Time-dependence of ionization and excitation by intense, short electric pulses

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To my family
Contents

1 Introduction 1

I Slowly-varying pulses: advanced adiabatic approach 5

2 The adiabatic approximation 7
   2.1 Introduction to the adiabatic approximation and historical survey 7
   2.2 Formulation of the problem in the adiabatic approximation 8
   2.3 Landau-Zener avoided crossings 9
   2.4 Analytic properties of the adiabatic potential curves and adiabatic wavefunctions 9
   2.5 Probability of nonadiabatic transitions between bound states and the adiabatic asymptote 12
   2.6 Hidden crossings 13
   2.7 Conclusions 14

3 Ionization and excitation of the hydrogen atom by an electric pulse 15
   3.1 Introduction 15
   3.2 Adiabatic basis of quasistationary states 15
   3.3 Numerical results in the case of a Gaussian-shaped electric pulse 18
   3.4 The advanced adiabatic approach 23
   3.5 Comparison of the advanced adiabatic approach and the DVR calculation for the Gaussian-shaped electric pulse 27
   3.6 The hydrogen atom in a rectangular electric field pulse 29
   3.7 Conclusions 30

II Ionization and recombination in intense, short pulses 33

4 Introduction 35

5 Basic analytic approximations 37

6 First-order perturbation theory 41
   6.1 Phase dependence 45

7 The strong-field short pulse case 49
   7.1 The modified FMA 51
Chapter 1

Introduction

The investigation of the interaction of lasers with matter has been studied for almost half a century. In the early days studies concentrated on the ionization with low-intensity continuous wave lasers. In this case the electromagnetic field of the laser has an enormous number of cycles, so that the photon picture is appropriate. If the energy of the photon is bigger than the ionization potential of the atom, one photon absorption suffices to ionize the atom, a process which can be described by the famous Fermi’s Golden Rule. Even when the energy of the photon is smaller than the ionization threshold the atom can be ionized by absorbing a minimal number of photons so that the electron can reach the continuum, that is, a multiphoton ionization occurs. However, if the laser intensity is increased, the atom can absorb more than the minimal number of photons, a process which is called above threshold ionization and first observed by Agostini et al. in 1979 [1]. Actually the ionization of atoms by high intensity lasers can occur at any frequency, provided the field is strong enough. Since the 70’s of the last century the intensity of lasers has been increased dramatically [2], to reach field strengths which are much larger than the strength of the Coulomb field which binds the electron in the hydrogen atom. In parallel with increasing intensity, the duration of typical laser pulses has been shortened to femtoseconds ($10^{-15}$ s), and very recently, fraction of a femtosecond pulses have been generated [3], approaching the attosecond regime. Depending on their frequency, these laser pulses can contain from hundreds down to one wave cycle. Since the technological advance in this field has been explosive, there is no doubt that stronger and shorter pulses will be produced in the near future. To date such pulses have been only used to measure the waveform of a relatively low-frequency laser pulse which generated them [4]. However with such laser pulses it is in principle possible to observe and control real-time electronic processes on the attosecond scale, an exciting possibility.

There has been an enormous amount of theoretical work on the ionization of atoms by strong lasers. Mostly this reduced to performing numerical calculations on the time-dependent Schrödinger equation, the first realistic calculation being reported in 1991 in reference [5]. In such calculations, one follows the time-development of the electron wavefunction during the pulse. However, a purely numerical calculation is limited by the computation time, and more importantly, does not provide an insight into the mechanism of strong-field ionization. Almost all analytic approaches treating the strong-field ionization of atoms have been based on the original work of Keldysh [7] as early as 1964, and subsequently of Faisal [8] and Reiss [9], known as the Keldysh-Faisal-Reiss approach. In this approach the atomic potential is taken into account as a perturbation with respect to the time-dependent electric field. In situations
where the field is strong and the evolution is adiabatic with respect to the dynamics of the electron in the initial state, the process of ionization is described by time-dependent tunnelling. However when only one or a few cycles of the strong field occur and its time-variation is not adiabatic, then the above analytic approach is invalid. In this thesis, to provide a detailed description of the ionization and excitation processes in strong fields, we will consider a unidirectional ‘half-cycle’ pulse at various time scales and peak electric fields. We will accomplish this by bringing ideas from the field of atomic collisions, exploiting the formal similarity of the charged particle collision process with the process of ionization and excitation by a half-cycle pulse. Even a half-cycle, on different time scales, can reveal very interesting physical mechanisms of ionization and excitation, as shown below. On the basis of such considerations for a half-cycle we develop an original analytic approach for excitation and ionization by a few-cycle pulse, in the limit of pulses of very short total duration. These analytic approximations are compared to "exact" results obtained by direct numerical solution of the time-dependent Schrödinger equation (TDSE).

The thesis is organized into three parts, presented in the chronological order in which the research unfolded. Each part contains a short introduction and conclusion, as well as explanation of the connection to the other parts. Here we will briefly go through the contents.

We start the thesis by analyzing the response of an atom to slowly-varying pulses in Part I. In the first chapter of this part we introduce the basic ideas and concepts of the adiabatic approximation resulting from the analyticity of the Hamiltonian with respect to the adiabatic parameter. In the second chapter of this part we concentrate on the process of ionization and excitation of the hydrogen atom by a slow-varying electric field pulse, where we compare the ab initio solutions of the TDSE with the advanced adiabatic approach, and formally derive an expression for the tunnelling probability.

In Part II we consider half-cycle as well as few-cycle pulses on the opposite time scale from the ones considered in Part I, that is in the limit of very short pulse duration. The basic approximations used in the short pulse limit are discussed in the second chapter of this part. In the third chapter of this part first-order time-dependent perturbation theory is used to investigate the weak-field limit of few-cycle pulse interaction with an atom, where we focus on the time-dependence of ionization and excitation and discuss the relative phase-envelope effects. In the fourth chapter of this part the strong-field limit of short few-cycle pulses is discussed. In particular a new process, the periodic occurrence of ionization and recombination in time, is uncovered. This coherent process we describe as "Rabi flopping involving the continuum". In the same chapter, an analytic method to obtain the probability of returning to the same state after Rabi flopping is formulated.

The analysis of the response of two different atomic systems - the hydrogen atom and a negative ion modelled by a zero range potential - to an electric field pulse with Gaussian time-dependence is presented in Part III. We cover a large interval of pulse durations - from the limit of very short pulses to the long-pulse (tunnelling) limit. In the first chapter of Part III we focus on the negative ion and demonstrate nonmonotonic behavior of the ionization probability with respect to the pulse width, which results in the appearance of a local maximum. The same effect appears in the case of the hydrogen atom, discussed in the second chapter of this part, where in addition we analyze the excitation probability and attribute the maximum as due to "resonance" between the interaction time of the pulse and the time corresponding to the inverse of the transition frequency.

In the final chapter of the thesis, Chapter 11, the most important results of this work are summarized and an outlook on further work is given.
In addition to the main body of the thesis, the details of the numerical approaches and derivations of analytic expressions are put into four different appendices. The details of the two numerical methods employed in the codes written to solve the TDSE are provided in appendices A (the numerical method based on the discrete variable representation) and D (integral-equation based numerical method). The mathematical details of the derivation of the transition probability in the advanced adiabatic approach and the asymptotic expressions in the short-pulse limit for the case of a 2s initial state are given in Appendix B and Appendix C respectively.

We use atomic units ($m_e = e = \hbar = 1$) throughout this work.
CHAPTER 1: Introduction
Part I

Slowly-varying pulses: advanced adiabatic approach
Chapter 2

The adiabatic approximation

2.1 Introduction to the adiabatic approximation and historical survey

The adiabatic approximation is a method developed in physics to treat systems in which the time-dependence of the Hamiltonian is slowly varying. In this way it is possible to approximately separate "fast" and "slow" motion of a dynamical system. The approximation consists in the assumption that the system can be well described by the eigenstates at fixed values of a set of variables which are slowly varying relative to the other set of variables. The former set of variables are called adiabatic parameters and the eigenstates are called adiabatic states. If the problem is such that one can find good adiabatic parameters, which change slowly in time, such that the system stays in one adiabatic state, then nothing happens. However, it is possible that in some region of the adiabatic parameter the adiabaticity breaks down and the system undergoes transition between the states, known as nonadiabatic transitions. The identification of the adiabatic parameters in a given problem gives us insight into the static properties of the system and, together with the nonadiabatic transitions, into its dynamical behavior.

Historically, the concept of adiabaticity (or adiabatic invariants) was introduced by Ehrenfest [10] to justify the Bohr-Sommerfeld quantization condition. The earliest and maybe the best-known adiabatic approximation in quantum mechanics is the Born-Oppenheimer approximation [11] for the approximate separation of the electronic, vibrational and rotational degrees of freedom in molecules on the grounds of the adiabaticity associated with the small value of the ratio between the nuclear and the electron velocities. The adiabatic theorem in quantum mechanics was formulated by Born and Fock [12] who proved that in the limit $v \to 0$ the population of eigenstates of the instantaneous Hamiltonian $\hat{H}(vt)$ (adiabatic states) does not change, i.e. the adiabatic states are the correct states of the zeroth order of the adiabatic approximation. Initially the two-level exactly soluble models of Landau, Zener and Stueckelberg [13, 14, 15] were considered. The most complete treatment was given by Stueckelberg in reference [15], where he obtained the adiabatic asymptote for the probability of inelastic transitions. His derivation is based on the analyticity of the Hamiltonian with respect to the adiabatic parameter $Q = vt$. Later studies of exactly-solvable models include the two-level model of Rosen, Zener and Demkov [16, 17], and of Nikitin [18] for transitions between bound electronic states, and the Demkov-Osherov model [19] for transitions from a bound state to a continuum (ionization).
The asymptotic theory of Stueckelberg [15] initially formulated for two-level systems and the Demkov-Osherov model [19] are the foundation of the advanced adiabatic approach (AAA) of Solov’ev [20, 21, 22]. As we will see below, in this approach, both transitions between the bound states and transitions to the continuum are included. Furthermore, it is an asymptotic theory which enables a treatment going beyond the restrictions valid for the exactly solvable models, the only requirement being \( v \to 0 \). Another important aspect of the adiabatic approach is the discovery of hidden crossings in reference [23]. The hidden crossings provide a complete description of non-adiabatic transitions and open the way to systematic applications mainly in the field of atomic collisions (for a review see references [21, 22]).

An adiabatic theory to describe electric field induced nonadiabatic transitions between rotational states of a water molecule through the hidden-crossings mechanism has been formulated in references [24, 25]. Most recently, the case of electric field pulse induced nonadiabatic transitions in hydrogen atom was studied in references [26, 27], where hidden crossings in the framework of advanced adiabatic approach were considered. The study of electric-field-induced nonadiabatic transitions in atomic systems will be presented in this part of the thesis.

### 2.2 Formulation of the problem in the adiabatic approximation

In the case of a system with a slowly varying (adiabatic) parameter \( Q = vt \), \( v \) is a small parameter and the time-dependent Schrödinger equation is

\[
\dot{H}(Q(t))\Psi(r, t) = i\frac{\partial \Psi(r, t)}{\partial t} \quad (2.1)
\]

where \( r \) is a set of electronic coordinates and \( \dot{H}(Q) \) is the Hamiltonian which depends on time through the adiabatic parameter. We note here that \( Q \) is a general adiabatic parameter which depends on the problem considered. We proceed by expanding the electronic wavefunction as follows

\[
\Psi(r, t) = \sum_p g_p(t) \varphi_p(r, Q) \exp \left( -i \int_{-\infty}^{t} E_p(Q(t'))dt' \right) \quad (2.2)
\]

in terms of the eigenfunctions and eigenvalues of the instantaneous Hamiltonian

\[
\dot{H}(Q)\varphi_p(r, Q) = E_p(Q)\varphi_p(r, Q). \quad (2.3)
\]

The eigenvalues \( E_p(Q) \) are called adiabatic potential curves. The adiabatic theorem of Born and Fock [12] states that the population of the adiabatic states does not change in the limit \( v \to 0 \), that is the adiabatic states are the correct states in the zeroth-order adiabatic approximation.

Inserting the expansion (2.2) into the Schrödinger equation (2.1) we obtain an equation describing the nonadiabatic transitions

\[
\frac{dg_p(t)}{dt} = -\sum_{p' \neq p} w_{pp'}(t) \exp \left( i \int_{-\infty}^{t} \Delta E_{pp'}(Q(t'))dt' \right) g_{pp'}(t), \quad (2.4)
\]
where $\Delta E_{pp'} = E_p - E_{p'}$ and $w_{pp'}$ is the matrix element of the nonadiabatic coupling,

$$w_{pp'} = \left\langle \varphi_p \left| \frac{d}{dt} \varphi_{p'} \right. \right\rangle. \quad (2.5)$$

If the system at $t \to -\infty$ was in the state $\varphi_p$ then the probability of nonadiabatic transition to the state $\varphi_{p'}$ is

$$P_{pp'} = \lim_{t \to -\infty} \left| g_{p'}(t) \right|^2. \quad (2.6)$$

### 2.3 Landau-Zener avoided crossings

To introduce avoided crossings between adiabatic potential curves we consider a two-level system with a Hamiltonian

$$H(Q) = \begin{pmatrix} V_1(Q) & V(Q) \\ V(Q) & V_2(Q) \end{pmatrix} \quad (2.7)$$

where $V(Q)$ is the coupling between the diabatic terms $V_1(Q)$ and $V_2(Q)$. The eigenenergies of this Hamiltonian matrix are the adiabatic potential curves $E_{1,2}(Q)$, given by

$$E_{1,2}(Q) = \frac{1}{2} \left[ V_1(Q) + V_2(Q) \pm \sqrt{(V_1(Q) - V_2(Q))^2 + 4V^2(Q)} \right] \quad (2.8)$$

and are plotted in figure 2.1. We can assume that the diabatic terms are such that they cross at $Q = Q_R$ as illustrated in figure 2.1. However, the coupling between them makes the adiabatic energy curves come together, but not to cross, which is in accordance with the von Neumann-Wigner theorem \[28\]. The region of the closest approach of adiabatic potential curves occurs at $Q_R$ (see figure 2.1), and such behavior of the adiabatic potential curves is called an avoided crossing. Actually it is the point at which the probability of transition between the two adiabatic states has a maximum.

In figure 2.1 the case when the diabatic potentials are such that

$$V_1(Q) - V_2(Q) = Wvt,$$

where $W$ is the slope difference of the diabatic terms, is illustrated. When the coupling is constant ($V(Q) = A$), then the probability of nonadiabatic transitions is given by the famous Landau-Zener formula \[13, 14\]

$$P_{LZ} = \exp \left[ -\frac{2\pi A^2}{v|W|} \right]. \quad (2.9)$$

In the next section we will consider the adiabatic potential curves as an analytic function of complex adiabatic parameter and discuss the possible implications.

### 2.4 Analytic properties of the adiabatic potential curves and adiabatic wavefunctions

It is advantageous to treat $Q$ as a complex variable. Namely if one moves away from the real axis of $Q$ one finds that the avoided crossing of two curves $E_1(Q)$ and $E_2(Q)$ reflects their
CHAPTER 2: The adiabatic approximation

2.4 Analytic properties of the adiabatic potential curves and adiabatic wavefunctions

Figure 2.1: Avoided crossings between two potential curves. The adiabatic potential curves are plotted with full lines and dashed lines are the diabatic terms.

exact crossing at the complex value $Q_c$ near the real axis of $Q$. The degeneracy of the energy levels at $Q = Q_c$ results in specific features. In the complex $Q$-plane the Hamiltonian $\hat{H}(Q)$ is no longer self-adjoint so that, when two eigenvalues merge $E_1(Q_c) = E_2(Q_c) \equiv E_c$, the Hamiltonian reduces not to a diagonal form but rather to the Jordan form

$$H(Q_c) = \begin{pmatrix} E_c & 1 \\ 0 & E_c \end{pmatrix}$$ \hspace{1cm} (2.10)

In the vicinity of $Q_c$ the values of $E_1(Q)$ and $E_2(Q)$ can be found using perturbation theory with respect to the small parameter $\Delta Q = Q - Q_c$. The most typical case is the case of a linear perturbation with respect to the adiabatic parameter $Q$

$$U(Q) = \Delta Q \begin{pmatrix} U_{11} & U_{12} \\ U_{21} & U_{22} \end{pmatrix},$$ \hspace{1cm} (2.11)

where $U_{ij}$ are constants. Diagonalizing the matrix $H(Q) + U(Q)$ in the first approximation for $\Delta Q \to 0$ yields

$$E_{1,2}(Q) = E_c \pm (U_{21} \Delta Q)^{1/2},$$ \hspace{1cm} (2.12)
i.e., instead of a linear dependence on the small parameter $\Delta Q$, we have a square-root dependence. The square-root branch point combines the two adiabatic potential curves into a single analytic function, so that when the point $Q_c$ is gone around, the sign in front of the radical in (2.12) is reversed; i.e. the first adiabatic potential curve transforms into the second one, and vice versa. The corresponding adiabatic wavefunctions $\varphi_{1,2}$ exhibit the same property. The adiabatic eigenfunctions $\varphi_{1,2}$ are orthonormal

$$\int \varphi_{p'}(r, Q)\varphi_{p}^*(r, Q')d^3r = \delta_{pp'}, \quad p, p' = 1, 2.$$  (2.13)

Note that the normalization condition is valid also for values in the complex $Q$-plane. Therefore the requirement that the eigenfunctions collapse into a single eigenfunction at the branch point could be viewed as paradoxical. This can be resolved by introducing wavefunctions $\chi_{1,2}(r, Q)$ such that they are bounded for all values of $Q$ and

$$\varphi_p(r, Q) = C_p(Q)\chi_p(r, Q)$$  (2.14)

In addition, the wavefunctions $\chi_{1,2}(r, Q)$ can be chosen so that at the branch point $Q_c$ we have

$$\chi_1(r, Q_c) = \chi_2(r, Q_c)$$  (2.15)

and

$$\int \chi_p(r, Q_c)\chi_{p'}^*(r, Q_{c}')d^3r = 0.$$  (2.16)

Clearly this is only possible in the case when the normalization factors $C_p(Q)$ become infinite at the branch point $Q_c$. This singularity multiplies the zero matrix element (2.14) and creates indeterminacy which can be resolved* so that the normalization conditions (2.13) are satisfied. The singularity of the normalization factors creates a singularity in all nonadiabatic matrix elements $w_{1,2}$ at the branch point $Q_c$ and this is mirrored on the real axis at $Q_R \approx \Re Q_c$ as a maximum in the nonadiabatic coupling between the states. In summary, the adiabatic potential curves are in fact single analytic function $E(Q)$ of the complex adiabatic parameter $Q$ with two sheets $E_1(Q)$ and $E_2(Q)$ whose common branch point is $Q_c$. The normalization factors $C_{1,2}(Q)$ are singular at the branch point which results in a peak of the nonadiabatic matrix elements $w_{1,2}$ in the region $Q_R \approx \Re Q_c$. The maximum in the nonadiabatic matrix elements means intensive transitions between the states $\varphi_1(r, Q)$ and $\varphi_2(r, Q)$.

The notion of analytic function of a complex variable can be easily extended to a situation when we have $N$ levels. If we approximate a given Hamiltonian, which is an analytic function of the adiabatic parameter $Q$, having $N$-bound states of the same symmetry then its eigenvalues are found from the equation

$$\det (H(Q) - EI) = 0,$$  (2.17)

where $I$ is the unit matrix. Since the determinant is an analytic function of $E$ and $Q$, the solution of the transcendental equation (2.17) is, according to the theory of the functions of complex variable one analytic function $E(Q)$ which has $N$ branches $E_p(Q)$ ($p = 1, 2, ..., N$) connected through branch points. In principle one can construct functions $Q_p(E)$ inverse to $E_p(Q)$, and an analytic function $Q(E)$ inverse to $E(Q)$. We will use the property of analyticity of adiabatic potential curves in this part of the thesis.

*More about the normalization factors can be found in reference [21].
2.5 Probability of nonadiabatic transitions between bound states and the adiabatic asymptote

The equation (2.4) which describes nonadiabatic transitions in principle can be solved when we know the matrix elements of nonadiabatic coupling. When the problem is such that there are only discrete levels and when their number and identity are conserved during the slowly-varying perturbation, the numerical solution of the equation (2.4) is exact. However an "exact" numerical solution is frequently not possible, and even when it is, it does not give us insight into the dynamics of the system. Therefore it is always desirable to find approximate solutions.

One can apply asymptotic methods by using the analyticity of the $\hat{H}(Q)$ and $E(Q)$ as follows (see [29]). Namely the adiabatic problem has a semiclassical character in the sense that the transition times are long and the change in action which is given by the integral $\int E(t)dt$ is also large. Hence we have a situation to deal with semiclassical solution with respect to time, and not with respect to the coordinate as usual. If we consider the case when a nonadiabatic transition has occurred from the adiabatic state $\varphi_p$ to the adiabatic state $\varphi_q$, then in the limit $t \to \infty$ the semiclassical wavefunction has the form $\Psi(t) = c\varphi_q \exp(-iE_q t)$

The procedure to find the transition probability from the term $E_p$ to the term $E_q$ reduces to finding the coefficient $c = g_q(t)$, in front of the $q$-th adiabatic state in $t \to \infty$ assuming that one starts from a wavefunction $\Psi = \varphi_p \exp(-iE_p t)$ in the limit $t \to -\infty$. To do that, one requires the analyticity of the adiabatic potential curves with respect to time. Since, as we have demonstrated in the previous section, the adiabatic potential curves are analytic with respect to the adiabatic parameter, this can only be satisfied when the time-dependence of the adiabatic parameter is analytic. Deriving an asymptotic expression for $g_q(t)$ in the limit $t \to \infty$ proceeds by considering a complex time. The only way we can go to the sheet $E_q$ starting from the sheet $E_p$ is to go around the branch point in the complex $t$-plane connecting the above sheets. The analogy of this procedure with the one of finding the semiclassical wavefunction of the reflected wave from a potential wall that has smaller height than the energy of the incident particle is considered in the book of Landau and Lifshitz [29]. The final result is that the probability amplitude of nonadiabatic transition from the term $E_p$ to the term $E_q$ in the limit of $v \to 0$ has the asymptotic form (accurate to within a preexponential factor),

$$g_q(t) \sim \exp \left( i \int_{-\infty}^{t} (E_q(Q(t')) - E_p(Q(t')))dt' \right). \tag{2.18}$$

However, although this asymptotic solution is correct, the situation is more complicated than the one presented in reference [29]. This asymptotic expression is valid everywhere, except for a small region in the vicinity of the branch point $Q_c$ (or $t_c$ in the complex $t$-plane). The standard way of solving such a problem would be to analyze the nature of the singularity $Q_c$ and to solve exactly the system of coupled differential equations (2.4) in this region. Then one matches this solution at the border region to the asymptotic one, a procedure analogous to matching the solutions of a semiclassical wavefunction left and right of the turning points with the exact solution obtained at the turning point.

Another and more effective method of calculation is Zwaan’s method using contour integration around the branch point and taking into account the Stoke’s phenomenon, possible
2.6 Hidden crossings

The application of the adiabatic approximation to a particular class of problem is usually restricted to obtaining the adiabatic potential curves and matrix elements of the nonadiabatic coupling for real values of the adiabatic parameter \( Q \). Then the coupled differential equations (2.4) are solved numerically. A method to obtain the nonadiabatic transitions analytically is usually limited to application of the Landau-Zener formula (2.9). However in many situations the diabatic potential curves simply cannot be constructed since the avoided crossings are either wide, or in some cases become indistinguishable in the overall pattern of adiabatic curves.

The asymptotic adiabatic theory reviewed in the previous section makes it possible to use the property of analyticity of the instantaneous Hamiltonian with respect to the adiabatic parameter. In fact use is made of the multi-valued analytic function \( E(Q) \) in the complex \( Q \)-plane and its branch points. The real part of the branch points gives the region of the adiabatic parameter where one has a possibility for nonadiabatic transitions and the corresponding probability is calculated according to equation (2.19). The branch points reveal both Landau-Zener avoided crossings (which are close to the real axis), but also crossings which cannot be accounted for in the traditional adiabatic approach, called hidden crossings [23]. The probability of nonadiabatic transitions in the case of hidden crossings is formally given by the expression (2.19).

Not only that, mathematically speaking, the complex branch points reveal couplings between the adiabatic terms which cannot be found on the real axis of the adiabatic parameter, they also reveal a physically different mechanism of nonadiabatic transitions. More precisely, the mechanism of nonadiabatic transitions arising from the hidden crossings is different from the Landau-Zener transitions. A semiclassical analysis reveals this difference [22, 23]. To

\[\text{CHAPTER 2: The adiabatic approximation}\]
illustrate this we use an example of a particle in a double-well potential and the distance between the minima of the well as adiabatic parameter. The Landau-Zener avoided crossings can be related semiclassically to the underbarrier interaction between two adiabatic states located in each potential well and with energy smaller than the potential barrier separating the wells. On the other hand, the hidden-crossings transitions occur when the energy of the particle touches the top of the barrier separating both wells [22].

2.7 Conclusions

In the traditional application of the adiabatic approximation one either restricts oneself to a two-state approximation and uses the Landau-Zener formula (2.9) to calculate the probability of nonadiabatic transitions between potential curves that exhibit avoided crossings, or one uses the coupled differential equations (2.4) for numerical calculation. In contrast, in the adiabatic approach using the adiabatic asymptote, one uses the analyticity of the Hamiltonian in the complex plane of the adiabatic parameter $Q$. The adiabatic potential curves are in fact one multivalued analytic function $E(Q)$ whose sheets correspond to different adiabatic states. The complex branch points (hidden crossings) connecting these sheets are related to the nonadiabatic transitions between the states and include all possible crossings between the curves whether they are visible or not on the real axis of the adiabatic parameter. Therefore in the adiabatic approach adopted in this thesis, instead of looking at the real axis of the adiabatic parameter searching for avoided crossings, one solves the stationary problem for the adiabatic parameter in the complex plane and then uses formula (2.19) to calculate the probability of nonadiabatic transition. In the next chapter, we will look at the process of excitation and ionization of the hydrogen atom by an electric pulse from the viewpoint of the adiabatic approximation.
Chapter 3

Ionization and excitation of the hydrogen atom by an electric pulse

3.1 Introduction

The dynamics of the interaction of a hydrogen atom with an electric pulse has been the subject of many theoretical investigations treating this process beyond the perturbative analysis. In the limit of strong fields this process becomes nonlinear and usually the only way to solve this problem is through numerical calculation. There has been an enormous number of numerical one-, two- and three-dimensional calculations for laser pulse ionization of an one-electron atom from its ground state, the first realistic three-dimensional calculation being given in the reference [6]. However there have been relatively few studies of unidirectional electric pulse ionization and excitation of hydrogen. Examples are a recent theoretical study of the ionization dynamics of hydrogen interacting with an ultra-short intense laser pulse [30] and studies of the short-time response of the hydrogen atom to a suddenly switched-on constant electric field [31, 32].

The problem of an atom in electric field is interesting also from the point of view of the adiabatic approximation. In the previous chapter we have introduced the adiabatic approximation for bound states. In the limit of a stationary electric field the adiabatic states are unbound and decay, and therefore the basis expansion over adiabatic states of the type (2.2) does not exist in this case. The development of an asymptotic adiabatic theory adapted to this case was begun in references [26, 27] and will be presented in this chapter.

3.2 Adiabatic basis of quasistationary states

The dynamics of a hydrogen atom in a time-dependent electric field is described by the time-dependent Schrödinger equation

\[
\left( -\frac{1}{2} \Delta - \frac{1}{r} + F(t)z \right) \Psi(r, t) = i \frac{\partial \Psi(r, t)}{\partial t}.
\]

(3.1)
3.2 Adiabatic basis of quasistationary states

When the electric field $F(t)$ is slowly-varying, one may use the adiabatic approach. In this case the adiabatic states are the eigenstates of the Stark problem

$$
\left( -\frac{1}{2}\Delta - \frac{1}{r} + Fz \right) \varphi_p(r, F) = E_p(F)\varphi_p(r, F),
$$

(3.2)

having only outgoing waves in the asymptotic region $z \to -\infty$. Here $E_p(F)$ are the adiabatic potential curves and $F$ is the adiabatic parameter. In the previous chapter we have used $Q = vt$, where $v$ is a small parameter, to denote the adiabatic parameter. Physically, the slowly-varying (adiabatic) parameter in this case is $F$ and its time-dependence is not restricted to the linear form. However, one can always find a parameter $Q = vt$ which is connected with $F$ through the actual time-dependence $F(t)$. We do this in order to use directly the adiabatic theory presented in the previous chapter. Therefore, in this chapter we will refer both to $Q$ and $F$ as adiabatic parameter interchangeably. The "mathematical" adiabatic parameter $Q$ will be defined in the next section where we restrict our analysis to a electric pulse with Gaussian time-dependence.

In the limit $F \to 0$, the adiabatic wavefunctions reduce to the atomic wavefunctions with parabolic quantum numbers $n_1$, $n_2$ and $m$. The description of the stationary Stark problem can be done using two alternative formalisms. The aim of the first method is to calculate the slowly-varying (adiabatic) parameter in this case is $Q = vt$, where $v$ is a small parameter, to denote the adiabatic parameter. Physically, the slowly-varying (adiabatic) parameter in this case is $F$ and its time-dependence is not restricted to the linear form. However, one can always find a parameter $Q = vt$ which is connected with $F$ through the actual time-dependence $F(t)$. We do this in order to use directly the adiabatic theory presented in the previous chapter. Therefore, in this chapter we will refer both to $Q$ and $F$ as adiabatic parameter interchangeably. The "mathematical" adiabatic parameter $Q$ will be defined in the next section where we restrict our analysis to a electric pulse with Gaussian time-dependence.

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The equation (3.2) can be separated in parabolic coordinates

$$
E_p(F) = W_p(F) - i\frac{\Gamma_p(F)}{2}, \quad W_p(F) = E_p^{(0)} + \Delta E_p(F).
$$

(3.3)

Here $E_p^{(0)}$ is the eigenenergy of the field-free atomic state, $\Delta E_p(F)$ is the DC Stark shift, $W_p(F)$ is the resonance position and $\Gamma_p(F)$ is the width of the state (resonance width).

The equation (3.2) can be separated in parabolic coordinates $\xi = r + z$, $\eta = r - z$ and $\phi$. In these coordinates $\varphi_p$ is represented as a product

$$
\varphi_p(r, F) = (\xi\eta)^{-1/2}X(\xi)Y(\eta)\exp(im\phi).
$$

(3.4)

The functions $X(\xi)$ and $Y(\eta)$ satisfy the differential equations

$$
\left( \frac{d^2}{d\xi^2} + \frac{E_p(F)}{2} - \frac{\beta_1}{\xi} - \frac{F}{4} + \frac{1}{4\xi^2} \right) X_p(\xi) = 0,
$$

(3.5)

$$
\left( \frac{d^2}{d\eta^2} + \frac{E_p(F)}{2} + \frac{\beta_2}{\eta} + \frac{F}{4} + \frac{1}{4\eta^2} \right) Y_p(\eta) = 0,
$$

(3.6)

where $\beta_1$ and $\beta_2$ are separation constants, and $\beta_1 + \beta_2 = 1$. The quasistationary states $\varphi_p$ are defined with the asymptotic behavior of the functions $X_p(\xi)$ and $Y_p(\eta)$ for $\xi, \eta \to \infty$:

$$
X_p(\xi) \sim \xi^{-1/4}\exp\left( -\frac{1}{3}F^{1/2}\xi^{3/2} + E_pF^{-1/2}\xi^{1/2} \right)
$$

(3.7)

$$
Y_p(\eta) \sim \eta^{-1/4}\exp\left( \frac{i}{3}F^{1/2}\eta^{3/2} + iE_pF^{-1/2}\eta^{1/2} \right).
$$

(3.8)
Restricting to the case $F > 0$, from the equations (3.7) - (3.8) one can see that the motion of the electron is bounded with respect to the coordinate $\xi$ and unbounded with respect to $\eta$.

In the adiabatic approximation using the adiabatic asymptote presented in the previous chapter, the curves for complex adiabatic parameter are used in order to find the complex branch points (hidden crossings) necessary to study the nonadiabatic transitions. The adiabatic potential curves $E_p(F)$ in the complex $F$-plane were calculated in reference [26], making use of the algorithm proposed in reference [34]. In figure 3.1 a fragment of the Riemann surface of an effective quantum number

$$n(F) = \frac{1}{\sqrt{-2E(F)}}$$  \hspace{1cm} (3.9)

is shown. One clearly sees the branch points $A$ and $B$ between the ground state and the states (in parabolic quantum numbers) $p = (0, n_2, 0)$, $n_2 = 1, 2$. By going in the complex $F$ plane along the red and blue paths indicated in figure 3.1 one goes from the ground state surface to the surfaces $(n_1, n_2, m) = (0, 1, 0)$ and $(n_1, n_2, m) = (0, 2, 0)$ respectively. Moreover, in reference [26], through a semiclassical analysis it is explicitly shown that $E_p(F)$ is an analytic function in the complex plane of $F$ which has different sheets corresponding to the same parabolic number $n_1$ and $m = 0$. 

In figure 3.2, the first three adiabatic potential curves (resonance positions $W_p$ and widths $\Gamma_p$) as a function of $F$ are displayed. When, under the influence of the stationary electric field, the resonance passes the top of the barrier, its width increases rapidly and it decays. Another point is that the positions of the real parts of the branch points, that is the region of $F$ in which the nonadiabatic transitions should take place, cannot be directly determined from the behavior of the adiabatic potential curves on the real axis, making the hidden crossings between the quasistationary Stark states completely different from the usual avoided crossings.

Figure 3.2: Resonance position $W$ and width $\Gamma$ for the ground and the two lowest excited states as functions of $F$. Continuous lines - $W_p$; dotted lines - $W_p \pm \Gamma_p/2$. The top of the 3D potential barrier is shown as a green continuous line. The positions of the real part of the branch points $F_A$ and $F_B$ (corresponding to the points A and B in figure 3.1) are indicated with arrows, and the transition between adiabatic potential curves is symbolically shown with dashed lines.

### 3.3 Numerical results in the case of a Gaussian-shaped electric pulse

In order to study the nonadiabatic transitions in the problem (3.1), we will consider excitation and ionization of a hydrogen atom from the ground state by an electric-field pulse characterized by a Gaussian time-dependence,

$$F(t) = F_0 e^{-\left(t/\tau\right)^2}.$$  \hspace{1cm} (3.10)
CHAPTER 3: Ionization and excitation of the hydrogen atom by an electric pulse

3.3 Numerical results in the case of a Gaussian-shaped electric pulse

The reasons for choosing the Gaussian time dependence are twofold. Firstly, the dependence of $F$ on time is analytic, which is required by the asymptotic adiabatic approach. The second reason is that the realistic half-cycle pulses used in experiments have approximately Gaussian time-dependence \[35\]. For the electric field time-dependence in question, we can define the "mathematical" adiabatic parameter as $Q = t/\tau$. This parameter is connected with the adiabatic parameter $F$ through the time-dependence \[(3.10)\], that is $F = F_0 \exp(-Q^2)$, which is an analytic function.

We proceed with the analysis by solving the problem \[(3.1)\] numerically. The numerical calculation is used as a benchmark with respect to the results obtained in the advanced adiabatic approach as will be illustrated in the next section. We have used the discrete variable representation (DVR) method in order to solve the problem \[(3.1)\] numerically. DVR is a discretized coordinate representation (the DVR basis functions are eigenfunctions of the coordinate operators) in which the potential energy matrix is diagonal and the kinetic energy matrix is calculated exactly and in multidimensional problems is sparse. We have used the cylindrical symmetry of the problem \[(3.1)\] to eliminate one dimension. Next, the two-dimensional space is separated in scaled parabolic coordinates. Each coordinate is represented by an one-dimensional DVR basis, and the total DVR basis is built as a direct product of one-dimensional bases. In the absence of an electric field, the diagonalization of the atomic Hamiltonian in the DVR basis gives a set of pseudo-states with negative and positive eigenenergies. The negative eigenenergies are in excellent agreement with the low-lying atomic bound-state levels for a large range of principal quantum numbers. The states with positive eigenenergies represent the continuum. Further details of the DVR basis representation used are given in Appendix A of this thesis.

The time evolution of the system was calculated using the explicit second-order propagation scheme

$$\Psi(r, t + \delta t) \approx \Psi(r, t - \delta t) - 2i\delta t \hat{H}(t)\Psi(r, t),$$ \[(3.11)\]

where both the wavefunction $\Psi$ and the Hamiltonian matrix $\hat{H}$ are represented by the DVR.

Transition probabilities were found by projecting the final wavepacket onto the atomic excited and continuum pseudo-states. The probabilities of population $P_n$ of the low-lying shells ($n=1-4$) were obtained by summing up moduli squared of the corresponding projections to individual atomic bound pseudo-states. For the basis sizes used, for these low-lying shells, these pseudostates are numerically equivalent to exact degenerate hydrogenic states. The ionization probability was calculated by summing up moduli squared of the projections to all continuum pseudo-states. Convergence was obtained by increasing the DVR basis size.

In practical calculations, as we have checked, it is sufficient to define the "pulse duration" by the interval $[t_0, t_0]$, where $\pm t_0$ correspond to instants when the electric field strength reaches the values of $10^{-3}F_0$. At the end of the time evolution, one obtains the population probability of different shells of the hydrogen atom, as well as the ionization probability. The range of maximum field strength $F_0$ considered was from the order of $10^{-3}$ a.u. to $6 \times 10^{-2}$ a.u. The maximum peak field considered is roughly equal to the real part of the branch point between the ground state and the first excited state as can be seen from figure \[32\]. Depending on the width $\tau$ of the pulse, we obtained convergence of the results with different sizes of the two-dimensional DVR bases: from $N_{DVR} = 25 \times 25$ for $\tau = 5$ a.u., up to $N_{DVR} = 60 \times 60$ for $\tau = 20$ a.u. The notation $N_{DVR} = M_u \times M_v$ means the total number of two-dimensional basis functions is $M_uM_v$. Both $M_u$ and $M_v$ are the number of one-dimensional basis functions.
Figure 3.3: Probabilities for excitation $P_n$ (of the $n$-th shell, $n=2,3,4$) and ionization $P_{ion}$ as functions of peak electric field strength $F_0$ of a Gaussian pulse with width $\tau=5$ a.u. DVR denotes calculations using the DVR basis. BSS denotes calculations using a discrete basis as in reference [26].
CHAPTER 3: Ionization and excitation of the hydrogen atom by an electric pulse

3.3 Numerical results in the case of a Gaussian-shaped electric pulse

Figure 3.4: Probabilities for excitation $P_n$ (of the $n$-th shell, $n=2,3,4$) and ionization $P_{\text{ion}}$ as functions of peak electric field strength $F_0$ of a Gaussian pulse with width $\tau=10$ a.u. Notation as in figure 3.3.
Figure 3.5: Probabilities for excitation $P_n$ (of the $n$-th shell, $n=2,3,4$) and ionization $P_{\text{ion}}$, as functions of peak electric field strength $F_0$ of a Gaussian pulse with width $\tau=20$ a.u. Notation as in figure 3.3.
CHAPTER 3: Ionization and excitation of the hydrogen atom by an electric pulse

3.4 The advanced adiabatic approach

representing the scaled parabolic coordinates $u$ and $v$, respectively (see Appendix A). Because of the high values of the ionization probability for $\tau > 20$ a.u., it was not possible to obtain convergence for reasonable sizes of the DVR bases in these cases.

Results for the DVR numerical calculations of the population probabilities $P_n$ of the $n$-th shell and the ionization probability $P_{\text{ion}}$, as functions of the maximum field strength $F_0$, are shown in figures 3.3-3.5. For comparison, also shown are the results obtained from the numerical solution of equation (3.1) but using an expansion in the basis of hydrogenic bound states only [26]. The reason for the discrepancy between the two sets of results, particularly at higher $\tau$, is the relatively high probability of ionization. More precisely, the calculations using a bound basis do not take into account the continuum states of the electron. Consequently, the results of the two numerical calculations do not differ when the probability of ionization is negligibly small, as can be seen for $\tau = 5$ in figure 3.3. On the other hand, when the probability of ionization becomes comparable with the probability of population of the given shell, then the results of the two methods start to differ. In the cases with higher $\tau$, the ionization probability becomes high enough at relatively smaller $F_0$ and the two sets of results become completely different. This happens because of the "reflection of the probability distribution" from the energy limit $E = 0$ in the case of the hydrogenic basis. As one increases $F_0$, population "reflects" from this energy limit and causes the appearance of spurious oscillatory structure, first in the population probability of the fourth shell ($P_4$), then of the third and finally of the second shell. The reflection from the energy limit is analogous to the reflection of a Gaussian wave packet from a spatial grid boundary under the influence of an external field when no absorbing potential is applied. In our case, levels with higher energy tend to be populated as $F$ is increased. If the basis lacks a representation of the continuum, or if the continuum is not represented to high enough energy, then the population probability has no other choice but to return to states of lower energy. This is also why the spurious oscillatory structure is first observed for the higher energy shells.

3.4 The advanced adiabatic approach

As it was already pointed out, the conventional adiabatic approach is not valid in the situation considered here because during the pulse all adiabatic states are unbound. They all become quasi-stationary and decay. To overcome this difficulty we use the advanced adiabatic approach developed in reference [20]. In this approach one seeks the solutions of the nonstationary Schrödinger equation (2.1) employing the Fourier ansatz

$$\Psi(r, t) = \int_C e^{i\xi_i(E)/v} \varphi_i(r, E) e^{-iEt} dE.$$  (3.12)

Here $\varphi_i$ are eigenfunctions of the adiabatic basis, $E_i(Q)$ are the adiabatic potential curves of the adiabatic parameter $Q = vt$, $v = 1/\tau$ is a small parameter. In addition, the eigenfunctions $\varphi_i(r, E) = \varphi_i(r, Q)|_{Q=Q_i(E)}$ are extended in the complex $E$-plane and $Q_i(E)$ is the function inverse to $E_i(Q)$. The idea behind the representation (3.12), as we will see below, is to take into account the time delay between the actual time and the time the ionization took place. Formally, the only requirement that we impose on the contour $C$ is to be such that integrand vanishes on its ends. After the substitution of (3.12) into the time-dependent Schrödinger
equation (2.14), one obtains an integral equation for the function $\zeta_i(E)$:

$$
\int C \left[ \hat{H}(Q) - E \right] e^{i\zeta_i(E)/v} \varphi_i(r, E)e^{-iEt} dE = 0.
$$

(3.13)

The advanced adiabatic approximation is an asymptotic solution of the integral equation (3.13) for $\zeta_i(E)$ in the limit $v \to 0$. The first two terms of the asymptotic series of $\zeta_i(E)$ with respect to $v$ were derived in [20], and the final expression for the wavefunction in the advanced adiabatic approximation reads:

$$
\Psi_{ad}(r, t) = \frac{1}{\sqrt{2\pi v}} \int C \left[ \frac{d\varphi_i}{dE} \right]^{1/2} \varphi_i(r, E) \exp \left[ \frac{i}{v} \int_{E_i^{(0)}}^{E} \varphi_i(E')dE' - iEt \right] dE.
$$

(3.14)

In the above equation, $E_i^{(0)}$ is the energy of the initial state ($E_i(Q) \to E_i^{(0)}$ as $t \to -\infty$). The integration contour $C$ is determined by the initial boundary conditions. At $t \to -\infty$ it begins at the initial state energy $E_i^{(0)}$ and goes up toward $+i\infty$. In this limit the integral can be calculated exactly and coincides with the initial atomic wavefunction $|i\rangle$. As the time changes from $-\infty$ to $+\infty$ the contour $C$ is deformed towards the lower half-plane, enclosing singularities related to the other limiting bound states $|f\rangle$. The probability $p_{if}$ for a transition between initial $|i\rangle$ and final $|f\rangle$ atomic bound states is obtained by using the steepest descent (or, equivalently, saddle point) method at bounded values of $r$. As stated above, the adiabatic eigenfunctions $\varphi_i(r, E)$, as well as eigenenergies $E_i(Q)$, are different branches of a single (multi-valued) analytic function which are connected pairwise by branch points (hidden crossings). Therefore the index $i$ can be omitted in the equation which determines the saddle point: $Q(E)/v - t = 0$. Apparently this equation has as many roots ($E = E_f(vt)$) as the number of the discrete energy levels. The final result for the probability coincides formally with the expression in the adiabatic approximation employing the adiabatic asymptote (2.19) presented in the previous chapter:

$$
p_{if} = \exp \left( -\frac{2}{v} \operatorname{Im} \int_L E(Q) dQ \right).
$$

(3.15)

Here $L$ is a contour in the complex $Q$-plane which begins at $t \to -\infty$ on the energy surface $E_i(Q)$, goes around the complex branch point (hidden crossing) $Q_c$ connecting $i$ and $f$ adiabatic states, and at $t \to +\infty$ ends on the energy surface $E_f(Q)$. The details of the derivation of the expression (3.15) are given in Appendix B. In the particular case $i = f$ we obtain the depletion of the initial state due to tunnelling:

$$
p_{ii} = \exp \left( -\int_{-\infty}^{+\infty} \Gamma_i(t) dt \right) = 1 - P_{\text{tun.}},
$$

(3.16)

where $\Gamma_i(t) = 2|\operatorname{Im}E_i(Q)|$ is the width of the adiabatic state $\varphi_i(r, Q)$ and $P_{\text{tun.}}$ is the tunnelling probability. This expression is widely used but, as far as we know, has not been
rigorously derived before. Its derivation requires a knowledge of the adiabatic representation \((3.14)\).

The wavefunction \((3.14)\) takes into account the time delay effect which is of crucial importance for ionization. We will illustrate this point by considering a case when the electric field is absent and the potential which is seen by the ejected electron has a finite range, a situation frequently considered in the field of atomic collisions. At \(t \to +\infty\) the wave packet of the ejected electron moves to infinite \(r\), where the adiabatic wavefunction can be replaced by its asymptotic form \(\varphi(r, E) \sim (1/r) \exp(ikr)\) where \(k = (2E)^{1/2}\). Now \(r\) is also a large parameter. Together with \(1/v\) and \(t\) it gives the saddle point equation

\[
\frac{r}{k} + \frac{Q(E)}{v} - t = 0
\]  

which has a time delay \(r/k\) between the actual time \(t\) and the time \(Q(E)/v\) at which the electron was emitted \([20, 21]\).

When the peak amplitude of the pulse is larger than the amplitude corresponding to the real part of \(F\) at the position of the hidden crossing, interference appears between the two possible paths to go from initial \(|i\rangle\) to final \(|f\rangle\) state, i.e. during the increasing or decreasing stages of the pulse. Restricting ourselves to a two-state approximation, the adiabatic asymptote \((3.14)\) can be extended to include this interference \([20]\) in terms of an Airy function

\[
\Psi^{ad.}(r, t) = \sqrt{\frac{2}{v}} e^{-\sigma(E)} \int_C \frac{dQ(E)}{dE} \left[ \varphi_i(r, E) \left( \frac{3}{2} \sigma(E) \right)^{1/6} \right] Ai \left( \frac{3}{2} \sigma(E) \right)^{2/3} e^{-iE't} dE
\]

where

\[
\sigma(E) = \frac{i}{v} \int \frac{Q_i(E') dE'}{E_i}
\]

and \(E_i = E(F_0)\) is the energy at the peak of the pulse \((3.10)\). Then, in the two-passage case the final expression for the transition probability between states \(|i\rangle\) and \(|f\rangle\) is

\[
P_{if} = 4p_{if}(1 - p_{if}) \sin^2 \left( \frac{1}{2} \text{Re} \left[ \int_{C_1} E(Q) dt - \int_{C_2} E(Q) dt \right] \right)
\]  

where \(C_1\) and \(C_2\) are contours in the complex time plane starting at \(t = -\infty\), going around branch points given by \((3.10)\) as,

\[
t_{1,2} = \pm\tau \left[ \ln \left( \frac{F_0}{F_c} \right) \right]^{1/2}
\]

respectively and ending at \(t = +\infty\).
Two points should be mentioned here. Firstly, because of the decay of the bound states in the continuum, the total probability of inelastic transitions is a sum of the probabilities from both inelastic and elastic channel. The inelastic channel consists of the nonadiabatic transitions arising from the hidden-crossings between bound states with probability (3.15) which, through nonadiabatic transitions to other bound states or decay eventually result with ionization. This probability will be denoted as $P_{hc}$ in the next section. On the other hand the "elastic" channel is the decay of the initial bound state into the continuum with a probability given in equation (3.16), which will be denoted as $P_{tun}$ in the next section. Therefore, the total probability of inelastic transitions in the advanced adiabatic approach is the sum $P_{hc} + P_{tun}$. Second, in our case the position of the real part of the branch point relative to the field strengths applied is such that we can take only the elementary probability of hidden-crossing transition (3.15) as an estimate of the total inelastic probability, that is $P_{hc} = p_{ij}$, instead of $P_{ij}$ defined in equation (3.19). This will be clarified in the next section.

Finally, we can estimate the expected range of validity of the advanced adiabatic approach by comparing electric field excitation and ionization with the charged ion impact excitation and ionization [26]. In the case of collision of a charged ion with a particle the perturbation of the atomic electron is

$$V(t) = -\frac{Z}{|r - R(t)|}$$ (3.21)

where $Z$ is the incident ion charge, $R(t)$ is the instantaneous distance between the atomic nucleus and the incident ion. In our case the perturbation of a hydrogen atom by a time-dependent electromagnetic field is given by $\frac{1}{2} \mathbf{p} \cdot \mathbf{A}(t)$, where $\mathbf{p}$ is the momentum operator of the atomic electron, $\mathbf{A}$ is the vector potential and $c$ is the speed of light in vacuum. We can perform a "space-translation" transformation [36] of the time-dependent wavefunction

$$\Psi'(r, t) = \Psi(r, t) \exp \left( i \mathbf{p} \cdot \mathbf{\alpha}(t) + i \int_{t_0}^{t} \frac{\mathbf{A}^2(t')}{2c^2} dt' \right), \quad \mathbf{\alpha}(t) = \frac{1}{c} \int_{t_0}^{t} \mathbf{A}(t') dt' .$$ (3.22)

This transformation leads to an effective Hamiltonian for the electron

$$-\frac{1}{2} \Delta r - \frac{1}{|r - \mathbf{\alpha}(t)|}$$ (3.23)

which has formally the same form as the case (3.21). The adiabatic criterion is given by the condition $\tau / \tau_{at} > 1$ where $\tau_{at}$ is the characteristic time associated with the transition and $\tau$ is the characteristic duration of perturbation. The characteristic atomic time is $1/\Delta E$ where $\Delta E$ is the transition energy. In the case of atomic collisions the characteristic time of perturbation is the collision time defined as $R/v$. This leads to the condition for adiabaticity

$$\frac{\tau}{\tau_{at}} = \Delta E \tau = \frac{\Delta E R}{v} > 1.$$ (3.24)

However, the combination $\Delta E \tau$ appears always as a phase, so a more precise condition would be

$$\frac{\Delta E R}{v} > 2\pi.$$ (3.25)
By comparison of the equations (3.23) and (3.21) it is clear that in the case of pulse excitation and ionization $\alpha(t)$ plays the role of $R(t)$. Therefore the criterion for adiabatic behavior in this case reads
\[
\frac{\Delta E\alpha}{\dot{\alpha}} > 2\pi.
\] (3.26)

For Gaussian pulses, the width of the pulse $\tau$ can be taken as estimate of the ratio $\alpha/\dot{\alpha}$. Therefore the adiabatic criterion reads
\[
\Delta E\tau > 2\pi.
\] (3.27)

Since for hydrogenic atom $\Delta E \sim 1/2$ a.u., the adiabatic condition holds when
\[
\tau > 4\pi.
\] (3.28)

In the next section we will test this crude criterion.

### 3.5 Comparison of the advanced adiabatic approach and the DVR calculation for the Gaussian-shaped electric pulse

Figure 3.6 shows the results of the exact DVR ($P_{\text{inel.}}$) and approximate adiabatic calculations for the total inelastic transition probability out of the ground state of the hydrogen atom induced by an electric pulse of the form (3.10) with $\tau = 10$ a.u. and $\tau = 20$ a.u. The probability of inelastic transitions was calculated numerically as $P_{\text{inel.}} = 1 - P_1$, where $P_1$ is the population probability of the ground state. According to the adiabatic criterion given in equation (3.28), the case $\tau = 10$ a.u. is in the non-adiabatic regime and the case $\tau = 20$ a.u. is in the adiabatic regime. The ground state is connected by the branch point $F_c = (0.0507988, -0.0392454)$ with the first excited state, as calculated in the reference [26]. The transition probability between the ground and the first excited states $p_{12}$ can then be taken as an estimate of $P_{\text{inel.}}$ by assuming that system passes the hidden crossing only once (there is no interference between increasing and decreasing stages of the pulse) and the probability flux is subsequently redistributed from the first excited state to other excited states and the ionization channel. In the case of the Gaussian-shaped pulse (3.10) expression (3.15) for $p_{12}$ can be rewritten in more definite form:
\[
p_{12} = \exp \left( -\tau \right) \left| \text{Im} \int_0^F \frac{[E_2(F) - E_1(F)]}{F \sqrt{\text{Im}(F_0/F)}} dF \right|.
\] (3.29)

This result is labelled as $P_{\text{hc}}$ in figure 3.6. The agreement between the exact DVR calculation and the adiabatic result, which is in fact the sum of $P_{\text{run.}}$ (calculated from the definition (3.10) and using the width of the ground state) and $P_{\text{hc}}$, is very good for the adiabatic case ($\tau = 20$ a.u.). In the case $\tau = 10$ a.u., which is beyond the range of the validity of the adiabatic approach ($\tau > 4\pi$), equation (3.29) overestimates the probability of inelastic transitions by an order of magnitude, indicating, as expected, that the adiabatic approximation is invalid.

Here we have applied expression (3.29) (or (3.10)) for the calculation of the estimate of the probability of inelastic transitions in the first-order adiabatic approximation because the amplitudes $F_0$ considered are less then or about equal to $\text{Re} F_c = 0.0507988$. In this case
CHAPTER 3: Ionization and excitation of the hydrogen atom by an electric pulse

3.5 Comparison of the advanced adiabatic approach and the DVR calculation for the Gaussian-shaped electric pulse

Figure 3.6: Total probability for inelastic transitions, calculated numerically $P_{\text{inel.}}$, and both in the zeroth ($P_{\text{tun.}}$) and in the first-order ($P_{\text{hc}}$) adiabatic approximation as functions of peak electric field strength $F_0$ of a Gaussian pulse with width $\tau$. The adiabatic result is a sum of $P_{\text{tun.}}$ and $P_{\text{hc}}$. 

---

[Graphs showing the probability $P$ as a function of $F_0$ for different values of $\tau$]
one can suppose that population probability does not return to the ground state, that is, the population which goes into the first excited state is subsequently redistributed to the other excited states and the ionization channel. More detailed calculations of the individual population probabilities within the adiabatic approach would require a knowledge of the location of the branch points between the excited states, which are not obtained from the numerical solution of the stationary problem (3.2) in the complex plane.

The comparison in figure 3.6 shows that for \( \tau = 20 \) a.u., where the criterion of adiabaticity is fulfilled, the tunnelling probability \( P_{\text{tun}} \) is much smaller than the probability of inelastic transitions via hidden crossings \( P_{hc} \). However when \( \tau \) is increased, the probability \( P_{hc} \) decreases rapidly and the contribution from the tunnelling in the total adiabatic result for the probability of inelastic transitions increases. For the pulse shape (3.10) in question, the decrease of \( P_{hc} \) is exponential with \( \tau \). Then in the limit \( \tau \to \infty \), \( P_{hc} \) vanishes and the total adiabatic result is given by \( P_{\text{tun}} \).

### 3.6 The hydrogen atom in a rectangular electric field pulse

In this section, to facilitate comparison with previous work [31, 32], we consider excitation and ionization of the hydrogen atom from the ground state by a rectangular electric field pulse with constant amplitude \( F_0 \). In particular, we have focused on the total probability of depletion of the ground state.

Figure 3.7 shows the ground state probability as a function of pulse duration \( \tau \) for \( F_0 = 0.08 \) a.u. obtained by numerical calculation in the DVR basis. As previously stated, for a fixed DVR basis size, results converge up to a certain value of \( \tau \). In this case, taking a basis size \( N_{DVR} = 50 \times 170 \), convergence has been obtained up to \( \tau \approx 42 \) a.u. On the same figure we show the decay of the ground state by tunnelling, using the width of the ground state for \( F_0 = 0.08 \) a.u. given in [26], as well as the results given in references [31] and [32].

Within the \( \tau \) limit of convergence of the results (\( \tau < 42 \) a.u.) the DVR calculation shown in figure 3.7 agrees perfectly with the results of Scrinzi [32], who used the method of complex scaling. One sees that after abrupt turn-on of the electric field, the ground state population decreases monotonically as higher excited states are populated. After around 5 a.u. the rate of population depletion varies (our agreement with [32] suggests this is a real physical effect) before settling down at \( \tau \sim 20 \) a.u. to become equal to the tunnelling rate. Therefore the exponential decay curve in figure 3.7 is the normalized curve \( (0.902 \exp(-\Gamma \tau)) \). The preexponential factor accounts for the initial drop of the ground state during the sudden turn-on of the pulse. This discrepancy with the result in the advanced adiabatic approximation for the probability of staying in the same state (3.16) is due to the non-analyticity of the rectangular pulse time-dependence. For this value of \( F_0 \), the value of \( \Gamma \) is taken from [26] as \( 4.54 \times 10^{-3} \) a.u. which is, to this accuracy, precisely the value obtained by Scrinzi [32].

Also shown in figure 3.7 are recent calculations of Geltman [31] who used a discrete basis of bound and continuum states. Interestingly, there is near perfect agreement of all calculations in the ‘switching-on’ phase, \( \tau < 5 \) a.u., but the calculations of [31] fail to reproduce the exponential decay, rather they show oscillations typical of those produced by reflection at an energy boundary.
3.7 Conclusions

We have studied the excitation and ionization of the hydrogen atom under the influence of an electric pulse with both Gaussian and step-function shape.

The numerical DVR method has shown itself capable of adequately describing the cases of both short and long (adiabatic) pulses. However, as the length of the pulse increases the demands on the size of the basis set required to obtain converged results increases rapidly. We have also shown, perhaps not surprisingly, how important it is to include a proper description of the continuum in order to avoid spurious oscillations in the occupation probabilities. The direct use of parabolic co-ordinates has been shown to be well-adapted to describing the directed motion of the electron in an electric field.

We used the numerical DVR calculation as a benchmark result to compare with the results of the advanced adiabatic approach. The advanced adiabatic approach in turn relies on the analytic properties of adiabatic potential curves in the complex plane of the adiabatic parameter and it describes all inelastic processes, including ionization. For a Gaussian pulse, excitation and ionization probabilities show a monotonic increase as the maximum field strength increases, for fixed pulse length. Using the present level of knowledge of the complex adiabatic eigenvalues of the hydrogen atom in a static electric field we have tested the predictions of the advanced adiabatic theory for the total inelastic transition probability out of the ground state. In the region of its applicability, the analytic adiabatic theory gives good agreement with the numerical DVR results. In addition, using the advanced adiabatic approach the expression for the tunnelling probability is rigorously derived.

In the case of a step-function pulse, which we have considered in order to compare with previous calculations [32, 31], after a rapid decrease of ground-state occupation probability
due to population of higher-lying states, the ground state probability is well described by the
tunnelling rate in the constant electric field. In this case we obtain perfect agreement over
the pulse length range $0 \leq \tau \leq 42$ a.u. with the results of Scrinzi [32], who used a completely
different numerical method. However, the alternative numerical approach of Geltman [31]
appears only to describe the initial depletion phase ($\tau < 5$ a.u.) correctly.

Considering the limits of applicability of the advanced adiabatic approach, one remarks
the time scale at which transition from adiabatic to nonadiabatic regime takes place: an order
of magnitude 10 a.u., that is order of magnitude 100 attoseconds! This is the typical time scale
the inelastic transitions governed by the hidden-crossings mechanism take place. Otherwise,
for longer times, the tunnelling mechanism (the elastic channel) takes over. This brings us
to the question what happens at smaller time scales. For the case of unidirectional pulse
excitation we will try to provide an answer in Part III of this thesis. The case of few-cycle
pulses of very short duration will be considered in Part II.
Part II

Ionization and recombination in intense, short pulses
Chapter 4

Introduction

An experiment with unidirectional electric-field pulses on time scales considered in Part I of this thesis is presently not possible. However, observation and control of quantum phenomena in atoms and molecules using newly-developed laser techniques producing pulses with only a few cycles of the electric field is an area of great current interest \[2\]. In particular, the development of atto-second pulses (more accurately "a fraction of a femtosecond" pulses), has been rapid in recent years \[3, 5, 37, 38, 39\]. Presently, the free electron laser source at Deutsches Elektronen-Synchrotron (DESY) produces pulses with frequency $\nu \approx 0.5$ a.u., total pulse duration of $50$ fs and intensities up to $7 \times 10^{13}$ W/cm$^2$ (corresponding to a peak electric field of $\approx 0.044$ a.u.)\[37, 38\], whereas the high-frequency laser pulses produced from a high harmonic generation have a frequency of $\omega \approx 3.3$ a.u. and minimal total duration of $0.65$ fs \[39\] and very recently of $0.25$ fs \[5\]. In both cases, the envelopes of the pulses produced are not well controlled and each pulse contains more than five (in the DESY case more than one hundred) cycles. Very recently a train of almost single-cycle pulses of duration $0.17$ fs has been realized \[4\]. A truly few-cycle pulse has been realized for $\omega \approx 0.05$ a.u. \[10\]. The attosecond few-cycle pulse awaits the development of attosecond high-power lasers with controllable pulse envelopes, but since progress in laser physics is explosive, there is reason to hope that such lasers will be available in the near future. Alternatively one can use the relativistic time dilation to obtain short, very strong field pulses in the frame of target particles moving at relativistic velocities, although here one is restricted to ions in storage rings.

There has been an enormous amount of theoretical work on the ionization of atoms by strong lasers. However, in the early days, this has been mostly confined to the c.w. laser regime. The observation of real-time electronic processes requires extremely short pulses where only a few cycles (in fact down to a half-cycle) of the electromagnetic field occur in the pulse duration. This opens up a completely new area for theory. Most of the theoretical approaches for studying several-cycle pulses employed so far, except a small number of analytic results based mainly on the Keldysh-Faisal-Reiss approximation \[7, 8, 9\] (for recent results see \[11, 32\]) and the Coulomb-Volkov approach \[13\] were wholly numerical. Here we will consider the situation where the oscillation period is short compared to the orbital time in the initial state. In this regime there are a large number of papers concerning ionization of Rydberg states (see for example \[11, 35, 40\]). Also purely analytic nonperturbative studies of Rydberg atom excitation and ionization are available for cases of half-cycle pulses \[47, 48, 49\]. However, for few-cycle pulses, so far the theoretical approaches have been limited to numerical studies only.
CHAPTER 4: Introduction

In this part of the thesis we will formulate a nonperturbative analytical approach for calculation of the probability of returning to the initial state. We will also identify a process of ionization and recombination which occurs periodically in time. By using suitably designed pulses, a control of the continuum occupation probability (or correspondingly that of the initial state) can be achieved. Parts of this work have been published in references [50] and [51]. In the first paper [50] the ionization of the ground-state hydrogen atom in a short half- or single-cycle electric field pulse is studied. The second paper [51] presents more extensive results and in particular generalizes the strong-field case to several cycle pulses and to ionization from excited states of the hydrogen atom. In addition, the energy and particularly angular distributions of ionized electrons are studied.

In the next chapter, we will consider the basic analytic approximations considered in this Part: the first-order time-dependent perturbation theory (FPA), the sudden approximation (SA) and the first-order Magnus approximation (FMA). Chapter 6 deals with the analysis of the response of a hydrogen atom to a several-cycle pulse in the FPA where we show the periodic occurrence of ionization and recombination in time, as well as the effect of the relative phase between envelope and carrier. The strong-field short-pulse case is considered in Chapter 7 where we present analytic expressions for the probability of returning to the initial state after interaction with a one or a few-cycle laser pulse, in the limit of large peak fields. Finally, we conclude this part in Chapter 8.
Chapter 5

Basic analytic approximations

To introduce the basic approximations used in this part we take an initial state \( \Phi_i(t_0) \) and calculate the propagation to time \( t \) i.e.

\[
|\Psi_i(t)\rangle = \hat{U}(t, t_0) |\Phi_i(t_0)\rangle
\]  

(5.1)

where the time-development operator \( U \) is defined by

\[
\hat{H}(t)\hat{U}(t, t_0) = i\partial\hat{U}/\partial t
\]

(5.2)

with, in dipole approximation,

\[
\hat{H}(t) = \hat{H}_0 + \mathbf{r} \cdot \mathbf{F}(t) \equiv \hat{H}_0 + V(t).
\]

(5.3)

Here \( \hat{H}_0 \) is the atomic Hamiltonian and \( \mathbf{F}(t) \) describes the magnitude (whose peak value we denote by \( F_0 \)) and polarization of the classical electric field.

The probability amplitude of occupation of any final state is then simply

\[
a_{fi}(t) = \langle \Phi_f(t) | \Psi_i(t) \rangle
\]

(5.4)

and the corresponding probability is \( P_{fi}(t) = |a_{fi}(t)|^2 \).

The most accurate method of calculating \( \Psi_f(t) \) from \( 5.1 \) is to propagate the wavefunction in time according to the time-dependent Schrödinger equation (TDSE)

\[
\hat{H}(t) |\Psi_i(t)\rangle = i \frac{\partial}{\partial t} |\Psi_i(t)\rangle
\]

(5.5)

obtained by applying \( 5.2 \) on \( |\Phi_i(t_0)\rangle \). This we have achieved by propagating the wavefunction, completely numerically with no approximations, on a three-dimensional grid using the discrete variable representation (DVR) method which we have also used in Part I. The details of this numerical approach are given in Appendix A.

As with all fully-numerical approaches, the results provide little insight into the physics underlying the time-development. Therefore we examine two limits where analytical solutions are possible. The first is standard first-order perturbation approximation (FPA), valid when \( F_0 \ll 1 \text{ a.u.} \). Here we give closed forms for \( N \)-cycle rectangular and sinusoidal pulses. Somewhat unusual in the case of very intense pulses \( (F_0 > 1 \text{ a.u.}) \) we can also give analytic
expressions for excitation and ionization probabilities when the half-cycle duration \( \tau \ll 1 \) a.u. These expressions are obtained using the first Magnus approximation (FMA) to the exact propagator defined in equation (5.2). Remarkably, the physics of ionization by short pulses of arbitrary intensity becomes rather simple, and, as we show, one can obtain analytic expressions for the ionization probability even in \( N \)-cycle pulses, so long as \( \tau \) is less than the initial orbital period.

The time propagator is defined formally also by the integral equation

\[
\hat{U}(t, t') = \hat{U}_0(t, t') - i \int_{t'}^t \hat{U}_0(t, t'')V(t'')\hat{U}(t'', t')dt''
\]  

(5.6)

where \( \hat{U}_0(t, t') = \exp(-i\hat{H}_0(t - t')) \) is the propagator of the atomic field alone. In FPA one replaces \( \hat{U} \) on the r.h.s. of equation (5.6) by \( \hat{U}_0 \) and substitutes in equation (5.4) and (5.1) to give:

\[
a_{f,i}(t) = \langle \Phi_f(t) | \hat{U}_0(t, t_0) | \Phi_i(t_0) \rangle - i \int_{t_0}^t \langle \Phi_f(t) | \hat{U}_0(t, t')V(t')\hat{U}_0(t', t_0) | \Phi_i(t_0) \rangle dt'.
\]  

(5.7)

If \( \Phi_i(t_0) = \phi_i \exp(-iE_it_0) \) and \( \Phi_f(t) = \phi_f \exp(-iE_ft) \), where \( \phi_i, \phi_f \) are eigenstates of \( \hat{H}_0 \) with different eigenvalues \( E_i \) and \( E_f \), then the first term in (5.7) is zero and one obtains

\[
a_{f,i}(t) = -i \int_{t_0}^t \langle \phi_f | V(t') | \phi_i \rangle \exp[i(E_f - E_i)t'] dt',
\]  

(5.8)

which is the standard first-order perturbation result.

For intense pulses, in general when the electric field is bigger than the atomic field potential, the perturbation theory does not converge. However, if the pulse time is very short one can employ an approximation to \( \hat{U}(t, t') \) first suggested by Magnus and considered in detail by Pechukas and Light. If \( \hat{H} \) and \( \hat{U} \) commute, equation (5.2) can be integrated to yield

\[
\hat{U}(t, t_0) = \exp\left(-i \int_{t_0}^t \hat{H}(t')dt'\right).
\]  

(5.9)

However this is not possible since \( \hat{H}(t_1) \) and \( \hat{H}(t_2) \) do not commute for any two times \( t_1 \) and \( t_2 \). Nevertheless, the Magnus expansion shows that, for small \( (t - t_0) \), (5.9) can be used as the first approximation to \( \hat{U}(t, t') \), the corrections involving, as one might expect, the nested commutators of \( \hat{H}(t) \) at different times. Then if one makes the further assumption that duration of \( V(t) \) is short compared to the orbital times of eigenstates of \( \hat{H}_0 \), one can neglect the non-commutativity of \( \hat{H}_0 \) and \( V(t) \) to write

\[
|\Psi_i\rangle = \hat{U}(t, t_0) |\Phi_i(t_0)\rangle = \exp\left[-i \int_{t_0}^t V(t')dt'\right] \exp\left[-i\hat{H}_0(t - t_0)\right] |\Phi_i(t_0)\rangle
\]

38
CHAPTER 5: Basic analytic approximations

\[
\exp \left[ -i \left( \int_{t_0}^{t} \mathbf{F}(t') dt' \right) \cdot \mathbf{r} \right] \exp \left( -iE_i t \right) \left| \phi_i \right> .
\] (5.10)

Then, defining

\[
\mathbf{q} = \int_{t_0}^{t} \mathbf{F}(t') dt'
\] (5.11)

as a momentum boost, one obtains the simple result

\[
P_{fi} = |\langle \phi_f | \exp(-i\mathbf{q} \cdot \mathbf{r}) | \phi_i \rangle|^2 ,
\] (5.12)

which we will call the FMA, elsewhere called "short-pulse approximation" [48] or "impulse approximation" [47].

One remarks here on the close analogy between the FMA for short light pulses and excitation and ionization by the electric fields of charged particles. For electron or heavy-ion impact in the first Born approximation, the transition matrix element is exactly that appearing in (5.12), where \( \mathbf{q} \) is then the change in momentum of the projectile, or equivalently the momentum transferred to the target atom. For heavy ions moving at velocities high enough that their motion can be described by a classical trajectory the analogy is even closer. Then, for distant collisions where the dipole term of the Coulomb force is dominant, the transition matrix element is again of the form (5.12) in FMA, with the momentum transfer \( \mathbf{q}(t) \) given exactly as in equation (5.11) by an integral over the electric field of the incident heavy ion.

When the momentum transfer becomes small so that \( e^{-i\mathbf{q} \cdot \mathbf{r}} \approx 1 - i\mathbf{q} \cdot \mathbf{r} \), the FMA transition amplitude becomes

\[
a_{fi} \approx -i \langle \phi_f | \mathbf{q} \cdot \mathbf{r} | \phi_i \rangle
\] (5.13)

Similarly, when \( (E_f - E_i) \tau \ll 1 \), i.e., for a short pulse the expression (5.8) in the first-order perturbation approximation reduces to equation (5.13). Hence, the FMA and FPA give identical results for short, weak pulses, that is equation (5.13) is the dipole limit of both FPA and FMA. The FPA remains valid for longer, weak pulses; the FMA for short, stronger pulses. The expression (5.13), following reference [54], will be referred to as the sudden approximation (SA). In the next chapters we will calculate the ionization probability as a function of time in these three analytic approximations.
Chapter 6

First-order perturbation theory

The FPA is normally applied to situations where the pulse contains an enormous number of cycles e.g. c.w. laser ionization. Then one obtains a constant ionization rate known as Fermi’s Golden Rule. In this case the ejected electrons are monochromatic corresponding to the absorption of a single photon from the ground state. However, for short pulses in time, as one might expect from elementary considerations of the time to energy Fourier transform embodied in equation (5.8), the spectrum of ejected electrons exhibits considerable structure extending over an extremely wide energy range [50].

As an example we consider specifically a pulse consisting of a train of $m$ alternating half-cycles each of duration $\tau$ and of either rectangular or sinusoidal form. The ionization probability from the ground state $1$, with binding energy $E_1$, to a final state $k$, of momentum $k$, integrated over all angles of emission is given by

$$\frac{dP}{dE} = k \int d\mathbf{k} |a(\mathbf{k})|^2$$

where

$$a(\mathbf{k}) = -i \int_0^{m\tau} \langle \phi_\mathbf{k} | \mathbf{F}(t) \cdot \mathbf{r} | \phi_1 \rangle \exp[i\epsilon t] dt, \quad \epsilon = E - E_1 \quad \text{and} \quad E = \frac{k^2}{2}. \quad (6.2)$$

If we fix the z-axis to be oriented along $\mathbf{F}$, then $\langle \phi_\mathbf{k} | \mathbf{F}(t) \cdot \mathbf{r} | \phi_1 \rangle = F(t) \langle \phi_\mathbf{k} | z | \phi_1 \rangle$ and

$$\langle \phi_\mathbf{k} | z | \phi_1 \rangle = \frac{1}{\sqrt{k}} \int^{l-l} \exp(-i\delta_1) Y_{l0}(\theta_k, \varphi_k) \langle \phi_{E10} | z | \phi_1 \rangle.$$  

Here the angles $\theta_k$ and $\varphi_k$ define the direction of $\mathbf{k}$, $Y_{l0}$ is the spherical harmonic for the orbital quantum number $l = 1$ and zero magnetic quantum number, and $\delta_1 = \arg \Gamma(2 + i/k)$ is the Coulomb phase for $l = 1$. The eigenfunction $\phi_{E10}$ is a continuum state with well-defined orbital quantum number $l = 1$ and magnetic quantum number $m' = 0^*$ normalized in terms of energy $E$. The continuum states with well-defined momentum and direction $\phi_\mathbf{k}$, satisfying the outgoing wave boundary conditions can be expanded in terms of $\phi_{Elm'}$

$$\phi_\mathbf{k}(r) = \frac{1}{\sqrt{k}} \sum_{l=0}^{\infty} \sum_{m'=-l}^{l} i^l \exp(i\delta_l) \phi_{Elm'}(r) Y_{lm'}^{*}(\theta_k, \varphi_k). \quad (6.4)$$

*Here we use $m'$ to denote magnetic quantum number since $m$ is reserved for the number of half-cycles.
CHAPTER 6: First-order perturbation theory

Figure 6.1: Energy distribution for \( q = 9 \times 10^{-3}, \tau = 0.3 \).

Figure 6.2: The energy distribution of ionized electrons for ten half-cycles of duration a) \( \tau = 0.3 \) a.u., \( q = 9 \times 10^{-3} \) a.u. and b) \( \tau = 3 \) a.u., \( q = 0.09 \) a.u., calculated from equations (6.5) and (6.7). The arrows mark the resonant peaks.
The relation between the matrix elements (6.3) follows from equation (6.4) and the dipole selection rules. The time integral in equation (6.2) can be performed to give

\[
\frac{dP}{dE} = F_0^2 u_1(E) \left| \frac{(1 - \exp(i\epsilon\tau))(1 - (-1)^m \exp(iem\tau))}{\epsilon(1 + \exp(i\epsilon\tau))} \right|^2
\]

for a sequence of rectangular pulses of magnitude \(F_0\) and duration \(\tau\). Here we defined the function

\[
u_1(E) = k \int |\langle \phi_k | z | \phi_1 \rangle|^2 dk = |\langle \phi_{E10} | z | \phi_1 \rangle|^2,
\]

which is explicitly equal to (6.5)

\[
u_1(E) = \frac{2^8}{3 (1 + 2E)^5 (1 - \exp(-2\pi/\sqrt{2E}))}.
\]

For a sequence of sinusoidal pulses i.e. \(F(t) = F_0 \sin(\pi t/\tau)\) and \(0 < t < m\tau\), one obtains

\[
\frac{dP}{dE} = \left( \frac{F_0\pi}{\tau} \right)^2 u_1(E) \left| \frac{(1 - (-1)^m \exp(iem\tau))}{\epsilon^2 - (\pi/\tau)^2} \right|^2
\]

\[
= 4 \left( \frac{F_0\pi}{\tau} \right)^2 u_1(E) \frac{\sin^2 \left( \frac{\pi}{2} (\epsilon - \pi/\tau)m\tau \right)}{(\epsilon^2 - (\pi/\tau)^2)^2}.
\]

The energy distributions resulting from 5 full cycle pulses are shown in figure 6.1. The rectangular pulse has field strength \(F_0\) and the peak of the sinusoidal pulse is chosen as \(\pi F_0/2\) so \(q\) is the same in both cases. For \(\tau = 0.3\) a.u. the energy distributions peak strongly at zero energy and show considerable structure. For sinusoidal pulses the harmonic peaks decrease smoothly as a function of energy whereas for square pulses the harmonics are folded with the Fourier transform of a single half cycle and the higher energy part of the distribution shows peaks at \(E_{1} + \omega_0 + \omega_0(1 + 2j)/m; j \geq 1; \omega_0 = \pi/\tau\). This behavior is illustrated further in figure 6.2 where we concentrate attention on the low-energy part of the electron emission spectrum, again for five-cycle pulses of rectangular or sinusoidal form. One sees that near threshold \(dP/dE\) is independent of pulse shape but differences appear at higher energies due to the differences in the Fourier transforms of the pulses, as detailed above. The energy distributions also show a broad peak, indicated by arrows in figure 6.2 near \(E = \pi/\tau + E_1\) which corresponds to the one-photon absorption. For \(\tau = 0.3\) a.u. this peak is much smaller than the \(E = 0\) emission probability. However, for longer pulses, for example, for ten half-cycles with \(\tau = 3\) a.u., corresponding to total pulse time of 30 a.u. (see figure 6.2(b)), this peak grows and dominates the emission of zero-energy electrons. Of course this is just the onset of the behavior appropriate to an infinitely long pulse, where this resonance peak becomes a \(\delta\)-function.

In figures 6.3 and 6.4 the effect of only one, two, or three alternating pulses is shown. Here the numerical DVR calculation and the analytic results give identical results. Moreover, in accordance with the previous consideration for the energy distribution for sine and rectangular pulses, the results presented in figures 6.3 and 6.4 are the same for both type of pulses provided
alternating pulses, $F_0=0.03$, $\tau=0.3$ each

Figure 6.3: Energy distribution from the DVR calculation for $F_0 = 0.03$ a.u. and $\tau = 0.3$ a.u.

$F_0=0.03$ a.u., $\tau=0.3$ a.u.

Figure 6.4: The excitation probability $P_n$ (of the $n$-th shell, $n = 2, 3$) and the ionization probability $P_{\text{ion}}$, as functions of time. The probability of population of the other bound shells with $n > 3$ is negligibly small.
the peak amplitudes of the pulses are such that the momentum transfer $q$ for a half-cycle is the same. In figure 6.3 the region of lower-energy electron emission ($\leq 2$ a.u.) is shown. The energy distribution $dP/dE$ exhibits an oscillatory behavior as a function of time, in that the ionization caused by a unidirectional rectangular half-cycle pulse is drastically reduced by a subsequent half-cycle of opposite direction. Adding a third half-cycle results essentially in the restoration of the ionization probability for one half-cycle. To our knowledge, that this oscillation of ionization and recombination occurs even in the perturbative regime has not been pointed out before. In figure 6.4 this behavior is made explicit by plotting the time-dependent occupation probability of the continuum ($dP/dE$ integrated over all $E$) and of the $n = 2$ and $n = 3$ shells, during a three half-cycle pulse. Although the absolute probabilities are low, one notes that ionization is as probable as excitation and that all probabilities oscillate so that at $t = 2\tau$, a one-cycle pulse, almost all probability has returned to the ground state. Note that in dipole approximation from the ground state only $p$-states ($l = 1$) are populated, so that the angular distribution is purely $\cos^2 \theta$.

The origin of the recombination is simply due to the quantum phase reversal which arises from reversing the electric field. Classically, one could view the polarization (ionization) caused by the first half-cycle simply being reversed by switching the electric field direction in the second half-cycle. The small residual ionization is just due to the high momentum components of the ionized wavepacket which leave the interaction region quickly enough to avoid recombination.

6.1 Phase dependence

A further interesting effect in the perturbation regime is the enormous dependence of the ionization probability on the phase of the electric field. We consider a one-cycle ($m = 2$) sinusoidal pulse with a $\sin^2$ envelope i.e. $F(t) = F_0 \sin^2(\pi t/2\tau) \sin(\pi t/\tau + \phi)$ where $\phi$ is the relative phase of envelope and carrier. Perturbation theory gives in this case,

$$\frac{dP}{dE} = \left(\frac{\pi}{\tau}\right)^2 F_0^2 u_1(E) \sin^2[\varepsilon \tau] \times$$

$$\times \left(\frac{1}{\varepsilon^2 - (2\pi/\tau)^2} - \frac{1}{\varepsilon^2 - (\pi/\tau)^2}\right)^2$$

for $\phi = 0$ (6.8)

$$\frac{dP}{dE} = F_0^2 u_1(E) \varepsilon^2 \sin^2[\varepsilon \tau] \times$$

$$\times \left(\frac{1}{\varepsilon^2 - (\pi/\tau)^2} - \frac{1}{2(\varepsilon^2 - (2\pi/\tau)^2)} - \frac{1}{2\varepsilon^2}\right)^2$$

for $\phi = \pi/2$. (6.9)

From figure 6.5(a) the shape of $dP/dE$ is largely independent of $\phi$, since it is decided essentially by the carrier envelope. However the magnitude of ionization is very sensitive to $\phi$ and in particular, as shown in figure 6.5(b), where the low-energy part of the spectrum is magnified, one sees that a phase change of $\pi/2$ brings more than two orders of magnitude change in the ionization probability near threshold. A one-cycle pulse with sine squared envelope might seem unrealistic since the integral over the pulse is not zero for arbitrary $\phi$, that is, in general, the pulse has a non-vanishing dc component. An electromagnetic pulse with a dc component cannot propagate, however, it is in principle possible to create such pulses with a use of a
Figure 6.5: Energy distribution of continuum electrons for a one-cycle laser pulse with $\tau = 0.3$ a.u. and $q = 9 \times 10^{-3}$ a.u. and an assumed $\sin^2$ envelope of duration one cycle for the $\phi = 0$ and $\phi = \pi/2$ cases.

capacitor. In order to show that such phase dependence is present in the result obtained by the FPA, we have considered a two-cycle pulse with the same (sine square) envelope, that is $F_0 \sin^2(\pi t/4\tau) \sin(\pi t/\tau + \phi)$, which does not have a dc component and can therefore model a realistic electromagnetic pulse. From the result of the energy distribution of the ionized electrons presented in figure 6.6, one can see that the same conclusions as in the one-cycle case apply in the two-cycle pulse as well. Namely one still observes strong dependence of the energy distribution on the phase $\phi$. In this case the change of $\phi$ from 0 to $\pi/2$ brings more than one order of magnitude of ionization probability near threshold.

Finally, we consider a general pulse with duration $T$

$$F(t) = F_0 \sin^2 \left( \frac{\pi t}{T} \right) \sin \left( \frac{\pi t}{\tau} + \phi \right), \quad (6.10)$$

where $\tau$ is the duration of a half-cycle. In the FPA the energy distribution of the ejected electrons after a pulse of the type (6.10) is

$$\frac{dP}{dE} = F_0^2 u_1(E) |A(\epsilon, \tau, T)|^2, \quad A(\epsilon, \tau, T) =$$

$$-\frac{1}{4} \left[ e^{i\phi} \left( e^{(\epsilon+\pi/\tau)T} - 1 \right) \left( \frac{1}{\epsilon + \pi/\tau} - \frac{0.5}{\epsilon + \pi/\tau + 2\pi/\tau} - \frac{0.5}{\epsilon + \pi/\tau - 2\pi/\tau} \right)$$

$$- e^{-i\phi} \left( e^{(\epsilon-\pi/\tau)T} - 1 \right) \left( \frac{1}{\epsilon - \pi/\tau} - \frac{0.5}{\epsilon - \pi/\tau + 2\pi/\tau} - \frac{0.5}{\epsilon - \pi/\tau - 2\pi/\tau} \right) \right].$$

46
6.1 Phase dependence

Figure 6.6: The same as in Figure 6.5, except the total duration of the pulse is two cycles.

Figure 6.7: Energy distribution at threshold of continuum electrons for $\tau = 0.3$ a.u. and $q = 9 \times 10^{-3}$ a.u. and an assumed $\sin^2$ envelope of duration $T$ as a function of the ratio $T/\tau$ for the $\phi = 0$ and $\phi = \pi/2$ cases. Graph (b) is the zoomed (a) for small ratios $T/\tau$. 
In the limit $E \to 0$, that is near threshold, the above expression as a function of $T/\tau$ depends on $\phi$ as a parameter. This dependence is illustrated in figures 6.7 and 6.8 where the energy distribution at threshold is plotted as a function of the ratio between the total pulse duration and the half-cycle duration ($T/\tau$), taking the relative phase envelope-carrier $\phi$ to be 0 or $\pi/2$. The high-frequency case (relative to the binding energy of the initial state) is considered in figure 6.7 and the case with 10 times smaller frequency in figure 6.8. Restricting to small values of the ratio $T/\tau$ as in the figures 6.7(b) and 6.8(b), the difference of the energy distribution near threshold for different $\phi$ values is significant, even in the case $\tau = 3$ a.u. This difference persists also for higher ratios $T/\tau$ in the high frequency case (see figure 6.7(a)). On the contrary, as shown in figure 6.8, in the case of ten times smaller frequency this difference disappears by increasing the total pulse duration $T$. Actually the sensitivity of the energy distribution at threshold to the carrier-envelope phase originates from the ionization and recombination which occur periodically in time (see figures 6.3 and 6.4). In the high-frequency case, there is not enough time for the wavefunction to move, so the ionization caused by an odd half-cycle is reversed by the recombination caused by the following (even) half-cycle. Therefore only a negligible ionization takes place during an even number of cycles, for the few-cycle case. On the other hand, in the low-frequency case, the time during a half-cycle is long enough and this results in a non-negligible fraction of the ionized wavepacket leaving the atom and not recombining after the second half-cycle. From figure 6.7 we see that in the FPA the phenomenon of ionization and recombination which occurs periodically in time is not only characteristic of few-cycle pulses, but also persists for longer times.
Chapter 7

The strong-field short pulse case

When $\tau$ is shorter than the initial-state orbital time but $q$ (i.e., $F_0$) is large, then the FMA of equations (5.11) and (5.12) is appropriate. One notes that in this approximation only the integral over the pulse duration appears corresponding to the momentum boost $q$ given by equation (5.11). For a single half-cycle rectangular pulse $q = F_0 \tau$ and for a single half-cycle sinusoidal pulse $q = 2F_0\tau/\pi$. However, the value of $q$ is independent of pulse shape and one can replace $F(t)$ by a $\delta$-pulse i.e.

$$F(t) = q\delta(t-t_1) \quad ; \quad t_1 \in (0, \tau)$$  \hspace{1cm} (7.1)

In the following, we will demonstrate the validity of this approximation explicitly and we will compare the FMA result to exact numerical DVR results for rectangular and sinusoidal pulses. Since, for hydrogenic atoms, the matrix elements of the momentum boost operator are known in closed form [56, 57, 58], the ionization probability (5.12) can be calculated analytically. This is somewhat unusual in the strong-field case where often, even in numerical work, the approximation of reduced dimensionality or cut-off Coulomb potentials have been made.

Initially we consider a single short pulse and examine the momentum spectra of ionized electrons as a function of $q$. In particular we see where the sudden approximation (5.13) is valid. In figure 7.1, we show $dP/dE$ for four values of $q$. On the insets of the same figure we show angular distributions given by

$$A(k) = \int |a(k)|^2 dk.$$  

When $q \ll 1$ a.u. (figure 7.1(a)), one sees that for $dP/dE$ the FMA and its dipole limit, the SA, agree perfectly. For the same case the agreement of the FMA angular distribution (shown on the inset) and the expected $p$-wave angular distribution in the dipole limit is not so good. The angular distribution in the dipole limit has forward-backward symmetry even though the field is unidirectional [59], and as can be seen from figure 7.1(a) the FMA result is not perfectly forward-backward symmetrical although $q$ is very small. This indicates that the angular distribution is a more sensitive test of approximations than the energy distribution. As $q$ is increased the SA breaks down as can be seen already for $q = 0.5$ a.u. in figure 7.1(b), the angular distribution becoming directed strongly along the field. The dipole contribution of the SA remains peaked at zero emission energy but the FMA gradually acquires a peak near to $E = q^2/2 - |E_i|$ as $q$ becomes large. This is the binary peak, well-known in collision physics, corresponding to the initially-bound electron receiving all the transferred momentum,
Figure 7.1: Energy distributions obtained after one short pulse ($\tau \ll 1$) in the FMA and in the SA. The insets show the angular distribution with respect to the field $z$-direction.
with the nucleus acting as a spectator. This simple physical picture is illustrated best in momentum space. The distribution of the initial momentum of the bound electron is given by the momentum space wavefunction \( \phi_i(p) \) i.e. for a 1s electron in a field of a nucleus of charge \( Z \)

\[
\left| \phi_i(p) \right|^2 = \frac{(2Z)^5}{4\pi^2} \frac{1}{(k^2 + Z^2)^4}.
\]

For a large momentum \( k \) of the ejected electron it is sufficient to replace the continuum Coulomb wave by a plane wave so that (5.12) becomes

\[
P_{fi} = \left| \phi_i(q + k) \right|^2 = \frac{(2Z)^5}{4\pi^2} \frac{1}{(|q + k|^2 + Z^2)^4}.
\]

Hence one sees that the initial momentum distribution, centered around momentum \( k = 0 \) from (7.2), is simply lifted, without change of shape, to be centered around \( k = q \) with corresponding energy shift \( q^2/2 + |E_i| \). One also sees from (7.3) that the energy distribution peaks near \( k = q \) \( (E = q^2/2) \) as shown in figure 7.1(d). On the same figure the dotted line, denoted as projection on plane waves, is the energy distribution according to (7.3). Indeed, as \( q \to \infty \) the distribution (7.3) is proportional to \( \delta(q + k) \) expressing the binary condition. From (7.3) the qualitative features of the small \( q \) energy distributions are also established. The distribution (7.2) has a width \( \langle p \rangle \sim Z \) so that for \( q < Z \), the peak of the distribution is not shifted appreciably and the equivalent energy shift \( q^2/2 \) is less than the binding energy \( |E_1| = Z^2/2 \). Hence only the tail of the distribution (7.3) is evident at positive energies i.e. the distribution peaks at \( E = 0 \) as in figure 7.1(a). By contrast for \( q \gg Z \) (= 1 for hydrogen), as in figure 7.1(d), the whole distribution, peaked at the binary condition \( k = q \), is evident. Such a "binary collision" interpretation of energy distributions has already been suggested in references [43] and [19].

7.1 The modified FMA

In the FMA, an even number of half-cycles with the same amplitude results, at the end of the pulse, in no ionization and excitation at all, i.e. it appears that nothing has happened. However, the numerical results show that this is not the case. Therefore, we have modified the FMA to allow propagation in the Coulomb field of the nucleus between the half-cycles. To illustrate this point precisely, in the case of a single-cycle pulse one approximates the influence of one cycle by two alternating \( \delta \)-pulses, each of them with an amplitude equal to the momentum transfer \( q \) as defined in (7.1), and a time shift between the \( \delta \)-pulses equal to a half-cycle duration (illustrated in figure 7.7(b)). Here one should mention two points. First, although this modified FMA is formally similar to the numerical split-operator method [60] we use only one \( \delta \)-function per half-cycle, the use of a \( \delta \)-function meaning that in the moment of interaction the Coulomb field is neglected. The second point concerns the short interaction time which is crucial for the validity of our modified FMA. Because of the short interaction time, the electronic wavefunction does not have time to move away from the Coulomb center and therefore the electron must be described by Coulomb waves i.e. approximating the continuum eigenstates as plane waves is inappropriate. Such an intuitive approximation of the sinusoidal time-dependence of the pulse by a train of alternating \( \delta \)-pulses has been already considered in a purely numerical study [61] where qualitative features of ionization from a softcore potential for pulses of around 50 cycles were considered.
In the modified FMA, $N$-cycles are equivalent to a sequence of $2N$ $\delta$-pulses of alternating sign separated by the half-cycle time $\tau$ i.e.

$$F(t) \approx F_N(t) = q \sum_{j=0}^{2N-1} (-1)^j \delta(t - j\tau). \quad (7.4)$$

In this case the transition amplitude becomes

$$a_{fi}(N) = \langle \phi_f | e^{iqr} e^{-iH_0\tau} \left(e^{-i\alpha r} e^{-iH_0\tau} e^{iqr} e^{-iH_0\tau}\right)^{N-1} e^{-iqr} | \phi_i \rangle. \quad (7.5)$$

### 7.2 Half-cycle case

We will consider the case of a single half-cycle pulse ($N = 1/2$ in (7.4)). From figure 7.2(a) one sees that for $q > 3$ a.u. all atoms are ionized after the pulse (the FMA result agrees perfectly with the DVR results in this case). As a function of $q$ the de-population of the ground state is continuous and monotonic. However, the population of the $n$-th shell shown in figure 7.2(b) first increases with $q$ and then decreases to zero. The probability of excitation of the $n$-th shell from the ground state in the FMA can be calculated following the general procedure outlined in [56] to give

$$P_{n1}(q') = \frac{2^8 n^7 q'^2 \left[n^2(3q'^2 + 1) - 1\right]}{3 \left[(n^2q'^2 + 1)^2 + 2n^2(n^2q'^2 - 1) + n^4\right]^3} \left(\frac{n^2q'^2 + (n - 1)^2}{n^2q'^2 + (n + 1)^2}\right)^n, \quad (7.6)$$

where $q' = q/Z$ is the momentum boost scaled by the nuclear charge $Z$. This function exhibits a maximum which is located at increasing $q'$ as $n$ increases. For $n = 2$ the maximum is at $q' \approx 0.75$ a.u., and as $n \to \infty$ it shifts to $q' \approx 0.9$ a.u. From figure 7.2(b) one sees that this is the $q$ region in which the excitation probability maximizes. As seen in figure 7.2(a), this also coincides with the rapid increase of ionization probability. In figure 7.2 the probabilities obtained from a DVR calculation using both rectangular and sinusoidal pulses are shown also. In all cases the exact DVR results for both pulse forms agree perfectly with the FMA result on the scale of figure 7.2.

### 7.3 One-cycle case

The fact that for large enough $q$ all atoms are 100% ionized after a half-cycle pulse can be used to advantage to derive approximate analytic expressions for initial-state populations after $N$ complete cycles of the field. We begin with $N = 1$ where equation (7.4) reduces to

$$a_{fi}(1) = \langle \phi_f | e^{iqr} e^{-iH_0\tau} e^{-iqr} | \phi_i \rangle. \quad (7.7)$$

If we introduce a complete set of hydrogen eigenstates as intermediate states then (7.7) becomes
CHAPTER 7: The strong-field short pulse case

7.3 One-cycle case

Figure 7.2: Probability of (a) ionization and population of the $Z = 1$ ground state, and (b) population of the $n=2,3,4$ shell, after one half-cycle pulse. The FMA is compared to the numerical calculation (DVR) for both sinusoidal and rectangular pulses.
\[ a_{f_1}(1) = \sum_{n=1}^{\infty} \langle \phi_f | \exp(i\mathbf{q} \cdot \mathbf{r}) | \phi_n \rangle \langle \phi_n | \exp(-i\mathbf{q} \cdot \mathbf{r}) | \phi_i \rangle \exp(-iE_n \tau) \]
\[ + \int d^3k \langle \phi_f | \exp(i\mathbf{q} \cdot \mathbf{r}) | \phi_k \rangle \langle \phi_k | \exp(-i\mathbf{q} \cdot \mathbf{r}) | \phi_i \rangle \exp(-i \frac{k^2}{2} \tau). \]  
(7.8)

In figure 7.3(a) the full circles show the decreasing probability of being in the ground state after a one-cycle pulse as \( q \) is increased. At \( q \approx 3 \) a.u. this amounts to around 75%. However this cannot be assigned to population which has remained in the ground state. In figure 7.3(a) is also shown (empty circles) the probability of ionization after a half-cycle pulse, obtained by numerical DVR calculation, which is in perfect agreement with the FMA half cycle result (dotted line). For \( q \approx 3 \) a.u. this amounts to almost 100%. Hence one concludes that on the first half-cycle all electrons are ionized and 80% of them are returned to the ground state by the second half-cycle. This extremely large probability of recombination corresponds then to "Rabi flopping" on the continuum [50]. That this interpretation is correct is also to be seen from the dashed line in figure 7.3(a). This denotes the final ground-state population emanating from the electrons in the continuum after a half-cycle. Above \( q \approx 2.5 \) a.u. the final population of the ground state has come exclusively from recombination of continuum electrons. Since this is so, we can see that, above \( q \approx 2.5 \) a.u., one can neglect the contribution of all bound states as intermediate states in equation (7.8). Then, if we assume that the discrete initial and the final states are identical, the probability of population of the initial state after the second \( \delta \)-pulse is

\[ P_{ii} = \left| \int d^3k |\langle \phi_k | \exp(-i\mathbf{q} \cdot \mathbf{r}) | \phi_i \rangle|^2 \exp(-i \frac{k^2}{2} \tau) \right|^2. \]  
(7.9)

In the case when the initial state is the ground state the above expression reduces to, (denoting \( P_{ii} \) simply as \( P_1 \))

\[ P_1 = \left| \int I(k') \exp(-i \frac{k'^2}{2} \tau') \, dk' \right|^2, \]  
(7.10)

where the scaling \( k' = k/Z, \tau' = \tau Z^2 \) is used and the function \( I(k') \) is given by [50, 51, 58].

\[ I(k') = \frac{2^8 q'^2 k'(3q'^2 + k'^2 + 1) \exp \left[-(2/k') \tan^{-1} \left(2k'/(q'^2 - k'^2 + 1)\right)\right]}{3[(q' - k')^2 + 1]^3[(q' + k')^2 + 1]^3[1 - \exp(2\pi/k')]}. \]  
(7.11)

In the limit \( q' \to \infty \), one obtains the following asymptote

\[ I(k') \approx \frac{8}{3\pi} \frac{1}{[1 + (q' - k')^2]^3}. \]  
(7.12)

If we linearize the \( k' \)-dependence of the energy phase factor in equation (7.10) i.e.

\[ \exp(-i \frac{k'^2}{2} \tau') \approx \exp(-i(k' - q')q' \tau') \exp(-i \frac{q'^2}{2} \tau') \]  
(7.13)
CHAPTER 7: The strong-field short pulse case

7.3 One-cycle case

Figure 7.3: a) The probability $P_1$ of occupation of the ground state after a one-cycle sine pulse and the probability $P_{ion}$ of occupation of continuum states after a half-cycle. b) The same probabilities for the 2s initial state. In both cases $Z = 1$. 
CHAPTER 7: The strong-field short pulse case

7.3 One-cycle case

Figure 7.4: Full lines: ground state occupation probability after a one cycle sine pulse for different $\tau$’s according to the asymptotic formula (7.14). Dashed line: probability of ionization after the first half cycle. Results are plotted for $Z = 1$.

then one can integrate the above asymptotic expression and the ground state occupation probability assumes the simple analytic form

$$P_{1}^{as.} = \exp(-2q'\tau') \left( 1 + q'\tau' + \frac{(q'\tau')^2}{3} \right)^2.$$ (7.14)

From figure 7.4(a) one sees that this analytic form for $P_1$ (denoted by the continuous line) agrees with the numerical DVR result for $q > 3$ a.u. However, although the approximation that only continuum states function as intermediate states is not justified for $q < 2.5$ a.u., the analytic asymptote is valid all the way down to $q = 0$. This is a happy accident caused by the fact that expression (7.14) has the correct $q = 0$ value and the probability is smooth and monotonic in $q$.

The monotonic decrease of $P_1$ as a function of $q$ is shown in figure 7.4 for various values of $\tau$. Also shown is the ionization probability after a half-cycle, which in the FMA depends only on $q$ and not on $\tau$. One sees that for $\tau = 0.1$ a.u. even at $q = 6$ a.u., 90% of the population returns to the ground state. Recombination at the 80% level is still achieved at $q = 0.9$ a.u. for $\tau = 0.9$ a.u. The qualitative behavior of the curves of figure 7.4 is readily understood in the region $q > 3$ a.u. The first pulse puts electrons in the continuum centered around $k = q$. Hence the electrons have time $\tau$ to diffuse away before the recombining pulse occurs. The larger is $q$ and the longer is $\tau$, the more electrons will diffuse out of the ground state wavepacket whose initial momentum-space coherent shape is unchanged by the impulsive transfer of momentum. The more electrons diffuse away, the fewer are available to be recombined by the second half of the one-cycle pulse.
CHAPTER 7: The strong-field short pulse case

7.3 One-cycle case

Figure 7.5: The time evolution of the probabilities of the population of the ground state ($P_1$) and the ionization probability ($P_{\text{ion}}$) during one-cycle sine pulse for $F_0 = 5\pi$ a.u., $\tau = 0.3$ a.u. Results are plotted for $Z = 1$.

Calculations have been performed also for initial 2s and 2p states. The results for 2s, for the same $q$ and $\tau$ values shown in figure 7.3(a) for 1s, are given in figure 7.3(b). One notes that already for $q > 1$ a.u., 100% ionization is caused by the first half-cycle pulse. Compared to the ground state, this lower value of $q$ to achieve ionization is simply due to the lower binding energy. The minimum "momentum kick" to be given to a bound electron to ionize is given by $\frac{1}{2}q^2 = \frac{1}{2}Z^2/n^2$, i.e. by $q = Z/n$. This gives $q = 1$ a.u. for the $n = 1$ ground state of hydrogen and $q = 0.5$ a.u. for $n = 2$. This is in rough agreement with the onset of ionization shown in figure 7.3. One also notes, from the exact DVR results for $P_{2s}$ after a one-cycle $\tau = 0.3$ a.u. pulse shown in figure 7.3(b), that now at $q = 3$ a.u., 90% of the ionized electrons recombine. For a 1s initial state this value is 80%. From the arguments given above one might expect that the number of electrons escaping before recombination depends only on $q$ and $\tau$. However the reduction for the 2s is readily explicable. The width of the continuum momentum distribution (the ground state distribution boosted by momentum $q$) is proportional to $Z/n$. Clearly it is the high momentum electrons which diffuse away fastest and, as the momentum spread of 2s is a factor of 2 smaller than for 1s, there is less diffusion out of the coherent momentum wavepacket and therefore a higher recombination probability.

Using a similar procedure as led to equation (7.14) (see Appendix C), one can obtain an asymptotic expression for the population of the 2s state after a full cycle pulse, when one starts from the 2s state. This is given by

$$P_{2s}^{as} = \exp(-q'\tau) \left(1 + \frac{q'^2}{2} + \frac{(q'\tau')^2}{12} + \frac{(q'\tau')^4}{240}\right)^2.$$ (7.15)
CHAPTER 7: The strong-field short pulse case

7.4 Few-cycle case

This curve is shown in figure 7.3(b) as a continuous line and, as in the 1s case, is in perfect agreement with DVR results, not only for asymptotically large \( q \) but over the complete range of \( q \) values.

In figure 7.6 we present the time-development of the occupation probability of initial 1s (\( P_{1s}(t) \)) and continuum states \( P_{\text{ion}}(t) \) which shows explicitly that in a single full-cycle pulse, almost 100% ionization occurs after a half-cycle and \( \sim 80\% \) recombination after a full cycle. Note that this process is entirely to be distinguished from the "stabilization" of the ground state. Rather, over a small range of of \( q \) one has a process more akin to "Rabi flopping" between continuum and the ground state.

In figure 7.6 we show the same plots for an initial 2s or 2p state, for the same \( q \) and \( \tau \) values. In this case one notes a rapid full depletion of the initial state into the continuum and then 90% repopulation of the initial state. One might question why re-population occurs almost exclusively into the original initial state, since after 100% ionization all bound states are unoccupied. Presumably, the answer simply lies in the fact that the initial bound-state momentum wave packet \( \hat{\phi}_i(p) \) is transferred unaltered to \( \hat{\phi}_i(p + q) \) on the first half-cycle. If there is no appreciable spreading of this packet before the second half-cycle, which provides momentum \( q \), then the whole wavepacket becomes \( \hat{\phi}_i(p) \) again, which has zero overlap with states other than the initial state \( i \).

7.4 Few-cycle case

Even more interesting is a train of \( N \) pulses. The TDSE equation (5.5) has been solved exactly numerically to obtain the initial state and continuum populations as a function of time and the results are presented for an initial 1s state in figure 7.8 for a two-cycle train and in figure 7.9 for a five-cycle train of pulses. The modified FMA for the transition amplitude is given by equation (7.5) and represented symbolically in figure 7.7 by a train of alternating \( \delta \)-pulses. A negative amplitude represents the pulse which returns the continuum electron to the initial state, where it remains until a positive amplitude pulse puts it back in the continuum after a lapse time \( \tau \). During this time the time-dependent wavefunction simply acquires a constant phase \( \exp(-iE_i\tau) \). For \( N \) pulses this is a phase \( \exp(-iE_iN\tau) \) which does not contribute to
Figure 7.7: (a) Electric field time dependence \( F(t) \). (b) A train of alternating \( \delta \) pulses modelling the electric field \( F_N(t) \). Shaded regions denote the time intervals in which the population is entirely in the continuum. (c) The equivalent one-cycle pulse \( F_1(t) \).

\[ P_{fi} = |a_{fi}|^2 \] from equation (7.5). This implies that in (7.5) one can put

\[ e^{-iqr} e^{-iH_0 \tau} e^{iqr} = 1 \]  

(7.16)

to give, as simplification

\[ a_{fi}(N) = \langle \phi_f | e^{iqr} e^{-iH_0 N \tau} e^{-iqr} | \phi_i \rangle . \]  

(7.17)

That is, a train of \( N \) cycles is equivalent, in this approximation to the modified FMA of (7.5), to a one-cycle pulse with a delay of \( N \tau \) between half cycles. This approximation is shown symbolically in figure (7.7(c)) with the equivalent one-cycle pulse \( F_1(t) \). Hence the analytic forms (equations (7.14) and (7.15)) for the population of the initial state after one cycle can be applied for \( N \) cycles, simply by replacing \( \tau' \) by \( N \tau' \). The results of this approximation are shown also in figures (7.8 and 7.9) after each cycle and are in very good (and sometimes perfect) agreement with the accurate DVR results.

Figure (7.8) illustrates the Rabi flopping from the ground state for relatively large \( q \) values and for \( \tau = 0.3 \) a.u. and 0.1 a.u., and a total duration of two cycles i.e. \( t = 4 \tau \). One sees clearly again that for larger \( q \) and shorter \( \tau \) the Rabi flopping is less damped. The \( N \)-cycle results are shown in figure (7.9) and illustrate that the rate of decrease of \( P_1 \) as \( q \tau \) increases...
Figure 7.8: Full lines: \( Z = 1 \) ground state occupation probability as a function of time for a pulse with different \( \tau \)'s. Dotted lines: probability of ionization. Full circles: analytic asymptotic expression for the ground state occupation probability after \( N \) full cycles (\( N = 1 \) to 2).
CHAPTER 7: The strong-field short pulse case

7.4 Few-cycle case

Figure 7.9: Full lines: $Z = 1$ ground state occupation probability as a function of time for a pulse with different $\tau$'s. Dotted lines: probability of ionization. Full circles: analytic asymptotic expression for the ground state occupation probability after $N$ cycles ($N = 1$ to 5).
Figure 7.10: Full line: 2s state occupation probability as a function of time for $Z = 1$. Dotted line: probability of ionization. Full circles: analytic asymptotic expression for the initial state occupation probability after $N$ cycles ($N = 1$ to 2).

is quite strong, i.e., as expected from equation (7.17), one needs $q \tau \ll 1$ a.u. but also $q > 1$ a.u. and therefore $\tau \ll 1$ a.u. to achieve significant Rabi flopping over a few cycles. The $N$-cycle formula (7.17) agrees also for the 2s state as we have explicitly checked by a numerical calculation, as illustrated in figure 7.10.
Chapter 8

Conclusions

In this part of the thesis we have examined the ionization of a hydrogenic atom from the $n = 1$ and $n = 2$ states by short laser pulses consisting of a half-cycle up to the order of five full cycles. The common characteristic of the pulses considered here is that the half-cycle duration is short compared to the electron orbital time. In the cases of both weak and strong peak amplitudes of the field we identify a process of ionization and recombination which occurs periodically in time. Three levels of analytic approximation have been compared and contrasted:

1. the FPA appropriate for weak pulses,
2. the FMA, appropriate for short pulses, and
3. the modified FMA which includes the propagation in the Coulomb field of the nucleus, appropriate to obtain the extent of recombination in the strong-field limit.

In the case of strong fields, we have used the DVR code to obtain fully converged numerical solutions of the time-dependent problem which were used as a benchmark to test the analytic approximations.

In the case of small peak amplitudes, we have used the FPA. For a finite number of pulses the energy distribution shows considerable structure, peaking at zero electron emission energy for $\tau < 1$ a.u. However, when $\tau > 1$ a.u. or the number $m$ of half-cycles tends to infinity, a peak appears in the energy spectrum correspondingly to the energy conservation condition for one-photon absorption i.e. at electron energy $E = -|E_i| + \pi/\tau$. For a small number of cycles, beginning with a half-cycle $N = 1/2$, we have shown that the population of excited and continuum states, though small, exhibits oscillations in time, with a maximum for odd $m$ and a minimum for even $m$. This is the reason why, particularly for low-energy electron emission, the ionization probability shows strong dependence on the phase of the pulse with respect to the maximum of the carrier envelope. Furthermore, we have shown that in the high-frequency case the dependence of the energy distribution at threshold from the carrier-envelope phase persists also for more cycles.

In the FMA for $\tau \ll 1$ a.u. we have shown that the ionization probability is independent of the precise shape of the pulse and in the modified FMA can be represented as a train of alternating $\delta$-pulses separated by a time $\tau$. Namely, in the original FMA applied to the whole pulse consisting of even half-cycles the effect of the opposite kicks is to cancel each other, resulting in no change of the initial state. This deficiency has been overcome by modifying
the FMA to include the propagation of the wavefunction in the Coulomb field of the nucleus. The transition amplitude after each half-cycle is decided by the momentum boost operator $\exp(-i\mathbf{q} \cdot \mathbf{r})$, where $-\mathbf{q}$ is the momentum transferred from field to the atom. The analogy here to the scattering of fast charged particles has been emphasized. For small $\mathbf{q}$, such that $\mathbf{q} \cdot \mathbf{r} \ll 1$ for all relevant $r$ values, only the dipole term is important and this "sudden approximation" gives a $\cos^2 \theta$ angular distribution, as in the FPA and an energy distribution peaking at $E = 0$ for a single half-cycle pulse. However, as $q$ increases the angular distribution becomes more and more peaked along the field direction. The energy shows a maximum at the "binary peak" corresponding to transfer of all momentum to the electron with the nucleus acting as spectator. In the FMA the angular distribution becomes more and more peaked along the field direction as the momentum transfer is increased.

For $N = 1/2$, all probability is transferred to the continuum when $q$ exceeds approximately 2 a.u. for the $1s$ state and 1 a.u. for the $2s$ state. For these $q$ values, for $N = 1$ almost all probability returns to the initial state, a process akin to Rabi flopping from the continuum. For the $n = 2$ state, this process is even more pronounced. So long as $\tau \ll 1$ a.u. this flopping continues for several cycles before the initial state is appreciably de-populated.

Under the approximation that, for $N$ equal to a half-integer, all population previously in the initial state is transferred to the continuum and in the subsequent half-cycle is transferred back to the initial state, a simple analytic form has been obtained for the population of the initial state ($1s$ or $2s$) after $N$ cycles (see equations (7.14) and (7.15)). This formula, strictly speaking, is an asymptotic expression in the modified FMA in the limit of infinite momentum transfer $q'$, but valid for all $q'$. Initially derived for one cycle, it has been extended to $N$-cycles. For both $1s$ and $2s$ as initial state this formula is in excellent agreement with the exact DVR result. Its remarkable simplicity and the range of validity makes the formula a possible candidate for rapid estimation of the initial-state occupation probability for strong-field attosecond pulse excitation and ionization.

The calculations have been carried out on the hydrogen atom so that numerical results can be obtained without further approximation and the analytic results in closed form. However the key results in short pulse ionization depend only on the fact that the orbital time in the initial state is much longer than the pulse duration $\tau$ and that the momentum transfer $q$ is much larger than the width of the momentum distribution of the initial state. For hydrogenic atoms this width is $Z/n$ or $|2E_i|^{1/2}$ where $|E_i|$ is the initial state binding energy. Hence for non-hydrogenic atoms equivalent results should be obtained with qualitatively similar character if $q\tau$ in atomic units is scaled by a factor $|2E_i|^{1/2}$.

In contrast to this and the previous part where we looked at the long pulse limit (Part I) and very short-time limit, in the next part we cover the entire time scale. In particular we focus on times "in between" the very short and very long pulse, that is when the time scale of the external excitation of the system is of the same order of magnitude as the dynamics of the system in its initial state. We uncover a phenomenon of resonant excitation and ionization by a unidirectional electric pulse, occurring in two different atomic systems, namely the hydrogen atom and a negative ion.
Part III

Resonant excitation and ionization
Chapter 9

Ionization of a negative ion by an electric field pulse

9.1 Introduction

In the previous two parts of the thesis we have analyzed the dynamics of the hydrogen atom both in the slowly-varying pulse limit (Part I) and the short-pulse limit (Part II). Here we will rather consider response of an atomic system to a unidirectional electric field pulse with Gaussian time-dependence and duration ranging from very short to very long. Two different atomic systems will be considered: a negative ion and the hydrogen atom. We will show and explain an effect of nonmonotonic dependence of the ionization probability on the pulse width at constant amplitude, present in both systems studied. Although in the case of a negative ion the process of promotion of the outer electron to the continuum is called \textit{detachment}, in this part of the thesis we will call it \textit{ionization} to facilitate comparison with the case of hydrogen.

The first chapter of this part of the thesis contains a study of ionization of negative ions by a Gaussian pulse. We begin the first chapter by introducing the three-dimensional zero-range potential (ZRP) which will serve to model the negative ion. In the second section, a survey of the studies using the ZRP to model atomic systems is presented. Next, the time-dependent problem is solved \textit{ab initio} in section 3, whereas the solution of the corresponding stationary problem considered in the context of the adiabatic approximation is presented in section 4. The analytic approaches valid in the short-time limit are reviewed in section 5. The last section of this chapter contains a detailed comparison of the numerical and analytic results.

The second chapter of this part, Chapter 10, focuses on the discussion of the nonmonotonic behavior of the ionization and excitation probability with respect to the pulse width.

9.2 The zero-range potential

The zero-range potential can be considered as a limiting case of a central potential well of depth $U_0$ and radius $b$ \cite{63}, that is a potential $V_c(r)$ defined as

$$V_c(r) = \begin{cases} 
-U_0, & r < b \\
0, & r > b 
\end{cases}$$

(9.1)
We assume that the electron is in the $s$-state ($l = 0$), that is the potential is such that it supports only one bound state. In order for this to be satisfied, the potential should be such that \( \pi^2/8 < U_0 b^2 < 9\pi^2/8 \). Then the wavefunction of the electron is

\[
\psi(r) = C \frac{\exp(-\alpha r)}{r}, \quad \text{for} \quad r > b.
\] (9.2)

where \( \alpha = \sqrt{2|E_0|} \), \( |E_0| \) is the binding energy, and \( C \) is a normalization constant. In the limiting case when one increases the depth of the well \( U_0 \to \infty \) in such a way that the binding energy stays constant (this is accomplished by keeping the product \( U_0 b^2 \) constant), the radius of the potential well goes to zero. Therefore the boundary condition for the logarithmic derivative of the function \( r \psi \) at \( r \to 0 \) is

\[
\left. \frac{1}{r \psi} \frac{\partial (r \psi)}{\partial r} \right|_{r=0} = -\alpha.
\] (9.3)

In order to find the form of the zero-range potential \( V(r) = \lim_{U_0 \to \infty} V(r) \) we first expand \( \Psi \) in the vicinity of \( r \to 0 \) as

\[
|\psi(0)|_{r \to 0} = C \left( \frac{1}{r} - \alpha \right) + O(r).
\] (9.4)

Applying the total Hamilton operator \( \hat{H} = -\Delta/2 + V(r) \) to the wavefunction \( \psi \) and taking into account its behavior at the origin we obtain the eigenvalue equation as

\[
\left( -\frac{1}{2} \Delta - E_0 \right) \psi = -\frac{2\pi}{\alpha} \delta(r) \frac{\partial (r \psi)}{\partial r}
\] (9.5)

from where one identifies the ZRP as

\[
V(r) = \frac{2\pi}{\alpha} \delta(r) \frac{\partial}{\partial r} r.
\] (9.6)

The normalized bound-state eigenfunction of this potential is given by

\[
\phi_0(r) = \left( \frac{\alpha}{2\pi} \right)^{1/2} e^{-\alpha r} \frac{1}{r},
\] (9.7)

and the continuum eigenfunctions are

\[
\phi_k(r) = (2\pi)^{-3/2} \left( e^{ikr} - \frac{1}{\alpha + ik} e^{ikr} \right).
\] (9.8)

The potential is the three-dimensional zero-range potential (3D ZRP). In the one-dimensional case (1D) a similar procedure as outlined above leads to the following form of the ZRP

\[
V_{1D}(x) = -\alpha \delta(x).
\] (9.9)

The above \( \delta \) potential has been used in many analytic and numerical studies which will be reviewed in the next section. However, in this chapter we will use the 3D ZRP.

Among the systems which can be modelled by a ZRP potential is the negative ion with outer weakly-bound electron in an $s$-state. This one-electron model of the negative ion will be adopted in this study, as done in many other studies (see, for example [64, 65, 66, 67, 68]. A detailed discussion of the possible application of the ZRP to problems in atomic physics can be found in the book of Demkov and Ostrovskii [63].
9.3 Historical survey of studies using zero-range potentials as a model of an atomic system

There has been a large number of studies involving electrons bounded by a ZRP in an electric field. They can be divided into studies considering either stationary fields, laser ionization or response to a step-like time-dependent electric field.

The first study of the decay of the bound state of a 3D ZRP by a stationary electric field was conducted forty years ago by Demkov in reference [64]. There the quasistationary problem for a 3D ZRP was investigated and expressions for the stationary Green’s function and tunnelling rate in a weak stationary field were derived. Much later the same problem was studied in reference [65] in the context of comparison between semiclassical and quasistationary approaches and essentially the same results were rederived.

Time-dependent studies involving ZRP begun with the paper of Geltman [69] where a 1D δ-potential atom model was used to study ionization of atoms by laser pulse. Since then many such studies were performed in order to model both negative ion detachment or ionization of one-electron atoms by laser fields. In the 90’s the ZRP was used as a model atom for multiphoton ionization studies. For example, the 3D ZRP was used to obtain multiphoton ionization rates [66] and to model high-harmonic generation [67] from atoms subject to intense circularly and elliptically polarized laser fields. One of the rare time-dependent numerical approaches, which in principle can be used to study the response to an electric field pulse was performed in the reference [70], however, only for a 1D ZRP. A review of multiphoton ionization (detachment) of negative ions can be found in reference [68]. The most recent studies involving ZRP consider ionization of a one-electron atom in very strong laser fields [71], where the 1D ZRP was employed, and negative ion detachment by a few cycle laser pulse [72], where the 3D ZRP was used.

The case of ionization of an electron, bound by a 1D ZRP, by an electric field with step-like (rectangular) time-dependence was considered in many papers. The calculation was carried out for the first time in reference [73] in the length gauge, whereas the first such calculation in the velocity gauge was done in reference [74]. Perhaps the most extensive study of this type was made in reference [75], where many different approximations were compared to "exact" numerical calculations. However to date there is no time-dependent study for a 3D ZRP in the presence of a unidirectional electric field pulse with non-step-like (non-rectangular) time dependence. We will solve this problem numerically in the next section.

9.4 Solution of the nonstationary problem

The nonstationary Schrödinger equation governing the dynamics of the outer electron of a negative ion in the presence of a time-dependent electric field is

\[
i \frac{\partial \psi(\mathbf{r}, t)}{\partial t} = \left( -\frac{1}{2} \Delta_{\mathbf{r}} + V(\mathbf{r}) + F(t)z \right) \psi(\mathbf{r}, t),
\]

where \( V(\mathbf{r}) \) is the 3D ZRP defined in equation (9.6). In this study we restrict our analysis to the response of a negative ion to a (half-cycle) pulse of Gaussian time dependence:

\[
F(t) = F_0 e^{-\left( t/\tau \right)^2}.
\]
We perform a transformation of the equation (9.10) by introducing scaled time and space coordinates: \( t' \to \alpha^2 t', \quad r' \to \alpha r \) and obtain the scaled version of (9.10):

\[
 i \frac{\partial \psi(r', t')}{\partial t'} = \left( -\frac{1}{2} \Delta_{r'} + 2\pi \delta(r') \frac{\partial}{\partial r'} r' + F'(t') \right) \psi(r', t') \tag{9.12}
\]

where \( F'(t') = F_0' e^{-(t'/\tau)^2} \) \( (F_0' = F_0/\alpha^3, \tau' = \alpha^2 \tau) \) is the scaled electric field and bound state energy \( E_0' = -1/2 \) a.u. The scaling enables us to carry out the calculations normalized to \( \alpha \). In this and the following section we will consider the scaled equation (9.12) and omit the primes.

The solutions of equation (9.12) satisfy the homogeneous integral equation [67]

\[
 \psi(r, t) = \int_{-\infty}^{t} dt' \int d^3r' G(r, t; r', t') V(r') \psi(r', t'), \tag{9.13}
\]

where \( G \) is the Volkov Green’s function

\[
 G(r, t; r', t') = G^{(0)}(r - r', t - t') e^{-i\mathcal{M}(t, t') - i\mathcal{R}(r, r', t')}, \tag{9.14}
\]

and

\[
 G^{(0)}(r, t) = -i \theta(t) \frac{\exp \left( i r^2 / 2t \right)}{(2\pi it)^{3/2}} \int_{t - t'}^{t} dt'' A^2(t'') - \frac{1}{t - t'} \left( \int_{t - t'}^{t} dt'' A(t'') \right)^2 \tag{9.15}
\]

\[
 \mathcal{M}(t, t') = \frac{1}{2} \left[ \int_{t}^{t'} dt'' A^2(t'') - \frac{1}{t - t'} \left( \int_{t}^{t'} dt'' A(t'') \right)^2 \right]
\]

\[
 \mathcal{R}(r, t; r', t') = -\left( A(t) \cdot r - A(t') \cdot r' - \frac{r - r'}{t - t'} \int_{t'}^{t} dt'' A(t'') \right).
\]

Here \( G^{(0)} \) is the Green’s function of a free electron, \( \theta(t) \) is the Heaviside step function and \( A(t) = -\int_{-\infty}^{t} dt' F(t') \) is, apart from a constant equal to the speed of light, the vector potential. The equation (9.13) does not contain the inhomogeneous term which one would normally have for an integral equation of Lippmann-Schwinger type. In our special case, starting from the bound state at \( t \to -\infty \), and using the properties of the zero-range potential, it can be shown that the solution of the form (9.13) satisfies the initial conditions of equation (9.12).

Since the potential \( V(r) \) includes a \( \delta \)-function, the integral equation (9.13) can be simplified [67]. We define a quantity \( R(t) \):

\[
 R(t) = -2(2\pi)^{1/2} e^{-i t^2 / 2} \lim_{r \to 0} \frac{\partial}{\partial r} r \psi(r, t), \tag{9.16}
\]

so the integral equation (9.13) transforms into

\[
 R(t) = 2\pi \lim_{r \to 0} \frac{\partial}{\partial r} r \int_{-\infty}^{t} dt' G^{(E)}(r, t, 0, t') e^{-i(t-t')/2} R(t'). \tag{9.17}
\]
CHAPTER 9: Ionization of a negative ion by an electric field pulse

9.4 Solution of the nonstationary problem

The integral and the limit \( r \to 0 \) in (9.17) do not commute, since as a result of integration one obtains a term proportional to \( r^{-1} \). We can regularize the integral by writing

\[
R(t) = 2 \pi \lim_{r \to 0} \frac{\partial}{\partial r} \left[ \int_{0}^{\infty} dt' \left( \frac{i}{2 \pi t'} \right)^{3/2} e^{i r^2 / 2 t'} \times \left[ e^{-i M(t,t-t')} e^{-i R(r,t,0,t-t')} e^{-i \frac{e}{2 t'} R(t-t') - R(t)} + R(t) \right] \right].
\]

(9.18)

Here the integration of the last term on the right hand side of the above equation gives a result directly proportional to \( r^{-1} \), that is,

\[
\int_{0}^{\infty} dt' \left( \frac{i}{2 \pi t'} \right)^{3/2} e^{i r^2 / 2 t'} R(t) = - \frac{R(t)}{2 \pi r}.
\]

(9.19)

Therefore the above term does not contribute and the limit now commutes with the rest of the terms so we obtain

\[
R(t) = - \left( \frac{1}{2 \pi i} \right)^{1/2} \int_{0}^{\infty} dt' \left[ e^{-i M(t,t-t')} e^{-i \frac{e}{2 t'} R(t-t') - R(t)} \right].
\]

(9.20)

When \( R(t) \) is calculated, one can obtain the wavefunction as

\[
\psi(r, t) = (2 \pi)^{-1/2} e^{i t f_0^2 / 2} \int_{0}^{\infty} dt' e^{i r^2 / 2 t'} e^{-i M(t,t-t')} e^{-i R(r,t,0,t-t')} R(t-t').
\]

(9.21)

The integral equation (9.20) is solved by using a numerical procedure outlined in Appendix D.

In cases where only the ground state probability or the probability of ionization is needed, calculating \( R(t) \) is sufficient since

\[
\lim_{t \to \infty} \left| \langle \phi_0 | \psi \rangle \right|^2 = \lim_{t \to \infty} |R(t)|^2.
\]

(9.22)

Note that equation (9.22) does not hold for arbitrary \( t \). The reason for this is that in the case of arbitrary \( t \), \( R(t) \) contains contributions both from the ground state and the spherical wave part of the continuum eigenfunctions since both contain the term \( r^{-1} \). As the field is turned off the spherical wave leaves the origin, and only the bound eigenfunction is left. That occurs immediately after the turning off of the pulse. The time needed for the spherical wave to propagate away from the origin depends on the momentum distribution of the ionized wavepacket. If \( \tau \) and \( F_0 \) are small, the momentum distribution of the ionized wavepacket will be concentrated at small momenta. In this case when doing a numerical calculation of \( R(t) \) one has to wait more time after the field turn-off so that the ionized wavepacket leaves the origin and \( R(t) \) attains a stationary value. On the other hand, for longer \( \tau \) and \( F_0 \), \( R(t) \) attains its stationary value immediately after the end of the pulse, that is at \( t = 3 \tau \).
CHAPTER 9: Ionization of a negative ion by an electric field pulse

9.5 The adiabatic approach

As it was pointed out in Part I of this thesis, in the adiabatic approach two steps are necessary: first, the definition of an adiabatic basis and solution of the stationary problem, and second, the calculation of the probability of nonadiabatic transition. Here, as in the case of the hydrogen atom in an external field, we take quasistationary (decaying) states as the adiabatic states.

9.5.1 Quasistationary state

In the case of an electron bound by a ZRP in the presence of a stationary electric field, there is only one quasistationary state, corresponding to the one bound state supported by the potential, in the limit $F \to 0$. The quasistationary state satisfies the eigenvalue equation

$$(E + \frac{1}{2} \Delta - Fz) \chi(r, F) = \frac{2\pi}{\alpha} \delta(r) \frac{\partial}{\partial r}(r \chi(r, F)).$$

(9.23)

In the above equation $E$ is the complex eigenvalue (the adiabatic potential curve), and $\chi$ is the instantaneous eigenfunction. Both $E$ and $\chi$ depend on the adiabatic parameter $F$. We can express $\chi$ in terms of the stationary Green’s function of the problem which satisfies

$$(E + \frac{1}{2} \Delta - Fz) G(r, r'; E) = \delta(r - r').$$

(9.24)

Comparing (9.23) with (9.24), one obtains

$$\chi(r, F) = \frac{2\pi}{\alpha} G(r, 0; E) \lim_{r \to 0} \frac{\partial(r \chi(r, F))}{\partial r}. \quad (9.25)$$

The stationary Green’s function can be calculated explicitly and expressed in terms of Airy functions (under the assumption $F > 0$).

$$G(r, 0; E) = \frac{1}{2r} \left( Ci(b + ar_<)Ai'(b + ar_<) - Ci'(b + ar_<)Ai(b + ar_<) \right), \quad (9.26)$$

where $r_> = (r + z)/2$, $r_< = -(r - z)/2$, $a = (2F)^{1/3}$, $b = -2E/a^2$, and $Ci$ is the complex Airy function defined as

$$Ci(z) = Bi(z) + iAi(z), \quad (9.27)$$

where $Ai(z)$ and $Bi(z)$ (Airy functions) are two linearly independent solutions of the Airy equation $w''(z) - zw(z) = 0$. Using the asymptotic expressions for the Airy functions, one obtains

$$Ci(-z) \sim \pi^{-1/2}z^{-1/4}e^{i(\frac{2}{3}z^{3/2} + \frac{\pi}{4})}, \quad z \to \infty. \quad (9.28)$$

that is, the above function has the form of an outgoing wave. Multiplying the equation (9.25) with $r$, differentiating with respect to $r$ and inserting $r = 0$, one obtains the eigenvalue equation for $E(F)$

$$1 - \frac{2\pi}{\alpha} \lim_{r \to 0} \frac{\partial}{\partial r}(rG(r, 0; E)) = 0. \quad (9.29)$$

72
which is explicitly the transcendental equation

\[ \pi a \left( bAi(b)Ci(b) - Ai'(b)Ci'(b) \right) = \alpha. \] (9.30)

Using the above equation one can calculate numerically the function

\[ E(F) = W(F) - \frac{i}{2} \Gamma(F), \] (9.31)

where \( W \) (resonance position) and \( \Gamma \) (resonance width) are both real. The equation (9.30) is satisfied for all \( \text{Re}F > 0 \), defined in the complex plane. In the weak field limit it is possible to derive simple expression for \( E(F) \) as follows. In the limit \( F \to 0 \), \( b = -2E/(2F)2/3 \to \infty \) since \( \text{Re}E < 0 \). Using the asymptotic expressions for the Airy functions [76] and retaining the first two terms of the real part and only the first term of the imaginary part, which is exponentially small, on the right hand side of the eigenvalue equation (9.30), we obtain its asymptotic version

\[ \kappa = \frac{F^2}{8\kappa^3} - \frac{iF}{4\kappa^2} \exp \left( -\frac{2\kappa^3}{3F} \right) = \alpha, \] (9.32)

where \( \kappa = \sqrt{-2E} \). Squaring the above equation, retaining the terms of the first and the second order of the real part and only of the first order of the imaginary part, and putting \( \kappa = \alpha \) in all terms except the term with \( \kappa^2 \), we obtain

\[ E(F) \approx -\frac{\alpha^2}{2} - \frac{F^2}{8\alpha^4} - \frac{iF}{4\alpha} \exp \left( -\frac{2\alpha^3}{3F} \right) \text{ when } F \to 0. \] (9.33)

Explicitly the width in the weak field limit is

\[ \Gamma(F) = \frac{F}{2\alpha} \exp \left( -\frac{2\alpha^3}{3F} \right). \] (9.34)

We note here that the expression for the width \( \Gamma \) for the three dimensional case given in references [65, 77] is wrong by a factor \( \sqrt{2} \), and the expression given in references [64, 63] is correct.

In the cases where the weak-field approximation does not work one has to solve equation (9.30) numerically in order to obtain \( E(F) \). We have used the Mathematica package to solve numerically equation (9.30) in the complex \( F \)-plane.

### 9.5.2 Tunnelling

A special feature of the quasistationary states is their decay which prevents the application of the conventional adiabatic approach. Therefore, as in Part I, we will use the advanced adiabatic approach. Initially we consider the elastic channel, that is, we derive the probability of staying in the same state. This was also the case for the hydrogen atom in an electric field, analyzed in Part I of this thesis, where it was shown that the elastic channel gives the decay of the quasistationary states through tunnelling.

The derivation of the tunnelling probability in the advanced adiabatic approach proceeds exactly in the same way as in the case of the hydrogen atom. We start with the adiabatic (instantaneous) eigenfunction \( \chi(r, E) \) and eigenvalue \( E(F) \) of the instantaneous Hamiltonian,
defined above. The "mathematical" adiabatic parameter is \( Q = vt \), \( v = \tau^{-1} \) is a small parameter). The connection between the adiabatic parameter \( F \) and \( Q \) is through the \( F \)-time dependence \((9.11)\), in our case \( F = F_0 \exp(-Q^2) \). We use the adiabatic asymptote of the solution of the time-dependent Schrödinger equation \([20]\), which in our case reads:

\[
\Psi^{ad}(r,t) = \frac{1}{\sqrt{2\pi v}} \int_C \left[ \frac{dQ(E)}{dE} \right]^{1/2} \chi(r,E) \exp \left[ \frac{i}{v} \int_{E(0)}^E Q(E')dE' - iEt \right] dE. \tag{9.35}
\]

Here \( E^{(0)} \) is the energy of the initial state \( E(Q) \to E^{(0)} \) as \( t \to -\infty \) and \( Q(E) \) is the inverse function to \( E(Q) \), both being extended into the complex \( E \) and \( Q \)-plane respectively. Also the eigenfunction \( \chi(r,E) = \chi(r,Q)|_{Q=Q(E)} \) is extended to the complex plane. The integration contour \( C \) in the complex \( E \)-plane is determined by the initial boundary conditions and is explained in detail in Appendix B. Applying the same procedure as in Part I, Chapter 3 of this thesis, we obtain the probability of staying in the same (unique) bound state \( p_{11} \).

\[
p_{11} = \exp \left( -\int_{-\infty}^{+\infty} \Gamma_i(t)dt \right) = 1 - P_{\text{tun}}, \tag{9.36}
\]

where \( P_{\text{tun}} \) is the tunnelling probability. This widely used expression for the tunnelling probability is usually introduced and defined as such in the semiclassical theory. The above derivation of the tunnelling probability, as well as the derivation which is conducted in Part I is based purely on the adiabatic representation of the wavefunction \((9.35)\).

### 9.5.3 Transition to the continuum in the advanced adiabatic approach

Looking at the the problem of the negative ion in the framework of the advanced adiabatic approach, the simple fact that there is only one bound state results in the absence of hidden crossings, since they are defined between bound states. Therefore the only way to describe transitions to the continuum is to consider that part of the wavefunction in the advanced adiabatic approximation \((9.35)\) belonging to the continuum electrons, when the initial state is a bound state. In the case of the hydrogen atom, due to the presence of excited bound states, it was possible to assume the main channel of transition to the continuum through the first excited state and the probability of such transition was calculated using the hidden crossings between the ground state and the first excited state (see Part I, Chapter 3). Here we will consider transitions from the initial bound state directly to the continuum in the advanced adiabatic approach.

The part of the wavefunction corresponding to the continuum electrons in the advanced adiabatic approach is given by the equation \((9.35)\), where the contour \( C \) coincides with the axis \( \text{Re}E > 0 \). The asymptotic form of \( \chi(r,E(F)) \) in the limit \( (r-z) \to \infty \) is

\[
\lim_{(r-z)\to\infty} \chi(r,E(F)) \to \frac{C(E(F),r)}{r} \exp(iu), \tag{9.37}
\]

where \( C(E(F),r) \) is the preexponential factor and

\[
u(E) = \frac{2}{3} \left( \eta - \frac{2E}{(2F)^{2/3}} \right)^{3/2}, \quad \eta = \frac{(2F)^{1/3}}{2}(r-z). \tag{9.38}
\]
The function \( u(E) \) contributes to the total exponent of the integrand in equation (9.35). In principle, the contour \( C \) can be deformed so that it goes through the saddle point \( E'(F') \), which is simultaneously a solution of the saddle-point equation

\[
\frac{du}{dE} + Q(E)/v - t = 0
\]

and the spectral equation \( (9.29) \). Assuming that \( E'(F') \) is calculated, by performing saddle-point integration one obtains the wavepacket of the ionized electron as

\[
\psi_{\text{ion}}(r, t) = \sqrt{\left( \frac{dQ}{dE'} \right)}_E=E' \times \frac{C(E'(F'), r)}{r} \exp \left[ i \left( u(E') + \frac{1}{v} \int_{E'^{(0)}}^{E'} Q(E'')dE'' - E't \right) \right].
\]

(9.40)

The above expression is much too involved. We have been unable to obtain physically accept-able and numerically converged solutions for the system of transcendental equations \( (9.29) \) and \( (9.39) \). Therefore the treatment of the nonadiabatic transitions from a bound state to the continuum is still an open question.

9.6 Short times: the Magnus approximation and time-dependent perturbation theory

At very short times (smaller than the electron orbital period), the electric field pulse can safely be treated as a delta kick, acting on the bound electron. Therefore one can apply the first Magnus approximation (FMA), defined in Part II of this thesis, where the influence of the electric field on the electron is approximated as a momentum kick

\[
q = \int_{t_0}^{t} F(t')dt'.
\]

Because of the unitarity of the FMA, the probability of ionization can be obtained indirectly *

\[
P_{\text{ion}} = 1 - |\langle \phi_0 | \exp(-iq \cdot r) | \phi_0 \rangle|^2 = 1 - \left( \frac{2\alpha}{q} \arctan \left( \frac{q}{2\alpha} \right) \right)^2,
\]

(9.41)

where \( \phi_0 \) is the bound-state eigenfunction \( (9.7) \). The Magnus approximation is valid in the limit of short times, and up to high value of peak electric field, as shown in Part II of the thesis.

In the case of relatively short times and weak amplitudes of the electric field pulse one can use the first-order time-dependent perturbation theory (FPA). The transition probability amplitude from the bound state to a continuum state with momentum \( k \) in the limit \( t \to \infty \) (at the end of the pulse) is

\[
a(k) = -i \int_{-\infty}^{\infty} dt \langle \phi_k | F(t) \cdot r | \phi_0 \rangle \exp \left( \frac{(k^2 + \alpha^2)t}{2} \right)
\]

*In this section we use the unscaled Schrödinger equation \( (9.10) \).
CHAPTER 9: Ionization of a negative ion by an electric field pulse

9.7 Results: resonant ionization

\[ P_{\text{ion}} = \int d^3k |a(k)|^2 = \frac{16}{3} (F_0 \tau)^2 \int_0^\infty dk \exp \left( -\frac{(k^2 + \alpha^2)^2}{8} \right) \frac{k^4}{(\alpha^2 + k^2)^2}. \]  

(9.43)

Figure 9.1: Ionization probability as a function of the scaled pulse duration for different values of the field amplitude. The dotted line denotes results which are not numerically converged.

9.7 Results: resonant ionization

Starting from the bound state of the outer electron in the negative ion (the bound state of the ZRP) as initial state, we have calculated numerically the ionization probability as a function of the pulse width \( \tau' = \alpha^2 \tau \) in the interval from \( 10^{-1} \) to \( 10^2 \) a.u. and peak field strengths \( F_0' = F_0/\alpha^3 \) in the interval from 0.05 to 0.5 a.u. The results of the calculation are presented in figure 9.1, where \( P_{\text{ion}}(\tau') \) is plotted, taking \( F_0' \) as a parameter.

For strong fields (peak amplitude \( F_0' \geq 0.2 \) a.u. in figure 9.1), \( P_{\text{ion}}(\tau') \) is a monotonically increasing function of \( \tau' \) which is in agreement with the intuitive expectation for this process: by increasing the width of the pulse one expects increased ionization probability. However, decreasing the peak electric field (\( F_0' \leq 0.05 \) a.u. in figure 9.1) one sees that a local maximum
CHAPTER 9: Ionization of a negative ion by an electric field pulse

9.7 Results: resonant ionization

Figure 9.2: Comparison of numerical results with theory (a) - $F_0'' = 0.5$ a.u.; (b) - $F_0'' = 0.3$ a.u.; (c) - $F_0'' = 0.2$ a.u.; (d) - $F_0'' = 0.1$ a.u.; (e) - $F_0'' = 0.08$ a.u.; (f) - $F_0'' = 0.05$ a.u. Black circles connected with linear segments - numerical results, blue lines - ionization probability in FMA, green line - ionization probability in FPA, red lines - tunnelling probability.
emerges at $\tau' \sim 1$ a.u. which is followed by a rapid decrease. The decrease is steeper the smaller is $F'_0$. In the limit of large $\tau'$ the monotonic increase is restored and this eventually leads to full ionization.

In the limit of very short times $\tau'$, as already discussed in Part II, the FMA of equation (9.41) is valid. In the limit of large $\tau'$ we expect that the correct answer is given by the expression for the tunnelling probability (defined in equation (9.36)). We also expect that for relatively short times and weak fields the FPA of equation (9.43) will be valid.

In figure 9.2 we compare the numerical results to the analytic expressions in the FMA, FPA and zero-order adiabatic approximation (tunnelling). We can see that we get excellent agreement with the analytic results in the limits of their validity, except in the limit of very weak fields and long-pulses (the dotted red line in figure 9.2 (f) for $F_0 = 0.05$ a.u.). This is due to the nature of the numerical method based on a solution of an integral equation. Namely in the case of very small ionization probability, the value of $R(t)$ defined in equation (9.10) is too close to unity, so after a long time propagation, any numerical error in unitarity results in a huge error in the ionization probability. Nevertheless, in all other cases the numerical tool proved very reliable as can be seen from the agreement with the analytic results.

In all cases, the curve of the ionization probability is bounded by two asymptotes. In the limit of very short pulses the FMA acts as asymptote from the left, and in the limit of long pulses, the asymptote is the tunnelling curve. In the cases of high peak electric fields, as in figures 9.2 (a)-(c), the relative position of both envelopes is such that the curve of the ionization probability goes smoothly from one to the other envelope, without exhibiting a maximum. As expected, at higher $F'_0$, the FPA result breaks down at smaller $\tau'$ compared to the weak-field case. Moreover, in the strong-field case, the interval of $\tau'$ between the validity of the first-order perturbation theory and the tunnelling result is very small, concentrated on an interval around $\tau' \sim 3$ a.u. (figures 9.2 (a)-(b)). Therefore in the limit of strong fields and slowly-varying pulses, it is safe to take into account only the tunnelling effect. This can also explain qualitatively the success of the Keldysh-Faisal-Reiss theory [7, 8, 9], where at strong fields and slowly-varying pulses one takes into account the time-dependent tunnelling at each half cycle of the electric field.

In contrast to the strong-field case, the behavior of the ionization curves in the weak-field case is totally different. Namely the FMA asymptote as a function of $F'_0$ does not fall so rapidly as the tunnelling asymptote. Therefore the tunnelling curve lies several orders of magnitude well below the FMA. This is the reason why the curve of the ionization probability exhibits a peak and decreases toward the tunnelling asymptote. The peak in the ionization probability is very well reproduced by the FPA, as can be seen in figures 9.2 (d)-(f), and it lies in the $\tau'$ interval $(1, 2)$. As the pulse duration increases the FPA breaks down and the ionization probability "locks" to the tunnelling curve.

We illustrate the process of the breaking down of FPA result by plotting the probability density of the wavefunction of the ionized electron $|\Psi_{\text{ion}}(r)|^2$ in figure 9.3 and the momentum distribution $|a(k)|^2$ in figure 9.4 both for the case $F'_0 = 0.1$ a.u. and $\tau' = 1, 2, 3$ a.u. The wavefunction of the ionized electron $\Psi_{\text{ion}}(r)$ is defined as

$$\Psi_{\text{ion}}(r) = \left(\Psi(r, T) - \phi_0(r) \int \phi_0^*(r')\Psi(r', T) d^3r\right),$$

(9.44)

where $T$ is the time needed for the spherical wave to leave the origin. In accordance with the discussion of section 9.4., this happens when $|R(t)|^2$ attains stationary value. Afterwards
\[ |\Psi_{\text{ion}}(\mathbf{r})|^2 \times 10^6, \quad \tau' = 1 \text{ a.u.} \]

\[ |\Psi_{\text{ion}}(\mathbf{r})|^2 \times 10^6, \quad \tau' = 2 \text{ a.u.} \]

\[ |\Psi_{\text{ion}}(\mathbf{r})|^2 \times 10^6, \quad \tau' = 3 \text{ a.u.} \]

Figure 9.3: Probability density of the wavepacket corresponding to the ionized electron \(|\psi_{\text{ion}}(\mathbf{r})|^2\) for the case \(F_0/\alpha^3 = 0.1 \text{ a.u.}\). Cylindrical coordinate system is used.
\[ |a(k)|^2 \times 10^3, \quad \tau' = 1 \text{ a.u.} \]

\[ |a(k)|^2 \times 10^3, \quad \tau' = 2 \text{ a.u.} \]

\[ |a(k)|^2 \times 10^3, \quad \tau' = 3 \text{ a.u.} \]

Figure 9.4: Momentum distribution of the ionized electron (|a(k)|^2) for the case \( F_0/\alpha^3 = 0.1 \) a.u. Cylindric coordinate system is used.
a(k) is obtained as a Fourier transform of $\Psi_{\text{ton}}(r)$

$$a(k) = \frac{1}{(2\pi)^{3/2}} \int \Psi_{\text{ton}}(r) \exp(-i k \cdot r) d^3r.$$  \hspace{1cm} (9.45)

Going from $\tau' = 1$ to $3$ a.u. (figures 9.3 (a) to (c) and 9.4 (a) to (c)) one can clearly see the breaking of the forward-backward symmetry of the probability density and the momentum distribution. In the figures 9.3 and 9.4 the electric field vector is oriented along the negative $z$-axis, hence the motion of the wavepacket, from a totally symmetric form when $\tau' = 1$ a.u., becomes directed along the positive $z$-axis when $\tau' = 3$ a.u.

The only region of $\tau'$ in the weak-field limit which cannot be directly related to a simple analytic expression is the decrease of the ionization probability after the FPA breaks down up to the point when the ionization probability becomes equal to the tunnelling probability expression. This $\tau'$ interval becomes bigger with decrease of the peak electric field as can be seen from figure 9.2. The physical origin of the decrease of $P_{\text{ion}}(\tau')$ will be discussed in the next chapter.
CHAPTER 9: Ionization of a negative ion by an electric field pulse

9.7 Results: resonant ionization
Chapter 10

Resonant excitation and ionization of the hydrogen atom

The nonmonotonic behavior of the ionization probability as a function of pulse width found in the case of the negative ion prompted a similar study in the case of the hydrogen atom. This case was already studied in Part I of the thesis, but for a more restricted range of pulse widths. Here we concentrate on the behavior of the probability of excitation and ionization as a function of the pulse width, covering the whole range - from very short to very long pulses.

The nonstationary Schrödinger equation governing the dynamics of hydrogen in presence of nonstationary electric field oriented along the $z$-axis is

$$
\left( -\frac{1}{2} \Delta - \frac{1}{r} + F_z \right) \Psi(r,t) = i \frac{\partial \Psi(r,t)}{\partial t}.
$$

(10.1)

We will again consider the case of a field with Gaussian time-dependence and we will take the ground state as initial. The nonstationary problem is solved using the same numerical procedure as in Part I, Chapter 3 of the thesis, that is, using the DVR.

Similarly as in Chapter 9 we consider the FPA and the zero-order adiabatic approximation. In the FPA the probability of transition from the ground state to the excited state of the $n$-th shell of orbital quantum number $l = 1$ and magnetic quantum number $m = 0$ is given by

$$
P_n = |a_{n1}|^2, \quad a_{n1} = -i \langle \phi_{n10} | z | \phi_1 \rangle \int_{-\infty}^{\infty} F(t) \exp \left( i(E_n - E_1)t \right) dt,
$$

(10.2)

where $E_n$ is the eigenenergy of the states of the $n$-th state, $\phi_1$ is the ground-state eigenfunction and $\phi_{n10}$ is the eigenfunction of the state in the $n$-th shell with $l = 1$ and $m = 0$. In the FPA the probability amplitude of ionization from the ground state to a continuum state $\phi_{Elm}$ of energy $E$ and well-defined angular momentum is

$$
a(E) = -i \langle \phi_{Elm} | z | \phi_1 \rangle \int_{-\infty}^{\infty} F(t) \exp \left( i(E - E_1)t \right) dt.
$$

(10.3)

Due to the selection rules for dipole transitions, the dipole matrix element is nonzero for $l = 1$
and $m = 0$ only, and 

\[
(\phi_{E10}| z |\phi_1) = \frac{2^4}{\sqrt{3}} \frac{1}{(1 + 2E)^{5/2}} \exp\left(\frac{-2}{\sqrt{2E}} \arctan \sqrt{2E}\right) \frac{\exp\left(\frac{2}{\sqrt{2E}}\right)}{\sqrt{1 - \exp(-2\pi/\sqrt{2E})}}.
\] (10.4)

The probability of ionization is therefore

\[
P_{\text{ion}} = \int |a(E)|^2 \, dE = (F_0 \tau)^2 \pi \frac{2^8}{3} \int_0^\infty \frac{\exp\left(-\frac{(E-E_1)^2}{2}\right) \exp\left(-\frac{4}{\sqrt{2E}} \arctan \sqrt{2E}\right)}{(1 + 2E)^5 \left(1 - \exp(-2\pi/\sqrt{2E})\right)} \, dE. \tag{10.5}
\]

In the limit of long pulses we expect the expression for the tunnelling probability to be valid. To evaluate this probability it is necessary to know the width $\Gamma(E)$ of the Stark state corresponding to the ground state. For weak fields, one can use the expression for the width of the Stark states given in reference [78]:

\[
\Gamma(F) = \frac{4}{F} \exp\left(-\frac{2}{3F}\right). \tag{10.6}
\]

In order to obtain the width of the Stark state in the strong-field case, one has to solve the stationary problem \[\text{starting from the ground state. The eigenvalue } E(F) \text{ of the quasistationary state corresponding to the ground state has been solved numerically exactly as described in Part I, Chapter 3 of this thesis.}

Results of the numerical calculation, compared to the analytic expressions are presented in figure 10.1. The same behavior found in the case of the negative ion (ZRP potential) is observed. In the case of a strong field (figures 10.1 (a) and (b)), the ionization probability as a function of the pulse width $\tau$ exhibits a monotonic increase. On the other hand, in the weak-field case (figures 10.1 (c)-(e)), there is a maximum in the ionization probability at $\tau \approx 2$ a.u., followed by a fall towards the tunnelling probability curve. The decrease of the ionization probability is particularly large for the cases in figures 10.1 (e)-(f), since the width of the ground state in the weak-field limit decreases very rapidly with decrease of $F$ (see equation (10.6)). We have been unable to obtain converged DVR results for $\tau > 50$ a.u. but since in the strong-field case the ionization curve "locks" to the tunnelling curve it is natural to expect that $P_{\text{ion}}$ will follow this behavior in the weak-field case as well.

Exactly as in the case of the ZRP potential, the local maximum of the ionization probability can be reproduced perfectly with the FPA. After the maximum the FPA breaks down sharply, and this happens at smaller $\tau$’s for larger $F_0$’s as expected.

In addition to the ionization curves, in figure 10.1 the population probabilities of the first and the second excited shell (states with principal quantum number $n = 2$ and $n = 3$ respectively) are plotted. The total probability of inelastic transitions $P_{\text{inel}}$, defined as

\[
P_{\text{inel}} = 1 - P_1, \tag{10.7}
\]

where $P_1$ is the probability of ground state occupation, is plotted in figure 10.1 as well.

One notes that the probability of populating excited shells always exhibits a maximum as a function of $\tau$, no matter what the field strength. In the weak-field case these peaks can be described well in the FPA, whereas for high values of $F_0$ the FPA breaks down before the maximum. Moreover, the population probability $P_2$ peaks at $\tau \sim 3$ a.u. rather than
Figure 10.1: Ionization and excitation probability as a function of the pulse duration $\tau$ for different values of the field amplitude. Open circles connected with linear segments—numerical results; Dashed lines—result in FPA. Black curves—probability of ionization ($P_{\text{ion}}$); Magenta curves—probability of inelastic transitions ($P_{\text{inel}}$); Blue curves—population probability of the first excited shell ($P_2$); Green curves—population probability of the second excited shell ($P_3$); Red lines—tunnelling probability ($P_{\text{tun}}$).
$\tau \sim 2$ a.u., the position of the peak in the ionization probability. This reveals the nature of the peaks in ionization and excitation probability. The peaks can be related to a resonance of the interaction time of the pulse with respect to the transition time (inverse transition frequency) from the ground state to the continuum or from the ground state to excited states respectively.

Comparing the ionization and excitation probability, one can see that in the short-pulse limit, where the FPA is valid, the dominant contribution to the inelastic probability comes from the first excited state, which is in accord with the property of the dipole matrix elements. After the peak, the population probability of excited states decreases due to nonadiabatic transitions between the excited states and the continuum and this leads eventually to complete depletion of the excited states, when also $P_{\text{ion}}$ becomes equal to $P_{\text{inel}}$.

The nonmonotonic behavior of the ionization probability is not a feature of the potential used in this study or the electric field time-dependence. Such behavior of the ionization probability was observed for a one-dimensional $\delta$ potential in a numerical study \[69\] and relatively recently in reference \[79\], where a numerical close-coupling study of H(1s) ionization by a laser pulse with sine squared envelope was considered. In the latter paper, commenting on figure 3, where the probability of ionization versus number of cycles was plotted, the author was surprised by the huge fall at a fraction of a cycle and offered no theoretical explanation for this phenomenon. Most recently, in reference \[80\] this drop was confirmed but again no explanation is provided. Here we have provided a complete explanation of this effect.

The result of nonmonotonic behavior of the ionization probability and resonant structure of the excitation probability does not come as a surprise if we compare ionization and excitation by a unidirectional pulse with collision of a charged projectile with a hydrogen atom and the negative ion. When plotted as a function of the impact velocity of the projectile, the ionization cross-section exhibits a maximum at velocities corresponding to the collision time $\tau_{\text{col}} \sim \tau_{\text{at}}$. Here $\tau_{\text{at}}$ is the characteristic time associated with the transition to the continuum. This time is of order $1/\Delta E$, where $\Delta E$ is the transition energy. The collision time is inversely proportional to the impact velocity. With increase of the impact velocity (decrease of $\tau_{\text{col}}$) the cross-section goes to zero. The region of $\tau_{\text{col}} < \tau_{\text{at}}$ (high impact velocity) for collisions corresponds to the short-pulse situation and the region of $\tau_{\text{col}} > \tau_{\text{at}}$ (low impact velocity) corresponds to the long-pulse behavior. In the case of collisions, the nonadiabatic transitions explain the rise of the cross-section \[21\]. Therefore in the case of electric pulse ionization and excitation, the decrease of probability as a function of $\tau$ can be attributed to the nonadiabatic transitions. However, the situation of pulse ionization is a little more subtle than the collision because of the presence of the decay of the bound states into the continuum, which results in complete ionization in the limit of long pulses.

Finally, we discuss the possibility of reproducing the decrease of the inelastic probability using the advanced adiabatic approach. Looking at the expression for the transition probability \[80\] given in Part I one remarks that it decreases exponentially as a function of $\tau$, which is qualitatively correct. However, although the main channel for inelastic transition goes through the first excited state, we have checked that it is not possible to simply identify the total probability of inelastic transitions with the probability of nonadiabatic transitions between the ground state and the first excited state. This holds especially in the case of weak fields where the $\tau$ interval of the decreasing part of the total probability of inelastic transitions is the longest. A possible way to proceed further is to take into account the interference between two possible paths to go from the initial to the final state during increasing and decreasing stages of the pulse but this still remains an open question.
In summary, we have presented a study of ionization and excitation of two different one-electron atomic systems - the hydrogen atom and a negative ion - by electric field pulses of different amplitude and pulse widths. We have applied both numerical and analytic methods to obtain the results. The numerical solution of the nonstationary problem in the case of a negative ion is based on a solution of an integral equation. In the case of the hydrogen atom the numerical solution was obtained using the DVR. Depending on the pulse width and its amplitude various analytic approximations were used, ranging from the FMA in the short-pulse limit, via the FPA, to the advanced adiabatic approach in the long pulse limit.

The phenomenon of nonmonotonic behavior of the ionization probability in the weak-field case as a function of the pulse width $\tau$ is identified for both systems. The function $P_{\text{ion}}(\tau)$ exhibits a local maximum and then decreases to become equal to the analytic expression for tunnelling in the long-pulse limit. This probability then rises as a function of $\tau$ and eventually results in full ionization. The probability of population of excited states exhibits a maximum as a function of the pulse width, but then completely depletes in the long pulse limit. The peak in the ionization and excitation probability in the weak-field limit is readily described by the first-order time-dependent perturbation theory and corresponds to a resonant interaction time of the pulse with respect to the inverse of the transition frequency between the initial and the final states. By comparison with well-studied processes in the field of atomic collisions, the decrease of the ionization probability as a function of pulse duration is associated with the nonadiabatic transitions from the ground state to the excited states and from the excited states to the continuum. However, this point needs further investigation in the framework of the advanced adiabatic approach. Finally, the reason for the different behavior of the probability of excitation of the bound states and the ionization probability is the decay of the bound states to the continuum which becomes the dominant process in the long pulse limit.
Chapter 11

Conclusions and outlook

In this thesis we have performed studies of time-dependent electric pulse ionization and excitation of atomic systems with the aim of achieving a comprehensive understanding of this process. For most of the thesis the focus is on the hydrogen atom but in Part III the negative ion is analyzed also. Unidirectional (half-cycle) pulses are considered, as well as oscillating (up to several-cycle) pulses. The time scale of the pulses considered varied from very short to very long with respect to the time scale of the electron orbit in its initial state. The peak electric fields were mostly in the strong-field regime, although the weak-field case was considered as well.

Several complementary methods were used to attack the above problem - numerical, semi-analytic and analytic. Numerical methods for solving the three-dimensional time-dependent Schrödinger equation were used as a benchmark to test the validity of the analytic methods devised. In contrast to the numerical calculations the analytic methods gave us insight into the dynamics of the systems studied.

For the case of the hydrogen atom a numerical code based on the DVR representation of the state vectors was written. The DVR avoids the problem of the singularity of the Coulomb potential since the wavefunction is computed only at grid points related to the Laguerre polynomials. The matrix belonging to the kinetic energy part of the Hamiltonian is calculated exactly in the DVR representation, and the potential energy part is diagonal, which is a good approximation. In DVR one is not restricted to a certain pulse shape or Coulomb potential - these changes are easily incorporated in the code as long as the symmetry of the system is not changed. Another numerical method, based on the solution of the integral equation for the propagator was developed to provide numerical results for the negative ion modelled by a three-dimensional zero-range potential. This is an original numerical procedure which exploits the special properties of the potential and enables solution for any pulse shape which extends to infinity, such as the Gaussian pulse. The same numerical procedure can be used to treat both one and three-dimensional zero-range potentials.

The advanced adiabatic approach, developed by Solov’ev in the field of atomic collisions, was used to describe the process of ionization and excitation for slowly-varying pulses. In this approach the adiabatic parameter (in our case the field amplitude \( F \)) is treated as a complex variable. Use is made of the analyticity of the Hamiltonian in the complex plane of the adiabatic parameter. In the application of the advanced adiabatic approach two steps are necessary. The first step is a formulation of an adiabatic basis using quasistationary states as adiabatic states and solving the stationary problem in the complex plane of the adiabatic
parameter. The energy potential curves corresponding to the eigenenergies of the adiabatic states with the same symmetry are in fact different sheets of one analytic function in the complex plane, connected by branch points (hidden crossings). The hidden crossings are related to strong coupling between the adiabatic states. The second step is a calculation of the probability of nonadiabatic transitions by contour integration around the branch points in the complex plane.

Purely analytic methods were used in the limit of very short pulses, regardless of the field amplitude. These are the first-order time-dependent perturbation theory (FPA), first-order Magnus approximation (FMA) and a modification of the first-order Magnus approximation (modified FMA). The FPA has been used in the weak-field case, for both half- and several-cycle pulses. In the strong-field case and half-cycle duration much smaller than the orbital time of the electron in its initial state the FMA and its modification are used. For half-cycle pulses the FMA provides the answer by reducing the pulse, regardless of its shape, to a momentum kick with magnitude equal to the half-cycle pulse area. The modified FMA, developed in this thesis, in turn enables analysis beyond a half-cycle pulse by inclusion of the propagation in the Coulomb field of the nucleus between the kicks.

The results of this thesis can be divided with respect to the time scale of the pulse. In the limit of very long pulses the initial state depletes through tunnelling. Although the tunnelling has been known for a very long time, the original contribution here is its rigorous derivation starting from the representation of the wavefunction in the advanced adiabatic approach (Part I of the thesis). Namely the depletion of the initial state due to tunnelling corresponds to the zeroth-order adiabatic behavior in this problem. The tunnelling becomes the dominant process at very long times. This is true in both systems studied - the hydrogen atom (Part I and Part III) and the negative ion (Part III).

At smaller time scales the nonadiabatic transitions arising from the hidden crossings between the initial and the excited states dominate, that is, the inelastic channel takes over from the elastic one. In Part I of this thesis we have assumed that the dominant contribution comes from the nonadiabatic transition between the ground state as initial and the first excited state, ignoring the possible interference between the increasing and decreasing stages of the pulse. This provided a fair estimate of the total inelastic probability for the electric field amplitudes studied (see figure 3.6). During the course of the research we have investigated this problem more closely and this is presented in Part III of the thesis. There we extended the range of the electric peak amplitudes and pulse widths investigated and also presented the case of the negative ion. It turns out that the range of pulse widths for which the inelastic channel in the advanced adiabatic approach dominates becomes longer the smaller is the peak electric field (figures 9.2 and 10.1). Also, with decrease of the peak electric field the minimal pulse widths at which the tunnelling probability expression can be utilized increases. Since in the case of the negative ion excited states do not exist, the nonadiabatic transitions go from the ground state directly to the continuum.

Another effect emerged by considering the whole interval of pulse widths at various peak amplitudes of the pulse. Namely the plots of the ionization probability as a function of the pulse width (with peak electric field as a parameter, presented in figures 9.2 and 10.1) revealed a nonmonotonic behavior of the ionization probability as a function of the pulse width. At strong fields this effect is absent because of the relative position of the short time asymptote (the FMA) and the tunnelling asymptote - the ionization curve goes from one asymptote to the other, keeping the monotonic rise. On the other hand, for weak fields the situation is such that the tunnelling asymptote is well below the FMA asymptote so that ionization probability
exhibits a local maximum and then decreases to "lock" to the tunnelling curve and restore the monotonic rise. We have explained the above behavior, observed but not explained in several recent publications. The probabilities of occupation of excited states in turn always exhibit a maximum and then decrease to zero. By observing the position of the maxima in the excitation and ionization probabilities, we were able to relate the maximum to the situation where the pulse width is in resonance with the inverse transition frequency from the initial state to excited states or to the continuum.

Finally, in the case of very short pulses, we have considered both half-cycle pulses and few-cycle pulses. We have identified a periodic occurrence of ionization and recombination in time. More precisely, the ionization which occurs after an odd half cycle is reversed in the following even half cycle. In the weak field case this periodicity leads to a high sensitivity of the energy distribution to the relative envelope-carrier phase which is particularly pronounced, as expected, for one cycle (see figure 6.5). However, as illustrated in figure 6.7, the difference of the energy distributions at threshold for different phases persists, provided that the half-cycle duration is smaller than the orbital time of the electron in its initial state.

In the strong field the periodic occurrence of ionization and recombination in time is termed "Rabi flopping involving the continuum" because after each odd half-cycle of the field the atom is practically 100% ionized and then the even half-cycle returns most of this population back to the initial state. This is illustrated in many figures in Part II of the thesis. Effectively the electronic wavefunction does not have time to move during this process. In momentum space the odd half-cycle causes a shift of the wavefunction in one direction, and the even half-cycle shifts it back to approximately its original position, resulting in recombination in the initial state. Actually this process is an interplay between the initial state and the continuum which, depending on the parameters of the pulse, persists for several cycles. By considering this process in the modified FMA, we have been able to derive analytic formulas for the population probability of the initial state after one cycle, as asymptotic expressions in the limit of infinite momentum transfer (equations (7.14) and (7.15)). Remarkably, these analytic expressions are in excellent agreement with the numerical results even for small momentum transfers. We have even been able to reduce the analysis of the few-cycle pulse with constant envelope to an equivalent one-cycle pulse. This enabled application of the same asymptotic formulas derived in the one-cycle pulse for the few-cycle pulse as well.

The work presented in the thesis lays down a foundation on top of which one can proceed in different directions and consider further applications, but it also left some open questions. Many of these questions concern the long pulse limit. The first one is the formulation of a clear analytic criterion for the point at which a transition from the dominant inelastic channel (due to nonadiabatic transitions arising from the hidden crossings) to dominant tunnelling process takes place. The second is the examination of the nonadiabatic transitions from the bound states directly into the continuum and taking into account the interference effect for the bound-bound transitions during increasing and decreasing stages of the pulse. Such considerations will lead eventually to an approximate semianalytic expression for the region of the decrease of the total inelastic probability as a function of the pulse width.

Possible applications of this work are mostly related to control of ionization and to mapping and examining the coherence from the bound state to the continuum. For example the fact that the ionization probability in the weak field limit for a unidirectional pulse exhibits a maximum, gives one a possibility, with a suitable choice of the electric field pulse, to maximize the ionization yield. The opposite procedure is also possible - one obtains a maximum of the ionization or excitation probability for a certain one-electron system and then deduces the
dynamics of the electron in its initial state. Concerning the periodical occurrence of ionization and recombination we hope that in the near future, with the development of attosecond pulses, this can be tested experimentally. In the weak-field regime, by analyzing the energy distributions of the electrons at small energies it will be possible to give conclusions about the actual envelope and the relative envelope-carrier phase of the attosecond pulses. In the strong field limit, one can use the asymptotic formulas to provide a rapid estimate of the probability of returning to the initial state. One may also proceed by devising asymptotic formulas in the few-cycle case starting from Rydberg states where the time scales of the pulses and the peak fields are within experimental reach. Even more interesting is to start from a coherent state and observe ionization and recombination in this case. Finally, the availability of analytic expressions opens up the possibility of using the results of this thesis to tailor laser pulses to optimize the production of specific continuum electron states.
Appendix A

Numerical method based on the DVR

In this chapter we will introduce the discrete variable representation (DVR) which is a numerical method for solving the Schrödinger equation. Generally, the DVR is a discretized coordinate representation of the Hamiltonian and the state vectors of the system which in most cases is related to a given class of orthogonal polynomials. The most important property of the Hamiltonian matrix represented in DVR is that its potential energy part is diagonal while the kinetic energy matrix is sparse.

This method was first introduced in reference [81] and subsequently in [82] where it was called "generalized Lagrange mesh". At first, it was used mainly in chemical physics (see [83] and references cited therein). The first application of the DVR method in atomic physics was performed in [84] where a DVR basis was used in atomic structure calculations by discretizing the radial part of the eigenvalue equation for such systems. Later on, it was used for representing highly excited states of atoms in electric and magnetic fields [85, 86], as well as for time-dependent calculations of collisions of antiprotons with hydrogen atoms [87] and very recently hydrogen molecular ions [88].

In the next sections we will illustrate briefly the essence of the general method and specifically discuss the DVR based on Laguerre polynomials which is used as a numerical benchmark to support the analytical results presented in the thesis.

A.1 The general method

We will illustrate the general method on the problem of discretization of the one-dimensional eigenvalue equation with local potential $V(x)$ and kinetic energy operator $\hat{T}$ (in this section we will follow the reference [82])

$$\left(\hat{T} + V(x)\right)\Psi(x) = E\Psi(x), \quad (A.1)$$

where $x$ can be a cartesian, polar, radial or angular coordinate. In the DVR we discretize the wavefunction $\Psi(x)$ defined on the interval $(a, b)$ at $N$ given points $x_j$. One introduces a set of $N$ Lagrange functions $f_i(x)$ satisfying the conditions

$$f_i(x_j) = \delta_{ij}, \quad \text{and} \quad \int_a^b f_i^*(x)f_j(x)dx = w_{ij}. \quad (A.2)$$
APPENDIX A: Numerical method based on the DVR

A.1 The general method

The first condition is necessary to provide a Lagrange interpolation of the function $\Psi$ based on the values of the function on the grid points $x_i$

$$\Psi(x) \approx \sum_{i=1}^{N} \Psi(x_i)f_i(x), \quad (A.3)$$

and the orthogonality condition provides a means to calculate the scalar product of two approximated functions as

$$\int_{a}^{b} \Phi^*(x)\Psi(x)dx \approx \sum_{i=1}^{N} w_i\Phi^*(x_i)\Psi(x_i). \quad (A.4)$$

The above formula is alike to the usual Gauss quadrature formula for integration of functions i.e.

$$\int_{a}^{b} F(x)dx \approx \sum_{i=1}^{N} w_iF(x_i), \quad (A.5)$$

with $N$ quadrature points $x_i$ and weights $w_i$. We construct the Lagrange functions as a linear combination of a set of $N$ basis functions $\varphi_i$,

$$f_i(x) = w_i \sum_{k=0}^{N-1} \varphi^*_k(x_i)\varphi_k(x) \quad (A.6)$$

orthonormal on the interval $(a,b)$

$$\int_{a}^{b} \varphi^*_i(x)\varphi_j(x)dx = \delta_{ij}, \quad i, j = 0...N - 1, \quad (A.7)$$

which, as we shall see, are directly related to a given class of orthogonal polynomials. Since the Lagrange functions satisfy the conditions (A.2), the functions $\varphi_i$ must satisfy the condition

$$\sum_{k=0}^{N-1} \varphi^*_k(x_i)\varphi_k(x_j) = w_i^{-1}\delta_{ij} \quad (A.8)$$

With such a representation of $\Psi(x)$, the matrix elements of the kinetic energy operator in the basis of the normalized functions

$$f_i^{(DVR)}(x) = w_i^{-1/2}f_i(x), \quad (A.9)$$

which define the DVR basis, are calculated exactly\(^\dagger\) as

$$T_{ij} = \int_{a}^{b} f_i^{(DVR)*}(x)\hat{T}f_j^{(DVR)}(x)dx, \quad (A.10)$$

\(^\dagger\)In the literature, as in [76], the weights $w_i$ are defined as $\int_{a}^{b} w(x)F(x)dx \approx \sum w_iF(x_i)$, but we will use the notation of (A.5) as more compact.

\(^\dagger\)Here we have assumed that $\hat{T}$ contains derivatives which reduce the degree of the polynomial $f_j^{(DVR)}(x)$, so the Gauss quadrature formula is exact and not an approximation.
while the matrix elements of the potential are approximated using the Gauss quadrature formula

\[ V_{ij} = \int_a^b f_1^{(DVR)}(x)V(x)f_2^{(DVR)}(x)dx \approx V(x_i)\delta_{ij}. \]  

(A.11)

which is the basic approximation of the DVR. In this basis, the eigenvalue equation (A.1) reduces to the following matrix equation

\[ \sum_{j=1}^N (T_{ij} + V(x_i)\delta_{ij}) w_j^{1/2} \Psi(x_j) = E w_i^{1/2} \Psi(x_i) \]  

(A.12)

where, because of expansion (A.3), only the values of the wavefunction at the grid points appear. Notice that up to now we did not specify the conditions which should be satisfied by the grid points. Generally speaking, as we will see, \( x_i \) are directly dependent on the particular choice of the basis functions \( \varphi_i \).

### A.1.1 DVR related to orthogonal polynomials

We consider a class of orthogonal polynomials \( p_k(x) \) associated with a weight function \( w(x) \) defined on \((a, b)\), satisfying the orthogonality condition

\[ \int_a^b w(x)p_i(x)p_j(x)dx = h_i\delta_{ij}, \]  

(A.13)

where \( h_i \) is the norm of \( p_i \). Then it is possible to define the basis functions \( \varphi_k \) as

\[ \varphi_k(x) = h_k^{-1/2}p_k(x)w(x)^{1/2}. \]  

(A.14)

These basis functions should satisfy the condition (A.8) necessary for the existence of the grid. Using the Christoffel-Darboux formula for \( x \neq y \) one obtains

\[ \sum_{i=0}^{N-1} \varphi_i(x)\varphi_i(y) = \frac{k_{N-1}}{k_N} h_N^{1/2} \frac{\varphi_N(x)\varphi_{N-1}(y) - \varphi_N(y)\varphi_{N-1}(x)}{x - y}, \]  

(A.15)

and for \( x = y \)

\[ \sum_{i=0}^{N-1} \varphi_i^2(x) = \frac{k_{N-1}}{k_N} \frac{1}{h_{N-1}} w(x) \left( p_N'(x)p_{N-1}(x) - p_N'(x)p_{N-1}(x) \right), \]  

(A.16)

where \( k_n \) is the coefficient in front of \( x^n \) in \( p_n(x) \). From the condition (A.8), one can see that the grid points \( x_i \) should be chosen so that

\[ p_N(x_i) = 0, \quad \text{for} \quad i = 0...N - 1, \]  

(A.17)

that is, the grid points for a basis of \( N \) DVR functions \( f_i^{(DVR)} \) are the grid points associated with a given class of orthogonal polynomials. The weights \( w_i \) can be obtained from an application of equation (A.16) and then of equation (A.8) to give

\[ w_i = \frac{k_N}{k_{N-1}} \frac{1}{\sqrt{h_{N-1} h_N \varphi_N'(x_i)\varphi_{N-1}(x_i)}}. \]  

(A.18)
Finally by application of the relation \( A.6 \) and \( A.15 \) we obtain the basis functions of the DVR

\[
f^{(DVR)}_i(x) = w_i^{-1/2} \frac{\varphi_N(x)}{\varphi'_N(x_i)(x-x_i)}. \tag{A.19}
\]

As can be seen from the above equation, every DVR basis function of an \( N \)-dimensional basis related to a given class of orthogonal polynomials can be expressed as a product of an orthogonal polynomial of degree \( N-1 \) and \( w(x)^{1/2} \).

### A.1.2 Extension of the DVR method to \( n \)-dimensional problems

In the cases of more than one dimension, multidimensional DVR basis functions are formed simply as a direct product of DVR basis functions for each dimension [83]. The DVR basis functions in this case have the dimension

\[
N_{DVR} = \prod_{i=1}^n N_i, \tag{A.20}
\]

where \( N_i \) is the number of basis DVR functions in the \( i \)-th coordinate \( x^{(i)} \). We will denote the DVR functions as \( f^{(DVR)}_p(r) \), where \( r = (x^{(1)}, x^{(2)}, ..., x^{(n)}) \), and \( p = (i_1, i_2, ..., i_n) \), \( i_j = 1, N_j \). In order to keep relations \( A.10 \) and \( A.11 \) for the matrix elements of the kinetic and potential energy the same for each possible geometry, one should include explicitly the Jacobian \( J(r) \) for the transformation

\[
f^{(DVR)}_p(r) = J(r)^{-1/2} f^{(DVR)}_{i_1}(x^{(1)}) f^{(DVR)}_{i_2}(x^{(2)}) \cdots f^{(DVR)}_{i_n}(x^{(n)}),
\]

\[
i_1 = 1...N_1; \quad i_2 = 1...N_2; \quad \cdots \quad i_n = 1...N_n. \tag{A.21}
\]

The potential energy matrix elements are given by

\[
V_{pp'} = \int f^{(DVR)^*}_p(r)V(r)f^{(DVR)}_p(r) d^n r \approx V(r_p)\delta_{pp'}, \tag{A.22}
\]

where \( d^n r = J(r)dx^{(1)} dx^{(2)} \cdots dx^{(n)} \), \( \delta_{pp'} = \delta_{i_1'i_1}\delta_{i_2'i_2} \cdots \delta_{i_n'i_n} \) and \( r_p \) is a vector whose elements are grid points of the DVR bases for different coordinates, that is

\[
r_p = (x^{(1)}_{i_1}, x^{(2)}_{i_2}, ..., x^{(n)}_{i_n}). \tag{A.23}
\]

Finally the matrix elements of the kinetic energy matrix are evaluated exactly from

\[
T_{pp'} = \int f^{(DVR)^*}_p(r)T f^{(DVR)}_p(r) d^n r. \tag{A.24}
\]

### A.2 DVR related to Laguerre polynomials

Here we will illustrate the procedure of building a DVR representation for the problem of the hydrogen atom in a time-dependent electric field, which is the core of the numerical method used in this thesis and presented in reference [27]. The dynamics of a hydrogen atom in
a time-dependent electric field is described by the time-dependent Schrödinger equation (in atomic units):

\[
\left( -\frac{1}{2} \Delta - \frac{1}{r} + F(t) \right) \Psi(r, t) = i \frac{\partial \Psi(r, t)}{\partial t},
\]

(A.25)

where the time-dependent electric field \( F(t) \) is oriented along the \( z \)-axis. The projection of the electronic angular momentum \( L_z = m \) is an integral of motion, so we restrict the calculations to fixed \( m \), disregarding the dependence of the eigenfunctions on the azimuthal angle \((2\pi)^{-1/2} \exp(im\phi)\), and therefore reduce the problem to two spatial dimensions. We separate the problem in scaled parabolic coordinates \((u, v)\) such that

\[
\frac{u}{\lambda} = r + z, \quad \frac{v}{\lambda} = r - z,
\]

(A.26)

where \( \lambda \) is an arbitrary scaling parameter whose role is to be explained later in this section. In these coordinates, the Hamiltonian of the system can be written

\[
\hat{H}(t) = \hat{T} + V(u, v, t),
\]

(A.27)

where the kinetic energy operator \( \hat{T} \) in scaled parabolic coordinates has the form

\[
\hat{T} = \frac{2\lambda^2}{u + v} \left[ -\frac{\partial}{\partial u} \frac{\partial}{\partial u} - \frac{\partial}{\partial v} \frac{\partial}{\partial v} + \frac{m^2}{4} \left( \frac{1}{u} + \frac{1}{v} \right) \right],
\]

(A.28)

and the potential \( V \) is

\[
V(u, v, t) = -\frac{2\lambda}{u + v} + F(t)\frac{u - v}{2\lambda}.
\]

(A.29)

The eigenfunctions of the bound states of the field-free Hamiltonian separated in parabolic coordinates contain products of generalized Laguerre polynomials from both coordinates \( u \) and \( v \), that is

\[
\Phi_{n_1,n_2,m}(u, v, \phi) \sim \exp \left( -\frac{\epsilon}{2\lambda} (u + v) \right) (uv)^{\frac{1}{2}|m|} \times L_{n_1+|m|}^{\frac{\epsilon}{\lambda}u} L_{n_2+|m|}^{\frac{\epsilon}{\lambda}v} \exp(im\phi), \quad \epsilon = \frac{1}{n}.
\]

(A.30)

Therefore, it is intuitive to use DVR related to generalized Laguerre polynomials \( L_k^{[m]} \) for both \( u \) and \( v \) coordinates. The norm and the weight function of the generalized Laguerre polynomials are [76]

\[
h_k = \frac{(n + |m|)!}{n!}, \quad \text{and} \quad w(x) = x^{|m|}e^{-x},
\]

(A.31)

resulting in, as defined in [A.14],

\[
\varphi_n(u) = \left[ \frac{n!}{(n + |m|)!} \right]^{1/2} L_{n}^{[m]}(u)^{|m|/2}e^{-u/2}, \quad n = 0, 1, 2, ...N - 1
\]

(A.32)
The weights are calculated from equation (A.18) and using the properties of the Laguerre polynomials [76] this expression reduces to

$$w_i = \frac{1}{x_i (\varphi_N(x_i))}.$$  \hspace{1cm} (A.33)

The one-dimensional DVR basis functions we use are, from equation (A.6),

$$f_i^{(DVR)}(u) = w_i^{1/2} \sum_{n=0}^{N-1} \varphi_n(u_i) \varphi_n(u), \quad i = 1, 2, ..., N.$$ \hspace{1cm} (A.34)

In accordance with equation (A.2), the functions of the one-dimensional basis have the remarkable property

$$f_i^{(DVR)}(u_j) = w_i^{-1/2} \delta_{ij},$$ \hspace{1cm} (A.35)

that is, they are zero at all quadrature points except one. Moreover, the coordinate $u$ is diagonal in the basis (A.34) with eigenvalues equal to the grid points,

$$\int_0^\infty f_i^{(DVR)}(u)N_j^{(DVR)}(u)du = u_i \delta_{ij}.$$ \hspace{1cm} (A.36)

The two-dimensional basis is formed from a direct product of one-dimensional bases, taking care of the Jacobian, as defined in equation (A.21), i.e.,

$$f_{ij}^{(DVR)}(u, v) = \frac{2\lambda^{3/2}}{(u_i + v_j)^{1/2}} f_i^{(DVR)}(u) f_j^{(DVR)}(v).$$ \hspace{1cm} (A.37)

Using this basis, matrix elements of the potential energy are simply given by:

$$V_{ij,j'}(t) = V(u_i, v_j, t) \delta_{ii'} \delta_{jj'},$$ \hspace{1cm} (A.38)

where use has been made of the basic approximation of the DVR, that is, the substitution of the exact integration by the two-dimensional quadrature formula

$$\int_0^\infty du \int_0^\infty dv g(u, v) \approx \sum_{i=1}^{N_1} w_i \sum_{j=1}^{N_2} w_j g(u_i, v_j),$$ \hspace{1cm} (A.39)

where $g(u, v)$ is an arbitrary function. The matrix elements of the kinetic energy operator can be evaluated exactly by use of the differential equation satisfied by the functions $\varphi_k(u)$

$$\left(-\frac{\partial}{\partial u} \frac{\partial}{\partial u} - \frac{1}{4u} (m^2 - u^2)\right) \varphi_k(u) = \left(k + \frac{|m| + 1}{2}\right) \varphi_k(u),$$ \hspace{1cm} (A.40)

and taking into account the form of the kinetic energy operator (A.28). Explicitly, the matrix elements of the kinetic energy operator are

$$T_{ij,j'} = \int_0^\infty du \int_0^\infty dv f_{ij}^{(DVR)}(u, v) \hat{T} f_{ij'}^{(DVR)}(u, v) = \frac{2\lambda^2 (t_i \delta_{j,j'} + t_j \delta_{i,i'})}{(u_i + v_j)^{1/2}(u_i' + v_j')^{1/2}}.$$ \hspace{1cm} (A.41)
APPENDIX A: Numerical method based on the DVR

A.2 DVR related to Laguerre polynomials

where

\[ t_{ii}^u = \begin{cases} \frac{1}{2} \left( n + \frac{|m|+1}{2} - \frac{u_i + m^2 - 1}{2u_i} \right) & i = i' \\ 2(-1)^{i-i'} (u_i u_{i'})^{1/2} \left( u_i - u_{i'} \right)^{-2} & i \neq i' \end{cases} \] (A.42)

The exact evaluation of the kinetic energy term is a very useful property since the highly singular numerical derivatives are avoided, which is not the case with most of the other numerical methods based on propagation on a grid. The DVR also makes possible the inclusion of a realistic Coulomb potential since we only need the wavefunction at the grid points, thereby avoiding the singularity at the origin. Finally, the matrix elements of the kinetic energy term need to be evaluated only once for a particular symmetry of the problem, so changing the potential from Coulomb to some other local potential is straightforward.

Any arbitrary function \( g(u, v) \) can be decomposed in the DVR basis (A.37) and represented as a vector whose components are

\[ g_{ij} = \frac{((u_i + v_j)w_i w_j)^{1/2}}{2\lambda^{3/2}} g(u_i, v_j). \] (A.43)

This property enables one, in principle, to start doing the calculation from any initial wavefunction. It is also possible to reconstruct the complete wavefunction at arbitrary point from a given DVR vector by using the equation (A.3), but this injects an additional approximation into the calculations.

Note that in (A.34) and (A.37) it is possible to use symmetric bases, i.e. the same \( N \) for both \( u \) and \( v \) coordinates, or asymmetric bases, where the number of basis functions differ in each coordinate. In fact the asymmetric choice, for a given total number of basis functions, is more efficient since it more closely mirrors the physics of the directed electron motion which corresponds to bound motion in the \( u \) coordinate but unbound motion in the \( v \) coordinate, the bound motion requiring fewer basis functions.

Using the basis (A.37) the field-free atomic Hamiltonian matrix \( H_0 \) can be diagonalized to provide a finite set of atomic bound (with negative energies) and (discretized) continuum (with positive energies) pseudo-states. Both the dimension of the basis and the scaling parameter \( \lambda \) can be varied to reproduce the eigenenergies of the bound states very accurately and also to include enough states with positive energies so that the continuum is well represented. Clearly, by increasing the number of basis functions we obtain a better representation, but the maximum number of basis states is limited by the computation time and available memory. Therefore it is necessary to vary the scaling parameter \( \lambda \) to obtain better representation of the bound states of interest for minimal DVR basis size. For example, if one puts \( \lambda = 0.5 \) then one focuses onto the low-lying bound states. By decreasing \( \lambda \) the focus is lifted in the direction of highly excited bound states. For example in reference \[85\] the value of \( \lambda = 0.03 \) was chosen to obtain a good DVR representation of the Rydberg states. In both cases the continuum is well represented.

As already mentioned in Chapter 3, the time evolution of the system was calculated by using the explicit second-order propagation scheme:

\[ \Psi(r, t + \delta t) \approx \Psi(r, t - \delta t) - 2i\delta t \hat{H}(t)\Psi(r, t). \] (A.44)

In the above equation, the wavefunction is a vector in DVR representation and \( \hat{H} \) is represented as a matrix in DVR.
A.3 Concluding remarks

To summarize, a DVR basis can be associated with every class of orthogonal polynomial. A DVR basis function is related directly to the Gaussian points of the orthogonal polynomial in question, that is, the basis functions are evaluated only at the grid points. Hence the singularity of the Coulomb potential at the origin is avoided. The matrix elements of the Hamiltonian are calculated using the Gauss integration formula, thus making potential energy matrix elements diagonal in this basis, which is an approximation, and kinetic energy matrix exactly evaluated. Therefore the kinetic energy matrix is evaluated once for each problem, and is not affected by changing the potential energy term in the Hamiltonian. This is a very useful property since, in the problem of one-electron atom in an electric field, one can very easily change the atomic potential, which is diagonal in DVR, without the need to correct any other aspects of the calculation.
Appendix B

Derivation of transition probability in the advanced adiabatic approach

Here we show explicitly how one obtains the expression for the transition probability \( \Psi(15) \) from the expression for the wavefunction in the advanced adiabatic approach \( \Psi(14) \). In the advanced adiabatic approximation the wavefunction reads

\[
\psi_{\text{ad}}(r, t) = \frac{1}{\sqrt{2\pi v}} \int_C \left[ \frac{dQ(E)}{dE} \right]^{1/2} \varphi_i(r, E) \exp \left[ \frac{i}{v} \int_{E_i^{(0)}}^E Q(E')dE' - iEt \right] dE. \tag{B.1}
\]

In the above equation, \( E_i^{(0)} \) is the energy of the initial state \( (E_i(Q) \rightarrow E_i^{(0)} \text{ as } t \rightarrow -\infty) \), \( Q_i(E) \) is the inverse to the function \( E_i(Q) \) and

\[
\varphi_i(r, E) = \varphi_i(r, Q)|_{Q=Q_i(E)} \tag{B.2}
\]

is the eigenfunction extended into the complex \( E \)-plane. The function \( \varphi_i(r, E) \) represents an analytic continuation throughout the complex \( E \)-plane and carries information not only on the state \( |i\rangle \), but also on all adiabatic states linked to this state by the branch points, i.e. the states of the same symmetry. The indices \( i \) on the functions \( E \) and \( \varphi \) have the meaning of being on the \( i \)-th sheet of a given function, rather than denoting different analytic functions. Therefore the \( E_i(Q) \) and \( \varphi_i(r, Q) \) are the \( i \)-th sheet of the analytic function \( E(Q) \) and \( \varphi(r, Q) \) respectively. The analytic function \( Q(E) \) is inverse to \( E(Q) \).

The integration contour \( C \) should be such that the integrand vanishes at its ends. The contour is also determined by the initial boundary conditions. In the limit \( t \rightarrow -\infty \), and assuming that the initial state of the system is \( |i\rangle \) with energy \( E_i^{(0)} \), the contour (denoted as \( C' \) in figure \( \text{[B.1]} \) begins at \( E_i^{(0)} \) and goes to \(+\infty\). This is a contour of steepest descent, with the point \( E_i^{(0)} \) being the saddle point. In this way, the value of the integral \( \text{[B.1]} \) is determined by the integrand at the saddle point \( E_i^{(0)} \), so one obtains

\[
\lim_{t \rightarrow -\infty} \Psi_{\text{ad}}(r, t) = \varphi_i(r, E_i^{(0)}) \exp(-iE_i^{(0)}t), \tag{B.3}
\]

This solution obviously coincides with the eigenfunction of the atomic state \( |i\rangle \).
APPENDIX B: Derivation of transition probability in the advanced adiabatic approach

The contours at arbitrary $t$ could in principle be constructed, but at finite $t$ one is unable to use asymptotic methods for calculation of the integral (B.1). In the limit $t \to \infty$ the contour of integration starts at $-\infty$ and enclosing the bound-state eigenenergies goes to $\infty$. The reason for avoiding the bound-state energies is because of the singularities of the function $dQ(E)/dE$ at these points. This is illustrated in figure B.1 with the contour $C$. It is possible to deform the original contour $C$ in the lower half-plane so that we get a set of contours $C_n$, each corresponding to one bound state up to the last bound state (denoted as $E_f(0)$ in figure B.1) on the boundary with the continuum, plus a line coinciding with the positive Re$E$ axis which corresponds to the continuum. Since we want to calculate the probability of transition to a final state $|f\rangle$ we consider the contour $C_f$. The saddle point which determines the value of the integral can be found from the saddle-point equation

$$\frac{Q(E)}{v} - t = 0.$$  \hfill (B.4) 

This equation has as many roots $E_f = E(vt)$ as the number of discrete energy levels. For transition from the initial state $|i\rangle$ to the final state $|f\rangle$, the contour $C$ goes through the saddle-point $E_f$. Using saddle-point integration, from equation (B.1) we obtain

$$\Psi(r, t)^{ad} = \varphi_f (r, E_f(t)) \exp \left[ \frac{i}{v} \int_{E_i^{(0)}}^{E_f(t)} Q(E) dE - E_f(vt) vt \right], \hfill (B.5)$$

Figure B.1: The contours of integration $C$ (blue line) and $C'$ (cyan line). The set of contours $C_n$, obtained by deforming the contour $C$ are plotted in red.
APPENDIX B: Derivation of transition probability in the advanced adiabatic approach

and after a partial integration

\[
\Psi^{ad}(r, t) = \varphi_f(r, E_f(t)) \times \\
\times \exp \left[ -\frac{i}{v} \left( \int_{Q(E_f(t))} E(Q')dQ' + E_f(Q)Q + (\infty)E_i(-\infty) - vtE_f(vt) \right) \right]. \tag{B.6}
\]

In the limit \( t \to +\infty \), (B.6) transforms into

\[
\varphi_f(r, E_f(+\infty)) \exp \left[ -\frac{i}{v} \left( \int_{L} E(Q')dQ' + (\infty)E_i(-\infty) \right) \right], \tag{B.7}
\]

where \( E_f(+\infty) = E_f^{(0)} \) (the energy of the atomic state \(|f\rangle\)), and \( L \) is a contour in the complex \( Q \)-plane which begins at \( t \to -\infty \) on the energy surface \( E_i(Q) \), goes around the complex branch point (hidden crossing) \( Q_c \) connecting the adiabatic states \( i \) and \( f \), and at \( t \to +\infty \) ends on the energy surface \( E_f(Q) \). The final result for the probability of transitions \( p_{if} \) is

\[
p_{if} = \exp \left( -\frac{2}{v} \left| \operatorname{Im} \int_{L} E(Q)dQ \right| \right), \tag{B.8}
\]
APPENDIX B: Derivation of transition probability in the advanced adiabatic approach
Appendix C

Asymptotic expression in the case of a 2s initial state

In order to derive the asymptotic expression we start from the explicit expression for the matrix element $I(k') = k'^2 \int |\langle \phi_{k'} | \exp(-i\mathbf{q}' \cdot \mathbf{r}') | \phi_{2s} \rangle|^2 \, dk'$ given in [56]:

$$I = \frac{2^5 q'^2 k' \exp \left[ -(2/k') \tan^{-1}(k'/(q'^2 - k'^2 + 1/4)) \right]}{3[1 - \exp(2\pi/k')][(q' - k')^2 + 1/4]^5[(q' + k')^2 + 1/4]^5}$$

$$\times \left[ 3q'^{10} + \left( 8 - 11k'^2 \right) q'^8 + \left( \frac{41}{8} + 18k'^2 + 14k'^4 \right) q'^6 + \left( \frac{5}{16} - \frac{31}{8} k'^2 - 10k'^4 - 6k'^6 \right) q'^4 \right.$$  
$$+ \left( \frac{47}{320} - \frac{47}{80} k'^2 - \frac{7}{4} k'^4 - k'^6 \right) \left( \frac{1}{4} + k'^2 \right) q'^2 + \left( 1 + k'^2 \right) \left( \frac{1}{4} + k'^2 \right)^4 \right] \tag{C.1}$$

where we used the scaled quantities $k' = k/Z$, $q' = q/Z$, $r' = Zr$. We can use the fact that in the limit of $q' \to \infty$ there is a well defined peak in (C.1) at $k' = q'$, so we can factor the expression as follows,

$$I = f(k', q') \times g(k', q') \tag{C.2}$$

where $f(k', q') = \left((q' - k')^2 + 1/4\right)^{-5}$ is the part of the expression (C.1) which defines the peak at $k' = q'$. Next, by expanding $g(k', q')$ into Taylor series with respect to $k'$ at the point $k' = q'$ and subsequently taking the limit $q' \to \infty$ for the coefficients, one obtains,

$$\lim_{q' \to \infty} g(k', q') = \frac{1}{120\pi} - \frac{(k' - q')^2}{12\pi} + \frac{(k' - q')^4}{3\pi}. \tag{C.3}$$

Inserting (C.3) into (C.2) we get an asymptotic expression for $I(k')$. Using the linearization (7.13), the integral (7.10) reduces to

$$\int_{-\infty}^{\infty} \frac{\exp(-iu^2)}{(u^2 + 1/4)^5} \left( \frac{1}{120\pi} - \frac{u^2}{12\pi} + \frac{u^4}{3\pi} \right) \, du. \tag{C.4}$$

Integrating (C.4) and taking the squared modulus of the result one obtains the asymptotic expression (7.15).
APPENDIX C: Asymptotic expression in the case of a 2s initial state
Appendix D

Integral-equation based numerical method for ZRP

In this appendix we will explain the numerical method of solving the equation

\[ R(t) = -\left( \frac{1}{2\pi i} \right)^{1/2} \int_0^\infty \frac{dt'}{t'^{3/2}} \left[ e^{-i\mathcal{M}(t,t-t')} e^{-i\frac{t'^2}{2}} R(t - t') - R(t) \right], \quad (D.1) \]

where \( \mathcal{M}(t, t - t') \) is

\[ \mathcal{M}(t, t - t') = \frac{1}{2} \left[ \int_{t-t'}^t dt'' \mathbf{A}^2(t'') - \frac{1}{12} \left( \int_{t-t'}^t dt'' \mathbf{A}(t'') \right)^2 \right], \quad (D.2) \]

\[ \mathbf{A}(t) = -\int_{-\infty}^t dt' \mathbf{F}(t), \]

and \( \mathbf{F}(t) \) is the nonstationary electric field. The equation (D.1) is a homogeneous integral equation with singular kernel.

In the absence of the field, the solution of (D.1) is \( R(t) = 1 \) for all \( t \). Therefore, the initial condition of equation (D.1) is \( \lim_{t \to -\infty} R(t) = 1 \). We will solve the integral equation (D.1) for an electric field pulse of Gaussian shape

\[ F(t) = F_0 e^{-(t/\tau)^2}. \quad (D.3) \]

In this case it is safe to take \( R(t) = 1 \) for \( t \leq -3\tau \), and also to assume that the field is zero for \( t > 3\tau \).

We solve (D.1) on an equidistant time grid, that is, obtain \( R(t_n) \), \( t_n = nh - 3\tau \), \( n = 0, 1, 2, \ldots \) and \( t_n < 3\tau \), the initial condition being \( R(t_0) = 1 \). To calculate the integral on the right hand side of (D.1) we divide the integration space into two intervals - \([0, h] \) and \((h, \infty)\). In the first interval, by expanding the nonsingular part of the integral into Taylor series around the point \( t' = 0 \) and keeping the terms only up to the first order, we approximate:

\[
\int_0^h \frac{dt'}{t'^{3/2}} \left[ e^{-i\mathcal{M}(t_n,t_n-t')} e^{-i\frac{t'^2}{2}} R(t_n - t') - R(t_n) \right] \approx -\int_0^h \frac{dt'}{t'^{1/2}} \left[ \frac{i}{2} R(t_n) + R'(t_n) \right]
\]
\[ -(iR(t_n) + 2R'(t_n))\sqrt{h} \approx - \left( iR(t_n) + 2\frac{(R(t_n) - R(t_{n-1}))}{h} \right) \sqrt{h}, \quad (D.4) \]

since
\[ \lim_{t' \to 0} \frac{\partial M(t_n, t_n - t')}{\partial t'} = 0. \quad (D.5) \]

In the second interval \((h, \infty)\) we obtain
\[
\begin{align*}
\int_0^\infty \frac{dt'}{\sqrt{h}} \left[ e^{-iM(t_n, t_n - t')} e^{-i\frac{t'}{2}} R(t_n - t') - R(t_n) \right] \\
= \int_{h_{\text{max}}}^{h_{\text{max}}} \frac{dt'}{\sqrt{h}} e^{-iM(t_n, t_n - t')} e^{-i\frac{t'}{2}} R(t_n - t') \\
+ \int_{h_{\text{max}}}^{\infty} \frac{dt'}{\sqrt{h}} e^{-iM(t_n, t_n - t')} e^{-i\frac{t'}{2}} R(t_n - t') - \frac{2R(t_n)}{\sqrt{h}}.
\end{align*}
\]

We calculate the first term on the right hand side of (D.6) using the trapezoidal rule and then calculate the second term using the second-order cut-off formula
\[
\int_{h_{\text{max}}}^{\infty} e^{i\omega t} H(t) dt \approx - \frac{H(h_{\text{max}}) e^{i\omega h_{\text{max}}}}{i\omega} + \frac{H'(h_{\text{max}}) e^{i\omega h_{\text{max}}}}{(i\omega)^2} \quad (D.7)
\]

where in our case \(\omega = -1/2\). Using the equations (D.4) and (D.6) one can write the discretized version of the integral equation (D.1) as
\[
R(t_n) = - \left( \frac{1}{2\pi i} \right)^{1/2} \left( S - (ih^{1/2} + 4h^{-1/2}) R(t_n) \right), \quad (D.8)
\]

where \(S\) denotes the sum of all terms which do not depend on \(R(t_n)\), so the solution is
\[
R(t_n) = - \frac{S}{(2\pi i)^{1/2} - (ih^{1/2} + 4h^{-1/2})}. \quad (D.9)
\]

Since any error made in the calculation of \(R(t_n)\) will multiply itself in the solution of \(R(t_m)\), \(m > n\), one has to pay particular attention to the precision \(R(t_n)\) is calculated. Moreover, as we have checked for the case when electric field is absent and we know the exact solution, very small errors (relative error smaller than \(10^{-5}\)) made in calculation of \(R(-3\tau + h) \equiv R(t_1)\) result in completely wrong solution. Therefore one has to normalize the solution (D.9) after every time step, the normalization constant being obtained as the reciprocal value of \(R(-3\tau + h)\) in the absence of electric field. For the purpose of our calculation (calculating the response of the model negative ion to an electric field with \(\tau \in [0.1, 0.5] \) and \(F_0 \in [0.1, 0.5]\)) we used \(h = 5 \times 10^{-2}\) or \(h = 2.5 \times 10^{-2}\), and \(h_{\text{max}} \approx 5000\). We have verified that the calculations converge with respect to variations of both \(h\) and \(h_{\text{max}}\).
Once $R(t)$ is calculated, one is able to calculate the electron wavefunction according to equation (9.21). By means of variable substitution $t'(x) = -x + \sqrt{x^2 + r^2}$ we obtain

$$\psi(r, t) = (2\pi)^{-1} i^{-1/2} e^{i\frac{i}{2}} \int_{-\infty}^{\infty} dx \frac{e^{ix} e^{-iM(t, t - t'(x))} e^{-iR(r, t, 0, t - t'(x))}}{(-x + \sqrt{x^2 + r^2})^{1/2} \sqrt{x^2 + r^2}} R(t - t'(x)), \quad (D.10)$$

thereby removing the singularity in the integrand. This integral is numerically solved by trapezoidal integration in the interval $[h_{max}', h_{max}'']$ and then using the second order cut-off formula (D.7) and its equivalent for negative infinity. The values of the parameters $h_{max}'$, $h_{max}''$ and $h$ are varied to ensure converged calculation. The values of $R(t - t'(x))$ are interpolated from the calculated values $R(t_n)$ using standard spline interpolation procedure.

The same procedure for solving integral equation of type (D.1) can be applied to the case of the equivalent one-dimensional problem. In this case, the problem reduces to the following integral equation

$$\Phi(t) = \left( \frac{i}{2\pi} \right)^{1/2} \int_{0}^{\infty} dt' \frac{dM}{d^2} e^{-iM(t, t - t')} e^{-it'/2} \Phi(t - t'), \quad (D.11)$$

where $\mathcal{M}$ is defined in (D.2) by replacing $A$ with $A$. In the absence of the field $\Phi(t) = 1$ for all $t$ and therefore the initial condition of equation (D.11) is $\lim_{t \to -\infty} \Phi(t) = 1$. This makes the problem (D.11) formally equivalent to (D.1) and one can use the numerical procedure presented above to solve (D.11) as well.
APPENDIX D: Integral-equation based numerical method for ZRP
Bibliography


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