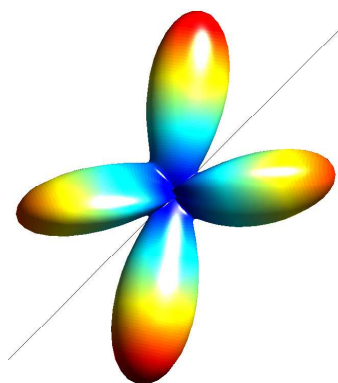


Contributions to the Theory of Atoms and Molecules in Strong Electromagnetic Fields



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*Når eg ser din himmel, eit verk av dine fingrar,
månen og stjernene som du har sett der,
kva er då eit menneske, sidan du kjem det i hug,
eit menneskebarn, sidan du tek deg av det?*

Salme 8,4-5.

*When I consider your heavens, the work of your fingers,
the moon and the stars, which you have set in place,
what is man that you are mindful of him,
the son of man that you care for him?*

Psalm 8,3-4.

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List of Papers

- Paper I** *Dynamics of $H(2p)$ ionization in ultrashort strong laser pulses.*
T. Birkeland, M. Førre, J. P. Hansen, and S. Selstø, Journal of Physics B **37**, 4205 (2004).
- Paper II** *Exact Nondipole Kramers-Henneberger Form of the Light-Atom Hamiltonian: An Application to Atomic Stabilization and Photoelectron Energy Spectra.*
M. Førre, S. Selstø, J. P. Hansen, and L. B. Madsen, Physical Review Letters **95**, 043601 (2005).
- Paper III** *Strong Orientation Effects in Ionization of H_2^+ by Short, Intense, High-Frequency Light Pulses.*
S. Selstø, M. Førre, J. P. Hansen, and L. B. Madsen, Physical Review Letters **95**, 093002 (2005).
- Paper IV** *Atoms and Molecules in Strong, High-frequency Fields.*
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- Paper V** *Geometrical dependence in photoionization of H_2^+ in high-intensity, high-frequency, ultrashort laser pulses.*
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- Paper VII** *Four-State (Two-Spin) Non-Stationary Models.*
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Paper VIII

Coherent Single-Electron Transport between Coupled Quantum Dots.

S. Selstø, and M. Førre, Submitted to Physical Review.

Paper IX

Electron angular distribution in resonance enhanced two-photon ionization of H_2^+ by ultrashort laser pulses

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Chapter 1

Introduction

In 1960 Theodore Harold Maiman reported the first working laser (1). Although interesting to scientist, few people could have predicted the usefulness of this new technology. In the early days it was said to be "a solution looking for a problem". At present, however, numerous such problems have been found. In our every day life lasers are encountered for instance when listening to CD-s and watching DVD-films, talking on the phone, on the dance floor, when going to the supermarket and during traffic controls. Maybe the most important applications are the ones that are *not* encountered every day, though. For example, laser technology is widely used within medicine and science.

The main application of lasers in medicine is various kinds of surgery. There are also applications to diagnostics (2). Within science, it proves very useful for measurements. For instance, very precise measurements of distances can be performed – on almost any scale. Lasers are used for spectroscopy, i.e. measuring the energies of microscopic systems, and with short pulses, one is able to monitor chemical reactions on the actual time scale of the reaction. Other interesting applications are laser cooling and optical tweezing. Finally, one hope for the future is that energy may be produced by fusion of small nuclei in combinations of very strong laser fields (3).

The acronym "laser" stands for "light amplification by stimulated emission of radiation". Contrary to "ordinary light", laser light is coherent and practically monochromatic, i.e. it contains only one wavelength. Typically it is very focused, so that the intensity of the radiation may be extremely high. Over the years different techniques have been used to make lasers. Maiman used a silver coated rod of ruby, which is an example of a solid state-state laser. Nowadays, semiconductor lasers are most common. The newest and maybe most impressive contribution to the family is the free electron laser, which uses a relativistic beam of electrons. With the improved technology, the intensity, the shortness of the pulses and the photon energy of lasers are also improved (5). Lasers with photon energies of about 100 eV and pulse duration as low as 250 as has been demonstrated (6), and intensities can reach beyond 10 TW/cm².

It is expected that, as the intensity and frequency of laser pulses become increasingly high, we will acquire new knowledge about the interaction between matter and light. Much theoretical effort has been made during the last decades in order to describe both atoms and molecules in strong attosecond laser fields.

For very high-frequency laser fields the oscillations of the field may be fast even on the atomic scale. This, in turn may cause electrons to experience some time-average effect of the field rather than the instantaneous one. This may be related to the phenomenon of atomic stabilisation (7).



Figure 1.1: This picture is from Starfire Optical Range on Kirtland Air Force Base, New Mexico, USA (4). The laser is used to eliminate atmospheric distortions in order to get as clear images as possible of objects in space.

Another issue raised by both the shortness of the wavelength of the field and its high intensity, is the importance of the magnetic interaction. In many cases, the spatial dependence of the laser field may be neglected so that it is adequately described by a homogeneous electric field. However, as intensities and frequencies increase, this approximation breaks down.

Both these issues are central parts of the present work. The thesis contains six chapters. Chapter 2 is a brief introduction to the Schrödinger equation, which is the starting point for most of the results presented. Chapter 3 describes the interaction between matter and light, and methods used to solve the time dependent Schrödinger equation are briefly outlined in chapter 4. The scientific papers, which are found in chapter 7, constitute the main part of the thesis. Each of these papers are introduced in chapter 5. Chapter 6 contains a summary of what has been done along with a few ideas about the direction of future work.

In most of the papers and in parts of the thesis atomic units are used. They are defined by choosing Planck's constant divided by 2π , $\hbar = 1.05 \cdot 10^{-34}$ Js, as the unit of angular momentum, the Bohr radius, $a_0 = 4\pi\epsilon_0\hbar^2/m_e e^2 = 5.29 \cdot 10^{-11}$ m, as the unit of length and the electron mass, $m_e = 9.1 \cdot 10^{-31}$ kg, as the unit of mass. Atomic units are practical since this choice simplifies the relevant equations considerably, and the magnitudes of the quantities become moderate on the atomic scale. However, they have the disadvantage that for most people they are not easily related to quantities encountered in every day life, as is the case for the SI-units.

Chapter 2

The Schrödinger Equation

At the end of the 19th century and in the beginning of the last one, various discoveries forced scientist to change their understanding of nature in a profound way. The consequences reached far beyond the realm of mere physics. For instance, the Michelson Morley experiment showed that the speed of light is the same regardless of the observer's velocity relative to the light source, which, in turn, lead Albert Einstein to put forward his famous theory of special relativity in 1905 (8; 9). With this theory, space and time could no longer be considered two separate, absolute concepts; measurements of lengths or time intervals are modified by the movement of the observer.

This was not the only revolutionary hypothesis put forward by Einstein this year. Among other things he was also able to explain the photo-electric effect (10), in which he claims that charges are liberated to carry current by absorbing light-quanta – one at a time – of a certain energy which is given by the wavelength of the light. However, the idea of light as consisting of small quanta does not originate from Einstein. It was first introduced by Max Planck in order to explain the spectrum of black body radiation (11). Planck intended this idea to be no more than a mathematical tool. He was even disappointed to learn that his "trick" turned out to change our understanding of light completely. The traditional understanding of light as waves was no longer sufficient; it had to be acknowledged that sometimes light behaves as particles. This new insight in the nature of light was soon to have consequences for our understanding of matter as well.

Bohr was among the very first to try and formulate the principles of quantum mechanics. His model of the hydrogen atom was able to explain the Rydberg formula for the spectral emission lines from hydrogen gas through the relation (12)

$$E_n = -\frac{me^4}{2(4\pi\epsilon_0)^2\hbar^2} \frac{1}{n^2}, \quad (2.1)$$

which was already known to agree very well with measured spectra. Here E_n is the energy of the atom in state number n , e is the elementary charge and ϵ_0 is the permittivity of free space. Although the Bohr model is considered obsolete nowadays, he should be accredited for having formulated the idea of a discretised energy spectrum of atoms.

In 1923 Luis de Broglie, inspired by Planck, Einstein and Bohr, among others, made the bold step of suggesting, in his Ph. D. thesis, that since light turns out to be particles as well as waves, also matter may behave as waves as well as particles. Few years later, his hypothesis was confirmed by experiments made by C. J. Davisson and L. H. Germer (13) and by G. P. Thomson (14).

All these observations paved the way for a completely new understanding of matter and its interactions. However, it was not at all trivial to formulate a theory that could embrace these new phenomena in a consistent manner. The process that finally led to the formulation of quantum mechanics is an excellent example of the fruitfulness of cooperation and exchange of ideas. Many letters were written and hours of discussions took place – not the least in Niels Bohr’s institute in Copenhagen.

Erwing Schrödinger was convinced that if particles are to be considered waves, they should be described by a wave equation. In 1926 he developed and presented these ideas in a famous series of six papers (15). His first published version of the equation for a particle in a static potential reads

$$\Delta\psi + \frac{8\pi^2m}{h^2}(E - V)\psi = 0 \quad (2.2)$$

Here $\Delta = \nabla^2$ is the Laplace operator, the eigenvalue E is the energy and V is the potential. He considered the particle to be represented by a standing wave. For the hydrogen atom the solution of this equation leads to the Bohr formula, Eq. (2.1), for the energies.

In fact, before this Schrödinger had already developed a relativistic version of the equation. This was not published, however, because the energies predicted did not coincide with the Sommerfeld correction to the Bohr formula (16). Schrödinger’s relativistic equation is actually the time independent version of the equation now known as the Klein-Gordon-Fock equation, which is valid for particles of spin zero.

In the following papers Schrödinger incorporated the description of an electric field in his wave equation, developed formalism for describing more complex systems, showed how perturbation theory could be applied to quantum mechanics, and finally formulated the dynamic generalisation of Eq. (2.2) (17). For a single particle the time-dependent Schrödinger equation may be written

$$\left\{ -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}, t) \right\} \Psi(\mathbf{r}, t) = i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r}, t). \quad (2.3)$$

Shortly before Schrödinger published his wave equation, Werner Heisenberg had formulated another theory of quantum mechanics called *matrix mechanics*. This was shown by Schrödinger to be equivalent to his wave mechanical formulation.

Schrödinger’s equation gained acceptance rather quickly. However, its *meaning* was to be subject to intense debate. Specifically, how was the wave function Ψ to be interpreted? Max Born suggested that the square of the absolute value of the wave function, $|\Psi|^2$ represents the probability density of finding the particle at position \mathbf{r} . These ideas were developed further by Bohr in cooperation with Heisenberg, among others.

2.1 The Hydrogen Atom

We will very briefly consider the solutions of the stationary Schrödinger equation for the hydrogen atom. For this system, Eq. (2.2) may be written

$$\left\{ -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} \right\} \psi(\mathbf{r}) = E\psi(\mathbf{r}). \quad (2.4)$$

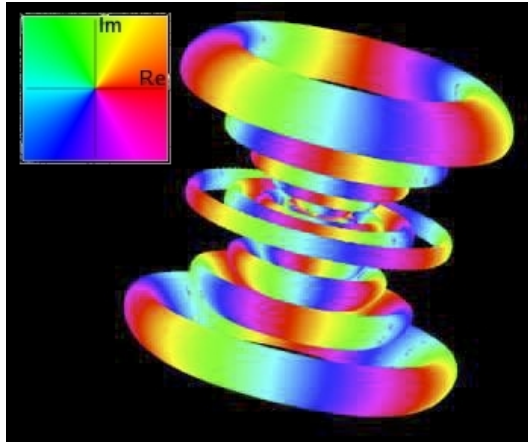


Figure 2.1: The wave function of a highly excited hydrogen bound state with quantum numbers $n=10$, $l=5$ and $m=3$. The picture is taken from Ref. (18). The picture shows an isosurface of the absolute value of the wave function. The colours encode the phase according to the colour circle convention in the upper left corner. The diameter of this structure is about $3 \cdot 10^{-8}$ m.

For a hydrogen atom the equation is analytically solvable. One discrete set of solutions for energies below zero, i.e. *bound states*, may be written as

$$\psi_{nlm} = R_{n,l}(r) Y_{l,m}(\theta, \varphi). \quad (2.5)$$

The radial part $R_{n,l}$ is proportional to $\rho^l e^{-\rho/2} L_{n+l}^{2l+1}(\rho)$ where $\rho = 2r/na_0$ and L^j are associated Laguerre polynomials, and the angular part $Y_{l,m}(\theta, \varphi)$ is proportional to $P_l^{|m|}(\cos \theta) e^{im\varphi}$ where P_l^m are associated Legendre functions.

The quantum numbers n , l and m are related to the energy (through Eq. (2.1)), the angular momentum of the system and the projection of the angular momentum on some pre-chosen axis, respectively. An example of such a wave function is illustrated in Fig. 2.1. Obtaining the energy spectrum of atomic hydrogen in such a consistent manner may be considered the first great triumph of Schrödinger's wave equation.

For unbound system the energy is no longer quantised, and the eigenfunctions, $\psi_{k,l,m} = R_{k,l}(r) Y_{l,m}(\theta, \phi)$, constitute a continuous basis in which the wave number $k = \sqrt{2mE}/\hbar$ may have any positive value.

The quantum numbers l , and m are subject to the constraints $l = 0, 1, \dots, n$ and $m = -l, -l+1, \dots, l$, respectively. Consequently, n^2 states corresponds to the same energy E_n . This high degree of *degeneracy* is a consequence of the special nature of the $\sim 1/r$ -potential. Since it is spherically symmetric, all three components of the angular momentum are conserved. Furthermore, another spatial vector, namely the Runge-Lenz vector, is also conserved. In group theoretical terms, this is a manifestation of the $SO(4)$ -symmetry (19).

For system with more than one electron, the degree of symmetry is strongly reduced due to the interaction between the electrons.

2.2 The Non-Local Nature of Quantum Mechanics

Einstein was very displeased about the direction quantum mechanics had taken. He felt that, although it may be *correct*, it could not possibly be a *complete* theory. He was particularly unhappy about the probabilistic, non-deterministic nature of the theory¹. In order to "prove" its inadequacy, he and two of his colleges formulated what they considered to be a paradox in which two particles, according to quantum mechanics, could have 100 % correlated, yet undecided, physical quantities at arbitrarily large separation (20). Thus, a measurement on one of the particles would completely determine the outcome of a measurement of the same quantity on the other particle instantly, which Einstein claimed to be in violation of the principle of relativity; no information can travel faster than the speed of light. They drew the conclusion that there had to be more to know about the system than what quantum mechanics was able to predict.

The correlation mentioned above arises from what is called *entanglement*; a system of, say, two particles is *not* described by the combination of the state of each one of them but rather by some global, common state. Schrödinger, who introduced the term "entanglement", said, referring to this phenomenon: "I would not call that *one* but rather *the* characteristic trait of quantum mechanics, the one that enforces its entire departure from classical lines of thought" (23).

In the early 1980s, one was able to investigate the issue of the EPR-paradox experimentally. Earlier, John Bell had shown that if we, inspired by Einstein, assumed that the correlation between seemingly entangled particle was due to some local *hidden variables*, measurements would be correlated in a different way than predicted by quantum mechanics. He suggested an experiment, which Alan Aspect and coworkers were able to perform. They found a very good agreement with the predictions of quantum mechanics (22).

Another manifestation of the non-local nature of dynamical, microscopic systems is interference. In classical mechanics, a system starts out in a well defined initial state and evolves uniquely into another. In quantum mechanics, however, the initial state is not precisely known – in the classical sense, and we may think of the system as following several separate evolutions simultaneously. When the amplitudes of these distinct "paths" interfere with each-other, the phases gives raise to an interference effect that does not have any classical analogue. The multiple path Landau-Zener model, which is described later in this thesis, may serve as an illustrative example of this phenomenon.

In addition to the heavy impact on physics and our understanding of nature, every day life has also felt the consequences of modern physics – for better and for worse. Inventions such as lasers (with all its applications), transistors and integrated circuits, nuclear magnetic resonance imaging (MRI), nuclear energy and weapons and GSM-navigation are all results of these theories. At present much effort is made in order to obtain control of quantum systems through manipulating them with electromagnetic fields. These efforts may enable us, among other things, to obtain optical control of chemical reactions, nano-fabrication and handling information on a quantum level. Our dream is that this may open new doors within medicine, information technology and energy production. This *may* make us better equipped to make conditions for life on earth more sustainable. In doing so, however, we should *not* wait until these new technologies are available.

¹The famous claim "God does not play dice" was put forward by Einstein in this context. Bohr's response is both simple and wise: "Who are you to tell God what to do?"

Chapter 3

The Interaction between Light and Matter

The electromagnetic field is governed by the well known Maxwell equations. In differential form they read

$$\nabla \cdot \mathbf{E} = \frac{1}{\epsilon_0} \rho \quad (3.1)$$

$$\nabla \cdot \mathbf{B} = 0 \quad (3.2)$$

$$\nabla \times \mathbf{E} = -\frac{\partial}{\partial t} \mathbf{B} \quad (3.3)$$

$$\nabla \times \mathbf{B} = \mu_0 \mathbf{J} + \mu_0 \epsilon_0 \frac{\partial}{\partial t} \mathbf{E}, \quad (3.4)$$

where \mathbf{E} and \mathbf{B} is the the electric and magnetic field, respectively, ρ is the charge density, and \mathbf{J} is the current density.

By expressing the fields by the vector potential, \mathbf{A} , and the scalar potential φ ,

$$\mathbf{E} = -\frac{\partial}{\partial t} \mathbf{A} - \nabla \varphi \quad (3.5)$$

$$\mathbf{B} = \nabla \times \mathbf{A}, \quad (3.6)$$

Eqs. (3.2) and (3.3) are automatically satisfied. The vector and scalar potentials are found by substituting Eqs. (3.5) and (3.6) into Eqs. (3.1) and (3.4). However, this does not determine the potentials completely; we may impose further restrictions which do not affect the physics. There are several possible ways of doing this, which are referred to as *gauges*. Here we will use the Coulomb gauge restriction, which demands that the divergence of the vector potential is zero:

$$\nabla \cdot \mathbf{A} = 0 \quad (3.7)$$

If we limit ourselves to free fields, i.e. with no charge nor current, the scalar potential is zero, and the vector potential (in the Coulomb gauge) is given by

$$c^2 \nabla^2 \mathbf{A} = \frac{\partial^2}{\partial t^2} \mathbf{A}, \quad (3.8)$$

which is the well known wave equation. Here $c = (\epsilon_0\mu_0)^{-1/2}$ is the speed of light. One is easily persuaded that any linear combination of functions of form $\mathbf{f}(\omega t - \mathbf{k} \cdot \mathbf{r})$ such that $\omega/|\mathbf{k}| = c$ is a solution of Eq. (3.8). Hence, the general solution may be written as

$$\mathbf{A}(\mathbf{r}, t) = \int d^3k \sum_{\lambda=1}^2 \{a(\mathbf{k}, \lambda) \exp[i(\omega t - \mathbf{k} \cdot \mathbf{r})] + a^*(\mathbf{k}, \lambda) \exp[-i(\omega t - \mathbf{k} \cdot \mathbf{r})]\} \boldsymbol{\varepsilon}_{\hat{\mathbf{k}}, \lambda}. \quad (3.9)$$

The polarisation vectors $\boldsymbol{\varepsilon}_{\hat{\mathbf{k}}, \lambda}$, $\lambda = 1, 2$, are orthogonal to each other and to the propagation direction $\hat{\mathbf{k}}$. The three components of \mathbf{k} may be discretised by imposing a cavity on the system.

In quantum mechanics, the electromagnetic field, as well as the system of matter particles, is described by a state vector in its own Hilbert space. Furthermore, the field, as any physical quantity, is represented by operators. In the case of the vector potential, which gives the physical quantities \mathbf{E} and \mathbf{B} , we let the expansion coefficients $a^{(*)}(\mathbf{k}, \lambda)$ become operators. The $a(\mathbf{k}, \lambda)$ -s are the annihilation operators, which reduce the number of field quanta in the mode given by the momentum \mathbf{k} and polarisation λ by one. Accordingly, $a^*(\mathbf{k}, \lambda) \rightarrow a^\dagger(\mathbf{k}, \lambda)$ is the creation operator, which increases the number of quanta, i.e. photons, in the mode by one.

However, for strong fields, the number of photons in a mode may be so high, in the order of 10^6 or more, that any basis representation of the photon states would be unfeasible. On the other hand, according to the correspondence principle of Bohr (24), for high quantum numbers, classical physics should be reproduced. Hence, we should be able to describe the field classically in the following, i.e. \mathbf{A} will be a scalar quantity, not an operator. A rigorous proof of the validity of this approximation for strong fields is found in Ref. (25).

Alternatively, this procedure may be justified by the ideas of Briggs and Rost (26). They have shown that for some small quantum system coupled to another much larger¹ system, the larger one may be described classically in the interaction. Furthermore, based on the same idea, they are able to deduce the time dependent Schrödinger equation from the time independent one with a statistical description of the interaction. This semi-classical approach has a long history within collision physics (27).

We will now turn to the issue of how the interaction between the (classical) electromagnetic field and matter is described.

3.1 Euler-Lagrange Formalism

The starting point is the classical Euler-Lagrange formalism (28). In this context, the classical Hamiltonian function for a particle with mass m is given by

$$H = \frac{1}{2m} \sum_{i=1}^3 p_i q_i + V, \quad (3.10)$$

where p_i are the components of the generalised momenta, q_i are the generalised coordinates and V is some external potential.

¹What is meant by "larger" is defined very precisely by an asymmetry condition on the energies of the systems.

The generalised momentum is defined by the Lagrangian function \mathcal{L} ,

$$p_i = \frac{\partial \mathcal{L}}{\partial \dot{q}_i}. \quad (3.11)$$

The Lagrangian is to be chosen such that it reproduces Newton's second law with the Lorentz force,

$$m\ddot{\mathbf{r}} = q(\mathbf{E} + \mathbf{v} \times \mathbf{B}), \quad (3.12)$$

through the Euler-Lagrange equation,

$$\frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{q}_i} - \frac{\partial \mathcal{L}}{\partial q_i} = 0. \quad (3.13)$$

This is achieved with

$$\mathcal{L} = \frac{1}{2}mv^2 - V + q\mathbf{v} \cdot \mathbf{A}. \quad (3.14)$$

Here q is the charge of the particle and \mathbf{v} is its velocity.

Inserting Eqs. (3.14) and Eq. (3.11) into Eq. (3.10), we arrive at the Hamiltonian

$$H = \frac{1}{2m}(\mathbf{p} - q\mathbf{A})^2 + V(\mathbf{r}) = H_0 + H_I \quad (3.15)$$

where $H_0 = 1/2m p^2 + V$ is the Hamiltonian of the unperturbed particle and the interaction is given by

$$H_I = -\frac{q}{m}\mathbf{A} \cdot \mathbf{p} + \frac{q^2}{2m}A^2. \quad (3.16)$$

3.2 The Dipole Approximation

For monochromatic light the wavelength may be much larger than the extension of the system at hand. For instance, red light has a wavelength of about 700 nm, whereas the typical size of a molecule in the ground state is about 1 nm. In such cases, when the extension of the atomic system is not greatly increased by the interaction, the spatial variation of the field may be neglected. This corresponds to a zeroth order expansion in the spatial variables of the field,

$$\exp[i(\omega t - \mathbf{k} \cdot \mathbf{r})] = \exp[i\omega t] + \mathcal{O}(\omega r/c).$$

When this approximation is applied to Eq.(3.15), it is referred to as the *dipole approximation*.

This approximation is widely used. However, as the wavelength grows shorter and the field grows stronger, non-dipole effects may come into play. Part of this work is devoted to the study of such effects.

It should be noted that large atomic system does not necessarily imply significant non-dipole effects since dynamics in many cases primarily takes place near the nucleus.

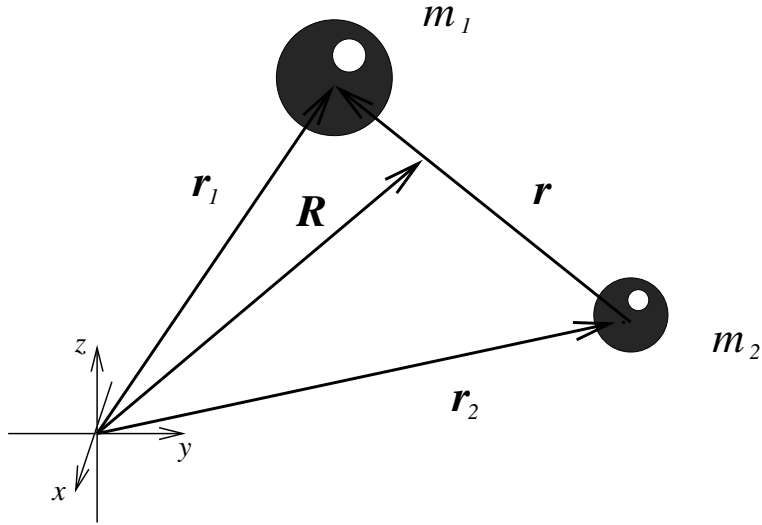


Figure 3.1: The coordinates of the two particles, \mathbf{r}_1 and \mathbf{r}_2 , along with the centre of mass and relative coordinates \mathbf{R} and \mathbf{r} .

3.2.1 Separability of the Schrödinger Equation

When solving the time dependent Schrödinger equation for, e.g., the hydrogen atom or a hydrogen like atom in an electromagnetic field, it is usually assumed that the proton may be considered fixed, and the only dynamics is that of the electron relative to the position of the nucleus. This seems reasonable considering the large ratio between the proton and the electron masses. However, for any system of two charged particles, the Schrödinger equation is easily reduced to an effective one particle equation when the dipole approximation applies.

For two particles in the field \mathbf{A} , Eq. (3.15) is straightforwardly generalised:

$$H = \frac{1}{2m_1}(\mathbf{p}_1 - q_1\mathbf{A}(\mathbf{r}_1, \mathbf{t}))^2 + \frac{1}{2m_2}(\mathbf{p}_2 - q_2\mathbf{A}(\mathbf{r}_2, t))^2 + \frac{q_1q_2}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad (3.17)$$

We define a new set of coordinates, namely the centre of mass (CoM) coordinates and the relative coordinates, by

$$\left. \begin{aligned} \mathbf{R} &= \frac{1}{M}(m_1\mathbf{r}_1 + m_2\mathbf{r}_2) \\ \mathbf{r} &= \mathbf{r}_1 - \mathbf{r}_2 \end{aligned} \right\} \Leftrightarrow \left\{ \begin{aligned} \mathbf{r}_1 &= \mathbf{R} + \frac{m_2}{M}\mathbf{r} \\ \mathbf{r}_2 &= \mathbf{R} - \frac{m_1}{M}\mathbf{r} \end{aligned} \right. \quad (3.18)$$

The coordinates are illustrated in Fig. 3.1.

The corresponding generalised momenta, \mathbf{P} and \mathbf{p} , respectively, are still given by Eq. (3.11). By expressing the Hamiltonian in these coordinates and neglecting the spatial dependence of the field, the Hamiltonian may be separated in three parts: H_R , corresponding to the \mathbf{R} -coordinate, H_r , corresponding to the \mathbf{r} -coordinate, and H_t , which is purely time dependent. Specifically we have:

$$\begin{aligned} H &= H_R + H_r + H_t \\ H_R &= \frac{P^2}{2M} - \frac{Q}{M}\mathbf{A}(t) \cdot \mathbf{P} \end{aligned} \quad (3.19)$$

$$\begin{aligned}
H_r &= \frac{p^2}{2\mu} - \frac{\tilde{q}}{\mu} \mathbf{A}(t) \cdot \mathbf{p} + V_C(r) \\
H_t &= (A(t))^2 \left(\frac{Q^2}{2M} + \frac{\tilde{q}^2}{2\mu} \right).
\end{aligned}$$

where the total mass M and the reduced mass μ are defined by

$$M \equiv m_1 + m_2, \quad (3.20)$$

$$\mu \equiv \frac{m_1 m_2}{m_1 + m_2}, \quad (3.21)$$

and the total charge Q and the reduced charge \tilde{q} are defined by

$$Q \equiv q_1 + q_2, \quad (3.22)$$

$$\tilde{q} \equiv \frac{1}{M}(q_1 m_2 - q_2 m_1) = \mu \left(\frac{q_1}{m_1} - \frac{q_2}{m_2} \right), \quad (3.23)$$

respectively. The last term in Eq. (3.19) may be removed by a trivial phase transformation of the wave function.

With the Hamiltonian reduced to separate terms depending only on \mathbf{R}, \mathbf{P} and \mathbf{r}, \mathbf{p} , respectively, the separation is trivial. As we will see later, separation is less trivial when the spatial dependence of the field is taken into consideration.

3.2.2 Alternative Formulations of the Hamiltonian

The form of the Hamiltonian Eq. (3.15) is commonly referred to as *velocity gauge*. This reflects the fact that the generalised momentum is shifted compared to the canonical momentum, $m\mathbf{v}$, by $q\mathbf{A}$ which corresponds to the momentum of a classical free particle in the presence of the electric field $\mathbf{E} = -\dot{\mathbf{A}}$.

Within the dipole approximation, there are various ways to formulate the the Hamiltonian of the interaction. In general, by imposing some norm conserving (unitary) transformation T on the state $|\Psi\rangle$,

$$|\Psi'\rangle \equiv T|\Psi\rangle,$$

the Hamiltonian may be brought from H to H' , which has generic form

$$H' = THT^\dagger + i\dot{T}T^\dagger. \quad (3.24)$$

In the following we will consider two other forms of the interaction, which constitute alternatives to the velocity gauge, namely the *length gauge* description and the *Kramers-Henneberger frame*.

The length gauge

If the unitary phase transformation

$$T_l = \exp(-iq\mathbf{r} \cdot \mathbf{A}(t)) \quad (3.25)$$

(in atomic units) is applied to Eqs. (3.15) and (3.24), the new Hamiltonian will be

$$H_l = \frac{1}{2m} p^2 + V(\mathbf{r}) - q\mathbf{r} \cdot \mathbf{E}. \quad (3.26)$$

In this case the interaction, $-q\mathbf{r} \cdot \mathbf{E}$, has a somewhat more intuitive form than in velocity gauge: It is the potential energy of a dipole of charges $\pm q$ at separation \mathbf{r} in the presence of the electric field \mathbf{E} . This is the origin of the term "dipole approximation".

In this formalism, the canonical and generalised momenta coincide, $\mathbf{p} = m\mathbf{v}$. It is also possible to arrive at Eq. (3.26) through the Lagrangian function by adjusting the vector and scalar potential in a way that does not change \mathbf{E} nor \mathbf{B} , i.e. by performing a gauge transformation – hence the name length *gauge*.

Kramers-Henneberger frame

The Kramers-Henneberger (KH) form of the Hamiltonian is obtained by the transformation (in atomic units)

$$T_{\text{KH}} = \exp(-i\boldsymbol{\alpha}(t) \cdot \mathbf{p}), \quad (3.27)$$

$$\boldsymbol{\alpha} \equiv \frac{q}{m} \int_{t_0}^t \mathbf{A}(t') dt', \quad (3.28)$$

which is a translation (24). The resulting Hamiltonian reads

$$H_{\text{KH}} = \frac{1}{2m} p^2 + V(\mathbf{r} - \boldsymbol{\alpha}) + \frac{q^2}{2m} A^2. \quad (3.29)$$

This description of the interaction was first derived by Pauli (29), and later by Kramers and Henneberger (30; 31), after whom it is named. In literature, one will also find that it is called *acceleration gauge*, which is somewhat misleading since it, contrary to the length gauge, cannot be achieved by a gauge transformation (32).

The interaction is induced by the time dependent translation $\boldsymbol{\alpha}$ of the position vector \mathbf{r} . This corresponds to a reference frame that follows the path of a classical free particle in the field. Rather than the direct influence from the field, the particle "experiences" a moving potential.

As we will see, it is possible to generalise this description in order to include non-dipole effects.

3.3 Non-Dipole Effects

Of course, no magnetic effects can be described with a vector potential independent of the spatial variables (see Eq. (3.6)). In the velocity gauge, Eq. (3.15), the spatial dependence of the field may be fully accounted for in a straightforward manner. But the description in the length gauge is not that straight forward without the dipole approximation (33). When it comes to the KH frame, the transition is somewhat more cumbersome than in the dipole case. However, we will demonstrate here that it may still be done.

3.3.1 The non-dipole form of the Kramers-Henneberger Hamiltonian

We will take the vector potential to be represented by a linearly polarised field of the form

$$\mathbf{A}(\eta) = A(\eta)\boldsymbol{\varepsilon} \quad (3.30)$$

where $\boldsymbol{\varepsilon} \equiv [\varepsilon_x, \varepsilon_y, \varepsilon_z]$ is a unit vector in the direction of the polarisation, and η is defined by

$$\eta \equiv \omega t - \mathbf{k} \cdot \mathbf{r}. \quad (3.31)$$

The Coulomb gauge restriction, Eq. (3.7), is here equivalent to

$$\mathbf{k} \cdot \mathbf{r} = k_x \varepsilon_x + k_y \varepsilon_y + k_z \varepsilon_z = 0. \quad (3.32)$$

The form of the transformation, Eq. (3.27), is maintained, but translation $\boldsymbol{\alpha}$ is slightly re-defined as compared to Eq. (3.28):

$$\boldsymbol{\alpha}(\eta) = \frac{q}{\omega m} \int_{\eta_0}^{\eta} \mathbf{A}(\eta') d\eta'. \quad (3.33)$$

In fact, it is not obvious that the transformation $T_{\text{KH}} = \exp(-\boldsymbol{\alpha}(\eta) \cdot \mathbf{p})$ actually is a translation since $\boldsymbol{\alpha}$ now depends on spatial variables in addition to time. However, within the Coulomb gauge restriction we find that indeed $T_{\text{KH}} V(\mathbf{r}) T_{\text{KH}}^\dagger = V(\mathbf{r} - \boldsymbol{\alpha})$. The transformation of the kinetic energy term, $T p^2 / 2m T^\dagger$, gives rise to three new terms.

All in all the final Hamiltonian in the generalised Kramers-Henneberger frame reads

$$\begin{aligned} H_{KH} = & \frac{1}{2m} p^2 + V(\mathbf{r} - \boldsymbol{\alpha}(\eta)) + \frac{1}{2m} (A(\eta))^2 - \\ & \frac{1}{2m} \left(k^2 (\boldsymbol{\alpha}'(\eta) \cdot \mathbf{p})^2 + ik^2 \boldsymbol{\alpha}''(\eta) \cdot \mathbf{p} + 2(\boldsymbol{\alpha}'(\eta) \cdot \mathbf{p})(\mathbf{k} \cdot \mathbf{p}) \right). \end{aligned} \quad (3.34)$$

In many cases the three last terms may be neglected. By comparing their magnitude to the kinetic energy terms of the same form, we find that a sufficient criterion for this is given by

$$\frac{|q| E_{\text{max}}}{\omega m c} \ll 1, \quad (3.35)$$

where E_{max} is the maximum amplitude of the electric field ($E_{\text{max}} = \omega A_{\text{max}}$). In App. A for all details are given.

The above formalism is easily generalised to a circularly polarised field and to any number of particles.

3.3.2 Separation of the two-particle Hamiltonian in the presence of a spatially dependent field

We have already seen that within the dipole approximation, the two-particle Schrödinger equation is easily reduced from a six dimensional to an effective three dimensional equation. With a spatially dependent field, which would necessarily depend on both the CoM coordinate \mathbf{R} and the relative coordinate \mathbf{r} , this is not possible in the general case (see Eqs. (3.17) and (3.18) or Ref. (34)). However, by expanding the vector potential to first order, we may find cases in which separation is permissible. For simplicity, we let the linearly polarised field of Eq. (3.30) propagate along the x axis. To first order in $\omega x/c$ and $\omega X/c$, the field at positions \mathbf{r}_1 and \mathbf{r}_2 are given by

$$\mathbf{A}(\mathbf{r}_1, t) \approx \mathbf{A}_0(t) + \frac{1}{c} \mathbf{E}_0(t) \left(X + \frac{m_2}{M} x \right) \quad (3.36)$$

and

$$\mathbf{A}(\mathbf{r}_2, t) \approx \mathbf{A}_0(t) + \frac{1}{c} \mathbf{E}_0(t) \left(X - \frac{m_1}{M} x \right), \quad (3.37)$$

respectively, where the time-only dependent fields A_0 and E_0 are the respective fields evaluated at the origin. Keeping only terms of first order, the velocity gauge Hamiltonian reads

$$H = H' + h' + \left(\frac{Q^2}{2M} + \frac{\tilde{q}^2}{2\mu} \right) A_0^2 - \frac{\tilde{q}}{M} \mathbf{P} \cdot \mathbf{E}_0 \frac{x}{c} - \frac{\tilde{q}}{\mu} \mathbf{P} \cdot \mathbf{E}_0 \frac{X}{c} \quad (3.38)$$

with

$$H' \equiv \frac{1}{2M} P^2 - \frac{Q}{M} \mathbf{P} \cdot \left(\mathbf{A}_0 + \mathbf{E}_0 \frac{X}{c} \right) + \left(\frac{Q^2}{M} + \frac{\tilde{q}^2}{\mu} \right) A_0 E_0 \frac{X}{c} \quad (3.39)$$

$$h' \equiv \frac{1}{2\mu} p^2 + V_C(r) - \frac{\tilde{q}}{\mu} \mathbf{P} \cdot \mathbf{A}_0 - \frac{q'}{\mu} \mathbf{P} \cdot \mathbf{E}_0 \frac{x}{c} + \left(\frac{Q\tilde{q}}{M} + \frac{\tilde{q}q'}{\mu} \right) A_0 E_0 \frac{x}{c}. \quad (3.40)$$

The total and reduced charges, Q and \tilde{q} , are already defined in Eqs. (3.22) and (3.23), respectively, whereas the effective charge q' is defined by

$$q' \equiv \frac{q_1 m_2^2 + q_2 m_1^2}{M^2}. \quad (3.41)$$

The two last terms of Eq. (3.38) prohibit separation. However, for a charged system ($Q \neq 0$) in a strong field they may be neglected upon comparison to other non-dipole terms that do not include any momentum operator. This is related to the fact that for strong enough fields, the p -distribution in the velocity gauge has a narrow peak centred at the origin (35). This argument also applies to the distribution of the relative momentum \mathbf{p} in the direction of the field. For neutral systems, the effect of the second last term in Eq. (3.38) may be estimated by assuming thermal motion of the CoM (34). This way its effect may be compared to, e.g., the last term of Eq. (3.40) and neglected when the latter is dominant. The resulting effective one particle Schrödinger equation takes the form

$$i \frac{\partial}{\partial t} \psi(\mathbf{r}, t) = \left\{ \frac{1}{2\mu} p^2 + \frac{q_1 q_2}{r} + \frac{\tilde{q}}{\mu} \mathbf{P} \cdot \mathbf{A} + \left(\frac{Q\tilde{q}}{M} + \frac{\tilde{q}q'}{\mu} \right) A E \frac{x}{c} \right\} \psi(\mathbf{r}, t). \quad (3.42)$$

Another interesting observation is that when the reduced charge \tilde{q} vanish, as is the case, e.g., for a system consisting of two identical particles, the Schrödinger equation separates exactly (to first order in $\omega x/c$). Recently Smirnova et al. demonstrated that, within the dipole approximation, a proton and a deuterium particle may be quasi bound by combined linearly and circularly polarised laser fields (3). This raises the question of whether inclusion of non-dipole effects makes binding of two protons feasible in a similar manner. With a linearly polarised field \mathbf{A}^{\parallel} polarised in the z -direction propagating in the x direction and a circularly polarised field \mathbf{A}° polarised in the xy plane propagating in the z direction, the Schrödinger equation of system may be written as

$$i \frac{\partial}{\partial t} \Psi(\mathbf{r}, t) = \left\{ \frac{1}{m_p} p^2 + \frac{1}{r} - \frac{1}{m_p c} \mathbf{P} \cdot \left(\mathbf{E}^{\circ} z + \mathbf{E}^{\parallel} x \right) \right\} \Psi(\mathbf{r}, t), \quad (3.43)$$

where m_p is the proton mass and $\mathbf{E}^{\parallel(\circ)} = -\dot{\mathbf{A}}^{\parallel(\circ)}$.

3.4 Classical Dynamics

When describing complex systems, Monte Carlo methods, i.e. methods making use of arbitrary numbers, may be quite useful. The description of the interaction between microscopic systems and light is no exception. Furthermore, in surprisingly many cases adapted classical methods may be applied successfully to study atomic and molecular processes. The classical trajectory Monte Carlo (CTMC) method is an example of such a method. In this scheme, the dynamics is given by classical equations, i.e. Newton's second law. A large number of initial positions and momenta are chosen at random from some initial distribution. Then the classical equations corresponding to each of these initial conditions are solved, and the results are obtained by investigating the whole set of such solutions. There are various ways of constructing initial distributions. One possible choice is the micro-canonical distribution in which the energy of each set of initial conditions is fixed. Specifically, the initial coordinates $\mathbf{r}_0, \mathbf{p}_0$, subject to the condition $1/2 p_0^2 + V(\mathbf{r}_0)$, are substituted by a new set of coordinates in which the distribution is uniform. This method was introduced by Abrines and Percival in 1966 (36).

Ideally, the distribution of initial conditions should reassemble the quantum mechanical probability distribution as closely as possible – both in position and momentum space. For the micro-canonical distribution, this is impossible, however, since there is an outer limit to the classical position of a bound electron in a potential, and there are no such limit on the quantum mechanical wave function.

For a particle subject to the static potential $V(\mathbf{r})$ and the external electric field $\mathbf{E}(\mathbf{r}, t)$ and magnetic field $\mathbf{B}(\mathbf{r}, t)$, Newton's second law may be written as a set of coupled ordinary differential equations:

$$\begin{aligned}\dot{\mathbf{r}} &= \mathbf{v} \\ \dot{\mathbf{v}} &= \frac{q}{m}(\mathbf{E} + \mathbf{v} \times \mathbf{B}) - \frac{1}{m}\nabla V.\end{aligned}\tag{3.44}$$

This classical problem is of course much less costly to solve than the quantum mechanical one – also for relatively large sets of initial conditions.

Again referring to the system of quasi bound proton and deuterium, Ref. (3), the above method has been used to investigate the effect of non-dipole terms in binding of bare nuclei (37). These calculations indicate that inclusion of spatial variables in the fields have detrimental effect on the binding of the system. However, we will demonstrate later that this detrimental effect is less pronounced in a fully quantum mechanical description.

Chapter 4

Solving the Schrödinger Equation

When solving the Schrödinger equation, analytical solutions are desirable. In addition to being elegant, such solutions represent a very compact way of obtaining results which makes it easier to investigate how the outcome depends on the parameters involved. However, in most cases we are forced to settle for some numerical solution. A wide range of schemes for solving the Schrödinger equation numerically is available. In this chapter we will consider two of them and give practical examples of their application. We will start by considering an analytical method, though.

Throughout this chapter atomic units are used unless stated otherwise.

4.1 The Landau-Zener Model

In 1932 no less than four different scientists were able to find analytical solutions to the Schrödinger equation of a quantum system consisting of two states, $|1\rangle$ and $|2\rangle$ with some constant coupling V and linear difference in diagonal energy, $\langle 2|H|2\rangle - \langle 1|H|1\rangle = bt$. These four people, who used quite different approaches, were Ettore Majorana (38), Ernst Carl Gerlach Stückelberg (39), Lev Davidovich Landau (40) and Clarence Melvin Zener (41). However, usually only the last two have their names attached to the model.

The model provides an analytical expression for the probability of transition between the two states. Although derived for a very particular – and very small – system, it is widely used today. Reason being that the model invites us to an intuitive understanding of the dynamics which may easily be generalised and applied to larger systems. The underlying idea is that transitions between states take place more or less instantly as the energies, or potential curves, of the two states cross. For a system consisting of several states, transitions between crossing states take place with probability given by the LZ model, whereas the populations of all other states are assumed to be unaltered. An example of such a system to which the LZ model has been applied successfully is shown in Fig. 4.1 (43). It should be noted that in general the phases of the amplitudes of the states involved in crossings are important, not just the populations.

The assumption that transitions take place at the instant of crossing may be motivated by turning to the basis consisting of instantaneous eigenstates of the time dependent Hamiltonian. We label these time dependent states $|\chi_j(t)\rangle$ and define them by

$$H(t)|\chi_j(t)\rangle = \epsilon_j(t)|\chi_j(t)\rangle, \quad (4.1)$$

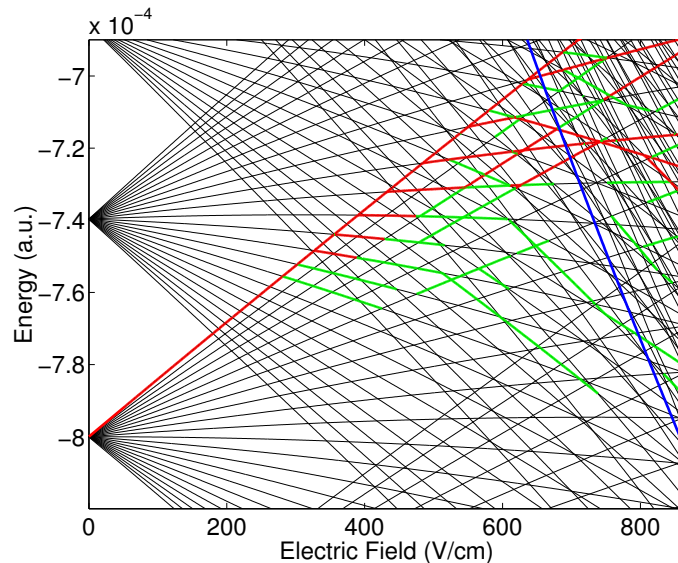


Figure 4.1: The energies of three sub-shell in a lithium atom in the presence of a dc field. The figure is taken from Ref. (43). The red curves correspond to states with population probability P larger than 1 %, whereas the the green curves correspond to $0.5 \% \leq P \leq 1 \%$. The classical ionisation limit is shown as a blue line.

where the ϵ_j -s are the eigenenergies of $H(t)$. In this basis, which is referred to as the *adiabatic* basis, the potential curves in general exhibit an avoided crossing rather than a crossing according to the von Neumann-Wigner non crossing rule, see, e.g., Ref. (28). If we write the state as a linear combination of the adiabatic states as

$$|\Psi\rangle = \sum_j a'_j \exp\left(-i \int_{t_i}^t \epsilon_j(t') dt'\right) |\chi_j\rangle, \quad (4.2)$$

the Schrödinger equation is equivalent to

$$\frac{\partial}{\partial t} a'_k = \sum_{j \neq k} \frac{\langle \chi_k | \frac{\partial H}{\partial t} | \chi_j \rangle}{\epsilon_k - \epsilon_j} e^{-i \int_{t_i}^t \epsilon_j(t') dt'} a'_j(t). \quad (4.3)$$

From this we see that couplings, and hence the possibility of transitions, between the adiabatic states vanish when the energy separation between two states become large. Furthermore, the above expression together with the non-crossing rule, proves the adiabatic theorem, which says that if the Hamiltonian varies slowly with time, $\partial H / \partial t \approx 0$, a system that starts out in the n 'th eigenstate will remain in the n th state (42).

In the following we will outline the relevant concepts of the LZ model a bit more precisely.

4.1.1 The two state case

We start out by a two state system, which in some basis has a linear energy difference and constant coupling. We will refer to this basis as the *diabatic* basis. We may write the Schrödinger equation

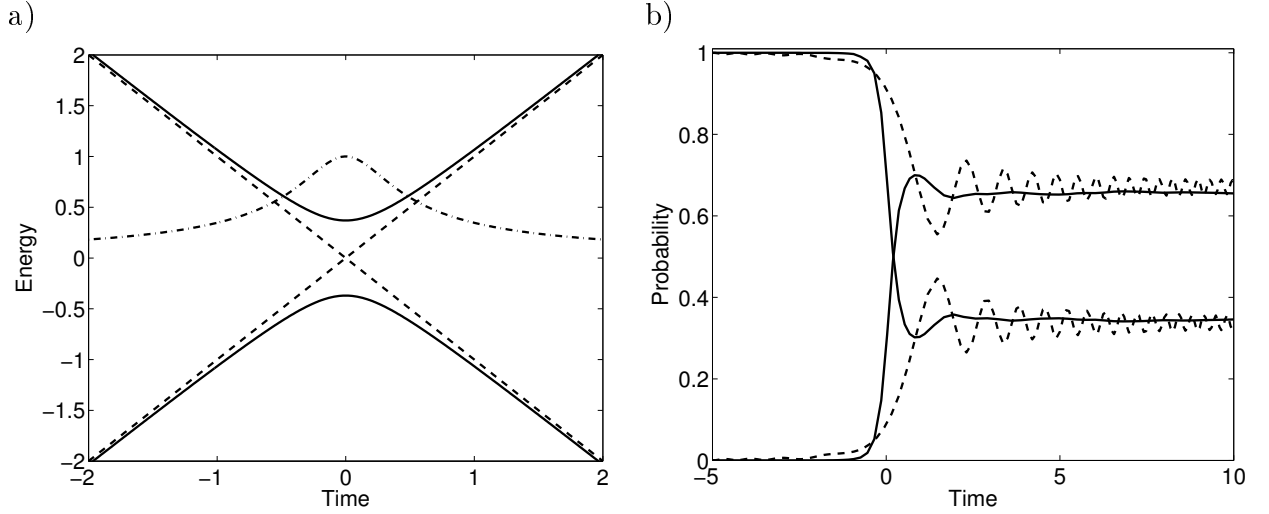


Figure 4.2: *a)* The diabatic (dashed curve) and adiabatic (full curve) diagonal energies. The absolute value of the Lorentzian shaped coupling is also included (dash-dotted curve). *b)* The populations of the two states as functions of time in the diabatic (dashed curve) and adiabatic basis (full curve). In this example we have $b = 2$ a.u. and $V = 0.37$ a.u..

as matrix equation, $i\dot{\mathbf{c}} = H_D \mathbf{c}$, with the Hamiltonian matrix

$$H_D = \begin{pmatrix} -\frac{1}{2}bt & V \\ V^* & \frac{1}{2}bt \end{pmatrix}, \quad (4.4)$$

The coupling V is assumed to be real in the following.

In the adiabatic basis, which is obtained by diagonalising the matrix (4.4), the Hamiltonian takes the form:

$$H_A = \begin{pmatrix} -\sqrt{(bt/2)^2 + V^2} & i\frac{bV}{b^2t^2 + 4V^2} \\ -i\frac{bV}{b^2t^2 + 4V^2} & \sqrt{(bt/2)^2 + V^2} \end{pmatrix}. \quad (4.5)$$

The diagonal energies within both bases are illustrated in Fig. 4.2 *a)*. The adiabatic diagonal energies and basis states coincide with the diabatic ones in the limit $t \rightarrow \pm\infty$. At the instant when the diabatic curves cross, the splitting of the adiabatic curves gives the magnitude of the coupling:

$$\Delta\epsilon(t=0) = 2|V|. \quad (4.6)$$

The adiabatic coupling has a well localised Lorentzian shape, whereas it remains constant in the diabatic basis. It is evident that transitions take place much faster in the adiabatic basis than in the diabatic one. This is illustrated in Fig. 4.2 *b)*.

In the adiabatic basis, the dynamics may be described through propagators in the form of 2×2 matrices:

$$\mathbf{c}(t_f) = J(t_f, 0)S J(0, t_i)\mathbf{c}(t_i), \quad (4.7)$$

where $\mathbf{c}(t) = (c_1, c_2)^T$ is defined by $|\Psi(t)\rangle = c_1|\chi_1\rangle + c_2|\chi_2\rangle$. The initial and final times, t_i and t_f , are to be chosen well separated from the crossing. Before and after the crossing, the only

time-evolution is the one corresponding to the adiabatic phase, given by the J -matrices:

$$J(t_2, t_1) \equiv \text{diag} \left\{ \int_{t_1}^{t_2} \epsilon_1(t') dt', \int_{t_1}^{t_2} \epsilon_2(t') dt' \right\}. \quad (4.8)$$

The transition matrix S reads

$$S^{(\pm)} = \begin{pmatrix} \sqrt{1-p} e^{i\alpha} & \pm \sqrt{p} \\ \mp \sqrt{p} & \sqrt{1-p} e^{-i\alpha} \end{pmatrix}, \quad (4.9)$$

where p is the probability of a non-adiabatic evolution (38; 39; 40; 41),

$$p \equiv \exp(-2\pi\delta), \quad \delta \equiv V^2/|b|, \quad (4.10)$$

and the Stokes phase,

$$\alpha \equiv \frac{\pi}{4} + \delta(\ln \delta - 1) - \arg[\Gamma(1 + i\delta)], \quad (4.11)$$

is the phase shift introduced by the crossing.

We emphasise that this description only applies to the adiabatic basis. In the diabatic basis, the phase shift that arises from the crossing is time-dependent.

The sign in Eq. (4.9) is crucial; care must be taken when choosing the right expression. It depends on both the signs of the parameters b and V and also the topology of the potential curves of the system.

4.1.2 The multi-state case

Within the framework of matrix propagators, the generalisation from two state to multi-state Landau-Zener (MLZ) theory is straightforward. Suppose a system of N states is subject to m crossings at times t_i , $i = 1, \dots, m$. Then

$$\begin{pmatrix} c_1(t_f) \\ c_2(t_f) \\ \vdots \\ c_N(t_f) \end{pmatrix} = J(t_f, t_m) S_m J(t_m, t_{m-1}) S_{m-1} \cdots J(t_3, t_2) S_2 J(t_2, t_1) S_1 J(t_1, t_i) \begin{pmatrix} c_1(t_i) \\ c_2(t_i) \\ \vdots \\ c_N(t_i) \end{pmatrix}. \quad (4.12)$$

The S -matrices are constructed by inserting the elements of the 2×2 matrix Eq. (4.9) in the entries corresponding to the adiabatic states involved in the avoided crossing, and the rest of it corresponds to the identity matrix. The J -matrices are constructed by a direct generalisation of Eq. (4.8).

In this propagation scheme, there are three kinds of phases involved, namely the adiabatic or dynamic phases given by the time integral of the adiabatic energies, the instantaneous phase shift α and signs arising from "book-keeping" arguments. In some particular cases, these phases are unimportant. (44; 45). However, unless the system has some special topology, they all play a crucial role.

In order to be able to apply Eq. 4.12, it is crucial that the transition dynamics at one crossing do not interfere with the dynamics corresponding to the next one. From Eq. (4.5) we may find a

criterion for this. We define the interaction time τ as the width of the Lorentzian coupling at 10 % of its maximum value, $1/(b^2\tau^2 + 4V^2) = \frac{1}{10} \cdot 1/(4V^2)$, which gives

$$\tau = 6 \left| \frac{V}{b} \right|. \quad (4.13)$$

By demanding that two consecutive couplings do not overlap considerably we arrive at

$$t_{n+1} - t_n > \frac{1}{2}(\tau_{n+1} + \tau_n) \quad \forall n. \quad (4.14)$$

Although this is only a necessary condition, not a sufficient one, we expect that it should serve at least as an estimate of the applicability of the MLZ model.

Second order transitions

Obviously, if the coupling V in Eq. (4.4) vanishes, no transition takes place. Analogously, one may expect that no transitions will take place between two uncoupled crossing diabatic states in some system consisting of more than two states. However, this is not necessarily the case. The Hamiltonian matrix of such a diabatic system may still feature avoided crossings between the eigenenergies. The splitting will in general be of order $\sim V^2$ as opposed to $\sim V$, cf. Eq. (4.6). From this a "pseudo-coupling" may be found and inserted into Eq. (4.10) in order to find the probability of such a second order transition. Although the transition probabilities between uncoupled diabatic states tend to be rather low, they may play a surprisingly crucial role. This is rather puzzling seen from the semi classical point of view in which propagation takes place only forward in time following diabatic energy curves between crossings with possible hopping between diabatic states at the crossings due to the coupling.

4.2 Basis Expansion

One very common way of solving the Schrödinger equation numerically, is to expand the wave function in some basis, $|\Psi\rangle = \sum_{i=1}^N c_i |\phi_i\rangle$, where the finite set of basis states $\{|\phi_i\rangle\}$ to as large an extent as possible spans the relevant space. When doing so, the Schrödinger equation takes the form of a coupled set of ordinary differential equations, which can be expressed as a matrix equation. If the basis is orthonormal and the basis states are independent of time, the equation reads

$$i \frac{\partial}{\partial t} \mathbf{c} = \tilde{H}(t) \mathbf{c}, \quad (4.15)$$

with $\mathbf{c} = (c_1, \dots, c_N)^T$ and \tilde{H} is a matrix with its elements given by $\langle \phi_i | H(t) | \phi_j \rangle$. This system of coupled first order differential equations may be solved by, e.g., the Runge-Kutta method (46). Of course, obtaining the couplings $\langle \phi_i | H | \phi_j \rangle$ may be far from trivial.

In principle, for sufficiently large N , any set of basis states will do. However, we want to keep N as low as possible. Furthermore, maximum sparsity of the Hamiltonian matrix is desired in order to make the numerical solution as fast and stable as possible. Quite frequently a basis that solves some corresponding time independent Schrödinger equation is applied. Specifically, if the Hamiltonian can be written as $H = H_0 + H'(t)$ where H_0 does not depend on time, the eigenstates of H_0 may be a good choice of basis.

4.2.1 B-spline basis sets

The method of basis expansion may be used in order to solve the time independent Schrödinger equation, $H_0|\phi_i\rangle = \varepsilon_i|\phi_i\rangle$, as well as the time dependent one. In that respect, b-splines is a popular choice of basis (47). These basis functions are piecewise polynomials which are non-zero only on some limited interval. They are defined on the interval $[0, r_{\max}]$ by a knot sequence $\{t_i\}$ consisting of N points on the interval. The i 'th b-spline of order k is given by the recursion formula

$$\begin{aligned} B_i^1(r) &= \begin{cases} 1, & t_i < r < t_{i+1} \\ 0, & \text{otherwise} \end{cases} \\ B_i^k(r) &= \frac{r - t_i}{t_{i+k-1} - t_i} B_i^{k-1}(r) + \frac{t_{i+k} - r}{t_{i+k} - t_{i+1}} B_{i+1}^{k-1}(r). \end{aligned} \quad (4.16)$$

Since these functions are non-zero only on a limited interval, the Hamiltonian matrix \tilde{H}_0 becomes band-diagonal. The degree of differentiability of the basis functions is given by the order k , as well as the width of the diagonal band of the Hamiltonian matrix.

The basis is very flexible in the sense that different parts of space may be given particular significance by an appropriate choice of knot sequence. In this way, by expanding the position wave function on a basis consisting of spherical harmonics for the angular part and b-splines for the radial part,

$$\begin{aligned} \psi_n(r, \theta, \phi) &= \sum_{l,m} \frac{f_{l,m}^n(r)}{r} Y_{l,m}(\Omega) \\ f_{l,m}^n(r) &= \sum_i c_{i,lm}^n B_i^k(r), \end{aligned} \quad (4.17)$$

the eigenfunctions of both atoms and molecules may be found to a very high degree of precision (48; 49; 50).

Angular spectra for the photo electron of H_2^+

The procedure described above has been applied to find the angular distribution of the photo electron of the hydrogen molecular ion ionised by a linearly laser field oriented along the internuclear axis. The internuclear separation is assumed to be fixed at $R = 2$ a.u.. The eigenstates are found using a set of b-splines of order $k = 8$ with 220 knot-points distributed linearly from 0 to $r_{\max} = 60$ a.u.. The continuum states, representing outgoing waves, are subject to the boundary condition that the angular momentum quantum number l become well defined for the continuum states in the limit $r \rightarrow \infty$. This is imposed through Lippmann-Schwinger formalism (48).

Having obtained the adequate eigenfunctions, couplings may be calculated and the time dependent Schrödinger equation is solved.

The angular distribution of the electron of H_2^+ after being ionised by a laser pulse may be written as

$$\frac{dP_I}{d\Omega} = \int d\varepsilon \left| \sum_l i^{-l} e^{-i\sigma_l} Y_{lm}(\Omega) \langle \psi_{\varepsilon lm} | \Psi_f \rangle \right|^2. \quad (4.18)$$

Here $\varepsilon = k_e^2/2$ is the electron energy, $\sigma_l \equiv \arg \Gamma(l + 1 + i2/k_e)$ is the Coulomb phase shift, and $\psi_{\varepsilon lm}$ is the continuum state corresponding to an outgoing wave with energy ε , azimuthal quantum

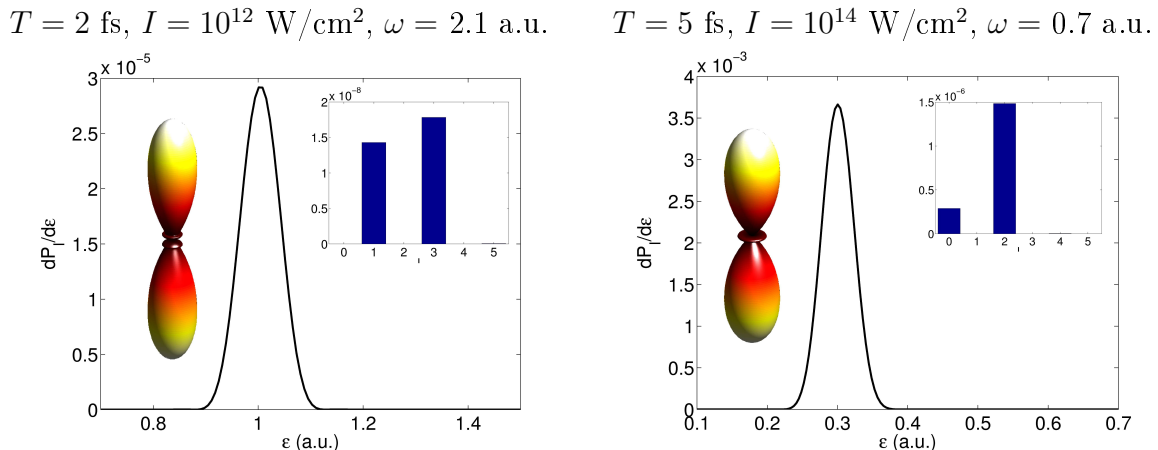


Figure 4.3: The energy distribution of the photo electron from a H_2^+ molecule exposed to a laser pulse in the fixed nuclei approximation. The left panel is for a one photon transition, whereas the right panel corresponds to a two photon transition. Also inserted in the figure are the distribution between the final channels and the angular distribution.

number m , which is conserved in this particular process, and asymptotic angular momentum quantum number l . The final amplitudes $\langle \psi_{\epsilon lm} | \Psi_f \rangle$ correspond directly to the amplitudes in Eq. (4.15).

The angular distribution, along with the energy and channel distribution, for processes in which the electron in the ground state Σ_g is ionised by absorption of one photon and by two photons is shown in Fig. 4.3. In representing the energy distribution of the photo electron, $dP_I/d\epsilon$, the amplitudes must be multiplied by the proportionality factor between the true continuum states and the box normalised continuum states, which is simply the square root of the density of states in the box. Also the distributions within the final l -channels are shown. We see that, in accordance with the dipole selection rules, only odd l -s are populated by one photon absorption and only even l -s are populated in the two photon process. The two-photon angular distribution is essentially a d -wave, whereas the outgoing wave is a mixture of p and f -waves in the one photon case.

4.3 The Split Operator Method

Formally, the solution of the Schrödinger equation may be written as

$$\Psi(t) = \hat{T} \exp \left(-i \int_{t_0}^t H(t') dt' \right) \Psi(t_0), \quad (4.19)$$

where \hat{T} indicates that the products in the expansion of the exponential operator should be time ordered (24). If we neglect time ordering and split the time interval into sub intervals of length Δt ,

$$\Psi(t + \Delta t) \approx \exp(-iH(t)\Delta t) \Psi(t), \quad (4.20)$$

the error made in each time step is of order Δt^2 and proportional to the time derivative of the Hamilton operator (51). In practical implementations the appearance of both kinetic energy T

and potential energy V in the exponent may be troublesome to handle. Therefore we would like to split the propagator into products corresponding to the distinct parts of the Hamiltonian. The error in doing so is minimised by "sandwiching" the propagator of the potential by half steps of the kinetic energy operator, i.e. by writing $\Psi(t + \Delta t) \approx e^{-iT\Delta t/2} e^{-iV\Delta t} e^{-iT\Delta t/2} \Psi(t)$, $H = T + V$. In doing this an error of order Δt^3 is introduced (52).

This method has been developed further in order to describe dynamical systems of cylindrical symmetry in spherical coordinates (53) and finally to describe any three dimensional system in spherical coordinates (54). The method is widely used in this work, so it merits being reviewed in detail.

The Schrödinger equation of one particle subject to some time dependent potential $W(\mathbf{r}, t)$ may be written in the following form:

$$i \frac{\partial}{\partial t} \Phi(\mathbf{r}, t) = \left\{ \frac{1}{2m} \frac{\partial^2}{\partial r^2} + \frac{L^2}{2mr^2} + V_S(r) + W(\mathbf{r}, t) \right\} \Phi(\mathbf{r}, t). \quad (4.21)$$

Φ is the reduced wave function, $r\Psi(\mathbf{r}, t)$, V_S is any spherically symmetric part of the potential and L is the angular momentum operator.

The reduced wave function is expanded in spherical harmonics,

$$\Phi(r, \Omega, t) = \sum_l^{l_{\max}} \sum_{m=-l}^l f_{lm}(r, t) Y_{lm}(\Omega). \quad (4.22)$$

In order to minimise errors, the propagator is constructed as

$$U(t + \Delta t, t) = e^{-iA\Delta t/2} e^{-iB\Delta t/2} e^{-iW(t)\Delta t} e^{-iB\Delta t/2} e^{-iA\Delta t/2}, \quad (4.23)$$

with

$$A = \frac{1}{2m} \frac{\partial^2}{\partial r^2}, \quad (4.24)$$

$$B = \frac{L^2}{2mr^2} + V_S(r). \quad (4.25)$$

Correspondingly, propagating the wave function from time t to $t + \Delta t$ is performed in five steps. The first one is multiplication with $e^{-iA\Delta t/2}$. This part only operates on the radial part of the wave function. By Fourier transforming the radial functions, the operator $\partial^2/\partial r^2$ amounts to simply multiplying by k^2 . Afterwards, the new radial functions are constructed by an inverse Fourier transform. Very fast numerical routines for doing so are available.

The second step is very simple since the spherical harmonics are eigenfunctions of L^2 . Specifically, $e^{-iB\Delta t/2} f_{lm} Y_{lm} = f_{lm} \exp[-i(l(l+1)/2mr^2 + V_S(r))] Y_{lm}$.

The most time consuming part of the propagation is the third one, $e^{-iW\Delta t}$. The entire wave function Φ must be constructed from Eq. (4.22) and then multiplied by the exponential operator. Afterwards, the new radial parts f_{lm} must be obtained, which is done by projecting of the new Φ on spherical harmonics,

$$f_{lm}(r) = \int \Phi(r, \Omega) Y_{lm}^*(\Omega) d\Omega \approx \sum_n w_n \Phi(r, \Omega_n) Y_{lm}^*(\Omega_n). \quad (4.26)$$

Angular grid points $\{\Omega_n\}$ and the corresponding weights $\{w_n\}$ of the quadrature are provided by Sloan and Wommersley (55). See Fig. 4.4.

The fourth and fifth step consist in repeating the second and third ones, respectively.

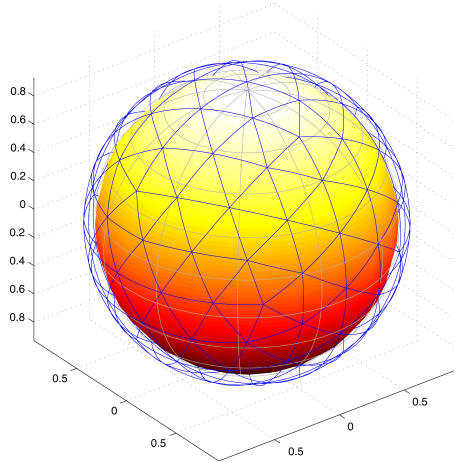


Figure 4.4: The angular grid points of a grid consisting of 122 points. As we see, the points are distributed rather uniformly on the sphere. The Image is provided by Prof. Ladislav Kocbach (56).

4.3.1 Propagation in imaginary time

For certain systems, such as the hydrogen atom, analytical expressions for the bound states are accessible. But in general these wave functions are not that easily constructed. In such cases, any propagation scheme may provide at least the ground state by a very simple modification, namely substituting time by *imaginary time*, $t \rightarrow \tau = -it$. The time propagator given by the time independent Hamiltonian H_0 is modified accordingly:

$$\Psi(t) = e^{-iH_0 t} \Psi_0 \rightarrow e^{-H_0 \tau} \Psi_0, \quad (4.27)$$

where Ψ_0 is some test function with a non-vanishing projection on the ground state. This state may always be written as a linear combination of eigenstates of H_0 , $\Psi_0 = \sum_n c_n \phi_n$ with $H_0 \phi_n = \varepsilon_n \phi_n$. Consequently, $\Psi(\tau) = \sum_n c_n e^{-i\varepsilon_n \tau} \phi_n$. The amplitude of all excited states die out exponentially faster than that of the ground state ϕ_0 . Therefore, after a short "time", the only surviving state is the ground state.

The energy of the ground state is easily found from the norms of the wave functions of two consecutive time steps. Assuming that it has already converged rather close to the ground state, we have $\Psi(\tau + \Delta\tau) = e^{-H_0 \Delta\tau} \Psi(\tau) \approx e^{-\varepsilon_0 \Delta\tau} \Psi(\tau)$. Thus

$$\varepsilon_0 = -\frac{1}{2\Delta\tau} \ln \left(\frac{\langle \Psi(\tau + \Delta\tau) | \Psi(\tau + \Delta\tau) \rangle}{\langle \Psi(\tau) | \Psi(\tau) \rangle} \right). \quad (4.28)$$

The convergence towards the ground state can be checked by monitoring this value. An example of such a convergence is illustrated in Fig. 4.7. When the ground state energy of the system is known in advance, it provides a test of the accuracy of the numerical parameters at hand.

In principle, this method may be used to find excited states as well. By removing any projection of lower lying states at each time step, the resulting wave function should be the desired excited state.

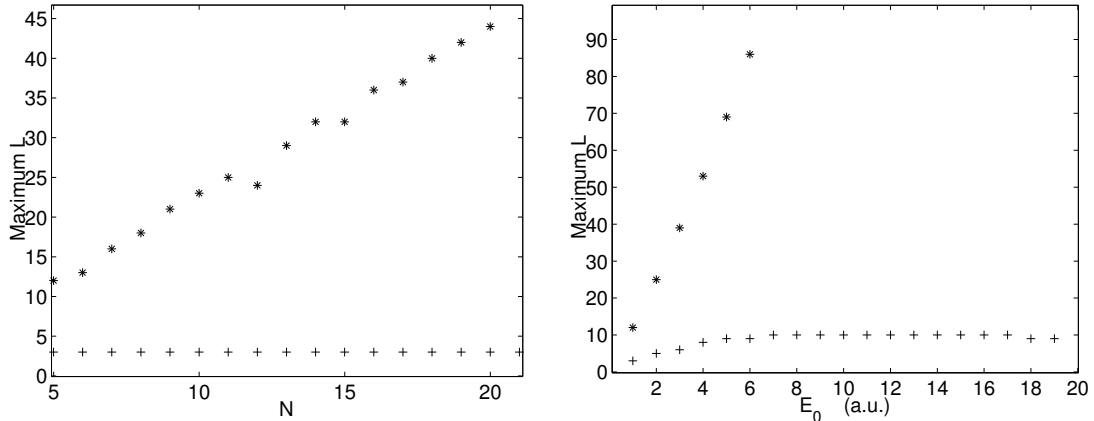


Figure 4.5: l_{\max} , the number of l -s needed to achieve convergent results, in the length gauge (*) and the Kramers-Henneberger frame (+) as a function of the number of optical cycles (left) and maximum field strength (right) for a hydrogen atom initially prepared in the $2p$ state exposed to a linearly polarised laser field. The figures are taken from paper I in this thesis.

4.3.2 Practical examples challenges

The split operator method is very useful and seemingly quite powerful. In principle, any three dimensional dynamic system of one effective particle may be described by this method; any interaction may be implemented in the $W(\mathbf{r}, t)$ -potential. However, an interaction given by a scalar operator is much more easily implemented than non scalar ones. Specifically, for interaction with electromagnetic fields, the length gauge, Eq. (3.26), and KH form of the interaction, Eq. (3.29), is preferable to the velocity gauge, Eq. (3.15), which involves the operator $\mathbf{A} \cdot \mathbf{p} = -i\mathbf{A} \cdot \nabla$.

In the following some of the possibilities and challenges of the method will be illuminated by briefly outlining some particular applications.

The hydrogen atom in laser fields

When describing a hydrogen atom in an electromagnetic field in the length gauge, the Coulomb potential may be included in the spherical part of the potential, V_S in Eqs. (4.21) and (4.25). In the KH frame the translated Coulomb potential, $1/|\mathbf{r} + \int_{t_0}^t \mathbf{A}(t') dt'|$, is included in the time dependent potential W . As it turns out, for strong fields much lower l_{\max} is needed in order to obtain convergence in the latter case than in the length gauge. In Fig. 4.5 we see that the numbers of l -s needed in the length gauge seems to increase linearly with both field strength and pulse duration, whereas it is more or less constant in the KH frame.

A problem that must always be tackled in atomic and molecular physics, is the singularity of the Coulomb potential, $V = 1/r$. Since the field is calculated directly in this method, some finite value must be assigned to $V(r = 0)$. One way of avoiding this problem, is to impose a softening, $V \rightarrow 1/\sqrt{r^2 + s^2}$. However, this may change the dynamics of the system rather dramatically (57). In this work, the problem has been minimised by arranging the geometry relative to the angular grid-points, such that the singularity is encountered as little as possible.

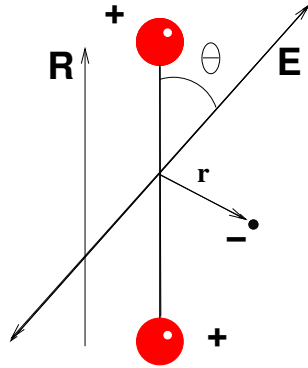


Figure 4.6: The geometry of the system of a H_2^+ molecule exposed to a linearly polarised laser field. The protons are separated by the distance R and the angle between the internuclear axis and the electric field of the laser define the orientation angle θ .

Dynamics involving the hydrogen molecular ion

In the fixed nuclei approximation, the Hamiltonian of an H_2^+ molecule exposed to a linearly polarised field is given in atomic units by

$$H_l = -\frac{1}{2}\nabla^2 - \frac{1}{|\mathbf{r} - \mathbf{R}/2|} - \frac{1}{|\mathbf{r} + \mathbf{R}/2|} + \mathbf{r} \cdot \mathbf{E}(t)$$

in the length gauge and by

$$H_{\text{KH}} = -\frac{1}{2}\nabla^2 - \frac{1}{|\mathbf{r} - \mathbf{R}/2 + \boldsymbol{\alpha}|} - \frac{1}{|\mathbf{r} + \mathbf{R}/2 + \boldsymbol{\alpha}|}$$

in the Kramers-Henneberger frame, cf. Eqs. (3.26), (3.28) and (3.29). See Fig. 4.6. Since the Coulomb potential is not isotropic, both the Coulomb potential and the interaction with the field is incorporated in the potential W in Eq. (4.21) in both gauges.

Although an analytical expression for the ground state of this system is known (58), it is more convenient to construct it by propagation in imaginary time. In Fig. 4.3.2 the energy calculated from Eq. (4.28) is shown as a function of the imaginary time τ . The convergence towards the ground state energy is seen to be very fast.

In order to find the final ionisation probability an absorber is imposed on the boundary of the grid. The remaining wave function is propagated until the the norm is converged, so that the ionisation probability is found as $P_I = 1 - \int_{\text{grid}} |\Psi|^2 dV$.

As mentioned, the projection of the explicit wave function $\Phi(r, \Omega)$ onto spherical harmonics is the most time consuming part of the propagation. Therefore the scheme may be "speeded up" considerably if we are able to calculate the matrix elements of type $\langle l'm' | W | lm \rangle$. Furthermore, since numerical integration over the angles is avoided, the precision of the method is improved, and truncation errors induced by the coupling to l -values higher than l_{max} may be removed.

Specifically, for the case of a H_2^+ molecule in an electromagnetic field of arbitrary orientation in the length gauge, this can be done analytically by expanding the Coulomb potential in spherical harmonics and performing subsequent Euler rotations of the interaction term in order to align

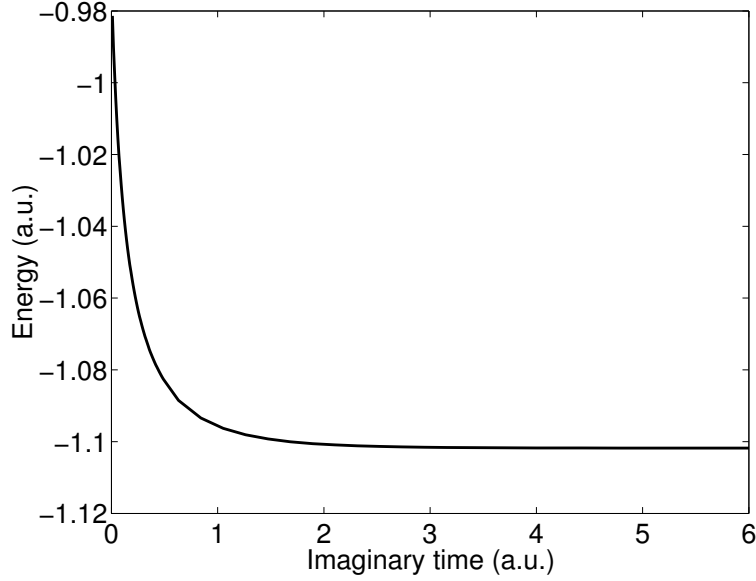


Figure 4.7: The convergence towards the ground state energy for a H_2^+ molecule at internuclear separation $R = 2$ a.u..

it with the quantisation axis (59). In this way, also the problem related to the singularities is avoided since the potential is always finite and still consistent with the l_{max} of Eq. (4.22).

Binding bear nuclei: Non-dipole effects

As mentioned previously, it has been demonstrated that, within the dipole approximation, deuterium and proton may be quasi bound by a combined circularly and linearly polarised laser field (3) and that classical calculations indicate that this binding does not sustain inclusion of non-dipole effects (60).

The Hamilton operator for the system, with the circularly polarised field \mathbf{A}° propagating in the z -direction and the linearly polarised field $\mathbf{A}^|$ polarised in the z -direction and propagating in the x -direction may be written in the Kramers-Henneberger form as

$$H = \frac{3}{2m_p} p^2 + \frac{1}{|r - \boldsymbol{\alpha}_0|} + \frac{1}{2m_p c} \mathbf{A}_0 \cdot \mathbf{E}_0^| x, \quad (4.29)$$

where m_p is the proton mass and $\boldsymbol{\alpha} = 1/2m_p \int_{t_i}^t \mathbf{A}_0(t') dt' \hat{\mathbf{z}}$. The index "0" indicates that the fields are evaluated at $\mathbf{r} = \mathbf{0}$. The details of the separation in relative and centre of mass coordinates are explained in App. B.

In this particular case, the linearly polarised field is much stronger and has a higher frequency than the circular one, so that only non-dipole terms arising from this field is included. This is done by expanding the field to first order in $\mathbf{k}^| \cdot \mathbf{r}$.

Using a Cartesian version of the split-operator scheme, it is found that inclusion of non-dipole effects does have a certain detrimental effect on the binding of the system, but not to such an extent that binding is not feasible. This is illustrated in Fig. 4.8.

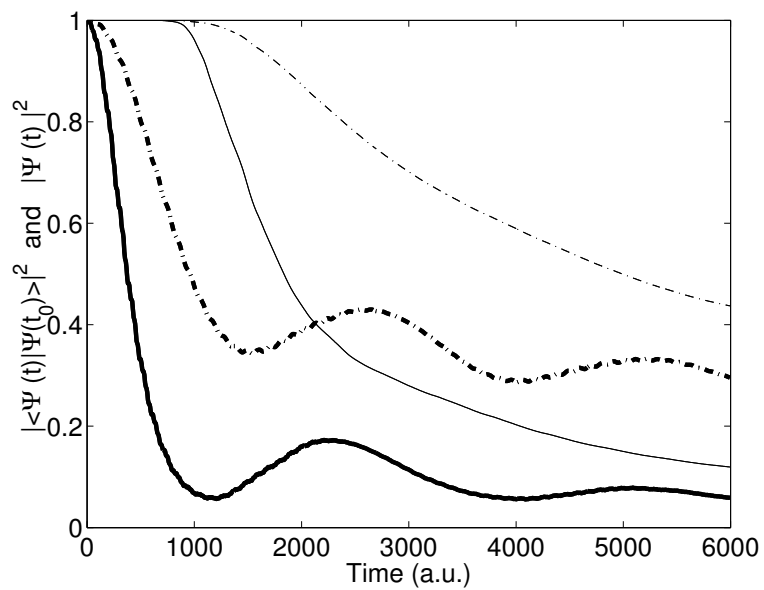


Figure 4.8: The norm of the wave function (thin lines) and the projection on the initial state (thick lines) as functions of time with the dipole approximation (dash-dotted curves) and without the dipole approximation (full curves). The field strengths are $E^\circ = 33$ a.u. for the circularly polarised field and $E^l = 260$ a.u. for the linearly polarised field, and the frequencies are $\omega^\circ = 0.060$ a.u. and $\omega^l = 0.11$ a.u., respectively. This image is based on a calculation by Ingrid Sundvor.

Chapter 5

Introduction to the Papers

The present scientific results are all products of teamwork. Many of the underlying ideas have emerged from discussions and interaction between various people so that they cannot be accredited one single person.

The content of the papers may seem somewhat diverse. However, they are all, in some way, related to the dynamic interaction between matter and light. In the following the content of each one of them will be briefly outlined, and my specific contributions in each case – in addition to taking part in writing the papers – in is indicated.

Paper I concerns geometrical dependencies in photo-ionisation of a hydrogen atom initially prepared in the $2p, m = 0$ state. It is found that for high photon energy, the ionisation probability features a very strong dependence of the angle between the quantisation axis and the polarisation of the laser field. This dependence is explained as a consequence of the multi photon channel closing due to an effectively lower binding energy for the perpendicular geometry than the for the parallel one. This hypothesis is confirmed by investigating the energy spectra of the photo-electron.

My specific contribution to this work is mainly modifying the computer codes used to describe this system.

Paper II addresses some of the same issues as the previous one. By investigating the energy spectra of photo-electrons from hydrogen atoms initially prepared in the ground state, it is found that multi-photon-ionisation is suppressed as the field strength increases. This explains the mechanism of atomic stabilisation. At sufficiently high intensity, the electron only "experiences" the time independent zeroth order Floquet component of the Coulomb potential in the Kramers-Henneberger frame. Furthermore, the non-dipole version of the Kramers-Henneberger frame Hamiltonian is presented. It is demonstrated that atomic stabilisation prevails inclusion of non-dipole effects, contrary to what others have claimed, and that the photoelectrons have low energy in this regime.

In this work I have worked out the non-dipole form of the Kramers-Henneberger Hamiltonian.

Paper III, as paper I, addresses the issue of orientational dependence in photo-ionisation.

This time the system is the hydrogen molecular ion, however. Also in this case, for high photon energy, very strong dependence on geometry is found. Specifically, at polarisation parallel to the internuclear axis, the ionisation probability exhibits oscillatory behaviour as a function of the internuclear distance. As the field strength increases, the ionisation probability ceases to increase, i.e. the system is stabilised. As the angle between the polarisation and internuclear axis is varied, the oscillations are reduced and vanish at perpendicular polarisation. This phenomenon is explained in terms of interference between outgoing waves originating from each of the scattering centres (protons). This idea is also able to explain the angular distribution of the photo-electron.

In this case, obtaining the numerical results and presenting them graphically has been done by myself.

Paper IV is a proceeding to the 2nd International Conference on Developments in Atomic, Molecular and Optical Physics with Applications in Delhi, India 2006. It may be considered a brief summary of the results of the three preceding articles. Furthermore, results concerning the nuclear motion in photo-ionisation of H_2^+ are presented. Three such methods are considered, namely the fixed nuclear approximation, classical description of the nuclear motion, and full quantum mechanical description.

Paper V is an elaboration and continuation of paper III. Specifically, the photo-electron spectra are investigated in more detail through a Fourier transform of the outgoing wave function after the interaction. The model of two interfering outgoing waves is developed further to include Coulomb scattering by the other scattering centre. This way, the angular distributions predicted by the model agree quantitatively with the ones obtained from the *ab initio* calculations. Finally, the importance of the initial distribution of the internuclear separations is considered.

As in the case of paper III, the *ab initio* calculations has been performed by myself, as well as presenting them. This includes the method of finding the photo-electron spectra through a Fourier transform.

In *paper VI* non-dipole effects in photo-ionisation of the hydrogen atom is investigated. The before mentioned non-dipole form of the Kramers-Henneberger frame is applied. Clear manifestations of the magnetic field are found by investigating the angular distribution of the photo-electron. The angular distribution has a third lobe in addition to the two which are present also in the dipole approximation. The non-dipole effects are reproduced by classical calculations.

In *Paper VII* we investigate the applicability of the Landau-Zener model to a four level system, which may, e.g., consist of two spin-1/2 particles exposed to a magnetic field. Special emphases is put on cases of exact solvability. Furthermore, the importance of interference effects and second order transitions is demonstrated.

Numerical solutions to the specific examples are provided by myself. However, my main contribution to this paper has been on the application of the Multi-state Landau-Zener model to systems of multiple paths and describing the consequent interference effect in addition to investigating the significance of second order crossings.

Paper VIII describes the transport of an electron between adjacent quantum dots using a linearly polarised oscillating field in the radio frequency regime. The process is understood within a simple four level model, which I have solved analytically. The framework of the Landau-Zener model is applied, although the parameters predicted by this model does not apply to this particular system.

Paper IX addresses some of the same issues as those of papers III and V, namely the angular distribution of the electron arising from photon ionisation of the hydrogen molecular ion. The method is quite different, however. In this case, the Schrödinger equation is solved as described in Sect. 4.2.1 using a basis set consisting of b-spines and spherical harmonics. The dynamics is contained within the Σ ($m = 0$)-symmetry, and the dynamics include description of nuclear vibration. It is demonstrated that the angular distribution of the photo electron ionised by two photons is strongly altered when the ionisation process involves resonant transitions between bound electronic states.

The distributions displayed in the article are calculated by myself from calculations involving nuclear vibration performed by Dr. Alicia Palacios. Furthermore, solving the Schrödinger equation in the fixed nuclei approximation, used for comparison with the proton kinetic energy integrated angular distributions, has been done by me.

Chapter 6

Summary and Outlook

The main focus in this work has been the dynamics of atoms and molecules in the presence of intense, short, high frequency laser fields. Within this scope special emphasis has been put on geometrical aspects. It has been found that the relative orientation of the linearly polarised field is quite significant – both for atoms and diatomic molecules. Furthermore, in the latter case, also the internuclear separation is crucial. For both hydrogen and the hydrogen molecular ion, the dependence is understood theoretically. For the molecule it has been shown that it may be understood as a consequence of interference and refraction of two outgoing partial waves.

Some more fundamental theoretical concepts has been investigated as well. First of all, we have considered the general applicability of the Landau-Zener model and found that its generalisation to systems of many states and crossings can be done. Careful treatment of phase-interference effects is necessary in the general case. It has also been found that transitions at second order avoided crossings may be significant, which is rather puzzling from a semi-classical point of view. The framework of the Landau-Zener model has also been applied to describe coherent electron transport between adjacent quantum dots.

Furthermore, effort has been made in order to describe non-dipole effects in the interaction with the electromagnetic field. We have found that for very strong fields in the high frequency regime, the magnetic field causes the angular distribution of the photo electron from an atom to feature a three lobe shape rather than a two lobe shape, as would be the situation in the dipole approximation. We have also demonstrated that the phenomena of atomic stabilisation sustains inclusion of non-dipole terms.

Another aspect of these non-dipole terms is their importance to the separability of the Schrödinger equation. In general, these terms prohibit separation. However, in some cases separation may be performed – either approximatively or exactly to first order in the spatial variables of the field. The question of separability will be investigated further by numerical calculations.

Since H_2^+ has been much investigated in this work, the two electron system H_2 represents a natural step forward. The *ab initio* description of this system is far more complex than the one with only one electron – not just because the dimensionality is increased from three to six, or seven if internuclear vibration is to be included, but also because electron correlation and entanglement are introduced.

On the other hand, the *reduction* of one electron from H_2^+ to H_2^{2+} is also an interesting challenge. We have found that two protons, for which the relative motion does not have any dipole interaction with any external field, first order spatial terms *does* induce an interaction. This raises

the question of whether this system may be bound by a combination of strong electromagnetic fields in a manner analogous to that for proton - deuterium.

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