}}$$

and

$$K_1\left(\vec{r},t\right)=\partial_t K_2\left(\vec{r},t\right)=\frac{1}{(2\pi)^3}\int d^3k\ \cos\left(\epsilon t/\hbar\right)e^{i\overrightarrow{k}\cdot\overrightarrow{r}}$$

or

$$K_2\left(\vec{r},t\right)=\frac{i}{(2\pi)^3}\int d^3k\ d\omega\ e^{i\overrightarrow{k}\cdot\vec{r}-i\omega t}\delta\left(\omega^2-\frac{\epsilon^2}{\hbar^2}\right)\frac{\omega}{|\omega|}\tag{2.10}$$

and

$$K_1\left(\vec{r},t\right)=\frac{1}{\hbar\,(2\pi)^3}\int d^3k\ d\omega\ e^{i\overrightarrow{k}\cdot\vec{r}-i\omega t}\delta\left(\omega^2-\frac{\epsilon^2}{\hbar^2}\right)\epsilon$$

Important feature of the functions $K_1\left(\vec{r},t\right)$ and $K_2\left(\vec{r},t\right)$ is that they are analytic in the variable k, which is essential if for the solutions it is required not to transmit signals faster than the speed of light. As the consequence, however, both signs of energy are present in solution, which is explicitly evident if it is written in the expanded form

$$f\left(\vec{r},t\right)=\frac{1}{2\,(2\pi)^3}\left[\int d^3k\ e^{i\overrightarrow{k}\cdot\vec{r}+i\epsilon t/\hbar}K^+\left(\overrightarrow{k}\right)+\int d^3k\ e^{i\overrightarrow{k}\cdot\vec{r}-i\epsilon t/\hbar}K^-\left(\overrightarrow{k}\right)\right]$$

where

$$K^{\pm}\left(\overrightarrow{k}\right)=\int d^3u\ e^{-i\overrightarrow{k}\cdot\overrightarrow{u}}\left[F_0(\overrightarrow{u})\pm\frac{\hbar}{i\epsilon}G_0(\overrightarrow{u})\right]$$

Solution is a combination of two plane waves, whose physical meaning is deduced by noting that velocity of a relativistic particle is

$$\overrightarrow{v}=\frac{\overrightarrow{p}}{e}c^2=-c^2\nabla\left(\partial_t\right)^{-1}$$

where the operators act on a plane wave. Thus the velocity of the component with $K^+\left(\overrightarrow{k}\right)$ in the solution $f\left(\vec{r},t\right)$ is

$$\overrightarrow{v}=-\frac{\hbar\overrightarrow{k}}{\epsilon}c^2$$

and points in the opposite direction with respect to the momentum of particle. For the other component velocity is in direction of momentum. In general, therefore, solution always consists of two components, one going in the opposite direction with respect to the other. The question is could one form solution with a single energy component, for example only for the positive one?

For a single energy component solution, for example positive, one should require that

$$K^{+}\left(\overrightarrow{k}\right) = 0$$

for all $\overrightarrow{k}$. It follows that $F_0(\overrightarrow{r})$ and $G_0(\overrightarrow{r})$ are not independently determined but they are related by

$$F_0(\overrightarrow{r}) = \frac{\hbar i}{(2\pi)^3} \int d^3u \; G_0(\overrightarrow{u}) \int d^3k \; \frac{e^{i\overrightarrow{k}\cdot(\overrightarrow{u}-\overrightarrow{r})}}{\epsilon} \tag{2.11}$$

and if $G_0(\overrightarrow{u})$ is spherically symmetric then

$$F_0(r) = -\frac{2i\hbar}{\pi c\hbar r} \int dk \; \frac{\sin kr}{\sqrt{k^2 + \frac{m^2c^2}{\hbar^2}}} \int du \; u \; G_0(u) \sin ku$$

In the limit $m \to 0$ (for the electromagnetic field)

$$F_0(r) = -\frac{2i\hbar}{4\pi c\hbar r} \int du \; u \; G_0(u) \ln\left[\frac{(r+u)^2}{(r-u)^2}\right] \underset{r\to\infty}{\approx} -\frac{2i\hbar}{\pi c\hbar r^2} \int du \; u^2 \; G_0(u)$$

which shows that $F_0(r)$ is nowhere zero even if $G_0(r)$ may be strictly so beyond some r. This, however, means that for a single energy component solution particle cannot be localized within finite space.

On the other hand, in the limit $m \to \infty$

$$F_0(r) = -\frac{i\hbar}{mc^2} G_0(r)$$

and the solution is determined by only single initial function, which is the non relativistic limit.

Solution (2.9) could also be used for solving homogeneous Dirac equation, however, it would appear that since it is first order in time derivative there is no need for this initial condition. This is not the case because solution is having four components and requires formally four initial conditions at $t = 0$. The simplest generalization in (2.9) would be to replace $F_0(\overrightarrow{u})$ and $G_0(\overrightarrow{u})$ by four row matrices, but that means eight initial functions amongst which four matrix elements are not independent functions. For selecting these elements one starts with the solution of Dirac equation as it is formally derived from (2.9)

$$f(\vec{r},t)=\left(\frac{1}{c}\gamma_0\partial_t+\overrightarrow{\gamma}\cdot\nabla-i\frac{mc}{\hbar}\right)$$
$$\int d^3u\ \left[K_1\left(\vec{r}-\overrightarrow{u},t\right)F_0(\overrightarrow{u})+K_2\left(\vec{r}-\overrightarrow{u},t\right)G_0(\overrightarrow{u})\right]$$

but it is more convenient to give it in the Fourier transformed form. If one makes replacement

$$f(\vec{r},t)=\int d^3k\ \widehat{f}\left(\overrightarrow{k},t\right)e^{i\overrightarrow{k}\cdot\overrightarrow{r}} \tag{2.12}$$

and defines matrix E as

$$E=e^{-it\gamma_0\epsilon/\hbar} \tag{2.13}$$

then

$$\widehat{f}(\overrightarrow{k},t)=\frac{1}{2}\left(\frac{1}{c}\gamma_0\partial_t+i\overrightarrow{\gamma}\cdot\overrightarrow{k}-i\frac{mc}{\hbar}\right)E\left[\frac{\hbar}{i\epsilon}\gamma_0\widehat{g}_0(\overrightarrow{k})+\widehat{F}_0(\overrightarrow{k})\right]$$

This is a linear combination

$$\widehat{f}(\overrightarrow{k},t)=\Upsilon Ea$$

where a is a single column matrix and Υ is a 4×4 unitary matrix with the property

$$\Upsilon^+\Upsilon=I$$

where I is the unit matrix. The matrix a is determined from the initial $\widehat{f}_0(\overrightarrow{k})=\widehat{f}(\overrightarrow{k},t=0)$, whose matrix elements are arbitrary functions of $\overrightarrow{k}$, in which case

$$a=\Upsilon^+\widehat{f}_0(\overrightarrow{k})$$

and

$$\widehat{f}(\overrightarrow{k},t)=\Upsilon E\Upsilon^+\widehat{f}_0(\overrightarrow{k})$$

Solution in terms of $\widehat{F}_0(\overrightarrow{k})$ and $\widehat{g}_0(\overrightarrow{k})$ is then

$$\Upsilon E\Upsilon^+\widehat{f}_0(\overrightarrow{k})=\frac{1}{2}\left(\frac{1}{c}\gamma_0\partial_t+i\overrightarrow{\gamma}\cdot\overrightarrow{k}-i\frac{mc}{\hbar}\right)E\left[\frac{\hbar}{i\epsilon}\gamma_0\widehat{g}_0(\overrightarrow{k})+\widehat{F}_0(\overrightarrow{k})\right]$$

where either of the two coefficients is arbitrary, and one could choose

$$\widehat{F}_0(\overrightarrow{k})=\frac{\hbar}{i\epsilon}\gamma_0\widehat{g}_0(\overrightarrow{k})$$

when

$$\widehat{f}(\overrightarrow{k},t)=\Upsilon E\Upsilon^{+}\widehat{f}_0(\overrightarrow{k})=\frac{\hbar}{i\epsilon}\left(\frac{1}{c}\gamma_0\partial_t+i\overrightarrow{\gamma}\cdot\overrightarrow{k}-i\frac{mc}{\hbar}\right)E\,\gamma_0\widehat{g}_0(\overrightarrow{k}) \quad (2.14)$$

One shows that

$$\left(\frac{1}{c}\gamma_0\partial_t+i\overrightarrow{\gamma}\cdot\overrightarrow{k}-i\frac{mc}{\hbar}\right)E=-i\frac{\sqrt{2\epsilon\left(\epsilon+mc^2\right)}}{\hbar c}UE$$

where U is a unitary matrix and could be identified with Υ, which is explicitly given as

$$\Upsilon=\sqrt{\frac{\epsilon+mc^2}{2\epsilon}}\begin{vmatrix} I & -c\hbar\frac{\overrightarrow{S}\cdot\overrightarrow{k}}{\epsilon+mc^2} \\ c\hbar\frac{\overrightarrow{S}\cdot\overrightarrow{k}}{\epsilon+mc^2} & I \end{vmatrix} \quad (2.15)$$

and

$$\widehat{g}_0(\overrightarrow{k})=-\frac{c\sqrt{\epsilon}}{\sqrt{2\left(\epsilon+mc^2\right)}}\gamma_0\Upsilon^{+}\widehat{f}_0(\overrightarrow{k}) \quad (2.16)$$

In this way $\widehat{F}_0(\overrightarrow{k})$ and $\widehat{g}_0(\overrightarrow{k})$ are determined in terms of the initial condition $\widehat{f}_0(\overrightarrow{k})$.

What is the condition for the solution with only one energy component? The one (2.11) does not apply here instead one imposes it on $\widehat{g}_0(\overrightarrow{k})$ in (2.16), thus for the solution with only the positive energy component the last two matrix elements should be zero. This means that the four elements of $\widehat{f}_0(\overrightarrow{k})$ cannot be chosen independently, instead they are related by

$$\widehat{f}^{(-)}(\overrightarrow{k},0)=\frac{c\hbar}{\epsilon+mc^2}\overrightarrow{S}\cdot\overrightarrow{k}\;\widehat{f}^{(+)}(\overrightarrow{k},0) \quad (2.17)$$

and so

$$\widehat{G}_0^{(+)}(\overrightarrow{k})=-\frac{c\epsilon}{\epsilon+mc^2}\widehat{f}^{(+)}(\overrightarrow{k},0),\quad \widehat{G}_0^{(-)}(\overrightarrow{k})=0 \quad (2.18)$$

This result implies a general question of initial conditions for Dirac equation. In particular one would like to know if they are specified, for example, in the coordinate space how do they appear in the momentum space, and vice verse.

If in the coordinate space the initial condition is $f_0\left(\overrightarrow{r}\right)$ then in the momentum space the matrix $\widehat{g}_0(\overrightarrow{k})$ plays the same role and it is given by

$$\widehat{g}_0(\overrightarrow{k})=-\frac{c}{2}\left[1+\frac{c\hbar}{\left(\epsilon+mc^2\right)}\overrightarrow{\gamma}\cdot\overrightarrow{k}\right]\gamma_0\widehat{f}_0(\overrightarrow{k}) \quad (2.19)$$

In particular if one specifies that $f_0\left(\overrightarrow{r}\right)$ contains only the positive energy components then $\widehat{g}_0(\overrightarrow{k})$ is

$$\widehat{G}_0^+(\overrightarrow{k}) = -\frac{c}{2}\widehat{f}_0^+(\overrightarrow{k});\ \ \widehat{G}_0^-(\overrightarrow{k}) = \frac{\hbar c^2}{2\left(\epsilon + mc^2\right)}\overrightarrow{S}\cdot\overrightarrow{k}\ \ \widehat{f}_0^+(\overrightarrow{k})$$

which shows that in the momentum space both energy components in the coefficients are present. At any other time in the coordinate space the solution is given by the transformation (2.12) of solution (2.14) and hence both energy components are present. In other words, if in the coordinate space one determines initial conditions to have only a single energy component, in the time evolution both appear.

The only way to ensure that at any time only single energy component is present in the coordinate space is to choose correct $\widehat{g}_0(\overrightarrow{k})$, as in the example (2.18). For example solution with only the positive energy component is

$$f\left(\overrightarrow{r},t\right) = \frac{\hbar}{i}\left(\frac{1}{c}\gamma_0\partial_t + \overrightarrow{\gamma}\cdot\overrightarrow{\nabla} - i\frac{mc}{\hbar}\right)\int d^3k\,\frac{e^{i\overrightarrow{k}\cdot\overrightarrow{r}-it\epsilon/\hbar}}{\epsilon}\begin{vmatrix}\widehat{G}_0^{(+)}(\overrightarrow{k})\\ 0\end{vmatrix}$$

but as the initial conditions are normally selected in the coordinate space finding $\widehat{G}_0^{(+)}(\overrightarrow{k})$ that matches it is not a simple task. One solves the problem by using the relationship (2.17) when

$$f\left(\overrightarrow{r},0\right) = \int d^3k\,e^{i\overrightarrow{k}\cdot\overrightarrow{r}}\begin{vmatrix}\widehat{f}^{(+)}(\overrightarrow{k},0)\\ \frac{c\hbar}{\epsilon+mc^2}\overrightarrow{S}\cdot\overrightarrow{k}\ \ \widehat{f}^{(+)}(\overrightarrow{k},0)\end{vmatrix}$$

which shows that only the first two components of $f\left(\overrightarrow{r},0\right)$ are arbitrary. If one chooses $f^+\left(\overrightarrow{r},0\right)$ then

$$\widehat{f}^{(+)}(\overrightarrow{k},0) = \frac{1}{(2\pi)^3}\int d^3r\,e^{-i\overrightarrow{k}\cdot\overrightarrow{r}}f^+\left(\overrightarrow{r},0\right)$$

and the other two components in the coordinate space are

$$f^-\left(\overrightarrow{r},0\right) = \frac{c\hbar}{i}\overrightarrow{S}\cdot\overrightarrow{\nabla}\int d^3k\,\frac{e^{i\overrightarrow{k}\cdot\overrightarrow{r}}}{\epsilon+mc^2}\,\widehat{f}^{(+)}(\overrightarrow{k},0)$$

2.3 Inhomogeneous Equation

2.3.1 General Features

Inhomogeneous term in (2.1) is charge or current density for the electromagnetic field, whilst for Klein-Gordon equation it is

$$\rho = \frac{2iq}{\hbar c}\left(\overrightarrow{A}\cdot\nabla + \frac{1}{c}V\partial_t\right) f(\vec{r},t) + \frac{q^2}{c^2\hbar^2}\left(\overrightarrow{A}^2 - V^2\right) f(\vec{r},t) \tag{2.20}$$

and for Dirac equation

$$\rho = \frac{iq}{\hbar c}\left(\overrightarrow{\gamma}\cdot\overrightarrow{A} - \gamma_0 V\right)\left(\frac{1}{c}\gamma_0\partial_t + \overrightarrow{\gamma}\cdot\nabla - i\frac{mc}{\hbar}\right) g(\vec{r},t) \tag{2.21}$$

where the replacement (2.6) was made.

Green function that enters integral equation (2.7) is formally defined as solution of equation (2.8) and its Fourier transform

$$K(\vec{r},t) = \int d^3k\, de\, \widehat{K}\left(\overrightarrow{k}, e\right) e^{i\overrightarrow{k}\cdot\vec{r} - iet/\hbar}$$

is

$$\widehat{K}\left(\overrightarrow{k}, e\right) = \frac{1}{(2\pi)^4}\frac{c^2\hbar^2}{e^2 - c^2\hbar^2k^2 - m^2c^4}$$

which is a function with two first order singular points. There are various ways to avoid integrating over the singular points and the results represent different boundary conditions. Important integration variable is e and one way of evaluating this integral is to calculate its principal value

$$\int de\, \widehat{K}\left(\overrightarrow{k}, e\right) e^{-iet/\hbar} = \frac{c^2\hbar^2}{(2\pi)^4}\mathbf{P}\left[\int \frac{de}{e^2 - \epsilon^2} e^{-iet/\hbar}\right]$$

the result being

$$\int de\, \widehat{K}\left(\overrightarrow{k}, e\right) e^{-iet/\hbar} = -\frac{c^2\hbar^2}{16\pi^3\epsilon}\sin\frac{\epsilon t}{\hbar}$$

The other way is to replace e by $e + i\eta$, where η is small and positive, and after integration it is taken to zero.[1] In this case

$$\int de\, \widehat{K}\left(\overrightarrow{k}, e\right) e^{-iet/\hbar} = \Theta(t)\frac{c^2\hbar^2}{8\pi^3\epsilon}\sin\frac{\epsilon t}{\hbar}$$

[1] Analogous way is to retain the integration variable e real but shifting the integration path into the complex e plane. The result is the same.

where $\Theta(t)$ is the unit step function. Green function that results from such integration is called retarded. Similarly one could show that if $\eta < 0$ the right hand side is multiplied by $\Theta(-t)$, and this is advanced Green function.

The third way to evaluate the integral is to make replacement $\epsilon \to \epsilon - i\eta$ when the results is

$$\int de\ \widehat{K}(\overrightarrow{k}, e)\ e^{-ie t/\hbar} = i\frac{c^2\hbar^2}{16\pi^3\epsilon}\left[\Theta(t)\, e^{-ie t/\hbar} + \Theta(-t)\, e^{ie t/\hbar}\right]$$

If $\eta < 0$ then the sign of ϵ in the exponent is changed. This is known as the Feynman Green function.

Although (2.1) is the same for all three relativistic applications, with some not so essential modifications, the meaning of solutions does not reflect that observation. This is demonstrated on the conservation laws that are deduced from these three applications. In electrodynamics the wave equation is for the scalar V and vector $\overrightarrow{A}$ potentials

$$\begin{aligned} \Delta V - \frac{1}{c^2}\partial_t^2 V &= -4\pi\rho \\ \Delta\overrightarrow{A} - \frac{1}{c^2}\partial_t^2\overrightarrow{A} &= -\frac{4\pi}{c}\overrightarrow{j} \end{aligned} \tag{2.22}$$

and from the continuity equation for the charge ρ and current $\overrightarrow{j}$ densities

$$\partial_t\rho = -\nabla\cdot\overrightarrow{j}$$

one shows that

$$\frac{1}{c}\partial_t V + \nabla\cdot\overrightarrow{A} = 0$$

This is formally the continuity equation for the two potentials but it does not have the same meaning as for the charge and current densities for which it implies conservation law for the charge. The continuity equation for potentials is called the Lorentz condition, and about its meaning and importance shall be discussed in Chap. 3. There is indeed a conservation law in electrodynamics, which relates the energy change in the field at the expense of its flow from or into some volume, but it cannot be deduced from the two equations for the potentials (see Chap. 3).

For the Klein-Gordon equation one derives the continuity equation

$$\partial_t P = -\nabla\cdot\overrightarrow{J} \tag{2.23}$$

where

$$P = -\hbar\ \mathrm{Im}\left(f^*\partial_t f\right) - Vf^*f$$

and

$$\overrightarrow{J} = \hbar c^2 \,\mathrm{Im}\,\left(f^* \nabla f\right) - c\,\overrightarrow{A}\, f f^*$$

and about its meaning in Sect. 2.3.3. In short, this continuity equation implies conservation of energy law because P could be associated with the energy density.

From Dirac equation (2.4) one derives the continuity equation

$$\partial_t \left(f^+ f\right) = -c\nabla \cdot \left(f^+ \gamma_0 \overrightarrow{\gamma}\, f\right)$$

where

$$P = f^+ f \tag{2.24}$$

is associated with the probability density and

$$\overrightarrow{J} = c f^+ \gamma_0 \overrightarrow{\gamma}\, f \tag{2.25}$$

with the probability current. The continuity equation for Dirac equation implies conservation of the probability law, more about it in Sect. 2.3.4.

2.3.2 *Electromagnetic Field*

Properties of solutions for the two basic equations of electrodynamics (2.22) are demonstrated on the equation for the scalar potential because no additional information is obtained by discussing the one for the vector potential. More detailed analysis that includes both equations is given in Chap. 3.

Equation for the scalar potential is

$$\Delta V(\vec{r}, t) - \frac{1}{c^2}\partial_t^2 V(\vec{r}, t) = -4\pi\rho(\vec{r}, t) \tag{2.26}$$

where $\rho(\vec{r}, t)$ is charge density, which could have two sources. It is either distribution of classical charges or it could be the probability density that plays the role of the charge density. The latter is (2.21), times the charge of the particle, and not (2.20) because it cannot be associated with the probability density, as it is discussed in Sect. 2.3.3.

Solution of equation (2.26) depends on the choice of the boundary conditions, and consequently appropriate Green function is chosen from those that are defined in Sect. 2.3.1. The most often used is the retarded boundary condition for which the appropriate Green function is defined as

$$K_r(\vec{r}, t) = \frac{1}{(2\pi)^4}\int d^3k\, d\omega \quad \frac{c^2}{(\omega + i\eta)^2 - c^2 k^2} e^{i\overrightarrow{k}\cdot\vec{r} - i\omega t} \tag{2.27}$$

from which its intermediate form is

$$K_r(\vec{r},t) = -\frac{c}{2\,(2\pi)^3}\int d^3k\;\frac{\sin(ckt)}{k}\;e^{i\,\vec{k}\cdot\vec{r}}\;\Theta(t)$$

and the final one

$$K_r(\vec{r},t) = -\frac{1}{4\pi r}\delta\left(t-\frac{r}{c}\right)\Theta(t)$$

Solution of the wave equation is now

$$V_r(\vec{r},t) = \int d^3u\;\frac{1}{\left|\vec{r}-\overrightarrow{u}\right|}\rho\left(\overrightarrow{u},\,t-\frac{\left|\vec{r}-\overrightarrow{u}\right|}{c}\right) \tag{2.28}$$

and it represents (the details in Chap. 3) outflow of electromagnetic energy from a sphere within which all charge density is contained. Similarly one derives advanced Green function, which is given by

$$K_a(\vec{r},t) = -\frac{1}{4\pi r}\delta\left(t+\frac{r}{c}\right)\Theta(-t)$$

Retarded and advanced Green functions in the combination

$$K^-(\vec{r},t) = \frac{1}{2}\left[K_r(\vec{r},t) - K_a(\vec{r},t)\right] \tag{2.29}$$

define standing wave solution. From their definition the standing wave Green function is

$$K^-(\vec{r},t) = -\frac{ic^2}{2\,(2\pi)^3}\int d^3k\;d\omega\;e^{i\,\vec{k}\cdot\vec{r}-i\omega t}\,\delta\left(\omega^2-c^2k^2\right)\frac{\omega}{|\omega|}$$

in the intermediate form

$$K^-(\vec{r},t) = -\frac{c}{16\pi^3}\int d^3k\;e^{i\,\vec{k}\cdot\vec{r}}\,\frac{\sin(ckt)}{k}$$

and in the final

$$K^-(\vec{r},t) = -\frac{1}{8\pi r}\left[\delta\left(t-\frac{r}{c}\right)-\delta\left(t+\frac{r}{c}\right)\right]$$

which is the same as the Green function (2.10) for homogeneous equation, when the mass of particle is formally set to zero. The Green function $K^-(\vec{r},t)$ also solves the initial value problem for the inhomogeneous equation, producing the standing wave solution.

The basic assumption in the derivation of the previous Green functions is to shift the poles of integrand (2.27) in the frequency variable, however, the same could be done by shifting them in the wave number. One then obtains Feynman Green function, which is defined as

$$K_F(\vec{r},t) = -\frac{1}{(2\pi)^4}\int d^3k\, d\omega\, \frac{c^2}{\omega^2 - c^2(k-i\eta)^2}\, e^{i\overrightarrow{k}\cdot\vec{r}-i\omega t}$$

and in the intermediate form it is given by

$$K_F(\vec{r},t) = \frac{ic}{2(2\pi)^3}\int d^3k\, \frac{e^{-ickt}\Theta(t) + e^{ickt}\Theta(-t)}{k}\, e^{i\overrightarrow{k}\cdot\vec{r}}$$

and finally

$$K_F(\vec{r},t) = \frac{ic}{4\pi^2}\left[\mathbf{P}\left[\frac{1}{r^2 - c^2t^2}\right] - \frac{i\pi}{2r}\delta(r - c|t|)\right]$$

Physical meaning of those Green functions is analyzed on two examples.

2.3.2.1 Charge Density

In order to understand the meaning of various solutions that the Green functions produce it is assumed that a point charge is created at $t = 0$[2] and after it oscillates harmonically. Charge density for this example is

$$\rho\left(\overrightarrow{r},t\right) = \sin(\omega_0 t)\,\delta\left(\overrightarrow{r}\right)\Theta(t) \tag{2.30}$$

in which case retarded solution is

$$V_r\left(\overrightarrow{r},t\right) = \frac{1}{r}\sin\left[\omega_0\left(t - \frac{r}{c}\right)\right]\Theta\left(t - \frac{r}{c}\right)$$

As anticipated the field expands at the speed of light, being zero for all time that is smaller than the time to reach the point r at this speed. After that the field oscillates out of phase with the source, the phase being determined by the information that travels with c.

Standing wave solution, on the other hand, is given by

$$V_{st}\left(\overrightarrow{r},t\right) = \frac{\sin\left[\omega_0\left(t - \frac{r}{c}\right)\right]\Theta\left(t - \frac{r}{c}\right) - \sin\left[\omega_0\left(t + \frac{r}{c}\right)\right]\Theta\left(t + \frac{r}{c}\right)}{2r}$$

that has two time sections. For $0 < t < r/c$ solution is the wave that travels from infinity towards the origin, whilst for $t > r/c$ it is in the form

$$V_{st}\left(\overrightarrow{r},t\right) = \frac{\cos(\omega_0 t)\sin\left(\frac{\omega_0 r}{c}\right)}{r}$$

[2]The meaning of this charge density is not very physical but it is instructive for understanding how its sudden change affects the electromagnetic field.

which describes standing wave being formed by two oppositely propagating waves that extend to infinity. For the assumed charge density standing wave is formed when t is very large.

Solution for the Feynman Green function is not given in simple form as for the previous two solutions. Furthermore solution is not easily interpreted for charge density, which is evident from two extreme limits. One limit is for large $r > ct$ when

$$V_F\left(\overrightarrow{r}, t\right) \approx \frac{i}{2r} e^{-i\omega_0\left(t+\frac{r}{c}\right)}$$

which is complex and therefore not regarded as the physical solution. On the other hand, for large $t > r/c$ solution is

$$V_F\left(\overrightarrow{r}, t\right) \approx \frac{1}{r} \sin\left(\omega_0 t\right) e^{i\frac{\omega_0 r}{c}}$$

which is again complex and resembles the standing wave solution $V_{st}\left(\overrightarrow{r}, t\right)$. The difference is that the standing wave solution is formed as interference of two waves, incoming and outgoing

$$V_{st}\left(\overrightarrow{r}, t\right) \sim \sin\left(\frac{\omega_0 r}{c} - \omega_0 t\right) + \sin\left(\frac{\omega_0 r}{c} + \omega_0 t\right)$$

whilst the Feynman is result of interference of the same kind of waves, but in the form of plane waves

$$V_F\left(\overrightarrow{r}, t\right) \sim e^{i\frac{\omega_0 r}{c} - i\omega_0 t} - e^{-i\frac{\omega_0 r}{c} - i\omega_0 t}$$

As the result the modulus of the standing wave solution is time dependent, oscillates as $\cos\left(\omega_0 t\right)$, whilst that of the Feynman is time independent. For this reason Feynman solution for charge density has no meaning but it has for quantum densities.

2.3.2.2 Quantum Density

Inhomogeneous term in (2.26) could also be the quantum probability density or the probability current for a charged particle. As mentioned in Sect. 2.3.1 the only densities that could play that role are derived from Dirac equation, and the charge density is

$$\rho(\vec{r}, t) = q\ f^{+}(\vec{r}, t) f(\vec{r}, t) \tag{2.31}$$

whilst the charge current is

$$\overrightarrow{J}(\vec{r}, t) = cq\ f^{+}(\vec{r}, t)\gamma_0 \overrightarrow{\gamma} f(\vec{r}, t) \tag{2.32}$$

where q is charge of the particle (in further discussion $q = 1$). Function $f(\vec{r}, t)$ appears in two basic forms, either as a combination of bound state eigenfunctions or it is a solution for unbound particle. General form of the density in both cases is

$$\rho(\vec{r}, t) = \; f_1^+(\vec{r}) f_2(\vec{r}) e^{i\omega_0 t} + f_2^+(\vec{r}) f_1(\vec{r}) e^{-i\omega_0 t}$$

where ω_0 could either be the energy difference of the states 1 and 2 or it could also contain frequency of the external electromagnetic wave if it interacts with the charge. For simplicity it is assumed that both $f_1(\vec{r})$ and $f_2(\vec{r})$ represent bound state functions and ω_0 is arbitrary. Furthermore it is assumed that there is no onset of time dependence, which implicitly assumes that if there is then solution is analyzed long time after it.

Retarded solution is obtained in a straightforward way, its structure is not very revelling, however, in the limit far away from the source it is given by

$$\begin{aligned} V_r(\vec{r}, t) \sim \frac{e^{i\omega_0\left(\frac{r}{c}-t\right)}}{r} \int d^3k_1 \; \widehat{f_2^+}(\overrightarrow{k_1} - \frac{\omega_0}{c}\widehat{n}) \; \widehat{f_1}(\overrightarrow{k_1}) \\ + \frac{e^{-i\omega_0\left(\frac{r}{c}-t\right)}}{r} \int d^3k_1 \; \widehat{f_1^+}(\overrightarrow{k_1}) \; \widehat{f_2}(\overrightarrow{k_1} + \frac{\omega_0}{c}\widehat{n}) \end{aligned} \tag{2.33}$$

where the replacement

$$\int d^3u e^{-i\,\overrightarrow{k}\cdot\overrightarrow{u}} \, f_1^+(u) f_2(u) = \frac{1}{(2\pi)^3} \int d^3k_1 \; \widehat{f_1^+}(\overrightarrow{k_1} - \overrightarrow{k}) \; \widehat{f_2}(\overrightarrow{k_1})$$

was made, the Fourier transform of the density. The result is important because it shows that the frequency of radiated field equals that of the frequency of the density, however, the amplitude of $V_r(\vec{r}, t)$ depends on the momentum width of individual solutions $f_j(\vec{r})$. If those widths are Δk_j and $\omega_0/c \gg \Delta k_j$ then this amplitude is negligible.

Standing wave solution is obtained in the same way, and in the far away limit it is given by

$$V_{st}(\vec{r}, t) \sim \frac{1}{r} \sin\left(\omega_0 t + \alpha\left(\widehat{n}\right)\right) \cos\left(\omega_0 \frac{r}{c}\right) I\left(\widehat{n}\right)$$

where

$$I\left(\widehat{n}\right) e^{i\alpha(\widehat{n})} = \int d^3u \sin\left(\omega_0 \frac{\widehat{n}\cdot\overrightarrow{u}}{c}\right) \; f_1^+(\overrightarrow{u}) f_2(\overrightarrow{u})$$

and $\widehat{n} = \vec{r}/r$. The solution is typical for this wave, it is a product of the time and space dependent functions. It could be shown (in later analysis) that resulting flow of energy from the source is zero, in contrast to the retarded solution when this flow is outward from the source.

Feynman solution is

$$V_F(\vec{r},t) = -e^{it\omega_0}\int d^3u\,\frac{e^{i\frac{\omega_0}{c}|\vec{r}-\overrightarrow{u}|}}{|\vec{r}-\overrightarrow{u}|}\,f_1^+(\overrightarrow{u})\,f_2(\overrightarrow{u}) - e^{-it\omega_0}\int d^3u\,\frac{e^{i\frac{\omega_0}{c}|\vec{r}-\overrightarrow{u}|}}{|\vec{r}-\overrightarrow{u}|}\,f_2^+(\overrightarrow{u})\,f_1(\overrightarrow{u})$$

which is complex and in classical electromagnetic theory it has no meaning. However, some of its meaning is deduced by considering its asymptotic limit far away from the source. In this case

$$V_F(\vec{r},t) \sim \frac{e^{it\omega_0+i\frac{\omega_0}{c}r}}{r}\int d^3k_1\;\widehat{f_1^+}(\overrightarrow{k_1})\;\widehat{f_2}(\overrightarrow{k_1}+\frac{\omega_0}{c}\widehat{n}) + \frac{e^{-it\omega_0+i\frac{\omega_0}{c}r}}{r}\int d^3k_1\;\widehat{f_2^+}(\overrightarrow{k_1}-\frac{\omega_0}{c}\widehat{n})\;\widehat{f_1}(\overrightarrow{k_1}) \tag{2.34}$$

which resembles retarded V_r solution. The essence of the two solutions, however, is different. In both solutions time has two signs but the sign of the radial component is always positive in V_F whilst in V_r changes. In the Feynman solution this indicates that the two components move in different directions whilst in the retarded they move in the same. In that respect Feynman solution is similar to the standing wave solution rather than the retarded one. There is, however, much more important difference in their physical meaning.

In the integrals of the three solutions the variable $\overrightarrow{k}$ is associated with the momentum of particle, given by $\hbar\overrightarrow{k}$. Change in the argument from one eigenfunction (the same applies if these are solutions for the unbound particles) to the other indicates that radiation by charge has the effect on its momentum distribution. If one associates $\widehat{f_1}(\overrightarrow{k_1})$ with the "incoming" solution[3] and $\widehat{f_2}(\overrightarrow{k_2})$ with the "outgoing" then the radiated field has impact on the momentum distribution of the latter. In the retarded solution (2.33) both plane wave components represent the radiated waves going outward, regardless of the sign in the time component of their phase. If this sign is negative then the corresponding momentum distribution of the "outgoing" solution is shifted, as if the charge lost its momentum by $\hbar\frac{\omega_0}{c}\widehat{n}$ from its "incoming" value. This demonstrates particle like feature of the radiation field, because if the outgoing radiation carries momentum $\hbar\frac{\omega_0}{c}\widehat{n}$ then it should be subtracted from the particle in order to preserve momentum conservation law. On the other hand, if the sign of time is positive the wave also goes outward but the momentum of the "outgoing" charge acquires momentum $\hbar\frac{\omega_0}{c}\widehat{n}$, which is contrary to the idea that the radiation field behaves as a particle. The same applies for the standing wave solution.

[3]The product of two eigenfunctions results from applying perturbation method in analysis of the effect on a charge by external force. In that case one of the eigenfunction, $f_1(\overrightarrow{u})$, corresponds to the unperturbed solution ("incoming") and $f_2(\overrightarrow{u})$ is from the set in which perturbed solution is expanded ("outgoing").

The Feynman solution (2.34), on the other hand, demonstrates the particle like feature of radiation field, because the two plane waves are going in different directions. Thus, for example, the incoming wave (having the positive sign of the time component in its phase) transfers momentum onto the charge. On the other hand, the wave that is outgoing carries away momentum thus reducing initial momentum of the charge.

Free Particle

Additional features of the radiation field are demonstrated for the probability density that describes a charge which is initially localized in a finite space, but otherwise it is free (for example an electron produced in a nuclear beta decay). A general solution of Dirac equation for this circumstance is given by

$$f\left(\overrightarrow{r},t\right)=\int d^3k\ \widehat{f}\left(\overrightarrow{k},t\right)e^{i\overrightarrow{k}\cdot\overrightarrow{r}} \tag{2.35}$$

where

$$\widehat{f}(\overrightarrow{k},t)=\frac{\hbar}{i\epsilon}\left(\frac{1}{c}\gamma_0\partial_t+i\overrightarrow{\gamma}\cdot\overrightarrow{k}-i\frac{mc}{\hbar}\right)E\,\gamma_0\widehat{g}_0(\overrightarrow{k})$$

$\widehat{g}_0(\overrightarrow{k})$ is connected with the initial $\widehat{f}_0(\overrightarrow{k})$ through the relationship (2.16).

Charge density for this example is time dependent because it spreads in time, however, there is a specific important feature of it that should be analyzed in detail. Initially localized charge implies that $\widehat{f}_0(\overrightarrow{k})$ is also bound within certain interval of k and there are two limits that could be analyzed depending on its range. One is the non-relativistic limit, meaning that for all k within this interval applies the inequality $k\ll\frac{mc^2}{c\hbar}$, in which case $\epsilon\approx mc^2+\frac{\hbar^2k^2}{2m}$, and $\widehat{f}(\overrightarrow{k},t)$ is approximately

$$\widehat{f}(\overrightarrow{k},t)\approx E\widehat{f}_0(\overrightarrow{k})-i\frac{\hbar}{mc}\gamma_0\overrightarrow{\gamma}\cdot\overrightarrow{k}\ \sin\left(\frac{\epsilon}{\hbar}t\right)\widehat{f}_0(\overrightarrow{k})$$

and the density is

$$\rho(\overrightarrow{r},t)\approx\rho_o(\overrightarrow{r},t)+\rho_s(\overrightarrow{r},t) \tag{2.36}$$

where

$$\rho_o(\overrightarrow{r},t)=\int d^3k\int d^3q\ \widehat{f}_0^{+}(\overrightarrow{q})e^{i\gamma_0\frac{\hbar\left(q^2-k^2\right)}{2m}t+i\left(\overrightarrow{k}-\overrightarrow{q}\right)\cdot\overrightarrow{r}}\ \widehat{f}_0(\overrightarrow{k})$$

and

$$\rho_s(\overrightarrow{r},t)=\frac{\hbar}{2mc}e^{-2i\gamma_0\frac{mc^2}{\hbar}t}\int d^3k\int d^3q\ \widehat{f}_0^{+}(\overrightarrow{q})\gamma_0\overrightarrow{\gamma}\cdot\left(\overrightarrow{k}+\overrightarrow{q}\right)e^{i\gamma_0\frac{\hbar\left(q^2+k^2\right)}{2m}t+i\left(\overrightarrow{k}-\overrightarrow{q}\right)\cdot\overrightarrow{r}}\ \widehat{f}_0(\overrightarrow{k})$$

$\rho_0(\overrightarrow{r},t)$ is the nonrelativistic time evolution of the charge density, the same as derived from Schroedinger equation. Depending on the initial mixture of states in $\widehat{f_0}(\overrightarrow{k})$ the time evolution could also include negative energy terms. The density $\rho_s(\overrightarrow{r},t)$ is combination of terms that are essentially the same as $\rho_0(\overrightarrow{r},t)$ but with the oscillating factor $e^{-2i\gamma_0\frac{mc^2}{\hbar}t}$.

Retarded solution is calculated from (2.28), and far away from the source the density $\rho_o(\overrightarrow{r},t)$ in (2.36) gives

$$V_{ro}(\vec{r},t) \sim \frac{(2\pi)^3}{r}\int d^3k\ \ \widehat{f_0^+}(\overrightarrow{k})\left(1-\gamma_0\frac{\hbar}{mc}\widehat{n}\cdot\overrightarrow{k}\right)^{-1}\widehat{f_0}(\overrightarrow{k}) \sim \frac{1}{r} \tag{2.37}$$

where the identity

$$\int d^3u\ e^{i\gamma_0\frac{\hbar\left(q^2-k^2\right)}{2m}\frac{\widehat{n}\cdot\vec{u}}{c}+i\left(\overrightarrow{k}-\overrightarrow{q}\right)\cdot\vec{u}} = (2\pi)^3\left(1-\gamma_0\frac{\hbar}{mc}\widehat{n}\cdot\overrightarrow{k}\right)^{-1}\delta\left(\overrightarrow{k}-\overrightarrow{q}\right)$$

was used. This is the Coulomb potential of a point like charge, which is slightly modified from its unit value and correction is of the order $k\hbar/(mc)$. The density $\rho_s(\overrightarrow{r},t)$ is essential the same as $\rho_0(\overrightarrow{r},t)$ except that it is oscillating with the mass dependent frequency, and so the potential has the same structure.

The other extreme is when $k \gg \frac{mc^2}{c\hbar}$ and $\epsilon \approx c\hbar k + \frac{m^2c^3}{2\hbar k}$, which is relativistic time evolution of the density. In this case

$$\widehat{f}(\overrightarrow{k},t) \approx \left[I\cos\left(\frac{\epsilon}{\hbar}t\right) - i\gamma_0\overrightarrow{\gamma}\cdot\frac{\overrightarrow{k}}{k}\sin\left(\frac{\epsilon}{\hbar}t\right)\right]\widehat{f_0}(\overrightarrow{k})$$

and the density is

$$\rho(\overrightarrow{r},t) \approx \rho_0(\overrightarrow{r},t) + \rho_s(\overrightarrow{r},t) \tag{2.38}$$

where

$$\rho_0(\overrightarrow{r},t) = \int d^3k\int d^3q\ \widehat{f_0^+}(\overrightarrow{q})\widehat{f_0}(\overrightarrow{k})\cos(cqt)\cos(ckt)\,e^{i\left(\overrightarrow{k}-\overrightarrow{q}\right)\cdot\overrightarrow{r}}$$

and

$$\rho_s(\overrightarrow{r},t) \approx -i\int d^3k\int d^3q\ e^{i\left(\overrightarrow{k}-\overrightarrow{q}\right)\cdot\overrightarrow{r}}$$
$$\widehat{f_0^+}(\overrightarrow{q})\gamma_0\overrightarrow{\gamma}\cdot\left(\frac{\overrightarrow{q}}{q}\sin(cqt)\cos(ckt)+\frac{\overrightarrow{k}}{k}\cos(cqt)\sin(ckt)\right)\widehat{f_0}(\overrightarrow{k})$$

where again only the dominant terms were retained. There is now no distinction between contributions from negative and positive energy components. The density spreads at (nearly) the speed of light, in contrast with the non-relativistic solution, more about it shortly.

The potential that is derived from the density (2.38) has complicated structure but overall it is negligible, and the reason shall be described on one example. However, before that a general comment is necessary. Relativistic time evolution of the density (2.38) is given by $\rho_0(\overrightarrow{r}, t)$ and $\rho_s(\overrightarrow{r}, t)$ for which it could be shown to spread at (nearly) the speed of light. This causes the problem of fundamental importance that should be discussed in more details. By the very nature of retarded solution (2.28) the potential $V(\vec{r}, t)$ is determined by the value of charge density prior to time t, which also includes the instant $t = 0$. This means that for the initial value of potential one requires charge density from its past, which is not known by default because the assumption is that its time evolution is determined from that instant on. In the non relativistic limit this was not the problem because the assumption is that velocity of light is nearly infinite and the past of the charge density is not essential. In general, therefore, initial value problem for potential is not solvable unless some assumptions are made on the past of the charge density. The simplest is to assume that it is constant up to $t = 0$ and after that its time evolution is for a free particle. For simplicity $\widehat{f_0}(\overrightarrow{k})$ is assumed to be dependent only on the modulus k.

Charge density $\rho_0(\overrightarrow{r}, t)$ with these properties is

$$\rho_0(\overrightarrow{r}, t) = \left| f\left(\overrightarrow{r}, t\right)\right|^2$$

where

$$\begin{aligned} f\left(\overrightarrow{r}, t\right) &= \int d^3k \widehat{f}(k, 0) \cos\left[ckt\ \Theta(t)\right] e^{i\overrightarrow{k}\cdot\overrightarrow{r}} \\ &= \frac{1}{2}\left[\frac{r + ct_r}{r} f\left(r + ct_r, 0\right) + \frac{r - ct_r}{r} f\left(r - ct_r, 0\right)\right] \end{aligned}$$

where

$$t_r = t\ \Theta(t)$$

Relativistic dynamics assumes that $f\left(\overrightarrow{r}, 0\right)$ is very narrow which means that $f\left(\overrightarrow{r}, t\right)$ is essentially of the shape of a sphere whose radius is expanding at (nearly) the speed of light and the thickness of its perimeter is of width for $\left|f\left(\overrightarrow{r}, 0\right)\right|$. The density $\rho_0(\overrightarrow{r}, t)$ is therefore concentrated on the perimeter of the sphere, of a narrow thickness, in which case one distinguishes three regions for potential: inside the sphere, within its perimeter and outside of it. The retarded potential is

$$V_r(\vec{r}, t) = \frac{1}{4}\int d^3u\ \frac{1}{\left|\vec{r} - \overrightarrow{u}\right|}\left|\frac{u + ct_r}{u} f\left(u + ct_r, 0\right) + \frac{u - ct_r}{u} f\left(u - ct_r, 0\right)\right|^2$$

where t in t_r is replaced by $t - \frac{|\vec{r}-\overrightarrow{u}|}{c}$, and for inside the sphere the inequality $ct \gg r$ should be satisfied. By writing $\overrightarrow{u} = u\widehat{n}_u$ one makes estimate

$$u \pm ct_r \approx \left(1 \pm \widehat{n} \cdot \overrightarrow{n_u}\right) u \pm ct \mp r \approx (1 \pm \widehat{n} \cdot \widehat{n}_u)\, u \pm ct$$

and the only non negligible contribution is for the negative sign and $u \approx ct$. This means that the potential is approximately

$$V_r(\vec{r}, t) \sim \frac{1}{ct} \int d^3u \left| \frac{u - ct}{u} f\,(u - ct, 0) \right|^2$$

which is constant in the coordinates and hence the field is zero. This is precisely the case for the field inside a sphere with only the surface charge.

For outside of the sphere $r \gg ct$ when

$$u \pm ct_r = u$$

and

$$V_r(\vec{r}, t) \approx \frac{1}{r} \int d^3u \;\; |f\,(u, 0)|^2$$

which is the Coulomb potential, as it should. Correction to the Coulomb law, of the kind given in (2.37), is not done.

Within the perimeter of the density, which arrives at distance r in time $t = r/c$, the potential makes a sudden change from $1/r$ functional form to a constant value inside the sphere. The change occurs within the width of $|f\,(r, 0)|^2$, which is small and hence the field could have large value.

Standing wave solution, and likewise the Feynman solution, have essentially no meaning for these narrow charge densities because the components of the retarded and advanced solutions are well separated in their time evolution. It is only when the latter overlap for a long period of time one could talk about their physical meaning.

2.3.3 Klein-Gordon Equation

Klein-Gordon equation is

$$\Delta f(\vec{r}, t) - \frac{1}{c^2}\partial_t^2 f(\vec{r}, t) - \frac{m^2c^2}{\hbar^2} f(\vec{r}, t) = g(\vec{r}, t) \tag{2.39}$$

and its solution is

$$f(\vec{r}, t) = f_0(\vec{r}, t) + \int d^3u\, ds\; K\left(\vec{r} - \overrightarrow{u}, t - s\right) g(\overrightarrow{u}, s) \tag{2.40}$$

where the Green function satisfies equation

$$\Delta K\left(\vec{r},t\right)-\frac{1}{c^2}\partial_t^2 K\left(\vec{r},t\right)-\mu^2 K\left(\vec{r},t\right)=\delta\left(\vec{r}\right)\delta\left(t\right)$$

The inhomogeneous term in (2.39) is the difference between (2.2) and the homogeneous equation for a free particle $f_0(\vec{r},t)$ that is discussed in (2.2).

Solutions of Klein-Gordon equation have very specific properties that cannot be understood in terms of the basic principles of quantum theory. These will be reviewed rather than discussing solutions based on different Green functions.

Important identity follows from (2.2)

$$c\nabla\left[c\hbar\left(f^*\nabla f-f\nabla f^*\right)-2iq\overrightarrow{A}f^*f\right]=-\hbar\,\partial_t\left[f\partial_t f^*-f^*\partial_t f-\frac{2iq}{\hbar}Vf^*f\right] \tag{2.41}$$

which is in the form of the continuity equation. As in the case of non-relativistic dynamics one could associate

$$P=\frac{\hbar}{2i}\left(f\partial_t f^*-f^*\partial_t f-\frac{2iq}{\hbar}Vf^*f\right) \tag{2.42}$$

with the probability density, but there is a problem with this interpretation because the function P is not always positive. Alternative interpretation is in terms of the charge density, but again it is not correct for the reasons that will be described, however, before doing that it is necessary to make a short digression about classical relativistic dynamics.

There are three types of energy of particle: its rest energy, or the energy equivalent of its rest mass, kinetic energy and potential energy. Total energy is combination of these three terms. In addition there is also momentum of particle and together with energy one derives fundamental equation of relativity

$$(e-qV)^2-c^2p^2=m^2c^4$$

where e is its total and V potential energy. The difference $e-qV$ is called energy of particle and it is given by

$$e-qV=\frac{mc^2}{\sqrt{1-\frac{v^2}{c^2}}}=mc^2+e_{kin} \tag{2.43}$$

where e_{kin} is kinetic energy. From relativistic definition of velocity v, essentially as the ratio of momentum and energy, one obtains

$$v=c\frac{\sqrt{(e-qV)^2-m^2c^4}}{e-qV} \tag{2.44}$$

from where one concludes that momentum and velocity of particle may not point in the same direction. In non relativistic dynamics they point in the same direction because by default mass is defined as a positive parameter. In relativistic dynamics, however, the mass is replaced by the energy of particle that could also be negative. This result will be of particular importance in later analysis of quantum dynamics.

In the function P the product $f\partial_t f^*$ could be replaced by $\frac{e}{\hbar} ff^*$, where e is the average total energy of the particle,[4] when (2.42) is approximately

$$P \approx (e - V)\, f^* f$$

One could interpret P as the product of energy of particle and the probability density, but for that to be correct $f^* f$ should obey continuity equation, which is not true. Furthermore the current that is defined from (2.41) (for simplicity the vector potential is omitted) is[5]

$$\overrightarrow{j} = \frac{c^2\hbar}{2i}\left(f^*\nabla f - f\nabla f^*\right)$$

which is interpreted as the momentum of particle, and the ratio $\overrightarrow{j}/P$ has dimension of velocity. This means that P could only be interpreted as the energy density and not probability of energy of a particle, and not as the probability density or charge density.

2.3.4 Dirac Equation

2.3.4.1 General Theory

Dirac set of equations for a charge in the electromagnetic field is given by (2.4)

$$\left(\frac{1}{c}\gamma_0\partial_t + i\frac{qV}{\hbar c}\gamma_0 + \overrightarrow{\gamma}\cdot\nabla - \frac{iq}{\hbar c}\overrightarrow{\gamma}\cdot\overrightarrow{A} + i\frac{mc}{\hbar}\right) f(\vec{r},t) = 0$$

and its homogeneous form had been discussed. The equation could be transformed in other forms, each one of them having certain merits. One form that resembles Klein-Gordon equation is obtained by generalizing parametrization (2.6) as

$$f(\vec{r},t) = \left(\frac{1}{c}\gamma_0\partial_t + i\frac{qV}{\hbar c}\gamma_0 + \overrightarrow{\gamma}\cdot\nabla - \frac{iq}{\hbar c}\overrightarrow{\gamma}\cdot\overrightarrow{A} - i\frac{mc}{\hbar}\right) g(\vec{r},t) \qquad (2.45)$$

[4] For a very narrow probability amplitude in momentum space (a very wide in the coordinate space) this assumption is nearly exact.

[5] It should be noted that from the continuity equation the current is not uniquely determined, as discussed in Chap. 3.

If it is replaced in Dirac equation one derives equation for $g(\vec{r},t)$

$$(\hbar\partial_t + iqV)^2 g - \left(c\hbar\nabla - iq\overrightarrow{A}\right)^2 g + m^2c^4 g$$
$$- ic\hbar q\,\gamma_0\overrightarrow{\gamma}\cdot\left(\frac{1}{c}\partial_t\overrightarrow{A} + \nabla V\right)g + ic\hbar q\,\overrightarrow{\Sigma}\cdot\left(\nabla\times\overrightarrow{A}\right)g = 0$$

where

$$\overrightarrow{\Sigma} = \begin{vmatrix} \vec{S} & 0 \\ 0 & \vec{S} \end{vmatrix}$$

and the identity

$$\left(\vec{S}\cdot\overrightarrow{a}\right)\left(\vec{S}\cdot\overrightarrow{b}\right) = \overrightarrow{a}\cdot\overrightarrow{b} + i\,\vec{S}\cdot\left(\overrightarrow{a}\times\overrightarrow{b}\right)$$

was used. The equation is the Klein-Gordon type, except that the solution $g(\vec{r},t)$ has four elements and there are two additional terms, one that describes interaction of electric field with the charge and the other that represents interaction of its spin with magnetic field. The difficulty appears to be in the order of the equation, which is the second order in both time and coordinates, and this requires more initial conditions than for (2.4). This observation, however, is superficial because $g(\vec{r},t)$ is parametrized as (2.45) and therefore the additional conditions are deduced from it. If in the small vicinity of the initial instant $t=0$ electromagnetic field is zero then in the momentum space solution for $f(\vec{r},t)$ is given by (2.14). The function $\widehat{g}_0(\overrightarrow{k})$ is determined from the initial $f(\vec{r},0)$ by using (2.19) and therefore $g(\vec{r},t)$, in the small vicinity of $t=0$ is given by

$$g(\vec{r},t) = \frac{\hbar}{i}\int d^3k\frac{1}{\epsilon}E\,\gamma_0\widehat{g}_0(\overrightarrow{k})e^{i\overrightarrow{k}\cdot\overrightarrow{r}}$$

from where additional initial conditions are

$$\partial_t g(\vec{r},0) = -i\frac{\hbar}{i\hbar}\int d^3k\,\widehat{g}_0(\overrightarrow{k})e^{i\overrightarrow{k}\cdot\overrightarrow{r}}$$
$$\nabla g(\vec{r},0) = \hbar\int d^3k\frac{\gamma_0\overrightarrow{k}}{\epsilon}\,\widehat{g}_0(\overrightarrow{k})e^{i\overrightarrow{k}\cdot\overrightarrow{r}}$$

If the scalar potential is time independent one derives another form of Dirac set of equations. The set is first decoupled into two, the first is formally written as

$$f_1 = -\left(\frac{1}{c}\partial_t + i\frac{qV}{\hbar c} + i\frac{mc}{\hbar}\right)^{-1}\vec{S}\cdot\left(\nabla - \frac{iq}{\hbar c}\overrightarrow{A}\right)f_2 \tag{2.46}$$

whilst the second is

$$\left(-\frac{1}{c}\partial_t - i\frac{qV}{\hbar c} + i\frac{mc}{\hbar}\right) f_2 - \overrightarrow{S}\cdot\left(\nabla - \frac{iq}{\hbar c}\overrightarrow{A}\right) f_1 = 0 \tag{2.47}$$

where f_1 contains the two upper elements of f whilst f_2 the lower two. Inverse of the operator in (2.46) is obtained by solving the Green function equation

$$-\left(\frac{1}{c}\partial_t + i\frac{qV}{\hbar c} + i\frac{mc}{\hbar}\right) D(t) = \delta(t)$$

with the solution

$$D(t) = -ce^{i\frac{t}{\hbar}(-qV-mc^2)}\Theta(t) \equiv -\left(\frac{1}{c}\partial_t + i\frac{qV}{\hbar c} + i\frac{mc}{\hbar}\right)^{-1}$$

and (2.46) is

$$f_1 = -c\overrightarrow{S}\cdot\int_0^t e^{-i\frac{(t-s)}{\hbar}(qV+mc^2)}\left(\nabla - \frac{iq}{\hbar c}\overrightarrow{A}(s)\right) f_2(s) + e^{-i\frac{t}{\hbar}(qV+mc^2)} f_1(0)$$

Equation (2.47) is now in the form of integro-differential equation that simplifies for the scalar potential only

$$\begin{aligned}&\frac{i}{\hbar c}\left(i\hbar\partial_t - qV + mc^2\right) f_2\\ &\quad = -c\overrightarrow{S}\cdot\nabla\left[\int_0^t e^{-i\frac{(t-s)}{\hbar}(qV+mc^2)}\overrightarrow{S}\cdot\nabla f_2(s)\right] + \overrightarrow{S}\cdot\nabla\left[e^{-i\frac{t}{\hbar}(qV+mc^2)} f_1(0)\right]\end{aligned}$$

The equation is solved by iteration, thus on the right side it is assumed that solution is stationary

$$f_2(t) = e^{-i\frac{e_0 t}{\hbar}} f_2(0) \tag{2.48}$$

and it reduces to differential equation

$$\left(i\hbar\partial_t - qV + mc^2\right) f_2 = c^2\hbar^2 e^{-i\frac{t}{\hbar}e_0}\overrightarrow{S}\cdot\nabla\frac{\overrightarrow{S}\cdot\nabla f_2(0)}{Vq - e_0 + mc^2}$$

Solution is

$$\begin{aligned}f_2 = {} & \frac{c^2\hbar^2}{e_0 - Vq + mc^2} e^{-i\frac{t}{\hbar}e_0}\left[1 - e^{i\frac{t}{\hbar}(e_0+mc^2-qV)}\right]\overrightarrow{S}\cdot\nabla\frac{\overrightarrow{S}\cdot\nabla f_2(0)}{Vq - e_0 + mc^2}\\ & + e^{i\frac{t}{\hbar}(mc^2-qV)} f_2(0)\end{aligned}$$

and if rapidly oscillating terms are neglected one obtains equation for the time independent component of the solution

$$\Delta f_2 + \frac{(e_0 - Vq)^2}{c^2\hbar^2} f_2 - \frac{m^2c^2}{\hbar^2} f_2 = q\frac{\nabla V \cdot \nabla + i\vec{S}\cdot(\nabla V \times \nabla)}{Vq - e_0 + mc^2} f_2 \tag{2.49}$$

where the relationship

$$\left(\vec{S}\cdot\overrightarrow{a}\right)\left(\vec{S}\cdot\overrightarrow{b}\right) = \overrightarrow{a}\cdot\overrightarrow{b} - i\overrightarrow{a}\cdot\left(\vec{S}\times\overrightarrow{b}\right)$$

was used.

2.3.4.2 Free Particle

Free particle is the simplest example to study from Dirac equation, which was partially discussed in Sect. 2.2. Motivation is that solutions of this equation have some specific features and their implications are best analyzed for a free particle, when interaction is included no essential additional insight is obtained.

Few comments about the choice of initial conditions, which were in part discussed in Sect. 2.2, because they determine the physics of the problem. Alternatives are either to choose them in the coordinate space, at $t = 0$, or in the momentum space. The "natural" choice is the coordinate space, however, in doing so some important features of dynamics could be missed. For example, choosing solution that has only one energy component cannot be easily decided upon if one works in the coordinate space only (apart from a trivial case of a plane wave), as discussed in Sect. 2.2. It is therefore necessary to analyze the consequences of the choice of initial conditions in the two spaces in order to select physically meaningful solution.

If solution in the coordinate space is $f(\vec{r}, t)$ then in the momentum space it is defined through the transformation

$$f(\vec{r}, t) = \int d^3k\ \widehat{f}(\overrightarrow{k}, t)e^{i\overrightarrow{k}\cdot\overrightarrow{r}}$$

and for a free particle

$$f(\vec{r}, t) = \int d^3k\ \Upsilon E\Upsilon^+ \widehat{f}_0(\overrightarrow{k})e^{i\overrightarrow{k}\cdot\overrightarrow{r}} \tag{2.50}$$

where the symbols are defined in Sect. 2.2. From this relationship one gets initial $f(\vec{r}, 0)$ from $\widehat{f}_0(\overrightarrow{k})$. However, instead of $\widehat{f}_0(\overrightarrow{k})$ one defines

$$\widehat{g}_0(\overrightarrow{k}) = (2\pi)^{3/2}\gamma_0\Upsilon^+\widehat{f}_0(\overrightarrow{k})$$

in which case solution in the coordinate space is

$$f(\vec{r},t)=(2\pi)^{-3/2}\int d^3k\ \Upsilon E\gamma_0\widehat{g}_0(\overrightarrow{k})e^{i\overrightarrow{k}\cdot\overrightarrow{r}} \tag{2.51}$$

and $\widehat{g}_0(\overrightarrow{k})$ also defines initial conditions for $f(\vec{r},t)$.

For further discussion it is necessary to review the initial conditions in more details. They have four components, as it is shown in discussing initial conditions for Dirac equation in (2.2), and could be separated into two sets where each one has two components. In the coordinate space it is not simple to associate physically meaningful interpretation to each group although when the plane wave solutions are analyzed one is associated with positive and the other with negative energy of particle. When the localized particle is analyzed then this interpretation is no longer valid, as discussed in Sect. 2.2. For this, and other examples, choosing initial conditions in the momentum space often takes priority over taking them in the coordinate space, and to show this few examples shall be analyzed.

In the momentum space there are two classes of initial conditions, either one chooses them for $\widehat{f}_0(\overrightarrow{k})$ or $\widehat{g}_0(\overrightarrow{k})$, however, in both cases their four components are split into a set of two matrices each one with two elements. It is shown on the example of $\widehat{g}_0(\overrightarrow{k})$ how each matrix is parametrized, the same is true for $\widehat{f}_0(\overrightarrow{k})$. The first two elements of $\widehat{g}_0(\overrightarrow{k})$ shall be associated with the positive energy and they are parametrized as[6]

$$\widehat{g}_0^{(+)}(\overrightarrow{k})=\begin{vmatrix} s_1^{(+)}(\overrightarrow{k}) \\ s_2^{(+)}(\overrightarrow{k}) \end{vmatrix}\widehat{G}^{(+)}(\overrightarrow{k})=s^{(+)}(\overrightarrow{k})\widehat{G}^{(+)}(\overrightarrow{k})$$

where each element is in general complex, $s^{(+)}(\overrightarrow{k})$ is unitary and $\widehat{G}^{(+)}(\overrightarrow{k})$ is a scalar function. Similarly the other two elements are defined and $s^{(\pm)}$ are parametrized as

$$s^{(+)}=\begin{vmatrix} e^{-i\frac{\phi}{2}}\cos\frac{\theta}{2} \\ e^{i\frac{\phi}{2}}\sin\frac{\theta}{2} \end{vmatrix}\cos\frac{\beta}{2},\quad s^{(-)}=\begin{vmatrix} e^{-i\frac{\phi}{2}}\cos\frac{\theta}{2} \\ e^{i\frac{\phi}{2}}\sin\frac{\theta}{2} \end{vmatrix}\sin\frac{\beta}{2}$$

where the angle β measures relative contributions of the positive and negative energy components. A word of warning, previous parametrization is the simplest, in the following section a more general one shall be given.

In the momentum space one defines either $\widehat{f}_0(\overrightarrow{k})$ or $\widehat{g}_0(\overrightarrow{k})$ as the initial conditions, and the choice has repercussions on the averages of physically relevant parameters. For example, average of the coordinates is defined as

$$\vec{r}_{av}=\int d^3r\ \vec{r}\ f^+(\vec{r},t)f(\vec{r},t)$$

[6]The same is valid for $\widehat{f}_0(\overrightarrow{k})$ but the signs in superscript is left for convenience and does not imply positive energy component.

and if one chooses (2.50) then

$$\vec{r}_{av} = (2\pi)^3\, i \int d^3k\ \widehat{f}_0^{+}(\overrightarrow{k})\Upsilon E^{+}\Upsilon^{+}\ \nabla_k \left[\Upsilon E \Upsilon^{+} \widehat{f}_0(\overrightarrow{k})\right] \tag{2.52}$$

or else for (2.51)

$$\vec{r}_{av} = i \int d^3k\ \widehat{g}_0^{+}(\overrightarrow{k})\gamma_0 E^{+}\Upsilon^{+}\ \nabla_k \left[\Upsilon E \gamma_0 \widehat{g}_0(\overrightarrow{k})\right] \tag{2.53}$$

In further discussion it is assumed that $\widehat{f}_0(\overrightarrow{k})$ parametrizes as

$$\widehat{f}_0(\overrightarrow{k}) = \begin{vmatrix} s^{(+)}\widehat{F}^{(+)}(\overrightarrow{k}) \\ s^{(-)}\widehat{F}^{(-)}(\overrightarrow{k}) \end{vmatrix} = s\ \widehat{F}(\overrightarrow{k})$$

and similarly for $\widehat{g}_0(\overrightarrow{k})$. For both initial conditions s is the same and independent of $\overrightarrow{k}$. The matrix s is diagonal with the elements of $s^{(\pm)}$ and $\widehat{F}(\overrightarrow{k})$ is the single column matrix of the scalar functions $\widehat{F}^{(\pm)}(\overrightarrow{k})$. The averages are calculated for two extreme cases: for the positive energy component ($\beta = 0$) and for the negative one ($\beta = \pi$) with the result for (2.52)

$$\begin{aligned}\vec{r}_{av}^{(\pm)} = \ & \pm (2\pi)^3 c^4 \hbar m \int d^3k\ \ \widehat{F}^{(\pm)*} \frac{\overrightarrow{k}}{\epsilon^2}\left(t - \frac{\hbar}{2\epsilon}\sin\frac{2\epsilon t}{\hbar}\right)\widehat{F}^{(\pm)} \\ & + (2\pi)^3 c^2\hbar^2 \int d^3k\ \ \widehat{F}^{(\pm)*}\frac{\overrightarrow{k}\times\widehat{n}}{\epsilon^2}\sin^2\frac{\epsilon t}{\hbar}\widehat{F}^{(\pm)} + (2\pi)^3\, i \int d^3k\ \ \widehat{F}^{(\pm)*}\nabla_k\ \widehat{F}^{(\pm)}\end{aligned}$$

where $\widehat{n}$ is the unit vector that is determined by the angles θ and ϕ in $s^{(\pm)}$. On the other hand the average for (2.53) is

$$\begin{aligned}\vec{r}_{av}^{(\pm)} = \ & \int d^3k\ \ \widehat{G}^{(\pm)*}\left[\pm\frac{c^2\hbar\overrightarrow{k}}{\epsilon}t + \frac{c^2\hbar^2}{2\epsilon\left(\epsilon + mc^2\right)}\overrightarrow{k}\times\widehat{n}\right]\widehat{G}^{(\pm)} \\ & + (2\pi)^3\, i \int d^3k\ \ \widehat{G}^{(\pm)*}\nabla_k\widehat{G}^{(\pm)}\end{aligned}$$

and there is difference between the two averages. In fact it is even more so if the average velocity is calculated, the time derivative of $\vec{r}_{av}^{(\pm)}$. The average velocity for $\widehat{f}_0(\overrightarrow{k})$ rapidly oscillates around its constant value, which is quite surprising considering that single energy solutions are selected. Even more surprising is the constant component, which has the value that is not related to how one defines relativistic velocity. On the other hand the average velocity for $\widehat{g}_0(\overrightarrow{k})$ is non oscillatory, as one would expect, and it is in accord with the standard definition of relativistic velocity.

Interesting feature of $\vec{r}_{av}^{(\pm)}$ is that it has a constant, time independent, component of the order $\frac{c^2\hbar^2}{\epsilon^2}\overrightarrow{k}\times\widehat{n}$. In the nonrelativistic limit $\epsilon\approx mc^2$ and it has the value $\frac{\hbar}{mc^2}\frac{\hbar\overrightarrow{k}}{m}\times\widehat{n}$ which is the product of velocity of particle and the period time of the oscillations that result from the energy equivalent of particle's rest mass. At the other extreme in the relativistic limit $\epsilon\approx c\hbar k$ this term has the estimate $k^{-1}\widehat{k}\times\widehat{n}$ which is shorter than the Compton wavelength.

Even more revelling is the average energy, which is by definition

$$\epsilon_{av}=(2\pi)^3\,i\hbar\int d^3k\;\;\widehat{F}^{+}(\overrightarrow{k})s^{+}\Upsilon E^{+}\Upsilon^{+}\,\partial_t\left[\Upsilon E\Upsilon^{+}s\;\widehat{F}(\overrightarrow{k})\right]$$

and for $\widehat{f}_0(\overrightarrow{k})$

$$\epsilon_{av}^{(\pm)}=\pm mc^2$$

whilst for $\widehat{g}_0(\overrightarrow{k})$

$$\epsilon_{av}^{(\pm)}=\pm\epsilon$$

The second choice produces result that is expected whilst the first one gives the rest energy of particle and not its true value.

Important parameter is the angular momentum, which is defined as

$$\overrightarrow{L}_{av}=-i\hbar\int d^3r\;\;f^{+}(\vec{r},t)\vec{r}\times\nabla f(\vec{r},t)$$

and for the initial $\widehat{f}_0(\overrightarrow{k})$

$$\begin{aligned}\overrightarrow{L}_{av}^{\pm}=\;& c^2\hbar^3(2\pi)^3\int d^3k\;\;\frac{\sin^2\left(\frac{\epsilon t}{\hbar}\right)}{\epsilon^2}\left[\left(\overrightarrow{k}\times\widehat{n}\right)\times\overrightarrow{k}\right]\left|\widehat{F}^{(\pm)}\right|^2\\&-i\hbar(2\pi)^3\int d^3k\;\;\widehat{F}^{(\pm)+}\overrightarrow{k}\times\nabla_k\,\widehat{F}^{(\pm)}\end{aligned}$$

whilst for $\widehat{g}_0(\overrightarrow{k})$

$$\overrightarrow{L}_{av}^{\pm}=\frac{c^2\hbar^3}{2}\int d^3k\;\;\frac{\left(\overrightarrow{k}\times\widehat{n}\right)\times\overrightarrow{k}}{\epsilon\left(\epsilon+mc^2\right)}\left|\widehat{G}^{(\pm)}\right|^2-i\hbar\int d^3k\;\;\widehat{G}^{(\pm)+}\overrightarrow{k}\times\nabla_k\widehat{G}^{(\pm)}$$

The last term is the angular momentum that results from the motion of the probability density as the whole. The first term oscillates very rapidly.

Once the initial conditions are determined one must decide on the choice of boundary conditions for propagation of solution. There is essentially only one choice, retarded solution which is defined as having the value of the initial condition up to the initial instant ($t=0$). For $t>0$ it corresponds to the solution of Dirac equation with that initial condition, and for a free particle one can write it as

$$f(\vec{r},t)=\Theta(t)\left(\frac{1}{c}\gamma_0\partial_t+\overrightarrow{\gamma}\cdot\nabla-i\frac{mc}{\hbar}\right)\int d^3k\,\frac{\sin\frac{\epsilon t}{\hbar}}{\epsilon}e^{i\overrightarrow{k}\cdot\overrightarrow{r}}\,\widehat{f_0}(\overrightarrow{k}) \tag{2.54}$$

and when the integral representation (C.6) is used then (2.54) takes equivalent form[7]

$$f\left(\overrightarrow{r},t\right)=\frac{\hbar}{2\pi}\left(\frac{1}{c}\gamma_0\partial_t+\overrightarrow{\gamma}\cdot\nabla-i\frac{mc}{\hbar}\right)\int\frac{de\,d^3k\,e^{i\overrightarrow{k}\cdot\overrightarrow{r}-iet/\hbar}}{\epsilon^2-(e+i\eta)^2}\widehat{f_0}(\overrightarrow{k})$$

where $\eta>0$ and the limit $\eta\to 0$ is assumed. Equation that the retarded solution satisfies is

$$\left(\frac{1}{c}\gamma_0\partial_t+\overrightarrow{\gamma}\cdot\nabla+i\frac{mc}{\hbar}\right)f\left(\overrightarrow{r},t\right)=\frac{1}{c^2\hbar}f_0\left(\overrightarrow{r}\right)\delta(t) \tag{2.55}$$

where the inhomogeneous term is indeed the initial condition for $f\left(\overrightarrow{r},t\right)$ which is shown from (2.54)

$$f\left(\overrightarrow{r},0\right)=\frac{1}{2\hbar c}\gamma_0 f_0\left(\overrightarrow{r}\right)$$

The inhomogeneous term $f_0\left(\overrightarrow{r}\right)\delta(t)$ could be of a more general form $\Gamma\left(\overrightarrow{r},t\right)$, for example it could be collection of terms resulting from interaction of particle with electromagnetic field. Solution is then

$$f\left(\overrightarrow{r},t\right)=\frac{\hbar}{(2\pi)^4}\left(\frac{1}{c}\gamma_0\partial_t+\overrightarrow{\gamma}\cdot\nabla-i\frac{mc}{\hbar}\right)\int ds\,d^3u\int\frac{de\,d^3k\,e^{i\overrightarrow{k}\cdot(\overrightarrow{r}-\overrightarrow{u})-ie(t-s)}}{\epsilon^2-(e+i\eta)^2}\Gamma\left(\overrightarrow{u},s\right)$$

It is convenient to define (retarded) Green function as

$$K_r(\overrightarrow{r},t)=\frac{\hbar^2c^2}{(2\pi)^4}\int de\,d^3k\,\frac{e^{i\overrightarrow{k}\cdot\overrightarrow{r}-iet/\hbar}}{\epsilon^2-(e+i\eta)^2}$$

which satisfies equation

$$\left(\frac{1}{c}\gamma_0\partial_t+\overrightarrow{\gamma}\cdot\nabla+i\frac{mc}{\hbar}\right)\left(\frac{1}{c}\gamma_0\partial_t+\overrightarrow{\gamma}\cdot\nabla-i\frac{mc}{\hbar}\right)K_r(\overrightarrow{r},t)=\delta\left(\overrightarrow{r}\right)\delta(t)$$

when retarded solution is then

$$f\left(\overrightarrow{r},t\right)=\frac{1}{\hbar c^2}\left(\frac{1}{c}\gamma_0\partial_t+\overrightarrow{\gamma}\cdot\nabla-i\frac{mc}{\hbar}\right)\int ds\,d^3u\,K_r(\overrightarrow{r}-\overrightarrow{u},t-s)\Gamma\left(\overrightarrow{u},s\right)$$

[7] $\Theta(t)$ and ∂_t can interchange their order because $\delta(t)$ that results from this gives zero contribution in f.

Time evolution (2.54) involves both energy components ϵ, one with the factor $e^{-it\epsilon/\hbar}$ and the other with $e^{it\epsilon/\hbar}$. As the consequence for increasing time initial $f_0\left(\overrightarrow{r}\right)$ splits into two components, one that propagates in one direction and the other in the opposite. For the reason that was discussed in Sect. 2.3.2.2 one requires solution that propagates only single energy component, for example the one with $e^{-it\epsilon/\hbar}$ (positive energy component), for $t > 0$ and the other with $e^{it\epsilon/\hbar}$ (negative energy component), for $t < 0$, however both components move in the same direction. In short, this solution expresses particle like feature of solution whilst the retarded describes wave like feature. To find this solution the simplest would be to replace (2.54) with

$$f_F\left(\overrightarrow{r},t\right) = \frac{i\hbar}{2}\left(\frac{1}{c}\gamma_0\partial_t + \overrightarrow{\gamma}\cdot\nabla - i\frac{mc}{\hbar}\right) \int \frac{d^3k}{\epsilon}\left[e^{-it\epsilon/\hbar}\Theta\left(t\right) + e^{it\epsilon/\hbar}\Theta\left(-t\right)\right]e^{i\overrightarrow{k}\cdot\overrightarrow{r}}\,\widehat{f_0}\left(\overrightarrow{k}\right)$$

where the time derivative that includes step functions is zero. By following the steps as for the retarded solution one derives $f_F\left(\overrightarrow{r},t\right)$ in the equivalent form

$$f_F\left(\overrightarrow{r},t\right) = \frac{\hbar}{2\pi}\left(\frac{1}{c}\gamma_0\partial_t + \overrightarrow{\gamma}\cdot\nabla - i\frac{mc}{\hbar}\right)\int de\, d^3k\, \frac{e^{i\overrightarrow{k}\cdot\overrightarrow{r}-iet/\hbar}}{\left(\epsilon - i\eta\right)^2 - e^2}\,\widehat{f_0}\left(\overrightarrow{k}\right) \tag{2.56}$$

It is straightforward to show that $f_F\left(\overrightarrow{r},t\right)$ satisfies inhomogeneous equation

$$\left(\frac{1}{c}\gamma_0\partial_t + \overrightarrow{\gamma}\cdot\nabla + i\frac{mc}{\hbar}\right)f_F\left(\overrightarrow{r},t\right) = \frac{1}{c^2}f_0\left(\overrightarrow{r}\right)\delta\left(t\right) \tag{2.57}$$

On the other hand Feynman solution at the initial instant is

$$f_F\left(\overrightarrow{r},0\right) = \frac{\hbar}{2}\int\frac{d^3k}{\epsilon}\left(-\overrightarrow{\gamma}\cdot\overrightarrow{k} + \frac{mc}{\hbar}\right)e^{i\overrightarrow{k}\cdot\overrightarrow{r}}\,\widehat{f_0}\left(\overrightarrow{k}\right) \tag{2.58}$$

which is not identical with f_0, as for (2.55). This means that the initial condition is determined by $\widehat{f_0}\left(\overrightarrow{k}\right)$, and it is given by (2.58), whilst the solution $f_F\left(\overrightarrow{r},t\right)$ satisfies the inhomogeneous equation (2.57).

For a more general form of the inhomogeneous term $\Gamma\left(\overrightarrow{r},t\right)$ Feynman solution is

$$\Phi_F\left(\overrightarrow{r},t\right) = \left(\frac{1}{c}\gamma_0\partial_t + \overrightarrow{\gamma}\cdot\nabla - i\frac{mc}{\hbar}\right)\int ds\, d^3u\, K_F(\overrightarrow{r}-\overrightarrow{u},t-s)\Gamma\left(\overrightarrow{u},s\right)$$

where the Green function is

$$K_F(\overrightarrow{r},t)=\frac{\hbar c^2}{(2\pi)^4}\int de\,d^3k\;\frac{e^{i\overrightarrow{k}\cdot\overrightarrow{r}-iet/\hbar}}{(\epsilon-i\eta)^2-e^2}$$

There is a basic difference between Feynman solution (2.56) and the retarded (2.54). For the latter its initial value is arbitrarily specified in the coordinate space whilst for the Feynman solution it should be specified in the momentum space from which one derives in the coordinate space from (2.58). This difference is demonstrated on the example in which $f_0\left(\overrightarrow{r}\right)$ is zero beyond r_0, and the simplest example is (normalization is not important)

$$f_0\left(\overrightarrow{r}\right)=\frac{1}{r}\Theta\left(r_0-r\right)C$$

where C is constant matrix. Fourier transform of $f_0\left(\overrightarrow{r}\right)$ is

$$\widehat{f_0}\left(\overrightarrow{k}\right)=\frac{1}{2\pi^2}\;\frac{1-\cos kr_0}{k^2}C$$

Initial $f\left(\overrightarrow{r},0\right)$ is identical with $f_0\left(\overrightarrow{r}\right)$ and the estimate for $f_F\left(\overrightarrow{r},0\right)$ is

$$f_F\left(\overrightarrow{r},0\right)\sim\frac{1}{r}\int dk\frac{\sin kr}{\sqrt{k^2+\frac{m^2c^2}{\hbar^2}}}\;\frac{1-\cos kr_0}{k}\sim\frac{1}{r^{3/2}}e^{-\frac{mc}{\hbar}r};\quad r\gg r_0$$

which is not zero beyond $r=r_0$. In the time evolution of f the cut at $r=r_0$ moves outward at the speed of light, the same applies for f_F and the tail beyond this cut also moves at the same speed.

Difference between initial $f\left(\overrightarrow{r},0\right)$ and $f_F\left(\overrightarrow{r},0\right)$ is removed in the limit when $f_0\left(\overrightarrow{r}\right)$ is very wide, in the plane wave limit. In this case $f\left(\overrightarrow{r},0\right)\sim e^{i\overrightarrow{k}_0\cdot\overrightarrow{r}}$ and

$$f_F\left(\overrightarrow{r},0\right)\sim\frac{1}{\epsilon_0}\left(c\overrightarrow{\gamma}\cdot\overrightarrow{k}_0-\frac{mc^2}{\hbar}I\right)e^{i\overrightarrow{k}_0\cdot\overrightarrow{r}}$$

which, apart from normalization, it is identical with $f_0\left(\overrightarrow{r}\right)$.

2.3.4.3 Spherically Symmetric Potential

Special interest is interaction of particle with a spherically symmetric potential, which is analyzed from (2.46) and (2.49) in the limit (2.48) when they are time independent

$$\left(e_0-Vq-mc^2\right)f_1=-i\hbar c\vec{S}\cdot\nabla f_2,\quad\left(e_0-Vq+mc^2\right)f_2=-i\hbar c\overrightarrow{S}\cdot\nabla f_1 \tag{2.59}$$

It is expected that for these potentials the total angular momentum is conserved which means that the solution is parametrized as

$$f_1 = \frac{1}{r} u_1(r)\ \Phi_1(\theta,\phi), \quad f_2 = \frac{i}{r} u_2(r)\ \Phi_2(\theta,\phi)$$

where $u_{1,2}(r)$ are scalars. At this point one defines the spin matrices in the spherical coordinates, which are given by

$$S_r = \begin{vmatrix} \cos\theta & e^{-i\phi}\sin\theta \\ e^{i\phi}\sin\theta & -\cos\theta \end{vmatrix}, \quad S_\theta = \begin{vmatrix} -\sin\theta & e^{-i\phi}\cos\theta \\ e^{i\phi}\cos\theta & \sin\theta \end{vmatrix},$$
$$S_\phi = \begin{vmatrix} 0 & -ie^{-i\phi} \\ ie^{i\phi} & 0 \end{vmatrix}$$

and for them one can show these identities

$$\vec{S}\cdot\nabla = \vec{S}\cdot\widehat{r}\left[\left(\vec{S}\cdot\widehat{r}\right)\left(\vec{S}\cdot\nabla\right)\right] = S_r\left(\frac{\partial}{\partial r} + i\ \vec{S}\cdot(\widehat{r}\times\nabla)\right)$$
$$\vec{S}\times\nabla = S_r\left(\frac{\widehat{\phi}}{r}d_\theta + \frac{\widehat{\theta}}{r\sin\theta}d_\phi\right) + S_\theta\frac{\widehat{r}}{r\sin\theta}d_\phi - S_\phi\frac{\widehat{r}}{r}d_\theta$$

In order that in the set (2.59) radial and angular components are decoupled one must assume that the angular functions satisfy identities

$$\vec{S}\cdot(\widehat{r}\times\nabla)\,\Phi^{(\sigma)}(\theta,\phi) = \frac{i}{r}\lambda_\sigma\Phi^{(\sigma)}(\theta,\phi); \quad \sigma = -1, 1$$

and

$$S_r\Phi_{1,2} = \Phi_{2,1}$$

Furthermore the angular functions must be eigenfunctions of the angular part of the Laplace operator in (2.49), eigenfunctions of the angular momentum operator squared. The two eigenvalue problems do not have single solution, there are two angular functions that satisfy those two criteria, hence for Φ_1 they are

$$\Phi^{(-1)}_{l,m}(\theta,\phi) = \frac{1}{\sqrt{2l+1}}\begin{pmatrix}\sqrt{l-m+1}\,Y^{m-1}_l \\ -\sqrt{l+m}\,Y^m_l\end{pmatrix};\ \lambda^{(-1)} = -l-1;\ l = 1,2,\ldots \tag{2.60}$$
$$\Phi^{(1)}_{l,m}(\theta,\phi) = \frac{1}{\sqrt{2l+1}}\begin{pmatrix}\sqrt{l+m}\,Y^{m-1}_l \\ \sqrt{l-m+1}\,Y^m_l\end{pmatrix};\ \lambda^{(1)} = l;\ l = 0,1,2,\ldots$$

and they are interrelated by

$$S_r\Phi^{(\sigma)}_{l,m}(\theta,\phi) = \Phi^{(-\sigma)}_{l+\sigma,m}(\theta,\phi); \quad \sigma = \pm 1$$

The completeness relation for the functions (2.60) is

$$\sum_{l,m,\sigma} \Phi_{l,m}^{+(\sigma)}\left(\theta',\phi'\right)\ \Phi_{l,m}^{(\sigma)}\left(\theta,\phi\right) = \delta\left(\phi-\phi'\right)\delta\left(\sin\theta-\sin\theta'\right)$$

These are called the spin angular functions because they represent the states that result from addition of the spin and the angular momentum. Thus the spin angular function $\Phi_{l,m}^{(-1)}(\theta,\phi)$ represents the state of the total angular momentum $j=l-1/2$ whilst $\Phi_{l,m}^{(1)}(\theta,\phi)$ represents $j=l+1/2$.

The two solutions of Dirac equation are now parametrized as

$$f^{(\sigma)} = \frac{1}{r}\begin{vmatrix} u_1^{(\sigma)}(r)\ \Phi_{l,m}^{(\sigma)}(\theta,\phi) \\ iu_2^{(\sigma)}(r)\ \Phi_{l+\sigma,m}^{(-\sigma)}(\theta,\phi)\end{vmatrix}$$

where the radial functions satisfy the set of equations

$$\begin{aligned} c\hbar\left(\frac{d}{dr}-\frac{\sigma\left(l+1/2+\sigma/2\right)}{r}\right)u_1^{(\sigma)}+\left(mc^2+e_0-qV\right)u_2^{(\sigma)}=0 \\ c\hbar\left(\frac{d}{dr}+\frac{\sigma\left(l+1/2+\sigma/2\right)}{r}\right)u_2^{(\sigma)}+\left(qV+mc^2-e_0\right)u_1^{(\sigma)}=0\end{aligned} \tag{2.61}$$

with the normalization

$$\int d^3r\ f^{+(\sigma)}f^{(\sigma)} = \int dr\ \left[u_1^{(\sigma)2}(r)+u_2^{(\sigma)2}(r)\right]=1$$

and the overlap integral

$$\int dr\ u_1^{(\sigma)}u_2^{(\sigma)} = \frac{\hbar}{2mc}\left[u_1^{(\sigma)2}(0)+u_2^{(\sigma)2}(0)-\sigma\left(2l+1+\sigma\right)\int dr\frac{u_1^{(\sigma)2}-u_2^{(\sigma)2}}{r}\right]$$

Non-relativistic limit implies $e_0\approx mc^2\gg|qV|$ when one talks about the dominant $u_1^{(\sigma)}$ component of the solution and its subdominant $u_2^{(\sigma)}$.

Average current is now calculated, and from its definition (2.25) when

$$\begin{aligned}\overrightarrow{J}^{(\sigma)} = & \frac{2c}{r^2}\,\mathrm{Im}\left[u_2^{*(\sigma)}u_1^{(\sigma)}\right]\left|\Phi_{l,m}^{(\sigma)}\right|^2\widehat{n} \\ & -\frac{2c}{r^2}\,\mathrm{Re}\left[u_2^{*(\sigma)}u_1^{(\sigma)}\right]\widehat{n}\times\Phi_{l,m}^{+(\sigma)}(\theta,\phi)\,\vec{S}\Phi_{l,m}^{(\sigma)}(\theta,\phi) \\ & +\frac{2c}{r^2}\,\mathrm{Im}\left[u_2^{*(\sigma)}u_1^{(\sigma)}\right]\left|\Phi_{l,m}^{(\sigma)}\right|^2\widehat{n}-\frac{2c}{r^2}\,\mathrm{Re}\left[u_2^{*(\sigma)}u_1^{(\sigma)}\right]\widehat{n}\times\widehat{z}P_{l,m}^{+(\sigma)}(\theta)\end{aligned}$$

where $P_{l,m}^{+(\sigma)}(\theta)$ is a polynomial. One shows

$$\int d^3r\ \overrightarrow{J}^{(\sigma)} = -2c \int dr\ u_1^{(\sigma)}(r)\, u_2^{(\sigma)}(r) \int d\Omega\ \Phi_{l,m}^{+(\sigma)}(\theta,\phi)\, S_\theta \Phi_{l,m}^{(\sigma)}(\theta,\phi)\ \widehat{\phi}$$

and indicates that whilst there is no flow of probability in the radial direction there is always its component that goes around the origin. A note here, strictly speaking the unit azimuthal angle should have been given in the Cartesian coordinates, in which case, on average, even this current is zero. This is simply the consequence of the current going in circle, when its tangential component is not zero, but in Cartesian coordinates, on average, it is zero.

Another important parameter to calculate is the angular momentum, and it would be natural to define it as

$$\overrightarrow{L}_{l,m}^{(\sigma)} = -i\hbar \int d^3r\ f^{+(\sigma)} \overrightarrow{r} \times \nabla f^{(\sigma)} = m\hbar \widehat{z} \tag{2.62}$$

For a spherically symmetric potential the angular momentum is constant and to check that one calculates its time derivative, which must be zero. It is straightforward to show that

$$d_t \overrightarrow{L}_{l,m}^{(\sigma)} = -ic\hbar \int d^3r\ f^{+(\sigma)} \gamma_0 \overrightarrow{\gamma} \times \nabla f^{(\sigma)}$$

which means that the definition is not complete. One can show that its complete definition is

$$\overrightarrow{L}_{l,m}^{(\sigma)} = \int d^3r\ f^{+(\sigma)} \left(-i\hbar \overrightarrow{r} \times \nabla + \frac{\hbar}{2} \overrightarrow{\Sigma} \right) f^{(\sigma)}$$

which is indeed constant. The first part is orbital angular momentum whilst the second is the spin. It should be noted that whilst the orbital angular momentum has simple expression (2.62) the same is not true, in general, for the spin component. It is only in the non-relativistic limit that the spin component acquires simple expression

$$\int d^3r\ f^{+(\sigma)} \overrightarrow{\Sigma} f^{(\sigma)} \approx \sigma \frac{2m-1}{2l+1}; \quad -l + \frac{1}{2}(1-\sigma) \le m \le l + \frac{1}{2}(1+\sigma)$$

Chapter 3
Electrodynamics

Abstract Basic principles of electrodynamics are reviewed with the emphases on the parts that are of importance in manipulating dynamics of charges; short pulses, modulated waves and focusing the waves to increase there amplitude.

Basic principles and applications of electrodynamics are thoroughly described in the available literature [10–12], however, there are still areas of its use which are not often reviewed and specifically when it comes to investigate interaction with charges under extreme conditions. For this purpose electrodynamics is reviewed with the emphases on the features that are important in such extremes.

3.1 Basic Principles

Electromagnetic field has two components: electric and magnetic, which means that in general it is defined by six vector components. However, it could be uniquely represented by recalling definition of a field, it is a force that it exerts on a test charge.[1] Gravitational field is gravitational force on a unit mass whilst electromagnetic field is electromagnetic force on a unit charge. Electromagnetic force is also called Lorentz force and when normalized to unit charge one could define electromagnetic field as (for simplicity from now on the CGS units will be used)

$$\overrightarrow{\Phi} = \vec{E} + \frac{\vec{v}}{c} \times \vec{H} \tag{3.1}$$

where $\vec{v}$ is velocity of the test charge and c is velocity of light. The Lorentz force is therefore

$$\vec{F} = e\,\overrightarrow{\Phi}$$

[1] Test charge is the name of a fictitious charge that measures the strength of the field.

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where e is charge of the particle on which the field is applied. In general stationary charges determine electric component (or electric field) whilst the charges in motion determine magnetic component (or magnetic field). Exact relationship between charges in motion and the electromagnetic field is given by Maxwell equations, four of them are (these equations could be derived from more general principles, also the Lorentz force [9])

$$\nabla \times \vec{E} = -\frac{1}{c}\partial_t \vec{H} \ , \quad \nabla \times \vec{H} = \frac{1}{c}\partial_t \vec{E} + \frac{4\pi}{c}\vec{j} \ ,$$
$$\nabla \cdot \vec{E} = 4\pi\rho, \quad \nabla \cdot \vec{H} = 0$$

where ρ is charge density and $\vec{j}$ is charge current. For a point-like electron (in traditional, or classical, description) these two quantities are

$$\rho = e\ \delta(\vec{r} - \vec{r}_0), \quad \vec{j}\ = e\vec{v}_0\ \delta(\vec{r} - \vec{r}_0)$$

where $\vec{r}_0$ is position of the electron and $\vec{v}_0$ is its velocity. On the other hand, if position of the electron is given as the probability density then the two quantities are

$$\rho = e\ |f(\vec{r})|^2 \, , \quad \vec{j}\ = \frac{e\hbar}{m}\,\mathrm{Im}\left[f^*(\vec{r})\nabla f(\vec{r})\right]$$

where $f(\vec{r})$ is the probability amplitude.

Electromagnetic field propagates in space and interacts with the other charges, however, it also interacts with its own source. In the traditional picture[2] a charge is treated as a point-like particle, for which the self force of this kind is not well defined (again, treatment of this force goes back more than hundred years ago and is considered as one of the unsolved problems in classical electrodynamics). However, in the real world dynamics of particles one must take into account their delocalization due to the uncertainty principle, in which case instead of being treated as the point like objects their position is described by probability density [9]. For the probability density, however, this self force is well defined only if the effect of retardation is taken into account, i.e. at certain point electromagnetic field that exerts a force on the charge density originated at some earlier time at another location.

Electromagnetic field is the carrier of energy, and the energy balance is obtained from Maxwell equations, from which one derives equation

$$\nabla \cdot (\vec{E} \times \vec{H}) = -\frac{1}{2c}\partial_t \left(\vec{H} \cdot \vec{H} + \vec{E} \cdot \vec{E}\right) - \frac{4\pi}{c}\vec{E} \cdot \vec{j}$$

In this equation one recognizes the continuity equation, which always expresses a conservation law. For example, for the charge and the current densities it is given by

[2]By *traditional picture* it is meant classical dynamics, or more precisely, dynamics of particles where the uncertainty principle is not implemented.

$$\nabla \cdot \vec{j} = -\partial_t \rho \tag{3.2}$$

which is homogeneous because besides derivatives there are no other terms. It follows from this equation that the total probability in space is always conserved. The continuity equation for the electromagnetic field is similar but contains additional term, which makes it inhomogeneous instead homogeneous equation. Therefore, if with the current density one associates the vector

$$\vec{P} = \frac{c}{4\pi}\vec{E} \times \vec{H} \tag{3.3}$$

and with the charge density one associates

$$\epsilon = \frac{1}{8\pi}\left(\vec{H} \cdot \vec{H} + \vec{E} \cdot \vec{E}\right)$$

then the relationship between them, in the form of the continuity equation, suggests that the total ϵ in space is conserved if there are no currents in it. One then associates ϵ with energy density of the electromagnetic field and $\vec{P}$ is Poyting vector and measures energy flow per unit time and unit area, which is also associated with the momentum density of the field. The presence of other charges in the total volume affects the energy of the field, it is either absorbed or released by them, and the extent of this exchange is measured by the additional inhomogeneous term $\vec{E} \cdot \vec{j}$, where these charges are represented by their respective currents.

It should be noted that the continuity equation does not specify the energy flow uniquely. One can make replacement

$$\vec{P} \Longrightarrow \vec{P} + \nabla \times \vec{U}$$

where $\vec{U}$ is arbitrary vector, and the continuity equation is not altered. The additional term represents the flow of energy that does not exit enclosed volume, it flows in a circle around its source.

Closely related to the Poyting vector is the radiation pressure, which is the force of the electromagnetic radiation per unit area, and it is given by

$$\overrightarrow{F} = \frac{1}{4\pi}\vec{E} \times \vec{H}$$

3.2 Vector and Scalar Potentials

Analysis of the electromagnetic field is considerably simplified if one defines potentials. Scalar potential was already defined when the electric, time independent, force was introduced, in which case the appropriate electric field is given by

$$\vec{E} = -\nabla V$$

The advantage of using the potential is obvious, instead of working with the three component quantities, the electric field, one needs to know a single component, scalar, function. However, the disadvantage is that the potential is not a uniquely defined quantity, because it is the field that manifests itself as a force on a charge. Any constant could be added to the potential and the force remains the same.

In the same spirit one defines a vector function for the magnetic field by noting its basic property

$$\nabla \cdot \vec{H} = 0$$

from where it follows that $\vec{H}$ could be represented as

$$\vec{H} = \nabla \times \vec{A} \tag{3.4}$$

where $\vec{A}$ is the vector potential. The scalar potential is derived from the charge density and it is expected that the vector potential is derived from the charge current.

To find relationship of the scalar and vector potentials to the charge density and the charge current one must find their relationship to Maxwell equations. From the first Maxwell equation one obtains

$$\nabla \times \vec{E} = -\frac{1}{c}\partial_t \nabla \times \vec{A} \ = -\nabla \times \frac{1}{c}\partial_t \vec{A}$$

and hence

$$\vec{E} = -\frac{1}{c}\partial_t \vec{A} - \nabla V \tag{3.5}$$

The second term on the right expresses the fact that the Maxwell equation determines the electric component up to a gradient of a scalar function.

From the second Maxwell equation one obtains

$$\nabla \times \left(\nabla \times \vec{A}\right) = \frac{1}{c}\partial_t \left(-\frac{1}{c}\partial_t \vec{A} - \nabla V\right) + \frac{4\pi}{c}\vec{j}$$

or

$$\nabla \left(\nabla \cdot \vec{A}\right) - \Delta \vec{A} = -\frac{1}{c^2}\partial_t^2 \vec{A} - \nabla \left(\frac{1}{c}\partial_t V\right) + \frac{4\pi}{c}\vec{j}$$

In this equation one recognizes the wave equation

$$\Delta \vec{A} - \frac{1}{c^2}\partial_t^2 \vec{A} = -\frac{4\pi}{c}\vec{j} \tag{3.6}$$

which one needs to assume if the vector potential is to describe electromagnetic waves. This requirement is fulfilled if the vector and the scalar potentials are inter

related through equation

$$\nabla \cdot \vec{A} + \frac{1}{c}\partial_t V = 0 \tag{3.7}$$

which is also known as the Lorentz condition.

The third Maxwell equation then gives

$$\nabla \cdot \left(-\frac{1}{c}\partial_t \vec{A} - \nabla V \right) = -\frac{1}{c}\partial_t \nabla \cdot \vec{A} - \Delta V = \frac{1}{c^2}\partial_t^2 V - \Delta V = 4\pi\rho$$

or finally

$$\Delta V - \frac{1}{c^2}\partial_t^2 V = -4\pi\rho \tag{3.8}$$

where the Lorentz condition was used. Again this is now a wave equation, but for the scalar potential.

Both potentials obey inhomogeneous wave equation, and its general solution is

$$h\left(\vec{r}, t\right) = h_{\text{hom}}\left(\vec{r}, t\right) + \int d^3r'\, dt'\; K\left(\vec{r} - \vec{r}', t - t'\right) \boldsymbol{g}\left(\vec{r}', t'\right) \tag{3.9}$$

where $K\left(\vec{r} - \vec{r}', t - t'\right)$ is the Green function for the electromagnetic field, which is derived in Appendix 2, and $\boldsymbol{g}\left(\vec{r}', t'\right)$ is inhomogeneous term in the wave equations. Solution for the potentials, without the homogeneous term $h_{\text{hom}}\left(\vec{r}, t\right)$ (it corresponds to the electromagnetic field without a source), is in the explicit form (see Appendix 2)

$$\begin{aligned} \vec{A} &= \frac{1}{c}\int \frac{\vec{j}\left(\vec{r}', t_{ret}\right)}{|\vec{r} - \vec{r}'|} d^3r' \\ V &= \int \frac{\rho\left(\vec{r}', t_{ret}\right)}{|\vec{r} - \vec{r}'|} d^3r' \end{aligned} \tag{3.10}$$

where t_{ret} is the retarded time, which is defined as the solution of equation

$$t - t_{ret} = \frac{1}{c}\left|\vec{r} - \vec{r}'\right|$$

Its essence is to give time when the disturbance in the field should be produced by its source at the coordinates $\vec{r}'$ in order to interact with the charge density at the position $\vec{r}$ and time t.

Despite the fact that both potentials are determined by charge and current they are in fact not uniquely determined quantities. If any scalar function W satisfies the homogeneous wave equation

$$\Delta W - \frac{1}{c^2}\partial_t^2 W = 0$$

then the electric and magnetic components of the electromagnetic field remain unaltered if one makes replacements

$$\vec{A} \Longrightarrow \vec{A} + \nabla W$$
$$V \Longrightarrow V - \frac{1}{c}\partial_t W$$

The Lorentz condition is also satisfied. This arbitrariness in the definition of the potentials plays important role in dynamics of the electromagnetic field, and it has a special name, the gauge invariance. Related to this invariance is a theorem, which is mentioned but not proved. Any vector could be uniquely decomposed into two components

$$\vec{A} = \vec{A}_{\parallel} + \vec{A}_{\perp}$$

where they are defined to satisfy the equations

$$\nabla \times \vec{A}_{\parallel} = 0$$
$$\nabla \cdot \vec{A}_{\perp} = 0$$

$\vec{A}_{\parallel}$ is called the longitudinal component because in general it is given as a gradient of a certain scalar function

$$\vec{A}_{\parallel} = \nabla \Phi$$

On the other hand, $\vec{A}_{\perp}$ is called the orthogonal component because it is given as the curl of a vector

$$\vec{A}_{\perp} = \nabla \times \vec{S}$$

These components could be extracted from the equations

$$\vec{A}_{\parallel} = -\frac{1}{4\pi}\nabla \left[\nabla \cdot \int \frac{\vec{A}(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|} d^3 r' \right] \tag{3.11}$$
$$\vec{A}_{\perp} = \frac{1}{4\pi}\nabla \times \left[\nabla \times \int \frac{\vec{A}(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|} d^3 r' \right]$$

but directly if one defines Green function for the orthogonal component (longitudinal is then easily extracted). By using (C.8) and definition of Green functions in Chap. 2 one derives orthogonal Green function for the retarded field

$$K^{tr}_{n,m}(\vec{r}, t) = \frac{2}{(2\pi)^3} \int d^3\kappa \, d\omega \, \frac{\delta_{n,m} - \widehat{\kappa}_n \widehat{\kappa}_m}{\vec{\kappa}^2 - \left(\frac{\omega}{c} + i\eta\right)^2} e^{i\vec{\kappa}\cdot\vec{r} - i\omega t}$$

where $\eta > 0$ and $\widehat{\kappa} = \vec{\kappa}/\kappa$ is unit vector. The n-th orthogonal component of the vector potential is now

$$\left(\overrightarrow{A}_{\perp}\right)_n = \frac{1}{c}\sum_m \int d^3q\, ds\, K^{tr}_{n,m}\left(\vec{r}-\vec{q}, t-s\right)\, \overrightarrow{j}_m\left(\vec{q}, s\right)$$

These components are of importance in quantum dynamics of a charge that is interacting with the electromagnetic field. Momentum operator is modified by the transversal component of the vector potential whilst the longitudinal goes together with the scalar potential. External electromagnetic field without a source (for example a plane wave) could always be modified by using the gauge invariance to eliminate scalar and longitudinal components.

From homogeneous equations (3.6) and (3.8) (they do not necessarily reflect solutions without source, they also represent standing wave solutions, as it will be shown later) one derives expression for the energy of the field and its momentum, which are given by

$$T_0 = \frac{1}{8\pi}\int d^3r \left(\vec{H}\cdot\vec{H} + \vec{E}\cdot\vec{E}\right)$$

and

$$\overrightarrow{T} = \frac{c}{4\pi}\int d^3r\, \vec{E}\times\vec{H}$$

respectively. They assume more convenient form when given in terms of the potentials. By replacing electric and magnetic components from (3.5) and (3.4), respectively, the Lorentz condition (3.7) is used and after partial integrations one gets for the total electromagnetic energy (and removing scalar potential by gauge transformation)

$$T_0 = \frac{1}{8\pi}\int d^3r \left(\frac{1}{c^2} d_t\overrightarrow{A}\cdot d_t\overrightarrow{A} + d_x\overrightarrow{A}\cdot d_x\overrightarrow{A} + d_y\overrightarrow{A}\cdot d_y\overrightarrow{A} + d_z\overrightarrow{A}\cdot d_z\overrightarrow{A}\right)$$

and for the total electromagnetic momentum

$$\overrightarrow{T} = -\frac{1}{4\pi c^2}\int d^3r\, \left(d_t\overrightarrow{A}\cdot d_x\overrightarrow{A}\,\hat{x} + d_t\overrightarrow{A}\cdot d_y\overrightarrow{A}\,\hat{y} + d_t\overrightarrow{A}\cdot d_z\overrightarrow{A}\,\hat{z}\right)$$

If the vector potential is represented as

$$\overrightarrow{A} = \int d^3k\, \left[e^{i\vec{k}\cdot\vec{r}-ktc}\,\overrightarrow{a}\left(\overrightarrow{k}\right) + e^{-i\vec{k}\cdot\vec{r}+ktc}\,\overrightarrow{a}^*\left(\overrightarrow{k}\right)\right]$$

then these two expressions take the form

$$T_0 = 2\pi^2\int d^3k\, k^2\left[\overrightarrow{a}\left(\overrightarrow{k}\right)\cdot\overrightarrow{a}^*\left(\overrightarrow{k}\right) + \overrightarrow{a}^*\left(\overrightarrow{k}\right)\cdot\overrightarrow{a}\left(\overrightarrow{k}\right)\right]$$

and

$$\overrightarrow{T} = \frac{2\pi^2}{c} \int d^3k \, k \overrightarrow{k} \left[\overrightarrow{a} \left(\overrightarrow{k} \right) \cdot \overrightarrow{a}^* \left(\overrightarrow{k} \right) + \overrightarrow{a}^* \left(\overrightarrow{k} \right) \cdot \overrightarrow{a} \left(\overrightarrow{k} \right) \right]$$

Importance of these expressions is in formulation of quantum electromagnetic field theory [24–26].

3.3 Electromagnetic Waves

3.3.1 General Features

Charges in a non uniform motion produce electromagnetic waves and if this change in velocity is for a finite time interval then the wave has a finite length. Far away from the source equation for this field is then

$$\Delta \vec{A} - \frac{1}{c^2} \partial_t^2 \vec{A} = 0$$
$$\Delta V - \frac{1}{c^2} \partial_t^2 V = 0$$

These are wave equations without a source, and they are basic in the analysis of interaction of the electromagnetic wave with charges. Their solution is simple, for example, a single source produces waves that far away from it propagate in the radial direction, in the outward direction, for which a general solution is

$$h = \frac{1}{r} \sum_{l,m} a_{l,m} Y_{l,m}(\theta, \phi) f_{l,m}(r - ct)$$

The waves of this kind are seldom encountered, only in dynamics of individual source, more often one observes a collective effect of huge number of sources (e.g. atoms) in which case a wave of particular character is encountered. This wave propagates in a certain direction, along which it has coordinate dependence, and perpendicular to it is in general constant (not always, as discussed in Sect. 3.3.4). When referring to the wave one assumes this functional dependence, whilst the wave produced by a single charge is referred to as the spherical wave.

A general solution of the wave equation for the potentials (without the source) is

$$\vec{A} = \vec{f} \left(\hat{n} \cdot \vec{r} \pm ct \right) \qquad (3.12)$$
$$V = \boldsymbol{g} \left(\hat{n} \cdot \vec{r} \pm ct \right)$$

where $\vec{f}$ and $\boldsymbol{g}$ are arbitrary functions, however, they are determined by how the wave is formed. As it was shown earlier there is arbitrariness in the choice of the potentials, having the roots in the gauge invariance. This invariance can be used with the specific purpose to make the scalar potential zero. In other words, one defines new potentials as

$$\vec{A}_{new} = \vec{A} + \nabla W$$
$$V_{new} = V - \frac{1}{c}\partial_t W = 0$$

where the correcting scalar potential that does that is

$$W = c \int \boldsymbol{g}\left(\hat{n} \cdot \vec{r} \pm ct\right)\, dt$$

Therefore electromagnetic waves, when they have no source, are uniquely described entirely by the vector potential. This is also called the Coulomb gauge.

Important property of the vector potential is deduced from the Lorentz condition. When applied to the potentials in the Coulomb gauge one finds

$$\nabla \cdot \vec{A} + \frac{1}{c}\partial_t V = \nabla \cdot \vec{A} = \hat{n} \cdot \vec{f}\,' = 0$$

where $'$ indicates derivative with respect to the argument of the functions. This means that the unit vector $\hat{n}$ in the argument of the vector potential is always perpendicular to its polarization. From the Poyting vector (3.3) one deduces physical meaning of the unit vector. The electric and magnetic components are

$$\vec{E} = -\frac{1}{c}\partial_t \vec{A} - \nabla V = \mp \vec{f}\,'\left(\hat{n} \cdot \vec{r} \pm ct\right)$$
$$\vec{H} = \nabla \times \vec{A} = \hat{n} \times \vec{f}\,'\left(\hat{n} \cdot \vec{r} \pm ct\right)$$

and the Poyting vector is

$$\vec{P} = \frac{c}{4\pi}\vec{E} \times \vec{H} == \mp \frac{c}{4\pi}\hat{n}\left(\vec{f}\,' \cdot \vec{f}\,'\right)$$

The unit vector $\hat{n}$, therefore, determines direction of the energy flow, it is along its direction when the argument of the vector potential is $\hat{n} \cdot \vec{r} - ct$ whilst in the opposite when it is $\hat{n} \cdot \vec{r} + ct$. Both choices are allowed, but in the case of spherical waves the former one indicates that the wave travels away from the source, whilst in the latter it travels towards the source. Obviously the latter choice is not physical and therefore the former will always be used for the spherical waves. However, for the waves (not spherical) both choices are used, depending on where the sources of the wave are, e.g. if they are placed in the space $x > 0$ then for the waves that propagate towards $x \to -\infty$ the appropriate choice of the argument in the function f would

be $\hat{n}\cdot\vec{r}+ct$. The unit vector $\hat{n}$ is called the propagation vector of the electromagnetic waves.

Direction of the vector potential is polarization of the electromagnetic wave. In general one distinguishes two types of polarizations. The most common is when the direction of the vector potential does not changes in time, in which case one talks about the linear polarization of the wave. When it changes in time then it is called non-linearly polarized light. There are more specific choices, but they are only well defined for the plane waves, which will be discussed shortly.

Very often a detailed shape of vector potential is not known, in which case one makes models on the bases of the available general information. The simplest model is a linearly polarized wave, say along the z direction, that propagates along the x axes. The vector potential is then determined by a single component, a single scalar function. If this wave has finite length then one acceptable form that describes it is

$$\vec{A} = A_0\, e^{-\frac{(x-ct)^2}{c^2T^2}} \cos\left[\frac{\omega}{c}(x-ct)\right]\hat{z} \tag{3.13}$$

T is normally estimated, ω is known, but the amplitude A_0 must be determined. The available information for this is the total energy carried by this wave, but normalized to the unit area that is perpendicular to the propagation of the wave. The amplitude is therefore obtained from the relationship

$$en = \int_{-\infty}^{\infty} dt\ P = \frac{c}{4\pi}\int_{-\infty}^{\infty} dt\ \left(\vec{f}\,'\cdot\vec{f}\,'\right)$$

where P is the modulus of the Poyting vector and en is the energy that is carried by this wave. By assuming the shape (3.13) one gets

$$en = \frac{A_0^2}{8cT\sqrt{2\pi}}\left(1+T^2\omega^2+e^{-\frac{1}{2}T^2\omega^2}\right)$$

There are two limiting cases: very long wave, when $T\omega \gg 1$, and a short wave, when $T\omega \approx 1$. However, the energy en is not the proper choice for getting information about the wave, instead one should calculate the time average power that it transmits, i.e. the time average of the Poyting vector. This average is

$$\frac{en}{T} = P_{av} = \frac{A_0^2}{8cT^2\sqrt{2\pi}}\left(1+T^2\omega^2+e^{-\frac{1}{2}T^2\omega^2}\right)$$

from which, in principle, the amplitude A_0 could be calculated.

For a long wave the amplitude is

$$P_{av} = \frac{A_0^2}{8c\sqrt{2\pi}}\omega^2 \Longrightarrow A_0 = 2^{7/4}\pi^{1/4}\frac{\sqrt{cP_{av}}}{\omega}$$

but for a short

$$P_{av} = \frac{A_0^2}{4cT^2\sqrt{2\pi}} \Longrightarrow A_0 = 2^{5/4}\pi^{1/4}T\sqrt{cP_{av}}$$

Measure of the strength of the field is not the vector potential but the electric and magnetic components, which are derived from the vector potential. For a long wave the electric component is

$$\vec{E} = -\frac{1}{c}\partial_t \vec{A} \approx -\frac{A_0\omega}{c} \sin\left(\frac{\omega}{c}x - \omega t\right) \hat{z}$$

whilst for a short

$$\vec{E} \approx -\frac{2A_0}{cT^2\omega}\left(\frac{\omega}{c}x - \omega t\right)\cos\left(\frac{\omega}{c}x - \omega t\right) \hat{z}$$

In general, for a short wave the strength of the field increases as T^{-1} , i.e. the shorter the wave the electric and magnetic components are larger.

3.3.2 Plane Waves

Special type of the electromagnetic wave is a plane wave. Its typical feature is that it has single frequency, which uniquely specifies its other characteristics, except polarization. There are, however, no perfect plane waves, because single frequency implies also infinite length along the line of propagation, which means that it carries infinite energy. Nevertheless, the concept of a plane wave is very useful because in many circumstances describes well real situations, and in addition simplifies theoretical analysis. Plane wave approximation fails when transient effects are analyzed, impact of onset or the end of interaction with charges, when this could have important consequences on the resulting dynamics, as it will be discussed in Chap. 4.

The most general form of a plane wave is

$$\vec{A} = A_x \cos\left(\frac{\omega}{c}z - \omega t\right) \hat{x} + A_y \cos\left(\frac{\omega}{c}z - \omega t + \alpha\right) \hat{y} \tag{3.14}$$

where now it is assumed that it propagates along the z axes. The assumption is not restriction on its generality, because the wave that propagates in any other direction is obtained from this by rotation of the coordinate system. α is the phase shift between oscillations along the x and y coordinates, and in general the amplitudes of the vector potential along these axes are not equal. Depending on the phase shift one distinguishes various types of polarizations of the electromagnetic wave.[3]

[3]Polarization of electromagnetic field is defined as direction of its electric component, but for the plane waves this coincides with the direction of the vector potential, because the former is just the time derivative of the latter.

Polarization is defined as time dependence of the vector potential direction at a fixed point in space. For simplicity one takes $z = 0$ as the reference point, in which case the direction angle ϕ with respect to the x axes is

$$\tan\phi = \frac{A_y}{A_x}\left[\cos\alpha - \tan(ct)\sin\alpha\right]$$

which in general is time dependent, except for two special cases: $\alpha = 0,\ \pi$. The polarization is in this case called linear. There are another two special cases for $\alpha = \pi/2,\ 3\pi/2$, and their meaning is obtained by calculating modulus of the vector potential

$$A = \sqrt{A_x^2\cos^2(ct) + A_y^2\sin^2(ct)}$$

and if the relationship

$$\tan\phi = \frac{A_y}{A_x}\tan(ct)$$

is used then

$$A = \frac{A_y A_x}{\sqrt{A_x^2 + A_y^2 - \left(A_x^2 - A_y^2\right)\cos(2\phi)}}$$

This is equation for an ellipse with the axes A_x and A_y, and therefore polarization is called elliptic, and the special case of it is circular when $A_x = A_y$. Any other choice of the phase shift α does not produces simple polarization.

Plane wave is a very useful model because in a number of circumstances it realistically describes interaction of the electromagnetic field with charges. For example, a continuous laser produces almost a steady stream of the electromagnetic radiation of nearly a single frequency. The concept of a plane wave is, however, primarily a very useful mathematical object, and therefore it is important to define it in a suitable way. One of its forms is

$$\vec{A}_j^{+}(\vec{k}) = \hat{a}_j\, e^{i\,\vec{k}\cdot\vec{r} - wt} \tag{3.15}$$

where $\vec{k} = \frac{w}{c}\hat{n}$, and the index $j = 1, 2$ refers to one of directions of polarization (there are at most two), which, from the Lorentz condition, have the property

$$\hat{a}_j \cdot \vec{k} = 0$$

Polarization vectors are not uniquely defined from this property, one of them is arbitrary but the other one is then (almost) uniquely determined (its sign is arbitrary). The last equation implies

$$\hat{a}_j \cdot \vec{k} = k\left[\cos\theta_a\cos\theta_k + \cos(\phi_a - \phi_k)\sin\theta_a\sin\theta_k\right]$$

where the spherical angles are for each vector. The choice of direction of $\hat{a}_1$ is arbitrary and the simplest is to take $\phi_a = \phi_k$ in which case $\theta_a = \theta_k + \pi/2$. The other polarization vector is then $\hat{a}_2 = \hat{a}_1 \times \vec{k}/k$. In the explicit form

$$\hat{a}_1 = \cos\theta_k \cos\phi_k \, \widehat{x} + \cos\theta_k \sin\phi_k \, \widehat{y} - \sin\theta_k \, \widehat{z}$$

and

$$\hat{a}_2 = \sin\phi_k \, \widehat{x} - \cos\phi_k \, \widehat{y}$$

Any wave is described as a linear combination of these elementary plane waves, however, $\vec{A}_j^+(\vec{k})$ do not form a complete set of functions, additionally one must define

$$\vec{A}_j^-(\vec{k}) = \hat{a}_j \, e^{-i \, \vec{k}\cdot\vec{r} + wt} \tag{3.16}$$

so that a general plane wave (3.14) is given as a sum

$$\overrightarrow{A} = \boldsymbol{g}_1 \vec{A}_1^+(\vec{k}) + \boldsymbol{g}_2 \vec{A}_2^+(\vec{k}) + h_1 \vec{A}_1^-(\vec{k}) + h_2 \vec{A}_2^-(\vec{k})$$

Vector $\hat{n}$ has only component in the z direction therefore the unit polarization vectors $\hat{a}_j$ must be a linear combination of the unit vectors $\hat{x}$ and $\hat{y}$. One of them is arbitrary, say it is given by

$$\hat{a}_1 = \cos\beta \, \hat{x} + \sin\beta \, \hat{y}$$

but the other one, which is orthogonal to it, is

$$\hat{a}_2 = \sin\beta \, \hat{x} - \cos\beta \, \hat{y}$$

If they are replaced in the linear combination then

$$\begin{aligned}
&\frac{A_x}{2}\left(e^{i(k\,z-ct)} + e^{-i(k\,z-ct)}\right)\,\hat{x} + \frac{A_y}{2}\left(e^{i(k\,z-ct+\alpha)} + e^{-i(k\,z-ct+\alpha)}\right)\,\hat{y} \\
&\quad = \boldsymbol{g}_1(\cos\beta\,\hat{x} + \sin\beta\,\hat{y})e^{i(k\,z-ct)} + \boldsymbol{g}_2\left(\sin\beta\,\hat{x} - \cos\beta\,\hat{y}\right)e^{i(k\,z-ct)} \\
&\qquad + h_1(\cos\beta\,\hat{x} + \sin\beta\,\hat{y})e^{-i(k\,z-ct)} + h_2\left(\sin\beta\,\hat{x} - \cos\beta\,\hat{y}\right)e^{-i(k\,z-ct)}
\end{aligned}$$

and by comparing the coefficients in front of the same unit vectors, and the exponential functions, then

$$\begin{aligned}
\frac{A_x}{2} &= \boldsymbol{g}_1\cos\beta + \boldsymbol{g}_2\sin\beta, \quad \frac{A_x}{2} = h_1\cos\beta + h_2\sin\beta, \\
\frac{A_y}{2}e^{i\alpha} &= \boldsymbol{g}_1\sin\beta - \boldsymbol{g}_2\cos\beta, \quad \frac{A_y}{2}e^{-i\alpha} = h_1\sin\beta - h_2\cos\beta
\end{aligned}$$

Solution for the expansion coefficients is

$$g_1 = \frac{1}{2}\left(A_x \cos\beta + A_y e^{i\alpha}\sin\beta\right), \quad g_2 = \frac{1}{2}\left(A_x \sin\beta - A_y e^{i\alpha}\cos\beta\right),$$
$$h_1 = \frac{1}{2}\left(A_x \cos\beta + A_y e^{-i\alpha}\sin\beta\right), \quad h_2 = \frac{1}{2}\left(A_x \sin\beta - A_y e^{-i\alpha}\cos\beta\right)$$

That simple exercise showed how to use plane waves (3.15) and (3.16) to represent any wave as their linear combination. The first step is to define polarization vectors, based on the knowledge of the unit vector $\hat{n}$. One then forms a general linear transformation

$$\vec{A}(u) = \int dw \left[\left(g_1(w)\hat{a}_1 + g_2(w)\hat{a}_2\right) e^{i\ w\ u} + \left(h_1(w)\hat{a}_1 + h_2(w)\hat{a}_2\right) e^{-i\ w\ u}\right]$$

and from that the polarization components are obtained as

$$\vec{A}(u)\cdot\hat{a}_j = \int_0^\infty dw \left[g_j(w)e^{i\ w\ u} + h_j(w)e^{-i\ w\ u}\right]$$

The coefficients in the expansion are now

$$g_j(w) = \frac{1}{2\pi}\int_{-\infty}^{\infty} du\ \vec{A}(u)\cdot\hat{a}_j\ e^{-i\ w\ u}, \quad h_j(w) = \frac{1}{2\pi}\int_{-\infty}^{\infty} du\ \vec{A}(u)\cdot\hat{a}_j\ e^{i\ w\ u}$$

3.3.3 Short Pulses

A special type of a time varying electromagnetic field is produced by a uniformly moving charge. It does not have characteristics of an electromagnetic wave because it is not produced by a non uniformly moving charge, but a pulse that travels with its source which is of a very short duration and of the extreme strength. These pulses could be used also for manipulating charges, atoms or molecules, with a possible advantage that they do not have a single frequency carrier. e.g. as the pulse that was modelled by (3.13). The disadvantage of these pulses, however, is that their strength depends on the distance from the source, and in that respect cannot be used with the same intention as, for example, the plane electromagnetic waves. Modelling of these pulses assumes the point like character of their source, e.g. of the electron or the proton, and that their velocity approaches the speed of light.[4] One manifestation of the effect of relativistically moving charge on the surrounding media through the electromagnetic pulse that it produces is in particle detectors, say a bubble chamber.

[4]The electron with kinetic energy 3 MeV has the speed 0.99 that of light, whilst proton of the same speed must have kinetic energy 5713 MeV. This gives roughly the energy range when these short pulses are important.

Vector potential, for a point like source,[5] is

$$\vec{A}\left(\vec{r},t\right)=-\frac{1}{4\pi^3 c}\int d^3q\int ds\;K\left(\vec{r}-\vec{q},t-s\right)\;\vec{j}\left(\vec{q},s\right)$$

where $K\left(\vec{r}-\vec{q},t-s\right)$ is the Green function for the electromagnetic field, and its explicit form is derived in Appendix 2. By assuming that the charge moves with velocity v_0 along the z axis, and that its current is given by

$$\vec{j}\left(\vec{q},s\right)=ev_0\hat{z}\,\delta\left(q_z-v_0 s\right)\delta\left(q_x\right)\delta\left(q_y\right)$$

then the vector potential is

$$\begin{aligned}\vec{A}\left(\vec{r},t\right)&=\frac{1}{4\pi^3 c}\int d^3q\int ds\int d^3k\int dw\;\frac{e^{i\,\vec{k}\cdot\left(\vec{r}-\vec{q}\right)-iw(t-s)}}{k^2-\left(\frac{w}{c}+i\eta\right)^2}\;\vec{j}\left(\vec{q},s\right)\\&=\frac{\hat{z}\,ev_0}{2\pi^2 c}\int d^2k\,dk_z\frac{e^{i\vec{k}\cdot\vec{r}+ik_z z-iv_0k_z t}}{k^2+k_z^2-\left(\frac{v_0}{c}k_z+i\eta\right)^2}\end{aligned}$$

where the integral in $\vec{k}$ was split into the integration along its z component and the components that are perpendicular to it. The integrals could be evaluated exactly, and the final result is

$$\vec{A}\left(\vec{r},t\right)=\frac{ev_0}{c}\frac{\hat{z}}{\sqrt{\left(z-v_0t\right)^2+\left(1-\frac{v_0^2}{c^2}\right)\left(x^2+y^2\right)}}$$

and similar derivation gives for the scalar potential

$$V\left(\vec{r},t\right)=\frac{e}{\sqrt{\left(z-v_0t\right)^2+\left(1-\frac{v_0^2}{c^2}\right)\left(x^2+y^2\right)}}$$

The electric and magnetic components of the field are then derived from the known expressions, however, it is the electromagnetic field (3.1) that matters, which is given by

$$\overrightarrow{\Phi}=e\gamma\frac{x\left(c^2-v_0\mathring{z}\right)}{c^2R^3}\hat{x}+e\gamma\frac{y\left(c^2-v_0\mathring{z}\right)}{c^2R^3}\hat{y}+e\gamma\frac{c^2\left(z-v_0t\right)+v_0\left(x\,\mathring{x}+y\,\mathring{y}\right)}{c^2R^3}\hat{z}\tag{3.17}$$

[5]For elementary particles one should use the fact that their dynamics is described by the probability amplitude. However, in the extreme circumstances when their speed approaches that of the electromagnetic waves the spread of their probability amplitude is negligible, and it is confined to a narrow space. This means that the elementary particles could indeed be treated as the point like objects.

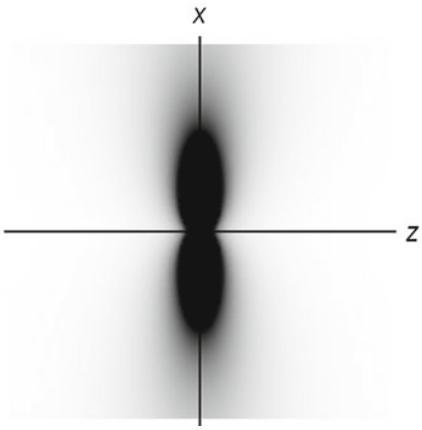

Fig. 3.1 Modulus of the electromagnetic field $\overrightarrow{\Phi}$ of a charge that is moving with velocity at nearly the speed of light along the z axes

where

$$\gamma = \left(1 - \frac{v_0^2}{c^2}\right)^{-1/2}$$

and

$$R = \sqrt{\gamma^2 (z - v_0 t)^2 + \left(x^2 + y^2\right)}$$

A typical modulus of the electromagnetic field $\overrightarrow{\Phi}$ is shown in Fig. 3.1 when velocity of charge that produces the field is nearly the speed of light.

As an example the electron having kinetic energy of 100 MeV, and at distance 5×10^{-11} m (approximately the Bohr radius) from the z axes, produces time dependence of the z and the x components of the field $\overrightarrow{\Phi}$ as shown in Fig. 3.2, left and right graphs, respectively. At the same distance in Hydrogen atom the Coulomb field of the proton is of the order $E_{Coulomb} \approx 6 \times 10^{11}$ Volt/m. The z component is smaller whilst the x component is much larger than the field that keeps the electron bound to the proton.

By assumption velocity v_0 of the charge is nearly the speed of light, and if z is not close to $v_0 t$, then the two potentials are

$$\vec{A}\left(\vec{r}, t\right) = \frac{e\,\hat{z}}{\sqrt{(z - v_0 t)^2}} sign(v_0), \quad V\left(\vec{r}, t\right) = \frac{e}{\sqrt{(z - v_0 t)^2}}$$

which is a valid approximation within the interval

$$\sqrt{x^2 + y^2} < \gamma \ |z - ct|$$

This inequality defines a conus within which the potentials are longitudinal, i.e. depend only on the coordinate along which the charge moves. Outside the conus,

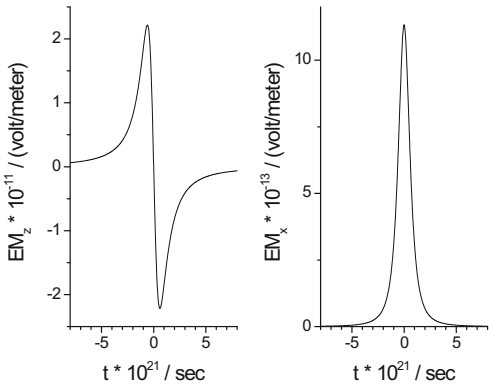

Fig. 3.2 Components of the electromagnetic field (3.17) of a charge that is moving along the z axes at nearly the speed of light

when the inequality is reversed, the potentials depend on the transversal coordinates, and within the time interval

$$t < \frac{1}{c\gamma}\sqrt{x^2 + y^2} \tag{3.18}$$

reach the maximal value

$$\vec{A}_{\max}(\vec{r}, t) = \frac{e\gamma\,\hat{z}}{\sqrt{x^2 + y^2}} sign(v_0), \quad V_{\max}(\vec{r}, t) = \frac{e\gamma\,\hat{z}}{\sqrt{x^2 + y^2}}$$

This means that although a fast moving charge exerts a strong force on the neighboring charges, its time duration is very short.

The structure of the field of a fast moving charge is almost equivalent of an electromagnetic wave, because its functional dependence on time and coordinates is essentially the same as in (3.12). More specifically it is the same as the electromagnetic wave beam, which is discussed in the following Sect. 3.3.4.

Previous analysis of the electromagnetic field that is produced by a single, fast moving, charge one could generalize by considering more charges, for example two charges (of the same mass, for simplicity) that move against each other with the same velocity. If one moves along the z axes with velocity v_0, having the charge e_1 and being at the distance d along the x axes, whilst the other one having the charge e_2 at $-d$ along the same axis but moving in the opposite direction then the charge and the current densities are

$$\rho(\vec{r}, t) = e_1\,\delta\left(\vec{r} - v_0 t\,\hat{z} - d\,\hat{x}\right) + e_2\,\delta\left(\vec{r} + v_0 t\,\hat{z} + d\,\hat{x}\right),$$
$$\vec{j}(\vec{r}, t) = \left[e_1\,v_0\,\delta\left(\vec{r} - v_0 t\,\hat{z} - d\,\hat{x}\right) - e_2\,v_0\,\delta\left(\vec{r} + v_0 t\,\hat{z} + d\,\hat{x}\right)\right]\hat{z}$$

The vector potential is derived in the same way as in the previous analysis, and the result is

$$\vec{A}(\vec{r}, t) = \frac{\hat{z}\,\gamma v_0}{c}\left(\frac{e_1}{R^-} - \frac{e_2}{R^+}\right)$$

whilst the scalar potential is

$$V(\vec{r},t)=\frac{e_1\gamma}{R^-}+\frac{e_2\gamma}{R^+}$$

where

$$R^{\pm}=\sqrt{\gamma^2\left(z\pm v_0t\right)^2+\left[(x\pm d)^2+y^2\right]}$$

The electromagnetic field that is derived from the two potentials is

$$\begin{aligned}\overrightarrow{\Phi}\ =&\left[\frac{e_1\gamma\left(v_0v_z-c^2\right)(d-x)}{c^2R^{-^3}}+\frac{e_2\gamma\left(v_0v_z+c^2\right)(d+x)}{c^2R^{+^3}}\right]\hat{x}\\&+y\left[\frac{e_1\gamma\left(v_0v_z-c^2\right)}{c^2R^{-^3}}+\frac{e_2\gamma\left(v_0v_z+c^2\right)}{c^2R^{+^3}}\right]\hat{y}+\left[\frac{e_2\gamma s^+}{c^2R^{-^3}}-\frac{e_1\gamma s^-}{c^2R^{-^3}}\right]\hat{z}\end{aligned}$$

where

$$s^{\pm}=c^2\left(tv_0\pm z\right)-v_0\left(\pm dv_x+xv_x+yv_y\right)$$

The interesting space is around the origin when the two charges meet, say this instant is $t=0$, where the electromagnetic field for $e_1=e_2=e$ approximates as

$$\overrightarrow{\Phi}\approx\frac{2\gamma e}{d^3}\left[\left(d\frac{v_0v_z}{c^2}-2x\right)\hat{x}+y\,\hat{y}+\left(z-d\frac{v_0v_x}{c^2}\right)\hat{z}\right]$$

For small velocity of the test charge the components of the electromagnetic field are either binding harmonic force or repulsive. Thus if the test charge has the same sign as e then in x direction the force is harmonic and binding

$$F_x=-\frac{4\gamma e}{d^3}x$$

whilst in the other directions it is repulsive. On the other hand, if $e_1=-e_2=e$ then

$$\overrightarrow{EM}\approx\frac{2\gamma e}{d^3}\left[\left(\frac{2v_0v_z}{c^2}x-d\right)\hat{x}-\frac{v_0v_z}{c^2}y\,\hat{y}+\left(y\frac{v_0v_y}{c^2}-2x\frac{v_0v_x}{c^2}\right)\hat{z}\right]$$

which is in x direction constant and in the others it is velocity dependent, and negligible for a slowly moving test charge.

For the electron and the positron, when each has the kinetic energy of 100 MeV and are at the distance 5×10^{-11} m (again approximately the Bohr radius) from the z axes along the x direction, produce time dependence of the z and the x components of the field $\overrightarrow{\Phi}$ at the origin as shown in Fig. 3.3. This field should be compared with the Coulomb of the proton, which is of the order $E_{Coulomb}\approx6\times10^{11}$ Volt/m. The z

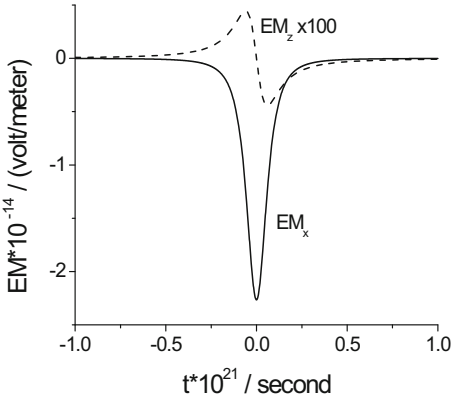

Fig. 3.3 Time dependence of the components of the electromagnetic field between two charges of different sign that move in the opposite direction

component is smaller whilst the x component much larger than the field that keeps the electron bound to the proton.

Impact that the electromagnetic field of this kind has on atoms is discusses in Sect. 4.2.

3.3.4 Finite Width Waves

So far electromagnetic waves were treated as having infinite width. In practice, however, they are either radiated from a single source, in which case they are spherical like, or they are in the form of a directed beam, for example radar beam or laser beams. In almost all analysis of these beams the assumption is that they are plane waves, meaning that their width is infinitely wide. There are several problems in the treatment of a beam of electromagnetic waves with the finite width. The problem is not only with the edges of the beam but one must also allow that their polarization has coordinate dependence. One should make distinction with the amplitude modulation in which interference of several plane waves produces a wave whose amplitude varies with the coordinate along its propagation direction, but not in the direction of polarization. For simplicity linearly polarized waves are treated.

Simple functional form for a vector potential that appears to describe electromagnetic wave is

$$\vec{A}(x, z, t) = a(z)\, e^{-iwt+ikx}\, \hat{z} \tag{3.19}$$

which has coordinate dependence of its polarization, but to be the wave there are two problems with it. First, this potential is not sufficient for describing the wave, the scalar potential is missing because the Lorentz condition (3.7) for (3.19) is not satisfied, as it should. Second the wave equation (3.6) is not satisfied (the current is zero). However, (3.19) could be treated as the initial condition for electromagnetic wave that evolves from it, for example taken at $t = 0$, but the problem is finding the

basis that would be used for solving the problem. This basis is derived by generalizing (3.19) to the form that satisfies the wave equation, and the simplest is

$$\vec{A}(x,z,t) = f[x,z]\, e^{-iwt}\, \hat{z}$$

where the function $f(x,z)$ satisfies equation

$$\partial_x^2 f(x,z) + \partial_z^2 f(x,z) + k^2 f(x,z) = 0$$

One then uses the required form for the vector potential as the initial condition

$$f(0,z) = a(z), \qquad \partial_x f(0,z) = ika(z)$$

for the solution of this equation and analyze to what extent (3.19) is preserved along the x axes.

The equation is solved by writing

$$f(x,z) = \int dq\; e^{iqz} \boldsymbol{g}(q,x)$$

and equation for the function $\boldsymbol{g}(q,x)$ is

$$\partial_x^2 \boldsymbol{g}(q,x) = -\left(k^2 - q^2\right) \boldsymbol{g}(q,x)$$

with the solution

$$\boldsymbol{g}(q,x) = \boldsymbol{g}(q,0)\left[\cos\left(x\sqrt{k^2-q^2}\right) + i\frac{k}{\sqrt{k^2-q^2}}\sin\left(x\sqrt{k^2-q^2}\right)\right]$$

where

$$\boldsymbol{g}(q,0) = \frac{1}{2\pi}\int dz\; e^{-iqz} a(z)$$

In principle the equation is solved, one only has to calculate the integral in the variable q, but this is not straightforward. The problem are the square root branching points at $q = \pm k$, and if the choice of the integration paths around them is not correct the result may be meaningless. In order to avoid problems of this kind one splits $\boldsymbol{g}(q,x)$ as

$$\boldsymbol{g}(q,x) = \boldsymbol{g}^{+}(q,x) + \boldsymbol{g}^{-}(q,x) \tag{3.20}$$

where

$$\boldsymbol{g}^{\pm}(q,x) = \frac{1}{2}\left(1 \pm \frac{k}{\sqrt{k^2-q^2}}\right)\boldsymbol{g}(q,0) e^{\pm ix\sqrt{k^2-q^2}}$$

The integration path q for $\boldsymbol{g}^+(q,x)$ is now defined having a small positive imaginary part for $\mathrm{Re}(q) < 0$ and negative for $\mathrm{Re}(q) > 0$. For the function $\boldsymbol{g}^-(q,x)$ it is the other way around.

The question of importance is the stability criterion for the initial shape of the wave. In other words, if at $x = 0$ a particular choice for the cross section of the beam of the electromagnetic wave is made at what distance x one still finds approximately the same form. In order to find the answer one must evaluate the integral

$$f^{\pm}(x,z) = \frac{1}{2}\int^{\pm} dq \left(1 \pm \frac{k}{\sqrt{k^2-q^2}}\right)\boldsymbol{g}(q,0)e^{iqz\pm ix\sqrt{k^2-q^2}}$$

for large x, which could be done by various techniques but the choice depends very much on the initial function $a(z)$, or on $\boldsymbol{g}(q,0)$. The most used function is Gaussian

$$a(z) = e^{-\frac{z^2}{d^2}} \quad \Rightarrow \quad \boldsymbol{g}(q,0) = \frac{d}{2\sqrt{\pi}}e^{-d^2q^2/4}$$

and so the integrals are

$$f^{\pm}(x,z) = \frac{d}{4\sqrt{\pi}}\int^{\pm} dq \left(1 \pm \frac{k}{\sqrt{k^2-q^2}}\right)e^{-d^2q^2/4+iqz\pm ix\sqrt{k^2-q^2}}$$

and if d is large compared to the wave length of the wave, i.e. $kd \gg 1$, then most of contribution comes from (relatively) small values of q. In this case one makes expansion

$$\sqrt{k^2-q^2} \approx k - \frac{q^2}{2k}$$

and so the dominant integral is

$$f^{+}(x,z) = \frac{1}{\Delta^+(x)}e^{ikx\left(1+\frac{2z^2}{d^2k^2\Delta^2(x)}\right)-\frac{z^2}{\Delta^2(x)}} \tag{3.21}$$

where

$$\Delta^{\pm}(x) = d \pm \frac{2ix}{dk} \quad ; \quad \Delta^2(x) = \Delta^+(x)\Delta^-(x)$$

The subdominant component is

$$f^{-}(x,z) = \frac{z^2 - 2d\Delta^-(x)}{8k^2d^2\left[\Delta^-(x)\right]^3}e^{-ikx\left(1+\frac{2z^2}{d^2k^2\Delta^2(x)}\right)-\frac{z^2}{\Delta^2(x)}}$$

The beam of electromagnetic wave therefore spreads with the distance x, in general this spread is considerable when its width is larger than $\sqrt{2}$, which happens at $x \approx 4dn$, where n is the number of wave lengths that goes into the width d. Also the wave

length of the wave changes as

$$\lambda(x,z) = \frac{\lambda_0}{1+\frac{2z^2}{d^2k^2\Delta^2(x)}}$$

which is also a function of z. For a typical wave length of $\lambda_0 = 5\times10^{-7}\,\mathrm{m}$ and the width of the beam $d = 5\times10^{-3}\,\mathrm{m}$ the distance along which it is stable is $x \approx 200\,\mathrm{m}$.

Generalization to three dimensions is straightforward. The equation is in this case

$$\partial_x^2 f(x,z) + \partial_y^2 f(x,z) + \partial_z^2 f(x,z) + k^2 f(x,z) = 0$$

and it is assumed now that the wave propagates along the z axes. The initial conditions are chosen for $z = 0$, and they are defined as

$$f(x,y,0) = a(x,y); \qquad \partial_z f(x,y,0) = ika(x,y)$$

The formal solution is written as

$$f(x,y,z) = \int dq_x\, dq_y\, e^{iq_x x + iq_y y}\boldsymbol{g}(q_x,q_y,z)$$

where

$$\partial_z^2\boldsymbol{g}(q_x,q_y,z) = -\left(k^2 - q_x^2 - q_y^2\right)\boldsymbol{g}(q_x,q_y,z)$$

and the solution of this equation is

$$\begin{aligned}&\boldsymbol{g}(q_x,q_y,z)\\ &\quad= \boldsymbol{g}(q_x,q_y,0)\left[\cos\left(z\sqrt{k^2-q_x^2-q_y^2}\right) + i\frac{k}{\sqrt{k^2-q_x^2-q_y^2}}\sin\left(z\sqrt{k^2-q_x^2-q_y^2}\right)\right]\end{aligned}$$

In this way formal solution in three dimensions is obtained, only the function $a(x,y)$ needs to be specified. One particularly interesting example is

$$a(x,y) = re^{-\frac{r^2}{d^2}}\sin\phi$$

when

$$\begin{aligned}\boldsymbol{g}(q_x,q_y,0) &= \frac{1}{(2\pi)^2}\int dx\, dy\, e^{-iq_x x - iq_y y} y e^{-\frac{x^2}{d^2}-\frac{y^2}{d^2}}\\ &= N\, q_y e^{-\frac{1}{4}d^2q_x^2 - \frac{1}{4}d^2q_y^2}\end{aligned}$$

and the solution is

$$f^{\pm}(x,y,z) = N\int_0^{\infty} dq \int_0^{2\pi} d\gamma \left(1 \pm \frac{k}{\sqrt{k^2-q^2}}\right) q^2 \sin\gamma \, e^{-\frac{1}{4}d^2q^2 + iqr\cos(\gamma-\phi) \pm iz\sqrt{k^2-q^2}}$$

where again separation (3.20) was used. After the angular integration one gets

$$f^{\pm}(x,y,z) = N\sin\phi \int_0^{\infty} dq \left(1 \pm \frac{k}{\sqrt{k^2-q^2}}\right) q^2 \, J_1(qr) e^{-\frac{1}{4}d^2q^2 \pm iz\sqrt{k^2-q^2}}$$

where $J_n(u)$ is the Bessel function. By assuming that d is large, in the units of the wave length of the wave, dominant solution is

$$f^{+}(x,y,z) = \frac{8N\, y}{d^2\left[\Delta^{+}(z)\right]^2} e^{izk\left(1+\frac{2r^2}{d^2k^2\Delta^2(z)}\right) - \frac{r^2}{\Delta^2(z)}}$$

where

$$\Delta^{\pm}(z) = d \pm \frac{2iz}{dk} \quad ; \quad \Delta^2(z) = \Delta^{+}(z)\Delta^{-}(z)$$

The subdominant component is

$$f^{-}(x,y,z) = \frac{8N\, y}{k^2 d^4\left[\Delta^{-}(z)\right]^4}\left[r^2 - 2d\Delta^{-}(z)\right] e^{-izk\left(1+\frac{2r^2}{d^2k^2\Delta^2(z)}\right) - \frac{r^2}{\Delta^2(z)}}$$

which differs from the result in two dimensions (3.21) in some obvious factors, but in essence it is the same form for the wave. Therefore the same conclusions apply as before, the beam is stable up to the point where $z \approx kd^2$.

The vector potential that is polarized along the y axes is now, by taking into account only the dominant component

$$\begin{aligned}\vec{A}(x,y,z,t) &= \mathrm{Re}\left[f^{+}(x,y,z)\, e^{-iwt}\right]\hat{y} \\ &= a_0 y\, e^{-\frac{r^2}{\Delta^2(z)}} \cos\left[zk\left(1+\frac{2r^2}{d^2k^2\Delta^2(z)}\right) - wt\right]\hat{y}\end{aligned}$$

whilst the subdominant represents the wave that propagates in the opposite direction. It is interesting to note that any "localization" of the electromagnetic wave produces this component, the result that is derived also in the relativistic quantum theory, however, there this is interpreted as creation of negative energy states of particle.

Very often one uses the initial shape of the vector potential as being constant, which obviously only applies within the space where its spreading is negligible, its general form being (for the model that is used earlier on)

$$\vec{A}(x, y, z, t) = a_0 y \, e^{-\frac{r^2}{d^2}} \cos[zk - wt] \; \hat{y}$$

from which the scalar potential is derived from the Lorentz condition

$$V = \frac{a_0}{k}\left(1 - \frac{2y^2}{d^2}\right) e^{-\frac{r^2}{d^2}} \sin[zk - wt]$$

The electric field is

$$\vec{E} = a_0 \vec{f}\,(x, y, z, t) e^{-\frac{r^2}{d^2}}$$

where

$$\vec{f}\,(x, y, z, t) = -\frac{2x}{kd^2}\left(1 - \frac{2y^2}{d^2}\right) \sin[zk - wt] \; \hat{x}$$
$$-\frac{y}{kd^2}\left(6 - \frac{4y^2}{d^2} + k^2 d^2\right) \sin[zk - wt] \; \hat{y} + \left(1 - \frac{2y^2}{d^2}\right) \cos[zk - wt] \; \hat{z}$$

The dominant component is in y direction, followed by that in the z direction, whilst the weakest is in the x direction, the estimates that are based on the assumption that $kd \gg 1$. The magnetic field is

$$\vec{H} = a_0 k y \sin[zk - wt] \, e^{-\frac{r^2}{d^2}} \, \hat{x} - \frac{2a_0 xy}{d^2} \cos[zk - wt] \, e^{-\frac{r^2}{d^2}} \hat{z}$$

Two typical values of the modulus of the electric field are shown in Figs. 3.4 and 3.5 for a fixed z and variable x and y. In the first the phase of the wave was chosen so that only the x and y components are present, whilst in the second only the z component is present. The ratio of the maxima $|E_{xy}|$ in Fig. 3.4 to the maxima $|E_z|$ in Fig. 3.5 is

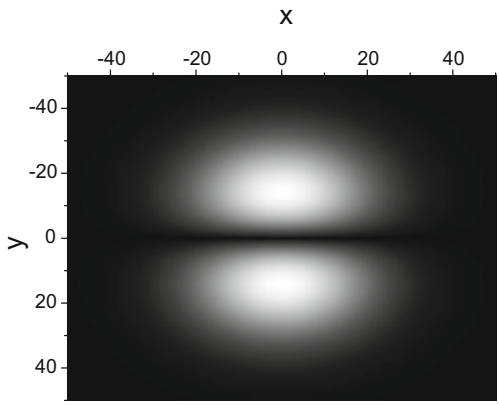

Fig. 3.4 Modulus of electric field in the beam of electromagnetic wave of the width $d = 50\lambda$. It has only x and y components, but the former are almost negligible

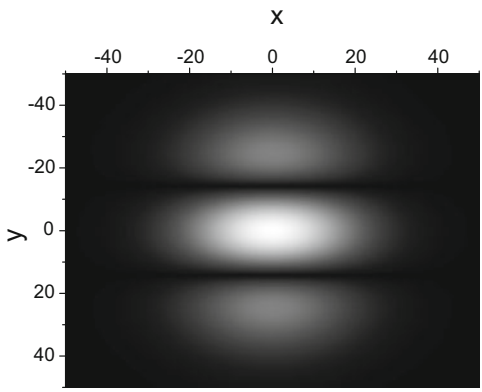

Fig. 3.5 Modulus of electric field in the beam of electromagnetic wave of the width $d = 50\lambda$, which has only z component. The modulus of the field is considerably smaller than that in Fig. 3.4

$$\frac{|E_{xy}|}{|E_z|} \approx \frac{dk}{\sqrt{2e}}$$

which is large.

3.3.5 *Beam Focusing (Paraxial Approximation)*

Electromagnetic wave could be manipulated in order to achieve its high intensity in a particular region of space. The best know example is squeezing plane wave into a point by a lens. However, the effect of high intensity could also occur along the lines or confined to planes, and an example are high intensity lines of light on a sandy seabed when the choppy sea surface is in the sunlight. The intensity, as opposed to the focal point, persist regardless of the depth of the sea. These high intensity regions are result of the caustic effect, whereby rays of light concentrate on the line or surface being tangent on them. The caustics are result of the inhomogeneous character of media through which rays of electromagnetic wave travel, where each ray satisfies equation

$$\frac{d\overrightarrow{v}}{dt} = -\overrightarrow{v} \times \left(\overrightarrow{v} \times \nabla n\right) - \overrightarrow{v}\left(\overrightarrow{v} \cdot \nabla n\right)$$

where $\overrightarrow{v}$ is speed of light in the medium with the refraction index $n\,(x, y, z)$. The caustic effect is demonstrated in Fig. 3.6 where the surface between two media is irregular (light rays come from above the surface) on a two dimensional example.

Caustics could also form high intensity lines on a surface, resulting of formation of patterns on seabed, as shown in Fig. 3.7.

The effect of caustics is described within geometric optics, however, there is another effect that results in the similar outcome but its cause is in the wave nature of electromagnetic waves. The basic idea is that along its line of propagation a beam

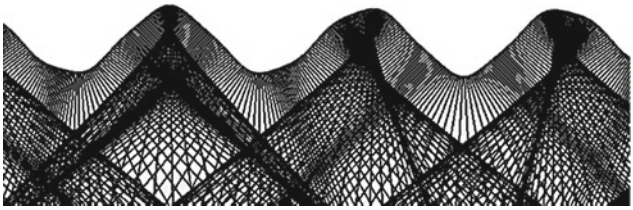

Fig. 3.6 Caustic effect that is the cause of high intensity lines of light

Fig. 3.7 Simulation of high intensity lines on a seabed that are caused by a choppy sea surface

is essentially the plane wave whilst perpendicular to it is slowly spreading, being dissimilar to the effect of caustics where for the definition of rays it is essential that no spread of beam occurs. The assumption implies that the wave length of the carrier wave is much smaller than the width of the beam, and so the functional form for the vector potential that describes a wave with this properties is

$$\vec{A}(x, y, z, t) = f(x, y, z)\, e^{-iwt+ikx}\, \hat{z}$$

From the equation for the vector potential one gets equation for the scalar function

$$ik\partial_x f = -\frac{1}{2}\left(\partial_y^2 f + \partial_z^2 f\right) \tag{3.22}$$

where in the derivation the following assumption is implemented

$$|k\partial_x f| \gg \left|\partial_x^2 f\right|$$

but the second derivatives in the coordinates y and z are retained. The choice of parametrization for f determines the scalar potential Φ from the Lorentz condition

$$\Phi = -i\frac{c}{\omega}\partial_z f$$

and so the electric field is

$$\overrightarrow{E} = \frac{i}{k}\left(\nabla\partial_z f + k^2 f\,\hat{z}\right)e^{-iwt+ikx}$$

Solving (3.22) is, therefore, central in calculating magnetic and electric fields, and the equation resembles Schroedinger equation [27], albeit in two dimensions, for a free particle if one associates k with $\hbar^{-1}$ and x with time t. Based on this observation, and in order to have complete symmetry with quantum dynamics, one defines dimensionless coordinates as $x \Rightarrow kx$ to obtain final equation

$$i\partial_s f = -\frac{1}{2}\left(\partial_y^2 f + \partial_z^2 f\right) \tag{3.23}$$

where now the variable x is replaced by s to emphasize that it plays the role that could be either coordinate or time.

For solving (3.23) with the initial condition $f_0\,(y, z)$ at $s = 0$ one uses techniques that are developed in quantum dynamics. The most straightforward solution is

$$f\,(\vec{r}, s) = \int d^2k\; A\left(\overrightarrow{k}\right)e^{i\overrightarrow{k}\cdot\vec{r}-\frac{i}{2}k^2 s}$$

where

$$\vec{r} = y\,\widehat{y} + z\,\widehat{z}$$

and $A\left(\overrightarrow{k}\right)$ is the amplitude that is determined from f_0. Alternatively solution could be formulated in the phase space, in quantum dynamics its components are coordinate and momentum and here coordinate and wave number. Formulating solution in this way has advantage that also classical dynamics could be used for solving this initial value problem for (3.23). In the phase space the solution is given by

$$\rho\,(\vec{r}, \vec{p}, s) = \frac{1}{\pi^2}\int d^2q\;\; f^*(\vec{r}+\vec{q}, s)\,f\,(\vec{r}-\vec{q}, s)\,e^{2i\vec{p}\cdot\vec{q}} \tag{3.24}$$

where now the vector $\vec{r}$ is defined as

$$\vec{r} = y\,\widehat{y} + z\,\widehat{z}$$

and likewise the other vectors. Formulation of solution through the phase space density (3.24), which is also know as the Wigner function, has advantage that it

could also be solved by classical dynamics but at the same time the uncertainty principle is preserved. The basis of quantum dynamics is this principle, but it is also in electrodynamics, where the width of electromagnetic pulse in coordinates is inverse proportional to its width in the wave number (frequency) space.

From the phase density one obtains the modulus of f squared by integrating it over the momentum variables

$$P(\vec{r}, s) = |f(\vec{r}, s)|^2 = \frac{1}{\pi^2} \int d^2p \int d^2q \;\; f^*(\vec{r} + \vec{q}, s) f(\vec{r} - \vec{q}, s) e^{2i\vec{p}\cdot\vec{q}}$$

whilst the phase $\arg(f) = \gamma$ is derived from the current

$$\overrightarrow{j} = \mathrm{Im}\left[f^* \nabla_2 f\right] = |f|^2 \;\; \nabla_2 \gamma \tag{3.25}$$

where ∇_2 is two dimensional gradient and

$$\overrightarrow{j} = \int d^2p \;\; \vec{p}\rho(\vec{r}, \vec{p}, s) \tag{3.26}$$

Time evolution of the phase space density (3.24) has simple solution. One defines trajectory

$$\vec{r} = \vec{r}_0 + \vec{p}\, s$$

and makes replacement [9]

$$\rho(\vec{r}, \vec{p}, s) = \frac{1}{\pi^2} \int d^2q \;\; f_0^*(\vec{r} - \vec{p}\, s + \vec{q}) f_0(\vec{r} - \vec{p}\, s - \vec{q}) e^{2i\vec{p}\cdot\vec{q}}$$

where now the phase space density is given entirely in terms of the initial condition for f. Few words about the initial conditions. It should be emphasized that the variable s is the coordinate and therefore the phase space density, and as the consequence the solution f is time independent. The solution represents stationary situation when the electromagnetic wave is of the infinite extent. As opposed to quantum dynamics, where s plays the role of time, one does not describe time evolution of wave. This should be kept in mind because the temptation to associate s with time, in resemblance with quantum dynamics, may lead to misinterpretation of results, such as coining the phrase "self-accelerating" beam for the effects that will be described [14–16].

There is a choice to formulate initial conditions in either the coordinate or the momentum space. If specified in the coordinate space it is implied that this is perpendicular to the line of propagation, it cannot be along parallel with it. The reason is simple, the variable s plays the role of the evolution parameter and at some point, say $s = 0$, the initial conditions are specified and this is along the y and z axes. If this initial condition is specified in such a way then one could only analyze the situation of a finite size beams, of the sort that were discussed in Sect. 3.3.4. The situation that one wants to analyze is infinitely, or practically so, wide beam that is

phase modulated in y and z directions, and the best way to ensure it is to specify initial conditions in the momentum space, which is defined as

$$f_0(\vec{r}) = \frac{1}{4\pi^2} \int d^2p \; \boldsymbol{g}_0(\vec{p}) \, e^{i\vec{p}\cdot\vec{r}}$$

when the phase space density is

$$\rho(\vec{r}, \vec{p}, s) = \frac{1}{\pi^2} \int d^2q \; \boldsymbol{g}_0^*\left(\vec{p} - \overrightarrow{q}\right) \; \boldsymbol{g}_0\left(\overrightarrow{p} + \overrightarrow{q}\right) e^{2i\overrightarrow{q}\cdot(\vec{r} - \vec{p}\, s)}$$

Initial function $\boldsymbol{g}_0$ should be of a special kind, any localization in the momentum variable reflects on localization in the coordinate space, the situation one wants to avoid. One way to ensure that the initial conditions reflect those requirements is that $\boldsymbol{g}_0(\vec{p})$ is of the exponential type with the exponent being imaginary.

Few examples shall be analyzed in one dimension, when the phase space density is

$$\rho(y, p, s) = \frac{1}{\pi} \int dq \; \boldsymbol{g}_0^*(p - q) \; \boldsymbol{g}_0(p + q) \, e^{2iq(y - p\, s)} \tag{3.27}$$

The simplest choice for $\boldsymbol{g}_0$ is Gaussian function with imaginary exponent, for which one shows that f is the delta function. The next more complicated is a polynomial type phase for $\boldsymbol{g}_0$ and the simplest non trivial is

$$\arg \boldsymbol{g}_0 = \frac{1}{3}p^3 + \frac{a}{2}p^2 + pc \tag{3.28}$$

where c and a are "the control parameters". The phase of the integrand is now

$$\delta = \frac{2}{3}q^3 + 2q\left[\left(p + \frac{a - s}{2}\right)^2 - \frac{1}{4}(s - a)^2 + (y + c)\right] \tag{3.29}$$

and when integration in q and p are performed then $P(y, s)$ is a function of $s - a$ and $y + c$. This shows that the parameter a plays the role of the shift of the "instant" when one specifies the initial condition and c moves the entire P along the perpendicular direction with respect to x. In that sense these two parameters do not play essential role, they only move the entire graph in those specified directions, and that is why they are referred to as "the control parameters". By setting both control parameters to zero the expression for $P(y, s)$ is

$$P(y, s) \sim \int_{-\infty}^{\infty} dp \; Ai\left[2^{2/3}\left(p^2 - \frac{1}{4}s^2 + y\right)\right] \tag{3.30}$$

where $Ai(u)$ is Airy function, and its typical contour is shown in Fig. 3.8a.

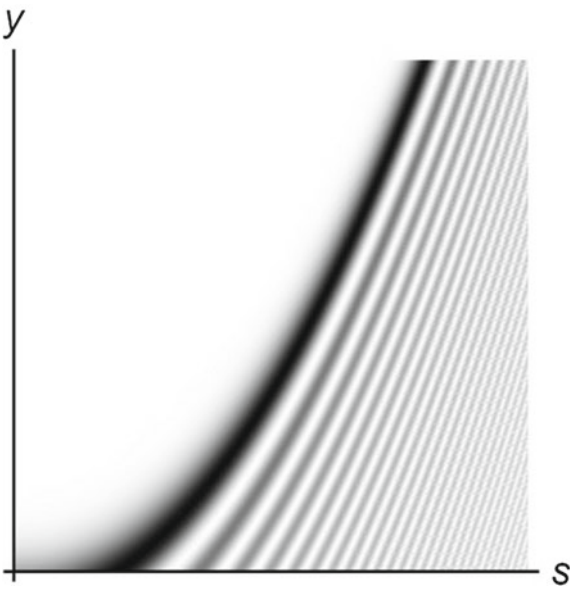

Fig. 3.8 The density $P(y, s)$ for the cubic phase (3.28) of initial condition $\boldsymbol{g}_0$

Qualitative features in Fig. 3.8 are determined from the properties of Airy function in (3.30). It is negligible for positive argument and oscillatory for negative, and the dividing line

$$y = \frac{1}{4}s^2$$

separates two regions. For s greater than $2\sqrt{y}$ the argument of the Airy function is negative and it is oscillatory, whilst in the opposite case the solution is negligible. More accurate features of $P(y, s)$ are determined from the stationary phase method C.3 for calculating integrals of the type (3.27). In this example this is a two dimensional integral, in the variables q and p, and the stationary points are calculated from two equations

$$\partial_q \delta = 2q^2 + 2\left(p^2 - ps + y\right) = 0, \quad \partial_p \delta = 2q\,(2p - s)$$

where δ is given by (3.29). There are four solutions of the set, two are

$$q_{1,2} = 0, \quad p_{1,2} = \frac{1}{2}s \pm \frac{1}{2}\sqrt{s^2 - 4y}$$

and the remaining two

$$q_{3,4} = \pm\frac{1}{2}\sqrt{s^2 - 4y}, \quad p_{3,4} = \frac{s}{2}$$

By using formulae from C.3 the estimate for $P\,(y,s)$ is

$$P_{st}\,(y,s) \approx \frac{2\pi}{\sqrt{s^2-4y}}\left[1+\sin\left(\frac{1}{6}\left(s^2-4y\right)\right)^{3/2}\right];\quad s^2>4y$$

and for $s^2 < 4y$ it is zero. $P_{st}\,(y,s)$ is in a very close agreement with the result in Fig. 3.8, except in the region around the border line, where the stationary phase method is not very accurate. It could be verified that $P_{st}\,(y,s)$ is the asymptotic expansion of the function

$$P\,(y,s) \sim Ai\left[-\frac{1}{4}\left(s^2-4y\right)\right]^2$$

The current is also needed to get solution f of equation (3.23), which is defined in (3.26) and for the phase (3.29) it is given by

$$j\,(y,s) = \frac{s}{2}P\,(y,s)$$

from where the phase γ in (3.25) is

$$\gamma = \frac{s}{2}y$$

and f is

$$f \sim Ai\left[\frac{1}{4}\left(4y-s^2\right)\right]e^{i\frac{s}{2}y}$$

It is straightforward to calculate f directly from (3.23) with the result

$$f_{dir} \sim Ai\left[\frac{1}{4}\left(4y-s^2\right)\right]e^{i\frac{s}{2}y\,-i\frac{1}{12}s^3}$$

and the two solutions are identical, apart from additional contribution in the phase of f_{dir} that is independent of y and therefore cannot be derived from (3.25).

The phase (3.28) is an example of the polynomial type for the elementary catastrophes, when $a = 0$, called *fold* or *rainbow* [27] and the next one is the *cusp* with the phase (the catastrophes were analyzed in details by Berry [17]

$$\arg \boldsymbol{g}_0 = \frac{1}{4}p^4 + \frac{a}{2}p^2 + pc \tag{3.31}$$

when the phase of the integrand in the phase space density is

$$\delta = 2pq^3 + 2q\left[p^3 + p\,(a-s) + y + c\right]$$

Again the parameters a and c could be omitted because they play the role of translation for the variables s and y, respectively. One could show that the phase space density is (non essential constant pre-factors are omitted)

$$\rho(y, p, s) \sim \frac{1}{p^{1/3}} Ai\left[\frac{2^{2/3}}{3^{1/3} p^{1/3}}\left(p^3 - ps + y\right)\right]$$

and getting from it the density $P(y, s)$ could only be done numerically. A typical $P(y, s)$ is shown in Fig. 3.9 and resemblance with that in Fig. 3.8 is again that there are two regions of space, one where $P(y, s)$ is (nearly) zero and the other where it oscillates. The line that separates the two spaces is estimated by evaluating the phase space density by the stationary phase method (see C.3). The two equations that determine the stationary points are

$$\partial_q \delta = 6pq^2 + 2p^3 - 2ps + 2y = 0, \quad \partial_p \delta = 2q^3 + 6qp^2 - 2qs = 0$$

where the second has three solutions

$$q_{st} = 0, \ \pm\sqrt{s - 3p^2}$$

For each of these the first equation has three roots in the variable p, however, as this equation is quadratic in q there is in fact only one equation to be solved. For $q_{st} = 0$ the equation is

$$p^3 - ps + y = 0 \tag{3.32}$$

whilst for the other two q_{st} there is only one equation

$$8p^3 - 2ps - y = 0$$

If solution of the first equation is p_{st} then the solution of the second is $-p_{st}/2$ which means that only the (3.32) needs to be solved. The three solutions of equation (3.32) are functions of parameter φ, which is defined as

$$\cos\varphi = \frac{9y}{\sqrt{12s^3}}$$

and they are given by

$$p_{st}^{\pm} = \frac{2\sqrt{s}}{\sqrt{3}} \cos\left(\frac{\varphi}{3} \mp \pi/3\right), \quad p_{st} = -\frac{2\sqrt{s}}{\sqrt{3}} \cos\left(\frac{\varphi}{3}\right)$$

Definition of the parameter φ specifies the dividing line between the space where $P(y, s)$ is negligible and where it is not, the latter is in the space

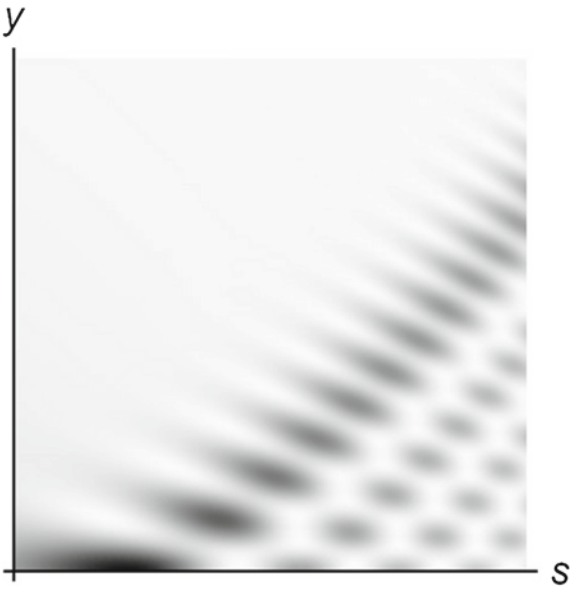

Fig. 3.9 The density $P(y, s)$ for the quartic phase (3.31) of initial condition g_0

$$y < \frac{2}{3\sqrt{3}} s^{3/2} \tag{3.33}$$

Having the stationary points of the phase in the integrand (3.27), and by using the expressions C.3 one calculates $P_{st}(y, s)$, which almost exactly reproduces $P(y, s)$ in Fig. 3.9, except around the border line where the stationary phase method fails.

The last to analyze polynomial is for elementary catastrophe *swallowtail*

$$\arg g_0 = \frac{1}{5} p^5 + \frac{a}{3} p^3 \tag{3.34}$$

where the coefficients with the second and the first power in p are omitted, for the reason that was discussed earlier. The phase of the integrand in $P(y, s)$ is now

$$\delta = \frac{2}{5} q^5 + \frac{2}{3} \left(a + 6p^2\right) q^3 + 2 \left(p^4 + ap^2 - ps + y\right) q$$

General features of $P(y, s)$ are obtained by the stationary phase method C.3. The stationary points are calculated numerically although they are given in a closed, somewhat complicated, form. There are 16 roots of the stationary equations, however, only 4 are real and only in a certain region in the plane (s, y). The line that separates the space where $P(y, s)$ is negligible (all the four roots are complex) from that where it is not (the four roots are real) is not given in a simple form as for the previous polynomials, however, it could be estimated for large s and the analytic expression for the four real roots. One shows that the line has asymptotic expansion

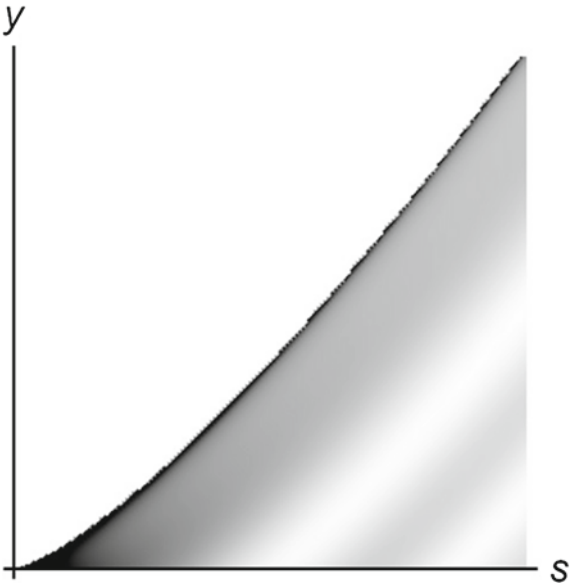

Fig. 3.10 The density $P(y, s)$ for the quintic phase (3.34) of initial condition g_0 for $a = 100$ (**a**). The density for $a = 0$ (**b**)

$$y \approx 6\, 2^{1/3} s^{4/3} - 2^{2/3} a s^{2/3} + \frac{1}{6} - \ldots$$

whilst in the vicinity of $s = 0$ the line has quadratically dominant term s^2 (Fig. 3.10).

Chapter 4
Charge in Electromagnetic Wave

Abstract Dynamics of a single charge is analyzed when electromagnetic wave of finite length interacts with it. Extreme case of impact on atom by a very short pulse, which is produced by relativistic motion of a charge, is examined. Theory for the field reaction force is developed, which is the missing link between dynamics of charge and radiation that it generates.

Some of the most basic features of dynamics of atoms and molecules in the electromagnetic field could be deduced from the simplest system: single charge in the electromagnetic field. The system is analyzed in details here both in classical and quantum treatment. The former has advantage to give intuitive insight into this dynamics, whilst the latter describes it more accurately. Classical mechanics is used in its most elementary form, without the treatment through the Liouville equation in the phase space. This simplifies considerably the analysis but gives a qualitative overview of the basic effects.

4.1 Basic Effects

4.1.1 Classical Dynamics

Information on dynamics of a charge in the electromagnetic wave is obtained from equation of motion

$$m\, d_t^2 \vec{r} = -\frac{e}{c}\, \partial_t \vec{A}(u) + \frac{e}{c}\, \vec{v} \times \left[\nabla \times \vec{A}(u)\right]$$

where

$$u = \frac{\hat{n}}{c} \cdot \vec{r} - t$$

S.D. Bosanac, *Electromagnetic Interactions*,
Springer Series on Atomic, Optical, and Plasma Physics 94,
DOI 10.1007/978-3-662-52878-5_4

For a linearly polarized wave, which is from now on assumed, one writes

$$\vec{A}(u) = \hat{s}\, a(u) \tag{4.1}$$

where $\hat{n} \cdot \hat{s} = 0$, and equation of motion is

$$\begin{aligned} m\, d_t^2\, \vec{r} &= \frac{e}{c}\, \hat{s}\, a'(u) + \frac{e\, a'(u)}{c^2}\, \vec{v} \times \left[\hat{n} \times \hat{s}\right] \\ &= \frac{e}{c} a'(u) \left[\hat{s}\left(1 - \frac{\vec{v}}{c} \cdot \hat{n}\right) + \hat{n}\left(\frac{\vec{v}}{c} \cdot \hat{s}\right)\right] \end{aligned} \tag{4.2}$$

Typical for dynamics of atoms and molecules in the electromagnetic field is that the velocity of light c is large compared to the typical velocities of charges. In such cases one makes assumption that the ratio v/c is small, and (4.2) simplifies

$$m\, d_t^2\, \vec{r} = \frac{e}{c}\, a'(u)\, \hat{s}$$

If one scalar multiplies the equation with $\hat{n}/c$ then

$$m\, d_t^2 \left(\frac{\hat{n}}{c} \cdot \vec{r}\right) = m\, d_t^2\, u = 0$$

which means that

$$u = a + bt$$

where a and b are constants that are determined from the initial conditions. If at $t = 0$ the initial position of the charge is $\vec{r}_0$ and its velocity $\vec{v}_0$ then

$$u = \frac{\hat{n}}{c} \cdot \vec{r}_0 + \left(\frac{\hat{n}}{c} \cdot \vec{v}_0 - 1\right) t$$

which means its trajectory satisfies condition

$$\hat{n} \cdot \vec{r} = \hat{n} \cdot \vec{r}_0 + \hat{n} \cdot \vec{v}_0\, t$$

It says that the parallel component of velocity of charge with respect to $\hat{n}$ is not affected by the electromagnetic wave, despite the fact that $a(u)$ has coordinate dependence. Therefore motion of a charge in the electromagnetic wave is primarily in the plane that is perpendicular to its propagation.

If one makes correction to the trajectory due to the finite, but large, value of c then the equation of motion is

$$m\, d_t^2\, \vec{r} = \frac{e}{c} a'(u) \left[\hat{s} + \varepsilon\, \hat{n}\left(\frac{\vec{v}}{c} \cdot \hat{s}\right)\right]$$

where the term $\frac{\hat{n}}{c} \cdot \vec{v}$ was neglected. Parameter ε was introduced only to indicate that the additional term in the equation of motion is small. Solution of the equation is a function of this parameter, and is expanded in the series

$$\vec{r}\ (t;\varepsilon) = \vec{r}^{(0)}\ (t) + \varepsilon\, \vec{r}^{(1)}\ (t) + \cdots$$

where the unperturbed trajectory $\vec{r}^{(0)}\ (t)$ satisfies equation

$$m\ d_t^2\ \vec{r}^{(0)}\ (t) = \frac{e}{c}\ a'(-t)\ \hat{s} \tag{4.3}$$

with the solution

$$\vec{r}^{(0)}(t) = \hat{s}\ f(t)$$

Correction $\vec{r}^{(1)}\ (t)$ is obtained by finding the equation that it satisfies, and this is done by first expanding the function $a'(u)$ as

$$\begin{aligned} a'(u) &= a'\left(\frac{\hat{n}}{c} \cdot \hat{s}\ f(t) + \varepsilon \frac{\hat{n}}{c} \cdot\ \vec{r}^{(1)} - t\right) = a'\left(\varepsilon \frac{\hat{n}}{c} \cdot \vec{r}^{(1)} - t\right) \\ &= a'(-t) + \varepsilon \left(\frac{\hat{n}}{c} \cdot\ \vec{r}^{(1)}\right) a''(-t) \end{aligned}$$

in which case equation for the trajectory is

$$m\ d_t^2\ \left(\hat{s}\ f(t) + \varepsilon\, \vec{r}^{(1)}\right) = \frac{e}{c}\left[a'(-t) + \varepsilon \frac{\hat{n} \cdot\ \vec{r}^{(1)}}{c} a''(-t)\right]\left[\hat{s} + \varepsilon\ \frac{f\,'(t)\hat{n}}{c}\right]$$

By collecting the terms of the same order ε the equation for the correction is

$$m\ d_t^2\ \vec{r}^{(1)} = \frac{e}{c^2} a'(-t)\ f\,'(t)\ \hat{n} + \frac{e}{c^2}\left(\hat{n} \cdot\ \vec{r}^{(1)}\right) a''(-t)\ \hat{s}$$

and contains two mutually orthogonal terms. The component of $\vec{r}^{(1)}$ that is parallel to the line of propagation is obtained by scalar multiplying the equation by $\hat{n}$, in which case it is solution of equation

$$m\ d_t^2\ r_n^{(1)} = \frac{e}{c^2} a'(-t)\ f\,'(t) \tag{4.4}$$

and if the initial conditions are $r_n^{(1)}(0) = d_t\ r_n^{(1)}(0) = 0$ then

$$r_n^{(1)}(t) = f_n^{(1)}(t)$$

On the other hand, parallel component with the polarization vector satisfies equation

$$m\, d_t^2\, \left(\hat{s}\cdot\vec{r}^{(1)}\right) = m\, d_t^2\, r_s^{(1)} = \frac{e}{c^2} f_n^{(1)}(t) a''(-t)$$

and if the initial conditions are $r_s^{(1)}(0) = d_t\, r_s^{(1)}(0) = 0$ then

$$r_s^{(1)}(t) = f_s^{(1)}(t)$$

so that the final (approximate to the order ε) solution for trajectory is

$$\vec{r}^{(0)}(t) = \hat{s}\, f(t) + \hat{s}\, f_s^{(1)}(t) + \hat{n}\, f_n^{(1)}(t)$$

Essential dynamic features of a charge that interacts with the electromagnetic wave which is polarized along the x axes and propagates along the z axes are illustrated on one example. The vector potential for this wave is

$$\vec{A}(u) = a(u)\, \vec{x}$$

and for the amplitude function $a(u)$ one takes

$$a(u) = \frac{a_0}{\left(1 + e^{\frac{cu - z_1}{d}}\right)\left(1 + e^{-\frac{cu - z_2}{d}}\right)} \cos(wu + \delta)$$

This form is typical of a wave that has beginning and end (electromagnetic pulse), whilst in between oscillates with the frequency w (carrier wave of single frequency). The onset of the wave has the width d and the same at its end. Typical amplitude $a(u)$ at $t = 0$ is shown by the left graph in Fig. 4.1. At some later time, when the wave interacts with the charge, the vector potential is

$$\vec{A}(z,t) = a\left(\frac{z}{c} - t\right)\, \vec{x}$$

and it is shown in Fig. 4.1 (right graph).

If at $t = 0$ the beginning of the electromagnetic pulse is at the position $z_1 < 0$ then it reaches the charge in time $t = |z_1/c|$. The vector potential then increases its amplitude to a_0 in time $t_{int} \approx d/c$, exerting the force on the charge being approximately

$$F \approx e a_0/(c t_{int}).$$

From the relationship

$$F t_{int} = m v$$

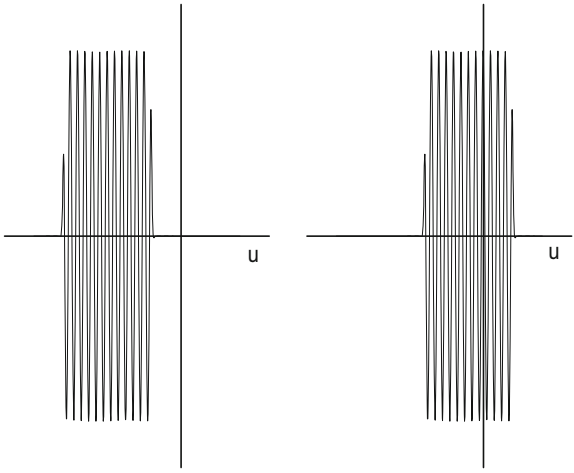

Fig. 4.1 Vector potential for electromagnetic wave of finite length and a carrier wave of single frequency, before the onset of interaction with the charge at the origin (*left graph*) and during interaction (*right graph*)

velocity that the particle acquires is

$$v = \frac{F t_{int}}{m} \approx \frac{e a_0 t_{int}}{m c t_{int}}$$

Along the length of the wave the force is oscillatory and acts during time $t_{osc} = |z_2 - z_1|/c$. In this interval it makes

$$n_{osc} = t_{osc} w/(2\pi) = |z_2 - z_1| w/(2\pi c) \tag{4.5}$$

oscillations, and after the wave has gone velocity of the particle could be estimated from the approximate solution for the trajectory. The dominant solution is $\vec{r}^{(0)}(t)$, which means that along the z axes the velocity is small, but along the x axes (in the direction of polarization) it is given by

$$d_t \, \vec{r}^{(0)}\,(t) = \frac{e\,\hat{s}}{cm} \int_0^T a'(-t)\, dt = -\frac{e\,\hat{s}}{cm} \left[a(-T) - a(0)\right] = 0$$

where it was taken into account that interaction with the charge is zero before its onset, and after the wave departed. Likewise the component of the velocity that is parallel with the propagation of the wave, in the z direction, is estimated from

$$\begin{aligned} d_t \, r_n^{(1)} &= \frac{e}{mc^2} \int_0^T a'(-t)\; f\,'(t)\, dt = -\frac{e^2}{m^2 c^3} \int_0^T a'(-t)\; \left[a(-t) - a(0)\right]\, dt \\ &= \frac{e^2}{m^2 c^3} \left[\frac{1}{2} a^2(-T) + \frac{1}{2} a^2(0) - a(0) a(-T)\right] \end{aligned}$$

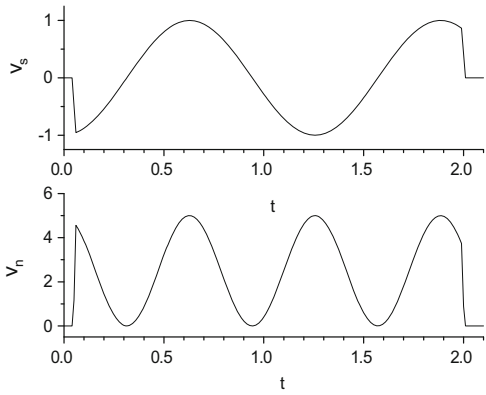

Fig. 4.2 Time dependence of two components of velocity of a charge in the electromagnetic wave in Fig. 4.1. One is parallel with the polarization of the wave (*upper graph*) and the other parallel with its propagation vector

and it is also zero. Therefore if the particle is at rest before the onset of interaction with the electromagnetic wave then it is at rest after the interaction is over. Typical time dependence of the two components of velocity of the charge are shown in Fig. 4.2, component parallel with $\hat{s}$ (upper graph) and component parallel with $\hat{n}$ (lower graph). Both velocity components were calculated numerically for some given parameters, and the approximate velocities, which are obtained from (4.3) and (4.4), are not distinguishable from the exact ones.

By increasing length of the pulse number of its oscillations within it increases, which is reflected in the number of oscillations of the charge during the interaction. For the parallel component with the polarization the number of oscillations of the charge is estimated from (4.5), but for the parallel component with the propagation of the wave (see Fig. 4.2) this number is doubled. The latter has also a constant component thus implying that the charge acquired uniform velocity, whilst the former averages to zero. Doubling of the frequency, and acquiring uniform velocity, is explained from the solution of (4.4). Within the wave, far away from its front or end, parallel velocity with $\hat{n}$ is approximated as

$$\begin{aligned} v_n &= \frac{e^2}{2m^2c^3} a^2(-t) \\ &\approx \frac{e^2 a_0^2}{4m^2c^3} \left[1 + \cos\left(2wt\right)\right] \end{aligned}$$

This component of velocity oscillates at twice the frequency of the wave, and furthermore it has a constant component

$$v_{drift} = \frac{e^2 a_0^2}{4m^2c^3} \tag{4.6}$$

meaning that a charge in a plane electromagnetic wave acquires a constant velocity, the drift velocity.

The choice of small width d is an extreme case, because in real situation it may be much larger. However, this example describes an often made mistake in the theoretical modeling of interaction between the electromagnetic plane wave and a charge. The most common assumption is that the magnetic component is neglected so that the basic equation of motion is

$$m\, d_t^2\, z\,(t) = e\, E_0\, \cos(w\, t + \delta) \tag{4.7}$$

where the electric component points in the z direction. Initial conditions $z = z_0$ and $v = v_0$ are set at $t = 0$, but that says nothing about the field prior to that instant, whether it was zero or had the value that is extrapolation of the functional form (4.7). In the modelling one should assume that it is zero, because otherwise the results do not have meaning for the simple reason that there is no telling how the initial conditions for the particle are determined. They could have been chosen at any other instant in time, of course with their value appropriate for it. Strictly speaking it should be assumed that the field is zero prior to $t = 0$, but one has a choice whether to model the interaction either with the vector potential or with the electromagnetic field. In the latter case one assumes the electric component to have the functional form

$$\vec{E} = E_0 \cos(wt + \alpha)\Theta(t)\, \hat{z}$$

where $\Theta(t)$ is the step function. However, the vector potential from which it is derived is

$$\vec{A} = -c \int dt\ \vec{E} = -cE_0 \frac{\sin(wt + \alpha)\Theta(t)}{w} \hat{z}$$

which does not give back the electric component because

$$\vec{E} == -\frac{1}{c}\partial_t \vec{A} = E_0 \left[\cos(wt + \alpha)\Theta(t) + \frac{\sin(wt + \alpha)}{w} \delta\,(t) \right] \hat{z}$$

i.e. it has contribution from the delta function. This inconsistency only tells that when it comes to modeling interaction of the electromagnetic wave with the charges one must start from the vector potentials.

The exact equation of motion that includes the onset of interaction is therefore

$$m\, d_t^2\, z\,(t) = e\, E_0 \left[\cos(wt + \alpha)\Theta(t) + \frac{\sin(wt + \alpha)}{w} \delta\,(t) \right]$$

The initial conditions are defined before the onset of interaction, for example those already mentioned in the previous analysis. The equation could now be integrated in the interval from $t = 0^-$ (just before the onset of interaction) to $t = 0^+$ (just after the onset of interaction) to give for velocity

$$m\ v\left(0^{+}\right) = e\ E_0 \int_{0^{-}}^{0^{+}} \left[\cos(wt+\alpha)\Theta(t) + \frac{\sin(wt+\alpha)}{w}\delta\left(t\right)\right] dt$$
$$= e\ E_0 \frac{\sin(\alpha)}{w} + mv_0$$

and the coordinate

$$z\left(0^{+}\right) = z_0$$

Therefore if (4.7) is solved for the trajectory by taking into account the onset of the field then the initial velocity should be modified as

$$v\left(0^{+}\right) = e\ E_0 \frac{\sin(\alpha)}{mw} + v_0 \tag{4.8}$$

whilst the coordinate is the same.

4.1.2 Quantum Dynamics

The basic equation of quantum dynamics for a charge that interacts with the electromagnetic wave is

$$i\hbar\partial_t f = -\frac{\hbar^2}{2m}\left[\nabla - \frac{ie}{\hbar c}\vec{A}\left(\frac{\hat{n}\cdot\vec{r}}{c} - t\right)\right]^2 f \tag{4.9}$$

which is solved by transforming it into the integral equation, and then by iteration. It is shown in Appendix B how to do this transformation, and if (4.9) is written as

$$i\hbar\partial_t f + \frac{\hbar^2}{2m}\nabla^2\ f = \left[\frac{ie\hbar}{mc}\vec{A}\left(\frac{\hat{n}\cdot\vec{r}}{c} - t\right)\cdot\nabla + \frac{e^2}{2mc^2}\ \vec{A}^2\left(\frac{\hat{n}\cdot\vec{r}}{c} - t\right)\right]\ f$$

then the appropriate integral equation is

$$f(\vec{r},t) = f_0(\vec{r},t)$$
$$+ \int d^3q\ ds\ G(\vec{r}-\vec{q},t-s)\left[\frac{ie\hbar}{mc}\vec{A}\left(\frac{\hat{n}\cdot\vec{q}}{c} - s\right)\cdot\nabla + \frac{e^2}{2mc^2}\ \vec{A}^2\left(\frac{\hat{n}\cdot\vec{q}}{c} - s\right)\right] f(\vec{q},s)$$

where $G(\vec{r}-\vec{q},t-s)$ is Green function. The unperturbed solution $f_0(\vec{r},t)$ is determined before the onset of interaction, and typical initial conditions are shown in Fig. 4.3 where at $t=0$ the probability density $|f_0(\vec{r},0)|^2$ is shown by a filled shape and the electromagnetic wave by solid line. One possible choice for the initial probability density is

$$P(\vec{r}) = |f_0(\vec{r},0)|^2 = \frac{1}{d^3\pi^{3/2}}\ e^{-\frac{r^2}{d^2}}$$

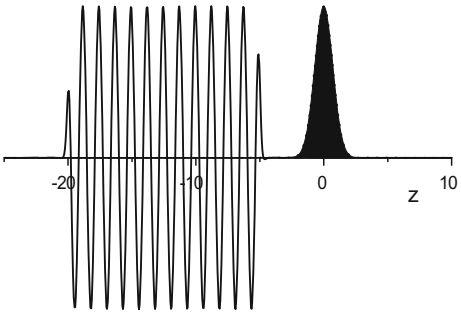

Fig. 4.3 Initial conditions for scattering of the finite length electromagnetic wave (*solid line*) on a particle whose initial probability amplitude is shown filled shape

and if the charge has average velocity $\vec{v}_0$ then the probability amplitude that describes these data is

$$f_0(\vec{r},0) = \sqrt{P(\vec{r})}e^{im\vec{v}_0\cdot\vec{r}/\hbar} = \frac{1}{d^{3/2}\pi^{3/4}}\, e^{im\vec{v}_0\cdot\vec{r}/\hbar - \frac{r^2}{2d^2}} \tag{4.10}$$

At any time later this probability amplitude is

$$f_0(\vec{r},t) = \frac{1}{\pi^{3/4}d^{3/2}\Delta^{3/2}(t)} e^{-\frac{1}{2\Delta(t)}\left[\frac{r^2}{d^2} + imv_0(v_0t-2x)/\hbar\right]}$$

where

$$\Delta(t) = 1 + i\frac{t\hbar}{md^2}$$

The integral equation is solved by iteration, meaning that in the first approximation one neglects interaction with the electromagnetic wave, and the solution is

$$f^{(0)}(\vec{r},t) = f_0(\vec{r},t)$$

In the next step this solution is replaced in the integral, so that the correction is

$$f^{(1)}(\vec{r},t) = f_0(\vec{r},t) + \int d^3q\, ds\, G(\vec{r}-\vec{q},t-s)\left[\frac{ie\hbar}{mc}\vec{A}\left(\frac{\hat{n}\cdot\vec{q}}{c}-s\right)\cdot\nabla + \frac{e^2}{2mc^2}\,\vec{A}^2\left(\frac{\hat{n}\cdot\vec{q}}{c}-s\right)\right] f_0(\vec{q},s)$$

and in the following iteration the exact solution in the integral is replaced by $f^{(1)}(\vec{r},t)$. Higher order corrections are getting considerably more complicated for analysis and therefore this procedure is only implemented when the first one already gives reasonable accurate answer. There is, however, another problem with the integral equation, which should be mentioned because of possible problems in the analysis of its solution. If one assumes a plane wave, for example of the form

$$\vec{A} = A_0\hat{x}\,\cos w\left(\frac{z}{c}-t\right)$$

then the first iteration of the integral equation is

$$f^{(1)}(\vec{r},t) = f_0(\vec{r},t) + \int d^3q\; ds\; G(\vec{r}-\vec{q},t-s)\left[\frac{ie\hbar}{mc}A_0\cos\left(w\frac{q_z}{c}-ws\right)\partial_{q_x}+\frac{e^2}{4mc^2}\;A_0^2\right] f_0(\vec{q},s)$$

where one made approximation

$$\vec{A}^2 = A_0^2\;\cos^2 w\left(\frac{z}{c}-t\right) = \frac{1}{2}A_0^2\;\left[1+\cos 2w\left(\frac{z}{c}-t\right)\right] \approx \frac{1}{2}A_0^2$$

There are now two terms in the integrand, and the second gives

$$\int d^3q\; ds\; G(\vec{r}-\vec{q},t-s)\left[\frac{e^2}{4mc^2}\;A_0^2\right] f_0(\vec{q},s) = \frac{e^2}{4mc^2}\;A_0^2\int d^3q\; ds\; G(\vec{r}-\vec{q},t-s)\; f_0(\vec{q},s) \to \infty$$

which could be shown by using expressions for the Green function from Appendix B.

The first term, on the other hand, gives

$$I_1 = \int d^3q\; ds\; G(\vec{r}-\vec{q},t-s)\left[\frac{ie\hbar}{mc}A_0\cos\left(w\frac{q_z}{c}-ws\right)\partial_{q_x}\right] f_0(\vec{q},s)$$
$$= \frac{ie\hbar}{2mc}A_0\int d^3q\; ds\; G(\vec{r}-\vec{q},t-s)\left(e^{iw\frac{q_z}{c}-iws}+e^{-iw\frac{q_z}{c}+iws}\right)\partial_{q_x}\; f_0(\vec{q},s)$$

and when the retarded Green function is used and

$$f_0(\vec{q},s) = \int d^3p\; B(\vec{p})e^{i\vec{p}\cdot\vec{q}-i\frac{\hbar p^2 s}{2m}} \tag{4.11}$$

then

$$I_1 = -\frac{e\hbar^2 i A_0}{2mc(2\pi)^3}\int d^3q\; ds\;\int\; d^3\kappa\; e^{i\vec{\kappa}\cdot(\vec{r}-\vec{q})-i\frac{\hbar\kappa^2}{2m}(t-s)}\;\Theta(t-s)$$
$$\left(e^{iw\frac{q_z}{c}-iws}+e^{-iw\frac{q_z}{c}+iws}\right)\int d^3p\; p_x B(\vec{p})e^{i\vec{p}\cdot\vec{q}-i\frac{\hbar p^2 s}{2m}}$$

The integral in the variables q gives the delta function

$$\int d^3q.... = (2\pi)^3\delta(-\vec{\kappa}\pm\frac{w}{c}\,\hat{z}\;+\overrightarrow{p}) \tag{4.12}$$

whilst the integral in s is

$$\int_0^t ds\; e^{i\frac{\hbar\kappa^2}{2m}s\mp iws-i\frac{\hbar p^2}{2m}s} = \pi\delta\left(\frac{\hbar\kappa^2}{2m}\mp w-\frac{\hbar p^2}{2m}\right)-i\P\left[\frac{1}{\frac{\hbar\kappa^2}{2m}\mp w-\frac{\hbar p^2}{2m}}\right] \quad (4.13)$$

where it was assumed that the field was turned on at $t = 0$ and that the effect on the probability amplitude is analyzed long after that time. The sign ¶ indicates the Cauchy principal value of the integral, which is defined in (C.1).

When one takes into account the delta function (4.12) then the argument of the functions in (4.13) is

$$\frac{\hbar\kappa^2}{2m}\mp w-\frac{\hbar p^2}{2m} = \frac{\hbar}{cm}\left(\pm p_z\mp\frac{cm}{\hbar}+\frac{w}{2c}\right)$$

which can never be zero because $\frac{cm}{\hbar}$ is much larger than the possible momentum of the particle. Therefore contribution from the delta function in (4.13) is zero and the principal value sign can be omitted because the argument is not singular, and the integral is

$$I_1 = -\frac{e\hbar^2A_0}{2mc}\int d^3p\; p_x B\left(\vec{p}-\frac{w}{c}\hat{z}\right)e^{i\;\vec{p}\cdot\vec{r}-i\frac{\hbar p^2}{2m}t}$$
$$-\frac{e\hbar^2A_0}{2mc}\int d^3p\; p_x B\left(\vec{p}+\frac{w}{c}\hat{z}\right)e^{i\vec{p}\cdot\vec{r}-i\frac{\hbar p^2}{2m}t}$$

Approximate probability amplitude is now

$$f^{(1)}(\vec{r},t) = f_0(\vec{r},t)+\frac{ie\hbar^2A_0}{2mc}\partial_x\int d^3p\; B\left(\vec{p}-\frac{w}{c}\hat{z}\right)e^{i\;\vec{p}\cdot\vec{r}-i\frac{\hbar p^2}{2m}t} \quad (4.14)$$
$$+\frac{ie\hbar^2A_0}{2mc}\partial_x\int d^3p\; B\left(\vec{p}+\frac{w}{c}\hat{z}\right)e^{i\vec{p}\cdot\vec{r}-i\frac{\hbar p^2}{2m}t}$$

where the unperturbed probability amplitude $f_0(\vec{r},t)$ is given by (4.11). All three terms have the same structure as in (4.11), which means that they represent motion of a free probability amplitude, the only difference being in their momentum distribution $B(\vec{p})$. For example the contribution with $B\left(\vec{p}-\frac{w}{c}\hat{z}\right)$ means that the free probability amplitude has additional component $\frac{w\hbar}{c}\hat{z}$ in the moment and hence it moves with the additional velocity $\frac{w\hbar}{mc}\hat{z}$. It appears as if part of the initial probability amplitude acquires velocity that is related to the frequency of the electromagnetic wave and not its amplitude. This result differs in essential way from the classical treatment, where the translational velocities of the particle depend only on the amplitude of the wave. However, it should be emphasized that this finding only applies to a small fraction of the initial probability amplitude, but the classical change of velocity affects all. The effect that the momentum of particle depends on the frequency is called the

frequency dependent momentum transfer, the finding that is normally associated with the concept that the electromagnetic interaction is mediated by a photon.

The problem of the onset of interaction with the electromagnetic wave also exists here, as in the classical treatment. Here it is somewhat more complicated to derive this effect because one works with the probability amplitude rather than the precise position of the particle. The equation for the onset of interaction is

$$i\hbar\partial_t f = -\frac{\hbar^2}{2m}\left[\nabla - \frac{ie}{\hbar c}\vec{A}\left(\frac{\hat{n}\cdot\vec{r}}{c} - t\right)\Theta\left(t - \frac{\hat{n}\cdot\vec{r}}{c}\right)\right]^2 f$$

and the assumption is that the probability amplitude f is localized around the origin, not moving but spreading according to the laws of dynamics. If one makes replacement

$$f = e^{\frac{ie}{\hbar c}\vec{r}\cdot\vec{A}\left(\frac{\hat{n}\cdot\vec{r}}{c}-t\right)\Theta\left(t-\frac{\hat{n}\cdot\vec{r}}{c}\right)} g$$

then the equation for g is quite complicated but simplifies if one notices that the time derivative of the phase is of the order c, which is orders of magnitude larger than the derivative of the vector potential with respect to the coordinates. If one neglects the latter derivative the equation for g is

$$-\frac{e}{c}\left[-\vec{r}\cdot\vec{A}'\left(\frac{\hat{n}\cdot\vec{r}}{c} - t\right)\Theta\left(t - \frac{\hat{n}\cdot\vec{r}}{c}\right) + \vec{r}\cdot\vec{A}\left(\frac{\hat{n}\cdot\vec{r}}{c} - t\right)\delta\left(t - \frac{\hat{n}\cdot\vec{r}}{c}\right)\right] g + i\hbar\partial_t g = -\frac{\hbar^2}{2m}\Delta g$$

One now integrates the equation in the time interval around the non zero contribution of the delta function, from $t - \varepsilon$ to $t + \varepsilon$, where the limit $\varepsilon \to 0$ is assumed. The only contribution is from the delta function, and the result is

$$-\frac{e}{c}\vec{r}\cdot\vec{A}(0)\, g^-\left(r, \frac{\hat{n}\cdot\vec{r}}{c}\right) + i\hbar g^+\left(r, \frac{\hat{n}\cdot\vec{r}}{c}\right) - i\hbar g^-\left(r, \frac{\hat{n}\cdot\vec{r}}{c}\right) = 0$$

One writes this equation as

$$i\hbar g^+\left(r, \frac{\hat{n}\cdot\vec{r}}{c}\right) = i\hbar g^-\left(r, \frac{\hat{n}\cdot\vec{r}}{c}\right) + \frac{e}{c}\vec{r}\cdot\vec{A}(0)\, g^-\left(r, \frac{\hat{n}\cdot\vec{r}}{c}\right)$$

or alternatively

$$g^+\left(r, \frac{\hat{n}\cdot\vec{r}}{c}\right) = e^{-\frac{ie}{\hbar c}\vec{r}\cdot\vec{A}(0)} g^-\left(r, \frac{\hat{n}\cdot\vec{r}}{c}\right)$$

because higher order corrections in c^{-1} were neglected. From the rules of quantum mechanics the phase indicates that the charge acquires velocity, which is exactly the same as given by (4.8) in classical mechanics.

Simplification in (4.9) is made by assuming that c is very large, meaning that within one period of its oscillation the wave travels much further than the width of the probability amplitude spreads. One, therefore, assumes the inequality

$$\frac{2\pi}{w}c \gg L = \frac{\hbar 2\pi}{d_p}$$

where the uncertainty principle $d_p L \approx \hbar$ was assumed. By rearranging the inequality one gets

$$\frac{d_p}{w\hbar}c = \frac{d_p}{\hbar k} \gg 1$$

which expresses the fact that the momentum transfer by the photon is much smaller than the width of the momentum distribution in the probability amplitude. Under this condition one makes expansion

$$\vec{A}\left(\frac{\hat{n}\cdot\vec{r}}{c} - t\right) \approx \vec{A}(-t) + \frac{\left(\hat{n}\cdot\vec{r}\right)}{c}\vec{A}'(-t)$$

in which case (4.9) is

$$i\hbar\partial_t f = -\frac{\hbar^2}{2m}\left[\nabla - \frac{ie}{\hbar c}\vec{A}(-t) - \frac{ie}{\hbar c^2}\left(\hat{n}\cdot\vec{r}\right)\vec{A}'(-t)\right]^2 f$$

or in the expanded form

$$\begin{aligned} i\hbar\partial_t f = &-\frac{\hbar^2}{2m}\left[\Delta f - 2\left(\tfrac{ie}{\hbar c}\vec{A}(-t) + \tfrac{ie}{\hbar c^2}\left(\hat{n}\cdot\vec{r}\right)\vec{A}'(-t)\right)\cdot\nabla f\right] \\ &+ \frac{e^2}{2c^2 m}\left[\vec{A}^2(-t) + \left(\hat{n}\cdot\vec{r}\right)^2\vec{A}'^2(-t)\right] f + \frac{e^2}{c^3 m}\left(\hat{n}\cdot\vec{r}\right)\vec{A}(-t)\cdot\vec{A}'(-t)\, f \end{aligned}$$

This complicated expression has in fact relatively simple solution. It can be shown, but not derived here, that a general solution for a charge in the electromagnetic wave is

$$f = \int d^3k\; B(\vec{k}) e^{i\,\vec{k}\cdot\vec{r} - i\frac{\hbar k^2}{2m}t + i\frac{e}{2mc}\int_{u_0}^{\hat{n}\cdot\vec{r}/c - t} du\left[\frac{e}{c\hbar}A^2(u) - 2\,\vec{k}\cdot\vec{A}(u)\right]} \tag{4.15}$$

which is generalization of the expression (4.11) for a free probability amplitude. The amplitude $B(\vec{k})$ is determined from the initial probability amplitude from

$$f(\vec{r},0) = \int d^3k\; B(\vec{k}) e^{i\,\vec{k}\cdot\vec{r}} \implies B(\vec{k}) = \int d^3r\; f(\vec{r},0)\, e^{-i\,\vec{k}\cdot\vec{r}}$$

By assuming large c the exponent in the general solution is expanded into the powers of c^{-1}, and after rearranging it one gets solution in a general form

$$f = e^{i\ \gamma(t)+i\ \vec{v}_{drift}\cdot\vec{r}} \int d^3k\ B(\vec{k}) e^{i\ \vec{k}\cdot(\vec{r}-\vec{r}_{osc})-i\frac{\hbar k^2}{2m}t+i\ \Phi} \tag{4.16}$$

where

$$\vec{v}_{drift} = \frac{e^2}{2m\hbar c^3} A^2(-t)\ \hat{n}$$

is the classical drift velocity, whilst

$$\vec{r}_{osc} = \frac{e}{mc} \int_{u_0}^{-t} du\ \vec{A}(u)$$

is the classical expression for the oscillations in the direction of polarization and

$$\gamma(t) = \frac{e^2}{2m\hbar c^2} \int_{u_0}^{-t} du\ A^2(u)$$

is the phase that gives the energy of the particle due to these oscillations. The latter can be shown by noting that the time derivative of the probability amplitude gives the energy of the particle i.e.

$$i\hbar\partial_t f = Ef = i\hbar\partial_t\left[\gamma(t)\right]\ f + \cdots$$

where the additional term comes from derivatives of the other factors in f. Therefore the contribution to energy from the phase γ is

$$E_\gamma = \frac{e^2}{2mc^2} A^2(-t)$$

On the other hand, velocity from $\vec{r}_{osc}$ is

$$\vec{v}_{osc} = -\frac{e}{mc}\ \vec{A}(-t)$$

and the appropriate kinetic energy is

$$E_{osc} = \frac{m\vec{v}_{osc}^2}{2} = E_\gamma$$

The remaining term is

$$\Phi = -\frac{e}{mc^2}\vec{k}\cdot\vec{A}(-t)\ \hat{n}\cdot\vec{r}$$

which is also a classical quantity. In order to show this one starts by solving classical equation (4.3), which gives for velocity

$$d_t\,\vec{r}^{(0)}\,(t) = -\frac{e}{mc}\,a(-t)\,\hat{s} + v_{0s}\hat{s}$$

where v_{0s} is parallel component of initial velocity with the polarization of the electromagnetic wave. Correction to the component of the velocity that is parallel with the propagation of the electromagnetic wave is given by

$$d_t\,r_n^{(1)} = -\frac{e}{mc^2}a(-t)\;v_{0s} = -\frac{e}{mc^2}\vec{v}_0\cdot\vec{A}(-t)$$

or the appropriate momentum is

$$\vec{p}_{in} = -\frac{e}{c^2}\left[\vec{v}_0\cdot\vec{A}(-t)\right]\,\hat{n}$$

where the index in indicates that this component of momentum is associated with the initial velocity of the charge. In the probability amplitude the function $B(\vec{k})$ determines distribution of momenta, and $\hbar\vec{k}$ is initial momentum of the charge and $\vec{v}_0$ is associated with the initial velocity $\frac{\vec{k}\hbar}{m}$. The phase Φ is now derived as

$$\Phi = -\frac{e}{mc^2}\vec{k}\cdot\vec{A}(-t)\,\hat{n}\cdot\vec{r} = -\frac{e}{mc^2}\frac{m}{\hbar}\left[\vec{v}_0\cdot\vec{A}(-t)\;\right]\hat{n}\cdot\vec{r} = \frac{\vec{p}_{in}}{\hbar}\cdot\vec{r}$$

which shows that it is derivable from classical concepts, and hence it is of classical origin. According to the rules of quantum theory, the factor that multiplies $\vec{r}$ in the phase Φ represents additional velocity of the charge (see discussion of (4.10)).

There is one important consequence of using vector potential. Dynamics of charge is affected even when it is assumed that vector potential is time independent, in which case force on it is zero (contribution from magnetic component is neglected). This effect is also in classical mechanics as it follows from (4.3). Velocity of charge is in this case

$$d_t\,\vec{r}^{(0)}\,(t) = -\frac{e}{mc}\,a\,\hat{s} \tag{4.17}$$

where a is arbitrary constant. The answer to this paradox, in classical mechanics, is that one should be very careful about understanding the initial conditions. The choice of the constant a is intimately connected with how they are determined. If one assumes that prior to the instant $t = 0$ velocity of the particle is zero then a must be zero, from the previous conclusion. At $t = 0$ the potential changes its value to a, which is instantaneous by implicit assumption, and therefore the correct vector potential is $a\Theta(t)$ and the correct equation that one needs to solve is

$$m\,d_t^2\,\vec{r}^{(0)}\,(t) = -\frac{e}{c}\,\delta(t)\,\hat{s}$$

Its solution for velocity after $t = 0$ is

$$d_t \, \vec{r}^{(0)} \, (t) = -\frac{e}{mc} \, a \, \hat{s}$$

which is the same as (4.17). Therefore working with vector potentials needs great care so that the results may not be interpreted in non physical terms.

The same analysis applies in quantum dynamics. In the solution (4.16) one could formally replace the vector potential by a constant value, and all the parameters that determine it are not zero. However, without repeating the analysis with the onset of vector potential, the answer to this paradox is the same as in classical mechanics; one needs to make sure that the correct initial conditions are chosen. By replacing the vector potential with its constant value one is implicitly assuming that the initial velocity of the particle is modified according to the discussion in classical mechanics, however, adapted to the quantum rules.

Related to the last discussion is transformation that is normally used in the electromagnetic wave-charge interaction. In (4.9) one assumes that the vector potential is not coordinate dependent, in which case

$$i\hbar\partial_t f = -\frac{\hbar^2}{2m}\left[\nabla - \frac{ie}{\hbar c}\vec{A}\,(t)\right]^2 \, f$$

and writes

$$f = e^{i\frac{ie}{\hbar c}\vec{r}\cdot\vec{A}(t)} g$$

to obtain equation for g as

$$i\hbar\partial_t g = -\frac{\hbar^2}{2m}\Delta \, g + \frac{e}{c}\vec{r}\cdot\partial_t\vec{A}\,(t) \;\; g = -\frac{\hbar^2}{2m}\Delta \, g - e\,\vec{r}\cdot\vec{E}\,(t) \;\; g$$

where $\vec{E}\,(t)$ is electric field. This equation is the bases for almost all analysis of interaction between the electromagnetic field with charges, however, in the step from the vector potential to the electric field one modifies the probability amplitude by a phase, and the question is what is its nature. In the exact solution for this problem the probability amplitude f is given by (4.16) and in it there is no term of the kind that transforms it onto g, which means the phase of this term is the artificial one, with no particular physical meaning. In fact the only physical meaning that one could deduce is that the velocity of the particle is modified at each instant in time by

$$\vec{v}_{\text{mod}} \; = -\frac{e}{mc}\vec{A}\,(t)$$

so that according to the rules of quantum mechanics the new probability amplitude is

$$g = e^{-i\frac{ie}{\hbar c}\vec{r}\cdot\vec{A}(t)} f$$

The reason for such modification is only justified mathematically because equation for the probability amplitude g is simpler for analysis then that for f. However, great care must be taken when setting initial conditions, besides that for the onset of interaction. If before the onset the probability amplitude is f_0 then after the onset it is

$$f_0 \to e^{i\frac{ie}{\hbar c}\vec{r}\cdot\vec{A}(0)} f_0$$

and this means that the initial g is

$$g_0 = f_0$$

After time t solution is g but the required is the probability amplitude f, and this is given by

$$f = e^{i\frac{ie}{\hbar c}\vec{r}\cdot\vec{A}(t)} g$$

That this is not a simple matter of the phase is shown by calculating the momentum distributions of the two probability amplitudes at time t. This is done by taking the Fourier transform of both sides of the last equation

$$\int d^3r\ f(\vec{r})e^{-i\ \vec{k}\cdot\vec{r}} = B(\vec{k}) = \int d^3r\ e^{-i\ \vec{k}\cdot\vec{r}} e^{i\frac{ie}{\hbar c}\vec{r}\cdot\vec{A}(t)} g(\vec{r})$$
$$= \int d^3r\ e^{-i\ \left(\vec{k}-\frac{ie}{\hbar c}\vec{A}(t)\right)\cdot\vec{r}} g(\vec{r}) = C\left(\vec{k} - \frac{e}{\hbar c}\vec{A}\ (t)\right)$$

where $C\left(\vec{k}\right)$ is the momentum probability amplitude for g. Therefore momentum probability amplitude $B(\vec{k})$ for f (the one that is required) is shifted by $-\frac{e}{\hbar c}\vec{A}\ (t)$ in the momentum probability amplitude for g. This finding is very important to bare in mind whenever transforming the exact (4.9) into some equivalent form.

4.1.2.1 Weak Electromagnetic Field

A very important limiting case is when the coupling of the charge with the electromagnetic field is weak. The amplitude (4.15) is then approximately

$$f \approx f_0\ (\vec{r}, t) - i\frac{e}{mc}\int d^3k\ B(\vec{k})e^{i\ \vec{k}\cdot\vec{r} - i\frac{\hbar k^2}{2m}t} \int^{\frac{\hat{n}\cdot\vec{r}}{c}-t} du\ \vec{k}\cdot\vec{A}(u)$$

where $f_0\ (\vec{r}, t)$ is the probability amplitude for a free charge, which is given by (4.11). The quadratic terms in the vector potential are omitted. Special example is when the the electromagnetic field is a plane wave

$$\vec{A}(u) = \vec{A}_0 \cos\omega u = \vec{A}^+ + \vec{A}^- \tag{4.18}$$

when the correction to the probability amplitude is

$$f_1 = f_{ph}^{+} + f_{ph}^{-} \tag{4.19}$$

where

$$f_{ph}^{\sigma} = -\sigma \frac{e}{2m\omega c} e^{\sigma i \overrightarrow{q} \cdot \vec{r} - \sigma i \omega t} \int d^3k \; B(\vec{k}) e^{i \; \vec{k} \cdot \vec{r} - i \frac{\hbar k^2}{2m} t} \; \vec{k} \cdot \vec{A}_0$$

and

$$\overrightarrow{q} = \frac{\omega \hat{n}}{c}$$

In order to understand physical significance of this result one should discuss a simpler problem, probability amplitude consists of a dominant contribution and a subdominant whose phase is modified by $i \overrightarrow{q} \cdot \vec{r}$. The question is what is the time evolution of the entire probability amplitude? Straightforward answer would be

$$f(\vec{r}, t) = f_0(\vec{r}, t) + \varepsilon f_0(\vec{r}, t) e^{i \overrightarrow{q} \cdot \vec{r}}$$

where for simplicity it was assumed that the two components differ in the small factor ε. The probability density is then (the term with ε^2 is neglected)

$$P(\vec{r}, t) \approx |f_0(\vec{r}, t)|^2 \left[1 + 2\varepsilon \cos\left(\overrightarrow{q} \cdot \vec{r}\right)\right]$$

and it is not different from the one without the phase except that its modulus oscillates. However, the reasoning is not correct because phase modification of the second component affects its initial conditions, instead of being $f_0(\vec{r}, 0)$ it is $f_0(\vec{r}, 0) e^{i \overrightarrow{q} \cdot \vec{r}}$. Therefore, if the initial condition for the dominant component is

$$f_0(\vec{r}, 0) = \int d^3k \; g\left(\overrightarrow{k}\right) e^{i\vec{k} \cdot \vec{r}} \Rightarrow g\left(\overrightarrow{k}\right) = \frac{1}{(2\pi)^3} \int d^3r \; f_0(\vec{r}, 0) e^{-i\vec{k} \cdot \vec{r}}$$

then for the subdominant it is

$$g\left(\overrightarrow{k} - \overrightarrow{q}\right) = \frac{1}{(2\pi)^3} \int d^3r \; f_0(\vec{r}, 0) e^{i \overrightarrow{q} \cdot \vec{r} - i\vec{k} \cdot \vec{r}}$$

and the time evolution of the probability amplitude is

$$f(\vec{r}, t) = \int d^3k \; g\left(\overrightarrow{k}\right) e^{i\vec{k} \cdot \vec{r} - i \frac{\hbar k^2}{2m} t} + \varepsilon \int d^3k \; g\left(\overrightarrow{k} - \overrightarrow{q}\right) e^{i\vec{k} \cdot \vec{r} - i \frac{\hbar k^2}{2m} t}$$

If $g\left(\overrightarrow{k}\right)$ gives zero for the average value of the velocity of particle then $f_0(\vec{r}, t)$ only spreads without the overall translation. However, in the subdominant component the momentum distribution is shifted by $\overrightarrow{q}$ and as the result this component moves

with the average velocity $\hbar\overrightarrow{q}/m$. It appears as if the particle was hit by another particle, called the photon, having the momentum that is related to the frequency of the electromagnetic wave. The two components separate in space thus becoming independent entities.

Based on the foregoing discussion one deduces from the expression for the correction amplitude (4.19) that in a plane electromagnetic wave there will be two types of momentum transfers onto the charge. The subdominant component moves either in direction of the wave propagation or in the opposite one. That appears to be contrary to what the model with the photon predicts, which is derived from the assumption that the vector potential (4.18) represents wave moving in direction of the vector $\overrightarrow{q}$. However, if the vector potential is defined as a linear combination of two complex exponential functions then each component separately represents two distinctive momentum transfers. The component $\overrightarrow{A}^{+}$ represents a wave going in direction $\overrightarrow{q}$ whilst $\overrightarrow{A}^{-}$ represents the one going in the opposite direction $-\overrightarrow{q}$. In this way arbitrariness in the formulation of the model with the photon is removed because one could formulate the theory, the quantum field theory, with a particular momentum transfer.

4.2 Very Short Electromagnetic Pulse

4.2.1 Impact on Hydrogen Atom

In most applications electromagnetic waves are typically in the form of a wave carrier (wave of a single frequency) and the amplitude modulation, one example is shown in Fig. 4.1. For this reason the name "wave" is used, the extreme limit being a "plane wave" when only the wave carrier is present. There are circumstances, however, when there is no wave carrier in which case one talks of the electromagnetic pulse. One important example of the electromagnetic pulse is produced by a charge that is moving at nearly the speed of light, which is discussed in Sect. 3.3.3. The field has large strength in a narrow space that is perpendicular to the line of motion of the charge, and the question is what impact it has on the charges, in particular the bound ones, that are in its vicinity. The problem is defined more precisely by assuming that the charge es, where s is its sign, moves with velocity v_0 parallel with the z axes and at the distance d along the x axes (the impact parameter), its y coordinate being zero. As a typical example of a bound charge it is assumed that Hydrogen atom is placed at the origin of the coordinates, and the effect is analyzed for the electron. The field of the moving charge affects both the electron and the proton, however, the analysis will be made only for the electron, because it is expected that the proton is affected little compared to the electron. The electron is assumed to be initially in the ground $1S$ state, and before commencing analysis one chooses a convenient scaling. As the reference mass one chooses that of the electron, and scale all lengths with respect to the appropriate Compton wave number $\kappa = mc/\hbar$, i.e. one writes $\overrightarrow{r}$ for $\kappa\overrightarrow{r}$ and t

for $ct\kappa$. In this scaling the probability amplitude for the electron satisfies equation (for the details of the field that is produced by the moving charge see Sect. 3.3.3)

$$i\partial_t f = -\frac{1}{2}\left[\partial_z - i\frac{\alpha s\gamma v_0}{R}\right]^2 f - \frac{1}{2}\partial_x^2 f - \frac{1}{2}\partial_y^2 f + \frac{\alpha s\gamma}{R} f \tag{4.20}$$

where

$$R = \sqrt{\gamma^2 (z - v_0 t)^2 + (x - d)^2 + y^2}$$

and

$$\gamma = \left(1 - v_0^2\right)^{-1/2}$$

The Coulomb potential of the proton is not included because in this energy transfer, as it will be shown, it is not required.

The ground state probability amplitude is

$$f_0(r) = \frac{\alpha^{3/2}}{\sqrt{\pi}} e^{-\alpha r}$$

and its momentum space representation is

$$g_0(k) = \frac{2\sqrt{2}\alpha^{5/2}}{\pi} \frac{1}{\left(k^2 + \alpha^2\right)^2}$$

where α is the fine structure constant. As it was shown in Sect. 3.3.3 electromagnetic field of a moving charge is confined into a narrow space interval along the z axes, being of the order

$$\Delta z = \sqrt{1 - v_0^2} = \gamma^{-1}$$

where $|v_0| \lessapprox 1$. Therefore when the charge is at the distance from Hydrogen atom larger than $|z| > \alpha^{-1}$ the impact of the field on the electron is negligible. The time that it takes the charge to cross the atom is

$$t_{cross} \approx \frac{2r_H}{c} \Rightarrow t_{tran} = \frac{2}{\alpha}$$

and during that time the electron moves the distance

$$\Delta s = v_{el}\, t_{cross} \Rightarrow \Delta s = \alpha \frac{2}{\alpha} = 2$$

where the estimate $k = v_{el} = \alpha$ for the velocity of the electron was taken from the momentum distribution. During the crossing time of the charge the electron stays virtually at the same position. The estimate of the interaction time with the electron is also important, and it is given by

$$t_{int} = \frac{\Delta z}{|v_0|} \Rightarrow t_{int} = \gamma^{-1}$$

which is very short, and it could be assumed to be impulsive, i.e. during the interaction time the electron does not changes position and velocity. Having given those estimates it is clear that in (4.20) it is indeed not necessary to include the Coulomb potential of Hydrogen atom because the energy transfer is instantaneous.

Initial condition for (4.20) is not defined as usual at $t = 0$ because this is the instant when the field of the moving charge overlaps with Hydrogen atom. Instead it is defined at some earlier time when the field does not overlap with it, and because of the estimate (3.18) of the field width this instant should be at least earlier than

$$t < -1/\alpha$$

In practical calculations the initial instant could be defined at

$$t_0 = -3/\alpha$$

The impact parameter d is in general arbitrary but for the sake of estimates it could be taken as $d = 3/\alpha$, in which case for the incident energy of the moving electron at 100 MeV the width of the electromagnetic field on the z axes is

$$\Delta z = \frac{d}{\gamma} \approx 2$$

which is small compared to the "radius" of the atom $\alpha^{-1} \approx 137$. The initial instant for this scattering is shown in Fig. 4.4, where the red shaded region shows the initial electromagnetic field (its width somewhat exaggerated) and the gray shaded region is the probability density of the electron.

Having defined initial condition one now solves (4.20), and the first step is to make transformation

$$f = e^{i\alpha s\gamma v_0 \int^{z-v_0 t} dz' \frac{1}{R}} g$$

when equation for g is

$$i\partial_t g = -\frac{1}{2}\partial_z^2\, g - \frac{1}{2}\left(\partial_x + i\alpha s v_0 a_x\right)^2\, g - \frac{1}{2}\left(\partial_y + i\alpha s v_0 a_y\right)^2\, g + \frac{\alpha s}{\gamma R} g \quad (4.21)$$

where

$$a_x = \frac{x-d}{R\left[\gamma\left(z - v_0 t\right) + R\right]} \quad ; \quad a_y = \frac{y}{R\left[\gamma\left(z - v_0 t\right) + R\right]}$$

Velocity of charge is very close to the speed of light, hence $v_0 \approx 1$ and $\gamma >> 1$, and the function R is approximately

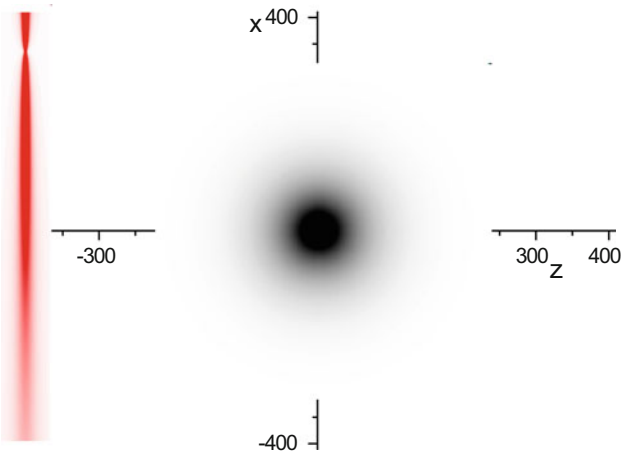

Fig. 4.4 Initial instant for calculating impact of the electromagnetic field (*blue* region) on Hydrogen atom (*gray shaded* region). The field is produced by a charge which is moving at nearly the speed c

$$R = \gamma \left| z - v_0 t \right| + \frac{(x-d)^2 + y^2}{2\gamma \left| z - v_0 t \right|}$$

except in a small vicinity of $|z - v_0 t| < \gamma^{-1}$ when it is of the order $R = O\left(\sqrt{(x-d)^2 + y^2}\right)$. Therefore a_x and a_y are step-like functions of the form

$$a_x = \frac{2\,(x-d)}{(x-d)^2 + y^2} \Theta\,(v_0 t - z) \quad ; \quad a_y = \frac{2y}{(x-d)^2 + y^2} \Theta\,(v_0 t - z)$$

which are independent of the z coordinate and time.

In (4.21) the last term is negligible because it is of the order γ^{-1}, but it is further simplified by defining a new function h as

$$g = e^{-i\alpha s v_0 \ln\left[(x-d)^2 + y^2\right] \Theta(v_0 t - z)} h$$

which satisfies equation

$$i\partial_t h = -\frac{1}{2}\partial_x^2 h - \frac{1}{2}\partial_y^2 h - \frac{1}{2}\partial_z^2 h$$

This is an equation for a free particle, but because interaction with the electromagnetic pulse takes very short time it could be assumed that the solution is

$$h = h_0(x, y, z) e^{-iEt}$$

However, the initial condition is defined for the function f, and by taking into account the two transformations the final solution is

$$f = e^{i\chi} f_0(x, y, z)$$

where the phase χ is

$$\chi = \alpha s \gamma v_0 \int_{z-v_0 t_0}^{z-v_0 t} \frac{dz'}{R} - \alpha s v_0 \ln\left[(x-d)^2 + y^2\right] \Theta\left(v_0 t - z\right) - E(t - t_0)$$

The probability amplitude is calculated when the interaction is over, which is at $t = -t_0$, when its phase is approximately

$$\chi = \frac{2\alpha s z}{t_0} - \alpha s \ln\left[(x-d)^2 + y^2\right] - E(t - t_0) + O\left(t_0^{-3}\right)$$

where $v_0 = 1$ was assumed. The term of the order t_0^{-1} could be neglected because for the stationary probability amplitude, as the one it is assumed, the limit $t_0 \to \infty$ could be taken. Therefore, after the interaction the probability amplitude is

$$f = e^{-i\alpha s \ln\left[(x-d)^2+y^2\right] - i E(t-t_0)} f_0(x, y, z)$$

which indicates that the electron acquired momentum

$$\vec{p} = -2\hbar\alpha s \frac{(x-d)\ \hat{x} + y\ \hat{y}}{(x-d)^2 + y^2} \tag{4.22}$$

where now the coordinates are not scaled.

The estimate could also be made from classical equation, which is given by (in the scaled coordinates)

$$d_t^2 \overrightarrow{r} = \frac{\alpha s \gamma\,(x-d)\,(1-v_z)}{R^3}\hat{x} + \frac{\alpha s \gamma y\,(1-v_z)}{R^3}\hat{y} + \frac{\alpha s \gamma\left[(x-d)\,v_x + y v_y\right]}{R^3}\hat{z}$$

where $v_0 = 1$ was assumed. Velocity of the electron (charge) is v with the index of the appropriate component. As in the quantum calculation it is assumed that the velocity of the electron is small, and that during the interaction it does not move. In this case the equation is

$$d_t^2 \overrightarrow{r} = \frac{\alpha s \gamma\,(x-d)}{R^3}\hat{x} + \frac{\alpha s \gamma y}{R^3}\hat{y}$$

and velocity of the electron is

$$d_t \overrightarrow{r} = -2\alpha s \frac{(x-d)\ \hat{x} + y\ \hat{y}}{(x-d)^2 + y^2}$$

which is precisely the result (4.22), when appropriately transformed into the momentum and into the non scaled coordinates. Therefore for all practical purpose energy transfer from the electromagnetic pulse that is produced by a fast moving charge onto a charge is impulsive and classical in nature. However, this is precisely the model by which momentum transfer from the electromagnetic field to a charge is mediated by a photon. This could be further demonstrated by assuming that the line of impact of a charge d is large compared to the size of the probability density for Hydrogen atom. In this case

$$\ln\left[(x-d)^2 + y^2\right] \approx -\frac{2x}{d}$$

and the probability amplitude after the interaction is over is

$$f = e^{isx\eta - iEt} f_0(r)$$

where η is the wave number for a "virtual photon", which is given by

$$\eta = \frac{2\alpha}{d}$$

and its corresponding frequency is

$$\nu = \frac{c\eta}{2\pi}$$

For the impact parameter $d = 10^{-9}$m the frequency of the virtual photon is $\nu \approx 7 \times 10^{14}\ \mathrm{sec}^{-1}$. Therefore, in this approximation it appears that the energy transfer is given in terms of a photon mediated interaction, but there is essential difference with the result for the "true photon", which is given by (4.14) (see discussion that follows). Whilst for the "true photon" only a small fraction of the initial probability amplitude is affected by the electromagnetic wave, which is proportional to its amplitude, for the "virtual photon" the whole is affected.

In the virtual photon approximation the momentum space distribution for the $1S$ state of Hydrogen atom, after the interaction is over, is given by

$$Q(\vec{p}) = \frac{2\sqrt{2}\alpha^{5/2}}{\pi} \frac{1}{\left[\left(\vec{p} - \frac{2\alpha s}{d}\hat{x}\right)^2 + \alpha^2\right]^2}$$

from where one calculates energy of the electron

$$E = \int d^3p \, \frac{p^2}{2} Q^2(\vec{p}) = \frac{\alpha^2}{2} + \frac{2\alpha^2}{d^2}$$

and by noting that d is scaled in terms of the Compton wave number of the electron, the energy transfer is very small, being of the order

$$\Delta E = \frac{2\alpha^2\hbar^2}{md^2} \approx \frac{8.1 \times 10^{-4}}{d^2} eV$$

where d is now in the units of Angstroms. Energy transfer is small, but depends on the distance d, however, for smaller values the "virtual photon" approximation is no longer applicable.

4.2.2 Impact On Atom

Electromagnetic field of a rapidly moving charge was analyzed in Sect. 3.3.3, whilst its impact on a target particle is analyzed in Sect. 4.2. The finding is that although the field has extremely large amplitude (essentially it increases by a factor that is the ratio of the kinematic mass of the charge to its rest mass) its duration is short and the overall impact on a charge, in terms of the energy transfer, is small. The energy transfer has a similar structure, at least when the moving charge is at the distance that is larger than the size of confinement of the particle, as if the interaction is mediated by a photon (for the photon concept see discussion following (4.14)); it is instantaneous and depends on the "frequency" of the field. The question is what impact this field has on atom?

As the field is confined within a narrow strip that is perpendicular to the velocity of the moving charge and having large strength, it affects all charges in atom in equal fashion. This means that all the electrons and the nucleus acquire instantaneous momentum, according to the analysis in Sect. 4.2 and as the result atom is left with an excess of internal energy (that of electrons) and acquires translational energy. Both energy transfer components are of interest, and they are calculated from the probability amplitude for the whole atom at the initial instant

$$f(\vec{R}_N, \vec{R}_1, \vec{R}_2, \ldots \vec{R}_n)$$

which acquires the phase

$$e^{i\,\vec{\gamma}\cdot(\vec{R}_1+\vec{R}_2+\cdots+\vec{R}_n)-i\,\vec{\Gamma}\cdot\vec{R}_N} f(\vec{R}_N, \vec{R}_1, \vec{R}_2, \ldots \vec{R}_n)$$

according to the analysis of Sect. 4.2. The probability amplitude is expressed in absolute coordinates, where the index N refers to the nucleus and the other indices

to the electrons. The "virtual" photon momentum is given by

$$\vec{\gamma} = \frac{2\alpha s}{d}\hat{d}$$

where the unit vector $\hat{d}$ points from the moving charge to the charge within atom at their closest approach and d is their separation. The factor s is the relative sign of the two charges, e.g. for two electrons $s = 1$. Therefore impact on all the electrons is

$$\vec{\Gamma} = -\frac{2n\alpha s}{d}\hat{d}$$

where n is the number of electrons.

By transforming into the centre of mass coordinates, which is identified with the nucleus, the probability amplitude transforms into

$$g(\vec{R}_N, \vec{r}_1, \vec{r}_2, ...\vec{r}_n) = e^{i\ \vec{\gamma}\cdot(\vec{r}_1+\vec{r}_2+\cdots+\vec{r}_n)} f(\vec{R}_N, \vec{r}_1, \vec{r}_2, ...\vec{r}_n)$$

where the relative coordinates are defined as $\vec{r}_j = \vec{R}_j - \vec{R}_N$. The centre of mass coordinates are not present in the phase, therefore, there is no energy transfer onto the translation of the atom as the whole. On the other hand probability amplitude to find the electron state μ after the interaction is

$$a_\mu = \int d^3r_1 d^3r_2 \ldots d^3r_n\ f^*_\mu(\vec{r}_1, \vec{r}_2, ...\vec{r}_n) e^{i\ \vec{\gamma}\cdot(\vec{r}_1+\vec{r}_2+\cdots+\vec{r}_n)} f(\vec{r}_1, \vec{r}_2, ...\vec{r}_n)$$

where the reference to the nucleus is omitted. These coefficients are relatively simply calculated for Hydrogen atom, in which case the amplitudes are

$$a_\mu = \sum_{l=0}^{\infty}\sum_{m=-l}^{l} i^l \sqrt{\frac{\pi}{2\gamma}} Y^*_{l,m}\left(\theta_\gamma, \phi_\gamma\right) \int d^3r\ f^*_\mu(\vec{r}) \frac{1}{\sqrt{r}} J_{l+1/2}\left(\gamma r\right) Y_{l,m}\left(\theta, \phi\right) f(\vec{r})$$

where the plane wave expansion (C.7) for $e^{i\ \vec{\gamma}\cdot\vec{r}}$ was used. If the index of the electron probability amplitude is the set $\mu = [\nu, \lambda, \upsilon]$, the initial probability amplitude is the ground state and

$$f_\mu(\vec{r}) = \frac{1}{r} R_{\nu,\lambda}(r) Y_{\lambda,\upsilon}\left(\theta, \phi\right)$$

then the coefficients are

$$a_{\nu,\lambda,\upsilon} = i^\lambda \sqrt{\frac{\pi}{2\gamma}} Y^*_{\lambda,\upsilon}\left(\theta_\gamma, \phi_\gamma\right) \int_0^\infty dr\ R_{\nu,\lambda}(r) \frac{1}{\sqrt{r}} J_{\lambda+1/2}\left(\gamma r\right) R_{1,0}(r)$$

They are given as the polynomials in the powers of $\varepsilon = \gamma/\alpha$, and because this ratio is small, of the order d^{-1}, only the leading powers are retained. Few coefficients

Table 4.1 Leading powers in $\epsilon = \gamma/\alpha$ in the probability amplitudes for the stationary states of Hydrogen atom after interaction of its ground state with the electromagnetic field that is produced by a fast moving charge

$\upsilon\backslash\lambda$	0	1	2	3
1	1–0.5 ε^2	–	–	–
2	0.497 ε^2	i 0.172 ε	–	–
3	0.183 ε^2	i 0.102 ε	–0.053 ε^2	–
4	0.105 ε^2	i 0.070 ε	–0.040 ε^2	–i 0.013 ε^3
5	0.071 ε^2	i 0.052 ε	–0.032 ε^2	–i 0.009 ε^3

are given in Table 4.1, where only the leading powers in ε are retained. The leading coefficients are for $\lambda = 1$ and arbitrary $n \geq 2$, when they are of the order ε, which means that the expansion of the probability amplitude is

$$g(\vec{r}) = f_{1,0} + \frac{3\varepsilon}{4\pi}\left[\cos\theta_\gamma \cos\theta + \sin\theta_\gamma \sin\theta \cos\left(\phi_\gamma - \phi\right)\right] \sum_{\nu=2} \widetilde{a}_\nu \; f_{\nu,1}$$

where the coefficients $\widetilde{a}_\nu$ are $a_{\nu,1,\upsilon}$ when ε is factored out. The sum is just another way of expressing $f_{1,0}$, which follows from the initial form for $g(\vec{r})$, however, it starts to deviate from it for different instants when the probability amplitude is

$$g(\vec{r}, t) = f_{1,0} e^{-iE_{1,0}t} + \frac{3\varepsilon}{4\pi}\left[\cos\theta_\gamma \cos\theta + \sin\theta_\gamma \sin\theta \cos\left(\phi_\gamma - \phi\right)\right] \sum_{\nu=2} \widetilde{a}_\nu \; f_{\nu,1} e^{-iE_{\nu,1}t}$$

4.3 Field Reaction

Electromagnetic field that is produced by moving charges could be divided up into two regions of analysis, far away from the source and in its close proximity. Focus of interest in most applications is on radiation that results from dynamics of charges, which is far away space, however, the field that overlaps with the probability density of its source (or the classical charge density) is of fundamental importance as the source of the effect without which energy conservation law would be violated. Electromagnetic field in the latter is important for formulating the field reaction force. In this section the basic principles that formulate this force are described.

Importance of the field reaction was recognized ever since it was discovered in the work of Maxwell and Herz that electromagnetic field produces wave that takes away energy from its source in accelerated motion. Calculating that energy, from the motion of charges, is done in a straightforward manner, and vice verse, from the

knowledge of the electromagnetic field motion of charges could have been deduced. It does not need special insight into that dynamics to deduce that what is needed is the force that would couple energy taken away by radiation at the expense of the energy of charges, kinetic and potential. In other words, radiated field takes away energy that must affect motion of charges, but the force that does that remains to a great extend the mystery even today. In fact, formulating the force that does that is as old as the problem itself, and effectively there are two models that one would use for its description. One is based on classical model for charges, but it is based on non physical assumptions and leads to non physical solutions for dynamics of charges (for a good account of the problems see [10]). The other model is based on assuming quantum charges and classical electromagnetic field, which dispenses with the inadequacies of the classical model (for account of the model see [9, 18, 19]), but still cannot answer some of the finer effects of this force. Much of the pursuit to formulate the force was scaled down by development of quantum electrodynamics, which was successful in giving accurate account of these fine details, for example Lamb shift. However, it should be remarked that, for example, the Lamb shift cannot be explained by the field reaction because this force is the consequence of motion of charges. The Lamb shift is intrinsic property of bound states of charges, and if it would have the source in the field reaction then its magnitude would depend on dynamics of charges. Therefore the criterion of validity of the models for field reaction cannot be failure to describe the fine effects of quantum electrodynamics, besides Lamb shift there is also anomalous magnetic moment of the electron. In mathematical terms, field reaction in order to have effect on the charge that is its source one uses either retarded or Feynman Green function (2.3.2) (depending if either wave or particle (photon) nature, respectively, of electromagnetic field is assumed), whilst for Lamb shift one uses standing wave Green function (2.3.2).

In order to understand the basic principle in formulating the field reaction force one starts with simple observation. As it was argued in Sect. 1.2 probability density plays the role of charge density for the charged particles. This means that if two particles interact then their total potential energy is

$$V = e^2 \int d^3r_1 \, d^3r_2 \, \frac{|f(\vec{r}_1)|^2 \, |f(\vec{r}_2)|^2}{|\vec{r}_1 - \vec{r}_2|}$$

where $f(\vec{r}_1)$ and $f(\vec{r}_2)$ are their respective probability amplitudes. However, treatment of $|f(\vec{r}_1)|^2$ as the charge density cannot be extended when the particle acts on itself, which is expected of the normal charge density. This extension leads to paradoxes that are discussed in Sect. 1.2.1. Nevertheless, probability density could act on itself, as if it were the charge density, provided it is time dependent. In this circumstances the field at time t and at the coordinate $\overrightarrow{q}$ is produced by the probability (charge) density $|f(\vec{r})|^2$ at some earlier time t_{ret}, and it could be treated as originating from the probability density of another charge. Therefore, the field that interacts with the charge density $|f(\vec{r})|^2$ at $\overrightarrow{q}$ and time t is produced by the same

probability density $|f(\vec{r})|^2$ but originating at time t_{ret}. Inclusion of this field affects dynamics of the particle, and because it arrises from the particle itself it is called field reaction force, or simply field reaction. This means that in principle equation[1]

$$i\,\partial_t f(\vec{r},t) = \frac{1}{2}\left[i\,\nabla + \vec{A}_{fr}(\vec{r},t) + \vec{A}_{ext}(\vec{r},t)\right]^2 f(\vec{r},t) + V_{fr}(\vec{r},t)\;\; f(\vec{r},t) + V_{ext}\;\;(\vec{r},t)\, f(\vec{r},t) \tag{4.23}$$

gives a complete dynamics of a charge in the external field (indicated by the subscript ext) which also includes field reaction (indicated by the subscript fr) given by (7.2) and (7.3). In this section time and spatial coordinates are scaled as

$$\vec{r} \equiv \vec{r}\,\kappa \quad ; \quad t \equiv ct\kappa$$

whilst the potentials are normalized as

$$eV \equiv \frac{eV}{mc^2} \quad ; \quad e\vec{A} \equiv \frac{e\vec{A}}{mc^2}$$

where

$$\kappa = \frac{mc}{\hbar}$$

is the Compton wave number.

There are certain features of the field reaction that should be taken into account for its correct formulation. One is that the leading term in the field reaction that comes by taking velocity of light infinite (see discussion in Sect. 7.1) should not be present. This contribution describes instantaneous interaction of the probability density with itself and it is a self repelling term of the kind that was discussed in Sect. 1.2.1. Impact of field reaction on its own source should not result in radiation, because only the external force should be responsible for that, for the following reason. A bound charge in an excited state radiates, and its sole cause is the binding potential whilst the field reaction should compensate for this lose of energy at the expense of the kinetic and potential energies of the charge. There is yet another feature of the force that needs attention and this is the nature of the energy/momentum exchange with the charge. At this stage, however, discussion about it is set aside until after few steps are made in derivation of the final $\vec{A}_{fr}(\vec{r},t)$ and $V_{fr}(\vec{r},t)$.

In order to find expression for the field reaction interaction one starts from (4.23) where the external field is omitted

$$i\,\partial_t f(\vec{r},t) = \frac{1}{2}\left[i\,\nabla + \vec{A}_{fr}(\vec{r},t)\right]^2 f(\vec{r},t) + V_{fr}(\vec{r},t)\;\; f(\vec{r},t)$$

[1] Charge of the particle is incorporated in the potentials, for the sake of simplicity.

From the wave equation for the scalar potential one obtains useful identity

$$-\frac{1}{4\pi}\int d^3q\ \frac{1}{|\vec{r}-\vec{q}|}\left[\Delta V_{fr}\left(\vec{q},t\right)-\partial_t^2 V_{fr}\left(\vec{q},t\right)+4\pi\alpha\rho\left(\vec{q},t\right)\right]=0$$

where α is fine structure constant. By partial integration, and using identity

$$\Delta\frac{1}{|\vec{r}-\vec{q}|}=-4\pi\ \delta\left(\vec{r}-\vec{q}\right)$$

one obtains

$$V_{fr}\left(\vec{r},t\right)+\frac{1}{4\pi}\partial_t\int d^3q\ \frac{1}{|\vec{r}-\vec{q}|}\partial_t V_{fr}\left(\vec{q},t\right)=\alpha\int d^3q\ \frac{\rho\left(\vec{q},t\right)}{|\vec{r}-\vec{q}|}$$

On the right is the instantaneous interaction and if the Lorentz condition (3.7) is used then the relationship is

$$V_{fr}\left(\vec{r},t\right)-\frac{1}{4\pi}\partial_t\int d^3q\ \frac{1}{|\vec{r}-\vec{q}|}\nabla\bullet\vec{A}_{fr}\left(\vec{q},t\right)=V_{fr}^{\infty}\left(\vec{r},t\right)$$

By defining new probability amplitude as

$$f\left(\vec{r},t\right)=g\left(\vec{r},t\right)e^{-i\Phi\left(\vec{r},t\right)}$$

where

$$\Phi\left(\vec{r},t\right)=\frac{1}{4\pi}\int d^3q\frac{1}{|\vec{r}-\vec{q}|}\nabla\bullet\vec{A}_{fr}\left(\vec{q},t\right)$$

equation for $g\left(\vec{r},t\right)$ is

$$i\ \partial_t g\left(\vec{r},t\right)=\frac{1}{2}\left[i\ \nabla+\vec{A}_{fr}\left(\vec{r},t\right)+\nabla\Phi\left(\vec{r},t\right)\right]^2 g\left(\vec{r},t\right)$$

In the gradient $-\nabla\Phi\left(\vec{r},t\right)$ one recognizes the parallel component of the vector $\vec{A}_{fr}\left(\vec{r},t\right)$, as defined by (3.11), so that the equation is

$$i\ \partial_t g\left(\vec{r},t\right)=\frac{1}{2}\left[i\ \nabla+\vec{A}_{fr}^{\perp}\left(\vec{r},t\right)\right]^2 g\left(\vec{r},t\right) \tag{4.24}$$

where the orthogonal component is

$$\vec{A}_{fr}^{\perp}\left(\vec{r},t\right)=\frac{1}{4\pi}\nabla\times\nabla\times\int\frac{d^3q}{|\vec{r}-\vec{q}|}\vec{A}_{fr}\left(\vec{q},t\right)$$

In this way field reaction interaction is defined entirely in terms of the, transversal, vector potential.

The source of $\vec{A}_{fr}(\vec{q},t)$ is in the probability current for the charge, and for its propagation from the source one uses Green functions that are discussed in Sect. 2.3.2. One is retarded Green function, which one would first use, however, it refutes the principle that no radiation emanates from the source, i.e. far away from the source the intensity of radiation decays as r^2. One is left with the choice of either standing wave Green function or the Feynman. Both are acceptable and here additional requirement is made on the field reaction, in its interaction with a charge it should manifest itself as a photon, i.e. as a particle. This feature could be satisfied if the field $\vec{A}_{fr}$ has the form of a plane wave as the Feynman Green function has. For detailed discussion how electromagnetic field manifests itself as a particle in the interaction with a charge see Chap. 17 in [9].

Feynman Green function is defined in Sect. 2.3.2 and solution for $\vec{A}_{fr}(\vec{q},t)$ is

$$\vec{A}_{fr}(\vec{r},t) = -4\pi\alpha \int d^3u\, ds\, K_F(\overrightarrow{r} - \overrightarrow{u}, t-s) \times \vec{j}\left(\overrightarrow{u}, s\right)$$

where the current is derived from (4.24), and it is given by

$$\vec{j}(\vec{r},t) = \frac{1}{2i}\left[g^*(\vec{r},t)\nabla g(\vec{r},t) - g(\vec{r},t)\nabla g^*(\vec{r},t)\right] - \vec{A}_{fr}(\vec{r},t)\, g^*(\vec{r},t)\, g(\vec{r},t) \tag{4.25}$$

where the field reaction is also present. This means that the wave equation which $\vec{A}_{fr}$ satisfies is

$$\Delta\vec{A}_{fr} - \partial_t^2\vec{A}_{fr} - 4\pi\alpha\, g^*g\,\vec{A}_{fr} = -4\pi\alpha\ \mathrm{Im}\left[g^*\nabla g\right]$$

where one recognizes Klein-Gordon type equation, inhomogeneous for a "particle" of "mass" $4\pi\alpha\, g^*g$. Transversal component is now

$$\vec{A}^{\perp}_{fr}(\vec{r},t) = -\alpha\int\frac{d^3q}{|\vec{r}-\vec{q}|}\int d^3u\, ds\, K_F(\vec{q} - \overrightarrow{u}, t-s)\,\nabla\times\nabla\times\vec{j}\left(\overrightarrow{u}, s\right)$$

and when the Feynman Green function is used then

$$\vec{A}^{\perp}_{fr}(\vec{r},t) = \frac{ic\alpha}{\pi}\nabla\times\nabla\times\int\frac{d^3u}{u}\int_0^{\infty} ds\left[I^-\,\vec{j}\left(\overrightarrow{r}+\overrightarrow{u}, t-s\right) - I^+\,\vec{j}\left(\overrightarrow{r}+\overrightarrow{u}, t+s\right)\right]$$

where

$$I^{\pm} = -u\left(\ln k - 1 + \ln c + E_{\gamma}\right) + \frac{c}{2}\left(s - \frac{u}{c}\right)\ln\left|s - \frac{u}{c}\right| - \frac{c}{2}\left(s + \frac{u}{c}\right)\ln\left|s + \frac{u}{c}\right| \pm\frac{ic\pi}{4}\left(\left|s + \frac{u}{c}\right| - \left|s - \frac{u}{c}\right|\right)$$

The parameter k is small, and represents the limit $k \to 0$, which means that $I^{\pm}$ has logarithmic singularity, however its contribution to $\vec{A}^{\perp}_{fr}(\vec{r}, t)$ is zero. In fact all the contributions from the terms in $I^{\pm}$ that are linear in u are zero, and based on this observation in the limit $c \to \infty$ the field reaction $\vec{A}^{\perp}_{fr}(\vec{r}, t)$ goes to zero as c^{-2}. This also means that indeed $\vec{A}^{\perp}_{fr}(\vec{r}, t)$ represents field reaction because the static interaction is removed.

Chapter 5
Confinement of Charge

Abstract Controlling motion of a charged particle is to control its phase space, in particular the momentum part. Particle with relativistic velocity is one model, when owing to relativistic effects the phase space is almost stationary, except for translational degrees of freedom. Relativistic motion is an example of the universal recipe to control motion of, charged, particles; they should be confined to a small volume of space and then manipulated by electromagnetic field. Confinement is achieved by static and time dependent magnetic field and electromagnetic waves of various properties. Extreme confinement of charges when their motion is in the relativistic regime, have specific features that are manifested in distribution of their momenta and energies when the system decays, and also in distribution of charges densities within the bound system, for which two body Dirac equation is used.

One of the basic uses of the electromagnetic field is to control motion of charges. For solving this task it is important to learn about the elementary processes that govern motion of the simplest system, a single charge in the electromagnetic field. This had been done in Chap. 4, by using both quantum and classical dynamics because they give complementary information about dynamics of a charge, the former gives the accuracy whilst the latter physical insight. Yet the analysis in Chap. 4 is not complete, at least in classical dynamics, because the true nature of a charge is that of a delocalized particle, which was not taken into account. Therefore instead of assuming that controlling motion of a charge means controlling its trajectory one should modify the question and seek to control its phase space density. Although the concept of probability is incorporated in quantum dynamics the shortcoming of this approach is that analysis is not in the phase space and in that sense the dynamics is not complete. In contrasts phase space analysis is inherent in classical dynamics and in this respect the two dynamics are complementary. Phase space analysis in classical dynamics is done with relative ease, but result may not be sufficiently accurate, on the other hand quantum dynamics gives accuracy but the physical insight is missing.

Having these two tools one has at disposal ways of studying the basic principles behind controlling motion of charges. However, the task should be defined more precisely by asking what is meant by the control of motion? In short, the control means moving most of the probability density from one part of the phase space to

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another. In simpler terms this means moving the average position of the particle from one point to another, and also leaving it with a predetermined average velocity. The emphases is on most of the probability density, or a weaker statement on the average position and velocity.

5.1 General Remarks

The simplest system to control is a free particle, and the task is simple, at least it appears so, to move particle from its averaged position, say at $\vec{r} = \vec{r}_i$ to $\vec{r} = \vec{r}_f$ in time t. For simplicity it is required that initial and final velocity of particle should be zero. This, very simple definition of the task should be made more exact in order to have any meaning for the particles that one is interested to control, e.g. electrons, protons, atoms and molecules. In classical terms instead of initial position and velocity of a particle one defines its initial phase space probability density. Likewise one defines its final phase space probability density, and the average quantities replace position and velocities. In quantum terms initial is the probability amplitude in the coordinate space, which is defined by its modulus (related to the coordinate probability density, equivalent of the position) and the phase (related to the probability current, equivalent of the velocity). The phase space analysis in quantum dynamics is obsolete because by implementing the uncertainty principle on the phase space one of its components is redundant, usually the momentum component. This is why the essential equation in classical dynamics is in the coordinate and momentum (phase) space whilst the same equation in quantum dynamics is only in one space, most commonly in the coordinate space.

From the definition of the task it is immediately clear where the basic problem is. Whilst for a single trajectory control of the motion of a particle means essentially control of a single set of parameters, initial position and velocity, in reality one has to control a set of its continuum values. This means that one has to find the ways of controlling at least majority of the initial conditions, because one could hardly expect to control all of them. For example, if one assumes initial phase space probability density that gives zero average velocity for the particle, then even if no force is applied it evolves in time and eventually spreads all over the space. Therefore control of the motion of a particle does not only involves control of its average position and velocity but also the width of its phase space density. This makes the task considerably more difficult than the same task for a single trajectory.

Few general estimates are in order before going into the more detailed analysis of the possible ways of solving the task. For simplicity single dimension dynamics is assumed, the coordinate is z and the momentum p. First, it is necessary to know what the initial conditions are, and in the case of a free particle this essentially means assuming the shape of the initial phase space density (it is tentatively assumed that the average velocity of the particle is zero). In general it could be assumed that its width in the coordinate space is Δz and in the momentum space is Δp, and their product is

$$\Delta z\, \Delta p_z = b > \frac{\hbar}{2}$$

from where the estimate for the spread of velocities is

$$\Delta v < \frac{\hbar}{2m\, \Delta z} \tag{5.1}$$

Few typical values of b are[1]

Gaussian	$f = \frac{1}{a^{3/2}\pi^{3/4}} e^{-\frac{r^2}{2a^2}}$	$b = \frac{\hbar}{2}$
$1S$ *state of* H	$f = \frac{\alpha^{3/2}}{\pi^{1/2}} e^{-\alpha r}$	$b = \frac{\hbar}{\sqrt{3}}$
$3D$ *square well*	$f = \frac{1}{r\sqrt{r_0}\sqrt{2\pi}} \sin\left(\frac{\pi r}{r_0}\right)$	$b = 0.56\ \hbar$

The two parameters that need to be controlled are the width of the probability density in the coordinate and its average position, which is done by controlling the momentum space. To control the momentum space the force should be sufficiently strong to easily manipulate particle with extreme momenta, whose estimate is (5.1). In terms of the energy parameter the confining potential should be much larger than the average kinetic energy of particle, which is estimate from the momentum distribution $Q(p)$. If it is assumed that $Q(p)$ is constant within the interval Δp then the average kinetic energy of the particle is

$$\langle E_{kin} \rangle = \int d^3p\, Q(p) \frac{p^2}{2m} = \frac{3}{10m} \frac{\hbar^2}{\Delta z^2} \tag{5.2}$$

For example the proton that is confined within $\Delta r = 10^{-10}$ m (as in Hydrogen molecule) has the average kinetic energy $\approx 10^{-3}$ eV, whilst if it is confined within $\Delta r = 10^{-15}$ m (as in a nucleus) it has kinetic energy $\approx 10^{7}$ eV. The electron within $\Delta r = 10^{-10}$ m (as in Hydrogen atom) has the average kinetic energy ≈ 2 eV. These are the relevant parameters but another one is also the speed at which the probability density spreads, which determines the time interval within which the confining force acts and its time dependence to be properly defined to control the motion. Estimate of the spreading time for the probability density in the coordinates of a free particle starts by noting that in the momentum space the appropriate probability density is constant, but the probability amplitude has time dependence

$$g(p) = |g(p)|\, e^{-it\frac{p^2}{2m\hbar}}$$

[1] Δu is standard deviation, which is defined as $(\Delta u)^2 = \left(u^2\right)_{aver} - (u_{aver})^2$ and it is used in calculation of the uncertainty relationship.

From this time dependence one gets the rate at which the width of the probability density spreads in the coordinates by calculating standard deviation of the coordinate z. The average of the coordinate squared is

$$\begin{aligned}\langle z^2\rangle &= -\hbar^2 \int d^3p\; g^*(p)\partial_{p_z}^2 g(p)\\ &= \hbar^2 \int d^3p\; \left(\partial_{p_z}|g(p)|\right)^2 + \frac{t^2}{m^2}\int d^3p\, p^2\,|g(p)|^2\end{aligned}$$

and the standard deviation for large time is

$$\Delta z \approx \frac{t}{m}\sqrt{\int d^3p\, p^2\,|g(p)|^2} \approx \frac{t\hbar\sqrt{3}}{m\Delta z_0\sqrt{5}}$$

where Δz_0 is initial width of the probability density. Average kinetic energy (5.2) was used in the last step.

5.1.1 Uniform Velocity

One relatively simple way of controlling the spread of the probability density is to give particle velocity that is nearly the speed of light. This effect is at work with the elementary particles, and examples are shown in Fig. 5.1. Fragments, elementary particles, that are produced leave a visible trek of perturbed matter through which they move (provided that they are charged) and they are identified by their classical trajectories. It should be noted though that these particles are initially confined within the space within which their host particle, from which they are produced either by collision or decay, is confined. The simplest is to assume that this is the radius of the host particle, and this uncertainty is represented by the probability density of this width. The probability density for the fragment evolves from that instant on as predicted from quantum dynamics, and in the rest frame of the parent particle, for simplicity, evolves in radial direction. This means that for a spherically symmetric probability density detecting fragment is equally probable in any direction, however, as Fig. 5.1 shows individual events are observed. One event does not reveal quantum nature of the fragment, but it would if one is to follow its path.

For better understanding of this effect analogous one is analyzed. A particle that approaches a screen with a slit in it serves as detector that determines its position which is parallel with the screen. This measurement has meaning only if prior to reaching the screen the uncertainty in the position of the fragment is wider than the slit. The width of the slit determines a new probability density, together with the appropriate momentum probability density, according to the quantum principles. This means that upon exiting the slit the new probability density evolves in time irrespective of its form before the screen. Motion of a single particle is then determined

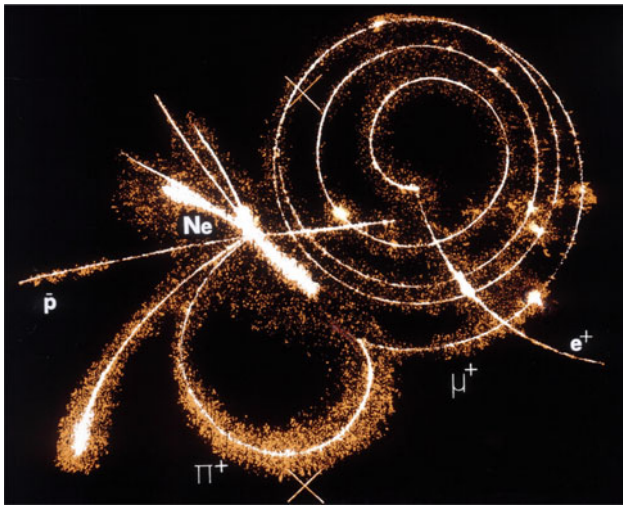

Fig. 5.1 Traces of elementary particles in detector. Although quantum objects elementary particles obey classical dynamics equations. *Credit* CERN

with random initial conditions that are determined by the probability densities on the exit from the slit. If the trajectory after the screen is to be followed one needs layers of screens each with array of slits that serve as detectors of the particle position. Each slit works in the same way as in the initial screen, and upon exiting from one of them motion of the particle is again determined by random choice of initial conditions, irrepsective of its motion prior to entering the slit. The entire trajectory looks more like random walk rather than obeying classical equation of motion.

The same reasoning applies for the fragment in the decay of the parent particle. However, the detectors of position are ionized molecules[2] in Fig. 5.1 and virtually there is no difference with the experiment with the slits. The difference is that motion of the fragments is relativistic, and this fact should be taken into account because otherwise the trajectories indeed would look like random walk.

Relativistic treatment for the time evolution of the probability densities is demonstrated on the example of a convenient initial phase space density, nevertheless quite general, that has functional form

$$\rho_0(\vec{r},\vec{p}) = \left(\frac{\hbar}{d\pi}\right)^3 e^{-\frac{1}{d^2}r^2-\frac{d^2}{\hbar^2}(\overrightarrow{p}-\overrightarrow{p}_0)^2}$$

where $\overrightarrow{p}_0$ is initial momentum of the particle given by an impulsive force.

[2]Using bubble chamber is only one way of determining trajectories of charged elementary particles, however, the same argument applies to the other methods. The essence is to trace trajectories by measuring with high accuracy the sequence of their positions.

Time evolution of the phase space density with a given initial value $\rho_0(\vec{r},\vec{p})$ is determined by knowing classical trajectories for arbitrary initial conditions $\vec{r}_i$ and $\vec{p}_i$, which for a free particle of mass m have simple form

$$\vec{r} = \vec{r}_i + \frac{\vec{p}_i}{\sqrt{p_i^2 + c^2m^2}}ct \quad , \quad \vec{p} = \vec{p}_i$$

Time dependence of the phase space density is then [9]

$$\rho(\vec{r},\vec{p},t) = \rho_0(\vec{r}^{\,-},\ \vec{p}^{\,-})$$

where[3]

$$\vec{r}^{\,-} = \vec{r} - \frac{\vec{p}}{\sqrt{p^2 + c^2m^2}}ct, \quad \vec{p}^{\,-} = \vec{p} \tag{5.3}$$

and time evolution of the coordinate probability density is

$$P(\vec{r},t) = \int d^3p\ \rho(\vec{r},\vec{p},t)$$

The simplest example is time evolution for a stationary particle that is defined with $p_0 = 0$. In that case $P(\vec{r},t)$ is

$$P(\vec{r},t) = \frac{N}{rt}\int dp\ p\sqrt{p^2+c^2m^2}\ e^{-\frac{d^2p^2}{\hbar^2}}\left[e^{-\frac{1}{d^2}\left(r-\frac{cpt}{\sqrt{p^2+c^2m^2}}\right)^2} - e^{-\frac{1}{d^2}\left(r+\frac{cpt}{\sqrt{p^2+c^2m^2}}\right)^2}\right]$$

and if relativistic limit is assumed then d should be small, later the meaning of this shall be defined more precisely. In this limit the second term in the integral could be neglected and the first is approximately the delta function (see C.1). The integral then has solution so that final expression for $P(\vec{r},t)$ is

$$P(\vec{r},t) = N\frac{t^2}{r\left(c^2t^2-r^2\right)^{5/2}}e^{-\frac{c^2d^2m^2}{\hbar^2\left(c^2t^2-r^2\right)}r^2}$$

Typical time evolution of the relativistic probability density $P(\vec{r},t)$ is shown in Fig. 5.2, its two dimensional cross section (a) and its one dimensional cross section across its centre (b). The density spreads as a radially expanding pulse where its furthest point from the centre moves at the sped of light. From $P(\vec{r},t)$ one calculates

[3] Classical results here are almost identical (negative energy trajectories not included for simplicity) with quantum for free particles. This treatment appears to be more in line with Klein-Gordon solution rather than Dirac one, because in the latter the spin degree of freedom is taken into account. However, for a free particle spin is not significant and the results are identical in both cases. More detailed relativistic quantum analysis is given in a separate chapter.

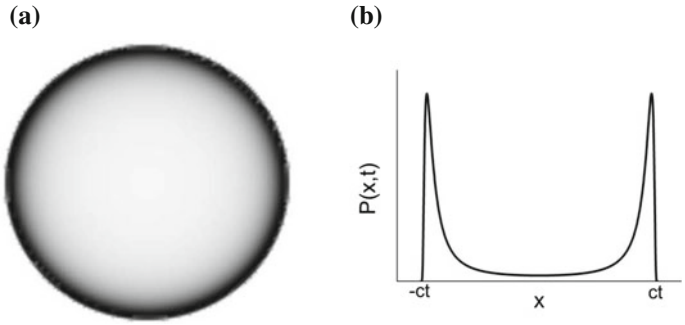

Fig. 5.2 Gaussian initial probability density after certain time in the relativistic regime, its two dimensional cross section (**a**) and one dimensional across the centre of expansion (**b**)

position of the maximum, which is at the distance

$$r = ct\sqrt{1 - \frac{2c^2m^2d^2}{5\hbar^2}}$$

from the centre. The maximum moves at nearly the speed of light, and from its value one derives the criterion for the relativistic approximation

$$\frac{cm}{\hbar}d \approx 0 \tag{5.4}$$

which is the same as saying that the Compton wave length of the particle should be much greater than the initial width of the probability density.

When particle moves with momentum p_0 in the z direction the expression for the probability density is

$$P(\vec{r}, t) = N \int dp_z dp_n \, p_n \, I_0\left(\frac{2cp_n r_n t}{d^2\sqrt{p^2 + c^2m^2}}\right) e^{\Omega}$$

where

$$\Omega = -\frac{1}{d^2}\left(z - \frac{ctp_z}{\sqrt{p^2 + c^2m^2}}\right)^2 - \frac{1}{d^2}\frac{t^2c^2p_n^2}{p^2 + c^2m^2} - \frac{r_n^2}{d^2} - \frac{d^2}{\hbar^2}(p_z - p_0)^2 - \frac{d^2}{\hbar^2}p_n^2$$

where p_n is component of momentum that is perpendicular to $\overrightarrow{p}_0$ in which case $p = \sqrt{p_z^2 + p_n^2}$, and similarly r_n is perpendicular distance with respect to $\overrightarrow{p}_0$ and $r = \sqrt{z^2 + r_n^2}$. Modified Bessel function of the first kind is $I_0(u)$. In the short time

limit the argument of the Bessel function is small and hence $I_0(u) \approx 1$ and the expression simplifies. In the relativistic limit, when $p_0 >> mc$ and d is small, the criterion being (5.4), one expects that $p_z \approx p_0$ whilst p_n is small and comparable to mc. Based on those comments one expands Ω for large p_0 giving

$$\Omega \approx -\frac{(z-vt)^2}{d^2} - \frac{R^2}{d^2} - \frac{d^2}{\hbar^2}p_z^2 - \frac{d^4p_0^2 + \hbar^2 ctz}{d^2\hbar^2 p_0^2}p_n^2$$

where velocity v is

$$v = c\left(1 - \frac{m^2c^2}{2p_0^2}\right) \approx c\frac{p_0}{\sqrt{p_0^2 + m^2c^2}}$$

The integrals are now straightforward to calculate and result is

$$P(\vec{r}, t) \sim \frac{e^{-\frac{R^2}{d^2} - \frac{(z-vt)^2}{d^2}}}{1 + \frac{\hbar^2 ctz}{d^4 p_0^2}}$$

which is copy of the initial probability density moving with velocity v. In the relativistic limit probability density is stable, in contrast with the example when $p_0 = 0$ and shown in Fig. 5.2.

The other extreme is the limit for large t when

$$P(\vec{r}, t) = N \int dp_z dp_n \, p_n \sqrt{\frac{p}{p_n r_n t}} e^{\Omega}$$

where now the exponent has additional contribution to its short time approximation

$$\Omega = \cdots + \frac{2ctRp_n}{p}$$

and in the asymptotic expansion for large p_0 it is modified by

$$\Omega \approx \cdots + \frac{2ctRp_n}{p_0}$$

The integral in p_z is again straightforward whilst in p_n it is given in terms of error function and for large t the probability density is

$$P(\vec{r}, t) \sim \frac{e^{-\frac{R^2}{D^2} - \frac{(z-vt)^2}{d^2}}}{1 + \frac{\hbar^2 ctz}{d^4 p_0^2}}$$

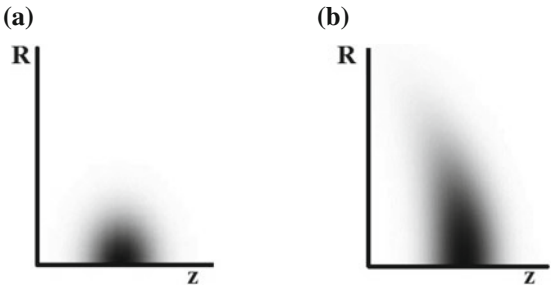

Fig. 5.3 Time evolution of the probability density in the relativistic regime with relativistic initial momentum. Short time evolution is shown in (**a**) and its long time in (**b**). The scale in (**b**) is 3 times larger than in (**a**) in vertical direction

where

$$D = d\sqrt{1 + \frac{\hbar^2 c^2 t^2}{d^4 p_0^2}}$$

Again the initial probability density moves with velocity v but its width in the perpendicular direction expands. Its rate of expansion determines stability of $P(\vec{r}, t)$, and from the expression for D one gets the value of time

$$t = \sqrt{3}\frac{d^2 p_0}{\hbar c} \tag{5.5}$$

when it expands by twice the original width. However, the angular spread α of $P(\vec{r}, t)$ is determined from the ration of D to ct (approximate position of its maximum on the z axis) and it is

$$\tan\alpha = d\sqrt{\frac{1}{c^2 t^2} + \frac{\hbar^2}{d^4 p_0^2}} \tag{5.6}$$

which is constant for infinite time. This angle is small considering the implicit assumption that was made so far that the product $p_0 d/\hbar$ is large, meaning that p_0 is much larger than the spread of momenta owing to confinement width d for the particle.

Typical example for the time evolution is shown in Fig. 5.3, one for short time (a) and the other for long time (b). The scales of (a) and (b) in the vertical direction are not the same, the latter is factor 3 lager. After the period of stable time evolution, which is a copy of the initial probability density, $P(\vec{r}, t)$ evolves radially however confined within the angle (5.6).

5.1.2 Decay of Two Particle System

Important issue that results from the model for relativistic translation of the phase space density in Sect. 5.1.1 is analysis of kinematics of a decay process, when two

particles are involved. Decaying system assumes that the two particles are bound together up to a certain instant (precise mechanism of their confinement is not important) and it is described by a phase space density for which two essential parameters are known. One is the width of their confinement by the mutual interaction (for example within a square well) and the other is the width of the localization of the system as the whole. The former width is measured in terms of the relative coordinates $\vec{r}_1 - \vec{r}_2$ of the two particles, and it is d, whilst the latter is given with respect to the center of mass coordinates, and it is D. From the meaning of the two widths D is always greater than d. A general functional form that describes this phase space density is

$$\rho_0(\vec{r}_1, \vec{r}_2, \vec{p}_1, \vec{p}_2) = f\left(\vec{r}_1 - \vec{r}_2, \frac{m_1\vec{r}_1 + m_2\vec{r}_2}{m_1 + m_2}, \frac{m_2\vec{p}_1 - m_1\vec{p}_2}{m_1 + m_2}, \vec{p}_1 + \vec{p}_2\right)$$

where one momentum variable is the total momentum of the two particles in the confinement and the other is the total momentum of the system as the whole. Mass of the two particles are m_1 and m_2. For the convenience one assumes explicit form for the initial phase space density of this system

$$\rho_0(\vec{r}_1, \vec{r}_2, \vec{p}_1, \vec{p}_2) = N\, e^{-\frac{1}{d^2}(\vec{r}_1-\vec{r}_2)^2 - \frac{d^2}{\hbar^2}\left(\frac{m_2\vec{p}_1 - m_1\vec{p}_2}{m_1+m_2}\right)^2 - \frac{1}{D^2}\left(\frac{m_1\vec{r}_1+m_2\vec{r}_2}{m_1+m_2}\right)^2 - \frac{D^2}{\hbar^2}(\vec{p}_1+\vec{p}_2)^2} \tag{5.7}$$

which assumes that the system as the whole does not move, in other words, average momentum of the system is zero. On the other hand, average total (kinetic) energy is

$$\begin{aligned}\langle E\rangle &= \int dV \left(\frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2}\right)\rho_0(\vec{r}_1, \vec{r}_2, \vec{p}_1, \vec{p}_2) \\ &= \frac{3\hbar^2\,(m_1+m_2)}{4d^2 m_1 m_2} + \frac{3\hbar^2}{4D^2\,(m_1+m_2)}\end{aligned} \tag{5.8}$$

At $t = 0$ a delta like repulsive force acts between the two particles that has a property to act along the line that joins the particles, in which case their total momentum is not changed. The force modifies momenta of the particles as

$$\overrightarrow{p}_1 \to \overrightarrow{p}_1 + \widehat{n}_{12}p_0 \quad , \quad \overrightarrow{p}_2 \to \overrightarrow{p}_2 - \widehat{n}_{12}p_0 \tag{5.9}$$

where

$$\widehat{n}_{12} = \frac{\overrightarrow{r}_1 - \overrightarrow{r}_2}{\left|\overrightarrow{r}_1 - \overrightarrow{r}_2\right|}$$

and p_0 is the momentum from the force. As a model for p_0 it could be assumed that the change in energy of the two particles is a fraction of the total energy $\langle E\rangle$ i.e.

$$\frac{\left(\overrightarrow{p}_1 + \widehat{n}_{12}p_0\right)^2}{2m_1} + \frac{\left(\overrightarrow{p}_2 - \widehat{n}_{12}p_0\right)^2}{2m_2} - \frac{\overrightarrow{p}_1^{\,2}}{2m_1} - \frac{\overrightarrow{p}_2^{\,2}}{2m_2} = \eta\langle E\rangle$$

then

$$p_0 = \sqrt{\frac{2m_1m_2}{m_1+m_2}\eta\langle E\rangle}$$

where it was assumed that the averages of $\overrightarrow{p}_1 \cdot \widehat{n}_{12}$ and $\overrightarrow{p}_2 \cdot \widehat{n}_{12}$ are zero. Time evolution of the phase space density is obtained by sampling method. By generating random $\overrightarrow{r}_n$ and $\overrightarrow{p}_n$ with the weight of the initial phase space density and replacing the coordinates with

$$\overrightarrow{r}_n \to \overrightarrow{r}_n + \frac{1}{m_n}\overrightarrow{p}_n t$$

where $\overrightarrow{p}_n$ is replaced by (5.9) one generates a density of points that represents phase space density at time t.

From the phase space density one determines kinematics of decay process, and two results are of particular interest: distribution of decay products $P(\Delta)$ with respect to the angle $\Delta = \frac{\overrightarrow{p}_1 \cdot \overrightarrow{p}_2}{p_1 p_2}$ (correlation in decay) and the probability of the absolute momenta difference $P(p_1 - p_2)$ for decaying products. Common assumption is that distribution $P(\Delta)$ is delta function at $\Delta = -1$ that is based on the classical picture that if initial momentum of the composed system is zero then the two fragments should fly apart in the opposite directions. The same applies for $P(p_1 - p_2)$ that should give $p_1 = p_2$ which is again based on the classical conservation laws.

For the calculation of both distributions one needs momentum probability density $P\left(\overrightarrow{p}_1, \overrightarrow{p}_2\right)$

$$P\left(\overrightarrow{p}_1, \overrightarrow{p}_2\right) = \int \rho_0\left(\overrightarrow{r}_1, \overrightarrow{r}_2, \overrightarrow{p}_1, \overrightarrow{p}_2\right) d^3r_1 d^3r_2$$

and because the particles are free this density is time independent. It is therefore sufficient to calculate $P(\Delta)$ and $P(p_1 - p_2)$ from the initial phase space density (5.7). The most straightforward way is to do that numerically by sampling method, whereby random choice for $\overrightarrow{p}_1$ and $\overrightarrow{p}_2$ is made with the weight $P\left(\overrightarrow{p}_1, \overrightarrow{p}_2\right)$,[4] one of the parameters is calculated and for its value add 1 into the box around it. After N steps the boxes are normalized with respect to this number and the width of the boxes and the result is the required probability distribution.

Electron-positron pair creation is an example of two particles being initially "bound"[5] and they fly away in opposite directions. For the modelling purpose it is assumed that initially the size of their confinement is approximately the size of Hydrogen atom (the mechanism of confinement is not essential in this example).

[4]For a general $\rho_0\left(\overrightarrow{r}_1, \overrightarrow{r}_2, \overrightarrow{p}_1, \overrightarrow{p}_2\right)$ one takes N random choices of the four coordinates, with the weight of the absolute value for initial phase space density. Sampling is made by adding or subtracting the outcome depending on the sign of ρ_0, which allows for the possibility that it could have negative values. For more details see [9].

[5]Being "bound" is here used for the modelling purpose. The pair is created in collision and its precise history prior to that is essentially not known. In this context the term "bound" means that between separating and creation the two particles were confined in a certain space.

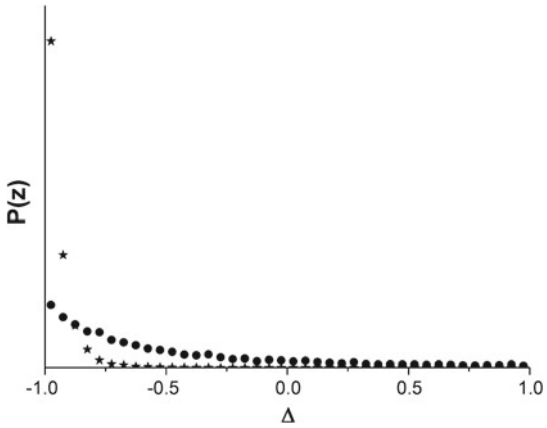

Fig. 5.4 Correlation probability in positron-electron decay when no internal release of energy ($\eta = 0$) is taking place (*circles*) and when it does ($\eta = 5$) (*stars*)

Average kinetic energy of the system (potential energy is significant but it is neglected in order to simplify the arguments of final conclusions) is $\langle E \rangle \approx 57\,\text{eV}$. Correlation probability is analyzed first for two cases, one when no internal energy is released and the other when it is factor $\eta = 5$ greater than $\langle E \rangle$. The results are shown in Fig. 5.4 where $\eta = 0$ example is displayed by circles and $\eta = 5$ by stars. In both cases motion of fragments is not correlated, in other words there is no way if one determines motion of positron that one knows in what direction the electron goes. By increase of internal release of energy the correlation goes towards the classical limit $\Delta = -1$ but it is only achieved for $\eta = \infty$. Classical limit is also achieved by increase of D, the width of the system as the whole, and in the limit $D \to \infty$ the correlation is delta function in $\Delta + 1$.

From classical dynamics one infers that the positron and the electron absolute momenta are the same, but the results in Fig. 5.5 for the probability $P\,(p_1 - p_2)$ show that this is not correct prediction. The results for $\eta = 0$ are shown by circles but since the effect of increasing η has very little effect on the distribution the stars show results for $\eta = 100$ (p_0 is momentum that is associated with $\langle E \rangle$). The distribution $P\,(p_1 - p_2)$ has large width, if compared with the typical momentum p_0 of the particles. This means that if momentum of one particle is known then momentum of the other is determined with large error bar. It does not help if internal energy is released the error bar stays almost the same. However, in absolute terms the error decreases with increasing p_0. Classical limit, delta function in $p_1 - p_2$, is achieved in the limit $D \to \infty$.

5.1.2.1 Neutron Decay

Results of the previous analysis show that classical conservation laws, if implemented without considering quantum nature of the systems, could lead to incorrect conclusions. This does not mean that the conservation laws do not apply for the quantum

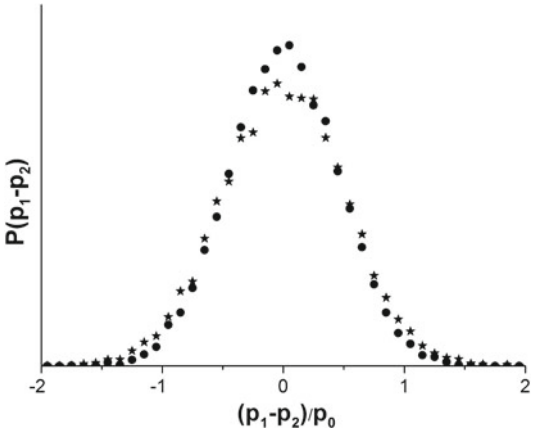

Fig. 5.5 Momentum difference probability in positron-electron decay when no internal release of energy ($\eta = 0$) is taking place (*circles*) and when it does ($\eta = 100$) (*stars*)

systems, the difference is that in the classical they apply for single trajectories with well determined initial conditions but in the quantum they apply for the averages. In fact if classical dynamics is formulated in the phase space then the same conclusion would be reached as in the quantum dynamics, the only difference being that in the latter the uncertainty principle applies for the choice of the phase space density [9].

Neutron decay is the prime example of this observation. In this decay the conjecture is that the mass difference between the neutron and the sum of proton and the electron masses (the most elementary model for the decay of the neutron) goes into the kinetic energy of the latter. By classical analysis it is shown that the fragments, proton and the electron, should have well determined kinetic energies and they fly in the opposite directions, $\Delta = -1$. It was experimentally determined that this conjecture is not correct because energy (momentum) of the electron momentum does not have single value but a distribution. New particle, antineutrino, was proposed as the third product of the neutron decay in order to fit this data. Applying the conservation laws to this three particle decay model it is straightforward to show that energy and momentum of the electron do not have single value, and the correlation angle between the electron and the proton is no longer $\Delta = -1$. Distribution for the electron energy and momentum that was calculated agreed very well with the experimental result, which was essentially the proof for antineutrino.

Energy conservation law is

$$m_n c^2 = c\sqrt{p_p^2 + m_p c^2} + c\sqrt{p_e^2 + m_e c^2} + cp_\nu$$

whilst for the momentum it is

$$0 = \overrightarrow{p}_p + \overrightarrow{p}_e + \overrightarrow{p}_\nu$$

where the assumption is that the neutron is at rest and antineutrino has zero mass.[6] Correlation angle is then given by

$$\cos\Delta = \frac{\left(m_n c - \sqrt{p_p^2 + m_p^2 c^2} - \sqrt{p_e^2 + m_e^2 c^2}\right)^2 - p_p^2 - p_e^2}{2p_p p_e}$$

where the arbitrary parameters are momenta of proton and the electron. Similarly one calculates momentum of the electron but its expression is too complicated for any analysis and one proceeds numerically, however, it is a function of arbitrary parameters momentum of proton and the correlation angle Δ. The correlation probability, and likewise the momentum of the electron probability, is calculated by taking a number of random choices for the arbitrary parameters and do the appropriate summation of the final outcomes.

Decay of neutron could be examined as a process that involves only two particles as its fragments, the electron and proton. Motivation to analyze this model follows from the previous discussion: in the original analysis of the decay products spread of initial conditions was not taken into account. By neglecting antineutrino as the third product the intention is to see to what degree distribution of energy and momentum among the electron and proton could be reproduced by taking into account this spread. There is, however, a problem with the two particle decay mode of neutron. In the decay model that is discussed the initial state consists of the electron and proton that are confined to a certain volume, and for the model to have some degree of authenticity one should take into account that they originated as decay products of the neutron. The parameter that should be taken into account is the mass of neutron that is greater than the sum of masses of proton and the electron. The answer is in the confinement energy for the two particles just prior to decay, which is for the Gaussian given by (5.8). By accepting that its mass equivalent equals the mass difference one determines the appropriate width d (the result is almost independent of D), and for the neutron it is $d = 2.7 \times 10^{-13}$ m.

Probability distribution $P\,(p_{electron})$ for the momentum of the electron is shown in Fig. 5.6 as calculated from the standard model for the neutron decay (stars) and in comparison with the model that two fragments are involved (solid circles). Spread of solid circles is larger than the experimental value for the threshold value of $p_{electron}$ and the optimal value $d = 4.5 \times 10^{-13}$ m for the width is found that reproduces it (line). However, in this case the "mass of neutron" is not reproduced, only its half value.

Correlation probability $P\,(\Delta)$ between the directions of the electron and proton momenta is shown in Fig. 5.7 as calculated from the standard model for the neutron decay (stars) and in comparison with the model that two fragments are involved (solid circles). Solid line is correlation for $d = 4.5 \times 10^{-13}$ m.

[6] If the mass of antineutrino is assumed to be not zero, but small, the final results do not change in essential way.

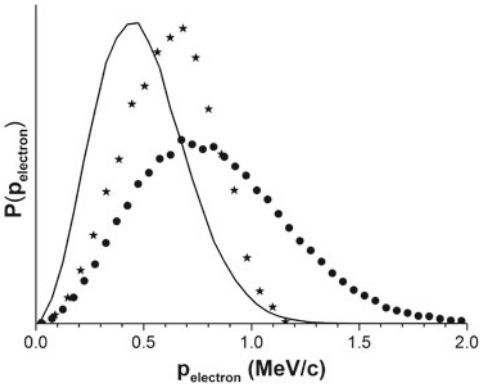

Fig. 5.6 Distribution of the electron momenta in neutron decay when antineutrino is taken into account (*stars*) and from the two fragment decay model (*solid circles*). *Line* is calculated from the model by fitting the width d to reproduce, approximately, the threshold value the electron momentum

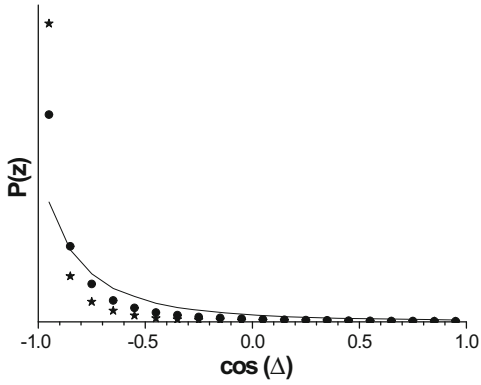

Fig. 5.7 Distribution of the electron-proton correlation angle Δ in neutron decay when antineutrino is taken into account (*stars*) and from the two fragment decay model (*solid circles*). Line is calculated from the model by fitting the width d to reproduce, approximately, the threshold value the electron momentum

The aim of the exercise was not to give the proof that there is non need for antineutrino, it is only to show that strict analysis of the decay processes should also include uncertainty of initial conditions. Results shown in Figs. 5.6 and 5.7 indicate that this effect is considerable and cannot be neglected.

5.2 Confinement by Magnetic Field

One way to control the momentum space is by magnetic field. The idea is to use property of the magnetic force to bend trajectories of charged particles into a circular motion. This means that all components of momenta that are perpendicular to the magnetic field do not contribute towards the spread of the probability density. The problem that remains is to choose sufficiently strong field so that the radius of trajectories is comparable to the width of the probability density. However, the effect does not control spread in the direction of the magnetic field, which should be done by other means.

To obtain parameters that are essential for the control of the spread of the probability density one should solve equation

$$i\hbar\partial_t f = -\frac{\hbar^2}{2m}\left[\nabla - \frac{ie}{\hbar c}\vec{A}\,(\vec{r})\right]^2 f \tag{5.10}$$

subject to some initial condition. It is assumed that the charge is in a homogeneous magnetic field along the z axes and the vector potential for it is

$$\vec{A}\,(\vec{r}) = A_0\,\hat{z}\times\vec{r}$$

Solving equation (5.10) is not straightforward, however, it is much simpler to calculate the probability density from classical mechanics with the constraint that the uncertainty principle is implemented. One starts by parametrizing the initial phase space density as

$$\rho_0(\vec{r},\vec{\pi}) \;=\; \frac{1}{\hbar^3\pi^3}\int d^3q\, f_0^*(\vec{r}+\vec{q}) f_0(\vec{r}-\vec{q})\, e^{2i\vec{\pi}\cdot\vec{q}/\hbar} \tag{5.11}$$

where $f_0(\vec{r})$ is initial probability amplitude and for the electromagnetic field ordinary momentum $\vec{p}$ is replaced by

$$\vec{\pi} = \vec{p} + \frac{e}{c}\vec{A}\,(\vec{r})$$

Obtaining time evolution of the phase space density with that initial value starts by solving Newton equation for the Lorentz force

$$\vec{F} = e\frac{\vec{v}}{c}\times\left(\nabla\times\vec{A}\right) = \frac{e}{c}a_0\dot{\vec{r}}\times\hat{z} \tag{5.12}$$

Motion of the charge in the z direction is not affected by the field, which means that it is sufficient to study time evolution of the phase space density in the $x-y$ plane. The only condition is that the initial phase space density is product separable in all the phase space components, which for simplicity it is assumed. For example, the initial probability amplitude with this property is a Gaussian function. This simplification does not alter general conclusions but emphases the essence of dynamics, and that is control over dynamics of the probability density in two dimensions.

Newton equation for the force (5.12) has solution in a closed form, which is obtained by defining complex coordinate $u = x + i\,y$ that satisfies equation

$$m\ddot{u} = -i\frac{e}{c}a_0\,\dot{u}.$$

For the initial conditions

$$u_0 = x_0 + iy_0, \qquad \dot{u}_0 = \dot{x}_0 + i\dot{y}_0$$

at $t = 0$ solution in the $x - y$ plane is given by

$$x = x_0 + \frac{v_{y0}}{\omega} + \frac{v_{x0}}{\omega}\sin(\omega t) - \frac{v_{y0}}{\omega}\cos(\omega t),$$
$$y = y_0 - \frac{v_{x0}}{\omega} + \frac{v_{x0}}{\omega}\cos(\omega t) + \frac{v_{y0}}{\omega}\sin(\omega t).$$

where $\omega = \frac{ea_0}{mc}$. Time dependence of the phase space density is now obtained by using the following rule. If one wants the value of the phase space density at the points $\overrightarrow{r}$ and $\overrightarrow{p}$ at time t then trajectory is calculated with these initial conditions and followed it backward in time to $t = 0$. At the final point one calculates the value of the initial phase space density, which is the value of it at time t. The rule is based on the basic feature of the phase space density that its value is preserved along a classical trajectory. The coordinates of trajectory are, therefore, replaced by

$$x \to x + \frac{p_y}{m\omega} - \frac{p_x}{m\omega}\sin(\omega t) - \frac{p_y}{m\omega}\cos(\omega t), \tag{5.13}$$
$$y \to y - \frac{p_x}{m\omega} + \frac{p_x}{m\omega}\cos(\omega t) - \frac{p_y}{m\omega}\sin(\omega t).$$

and the same replacement is done for the momentum components, where time changed the sign implying that charge moves backward in time.

For the initial probability amplitude

$$f_0 = \frac{1}{d\sqrt{\pi}} e^{-\frac{x^2+y^2}{2d^2}} \tag{5.14}$$

the initial phase space density is

$$\rho_0(x, y, p_x, p_y) = \frac{1}{\hbar^2\pi^2} e^{-\frac{x^2+y^2}{d^2} - \frac{d^2}{\hbar^2}\left[\left(p_y + \frac{1}{2}m\omega x\right)^2 + \left(p_x - \frac{1}{2}m\omega y\right)^2\right]}$$

where one replaces coordinates by (5.13), and likewise momenta, to get its time dependence. Probability density in the coordinates is now

$$P(x, y, t) = \int dp_x\, dp_y\, \rho(x, y, p_x, p_y, t)$$
$$= \frac{1}{\pi\gamma(t)} e^{-\frac{1}{\gamma(t)}(x^2+y^2)}$$

where

$$\gamma(t) = d^2\cos^2\left(\frac{\omega t}{2}\right) + 4D^2\sin^2\left(\frac{\omega t}{2}\right)$$

and

$$D = \frac{c\hbar}{eda_0}$$

Probability density at any time is a copy of the initial one except that its width oscillates between d and $2D$, however, when

$$d = 2D \;\Rightarrow\; a_0 = \frac{2c\hbar}{ed^2}$$

then it is constant and equal to the initial one. It is interesting that the width D does not depend on the mass of charge only the strength of the magnetic field, on the other hand the period of oscillations between the two widths is mass dependent. Thus for example, for the proton in magnetic field of the strength 1 T and the width $d = 10^{-10}$ m the frequency is $\nu = \frac{ea_0}{2\pi mc} \approx 1.5 \times 10^7 \mathrm{s}^{-1}$ and $D \approx 6.6 \times 10^{-6}$ m. The field that controls the probability density within its original width is $a_0 \approx 1.3 \times 10^7$ T, however, its value is inverse proportional as d^2 and so $a_0 = 1$ T would confine the one with the width $d \approx 3.6 \times 10^{-8}$ m.

5.2.1 Time Dependent Magnetic Field

Homogeneous magnetic field that is also time dependent induces circular electric field around its field lines, which also contributes towards confinement of the probability density. Force on charge is in this case (it is assumed that the magnetic field is parallel along the z axes)

$$\vec{F} = -\frac{e}{2c}\,\hat{z} \times \vec{r}\; d_t a_0(t) + \frac{e}{c} a_0(t)\dot{\vec{r}} \times \hat{z}$$

which has no component along the z axes and therefore only dynamics in the $x - y$ plane affects motion of charge. Equation of motion in the $x - y$ plane is simplified by defining function

$$u(t) = r\,(t)\, e^{-\frac{ie}{2cm}\int_0^t dt'\; a_0(t')}$$

where

$$r\,(t) = x(t) + i\, y(t)$$

It is shown that $u(t)$ satisfies equation

$$d_t^2 u(t) = -\frac{e^2}{4c^2m^2}\; a_0^2(t)\; u(t)$$

The simplest time dependence for the magnetic field is linear increase from its zero value, and the equation to solve is

$$d_t^2 u(t) = -\frac{e^2}{4c^2m^2}\; a_0^2\, t^2\; u(t)$$

with the initial conditions at $t = 0$

$$u_0 = r\,(0)\,, \qquad v_0 = D[r\,(s)\,, s]\,|_{s=0}$$

Further simplification is made by defining dimensionless time variable

$$s = bt = \sqrt{\frac{ea_0}{2cm}}t$$

in which case the equation is

$$d_s^2 u(s) = -\,s^2 u(s)$$

with a general solution

$$u = \sqrt{s}J_{1/4}\left(\frac{s^2}{2}\right)c_1 + \sqrt{s}Y_{1/4}\left(\frac{s^2}{2}\right)c_2 \tag{5.15}$$

where $J_a(z)$ and $Y_a(z)$ are Bessel functions. From the initial values u_0 and v_0 the coefficients c_1 and c_2 are

$$c_1 = \frac{1}{4}\left[\sqrt{2}v_0\Gamma\left(\frac{1}{4}\right) + 2u_0\Gamma\left(\frac{3}{4}\right)\right]$$
$$c_1 = -\frac{\pi}{\sqrt{2}\Gamma\left(\frac{1}{4}\right)}u_0$$

Trajectory of charge is obtained from (5.15), and a typical is shown in Fig. 5.8. Irrespective of initial conditions the trajectory spirals into the origin, with a rate $t^{-1/2}$, however, its angular frequency increases as s^2.

Having a general solution for trajectories one obtains time evolution of the phase space density and the rules how to do that for a time independent force are described in Sect. 5.2. The force here is time dependent when these rules are somewhat more elaborate because one must take into account that the force changes its value with time (for more details see [9]). If initial conditions are chosen at time $t = t_0$ then the force should be appropriate for this instant and not for $t = 0$. This is formally accomplished by replacing t by $t_0 - t$ in the force and in the other places where time shows up explicitly. In the new time variable classical trajectory is evolved from $t = 0$ to $t = t_0$.

The first step towards the time evolution of the phase space density is to define initial conditions at $s = s_0$

$$r_1 = r\,(s_0)\,, \qquad v_1 = d_{s_0} r_1$$

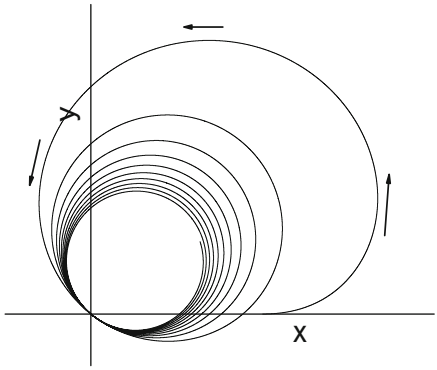

Fig. 5.8 Trajectory of a charge in homogeneous magnetic field when it linearly increases in time. The *arrows* indicate direction of motion of charge

where the coefficients c_1 and c_2 are

$$c_1 = \frac{\pi\sqrt{s_0}}{4}\left[r_1 s_0 Y_{-3/4}\left(\frac{s_0^2}{2}\right) + (ir_1 s_0 - v_1)\, Y_{1/4}\left(\frac{s_0^2}{2}\right)\right] e^{-i\frac{s_0^2}{2}}$$

$$c_2 = -\frac{\pi\sqrt{s_0}}{4}\left[r_1 s_0 J_{-3/4}\left(\frac{s_0^2}{2}\right) + (ir_1 s_0 - v_1)\, J_{1/4}\left(\frac{s_0^2}{2}\right)\right] e^{-i\frac{s_0^2}{2}}$$

and solution for the trajectory is

$$r(s) = \left[\sqrt{s} J_{1/4}\left(\frac{s^2}{2}\right) c_1 + \sqrt{s} Y_{1/4}\left(\frac{s^2}{2}\right) c_2\right] e^{i\frac{s^2}{2}}$$

The time variable is now replaced by $s \to s_0 - s$ when evolution of the trajectory backward in time from its initial values at $s = s_0$ is obtained by varying s from $s = 0$ till $s = s_0$. The coordinates and velocities for $s = s_0$, or $s = 0$ if one now considers time before it was replaced for the purpose of time reversal, are

$$r\,(0) = \frac{\sqrt{s_0}\,\Gamma\left(\frac{1}{4}\right)}{2\sqrt{2}}\left[r_1 s_0 J_{-3/4}\left(\frac{s_0^2}{2}\right) + (ir_1 s_0 - v_1)\, J_{1/4}\left(\frac{s_0^2}{2}\right)\right] e^{-i\frac{s_0^2}{2}}$$

and

$$d_s r\,(0) = \frac{i\pi\sqrt{s_0}}{\Gamma\left(\frac{1}{4}\right)}\left[r_1 s_0 J_{3/4}\left(\frac{s_0^2}{2}\right) + (-ir_1 s_0 + v_1)\, J_{-1/4}\left(\frac{s_0^2}{2}\right)\right] e^{-i\frac{s_0^2}{2}}$$

Formally the variables are now replaced as $s_0 \to s$, $r_1 \to r$ and $v_1 \to v$ in which case the time reversed solution is obtained: it gives the initial values at $t = 0$ for the coordinates and velocities if at t their values are specified. Finally the coordinates and velocities are

$$r^- = \frac{\sqrt{s}\,\Gamma\left(\frac{1}{4}\right)}{2\sqrt{2}}\left[rsJ_{-3/4}\left(\frac{s^2}{2}\right) + (irs - v)\,J_{1/4}\left(\frac{s^2}{2}\right)\right]e^{-i\frac{s^2}{2}} \tag{5.16}$$

and

$$v^- = \frac{i\pi\sqrt{s}}{\Gamma\left(\frac{1}{4}\right)}\left[rsJ_{3/4}\left(\frac{s^2}{2}\right) + (-irs + v)\,J_{-1/4}\left(\frac{s^2}{2}\right)\right]e^{-i\frac{s^2}{2}} \tag{5.17}$$

where the superscript $-$ indicates that the variables are calculated from the time reversed solution for trajectory.

Time dependence of the phase space density with its initial value (5.11) is now determined from[7]

$$\rho(\vec{r},\vec{p},t) \;=\; \frac{1}{\hbar^2\pi^2}\int d^2q f_0^*(\vec{r}^- + \vec{q}) f_0(\vec{r}^- - \vec{q})\, e^{2i\vec{\pi}^-\cdot\vec{q}/\hbar}$$

The "momentum" $\vec{\pi}^-$ is calculated for initial instant, and because of time dependence of the vector potential it is given by

$$\vec{\pi} = m\,\vec{v} = mb\,d_s\vec{r}$$

and when integrating in the variables $\vec{q}$ for the initial probability amplitude (5.14) the phase space density is

$$\rho(\vec{r},\vec{p},t) \;=\; \frac{1}{\hbar^2\pi^2}e^{-\frac{1}{d^2}\left(x^{-2}+y^{-2}\right)-\frac{d^2m^2b^2}{\hbar^2}\left(v_x^{-2}+v_y^{-2}\right)}$$

Solutions (5.16) and (5.17) are now to be replaced in the phase space density, which is a complicated function in four variables. Unless there is a special reason to use the phase space density (e.g. for calculating angular momentum) there is no need to investigate it in details, more import is the probability density $P(x, y, t)$ which is obtained by integrating it in the variables v_x and v_y, with the result

$$P(x,y,t) = \frac{1}{\pi\Delta^2(tb)}e^{-\frac{x^2+y^2}{\Delta^2(tb)}}$$

where

$$\Delta^2(s) = s\left[\frac{d^2\pi^2}{\Gamma^2\left(\frac{1}{4}\right)}J_{-1/4}^2\left(\frac{s^2}{2}\right) + \frac{\hbar^2\Gamma^2\left(\frac{1}{4}\right)}{8d^2m^2b^2}J_{1/4}^2\left(\frac{s^2}{2}\right)\right]$$

The probability density retains its original shape except that its width oscillates between two extremes. This is confirmed by taking the asymptotic value for the Bessel function, when the width is

[7] For potentials, scalar or vector, that are linear in spatial coordinates, regardless of time dependence, phase space and quantum dynamics give identical results. In this example phase space analysis is simpler.

$$\Delta^2(s) \approx \frac{4d^2\pi}{s\Gamma^2\left(\frac{1}{4}\right)}\cos^2\left(\frac{s^2}{2}-\frac{\pi}{8}\right)+\frac{\hbar^2\Gamma^2\left(\frac{1}{4}\right)}{ea_0m\pi sd^2}\sin^2\left(\frac{s^2}{2}+\frac{\pi}{8}\right)$$

which indeed goes to zero as $\Delta \sim t^{-1/2}$, but oscillates approximately between the values d and d^{-1}. The period of oscillations is not constant but decreases linearly in time.

Asymptotic value of the width of the probability density is reached when $s >> 1$ or

$$t >> b^{-1} = \sqrt{\frac{2cm}{ea_0}}$$

For the proton and the time gradient for the magnetic field $a_0 = 1\,\mathrm{T/s}$ this gives

$$t >> 1.4 \times 10^{-4}\,\mathrm{s}$$

whilst for the electron

$$t >> 3.4 \times 10^{-6}\,\mathrm{s}$$

Short time evolution $\Delta(s)$ for $d = 10^{-10}\,\mathrm{m}$ is shown in Fig. 5.9 for proton and the electron.

Similarly momentum space probability density is calculated. The details are omitted, and the final width for the velocity distribution (velocity gives better insight then momentum)

$$\Delta_v^2(s) = \frac{ea_0d^2\pi^2s^3}{2m\Gamma^2\left(\frac{1}{4}\right)}\left[J^2_{-1/4}\left(\frac{s^2}{2}\right)+J^2_{3/4}\left(\frac{s^2}{2}\right)\right]+\frac{\hbar^2s^3\Gamma^2\left(\frac{1}{4}\right)}{8d^2m^2}\left[J^2_{-3/4}\left(\frac{s^2}{2}\right)+J^2_{1/4}\left(\frac{s^2}{2}\right)\right]$$

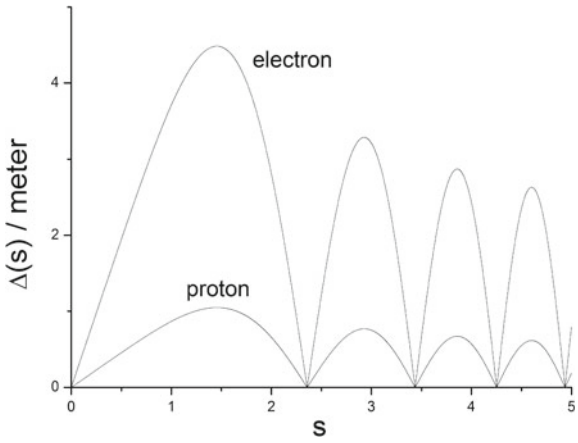

Fig. 5.9 Width $\Delta(s)$ of a Gaussian probability density for proton (its exact value is multiplied by factor 10) and the electron in time dependent homogeneous magnetic field. The width does not go to zero but a small value of the order $d = 10^{-10}\,\mathrm{m}$ that is assumed in the example

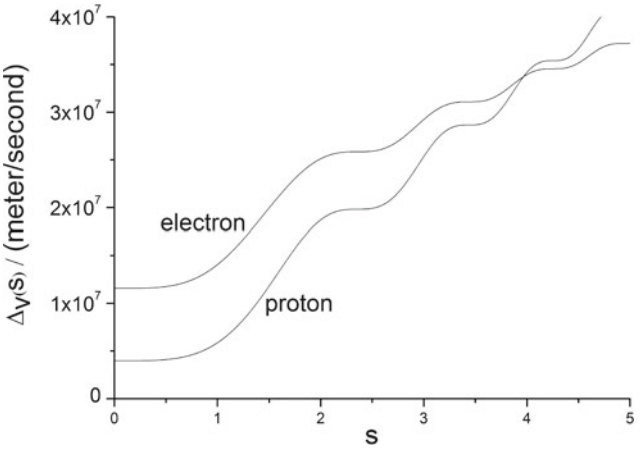

Fig. 5.10 Width $\Delta_v(s)$ of velocity probability density for proton (its exact value is multiplied by factor 10) and the electron in time dependent homogeneous magnetic field. The width increases in time as the result of the electric force which is induced by magnetic field

In the long time limit its value is

$$\Delta_v^2(s) \approx \left(\frac{2ea_0d^2\pi}{m\Gamma^2\left(\frac{1}{4}\right)} + \frac{\hbar^2\Gamma^2\left(\frac{1}{4}\right)}{2d^2m^2\pi}\right)s$$
$$-\left(\frac{ea_0d^2\pi}{m\Gamma^2\left(\frac{1}{4}\right)}\cos\left(\frac{s^2}{2}+\frac{\pi}{4}\right) + \frac{\hbar^2\Gamma^2\left(\frac{1}{4}\right)}{4d^2m^2\pi}\sin\left(\frac{s^2}{2}+\frac{\pi}{4}\right)\right)\frac{1}{s}$$

and the width increases as $t^{1/2}$, which indicates that the velocity of particle increases as the result of induced electric field (Fig. 5.10).

5.3 Confinement with Electromagnetic Wave

5.3.1 Classical Dynamics

Charge in electromagnetic field is analyzed in Chap. 4, and the results could be used to model control of its motion. Several effects are described as the result of this interaction, but one in particular is important to keep in mind and this is the frequency dependent (photon) momentum transfer. Its main feature is that for the waves of the form (4.1) momentum of a charge changes instantaneously and its subsequent motion is essentially not controllable. One way to avoid the effect is to form a standing wave, two counter propagating electromagnetic waves of equal amplitude, and the net result

is no frequency dependent momentum transfer on a charge. There are other useful features of such a wave, which are investigated in this section.

The simplest example of a standing wave is

$$\vec{A} = a \sin wt \ \cos kx \ \hat{z} \tag{5.18}$$

which is equivalent of a plane wave.[8] Although the use of the plane waves should be done with some caution, as discussed in details in Chap. 4, the analysis here is done within this model. The main rationale is that the essence of the effects that are discussed are not greatly affected by taking into account the onset of interaction. Also the field is assumed (relatively) weak, in which case the contribution from the effects that result by taking into account magnetic interaction are negligible. The rationale is that once the magnetic component becomes non negligible motion of a charge becomes multidimensional with less prospect to be controllable, and the goal here is to use the electromagnetic waves to control motion in one dimension, essentially in the direction of polarization. Based on this assumption Newton equation for a charge is

$$m \ddot{\vec{r}} = -eka \cos wt \ \cos kx \ \hat{z}$$

from which it is deduced that only motion in z direction is affected. In the x direction the solution is

$$x = x_0 + v_{x0} t$$

and equation in the z direction is

$$m \ddot{z} = -eka \ \cos wt \ \cos \left[k \left(x_0 + v_{x0} t\right)\right] \tag{5.19}$$

with the solution

$$z = z_0 + \left[v_{z0} - \frac{aev_{x0}}{mc^2} \sin \left(kx_0\right)\right] t + \frac{ae}{mwc} \cos \left(wt\right) \ \cos \left[k(x_0 + v_{x0} t)\right] + \frac{2aev_{x0}}{mwc^2} \sin \left(wt\right) \ \sin \left[k(x_0 + v_{x0} t)\right] - \frac{ae}{mwc} \cos \left(kx_0\right)$$

if the speed of light is large.

Typical for the solution is that it has linear increase in time, which indicates that the probability density in the z cannot be confined. However, the coefficient with the linear increase could be made zero if

$$v_{z0} - \frac{aev_{x0}}{mc^2} \sin \left(kx_0\right) = 0$$

[8] The phase of a plane standing wave in time and coordinate dependence is removed by a suitable choice of the initial instant in time and initial position of a charge.

which in principle could be satisfied for various combinations of parameters. The crucial is the amplitude of the vector potential, because if it is too small then the equation has no solution. If v_{z0} and v_{x0} are assumed to be of the same order of magnitude then the estimate of the minimal value for a is

$$ae = mc^2$$

but better estimate is given in terms of the required power of the plane wave to produce this amplitude. The amplitude of the Poyting vector is

$$P = \frac{1}{4\pi}\frac{a^2w^2}{c} = \frac{1}{4\pi\alpha}\frac{m^2c^2w^2}{\hbar}$$

because for a plane wave $E = H$ and

$$H = \left|\nabla \times \vec{A}\right| \sim a\frac{w}{c}$$

For a typical frequency of radiation of $\nu = 10^{15}\,\mathrm{s}^{-1}$ this estimates gives (see for the units conversion A) $P \approx 3 \times 10^{23}\,\mathrm{Wm}^{-2}$, which is so a large value that all practical purpose there is no way to prevent spread of the probability density in the z direction by using standing plane wave.

5.3.2 Charge in Standing Wave

Time evolution of a probability density for a charge in a plane standing wave (5.18) is analyzed in two dimensions, one along the coordinate dependence of the wave and the other along its polarization The condition is that the velocity of light is much larger than the spread of velocities in the phase space density

$$\rho_0 = \frac{1}{\hbar^2\pi^2}e^{-\frac{x^2+z^2}{d^2}-\frac{m^2d^2}{\hbar^2}[v_z^2+v_x^2]}$$

where it was taken into account that at $t = 0$ the vector potential is zero, and because of that it is not present in the momentum variable p_z. The condition means that $\hbar/(md) << c$. Probability density is calculated from the phase space density, and the first step is to find solution for the time reversed trajectory for general initial conditions. In the x coordinate the trajectory is simple

$$x = x_0 - v_{x0}t \tag{5.20}$$

however, in the z coordinate one obtains it by first solving a general Newton equation

$$\ddot{z} = F(t)$$

for the initial conditions at $t = t_0$. It could be shown that this solution is

$$z = z_0 - v_{z0}(t_0 - t) + (t_0 - t)\int_0^{t_0} dt''\, F(t'') + \int_{t_0}^{t} dt' \int_0^{t'} dt''\, F(t'')$$

and by taking the limit $t \to 0$ one gets

$$z = z_0 - v_{z0}t + t\int_0^t dt''\, F(t'') - \int_0^t dt' \int_0^{t'} dt''\, F(t'')$$
$$v = v_{z0} - \int_0^t dt''\, F(t'')$$

Time reversal is obtained by replacing t_0 by t (for more details about the rules to calculated time reversed trajectory for time dependent force see Sect. 5.2.1). Solution for the equation (5.19) is therefore

$$z = z_0 - \left[v_{z0} - qv_{x0}\sin\left[k(x_0 + v_{x0}t)\right]\cos(wt) + qc\cos\left[k(x_0 + v_{x0}t)\right]\sin(wt)\right]t \quad (5.21)$$
$$- \frac{qc}{w}\cos\left[k(x_0 + v_{x0}t)\right]\cos(wt) - \frac{2qv_{x0}}{w}\sin\left[k(x_0 + v_{x0}t)\right]\sin(wt) + \frac{qc}{w}\cos(kx_0)$$

and

$$v_z = v_{z0} - qv_{x0}\sin\left[k(x_0 + v_{x0}t)\right]\cos(wt) + qc\cos\left[k(x_0 + v_{x0}t)\right]\sin(wt) + qv_{x0}\sin[kx_0] \quad (5.22)$$

where

$$q = \frac{ae}{mc^2} = \frac{\sqrt{4\pi\alpha\hbar}}{wmc}\sqrt{P}$$

The parameter q is small, for example for the proton in the plane wave with the power $P = 1\ \mathrm{W/m^2}$ and the frequency $\nu = 10^{15}\ \mathrm{s^{-1}}$ it has the value $q \approx 10^{-15}$. Therefore correction to the trajectory in the z direction due to the spatial dependence of the standing wave is small.

The phase space density at time t is obtained by replacing coordinates and velocities in ρ_0 by expressions (5.20), (5.21) and (5.22), and subsequently remove the index 0 in them. Probability density is then obtained by integrating it in the velocity components, and after integration in v_z one gets

$$\int dv_z\, \rho(x, z, v_x, v_z) = \frac{N}{\Delta(t)} e^{-\frac{1}{\Delta^2(t)}[z+u(t)]^2 - \frac{1}{d^2}[x - v_x t]^2 - \frac{m^2 d^2}{\hbar^2}v_x^2}$$

where

$$u(t) = \frac{cq}{w}\cos(kx) + qtv_x \sin(kx) - \varepsilon\frac{cq}{w}\cos(wt)\cos[k(x + v_x t)]$$

and

$$\Delta^2(t) = d^2 + \frac{\hbar^2 t^2}{d^2 m^2}$$

The factor ε was introduced as the expansion parameter. For $\varepsilon = 0$ the integral in v_x (probability density) is quite lengthy, but one is interested in its limiting case for large t, which indicates whether the charge is contained or not. In this limit

$$P(x, z, t) = \frac{N}{t} e^{-\frac{d^2 m^2}{\hbar^2 t^2}\left[x^2 + \left(z + \frac{cq}{w}\cos(kx) + qx\sin(kx)\right)^2\right]}$$

probability density spreads in time and it has oscillatory structure in unison with the standing wave.

Correction to the probability density is obtained by expanding the phase space density in the powers of ε, and even in the first order it is again a lengthy expression which has functional structure

$$P^{(1)}(x, z, t) \sim \frac{qz}{t^3}\cos(2kx)\cos(wt)e^{-\frac{1}{t^2}\delta(x,z)}$$

where $\delta(x, z)$ as a quadratic form in the coordinates. Therefore, correction decays more rapidly but it is oscillatory in time.

5.3.3 *Generalized Standing Wave*

Lack of confinement by the standing wave could be remedied by treating a more general form for the field. One does not have much freedom in the choice of the field along the line of propagation, because by its definition standing wave is formed as interference of identical and counter propagating waves of infinite length, the plane waves. The only freedom that remains is to allow their polarization to be coordinate dependent, for example the standing wave could have a form

$$\vec{A} = a(z)\sin(wt)\ \cos(kx)\ \hat{z} \tag{5.23}$$

This simple generalization, however, is in contradiction with the wave equation that this vector potential should satisfy. In addition to this problem the implicit assumption that the scalar potential is zero is not correct, however, formally this is solved by deriving it from the Lorentz condition (3.7). Therefore, one should find a proper parametrization of the vector potential (the scalar is derived from it) that allows coordinate dependence of its polarization but at the same time that it should satisfy the wave equation.

The simplest non trivial solution is

$$h(x,z) = z\,; \quad g(x,z) = \cos x$$

and the eikonal function is

$$f(x,z) = \frac{c}{w}\ln z + \frac{c}{w}\ln\left[\cos\left(\frac{w}{c}x\right)\right]$$

which gives for the vector potential

$$\vec{A}(x,z,t) = az\ \sin(wt)\cos\left(\frac{w}{c}x\right)\ \hat{z}$$

and the scalar

$$V(x,z,t) = -\frac{ac}{w}\ \cos(wt)\cos\left(\frac{w}{c}x\right)$$

where the imaginary parts were taken. The Lorentz force is now, without including magnetic interaction

$$\vec{F} = ea\ \cos(wt)\sin\left(\frac{w}{c}x\right)\hat{x} - \frac{eawz}{c}\cos(wt)\cos\left(\frac{w}{c}x\right)\hat{z}$$

which has now two components, one along the polarization direction and the other parallel to the direction of the two counter propagating waves.

Linear increase in the polarization is not physical, because that implies infinite power carried by the wave. It is therefore necessary to make a cutoff in this increase, and for the moment the problem how to adjust the potentials to accommodate this change is of no concern. It is assumed that the essential dynamics of a charge in this field is all contained well within these bounds. In general the cutoff will be at the distance that is much larger than the wave length of the standing wave, for the reasons that will be discussed in Sect. 5.3.4.

Few estimates will be given in order to get insight into the general features of dynamics of a charge in this standing wave. In general one solves trajectory equation along the x axes first, which is

$$m\,\ddot{x} = ea\ \cos(wt)\sin\left(\frac{w}{c}x\right)$$

and its solution is not given in a closed form. However, for the sake of estimate it is assumed that because the interaction is weak solution is that for a free particle

$$x = x_0 + v_{x0}t$$

and trajectory equation in the z direction is

$$m\,\ddot{z} = -eakz\ \cos(wt)\ \cos\left[k\left(x_0 + v_{x0}t\right)\right] \tag{5.24}$$

This is equation for a harmonic force with a time dependent frequency, which could be either attractive or repulsive. Therefore in general the electromagnetic wave of this form does not necessarily confine a charge, this only happens under special circumstances. Simple qualitative arguments could be given why this is the case. If the force is slowly oscillating then in the repulsive regime the charge would not have a bounded trajectory, and in general its time dependence is an exponential increase. As soon as the sign of the force is reversed trajectory becomes bounded and therefore it is confined to a limited space. Upon the next reversal of the sign the trajectory is again unbounded with the rapid increase in the coordinate, and the result of these successive reversals of sign is in general a non confinement of the charge. However, if the time between the two reversals is short then on the average the charge is confined.

Equation (5.24) does not have a general solution, instead one takes into account that v_{x0} is small compared to c, in which case one writes

$$\cos(wt)\ \cos[k(x_0 + v_{x0}t)] \approx \cos(wt)\cos(kx_0) - wt\frac{v_{x0}}{c}\cos(wt)\sin(kx_0) \tag{5.25}$$

and the zeroth order equation is

$$\ddot{z} = -\epsilon\, z\ \cos(wt) \tag{5.26}$$

where

$$\epsilon = \frac{eka\cos(kx_0)}{m}$$

Solution is

$$z = b_1 C\left(0, -\frac{2\epsilon}{w^2}, \frac{tw}{2}\right) + b_2 S\left(0, -\frac{2\epsilon}{w^2}, \frac{tw}{2}\right)$$

where $C(0, s, u)$ is even Mathieu function and $S(0, s, u)$ is odd. It is typical of the Mathieu functions that they could be given in the form

$$M(0, s, u) = e^{iru} g(u)$$

where $g(u)$ is a function with the period 2π and r is their characteristic exponent. In general r is either real or complex, and in the latter case trajectory for the charge is not bounded. Therefore, depending on the arguments of the Mathieu functions the charge is either confined or it is not. For the particular Mathieu functions in the solution for the trajectory approximate condition that r is real is

$$|s| = \left|\frac{2ea\cos(kx_0)}{mwc}\right| < 0.9$$

or

$$\eta = \frac{ea}{mwc} = \frac{\sqrt{4\pi\alpha\hbar}}{mcw}\sqrt{P} < 0.45$$

where P is the modulus of the Poyting vector. The condition is well satisfied for proton, the frequency of the field $\nu = 10^{15}\,\mathrm{s}^{-1}$ and $P = 1\,\mathrm{W/m}^2$, when $\eta \approx 10^{-15}$. For such a small parameter η the Mathieu functions approximate as

$$C(0, s, z) \approx \cos\left(\frac{s}{\sqrt{2}}z\right) \quad ; \quad S(0, s, z) \approx \sin\left(\frac{s}{\sqrt{2}}z\right)$$

and solution for trajectory is

$$z = z_0 \cos\left(\frac{\epsilon}{\sqrt{2}w}t\right) + v_{z0}\frac{\sqrt{2}w}{\epsilon}\sin\left(\frac{\epsilon}{\sqrt{2}w}t\right) \tag{5.27}$$

which oscillates with either the amplitude (approximate) $z_{\max} = z_0$ or

$$z_{\max} = \left| v_{z0}\frac{\sqrt{2}}{w\eta\cos(kx_0)} \right|$$

whichever is greater. For confinement it is necessary that both amplitudes should be approximately equal, in which case

$$\left| v_{z0}\frac{\sqrt{2}}{w\eta\cos(kx_0)} \right| = z_0 \Rightarrow |v_{z0}| \approx \frac{|z_0|\, w\eta}{\sqrt{2}}$$

A fundamental question is being now suggestive: is the uncertainty principle violated for this condition? The principle requires that

$$|v_{z0}| = \frac{dw\eta}{\sqrt{2}} > \frac{\hbar}{2md} \Rightarrow d > \sqrt{\frac{\hbar}{mw\eta\sqrt{2}}}$$

where d is the width of the probability density. For the parameters that were used earlier the width should be greater than $d > 8.5 \times 10^{-5}\,\mathrm{m}$.

5.3.4 Gaussian Polarization

Results based on linearly dependent polarization with coordinate could be used for analyzing more general functional dependence. In general, however, this dependence should be of a particular symmetry. The argument is qualitative but it applies for a general case. If polarization has a general functional dependence $a(z)$ then it is reasonable to assume that it is either symmetric function, i.e. $a(-z) = a(z)$, or antisymmetric, i.e. $a(-z) = -a(z)$. As this function plays the role of a force then the scalar potential that is derived from it is in the former case antisymmetric function

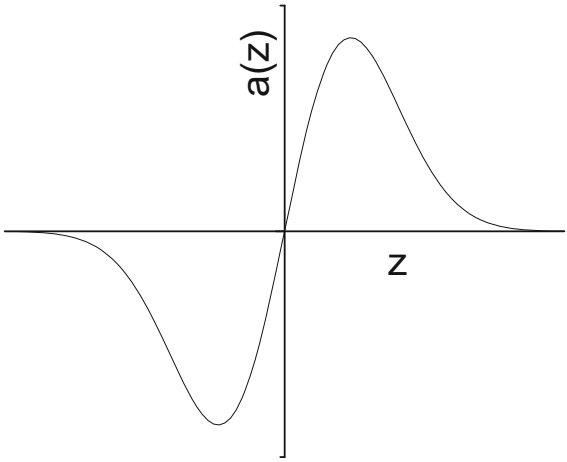

Fig. 5.11 Typical antisymmetric polarization function with two extrema

and in the latter it is symmetric. The first is a non binding potential and the latter is binding, which means that symmetric $a(z)$ does not stabilizes the probability density in the z coordinate.

It is therefore reasonable to assume that dynamics of a charge is approximately governed by the linearized polarization, in which case the dynamics equation is (5.26) where

$$\epsilon = \frac{ek\left|a'(0)\right|\cos\left(kx_0\right)}{m}$$

with the approximate solution (5.27). Physically acceptable assumption for $a(z)$ is that it goes to zero for large $|z|$, and because it is antisymmetric function it is zero at $z = 0$. From this general property it follows that in between these two extremes polarization has a maximum/minimum at $\pm z_{\max}$, which are dividing points[9]: for smaller $|z|$ than $z_{\max}$ polarization is confining and for larger it is not. Typical function $a(z)$ is shown in Fig. 5.11. Based on this property of the polarization function condition for confinement is that the trajectories should stay in the space $|z| < |z_{\max}|$. However, this means that the initial position of the charge should also be within these bounds, and because approximate trajectories are given by

$$z = z_0 \cos\left(\frac{\epsilon}{\sqrt{2}w}t\right) + v_{z0}\frac{\sqrt{2}w}{\epsilon}\sin\left(\frac{\epsilon}{\sqrt{2}w}t\right) \tag{5.28}$$

then the condition implies

$$\left|v_{z0}\frac{\sqrt{2}w}{\epsilon}\right| < z_{\max} \Rightarrow |v_{z0}| < z_{\max}\left|\frac{\epsilon}{\sqrt{2}w}\right|$$

[9]Function $a(z)$ may have several maxima but here the assumption is that there is only one.

A possible functional form that describes the antisymmetric polarization function with that general shape is

$$a(z) = a_0 z e^{-\frac{z^2}{D^2}} \tag{5.29}$$

for which the extremes are at

$$d_z a(z) = 0 \Rightarrow z_{\max} = \pm \frac{D}{\sqrt{2}}$$

However, it is not clear that such a choice could in principle be made, but as discussion in Sect. 3.3.4 showed it could be done but the question is of stability of this wave. Here it is assumed that these conditions are met and proceed with the confinement properties of it. As the consequence of the finite width of the wave scalar potential appears, which is calculated from the Lorentz condition (3.7), and it is given by

$$V = \frac{a_0}{k}\left(1 - \frac{2z^2}{D^2}\right) e^{-\frac{z^2}{D^2}} \cos(kx)\cos(wt)$$

and so the Lorentz force, without the magnetic component because velocities of charges are small, is

$$\vec{F} = e a_0 \left(1 - \frac{2z^2}{D^2}\right) e^{-\frac{z^2}{D^2}} \sin(kx)\cos(wt)\,\hat{x} - e a_0 k z e^{-\frac{z^2}{D^2}} \cos(kx)\cos(wt)\,\hat{z}$$

where only the leading term in the z component was retained. The force along the line of the wave propagation is small compared to the force along the direction of polarization, it is of the order kD smaller, therefore it could be neglected in further analysis. However, one should bear in mind that if fine effects are investigated then this neglect is to be accounted for.

It is convenient to re-scale the coordinates and time in units of the wave length λ of the electromagnetic wave. One writes for the coordinate $z \to z/\lambda$ and time $t \to ct/\lambda$, in which case equation for trajectory is[10]

$$\ddot{z} = -\epsilon z e^{-\frac{z^2}{D^2}} \cos(2\pi t) \tag{5.30}$$

where the coupling parameter is

$$\epsilon = \frac{2\pi e \lambda a_0}{mc^2}$$

and D is dimensionless, being defined as a fraction of λ. It is more convenient to relate the coupling parameter to the power that is transmitted by the plane wave, but

[10]For simplicity it is assumed that the effects due to the motion in the x direction are not essential for investigating confinement in the z direction, and so the choice $x = 0$ is made.

this time the Poyting vector has no meaning because the cross section of the beam of the electromagnetic wave is finite. Instead one uses the total power as the relevant parameter, which gives

$$W = 2\pi \int_0^\infty dz\, z\, \langle P(z,t)\rangle = \frac{ck^2a_0^2}{4} \int_0^\infty dz\, z^3 e^{-\frac{z^2}{D^2}} = \frac{ck^2a_0^2D^4}{32}$$

The coupling parameter is now

$$\epsilon = \frac{4e\lambda^2}{mc^2D^2}\sqrt{\frac{2W}{c}} = \frac{4\lambda^2}{mc^2D^2}\sqrt{2W\alpha\hbar}$$

and for the proton and the power $W = 1\,\mathrm{W}$ its numerical value is $\epsilon \approx 3.3 \times 10^{-8}\lambda^2/D^2$.

For the initial phase space density one chooses

$$\rho_0(z, v_z) = Ne^{-\frac{z^2}{d^2} - \kappa^2 d^2 v_z^2}$$

where κ is the wave number for the proton. Even if a moderately large value for d, say $d = 10^{-8}\,\mathrm{m}$, the product κd is very large, being of the order $\kappa d \approx 3 \times 10^8$. Such a large parameter implies that typical velocities of the proton are so small that during one oscillation of the field the proton makes a tiny move, whilst it should transverse large distance before confinement sets in. Therefore one needs to calculate $z(t)$ for long time during which the oscillatory term in equation (5.30) makes large number of oscillations.

The confinement problem could be solved approximately by noting that the coupling parameter is small. In the first approximation, therefore, solution of the equation is

$$z^{(0)} = z_0 + tv_0$$

and together with the correction to it is

$$z = \frac{\epsilon}{(2\pi)^2} z^{(0)} e^{-\frac{z^{(0)2}}{D^2}} \cos(2\pi t) - \frac{\epsilon}{(2\pi)^2} z^{(0)} e^{-\frac{z^{(0)2}}{D^2}} + z^{(0)}$$

In the trajectory equation (5.30) the coordinate z is replaced by the approximate solution, and subsequently the replacement $z^{(0)} \to z$ is made. Averaging over time gives

$$z\, \cos(2\pi t) \to \frac{\epsilon}{(2\pi)^2} z e^{-\frac{z^2}{D^2}} \cos^2(2\pi t) \to \frac{\epsilon}{2(2\pi)^2} z e^{-\frac{z^2}{D^2}}$$

and the force in the equation is now of the order ϵ^2. Equation that one solves now is

$$\ddot{z} = -\frac{\epsilon^2 z}{2(2\pi)^2} e^{-\frac{2z^2}{D^2}} \tag{5.31}$$

which does not have a rapidly oscillating component. This, however, means that the charge moves in a time independent potential, which in this case is a potential well of the width $\Delta z = D/2$ and the height

$$V_0 = \frac{D\epsilon^2}{16\pi^2\sqrt{e}}$$

5.3.5 *Quantum Dynamics*

Classical dynamics in the previous analysis is very useful for getting insight into the basic parameters that determine confinement, but for accurate results one need to use quantum dynamics. The basic equation for the vector potential (5.23) is

$$2\pi i\partial_t f = -\frac{\eta}{2}\partial_x^2 f - \frac{\eta}{2}\left[\partial_z - i\frac{\epsilon}{\eta}za(z)\sin(2\pi t)\ \cos(2\pi x)\right]^2 f \tag{5.32}$$

where only the dominant term in the vector potential is taken and the scalar potential is neglected. The equation is given in the same scaling as that used for equation (5.30), where $\eta = k/\kappa$ and $\kappa = mc/\hbar$ is the wave number of the charge. The parameter η is very small, its value for proton and a typical wave length $\lambda = 5 \times 10^{-7}$ m of the electromagnetic wave is $\eta = 2.642\,8 \times 10^{-9}$. By assuming that the width of the electromagnetic wave is finite, with a typical functional form (5.29), the coupling term for the same λ and the mass is

$$\frac{\epsilon}{\eta} = \frac{2\lambda^3}{\pi cD^2}\sqrt{\frac{2W\alpha}{\hbar}} = 12\frac{\sqrt{W}}{D^2}$$

where W is power in watts and D is in the units of λ.

In further analysis dependence on the x coordinate is neglected, because the interest is to investigate the possible confinement along the polarization of the wave. Equation to be solved is

$$2\pi i\partial_t f = -\frac{\eta}{2}\left[\partial_z - i\frac{\epsilon}{\eta}za(z)\sin(2\pi t)\right]^2 f$$

where η is small, which means that during one period of oscillations of the field, which is $T = 1$, the probability amplitude does not changes appreciable. Linear term in ϵ could be neglected and the term with ϵ^2 averages to $1/2$ and the equation is now

$$\frac{4\pi}{\eta}i\partial_t f = -\partial_z^2 f + \frac{\epsilon^2}{2\eta^2}\left[za(z)\right]^2 f \tag{5.33}$$

and represents dynamics of a particle in a time independent potential, which is solved by standard numerical methods. Approximation is valid under the condition that the right side is small, in other words

$$\frac{\eta}{4\pi}\left\langle -\partial_z^2 + \frac{\epsilon^2}{2\eta^2}\left[za(z)\right]^2\right\rangle << 1$$

where the bracket indicates an estimate. For the second derivative one has

$$\langle \partial_z^2 \rangle = \frac{1}{D^2}$$

which is assumed to be smaller than the estimate of the second term. The approximate equation, therefore, fails when

$$\left\langle \frac{\eta}{4\pi}\frac{\epsilon^2}{2\eta^2}\left[za(z)\right]^2\right\rangle \approx \frac{\epsilon^2 D^2}{8\pi\eta} \gtrsim 1$$

Equation (5.33) describes dynamics of a particle in a potential well, which has a typical shape as shown in Fig. 5.12. It is formally solved by writing solution as

$$f(z,t) = \int_0^\infty dE\, A(E) g(E,z) e^{-i\frac{\eta E}{4\pi}t}$$

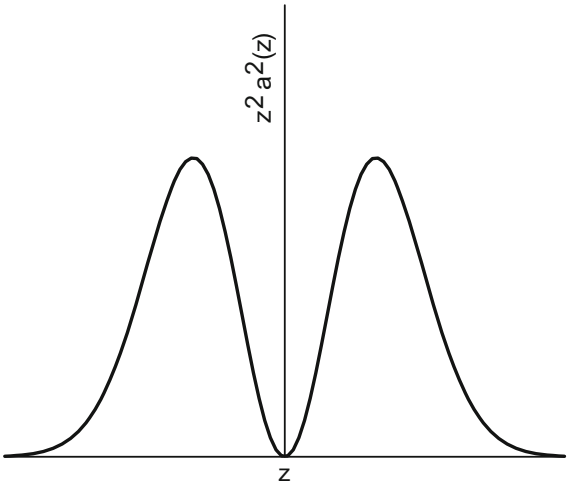

Fig. 5.12 Effective confining potential for a charge in the electromagnetic standing wave with coordinate dependent polarization

where $g(E,z)$ satisfies stationary equation

$$Eg = -\partial_z^2\, g + \frac{\epsilon^2}{2\eta^2}\,[za(z)]^2\; g = -\partial_z^2\, g + V(z)\, g \tag{5.34}$$

subject to appropriate boundary conditions. The simplest is to assume the scattering boundary conditions, which should be defined in both asymptotic spaces $z \to \pm\infty$. Thus the two solutions are defined as

$$e^{ikz} + u_r^+(E)e^{-ikz} \underset{z\to-\infty}{\longleftarrow} g^+(E,z) \underset{z\to\infty}{\longrightarrow} u_t^+(E)e^{ikz}$$

and

$$u_t^-(E)e^{-ikz} \underset{z\to-\infty}{\longleftarrow} g^-(E,z) \underset{z\to\infty}{\longrightarrow} e^{-ikz} + u_r^-(E)e^{+ikz}$$

where $k = \sqrt{E}$, and they are complex conjugate of each other, i.e. $\left[g^+(E,z)\right]^* = g^-(E,z)$. One derives a very important property for any two of these solutions by forming a combination

$$\left(E' - E\right) g_1^*(E',z)g_2(E,z) = g_1^*(E',z)\partial_z^2\, g_2(E,z) - g_2(E,z)\partial_z^2 g_1^*(E',z)$$

from which it is obtained

$$\begin{aligned}\left(E' - E\right)\int_{-L}^{L} dz\, g_1^*(E',z)g_2(E,z) = {} & g_1^*(E',L)\partial_z\, g_2(E,L) - g_2(E,L)\partial_z g_1^*(E',L) \\ & + g_2(E,-L)\partial_z g_1^*(E',-L) - g_1^*(E',-L)\partial_z\, g_2(E,-L)\end{aligned}$$

where the limit $L \to \infty$ is assumed. It follows that

$$\int_{-L}^{L} dz\, \left[g^+(E',z)\right]^* g^-(E,z) = 0$$

whilst (the details of derivation are omitted)

$$\left(E' - E\right)\int_{-L}^{L} dz\, \left[g^+(E',z)\right]^* g^+(E,z) = 2(\sqrt{E'} + \sqrt{E})\sin\left[\left(\sqrt{E'} - \sqrt{E}\right)L\right]$$

where it was taken into account that

$$\left|u_r^+(E)\right|^2 + \left|u_r^-(E)\right|^2 = 1$$

From the definition of delta function (see C.1)

$$\int_{-\infty}^{\infty} dz\, \left[g^\pm(E',z)\right]^* g^\pm(E,z) = 2\pi\delta\left(\sqrt{E'} - \sqrt{E}\right) = 4\pi\sqrt{E}\delta\left(E' - E\right)$$

From the two stationary solutions one derives the probability amplitude as

$$f(z,t) = \int_0^\infty dE \ \left[A^+(E)g^+(E,z) + A^-(E)g^-(E,z)\right] e^{-i\frac{4\pi E}{\eta}t}$$

where the coefficients are

$$A^\pm(E) = \frac{1}{4\pi\sqrt{E}} \int dz \ \left[g^\pm(E,z)\right]^* f_0(z) \tag{5.35}$$

where $f_0(z)$ is the initial probability amplitude. The most interesting energy range is when $E < \max[V(z)]$, in which case solution $g^+(E,z)$, because the amplitude of its incoming component is fixed to unity, is asymptotically

$$e^{ikz} + e^{-ikz+i\alpha} \underset{z\to-\infty}{\longleftarrow} g^+(E,z) \underset{z\to\infty}{\longrightarrow} \approx 0$$

and similarly for the other solution. However, around certain discrete values of E the probability amplitude undergoes a rapid change from this form into

$$e^{ikz} + u_r^+(E)e^{-ikz} \underset{z\to-\infty}{\longleftarrow} g^+(E,z) \underset{z\to\infty}{\longrightarrow} u_t^+(E)e^{ikz}$$

which is parametrized as

$$e^{ikz} + \left(1 + \frac{\gamma_r E_i}{E - E_r + iE_i}\right) e^{-ikz} \underset{z\to-\infty}{\longleftarrow} g^+(E,z) \underset{z\to\infty}{\longrightarrow} \frac{\gamma_t E_i}{E - E_r + iE_i} e^{ikz} \tag{5.36}$$

where $E_i > 0$ is small. There are discrete number of these energies, and so the probability amplitudes could be parametrized as

$$g^\pm(E,z) = g_b^\pm(E,z) + \sum_n \frac{\gamma_n^\pm(E,z)}{E - E_{res}^{(n)}}$$

where $g_b^\pm(E,z)$ is the background probability amplitude and $\gamma_n^\pm(E,z)$ is the residue of the probability amplitude. $E_{res}^{(n)}$ is the resonance energy, which is complex with a small negative imaginary part. It is important to note that both the background and the residue of the probability amplitudes are smoothly varying functions of the variable E. The probability amplitude is now

$$f(z,t) = f_b(z,t) + \sum_n \int_0^\infty \frac{dE}{E - E_{res}^{(n)}} \left[A^+(E)\gamma_n^+(E,z) + A^-(E)\gamma_n^-(E,z)\right] e^{-i\frac{\eta E}{4\pi}t}$$

and if the width of $A^\pm(E)$ is contained within the interval $E < \max[V(z)]$ then the background probability amplitude $f_b(z,t)$ is negligible or not important. The resonance term, however, has special significance because by shifting the integration

path in E into the lower half complex plane one gets

$$f(z,t) \sim -2\pi i \sum_n \left[A^+(E_{res}^{(n)})\gamma_n^+(E_{res}^{(n)},z) + A^-(E_{res}^{(n)})\gamma_n^-(E_{res}^{(n)},z)\right] e^{-i\frac{\eta E_{res}^{(n)}}{4\pi}t} \quad (5.37)$$

and diminishes in time with the decay rate of the form

$$f(z,t) \sim \sum_n f_{res}^{(n)} e^{-\frac{\eta E_I^{(n)}}{4\pi}t}$$

If imaginary part of a resonance is very small then this component of the probability amplitude stays nearly constant for a long time, longer that any other contribution, and so it acts as a bound state, but called *quasi bound* because it has no infinite lifetime.

Calculation of resonance energies $E_{res}^{(n)}$ is therefore essential for understanding confinement in a potential, however, it is not a simple task. The most straightforward would be to integrate equation (5.34) for the known initial conditions, for example by starting in the space $z \to \infty$ with the boundary condition

$$g(E,z) = e^{i\sqrt{E}z}$$

and integrate the equation to $z \to -\infty$ and fit it to the asymptotic form

$$g(E,z) = c(E)e^{ikz} + d(E)e^{-ikz}$$

and vary E until the coefficients undergo a rapid change, and find when it is maximal. This task is far from being simple, and in fact entirely impractical because of severe accumulation of numerical errors in the space of the potential barrier. However, even if the coefficients are calculated there is still the task of obtaining complex resonance energies, most importantly their imaginary part. Therefore that integration should have been done for complex E with negative imaginary part, and find the roots of equation

$$c(E) = 0$$

which, by definition, defines resonance energies. Again, this is not a simple task because for complex E the probability density increases exponentially with z, thus also contributing towards severe numerical instabilities. This implies that all the numerical methods must relay on using real values of E, however, in that case no resonance energies could be calculated, except by perturbation method. The equation to be solved by perturbation for the resonance energy is

$$c(E_{res}) = c(E_0 + E_1) \approx c(E_0) + E_1\, \mathring{c}(E_0) = 0$$

where the dot designates derivative with respect to E. E_0 is real approximation to the resonance energy and E_1 is complex correction that contains its width. Resonance energy is then approximately

$$E_{res} \approx E_0 - \frac{c(E_0)}{\mathring{c}(E_0)} \tag{5.38}$$

and the energy derivative of solution $g(E, z)$ satisfies equation

$$g + E\,\mathring{g} = -\partial_z^2\,\mathring{g} + V(z)\,\mathring{g} \tag{5.39}$$

5.3.5.1 Properties of Resonances

One model example illustrates properties of resonances in a potential well that is discussed in Sect. 5.3.5, but somewhat more general by being asymmetric

$$V(z) = \left(z + z^2\right) e^{-\frac{1}{25}z^2}$$

which is shown in Fig. 5.13.

By definition probability amplitude for a resonance state that is formed inside a potential well, i.e. for $E < 7$ in Fig. 5.13, have the same property as for a bound state. This means that it decrease exponentially through the potential barrier at both its ends, but instead of going asymptotically to zero it goes to a finite, but small, value, which in this respect makes resonance different from a bound state. Locating the energies at which resonances are formed is therefore the first task, which is done by integrating equation (5.34) from both ends of the potential. One fixes z_1 on the left side of the potential and z_2 on the right, both far away from it, and assumes that $g(z_1) = g(z_2) = 0$ whilst derivatives are arbitrary, say $g'(z_1) = g'(z_2) = 1$. Equation (5.34) is then integrated towards the origin, say a point z_0 inside the potential, and E is varied until

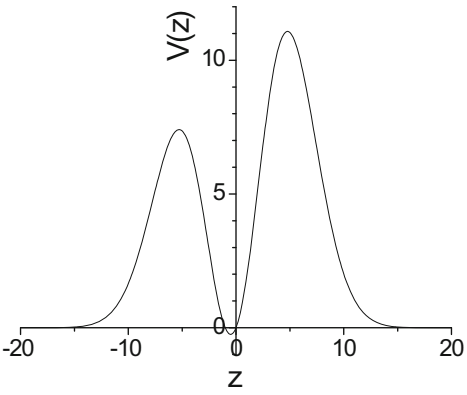

Fig. 5.13 Model potential that is typical of asymmetric confining potential

the log-derivative g'/g of both branches are identical. In other words, if solution from the left is g_1 whilst that from the right is g_2 then one is looking for a root of equation

$$\delta(E, z_0) = g_1'(z_0)/g_1(z_0) - g_2'(z_0)/g_2(z_0) = 0$$

The plot of function $\delta(E, z_0)$ is shown in Fig. 5.14, from where one finds that there are 5 solutions of equation (5.34) that satisfy the imposed boundary condition, except the one encircled. In general the curve $\delta(E, z_0)$ is a smooth function of E, except for few singularities where solution $g(z_0)$ goes through zero. However, there are very narrow intervals of E where this change is very rapid, as indicated by a circle, and within them the curve $\delta(E, z_0)$ has also a zero value. The corresponding probability amplitude is not representative of a bound state, in fact its modulus is at the minimum with respect to its value outside of potential well, and in this respect it is like an "anti-bound" state.

For the obtained E_n one solves the following boundary problem. For the positive and large z it is assumed that solution of equation (5.34) is in the form

$$g_2^+(z) = e^{i\sqrt{E_n}z}$$

and the equation is integrated from z_2 to z_0. For z negative and far away from the potential two solutions are assumed with the boundary conditions

$$g_1^{\pm}(z) = e^{\pm i\sqrt{E_n}z}$$

and the equation is integrated from z_1 to z_0. At the mid point all three solutions are joined smoothly into the connection

$$c\, e^{ikz} + de^{-ikz} \underset{z\to-\infty}{\longleftarrow} g_r^+(E, z) \underset{z\to\infty}{\longrightarrow} e^{ikz} \tag{5.40}$$

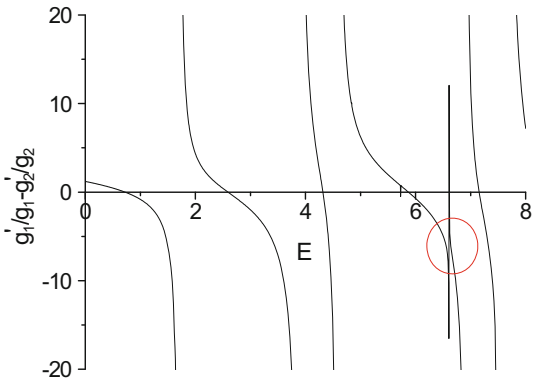

Fig. 5.14 Functional dependence of the difference of logderivatives on E for potential in Fig. 5.13 for a given boundary condition

Table 5.1 Resonance energies for potential in Fig. 5.13, and estimates of their widths by the WKB tunneling probabilities

n	$\mathbf{E}_n$	$\mathbf{\Gamma}$	P_{tunn}
1	0.7216	-4.354×10^{-10}	1.3×10^{-15}
2	2.5916	4.151×10^{-11}	2.7×10^{-10}
3	4.3171	2.411×10^{-7}	1.7×10^{-6}
4	5.8695	2.193×10^{-4}	1.8×10^{-3}
5	7.1647	0.0376	0.38

and resonances are calculated from equation (5.38) where $E_0 = E_n$. In the perturbation formula one still needs solution of equation (5.39) with the boundary conditions in the space $z \to \infty$ that is appropriate for the solution g_r^+, and these are

$$\mathring{g}_r^+(E,z) = \frac{iz}{2\sqrt{E_n}} e^{i\sqrt{E_n}z} \quad , \quad d_z\mathring{g}_r^+(E,z) = \frac{i}{2\sqrt{E_n}} e^{i\sqrt{E_n}z} - \frac{z}{2} e^{i\sqrt{E_n}z}$$

The equation is integrated backwards to $z \to -\infty$ by using already obtained solution $g_r^+(z)$. The energy derivative of the coefficient $c(E)$ is then

$$\mathring{c}(E_n) = \frac{e^{-ikz_1}}{2ik}\left[ik\mathring{g}_r^+ + d_z\mathring{g}_r^+ - \left(\frac{iz_1}{2k} + \frac{1}{2E_n}\right) d_z g_r'^+ + \frac{z_1}{2} g_r^+\right]$$

where $k = \sqrt{E_n}$. Resonance energy is then given by equation (5.38).

"Bound" state energies and the (negative) imaginary part of resonance energies $\Gamma = -\,\mathrm{Im}(E_{res})$ are given in Table 5.1. All except the first have the correct sign, which is attributed to extremely narrow energy width of resonance and this causes numerical instabilities in calculation. However, these widths could be approximately calculated by another method that is based on the WKB method for solving equation (5.34). From the method one calculates the tunneling probabilities

$$P_{tunn} = e^{-2\int_a^b dz\, \sqrt{V(z)-E_n}}$$

where a and b are the turning points of kinetic energy in the lower potential barrier, which gives reasonable widths as shown in Table 5.1. Although they are nearly an order of magnitude larger than the resonance widths, nevertheless as the quick estimates they are valuable data.

5.3.5.2 Confinement of Quantum Particle

Based on the classical analysis in Sect. 5.3.4 the potential (5.29) supports bound states, however, quantum analysis should give a more precise answer and one of

them is that bound states are not formed but resonances of certain lifetime. This is shown here by calculating resonance energies for those examples, by using the method that is described in Sect. 5.3.5.

The choice $D = 10$ is analyzed first, for which $\epsilon = 10^{-9}$ and $\eta = 2.64 \times 10^{-9}$. One finds 3 decaying states, whose widths are calculated from equation (5.38), however, they are in the units that are not directly related to their real lifetimes. These are obtained by using expansion (5.37) and express each term in the form

$$f(z,t) \sim e^{-i\frac{\eta E_{res}^{(n)}}{4\pi}t} \sim e^{-\frac{t}{\Gamma}}$$

and by recalling the units that are used here then

$$\frac{\eta E}{4\pi}t \rightarrow \frac{\eta^2 E}{8\pi^2}\frac{mc^2}{\hbar}t = \frac{t}{\Gamma}$$

or

$$\Gamma_m = \frac{8\pi^2}{\eta^2\left|\mathrm{Im}\left(E_{res}^{(m)}\right)\right|}\frac{\hbar}{mc^2}$$

Numerical values for each decaying state are given in Table 5.2, and they range from very long to short lived, however, the short lived are still long on the scale of typical motion in the confining potential (Fig. 5.15).

Similar analysis for parameter $D = 1$ in Sect. 5.3.4 does not produces any decaying state, thus contradicting the classical prediction. As already mentioned, classical study did not have the aim at giving precise prediction, but indication that bound (decaying) states could be formed. However, such contradictory predictions are expected when the potential marginally supports one or two states, but when there are more than both are in agreement.

Interesting question to analyze is time evolution of an initial probability density of a width d (in units of λ), which is centred around $z = 0$ and for simplicity it is symmetric. As an example a Gaussian probability amplitude is taken

$$f_0(z) = Ne^{-\frac{z^2}{2d^2}}$$

Table 5.2 Resonance energies and their lifetimes for a confining potential

m	$\mathbf{E}_{res}$	$\boldsymbol{\Gamma}$/s
1	$0.252 - i\,1.46 \times 10^{-9}$	5443
2	$0.721 - i\,9.71 \times 10^{-6}$	0.818
3	$1.103 - i\,2.64 \times 10^{-3}$	3.01×10^{-3}

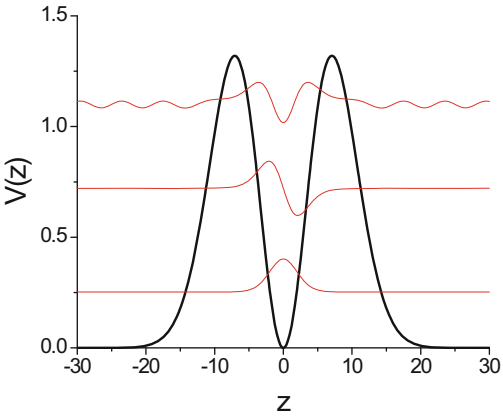

Fig. 5.15 Decaying states in confining potential (*black line*)

which gives probability amplitude in momentum space (in non scaled parameters)

$$G_0(p) = Ne^{-\frac{d^2p^2}{2\hbar^2}}$$

From this momentum distribution one derives a quantity that is of particular interest in theoretical modelling, the time that it takes for a free particle to spread over the range of potential whose width is D. This quantity gives an indication of the relative importance of the decaying states in the time evolution of the probability density. The time could be defined as

$$t_{spread} = \frac{D}{v}$$

where v is average velocity of particle, which is approximately $v = \hbar/(md)$. The right side is now transformed into the units in terms of λ, when

$$t_{spread} = \frac{8\pi^2 D}{w\eta\sqrt{E}} \approx \frac{4\pi^2 dD}{w\eta} \tag{5.41}$$

where w is the angular frequency of the standing wave. For the parameters that were used in Table 5.2 the spreading time for the free probability density is $t_{spread} = 4 \times 10^{-5}$ s, which is short even for the fastest decaying resonance.

In the process of confinement it is important to calculate what fraction of the initial probability density stays within the potential well, bound in decaying states. The unbound components of the probability density leave the confining potential in time (5.41) and therefore by the bound components it is meant those that decay with the much longer lifetime than this. Formally this fraction should be obtained by calculating

$$f_0(z) = \int_0^\infty dE \left[A^+(E)g^+(E,z) + A^-(E)g^-(E,z)\right]$$

where the coefficients are given by equation (5.35), but one should be careful about the exact procedure. Initial idea is to assume that the resonance states are like bounds states, they are normalized to unity and then for them the relevant projections are obtained as in expansion in a complete set of discrete functions. Whilst this procedure might be plausible for the resonance states with very narrow width, it does not have meaning for those with wider because they have a non negligible tail outs the potential well, and hence they are not normalizable. Therefore the answer must be derived from the first principles, and this is to start from the fact that $f_0(z)$ is normalized to unity, which means

$$\int dz\ |f_0(z)|^2 = 4\pi \int_0^\infty dE\ \sqrt{E}\ \left[\left|A^+(E)\right|^2 + \left|A^-(E)\right|^2\right] = 1$$

The coefficient $A^+(E)$ is calculated from equation (5.35)

$$A^+(E) = \frac{1}{4\pi\sqrt{E}} \int dz\ \left[g^+(E,z)\right]^* f_0(z)$$

but the irregular solution $g^+(E,z)$ is not normally calculated, instead one does that for the regular one, which is defined by the boundary condition (5.40). However, the two are related and so the coefficient is

$$A^+(E) = \frac{1}{4\pi c^*(E)\sqrt{E}} \int dz\ \left[g_r^+(E,z)\right]^* f_0(z)$$

and because in vicinity of a resonance energy E_r one has approximately

$$\frac{1}{c(E)} \approx \frac{iE_i\gamma_t(E_r)}{E - E_r + iE_i} e^{i\delta_t(E_r)}$$

the coefficient is finally

$$A^+(E) = -\frac{1}{4\pi\sqrt{E_r}} \frac{iE_i\gamma_t(E_r)}{E - E_r - iE_i} e^{-i\delta_t(E_r)} \int dz\ \left[g_r^+(E_r,z)\right]^* f_0(z)$$

It was assumed that near the resonance energy the regular solution $g_r^+(E,z)$ is nearly constant because it is essentially determined by the boundary condition at $z \to \infty$, which is nearly constant in the same vicinity.

From the amplitude $A^+(E)$ one calculates contribution to the probability of finding particle in the resonance state with the energy E_r

$$\begin{aligned} P_r^+ &= 4\pi \int_{E_r} dE\ \sqrt{E}\ \left|A^+(E)\right|^2 \\ &= \frac{|\gamma_t(E_r)|^2}{4\pi\sqrt{E_r}} \left|\int dz\ \left[g_r^+(E_r,z)\right]^* f_0(z)\right|^2 \int_{E_r} dE\ \frac{E_i^2}{(E-E_r)^2 + E_i^2} \end{aligned}$$

Similarly the contribution from $A^-(E)$ is calculated, but for real and symmetric $f_0(z)$ it is equal to the contribution from $A^+(E)$, therefore the total probability is

$$P_r = \frac{E_i\,|\gamma_t\,(E_r)|^2}{2\sqrt{E_r}}\left|\int dz\,\left[g_r^+(E_r,z)\right]^* f_0(z)\right|^2$$

For $d = 1$ the probability to find the particle in state $m = 1$ is $P_1 = 0.245$ whilst in state $m = 3$ it is $P_1 = 0.115$ (in state $m = 2$ the probability is zero because of symmetry), which is about one half of that predicted by classical mechanics in Sect. 5.3.4.

5.4 Extreme Confinement

5.4.1 One Particle

By extreme confinement one understands that a particle is localized within a very small volume, the definition that needs clarification. A small volume is the one in which average momentum of a particle implies that its velocity is very close to the speed of light, as deduced from uncertainty principle. If a particle of mass m is confined to a space of radius r_0 then by the uncertainty principle its typical momentum is

$$p = \frac{\hbar}{2r_0}$$

and velocity

$$v = \frac{pc}{\sqrt{c^2m^2 + p^2}} = \frac{c}{\sqrt{4\kappa^2 r_0^2 + 1}}$$

where $\kappa = mc/\hbar$ is the Compton wave number. For a Hydrogen like atom with Z protons, and Zr_0 being the Bohr radius of the ground state, velocity of the electron is $v \approx 3.6 \times 10^{-3}$ cZ, and even for a nucleus with large Z it is non-relativistic. On the other hand if the electron is confined to a nucleus, with a typical radius $r_0 = 10^{-15}$ m then it has velocity $v \approx 0.99999c$ whilst that of the proton is $v \approx 0.1c$, which is nearly relativistic.

Dispersion of momenta due to the uncertainty principle has a very important impact on dynamics of particles. One particular consequence is discussed in the context of a decaying system, in Sect. 5.1.2. In here discussion is devoted to the change in mass of a particle due to this effect. The mass effect, on its the most elementary level, is derived by calculating the relativistic energy due to the dispersion of momenta. The simplest distribution is

$$P(p) = \frac{d^3}{\hbar^3 \pi^{3/2}} e^{-\frac{d^2 p^2}{\hbar^2}}$$

where p is momentum of particle. The mass of particle is then its relativistic energy equivalent

$$m = \frac{1}{c} \int d^3 p \, P(p) \sqrt{m_0^2 c^2 + p^2}$$

where m_0 is its rest mass. Definition of the rest mass should be carefully examined, but at this point it is used as an arbitrary parameter. For the Gaussian distribution the mass is

$$m = \frac{c d m_0^2}{\sqrt{\pi}\hbar} e^{\frac{c^2 d^2 m_0^2}{2\hbar^2}} K_1 \left(\frac{c^2 d^2 m_0^2}{2\hbar^2} \right)$$

where $K_1(u)$ is Bessel function. In the non-relativistic limit $d \to \infty$ the mass has the value $m = m_0$, with the correction of the order d^{-2}. The rest mass is now defined as that which corresponds to a particle delocalized over the whole space. On the other hand in the relativistic limit for small d the mass of particle is

$$m \approx \frac{2\hbar}{\sqrt{\pi} c d} \tag{5.42}$$

and irrespective of its rest mass m_0. Similar analysis for more general distributions give the same result, thus for example for the Hydrogen atom this limit gives the same order d^{-1} and with approximately the same coefficient.

If particle has the overall relativistic momentum $\overrightarrow{p}_0$, with the property $\frac{p_0 d}{\hbar} >> 1$, then its relativistic energy is

$$m = \frac{1}{c} \int d^3 p \, P(p) \sqrt{m_0^2 c^2 + \left(\overrightarrow{p} - \overrightarrow{p}_0 \right)^2}$$

and by expanding it for large p_0 the dominant terms are

$$m = \frac{p_0}{c} + \frac{c m_0^2}{2 p_0} + \frac{\hbar^2}{2 c p_0 d^2} + O\left(k_0^{-3}\right)$$

The expression is approximation of

$$m \approx \frac{1}{c} \sqrt{p_0^2 + m_0^2 c^2 + \frac{\hbar^2}{d^2}}$$

which means that the rest mass m_0 is modified by

$$m_0^2 \to m_0^2 + \frac{\hbar^2}{c^2 d^2}$$

thus giving the same estimate for the change in mass as earlier, i.e. correction is of the order d^{-1}.

Previous analysis is demonstrated on the experiments with elementary particles, and one example is decay of charged negative pion into a muon and muon antineutrino. Initially pion, like in almost all other examples, is moving with relativistic velocity, resulting from collision of, say, two protons. Previous analysis, however, assumes that decay takes place in the rest frame of pion, when it is greatly simplified, and so direct comparison of theory with the experimental evidence should take this fact into account. The objective of this simplification is to emphasize the role of confinement and the consequences on kinematics and dynamics of particles, and the example is pion.

Mechanism that leads to decay of pion is of no consequence on the outcome of the subsequent kinematics. The fact is that muon is produced (muon antineutrino is not essential in the analysis, only in determining initial conditions) within the size of pion, which determines initial probability density for its position. Initial overall momentum of muon is determined from the energy and momentum conservation laws, and by assuming that the rest mass of antineutrino is zero the two laws give

$$\frac{p_0}{mc} = k_0 = \frac{1}{2m_\pi}\left(m_\pi^2 - m_\mu^2\right) = 59$$

where m is mass of the electron. Mass of pion and muon are with respect to the mass of the electron. Radius of pion (charged) is approximately 7×10^{-16} m and if this is assumed to be the size of confinement for the muon then its mass (5.42), in the units of the electron mass, would appear to be $m_\mu \approx 622$. This value exceeds by far all that is known about the mass of muon, and therefore it should be assumed that its initial confinement is orders of magnitude larger. For the extreme case of the radius of confinement 10^{-12} m stability of the initial probability density is preserved up to time (5.5), which in this example is $t \approx 10^{-18}$ s. It appears that the probability density spreads fast, so fast that experimental detection of muon would be almost impossible. At infinite time, however, the probability density spreads by angle (5.6), and in this example it is $\alpha \approx 6.5 \times 10^{-3}$ rad, which means that it looks like a very collimated beam enabling detection of muons.[11]

The true test of the impact of momentum distribution on the mass of a particle is to do dynamic calculations, essentially "mass time acceleration equals force". The problem with this test is that one can do this analysis provided the coordinate probability distribution stays stable for sufficiently long time. There are two ways to achieve this, one is that the particle has relativistic velocity, when according to discussion in Sect. 5.1.1 the coordinate probability density is stable. The other way is to do the test on a bound particle, for example on a Hydrogen like ion where the increase of its mass is due to the confined electron.

[11] This conclusion does not take into account other effects in detection of elementary particles, which are not reviewed here.

5.4.1.1 Force on Unbound Particle

The mass effect is analyzed for an unbound particle when it has large momentum p_0 in the x direction and the force that is applied is constant and perpendicular in the z direction. The idea is that if there is an effect on the mass of the particle which arrises from the momentum distribution then the solution for the average trajectory would be different from that which is expected from classical relativistic dynamics.[12] According to it particle that has momentum p_0 is introduced in dynamics equations with the increased, relativistic, mass. More precisely, relativistic dynamics equation for a particle that is subject to the force $\overrightarrow{F}$ is

$$d_t \overrightarrow{p} = d_t \left(\frac{m}{\sqrt{1 - \frac{v^2}{c^2}}} \overrightarrow{v} \right) = d_t \left(\gamma \overrightarrow{v} \right) = \overrightarrow{F} \tag{5.43}$$

where $\overrightarrow{v}$ is its velocity and γ is its relativistic mass. Before further steps it is convenient to work with scaled variables, thus one introduces $k = p/(\hbar\kappa)$ instead of momentum, d stand for $d\kappa$ and $\tau = ct\kappa$, where $\kappa = mc/\hbar$ is Compton wave number. For a particle that is subject to a constant force in z direction, with general initial conditions, solution of equation (5.43) is

$$\begin{gathered} x = x_0 + k_{x0} u, \quad y = y_0 + k_{y0} u, \\ z = z_0 + \frac{\sqrt{1 + \overrightarrow{k}^2} - \sqrt{1 + \overrightarrow{k}_0^2}}{F} \end{gathered} \tag{5.44}$$

where

$$u = \frac{1}{F} \log \frac{k_z + \sqrt{1 + \overrightarrow{k}^2}}{k_{z0} + \sqrt{1 + \overrightarrow{k}_0^2}}, \quad \overrightarrow{k} = \overrightarrow{k}_0 + \tau \overrightarrow{F}$$

Variables with the subscript 0 are their initial values at $\tau = 0$.

Initial phase space density is

$$\rho \left(\overrightarrow{r}, \overrightarrow{k}, \tau \right) = N e^{-\frac{r^2}{d^2} - d^2 \left(\overrightarrow{k} - \overrightarrow{k}_0 \right)^2}$$

and its time evolution is obtained by replacing $\overrightarrow{r}$ with (5.44) but τ is replaced by $-\tau$. Momentum $\overrightarrow{k}$ is replaced by $\overrightarrow{k} - \overrightarrow{F}\tau$. Resulting expression is quite complicated but one is not interested in detailed structure of the coordinate probability density

[12] It should be noted here that the tracks which the charged elementary particles produce in detectors are analyzed precisely in this way.

but the average coordinate in the z direction, along which the force is applied. This average is

$$z(\tau) = \int d^3r\, d^3k\, z\, \rho\left(\overrightarrow{r}, \overrightarrow{k}, \tau\right)$$

where the integrals in the coordinates and k_y could be evaluated without too many difficulties. The result is

$$z(\tau) = \int dk_x\, dk_z\, Z(k_x, k_z, \tau)$$

where

$$Z(k_x, k_z, \tau) = \frac{N}{F} e^{-d^2P^2(k_x, k_z - F\tau)} U\left(-\frac{1}{2}, 0, d^2P^2(k_x + k_0, k_z)\right) - \frac{N}{F} e^{-d^2P^2(k_x, k_z - F\tau)} U\left(-\frac{1}{2}, 0, d^2P^2(k_x + k_0, k_z - F\tau)\right)$$

where

$$P^2(k_x, k_z) = 1 + k_x^2 + k_z^2$$

$U(a, b, u)$ is hypergeometric function. From the relativistic assumption for k_0 it follows that the argument u in $U(a, b, u)$ is large, when one replaces it by its asymptotic expansion

$$U(a, b, u) \approx \sqrt{u} + \frac{1}{4\sqrt{u}}$$

$Z(k_x, k_z, \tau)$ is now a function of $P(k_x - k_0, k_z)$ with large k_0 and small other parameters, the fact to use to expand combination of the hypergeometric functions for large k_0. The result is a combination of powers in k_x and k_z when the integrals could be evaluated with the result (non scaled variables are used)

$$z(t) \approx \left(1 - \frac{m^2c^2}{2p_0^2} - \frac{\hbar^2}{4d^2p_0^2}\right)\frac{cFt^2}{2p_0} \approx \frac{cFt^2}{2\sqrt{p_0^2 + m^2c^2 + \frac{\hbar^2}{2d^2}}}$$

The dominant term is relativistic trajectory for a point-like particle under the impact of a constant force, but with a correction to its rest mass. This correction is only dependent on the width of the probability density.

5.4.2 Two Particles

Two particles that are bounded together, and the system as the whole is confined within a small space, should be analyzed within relativistic dynamics. Transition

from non relativistic to relativistic dynamics is not straightforward, and even for a single particle some of the problems are revealed in Sect. 5.4.1. Difficulties that are encountered when treating more than one particle are much greater, even to the extent that one could assume to be insurmountable. Few of these problems shall be discussed here on a simplified model, but two the greatest should be mentioned. One is that with each particle one should associate its own time, therefore for two particles there is no unique time variable that is used for describing their dynamics. Their dynamics should be treated with the invariant time, and in quantum dynamics it is not clear what it should be. The second problem is that one should taken into account finite speed of propagation for their mutual interaction. If this is done then the two particle system is not a solvable dynamics unless some simplifying assumptions are made. The source of the problem is that the initial conditions are not well defined, in particular force that acts between the particles (for more details see [9]).

Before attempting to analyze two particle relativistic systems, however, one should select the problems of interest. In fact there are not many examples of the systems that one should attempt to analyze, for example, one is Hydrogen like Uranium ion. Strictly speaking this ion is marginally relativistic, much better example would be, say the neutron as a bound state of proton and the electron. This, however, is dismissed as a non physical problem because the structure of the neutron has different description. The same is with the other elementary particles. Therefore discussion that follows could be treated as an exercise to describe problems, and the effects, that result from treating relativistically a two particle system.

The simplest system to analyze consists of a heavy particle and a light one (for example proton and the electron) mutually bound by a scalar potential.[13] In the examples like this a simplification is possible: dynamics of the heavier particle could be treated as non relativistic and therefore one could define universal time variable. Further simplification is that a one dimensional problem is treated, however, the conclusions are of a general nature that could be applied for systems in three dimensions. Additionally it is assumed that a constant, but time dependent, force is applied on the particle with large mass.

Classical equations of motion for this system are

$$q\ddot{X} = F(t) - G(x - X), \; d_t p = G(x - X)$$

where X is the coordinate of the particle with large mass, $q = M/m$ is the ratio of the large and small mass and

$$p = \frac{\dot{x}}{\sqrt{1 - \frac{\dot{x}^2}{c^2}}}.$$

The force between the two particles is $G(x - X)$ and it is normalized with respect to m.

[13] Again an approximation because this is not relativistically invariant interaction. Justification for it is that one of the partner particles has large mass and therefore moves non relativistically.

From the equations one derives two essential conservation laws. One is conservation of momentum law, which is given by

$$\frac{d}{dt}(p+P) = F(t) \tag{5.45}$$

where

$$P = q\dot{X}$$

If the external force is zero the total momentum is constant. The other is conservation of energy law, and for relativistic particle it is derived from equation for the fourth component of the four momentum

$$\frac{d}{dt}p_4 = \dot{x}G(x-X) = -\dot{x}\partial_x V(x-X)$$

where

$$p_4 = \sqrt{1+p^2}$$

and it is assumed that the force G is derived from a scalar potential V. By combining equation for p_4 with the one for the non relativistic particle it is shown that (contribution from the external force is neglected)

$$p_4 + \frac{1}{2q}P^2 + V(x-X) = E$$

is conserved, the total energy of the system. In the non relativistic dynamics for both particles the total energy could be conveniently divided up into contributions from the motion of their centre of mass and their relative motion (in the scaling here energy is normalized with respect to m)

$$E_{nr} = \frac{\left(\dot{x}+P\right)^2}{2(1+q)} + \frac{q\left(\dot{x}-\dot{X}\right)^2}{2(1+q)} + V(x-X)$$

This is the necessary step towards reducing the problem from a two particle dynamics into a single particle dynamics in the relative coordinates. Motion of the centre of mass is associated with the conservation of the the total momentum for the two particles. When the motion of one particle is relativistic the same fragmentation of the total energy is in a more complicated form. The details are omitted and the final result is

$$E = \frac{1}{2}\left(p_4 + \frac{1}{p_4}\right) + \frac{(p+P)^2}{2(p_4+q)} + \frac{qp_4}{2(p_4+q)}\left(\frac{p}{p_4} - \frac{P}{q}\right)^2 + V(x-X) \tag{5.46}$$

where one recognizes the same structure as in the non relativistic dynamics except for the first term, which in the limit of small velocity is the energy equivalent of the rest mass. Furthermore, each term is a function of p_4, therefore a function of p, and this means that in two particle relativistic dynamics there is no way one could disentangle motion of their centre of mass (the second term) from that for their relative motion (the third term).

Solving dynamics of the system when external force is applied requires formulation of initial phase space density, for which certain assumptions should be made. One is that initial, average, total momentum of the system is zero. The next is that bound state of the two particles is stationary, the assumption that could be made in the nonrelativistic dynamics because their relative motion is disentangle from that for their centre of mass. In the relativistic dynamics this disentanglement is not possible and therefore a more general assumption should be made. By a general theorem a stationary phase density is a function of dynamic invariants (conservation laws) and one of them is the total energy for the system of, in this case two, particles. This means that in relativistic dynamics the total energy for two particles (5.46) should be used as dynamic invariant. Another dynamic invariant is the total momentum of the system, and through the functional dependence of the phase space density on it one defines its initial value. Yet another dynamic invariant is the total angular momentum of the system, but in this discussion it will not be considered.

For those initial conditions the phase space density should be a function of total energy and the total momentum of the two particles.[14] Indeed the initial phase space density is stationary but in the trivial sense. The total energy is function of only the relative coordinates of the two particles and therefore the phase space density is spread over the whole space and as such stationary, regardless of nonrelativistic or relativistic dynamics. The term that is missing is localizing the system as the whole around certain point in space and for that one uses the coordinates for the centre of mass and this parameter needs some discussion. Total momentum of the two particles is well defined, and it is the invariant of motion if no force is applied, as it follows from (5.45). In non relativistic dynamics centre of mass is deduced from this law, however, the same is not possible in the relativistic dynamics and therefore it should be defined as its generalization. From (5.46) it could be inferred that the variable p_4 plays the role of mass for the relativistic particle and then the obvious definition for the centre of mass coordinate is

$$x_{cm} = \frac{qX + p_4 x}{q + p_4}$$

[14]It should be noted that the total energy, both in nonrelativistic and relativistic dynamics, has term with the total momentum of the particles. In the former this term could be omitted, being replaced by explicit reference in the phase space density by the total momentum. In the latter this is not possible and therefore the total momentum term appears in two places.

Phase space density has therefore a functional form

$$\rho\left(x, X, p, P\right) = f\left(E, d_x^2\left(p+P\right)^2, \frac{x_{cm}^2}{d_x^2}\right)$$

from which the average total energy E

$$E_{av} = \int dx\, dX\, dp\, dP\, E\, f\left(E, d_x^2\left(p+P\right)^2, \frac{x_{cm}^2}{d_x^2}\right),$$

has contribution from two terms with the total momentum. The same is also true in nonrelativistic dynamics if this term is not omitted from the total energy, and a model example is analyzed in order to demonstrate how this affects E_{av}. Convenient functional form of the phase space density is assumed with a note that in classical dynamics there is no restriction on its choice, and also bound state energy is not quantized. The simplest is to choose exponential function, in which case phase space density is (scaling is the same as in Sect. 5.4.1)

$$\rho = Ne^{-\frac{E}{d_e} - d_x^2\left(p+P\right)^2 - \frac{x_{cm}^2}{d_x^2}}$$

where the uncertainty principle is incorporated by the choice of the widths for momentum and coordinate variables. The parameter d_e is the measure for the width of (5.46) whilst d_x gives the range of the confinement for the system as the whole. From the phase space density one calculates the average total energy of the system, which is given by

$$E_{av} = N\int dx\, dX\, dp\, dP\, Ee^{-\frac{E}{d_e} - d_x^2\left(p+P\right)^2 - \frac{x_{cm}^2}{d_x^2}}$$

Potential is assumed for harmonic oscillator

$$V\left(u\right) = \frac{1}{2}\omega^2 u^2$$

when E_{av} is

$$E_{av} = d_e + \frac{1}{1 + 2d_e\frac{d_x^2}{\hbar^2}\left(m+M\right)}\frac{d_e}{2}$$

where the parameters are again non-scalled. The total energy equals essentially to d_e, in particular in the limit of infinite delocalization of the system, $d_x \to \infty$.

5.4.2.1 Classical Dynamics of Bound States

Before further analysis it is instructive to discuss relativistic theory of bound states and the problems one encounters. They are reviewed on a one dimensional example of a particle in harmonic oscillator. There are two basic quantities that play important role in relativistic dynamics, one is momentum of particle and the other its velocity. The first is very important because one of the basic laws, conservation of momentum law, could be formulated, and the other is that it has the property, together with its fourth component, of the relativistic four vector. On the other hand velocity is a directly measured quantity given as the time rate of coordinates, the two basic parameters of dynamics. The two quantities are related by a parameter, the mass of particle, which is by default taken positive because it essentially measures amount of matter. However, there is nothing to prevent defining the mass parameter negative, one could very well use the existing force law but the force should have to be defined with the opposite sign. On the other hand if the sign of the force is not changed then the two signs of the mass describe two separate space regions where the particle moves. This is best described from the expression for the total energy of the particle (for harmonic force)

$$E = \frac{p^2}{2m} + \frac{k}{2}x^2$$

If the mass is positive that he trajectory of the particle is bounded within the interval $-\sqrt{\frac{2}{k}E} < x < \sqrt{\frac{2}{k}E}$ whilst if it is negative then it moves in the intervals $x > \sqrt{\frac{2}{k}E}$ or $x < -\sqrt{\frac{2}{k}E}$. In both cases trajectories are solution of the force law, except that when the mass is negative velocity of particle points in opposite direction to the momentum.

The discussion about mass appears rather artificial but it is not so in relativistic dynamics. The basic equations of relativistic classical dynamics are (there are now four equations, three for the spatial coordinates and one for the time coordinate)

$$d_t \overrightarrow{p} = \overrightarrow{F}, \quad d_t p_4 = \overrightarrow{v} \cdot \overrightarrow{F}$$

where $\overrightarrow{v}$ is velocity of the particle and

$$\overrightarrow{p} = m\overrightarrow{v}, \quad p_4 = mc^2$$

where

$$m = m_0\gamma = \pm\frac{m_0}{\sqrt{1 - \frac{v^2}{c^2}}}$$

Relationship between momentum $\overrightarrow{p}$ and velocity $\overrightarrow{v}$ is formally the same as in the non relativistic dynamics except that now what one calls mass is no longer a fixed

parameter, and furthermore it has arbitrary sign. This mass is called *kinematic mass* in order to distinguish it from the (rest) mass m_0 in the non relativistic theory. By convention, but mainly to be in the unison with non relativistic dynamics, the sign of the mass is chosen positive. However, this choice, if it is not treated carefully, may lead to missleading conclusions. In order to see this one derives the conservation law from that set of equations, by assuming that the force is a (negative) gradient of a scalar function $V\left(\overrightarrow{r}\right)$, the potential. By combining together the four equations one gets the fundamental relationship

$$p_4^2 - c^2 p^2 = m_0^2 c^4 \tag{5.47}$$

and from the fourth equation

$$p_4 = E - V$$

where E is defined as the total energy of the particle and it has arbitrary sign. As it was mentioned, the concept of momentum is important but it is velocity that has physical significance,[15] which is deduced from the relationship (5.47)

$$v = \frac{c^2}{|E-V|}\sqrt{\frac{1}{c^2}(E-V)^2 - c^2 m_0^2} \equiv \frac{p}{|m|} \tag{5.48}$$

In this relationship positive sign is implicitly assumed for the square root and also absolute value of mass. It follows from (5.48) that velocity is real in two disjoint intervals, which are divided by the interval where the square root is imaginary. This means that a particle could move even in the interval where its potential energy greatly exceeds its kinetic energy, which in non relativistic dynamics is forbidden, however, provided its mass is fixed positive. On the other hand if in non-relativistic dynamics mass is taken negative then in that region velocity is real. In order to bring the two findings in agreement velocity of the particle is defined more precisely as

$$v = \frac{c^2}{E-V}\left(\frac{E-V}{c} - cm_0\right)^{1/2}\left(\frac{E-V}{c} + cm_0\right)^{1/2}$$

This form has another important property, which must be satisfied in both classical and quantum dynamics, it is analytic function of the coordinates. Without satisfying it many erroneous conclusions are easily obtained.

Nonrelativistic limit is defined when kinetic energy of particle is much smaller than the energy equivalent of its rest mass $m_0 c^2$. Although one should also apply the same reasoning for the potential energy, however, for harmonic oscillator, in principle, the potential may go to infinity yet kinetic energy of the particle could

[15] One should be careful when using the term "physical significance", in this context it is meant that velocity does not have arbitrary signature whilst momentum does.

be non-relativistic. One writes $E = m_0c^2 + E_n$ and because E_n is small velocity is approximately

$$v \approx \frac{c^2}{-V + c^2 m_0}\sqrt{2cm_0 - \frac{V}{c}}\sqrt{\frac{E_n}{c} - \frac{V}{c}}$$

The expression simplifies further for small V, for example around the equilibrium point of harmonic oscillator, when $v \approx \sqrt{\frac{2}{m_0}}\sqrt{E_n - V}$, which is a well known expression for a particle whose total energy is E_n. On the other hand, when $V > 2m_0c^2$ then velocity is again real which agrees with the previous discussion about the sign for the mass of particle.

For potentials that go to infinity at large distances classical relativistic, but also non-relativistic, dynamics allows particle to move in two mutually disjoint regions of space. Between the two regions there is a barrier that prevents particle to get across from one to the other, however, in quantum dynamics the barrier is not the obstacle because of the tunneling effect. The implication is that such potentials do not support bound states.

It is entirely different situation with potentials that have finite well depth, for example harmonic potential that has a finite height V_0. For convenience one could shift the potential to have negative well depth $-V_0$ in which case if $-m_0c^2 < E < m_0c^2$ then particle could only move in one region and in this energy range particle is bound. For $E < -m_0c^2$ particle again could move in two space regions and for $E > m_0c^2$ it moves in the whole space.

If the well is very deep, and $|E|$ is smaller than m_0c^2 (bound state regime) then velocity of the particle is

$$v \approx c - \frac{m_0^2 c^5}{2V^2}$$

and its mass is $m \approx V/c^2$.

5.4.2.2 Quantum Dynamics

Strictly speaking bound state problems should be treated within quantum dynamics, and as discussed in Chap. 2 Dirac set of equations is the proper to use.[16] For a particle in a scalar potential V this set is (in the scaling with the Compton wave number for the electron)

$$\begin{aligned} i\partial_t F &= -i\vec{S}\cdot\nabla G + VF \ + F, \\ i\partial_t G &= -i\vec{S}\cdot\nabla F + VG \ - G. \end{aligned} \tag{5.49}$$

[16] Chapter 2 is devoted to relativistic dynamics, and here the emphasis is on bound states.

where F and G are two component single row matrices and the spin matrices $\vec{S}$ (details of Dirac equations are found in Sect. 2.3.4). This set is solved by writing

$$F = \int_{-\infty}^{\infty} de\, f\,(\vec{r}, e)\, e^{-iet}, \qquad G = \int_{-\infty}^{\infty} de\, g\,(\vec{r}, e)\, e^{-iet} \tag{5.50}$$

where now the functions f and g satisfy equations

$$ef = -i\vec{S} \cdot \nabla g + Vf \ + f, \qquad eg = -i\vec{S} \cdot \nabla f + Vg \ - g \tag{5.51}$$

For spherically symmetric potential solution is factored in a product of angular and radial functions

$$f\left(\overrightarrow{r}\right) = \frac{1}{r} F\,(r)\ \ \Omega\,(\theta, \phi)$$

and similarly for the function g.

Time evolution of the probability amplitude (5.50) for a spherically symmetric potential reduces to time evolution of its radial component. By omitting from analysis the angular functions, and by replacement $F \to F/r$ and $G \to G/r$ one has

$$F = \int_{-\infty}^{\infty} de\, A\,(e) f\,(r, e)\, e^{-iet}, \qquad G = \int_{-\infty}^{\infty} de\, B\,(e)\, g\,(r, e)\, e^{-iet}$$

If the radial functions are defined with the asymptotic limit $r \to \infty$ (it applies only for those that represent unbound states)

$$f\,(r, e) \Rightarrow \cos\left[r\sqrt{e^2 - 1} + \delta\,(e)\right] \qquad g\,(r, e) \Rightarrow \frac{\sqrt{e^2 - 1}}{1 + e} \sin\left[r\sqrt{e^2 - 1} + \delta\,(e)\right]$$

one shows that they are normalized as

$$\int_0^{\infty} dr\ \left[f\left(e'\right) f\,(e) + g\left(e'\right) g\,(e)\right] = \pi\sqrt{\frac{e-1}{e+1}}\,\delta\left(e' - e\right) \tag{5.52}$$

From their asymptotic limit one could also show that individual radial functions are normalized as

$$\lim_{r\to\infty} \int_0^R dr\, f\,(r, e) f\left(r, e'\right) = \frac{\pi\sqrt{e^2 - 1}}{2\,|e|}\left[\delta\left(e' - e\right) + \delta\left(e' + e\right)\right],$$

$$\lim_{r\to\infty} \int_0^R dr\, g\,(r, e)\, g\left(r, e'\right) = \frac{\pi\sqrt{e^2 - 1}}{2\,|e|}\left[\frac{e-1}{e+1}\delta\left(e' - e\right) - \delta\left(e' + e\right)\right]$$

which is consisted with the normalization (5.52). The coefficients are then

$$A(e) = \frac{|e|}{\pi\sqrt{e^2-1}} \int f(r,e)\, F_0(r)\ dr$$
$$B(e) = \frac{|e|}{\pi\sqrt{e^2-1}} \frac{e+1}{e-1} \int g(r,e)\, G_0(r)\ dr$$

which are only defined in the interval $|e| > 1$.

The details of how to find the angular functions, and what are the equations that the radial functions satisfy could be found in Sect. 2.3.4. Important term in the radial equations is the centrifugal energy having a general form as in non-relativistic dynamics, with one exception for the indices $\sigma = 1$ and $l = 0$ (these are defined in (2.61)) when it is zero. In this case one could show from (2.61) that $F(r)$ satisfies equation

$$d_r^2 F = \frac{(F - r d_r F)\, d_r V}{r\,(e - V\ + 1)} - \left[(e - V\ )^2 - 1\right] F \tag{5.53}$$

whilst the other function is

$$G = \frac{F - r d_r F}{r\,(e - V\ + 1)}$$

In the same spirit one could isolate the radial function G that corresponds to $\sigma = -1$ and $l = 1$ for which the equation is

$$d_r^2 G = \frac{(G - r d_r G)\, d_r V}{r\,(e - V\ - 1)} - \left[(e - V\ )^2 - 1\right] G$$

and

$$F = -\frac{G - r d_r G}{r\,(e - V\ - 1)}$$

Those equations do not include the centrifugal contribution, and its impact could be estimated from a simple model. Relativistic effects are expected for potentials of a small width, for example of the order 10^{-15} m, which is the scale of a nucleus. The lowest centrifugal energy is $E_c = 2\hbar^2/(mr^2)$ and for the assumed range of interaction its estimated value is $E_c \approx 2.7 \times 10^3$ MeV, which is so large that the only relevant equation to describe these systems is (5.53).

Often in the analysis of dynamics one uses model potentials with sharp edges, for example a square well. Sharp edges require the use of the connection formula that propagates the solution smoothly across it. In the nonrelativistic dynamics the connection is simple, the log-derivate of the probability amplitude upon crossing does not changes the value. However, in the relativistic dynamics this is not the case because in equation (5.53) there is derivative of potential that in the vicinity where the potential changes as the step function it is a delta function. If the potential makes a step from V_0 to zero at $r = r_0$ then in its vicinity equation (5.53) is approximately

$$d_r^2 F = -\frac{(F - r d_r F)\, V_0 \delta\,(r - r_0)}{r\,(e - V\ + 1)} - \left[(e - V\ )^2 - 1\right] F$$

and by integrating it from $r = r_0 - \varepsilon$ to $r = r_0 + \varepsilon$, where ε in the end is taken zero, then

$$d_r F^+ - d_r F^- \approx \frac{\left(F^- - \frac{r_0}{2}\left(d_r F^+ + d_r F^-\right)\right) V_0}{r_0\,(e - V_0/2\ + 1)}$$

where the signs $\pm$ refers to $r = r_0 \pm \varepsilon$, and for V at $r = r_0$ one takes the value $V_0/2$. In the limit $\varepsilon \to 0$ the last relationship is exact, from which one gets the connection formula

$$d_r F^+ = \frac{F^- V_0}{r_0\,(e + 1)} + \frac{e - V_0 + 1}{e + 1} d_r F^-$$

besides the one $F^+ = F^-$, which is implicitly assumed. This is relativistic generalization of the nonrelativistic connection formula (which is derived in the limit $e \to \infty$) for Dirac equation. The same steps could be repeated for the other function G, thus obtaining

$$d_r G^+ = \frac{G^- V_0}{r_0\,(e - 1)} + \frac{e - V_0 - 1}{e - 1} d_r G^-$$

These connection formulas are used for the analysis of bound states for a square well potential with the well depth V_0. For $r < r_0$ the radial function is

$$R\,(r) = \sin\,(rK) \tag{5.54}$$

for both indices σ, whilst $K = \sqrt{(e - V_0)^2 - 1}$. Thus $F\,(r) = R\,(r)$ for $\sigma = 1$ and

$$G = \frac{\sin\,(rK) - rK\cos\,(rK)}{r\,(e - V_0\ + 1)}$$

whilst $G\,(r) = R\,(r)$ is for $\sigma = -1$ and

$$F = -\frac{\sin\,(rK) - rK\cos\,(rK)}{r\,(e - V\ - 1)}$$

In the space $r > r_0$ the radial functions are

$$R\,(r) = a_s\, e^{rk} + b_s\, e^{-rk}$$

where s is the sign of mass and $k = \sqrt{1 - e^2}$. It should be recalled that $e^2 < 1$. The coefficients are calculated from the connection formula, thus the coefficient a_s is

$$2a_s e^{r_0 k} = \left(1 + \frac{V_0}{k r_0\,(e + s)}\right) \sin\,(r_0 K) + \left(1 - \frac{V_0}{e + s}\right) \frac{K\cos\,(r_0 K)}{k}$$

and condition for a bound state is that $a_s = 0$. For $|V_0|$ very large the approximate equation for the energies of these states is (V_0 is negative)

$$a_s \sim \cos(r_0 K) = 0$$

with the solution

$$r_0\sqrt{(e_n - V_0)^2 - 1} = \left(n + \frac{1}{2}\right)\pi \Rightarrow e_n = -|V_0| + \sqrt{\frac{\left(n + \frac{1}{2}\right)^2 \pi^2}{r_0^2} + 1} \quad (5.55)$$

where the integer n is chosen so that e_n is from that interval $-1 < e_n < 1$. On this level of approximation these energies are degenerate with respect to the sign s of the mass, and degenerate with respect to spin states (for their definition see 2.60).

For the bound states the coefficient b_s is exactly

$$b_s e^{-r_0 k} = \sin(r_0 K) \approx \pm 1$$

Typical graph for $-K^2$ is shown in Fig. 5.16 and in the space with the negative values classical trajectory for particle is real. For example when $e > 1$, or mc^2 in the non scaled variables, this is the whole range of the radial coordinate. On the other hand, for $e < -mc^2$ there are two disjoint intervals where this is the case and the shape of the curve is very much like in the nonrelativistic quantum dynamics when potential has a barrier. Particle could tunnel through this barrier and hence the potential does not support bound states, instead resonances are formed. For the sharp square well that is discussed here the width of this barrier is zero and therefore no resonances could be formed because of the their important property: their energy width is proportional to the tunneling probability.

Few general properties could be derived for the bound states from the assumption that the width of the potential is very small, and by that it is meant it is much smaller than the Compton wave length for the bound particle. If the potential is modelled by a square well then it means that in (5.55) there is inequality $r_0 << 1$. Very small space within which a bound state is formed means that the potential well should be deep,

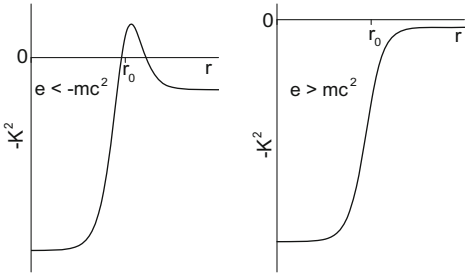

Fig. 5.16 Graph that shows classically allowed intervals of radial coordinates where particle could move for two energy intervals. The example is for a square well that is much deeper than the energy equivalent of its mass, and goes to zero beyond r_0

$V_0 >> 1$ in the model. The equation for the bound states then assumes approximate form

$$a_s \sim \frac{1}{r_0} \sin\left(r_0\left(e + |V_0|\right)\right) - |V_0| \cos\left(r_0\left(e + |V_0|\right)\right) = 0$$

where dependence on e is negligible because $|e| < 1$. It is, therefore, expected that the bound states energies are determined by $|V_0|$, and the role of e is marginal as long as it is from the interval $-1 < e < 1$.

There is, however, another important property of the relativistic bound states. On the approximate level probability density for bound states could be divided up into two regions, one inside the potential and the other outside of it, the tunneling space. If inside the potential probability density has constant value P and outside it is exponentially decaying then the total probability is

$$P\, r_0 + P \int_{r_0}^{\infty} dr\, e^{-2k(r-r_0)} = 1$$

where it is assumed that the probabilities connect smoothly across $r = r_0$. By calculating the integral the ratio of the two probabilities, that from outside to that within the potential, is

$$Q = \frac{1}{2kr_0} \tag{5.56}$$

which is large by the assumption that the Compton wave length is much larger than r_0. This means that finding particle outside the potential, in the tunneling space, is much larger than finding it inside.

Exact, numerical, calculation is done for the probability density in the Gaussian potential

$$V(r) = V_0 e^{-\frac{r^2}{r_0^2}}$$

by solving (5.53). The parameters are those that mimic the electron confined within the radius of a nucleus: $r_0 = 0.0025$ (approximately 10^{-15} m). For the chosen parameter r_0 bound state solution of (5.53) with no nodes (ground state, so to speak, but meaning the shallowest potential that supports a bound state) is not taken as an example but the one with 6 nodes. For the well depth $V_0 = -9116.91\ mc^2$ (m is mass of the electron and so the well depth is ≈4.7 GeV) energy of this bound state is $e = -0.9\ mc^2$. The probability density within the potential, and its tail within the tunneling space, is shown in Fig. 5.17, upper graph (the curve is not normalized as the probability density, for convenience of presentation). Its shape resembles that of classical probability density for a particle in a square well, it is constant with slight oscillations, which is in contrast with a nonrelativistic probability density that oscillates with a variable amplitude.

In the graph bellow in Fig. 5.17 the probability density is shown in all its extent, and as noticed it goes to the distance far exceeding r_0, in fact the average distance of the particle from the centre of potential is $r_{av} \approx 1.1 \approx 4.2 \times 10^{-13}$ m. This is more

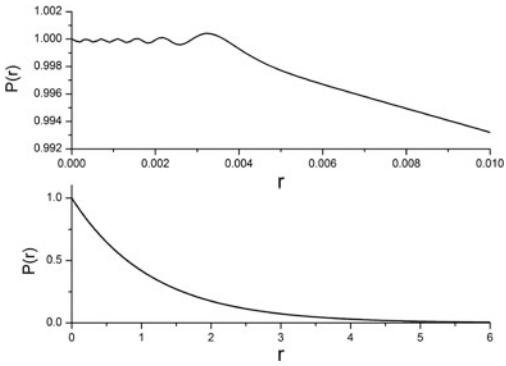

Fig. 5.17 Probability density

than 100 times larger than the range of potential, and this means that probability of finding particle within the tunneling space far exceeds the probability of finding it within $r = r_0$. The ration of the two probabilities is

$$Q = 381$$

and in fact it is almost independent of the order of a bound state. The estimate (5.56) gives ≈459, relatively a good guess, which depends very much on the choice of r_0 in its derivation. In any case, both results indicate that in fact the electron is not confined within the potential well, its presence could be noticed at distance that are relevant for the atomic structure.

Negative Energy States

Integration variable e in the solution (5.50) is defined in the whole interval from negative to positive values. However, for potentials that go to zero at infinity this energy range is interrupted for the values from the interval $-mc^2 < e < mc^2$, where solutions are either bound states or not defined. In the case of bound states the integral is replaced by a sum over the corresponding energy values. For a free particle, as the simplest example, the integral is split into two, one over the negative energies below $-mc^2$ and the other over the positive ones larger than mc^2. Negative energy states attract particular attention because for a free particle they do not appear to have much meaning, they appear as non-physical. It is shown here in the analysis for a free particle dynamics in one dimension that these states are essential when its motion is relativistic. For this example the set of Dirac equations is

$$i\partial_t F = -i\partial_z G + F \quad , \quad i\partial_t G = -i\partial_z F - G \tag{5.57}$$

where now F and G are ordinary functions. Solution for these functions is

$$F = \int_{-\infty}^{\infty} dp \left[a(p)\, e^{-ite(p)} + b(p)\, e^{ite(p)}\right] e^{ipz} \qquad (5.58)$$
$$G = \int_{-\infty}^{\infty} dp \left[c(p)\, e^{-ite(p)} + d(p)\, e^{ite(p)}\right] e^{ipz}$$

where $e = \sqrt{1+p^2}$. Integration variable is now changed from the energy to momentum in order to take explicitly into account two separate signs of energy. Components of the solution with $a(p)$ and $c(p)$ correspond to the positive energy states for $e > 1$ and those with $b(p)$ and $d(p)$ correspond to the negative ones for $e < -1$. If one assumes that the negative energy states are not physical, and they are omitted from expansion, then the "proper" solution is

$$F(z,t) = \int_{-\infty}^{\infty} dp\, a(p)\, e^{ipz - ite(p)} \qquad (5.59)$$

and the coefficient $a(p)$ is determined from the initial condition

$$F_0(z) = \int_{-\infty}^{\infty} dp\, a(p)\, e^{ipz} \Rightarrow a(p) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dz\ F_0(z) e^{-ipz} \qquad (5.60)$$

In order to understand the meaning of the "negative energy" states one chooses the initial probability amplitude that is zero outside certain interval in the coordinate z. The simplest choice is[17]

$$F_0(z) = \begin{cases} f(z) & ; \quad |z| < z_0 \\ 0 & ; \quad |z| > z_0 \end{cases} = \begin{cases} \left(z^2-1\right)^2 & ; \quad |z| < 1 \\ 0 & ; \quad |z| > 1 \end{cases} \qquad (5.61)$$

and the amplitude $a(p, z_0)$ is analytic in the complex p plane. If this were not the case, say the amplitude has a branch point in the half plane $\mathrm{Im}(p) > 0$, then for any $z > z_0$ in $F_0(z)$ one could not transform the integral in p along the path $\mathrm{Im}(p) \to \infty$ in order to get its zero value. Indeed for the explicit choice of $F_0(z)$ one gets

$$a(p, z_0) = -\frac{8}{\pi p^5}\left[3z_0 p \cos(z_0 p) + \left(z_0^2 p^2 - 3\right)\sin(z_0 p)\right]$$

which is indeed analytic in the whole p-plane. As the result for any $z > z_0$ the integral in p is transformed to the semi-circle $p = Pe^{i\beta}$, where $P \to \infty$, along which the integrand is zero and hence $F_0(z) = 0$, as it should. Similarly for $z < -z_0$ the integration path is transformed into the half plane $\mathrm{Im}(p) < 0$.

[17] When the probability amplitude is strictly zero outside certain finite nterval then it should also be zero at the end points of the interval, otherwise uncertainty principle is violated. For example, constant probability amplitude within the interval is not a physically acceptable choice.

Those observations about the general properties of $a(p)$ are essential for the time evolution of the probability amplitude $F(z,t)$. Physical requirement is that if this amplitude is strictly localized within the interval $|z| < z_0$ then at time t it cannot extend beyond the coordinates $|z| > z_0 + t$, i.e. it should be strictly zero there. However, this means that at any time the integrand in equation (5.59) should be analytic, but this is not the case because the function $e(p)$ introduces the branch points at $p = \pm i$. As the consequence $F(z,t)$ is not zero for large $|z|$ and the principle of Lorentz invariance is violated. This problem could only be remedied by introducing the "negative energy" component into the expansion of the solution of Dirac equation, because the combination of the two removes the branch points of $e(p)$.

In order to show that one needs both energy components to get physically acceptable solution of Dirac equation one first writes solutions (5.58) in the form that is consistent with the differential equations (5.57). These are

$$F = \int dp \left[a(p)\, e^{-ite(p)} - \frac{p}{e(p)+1} d(p)\, e^{ite(p)} \right] e^{ipz}$$
$$G = \int dp \left[\frac{p}{e(p)+1} a(p) e^{-ite(p)} + d(p)\, e^{ite(p)} \right] e^{ipz}$$

and if the initial functions are $F_0(z)$ and $G_0(z)$ then in terms of the coefficients

$$A(p) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dz\ F_0(z) e^{-ipz}$$
$$B(p) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dz\ G_0(z) e^{-ipz}$$

the solutions are

$$F = \int dp \left\{ \frac{e(p)\cos\left[te(p)\right] - i\sin\left[te(p)\right]}{e(p)} A(p) - \frac{ipB(p)}{e(p)} \sin\left[te(p)\right] \right\} e^{ipz}$$
$$G = \int dp \left\{ \frac{e(p)\cos\left[te(p)\right] + i\sin\left[te(p)\right]}{e(p)} B(p) - \frac{ipA(p)}{e(p)} \sin\left[te(p)\right] \right\} e^{ipz}$$

The integrand in both functions is an even function of $e(p)$, which means that the square root branch point is removed and it is analytic function in the whole p-plane. In this way physics of solution is preserved, but for that both "energy components" must be included.

As an illustrative example it is assumed that G is zero (initial probability current is zero), in which case

$$F(z,t) = \int dp \, \frac{e(p)\cos\left[te(p)\right] - i\sin\left[te(p)\right]}{e(p)} A(p)e^{ipz}$$
$$G(z,t) = -i\int dp \, \frac{pA(p)}{e(p)} \sin\left[te(p)\right] e^{ipz}$$

For the initial F one chooses (5.61) when

$$A(p) = -\frac{8}{p^5\pi}\left[3p\cos p + \left(p^2-3\right)\sin p\right]$$

but the integrals do not have solution in a closed form. Probability density

$$P(z,t) = |F(z,t)|^2 + |G(z,t)|^2$$

that is calculated numerically at $t = 8$ is shown in Fig. 5.18 by solid line (initial probability density is shown by broken line). It is strictly zero beyond the interval $|z| > 9$, as it should from the requirement of the Lorentz invariant dynamics.

It was shown that the negative energy components are essential for getting physically correct solution of Dirac equation. The question is if these components are always required for solving Lorentz invariant dynamics? The answer depends very much on the initial probability amplitudes F and G, which if they are strictly localized within certain interval negative energy components cannot be avoided. However, if this requirement is relaxed by allowing the amplitudes to have infinite extent then indeed one could have solution of Dirac equation with only a single energy component, say positive, in which case

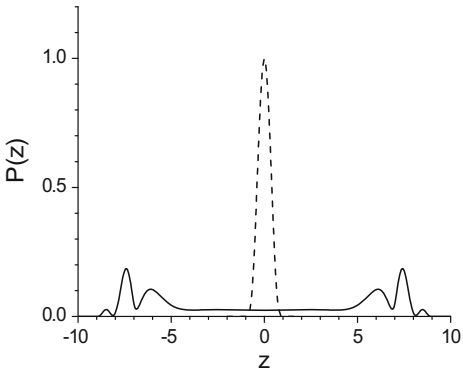

Fig. 5.18 Probability density in Lorentz invariant dynamics, which is initially strictly zero outside the interval $|z| < 1$ (*dashed line*), after time $t = 8$ (*solid line*)

$$F = \int dp\, a(p)\, e^{-ite(p)} e^{ipz} \quad , \quad G = \int dp\, \frac{e(p)-1}{p} a(p) e^{-ite(p)} e^{ipz}$$

From the structure of the integrand in G it is explicitly evident that having a single energy component in solution one cannot form the initial probability density other than of the infinite extent. In fact the square root branch point of $e(p)$ determines the asymptotic form of this probability density, which is of the order

$$P(z) \underset{|z|\to\infty}{\sim} e^{-|z|}$$

Possibility of solution with only single energy component does not invalidate previous remark that both components are required for getting physically correct solution. The latter applies to the examples where the Lorentz invariance is directly tested, but if this is not possible, such as when the probability density has infinite extent, then single energy component solutions are also acceptable. The only problem is how does one form such states, but this is the matter of other discussion.

5.4.3 Charge Density

When two oppositely charged particles are bound together there is separation of charge density within the system, as discussed in Sect. 1.2.3. It is shown that the separation depends on the mass ratio between the two charges, two examples of Hydrogen and Muonic Hydrogen showed that. However, there are two approximations made in that analysis, one is that position of the centre of mass of the system is delta function and the other is that relativistic effects on the mass of particles is not taken into account. The choice of delta function for the position of the centre of mass is in direct contradiction with the nonrelativistic approximation, the width in the momentum distribution is infinite.

Charge distribution for two oppositely charged particles that are bound together is analyzed here by amending previously mentioned drawbacks in the case of a Hydrogen-like atom. Two particles, one with the mass of the electron and the other with that of proton, are interacting through a scalar potential.[18] The model lacks rigor if it is not analyzed in the Lorentz invariant dynamics, but in this case one confronts four important obstacles. The most obvious is that proper Lorentz invariant interaction between the two partners is not taken into account because scalar potential[19] should be properly generalized for the systems where a typical velocity is nearly the speed of light. Generalization from the scalar potential towards the Lorentz invariant four vector interaction is not a unique procedure, for example, Maxwell equations

[18] This choice is inspired by measurement of the charge density in neutron [20], and as the model it is assumed that it is result of bound state of the electron and proton.

[19] Scalar interaction could be Lorentz invariant if it is function of the Lorentz scalar, which in this case this is not the case. The interaction is function of the relative distance of two particles.

could be derived from the Coulomb potential, but only if certain additional constraints are assumed [9].

The second problem is the question of defining the centre of mass of the system, which was discussed earlier in this chapter.

The third problem is even more serious. Interaction among particles are delayed, e.g. in analysis of Hydrogen atom one should in principle take into account delay of interaction due to the finite speed of electromagnetic field. The delay is in this case negligible because (a) velocity of the electron is less than 1% of c and (b) proton is assumed to be infinitely massive and so dynamics around the common centre of mass is negligible (motion around this centre results in the time variation of the Coulomb interaction and hence delay). In the case when particles move fast, and there is no apparent stationary centre of mass, this delay could affect dynamics in an essential way.

The fourth problem is that in relativistic dynamics one works with four coordinates, space and time define whereabouts of a particle and therefore for two particles there are two separates sets of these variables. In classical relativistic dynamics one defines invariant time that is universal for both particles, in terms of which their equations of motion are solved. In quantum relativistic dynamics it is not clear what analogous "time variable" should be. It is assumed here that ordinary time variable is universal for both particles, in fact only stationary states are analyzed when it does not enter the equations.

Proper formulation of Lorentz invariant dynamics for two particles therefore appears an impossible task, especially in the view of the fourth comment. However under some conditions one could formulate a solvable model but it is not strictly Lorentz invariant. One assumption is that stationary systems are studied when the time component is not present and the second is that the particles interact by a scalar potential that is function of their relative distance.

As it had been discussed proper quantum relativistic treatment is by Dirac equation, however, its generalization for two particle interaction is not straightforward. One way to derive it for the previous assumptions is to start from the nonrelativistic equation for stationary states for two particles

$$ef = -\frac{\hbar^2}{2m_1}\Delta_1 f - \frac{\hbar^2}{2m_2}\Delta_2 f + V\left(\overrightarrow{r}_2 - \overrightarrow{r}_1\right) f$$

The equation could be put in a set of first order equations in the space variables

$$\begin{aligned} eF &= -i\hbar\left(\overrightarrow{\Sigma}_1 \cdot \nabla_{s_1} + \overrightarrow{\Sigma}_2 \cdot \nabla_{s_2}\right) G + VF \\ G &= -\frac{i\hbar}{2m}\left(\overrightarrow{\Sigma}_1 \cdot \nabla_{s_1} + \overrightarrow{\Sigma}_2 \cdot \nabla_{s_2}\right) F \end{aligned} \tag{5.62}$$

where F and G are single column matrices and the number of rows depends on the properties of the matrices $\overrightarrow{\Sigma}_1$ and $\overrightarrow{\Sigma}_2$. The parameter m plays the role of mass and its value is as yet arbitrary. These matrices are defined by the requirements

$$\vec{\Sigma}_1 \vec{\Sigma}_1 = \vec{\Sigma}_2 \vec{\Sigma}_2 = I$$
$$\vec{\Sigma}_1 \vec{\Sigma}_2 + \vec{\Sigma}_2 \vec{\Sigma}_1 = 0$$

and for one dimensional model they are

$$\Sigma_1 = \begin{vmatrix} 1 & 0 \\ 0 & -1 \end{vmatrix} \quad , \quad \Sigma_2 = \begin{vmatrix} 0 & 1 \\ 1 & 0 \end{vmatrix} \tag{5.63}$$

for two dimensional model

$$\Sigma_{1x} = i\gamma_x \quad , \quad \Sigma_{1y} = i\gamma_y \quad , \quad \Sigma_{2x} = i\gamma_z \quad , \quad \Sigma_{2y} = \begin{vmatrix} 0 & I \\ I & 0 \end{vmatrix}$$

and three dimensional model

$$\vec{\Sigma}_1 = \begin{vmatrix} 0 & -\vec{\gamma} \\ \vec{\gamma} & 0 \end{vmatrix} \quad ,$$
$$\Sigma_{2x} = \begin{vmatrix} 0 & 0 & I & 0 \\ 0 & 0 & 0 & I \\ I & 0 & 0 & 0 \\ 0 & I & 0 & 0 \end{vmatrix} \quad , \quad \Sigma_{2y} = \begin{vmatrix} 0 & 0 & iI & 0 \\ 0 & 0 & 0 & -iI \\ -iI & 0 & 0 & 0 \\ 0 & iI & 0 & 0 \end{vmatrix} \quad ,$$
$$\Sigma_{2z} = \begin{vmatrix} 0 & 0 & 0 & iI \\ 0 & 0 & iI & 0 \\ 0 & -iI & 0 & 0 \\ -iI & 0 & 0 & 0 \end{vmatrix}$$

where the gamma matrices are defined in (2.4) and I is two dimensional unit matrix. The scaled coordinates $\vec{s}_2$ and $\vec{s}_1$ are defined as

$$\vec{s}_1 = \sqrt{\mu_1}\vec{r}_1 \quad , \quad \vec{s}_2 = \sqrt{\mu_2}\vec{r}_2$$

where μ_1 and μ_2 are dimensionless parameters, masses of the two particles that are normalized with respect to m. The set (5.62) is generalized into the Lorentz invariant form in the same manner as it is done for a single particle, with the final result

$$eF = -i\hbar c\left(\vec{\Sigma}_1 \cdot \nabla_{s_1} + \vec{\Sigma}_2 \cdot \nabla_{s_2}\right) G + VF + mc^2 F \tag{5.64}$$
$$eG = -i\hbar c\left(\vec{\Sigma}_1 \cdot \nabla_{s_1} + \vec{\Sigma}_2 \cdot \nabla_{s_2}\right) F + VG - mc^2 G$$

By defining new coordinates

$$\vec{r} = \vec{r}_2 - \vec{r}_1 = \frac{\vec{s}_2}{\sqrt{\mu_2}} - \frac{\vec{s}_1}{\sqrt{\mu_1}} \quad , \quad \vec{R} = a\vec{s}_1 + b\vec{s}_2$$

where the parameters a and b are determined later, the set of equations transforms into

$$eF = i\hbar c\left[\overrightarrow{\Sigma}\cdot\nabla_r - \overrightarrow{\Sigma}_c\cdot\nabla_R\right]G + VF + mc^2F$$
$$eG = i\hbar c\left[\overrightarrow{\Sigma}\cdot\nabla_r - \overrightarrow{\Sigma}_c\cdot\nabla_R\right]F + VG - mc^2G$$

where

$$\overrightarrow{\Sigma} = \frac{1}{\sqrt{\mu_1}}\overrightarrow{\Sigma}_1 - \frac{1}{\sqrt{\mu_2}}\overrightarrow{\Sigma}_2 \quad , \quad \overrightarrow{\Sigma}_c = a\overrightarrow{\Sigma}_1 + b\overrightarrow{\Sigma}_2$$

and the matrices have the property

$$\overrightarrow{\Sigma}\cdot\overrightarrow{p}\ \overrightarrow{\Sigma}\cdot\overrightarrow{p} = \frac{\mu_2+\mu_1}{\mu_2\mu_1}p^2 \quad , \quad \overrightarrow{\Sigma}_c\cdot\overrightarrow{p}\ \ \overrightarrow{\Sigma}_c\cdot\overrightarrow{p} = \left(a^2+b^2\right)\ p^2$$

The two equations are transformed into a single one and for a spherically symmetric potential it is

$$c^2\hbar^2\frac{\mu_2+\mu_1}{\mu_2\mu_1}\Delta_rF + \frac{c^2\hbar^2}{\mu_1+\mu_2}\Delta_RF + \frac{c^2\hbar^2\ \Sigma_r\partial_rV}{e-V+mc^2}\left(\overrightarrow{\Sigma}\cdot\nabla_rF - \overrightarrow{\Sigma}_c\cdot\nabla_RF\right)$$
$$= -\left[(e-V)^2 - m^2c^4\right]F \tag{5.65}$$

and

$$G = \frac{i\hbar c}{e-V+mc^2}\left[\overrightarrow{\Sigma}\cdot\nabla_r - \overrightarrow{\Sigma}_c\cdot\nabla_R\right]F$$

In the derivation it was assumed that

$$\overrightarrow{\Sigma}\cdot\nabla_r\overrightarrow{\Sigma}_c\cdot\nabla_R + \overrightarrow{\Sigma}_c\cdot\nabla_R\overrightarrow{\Sigma}\cdot\nabla_r = 0$$

from where the parameters a and b are determined

$$a = \frac{\sqrt{\mu_1}}{\mu_1+\mu_2} \quad , \quad b = \frac{\sqrt{\mu_2}}{\mu_1+\mu_2}$$

Equation (5.65) resembles two body equation in the center of mass coordinates, except for the term containing spin matrices $\overrightarrow{\Sigma}$ and $\overrightarrow{\Sigma}_c$. However, even without this term separation of solution into two independent for the relative and the centre of mass coordinates is not straightforward, as it is in the non relativistic dynamics. Before further discussion it is advatnageous to introduce scaling that would simplify equations. The dimensionless mass μ_1 is set to unity $\mu_1 = 1$, meaning that $m = m_1$ is assumed. It is also assumed that μ_2 is larger than μ_1 in which case one parametrizes

$\mu_2 = 1/\varepsilon^2$ where ε plays the role of perturbation parameter. Energy is scaled with respect to mc^2 and the coordinate with respect to the Compton wave number. Equation (5.65) is now

$$\left(1+\varepsilon^2\right)\Delta_r F + \frac{\varepsilon^2}{1+\varepsilon^2}\Delta_R F + \frac{\partial_r V}{e-V+1}\Sigma_r\left(\overrightarrow{\Sigma}\cdot\nabla_r F - \overrightarrow{\Sigma}_c\cdot\nabla_R F\right) = -\left[(e-V)^2-1\right]F \tag{5.66}$$

For further analysis the spin matrices $\overrightarrow{\Sigma}$ and $\overrightarrow{\Sigma}_c$ should be represented in the spherical coordinates, and it could be shown that for the relative coordinates spherical components of $\overrightarrow{\Sigma}$ are

$$\Sigma_n = \begin{vmatrix} 0 & \sigma_n \\ \widetilde{\sigma}_n^* & 0 \end{vmatrix} \quad ; \quad n = r, \theta, \phi$$

where σ_n are 4×4 matrices that are defined as

$$\sigma_r = -\gamma_r - \varepsilon \begin{vmatrix} I_2\sin\theta e^{i\phi} & iI_2\cos\theta \\ iI_2\cos\theta & I_2\sin\theta e^{-i\phi} \end{vmatrix},$$
$$\sigma_\theta = -\gamma_\theta + \varepsilon \begin{vmatrix} -I_2\cos\theta e^{i\phi} & iI_2\sin\theta \\ iI_2\sin\theta & -I_2\cos\theta e^{-i\phi} \end{vmatrix},$$
$$\sigma_\phi = -\gamma_\phi + \varepsilon \begin{vmatrix} -iI_2 e^{i\phi} & 0 \\ 0 & iI_2 e^{-i\phi} \end{vmatrix}$$

where I_o is a $o\times o$ unit matrix and γ_n are defined in (2.5). The matrices Σ_n are normalized as

$$\Sigma_n\Sigma_n = 1+\varepsilon^2$$

Similarly one could show that for the spherical components of $\overrightarrow{\Sigma}_c$ the matrices σ_n are replaced by

$$\sigma_R = -\frac{\varepsilon^2}{1+\varepsilon^2}\gamma_R + \frac{\varepsilon}{1+\varepsilon^2}\begin{vmatrix} I_2\sin\theta e^{i\phi} & iI_2\cos\theta \\ iI_2\cos\theta & I_2\sin\theta e^{-i\phi} \end{vmatrix},$$
$$\sigma_\Theta = -\gamma_\Theta + \varepsilon \begin{vmatrix} -I_2\cos\theta e^{i\phi} & iI_2\sin\theta \\ iI_2\sin\theta & -I_2\cos\theta e^{-i\phi} \end{vmatrix},$$
$$\sigma_\Phi = -\gamma_\Phi + \varepsilon \begin{vmatrix} -iI_2 e^{i\phi} & 0 \\ 0 & iI_2 e^{-i\phi} \end{vmatrix}$$

It should be noted that because of the structure of the Σ_n matrices the set of eight equations (5.66) de-couples into two sets with four equations. The two sets are coupled only if external field is included that couples the spin of particles.

The set (5.66) de-couples radial and angular components only if solution F is eigenfunction of three angular momentum operators: two for the angular momentum squared operators in the kinetic energies of the relative and the centre of mass

coordinates, and the angular part of the operator

$$\Sigma_r \left(\overrightarrow{\Sigma} \cdot \nabla_r - \overrightarrow{\Sigma}_c \cdot \nabla_R \right) = \left(1 + \varepsilon^2\right) \partial_r - \Sigma_r \Sigma_R \partial_R$$
$$+ \frac{1}{r} \Sigma_r \left(\Sigma_\theta \partial_\theta + \frac{\Sigma_\phi}{\sin\theta} \partial_\phi \right) - \frac{1}{r} \Sigma_r \left(\Sigma_\Theta \partial_\Theta + \frac{\Sigma_\Phi}{\sin\Theta} \partial_\Phi \right)$$

From the form of the operator it is evident that the radial center of mass coordinate is coupled to the angular coordinates for both the centre of mass and the relative coordinates, as it was qualitatively argued before. As the result the radial and angular motions cannot be de-coupled. Nevertheless one solves the set by deriving a complete set of angular functions for one of the set of coordinates, for example for the relative ones, and the complete solution is then expand in this bases. For the remaining coordinates the resulting set of equations is solved numerically.

Angular eigenfunctions for the relative coordinates satisfy the eigenvalue equation (in addition they also satisfy eigenvalue equation for the angular part of the kinetic energy operator for the relative motion)

$$\Sigma_r \left(\Sigma_\theta \partial_\theta + \frac{\Sigma_\phi}{\sin\theta} \partial_\phi \right) \Omega = \lambda_r \Omega$$

where Ω is a single column matrix with 8 elements. If the elements are parametrized as

$$\Omega_j = P_j(\theta)\, e^{i\mu_j \phi}$$

then the eigenvalue equation becomes

$$\Sigma_r \left(\Sigma_\theta \partial_\theta + \frac{i\Sigma_\phi}{\sin\theta} M \right) P = \lambda_r P$$

where M is a diagonal matrix with the elements

$$M_{j,j} = m\,\delta_{j,1} + (m+1)\,\delta_{j,2} + (m-1)\,\delta_{j,3} + m\,\delta_{j,4} + (m-1)\,\delta_{j,5}$$
$$+ m\,\delta_{j,6} + m\,\delta_{j,7} + (m+1)\,\delta_{j,8}$$

It is convenient to define new matrix A such that the eigenvalue equation is parametrized as

$$A \left(\Sigma_\phi \partial_\theta - \frac{i\Sigma_\theta}{\sin\theta} M \right) P = \lambda_r P$$

and in the next step one transforms the solution by defining an 8×8 transformation matrix Υ whose elements are

$$\Upsilon_{i,j} = \delta_{i,1}\delta_{j,1} + \delta_{i,2}\delta_{j,4} + \delta_{i,3}\delta_{j,2} + \delta_{i,4}\delta_{j,3} + \delta_{i,5}\delta_{j,6} + \delta_{i,6}\delta_{j,7} + \delta_{i,7}\delta_{j,8} + \delta_{i,8}\delta_{j,5}$$

In the new basis the transformed eigenfunction and the other components in the eigenvalue equation are

$$O = \Upsilon P \quad , \quad \Sigma_n^{\Upsilon} = \Upsilon \Sigma_n \Upsilon^{-1} \quad , \quad A^{\Upsilon} = \Upsilon A \Upsilon^{-1}$$

where

$$A^{\Upsilon} = \begin{vmatrix} 0 & \alpha & 0 & 0 \\ -\widetilde{\alpha}^* & 0 & 0 & 0 \\ 0 & 0 & 0 & \beta \\ 0 & 0 & -\widetilde{\beta}^* & 0 \end{vmatrix} \quad , \quad A_R^{\Upsilon} = \frac{i\varepsilon}{1+\varepsilon^2} \begin{vmatrix} 0 & \alpha & 0 & 0 \\ \widetilde{\alpha}^* & 0 & 0 & 0 \\ 0 & 0 & 0 & \beta \\ 0 & 0 & \widetilde{\beta}^* & 0 \end{vmatrix}$$

where

$$\alpha = \begin{vmatrix} \frac{2\varepsilon}{\varepsilon+i} & \frac{1-\varepsilon^2}{\varepsilon+i} \\ \frac{\varepsilon^2-1}{\varepsilon+i} & \frac{2\varepsilon}{\varepsilon+i} \end{vmatrix} \quad , \quad \beta = \begin{vmatrix} 0 & -i-\varepsilon \\ i+\varepsilon & 0 \end{vmatrix}$$

In this form the set of equations is block diagonal, where on the diagonal are 4×4 matrices, so that finally the set of equations is in the matrix form

$$\partial_\theta \begin{vmatrix} O^{(1)} \\ O^{(2)} \end{vmatrix} = \begin{vmatrix} U^{(1)} & 0 \\ 0 & U^{(2)} \end{vmatrix} \begin{vmatrix} O^{(1)} \\ O^{(2)} \end{vmatrix}$$

or

$$\partial_\theta O^{(n)} = U^{(n)} O^{(n)}$$

Each $O^{(n)}$ could be divided up into 2×2 block matrices and for these the set of equations to be solved is

$$\begin{aligned} \partial_\theta O_1^{(n)} &= U_{1,1}^{(n)} O_1^{(n)} + U_{1,2}^{(n)} O_2^{(n)} \\ \partial_\theta O_2^{(n)} &= U_{2,1}^{(n)} O_1^{(n)} + U_{2,2}^{(n)} O_2^{(n)} \end{aligned}$$

From the first equation

$$O_2^{(n)} = U_{1,2}^{(n)-1} \left[\partial_\theta O_1^{(n)} - U_{1,1}^{(n)} O_1^{(n)} \right]$$

and by replacing it in the second the equation to be solved is

$$\begin{aligned} &\partial_\theta^2 O_1^{(n)} - \left[U_{1,1}^{(n)} + U_{1,2}^{(n)} U_{2,2}^{(n)} U_{1,2}^{(n)-1} \right] \partial_\theta O_1^{(n)} \\ &- \left[\partial_\theta U_{1,1}^{(n)} + U_{1,2}^{(n)} U_{2,1}^{(n)} - U_{1,2}^{(n)} U_{2,2}^{(n)} U_{1,2}^{(n)-1} U_{1,1}^{(n)} \right] O_1^{(n)} = 0 \end{aligned}$$

The set of two equations is de-coupled and the solutions are Legendre polynomials from which the eigenvalues are

$$\lambda_r = -\left(1+\varepsilon^2\right) l_r \quad ; \quad l_r = l, \ -l-1$$

where $l = 0, 1, 2, \ldots$ Solution, for example for $\Omega^{(1)}$, when all the back transformations are made, is

$$\Omega^{(1)} = \begin{vmatrix} c_1 Y_l^m(\theta,\phi) \\ \frac{i(c_1+\varepsilon c_2)\sqrt{(l-m)(l+1+m)}}{(i-\varepsilon)(l_r+m+1)} Y_l^{m+1}(\theta,\phi) \\ \frac{i(c_2-\varepsilon c_1)\sqrt{(l+m)(l+1-m)}}{(i-\varepsilon)(l_r-m+1)} L_l^{m-1}(\cos\theta) \\ c_2 Y_l^m(\theta,\phi) \end{vmatrix}$$

which is determined by four "quantum numbers", the choice for l_r and the constants c_1 and c_2. The same also applies for $\Omega^{(2)}$. The constants c_n are determined by requiring that the solutions are ortho-normal for any combination of the "quantum numbers", and when this is imposed on them the solutions are

$$\Omega^{(1)}_{s_l,s} = \begin{vmatrix} \frac{\varepsilon\sqrt{2l+1-(2m-1)s_l}+is\sqrt{2l+1+(2m+1)s_l}}{2\sqrt{2}\sqrt{1+\varepsilon^2}\sqrt{2l+1}} Y_l^m(\theta,\phi) \\ \frac{ss_l\sqrt{1+\varepsilon^2}\sqrt{(l-m)(l+m+1)}}{(-i+\varepsilon)\sqrt{2}\sqrt{2l+1}\sqrt{2l+1+(2m+1)s_l}} Y_l^{m+1}(\theta,\phi) \\ \frac{is_l\sqrt{1+\varepsilon^2}\sqrt{(l+m)(l-m+1)}}{(-i+\varepsilon)\sqrt{2}\sqrt{2l+1}\sqrt{2l+1-(2m-1)s_l}} Y_l^{m-1}(\theta,\phi) \\ -\frac{\sqrt{2l+1-(2m-1)s_l}-is\varepsilon\sqrt{2l+1+(2m+1)s_l}}{2\sqrt{2}\sqrt{1+\varepsilon^2}\sqrt{2l+1}} Y_l^m(\theta,\phi) \end{vmatrix}$$

and

$$\Omega^{(2)}_{s_l,s} = \begin{vmatrix} \frac{is_l\sqrt{1+\varepsilon^2}\sqrt{(l+m)(l-m+1)}}{(i+\varepsilon)\sqrt{2}\sqrt{2l+1}\sqrt{2l+1-(2m-1)s_l}} Y_l^{m-1}(\theta,\phi) \\ \frac{\sqrt{2l+1-(2m-1)s_l}+is\varepsilon\sqrt{2l+1+(2m+1)s_l}}{2\sqrt{2}\sqrt{1+\varepsilon^2}\sqrt{2l+1}} Y_l^m(\theta,\phi) \\ -\frac{\varepsilon\sqrt{2l+1-(2m-1)s_l}-is\sqrt{2l+1+(2m+1)s_l}}{2\sqrt{2}\sqrt{1+\varepsilon^2}\sqrt{2l+1}} Y_l^m(\theta,\phi) \\ \frac{ss_l\sqrt{1+\varepsilon^2}\sqrt{(l-m)(l+m+1)}}{(i+\varepsilon)\sqrt{2}\sqrt{2l+1}\sqrt{2l+1+(2m+1)s_l}} Y_l^{m+1}(\theta,\phi) \end{vmatrix}$$

where s_l takes values ± 1 that correspond to l or $-l-1$, respectively. Likewise s also takes values ± 1 that correspond to two linearly independent choices of coefficients c_n.

Equation (5.66) in the expanded form is now

$$\begin{aligned} &\left(1+\varepsilon^2\right)\Delta_r F + \frac{\left(1+\varepsilon^2\right)\partial_r V}{e-V+1}\partial_r F + \frac{\partial_r V}{r\,(e-V+1)}\Sigma_r\left(\Sigma_\theta\partial_\theta + \frac{\Sigma_\phi}{\sin\theta}\partial_\phi\right)F \\ &+ \frac{\varepsilon^2}{1+\varepsilon^2}\Delta_R F - \frac{\partial_r V}{e-V+1}\Sigma_r\Sigma_R\partial_R F - \frac{\partial_r V}{r\,(e-V+1)}\Sigma_r\left(\Sigma_\Theta\partial_\Theta + \frac{\Sigma_\Phi}{\sin\Theta}\partial_\Phi\right)F \\ &= -\left[(e-V)^2-1\right]F \end{aligned}$$

and one way of solving it is to represent the solution in the series

$$F = \sum_{l,m,s_l,s} G_{l,m,s_l,s}\Omega^{(n)}_{l,m,s_l,s}(\theta,\phi)$$

when the coefficients $G_{l,m,s_l,s}(r, R, \Theta, \Phi)$ satisfy the set of multichannel equations

$$\frac{\left(1+\varepsilon^2\right)}{r^2}\partial_r\left(r^2\partial_r\right)G_{l,m,s_l,s} - \frac{\left(1+\varepsilon^2\right)l\,(l+1)}{r^2}G_{l,m,s_l,s}$$
$$+\frac{\left(1+\varepsilon^2\right)\partial_r V}{e-V+1}\partial_r G_{l,m,s_l,s} + \frac{\partial_r V}{r\,(e-V+1)}\lambda_r G_{l,m,s_l,s}$$
$$+\frac{\varepsilon^2}{1+\varepsilon^2}\Delta_R G_{l,m,s_l,s} - \frac{\partial_r V}{e-V+1}\sum_{l,'m,'s_l',s'}\partial_R G_{l,'m,'s_l',s'}T_{(l,m,s_l,s),\left(l,'m,'s_l',s'\right)}(\Theta,\Phi)$$
$$-\frac{\partial_r V}{r\,(e-V+1)}\sum_{l,'m,'s_l',s'}\widehat{Q}_{(l,m,s_l,s),\left(l,'m,'s_l',s'\right)}G_{l,'m,'s_l',s'} = -\left[(e-V)^2-1\right]G_{l,m,s_l,s}$$

where

$$T_{(l,m,s_l,s),\left(l,'m,'s_l',s'\right)}(\Theta,\Phi) = \int d\theta\, d\phi\, \Omega^{(n)+}_{l,m,s_l,s}(\theta,\phi)\,\Sigma_r\Sigma_R\Omega^{(n)}_{l,'m,'s_l',s'}(\theta,\phi)\sin\theta$$

and

$$\widehat{Q}_{(l,m,s_l,s),\left(l,'m,'s_l',s'\right)} = \int d\theta\, d\phi\, \Omega^{(n)+}_{l,m,s_l,s}(\theta,\phi)\,\Sigma_r\left(\Sigma_\Theta\partial_\Theta + \frac{\Sigma_\Phi}{\sin\Theta}\partial_\Phi\right)\Omega^{(n)}_{l,'m,'s_l',s'}(\theta,\phi)\sin\theta$$

Solving the set is quite a demanding task, but for the physical content of the solution it is instructive to solve much simpler one dimensional problem.

5.4.3.1 One Dimensional Model

One dimensional dynamics of two bodies that interact by a bounding potential is described by equations

$$eF = i\left(\Sigma\partial_x - \Sigma_X\partial_X\right)G + VF + F$$
$$eG = i\left(\Sigma\partial_x - \Sigma_X\partial_X\right)F + VG - G$$

that are reduced from the set (5.64) to single dimension. The matrices are

$$\Sigma = \Sigma_1 - \varepsilon\Sigma_2 = \begin{vmatrix} 1 & -\varepsilon \\ -\varepsilon & -1 \end{vmatrix},$$
$$\Sigma_X = \frac{\varepsilon^2}{1+\varepsilon^2}\Sigma_1 + \frac{\varepsilon}{1+\varepsilon^2}\Sigma_2 = \frac{\varepsilon}{1+\varepsilon^2}\begin{vmatrix} \varepsilon & 1 \\ 1 & -\varepsilon \end{vmatrix}$$

where Σ_1 and Σ_2 are defined in (5.63). Solution is represented in the form

$$F(x,X) = \int dk\, A(k)\, e^{ikX} f(x,k) \qquad (5.67)$$
$$G(x,X) = \int dk\, A(k)\, e^{ikX} g(x,k)$$

where now the functions f and g satisfy equations

$$ef = i(\Sigma\partial_x - ik\Sigma_X)g + Vf + f$$
$$eg = i(\Sigma\partial_x - ik\Sigma_X)f + Vg - g$$

or in a more explicit form

$$\partial_x g - \frac{ik\varepsilon}{1+\varepsilon^2}\begin{vmatrix} 0 & 1 \\ -1 & 0 \end{vmatrix} g - i\frac{V+1-e}{1+\varepsilon^2}\begin{vmatrix} 1 & -\varepsilon \\ -\varepsilon & -1 \end{vmatrix} f = 0 \qquad (5.68)$$
$$\partial_x f - \frac{ik\varepsilon}{1+\varepsilon^2}\begin{vmatrix} 0 & 1 \\ -1 & 0 \end{vmatrix} f - i\frac{V-1-e}{1+\varepsilon^2}\begin{vmatrix} 1 & -\varepsilon \\ -\varepsilon & -1 \end{vmatrix} g = 0$$

The amplitude $A(k)$ determines the probability amplitude for the system as the whole, for example, for the Hydrogen atom that would be the delocalization of the atom as the whole.

The system of two equations is reduced to a single of the second order by replacing g from the second equation

$$g = \frac{i}{V-1-e}\begin{vmatrix} -1 & \varepsilon \\ \varepsilon & 1 \end{vmatrix}\partial_x f - \frac{k\varepsilon}{(V-1-e)\left(1+\varepsilon^2\right)}\begin{vmatrix} \varepsilon & 1 \\ 1 & -\varepsilon \end{vmatrix} f \qquad (5.69)$$

in the first equation, giving equation for f

$$f'' = -\frac{V'}{1+e-V}f' + \frac{1-(e-V)^2 + \frac{\varepsilon^2}{(1+\varepsilon^2)}k^2}{1+\varepsilon^2}f \qquad (5.70)$$
$$+\frac{i\varepsilon k V'}{\left(1+\varepsilon^2\right)(1+e-V)}\begin{vmatrix} 0 & 1 \\ -1 & 0 \end{vmatrix} f$$

The set is decoupled into two independent equations by diagonalizing the coupling matrix

$$U^+\begin{vmatrix} 0 & 1 \\ -1 & 0 \end{vmatrix} U = \begin{vmatrix} i & 0 \\ 0 & -i \end{vmatrix}$$

where

$$U = \frac{1}{\sqrt{2}}\begin{vmatrix} 1 & i \\ i & 1 \end{vmatrix}$$

and by parametrizing $f(x) = Uf_T(x)$ the equation (5.70) transforms into

$$f_T'' = -\frac{V'}{1+e-V}f_T' + \frac{1-(e-V)^2+\frac{\varepsilon^2}{(1+\varepsilon^2)}k^2}{1+\varepsilon^2}f_T - \frac{\varepsilon k V'}{\left(1+\varepsilon^2\right)(1+e-V)}\begin{vmatrix}1 & 0\\ 0 & -1\end{vmatrix}f_T$$

Solutions are degenerate with respect to the change in sign of k, and they are selected by initial conditions, thus $f_T^{(+)}$ is zero in the lower component (f_T is a single column matrix with two rows, the lower component implies the second row) whilst $f_T^{(-)}$ has the upper component zero. The two components differ in the sign of k. Based on this observation one parametrizes solutions as $f^{(\pm)} = f_T^{(\pm)}Ur^{(\pm)}$, where $f_T^{(\pm)}$ is now scalar function and satisfies equation

$$f_T^{(\pm)\prime\prime} = -\frac{V'}{1+e^{\pm}-V}f_T^{(\pm)\prime} + \frac{1-\left(e^{\pm}-V\right)^2+\frac{\varepsilon^2}{(1+\varepsilon^2)}k^2}{1+\varepsilon^2}f_T^{(\pm)} \mp \frac{\varepsilon k V'}{\left(1+\varepsilon^2\right)\left(1+e^{\pm}-V\right)}f_T^{(\pm)}$$

where

$$r^{(\pm)} = \frac{1}{2}\begin{vmatrix}1 \pm 1\\ 1 \mp 1\end{vmatrix}$$

For the component (5.69) one writes $g^{(\pm)} = Ug_T^{(\pm)}$ where now $g_T^{(\pm)}$ is given by

$$g_T^{(\pm)} = \frac{1}{1+e-V}\left[f_T^{(\pm)\prime}\begin{vmatrix}1 & 0\\ 0 & 1\end{vmatrix} - \frac{k\varepsilon f_T^{(\pm)}}{1+\varepsilon^2}\begin{vmatrix}1 & 0\\ 0 & -1\end{vmatrix}\right]s^{(\pm)}$$

where

$$s^{(\pm)} = \frac{1}{2}\begin{vmatrix}-(1+i\varepsilon)(1\mp 1)\\ (1-i\varepsilon)(1\pm 1)\end{vmatrix}$$

Bound state energies e are functions of k, the dependence vanishes for $\varepsilon = 0$ i.e. when one of the particles has infinite mass. The centre of mass motion is then decoupled from the relative motion of the two particles.

Function f_T has asymptotic form for $|x| \to \infty$ as

$$f_T \to e^{\frac{\sqrt{1-e^2+\frac{\varepsilon^2}{1+\varepsilon^2}k^2}}{\sqrt{1+\varepsilon^2}}x}u_1 + e^{-\frac{\sqrt{1-e^2+\frac{\varepsilon^2}{1+\varepsilon^2}k^2}}{\sqrt{1+\varepsilon^2}}x}u_2 \tag{5.71}$$

and for the solution to have the finite norm it is required that $u_2 = 0$ for $x \to -\infty$ whilst in the limit $x \to \infty$ this requirement is satisfied if $u_1 = 0$. This means that e should be within the bounds

$$|e| < \sqrt{1 + \frac{\varepsilon^2}{1+\varepsilon^2} k^2} \tag{5.72}$$

which is generalization of the requirement for a single particle when $|e| < 1$, and if the non-scaled parameters are used then $|e| < mc^2$. This means that in (5.72) the additional term plays the role of increased bare mass of the particle and therefore the energy interval within which the bound states are possible is increased. Furthermore this "increased mass" has additional effect on the solution f in its asymptotic tail. If the range of potential well is x_0 then beyond this limit the tail, its exponentially decreasing component, is given by (5.71). For $k = 0$ it is a slowly decaying function that extends much beyond x_0, however, as $|k|$ increases the decay is more rapid and in the limit $|k| \to \infty$ is of the order x_0.

Typical features of solutions are demonstrated on an explicit example, where the bound potential V is Gaussian

$$V(x) = V_0 \, e^{-\frac{x^2}{d^2}}$$

and the amplitude $A(k)$ in (5.67) is

$$A(k) = \sqrt{\frac{D}{\sqrt{\pi}}} e^{-\frac{D^2}{2}(k-k_0)^2} \tag{5.73}$$

which in the coordinate space represents Gaussian probability amplitude, and indicates that the system of the two particles has momentum $\hbar k_0$ (in the units of the Compton momentum) that corresponds to the velocity

$$v = c \frac{k_0}{\sqrt{k_0^2 + 1}}$$

of the system. The parameters chosen for the potential in this example are $d = 1$ and $V_0 = -10$ whilst $\varepsilon = 0.1$ (mass of particle 2 is 100 time larger that of particle 1). The width d of the potential well is in the units of the Compton wavelength of particle 1, and if this is the electron then the system is confined within 10^{-12} m.

Dependence of e on k is calculated and the results are shown in Fig. 5.19 for $k > 0$ (for negative k the line is symmetric) for two values of ε. As k increases so the bounds within which the bound states are possible increases, and in the example with $\varepsilon = 0.1$ for $k = 100$ this bounds are $e_{thr} = \pm 10.0$ (10 times the rest mass of the particle 1 with respect to which scaling is made).

Probability density

$$P(x) = f^+(x) \, f(x) + g^+(x) \, g(x)$$

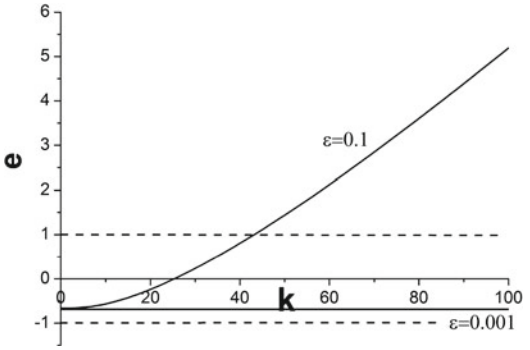

Fig. 5.19 $k-$dependence of bound state energy e for the system of two particles. *Dotted lines* represent the bounds within which relativistic bound states are possible for a single particle. The width of potential is $D = 1$ and dependence is shown for two values of the mass ratio ε

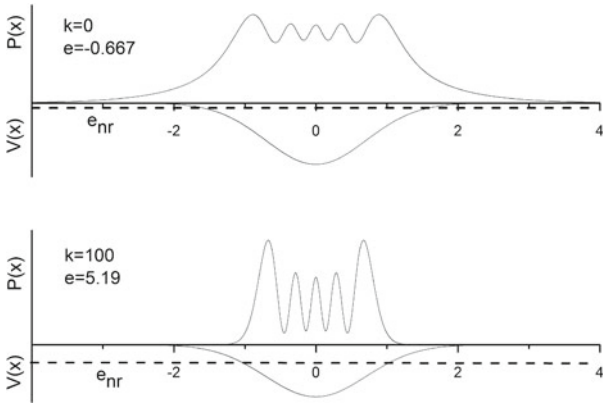

Fig. 5.20 Bound state probability densities for two extreme values of k shown against the potential well within which they are formed. The *broken line* represents energy at which these states are formed, and the index indicates its "non-relativistic" value * for the definition see discussion of equation (5.74)

for example in Fig. 5.19 with $\varepsilon = 0.1$ it is shown in Fig. 5.20 for the two extreme values of k. The curve $P(x)$ resembles closely the WKB solution for a particle in a well, more so for large k. However its oscillatory structure indicates that this is as an excited state for a non-relativistic particle in a well, but here it is ground state when $k = 0$ because no other is available below, until the limit $e = -1$. Furthermore one observes the shrinking effect in the width of $P(x)$, which is for large k nearly the width of the well, as explained in discussion following (5.71).

Energy interval within which bound states of the system are possible expands with increasing k and it is possible that new bound states appear. Thus for $k = 100$ in Fig. 5.20 ($\varepsilon = 0.1$) several new states appear and the lowest in energy is shown in Fig. 5.21 (upper curve). Natural question is what happens to this bound state when

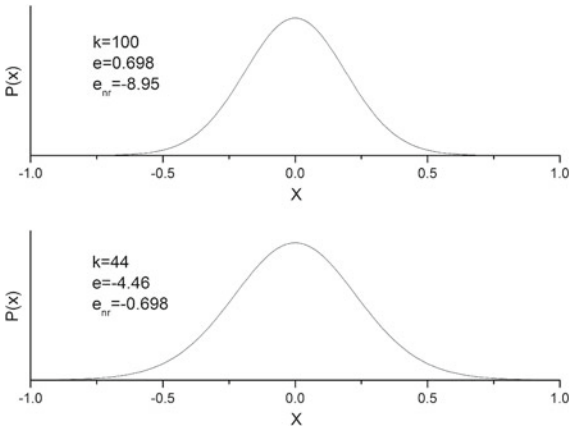

Fig. 5.21 For large k new bound states may appear, and one of them is shown for $k = 100$. In fact it is the true ground state for this system. When k is lowered this bound state disappears, and at this threshold it is shown in the lower graph together with its energy

k is lowered? In this case energy of this state decreases whilst the interval for the bound states shrinks and at some point e meets the lower boundary. For the state in Fig. 5.21 e meets the lower bound for $k \approx 44$, (enr $= -3.14$) and it is shown by the lower graph, together with its energy.

By decreasing k even further than the value that is shown in Fig. 5.21 the bound state becomes a resonance and the system decays into its constituents. Energy of the resonance states, which are complex and not real, are calculated by the same recipe as in non-relativistic dynamics, and follows from the physical reasoning. The states of this kind have only the outgoing components in the form of a plane wave, thus for $x < 0$ they have the form $\exp(iKx)$ (moving away from the origin) whilst for $x > 0$ they are $\exp(-iKx)$ (also moving away from the origin). It should be pointed out that because e is negative velocity of particle is opposite to its momentum, for this reason these boundary conditions have the chosen form. In order to satisfy the prescribed boundary conditions one makes the choice $\exp(iKx)$ for $x < 0$ but then from (5.71) it follows that resonance energies are solutions of equation

$$u_1(e) \sim J(e) = \delta f + f' = 0$$

where

$$\delta = \frac{\sqrt{\left(1 - e^2\right)\left(1 + \varepsilon^2\right) + \varepsilon^2 k^2}}{\left(1 + \varepsilon^2\right)}$$

Calculation of complex energies for resonances is a demanding task, but the simplest is to use perturbation technique. At real value of resonance energy e the module of function $J(e)$ (traditionally it is called the Jost function) has a minimum, close to zero, which means that the product $J^*(e)\, d_e J(e)$ is zero. If this is calculated then from perturbation theory the complex resonance energy is

$$e_r = e - \frac{J(e)}{d_e J(e)}$$

where the energy derivative of the Jost function is calculated by taking the energy derivative of the set (5.68), which is the most straightforward way of doing it.

For the example in Fig. 5.21 resonance at $k = 40$, just below the value of k where still the bound state prevails, has the energy $e = -4.80 - 0.00015i$, however for $k = 0$ it is $e = -6.73 - 0.047\ i$. The two resonances have large difference in their imaginary part, indicating that their decay time is different. Probability density for the two resonances is shown (5.22), together with

$$K^2(x) = 1 - [e - V(x)]^2 + \frac{\varepsilon^2}{1+\varepsilon^2}k^2$$

in order to show the source of this difference. The resonances are formed in the well around the origin but between it and the space where the particles move away from each other there is a barrier (positive value of $K^2(x)$) through which the system must tunnel. The barrier for $k = 40$ is much higher than that for $k = 0$. It should be noted that for $x >> 0$ the probability density oscillates, which is an artifact of using the perturbation technique for calculating resonance energies (the graphs are calculated for real e) (Fig. 5.22).

The energy e could be split into several components, and to show this it is assumed that $A(k)$ is non-zero around a narrow interval around k_0 and could be approximated by a delta function. Energy is defined as

$$e = \int dx\, dX \left| F^+ \; G^+ \right| \begin{vmatrix} V+1 & i(\Sigma\partial_x - \Sigma_X\partial_X) \\ i(\Sigma\partial_x - \Sigma_X\partial_X) & V-1 \end{vmatrix} \begin{vmatrix} F \\ G \end{vmatrix}$$

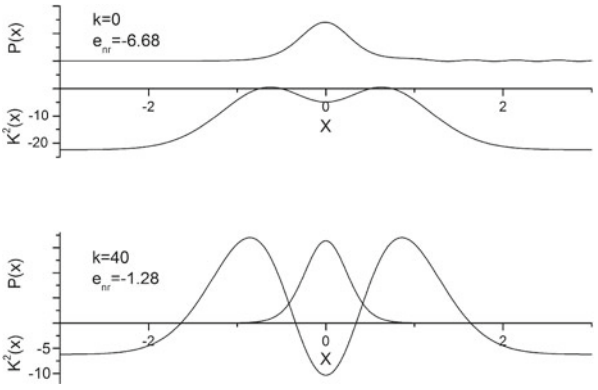

Fig. 5.22 Probability density $P(x)$ for resonances that are formed when k is lower than that in Fig. 5.21. Imaginary part of resonance energies is due to tunneling through the barrier that is formed in $K^2(x)$

and if

$$A(k) = \frac{1}{2\pi}\delta(k - k_0)$$

then

$$\begin{aligned} e = i\int dx\ \left[f^+(x)\,\Sigma\partial_x g(x) + g^+(x)\,\Sigma\partial_x f(x)\right] \\ + k_0\int dx\ \left[f^+(x)\,\Sigma_X\, g(x) + g^+(x)\,\Sigma_X f(x)\right] \\ + \int dx\, V(x)\ \left[f^+(x)\, f(x) + g^+(x)\ g(x)\right] \\ + \int dx\left[f^+(x)\, f(x) - g^+(x)\ g(x)\right] \\ = e_k + e_{kc} + e_v + e_m \end{aligned} \tag{5.74}$$

In the case of resonances this energy is infinite because solutions f and g are nor square integrable in which case one calculates it from

$$\begin{aligned} e = i\left[f_\infty^+\Sigma\partial_x g_\infty + g_\infty^+\Sigma\partial_x f_\infty\right]_N + k_0\ \left[f_\infty^+\Sigma_X\, g_\infty + g_\infty^+\Sigma_X f_\infty\right]_N \\ + \left[f_\infty^+ f_\infty - g_\infty^+\, g_\infty\right]_N = e_k + e_{kc} + e_m \end{aligned}$$

where ∞ indicates that solutions are calculated for $x \to \infty$ and N indicates that the bracket is normalized with respect to $P(x \to \infty)$.

Energy is a sum of four terms: first is kinetic energy (e_k), second is kinetic energy associated with the motion of the system (e_{kc}), the third is potential energy (e_v) and the last contribution is from the effective mass (e_m). The energy that is equivalent with the total energy in non-relativistic dynamics is the sum of kinetic and potential energies, and it is given by $e_{nr} = e_k + e_v$. Thus in example in Fig. 5.20 e_{nr} has the value $e_{nr} = -0.176$ for $k = 0$ and $e_{nr} = -1.96$ for $k = 100$. Both values are what one would consider "physical", meaning that they are negative, within the limits of the potential well. Interesting case is the example in Fig. 5.21 for $k = 100$ when $e_{kv} = -8.96$, which is close to the bottom of the potential well and plays the role of the ground state, which is confirmed by the shape of $P(x)$ in the same figure.

If the two particles are of different charge then one could calculate charge density in the system, along the lines in Sect. 1.2.3. One starts from the overall density

$$P(x, X) = F^+(x, X)\, F(x, X) + G^+(x, X)\, G(x, X)$$

and replacing solutions with (5.67), with the amplitude (5.73), one gets

$$P(x_1, u) = \digamma^+(x_1, u)\,\digamma(x_1, u) + \Gamma^+(x_1, u)\,\Gamma(x_1, u)$$

where

$$F\left(x_1,u\right)=\frac{1}{\sqrt{d_k\sqrt{\pi}}}\int dk\; e^{-\frac{k^2}{2d_k^2}+ik\left(x_1+\frac{1}{1+\varepsilon^2}u\right)}f\left(u,k\right)$$

and the same for $\Gamma\left(x_1,u\right)$ except that f is replaced by g. By taking $k_0=0$ it is assumed that the system is in the rest frame. The charge density for particle 1 (its mass is 1 in the scaled units) is then

$$\rho_1\left(x_1\right)=-Q\int du\,P\left(x_1,u\right)$$

where the minus sign of the charge Q indicates that it is negative.

Similarly the density could be parametrized as

$$P\left(x_2,u\right)=F^+\left(x_2,u\right)F\left(x_2,u\right)+\Gamma^+\left(x_2,u\right)\Gamma\left(x_2,u\right)$$

where now

$$F\left(x_2,u\right)=\frac{1}{\sqrt{d_k\sqrt{\pi}}}\int dk\;\; e^{-\frac{k^2}{2d_k^2}+ik\left(x_2-\frac{\varepsilon^2}{1+\varepsilon^2}u\right)}\;f\left(u,k\right)$$

and the charge density for particle 2 is

$$\rho_2\left(x_2\right)=Q\int du\,P\left(x_2,u\right)$$

and so the entire charge density is

$$\rho\left(x\right)=\rho_1\left(x\right)+\rho_2\left(x\right)$$

Charge density is not very sensitive on ε, the ratio of the mass of particle 1 with that for particle 2, except when ε is nearly one in which case it goes to zero. More important is dependence of the charge density on the width d_k, for a very physical reason. Larger d_k, which implies narrower width of the probability density in the coordinates, means that the system gets into the relativistic regime, and these affects the masses of particles and implication on the charge density. There is, however, the limit of taking d_k very large, in general there is no meaning for the system if $d_k>d^{-1}$ (the width of the potential well), and the largest to choose $d_k\approx d^{-1}$. The other extreme is $d_k\to 0$ and it is the simplest, the charge density is zero because individual densities are uniformly spread around the space.

In order to demonstrate the effect of confinement on the charge density it is assumed that $\varepsilon=1$ whilst the size of the potential well is $d=0.001$, which is the size of neutron (approximately) if particle 1 is the electron. The results for the entire charge densities are shown in Fig. 5.23 for two examples of confinements. The left graph is calculated when the confinement is hundred times larger than the size of the potential well, and distribution of charges is similar to that in Fig. 1.1 for Hydrogen

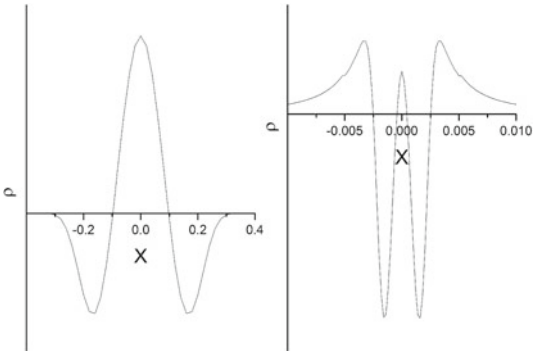

Fig. 5.23 Charge density for two oppositely charged particles, lighter particle has it negative. On the *left* is charge density when the width of confinement is about 100 times the size of the potential well. On the *right* the system is confined to the size of the potential well, approximately the size of neutron. In both case system is relativistic

like atom (for muon as particle 1). However, at extreme confinement, right graph, when it is of the size of the potential well, the distribution of charge density is reversed, most of the negative charge is around the centre of interaction.

Chapter 6
Atom in Electromagnetic Field

Abstract When electromagnetic wave interacts with atom both the electrons and its nucleus are affected. Several effects emerge that have roots in inter dependence of the electron and the atom as the whole dynamics. Some of the effects are classical in origin and the others are typical of quantum dynamics.

6.1 General Remarks

Atom is a conglomerate of many electrons and a single nuclei, and its interaction with the electromagnetic wave affects all of them, in principle. In typical approach many simplifying assumptions are made, but here this will be avoided as much as possible, or arguments will be given why they are used. For a free single charged particle in the electromagnetic wave both classical and quantum analysis were made, however, for atoms this is not possible. The reason is simple, motion of electrons even without the electromagnetic interaction is highly unstable in the classical treatment, meaning that the auto-ionization process occurs almost instantaneously (one electron in collision with another ejects it free but after that it is more tightly bound). There is a remedy in classical mechanics to avoid such events, but a complete reformulation of it in terms of probability densities is required. Application of classical mechanics will be used only when sufficient simplifications are made within the quantum treatment.

Isolated atom is described by a probability amplitude that includes both the electrons and its nuclei. Roughly speaking, atom as a whole is the same as a free particle, within which electrons are bound whose motion should be described in the relative coordinates with respect to its nuclei. The nuclei is normally associated with the centre of mass of atom, which is a good approximation, and therefore the probability amplitude could be written as a product

$$f\left(\vec{R};\vec{r}_1,\vec{r}_2,\vec{r}_3,\ldots\vec{r}_n\right) = f_N\left(\vec{R}\right) f_e\left(\vec{r}_1,\vec{r}_2,\vec{r}_3,\ldots\vec{r}_n\right)$$

S.D. Bosanac, *Electromagnetic Interactions*,
Springer Series on Atomic, Optical, and Plasma Physics 94,
DOI 10.1007/978-3-662-52878-5_6

where $\vec{R}$ is position of the nuclei with respect to some coordinate system (absolute coordinate system, for short) and $\vec{r}_j$ is position of the j-th electron with respect to the nuclei. This factorization is the bases of all analysis of electron structure because the nuclear degree of freedom is neglected. However, when the nuclear coordinate is taken into account then the probability amplitude for the electrons takes a more complicated form because relative to that coordinate electronic states are stationary but with respect to the absolute ones they are not. The probability amplitude for the nuclei evolves in time because it is that for a free particle, it spreads, and therefore probability density for, say, electron 1 it is given by

$$P\left(\vec{R}_1, t\right) = \int \left| f_N\left(\vec{R}, t\right) f_e\left(\vec{R}_1 - \vec{R}, \vec{R}_2 - \vec{R}, ..., \vec{R}_1 - \vec{R}\right)\right|^2 d^3R\, d^3R_2 ... d^3R_n$$

where $\vec{R}_j$ is the absolute position of the j-th electron. This may appear a somewhat artificial conclusion because the intrinsic properties of atoms do not depend on the whereabouts of atom as the whole. However, when it comes to interaction with forces that vary over the spatial distances then it is indeed necessary to work in the absolute coordinates for the electrons. Namely, variation of the force over the localization distance of the j-th electron in atom may be small but because localization of the atom as the whole is much larger, and spreading, then this variation may be large.

Probability density for the electron in Hydrogen atom is analyzed in order to demonstrate the difference when it is treated in terms of the absolute coordinates as opposed to the relative. Strictly speaking it should be done in the absolute, and one starts from the probability amplitude for the entire atom, nuclei (proton) and the electron. The simplest is to assume Gaussian type probability density of the width d for the proton and the $1S$ state for the electron in the relative coordinates. Together they give probability amplitude for the whole hydrogen atom as

$$f\left(\vec{R}; \vec{r}\right) = \sqrt{N}\, e^{-\frac{R^2}{2d^2}} e^{-\frac{r}{2a}}$$

However, position of the electron is determined in the absolute coordinates, in the same coordinate system in which position of the proton is given. If the coordinates for the electron are $\vec{R}_e$ then in the absolute coordinates the atom probability amplitude is

$$f\left(\vec{R}; \vec{R}_e\right) = \sqrt{N}\, e^{-\frac{R^2}{2d^2}} e^{-\frac{\left|\vec{R}_e - \vec{R}\right|}{2a}}$$

The probability density for the electron is now

$$P\left(\vec{R}_e\right) = N \int d^3R\, e^{-\frac{R^2}{d^2} - \frac{\left|\vec{R}_e - \vec{R}\right|}{a}} = N \int d^3R\, e^{-\frac{\left(\vec{R}_e - \vec{R}\right)^2}{d^2} - \frac{R}{a}}$$

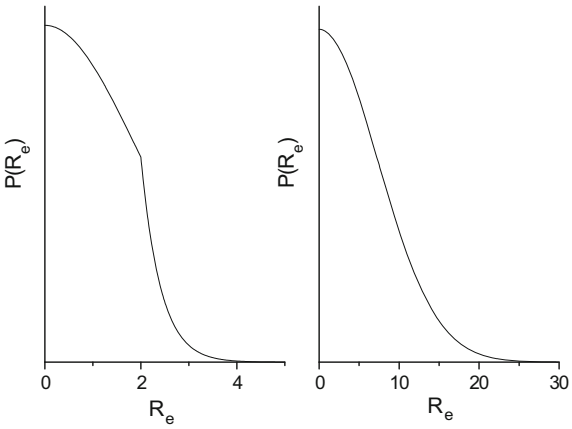

Fig. 6.1 Probability density for the electron in the $1S$ state of Hydrogen if delocalization of the atom is taken into account. For the atom that is localized to twice the width of the electron state the probability density is shown in *left figure* and when its delocalization is much wider (*right figure*)

and its explicit expression is

$$P\left(\vec{R}_e\right) = \frac{N}{R_e}\left[\left(\frac{d}{2a}+\frac{R_e}{d}\right)\mathrm{erf}\,c\left(\frac{d}{2a}+\frac{R_e}{d}\right)e^{\frac{R_e}{a}} - \left|\frac{d}{2a}-\frac{R_e}{d}\right|\mathrm{erf}\,c\left|\frac{d}{2a}-\frac{R_e}{d}\right|e^{-\frac{R_e}{a}}\right]$$

where

$$\mathrm{erf}\,c(z) = 1 - \mathrm{erf}(z)$$

and $erf(z)$ is the error function. Two extreme examples are shown in Fig. 6.1, one when $d = 2a$ (left graph) and the other when $d = 10a$ (right graph). For a very wide probability density of the nuclei the electron probability density is that of a Gaussian shape of the width that is comparable to d. On the other hand, for a small d the probability density for $R_e < d^2/(2a)$ is a Gaussian shape but otherwise it is that of the $1S$ state.

When the probability density evolves in time the only change is in the width of the Gaussian, when d is replaced by an increasing function in time. This means that eventually the probability density for the electron acquires the shape of the probability density for the nuclei, and gets delocalized over the entire space.

6.2 Atom in Electromagnetic Wave

6.2.1 Basic Equation

Equation for an atom in the electromagnetic wave is

$$i\hbar\partial_t f = -\frac{\hbar^2}{2M}\left[\nabla_R + \frac{ine}{\hbar c}\vec{A}\left(\frac{\hat{n}\cdot\vec{R}}{c} - t\right)\right]^2 f$$

$$-\frac{\hbar^2}{2m}\left[\nabla_{R_1}-\frac{ie}{\hbar c}\vec{A}\left(\frac{\hat{n}\cdot\vec{R}_1}{c}-t\right)\right]^2 f$$
$$\ldots-\frac{\hbar^2}{2m}\left[\nabla_{R_n}-\frac{ie}{\hbar c}\vec{A}\left(\frac{\hat{n}\cdot\vec{R}_n}{c}-t\right)\right]^2 f+V\ f$$

where $\vec{R}$ is position of the nuclei of the mass M and the total charge n, $\vec{R}_j$ is position of the j-th electron in the absolute coordinates and V is the Coulomb interaction among electrons and the nuclei. In order to simplify somewhat derivations indexing of the particles is modified. The nuclei is particle 1 and the electrons are particles 2, 3, …, N, so that there are N – 1 electrons. The equation is now

$$i\hbar\partial_t f=-\frac{\hbar^2}{2}\sum_{j=1}^{N}\frac{1}{m_j}\left[\nabla_{R_j}+\frac{ie_j}{\hbar c}\vec{A}\left(\frac{\hat{n}\cdot\vec{R}_j}{c}-t\right)\right]^2 f+V\ f \tag{6.1}$$

where $e_j=ne$ for $j=1$ but otherwise $e_j=-e$. The coordinates are transformed into the centre of mass system, but in such a way that the bilinear form

$$K=\sum_{j=1}^{N}\frac{1}{m_j}\left[\nabla_{R_j}\right]^2$$

is again diagonal. The final result of the necessary transformations are given in (D), and for the case of N – 1 identical particles (electrons) and the mass of the nuclei (particle 1) being much larger than the mass of the electrons, the expression for K is

$$K=\frac{1}{M}\Delta_R+\frac{1}{m}\sum_{j=1}^{n}\Delta_{r_j}$$

where now $\vec{R}$ is position of the centre of mass but it (approximately) coincides with the position of the nuclei and $\vec{r}_j$ is position of the j-th electron with respect to the nuclei, i.e.

$$\vec{r}_j=\vec{R}_j-\vec{R}$$

The vector potential in (6.1) can be approximated as

$$\vec{A}\left(\frac{\hat{n}\cdot\vec{R}_j}{c}-t\right)=\vec{A}\left(\frac{\hat{n}\cdot\vec{r}_j}{c}+\frac{\hat{n}\cdot\vec{R}}{c}-t\right)$$
$$\approx\vec{A}\left(\frac{\hat{n}\cdot\vec{R}}{c}-t\right)+\frac{\hat{n}\cdot\vec{r}_j}{c}\vec{A}'\left(\frac{\hat{n}\cdot\vec{R}}{c}-t\right)$$

with the argument that although over the distance R it may vary considerably, over the distances r_j it is nearly constant. When the square in (6.1) is evaluated then with this expansion the cross term is

$$T = \sum_{j=1}^{N} \frac{e_j}{m_j} \vec{A}\left(\frac{\hat{n}\cdot\vec{R}_j}{c} - t\right)\cdot\nabla_{R_j} \approx \vec{A}\left(\frac{\hat{n}\cdot\vec{R}}{c} - t\right)\cdot\sum_{j=1}^{N}\frac{e_j}{m_j}\nabla_{R_j} + \frac{1}{c}\vec{A}'\left(\frac{\hat{n}\cdot\vec{R}}{c} - t\right)\cdot\sum_{j=2}^{N}\frac{e_j}{m_j}\left(\hat{n}\cdot\vec{r}_j\right)\nabla_{R_j}$$

In the centre of mass coordinates the operators in this expression are given in (D), so that

$$T = -\frac{e}{m}\sum_{j=1}^{n}\left[\vec{A}\left(\frac{\hat{n}\cdot\vec{R}}{c} - t\right)\cdot\nabla_{r_j} + \frac{\left(\hat{n}\cdot\vec{r}_j\right)}{c}\vec{A}'\left(\frac{\hat{n}\cdot\vec{R}}{c} - t\right)\cdot\nabla_{r_j}\right] - \frac{e\sum_{j=1}^{n}\left(\hat{n}\cdot\vec{r}_j\right)}{Mc}\vec{A}'\left(\frac{\hat{n}\cdot\vec{R}}{c} - t\right)\cdot\nabla_R$$

Equation (6.1) is now

$$\begin{aligned} i\hbar\partial_t f = &-\frac{\hbar^2}{2M}\Delta_R f - \frac{\hbar^2}{2m}\sum_{j=1}^{n}\Delta_{r_j} f \\ &+ \frac{i\hbar e}{mc}\sum_{j=1}^{n}\left[\vec{A}\left(\frac{\hat{n}\cdot\vec{R}}{c} - t\right)\cdot\nabla_{r_j} + \frac{\left(\hat{n}\cdot\vec{r}_j\right)}{c}\vec{A}'\left(\frac{\hat{n}\cdot\vec{R}}{c} - t\right)\cdot\nabla_{r_j}\right] \\ &+ \frac{i\hbar e}{Mc^2}\sum_{j=1}^{n}\left(\hat{n}\cdot\vec{r}_j\right)\vec{A}'\left(\frac{\hat{n}\cdot\vec{R}}{c} - t\right)\cdot\nabla_R f + \left(\frac{n^2}{M} + \frac{n}{m}\right)\frac{e^2}{2c^2}\vec{A}^2\left(\frac{\hat{n}\cdot\vec{R}}{c} - t\right) f + V\, f \end{aligned} \tag{6.2}$$

where dependence of the vector potential on the coordinate of the nuclei was retained, to indicate that the probability amplitude for the atom as the whole may have large spread.

It is assumed that electrons are all bound, and that the eigenfunctions and eigenvalues of equation

$$E_\lambda\, h_\lambda = -\frac{\hbar^2}{2m}\sum_{j=1}^{n}\Delta_{r_j} h_\lambda + V\, h_\lambda$$

are known. The probability amplitude f then have expansion

$$f\left(\vec{R};\vec{r}_j\right) = \sum_\lambda g_\lambda\left(\vec{R},t\right) h_\lambda\left(\vec{r}_j\right) e^{-iE_\lambda t/\hbar} \tag{6.3}$$

which is replaced in (6.2) and a set of equations for $g_\lambda\left(\vec{R},t\right)$ is obtained. If for the vector potential one writes

$$\vec{A}\,(u) = a(u)\hat{s}$$

and if the orthonormal property of the eigenfunctions h_λ is used, this set is

$$\begin{aligned} i\hbar\partial_t g_\lambda\left(\vec{R},t\right) = &-\frac{\hbar^2}{2M}\Delta g_\lambda\left(\vec{R},t\right) \\ &+\frac{i\hbar e}{mc}\sum_\mu\left[a(u)\,r^{(s)}_{\lambda,\mu}+\frac{1}{c}a'(u)q_{\lambda,\mu}\right]e^{-i\left(E_\mu-E_\lambda\right)t/\hbar}g_\mu\left(\vec{R},t\right) \\ &+\frac{i\hbar e}{Mc^2}a'(u)\,\sum_\mu r^{(n)}_{\lambda,\mu}\,e^{-i\left(E_\mu-E_\lambda\right)t/\hbar}\,\hat{s}\cdot\nabla g_\mu\left(\vec{R},t\right) \\ &+\left(\frac{n^2}{M}+\frac{n}{m}\right)\frac{e^2}{2c^2}a^2\,(u)\,g_\lambda\left(\vec{R},t\right) \end{aligned} \tag{6.4}$$

where

$$\begin{aligned} r^{(s)}_{\lambda,\mu} &= \sum_{j=1}^{n}\int dV\; h_\lambda\left(\hat{s}\cdot\nabla_{r_j}\right)h_\mu \\ r^{(n)}_{\lambda,\mu} &= \sum_{j=1}^{n}\int dV\; h_\lambda\left(\hat{n}\cdot\nabla_{r_j}\right)h_\mu \\ q_{\lambda,\mu} &= \sum_{j=1}^{n}\int dV\; h_\lambda\left(\hat{n}\cdot\vec{r}_j\right)\left(\hat{s}\cdot\nabla_{r_j}\right)h_\mu \end{aligned}$$

and

$$u = \frac{\hat{n}\cdot\vec{R}}{c}-t$$

More convenient expression for the matrix elements $r^{(s,n)}_{\lambda,\mu}$ is obtained by using the relationship for two bound state eigenfunctions

$$(e_1-e_2)\int f_1\vec{r}\,f_2 = \frac{\hbar^2}{m}\int f_2\nabla f_1$$

in which case

$$\begin{aligned} r^{(s)}_{\lambda,\mu} &= \frac{nm}{\hbar^2}\left(E_\mu-E_\lambda\right)\int dV\; h_\lambda\left(\hat{s}\cdot\vec{r}_j\right)h_\mu \\ r^{(n)}_{\lambda,\mu} &= \frac{nm}{\hbar^2}\left(E_\mu-E_\lambda\right)\int dV\; h_\lambda\left(\hat{n}\cdot\vec{r}_j\right)h_\mu \end{aligned}$$

where the symmetry property of the probability amplitude with respect to interchange of two electrons was utilized.

6.2.2 First Order Interaction

There are various levels of approximation to the set of equations (6.4), and the leading one is to neglect all terms of the order c^{-2}, when

$$i\hbar\partial_t g_\lambda\left(\vec{R},t\right) = -\frac{\hbar^2}{2M}\Delta g_\lambda\left(\vec{R},t\right) + \frac{i\hbar e}{mc}a(u)\sum_\mu r^{(s)}_{\lambda,\mu}\, e^{-i\left(E_\mu - E_\lambda\right)t/\hbar} g_\mu\left(\vec{R},t\right) \tag{6.5}$$

which indicates that there is coupling between the motion of the atom and the electrons (degrees of freedom of electrons are contained in the indices λ and μ). However, before any further analysis one must specify initial conditions for this set of equations, for example initially the atom is in one of the eigenstates of electrons, say the ground state. The probability amplitude for the whole atom should represent its initial localization, and without much loss of generality the overall initial probability amplitude is

$$f_0\left(\vec{R};\vec{r}_j\right) = g_0\left(\vec{R}\right)h_{\lambda_0}\left(\vec{r}_j\right)$$

The simplest to assume is that $g_0\left(\vec{R}\right)$ is spherically symmetric, but that does not allow to decompose equations for g_λ in spherical coordinates, because of the argument in the vector potential. More appropriate would be cylindrical coordinates, where the z axes is chosen to lie along the vector $\hat{n}$.

Approximate solution g_λ is obtained by transforming the equation in the integral equation form, by using Green function (B.1.1). It is given by

$$\begin{aligned} g_\lambda\left(\vec{R},t\right) &= g_0\left(\vec{R},t\right)\delta_{\lambda,\lambda_0} \\ &+ \frac{i\hbar e}{mc}\sum_\mu r^{(s)}_{\lambda,\mu}\int d^3Q\int_0^t ds\; G\left(\vec{R}-\vec{Q},t-s\right)a\left(\frac{\hat{n}\cdot\vec{Q}}{c}-s\right)e^{-i\left(E_\mu-E_\lambda\right)s/\hbar}g_\mu\left(\vec{Q},s\right) \end{aligned}$$

and the first iteration gives correction

$$\begin{aligned} g_\lambda\left(\vec{R},t\right) &= g_0\left(\vec{R},t\right)\delta_{\lambda,\lambda_0} \\ &+ \frac{i\hbar e}{mc}\, r^{(s)}_{\lambda,\lambda_0}\int d^3Q\int_0^t ds\; G\left(\vec{R}-\vec{Q},t-s\right)a\left(\frac{\hat{n}\cdot\vec{Q}}{c}-s\right)e^{-i\left(E_{\lambda_0}-E_\lambda\right)s/\hbar}g_0\left(\vec{R},t\right) \\ &= g_0\left(\vec{R},t\right)\delta_{\lambda,\lambda_0} + \frac{i\hbar e}{mc}\, r^{(s)}_{\lambda,\lambda_0}\, I \end{aligned}$$

By replacing Green function with its explicit expression, and

$$g_0\left(\vec{R},t\right)=\frac{1}{(2\pi)^3}\int d^3k\ B\left(\vec{k}\right)e^{i\vec{k}\cdot\vec{R}-i\frac{\hbar k^2}{2M}t}$$

then the correction term I is

$$I=-\frac{i}{\hbar(2\pi)^3}\int d^3Q\int_0^t ds\int d^3\kappa\ e^{i\vec{\kappa}\cdot(\vec{R}-\vec{Q})-i\frac{\kappa^2\hbar}{2M}(t-s)}$$
$$a\left(\frac{\hat{n}\cdot\vec{Q}}{c}-s\right)e^{-i\left(E_{\lambda_0}-E_\lambda\right)s/\hbar}\int d^3k\ B\left(\vec{k}\right)e^{i\vec{k}\cdot\vec{Q}-i\frac{\hbar k^2}{2M}s}$$

The simplest assumption is that the electromagnetic interaction is a plane wave

$$a\left(u\right)=a_0\ \cos(u)=\frac{a_0}{2}\left(e^{iwu}+e^{-iwu}\right)$$

but, as argued before, one should take great care not to make conclusions that require the wave to have begging and end. If one uses expansion of the plane wave into a sum of two exponential functions, as shown, then the integrals I split into two, each corresponding to one of them. The integrals in the variables $\vec{Q}$ then given the delta function

$$\int d^3Q\ldots=(2\pi)^3\delta\left(-\vec{\kappa}\pm w\frac{\hat{n}}{c}+\vec{k}\right)$$

and in the variable s

$$\int_0^t ds\ldots=\frac{e^{i\left(\pm\frac{w\hbar}{cM}\ \vec{k}\cdot\hat{n}+\frac{w^2\hbar}{2c^2M}-\left(E_{\lambda_0}-E_\lambda\right)/\hbar\mp w\right)t}-1}{i\left(\pm\frac{w\hbar}{cM}\ \vec{k}\cdot\hat{n}+\frac{w^2\hbar}{2c^2M}-\left(E_{\lambda_0}-E_\lambda\right)/\hbar\mp w\right)}\tag{6.6}$$

where it was taken into account that

$$\vec{\kappa}=\pm w\frac{\hat{n}}{c}+\vec{k}$$

which follows from the delta function. It is assumed that the frequency w is close to the value when

$$\frac{1}{cM}\left(\pm\hbar\vec{k}\cdot\hat{n}+\frac{\hbar w}{2c}\right)w-\frac{E_{\lambda_0}-E_\lambda}{\hbar}\mp w=0\tag{6.7}$$

which is approximately satisfied for the resonance frequency

$$w=\frac{E_\lambda-E_{\lambda_0}}{\hbar}$$

under the assumption that $E_\lambda > E_{\lambda_0}$. Correction to this value comes from the other terms in (6.7), but it is small because

$$\frac{1}{cM}\left(\hbar\vec{k}\cdot\hat{n}+\frac{\hbar w}{2c}\right)$$

is the ratio between total momentum of the atom and its Compton momentum. Total momentum of the atom is a sum of its momentum from the dispersion of momenta in the initial probability amplitude and the momentum imparted by the electromagnetic wave. If this term is treated as perturbation then approximate solution of equation (6.7) is

$$w=\frac{E_\lambda-E_{\lambda_0}}{\hbar}+\frac{\vec{k}\cdot\hat{n}}{cM}\left(E_\lambda-E_{\lambda_0}\right)+\frac{\left(E_\lambda-E_{\lambda_0}\right)^2}{2c^2M\hbar}$$

The first correcting term, which includes $\vec{k}$ comes from the Doppler effect due to dispersion of momenta in the initial probability amplitude of the atom. The remaining term comes from the change in velocity of the atom due to the frequency dependent momentum transfer onto the atom (the photon effect). Frequency of the wave that has this value is also called resonance frequency.

For the resonance frequency of the electromagnetic wave the time integral is

$$\int_0^t ds\ldots=t$$

and so the correction term I is

$$\begin{aligned}I&=-\frac{a_0 i}{2\hbar}t\int d^3k\ B\left(\vec{k}\right)e^{i\left(w\frac{\hat{n}}{c}+\vec{k}\right)\cdot\vec{R}-i\frac{\left(w\frac{\hat{n}}{c}+\vec{k}\right)^2\hbar}{2M}t}\\&=-\frac{a_0 i}{2\hbar}t\int d^3k\ B\left(\vec{k}-w\frac{\hat{n}}{c}\right)e^{i\vec{k}\cdot\vec{R}-i\frac{k^2\hbar}{2M}t}\end{aligned}$$

where the contribution from the frequency term e^{iwt} in the plane wave was neglected. The probability amplitude for the atom is therefore

$$g_\lambda\left(\vec{R},t\right)=g_0\left(\vec{R},t\right)\delta_{\lambda,\lambda_0}+\frac{ea_0t}{2mc}r^{(s)}_{\lambda,\lambda_0}\int d^3k\ B\left(\vec{k}-w\frac{\hat{n}}{c}\right)e^{i\vec{k}\cdot\vec{R}-i\frac{k^2\hbar}{2M}t}$$

and increases linearly in time. However, correction to the probability amplitude for the atom is the same as the unperturbed except that it is moving with the additional velocity

$$\vec{v}_{atom}=\frac{w\hbar}{Mc}\hat{n} \tag{6.8}$$

Linear increase in time is obviously a sign of a very efficient energy transfer from a ground state into some excited one, and cannot go on indefinitely because perturbation expansion fails. In such a case alternative analysis that goes beyond perturbation theory is required. One obvious objection is that for the resonance frequency it was assumed that it has some fixed value, whilst in fact it varies with $\vec{k}$. More accurate assumption would be that it is solution of equation

$$\frac{w^2\hbar}{2c^2M} + \left(E_\lambda - E_{\lambda_0}\right)/\hbar - w = 0$$

and it has the value w_0. In this case I is

$$I = -\frac{cM}{2\hbar^2 w_0}\int d^3k\; B\left(\vec{k}\right) e^{i\left(w_0\frac{\hat{n}}{c}+\vec{k}\right)\cdot\vec{R}-i\frac{\left(w_0\frac{\hat{n}}{c}+\vec{k}\right)^2\hbar}{2M}t}\frac{e^{i\;\frac{w_0\hbar}{cM}\;\vec{k}\cdot\hat{n}\;t}-1}{\vec{k}\cdot\hat{n}}$$

and if one defines cylindrical coordinate system, with the z axes defined along the vector $\hat{n}$, then

$$I = -\frac{cM}{2\hbar^2 w_0}\int_{-\infty}^{\infty} dk_n e^{i\left(\frac{w_0}{c}+k_n\right)R_n - i\frac{\left(\frac{w_0}{c}+k_n\right)^2\hbar}{2M}t}$$
$$\frac{e^{i\;\frac{w_0\hbar}{cM}\;k_n t}-1}{k_n}\int d^2\kappa\; B\left(k_n\hat{n}+\vec{\kappa}\right) e^{i\vec{\kappa}\cdot\vec{R}-i\frac{\kappa^2\hbar}{2M}t}$$

where $k_n = \vec{k}\cdot\hat{n}$, $R_n = \hat{n}\cdot\vec{R}$ and the vector $\vec{\kappa}$ is perpendicular to $\hat{n}$. Formally the integral in k_n could now be calculated, and to demonstrate its properties it is assumed that $B\left(\vec{k}\right)$ is a Gaussian

$$B\left(\vec{k}\right) = N\, e^{-\frac{k^2}{d_k^2}} = N\, e^{-\frac{k_n^2}{2d_k^2}}\; e^{-\frac{\kappa^2}{2d_k^2}}$$

in which case

$$I = -\frac{icM\pi}{2\hbar^2 w_0\sqrt{d_k\sqrt{\pi}}} e^{-i\frac{\left(\hat{n}\cdot\vec{R}\right)w_0}{c}-i\frac{\hbar w_0^2}{2Mc^2}t}\left[\operatorname{erf}\left(\frac{R_n}{\sqrt{2}\Delta(t)}\right) - \operatorname{erf}\left(\frac{R_n - \frac{\hbar w_0}{Mc}t}{\sqrt{2}\Delta(t)}\right)\right]$$

where

$$\Delta(t) = \sqrt{\frac{1}{d_k^2} + i\frac{\hbar t}{M}}$$

where $\operatorname{erf}(z)$ is the error function. The remaining integrals in κ where omitted because they represent the unperturbed probability amplitude.

The function $I(t)$ is time dependent, and for short times it is approximately

$$I(t) \approx -i \frac{\sqrt{d_k \sqrt{\pi}}}{\sqrt{2}\hbar} t \; e^{-\frac{1}{2}(\hat{n}\cdot\vec{R})^2 d_k^2}$$

which has a linear increase in time, as expected, and it has the initial Gaussian shape. More general estimate of $I(t)$ is based on using property of the error function $\mathrm{erf}(z)$ that for $z < -2$ it has the value $\mathrm{erf}(z) = -1$ whilst for $z > 2$ its value is $\mathrm{erf}(z) = 1$, and $\mathrm{erf}(0) = 0$. As the time increases one error function remains centred at the origin and the centre of the other moves with the velocity (6.8). After sufficiently long time function I has estimate

$$I \sim \begin{cases} 0 \; ; & \frac{R_n}{\sqrt{2}\,|\Delta(t)|} < -2 \\ 2 \; ; & \frac{R_n}{\sqrt{2}\,|\Delta(t)|} > 2 \; ; \; \frac{R_n - \frac{\hbar w_0}{Mc} t}{\sqrt{2}\,|\Delta(t)|} < -2 \\ 0 \; ; & \frac{R_n - \frac{\hbar w_0}{Mc} t}{\sqrt{2}\,|\Delta(t)|} > 2 \end{cases} \tag{6.9}$$

and one typical example of this limiting case is shown in Fig. 6.2. The shape is result of the separation of the two centres of the error functions, and the transition time from the initial Gaussian shape is estimated from the following observation; if in time t the edge of the transition interval of the first error function is

$$\frac{R_n}{\sqrt{2}\Delta(t)} = 2$$

and this point is on the edge of the interval of the second error function, i.e.

$$\frac{2\sqrt{2}\Delta(t) - \frac{\hbar w_0}{Mc} t}{\sqrt{2}\,|\Delta(t)|} = -2$$

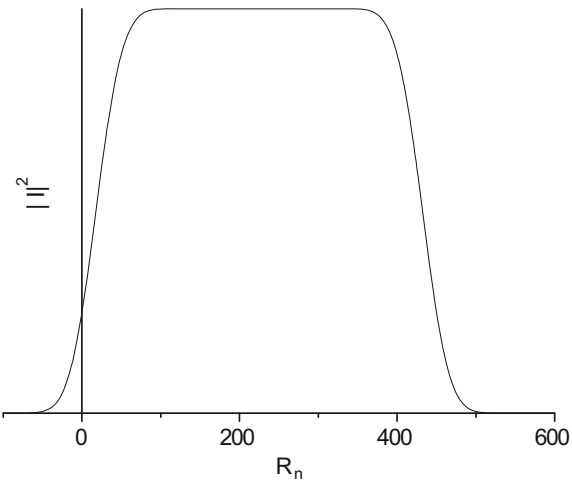

Fig. 6.2 Long time behavior of the correction to the probability amplitude for atom in interaction with a plane electromagnetic wave. Initial functional form of the probability amplitude for the atom is Gaussian

then for the times greater than this the function I acquires the shape (6.9) or as shown in Fig. 6.2. From the last equation one obtains

$$t = \frac{1}{w_0}\frac{16Mc^2}{\hbar w_0}\left(1+\sqrt{1+\frac{w_0^2}{8c^2d_k^2}}\right)$$

which gives time when the shape in Fig. 6.2 starts forming, before that being the Gaussian function whose maximum increases in time.

In the limit $t \to \infty$ the modulus of I is constant, in the interval given by (6.9), and within it

$$g_\lambda\left(\vec{R},t\right) = g_0\left(\vec{R},t\right)\delta_{\lambda,\lambda_0} + \frac{Ma_0e}{m\hbar w_0}\ \frac{\pi r^{(s)}_{\lambda,\lambda_0}}{\sqrt{d_k\sqrt{\pi}}}e^{-i\frac{\left(\hat{n}\cdot\vec{R}\right)w_0}{c}-i\frac{\hbar w_0^2}{2Mc^2}t}$$

therefore the correction term to the probability amplitude for the atom is constant, but large.

Very often the limit $t \to \infty$ is taken in the beginning of analysis, in the expression (6.6), where one of the integrals is delta function

$$\int_0^t ds\ldots \sim \delta\left(\frac{w\hbar}{cM}\vec{k}\cdot\hat{n}+\frac{w^2\hbar}{2c^2M}-\left(E_{\lambda_0}-E_\lambda\right)/\hbar - w\right)$$

and based on that very elaborate analysis for transitions between electronic states is made. In fact this limit is not allowed, because, as it was shown, the perturbation increases linearly in time and beyond certain value it fails. Various justifications of this limit, such as formulation of transition probabilities per second (derivative of perturbation is constant), only confuse the issue, and that is how to handle this limit. It was shown above how this can be done within the perturbation theory, but there is another approach by which one solves the problem beyond it.

One important finding of the previous analysis is importance of the resonance frequencies. Any other frequency perturbs atom but has little effect on it. Therefore from now on it is a very good approximation to consider only two states from the set (6.4) or (6.5). In order to simplify notation the two states are labeled as 1 and 2, where 2 is higher in energy than 1. The plane wave propagates in direction of z axes and it is polarized along the x axes. The set of two equations that one has to solve is

$$\begin{aligned}\partial_t g_1\left(\vec{R},t\right) &= \frac{i\hbar}{2M}\Delta g_1\left(\vec{R},t\right)\\ &\quad+\frac{ea_0r_{1,2}}{mc}\cos\left(\frac{wz}{c}-wt\right)e^{-i(E_2-E_1)t/\hbar}g_2\left(\vec{R},t\right)\\ \partial_t g_2\left(\vec{R},t\right) &= \frac{i\hbar}{2M}\Delta g_2\left(\vec{R},t\right)\\ &\quad-\frac{ea_0r_{1,2}}{mc}\cos\left(\frac{wz}{c}-wt\right)e^{-i(E_1-E_2)t/\hbar}g_1\left(\vec{R},t\right)\end{aligned} \tag{6.10}$$

where it was taken into account that $r_{1,2} = -r_{2,1}$. The frequency is nearly resonante, and therefore it is expected the dominant component of the plane wave that contributes to dynamics is[1]

$$\cos(\frac{wz}{c} - wt) \approx \frac{1}{2} e^{-i\frac{wz}{c}+iwt}$$

in the first equation, whilst the other is dominant in the second equation. The set that needs to be solved now is

$$\partial_t g_1\left(\vec{R},t\right) = \frac{i\hbar}{2M}\Delta g_1\left(\vec{R},t\right) + \varepsilon\, e^{-i\frac{wz}{c}+i\varpi t} g_2\left(\vec{R},t\right)$$
$$\partial_t g_2\left(\vec{R},t\right) = \frac{i\hbar}{2M}\Delta g_2\left(\vec{R},t\right) - \varepsilon\, e^{i\frac{wz}{c}-i\varpi t} g_1\left(\vec{R},t\right)$$

where de-tuning is

$$\varpi = w - \frac{(E_2 - E_1)}{\hbar}$$

and

$$\varepsilon = \frac{e a_0 r_{1,2}}{2mc}$$

One defines now new function by

$$g_1\left(\vec{R},t\right) = e^{-i\frac{wz}{2c}+i\frac{\varpi}{2}t} h_1\left(\vec{R},t\right) \quad ; \quad g_2\left(\vec{R},t\right) = e^{i\frac{wz}{2c}-i\frac{\varpi}{2}t} h_2\left(\vec{R},t\right) \tag{6.11}$$

and equations for them are

$$\Delta h_1 - \frac{iw}{c}\partial_z h_1 + \frac{2iM}{\hbar}\partial_t h_1 - \left(\frac{w^2}{4c^2} + \frac{M\varpi}{\hbar}\right) h_1 - \frac{2i\varepsilon M}{\hbar} h_2 = 0$$
$$\Delta h_2 + \frac{iw}{c}\partial_z h_2 + \frac{2iM}{\hbar}\partial_t h_2 - \left(\frac{w^2}{4c^2} - \frac{M\varpi}{\hbar}\right) h_2 + \frac{2i\varepsilon M}{\hbar} h_1 = 0$$

These functions in the Fourier transform are

$$h_1\left(\vec{R},t\right) = \int d^3k\; b_1(\vec{k},t) e^{i\vec{k}\cdot\vec{R}} \tag{6.12}$$
$$h_2\left(\vec{R},t\right) = \int d^3k\; b_2(\vec{k},t) e^{i\vec{k}\cdot\vec{R}}$$

[1] This choice is called the *rotating wave approximation* for the reasons that are somewhat mysterious, and go back to the early developments of quantum theory. In this text this name is not used for the sake of clarity of associating name with a substance of theory.

and equations for the coefficients are

$$d_t b_1 = -\left(\frac{i\hbar k^2}{2M} - \frac{i\hbar k_z w}{2Mc} + \frac{i\hbar w^2}{8Mc^2} + \frac{i\varpi}{2}\right) b_1 + \varepsilon b_2 \tag{6.13}$$
$$d_t b_2 = -\left(\frac{i\hbar k^2}{2M} + \frac{i\hbar k_z w}{2Mc} + \frac{i\hbar w^2}{8Mc^2} - \frac{i\varpi}{2}\right) b_2 - \varepsilon b_1$$

They have exact solution, which is

$$b_1(\vec{k},t) = e^{-i\frac{\hbar k^2}{2M}t - i\frac{\hbar w^2}{8Mc^2}t}\left[\cos\left(\frac{\Omega t}{2}\right) + i\left(\frac{\hbar k_z w}{Mc} - \varpi\right)\frac{\sin\left(\frac{\Omega t}{2}\right)}{\Omega}\right] b_1(\vec{k},0)$$
$$b_2(\vec{k},t) = -2\varepsilon\, e^{-i\frac{\hbar k^2}{2M}t - i\frac{\hbar w^2}{8Mc^2}t}\,\frac{\sin\left(\frac{\Omega t}{2}\right)}{\Omega} b_1(\vec{k},0)$$

where

$$\Omega = \sqrt{4\varepsilon^2 + \left(\frac{\hbar k_z w}{Mc} - \varpi\right)^2}$$

It was assumed in this solution that at $t = 0$ the initial conditions are

$$g_1\left(\vec{R},0\right) = e^{-i\frac{wz}{2c}}\int d^3k\; b_1(\vec{k},0)e^{i\vec{k}\cdot\vec{R}}$$
$$g_2\left(\vec{R},0\right) = 0 \quad \Rightarrow \quad b_2(\vec{k},0) = 0$$

or

$$b_1(\vec{k},0) = \frac{1}{(2\pi)^3}\int d^3R\; e^{+i\frac{wz}{2c} - i\vec{k}\cdot\vec{R}} g_1\left(\vec{R},0\right)$$

Time evolution of either $g_1\left(\vec{R},t\right)$ or $g_2\left(\vec{R},t\right)$ is very complicated, but numerically straightforward in particular this is a relatively simple task if initial $g_1\left(\vec{R},0\right)$ is a Gaussian. As noted before time evolution of the probability amplitude along the z axes is then de-coupled from its time evolution along the other axis. Coupling with the electromagnetic wave is along the z axes and therefore only this degree of freedom is considered. The assumed Gaussian is (the atom is at rest initially)

$$g_1(z,0) = \frac{1}{d^{1/2}\pi^{1/4}} e^{-\frac{z^2}{2d^2}}$$

and $b_1(k,0)$ is (only one coordinate is used, where now k stands for k_z)

$$b_1(k,0) = \sqrt{\frac{d}{2\pi^{3/2}}} e^{-\frac{d^2}{2}\left(k - \frac{w}{2c}\right)^2}$$

The coefficient $b_1(k,t)$ is now

$$b_1(k,t) = \sqrt{\frac{d}{2\pi^{3/2}}} e^{-i\frac{\hbar k^2}{2M}t - \frac{d^2}{2}\left(k-\frac{w}{2c}\right)^2} \left[\cos\left(\frac{\Omega t}{2}\right) + i\left(\frac{\hbar k w}{Mc} - \varpi\right)\frac{\sin\left(\frac{\Omega t}{2}\right)}{\Omega}\right]$$

where

$$\Omega = \sqrt{4\varepsilon^2 + \left(\frac{\hbar k w}{Mc} - \varpi\right)^2}$$

and the solution for $g_1(z,t)$ is

$$\begin{aligned} g_1(z,t) &= e^{-i\frac{wz}{2c}+i\frac{\varpi}{2}t}\int_{-\infty}^{\infty} dk\; b_1(k,t)e^{ikz} \\ &= \sqrt{\frac{d}{2\pi^{3/2}}} e^{i\frac{\varpi}{2}t}\int_{-\infty}^{\infty} dk\; e^{ikz - i\frac{\hbar\left(k+\frac{w}{2c}\right)^2}{2M}t - \frac{d^2}{2}k^2} \\ &\quad \left[\cos\left(\frac{\Omega t}{2}\right) + i\left(\frac{\hbar k w}{Mc} + \frac{\hbar w^2}{2Mc^2} - \varpi\right)\frac{\sin\left(\frac{\Omega t}{2}\right)}{\Omega}\right] \end{aligned}$$

where now

$$\Omega = \sqrt{4\varepsilon^2 + \left(\frac{\hbar k w}{Mc} + \frac{\hbar w^2}{2Mc^2} - \varpi\right)^2}$$

because the integration variable k was shifted.

Similarly the coefficient $b_2(k,t)$ is obtained as

$$b_2(k,t) = -\varepsilon\sqrt{\frac{2d}{\pi^{3/2}}}\, e^{-i\frac{\hbar k^2}{2M}t - \frac{d^2}{2}\left(k-\frac{w}{2c}\right)^2}\, \frac{\sin\left(\frac{\Omega t}{2}\right)}{\Omega}$$

and $g_2(z,t)$ is

$$\begin{aligned} g_2(z,t) &= e^{i\frac{wz}{2c}-i\frac{\varpi}{2}t}\int_{-\infty}^{\infty} dk\; b_2(k,t)e^{ikz} \\ &= -\varepsilon\sqrt{\frac{2d}{\pi^{3/2}}} e^{i\frac{wz}{c}-i\frac{\varpi}{2}t}\int_{-\infty}^{\infty} dk\;\; e^{ikz - i\frac{\hbar\left(k+\frac{w}{2c}\right)^2}{2M}t - \frac{d^2}{2}k^2}\;\frac{\sin\left(\frac{\Omega t}{2}\right)}{\Omega} \end{aligned} \tag{6.14}$$

Information that $g_2(z,t)$ gives is too detailed, one is more interested in the overall probability to find atom in the electronic state 2

$$P_2(t) = \int_{-\infty}^{\infty} dz\;\; |g_2(z,t)|^2$$

If solution (6.14) is replaced in the integral then

$$P_2(t) = \frac{4d\varepsilon^2}{\pi^{1/2}} \int_{-\infty}^{\infty} dk\, e^{-d^2k^2} \frac{\sin^2\left(\frac{t}{2}\sqrt{4\varepsilon^2 + \left(\frac{\hbar kw}{Mc} + \frac{\hbar w^2}{2Mc^2} - \varpi\right)^2}\right)}{4\varepsilon^2 + \left(\frac{\hbar kw}{Mc} + \frac{\hbar w^2}{2Mc^2} - \varpi\right)^2}$$

or if one changes the integration variable by writing

$$\frac{\hbar kw}{Mc} + \frac{\hbar w^2}{2Mc^2} - \varpi = \frac{\hbar w}{Mc} u$$

then

$$P_2(t) = \frac{4d\varepsilon^2}{\pi^{1/2}} \int_{-\infty}^{\infty} du\, e^{-d^2\left(u - \frac{w}{2c} + \frac{Mc}{w\hbar}\varpi\right)^2} \frac{\sin^2\left(\frac{t}{2}\sqrt{4\varepsilon^2 + \left(\frac{\hbar w}{Mc}\right)^2 u^2}\right)}{4\varepsilon^2 + \left(\frac{\hbar w}{Mc}\right)^2 u^2}$$

Typical features of the probability $P_2(t)$ depend on a number of parameters. Few typical choices are shown, and the other are gauged against them. In calculations the parameters M and $\hbar$ where set to unity, whilst $w = 15,\ c = 100$ and $d = 100$. For de tuning $\varpi = 0$ (w is the resonance frequency) two values of ε are chosen, and the corresponding $P_2(t)$ are shown in Fig. 6.3. One notices that the probability oscillates between the two extreme values with the period that depends on this parameter, and it is approximately given by

$$T = \frac{\pi}{\varepsilon} \tag{6.15}$$

It appears that the oscillations go indefinitely, with the amplitude between 0 and 1, however, on the longer time scale a different conclusion emerges, as shown in Fig. 6.4 where only the envelopes of the oscillations are shown because individual

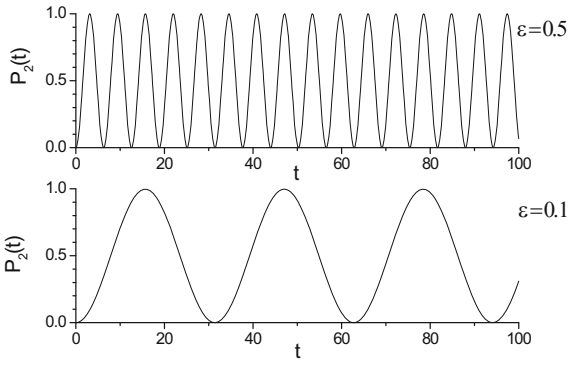

Fig. 6.3 Short time dependence of the probability for the excited state in a two level system under the impact of an electromagnetic wave with the resonance frequency, and two coupling parameters ε. The (Rabi) period is given by (6.15)

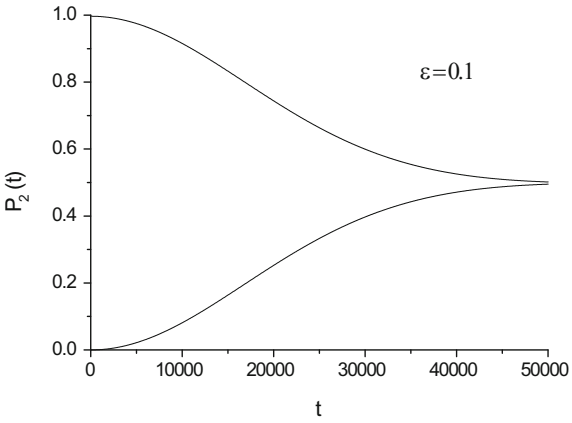

Fig. 6.4 Long time dependence of the probability for the excited state in a two level system under the impact of an electromagnetic wave with the resonance frequency. Only the envelope of the oscillations is shown

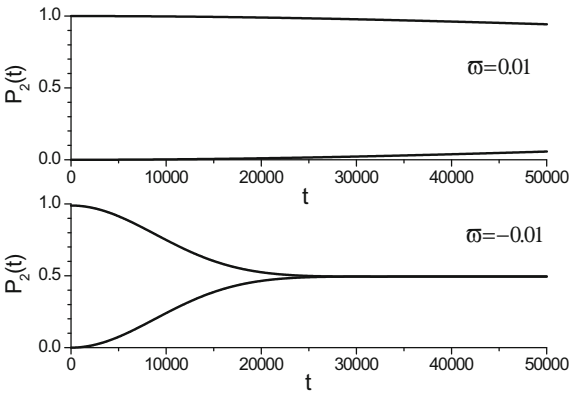

Fig. 6.5 Dumping of oscillations for the probability of the excited state in a two level system, as a function of de tuning

ones are not distinguishable. Dumping of the amplitudes occurs, and eventually the probability $P_2(t)$ acquires a stationary value. The time when this stationary value is achieved depends greatly on the chosen parameters. However, in the limit $c \to \infty$ this time is infinite when the period of oscillations, Rabbi oscillations, is (6.15), and it is referred to as the Rabbi period.

Dumping is also affected by de tuning ϖ, and two typical examples for $\varepsilon = 0.1$ are shown in Fig. 6.5, one for the positive and the other for the negative de tuning (again only the envelopes of the oscillations are shown). For the positive de tuning dumping gets negligible whilst for the negative it becomes more efficient.

The meaning of the dumping of the transition probability is that atom eventually acquires a permanent electric dipole moment. Namely, oscillations of the probability amplitude between two states occurs primarily between those that have different symmetry properties, which means that the electric dipole moment oscillates between zero value (when the electrons are in one of the eigenstates) and some maximal value

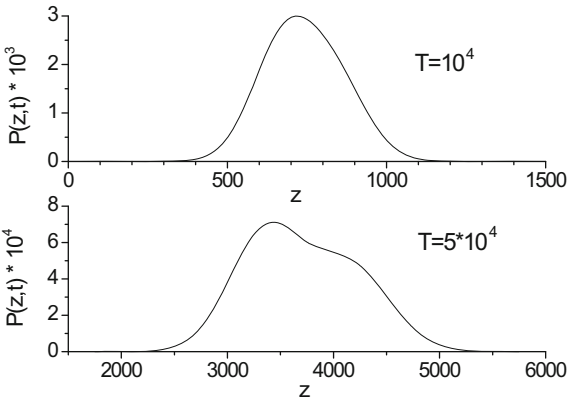

Fig. 6.6 Probability density of atom under the impact of a plane electromagnetic wave in resonance with its two levels. Short (*upper figure*) and long (*lower figure*) time behavior is shown

(for example when $P_2(t) = 0.5$). Eventually due to damping the probability acquires a constant value somewhere between its two extremes, which also means that the electric dipole moment of atom has a constant value.

Probability density for the atom, along the z direction, is defined as

$$P(z,t) = \int dV_{el}\ f^* f = \sum_{\lambda} g_{\lambda}^* \left(\vec{R},t\right) \nabla_R g_{\lambda} \left(\vec{R},t\right)$$
$$= g_1^*(z,t)\, g_1(z,t) + g_2^*(z,t)\, g_2(z,t)$$

Two typical instants in time are chosen, one when the probability $P_2(t)$ is still oscillating (in Fig. 6.4 this corresponds to $t = 10000$), and the other when this probability reached a constant value ($t = 50000$ in Fig. 6.4). The probability density retains its Gaussian shape for a long time, but spreads, and eventually it becomes a shape with two extremes, which are not well separated. Both examples are shown in Fig. 6.6.

Another useful quantity to calculate is velocity of atom, which is defined for the total probability amplitude (6.3) as

$$\vec{v}_{atom} = \int dV_{el}\, d^3R\ f^* \left(-\frac{i\hbar}{M}\nabla_R\right) f$$
$$= -\frac{i\hbar}{M} \int dV_{el}\, d^3R \sum_{\lambda} g_{\lambda}^* \left(\vec{R},t\right) h_{\lambda}\left(\vec{r}_j\right) e^{iE_{\lambda}t/\hbar} \nabla_R \sum_{\mu} g_{\mu}\left(\vec{R},t\right) h_{\mu}\left(\vec{r}_j\right) e^{-iE_{\mu}t/\hbar}$$

and if the orthonormal property of the electron eigenfunctions are used then

$$\vec{v}_{atom} = -\frac{i\hbar}{M} \sum_{\lambda} \int d^3R\ g_{\lambda}^* \left(\vec{R},t\right) \nabla_R g_{\lambda} \left(\vec{R},t\right)$$

For the example that is analyzed velocity, and only its component in the z direction is

$$
\begin{aligned}
&v_{atom} = \\
&\quad -\frac{i\hbar}{M}\left[\int d^3R\, g_1^*\left(\vec{R},t\right)\hat{z}\cdot\nabla_R g_1\left(\vec{R},t\right)+\int d^3R\, g_2^*\left(\vec{R},t\right)\hat{z}\cdot\nabla_R g_2\left(\vec{R},t\right)\right] \\
&= \frac{4d\hbar\varepsilon^2}{\pi^{1/2}M}\int_{-\infty}^{\infty} dk\, ke^{-d^2k^2}\,\frac{\sin^2\left(\frac{t}{2}\Omega\right)}{\Omega^2} \\
&\quad + \frac{d\hbar}{\pi^{1/2}M}\int_{-\infty}^{\infty} dk\, ke^{-d^2k^2}\left[\cos^2\left(\frac{\Omega t}{2}\right)+\left(\frac{\hbar k w}{Mc}+\frac{\hbar w^2}{2Mc^2}-\varpi\right)^2\frac{\sin^2\left(\frac{t}{2}\Omega\right)}{\Omega^2}\right]^2 \\
&\quad + \frac{w\hbar}{Mc}\frac{4d\varepsilon^2}{\pi^{1/2}}\int_{-\infty}^{\infty} dk\, ke^{-d^2k^2}\,\frac{\sin^2\left(\frac{t}{2}\Omega\right)}{\Omega^2}
\end{aligned}
$$

and from the definition of Ω one obtains

$$v_{atom} = \frac{w\hbar}{Mc}P_2(t) \tag{6.16}$$

This means that the atom acquires velocity that is proportional to the probability of finding electrons in the state 2 and the frequency dependent momentum from the electromagnetic wave, photon momentum transfer to the atom. Average value of the atom velocity is obtained by neglecting oscillating terms in $P_2(t)$, which gives

$$P_2(t) = \frac{2d\varepsilon^2}{\pi^{1/2}}\int_{-\infty}^{\infty} du\;\frac{e^{-d^2\left(u-\frac{w}{2c}+\frac{Mc}{w\hbar}\varpi\right)^2}}{4\varepsilon^2+\left(\frac{\hbar w}{Mc}\right)^2u^2}$$

The integral has analytic solution and the probability is

$$P_2(t) = \frac{Mcd\varepsilon\pi^{1/2}}{2w\hbar}e^{-a^2}\left[1-\operatorname{erf}(ia)\right]+C.C.$$

where $C.C.$ means the complex conjugate of the previous term, and

$$a = \frac{dw}{2c}-\frac{Mcd}{w\hbar}\varpi - i\frac{2Mcd}{w\hbar}\varepsilon$$

The argument of the error function $\operatorname{erf}(z)$ is large and from its asymptotic value

$$\operatorname{erf}(z) \approx 1-\frac{1}{z\sqrt{\pi}}e^{-z^2}$$

the average probability is

$$P_2(t) = \frac{2\varepsilon^2}{4\varepsilon^2 + \left(\frac{w^2\hbar}{2c^2M} - \varpi\right)^2}$$

For the example in Fig. 6.6 the average $P_2(t)$ gives the value ≈ 0.5, and so the motion of the maximum of the probability density $P(z,t)$ is governed by the equation

$$z_{atom} \approx \frac{15}{100} 0.5\, t = 0.075\, t$$

which is a good estimate.

6.2.3 Second Order Interaction

Second order interaction involves terms in the set (6.4) of the order c^{-2}

$$\begin{aligned} i\hbar\partial_t g_\lambda\left(\vec{R},t\right) = &-\frac{\hbar^2}{2M}\Delta g_\lambda\left(\vec{R},t\right) + \left(\frac{n^2}{M}+\frac{n}{m}\right)\frac{e^2}{2c^2}a^2(u)\, g_\lambda\left(\vec{R},t\right) \\ &+\frac{i\hbar e}{mc^2}\sum_\mu \frac{1}{c}a'(u) q_{\lambda,\mu} e^{-i\left(E_\mu - E_\lambda\right)t/\hbar} g_\mu\left(\vec{R},t\right) \\ &+\frac{i\hbar e}{Mc^2}a'(u)\sum_\mu r^{(n)}_{\lambda,\mu}\, e^{-i\left(E_\mu - E_\lambda\right)t/\hbar}\, \hat{s}\cdot\nabla g_\mu\left(\vec{R},t\right) \end{aligned}$$

Some of the terms have relatively simple explanation, which is based on the analysis in the previous chapters. Thus the time average of $a^2(u)$ is the contribution to the phase of $g_\lambda\left(\vec{R},t\right)$ that is interpreted as velocity of atom

$$V_{drift} = \left(\frac{n^2}{M}+\frac{n}{m}\right)\frac{e^2}{4Mc^3}a_0^2$$

in which the drift velocity (4.6) is recognized that gets contribution from both the nuclei and the electrons. The oscillatory part of $a^2(u)$ has double the frequency of the electromagnetic wave so that both the nuclei and the electrons oscillate at this frequency. It should be noted that V_{drift} increases as the square of the nuclear charge whilst it only increases linearly with the number of electrons, an indication that V_{drift} is indeed the drift velocity.

The term

$$V_{quadr} = \frac{i\hbar e}{mc^2}a'(u) q_{\lambda,\mu} e^{-i\left(E_\mu - E_\lambda\right)t/\hbar}$$

is very similar in its structure with that analyzed in the previous section, except that now it is of order c smaller and that it has also coupling along the propagation of the electromagnetic wave. The coupling element $r^{(s)}_{\lambda,\mu}$ (dipole interaction) in the previous section involves only the states that are connected by the polarization direction of the electromagnetic wave, on the other hand $q_{\lambda,\mu}$ is a product of the dipole terms in the $\hat{n}$ and $\hat{s}$ directions, which is a quadrupole interaction. These transitions are analyzed separately from those coupled by only the dipole interaction because the states involved may have different eigenenergies. Analyses of V_{quadr}, however, follows the same arguments as in the case for the dipole interaction.

The remaining term is

$$V_{long} = \frac{i\hbar e}{Mc^2} a'(u)\, r^{(n)}_{\lambda,\mu}\, e^{-i(E_\mu - E_\lambda)t/\hbar}\, \hat{s} \cdot \nabla$$

and involves the dipole interaction along propagation of the electromagnetic wave, the longitudinal interaction. Treating this term in isolation from the others should be done with some caution. Although the selection rules are different from the dipole interaction $r^{(s)}_{\lambda,\mu}$ the states involved may have equal eigenenergies., the states only couple different angular momentum states. Nevertheless, this interaction is analyzed here on its own.

By using the same arguments as in using the set (6.10) the two coupled equations that need to be solved are

$$\begin{aligned} i\hbar\partial_t g_1\left(\vec{R},t\right) &= -\frac{\hbar^2}{2M}\Delta g_1\left(\vec{R},t\right) + \frac{i\hbar e}{Mc^2}a'(u)\, r_{1,2}\, e^{-i(E_2-E_1)t/\hbar}\, \partial_x g_2\left(\vec{R},t\right) \\ i\hbar\partial_t g_2\left(\vec{R},t\right) &= -\frac{\hbar^2}{2M}\Delta g_2\left(\vec{R},t\right) - \frac{i\hbar e}{Mc^2}a'(u)\, r_{1,2}\, e^{-i(E_2-E_1)t/\hbar}\, \partial_x g_1\left(\vec{R},t\right) \end{aligned}$$

where polarization is assumed to be along the x axes, and the superscript (n) was omitted. Again the structure of equations is the same as in the set (6.10), except the selection rules are different and derivatives of $g_n\left(\vec{R},t\right)$ are involved. Analysis of the solutions is the same as for the set (6.10), which means that for a plane wave of the frequency w the set is transformed into

$$\begin{aligned} \partial_t g_1\left(\vec{R},t\right) &= \frac{i\hbar}{2M}\Delta g_1\left(\vec{R},t\right) - i\varepsilon\, e^{-i\frac{wz}{c}+i\varpi t}\, \partial_x g_2\left(\vec{R},t\right) \\ \partial_t g_2\left(\vec{R},t\right) &= \frac{i\hbar}{2M}\Delta g_2\left(\vec{R},t\right) + i\varepsilon\, e^{i\frac{wz}{c}-i\varpi t}\, \partial_x g_1\left(\vec{R},t\right) \end{aligned}$$

where

$$\varepsilon = \frac{ewr_{1,2}}{2Mc^2}$$

The set is first transformed by defining new functions, as in (6.11), which satisfy the equations

$$\Delta h_1 - \frac{iw}{c}\partial_z h_1 + \frac{2iM}{\hbar}\partial_t h_1 - \left(\frac{w^2}{4c^2} + \frac{M\varpi}{\hbar}\right) h_1 - \frac{2\varepsilon M}{\hbar}\partial_x h_2 = 0$$
$$\Delta h_2 + \frac{iw}{c}\partial_z h_2 + \frac{2iM}{\hbar}\partial_t h_2 - \left(\frac{w^2}{4c^2} - \frac{M\varpi}{\hbar}\right) h_2 + \frac{2\varepsilon M}{\hbar}\partial_x h_1 = 0$$

The solutions are represented in the Fourier transform as in (6.12), and for the coefficients the set of equations is

$$d_t b_1 = -\left(\frac{i\hbar k^2}{2M} - \frac{i\hbar k_z w}{2Mc} + \frac{i\hbar w^2}{8Mc^2} + \frac{i\varpi}{2}\right) b_1 + \varepsilon k_x b_2$$
$$d_t b_2 = -\left(\frac{i\hbar k^2}{2M} + \frac{i\hbar k_z w}{2Mc} + \frac{i\hbar w^2}{8Mc^2} - \frac{i\varpi}{2}\right) b_2 - \varepsilon k_x b_1$$

This is almost the same as the set (6.13) except that the coupling constant ε is multiplied by k_x, which means that instead with a single dimension problem one solves a two dimensional, at least. Detailed analysis of this dynamics is not made.

Chapter 7
Radiation by Charge

Abstract Charge under non uniform motion, more general than uniform acceleration, radiates and the radiation patter carries information about the structure of charge density. Radiation by created charge, by bound charge, rotating and vibrating molecule is calculated and analyzed. Line shift of atomic spectral lines is derived when atom is interacting with electromagnetic wave.

7.1 Radiation Zone

Charge in a nonuniform motion generates time dependent electromagnetic field that could be analyzed in two regions of space. One is far away from the source, the radiation zone where the outflowing electromagnetic field carries away energy and the measure of this is Poyting vector (3.3). The other region is where the electromagnetic field overlaps with the probability density of the charge and it is the source of field reaction (4.3). Electromagnetic field in the radiation zone is analyzed in this chapter and how its properties give information about its source.

A point-like classical charge has no meaning because of the uncertainty principle that should be imposed on dynamics of particles. Therefore, a single charge should be treated as an extended source of the electromagnetic field, of the sort as charge density that is discussed in Sect. 4.3. The two most important quantities that determine the field are the charge and the charge current, which in this case are defined as

$$\rho\left(\vec{r},t\right)=e\left|f\left(\vec{r},t\right)\right|^{2}\quad,\quad\vec{j}\left(\vec{r},t\right)=\frac{e\hbar}{m}\,\mathrm{Im}\,\left(f^{*}\nabla f\right) \tag{7.1}$$

where f is the probability amplitude for the particle of mass m and charge e (for more details see Sect. 1.2).

Vector and scalar potentials for a time varying charge distribution are derived from (3.9), and the acceptable retarded solution is derived in Chap. 2, with result for scalar

$$V\left(\vec{r},t\right)=\int d^{3}q\frac{\rho\left(\vec{q},t-\frac{1}{c}\left|\vec{r}-\vec{q}\right|\right)}{\left|\vec{r}-\vec{q}\right|} \tag{7.2}$$

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and vector

$$\vec{A}\left(\vec{r},t\right)=\frac{1}{c}\int d^3q\frac{\vec{j}\left(\vec{q},t-\frac{1}{c}\left|\vec{r}-\vec{q}\right|\right)}{\left|\vec{r}-\vec{q}\right|} \tag{7.3}$$

potential.

Both results indicate that the potentials at a certain point, and at certain time, are given by the charge density and the current at some earlier time, also called retardation time, being result of the finite velocity at which the perturbation in the field propagates. If the size of the source is small compared to the distance $\vec{r}$ where the field is observed then one could write

$$\left|\vec{r}-\vec{q}\right|\approx r-\hat{r}\cdot\vec{q} \tag{7.4}$$

and the scalar potential is

$$V\left(\vec{r},t\right)\approx\int d^3q\frac{\rho\left(\vec{q},t-\frac{1}{c}r+\frac{1}{c}\hat{r}\cdot\vec{q}\right)}{r}$$

It is tempting to conclude that because q is small compared to r one could write expansion

$$\rho\left(\vec{q},t-\frac{1}{c}r+\frac{1}{c}\hat{r}\cdot\vec{q}\right)\approx\rho\left(\vec{q},t-\frac{1}{c}r\right)+\frac{1}{c}\,\hat{r}\cdot\vec{q}\,\dot{\rho}\left(\vec{q},t-\frac{1}{c}r\right) \tag{7.5}$$

and that it is valid in all circumstances. However, this is not the case, which is shown by noting that the probability density for charge is determined roughly by the phase space density $\Gamma\left(\vec{r},\overrightarrow{v},t\right)$ as the integral (for simplicity velocity variable is used instead of the momentum variable)

$$\rho\left(\overrightarrow{q},t\right)=\int d^3v\,\Gamma\left(\overrightarrow{q},\overrightarrow{v},t\right)$$

If at some initial instant the phase space density is $\Gamma_0\left(\vec{r},\overrightarrow{v}\right)$ then after a short time interval, within which the particle is assumed to move freely, it is given by

$$\Gamma\left(\overrightarrow{q},\overrightarrow{v},\frac{1}{c}\hat{r}\cdot\vec{q}\right)=\Gamma_0\left(\overrightarrow{q}-\frac{\overrightarrow{v}}{c}\hat{r}\cdot\vec{q},\overrightarrow{v}\right)$$

where for simplicity it was assumed that $t=\frac{1}{c}r$. Expansion in the powers of c^{-1} is now

$$\begin{aligned}\Gamma\left(\overrightarrow{q},\overrightarrow{v},\frac{1}{c}\hat{r}\cdot\vec{q}\right)&\approx\Gamma_0\left(\overrightarrow{q},\overrightarrow{v}\right)+\frac{1}{c}\hat{r}\cdot\vec{q}\,\partial_t\Gamma\left(\overrightarrow{q},\overrightarrow{v},0\right)\\&=\Gamma_0\left(\overrightarrow{q},\overrightarrow{v}\right)-\frac{1}{c}\hat{r}\cdot\vec{q}\,\overrightarrow{v}\cdot\nabla_q\Gamma\left(\overrightarrow{q},\overrightarrow{v},0\right)-\frac{1}{c}\hat{r}\cdot\vec{q}\,\overrightarrow{F}\cdot\nabla_v\Gamma\left(\overrightarrow{q},\overrightarrow{v},0\right)\end{aligned}$$

where Liouville equation was used in the last step. The probability (charge) density is now

$$\rho\left(\vec{q}, \frac{1}{c}\hat{r}\cdot\vec{q}\right) \approx \rho\left(\vec{q}, 0\right) - \hat{r}\cdot\vec{q}\,\frac{\left\langle\overrightarrow{v}\right\rangle}{c}\cdot\nabla_q\rho\left(\vec{q}, 0\right)$$

where in the phase space $\left\langle\overrightarrow{v}\right\rangle$ is the average velocity of the particle. Expansion (7.5) is, therefore, accurate under more stringent conditions then suggested in the derivation (7.5), and in fact the condition $\left\langle\overrightarrow{v}\right\rangle \ll c$ should be more appropriate.

By assuming that expansion (7.5) is accurate the scalar potential is

$$V\left(\vec{r}, t\right) \approx \frac{1}{r} + \frac{1}{cr}\int d^3q\,\hat{r}\cdot\vec{j}\left(\vec{q}, t - \frac{1}{c}r\right)$$

where the continuity equation

$$\dot{\rho}\left(\vec{r}, t\right) = -\nabla\cdot\vec{j}\left(\vec{r}, t\right)$$

for the charge density and the current was used. Similarly the vector potential is obtained

$$\vec{A}\left(\vec{r}, t\right) = \frac{1}{cr}\int d^3q\,\vec{j}\left(\vec{q}, t - \frac{1}{c}r\right) - \frac{1}{c^2r}\int d^3q\,\hat{r}\cdot\vec{q}\,d_t\,\vec{j}\left(\vec{q}, t - \frac{1}{c}r\right)$$

and the second term can be neglected because it is of the order c^{-2}.

The electric component of the field is

$$\begin{aligned}\vec{E} = -\nabla V - \frac{1}{c}\partial_t\vec{A} &\approx \frac{\hat{r}}{c^2r}\int d^3q\,\hat{r}\cdot d_t\,\vec{j}\left(\vec{q}, t - \frac{1}{c}r\right) - \frac{1}{c^2r}\int d^3q\,d_t\,\vec{j}\left(\vec{q}, t - \frac{1}{c}r\right)\\ &= \frac{1}{c^2r}\hat{r}\times\left[\hat{r}\times\int d^3q\,d_t\,\vec{j}\left(\vec{q}, t - \frac{1}{c}r\right)\right]\end{aligned}$$

whilst the magnetic is

$$\vec{H} = \nabla\times\vec{A} \approx -\frac{1}{c^2r}\hat{r}\times\int d^3q\,d_t\,\vec{j}\left(\vec{q}, t - \frac{1}{c}r\right)$$

where only the dominant power of r was retained, which is r^{-1}. The Poyting vector from these components is

$$\vec{P} = \frac{c}{4\pi}\vec{E}\times\vec{H} = \frac{1}{4\pi c^3r^2}\hat{r}\left[\hat{r}\times\int d^3q\,d_t\,\vec{j}\left(\vec{q}, t - \frac{1}{c}r\right)\right]^2 \tag{7.6}$$

which shows that the energy flows in the radial direction, out of the surface surrounding the charge. Another finding is that the electric and magnetic components

are perpendicular to each other, which is characteristic of the electromagnetic wave. Total power outflow is the integral over the surface that surrounds the charge is

$$W = \int d\Omega\, \hat{r} \cdot \vec{P} = \frac{2}{3c^3 r^2} \left[\int d^3q\, d_t\, \vec{j} \left(\vec{q}, t - \frac{1}{c} r \right) \right]^2 \tag{7.7}$$

Previous derivation should be taken with some caution. In the expansion of the scalar and vector potentials one encounters the integral

$$\vec{v}_{av} = \int d^3q\, \vec{j} \left(\vec{q}, t - \frac{1}{c} r \right)$$

which has the meaning of the average velocity of the charge. It could be replaced by its classical result (in most cases, especially for unbound charges), in particular if the charge is acted upon by a constant force F then

$$\vec{v}_{av} = \frac{\vec{F}}{m}\, t$$

where m is mass of the charge. Scalar potential is in this case

$$\begin{aligned} V(\vec{r}, t) &\approx \frac{1}{r} + \frac{1}{mcr} \left(t - \frac{1}{c} r \right) \hat{r} \cdot \vec{F} \\ &= \frac{1}{r} + \frac{t}{mcr}\, \hat{r} \cdot \vec{F} - \frac{1}{mc^2}\, \hat{r} \cdot \vec{F} \end{aligned}$$

and likewise the vector potential

$$\vec{A}(\vec{r}, t) = \frac{t}{mcr} \vec{F} - \frac{1}{mc^2} \vec{F}$$

In the calculation of the electric and magnetic components one neglects contributions of the order r^{-2} or higher, in which case

$$\vec{E} \approx -\frac{1}{mc^2} \left(\vec{r} \cdot \vec{F} \right) \frac{\vec{r}}{r}$$

and

$$\vec{H} \approx \nabla \times \frac{t}{mcr} \vec{F} = 0$$

because magnetic component decays more rapidly with the distance then r^{-1}. Therefore a uniformly accelerating charge does not radiate, a surprising result in view of the intuitive belief that in these circumstances radiation is produced.

Analysis of W is the subject of spectroscopy, in particular connection between the structure of a cluster of charges, epitomized in their current, and the dominant frequencies at which the system radiates. The subject is well studied [21–23] because this is almost the only information that one gets about the structure of atoms and molecules. This aspect of radiation by charges is not discussed in details here, but few additional remarks are necessary for later analysis.

Poyting vector (7.6) gives very detailed information about the radiation intensity from non uniformly moving charges, because it is a function of time, and this is very difficult to measure. It also gives limited information because in its derivation it was assumed that over the range of the charge density the electromagnetic wave travels at infinite speed. The finite speed is taken into account by deriving the radiation intensity without expansion into the powers in c^{-1}, and as the result various correlation effects within the charge density are described. Correction that takes into account retardation effect within charge density is done by replacing the current in (7.6) with

$$\vec{j}\left(\vec{r}', t - \frac{r}{c}\right) \to \vec{j}\left(\vec{r}', t - \frac{r}{c} + \frac{\hat{n}\cdot\vec{r}'}{c}\right)$$

In addition to this modification one also replaces normalization of the power per unit surface area, the Poyting vector (7.6), with power per unit solid angle

$$\frac{dP}{d\Omega} = \frac{1}{4\pi c^3}\left[\int d^3r'\hat{n}\times\partial_t\vec{j}\left(\vec{r}', t - \frac{r-\hat{n}\cdot\vec{r}'}{c}\right)\right]^2, \quad \hat{n} = \frac{\vec{r}}{r} \tag{7.8}$$

As it was argued, information contained in (7.8) is too detailed, and it is replaced by integrating radiation power over the whole radiation time thus giving the total energy emitted in a given solid angle

$$W = \int_{-\infty}^{\infty} dt\, \frac{dP}{d\Omega} \tag{7.9}$$

where the limits of integration should be carefully examined. Formally they extend over the infinite time interval, but in fact the power $P(t)$ is non-zero over a finite time interval.

Having that in mind one defines Fourier transform of the current

$$\vec{j}(\vec{r}, t) = \frac{1}{(2\pi)^{7/2}}\int d^3k\, e^{-i\vec{k}\cdot\vec{r}}\int d\omega\, \vec{j}_{\vec{k},\omega}e^{i\omega t} \Rightarrow$$
$$\vec{j}_{\vec{k},\omega} = \frac{1}{(2\pi)^{1/2}}\int d^3r\, e^{i\vec{k}\cdot\vec{r}}\int dt\, \vec{j}(\vec{r}, t)\, e^{-i\omega t}$$

when the integral over the current, that enters the radiation intensity (7.8), is

$$\int d^3r'\hat{n}\times\partial_t\vec{j}\left(\vec{r}', t - \frac{r-\hat{n}\cdot\vec{r}'}{c}\right) = \frac{i}{(2\pi)^{1/2}}\hat{n}\times\int d\omega\, \omega\, \vec{j}_{\omega\frac{\hat{n}}{c},\omega}e^{i\omega(t-\frac{r}{c})}$$

and when replaced in the expression for emitted energy W one gets

$$W = \frac{1}{4\pi c^3} \int d\omega \omega^2 \left(\hat{n} \times \vec{j}_{\vec{k},\omega}\right)^2$$

where

$$\vec{k} = \frac{\omega}{c}\hat{n}$$

is the wave number of radiation. Instead of the unit vector $\hat{n}$ one now defines W as a function of the polarization vector $\hat{a}$ of the emitted radiation, whose property is $\vec{k} \cdot \hat{a} = 0$. This is achieved by replacing

$$\left(\hat{n} \times \vec{j}_{\vec{k},\omega}\right) \cdot \left(\hat{n} \times \vec{j}_{\vec{k},\omega}\right) \longrightarrow \left(\hat{a} \cdot \vec{j}_{\vec{k},\omega}\right)^2,$$

which differs from the original expression in the factor $\cos^2(\Delta)$, where Δ is the angle between $\hat{a}$ and the unit vector in direction of the perpendicular component of the current $\vec{j}_{\vec{k},\omega}$ with respect to $\vec{k}$. The radiation intensity gives now information about the polarization of the emitted radiation, besides its frequency dependence.

Spectrum is defined as emitted energy per unit frequency interval

$$W(\omega) = \frac{\omega^2}{4\pi c^3} \left|I(\hat{a}, \omega)\right|^2 \tag{7.10}$$

where

$$I(\hat{a}, \vec{k}, \omega) = \int d^3r \, e^{i\vec{k}\cdot\vec{r}} \hat{a} \cdot \vec{j}_\omega(\vec{r}) = \frac{1}{\sqrt{2\pi}} \int dt \int d^3r \, \vec{A}(\vec{r}, t) \cdot \vec{j}(\vec{r}, t) \tag{7.11}$$

is *radiation amplitude*, and

$$\vec{A} = \hat{a} \, e^{i\vec{k}\cdot\vec{r} - i\omega t} \tag{7.12}$$

is the vector potential of emitted electromagnetic wave. The current is in general given by

$$\vec{j}(\vec{r}, t) = \frac{\hbar e}{2im}\left(f^* \nabla f - f \nabla f^*\right) - \frac{e^2}{mc}\vec{A}_{in} \left|f(\vec{r}, t)\right|^2 \tag{7.13}$$

where $\vec{A}_{in}$ is vector potential of external electromagnetic field that determines dynamics of a charge. $f(\vec{r}, t)$ is probability amplitude for the charge, which in momentum space is

$$f(\vec{r}, t) = \int d^3p \, de \, \boldsymbol{g}(\vec{p}, e) \, e^{i\,\vec{p}\cdot\vec{r} - i\,et}$$

and the current is

$$\vec{j}\,(\vec{r},t)=\frac{\hbar e}{m}\int d^3p\,de\,d^3p'\,de'\boldsymbol{g}\,(\vec{p},e)\,\boldsymbol{g}^*\left(\vec{p}',e'\right)e^{i\,(\vec{p}-\vec{p}')\cdot\vec{r}-i\,(e-e')t}\left(\frac{\vec{p}+\vec{p}'}{2}-\frac{e}{c\hbar}\vec{A}_{in}\right)$$

It contains two terms, without and with the external field, and the radiation amplitude for the former is

$$\begin{aligned}I^{(1)}(\hat{a},\vec{k},\omega)&=\frac{1}{\sqrt{2\pi}}\int dt\int d^3r\;\hat{a}\;\cdot\vec{j}\,(\vec{r},t)\,e^{i\vec{k}\cdot\vec{r}-i\omega t}\\&=(2\pi)^{7/2}\frac{\hbar e}{2m}\;\hat{a}\;\cdot\int d^3p\,de\,\boldsymbol{g}^*\left(\vec{p}+\vec{k},e+\omega\right)\boldsymbol{g}\,(\vec{p},e)\left(2\vec{p}+\vec{k}\right)\end{aligned}$$

Contribution from the external field field $\vec{A}_{in}$ in radiation amplitude simplifies for a plane wave

$$\vec{A}_{in}=\vec{A}_{0in}\cos\left(\vec{k}_{in}\cdot\vec{r}-\omega_{in}t\right)$$

when it is parametrized as

$$I^{(2)}(\hat{a},\vec{k},\omega)=I^{(2)+}(\hat{a},\vec{k},\omega)+I^{(2)-}(\hat{a},\vec{k},\omega)$$

where

$$\begin{aligned}&I^{(2)\pm}(\hat{a},\vec{k},\omega)\\&\quad=-(2\pi)^{7/2}\frac{e^2}{2mc}\hat{a}\;\cdot\vec{A}_{0in}\int d^3p\,de\,\boldsymbol{g}^*\left(\pm\vec{k}_{in}+\vec{p}+\vec{k},\;\pm\omega_{in}+e+\omega\right)\boldsymbol{g}\,(\vec{p},e)\end{aligned}$$

Radiation amplitude is essentially an overlap integral between two momentum space probability amplitudes. One, $\boldsymbol{g}\,(\vec{p},e)$, is the original amplitude, before the interaction takes place, and the other, $\boldsymbol{g}^*\left(\vec{p}+\vec{k},e+\omega\right)$ or $\boldsymbol{g}^*\left(\pm\vec{k}_{in}+\vec{p}+\vec{k},\;\pm\omega_{in}+e+\omega\right)$, is the amplitude after the interaction. Both final state amplitudes indicate that momentum distribution of the charge changed by a discrete amount. In the amplitude without the external field the change is by the wave number of the radiated field whilst when the external field is included then there is additional change due to its wave number. If it is assumed that momentum probability amplitude has maximum for $\vec{p}=0$ then $\boldsymbol{g}^*\left(\vec{p}+\vec{k},e+\omega\right)$ means that the charge recoiled as if the wave number of the radiated field is associated with a momentum or as if a particle is emitted of momentum $\vec{k}$ rather than being the field. By the same token, the wave number of the external field could be treated in the same wave, it changes momentum of the charge.

7.2 Radiation by Created Charge

When a charge is created, or a charge changes its motions almost instantly, radiation is produced. Although the problem appears well defined, but it is not so if the retardation effect is strictly taken into account. The problem is that one does not have information about the charge prior to that instant. However, in specific situations this problem could be solved, and one is creation of a charge when it is initially confined to a small volume. By small it is meant that due to the uncertainty relation charge moves in confinement with relativistic velocity in which case its dynamics is relativistic, and its radiation should be treated accordingly. If Δr measures the width of this confining volume then in[1]

$$\Delta r\ \Delta v = \frac{h}{4\pi m}$$

one replaces Δv with the velocity of light and gets an estimate of its size. If Δr is smaller than the tenth of the Compton wave length of a charge then relativistic dynamics is required to describe its radiation when it is freed from the confinement. For Hydrogen atom Δr is of the order of the Bohr radius $h/\ (2\pi mc\alpha)$, where α is fine structure constant, and dynamics is not relativistic. However, relativistic effects for the lowest energy electron in Uranium atom would be appreciable. If the electron is confined to a nucleus, whose typical radius is roughly one hundredth of the electron Compton wavelength, it is required to use relativistic theory. Treatment here shall be relativistic, from Dirac equation.

The set of relativistic equations is

$$\frac{i\hbar}{c}\partial_t F = \vec{S}\cdot\frac{\hbar}{i}\nabla G\ + mcF, \qquad \frac{i\hbar}{c}\partial_t G = \vec{S}\cdot\frac{\hbar}{i}\nabla F - mcG \tag{7.14}$$

where $\vec{S} = S_x\widehat{x} + S_y\widehat{y} + S_z\widehat{z}$ are spin matrices. Solution is

$$\psi = \begin{pmatrix} F \\ G \end{pmatrix}$$

and for a free charge solution the two components are

$$F = \sqrt{\frac{e+mc^2}{2e}}e^{-iet/\hbar + i\vec{p}\cdot\vec{r}/\hbar}F_0, \qquad G = \sqrt{\frac{e+mc^2}{2e}}e^{-iet+i\vec{p}\cdot\vec{r}}G_0 \tag{7.15}$$

where

$$G_0 = \frac{c}{mc^2+e}\vec{S}\cdot\vec{p}F_0.$$

[1] Warning! The uncertainty relationship is non relativistic and so the estimate is used only as a crude guidance.

Solution is normalized as

$$1 = F^+F + G^+G$$

provided $F_0^+F_0 = 1$.

There are three initial conditions that determine dynamics of a charge: probability density, probability current and orientation of spin. One starts by parameterizing F_0 as

$$F_0 = \begin{pmatrix} e^{i\frac{\phi_0}{2}}\cos\frac{\theta_0}{2} \\ e^{-i\frac{\phi_0}{2}}\sin\frac{\theta_0}{2} \end{pmatrix}$$

in which case

$$F_0^+\vec{S}F_0 = \widehat{s}$$

is the unit vector that points in direction of the spin. The three initial conditions for ψ could now be fitted by parametrization (units in which $m = c = \hbar = 1$ are used, for details see Appendix A)

$$\psi_0 = \sqrt{\frac{e_0+1}{2e_0}}\begin{pmatrix} F_0 \\ \frac{1}{e_0+1}\vec{S}\cdot\vec{p}_0\, e^{i\beta}F_0 \end{pmatrix} f_0(\vec{r}) \tag{7.16}$$

when the probability density is

$$P_0 = F^+F + G^+G = |f_0(\vec{r})|^2$$

the probability current

$$\overrightarrow{J}_0 = F^+\vec{S}G + G^+\vec{S}F = |f_0(\vec{r})|^2\left(\frac{\vec{p}_0}{e_0}\cos\beta + \widehat{s}_0\times\frac{\vec{p}_0}{e_0}\sin\beta\right)$$

and spin

$$\overrightarrow{s}_0 = F^+\vec{S}G + G^+\vec{S}F = |f_0(\vec{r})|^2\,\widehat{s}_0$$

The phase β is determined from the initial condition for the current.

By defining initial conditions one formulates solution ψ in the form

$$\psi = \int d^3p\left[A^{(+)}(\vec{p})W^{(+)}e^{-iet+i\vec{p}\cdot\vec{r}} + A^{(-)}(\vec{p})W^{(-)}e^{iet+i\vec{p}\cdot\vec{r}}\right] \tag{7.17}$$

where

$$W^{(\pm)} = \begin{pmatrix} F_0 \\ \frac{1}{1\pm e}\vec{S}\cdot\vec{p}\,F_0 \end{pmatrix} \tag{7.18}$$

The unknown amplitudes $A^{\pm}(\vec{p})$ in (7.17) are obtained from the initial amplitude (7.16) by setting $t = 0$, in which case

$$A^{(\pm)}(\vec{p}) = \sqrt{\frac{e_0+1}{2e_0}}\frac{e \pm 1}{2e}\left(1 + \frac{e^{i\beta}}{1 \pm e}\frac{1}{e_0+1}\ (\vec{p}\cdot\vec{p}_0 - i\,\vec{p}\cdot\widehat{s}\times\vec{p}_0)\right)h(\vec{p})$$

where

$$h(\vec{p}) = \frac{1}{(2\pi)^3}\int d^3r\, f_0(\vec{r})e^{-i\vec{p}\cdot\vec{r}}. \tag{7.19}$$

and $\left(W^{(+)}\right)^+ W^{(-)} = 0$ was used.

Solution is

$$\psi = -i\int d^3p \begin{pmatrix} \left[\cos et - i\frac{\sin et}{e}\right]F_0 \\ -i\frac{\sin et}{e}\vec{S}\cdot\vec{p}\,F_0 \end{pmatrix} h(\vec{p})\, e^{i\vec{p}\cdot\vec{r}}$$

and the charge density is

$$P = P_r + P_s$$

where

$$P_r = |f|^2 + \left|\overrightarrow{j}\right|^2$$

and

$$P_s = -i\widehat{s}\cdot\left(\overrightarrow{j}^{\,*}\times\overrightarrow{j}\right)$$

with the definitions

$$\begin{aligned} f &= (2\pi)^{-3/2}\int d^3p\left(\cos et - i\frac{\sin et}{e}\right)h(\vec{p})\, e^{i\vec{p}\cdot\vec{r}} \quad , \\ \overrightarrow{j} &= (2\pi)^{-3/2}\,\nabla\int d^3p\frac{\sin et}{e}\,h(\vec{p})\, e^{i\vec{p}\cdot\vec{r}} \end{aligned} \tag{7.20}$$

The index r indicates that this is radial part and s the spin part of the probability density. In the same way one obtains the current

$$\overrightarrow{J} = -2\,\mathrm{Re}\left[f^*\left(\overrightarrow{j} + i\,\widehat{s}\times\overrightarrow{j}\right)\right]$$

There are two limits of interest. One is the non relativistic limit, which is when $f_0(\vec{r})$ is very broad whilst $h(\vec{p})$ is narrow and all p of significance are small compared to the rest mass of the charge (here this is $m = 1$). In this limit

$$e \approx 1 + \frac{p^2}{2}$$

and

$$f_{nr} = (2\pi)^{-3/2}\, e^{-it} \int d^3p\, h\,(\vec{p})\, e^{i\vec{p}\cdot\vec{r} - \frac{i}{2}p^2 t} \ ,$$

$$f_{nr}^{-} = (2\pi)^{-3/2}\, e^{it} \int d^3p\, h\,(\vec{p})\, e^{i\vec{p}\cdot\vec{r} + \frac{i}{2}p^2 t} \ ,$$

$$\overrightarrow{j}_{nr} = \frac{1}{2i}\nabla f_{nr}^{-} - \frac{1}{2i}\nabla f_{nr}$$

where the superscript $-$ indicates that sign of energy e is negative. The probability density is

$$P = P_{nr} + \left|\nabla f_{nr}^{-}\right|^2 + |\nabla f_{nr}|^2 - 2\,\mathrm{Re}\left[\ \left(\nabla f_{nr}^{-}\right)^* \cdot \nabla f_{nr}\right] + P_s \tag{7.21}$$

and the probability current

$$\overrightarrow{J} = \overrightarrow{J}_{nr} - \frac{1}{2}\widehat{s}\times\nabla\ |f_{nr}|^2 - \mathrm{Im}\left[f_{nr}^*\left(-i\widehat{s}\times\ \nabla f_{nr}^{-} + \ \nabla f_{nr}^{-}\right)\right]$$

The index *nr* indicates the quantities that have usual expression in the non relativistic theory. The corrections are of two kind, one is due to the spin, index s, but the other is the effect that needs little more attention. In the expression for the probability amplitude (7.17) there are two components differing in the sign of energy e. This fact is the source of many discussions, involving the concept of particle and anti particle, but in fact it has a very similar interpretation as the "negative frequency" solution for electromagnetic waves, as discussed in Chap. 2. Negative energy is not specific to only (relativistic) quantum theory but it is also important in classical relativistic dynamics, as discussed in [9, Sect. 8.3], where it must be introduced in order to resolve inconsistencies that appear if only positive energies are considered. Based on this finding negative energies do not have any deeper physical meaning, they are purely of mathematical significance specific to relativistic theory. They are needed for a proper mathematical formulation of the theory. Negative energy components in the solution have impact on the charge and current densities and one expects their effect on the radiation intensity, in this example, of a free charge. In the charge (probability) density the effect of the negative energy is in the interference term in (7.21), but an estimate shows that its contribution is of the order $(v/c)^2$, where v is typical velocity of the charge and c is the speed of light. However, in the non relativistic dynamics radiation intensity is determined by the probability (charge) current (7.8), and if the spin contribution is neglected then

$$\overrightarrow{J} = (2\pi)^{-3}\int d^3q\, h^*\left(\overrightarrow{q}\right) e^{-i\overrightarrow{q}\cdot\vec{r} + \frac{i}{2}q^2 t}\cdot$$
$$\nabla\left(\int d^3p\, h\,(\vec{p})\, e^{i\vec{p}\cdot\vec{r} - \frac{i}{2}p^2 t} - e^{2it}\int d^3p\, h\,(\vec{p})\, e^{i\vec{p}\cdot\vec{r} + \frac{i}{2}p^2 t}\right)$$

imaginary part of the right side being assumed. The second part contains the oscillatory term e^{2it}, which oscillates at the frequency that is equivalent to the energy of the two rest mass of the charge. This term is direct consequence of the interference between positive and negative energy contributions in the probability amplitude. However, the first and the second term are of the same order and the question is if the rapid oscillations of radiation could be observed? In order to verify this one calculates transform $\overrightarrow{J}_{\vec{k},\omega}$ of the current

$$\overrightarrow{J}_{\vec{k},\omega} = \frac{1}{(2\pi)^4} \int d^3r \int dt \ \overrightarrow{J} \left((\vec{r},t)\right) e^{i\vec{k}\cdot\vec{r}-i\omega t}$$

but here one encounters a problem. The integral in time variable runs from far past to far future, but the solution is determined in the far future by the initial condition at $t = 0$. Nothing is known about its past, but if formally the time is reversed at $t = 0$ then the solution evolves in the same way as in the future, and this is not very realistic. One assumption is that in the past the probability amplitude is zero, hence the solution describes creation of a charge. The time integral then runs from $t = 0$ to infinity, and $\overrightarrow{J}_{\vec{k},\omega}$ is

$$\overrightarrow{J}_{\vec{k},\omega} = i(2\pi)^{-4} \int dt \, h^* \left(\vec{k}+\vec{p}\right) e^{-i\omega t} \cdot$$
$$\left(\int d^3p \, \vec{p} h\left(\vec{p}\right) e^{i\vec{k}\cdot\vec{p}t+\frac{1}{2}ik^2t} - e^{2it} \int d^3p \, \vec{p} h\left(\vec{p}\right) e^{i\vec{k}\cdot\vec{p}t+\frac{1}{2}ik^2t+ip^2t} \right)$$

and the integral has the form as in (C.3). In this discussion only the estimate is required (more detailed analysis shall be in a separate section) and only the contribution from delta function is considered (equivalent to assuming that the probability amplitude evolves into the past as it does into the future). One then obtains for the spectrum (7.10)[2]

$$W(\omega) = \frac{\omega^2}{4\pi c^3} \left| \hat{n} \cdot \vec{j}_{\vec{k},\omega} \right|^2$$

where it was taken into account that $\vec{k}$ is parallel to $\hat{n}$ and $h\left(\vec{p}\right)$ depends only on the modulus p. The scalar product is then

$$\hat{n} \cdot \overrightarrow{J}_{\vec{k},\omega} \sim \frac{1}{\omega} \int dpp \, h\left(p\right) h\left(2\omega + p^2\right) + \frac{2-\omega}{\omega^2} \int dpp \, h\left(p\right) h\left(2\omega - p^2 - 4\right)$$

The first term is ordinary contribution that result from spreading of the non relativistic probability amplitude, and originates from only the positive energy component. As $h\left(p\right)$ is negligible outside a narrow interval around $p = 0$ this contribution in the

[2]Polarization vector $\widehat{a}$ is perpendicular to the vector $\overrightarrow{k}$ in which case radiation intensity is zero, and therefore the original expression with the vector $\widehat{n}$ is used.

spectrum decays rapidly when ω is larger than its width. On the other hand, the second term results from interference of positive and negative energy components, but for the same reason, it is negligible for all ω that are smaller than 2. In the standard units this means that the spectrum is non negligible in a very narrow frequency interval, which is determined by the width of $h\,(p)$, around $\omega \approx \frac{2mc^2}{\hbar}$. This line, if observed, is an indication of the presence of negative energy component in dynamics of a charge.

When considering relativistic dynamics one distinguishes two general cases. One is when a charge has relativistic velocity and the other when its probability amplitude is very narrow. For a relativistic charge one should also include the possibility that the probability amplitude is also very narrow but the modulus of momentum $\vec{p}_0$, that is associated with the motion of a charge, is also much larger than the width of $h\,(\vec{p})$, which in this case is also very large. The functions (7.20) are then

$$f \approx (2\pi)^{-3/2} \int d^3p \cos(et)\, h\,(\vec{p}-\vec{p}_0)\, e^{i\vec{p}\cdot\vec{r}} \quad , \quad \overrightarrow{j} = (2\pi)^{-3/2} \nabla \int d^3p \frac{\sin(et)}{e}\, h\,(\vec{p}-\vec{p}_0)\, e^{i\vec{p}\cdot\vec{r}}$$

and by decomposing the momentum $\vec{p}$ into the parallel $p_\parallel$ and orthogonal $p_\perp$ components with respect to $\vec{p}_0$ one gets for f

$$f \approx (2\pi)^{-3/2} \int dp_\parallel\, d^2p_\perp \cos(et)\, h\left(p_\parallel, \overrightarrow{p}_\perp\right) e^{ip_\parallel r_\parallel + i\overrightarrow{p}_\perp\cdot\overrightarrow{r}_\perp + ip_{0\parallel} r_\parallel}$$

where

$$e = \sqrt{\left(p_0+p_\parallel\right)^2 + p_\perp^2 + 1} \approx p_0 + \left(1 - \frac{1}{2p_0^2}\right) p_\parallel + \frac{p_\perp^2}{2p_0}$$

The integral is now

$$f \approx (2\pi)^{-3/2} \frac{e^{ip_{0\parallel} r_\parallel - ip_0 t}}{2} \int dp_\parallel\, e^{ip_\parallel r_\parallel - i\left(1-\frac{1}{2p_0^2}\right)p_\parallel t} \int d^2p_\perp h\left(p_\parallel, \overrightarrow{p}_\perp\right) e^{i\overrightarrow{p}_\perp\cdot\overrightarrow{r}_\perp - i\frac{p_\perp^2}{2p_0}t}$$

from where it follows that along the space coordinate that is parallel to $\vec{p}_0$ the probability amplitude translates with velocity

$$v = c\left(1 - \frac{m^2c^2}{2p_0^2}\right)$$

without changing shape, whilst along the orthogonal component it spreads as a non-relativistic charge but of the mass p_0/c. As this is much larger mass then the rest mass of the charge then the orthogonal spread is very slow. In other words, the probability amplitude for a charge moving at relativistic velocity is practically non spreading. Similar analysis for $\overrightarrow{j}$ shows that it represents a current-like non spreading vector function for a charge traveling at nearly a speed of light. For such a charge radiation

field is that of a classical charge density that does not spread (stationary probability density), a point-like classical charge when the density is narrow.

The other relativistic example is a very narrow probability amplitude but p_0 is small, for simplicity one puts $p_0 = 0$. In this case $e \approx p$ and for a spherically symmetric $h(\vec{p})$ one gets

$$f \approx \frac{(2\pi)^{-1/2}}{r} \int dp\, p\, h(p) \sin\left[p(r-t)\right] \quad , \tag{7.22}$$
$$\overrightarrow{j} \approx -(2\pi)^{-1/2} \frac{\widehat{r}}{r} \int dp\, p\, h(p) \sin\left[p(r-t)\right]$$

where it was assumed that r is large. This means that the initial shape is translated in time, at the speed of light (in fact nearly because higher order corrections in e are not taken into account). More detailed analysis of the functions f and $\overrightarrow{j}$ is made by using the stationary phase method (C.3) because $h(p)$ in (7.22) is broad, therefore a slowly varying function of p. Stationary point of the oscillatory function is

$$p_{st} = \frac{r}{\sqrt{t^2 - r^2}}$$

in which case the integral is

$$f \approx -\frac{t}{\left(t^2 - r^2\right)^{5/4}} h\left(\frac{r}{\sqrt{t^2 - r^2}}\right) \sin\left(\sqrt{t^2 - r^2} + \pi/4\right) \tag{7.23}$$

Figure 7.1 shows two typical examples of the modulus squared of f, when $h(p)$ is a Gaussian with large width, both from the exact expression (7.20) (broken line) and approximate (7.23) (solid line), for two time instances, one for $t = 200$ (upper graph) and $t = 2000$ (lower graph). The two results for f are nearly identical.

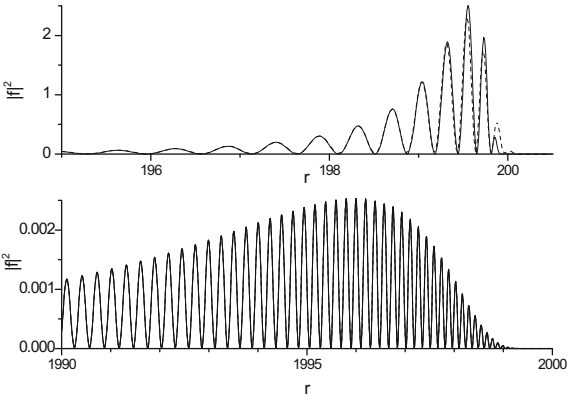

Fig. 7.1 Examples of the modulus squared of f. Exact expression (7.20) (*broken line*) and approximate (7.23) (*solid line*), for two time instances, one for $t = 200$ (*upper graph*) and $t = 2000$ (*lower graph*)

Similarly one calculates $\overrightarrow{j}$, in which case one gets for the probability density

$$P = \frac{t^4}{\left(t^2-r^2\right)^{7/2}} \sin^2\left(\sqrt{t^2-r^2}+\pi/4\right) h^2\left(\frac{r}{\sqrt{t^2-r^2}}\right) \tag{7.24}$$
$$\approx \frac{t^4}{2\left(t^2-r^2\right)^{7/2}} h^2\left(\frac{r}{\sqrt{t^2-r^2}}\right)$$

and the probability current

$$\overrightarrow{J} \approx \frac{t^2}{\left(t^2-r^2\right)^{5/2}} h^2\left(\frac{r}{\sqrt{t^2-r^2}}\right)\left(\frac{r}{\left(t^2-r^2\right)^{1/2}}\widehat{r}-\widehat{s}\times\widehat{r}\right) \tag{7.25}$$

where the oscillatory part was averaged over the oscillations and r was assumed large. Both functions are in a form of a pulse, being zero for $t < r$, of the width

$$r \approx ct\left(1-\frac{m^2c^2}{2\Delta^2}\right)$$

where Δ is the width of $h(p)$. Based on this estimate one makes further approximation $t + r \approx 2t$ in which case

$$P \approx \frac{1}{2^{9/2}} \frac{\sqrt{r}}{(t-r)^{7/2}} h^2\left(\frac{\sqrt{r}}{\sqrt{2}\sqrt{t-r}}\right)$$

where $\eta = t/r$. Similarly one obtains approximation for the current.

Radiation field is now calculated from the charge and current densities, thus the scalar potential is (7.2) but its explicit form from (7.24) is difficult to obtain. However, it could be shown that its general parametrization is (for a spherically symmetric $h(p)$)

$$V(r,t) = \frac{1}{r} U\left(\frac{t}{r}\right) \Theta(t-r)$$

where $\Theta(u)$ is the step function. Similarly one obtains for the vector potential

$$\overrightarrow{A} = \frac{1}{r}\left[A_r\left(\frac{t}{r}\right)\widehat{r} - A_s\left(\frac{t}{r}\right)\widehat{s}\times\widehat{r}\right]\Theta(t-r)$$

which has two components, the radial A_r and spin A_s. From the potentials one calculates the components of the electromagnetic field, the electric

$$\overrightarrow{E} = -\nabla V - \partial_t \overrightarrow{A} \approx \frac{1}{r}\left[U\left(\frac{t}{r}\right)\widehat{r} - A_r\left(\frac{t}{r}\right)\widehat{r} + A_s\left(\frac{t}{r}\right)\widehat{s}\times\widehat{r}\right]\delta(t-r)$$

and magnetic

$$\overrightarrow{H} = \nabla \times \overrightarrow{A} \approx \frac{1}{r} A_s(1)\,\delta(t-r)\,\widehat{r} \times (\widehat{s} \times \widehat{r})$$

where it was assumed that t is large. The Poyting vector is then

$$\begin{aligned}\overrightarrow{P} &= \frac{1}{4\pi}\vec{E} \times \vec{H} \\ &= \frac{1}{4\pi r^2}\left[A_s(1)\,[U(1) - A_r(1)\,]\widehat{r} \times \widehat{s} - A_s^2(1)\left(1 - (\widehat{s}\cdot\widehat{r})^2\right)\widehat{r}\right]\delta^2(t-r)\end{aligned}$$

which displays essential singularity because the total energy transmitted by radiation (7.9) is infinite due to the delta function squared. However, it should be noted that the delta function is an approximation, and in reality the front of the pulse is steep but not a step function, hence the field is of the delta function character. One thing, nevertheless, is correct, the intensity of the radiation power decreases as r^{-2}, characteristic feature of the radiation field that extends to infinity.

On encounter with a charge radiation field changes its momentum, due to the delta function (the same is correct if delta function is replaced by a more realistic one), in accordance with the theory that is described in Chap. 4. Another feature of the radiation field should also be mentioned, angular momentum that is carried by it. Its general definition is

$$\overrightarrow{S} = \int d^3r\, \overrightarrow{r} \times \overrightarrow{P}$$

from where one gets

$$\overrightarrow{S} = \frac{A_s(1)\,[U(1) - A_r(1)\,]}{4\pi} \int d^3r\, \frac{\delta^2(t-r)}{r}\,\widehat{s}$$

which is large (but not infinite) and points in direction of the spin of the charge. One could argue that the electromagnetic radiation, in this example, carries angular momentum that of the spin of the charge.

7.3 Radiation by a Bound Charge

7.3.1 Hydrogen Atom

The simplest radiation system of a bound charge is Hydrogen atom, which is in a mixture of states the origin of which is not discussed. Time evolution of this system is governed by equation

$$i\hbar\partial_t F\left(\overrightarrow{r}_p, \overrightarrow{r}_e, t\right) = \left(-\frac{\hbar^2}{2m_p}\Delta_p - \frac{\hbar^2}{2m_e}\Delta_e + V\right) F\left(\overrightarrow{r}_p, \overrightarrow{r}_e, t\right)$$

in which the term that includes loss of energy (field reaction) is not included. Radiation field is a combination of that produced by proton and the electron and it is calculated from the probability

$$P = q\int d^3 r_e \left|F\left(\overrightarrow{r}_p, \overrightarrow{r}_e, t\right)\right|^2 - q\int d^3 r_p \left|F\left(\overrightarrow{r}_p, \overrightarrow{r}_e, t\right)\right|^2$$

and current density

$$\overrightarrow{J} = \frac{q\hbar^2}{m_p}\,\mathrm{Im}\left(\int d^3 r_e\, F^*\nabla_p F\right) - \frac{q\hbar^2}{m_e}\,\mathrm{Im}\left(\int d^3 r_p\, F^*\nabla_e F\right)$$

where q is charge of proton. The probability amplitude is very well approximated as a product

$$F\left(\overrightarrow{r}_p, \overrightarrow{r}_e, t\right) = f\left(\overrightarrow{r}_e - \overrightarrow{r}_p, t\right)\boldsymbol{g}\left(\frac{m_p\overrightarrow{r}_p + m_e\overrightarrow{r}_e}{m_p + m_e}, t\right)$$

where f describes dynamics of the electron with respect to proton and $\boldsymbol{g}$ describes the atom as the whole in the centre of mass coordinates. Time evolution of the two functions is

$$f\left(\overrightarrow{r}, t\right) = \sum_n a_n f_n\left(\overrightarrow{r}\right) e^{-i\frac{e_n}{\hbar}t}$$

where $f_n\left(\overrightarrow{r}\right)$ are eigenstates of the atom (continuum states are excluded), and

$$\boldsymbol{g}\left(\overrightarrow{R}, t\right) = \frac{1}{(2\pi)^3}\int d^3 p\, G\left(\overrightarrow{p}\right)\, e^{i\overrightarrow{p}\cdot\overrightarrow{R} - it\frac{p^2\hbar}{2M}}$$

where $M = m_p + m_e$ is mass of Hydrogen atom.

Radiation field is obtained from the scalar and vector potentials, and the spectrum of radiation from (7.10). Scalar potential is

$$\begin{aligned} V \;&= q\int d^3 r_e d^3 r_p \frac{\left|f\left(\overrightarrow{r}_e - \overrightarrow{r}_p, t - \frac{1}{c}\left|\overrightarrow{r} - \overrightarrow{r}_p\right|\right)\right|^2 \left|\boldsymbol{g}\left(\frac{m_p\overrightarrow{r}_p + m_e\overrightarrow{r}_e}{m_p+m_e}, t - \frac{1}{c}\left|\overrightarrow{r} - \overrightarrow{r}_p\right|\right)\right|^2}{\left|\overrightarrow{r} - \overrightarrow{r}_p\right|} \\ &- q\int d^3 r_e d^3 r_p \frac{\left|f\left(\overrightarrow{r}_e - \overrightarrow{r}_p, t - \frac{1}{c}\left|\overrightarrow{r} - \overrightarrow{r}_e\right|\right)\right|^2 \left|\boldsymbol{g}\left(\frac{m_p\overrightarrow{r}_p + m_e\overrightarrow{r}_e}{m_p+m_e}, t - \frac{1}{c}\left|\overrightarrow{r} - \overrightarrow{r}_e\right|\right)\right|^2}{\left|\overrightarrow{r} - \overrightarrow{r}_e\right|} \end{aligned}$$

and by changing integration variables

$$V = q\int d^3u\, d^3r_p \frac{\left|f\left(\overrightarrow{u}, t-\frac{1}{c}\left|\overrightarrow{r}-\overrightarrow{r}_p\right|\right)\right|^2 \left|\boldsymbol{g}\left(\overrightarrow{r}_p+\frac{m_e}{m_p+m_e}\overrightarrow{u}, t-\frac{1}{c}\left|\overrightarrow{r}-\overrightarrow{r}_p\right|\right)\right|^2}{\left|\overrightarrow{r}-\overrightarrow{r}_p\right|}$$
$$-q\int d^3r_e\, d^3u \frac{\left|f\left(\overrightarrow{u}, t-\frac{1}{c}\left|\overrightarrow{r}-\overrightarrow{r}_e\right|\right)\right|^2 \left|\boldsymbol{g}\left(\overrightarrow{r}_e-\frac{m_p}{m_p+m_e}\overrightarrow{u}, t-\frac{1}{c}\left|\overrightarrow{r}-\overrightarrow{r}_e\right|\right)\right|^2}{\left|\overrightarrow{r}-\overrightarrow{r}_e\right|}$$

For sufficiently large r one makes approximation (7.4) in which case

$$V = \frac{q}{r}\sum_{l,n} a_n a_l^* e^{i\frac{e_l-e_n}{\hbar}\tau}\int d^3q\, \frac{e^{i\tau\frac{\hbar\Delta_{l,n}}{M}\widehat{r}\cdot\overrightarrow{q}}}{1-\frac{\hbar\,\widehat{r}\cdot\overrightarrow{q}}{cM}} G\left(\overrightarrow{q}+\frac{1}{2}\Delta_{l,n}\widehat{r}\right) G^*\left(\overrightarrow{q}-\frac{1}{2}\Delta_{l,n}\widehat{r}\right)$$
$$\int d^3u\, f_n\left(\overrightarrow{u}\right) f_l^*\left(\overrightarrow{u}\right)\left(e^{-i\frac{m_e\Delta_{l,n}}{m_p+m_e}\widehat{r}\cdot\overrightarrow{u}} - e^{i\frac{m_p\Delta_{l,n}}{m_p+m_e}\widehat{r}\cdot\overrightarrow{u}}\right)$$

where $\tau = t-\frac{r}{c}$ and

$$\Delta_{l,n} = \frac{e_l-e_n}{\hbar c\left(1-\frac{\hbar\widehat{r}\cdot\overrightarrow{q}}{cM}\right)}$$

In the simplest case when only one state is present the scalar potential is zero, as it should because Hydrogen atom is neutral. When two states are present then the potential gets contribution from the mixed terms of indices, for an insight into its structure one makes approximation that does not affect the essence of it but enables detailed calculation. The obvious approximation is to assume that M is large and m_e is small. In this approximation the potential is

$$V = \frac{q}{r}\,\mathrm{Re}\left[\begin{array}{c} a_1 a_2^* e^{i(e_2-e_1)\frac{\tau}{\hbar}}\int d^3q\, \frac{e^{i\tau\frac{e_2-e_1}{Mc}\widehat{r}\cdot\overrightarrow{q}}}{1+\frac{\hbar\,\widehat{r}\cdot\overrightarrow{q}}{cM}} \\ G\left(\overrightarrow{q}+\frac{e_2-e_1}{2\hbar c}\widehat{r}\right) G^*\left(\overrightarrow{q}-\frac{e_2-e_1}{2\hbar c}\widehat{r}\right)\int d^3u\, f_2\left(\overrightarrow{u}\right) f_1^*\left(\overrightarrow{u}\right)\left(1-e^{-i\frac{e_2-e_1}{\hbar c}\widehat{r}\cdot\overrightarrow{u}}\right) \end{array}\right] \tag{7.26}$$

where some terms that contain M were retained because they are essential for analysis. If for the momentum probability amplitude $G\left(\overrightarrow{p}\right)$ is taken Gaussian

$$G\left(\overrightarrow{p}\right) = \frac{1}{\pi^{3/4}\delta_p^{3/2}} e^{-\frac{p^2}{2\delta_p^2}}$$

then the integral in the momentum variable is

$$\int d^3q\, ... = \left(1+\frac{i\hbar\tau\,(e_2-e_1)}{2\delta_r^2 c^2 M^2}\right) e^{-\frac{\delta_r^2(e_2-e_1)^2}{4c^2\hbar^2}-\frac{\tau^2(e_2-e_1)^2}{4M^2c^2\delta_r^2}}$$

where the width δ_r of the probability density in the coordinates is used rather than the width δ_p in the momentum space, they are related by $\delta_r = 1/\delta_p$. This integral gives the overall effective charge density for Hydrogen atom as seen from large distance, and it is time dependent, decaying at a slow rate.

The other integral is in the relative coordinates between proton and the electron, and it is in general independent of the parity of the eigenfunctions for Hydrogen atom, however, its magnitude depends on the parity. Thus for example if the mixture is $1S$ and $2S$ states then

$$\int d^3u \ldots = -\frac{16384\sqrt{2}\alpha^2}{81\left(16+\alpha^2\right)^3}$$

where α is fine structure constant. Together the two contributions give small deviation from the neutral Hydrogen atom, which is also oscillating.

More interesting is calculation of the spectrum of the emitted radiation by Hydrogen atom, and for that one needs to calculate the probability current. The spectrum (or more appropriately, spectrum amplitude) is essentially given by the Fourier transform of the integral in (7.8)

$$I(\omega) = \int dt\, e^{i\omega t} \int d^3r' \overrightarrow{J}\left(\vec{r}', t - \frac{r - \hat{n}\cdot\vec{r}'}{c}\right)$$

where the current is given by

$$\overrightarrow{J} = \frac{q\hbar^2}{m_p}\,\mathrm{Im}\left(\int d^3r_e\, F^*\nabla_p F\right) - \frac{q\hbar^2}{m_e}\,\mathrm{Im}\left(\int d^3r_p\, F^*\nabla_e F\right) \tag{7.27}$$

and the coordinates $\vec{r}'$ are either for proton or the electron. The contribution of the individual currents is of similar form as (7.26) thus for proton is

$$\begin{aligned}&\int d^3r_p \overrightarrow{J}_p\left(\vec{r}_p, t - \frac{r - \hat{n}\cdot\vec{r}_p}{c}\right) \qquad (7.28)\\ &\sim \mathrm{Im}\sum_{l,n} a_l^* a_n e^{i\tau\frac{e_l - e_n}{\hbar}} \int d^3p\, \frac{G\left(\overrightarrow{p} + \frac{1}{2}\Delta_{l,n}\widehat{r}\right) G^*\left(\overrightarrow{p} - \frac{1}{2}\Delta_{l,n}\widehat{r}\right)}{1 - \frac{\hbar\,\widehat{r}\cdot\overrightarrow{p}}{cM}} e^{i\tau\frac{\hbar\Delta_{l,n}}{M}\widehat{r}\cdot\overrightarrow{p}}\overrightarrow{j}\end{aligned}$$

where

$$\overrightarrow{j} = \frac{q\hbar^2}{m_p}\int d^3u\left[-f_l^*\left(\overrightarrow{u}\right)\nabla f_n\left(\overrightarrow{u}\right) + \frac{i\left(\overrightarrow{p} + \frac{1}{2}\Delta_{l,n}\widehat{r}\right)m_p}{\left(m_p + m_e\right)} f_l^*\left(\overrightarrow{u}\right) f_n\left(\overrightarrow{u}\right)\right] e^{i\frac{m_e\Delta_{l,n}}{m_p + m_e}\widehat{r}\cdot\overrightarrow{u}} \tag{7.29}$$

For the electron one modifies $\overrightarrow{j}$ into

$$\overrightarrow{j} = \frac{q\hbar^2}{m_e}\int d^3u \left[f_l^*\left(\overrightarrow{u}\right)\nabla f_n\left(\overrightarrow{u}\right) + \frac{i\left(\overrightarrow{p} + \frac{1}{2}\Delta_{l,n}\widehat{r}\right)m_e}{\left(m_p + m_e\right)} f_l^*\left(\overrightarrow{u}\right) f_n\left(\overrightarrow{u}\right)\right] e^{-i\frac{m_p\Delta_{l,n}}{m_p+m_e}\widehat{r}\cdot\overrightarrow{u}}$$

Spectrum amplitude is therefore proportional to the Fourier integral of (7.28)

$$I(\omega) \sim \delta\left(\omega \pm \frac{e_l - e_n}{\hbar} \pm \frac{\hbar\Delta_{l,n}}{M}\widehat{r}\cdot\overrightarrow{p}\right) = \frac{Mc\,|e_l - e_n|}{\hbar^2\omega^2}\delta\left(\widehat{r}\cdot\overrightarrow{p} - \frac{Mc}{\hbar} \pm \frac{Mc\,(e_l - e_n)}{\hbar^2\omega}\right)$$

from where one also obtains that the frequency of radiation is

$$\omega = \mp\frac{(e_l - e_n)}{\hbar\left(1 - \frac{\hbar\widehat{r}\cdot\overrightarrow{p}}{cM}\right)}$$

which is Doppler shifted, due to dispersion of momenta in the probability density, familiar resonance frequency for transition between two discrete states. The integral over the momenta in (7.28) is now evaluated exactly and for the Gaussian momentum distribution it is given by

$$\int d^3p.... \sim \pm\frac{Mc}{\hbar\omega}\, e^{-\frac{1}{(2\delta_p c)^2}\left[\omega^2 + \left(\frac{2Mc^2}{\hbar}\right)^2\left(1 \mp \frac{e_l - e_n}{\hbar\omega}\right)^2\right]}$$

Properties of the spectrum depend on interplay of three parameters, one is the frequency ω_M that is associated with energy of the rest mass of the system (essentially that of proton) and the frequency $\omega_{l,n}$ that is associated with the energy difference between the states l and n. The third parameter is the width of the distribution of momenta δ_p. It could be assumed that δ_p is small (spectroscopic study of Hydrogen atom is in the environment where it is delocalized in relatively large space), ω_M is large and $\omega_{l,n}$ is small relative to it. In this case the spectrum consist of two lines at $\omega = \pm\,\omega_{l,n}$ when M is infinite, but only the one with the positive sign (if $e_l - e_n > 0$) gives contribution in the spectrum. For a finite value of M, but large, perturbation theory gives corrected position of the line

$$\omega = \frac{e_l - e_n}{\hbar}\left[1 - \frac{(e_l - e_n)^2}{4c^4M^2}\right]$$

and the spectroscopic width of the line is $\Delta\omega = 2\delta_p c$.

$$\Delta\omega = \frac{|e_l - e_n|\,\delta_p}{Mc}$$

The integral $\overrightarrow{j}$ is in the relative separation between proton and the electron, and in general determines the amplitude of the spectrum whilst the integral (7.28)

determines its structure as a function of ω. The first term in (7.29) is well known from analysis of transition probabilities, and involves momentum operator. Deviation from the standard form is in the additional exponential factor that contains the phase that indicates "photon" transfer of momentum to the proton (in the integral $\overrightarrow{j}$ for the electron the momentum transfer is to the electron). The momentum of the "photon", when M is large, is $\hbar\Delta_{l,n} \approx \frac{e_l - e_n}{c}$ and its direction where is emitted is $\widehat{r}$. This factor indicates that when atom emits radiation then both proton and the electron are affected in the form of a recoil as if a "particle" (a "photon") is emitted. As a consequence the transition probabilities are corrected by this effect, thus for the transition $1_{(n=2,l=1)} \to 2_{(n=1,l=0)}$ the first term in $\overrightarrow{j}$ is

$$\overrightarrow{j}^{\,I} = \frac{48\sqrt{2}\alpha^5 M^4 \left(3\alpha^2 M^2 + 4m_p^2\eta_{1,2}^2\right)}{\left(9\alpha^2 M^2 + 4m_p^2\eta_{1,2}^2\right)^3}\widehat{r}$$

where m_p is replaced by m_e when $\overrightarrow{j}$ is calculated for the electron and

$$\eta = \frac{\omega_{1,2}\hbar}{m_e c^2} \sim O\left(\alpha^2\right)$$

Impact of the "photon" emission has greater consequence on the "forbidden" transition $1_{(n=2,l=0)} \to 2_{(n=1,l=0)}$, when

$$\overrightarrow{j}^{\,I} = \frac{32\sqrt{2}i\alpha^4 M^3 m_p \eta_{1,2}\left(3\alpha^2 M^2 + 4m_p^2\eta_{1,2}^2\right)}{\left(9\alpha^2 M^2 + 4m_p^2\eta_{1,2}^2\right)^3}\widehat{r}$$

which is not zero, but it is smaller by a factor α relative to the "allowed" transition. However, the main consequence is that there are always "spontaneous" transitions from any excited states. The cause of instability of excited states is that the radiating system "jiggles" around the centre of mass which does not coincide with the nuclei. This is shown by taking the limit $m_p \to \infty$ when the "forbidden" transition intensity of radiation, when calculated from (7.27), is indeed zero.

The second term in $\overrightarrow{j}$ results from the motion of atom as the whole, and it is in the form of a product of momentum of atom and a function that is entirely a function of the internal coordinates of the atom. In the simplest case when $l = n$ this part of $\overrightarrow{j}$ is not zero, in contrast with the first term, and represents, together with the integral in the momentum, the current for the proton. When $l \neq n$ momentum of the atom $\overrightarrow{p}$ is modified by the momentum of the emitted radiation, thus indicating that it has an effect on the motion of atom. As an illustration contribution is calculated in $\overrightarrow{j}$ for the same transitions as in the examples before. Thus for $1_{(n=2,l=1)} \to 2_{(n=1,l=0)}$ it is given by

$$\overrightarrow{j}^{\,II} = \frac{\left(\overrightarrow{p} + \frac{1}{2}\Delta_{l,n}\widehat{r}\right)m_p}{\left(m_p + m_e\right)}\frac{384\sqrt{2}\alpha^5 M^5 m_p \eta_{1,2}}{\left(9\alpha^2 M^2 + 4m_p^2\eta_{1,2}^2\right)^3}$$

whilst for $1_{(n=2,l=0)} \to 2_{(n=1,l=0)}$

$$\overrightarrow{j}^{\,II} = -\frac{\left(\overrightarrow{p} + \frac{1}{2}\Delta_{l,n}\widehat{r}\right) m_p}{\left(m_p + m_e\right)} \frac{256\sqrt{2}\alpha^4 M^4 m_p^2 \eta_{1,2}^2}{\left(9\alpha^2 M^2 + 4m_p^2 \eta_{1,2}^2\right)^3}$$

Relativistic corrections are essential when analyzing fine details of radiated electromagnetic field from Hydrogen atom. Unfortunately one encounters a problem of fundamental nature, because strictly speaking one must take into account relativistic dynamics of both proton and the electron. In general, relativistic two body problem is not a solved problem (for details see discussion in Sect. 5.4.2) and it is not discussed here.

7.3.2 Radiation by Rotating Molecule

Molecules are structures that are defined by positions of nuclei of atoms, and the excess or lack of the electron charge density that surrounds them makes atoms slightly negatively or positively charged. Motion of nuclei, their vibrations around the equilibrium points or rotation around their centre of mass, causes this charge density to be time dependent resulting in electromagnetic radiation. Problem of radiation by this conglomerate of charges is solved by assuming a model for dynamics of such a system. At the extreme is the rigid rotor model, where the nuclei do not change their relative positions, but it is relaxed by allowing the nuclei to move around their equilibrium positions (semirigid model), in a harmonic potential. In both cases dynamics is solved for the eigenstates of the system and their set determines which lines in the spectrum are in principle observed. However, what is missing is information about charge density in molecule whose dynamics alone determines which lines shall in fact be observed, from the set of all possible.

Both classical and quantum dynamics is for a single, point-like, particle, and the concept such as the rigid rotor model is derivable by a suitable approximations in the many particle dynamics. In order to derive suitable model for analysis of radiation by a molecule one starts by defining suitable coordinates. Positions of the nuclei, if there are N of them, are given by r_n (notation is that of Sect. D.2), and their equilibrium positions are r_{n0}, which are either fixed or time dependent. Position of the centre of mass of the nuclei is always fixed (translation of molecule is not considered) and the origin of the coordinate system in which dynamics is described is centred there.

Radiation is emitted by charge density, which is distributed mainly on the surface of molecule but concentrated on individual atoms. As an approximation one defines charge for each of the atoms that represents charge density on it, and calculating this charge is described in Sect. 1.2.2. Therefore the main problem is to find dynamics of these charges as a function of internal coordinates of atoms in molecule, rotation of the equilibrium points r_{n0} and separation ε_n of nuclei from them.

General treatment of radiation by molecule starts from Schroedinger equation for the motion of nuclei in a potential that binds them together. In matrix form this equation is

$$-\frac{\hbar^2}{2}M^{-1}\Delta f + Vf = Ef \tag{7.30}$$

where M is diagonal matrix for the masses of atoms and Δ is also diagonal matrix. Eigenvalues of this equation give possible spectral lines that could in principle be observed when the molecule radiates. However, this analysis is very crude, because it does not say anything about relationship between actual charge density distribution in a molecule and radiation intensity. In other words, the spectrum that one obtains from (7.30) implicitly assumes that it is derived from probability density and probability current for atoms, which is associated with the charge density and charge current for these species as if they have unit charge. This assumption is based on the requirement that the probability density is normalized to unity, which also implicitly assumes that the total charge is unity. Much better description of distribution of charges is given in Sect. 1.2.4, where it is treated as an overall dipole moment of a molecule. The shortcoming of this treatment is that for relatively simple molecules, such as carbon dioxide, electric dipole moment is zero, nevertheless charge density is non zero on atoms thus allowing for radiation, in principle. For more complex molecules electric dipole moment may not have meaning.

Estimate of radiation intensity from a rotating molecule could be made by assuming that it comes from point like charges that are at the position of atomic nuclei. These charges are defined in Sect. 1.2.2. The simplest is to assume that molecule rotates around the z axes, in which case trajectory of the n-th atom is

$$r_n = R_n \cos(\omega_0 t + \delta_n)\ \widehat{x} + R_n \sin(\omega_0 t + \delta_n)\ \widehat{y} + z_n \widehat{z}$$

where R_n is its radius of rotation. Radiation energy per unit solid angle per unit frequency interval after s rotations is now

$$\frac{d^2P}{d\omega\, d\Omega} = \frac{1}{4\pi^2 c^3}\left|\sum_{n=1}^{N} q_n \int_0^{\frac{2\pi s}{\omega_0}} dt\, \widehat{r} \times \left(\widehat{r} \times \ddot{r}_n\right) e^{i\omega(t-\widehat{r}\cdot r_n/c)}\right|^2 \tag{7.31}$$

where $\widehat{r}$ is the unit vector that points in direction of the solid angle and q_n is charge on the n-th atom. This radiation energy is often too detailed and of sufficient interest is just the total energy per unit frequency (spectrum), which is obtained by integrating it over all angles, thus giving (retardation term in the exponent is neglected)

$$\frac{dP}{d\omega} = \frac{2\omega_0^4}{3\,\pi c^3}\left|\sum_n q_n R_n \int_0^{\frac{2\pi s}{\omega_0}} dt\ \left(\cos(\omega_0 t + \delta_n)\ \widehat{x} + \sin(\omega_0 t + \delta_n)\ \widehat{y}\right) e^{i\omega t}\right|^2$$

where trajectory of charges was taken into account. By integrating in time variable one gets

$$\frac{dP}{d\omega} = \frac{8\omega_0^4}{3\,\pi c^3}\frac{\omega^2+\omega_0^2}{\left(\omega^2-\omega_0^2\right)^2}\sin^2\left(\frac{\pi s\omega}{\omega_0}\right)\left[\left|\sum_n q_n x_n\right|^2+\left|\sum_n q_n y_n\right|^2\right]$$

and the total radiated energy is

$$P = \frac{4s\omega_0^3\pi}{3c^3}\left[\left|\sum_n q_n x_n\right|^2+\left|\sum_n q_n y_n\right|^2\right] \tag{7.32}$$

where x_n and y_n are the coordinates of charges. The absolute value of this energy gets more meaning if it is compared with some reference parameters, and the most obvious is rotational kinetic energy of molecule. If one defines angular momentum of rotating molecule from $I_{in}\omega_0 = \hbar L$, which is the classical equivalent of the quantum number, and rotational kinetic energy as

$$K = \frac{1}{2}I_{in}\omega_0^2$$

then normalized radiated energy is

$$\frac{P}{K} = \frac{2Ls\hbar}{3\varepsilon_0 c^3 I_{in}^2}\left(\left|\sum_k q_k y_k\right|^2+\left|\sum_k q_k x_k\right|^2\right)$$

where transformation to *SI* units was made. For convenience one defines momentum of inertia I_{in} in terms of proton mass and angstroms and charge in terms of the electron charge, in which case

$$\frac{P}{K} = \frac{2.7*10^{-13}sL}{I_{in}^2}\left(\left|\sum_k q_k y_k\right|^2+\left|\sum_k q_k x_k\right|^2\right)$$

This shows that rotating molecule radiates energy that is only a small fraction of the energy stored in its rotation.

In the same way one could estimate energy radiated by a vibrating molecule from its n-th vibration state, which has roughly the same structure as (7.32). $\widetilde{U}m^{1/2}\varepsilon$ could be normalized with respect to the energy of harmonic oscillator $n\hbar\omega_{vib}$, when one gets the rate of lose of energy from this state. However, one is interested in the relative importance of radiation from rotation of molecule and its vibration. The ratio of the two is

$$Q \sim \frac{Lm^2\eta^4}{nI_{in}^2}$$

where the distance η is obtained from the estimate for the frequency of harmonic oscillator from equation

$$\frac{m}{2}\omega_{vib}^2\eta^2 = n\hbar\omega_{vib}$$

Momentum of inertia of the molecule is roughly Mr_{mol}^2, where r_{mol} is of the order of the size of molecule and M is its mass, in which case

$$Q \sim \frac{L}{n}\left(\frac{m}{M}\right)^2\left(\frac{\eta}{r_{mol}}\right)^4$$

Since the ratio η/r_{mol} is small, and m is roughly of the order of M because there are N oscillators, it essentially determines the rate at which rotational energy of molecule is lost compared to energy lose from vibrations. This ratio is small meaning that molecule relaxes to its vibrational ground state much faster than to its rotational ground state. In that respect the two modes of dynamics of molecule are de-coupled in the first approximation.

Classical and quantum theory of rigid rotor is described in Appendix D.2, where also the charge current for a quantum system is given by (D.16). One starts by calculating radiation energy from the classical expression for point like charges (7.31), and when applied to the rigid rotor one has

$$\frac{d^2P}{d\omega\, d\Omega} = \frac{1}{4\pi^2c^3}\left|\sum_{n=1}^{N} q_n \int dt\, \widehat{r}\times\left(\widehat{r}\times\dot{v}_n\right)e^{i\omega(t-\widehat{r}\cdot r_n/c)}\right|^2 \tag{7.33}$$

where v_n is velocity of the n-th charge and for the rigid rotor (xyz rotation angles are used)

$$r_n = R\,(\alpha,\beta,\gamma)\,d_n(0)$$

where $d_n(0)$ is position of the n-th charge at some initial instant. $\widehat{r}\cdot r_n/c$ is small and therefore the exponential function could be expanded in the powers of c^{-1}. One word of caution, in principle ω could be large, meaning that the product $\omega\widehat{r}\cdot r_n/c$ could be large, however, for molecules this is not the case. For better understanding of radiation by rigid rotor two leading terms in the expansion are chosen and by integrating over the spherical angles Ω one gets

$$\int d\Omega\,\left[\widehat{r}\times\left(\widehat{r}\times\dot{v}_n\right)\right]\cdot\left[\widehat{r}\times\left(\widehat{r}\times\dot{v}_n'\right)\right] = \frac{8\pi}{3}\dot{v}_n\cdot\dot{v}_n'$$

and

$$\frac{\omega^2}{c^2}\int d\Omega\,\left[\widehat{r}\times\left(\widehat{r}\times\dot{v}_n\right)\right]\cdot\left[\widehat{r}\times\left(\widehat{r}\times\dot{v}_n'\right)\right](\widehat{r}\cdot r_n)\,(\widehat{r}\cdot r_n') = \frac{4\pi}{15}\left[\left(\dot{v}_n\times r_n\right)\cdot\left(\dot{v}_n'\times r_n'\right)+3\,(r_n'\cdot r_n)\left(\dot{v}_n\cdot\dot{v}_n'\right)-\left(\dot{v}_n\cdot r_n\right)\left(\dot{v}_n'\cdot r_n'\right)\right]$$

because contribution in (7.33) of the order c^{-1} is zero. In the last expression the second term could be written in alternative form, thus facilitating the final expression for the spectrum of radiation. One notices that the product in the second term could be written as

$$(r_n'\cdot r_n)\left(\dot{v}_n\cdot\dot{v}_n'\right) = Tr\left[\widetilde{X}'X\right]$$

where Tr is trace of a matrix and X is direct product of two vectors r_n and $\dot{v}_n$with the matrix elements

$$X_{i,j} = \left[r_n\otimes\dot{v}_n\right]_{i,j} = (r_n)_i\left(\dot{v}_n\right)_j$$

where the indices run over the three Cartesian coordinates.

The spectrum, with the two leading terms, is now

$$\begin{aligned}\frac{dP}{d\omega} &= \frac{2}{3\pi c^3}\left|\sum_{n=1}^{N}q_n\int dt\;\dot{v}_n e^{i\omega t}\right|^2 \\ &+\frac{\omega^2}{15\pi c^5}\left[\left|\sum_{n=1}^{N}q_n\int dt\;\left(\dot{v}_n\times r_n\right)e^{i\omega t}\right|^2-\left|\sum_{n=1}^{N}q_n\int dt\;\left(\dot{v}_n\cdot r_n\right)e^{i\omega t}\right|^2\right] \\ &+\frac{\omega^2}{5\pi c^5}Tr\left|\sum_{n=1}^{N}q_n\int dt\;Xe^{i\omega t}\right|^2\end{aligned} \tag{7.34}$$

where the absolute value of the last term should be understood as the product of Hermite conjugate matrix with the matrix itself. This is classical expression for the spectrum of radiation but the quantum is obtained by making replacement (D.16), and when integrated over all rotational angles one has

$$v_n e^{-i\omega\widehat{r}\cdot r_n/c}\Rightarrow-\hbar\int d\Omega\,R\,(\alpha,\beta,\gamma)\,\iota^{-1}d_n(0)\times\mathrm{Im}\;\left[f^*\widehat{\Lambda}f\right]e^{-i\omega\widehat{r}\cdot r_n/c}$$

Radiation intensity, when retardation is neglected, is then given by

$$\frac{dP}{d\omega} = \frac{\hbar^2}{3\pi c^3}\,|J_\omega|^2 \tag{7.35}$$

where

$$J_\omega = \int d\Omega\, R\,(\alpha, \beta, \gamma)\, \iota^{-1} \Pi \times \int dt\ \mathrm{Im}\ \left[f^* \dot{\widehat{\Lambda}} f\right] e^{i\omega t}$$

f is probability amplitude for the rigid rotor and

$$\Pi = \sum_{n=1}^{N} q_n d_n(0)$$

is its dipole moment.

The same thing could be done for the correction term to the spectrum, but obviously the expression is quite complicated. However, what it transpires is that the spectrum is no longer defined by dipole term, but radiation carries information about more detailed distribution of charges.

The spectrum is determined by the probability amplitude f for the rigid rotor. In the stationary state its time dependence is

$$f\,(\alpha, \beta, \gamma) = e^{-itE_\kappa/\hbar} \boldsymbol{g}_\kappa\,(\alpha, \beta, \gamma)$$

and there is no radiation. Therefore at least two, non degenerate, states should compose the probability amplitude, when the mixing term between the two in the charge current would produce radiation.

$\boldsymbol{g}_\kappa\,(\alpha, \beta, \gamma)$ is an eigenfunction for a rigid rotor (symbols are defined in Appendix D.2) that satisfies equation

$$-\frac{\hbar^2}{2} \widetilde{\widehat{\Lambda}}\, \iota^{-1} \widehat{\Lambda} \boldsymbol{g}_\kappa = E_\kappa \boldsymbol{g}_\kappa$$

where κ designates a set of quantum numbers that characterizes its rotational state. The equation, in the expanded form, is

$$\left(\frac{1}{\iota_x} - \frac{1}{\iota_y}\right) \left(\widehat{\Lambda}^+ \cdot \widehat{\Lambda}^+ + \widehat{\Lambda}^- \cdot \widehat{\Lambda}^-\right) \boldsymbol{g}_\kappa + \left(\frac{1}{\iota_x} + \frac{1}{\iota_y}\right) \left(\widehat{\Lambda}^+ \cdot \widehat{\Lambda}^- + \widehat{\Lambda}^- \cdot \widehat{\Lambda}^+\right) \boldsymbol{g}_\kappa +$$

$$\frac{1}{\iota_z} \widehat{\Lambda}_z \cdot \widehat{\Lambda}_z \boldsymbol{g}_\kappa = -\frac{8E_\kappa}{\hbar^2} \boldsymbol{g}_\kappa \tag{7.36}$$

where

$$\widehat{\Lambda}^\pm = \widehat{\Lambda}_x \pm i \widehat{\Lambda}_y$$

In order to solve this equation one must define basis functions that could be used for this purpose. These functions are Wigner rotation functions, eigenfunctions of the operator $\widehat{\Lambda}_E \cdot \widehat{\Lambda}_E$, however, the problem is that they are defined for the Euler angles whilst the formalism for the rigid body (and semi rigid body) dynamics here

is formulated in the *xyz* set of angles (for details see D.2). It could be shown that from the Wigner functions $D_l^{m,m'}(\alpha,\beta,\gamma)$ one obtains eigenfunctions $B_l^{m,m'}(\alpha,\beta,\gamma)$ of the operator $\widehat{\Lambda}\cdot\widehat{\Lambda}$ by replacement $\beta\to\beta+\pi/2$, but the problem is that the new angle β is defined in the limits $-\frac{\pi}{2}<\beta<\frac{\pi}{2}$. In applications in quantum dynamics it is therefore more convenient to use Wigner functions, but if required the functions $B_l^{m,m'}(\alpha,\beta,\gamma)$ are obtained through the replacements discussed in (D.2.2). Wigner functions have properties

$$\begin{aligned}
\widehat{\Lambda}^2 D_l^{m,m'}(\alpha,\beta,\gamma) &= -l(l+1)\,D_l^{m,m'}(\alpha,\beta,\gamma)\\
\widehat{\Lambda}_z D_l^{m,m'}(\alpha,\beta,\gamma) &= im' D_l^{m,m'}(\alpha,\beta,\gamma)\\
\widehat{\Lambda}^{\pm} D_l^{m,m'}(\alpha,\beta,\gamma) &= i\sqrt{l(l+1)-m'(m'\pm 1)}\,D_l^{m,m'\pm 1}(\alpha,\beta,\gamma)\\
\left(\widehat{\Lambda}^+\cdot\widehat{\Lambda}^- + \widehat{\Lambda}^-\cdot\widehat{\Lambda}^+\right) D_l^{m,m'}(\alpha,\beta,\gamma) &= -2\left[l(l+1)-m'^2\right] D_l^{m,m'}(\alpha,\beta,\gamma)
\end{aligned}$$

where $D_l^{m,m'}(\alpha,\beta,\gamma)=e^{-i(m\alpha+m'\gamma)}d^l_{m,m'}(\beta)$ and

$$d^l_{m,m'}(\beta)=\sqrt{(l+m)!\,(l-m)!\,(l+m')!\,(l-m')!}$$
$$\sum_s \frac{(-1)^{m-m'+s}\left(\cos\frac{\beta}{2}\right)^{2l+m'-m-2s}\left(\sin\frac{\beta}{2}\right)^{m-m'+2s}}{(l+m'-s)!s!\,(m-m'+s)!\,(l-m-s)!}$$

7.3.2.1 Dipole Radiation

The simplest rigid body is a two atom molecule. Its axis is assumed to be along the z coordinate axis, and its centre of mass is at the origin. Atom, of the mass m_1 is at the distance d_1 above the origin of the z axis whilst the other atom of the mass m_2 is below it. The starting point is to calculate the momentum of inertia of the molecule from the general expression for the coordinates of atoms. Thus if the spherical angles of atom 1 are θ_1 (polar angle) and ϕ_1 (azimuthal angle) then the position of atoms are

$$r_{1,2}=\pm d_{1,2}\{\sin\theta_1\cos\phi_1,\sin\theta_1\sin\phi_1,\cos\theta_1\}$$

from where the matrix X_n, defined in (D.10), is calculated, and then the momentum of inertia I is derived. Two eigenvalues ι of I are degenerate and one is zero, and their sequence in the diagonalization procedure is arbitrary. In this case they should be arranged so that degenerate eigenvalues should correspond to x and y components in the body fixed frame and the third (in this case zero) should correspond to the z component. The non zero diagonal components for a diatom molecule are

$$\iota_x=\iota_y=m_1d_1^2+m_2d_2^2$$

In the expression for the spectrum of rotating molecule (7.35) one also needs the dipole moment Π, and because the atoms are along the z axis of the body fixed frame then

$$\Pi = q\,(d_1 - d_2)\,\widehat{z}$$

where q is the charge on atom 1. The inverse ι^{-1} in the spectrum is infinite in its z component, but it has no impact because this component in the vector product of Π and the operator for the angular momentum $\widehat{\Lambda}$ is zero.

The integral over the current in the spectrum (7.35) is (Euler angle representation is used)

$$J = \int d\Omega\, R_E\,(\alpha, \beta, \gamma)\,\iota^{-1}\Pi \times \int dt\ \mathrm{Im}\left[f^*\widehat{\Lambda}_E f\right] e^{i\omega t}$$

where $f\,(\alpha, \beta, \gamma, t)$ is some arbitrary function, subject to symmetry properties, which is in general a linear combination of eigenfunctions for the rigid rotor. These are solutions of the equation (7.36), where the inverse ι^{-1} enters. Infinite value of ι_z^{-1} implies that the eigenvalues of the operator $\widehat{\Lambda}_z$ are zero, and so the eigenfunctions for the rigid rotor diatom molecule are

$$(\alpha, \beta, \gamma) = D_l^{m,0}\,(\alpha, \beta, \gamma) = e^{-im\alpha} d_{m,0}^l\,(\beta) = \sqrt{\frac{4\pi}{2l+1}}\, Y_l^{m*}\,(\beta, \alpha)$$

and the appropriate eigenvalues are

$$E_l = \frac{\hbar^2 l\,(l+1)}{2\left(m_1 d_1^2 + m_2 d_2^2\right)}$$

At this point it should be mentioned that the eigenfunctions are in terms of the Euler angles (zyz rotation). In the angles appropriate for the xyz rotation the angle β is replaced by $\beta + \pi/2$ and the orthogonality relationship among the eigenfunctions is

$$\int_{-\pi/2}^{\pi/2} d\beta\ \cos(\beta)\ \boldsymbol{g}_{l',m'}^*\,(\alpha, \beta, \gamma)\,\boldsymbol{g}_{l,m}\,(\alpha, \beta, \gamma) = \frac{4\pi}{2l+1}\delta_{l',l}$$

which defines the angle β in the interval that is not convenient for analysis.

The probability amplitude f, although general, it is not function of the angle γ, and so the vector product in the current $\boldsymbol{J}$ is

$$\begin{aligned} & q\,(d_1 - d_2)\,\widehat{z} \times \int dt\ \mathrm{Im}\left[f^*\widehat{\Lambda}_E f\right] e^{i\omega t} \\ & = q\,(d_1 - d_2) \int dt\, e^{i\omega t}\,\mathrm{Im} \begin{vmatrix} -\frac{\sin\gamma}{\sin\beta} f^* \partial_\alpha f - \cos\gamma f^* \partial_\beta f \\ -\frac{\cos\gamma}{\sin\beta} f^* \partial_\alpha f + \sin\gamma f^* \partial_\beta f \\ 0 \end{vmatrix} \end{aligned}$$

and the current itself is (the solid angle $d\Omega$ is the product $d\alpha\, d\beta\, d\gamma\, \sin\beta$)

$$J = \frac{q\,(d_1 - d_2)}{m_1 d_1^2 + m_2 d_2^2} \int d\Omega \int dt\; e^{i\omega t}\, \mathrm{Im} \begin{vmatrix} f^* \partial_\beta f\ \sin\beta \\ -f^* \partial_\alpha f\ \frac{\cos\alpha}{\sin\beta} - f^* \partial_\beta f\ \cos\beta \sin\alpha \\ -f^* \partial_\alpha f\ \frac{\sin\alpha}{\sin\beta} + f^* \partial_\beta f\ \cos\beta\cos\alpha \end{vmatrix}$$

From this current the spectrum (7.35) is obtained by taking time derivative of the vector in the integrand, which is not zero unless the probability amplitude is a mixture of the rigid rotor eigenstates. The simplest is a mixture of two

$$f\,(\alpha, \beta, \gamma, t) = a\, \boldsymbol{g}_{l,m}\,(\alpha, \beta, \gamma)\, e^{-itE_l/\hbar} + b\, \boldsymbol{g}_{k,n}\,(\alpha, \beta, \gamma)\, e^{-itE_k/\hbar}$$

in which case time derivative restricts the product $f^* \partial_{\beta,\alpha} f$ to the mixing terms

$$\mathrm{Im}\ \left[f^* \dot{\partial}_\beta f\right] = NA\,(\beta) \cos\left(n\alpha - m\alpha + tE_k/\hbar - tE_l/\hbar + \delta\right)$$

and

$$\mathrm{Im}\ \left[f^* \dot{\partial}_\alpha f\right] = NB\,(\beta)\,(m\ + n\ )\ \sin\left(n\alpha - m\alpha + tE_k/\hbar - tE_l/\hbar + \delta\right)$$

where

$$A\,(\beta) = P_k^n\,(\cos\beta)\, \partial_\beta P_l^m\,(\cos\beta) - \ P_l^m\,(\cos\beta)\, \partial_\beta P_k^n\,(\cos\beta)$$

and

$$B\,(\beta) = P_k^n\,(\cos\beta)\, P_l^m\,(\cos\beta)$$

The constant N is

$$N = \frac{E_k - E_l}{\hbar}\, |ab| \sqrt{\frac{(l-m)!}{(l+m)!} \frac{(k-n)!}{(k+n)!}}$$

When the time derivative is included in the current then

$$J_\omega = \frac{2\pi^3 q\,(d_1 - d_2)\, N}{m_1 d_1^2 + m_2 d_2^2} \delta\left(\omega - |E_k/\hbar - E_l/\hbar|\right) \left[J^I + (m\ + n\ )\, J^{II}\right]$$

where

$$J^I = \int d\beta A\,(\beta) \begin{vmatrix} 2\delta_{n,m} \sin^2\beta \\ -i\left(\delta_{n+1,m} - \delta_{n-1,m}\right) \sin\beta\cos\beta \\ \left(\delta_{n+1,m} + \delta_{n-1,m}\right) \sin\beta\cos\beta \end{vmatrix}$$

and

$$J^{II} = \int d\beta B\,(\beta) \begin{vmatrix} 0 \\ -i\left(\delta_{n+1,m} + \delta_{n-1,m}\right) \\ \left(\delta_{n+1,m} - \delta_{n-1,m}\right) \end{vmatrix}$$

It should be noted that the delta function is only approximately (limits in the time integral do not extend to infinity), and that when squared the result should be treated in the average sense, as shown in (C.5).

7.3.3 Radiation by Vibrating Molecule

In general molecule rotates and vibrates and as such it is called semirigid body, if vibrations of atoms around their equilibrium points are in a harmonic potential. General theory of such a body is described in D.3, which is a very complex dynamics, especially if external force is applied. Here it is assumed the simplest case when there is no external force on molecule and it is not rotating.

Position of the n-th atom in a molecule, with respect to its centre of mass, is (notation is defined in D.2)

$$r_n = d_n + \varepsilon_n$$

where d_n is position of its equilibrium point and ε_n is the distance from it (called local coordinates). For a non rotating molecule d_n is time independent. The potential within which the n-th atom moves is (D.18) which could be written in a more compact form as

$$V = \frac{1}{2}\widetilde{\varepsilon} W\,(d)\,\varepsilon$$

where the matrix elements of W are determined from the second derivatives of the exact potential around the equilibrium points of atoms. Classical equations of motion for the n-th atom are

$$m_n \ddot{\varepsilon}_n = \sum_j W_{n,j}\varepsilon_j$$

where the initial conditions for ε_j should satisfy the set of restrictions (D.28). On the other hand, quantum equation for this dynamics is

$$-\frac{\hbar^2}{2}\sum_n \frac{1}{m_n}\Delta_{\varepsilon_n} f + Vf = Ef \tag{7.37}$$

and it should be reminded that position of the n-th atom is $d_n + \varepsilon_n$, and hence f is a function of this variable. Both classical and quantum approaches give identical results for the dynamics of vibrating molecule, however, classical dynamics should be appropriately formulated from the Liouville equation [9]. Depending on the problem one could use one or the other.

In classical dynamics one first solves equations of motion for ε_n, details of which are given in (D.3.1). Slight generalization is made by including external force on the charges of atoms, for simplicity only that which is constant in coordinates but it has

arbitrary time dependence.[3] However, approximation is that molecule is fixed not to rotate and translate, which implies that the results could be used for large molecules when calculating internal flow of energy and its impact on radiation.

Classical equations, when external force F is included, are in the matrix notation

$$m\ddot{\varepsilon} = W\varepsilon + F \tag{7.38}$$

where for simplicity F is assumed to be only time dependent. One defines a unitary matrix with the property

$$\widetilde{U}\, m^{-1/2} W m^{-1/2}\, U = -\varpi^2$$

and when the local coordinates ε are transformed with this matrix as

$$\eta = \widetilde{U} m^{1/2} \varepsilon \tag{7.39}$$

then the set of equations for them is

$$\ddot{\eta} = -\varpi^2 \eta + \widetilde{U} m^{-1/2} F\,(t) \tag{7.40}$$

The set η is called normal coordinates. General solution of the set (7.40) is

$$\eta = \cos(\varpi t)\ \eta_0 + \varpi^{-1} \sin(\varpi t)\ \dot{\eta}_0 + \int_0^t du\, \varpi^{-1} \sin[\varpi\,(t-u)]\, \widetilde{U} m^{-1/2} F\,(u) \tag{7.41}$$

where η_0 and $\dot{\eta}_0$ are initial conditions and must be chosen in accordance with the conditions (D.28) for ε and $\dot{\varepsilon}$. It should be noted that also the average position of atoms d_n is for the normal coordinates given by $\widetilde{U} m^{1/2} d$.

The essential step in using classical dynamics is its formulation in the phase space and imposing the uncertainty principle (for details see [9]). One starts by choosing initial phase space probability density but for that there is a choice between either the local coordinates ε, and the appropriate conjugate momenta $\varkappa = m\dot{\varepsilon}$ or the normal coordinates η and the appropriate conjugate momenta $\kappa = \dot{\eta}$. Physically important are the local coordinates ε because their time dependence determines radiation, however, in the normal coordinates the equations are de-coupled, and so it is expected that the phase space density is product separable. Therefore it is of advantage to use normal coordinates for determining initial conditions but analysis of radiation should be done in the local ones.

[3] More general force that is linearly dependent on the coordinates also gives identical result as quantum dynamics.

Initial phase space density that is in accord with the uncertainty principle is parametrized for the normal coordinates[4] as

$$\rho_0(\eta,\kappa)=\frac{1}{\hbar^{3N}\pi^{3N}}\int d^{3N}q\, f_0^*(\eta+q) f_0(\eta-q)\, e^{2i\widetilde{q}\kappa/\hbar}$$

where $f_0(\eta)$ is initial probability amplitude which is determined from the initial probability density $P_0(\eta)$ as

$$f_0(\eta)=\sqrt{P_0(\eta)}e^{i\Phi_0(\eta)}$$

and the phase from the probability current. In the simplest case the phase could be chosen as

$$\Phi_0(\eta)=\widetilde{\varkappa}_0\varepsilon/\hbar$$

where $\varkappa_0$ is the average initial momentum of the particles. The phase of the amplitude, in the form that is given, indicates that the atoms are given initial momentum, say by impulsive collision by some external force. It is implicitly assumed that $f_0(\eta)$ has functional dependence $f_0\left(\eta+\widetilde{U}m^{1/2}d\right)$

Time evolution of the phase space density, for the initial phase space density $\rho_0(\eta,\kappa)$, is obtained by solving (7.40) and the solution for coordinates is given by (7.41) and for the momentum κ is

$$\begin{aligned}\kappa\ &=-\varpi\sin(\varpi t)\ \eta_0+\cos(\varpi t)\ \kappa_0\\ &\quad+\int_0^t du\ \cos[\varpi(t-u)]\,\widetilde{U}m^{-1/2}F(u)\end{aligned}$$

because $\kappa=\dot{\eta}$. The essence in the calculation of $\rho(\eta,\kappa,t)$ is to make replacements $\eta\longleftrightarrow\eta_0$, $\kappa\longleftrightarrow\kappa_0$, $t\to-t$ and $F(u)\to F(t-u)$ in the solutions (for the details see (Sect. 12.6 in [9])), which gives

$$\eta_0=\cos(\varpi t)\ \eta-\sin(\varpi t)\ \varpi^{-1}\kappa+\varpi^{-1}\int_0^t du\ \sin[\varpi(t-u)]\,\widetilde{U}m^{-1/2}F(t-u)$$

and

$$\kappa_0=\varpi\sin(\varpi t)\ \eta+\cos(\varpi t)\ \kappa-\int_0^t du\ \cos[\varpi(t-u)]\,\widetilde{U}m^{-1/2}F(t-u)$$

[4]It could be shown, but not elaborated, that the conditions (D.28) are automatically satisfied for any function that is dependant on one of the normal coordinates.

Time evolution of the phase space density is then given by

$$\begin{aligned}\rho(\eta,\kappa,t) &= \rho_0(\eta_0,\kappa_0)\\ &= \frac{1}{\hbar^{3N}\pi^{3N}}\int d^{3N}q\, f_0^*(\eta_0+q) f_0(\eta_0-q)\, e^{2i\widetilde{q}\kappa_0/\hbar}\end{aligned}$$

from where one calculates charge current for the n-th atom

$$j_n = \frac{q_n}{m_n}\frac{1}{\hbar^{3N}\pi^{3N}}\int d^{3N}\kappa\, \varkappa_n \int d^{3N}q\, f_0^*(\eta_0+q) f_0(\eta_0-q)\, e^{2i\widetilde{q}\kappa_0/\hbar} \tag{7.42}$$

where q_n is its effective charge. In this expression velocity of the n-th atom is given in the local coordinates because the appropriate current determines radiation.

Spectrum of radiation is given by (7.34) where the expressions for velocities and coordinates should be appropriately modified. Thus

$$q_n v_n \to \int d^{3N}\eta\, j_n$$

and

$$q_n(v_n \times r_n) \to \int d^{3N}\eta\, j_n \times r_n$$

where

$$\begin{aligned}j_n \times r_n = \frac{q_n}{\hbar^{3N}\pi^{3N}}\int d^{3N}\kappa\, \left(m^{-1/2}U\kappa\right)_n \times \left(m^{-1/2}U\eta\right)_n\\ \int d^{3N}q\, f_0^*(\eta_0+q) f_0(\eta_0-q)\, e^{2i\widetilde{q}\kappa_0/\hbar}\end{aligned}$$

and similarly

$$\begin{aligned}j_n \cdot r_n = \frac{q_n}{m_n\hbar^{3N}\pi^{3N}}\int d^{3N}\kappa\, \left(m^{-1/2}U\kappa\right)_n \cdot \left(m^{-1/2}U\eta\right)_n\\ \int d^{3N}q\, f_0^*(\eta_0+q) f_0(\eta_0-q)\, e^{2i\widetilde{q}\kappa_0/\hbar}\end{aligned}$$

The dominant term in the spectrum (7.34) is now

$$\frac{dI}{d\omega} = \frac{2}{3\pi c^3}\left|\sum_{n=1}^{N}\int dt \int d^{3N}\eta\, \dot{j}_n e^{i\omega t}\right|^2 \tag{7.43}$$

where

$$\begin{aligned}\int d^{3N}\eta\, j \;&= \hbar q m^{-1/2} U \cos(\varpi t)\,\mathrm{Im}\left[\int d^{3N}x\, f_0^*(x)\,\nabla_x f_0(x)\right]\\ &- \varpi \sin(\varpi t)\, q m^{-1/2} U \int d^{3N}x\, f_0^*(x) f_0(x)\, x\\ &+ q m^{-1/2} U \int_0^t du\, \cos(\varpi u)\,\widetilde{U} m^{-1/2} F(t-u)\end{aligned}$$

and apart from the term that contains external force the frequencies of radiation are ϖ_n. The intensity of particular line is, however, a complex function of the average value for x_n and ∇_{x_n} in the initial probability amplitude. One should note that in (7.43) the integral is infinite if t extends without limits, in that case it should be treated in the sense of the average value, as defined in (C.5).

Higher order correction in the spectrum are more complex, but in essence it produces frequencies of radiation that are combinations $\varpi_n \pm \varpi_m$.

Radiation by molecule is result to motion of charges on individual atoms, and this motion is determined from the probability density in the local coordinates. By definition this probability density is

$$P(\varepsilon) = \int d^{3N}\kappa\, \rho\left(\widetilde{U} m^{1/2}\varepsilon, \kappa, t\right)$$

and when the integrals are evaluated the final expression is

$$P(\varepsilon) = \frac{1}{(2\pi)^{3N}}\,|A|$$

where

$$\begin{aligned}A = \int d^{3N}u\; &e^{iu\int_0^t du\;\varpi^{-1}\sin[\varpi u]\widetilde{U}m^{-1/2}F(t-u) - iu\eta + i\frac{\hbar}{4}u^2\varpi^{-1}\sin 2t\varpi}\\ &f_0\left(u\hbar\varpi^{-1}\sin t\varpi + \widetilde{U}m^{1/2}d\right)\end{aligned}$$

where $\eta = \widetilde{U} m^{1/2}\varepsilon$.

7.3.3.1 Three Atom Linear Molecule

Linear, three atom, molecule is not the most general example to analyze vibrations of molecules, however it has specific features of its own. One starts by defining potential V that binds the molecule, which is a function of the relative separations among atoms. Thus if the relative separation of two atoms is

$$r_{l,k} = d_l - d_k + \varepsilon_l - \varepsilon_k \equiv d_{l,k} + \varepsilon_{l,k}$$

where d_l is equilibrium position of atom l and ε_l is its separation from it, then the potential is a function of combinations of the moduli[5]

$$\left|r_{l,k}\right| = \sqrt{\widetilde{r}_{l,k}\, r_{l,k}}$$

By convention position vector for atom l is $r_l = \{x_l, y_l, z_l\}$ and when written without the index its meaning is $r = \{r_1, r_2, r_3\}$ (for three atom molecule). The potential is then expanded into the series of powers ε, at most harmonic, and fitted into the bilinear form

$$V = V_0 + \frac{1}{2}\widetilde{\varepsilon} W \varepsilon \tag{7.44}$$

where W is symmetric 9×9 matrix. Specific feature of linear molecules is that motion of atoms is independent in their Cartesian coordinates, which implies that W is a diagonal block matrix provided that convention for the coordinates is redefined. The matrix r stands for $r = \{x, y, z\}$, where $x = \{x_1, x_2, x_3\}$ and x_l is the x Cartesian coordinate of atom l, and likewise for y and z. In this convention the matrix W is

$$W = \begin{vmatrix} W_x & 0 & 0 \\ 0 & W_y & 0 \\ 0 & 0 & W_z \end{vmatrix}$$

and the unitary matrix U that transforms local coordinates into the normal coordinates η, which is defined by (7.39), is also a diagonal block matrix

$$U = \begin{vmatrix} U_x & 0 & 0 \\ 0 & U_y & 0 \\ 0 & 0 & U_z \end{vmatrix}$$

The equilibrium positions of atoms are assumed to be along the x coordinate axis, which means that $d_x = \{d_1, d_2, d_3\}$ and $d_y = d_z = \{0, 0, 0\}$. In order to get results that are in an analytic form one simplifies the system by assuming that the masses of atoms 1 and 3 are equal and that $d_1 - d_2 = d_2 - d_3$; $d_1 > d_2 > d_3$. The block matrices in W are then given by

$$W_x = \begin{vmatrix} V^{(0,2,0)} + 2V^{(1,1,0)} + V^{(2,0,0)} & V^{(1,0,1)} - V^{(2,0,0)} & -V^{(0,2,0)} - V^{(1,0,1)} - 2V^{(1,1,0)} \\ V^{(1,0,1)} - V^{(2,0,0)} & -2V^{(1,0,1)} + 2V^{(2,0,0)} & V^{(1,0,1)} - V^{(2,0,0)} \\ -V^{(0,2,0)} - V^{(1,0,1)} - 2V^{(1,1,0)} & V^{(1,0,1)} - V^{(2,0,0)} & V^{(0,2,0)} + 2V^{(1,1,0)} + V^{(2,0,0)} \end{vmatrix}$$

[5]Potential could also be a function angles among the position vectors of atoms but here simpler case is assumed.

and

$$W_y = W_z = \begin{vmatrix} \frac{V^{(0,1,0)}}{d_{1,7}} + \frac{V^{(1,0,0)}}{d_{1,4}} & -\frac{V^{(1,0,0)}}{d_{1,4}} & -\frac{V^{(0,1,0)}}{d_{1,7}} \\ -\frac{V^{(0,1,0)}}{d_{1,7}} & 2\frac{V^{(1,0,0)}}{d_{1,4}} & -\frac{V^{(1,0,0)}}{d_{1,4}} \\ -\frac{V^{(0,1,0)}}{d_{1,7}} & -\frac{V^{(1,0,0)}}{d_{1,4}} & \frac{V^{(0,1,0)}}{d_{1,7}} + \frac{V^{(1,0,0)}}{d_{1,4}} \end{vmatrix}$$

where the short hand notation is used for derivatives of potential. Thus for example $V^{(1,1,0)}$ means

$$V^{(1,1,0)} = \frac{\partial}{\partial |r_{1,2}|} \frac{\partial}{\partial |r_{1,3}|} V\left(|r_{1,2}|, |r_{1,3}|, |r_{2,3}|\right)$$

The block matrices in the unitary matrix U are

$$U_x = U_y = U_z = \begin{vmatrix} \sqrt{\frac{m_1}{2m_1+m_2}} & \sqrt{\frac{m_2}{2(2m_1+m_2)}} & -\frac{1}{\sqrt{2}} \\ \sqrt{\frac{m_2}{2m_1+m_2}} & -\sqrt{\frac{2m_1}{2m_1+m_2}} & 0 \\ \sqrt{\frac{m_1}{2m_1+m_2}} & \sqrt{\frac{m_2}{2(2m_1+m_2)}} & \frac{1}{\sqrt{2}} \end{vmatrix}$$

and the eigenvalues (7.39) are

$$\varpi_x = \left(0, \frac{(2m_1+m_2)\left(V^{(1,0,1)} - V^{(2,0,0)}\right)}{m_1 m_2}, \frac{2V^{(0,2,0)} + V^{(1,0,1)} + 4V^{(1,1,0)} + V^{(2,0,0)}}{m_1}\right)$$

and

$$\varpi_y = \varpi_z = \left(0, \frac{(2m_1+m_2)\,V^{(1,0,0)}}{m_1 m_2 d_{1,4}}, \frac{2d_{1,4}V^{(0,1,0)} + d_{1,7}V^{(1,0,0)}}{m_1 d_{1,4} d_{1,7}}\right)$$

It is characteristic of the frequencies ϖ that at least three are zero, and additional two are also zero because

$$2d_{1,4}V^{(0,1,0)} + d_{1,7}V^{(1,0,0)} = 0$$

The equations of motion for the relevant normal coordinates are the same as for free particles, hence they are unbounded in time variable unless their initial time derivatives are zero. The requirements that select the initial conditions for these normal coordinates are that the molecule does not move, that ε do not shift its centre of mass and that molecule does not rotate along the axes that are perpendicular to the axis of the molecule. If the positions of atoms are

$$r_l = d_l + \varepsilon_l$$

then the centre of mass is

$$m_1 r_1 + m_2 r_2 + m_2 r_3 = \sqrt{2m_1 + m_2}\left\{\eta_{x1}, \eta_{y1}, \eta_{z1}\right\}$$

which is zero if the initial conditions for the normal coordinates $\{\eta_{x1}, \eta_{y1}, \eta_{z1}\}$ are zero. The centre of mass of the molecule does not move if the initial time derivatives of the same coordinates is zero.

Total angular momentum of the molecule is

$$L = m_1 r_1 \times \dot{r}_1 + m_2 r_2 \times \dot{r}_2 + m_2 r_3 \times \dot{r}_3$$

and the only condition that its y and z components are zero is that $\eta_{y3} = \eta_{z3} = \dot{\eta}_{y3} = \dot{\eta}_{z3} = 0$ in which case

$$L = \left\{\eta_{y2}\dot{\eta}_{z2} - \eta_{z2}\dot{\eta}_{y2}, \eta_{z2}\dot{\eta}_{x2} - \eta_{x2}\dot{\eta}_{z2}, \eta_{x2}\dot{\eta}_{y2} - \eta_{y2}\dot{\eta}_{x2}\right\}$$

Angular momentum has all three components, but according to the requirements on dynamics only the component along the x axis should be non zero. The only, non trivial, solution is that vibrations of molecule cannot be combination of three normal vibrations, one with frequency ϖ_{x2} and the other two with frequency $\varpi_{y2} = \varpi_{z2}$. When this selection is made only the normal mode η_{x2} is retained and then $L = 0$, whilst if the two normal modes with the degenerate frequencies are retained then the angular momentum is

$$L = \left\{\eta_{y2}\dot{\eta}_{z2} - \eta_{z2}\dot{\eta}_{y2}, 0, 0\right\} \tag{7.45}$$

and these normal modes are acceptable.

In the conclusion, vibrations of molecule that are acceptable are based on the normal modes $\eta_{x2}, \eta_{y2}, \eta_{z2}$ and η_{x3}, or their linear combinations, subject to the restrictions. Thus the mode η_{x3} could mix with any other mode, however, modes η_{x2} and η_{y2} (η_{z2}) cannot mix, the former having no angular momentum whilst the latter has and it is given by (7.45). The meaning of the modes is determined by calculating all r_l, from where one obtains that η_{x3} corresponds to asymmetric stretch, η_{x2} to symmetric stretch and η_{y2} (η_{z2}) to bending of molecule.

That analysis was classical, based on analysis of individual trajectories. Quantum dynamics is based on solving (7.37), however, the same result is obtained by using previous classical analysis but by appropriately solving Liouville equation. The result for the spectrum of radiation is summarized in (7.43), for which one needs to calculate the integral

$$\begin{aligned}\int d^{3N}\eta\, j \; &= \hbar \cos(\varpi t)\, qm^{-1/2} U \,\mathrm{Im}\left[\int d^{3N}\eta\, f_0^*(\eta)\, \nabla_\eta f_0(\eta)\right] \\ &- \varpi \sin(\varpi t)\, qm^{-1/2} U \int d^{3N}\eta \;\; |f_0(\eta)|^2\, \eta\end{aligned}$$

The frequencies ϖ are the same as those previously calculated. However, the role of initial conditions is now played by the probability amplitude, which is, in the simplest case, a product of $9 = 3N$ functions, each one for a different normal coordinate. Restrictions are now in the form of averages, thus the average angular momentum

should not have components other the one along the x axis. These conditions are satisfied provided the averages for the normal modes are satisfied. For example, from previous analysis η_{x1} mode and its time derivative should be zero, which means that

$$\int d\eta_{x1} \ \left|f_{\eta_{x1}0}\left(\eta_{x1}\right)\right|^2 \eta_{x1} = 0$$

and

$$\mathrm{Im}\left[\int d\eta_{x1} f^*_{\eta_{x1}0}\left(\eta_{x1}\right) \nabla_{\eta_{x1}} f_{\eta_{x1}0}\left(\eta_{x1}\right)\right] = 0$$

where $f_{\eta_{x1}0}\left(\eta_{x1}\right)$ is the probability amplitude for this mode. This condition is satisfied for any function that is symmetric with respect to reflection $\eta_{x1} \Leftrightarrow -\eta_{x1}$, despite the fact that it may be time dependent for $t > 0$.

Minimum requirement that the molecule radiates, for example in the normal mode η_{x3}, is that arbitrary function $f_{\eta_{x3}0}\left(\eta_{x3}\right)$ is a mixture of two functions of different symmetry, one symmetric and the other antisymmetric with respect to reflection $\eta_{x3} \Leftrightarrow -\eta_{x3}$, or that symmetric function is complex (for example that it has the phase $\gamma\eta_{x3}$).

7.3.4 Spectral Line Shifts

The spectral lines that result from the bound charges being placed in external electromagnetic field are shifted. This effect is the most pronounced when the field is static, for example in the Stark effect, and its analysis is primarily analyzed as the perturbation on the stationary states of the bound charge. On the other hand when the field is time dependent, for example if it is a plane wave, the effect needs alternative analysis. There are two distinctive situations, one is when the confining potential for the charge has no unbound states (harmonic potential) and the other when it does (Coulomb potential). In fact most of potentials do have unbound states, but very often the effect of ionization that result from the charge being placed in the external field is neglected. Calculation of the line shifts could be approached in two ways; from (i) perturbation theory and (ii) by solving the dynamics equations numerically.

7.3.4.1 Perturbation Theory

Dynamics of a charge that is bound in potential V and it is affected by external electromagnetic field in the form of a plane wave is described by equation

$$i\partial_t f = -\frac{1}{2}\left[\nabla - i\alpha\vec{A}\left(\widehat{\kappa}\cdot\vec{r} - t\right)\right]^2 f + Vf \approx$$
$$-\frac{1}{2}\nabla^2 f + i\alpha\vec{A}\left(\widehat{\kappa}\cdot\vec{r} - t\right)\cdot\nabla f + Vf$$

where the scaling is used in which interaction is measured in terms of the fine structure constant α. The simplest form of the vector potential is

$$\vec{A}\left(\widehat{\kappa}\cdot\vec{r}-t\right)=A_0\widehat{s}\sin\left[\omega\left(\widehat{\kappa}\cdot\vec{r}-t\right)\right]$$

where polarization vector $\widehat{s}$ is perpendicular to the line of the wave propagation $\widehat{\kappa}$. The equation is solved by converting equation into the integral one by using Green function (B.3)

$$f\left(r,t\right)=f_0\left(r,t\right)+i\alpha\int d^3r'dt'\;G\left(r-r,'t-t'\right)\vec{A}\left(\widehat{\kappa}\cdot\vec{r}\;'-t'\right)\cdot\nabla f\left(r,'t'\right)$$

and by replacing $f\left(r,t\right)$ with expansion

$$f\left(r,t\right)=\sum_n a_n(t)f_n(\overrightarrow{r})e^{-itE_n}+\int_0^\infty d^3k\,a_{\overrightarrow{k}}(t)f_{\overrightarrow{k}}(\overrightarrow{r})e^{-itE_k}\tag{7.46}$$

one gets

$$a_n=\delta_{n,n_0}+\frac{\alpha A_0}{2i}\sum_m\int_0^t dt'e^{i(E_n-E_m)t'}\left[e^{-i\omega t'}p^+_{n,m}-e^{i\omega t'}p^-_{n,m}\right]a_m\left(t'\right)\tag{7.47}$$

where the index n represents the set of numbers that specify bound states and also includes continuum states. The matrix elements are defined as

$$p^\pm_{n,m}=\int d^3r\,f_n\left(\overrightarrow{r}\right)e^{\pm i\omega\widehat{\kappa}\cdot\vec{r}}\widehat{s}\cdot\nabla f_m\left(\overrightarrow{r}\right)\tag{7.48}$$

The continuum basis functions are defined as

$$f_{\overrightarrow{k}}=\frac{\sqrt{2}}{kr\sqrt{\pi}}\sum_l\sum_{m=-l}^{l}f_l\left(r,k\right)Y^*_{l,m}\left(\theta_k,\phi_k\right)Y_{l,m}\left(\theta,\phi\right)\tag{7.49}$$

where the radial functions are defined with the asymptotic limit

$$f_l\left(r,k\right)\underset{r\to\infty}{\Rightarrow}\sin\left(kr+\delta_l\right)$$

when they are normalized as

$$\int dV\,f(\overrightarrow{r},\overrightarrow{k})f(\overrightarrow{r},\overrightarrow{k}')\;=\;\delta\left(\overrightarrow{k}-\overrightarrow{k}'\right)$$

The coefficients in (7.46) satisfy also set of differential equations

$$\dot{a}_n = \frac{\alpha A_0}{2i} \sum_m \left[e^{-i\omega t + itE_n - itE_m} p^+_{n,m} - e^{i\omega t + itE_n - itE_m} p^-_{n,m} \right] a_m$$

where the sum also implies integration over the continuum states. At $t = 0$ the only non zero coefficient is $a_{n_0} = 1$.

Integral equation (7.47) is solved by iteration. However, before that few words about the matrix elements (7.48). Their most revealing structure is obtained by transforming the basis functions into the momentum space

$$f_n\left(\overrightarrow{r}\right) = \frac{1}{(2\pi)^3} \int d^3p \, e^{i\overrightarrow{p}\cdot\overrightarrow{r}} \boldsymbol{g}_n\left(\overrightarrow{p}\right) \Rightarrow \boldsymbol{g}_n\left(\overrightarrow{p}\right) = \int d^3r \, e^{-i\overrightarrow{p}\cdot\overrightarrow{r}} f_n\left(\overrightarrow{r}\right)$$

and by manipulating equation for the stationary solutions $f_n\left(\overrightarrow{r}\right)$ and the plane waves one gets relationship

$$\left(E_k - E_p\right) \boldsymbol{g}_{\overrightarrow{k}}\left(\overrightarrow{p}\right) = \int d^3r \, V e^{-i\overrightarrow{p}\cdot\overrightarrow{r}} f_{\overrightarrow{k}}\left(\overrightarrow{r}\right) - \frac{1}{2} \lim_{r\to\infty} \left[r^2 \int d\Omega \, \left(f_0^* \nabla_r f - f \nabla_r f_0^* \right) \right]$$

which only applies for the continuum states. By using expansion (7.49) and (C.7) one gets relationship for the radial functions

$$\int dr \, \sqrt{r} J_{n+1/2}(pr) \boldsymbol{g}_n(r,k) = \frac{\pi\delta(k-p)}{\sqrt{2p\pi}} + \frac{2}{\left(k^2 - p^2\right)} \int dr \, V \sqrt{r} J_{n+1/2}(pr) \boldsymbol{g}_n(r,k)$$

or

$$\begin{aligned} \boldsymbol{g}_{\overrightarrow{k}}\left(\overrightarrow{p}\right) &= \frac{(2\pi)^{3/2}\,\delta(k-p)}{kp} \sum_{n=0} (-i)^n \sum_{\mu=-n}^{n} Y_{n,\mu}\left(\theta_p, \phi_p\right) Y^*_{n,\mu}\left(\theta_k, \phi_k\right) \\ &+ \frac{2}{\left(k^2 - p^2\right)} \int dr \, V(r) \, e^{-i\overrightarrow{p}\cdot\overrightarrow{r}} f_{\overrightarrow{k}}\left(\overrightarrow{r}\right) \end{aligned}$$

The matrix elements, in the momentum space, are therefore

$$p^{\pm}_{n,m} = \frac{i}{(2\pi)^3} \int d^3p \, \left(\widehat{s}\cdot\overrightarrow{p}\right) \, \boldsymbol{g}^*_n\left(\overrightarrow{p} \pm i\omega\widehat{\kappa}\right) \boldsymbol{g}_m\left(\overrightarrow{p}\right)$$

which shows that the electromagnetic wave transfers momentum $\pm\frac{\omega}{c}\hbar$ to the atom.

Iterating integral equation (7.47) produces a series

$$a_n = \sum_K a_n^{(K)} \tag{7.50}$$

where K indicates the K-th iteration and it is of the order α^K . The term $a_n^{(K)}$ is given in a closed form, which is a combination of exponentials and the appropriate coefficients, and each exponential is distinguished by a sequence $s_1\omega+s_2\omega+\cdots+s_K\omega$ in the exponent, where s_i is either of the sign $\pm$ of ω. There are 2^K such sequences. For a given sequence L the coefficient $a_n^{(K)}(L)$ is

$$a_n^{(K)}(L) = -\left(\frac{\alpha A_0}{2}\right)^K R\left[\sum_{l=1}^{K} \frac{(-1)^l}{\left(E_{m_l} - E_n - W_l\right) Q_l} e^{-it\left(E_{m_l} - E_n - W_l\right)} - \frac{1}{P_K}\right] \tag{7.51}$$

where

$$W_l = \omega \sum_{j=1}^{l} s_j \quad , \quad R = (-1)^K \prod_{j=1}^{K} s_j \, p_{m_{j-1},m_j}^{-s_j} \quad , \quad P_K = \prod_{l=1}^{K} \left(E_{m_l} - E_n - W_l\right)$$

$$Q_l = \exp\left[\sum_{i=1}^{K-1} \sum_{j=i+1}^{K} \left(\delta_{i,l} + \delta_{j,l}\right) \log\left(E_{m_i} - E_{m_j} + \omega \sum_{k=i+1}^{j} s_k\right)\right]$$

Summation is over all indices m_j except $m_0 = n$ and $m_K = n_0$. The overall $a_n^{(K)}$ is then

$$a_n^{(K)} = \sum_L a_n^{(K)}(L) \tag{7.52}$$

Iteration produces the coefficients a_n that could be represented as the series

$$a_n = \sum_{\nu=-\infty}^{\infty} b_{n,\nu}(t)\, e^{i\nu\omega t} = \sum_K \sum_{\nu=-K}^{K} b_{n,\nu}^{(K)}(t)\, e^{i\nu\omega t}$$

where the K-th iteration in (7.50) contributes with the terms from $e^{-iK\omega t}$ to $e^{iK\omega t}$. The coefficient $e^{i\nu\omega t - itE_n} b_{n,\nu}(t)$ in the expansion is interpreted as the probability amplitude for finding state n after time t, which is coupled to the frequency $\nu\omega$ of the external field, if initially the system is in the state n_0. The basic frequencies, therefore, at which the system oscillates in time are $E_n + \nu\omega$, albeit all $\nu \neq 0$ with smaller amplitudes. Typical term in the current (7.13) that produces radiation is then given by

$$j \sim b_{m_2,\nu_2}^*(t)\, b_{m_1,\nu_1}(t)\, e^{i(\nu_1-\nu_2)\omega t - i\left(E_{m_1} - E_{m_2}\right)t}$$

which means that radiation is composed of infinite number of basic spectral lines, and if $b_{m_1,\nu_1}(t)$ could be represented as $b_{m_1,\nu_1}(t) \sim \exp\left(it\varepsilon_{m_1,\nu_1}\right)$ then ε_{m_1,ν_1} is defined as the spectral line shift for the "state" whose "energy" is $E_{m_1} - \nu_1\omega\hbar$.

In general $b_{n,\nu}(t)$ could be parametrized as (the indices are omitted)

$$b(t) = \sigma(t)\, e^{-it\epsilon} \tag{7.53}$$

where the line shift ϵ and $\sigma(t)$ have expansion in the powers of α

$$\epsilon = \alpha\epsilon^{(1)} + \alpha^2\epsilon^{(2)} + \cdots$$
$$\sigma(t) = \sigma^{(0)}(t) + \alpha\sigma^{(1)}(t) + \alpha^2\sigma^{(2)}(t) + \cdots$$

These expansions are replaced in (7.53) and from the equality with the expansion for a_n in α, which results from iterating equation (7.47), one gets (the index n is not included for simplicity)

$$\sum_K b_{n,\nu}^{(K)}(t) \tag{7.54}$$
$$= \sigma^{(0)} + \alpha\left(\sigma^{(1)} - it\sigma^{(0)}\epsilon^{(1)}\right) + \alpha^2\left[\sigma^{(2)} - it\sigma^{(1)}\epsilon^{(1)} + \sigma^{(0)}\left(-it\epsilon^{(2)} - \frac{1}{2}t^2\epsilon^{(1)2}\right)\right] + \cdots$$

from where one deduces the line shift. Calculating line shifts is therefore the task of finding the terms in (7.50) that are in the form of powers in t. In doing so one distinguishes two situations, one is when the external frequency ω of the field is arbitrary and the other when it corresponds to one of the transition frequencies among the states.

7.3.4.2 Arbitrary Frequency ω

In general the coefficients $a_n^{(K)}$ are oscillatory and have terms of various orders in powers of t that play the role in the expansion (7.54) when extracting the level shifts. Those terms that are of the higher order than t^0 are selected by isolating the sequences L in (7.51) that have zero denominators. For the path L and the K-th perturbation order a typical factor in the denominator produces then the equation

$$E_{m_l} - E_n - W_l = 0 \quad ; \quad l \leq K$$

and for arbitrary ω the solution is

$$\sum_{j=1}^{l} s_j = 0$$

and

$$E_{m_l} = E_n$$

The sum of signs for ω could only be zero if l is even. The number of possible combinations when the sum is zero increases rapidly with l, for example if $l = 2$ there are 2 possible choices of signs: $\{+,-\}$ and $\{-,+\}$, but for $l = 4$ there are 6 : $\{+,-,+,-\}$, $\{+,-,-,+\}$, $\{-,+,+,-\}$, $\{-,+,-,+\}$, $\{+,+,-,-\}$, $\{-,-,+,+\}$. For a given l there are more than $2^{l/2}$ paths but one should also note

that this is only one set of these for a given order K, so that the overall number of them is quite large.

Initial and Final States Are the Same.

For the lowest order of perturbation $K = 0$ the initial state is n_0 and with this choice the next order $K = 1$ gives

$$\begin{aligned} a_n^{(1)} &= i\eta \left[\frac{e^{it\left(E_n - E_{n_0} + \omega\right)}}{\omega + E_n - E_{n_0}} p^-_{n,n_0} + \frac{e^{it\left(E_n - E_{n_0} - \omega\right)}}{\omega + E_{n_0} - E_n} p^+_{n,n_0} \right] \\ &\quad - i\eta \left[\frac{p^-_{n,n_0}}{\omega + E_n - E_{n_0}} + \frac{p^+_{n,n_0}}{\omega + E_{n_0} - E_n} \right] \end{aligned} \tag{7.55}$$

where

$$\eta = \frac{\alpha A_0}{2i}$$

and because $p^{\pm}_{n_0,n_0} = 0$ then $a^{(1)}_{n_0} = 0$. For the next order of perturbation $K = 2$ and arbitrary sequence L one gets

$$\begin{aligned} a_n^{(2)}(L) &= \eta^2 \sum_{m_1} \frac{s_1 s_2 p^{-s_2}_{n,m_1} p^{-s_1}_{m_1,n_0} e^{it\left(E_n - E_{m_1}\right)}}{\left(E_{m_1} - E_{n_0} + s_1\omega\right)\left(E_n - E_{m_1} + s_2\omega\right)} e^{its_2\omega} \\ &\quad - \eta^2 \sum_{m_1} \frac{s_1 s_2 p^{-s_2}_{n,m_1} p^{-s_1}_{m_1,n_0} e^{it\left(E_n - E_{n_0}\right)}}{\left(E_{m_1} - E_{n_0} + s_1\omega\right)\left(E_n - E_{n_0} + (s_1 + s_2)\,\omega\right)} e^{it(s_1+s_2)\omega} \\ &\quad + \eta^2 \sum_{m_1} \frac{s_1 s_2 p^{-s_2}_{n,m_1} p^{-s_1}_{m_1,n_0}}{\left(E_{m_1} - E_n - s_2\omega\right)\left(E_n - E_{n_0} + (s_1 + s_2)\,\omega\right)} \end{aligned} \tag{7.56}$$

and for $n = n_0$ the denominator is zero for two sequences, $s_1 = \pm$ and $s_2 = \mp$. When this limit is taken then

$$a^{(2)}_{n_0}(L) = it\eta^2 \sum_{m_1} \frac{p^{s_1}_{n,m_1} p^{-s_1}_{m_1,n_0}}{E_{m_1} - E_{n_0} + s_1\omega} + \eta^2 \sum_{m_1} \frac{p^{s_1}_{n_0,m_1} p^{-s_1}_{m_1,n_0} e^{it\left(E_{n_0} - E_{m_1}\right)}}{E^2_{n_0} - \left(E_{m_1} + s_1\omega\right)^2} e^{-its_1\omega}$$

where the first term is proportional to t. The coefficients in the series (7.54), when $n = n_0$, are now $\sigma^{(0)} = 1$, $\sigma^{(1)} = 0$ and $\epsilon^{(1)} = 0$ which gives

$$b_{n_0,0}(t) \approx 1 + \alpha^2 \left[\sigma^{(2)} - it\epsilon^{(2)}\right]$$

where $\sigma^{(2)}$ is the second term in $a^{(2)}_{n_0}(L)$ and

$$\epsilon^{(2)} = \left(\frac{A_0}{2}\right)^2 \sum_{m_1} \frac{2\left(E_{n_0} - E_{m_1}\right) p^-_{n_0,m_1} p^+_{m_1,n_0}}{\left(E_{n_0} - E_{m_1} + \omega\right)\left(E_{m_1} - E_{n_0} + \omega\right)}$$

is the second order correction in α for the level shift of the state n_0.

The next order is $K = 3$ and $a_n^{(3)}(L)$ is more complicated but the factors in the denominators in (7.51) that produce terms of the powers in t are $E_{n_0} - E_{m_2} + (s_1 + s_2)\omega$ and $E_{m_1} - E_n + (s_2 + s_3)\omega$. This means there are 4 paths that produce terms linear in t, two for the sum $s_1 + s_2 = 0$ and two for $s_2 + s_3 = 0$. However, for $n = n_0$ these terms are zero and hence the third order correction does not contribute to the level shift.

The fourth order $K = 4$ is even more complex, and without giving the details one obtains both the terms liner and quadratic in t. The coefficient $b_{n_0,0}(t)$ of this order is

$$b_{n_0,0}(t) \sim \alpha^4 \left(-\frac{t^2}{2}\epsilon^{(2)2} - it\epsilon^{(2)}\sigma^{(2)} - it\epsilon^{(4)} + \sigma^{(4)} \right)$$

and the quadratic term in t matches the same term in $a_{n_0}^{(4)}$. The term of the order t combines with the same term in $a_{n_0}^{(4)}$ and gives $\epsilon^{(4)}$.

Initial and Final States Are Not the Same.

When $n \neq n_0$ then

$$b_{n,0}(t) \approx \alpha\sigma^{(1)} + \alpha^2\sigma^{(2)} + \alpha^3 \left(-it\epsilon^{(2)}\sigma^{(1)} + \sigma^{(3)} \right) \ldots$$

and one expects that expansion in the third order $K = 3$ produces the level shift. $\sigma^{(1)}$ is extracted from $a_n^{(1)}$ in (7.55) but from there it is obvious that there would be 3 independent level shifts, each one corresponding to different exponential functions. The third order correction $a_n^{(3)}(L)$ is

$$\begin{aligned}
a_n^{(3)}(L) = i\eta^3 \sum_{m_1,m_2} & \frac{s_1 s_2 s_3 p_{n,m_2}^{-s_3} p_{m_2,m_1}^{-s_2} p_{m_1,n_0}^{-s_1} e^{it\left(E_n - E_{m_1}\right)} e^{it\omega(s_2+s_3)}}{\left(E_{m_1} - E_{n_0} + s_1\omega\right)\left(E_{m_2} - E_{m_1} + s_2\omega\right)\left(E_n - E_{m_1} + (s_2+s_3)\omega\right)} \\
- i\eta^3 \sum_{m_1,m_2} & \frac{s_1 s_2 s_3 p_{n,m_2}^{-s_3} p_{m_2,m_1}^{-s_2} p_{m_1,n_0}^{-s_1} e^{it\left(E_n - E_{m_2}\right)} e^{it\omega s_3}}{\left(E_{m_2} - E_{n_0} + (s_1+s_2)\omega\right)\left(E_{m_2} - E_{m_1} + s_2\omega\right)\left(E_n - E_{m_2} + s_3\omega\right)} \\
- i\eta^3 \sum_{m_1,m_2} & \frac{s_1 s_2 s_3 p_{n,m_2}^{-s_3} p_{m_2,m_1}^{-s_2} p_{m_1,n_0}^{-s_1} e^{it\left(E_n - E_{n_0}\right)} e^{it\omega(s_1+s_2+s_3)}}{\left(E_{m_1} - E_{n_0} + s_1\omega\right)\left(E_{m_2} - E_{n_0} + (s_1+s_2)\omega\right)\left(E_n - E_{n_0} + (s_1+s_2+s_3)\omega\right)} \\
+ i\eta^3 \sum_{m_1,m_2} & \frac{s_1 s_2 s_3 p_{n,m_2}^{-s_3} p_{m_2,m_1}^{-s_2} p_{m_1,n_0}^{-s_1}}{\left(E_n - E_{m_2} + s_3\omega\right)\left(E_n - E_{m_1} + (s_2+s_3)\omega\right)\left(E_n - E_{n_0} + (s_1+s_2+s_3)\omega\right)}
\end{aligned}$$

and there are three possible instances when one gets terms of the order t. One is when $s_1 + s_2 = 0$, in which case

$$a_n^{(3)}(L) = t\eta^3 \frac{s_3 p_{n,n_0}^{-s_3} e^{it\left(E_n - E_{n_0}\right)}}{E_n - E_{n_0} + s_3\omega} e^{it\omega s_3} \sum_{m_1} \frac{p_{n_0,m_1}^{-s_2} p_{m_1,n_0}^{s_2}}{E_{n_0} - E_{m_1} + s_2\omega}$$

where also the case $s_2 + s_3 = 0$ is included. Likewise when $s_2 + s_3 = 0$ then

$$a_n^{(3)}(L) = -t\eta^3 \frac{s_1 p_{n,n_0}^{-s_1}}{E_n - E_{n_0} + s_1\omega} \sum_{m_2} \frac{p_{n,m_2}^{s_2} p_{m_2,n}^{-s_2}}{E_n - E_{m_2} - s_2\omega}$$

and also $s_1 + s_2 = 0$ is included.

The level shifts are calculated from the expression for $b_{n,\nu}^{(3)}(t)$, but there are three of them, $b_{n,\pm 1}^{(3)}(t)$ and $b_{n,0}^{(3)}(t)$. The coefficient $\sigma^{(1)}$ for $b_{n,0}^{(3)}(t)$ is obtained from (7.55) and the level shift is calculated from

$$-t\eta^3 \frac{s_1 p_{n,n_0}^{-s_1}}{E_n - E_{n_0} + s_1\omega} \sum_{m_2} \frac{p_{n,m_2}^{s_2} p_{m_2,n}^{-s_2}}{E_n - E_{m_2} - s_2\omega} = -it\epsilon^{(2)}\sigma^{(1)}$$

where

$$\sigma^{(1)} = -i\eta \left(\frac{p_{n,n_0}^-}{\omega + E_n - E_{n_0}} + \frac{p_{n,n_0}^+}{\omega + E_{n_0} - E_n} \right)$$

and

$$\epsilon^{(2)} = \eta^2 \sum_{m_2} \frac{2\left(E_n - E_{m_2}\right) p_{n,m_2}^+ p_{m_2,n}^-}{\left(E_n - E_{m_2}\right)^2 - \omega^2}$$

Similar derivation gives for the level shifts for the lines $b_{n,\pm 1}^{(3)}(t)$

$$\epsilon^{(2)} = \eta^2 \sum_{m_2} \frac{2\left(E_n - E_{m_2}\right) p_{n_0,m_2}^+ p_{m_2,n_0}^-}{\left(E_n - E_{m_2}\right)^2 - \omega^2}$$

which is the same as the previous one except that the matrix elements $p_{n,m_2}^{\pm}$ are replaced by $p_{n_0,m_2}^{\pm}$.

Higher order corrections are obtained in the same way, but the procedure gets more complicated.

7.3.4.3 Resonant Frequency ω

When the frequency ω equals the difference $\frac{E_n - E_{n_0}}{\hbar}$ the analysis in Sect. 7.3.4.2 must be modified in order to take into account some specific differences. This is best demonstrated on the first order correction (7.55), which gives for this choice of ω

$$a_n^{(1)} = i\eta \frac{e^{2it\left(E_n - E_{n_0}\right)} - 1}{2\left(E_n - E_{n_0}\right)} p_{n,n_0}^- + t\eta p_{n,n_0}^+ \tag{7.57}$$

There is the term proportional to t, which is not present when ω is arbitrary. However, besides this term there is another one that does not have this structure, and as the consequence parametrization of the kind (7.53) is not adequate. Generalized parametrization that takes into account this feature of the first order correction is

$$\begin{aligned} a_n &= \sum_\nu \left[s_\nu(\alpha) \sin(t\alpha\epsilon_\nu)\, e^{\alpha\gamma_\nu t^2} + c_\nu(\alpha)\cos(t\alpha\epsilon_\nu)\, e^{\alpha\delta_\nu t^2} \right] e^{it\nu\left(E_n - E_{n_0}\right)} \\ &= \sum_\nu b_\nu e^{it\nu\left(E_n - E_{n_0}\right)} \end{aligned}$$

where ϵ_ν, γ_ν and δ_ν are functions of α. Exponential function that contains power t^2 shall become clear later, and in fact there is a succession of higher powers. After expansion in the powers of α one gets a series with the leading term $c_\nu(0)$ which must be zero if $n \neq n_0$. The series, up to the order α^2, is now (the superscript indicates order of derivative with respect to α)

$$\begin{aligned} b_{n,\nu} &= \alpha\left(ts^{(0)}_{n,\nu}\epsilon^{(0)}_\nu + c^{(1)}_{n,\nu}\right) \\ &\quad + \alpha^2\left(t^3 s^{(0)}_{n,\nu}\epsilon^{(0)}_\nu\gamma^{(0)}_\nu + t^2 c^{(1)}_{n,\nu}\delta^{(0)}_\nu + ts^{(0)}_{n,\nu}\epsilon^{(1)}_\nu + ts^{(1)}_{n,\nu}\epsilon^{(0)}_\nu + \frac{1}{2}c^{(2)}_{n,\nu}\right) + \cdots \end{aligned}$$

and by comparing it with the first order correction (7.57) one determines coefficients up to the power α

$$c^{(1)}_{n,0} = -\frac{A_0}{4}\frac{p^-_{n,n_0}}{E_n - E_{n_0}}, \quad c^{(1)}_{n,2} = \frac{A_0}{4}\frac{p^-_{n,n_0}}{E_n - E_{n_0}}, \quad c^{(1)}_{n,\nu} = 0;\ \nu > 2$$

$$s^{(0)}_{n,0}\epsilon^{(0)}_0 = \frac{A_0}{2i}p^+_{n,n_0}, \quad s^{(0)}_{n,\nu}\epsilon^{(0)}_\nu = 0;\ \ \nu > 0$$

The product $s^{(0)}_{n,0}\epsilon^{(0)}_0$ itself does not determine individual coefficients, but by noting that $\epsilon^{(0)}_0$ should be real one writes $p^+_{n,n_0} = e^{i\varphi}\left|p^+_{n,n_0}\right|$ in which case

$$s^{(0)}_{n,0} = -ie^{i\varphi}, \quad \epsilon^{(0)}_0 = \frac{A_0}{2}\left|p^+_{n,n_0}\right|$$

The second order correction $a^{(2)}_n$, it could be shown, does not contain powers of t, which implies that $\gamma_\nu(0) = \delta_\nu(0) = \epsilon^{(1)}_\nu = s^{(1)}_{n,\nu} = 0$, in which case the series up to the order α^3 is

$$\begin{aligned} b_{n,\nu} &= \alpha\left(ts^{(0)}_{n,\nu}\epsilon^{(0)}_\nu + c^{(1)}_{n,\nu}\right) + \frac{1}{2}\alpha^2 c^{(2)}_{n,\nu} \\ &\quad + \alpha^3\left(-\frac{t^3}{6}s^{(0)}_{n,\nu}\epsilon^{(0)3}_\nu + t^3 s^{(0)}_{n,\nu}\epsilon^{(0)}_\nu\gamma^{(1)}_\nu - \frac{t^2}{2}c^{(1)}_{n,\nu}\epsilon^{(0)2}_\nu + t^2 c^{(1)}_{n,\nu}\delta^{(1)}_\nu + \frac{t}{2}s^{(0)}_{n,\nu}\epsilon^{(2)}_\nu + \frac{t}{2}s^{(2)}_{n,\nu}\epsilon^{(0)}_\nu + \frac{1}{6}c^{(3)}_{n,\nu}\right) + \cdots \end{aligned}$$

The third order correction $a_n^{(3)}$ is quite lengthy, but the coefficient of the leading power t^3 is identical with the first term in the coefficient with the power α^3 and therefore $\gamma_\nu^{(1)} = 0$. The coefficient in $a_n^{(3)}$ with the power t^2 is

$$\begin{aligned} a_n^{(3)} \;&\approx i\eta^3 t^2 \frac{e^{2it\left(E_n - E_{n_0}\right)} - 1}{4\left(E_n - E_{n_0}\right)} \left|p^+_{n,n_0}\right|^2 p^-_{n,n_0} \\ &\quad - i\eta^3 t^2 \left[\sum_{m_2 \neq n_0} \frac{\left(E_{m_2} - E_n\right)\left|p^+_{m_2,n}\right|^2 p^+_{n,n_0}}{\left(E_{m_2} - E_{n_0}\right)\left(E_{m_2} + E_{n_0} - 2E_n\right)} + \sum_{m_1 \neq n} \frac{\left(E_{m_1} - E_{n_0}\right)\left|p^+_{m_1,n_0}\right|^2 p^+_{n,n_0}}{\left(E_{m_1} - E_n\right)\left(E_{m_1} + E_n - 2E_{n_0}\right)} \right] \end{aligned}$$

and by comparing with expansion for $b_{n,\nu}$ one verifies that

$$-\frac{\alpha^3}{2} c^{(1)}_{n,\nu} \epsilon^{(0)2}_\nu = i\eta^3 \frac{e^{2it\left(E_n - E_{n_0}\right)} - 1}{4\left(E_n - E_{n_0}\right)} \left|p^+_{n,n_0}\right|^2 p^-_{n,n_0}$$

The remaining term of the order t^2 gives

$$\begin{aligned} &p^-_{n,n_0} \delta_0^{(1)} \\ &\quad = -\frac{A_0^2}{2} \sum_{m_2 \neq n_0} \left[-\frac{\left(E_{m_2} - E_n\right)\left|p^+_{m_2,n}\right|^2}{\left(E_{n_0} - E_n\right)\left[\frac{\left(E_{m_2} - E_n\right)^2}{\left(E_{n_0} - E_n\right)^2} - 1\right]} + \frac{\left(E_{m_2} - E_{n_0}\right)\left|p^+_{m_2,n_0}\right|^2}{\left(E_n - E_{n_0}\right)\left[\frac{\left(E_{m_2} - E_{n_0}\right)^2}{\left(E_{n_0} - E_n\right)^2} - 1\right]} \right] p^+_{n,n_0} \end{aligned}$$

Appendix A
Units

Universally adopted are the *SI* units, however, one sometime uses another system of units, the CGS. The reason is that in the latter units dynamics equations are given in a relatively simple form, very convenient in theoretical analysis, and not the least of importance is that the velocity of light is explicitly present when the electromagnetic field is involved.[1] For this reason alone the CGS units are employed in this book when manipulating dynamics equations, but in the explicit examples the *SI* are used. Transformation of important quantities between the two unit systems is reviewed here.

One way to obtain electromagnetic quantity in a certain unit is to relate it to the quantities that are easy to transform from one units into the other. For example charge e is related to the scalar potential energy in two ways (sign in this case is not important)

$$V_{CGS} = \frac{e_{CGS}^2}{r};\ V_{SI} = \frac{e_{SI}^2}{4\pi\varepsilon_0 r}$$

where

$$\varepsilon_0 = vaccum\ permittivity = 8.854187817 \times 10^{-12}\frac{\mathrm{As}}{\mathrm{mV}}$$

Transformation of (potential) energy from one units into the other is simple, being related to the quantity

$$V = \frac{Mass\ Length^2}{Time^2}$$

[1] In the *SI* units it is the permeability and permittivity constants that are present in the equations of the electromagnetic field and not the speed of light.

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and so, for example, charge in the *SI* units is given by

$$e_{SI} = \sqrt{4\pi\varepsilon_0 r_{SI} V_{SI}} = \sqrt{4\pi\varepsilon_0 r_{SI} \frac{V_{SI}}{V_{CGS}} V_{CGS}} = e_{CGS}\sqrt{4\pi\varepsilon_0 \frac{V_{SI}}{V_{CGS}} \frac{r_{SI}}{r_{CGS}}}$$
$$= e_{CGS}\sqrt{4\pi\varepsilon_0 10^{-9}} = e_{CGS}\sqrt{\frac{4\pi 10^{-9}}{\mu_0}} \frac{1}{c_{SI}} = \frac{e_{CGS}}{10 c_{SI}}$$

where

$$\mu_0 = vacuum\ permeability = 1.2566370614 \times 10^{-6}\,\mathrm{NA}^{-2}$$

and the relationship

$$\varepsilon_0 \mu_0 c_{SI}^2 = 1$$

was used.

In the same way other quantities are interrelated. For example magnetic field (more exactly magnetic flux) is obtained from the force relationship

$$F_{CGS} = e_{CGS} \frac{v_{CGS}}{c_{CGS}} H_{CGS};\ F_{SI} = e_{SI} v_{SI} H_{SI}$$

where

$$F = \frac{Mass\ Length}{Time^2}$$

Therefore

$$H_{SI} = \frac{F_{SI}}{e_{SI} v_{SI}} = \frac{F_{SI}}{e_{SI} v_{SI} F_{CGS}} F_{CGS} = \frac{e_{CGS} v_{CGS} F_{SI}}{e_{SI} v_{SI} F_{CGS} c_{CGS}} H_{CGS}$$
$$= \frac{c_{SI} 10^{-2}}{c_{CGS}} H_{CGS} = 10^{-4}\, H_{CGS}$$

where the relationship between e_{SI} and e_{CGS} was used. Likewise transformation of the electric field is

$$E_{SI} = 10^{-6} c_{CGS} E_{CGS}$$

In the context of the magnetic field is vector potential A, which is obtained from its (symbolic) definition

$$H = \frac{1}{r} A$$

and its transformation is

$$A_{SI} = r_{SI} H_{SI} = \frac{r_{SI}}{r_{CGS}} \frac{H_{SI}}{H_{CGS}} A_{CGS} = 10^2 A_{CGS}$$

A very important quantity is the energy flux in the electromagnetic field, which is measured by the Poyting vector P, whose dimension is *Joule Second*$^{-1}$ *Meter*$^{-2}$. The flux is measured and from that one would want to extract information about the amplitude of the magnetic field, for a particular case of a plane wave. The Poyting vector in the two units is

$$P_{CGS} = \frac{c_{CGS}}{4\pi} E_{CGS} H_{CGS};\ P_{SI} = \frac{1}{\mu_0} E_{SI} H_{SI}$$

and by using transformations of the field one gets

$$P_{SI} = 10^{-3} P_{CGS}$$

For a plane wave the electric and magnetic components are interconnected through the relationship

$$E_{CGS} = H_{CGS};\ E_{SI} = c_{SI} H_{SI}$$

and therefore magnetic field in the *SI* units is

$$H_{SI} = \sqrt{\frac{\mu_0}{c_{SI}} P_{SI}}$$

In many applications one is confronted with a large number of constants, and for a general analysis they are often not required. One removes most of them by a proper re-scaling of coordinates, time and the amplitude of the field, in fact by making them dimensionless quantities. By doing that one also gains better insight into the importance or unimportance of certain parameters. The best known scaling uses as the basic parameters the Compton wave number for the electron and the energy equivalent of its mass. The wave number is

$$\kappa = \frac{m_{electron} c}{\hbar}$$

and so the dimensionless coordinates and time are defined as

$$\vec{\rho} = \kappa\, \vec{r};\ \tau = \kappa\, ct$$

Transformation into these units is formally achieved by putting $m = c = \hbar = 1$. The electromagnetic field is the simplest to scale through the potentials. Charge times scalar or vector potential have the units of energy, in the *CGS* units. One possibility for scaling is to divide them by the energy equivalent of the rest mass of the electron. In other words, one writes

$$\Phi = \frac{eV}{m_{electron} c^2}$$

for the scalar potential, and similarly for the vector potential. However, this is not a practical way of scaling because if it is done for the Coulomb potential then it is not consistent with the scaling of the coordinates. Therefore one first factors the potentials with charge by writing $V = eW$ in which case W has the unit of $length^{-1}$, which is scaled with the Compton wave number, hence

$$\Phi = \frac{e^2}{m_{electron}c^2} W = \frac{e^2}{m_{electron}c^2} \frac{m_{electron}c}{\hbar} U = \frac{e^2}{c\hbar} U = \alpha U$$

where α was given the name the fine structure constant. The potential is now

$$U = \frac{V}{e\kappa}$$

and α plays the role of charge. In these units the dynamics equations appear simpler, especially for the electron, when Newton equation with Lorentz force is

$$\ddot{\vec{r}} = \alpha \vec{E} + \alpha \vec{v} \times \vec{H}$$

and Schroedinger equation

$$i\partial_t f = -\frac{1}{2} \left[\nabla - i\alpha \vec{A} \right]^2 f + \alpha V f$$

where for simplicity the same notation for coordinates, time and potentials is used. The sign of α should be gauged against the sign of charges that define the fine structure constant. If other than the electron particle is chosen then its mass enters as a dimensionless parameter, it is the ratio with respect to the electron mass.

Appendix B
Nonrelativistic Green Functions

B.1 Time Dependent

Defining equation for the time dependent Green function for a free particle is

$$i\hbar\partial_t G(\vec{r}-\vec{q},t-s)+\frac{\hbar^2}{2m}\Delta G(\vec{r}-\vec{q},t-s)=\delta(\vec{r}-\vec{q})\delta(t-s)$$

and if the delta function is represented as

$$\delta(\vec{r}-\vec{q})\delta(t-s)=\frac{1}{(2\pi)^4}\int d^3\kappa\, d\omega\, e^{i\vec{\kappa}\cdot(\vec{r}-\vec{q})-i\omega(t-s)} \tag{B.1}$$

and Green function as

$$G(\vec{r},t)=\frac{1}{(2\pi)^4}\int d^3\kappa\, d\omega\, F(\vec{\kappa},w)\, e^{i\vec{\kappa}\cdot\vec{r}-i\omega t} \tag{B.2}$$

then the amplitude $F(\vec{\kappa},w)$ is

$$F(\vec{\kappa},w)=\frac{1}{\hbar}\frac{1}{\omega-\frac{\hbar\kappa^2}{2m}+i\eta}$$

where the parameter η is real and small, and it was introduced to avoid integration over the singular point of the integrand. In the end the limit $\eta\to 0$ is taken. Therefore, Green function is

$$G(\vec{r},t)=\frac{1}{\hbar(2\pi)^4}\int\frac{d^3\kappa\, d\omega}{\omega-\frac{\hbar\kappa^2}{2m}+i\eta}\, e^{i\vec{\kappa}\cdot\vec{r}-i\omega t}$$

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and the integral that is calculated first is in the variable ω, but the result depends in essential way on the sign of η. If it is positive then for $t < 0$ Green function is zero because the integrand is not singular in the complex plane $\mathrm{Im}\,\omega > 0$. However, for $t > 0$ the integration path in ω must be closed in the plane $\mathrm{Im}\,\omega < 0$, in which case the integral is not zero because of the presence of the first order pole there. The Green function for $t > 0$ is therefore

$$G(\vec{r}, t) = -\frac{i}{\hbar(2\pi)^3} \int d^3\kappa \; e^{i\vec{\kappa}\cdot\vec{r} - i\frac{\kappa^2\hbar}{2m}t} \; \Theta(t)$$

where $\Theta(z)$ is the step function. The integral is most conveniently calculated in the spherical coordinates of the vector $\vec{\kappa}$, in which case integration in the angular variables gives

$$G(\vec{r}, t) = -\frac{1}{\hbar(2\pi)r} \int_{-\infty}^{\infty} d\kappa \; \kappa \; e^{i\kappa r - i\frac{\kappa^2\hbar}{2m}t} \; \Theta(t)$$

and final integration gives

$$G^+(\vec{r}, t) = \frac{1}{\hbar}\left[\frac{mi}{2\pi\hbar t}\right]^{3/2} e^{i\frac{mr^2}{2t\hbar} + i\frac{\pi}{4}} \; \Theta(t).$$

From this Green function solution for the probability amplitude of the equation

$$i\hbar\partial_t f(\vec{r}, t) = -\frac{\hbar^2}{2m}\Delta f(\vec{r}, t) + W(\vec{r}, t) f(\vec{r}, t)$$

is obtained in the form of integral equation

$$f(\vec{r}, t) = f_{\mathrm{hom}}(\vec{r}, t) + \int d^3q \; ds \; G(\vec{r} - \vec{q}, t - s) W(\vec{q}, s) f(\vec{q}, s)$$

where $f_{\mathrm{hom}}(\vec{r}, t)$ is solution of the equation when the potential W is zero. Characteristic feature of this integral equation is that the solution at time t is obtained from the solution that is known from before this instant, which is consistent with the usual sequence of the cause and event, or the causality principle. This is why the Green function is called retarded, and will have the superscript $+$.

Green function could be generalized to arbitrary potential, when its defining equation is

$$i\hbar\partial_t G(\vec{r} - \vec{q}, t - s) + \frac{\hbar^2}{2m}\Delta G(\vec{r} - \vec{q}, t - s) - V(r) G(\vec{r} - \vec{q}, t - s) = \delta(\vec{r} - \vec{q})\delta(t - s)$$

There are two possibilities that give quite different results. One is when the potential allows only the bound states (e.g. harmonic oscillator), and the other when it allows

only the unbound ones (e.g. repulsive force). There is the third possibility when both bound and unbound states are allowed (e.g. attractive Coulomb potential), but this case is not considered.

If the potential allows only bound states then the corresponding eigenstates satisfy condition of completeness, in which case the product of two delta functions is written as

$$\delta(\vec{r}-\vec{q})\delta(t-s)=\frac{1}{2\pi}\sum_n f_n^*(\vec{q})f_n(\vec{r})\int dk\; e^{-ik(t-s)}$$

Likewise the Green function is written as expansion

$$G(\vec{r}-\vec{q},t-s)=\frac{1}{2\pi}\sum_n\int dk\; \boldsymbol{g}_n(k)e^{-ik(t-s)}f_n^*(\vec{q})f_n(\vec{r})$$

from where one obtains solution for the coefficients

$$\boldsymbol{g}(k,n)=\frac{1}{\hbar\left(k-\frac{e_n}{\hbar}+i\eta\right)}$$

where again a small parameter η is introduced for the same reason as for a free particle. For a retarded Green function $\eta>0$. Green function for $t>s$ is now

$$G(\vec{r}-\vec{q},t-s)=-\frac{i}{\hbar}\sum_n\; e^{-i\frac{e_n}{\hbar}(t-s)}f_n^*(\vec{q})f_n(\vec{r}) \tag{B.3}$$

where e_n are eigenvalues of equation

$$-\frac{\hbar^2}{2m}\Delta f_n+V(r)f_n=e_nf_n$$

that is subject to the boundary condition which makes the eigenfunctions f_n square integrable.

Deriving Green function for non binding potentials is more complicated and shall be demonstrated in one dimension. In three dimensions the procedure is the same but more complicated.

It is assumed that along the x axes potential is repulsive for $x<<0$ and $x>>0$, meaning that the force on the particle is directed towards the positive x values. One example of this potential linear, for example in the Starck effect. The basic equation that needs solution is

$$-\frac{\hbar^2}{2m}\partial_x^2f_e+V(x)f_e=e\,f_e$$

with the boundary condition

$$\lim_{x\to-\infty}f_e\to 0$$

and

$$\lim_{x\to\infty} f_e \sim \frac{1}{[e-V(x)]^{1/4}} \sin\left(\int dx\sqrt{e-V(x)}+\beta\right) \tag{B.4}$$

which implicitly assumes that for $x \to \infty$ the potential acquires large negative values, in which case e takes values on the whole real axes. In deriving Green function it is necessary to normalize the functions $f_e(x)$ as (for the assumed boundary conditions these functions are real)

$$\int_{-\infty}^{\infty} de\, f_e(x) f_e(y) = 2\pi\delta\,(x-y) \tag{B.5}$$

The easiest to obtain the proper normalization is for large x, where the asymptotic value for these functions is given by equation (B.4). The product of two of these asymptotics for different coordinates is

$$f_e(x)f_e(y) \approx \frac{1}{\left[-V(y)\right]^{1/4}[-V(x)]^{1/4}}$$
$$\sin\left(\int dx\sqrt{-V(x)}+\frac{1}{2}\int dx\frac{e}{\sqrt{-V(x)}}+\beta\right)$$
$$\sin\left(\int dy\sqrt{-V(y)}+\frac{1}{2}\int dy\frac{e}{\sqrt{-V(y)}}+\beta\right)$$

where it was assumed that $V(x)$ is large negative so that

$$\sqrt{e-V(x)} \approx \sqrt{-V(x)}+\frac{1}{2}\frac{e}{\sqrt{-V(x)}}$$

By transforming the product of the two sin functions into a sum of two, and when integrating in the variable e between the limits $\pm E$ one gets

$$\int_{-E}^{E} de\, f_e(x) f_e(y)$$
$$= \frac{2\cos\left(\int dx\sqrt{-V(x)}-\int dy\sqrt{-V(y)}\right)}{\left[-V(y)\right]^{1/4}[-V(x)]^{1/4}\left(\int dx\frac{1}{\sqrt{-V(x)}}-\int dy\frac{1}{\sqrt{-V(y)}}\right)}$$
$$\sin\left[\frac{E}{2}\left(\int dx\frac{1}{\sqrt{-V(x)}}-\int dy\frac{1}{\sqrt{-V(y)}}\right)\right]$$

and in the limit

$$\lim_{E\to\infty}\int_{-E}^{E} de\, f_e(x) f_e(y)$$
$$= \frac{\pi\cos\left(\int dx\sqrt{-V(x)} - \int dy\sqrt{-V(y)}\right)}{\left[-V(y)\right]^{1/4}\left[-V(x)\right]^{1/4}}$$
$$\delta\left[\frac{1}{2}\left(\int dx\frac{1}{\sqrt{-V(x)}} - \int dy\frac{1}{\sqrt{-V(y)}}\right)\right]$$
$$= 2\pi\delta\left[x-y\right]$$

which proves that (B.4) is the proper normalization for the identity (B.5).

Green function for this potential is obtained by generalizing it from (B.3) as

$$G(x-q,t-s) = -\frac{i}{2\pi\hbar}\int_{-\infty}^{\infty} de\, e^{-i\frac{e}{\hbar}(t-s)} f_e(q) f_e(x)$$

where the function $f_e(x)$ has asymptotic form (B.4).

B.1.1 Time Independent

Time independent Green function is defined as

$$\left[E - V(\vec{r}-\vec{q})\right] G(\vec{r}-\vec{q}) + \frac{\hbar^2}{2m}\Delta G(\vec{r}-\vec{q}) = \delta(\vec{r}-\vec{q})$$

where it is assumed that a particle interacts with a potential. As for the time dependent Green function one writes

$$G(\vec{r}) = \frac{1}{(2\pi)^3}\int d^3\kappa\, F(\vec{\kappa})\, e^{i\vec{\kappa}\cdot\vec{r}}$$

and so the equation is

$$\left[E - V(\vec{r}-\vec{q})\right]\int d^3\kappa\, F(\vec{\kappa})\, e^{i\vec{\kappa}\cdot(\vec{r}-\vec{q})} - \frac{\hbar^2}{2m}\int d^3\kappa\,\kappa^2 F(\vec{\kappa})\, e^{i\vec{\kappa}\cdot(\vec{r}-\vec{q})} = \int d^3\kappa\, e^{i\vec{\kappa}\cdot(\vec{r}-\vec{q})}$$

from which one obtains

$$\left(E - \frac{\hbar^2}{2m}p^2\right) F(\overrightarrow{p}) - \int d^3\kappa\, F(\vec{\kappa})\, W\left(\vec{\kappa}-\overrightarrow{p}\right) = 1 \tag{B.6}$$

where

$$W\left(\vec{\kappa}-\overrightarrow{p}\right) = \frac{1}{(2\pi)^3}\int d^3r V(\vec{r})\, e^{i\left(\vec{\kappa}-\overrightarrow{p}\right)\cdot\vec{r}}$$

The function $F(\overrightarrow{p})$ is solution of an integral equation, which is not easily solvable. However, if interaction is weak then it is solved by iteration resulting in the series

$$F(\overrightarrow{p}) = F^{(0)}(\overrightarrow{p}) + F^{(1)}(\overrightarrow{p}) + F^{(2)}(\overrightarrow{p}) + \ldots$$

which is essentially given in the powers of the potential. Thus the zeroth order solution is

$$F^{(0)}(\overrightarrow{p}) = \frac{1}{E - \frac{\hbar^2}{2m}p^2 + i\eta}$$

which gives Green function for a free particle. The parameter η is small and eventually its value is set to be zero, but depending on its sign one distinguishes two solutions. In order to investigate its role in the solution the Green function is calculated explicitly, for a free particle.

The Green function for a free particle is

$$G(\vec{r}) = \frac{1}{(2\pi)^3}\int d^3\kappa \, \frac{1}{E - \frac{\hbar^2}{2m}\kappa^2 + i\eta} \, e^{i\vec{\kappa}\cdot\vec{r}}$$

and after integrating over the angles one has

$$G(\vec{r}) = -\frac{1}{r(2\pi)^2}\int_{-\infty}^{\infty} d\kappa\kappa \, \frac{e^{ir\kappa}}{\frac{\hbar^2}{2m}\kappa^2 - E - i\eta}$$

The integration path along the real axes could now be extended into the upper half complex κ plane where the integrand is zero in the limit Im $(\kappa) \to \infty$. The value of the integral, however, is not zero because there is a pole of the integrand in that half of the plane, which is located at

$$\kappa_p = \sqrt{\frac{2m}{\hbar^2}E + i\eta}; \ \eta > 0$$

$$\kappa_p = -\sqrt{\frac{2m}{\hbar^2}E + i\eta}; \ \eta < 0$$

Final value of the integral, therefore, depends on the sign of η, hence

$$G(\vec{r}) = -\frac{im}{2\pi r\hbar^2}e^{ir\sqrt{2mE}/\hbar}; \ \eta > 0$$

and

$$G(\vec{r}) = -\frac{im}{2\pi r\hbar^2}e^{-ir\sqrt{2mE}/\hbar}; \ \eta < 0$$

As in the time dependent Green function the sign of η determines two different kind of solutions, when this parameter is positive then it represents outgoing waves and the incoming otherwise.

In the next iteration one gets the first order correction to the function $F(\overrightarrow{p})$, which is

$$F^{(1)}(\overrightarrow{p}) = \frac{1}{E - \frac{\hbar^2}{2m}p^2 + i\eta} \int d^3\kappa \, \frac{W\left(\vec{\kappa} - \overrightarrow{p}\right)}{E - \frac{\hbar^2}{2m}\kappa^2 + i\eta}$$

and for a spherically symmetric potential

$$W\left(\vec{\kappa} - \overrightarrow{p}\right) = \frac{1}{2\pi^2 \left|\vec{\kappa} - \overrightarrow{p}\right|} \int dr \, rV(r) \sin\left(\left|\vec{\kappa} - \overrightarrow{p}\right| r\right)$$

If this potential is of a Coulomb type

$$V(r) = \frac{q}{r} e^{-\gamma r}$$

then

$$W\left(\vec{\kappa} - \overrightarrow{p}\right) = \frac{q}{2\pi^2} \frac{1}{\left|\vec{\kappa} - \overrightarrow{p}\right|^2 + \gamma^2}$$

which gives

$$F^{(1)}(\overrightarrow{p}) = \frac{mi}{p\hbar^2} \frac{q}{E - \frac{\hbar^2}{2m}p^2 + i\eta} \ln \frac{i\gamma - p + \sqrt{\frac{2mE}{\hbar^2} + i\eta}}{i\gamma + p + \sqrt{\frac{2mE}{\hbar^2} + i\eta}}$$

In the derivation one encounters the integral of the form

$$I = \int_{-\infty}^{\infty} dz \, \frac{\ln(z - z_0)}{P(z)}$$

where z_0 is a complex number with $\mathrm{Im}(z_0) > 0$ and $P(z)$ is a polynomial of the order higher than the first and with the roots that are not real. The integral is then

$$I = 2\pi i \sum_{res} res\left[\frac{\ln(z - z_0)}{P(z)}\right] - 2\pi i \int_{-\infty + \mathrm{Im}(z_0)}^{z_0} \frac{dz}{P(z)}$$

where *res* is the residue at the pole with $\mathrm{Im}(z) > 0$ and it is the root of $P(z)$. Generalization to other than polynomials is straightforward.

Higher order corrections are obtained in the same way but they are obviously getting more complicated. However, a general solution could be found in a symbolical form by writing integral equation (B.6) as

$$\widehat{F} = \left(E - \frac{\hbar^2}{2m}\widehat{p}^2 + i\eta\right)^{-1} + \left(E - \frac{\hbar^2}{2m}\widehat{p}^2 + i\eta\right)^{-1} \widehat{V}\widehat{F} \tag{B.7}$$

where now the hat indicates that these are not ordinary functions but the "operators". On its own this equation has no meaning except when additional rules are defined. If one of the operators is multiplied as $\langle \vec{p} \,|\, \widehat{O}$ then the meaning of this as if one writes

$$\langle \vec{p} \,|\, \widehat{O} = \frac{1}{(2\pi)^{3/2}} O e^{-i\vec{p}\cdot\vec{r}}$$

and so one defines the matrix element

$$\langle \vec{p} \,|\, \widehat{O} \,|\, \vec{\kappa} \rangle \equiv O\left(\vec{\kappa} - \vec{p}\right)$$

In particular one defines the "vacuum state" as

$$|0\rangle = \frac{1}{(2\pi)^{3/2}}$$

then $\langle \vec{p} \,|\, \widehat{O} \,|0\rangle$ means

$$\langle \vec{p} \,|\, \widehat{O} \,|0\rangle \equiv O(\vec{p}) = \frac{1}{(2\pi)^3} \int d^3r \, O e^{-i\vec{p}\cdot\vec{r}}$$

Completeness of the plane waves is written as

$$|\vec{p}\rangle\langle\vec{p}\,| \equiv \frac{1}{(2\pi)^3} \int d^3p \, e^{i\vec{q}\cdot\vec{p} - i\vec{r}\cdot\vec{p}} = \delta\left(\vec{q} - \vec{r}\right)$$

in which case from the symbolic form of the integral equation one gets the "operational" by the following steps

$$\langle \vec{p} \,|\, \widehat{F} \,|0\rangle = \langle \vec{p} \,|\left(E - \frac{\hbar^2}{2m}\widehat{p}^2 + i\eta\right)^{-1} |0\rangle + \langle \vec{p} \,|\left(E - \frac{\hbar^2}{2m}\widehat{p}^2 + i\eta\right)^{-1} \widehat{V}\widehat{F} \,|0\rangle =$$

$$\left(E - \frac{\hbar^2}{2m}p^2 + i\eta\right)^{-1} + \langle \vec{p} \,|\left(E - \frac{\hbar^2}{2m}\widehat{p}^2 + i\eta\right)^{-1} |\vec{\kappa}\rangle\langle\vec{\kappa}\,|\, \widehat{V} \,|\vec{\lambda}\rangle\langle\vec{\lambda}\,|\, \widehat{F} \,|0\rangle =$$

$$\left(E - \frac{\hbar^2}{2m}p^2 + i\eta\right)^{-1} + \left(E - \frac{\hbar^2}{2m}p^2 + i\eta\right)^{-1} \int d^3\lambda W\left(\vec{\lambda} - \vec{p}\right) F\left(\vec{\lambda}\right)$$

where the identity

$$\langle \vec{p} \,|\left(E - \frac{\hbar^2}{2m}\widehat{p}^2 + i\eta\right)^{-1} |\vec{\kappa}\rangle = \left(E - \frac{\hbar^2}{2m}p^2 + i\eta\right)^{-1} \delta\left(\vec{\kappa} - \vec{p}\right)$$

was used.

The advantage of this formal treatment is that manipulation with the Green function is made easier, thus the iteration of equation (B.7) gives the series

$$\widehat{F} = \widehat{F}_0 + \widehat{F}_0 \left(\widehat{V}\widehat{F}_0\right) + \widehat{F}_0 \left(\widehat{V}\widehat{F}_0\right) \left(\widehat{V}\widehat{F}_0\right) + \ldots$$

where

$$\widehat{F}_0 = \left(E - \frac{\hbar^2}{2m}\widehat{p}^2 + i\eta\right)^{-1}$$

The series is formal expansion

$$\widehat{F} = \widehat{F}_0 \left(I - \widehat{V}\widehat{F}_0\right)^{-1} = \left[\left(I - \widehat{V}\widehat{F}_0\right)\widehat{F}_0^{-1}\right]^{-1} = \left(E - \frac{\hbar^2}{2m}p^2 - \widehat{V} + i\eta\right)^{-1}$$

which is also the Green function. However, it should again be emphasized that this is only a symbolic solution and that it has only meaning in the form of expansion, and as such it has a limited radius of convergence.

Appendix C
Useful Relationships

C.1 Delta Function

Standard symbol for one dimensional delta function is

$$delta\ function = \delta\left(x - x_0\right)$$

and its basic property is

$$\int_{x_0-\varepsilon}^{x_0+\varepsilon} dx\ \delta\left(x - x_0\right) f(x) = f\left(x_0\right)$$

where ε is arbitrarily small but not zero. There are various useful representations of the delta function, the most common are

$$\begin{aligned}
\delta\left(x - x_0\right) &= \frac{1}{2\pi}\int dk\ e^{ik(x-x_0)} \\
&= \frac{1}{2\pi} + \frac{1}{\pi}\sum_{n=1}^{\infty}\cos\left[n\left(x - x_0\right)\right] \\
&= \frac{1}{\pi}\lim_{\varepsilon\to 0}\frac{\varepsilon}{\left(x - x_0\right)^2 + \varepsilon^2} \\
&= \frac{1}{\pi}\lim_{\varepsilon\to\infty}\frac{\sin\left[\varepsilon\left(x - x_0\right)\right]}{x - x_0} \\
&= \frac{1}{2\sqrt{\pi}}\lim_{\varepsilon\to 0^+}\frac{1}{\sqrt{\varepsilon}}e^{-\frac{(x-x_0)^2}{4\varepsilon}}
\end{aligned}$$

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Delta function of a more complicated argument is expanded as

$$\delta\left[\boldsymbol{g}(x)\right] = \sum_n \frac{\delta\left(x - x_n\right)}{\left|\boldsymbol{g}'(x_n)\right|};\ \boldsymbol{g}(x_n) = 0$$

$$\delta\left[f(x,y)\right]\delta\left[\boldsymbol{g}(x,y)\right] = \frac{\delta\left[x - x_0\right]\delta\left[y - y_0\right]}{\left|\det\begin{vmatrix}\partial_x f & \partial_y f\\ \partial_x \boldsymbol{g} & \partial_y \boldsymbol{g}\end{vmatrix}\right|};\ f(x_0,y_0) = 0\ ,\ \ \boldsymbol{g}(x_0,y_0) = 0$$

where x_n is the nth root of $\boldsymbol{g}(x)$. Derivatives of delta function are evaluated by using the expression

$$\int dx\, f(x)\, d_x^n \delta\left(x - x_0\right) = -\int dx\, d_x f(x)\, d_x^{n-1}\delta\left(x - x_0\right)$$

Generalization of delta function to three dimensions is straightforward, and it is

$$\delta\left(\vec{r}\right) = \delta(x)\delta(y)\delta(z)$$

whilst in spherical coordinates it is given by

$$\begin{aligned}\delta\left(\vec{r} - \vec{r}_0\right) &= \frac{1}{r^2}\delta\left(r - r_0\right)\delta\left(\phi - \phi_0\right)\delta\left(\cos\theta - \cos\theta_0\right)\\ &= \frac{1}{r^2}\delta\left(r - r_0\right)\sum_{l,m} Y^*_{l,m}\left(\theta_0,\phi_0\right)Y_{l,m}\left(\theta,\phi\right)\end{aligned}$$

Closely related to delta function is the Cauchy principal value of integral. It is defined as

$$¶\left[\frac{f(x)}{x}\right] \equiv \lim_{\varepsilon\to 0}\left[\int_a^{-\varepsilon} dx\,\frac{f(x)}{x} + \int_{\varepsilon}^{b} dx\,\frac{f(x)}{x}\right] \tag{C.1}$$

and its connection to delta function is through the limit

$$\lim_{\eta\to 0}\frac{d}{dx}\ln\left(x - i\eta\right) = \lim_{\eta\to 0}\frac{1}{x - i\eta} = i\pi\delta(x) + ¶\left[\frac{1}{x}\right] \tag{C.2}$$

or

$$\lim_{X\to\infty}\int_{-X}^{0} dx\, e^{ikx} = \lim_{X\to\infty}\frac{1 - e^{-ikX}}{ik} = \tag{C.3}$$

$$\lim_{X\to\infty}\left[\frac{\sin\left(kX\right)}{k} - i\frac{1 - \cos\left(kX\right)}{k}\right] = \pi\delta(k) - i\,¶\left[\frac{1}{k}\right]$$

This relationship is shorthand for evaluation of integrals

$$\lim_{\eta\to 0}\int_a^b dx\frac{f(x)}{x-i\eta}=i\pi f(0)+¶\left[\frac{f(x)}{x}\right] \tag{C.4}$$

Cauchy principal value is calculated by using the formula

$$¶\left[\int_a^b\frac{f(x)}{x}\right]=\int_a^b\frac{f(x)-f(0)}{x}+\ln(\frac{b}{-a})f(0)$$

or by using perturbation method if the denominator is perturbed by a small value ε

$$¶\left[\int dx\frac{1}{x+\varepsilon}f\,(x)\right]=¶\left[\int dx\frac{1}{x}f\,(x-\varepsilon)\right]=¶\left[\int dx\frac{1}{x}f\,(x)\right]-\varepsilon¶\left[\int dx\frac{1}{x}f\,'(x)\right]$$

In applications one often requires the principal value of the integral that contains exponential function, which is given by

$$¶\left[\int dx\frac{e^{ixa}}{x-q}\right]=\begin{cases}-i\pi e^{-iaq};\ a>0\\ i\pi e^{-iaq};\ a<0\end{cases}$$

In various examples one gets integrals of the type

$$I=\int_{-\infty}^{\infty}dx\ \delta^2\,(x-x_0)f(x)=\frac{1}{\pi^2}\int_{-\infty}^{\infty}dx\ \left[\lim_{\varepsilon\to\infty}\frac{\sin\left[\varepsilon\,(x-x_0)\right]}{x-x_0}\right]^2 f(x) \tag{C.5}$$

For finite, but large, ε it is expected that most of contribution comes from the vicinity of $x=x_0$ hence one expands $f\,(x)$ in Taylor series and the dominant term I is

$$I=\frac{\varepsilon}{\pi}f(x_0)+O\left(\varepsilon^0\right)$$

which is large. One defines the average integral by

$$\langle I\rangle=\lim_{\varepsilon\to\infty}\frac{I}{\varepsilon}=\frac{f(x_0)}{\pi}$$

which is finite.

Closely related to delta function is the unit step function

$$\Theta\,(x)=\frac{1}{2}\left(1+\frac{x}{|x|}\right)\ =\lim_{d\to 0}\ \frac{1}{1+e^{-x/d}}$$

which has the integral representation

$$\Theta(x) = \frac{1}{2\pi i} \lim_{\eta \to 0} \int_{-\infty}^{\infty} dy \, \frac{e^{ixy}}{y - i\eta}; \; \eta > 0 \tag{C.6}$$

It follows from it

$$\frac{x}{|x|} = \frac{1}{\pi} \lim_{\eta \to 0} \int_{-\infty}^{\infty} dy \, \frac{\sin xy}{y - i\eta}$$

C.2 Expansions

A plane wave has expansion in spherical waves as

$$e^{i\,\vec{p}\cdot\vec{r}} = \sqrt{\frac{\pi}{2pr}} \sum_{n=0} i^n (2n+1) J_{n+1/2}(pr) P_n(\cos\Theta) \tag{C.7}$$

where

$$P_n(\cos\Theta) = \frac{4\pi}{2n+1} \sum_{m=-n}^{n} Y^*_{n,m}\left(\theta_p, \phi_p\right) Y_{n,m}(\theta, \phi)$$

Related to this expansion is that for the spherical wave

$$\frac{e^{\pm ik|\vec{r}-\vec{r}_0|}}{|\vec{r}-\vec{r}_0|} = \pm 4\pi k i \sum_{n=0}^{\infty} j_n(kr_<)\, h_n^{(3/2\mp 1/2)}(kr_>) \sum_{m=-n}^{n} Y^*_{n,m}(\theta_0, \phi_0)\, Y_{n,m}(\theta, \phi)$$

where the spherical Bessel j_n and Hankel $h_n^{(1)}$ functions are

$$j_n(z) = \sqrt{\frac{\pi}{2z}} J_{n+1/2}(z)$$

$$h_n^{(1)}(z) = \sqrt{\frac{\pi}{2z}} \left[J_{n+1/2}(z) + i\, N_{n+1/2}(z)\right]$$

In the limit $k \to 0$ the spherical wave has expansion

$$\frac{1}{|\vec{r}-\vec{r}_0|} = 4\pi \sum_{n,m} \frac{1}{2n+1} \frac{r_<^n}{r_>^{n+1}} Y^*_{n,m}(\theta_0, \phi_0)\, Y_{n,m}(\theta, \phi)$$

$$\frac{1}{|\vec{r}-\vec{q}|} = \frac{1}{2\pi^2} \int d^3\kappa \; \frac{1}{\kappa^2 + \eta^2} \, e^{i\,\vec{\kappa}\cdot(\vec{r}-\vec{q})} \tag{C.8}$$

$$|\vec{r}-\vec{q}| = \frac{1}{\pi^2}\int d^3k\ \frac{3\eta^2-k^2}{\left(k^2+\eta^2\right)^3} e^{i\ \vec{k}\cdot(\vec{r}-\vec{q})}$$

C.3 Stationary Phase Method

In the applications one often encounters integrals of the form

$$I = \int du\, Z(u) e^{i\phi(u)}$$

where the function $Z(u)$ is a slowly varying function of u[2] whilst the phase of the integrand $\phi(u)$ is large and also a slowly varying with u. The integral averages to a small value unless the phase at some points is stationary, meaning that its variation is second order in u. These points are solutions of equation

$$\frac{d\phi(u)}{du} = 0$$

and if there are several solutions they must be well separated, i.e. in between the points the phase oscillates very rapidly thus the contribution to the integral averages to a small value. From vicinity of one stationary point the integral approximates as

$$I \approx Z(u_{st}) \int du\, e^{i\phi(u_{st})+\frac{i}{2}(u-ust)^2\phi''(u_{st})} = \frac{\sqrt{2\pi}Z(u_{st})}{\sqrt{|\phi''(u_{st})|}} e^{i\phi(u_{st})+i\frac{\pi}{4}sign\left(\phi''(u_{st})\right)}$$

provided that $Z(u)$ is nearly constant within this interval. If there are several stationary points then the integral is the sum of the same contribution from all of them.

If the integral is two dimensional

$$I = \int du\, dv\, Z(u,v) e^{i\phi(u,v)}$$

then the condition for the stationary phase is

$$\partial_u Z(u,v) = 0 \quad , \quad \partial_v Z(u,v) = 0$$

in which case the phase in their vicinity approximates as

$$\phi(u,v) \approx \phi(u_{st},v_{st}) + \frac{1}{2}\Delta_u^2\phi''_u(u_{st},v_{st}) + \frac{1}{2}\Delta_v^2\phi''_v(u_{st},v_{st}) + \Delta_v\Delta_u\phi''_{u,v}(u_{st},v_{st})$$

[2] *Slowly* has a relative meaning, but in general it means that it is almost a constant function within the range in which the oscillatory part makes a large number of oscillations.

and the integral transforms into

$$I \approx e^{i\phi(u_{st})} Z(u_{st}, v_{st}) \int du\, dv\, e^{\frac{i}{2}\phi''_u \left(\Delta_u + \Delta_v \frac{\phi''_{u,v}}{\phi''_u}\right)^2 + \frac{i}{2}\Delta_v^2 \left[\phi''_v - \frac{(\phi''_{u,v})^2}{\phi''_u}\right]}$$

with the result

$$I \approx e^{i\phi(u_{st}, v_{st})} \frac{2\pi Z(u_{st}, v_{st})}{\sqrt{|\phi''|}\sqrt{\left|\phi''_v - \frac{(\phi''_{u,v})^2}{\phi''_u}\right|}} e^{i\frac{\pi}{4} sign(\phi'') + i\frac{\pi}{4} sign\left(\phi''_v - \frac{(\phi''_{u,v})^2}{\phi''_u}\right)}$$

Again, for several stationary points, well separated, the integral is the sum of the individual contribution.

Special case of the two dimensional integral is when the second derivatives are zero but the mixed is not, i.e.

$$I \approx e^{i\phi(u_{st})} Z(u_{st}, v_{st}) \int du\, dv\, e^{i\Delta_u \Delta_v \phi''_{u,v}}$$

when its value is

$$I \approx 2\pi e^{i\phi(u_{st})} \frac{Z(u_{st}, v_{st})}{\left|\phi''_{u,v}\right|}$$

C.4 Transformation of Volume Element

Volume element in Cartesian coordinates $\{x_1, x_2, \ldots, x_N\}$ is

$$dV = dx_1\, dx_2, \ldots,\ dx_N$$

By transforming the coordinates into the new ones by

$$y_n = f_n(x_1, x_2, \ldots, x_N)$$

the volume element transform into

$$dx_1\, dx_2, \ldots,\ dx_N = \frac{dy_1\, dy_2, \ldots,\ dy_N}{|J(y, x)|} = |J(x, y)|\, dy_1\, dy_2, \ldots,\ dy_N$$

where J is called Jacobian and it is defined as

$$J(y, x) = \det \begin{vmatrix} \partial_{x_1} y_1 & \partial_{x_1} y_2 & \cdots & \partial_{x_1} y_N \\ \partial_{x_2} y_1 & \partial_{x_2} y_2 & \cdots & \partial_{x_2} y_N \\ \vdots & \vdots & \ddots & \vdots \\ \partial_{x_1} y_1 & \partial_{x_1} y_1 & \cdots & \partial_{x_1} y_1 \end{vmatrix}$$

Appendix D
System of N Particles

D.1 Centre of Mass

In many applications it is necessary to transform the coordinates of N particles from arbitrary coordinate system, often referred to as the *laboratory*, into the *centre of mass* coordinate system. The centre of mass vector is defined as

$$\vec{R} = \frac{\sum_{n=1}^{N} m_n \vec{R}_n}{\sum_{n=1}^{N} m_n} \tag{D.1}$$

and the rest of $N-1$ position vectors are arbitrarily defined, but in here they must satisfy a specific requirement. The bilinear form of Laplacians

$$K = \sum_{n=1}^{N} \frac{1}{m_n} \Delta_{R_n}$$

must in new coordinates $\{\vec{R}, \vec{r}_1, \vec{r}_2, \ldots, \vec{r}_{N-1}\}$ be diagonal, i.e. again a sum of Laplacians. It can be shown that these new coordinates are defined as the following: the vector $\vec{r}_j$ is the difference between the vector $\vec{R}_{j+1}$ and the vector of the centre of mass of the previous j vectors $\vec{R}_n$; $n \leq j$. The first few vectors are

$$\begin{aligned}
\vec{r}_1 &= \vec{R}_2 - \vec{R}_1 \\
\vec{r}_2 &= \vec{R}_3 - \frac{m_1\vec{R}_1 + m_2\vec{R}_2}{m_1 + m_2} \\
\vec{r}_3 &= \vec{R}_4 - \frac{m_1\vec{R}_1 + m_2\vec{R}_2 + m_3\vec{R}_3}{m_1 + m_2 + m_3}
\end{aligned}$$

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By straightforward analysis it is shown that in these coordinates the bilinear form is

$$K = \frac{1}{\sum_{n=1}^{N} m_n}\Delta_R + \sum_{n=1}^{N-1}\frac{1}{\mu_n}\Delta_{r_n}$$

where μ_n is reduced mass of the particle $n+1$ and the mass of all particles with the indices $j < n+1$, i.e.

$$\mu_n = \frac{m_{n+1}\sum_{j=1}^{n} m_j}{\sum_{j=1}^{n+1} m_j}$$

Another important is the sum

$$\vec{T} = \sum_{n=1}^{N}\frac{1}{m_n}\nabla_{R_n}$$

which in the centre of mass coordinates is

$$\vec{T} = \frac{N}{\sum_{n=1}^{N} m_n}\nabla_R + \sum_{n=1}^{N-1}\frac{1}{\eta_n}\nabla_{r_n}$$

where the mass η_n is

$$\eta_n = \frac{m_{n+1}\sum_{j=1}^{n} m_j}{\sum_{j=1}^{n} m_j - n m_{n+1}}$$

Single gradient operator transforms into d

$$\frac{1}{m_j}\nabla_{R_j} = \frac{1}{\sum_{n=1}^{N} m_n}\nabla_R + \frac{1}{m_j}\nabla_{r_{j-1}} + \sum_{n=j}^{N-1}\frac{1}{\sum_{i=1}^{n} m_i}\nabla_{r_n};\ j = 2, 3, \ldots, N-1$$

$$\frac{1}{m_1}\nabla_{R_1} = \frac{1}{\sum_{n=1}^{N} m_n}\nabla_R + \sum_{n=1}^{N-1}\frac{1}{\sum_{i=1}^{n} m_i}\nabla_{r_n}$$
$$\frac{1}{m_N}\nabla_{R_N} = \frac{1}{\sum_{n=1}^{N} m_n}\nabla_R + \frac{1}{m_N}\nabla_{r_{N-1}}$$

Another transformation is with respect to the coordinates of the centre of mass (D.1), which shall be demonstrated for single dimension. If the coordinate of the nth particle is x_n, and its mass is m_n, then the centre of mass of the N particle is

$$X = \frac{m_1 x_1 + m_2 x_2 + m_3 x_3 + \cdots}{m_1 + m_2 + m_3 + \cdots}$$

One defines a coordinate d_n of the nth particle as

$$d_n = x_n - X$$

in which case derivatives

$$\partial \equiv \{\partial_{x_1}, \partial_{x_2}, \partial_{x_3}, ..\}$$

are transformed as

$$\partial = D\partial_d$$

where D has matrix elements

$$D_{i,j} = \frac{\partial d_j}{\partial x_i}$$

Kinetic energy operator is then transformed as

$$K = -\frac{\hbar^2}{2}\sum_{n=1}^{N}\frac{1}{m_n}\frac{\partial^2}{\partial x_n^2} = -\frac{\hbar^2}{2}\widetilde{\partial}\, m^{-1}\, \partial = -\frac{\hbar^2}{2}\widetilde{\partial}_d\, \widetilde{D} m^{-1}\, D\partial_d$$

One defines a unitary matrix U that diagonalizes symmetric matrix between the two operators ∂_d, to give

$$K = -\frac{\hbar^2}{2}\widetilde{\partial}_q\, \kappa^{-1}\partial_q$$

where κ is a diagonal matrix

$$\kappa^{-1} = \widetilde{U}\left(\widetilde{D} m^{-1}\, D\right) U \tag{D.2}$$

and the new coordinates are

$$q = \widetilde{U} d \tag{D.3}$$

D.2 Rigid Body

Special system of N particles is a rigid body, which is formed when all the separations among the constituents are fixed. This restriction on the motions of the individual particles greatly simplifies dynamics of the body, in fact it is reduced to three coordinates that determine its orientation in space and three coordinates that determine position of its centre of mass. For the analysis of dynamics of the rigid body one has two choices of reference frames, laboratory and centre of mass coordinate frames (see Sect. D.1). Laboratory coordinate frame is designated by X whilst the centre of mass one is C. Unit vectors that define X system are $\widehat{X}$, which are conveniently fixed and are time independent, whilst in the C system unit vectors may either be fixed, and conveniently chosen to be parallel with those in the X system and therefore designated by $\widehat{X}$, or time dependent and designated by $\widehat{C}$ (this referred to as the body fixed reference frame). Position of any particle is therefore determined from either of the coordinate systems and relationship among them is

$$\widetilde{R}_n(t)X = \widetilde{r}_n(t)X + \widetilde{r}_C(t)X = \widetilde{r}_n(0)C(t) + \widetilde{r}_C(t)X$$

where a simplified notation is used. X stands for the set of unit vectors along the axes that define laboratory frame, say they are $X = \{x_1, x_2, x_3\}$, $C(t)$ stand for the similar unit vectors $C(t) = \{c_1, c_2, c_3\}$ (which are time dependent), $r_n = \{x_1^{(n)}, x_2^{(n)}, x_3^{(n)}\}$ and

$$r_C = \frac{m_1 r_1 + m_2 r_2 + \cdots + m_N r_N}{m_1 + m_2 + \cdots + m_N}$$

is position of the centre of mass of this system.

Basic operation in analysis of motion of a system of particles is rotation of a vector, mainly to conveniently choose a coordinate frame in which the system appears simpler, analogous to translation transformation for the choice of the centre of mass point as the origin of it. Rotation of any vector is achieved in three steps, requiring three angles that represent three consequent rotations around Cartesian $\{x, y, z\}$ axes. The best known are the three Euler angles (zyz angles) representing rotations around z, y and z axes, in this order. For the rigid body dynamics, however, it is often more convenient to choose three consecutive rotations around x, y and z axes(xyz angles), both rotations are in the reference frame X. Rotation of a vector r_n, therefore, goes in three steps and this transformation is particularly convenient when the modulus of the vector is fixed, as in the rigid body, because time dependence of it is transferred to time dependence of rotation angles. So, for example, transforming vector $r_n(0)$ into $r_n(t)$, if its modulus is preserved, is by xyz rotation

$$r_n(t) = R(\alpha, \beta, \gamma)\, r_n(0) = R_x(\alpha)\, R_y(\beta)\, R_z(\gamma)\, r_n(0) \tag{D.4}$$

where

$$R(\alpha,\beta,\gamma)=\begin{vmatrix}1 & 0 & 0\\ 0 & \cos\alpha & -\sin\alpha\\ 0 & \sin\alpha & \cos\alpha\end{vmatrix}\begin{vmatrix}\cos\beta & 0 & \sin\beta\\ 0 & 1 & 0\\ -\sin\beta & 0 & \cos\beta\end{vmatrix}\begin{vmatrix}\cos\gamma & -\sin\gamma & 0\\ \sin\gamma & \cos\gamma & 0\\ 0 & 0 & 1\end{vmatrix}$$

which is unitary, meaning that $\widetilde{R}R$ is the unit matrix. The angles are time dependent. Rigid body is now defined as a system of particles when the scalar product

$$\widetilde{r}_n(t)X\cdot\widetilde{r}_m(t)X=x_1^{(n)}x_1^{(m)}+x_2^{(n)}x_2^{(m)}+x_3^{(n)}x_3^{(m)}$$

is time independent, or in other words rotation affects all positions of particles in the same way.

For the following analysis it is convenient to define relationship between an antisymmetric 3×3 (three independent elements) matrix and a single column matrix (vector), where the association between them is

$$A=\begin{vmatrix}0 & -a_3 & a_2\\ a_3 & 0 & -a_1\\ -a_2 & a_1 & 0\end{vmatrix}\Leftrightarrow a=\begin{vmatrix}a_1\\ a_2\\ a_3\end{vmatrix}\tag{D.5}$$

In this way a vector product with a could be alternatively written as a matrix product

$$a\times b=Ab$$

Important property of this association is that if a is rotated as (D.4) then A is transformed as

$$a'=R(\alpha,\beta,\gamma)\,a\Rightarrow R(\alpha,\beta,\gamma)\,A\widetilde{R}(\alpha,\beta,\gamma)=A'\tag{D.6}$$

In the laboratory frame velocity of particles is related to the time derivative of the rotation angles but it is convenient to define angular velocity vector ω with the property

$$\dot{r}_n(t)=\omega\times r_n(t)\equiv\Omega\,r_n(t)=\begin{vmatrix}0 & -\omega_3 & \omega_2\\ \omega_3 & 0 & -\omega_1\\ -\omega_2 & \omega_1 & 0\end{vmatrix}\begin{vmatrix}x_1^{(n)}\\ x_2^{(n)}\\ x_3^{(n)}\end{vmatrix}\tag{D.7}$$

From (D.4) one finds

$$\dot{r}_n(t)=\dot{R}(\alpha,\beta,\gamma)\,r_n(0)=\dot{R}(\alpha,\beta,\gamma)\,\widetilde{R}(\alpha,\beta,\gamma)\,r_n(t)=\Omega\,r_n(t)$$

and by comparing the elements the angular velocity vector is

$$\omega=\Upsilon\dot{q}=\begin{vmatrix}1 & 0 & \sin\beta\\ 0 & \cos\alpha & -\sin\alpha\cos\beta\\ 0 & \sin\alpha & \cos\alpha\cos\beta\end{vmatrix}\begin{vmatrix}\dot{\alpha}\\ \dot{\beta}\\ \dot{\gamma}\end{vmatrix}\tag{D.8}$$

Closely related, and important, quantity is total angular momentum of the system of particles that are forming a rigid body. It is defined as

$$L = \{L_1, L_2, L_3\} = \sum_{n=1}^{N} m_n r_n(t) \times \dot{r}_n(t) = I\, \Upsilon \dot{q} = I\omega \tag{D.9}$$

where (D.7) was used. The matrix I is momentum of inertia tensor

$$I = \sum_{n=1}^{N} m_n \widetilde{X}_n X_n$$

where

$$X = \begin{vmatrix} 0 & -x_3^{(n)} & x_2^{(n)} \\ x_3^{(n)} & 0 & -x_1^{(n)} \\ -x_2^{(n)} & x_1^{(n)} & 0 \end{vmatrix} \tag{D.10}$$

In general, the inertia tensor is a non-diagonal symmetric matrix, but there is a reference frame where it is diagonal. To find this frame one defines a unitary matrix U that diagonalizes I, in which case

$$\iota = \widetilde{U} I U = \sum_{n=1}^{N} m_n \widetilde{\left(\widetilde{U}\, X_n U\right)}\, \widetilde{U}\, X_n U$$

and from (D.6) one obtains rotation matrix

$$R\,(\alpha_d, \beta_d, \gamma_d) = \widetilde{U}$$

The angles α_d, β_d and γ_d determine rotation by which original reference frame should be transformed in the one where the inertia tensor is diagonal. If the new reference frame is defined by unit vectors X' then they are connected with the unit vectors X of the original frame by transformation

$$X' = \widetilde{R}\,(\alpha_d, \beta_d, \gamma_d)\, X = UX$$

Although it is convenient to define the *principal axes* reference frame, in the laboratory one, it should be emphasized that this applies only if the rigid body does not rotate. When it does then in this frame the inertia tensor becomes non-diagonal

$$I = \; R\,(\alpha, \beta, \gamma)\, \iota\, \widetilde{R}\,(\alpha, \beta, \gamma) \tag{D.11}$$

D.2.1 Classical Dynamics

When an external force is applied on a system of particles, that form a rigid body, then in general its centre of mass moves and the system rotates. Equation of motion for the particle n of mass m_n at the position r_n is

$$m_n \ddot{r}_n = F_n(r_n) + F_n^{in} \tag{D.12}$$

where $F_n(r_n)$ is a force that acts on this particle and F_n^{in} is the force that binds particles together, and it is in the form of a gradient of a potential that is a sum of the terms like

$$V_{i,j}^{in} \sim \delta\left(\left|r_i - r_j\right| - r_{ij}^{(0)}\right)$$

where $r_{ij}^{(0)}$ is a distance between the particles i and j. The coordinates r_n refer to a laboratory frame and they could be decomposed as

$$r_n = r_c + d_n \tag{D.13}$$

where r_c are coordinates of the centre of mass and d_n are the coordinates of the nth particle with respect to it. There are now two sets of equations, one for the motion of the centre of mass and the other for the nth particle. The former is obtained by summing the equations (D.12) when one gets

$$\sum_n m_n \ddot{r}_n = M\ddot{r}_c = \sum_n F_n(r_n)$$

where the sum of all internal forces is zero.

In order to obtain equation of motion for the rotation of the system one starts from equation for the nth particle

$$m_n \ddot{r}_n = m_n \ddot{d}_n + m_n \ddot{R} = \frac{d_n}{|d_n|}\frac{d_n}{|d_n|} \cdot F_n + \frac{d_n}{|d_n|} \times \left(F_n \times \frac{d_n}{|d_n|}\right)$$

where $d_n = r_n - r_c$. The binding force is omitted because it does not have effect on the moduli $|d_n|$, they are time independent. The force is decomposed into the parallel component with the distance d_n, and has impact on the centre of mass, and the one that is perpendicular to it. By vector product of the equation with d_n the result is

$$m_n \frac{d}{dt}\left(d_n \times \dot{d}_n\right) + m_n d_n \times \ddot{R} = d_n \times F_n$$

and when summing over all particles the final expression is

$$\frac{d}{dt}L = Q$$

where Q is total torque by the forces on the rigid body and L is the angular momentum of it.

This concludes setting up equations of motion for a system of particles that together form a rigid body. The two sets of equations describe motion of the centre of mass and the orientation of this system of particles, the rigid body. The two motions are coupled, which is shown by assuming that the external force changes by small amount from its value at the centre of mass, when one could write

$$F_n\left(r_c + d_n\right) \approx F_n\left(r_c\right) + \left(d_n \cdot \nabla\right) F_n\left(r_c\right)$$

The equation for the centre of mass is then

$$M\ddot{r}_c \approx \sum_n F_n\left(r_c\right) - \nabla_{r_c} \times Q\left(r_c\right) - \sum_n \nabla_{r_c}\left[d_n \cdot F_n\left(r_c\right)\right]$$

where $Q\left(r_c\right)$ is the torque on the rigid body in the approximation when the forces have the value at the centre of mass. Equation for the angular momentum, rotation of the rigid body, is approximately

$$\frac{d}{dt}L \approx Q\left(r_c\right) + \sum_n d_n \times \left[d_n \cdot \nabla\right] F_n\left(r_c\right) = Q\left(r_c\right) + Q'\left(r_c\right)$$

where $Q'\left(r_c\right)$ has the structure of a torque where the force is modification of the original one.

If no external force is applied on a rigid body then the angular momentum is constant, and the equations of motion for the angular velocities ω are derived from relationship

$$\frac{dL}{dt} == 0 = \frac{d\left(I\,\omega\right)}{dt} \tag{D.14}$$

and when the expression (D.11) is used one gets

$$\iota\dot{W} = -\Omega_W\,\iota\,W = -W \times \iota W \tag{D.15}$$

where (the set of angles $\{\alpha, \beta, \gamma\}$ equals $\{\alpha_d, \beta_d, \gamma_d\}$)

$$W = \widetilde{R}\left(\alpha, \beta, \gamma\right)\omega$$

and

$$\Omega_W = \widetilde{R}\left(\alpha, \beta, \gamma\right)\Omega\, R\left(\alpha, \beta, \gamma\right) = \begin{vmatrix} 0 & -W_3 & W_2 \\ W_3 & 0 & -W_1 \\ -W_2 & W_1 & 0 \end{vmatrix}$$

where the relationship (D.6) was used. Equation (D.15) has a special feature that momentum of inertia is angle independent and refers to the reference frame where it is diagonal, according to the definition that it is the body fixed frame. In this frame W plays the role of angular velocity and if multiplied by ι this is angular momentum in the body fixed frame. This is a convenient frame to analyze motion of a rigid body that is not subjected to an external force, however when it is applied then the laboratory frame should be used. Disadvantage is that in the body fixed frame angular momentum, in general, is not conserved, which follows from (D.15), however, its modulus is conserved.

Total energy of a rigid rotor is derived in an analogous way as angular momentum. By utilizing (D.13) in the set (D.12) equations of motion are

$$m_n \ddot{d}_n + m_n \ddot{r}_c = F_n$$

and by scalar product with R and d_n and combining the two products one obtains

$$\frac{m_n}{2}\frac{d}{dt}\dot{r}_c^{\,2} + \frac{m_n}{2}\frac{d}{dt}\dot{d}_n^{\,2} + m_n \frac{d}{dt}\dot{d}_n \cdot \dot{R} = -\dot{R}\nabla_n V - \dot{d}_n \nabla_n V$$

By summing over all particles the total energy is finally

$$E = \frac{M}{2}\frac{d}{dt}\dot{r}_c^{\,2} + \sum_n \frac{m_n}{2}\frac{d}{dt}\dot{d}_n^{\,2} + V\left(r_c + d_1, r_c + d_2, \ldots, r_c + d_N\right)$$

Initial conditions for a rotating rigid body are determined in the laboratory frame by specifying components of the angular momentum, however, these are derived quantities because the basic ones are angular velocities to which one would want to refer to. Components of ω are only formally called angular velocities, because they are related to the time derivatives of the rotation angles by (D.8), which one could call the true angular velocities but they are also not convenient to specify. The most intuitive to specify initial conditions are those in the reference frame which is defined by the principal axes of a rigid body, where the inertia tensor I is diagonal. Angular momentum in this body fixed reference frame is ιW where now component W_i is angular velocity around the axes i. In the laboratory frame the angular momentum is

$$L = R\left(\alpha, \beta, \gamma\right) \iota W = R\left(\alpha, \beta, \gamma\right) L_b$$

A very important parameter is velocity of a particle in a rigid body, and from its definition (D.7) one obtains

$$\dot{d}_n(t) = -R\left(\alpha, \beta, \gamma\right) \iota^{-1} d_n(0) \times L_b$$

which is related to the angular momentum L_b in the body fixed frame.

D.2.2 Quantum Dynamics

In order to formulate quantum equations for dynamics of rigid rotor one must define appropriate coordinates and derive the conjugate variables for which one applies the principle of correspondence. There are two sets of variables, coordinates of the centre of mass and the rotation angles for rotation of the rigid body. For the former the conjugate variables are components of the centre of mass momentum p_c, and hence by the correspondence principle the operator that is associated with it is $\widehat{p}_c = -i\hbar\nabla_{r_c}$. Conjugate variables for the rotation angles are derived from the Lagrangian, in fact only its kinetic energy part because potential is assumed to be only coordinate dependent. Kinetic energy of the rigid rotor is

$$K = \frac{1}{2}\sum_n m_n \dot{d}_n(t)\cdot\dot{d}_n(t) + \frac{1}{2}M\dot{r}_c(t)\cdot\dot{r}_c(t) = \frac{1}{2}\widetilde{\dot{q}}\,\widetilde{\Upsilon}\,I\Upsilon\dot{q} + \frac{1}{2}M\dot{r}_c(t)\cdot\dot{r}_c(t)$$

and momentum conjugate variables are

$$p_i = \frac{\partial K}{\partial \dot{q}_i}$$

where $\dot{q}_i$ is time derivative of one of the Euler angles. One finds that

$$p = \widetilde{\Upsilon}\,I\,\Upsilon\dot{q} \equiv Q\dot{q}$$

and the kinetic energy for the rotor is

$$K = \frac{1}{2}\widetilde{\dot{p}}\,\widetilde{Q^{-1}}p$$

The expression simplifies if one defines angular momentum in terms of the conjugate variables

$$L = I\,\Upsilon\dot{q} = \left(\widetilde{\Upsilon}\right)^{-1}\,p = \frac{1}{\cos\beta}\begin{vmatrix} \cos\beta & 0 & 0 \\ \sin\alpha\sin\beta & \cos\alpha\cos\beta & -\sin\alpha \\ -\cos\alpha\sin\beta & \sin\alpha\cos\beta & \cos\alpha \end{vmatrix} p \equiv \Omega_c p$$

or in the body fixed frame

$$L = R(\alpha,\beta,\gamma)\,L_b = \left(\widetilde{\Upsilon}\right)^{-1}\,p \Rightarrow$$
$$L_b = \frac{1}{\cos\beta}\begin{vmatrix} \cos\gamma & \cos\beta\sin\gamma & -\sin\beta\cos\gamma \\ -\sin\gamma & \cos\beta\cos\gamma & \sin\beta\sin\gamma \\ 0 & 0 & \cos\beta \end{vmatrix} p \equiv \Omega_b p$$

when

$$K = \frac{1}{2}\widetilde{L}\, I^{-1} L = \frac{1}{2}\widetilde{L_b}\, \iota^{-1} L_b$$

Going over to quantum dynamics one uses the correspondence principle and replaces

$$p \Rightarrow \widehat{p} = -i\hbar \begin{vmatrix} \partial_\alpha \\ \partial_\beta \\ \partial_\gamma \end{vmatrix} \equiv -i\hbar \nabla_\Psi$$

If one defines operator

$$\widehat{\Lambda} = \frac{i}{\hbar} \Omega_b p$$

with the explicit components

$$\widehat{\Lambda} = \begin{vmatrix} \widehat{\Lambda}_z \\ \widehat{\Lambda}_y \\ \widehat{\Lambda}_x \end{vmatrix} = \begin{vmatrix} \frac{\cos\gamma}{\cos\beta}\partial_\alpha + \sin\gamma\partial_\beta - \tan\beta\cos\gamma\partial_\gamma \\ -\frac{\sin\gamma}{\cos\beta}\partial_\alpha + \cos\gamma\partial_\beta + \tan\beta\sin\gamma\partial_\gamma \\ \partial_\gamma \end{vmatrix}$$

and

$$\widehat{\Lambda}^2 = \frac{1}{\cos^2\beta}\left(\partial_\alpha^2 + \partial_\gamma^2\right) - 2\frac{\tan\beta}{\cos\beta}\partial_\alpha\partial_\gamma + \frac{1}{\cos\beta}\partial_\beta\left(\cos\beta\partial_\beta\right)$$

then Schroedinger equation is

$$-\frac{\hbar^2}{2M}\Delta_{r_c} f - \frac{\hbar^2}{2}\widetilde{\widehat{\Lambda}}\, \iota^{-1}\widehat{\Lambda} f + V\left(r_c + d_1, r_c + d_2, \ldots, r_c + d_N\right) f = Ef$$

which, for simplicity, it is formulated in the body fixed frame. When the potential energy does not changes appreciable from its value at the centre of mass then the equation approximates

$$-\frac{\hbar^2}{2M}\Delta_{r_c} f - \frac{\hbar^2}{2}\widetilde{\widehat{\Lambda}}\, \iota^{-1}\widehat{\Lambda} f + V\left(r_c\right) f + \sum_n \left(d_n \cdot \nabla_{r_n}\right) V\left(r_c\right) f = Ef$$

Solution is approximately a product $f\left(r_c, r_n\right) = f_c\left(r_c\right) f_b\left(r_n\right)$ when the equation is replaced by two

$$-\frac{\hbar^2}{2M}\Delta_{r_c} f_c + V\left(r_c\right) f_c = E_c f_c$$

$$-\frac{\hbar^2}{2}\widetilde{\widehat{\Lambda}}\, \iota^{-1}\widehat{\Lambda} f_b + \sum_n \left(d_n \cdot \nabla_{r_n}\right) V\left(r_c\right) f_b = E_b f_b$$

Important quantity in the analysis is the probability current, which is essentially the average of the velocity of a particle. In classical dynamics velocity of the nth particle is

$$\dot{r}_n(t) = \dot{r}_c(t) - R(\alpha, \beta, \gamma)\, \iota^{-1} d_n(0) \times L_b$$

and by the correspondence principle it is replaced by the operator

$$\widehat{\dot{r}}_n(t) = -\frac{i\hbar}{M}\nabla_{r_c} + i\hbar R(\alpha, \beta, \gamma)\, \iota^{-1} d_n(0) \times \Omega_b \nabla_\Psi$$

The charge current for the nth particle is now

$$j_n = q_n \hbar \,\mathrm{Im}\left[f^*\left(\frac{1}{M}\nabla_{r_c} - R(\alpha, \beta, \gamma)\, \iota^{-1} d_n(0) \times \widehat{\Lambda}\right) f\right] \tag{D.16}$$

where q_n is its charge. The total charge current is

$$j = \sum_n j_n$$

Previous analysis was based on the xyz rotation matrix (D.4), which is convenient for classical dynamics but not in quantum. In the latter the most convenient is to use the zyz Euler rotation, which is represented by the rotation matrix

$$R(\alpha, \beta, \gamma) = R_z(\alpha)\, R_y(\beta)\, R_z(\gamma)$$

Following the same steps as previously one finds

$$\widehat{\Lambda}_E = \begin{vmatrix} -\frac{\cos\gamma}{\sin\beta}\partial_\alpha + \sin\gamma\partial_\beta + \cot\beta\cos\gamma\partial_\gamma \\ \frac{\sin\gamma}{\sin\beta}\partial_\alpha + \cos\gamma\partial_\beta - \cot\beta\sin\gamma\partial_\gamma \\ \partial_\gamma \end{vmatrix}$$

and

$$\widehat{\Lambda}_E^2 = \frac{1}{\sin^2\beta}\left(\partial_\alpha^2 + \partial_\gamma^2\right) - 2\frac{\cot\beta}{\sin\beta}\partial_\alpha\partial_\gamma + \frac{1}{\sin\beta}\partial_\beta\left(\sin\beta\partial_\beta\right)$$

Important quantity is the current (D.16), which with the Euler angles is

$$j_n = q_n \hbar \,\mathrm{Im}\left[f^*\left(\frac{1}{M}\nabla_{r_c} - R_E(\alpha, \beta, \gamma)\, \iota^{-1} d_n(0) \times \widehat{\Lambda}_E\right) f\right]$$

D.3 Semirigid Body

N particles that are bound together by a force that does not fixes their position with respect to the centre of mass of the system display collective motion in which motion

of a single particle is not independent of the motion of the others. The conglomerate of these particles form a semirigid body. In general this collective motion is chaotic but an important special case is when around the equilibrium points the force on particle is harmonic. The forces of this kind are result of approximating interparticle interaction around the equilibrium points by power expansion and by assuming that the resulting vibrations are of sufficiently small amplitude.

Position of the nth particle has three Cartesian components, and shall be denoted by $r_n = \{x_1, x_2, x_3\}$, where $n = 1, 2, \ldots, N$ (notation is along the lines as in Sect. D.2, except one should note additional complication that each constituent of the body is allowed to move). Thus the position of the nth particle is

$$r_n = r_c + d_n + \varepsilon_n \tag{D.17}$$

where r_c are coordinates of the centre of mass of the system, d_n are coordinates of its equilibrium position with respect to r_c and ε_n are its coordinates with respect to d_n. Coordinates d_n define rigid body, meaning that not only the moduli of d_n are time independent but also any scalar product $d_n \cdot d_i$. If the particles could move away from the equilibrium points d_n by a small distance ε_n then the body is a semirigid body. The potential that binds the particles into a stable system is in general a function of the separations between any two of them. This ensures that the forces which bind the particles into a single body are independent of the choice of the reference frame. However, the choice of the forces should ensure two additional requirements: vibrations of the particles should not have impact on the centre of mass motion and also should not change angular momentum of the body as the whole. It could be shown that the two requirements are fulfilled if the potential energy is a function of the modulus of the relative separations $r_i - r_j$ and the scalar products $\left(r_i - r_j\right) \cdot (r_i - r_k)$.

Potential energy is therefore a function of the form $V\left(r_i - r_j\right);\ i < j$, and harmonic approximation assumes that around the equilibrium points d_n one could replace it by expansion

$$V\left(d_{i,j} + \varepsilon_{i,j}\right) = V\left(d_{i,j}\right) + \tag{D.18}$$
$$\frac{1}{2}\sum_{i>j=1}^{N}\left(\varepsilon_{i,j}\cdot\nabla_i\right)\left(\varepsilon_{i,j}\cdot\nabla_i\right)V\left(d_{i,j}\right) + \sum_{i\neq j=1}^{N}\sum_{k>i,l>j}^{N}\left(\varepsilon_{i,k}\cdot\nabla_i\right)\left(\varepsilon_{j,l}\cdot\nabla_j\right)V\left(d_{i,k}, d_{j,l}\right)$$

where $d_{i,j} = d_i - d_j$ and $\varepsilon_{i,j} = \varepsilon_i - \varepsilon_j$. The expansion is written in a simplified form

$$V = V(d) + \frac{1}{2}\widetilde{\varepsilon}W(d)\,\varepsilon$$

where the matrix elements of $W(d)$ are deduced from the expansions (D.18) and $\varepsilon = \{\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_N\}$. The matrix elements satisfy two conditions, there is no net force on the body due to the forces among its constituents[3]

[3]The conditions are valid only if no external force is applied on the body.

$$\sum_{i,j} W_{i,j}(d) \cdot \varepsilon_j = 0$$

no net torque

$$\sum_{i,j} d_i \times W_{i,j}(d)\, \varepsilon_j = 0$$

Besides these there is also requirement that both d_i and ε_j are defined with respect to the centre of mass of the body, in which case

$$\sum_i m_i d_i = 0 \tag{D.19}$$

and

$$\sum_i m_i \varepsilon_i = 0$$

D.3.1 Classical Dynamics

Classical equation of motion for the nth particle is

$$m_n \ddot{r}_n = -\nabla_n V - \nabla_n V_{ext} \tag{D.20}$$

where V_{ext} is potential energy of the nth particle due to some external force. Internal potential is a function of the relative separations of the particles, whilst external potential is a function of the absolute positions (with respect to a laboratory frame) of the particles. The set should be manipulated in order to prepare it for analysis the basic problem, the motion of the semirigid body as the whole in which the amplitude of vibrations of its constituents is small compared to their average separations. The simplest transformation is to sum the equations in which case one obtains equation for the motion of its center of mass

$$M\ddot{r}_c = -\sum_n \nabla_n V_{ext}$$

where M is mass of the entire body.

For the next step on needs a small introduction. If the separation vector of the nth particle from the centre of mass r_c is s_n then one could define rotation (for definition of rotation transformation see Sect. D.2)

$$s_n = R(\alpha, \beta, \gamma)\, s_n^0$$

where the rotation angles are independent of the index n and rotate the position vectors from some of their initial orientations. Both the angles and s_n^0 are time dependent for the semirigid body, in which case time derivative of s_n is

$$\dot{s}_n = \omega \times s_n + R(\alpha, \beta, \gamma)\,\dot{s}_n^0 = \omega \times s_n + v_n \tag{D.21}$$

This time derivative has an important property

$$s_n \times \dot{s}_n = \omega \times s_n + R(\alpha, \beta, \gamma)\,\dot{s}_n^0 = s_n \times (\omega \times s_n) = \widetilde{X}_n X_n \omega$$

where the definition (D.9) was used. One also shows that

$$s_n \cdot \ddot{s}_n = s_n \cdot [\omega \times (\omega \times s_n)] + s_n \cdot \dot{v}_{s_n}$$

Equation that s_n satisfy are obtained by using the equation for the centre of mass coordinates, when one gets

$$m_n \ddot{s}_n = -\sum_j \frac{s_n - s_j}{|s_n - s_j|} V'(|s_n - s_j|) + \sum_i \left(\frac{m_n}{M} - \delta_{i,n}\right) \nabla_i V_{ext}$$

for which it could be shown that

$$\sum_n m_n \ddot{s}_n = 0$$

By vector multiplying the equation with s_n and summing them the resulting equation is

$$\frac{d}{dt} \sum_n m_n s_n \times \dot{s}_n = \sum_{i,n} \left(\frac{m_n}{M} - \delta_{i,n}\right) s_n \times \nabla_i V_{ext} = \frac{d}{dt} \sum_n m_n s_n \times (\omega \times s_n)$$

and when one uses definition for the momentum of inertia and the angular momentum (D.9)

$$\frac{d}{dt} L = \frac{d}{dt} I\omega = \sum_{i,n} \left(\frac{m_n}{M} - \delta_{i,n}\right) s_n \times \nabla_i V_{ext} \tag{D.22}$$

Similarly if equation for s_n is scalar multiplied by s_n and when they are summed one obtains

$$\sum_i m_i s_i \cdot \dot{v}_{s_i} = \sum_i m_i (\omega \times s_i)^2 - \frac{1}{2} \sum_{i,j} |s_i - s_j| V'(|s_i - s_j|) + \sum_i \sum_j \left(\frac{m_i}{M} - \delta_{i,j}\right) s_i \cdot \nabla_j V_{ext}$$

Equation for v_{s_n} is now derived by taking gradient of this equation with respect to s_n[4]

$$m_n \dot{v}_{s_n} = -2m_n \omega \times (\omega \times s_n) + F_n^0 + F_n \tag{D.23}$$

where the external force is

$$F_n = \sum_j \left(\frac{m_n}{M} - \delta_{n,j} \right) \nabla_j V_{ext} + \sum_i \sum_j \left(\frac{m_i}{M} - \delta_{i,j} \right) s_i \cdot \nabla_j \left(\nabla_n V_{ext} \right)$$

and the force, internal force, from the other particles

$$F_n^0 = -\sum_j \frac{s_n - s_j}{\left| s_n - s_j \right|} V' \left(\left| s_n - s_j \right| \right) - \sum_j \left(s_n - s_j \right) V'' \left(\left| s_n - s_j \right| \right)$$

The first term on the right is the Coriolis force, whilst the rest of the terms depend on the forces that act on particles.

Equation for the angular momentum of the body is (D.22), and besides it one should also derive equation for the total energy. From equation (D.20) one derives

$$\frac{d}{dt} \left(\frac{M}{2} \dot{r}_c^2 + \frac{1}{2} \sum_n m_n \dot{s}_n^2 \right) = -\frac{d}{dt} \left(V + V_{ext} \right)$$

and by using expression for $\dot{s}_n$ one finally obtains

$$\frac{d}{dt} \left(\frac{M}{2} \dot{r}_c^2 + \frac{1}{2} \widetilde{L} I^{-1} L + \frac{1}{2} \sum_n m_n v_n^2 \right) = -\frac{d}{dt} \left(V + V_{ext} \right)$$

On the left of equation is time rate of change of kinetic energy of the body, which is a sum of the kinetic energy for the motion of its centre of mass, rotation of the body and the motion of its constituents.

Previous equations are given in terms of the quantities that are only indirectly related to the parameters which are relevant for the study of dynamics of the body, such as the rotation angles α, β and γ and the stretching coordinates s_n^0. In order to transform them into these parameters one defines

$$\varpi = \widetilde{R} \left(\alpha, \beta, \gamma \right) \Upsilon \dot{q} = \Theta \dot{q} = \begin{vmatrix} \cos\beta \cos\gamma & \sin\gamma & 0 \\ -\cos\beta \sin\gamma & \cos\gamma & 0 \\ \sin\beta & 0 & 1 \end{vmatrix} \begin{vmatrix} \dot{\alpha} \\ \dot{\beta} \\ \dot{\gamma} \end{vmatrix} \tag{D.24}$$

[4]It should be noted that one is essentially saying that solution of equation $d \cdot r = 0$ is $r = 0$, which is not correct. However, if r is a function of t then the solution is correct if equation should be valid for any t. Solution is undetermined up to an additional component $d \times a$, where a is arbitrary vector.

Equations for (D.23) are then transformed into

$$m_n \ddot{s}_n^0 = -m_n\, \varpi \times \dot{s}_n^0 - 2m_n \varpi \times \left(\varpi \times s_n^0\right) - \sum_j \frac{s_n^0 - s_j^0}{\left|s_n^0 - s_j^0\right|} V'\left(\left|s_n^0 - s_j^0\right|\right) - \sum_j \left(s_n^0 - s_j^0\right) V''\left(\left|s_n^0 - s_j^0\right|\right) + \widetilde{R} F_n$$

where definition (D.21) was used. Similarly, equation for the angular momentum (D.22) is transformed into

$$\ddot{q} = -A\dot{q} - BI_0^{-1}\varpi \times I_0\varpi - BI_0^{-1}\dot{I}_0\varpi + BI_0^{-1}\widetilde{R}\sum_{i,n}\left(\frac{m_n}{M} - \delta_{i,n}\right) s_n \times \nabla_i V_{ext}$$

where

$$A = \Upsilon^{-1}\dot{\Upsilon} = \frac{1}{\cos\beta}\begin{vmatrix} 0 & -\dot{\alpha}\sin\beta & \dot{\beta} \\ 0 & 0 & -\dot{\alpha}\cos^2\beta \\ 0 & \dot{\alpha} & -\dot{\beta}\sin\beta \end{vmatrix},$$

$$B = \Upsilon^{-1}R = \frac{1}{\cos\beta}\begin{vmatrix} \cos\gamma & -\sin\gamma & 0 \\ \cos\beta\sin\gamma & \cos\beta\cos\gamma & 0 \\ -\sin\beta\cos\gamma & \sin\beta\sin\gamma & \cos\beta \end{vmatrix}$$

This equation simplifies considerably if there is no external force, in which case the total angular momentum is conserved and equal to L_0, when

$$I\omega = L_0 \;\Rightarrow\; \dot{q} = BI_0^{-1}\;\widetilde{R}L_0$$

Kinetic energy is transformed into

$$K = \frac{M}{2}\dot{r}_c^2 + \frac{1}{2}\widetilde{\varpi} I_0 \varpi + \frac{1}{2}\sum_n m_n \widetilde{\dot{s}_n^0}\dot{s}_n^0$$

Characteristic feature of a semirigid body is that s_n could be approximated as a sum of a large component d_n, whose modulus is fixed, and a small component η_n that measures the space within which the nth particle moves. Previous equations should be therefore formulated in terms of the new variables, and for that one uses perturbation analysis. If s_n is written as a sum

$$s_n = d_n + \eta_n \tag{D.25}$$

then

$$s_n^0 = \widetilde{R}s_n = d_n^0 + \varepsilon_n$$

where time derivatives of d_n^0 are zero. Force on the nth particle due to the other particles is then approximated as

$$F_n^0 = -\sum_{j\neq n} \frac{\left(d_n^0 - d_j^0\right)\left[\left(d_n^0 - d_j^0\right)\cdot\left(\varepsilon_n - \varepsilon_j\right)\right] + \left(\varepsilon_n - \varepsilon_j\right)}{\left|d_n^0 - d_j^0\right|^2} V''\left(\left|d_n^0 - d_j^0\right|\right)$$

where it was taken into account that $d_n^0 - d_j^0$ is the equilibrium distance of the two particles. Also, the leading term that is $\varepsilon_n - \varepsilon_j$ independent was neglected and it was assumed that the potential V is harmonic. For further convenience it is assumed that the force F_n^0 is represented in the matrix form

$$F_n^0 = \sum_j W_{n,j}\varepsilon_j;\ \ W_{n,n} = 0$$

Equation for s_n^0 transforms now into equation for the shifts ε_n

$$m_n\ddot{\varepsilon}_n = -m_n\,\varpi\times\dot{\varepsilon}_n - 2m_n\varpi\times\left(\varpi\times d_n^0\right) + \sum_j W_{n,j}\varepsilon_j + \widetilde{R}F_n$$

where the contribution of ε_j in the Coriolis term was neglected. For the rotation angles the equation approximates as

$$\ddot{q} = -A\dot{q} - BI_0^{-1}\varpi\times I_0\varpi - BI_0^{-1}\dot{I}_0\varpi + BI_0^{-1}\sum_{i,n}\left(\frac{m_n}{M} - \delta_{i,n}\right)s_n^0\times\left(\widetilde{R}\nabla_i V_{ext}\right)$$

Special attention should be devoted to the momentum of inertia, which is defined in terms of s_n^0, and from the definition of I_0 it approximates as

$$I_0 = \iota_0 + \sum_{n=1}^{N} m_n\left(\widetilde{E}_n D_n^0 + \widetilde{D}_n^0 E_n\right) \tag{D.26}$$

where D_n^0 is the matrix of the form (D.5) with the elements of d_n^0 whilst E_n has the elements ε_n. The equation for q is now

$$\ddot{q} = -A\dot{q} - B\iota_0^{-1}\varpi\times\iota_0\varpi + B\iota_0^{-1}\sum_{n=1}^{N} m_n\left[\dot{\varepsilon}_n\times\left(d_n^0\times\varpi\right) + d_n^0\times\left(\dot{\varepsilon}_n\times\varpi\right)\right] -$$
$$B\iota_0^{-1}d_n^0\times\left(\widetilde{R}\nabla_n V_{ext}\right)$$

where the term for the external force that is of the order ε was neglected. The first two terms on the right are the same as for the rotation of a rigid body. The third term is contribution due to the oscillations of the body, whilst the last term drives the body.

Kinetic energy is approximately

$$K = \frac{M}{2}\dot{r}_c^2 + \frac{1}{2}\widetilde{\varpi}\iota_0\varpi - \sum_{n=1}^{N} m_n\left(\dot{\varepsilon}_n \times \varpi\right)\cdot\left(d_n^0 \times \varpi\right) + \frac{1}{2}\sum_n m_n\dot{\varepsilon}_n\cdot\dot{\varepsilon}_n$$

Those were the most general equations that describe dynamics of a semirigid body, its rotation, vibration and translation under the impact of external force. However, in some circumstances it is sufficient to analyze vibrations only, without external force, which could only be de-coupled from rotations if the angular momentum of the body is zero. In this case the equations are

$$m_n\ddot{\varepsilon}_n = \sum_j W_{n,j}\varepsilon_j \tag{D.27}$$

and they are not coupled to the other degrees of freedom if initial conditions are chosen so that

$$\sum_n m_n\dot{\varepsilon}_n = \sum_n m_n\varepsilon_n = \sum_n m_n d_n^0 \times \varepsilon_n = 0 \tag{D.28}$$

Solving equations (D.27) is greatly facilitated if written in a matrix form

$$m\ddot{\varepsilon} = W\varepsilon$$

where W is a symmetric matrix. The equations are solved by modifying them as

$$\left(\ddot{m^{1/2}\varepsilon}\right) = m^{-1/2}Wm^{-1/2}\left(m^{1/2}\varepsilon\right)$$

and by defining coordinates ρ that are related to ε by transformation $m^{1/2}\varepsilon = U\rho$ where

$$\widetilde{U}\, m^{-1/2}Wm^{-1/2}\, U = -\varpi^2$$

then equations have simple solution

$$\varepsilon = m^{-1/2}U\left(\rho_0\ \cos\varpi t\ + \dot{\rho}_0\varpi^{-1}\ \sin\varpi t\right)$$

The initial conditions ρ_0 and $\dot{\rho}_0$ should be chosen in accordance with conditions (D.28).

D.3.2 Quantum Dynamics

Quantum dynamics for the semirigid body is formulated along the same lines as for the rigid body in Sect. D.2. One starts by defining the coordinates, and these are for the centre of mass, rotation angles and coordinates for vibrations. For these one must derive conjugate momentum variables from the Hamilton equations, entirely from kinetic energy of the semirigid body, which is given by

$$K = \frac{M}{2}\dot{r}_c^2 + \frac{1}{2}\dot{\widetilde{q}}\widetilde{\Theta}I_0\Theta\dot{q} + \frac{1}{2}\sum_n m_n\dot{\widetilde{s}}_n^0\dot{s}_n^0$$

The conjugate momentum for the centre of mass coordinates is therefore

$$p_c = \frac{\partial K}{\partial \dot{r}_c} = M\dot{r}_c \tag{D.29}$$

for the rotation angles

$$p_q = \widetilde{\Theta}I_0\Theta\dot{q} \tag{D.30}$$

and for vibrations

$$p_{s_n} = m_n\dot{s}_n^0 \tag{D.31}$$

In terms of the conjugate momenta the kinetic energy is

$$K = \frac{1}{2M}\widetilde{p}_c p_c + \frac{1}{2}\widetilde{p}_q\left(\widetilde{\Theta}I_0\Theta\right)^{-1}p_q + \frac{1}{2}\sum_n \frac{1}{m_n}\widetilde{p_{s_n}}p_{s_n}$$

Going over to quantum dynamics one uses the correspondence principle, which states that if the conjugate momentum of the coordinates $x = \{x_1, x_2, x_3\}$ is $p = \{p_1, p_2, p_3\}$ then

$$p \Rightarrow \widehat{p} = -i\hbar\begin{vmatrix}\partial_{x_1}\\ \partial_{x_2}\\ \partial_{x_3}\end{vmatrix} \equiv -i\hbar\nabla_x$$

From this correspondence one obtains kinetic energy operator, however, one should use the Laplace-Beltrami transformation. It states that for a bilinear form

$$B = \widetilde{x}\boldsymbol{g}^{-1}x$$

where $\boldsymbol{g}$ is a matrix with the elements that are functions of x, the corresponding Laplace operator in the derivatives ∇_x takes the form

$$\widehat{B} = G^{-1/2}\widetilde{\nabla}_x\left(G^{1/2}\boldsymbol{g}^{-1}\right)\nabla_x$$

where G is determinant of $\boldsymbol{g}$. It follows that the parts of the kinetic energy operator that correspond to the centre of mass motion and vibrations have simple structure. For the rotations one makes useful observation that

$$\widetilde{\Theta}^{-1}\widehat{p}_q = \cos^{-1}\beta\,\widehat{p}_q\,\Theta^{-1}\cos\beta$$

and if one defines the operator $\widehat{\Lambda}$ as

$$\widehat{\Lambda} = \frac{i}{\hbar}\widetilde{\Theta}^{-1}\widehat{p}_q = \begin{vmatrix} \frac{\cos\gamma}{\cos\beta}\partial_\alpha + \sin\gamma\partial_\beta - \tan\beta\cos\gamma\partial_\gamma \\ -\frac{\sin\gamma}{\cos\beta}\partial_\alpha + \cos\gamma\partial_\beta + \tan\beta\sin\gamma\partial_\gamma \\ \partial_\gamma \end{vmatrix}$$

then kinetic energy operator is

$$\widehat{K} = -\frac{\hbar^2}{2M}\Delta_c - \frac{\hbar^2}{2}\widetilde{\widehat{\Lambda}}\,I_0^{-1}\,\widehat{\Lambda} - \frac{\hbar^2}{2}\sum_n \frac{1}{m_n}\Delta_{s_n}$$

The operator $\widehat{\Lambda}$ corresponds, up to a constant, to the angular momentum, and has a very useful property

$$\widehat{\Lambda}\times\widehat{\Lambda} = \widehat{\Lambda}$$

For the semirigid body one replaces the coordinate vectors s_n by (D.25), in which case the inverse of the momentum of inertia that enters the kinetic energy operator is approximately

$$I_0^{-1} \approx \iota_0^{-1} - \iota_0^{-1}\left[\sum_{n=1}^{N} m_n\left(\widetilde{E}_n D_n^0 + \widetilde{D}_n^0 E_n\right)\right]\iota_0^{-1}$$

where the appropriate symbols are defined in (D.26). Approximate operator $\widehat{K}$ is now

$$\widehat{K} = -\frac{\hbar^2}{2M}\Delta_c - \frac{\hbar^2}{2}\widetilde{\widehat{\Lambda}}\,\iota_0^{-1}\,\widehat{\Lambda} - \frac{\hbar^2}{2}\sum_n \frac{1}{m_n}\Delta_{\varepsilon_n} - \frac{\hbar^2}{2}\widetilde{\widehat{\Lambda}}\,\iota_0^{-1}\left[\sum_{n=1}^{N} m_n\left(\widetilde{E}_n D_n^0 + \widetilde{D}_n^0 E_n\right)\right]\iota_0^{-1}\,\widehat{\Lambda}$$

One important quantity to calculate is the probability current that one could associate with each constituent of the body. It is derived from the classical expression for velocity of the nth particle, which is given by

$$\dot{r}_n = \dot{r}_c + \dot{d}_n + \dot{\eta}_n = \dot{r}_c - X_n\Upsilon\dot{q} + (\dot{R\varepsilon}_n)$$

which is further transformed into

$$\dot{r}_n = \dot{r}_c - X_n \Upsilon \dot{q} - R E_n \varpi + R \dot{\varepsilon}_n$$

where the matrix E_n is of the same character as X_n but with the components of ε_n. Finally one uses relationship with $\dot{q}$ to obtain

$$\dot{r}_n = \dot{r}_c - R \left(X_n^0 + E_n \right) \Theta \dot{q} + R \dot{\varepsilon}_n$$

and in terms of conjugate momenta

$$\dot{r}_n = \frac{1}{M} p_c + \frac{1}{m_n} R p_{\varepsilon_n} - R \left(X_n^0 + E_n \right) I_0^{-1} \widetilde{\Theta}^{-1} p_q$$

By replacing conjugate momenta with the operators one gets operator for the velocity

$$\widehat{v}_n = -\frac{i\hbar}{M} \nabla_c - \frac{i\hbar}{m_n} R \nabla_{\varepsilon_n} + i\hbar R \left(X_n^0 + E_n \right) I_0^{-1} \widehat{\Lambda}$$

and the current is defined as

$$j_n = \hbar \, \mathrm{Im} \left\{ f^* \left[\frac{1}{M} \nabla_c + \frac{1}{m_n} R \nabla_{\varepsilon_n} - R \left(X_n^0 + E_n \right) I_0^{-1} \widehat{\Lambda} \right] \right\}$$

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