Engineering and Control of Quantum Processes by Short Laser Pulses

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Declaration of Authorship

I, Felipe CAJIAO VÉLEZ, declare that this thesis titled, 'Engineering and Control of Quantum Processes by Short Laser Pulses’ and the work presented in it are my own. I confirm that:

■ This work was done wholly or mainly while in candidature for a research degree at this University.

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■ Where I have consulted the published work of others, this is always clearly attributed.

■ Where I have quoted from the work of others, the source is always given. With the exception of such quotations, this thesis is entirely my own work.

■ I have acknowledged all main sources of help.

■ Where the thesis is based on work done by myself jointly with others, I have made clear exactly what was done by others and what I have contributed myself.

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E ngineering and C ontrol of Quantum P rocesses by Sh ort Laser P ulses

b y F elipe C ajiao V éle z

We study two of the most important phenomena in strong-field physics: ionization by intense laser pulses and high-order harmonic generation. For the former one, we develop the generalized eikonal approximation which includes the interaction between the ionized electron and its parent ion. In contrast to the original eikonal approximation, it avoids a singularity at the Coulomb potential centre. Thus, it can be successfully applied to analyze rescattering phenomena in terms of quantum trajectories. The latter one is treated according to the Lewenstein model, which ignores the interaction between the electron and the ion after it penetrates the Coulomb barrier and before it recombines. Nevertheless, the model describes the process in a good qualitative way.

Employing the generalized eikonal approximation, we study the coherent interference patterns in photoelectron energy spectra and their modifications induced by the interaction of photoelectrons with the atomic potential. As well, we analyze how different factors characterizing the laser pulse (such as modulations of the pulse envelope or a number of cycles) influence these structures. In other words, we demonstrate the possibility of controlling the process by an external laser field. On the other hand, the Lewenstein model is used to analyze the harmonic responses from the $C_{20}$ carbon clusters ($C_{20}$ fullerene and two of its isomers: ring and bowl) and the nitrogen molecule. We show that the harmonic spectra present well-defined modulations in the peak intensities, which are directly related to the geometry of the molecule and the symmetry of its electron orbitals. Multicentre interferences and quantum trajectories interference are the main sources of such modulations. Other properties, e.g., polarization of the harmonic response and harmonic ellipticity from nitrogen molecule, are also analyzed and related to the molecular structure. Finally, we discuss the prospects of using the harmonic spectra from molecules to develop a simple spectroscopic technique to identify their geometric configuration. As well, we discuss the application of the generalized eikonal approximation to study strong-field ionization from multicentre atomic systems and to study other strong-field phenomena.
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To my wife, the light of my life.
To my parents, the light of my existence.
Chapter 1

Introduction

2015 has been declared the *International Year of Light and Light-based Technologies* [1]. This is in recognition of a revolutionary role of light and optical technology in many disciplines of our life such as medicine, communication, defense, security, etc. It is clear that many of these applications are directly related to the availability of sources of spatially and temporally coherent light, the *lasers* [2–4].

Before the invention of the laser, the analytical calculations to describe light-matter interactions were generally carried out according to the lowest order perturbation theory [5]. This theoretical approach was enough to describe one- and two-photon processes generated by the low-intensity light sources available at that time. In the early 1960’s, after the first lasers became operational, several nonlinear phenomena started to be observed, which involved multiple photons interacting with matter. It was the high intensity and the spatial and temporal coherence of radiation which made it possible to observe processes like laser-induced breakdown of gases and multiphoton ionization of hydrogen [5]. For such an intense radiation, and particularly when the interaction involves more photons than necessary for ionization, the lowest order perturbation theory is not valid anymore and a different theoretical approach is required in order to explain the new nonlinear phenomena [6]. In order to account for these effects, a nonperturbative theory was developed by Keldysh in 1964 [7] (which is also known as the Keldysh-Faisal-Reiss or KFR theory [8, 9], and sometimes recognized as the strong-field approximation or SFA). It describes the situation when the electric field characterizing the electromagnetic wave is considered to be much more intense than the atomic interaction experienced by ionized electrons with their residual ions. The fact that the SFA theory neglects the interaction of the electron with the parent ion after ionization makes its application to the analysis of photoionization of neutral atoms questionable, due to the long-range nature of the Coulomb potential. Moreover, direct comparison between spectra obtained under the SFA framework and the numerical solution of the time-dependent Schrödinger equation have shown significant differences at low photoelectron energies. This can be attributed to the longer time spent by the slow electrons near their parent ions, where the Coulomb interaction is more important [10].

Many efforts have been undertaken in order to include the effects of long-range potentials into the SFA theory. For example, in the improved strong-field approximation, the Coulomb potential
is included as a perturbation by means of the Born series expansion [11–13]. The zeroth order of the expansion accounts for the direct multiphoton ionization and represents the SFA matrix element, whereas the first order in the binding potential reflects the rescattering process [11–14]. The introduction of this new term explains several of the spectral characteristics, but again disagrees with the experimental data at the low-energy part of the photoelectron spectrum [13].

In another effort to introduce the binding potential in the theory, the eikonal approximation was applied to the description of photoionization processes. In general, this quasiclassical approximation is extensively used to analyze scattering processes at high energies and small angles [15, 16], regime for which the perturbation theory is not good enough (see, also Ref. [17]). It has been applied, for instance, to study the electron scattering with laser fields in the relativistic and nonrelativistic frameworks [18]. The application of the so-called Molière-Glauber eikonal [19, 20] to the ionization process provided a new tool for the treatment of photoelectron dynamics in the presence of strong laser fields [21, 22]. In this thesis, we develop the generalized eikonal approximation and we apply it to analyze the photoionization spectrum of hydrogen-like atoms interacting with short laser pulses.

In addition to the photoionization by strong laser fields, another phenomenon, the high-order harmonic generation (HHG), has attracted a lot of attention and can be considered as one of the most important processes of photon emission in intense laser fields [23]. In such process, after being ionized, the electron is later recombined with the parent ion with the consequent emission of a highly energetic photon. The first experimental evidence of this phenomenon was presented by Franken et al. in 1961 [23], when the second harmonic was observed after the interaction of strong coherent light with nonlinear crystals. One of the first approximated models applied successfully to the understanding and analysis of the HHG process in atoms is the so-called three step semiclassical model (TSM), developed in the early 1990’s [24–27]. The idea behind this model is to analyze the complete process as a sequence of three different events: ionization, propagation, and recombination. The first one, treated quantum-mechanically, describes the electron penetration through the distorted Coulomb barrier leading to ionization. The second step, the propagation, considers the classical trajectory of an electron in the presence of an electromagnetic wave ignoring any interaction with the atomic electrostatic potential, which is usually done in the strong-field approximation. The final step, the recombination, is again treated quantum-mechanically and describes the recombination of a highly energetic electron with the parent ion resulting in the emission of a harmonic photon [27, 28] (see, Section 3.1). The quantum-mechanical counterpart of the TSM is the so-called Lewenstein model. It accounts for quantum effects during the second step by considering an electron wave packet propagating in the continuum under the influence of an electromagnetic field [29].

The interaction of low-frequency, high-intensity laser fields with atomic systems is a source of coherent light with well-defined frequencies, which, in principle, can reach the keV regime [30]. Moreover, the HHG signal can be used to generate very short pulses, which is due to phase-matching properties of harmonic radiation in a macroscopic medium [31]. By controlling the macroscopic properties of the harmonic media and the individual atomic or molecular responses, it is possible to generate a train of ultrashort, coherent XUV pulses with duration around hundreds of attoseconds [32, 33]. Note that the intrinsic short time scale at which the HHG takes place makes it also an interesting tool to observe in real time and to control the electron dynamics in molecules and atoms [34]. For instance,
it was demonstrated that HHG can be used to image molecular orbitals [35], which is the starting point for orbital tomographic techniques allowing to monitor the evolution of chemical reactions.

It is important to note that the harmonic response obtained from atoms differs from the one obtained from molecules. When the molecular case is considered, new degrees of freedom can be used in order to control the properties of the harmonics. Different factors, including the molecular orientation and geometry, electron wave function properties, etc., are of great importance for a proper analysis of HHG. Therefore, an appropriate analysis of the harmonic response as a function of such parameters is fundamental for the understanding and application of HHG. It is the purpose of the second part of this thesis to develop a detailed analysis of the harmonic spectral properties obtained from different molecules, including carbon clusters like the $C_{20}$ fullerene, two of its isomers, and the nitrogen molecule.

The general aim of this thesis is to analyze two of the most important processes arising from the interaction of atoms or molecules with intense laser fields: the strong-field ionization and the high-order harmonic generation. In Chapter 2, we develop the generalized eikonal approximation in order to analyze the ionization of atomic targets by short laser pulses. This new approach avoids a singularity at the centre of the binding Coulomb potential and, in contrast to the Molière-Glauber eikonal, can be analyzed in terms of complex quantum trajectories. In order to illustrate this theory, the photoionization spectrum obtained by the interaction of ultrashort laser pulses with a hydrogen-like atom is analyzed. We show that, by changing certain parameters of the driving laser field, it is possible to control the characteristics of the photoelectron spectrum. Specifically, we demonstrate that, when the driving field consists of a sequence of two or more pulses, the photoelectron spectral response exhibits a comb-like structure due to inter-pulse interferences.

Chapter 3 provides a general description of the HHG process under the scope of the modified Lewenstein model, which accounts for multicentre systems. Problems related to the absence of gauge invariance and the influence of quantum trajectories in such model are studied.

Chapter 4 includes the analysis of the harmonic spectrum from molecules under the Lewenstein model. The responses arising from three carbon clusters (the $C_{20}$ fullerene, bowl, and ring) are analyzed by taking into account their geometrical properties and orientation. The $N_2$ molecule is also studied in order to understand the ellipticity properties of the harmonic response in the length and velocity gauges.

The last Chapter contains the conclusions and prospects for further development of the generalized eikonal approximation and investigations of the HHG from molecules.

Throughout this thesis we use atomic units (a.u.), for which $\hbar = 1$, but we explicitly express the electron charge, $e < 0$, and its mass, $m$, in the equations. For numerical calculations we set $|e| = 1$ and $m = 1$, unless stated otherwise.

The results presented in this thesis are based in part on the following publications:

and they have been presented at conferences as contributing papers:

• *Generalized eikonal approximation in strong field ionization* (poster), F. Cajiao Vélez, K. Krajewska, J. Z. Kamiński, and R. M. Potvliege, International Laser Physics Workshop LPHYS’12, Calgary, Canada (2012),

• *High harmonic generation from different isomers of C_{20} molecules* (talk), F. Cajiao Vélez and A. Jaroń-Becker, International Laser Physics Workshop LPHYS’14, Sofia, Bulgaria (2014),

• *Multielectron effects in molecular dynamics driven by intense laser pulses* (poster), Y. Xia, F. Cajiao Vélez, and A. Jaroń-Becker, 45th Annual Meeting of the APS Division of Atomic, Molecular and Optical Physics, Madison, USA (2014),

Chapter 2

Generalized eikonal approximation in strong-field ionization

Historically, the eikonal approximation was first introduced in relation to light scattering [36, 37]. Since then, such theory has been extensively applied not only in optics but also in atomic and molecular physics, quantum field theory, high energy physics, etc. The first application to modern theories was the analysis of scattering processes of energetic particles, as originally proposed by Molière [19]. The idea behind the Molière approximation was the interpretation of particle trajectories as classical, straight line paths, which can be explained provided that the de Broglie wavelength of the scattered particle is small compared with the size of the scatterer [17, 38, 39]. The pioneering work of Glauber [20] extended the Molière eikonal to the interaction of fast particles with complex atomic and nuclear systems, and established the basis of an exceptionally valuable technique to treat scattering processes at high energies.

After the theoretical bases were set, the eikonal approximation (EA) was successfully applied to more complex systems. For example, it was applied for the treatment of the inverse bremsstrahlung heating, which involves the electron scattering by a potential in the presence of intense electromagnetic fields [40–42]. In the original work of Choudhury and Bhakar [40, 41], and of Zon [42], the scattering amplitude was obtained by using the EA for the nonrelativistic Schrödinger equation and the laser field was considered as a monochromatic plane wave. The dipole approximation was extensively used in such calculations. Krstić and Mittleman [22] have shown that, for ionization in strong laser fields, the electron motion should be treated relativistically and the dipole approximation is not good enough to determine correctly the electron energy distribution and the transition rate as a function of the laser intensity. In order to account for those facts, the eikonal perturbation theory was proposed by Kamiński [18] for the nonrelativistic Schrödinger equation and the relativistic Klein-Gordon equation. For the nonrelativistic case the dipole approximation for the laser pulse was used and applied to free-free transitions, whereas for the relativistic ones the finite, in general, laser pulses in the plane-wave-front approximation were considered. Note that the approach developed by Kamiński in [18] was based on the proper-time method, which for propagators in quantum theories was proposed by Fock [43], and further developed by Schwinger [44, 45], and by Fradkin and co-workers [46–48] (see, also the review [49]).
It has been demonstrated that, for potential scattering in the presence of strong fields, the EA has certain limitations. Specifically, such a theory cannot be applied in regions far from the potential interaction zone [50]. Other considerations restrict the EA just to moderate laser intensities [51]. The so-called generalized eikonal approximation (GEA), which is the first order term of the eikonal perturbation theory [18], overcame part of the mentioned problems by including certain quantum properties of the system in the eikonal limit. The inclusion of such terms extended the range of applicability of the theory to large distances from the interaction site [50] allowing a proper treatment of the scattering amplitude. The GEA was further extended to solving the relativistic Dirac equation in order to account approximately for the electron spin effects [51].

In Refs. [52, 53], the so-called eikonal-Volkov approximation was introduced to treat strong-field ionization of atoms. This consisted in the inclusion of the laser field in its full extent by means of the Volkov wave function, together with the atomic potential treated within the EA (see, for instance, also Refs. [54–60]). This approach was further developed by Smirnova et al. [61, 62] to describe molecular ionization. It included the dynamical analysis of the electrons according to complex trajectories, which is a powerful tool for the overall understanding of the process (for complex trajectory method, see, for instance, recent reviews [5, 10]).

Another way to treat the photoionization by intense laser fields is by means of the strong-field approximation. The principal idea of the SFA approach is that, after the photoelectron appears in the continuum, it is treated as a free particle interacting with the laser field, ignoring any interaction with the atomic potential during its excursion. Even though the SFA theory is known as one of the most fruitful analytical approaches in strong-field physics, its application can be justified for short-range potentials only, not for the Coulomb-type potentials present during ionization of neutral atoms (see, also the most recent review by Popruzhenko [5]). The SFA theory gives, in general, a very good qualitative agreement with experimental and numerical results for laser light of moderate intensities in interaction with a short-range potential [6] but it fails to account for several well-documented spectral characteristics, including the wrong predictions obtained for the total ionization rate in the static-field limit [63].

Various methods have been proposed for taking the Coulomb interaction into account within the SFA. Except of the aforementioned eikonal-Volkov approach [52–62, 64], it has been done, for instance, by means of the Coulomb-Volkov ansatz [65–70] which accounts for the asymptotic phase of the atomic field-free wave function. In this context also, the saddle-point method was reformulated in terms of quantum trajectories by Popov and co-workers [71–74], by Gribakin and Kuchiev [75], and reviewed recently by Popruzhenko [5]. The quantum trajectories together with a detailed analysis of the saddle-point equations have shown to make considerable improvements in the SFA to include the Coulomb interactions [76]. In this Chapter, we use the quantum trajectories as presented in Ref. [63]. Note that the extension of this method to the Dirac equation has been also reported [77].

In this Chapter, we propose a generalization of the eikonal approximation in order to analyze the photoionization of atoms or ions by short laser pulses. This approach avoids a singularity at the centre of the binding potential and, in contrast to the EA, can be analyzed in terms of quantum trajectories, which simplifies the problem considerably.
We will start by describing the time-evolution in quantum mechanics in a very general way. Such description will be applied to a specific case, the atomic photoionization process. After the bases of the problem are established, we will develop the generalized eikonal approximation. We will demonstrate the generality and range of applicability of the GEA by comparing it with different theories of strong-field ionization including the Keldysh theory, the improved strong-field approximation, and the originally used eikonal approximation. We will demonstrate that, under certain conditions, the spectrum of ionized electrons presents coherent structures due to interference effects, which can be controlled by modifying the driving pulse parameters. In the last part of this Chapter, we will illustrate numerically the influence of the atomic potential, included in the calculations by means of the present theory, on the photoelectron spectrum of ionization.

2.1 Theoretical background

If the initial state of a quantum system, \( |\psi(t')\rangle \), and the Hamiltonian, \( \hat{H} \), that governs its evolution, are known, it is possible to determine the final state of the system at time \( t \) by applying a linear operator \( \hat{U}(t,t') \),

\[
|\psi(t)\rangle = \hat{U}(t,t')|\psi(t')\rangle ,
\]

known as the evolution operator. It is clear from this equation that \( \hat{U}(t,t') \) satisfies the initial condition

\[
\hat{U}(t',t') = \hat{I} ,
\]

where \( \hat{I} \) is the identity operator. In the following, we assume that the Hamiltonian depends on time, \( \hat{H}(t) \). Applying the definition (2.1) to the Schrödinger equation,

\[
i \frac{d}{dt} |\psi(t)\rangle = \hat{H}(t)|\psi(t)\rangle ,
\]

one obtains the following relation,

\[
i \frac{\partial}{\partial t} \hat{U}(t,t')|\psi(t')\rangle = \hat{H}(t)\hat{U}(t,t')|\psi(t')\rangle ,
\]

or, equivalently,

\[
i \frac{\partial}{\partial t} \hat{U}(t,t') = \hat{H}(t)\hat{U}(t,t') .
\]

The solution of this equation, which accounts for the initial condition (2.2), can be formally written as the integral Lippmann-Schwinger equation,

\[
\hat{U}(t,t') = \hat{I} - i \int_{t'}^{t} d\tau \hat{H}(\tau)\hat{U}(\tau,t').
\]
Generalized eikonal approximation in strong-field ionization

The final expression for the evolution operator is
\[
\hat{U}(t, t') = \hat{T} \exp \left( -i \int_{t'}^t \mathrm{d} \tau \hat{H}(\tau) \right),
\]  
(2.7)

where \( \hat{T} \) is the time-ordering operator \([39, 78]\) defined as
\[
\hat{T}(\hat{H}(t)\hat{H}(t')) = \begin{cases} 
\hat{H}(t)\hat{H}(t') & \text{if } t > t', \\
\hat{H}(t')\hat{H}(t) & \text{if } t' > t.
\end{cases}
\]  
(2.8)

Note that in the case when the Hamiltonian is time-independent or if, at different times, it happens that \([\hat{H}(t), \hat{H}(t')] = 0\), one can disregard the time-ordering operator in the definition (2.7).

Using the Dirac notation for the wave function in the position representation,
\[
\psi(r, t) = \langle r | \psi(t) \rangle
\]  
(2.9)

and Eq. (2.1), we can write that
\[
\psi(r, t) = \langle r | \hat{U}(t, t') | \psi(t') \rangle.
\]  
(2.10)

Next, by inserting here the closure relation (A.4), we arrive at the following expression,
\[
\psi(r, t) = \int \mathrm{d}r' \langle r | \hat{U}(t, t') | r' \rangle \psi(r', t').
\]  
(2.11)

The quantity
\[
K(r, t; r', t') = \langle r | \hat{U}(t, t') | r' \rangle
\]  
(2.12)

is called the propagator and it satisfies the initial condition
\[
K(r, t'; r', t') = \delta(r - r').
\]  
(2.13)

Now, in terms of the wave function, the time-evolution of the system takes the form
\[
\psi(r, t) = \int \mathrm{d}r' K(r, t; r', t') \psi(r', t').
\]  
(2.14)

This equation allows us to interpret the propagator as the probability amplitude of finding a particle at position \( r \) at time \( t \), provided that at time \( t' \) it was located at position \( r' \). Next, substituting Eq. (2.14) into the time-dependent Schrödinger equation, we find out that the propagator (2.12) satisfies the equation
\[
\frac{i}{\hbar} \frac{\partial K(r, t; r', t')}{\partial t} = H(r, -i \nabla, t) K(r, t; r', t').
\]  
(2.15)

Here, \( \hat{p} = -i \nabla \) is the momentum operator in the position representation. In other words, the propagator \( K(r, t; r', t') \) is the solution of the Schrödinger equation which satisfies the initial condition (2.13).
2.1.1 Retarded propagator

To emphasize that we are interested in the evolution of a particle forward in time (i.e., for \( t > t' \)), we introduce the notion of the \textit{retarded propagator} \cite{78, 79}. It is defined as

\[
K(r, t; r', t') = \theta(t - t') \langle r | \hat{U}(t, t') | r' \rangle, \tag{2.16}
\]

where \( \theta(t - t') \) is the Heaviside step function. While we keep the same notation, since now on we will deal only with the retarded propagators. In light of Eq. (2.13), we understand that the retarded propagator satisfies the initial condition

\[
K(r, t' + 0; r', t') = \delta(r - r'). \tag{2.17}
\]

In order to derive the differential equation that it satisfies, let us differentiate Eq. (2.16) with respect to \( t \). In doing so, we obtain

\[
\frac{\partial K(r, t; r', t')}{\partial t} = \delta(t - t') \langle r | \hat{U}(t, t') | r' \rangle + \theta(t - t') \langle r | \frac{\partial \hat{U}(t, t')}{\partial t} | r' \rangle. \tag{2.18}
\]

Here, taking into account Eqs. (2.2), (2.5), and the normalization condition (A.3), we rewrite the last equation such that

\[
i \frac{\partial K(r, t; r', t')}{\partial t} = i \delta(t - t') \delta(r - r') + \theta(t - t') \langle r | H(t) \hat{U}(t, t') | r' \rangle. \tag{2.19}
\]

Inserting here the closure relation (A.4), we obtain

\[
i \frac{\partial K(r, t; r', t')}{\partial t} = i \delta(t - t') \delta(r - r') + H(r, -i \nabla, t) K(r, t; r', t'). \tag{2.20}
\]

Hence, the retarded propagator satisfies the following partial differential equation,

\[
\left[ i \frac{\partial}{\partial t} - H(r, -i \nabla, t) \right] K(r, t; r', t') = i \delta(t - t') \delta(r - r'), \tag{2.21}
\]

with the initial condition (2.17).

Actually, one can derive an equivalent equation to (2.21) but in terms of the ‘\( \text{prime} \)’ variables. In order to show this, we take the derivative of Eq. (2.16) with respect to \( t' \). This leads us to

\[
\frac{\partial K(r, t; r', t')}{\partial t'} = -\delta(t - t') \langle r | \hat{U}(t, t') | r' \rangle + \theta(t - t') \langle r | \frac{\partial \hat{U}(t, t')}{\partial t'} | r' \rangle. \tag{2.22}
\]

In addition to employing here Eqs. (2.2) and (A.3), we make use of

\[
i \frac{\partial \hat{U}(t, t')}{\partial t'} = -\hat{U}(t, t') \hat{H}(t'), \tag{2.23}
\]
which follows from the definition of the evolution operator (2.7). Thus, Eq. (2.22) becomes
\[
\frac{i}{\partial t} \frac{\partial K(r, t; r', t')}{\partial t'} = -i\delta(t - t')\delta(r - r') - \theta(t - t')\langle r|\hat{U}(t, t')\hat{H}(t')|r'\rangle. \tag{2.24}
\]
Plugging here the closure relation (A.4) and using the definition (2.16), we find out that
\[
\frac{i}{\partial t} \frac{\partial K(r, t; r', t')}{\partial t'} = -i\delta(t - t')\delta(r - r') - H(r', i\nabla', t') K(r, t; r', t'). \tag{2.25}
\]
Thus, in terms of the prime variables, the retarded propagator satisfies the following differential equation,
\[
\left[-i\frac{\partial}{\partial t'} - H(r', i\nabla', t')\right] K(r, t; r', t') = i\delta(t - t')\delta(r - r'), \tag{2.26}
\]
which has to be solved accounting for the condition (2.17). Note that the Hamiltonian in Eqs. (2.21) and (2.26) is expressed differently. This difference follows from the fact that
\[
\langle r|\hat{p}|r'\rangle = -i\nabla\delta(r - r') = i\nabla'\delta(r - r'), \tag{2.27}
\]
which can be proven using the closure relation (A.9). In light of this relation,
\[
\langle r|\hat{p}|r'\rangle = \int \frac{dp}{(2\pi)^3} \langle r|p\rangle \langle p|\hat{p}|r'\rangle = \int \frac{dp}{(2\pi)^3} e^{ip\cdot r} p e^{-ip\cdot r'} = -i\nabla \int \frac{dp}{(2\pi)^3} e^{ip\cdot (r-r')} = -i\nabla\delta(r - r'). \tag{2.28}
\]
Similarly, one can show that \(\langle r|\hat{p}'|r'\rangle = i\nabla'\delta(r - r')\).

So far, our considerations have been very general. However, our purpose is to derive the form of the retarded propagator for a charged particle in an electromagnetic field. Later on, this will allow us to formulate the generalized eikonal approximation for strong-field ionization. However, before going further, we need to elaborate on a gauge invariance.

### 2.1.2 Retarded propagator for a particle in an electromagnetic field under the gauge transformation

Consider a particle of charge \(e\) and mass \(m\) that is placed in an electromagnetic field. The field is described by the scalar, \(\phi(\hat{r}, t)\), and the vector, \(A(\hat{r}, t)\), potentials so the Hamiltonian governing the particle dynamics equals
\[
\hat{H}(\hat{r}, \hat{p}, t) = \frac{1}{2m} [\hat{p} - eA(\hat{r}, t)]^2 + e\phi(\hat{r}, t). \tag{2.29}
\]
In order to derive the retarded propagator for this Hamiltonian, one can use either Eq. (2.21) or (2.26), as they are equivalent. For now, we will use Eq. (2.21) which for the given Hamiltonian (2.29) takes
the form
\[ \left[ i \frac{\partial}{\partial t} - \frac{1}{2m} \left( -i \nabla - eA(r, t) \right)^2 - e\phi(r, t) \right] K(r, t; r', t') = i\delta(t - t')\delta(r - r'). \quad (2.30) \]

As it is known, the scalar and vector potentials are not unique. Meaning that two sets of potentials \((\phi, A)\) and \((\tilde{\phi}, \tilde{A})\) may correspond to the same electromagnetic field characterized by the electric and magnetic vectors, \(E(r, t)\) and \(B(r, t)\), respectively. This happens if the following gauge transformation is established \([79]\),
\begin{align*}
\tilde{\phi}(r, t) &= \phi(r, t) - \frac{\partial \Lambda(r, t)}{\partial t}, \quad (2.31) \\
\tilde{A}(r, t) &= A(r, t) + \nabla \Lambda(r, t), \quad (2.32)
\end{align*}
where \(\Lambda(r, t)\) is an arbitrary function. Taking into account that \([80]\)
\begin{align*}
E(r, t) &= -\nabla \phi(r, t) - \frac{\partial A(r, t)}{\partial t}, \quad (2.33) \\
B(r, t) &= \nabla \times A(r, t), \quad (2.34)
\end{align*}
one can show that both sets of potentials, related through Eqs. (2.31) and (2.32), lead to the same fields, (2.33) and (2.34). In other words, that the same equations (2.33) and (2.34) are satisfied if we replace \((\phi, A)\) by \((\tilde{\phi}, \tilde{A})\). The change of potentials according to (2.31) and (2.32) seems to change the Hamiltonian (2.29). This would result, in turn, in the change of physical observables such as the energy of the particle. In order to avoid this problem, one has to remember that under the gauge transformation, the wave function also changes such that \([79]\)
\[ \tilde{\psi}(r, t) = e^{ie\Lambda(r, t)}\psi(r, t). \quad (2.35) \]
One can check that if \(\psi(r, t)\) is the solution of the Schrödinger equation for the potentials \((\phi, A)\) then \(\tilde{\psi}(r, t)\), defined by Eq. (2.35), is the solution of the Schrödinger equation for the potentials \((\tilde{\phi}, \tilde{A})\). When it comes to the retarded propagator, the respective transformation has the form
\[ \tilde{K}(r, t; r', t') = e^{ie\Lambda(r, t)} K(r, t; r', t')e^{-ie\Lambda(r', t')}. \quad (2.36) \]
In order to prove it, we substitute
\[ K(r, t; r', t') = e^{-ie\Lambda(r, t)} \tilde{K}(r, t; r', t')e^{ie\Lambda(r', t')} \]
into Eq. (2.30). As a result, we arrive at
\[ \left[ i \frac{\partial}{\partial t} - \frac{1}{2m} \left( -i \nabla - eA(r, t) - e\nabla \Lambda(r, t) \right)^2 - e\phi(r, t) + e\frac{\partial \Lambda(r, t)}{\partial t} \right] \tilde{K}(r, t; r', t') \]
\[ = i\delta(t - t')\delta(r - r'). \quad (2.38) \]
Here, we recognize that the transformation of the propagator (2.36) is in agreement with the gauge transformation of the potentials (2.31) and (2.32). Therefore, using these equations, we can write
down that
\[
\left[ i \frac{\partial}{\partial t} - \frac{1}{2m} \left( -i \nabla - e \tilde{A}(r, t) \right)^2 - e \tilde{\phi}(r, t) \right] \tilde{K}(r, t; r', t') = i \delta(t - t') \delta(r - r') .
\] (2.39)

The same can be checked starting with Eq. (2.26).

### 2.1.3 Dipole and single-active-electron approximations

The above general formulation will be used in this thesis to describe ionization of an atomic system by a strong laser field. In order to describe the interaction with the laser field, the so-called dipole approximation will be used [79]. It is based on the assumption that the wavelength of the laser field is large compared to the size of the atom. Since the typical extension of atomic orbits is of the order of angstroms, this condition is well satisfied for radiation corresponding to the infrared, visible, and ultraviolet part of the electromagnetic spectrum. In this case, the vector potential describing the laser field is assumed to be spatially homogeneous, meaning that \( \tilde{A}(r, t) = \tilde{A}(t) \). Actually, one has also to assure that the laser field is not too strong which excludes the relativistically-strong laser fields. On the other hand, the atomic interaction is taken care of by assuming that, at each time, there is only one electron which interacts with the laser field. This is known as the single-active-electron approximation (SAE) [25, 81, 82], and it is represented by a one-electron scalar potential, \( \phi(r, t) = \phi(r) \). In this case, the Hamiltonian (2.29) can be written in the velocity gauge [83],

\[
\hat{H}_V(\hat{r}, \hat{p}, t) = \frac{1}{2m} [\hat{p} - eA(t)]^2 + e \phi(\hat{r}).
\] (2.40)

Using the function
\[
\Lambda(\hat{r}, t) = -A(t) \cdot \hat{r},
\] (2.41)
one can derive the form of the new set of potentials,

\[
\tilde{\phi}(\hat{r}, t) = \phi(\hat{r}) - E(t) \cdot \hat{r},
\] (2.42)

\[
\tilde{A}(\hat{r}, t) = 0 .
\] (2.43)

Thus, the Hamiltonian (2.40) can be written in the length gauge such that [83]

\[
\hat{H}_L(\hat{r}, \hat{p}, t) = \frac{\hat{p}^2}{2m} - eE(t) \cdot \hat{r} + e \phi(\hat{r}) .
\] (2.44)

As discussed in the previous Section, along with the gauge transformation of potentials [Eqs. (2.42) and (2.43)], one has to transform the wave function and the propagator. If \( K_V(r, t; r', t') \) denotes the retarded propagator in the velocity gauge, which corresponds to the Hamiltonian (2.40), thus, in the length gauge, the propagator \( K_L(r, t; r', t') \) will have the form

\[
K_L(r, t; r', t') = e^{-ieA(t) \cdot r} K_V(r, t; r', t') e^{ieA(t')} r' .
\] (2.45)

This equation will be used in the next Section.
2.2 Generalized eikonal approximation (GEA)

In this Section, the generalized eikonal approximation will be formulated. To this end, we first derive the formula for the retarded propagator being the solution of Eq. (2.26). In this equation, we assume that the Hamiltonian describes the electron coupled to the laser field under the dipole approximation. While in our case, the electron couples also to the static atomic potential, for the time being we will consider a more general case in which \( \phi \) also depends on time, \( \phi(r, t) \). For convenience, from now on we will use the potential energy \( V(r, t) \equiv e\phi(r, t) \). Therefore, the equation that we are going to solve (2.26) takes the form

\[
-\frac{i}{\partial t} - \frac{1}{2m} (i \nabla' - eA(t'))^2 - V(r', t') = i\delta(t - t')\delta(r - r').
\]

(2.46)

Here, we explicitly write \( K_V(r, t; r', t') \) to emphasize that the propagator is calculated in the velocity gauge.

Our further development is based on the Fock-Schwinger proper time treatment [18, 43–49]. One can check that for a free particle, for which \( A(t') = 0 \) and \( V(r', t') = 0 \), the following function

\[
K(r, t; r', t') = \int_0^\infty ds \int \frac{d\Omega dk}{(2\pi)^{d+1}} \exp\left[-i\Omega(t - t') + ik \cdot (r - r') + is\left(\Omega - \frac{k^2}{2m} + i\epsilon\right)\right]
\]

(2.47)

is the solution of Eq. (2.46). Note that (2.47) solves this equation in an arbitrary number of dimensions \( d \). In addition, \( s \) is called the proper time and \( \epsilon > 0 \) is an infinitesimally small, real number. In analogy to the free particle solution (2.47), we propose to look for the solution of Eq. (2.46) for arbitrary \( A(t') \) and \( V(r', t') \) in the Fock-Schwinger representation as well. Namely, in \( d \) dimensions, we propose that

\[
K_V(r, t; r', t') = \int_0^\infty ds \int \frac{d\Omega dk}{(2\pi)^{d+1}} \exp\left[-i\Omega(t - t') + ik \cdot (r - r') + is\left(\Omega - \frac{k^2}{2m} + i\epsilon\right)\right]
\]

\[
+ i\Phi_k(t', s) + i\chi_k(r', t', s)
\]

(2.48)

is the solution of Eq. (2.46). Here, we have introduced the unknown functions \( \Phi_k(t', s) \) and \( \chi_k(r', t', s) \). We have purposely extracted \( \Phi_k(t', s) \) which depends only on time variables, similar to a part of the Hamiltonian containing the vector potential in the dipole approximation. The remaining part, \( \chi_k(r', t', s) \), which is called eikonal, contains both time- and space-dependence, similar to \( V \). Thus, both unknown functions must satisfy the following conditions,

\[
\Phi_k(t', s) = 0 \quad \text{when} \quad A = 0,
\]

\[
\chi_k(r', t', s) = 0 \quad \text{when} \quad V = 0.
\]

(2.49)

(2.50)

It is clear that, when \( A = 0 \) and \( V = 0 \), Eq. (2.48) is consistent with the free particle propagator (2.47).
After inserting Eq. (2.48) into Eq. (2.46), we obtain

\[
\int_0^\infty ds \int \frac{d\Omega d\mathbf{k}}{(2\pi)^{d+1}} e^{-i\Omega(t-t')-i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')} \left[ \Omega - \frac{k^2}{2m} + \frac{e}{m} \mathbf{k} \cdot \mathbf{A}(t') - \frac{e^2}{2m} \mathbf{A}^2(t') - V(r', t') + \frac{\partial}{\partial t'} \Phi_k + \frac{\partial}{\partial t'} \chi_k + \frac{1}{m}(\mathbf{k} - e\mathbf{A}(t')) \cdot \nabla' \chi_k + \frac{i}{2m} \Delta' \chi_k - \frac{1}{2m} (\nabla' \chi_k)^2 \right] 
\times \exp \left[ is \left( \Omega - \frac{k^2}{2m} + i\varepsilon \right) + i\Phi_k + i\chi_k \right] 
= i\delta(t - t') \delta(\mathbf{r} - \mathbf{r}').
\] (2.51)

On the other hand, one can show that the Dirac delta functions in Eq. (2.51) can be represented as

\[
\delta(t - t') \delta(\mathbf{r} - \mathbf{r}') = -i \int_0^\infty ds \int \frac{d\Omega d\mathbf{k}}{(2\pi)^{d+1}} \left( \Omega - \frac{k^2}{2m} + \frac{\partial \Phi_k}{\partial s} + \frac{\partial \chi_k}{\partial s} \right) 
\times \exp \left[ -i\Omega(t - t') + i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}') + is \left( \Omega - \frac{k^2}{2m} + i\varepsilon \right) + i\Phi_k + i\chi_k \right],
\] (2.52)

provided that

\[
\int_0^\infty ds \frac{\partial}{\partial s} \exp \left[ is \left( \Omega - \frac{k^2}{2m} + i\varepsilon \right) + i\Phi_k + i\chi_k \right] = i.
\] (2.53)

Combining Eqs. (2.51) and (2.52), we arrive at the following equation for the functions \(\Phi_k(t', s)\) and \(\chi_k(r', t', s)\),

\[
\frac{\partial \Phi_k}{\partial s} + \frac{\partial \chi_k}{\partial s} = \frac{\partial \Phi_k}{\partial t'} + \frac{\partial \chi_k}{\partial t'} + \frac{e}{m} \mathbf{A}(t') \cdot (\mathbf{k} - e\mathbf{A}(t')) + \frac{1}{m}(\mathbf{k} - e\mathbf{A}(t')) \cdot \nabla' \chi_k 
- V(r', t') - \frac{1}{2m} (\nabla' \chi_k)^2 + \frac{i}{2m} \Delta' \chi_k.
\] (2.54)

This equation is equivalent to a set of two differential equations, one depending only on time variables and the other one depending also on the position variable,

\[
\left( \frac{\partial}{\partial t'} - \frac{\partial}{\partial s} \right) \Phi_k(t', s) = -\frac{e}{m} \mathbf{A}(t') \cdot (\mathbf{k} - \frac{e}{2} \mathbf{A}(t')),
\] (2.55)

\[
\left( \frac{\partial}{\partial t'} - \frac{\partial}{\partial s} \right) \chi_k(r', t', s) = -\frac{1}{m}(\mathbf{k} - e\mathbf{A}(t')) \cdot \nabla' \chi_k(r', t', s) + V(r', t') + \frac{1}{2m} (\nabla' \chi_k(r', t', s))^2 - \frac{i}{2m} \Delta' \chi_k(r', t', s).
\] (2.56)

The function \(\Phi_k(t', s)\) can be directly obtained from Eq. (2.55). Namely, one can show that

\[
\Phi_k(t', s) = \int_0^{t'+s} d\sigma \frac{e}{m} \mathbf{A}(\sigma) \cdot (\mathbf{k} - \frac{e}{2} \mathbf{A}(\sigma))
\] (2.57)

is the solution of Eq. (2.55).

Note that in the absence of the potential \((V = 0)\), the function \(\chi_k\) vanishes [Eq. (2.50)] and the exact propagator (2.48) reduces to the Volov propagator (known also as the Gordon-Volov propagator). For more details on the Volov propagator, see Appendix B. To see this better, let us go back
to Eq. (2.48). After neglecting here \( \chi_k \), we can write down its explicit form,

\[
K_V(r, t; r', t') = \int_0^\infty ds \int \frac{d\Omega dk}{(2\pi)^{d+1}} \exp \left[ -i\Omega(t - t') + ik \cdot (r - r') + is \left( \Omega - \frac{k^2}{2m} + i\epsilon \right) \right] + i \int_t^{t+s} d\tau \frac{e}{m} A(\tau) \cdot (k - \frac{e}{2} A(\tau)) \right].
\] (2.58)

Here, the integral over \( \Omega \) leads to a Dirac delta function \( \delta(t - t' - s) \). By noting that for an arbitrary function \( f(s) \),

\[
\int_0^\infty ds \delta(t - t' - s) f(s) = \theta(t - t') f(t - t'),
\] (2.59)

we end up with

\[
K_V(r, t; r', t') \equiv K^{GV}_V(r, t; r', t') = \int \frac{dk}{(2\pi)^d} \exp \left[ i\kappa \cdot (r - r') - \frac{i}{2m} \int_t^{t'} d\tau (k - eA(\tau))^2 \right],
\] (2.60)

which, according to Eq. (2.59), holds at times \( t > t' \). This is the retarded propagator describing the dynamics of a charged particle in the laser field, given in the velocity gauge. For completeness, let us write it down in the length gauge as well. With the help of the gauge transformation (2.45), we find out that for \( t > t' \),

\[
K_L(r, t; r', t') \equiv K^{GV}_L(r, t; r', t')
\] (2.61)

\[
= \int \frac{dk}{(2\pi)^d} \exp \left[ i(k - eA(t)) \cdot r - i(k - eA(t')) \cdot r' - \frac{i}{2m} \int_t^{t'} d\tau (k - eA(\tau))^2 \right].
\]

These formulas define the retarded Volkov propagator either in the velocity or in the length gauge, \( K^{GV}_V(r, t; r', t') \) or \( K^{GV}_L(r, t; r', t') \), respectively, and are presented in Appendix B.

Note that Eq. (2.56) is a nonlinear second order differential equation for the function \( \chi_k(r', t', s) \), which can be solved explicitly only for particular potentials. As we will show below, for an arbitrary \( V \), a general method of solving this equation can be formulated.

In order to solve Eq. (2.56), let us rewrite this equation such that

\[
\left( \frac{\partial}{\partial t'} - \frac{\partial}{\partial s} + \frac{1}{m} [k - eA(t')] \cdot \nabla' + \frac{i}{2m} \Delta' \right) \chi_k(r', t', s) = W_k(r', t', s),
\] (2.62)

where the function \( W_k(r', t', s) \) is defined as

\[
W_k(r', t', s) = V(r', t') + \frac{1}{2m} \left[ \nabla' \chi_k(r', t', s) \right]^2.
\] (2.63)
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Note that in the case when \( V(r', t') = 0 \), meaning that \( \chi_k(r', t', s) = 0 \) in accordance with Eq. (2.50), \( W_k(r', t', s) \) also vanishes. Now, with the help of the Fourier transforms,

\[
\chi_k(r', t', s) = \int \frac{d\mu}{(2\pi)^d} e^{i\mu \cdot r'} \tilde{\chi}_k(\mu, t', s),
\]

\[
W_k(r', t', s) = \int \frac{d\mu}{(2\pi)^d} e^{i\mu \cdot r'} \tilde{W}_k(\mu, t', s),
\]

Eq. (2.62) can be represented as

\[
\left( \frac{\partial}{\partial t'} - \frac{\partial}{\partial s} + \frac{i\mu}{m} \cdot [k - eA(t')] - \frac{i\mu^2}{2m} \right) \tilde{\chi}_k(\mu, t', s) = \tilde{W}_k(\mu, t', s).
\]

We look for the solution of this equation in the form

\[
\tilde{\chi}_k(\mu, t', s) = \exp \left[ i \int_{t'}^{t'+s} d\tau \left( \frac{\mu}{m} \cdot [k - eA(\tau)] - \frac{\mu^2}{2m} \right) / \right] \tilde{\chi}_k'(\mu, t', s).
\]

By putting this ansatz into Eq. (2.66), we find that the new function \( \tilde{\chi}_k'(\mu, t', s) \) satisfies the following equation,

\[
\left( \frac{\partial}{\partial t'} - \frac{\partial}{\partial s} \right) \tilde{\chi}_k'(\mu, t', s) = \tilde{W}_k(\mu, t', s) \exp \left[ -i \int_{t'}^{t'+s} d\sigma' \left( \frac{\mu}{m} \cdot [k - eA(\sigma')] - \frac{\mu^2}{2m} \right) \right],
\]

which leads to

\[
\tilde{\chi}_k'(\mu, t', s) = - \int_{t'}^{t'+s} d\sigma \tilde{W}_k(\mu, \sigma, t' + s - \sigma) \exp \left[ -i \int_{\sigma}^{t'+s} d\sigma' \left( \frac{\mu}{m} \cdot [k - eA(\sigma')] - \frac{\mu^2}{2m} \right) \right].
\]

From here and Eq. (2.67), it follows that

\[
\tilde{\chi}_k(\mu, t', s) = - \exp \left[ i \int_{t'}^{t'+s} d\tau \left( \frac{\mu}{m} \cdot [k - eA(\tau)] - \frac{\mu^2}{2m} \right) \right] \\
\times \int_{t'}^{t'+s} d\sigma \tilde{W}_k(\mu, \sigma, t' + s - \sigma) \exp \left[ -i \int_{\sigma}^{t'+s} d\sigma' \left( \frac{\mu}{m} \cdot [k - eA(\sigma')] - \frac{\mu^2}{2m} \right) \right].
\]

Before we proceed further, we introduce new quantities,

\[
a_k(t) = \frac{1}{m} \int_0^t d\tau (k - eA(\tau)),
\]

\[
R_k(r', t', \sigma) = r' + a_k(\sigma) - a_k(t') = r' + \frac{1}{m} \int_{t'}^{\sigma} d\tau (k - eA(\tau)).
\]

One can check that \( R_k(r', t', \sigma) \) satisfies the classical Newton equation for a charged particle in a laser field. Now, Eq. (2.70) can be rewritten in a more compact form,

\[
\tilde{\chi}_k(\mu, t', s) = - \int_{t'}^{t'+s} d\sigma \tilde{W}_k(\mu, \sigma, t' + s - \sigma) \exp \left( i\mu \cdot [a_k(\sigma) - a_k(t')] - i\frac{\mu^2}{2m} (\sigma - t') \right). 
\]
Taking into account that
\[ \hat{W}_k(\mu, \sigma, t' + s - \sigma) = \int d\rho \, e^{-i\mu \cdot \rho} \, W_k(\rho, \sigma, t' + s - \sigma), \tag{2.74} \]
we can rewrite Eq. (2.73) such that
\[ \tilde{\chi}_k(\mu, t', s) = -\int_{t'}^{t'+s} d\sigma \int d\rho \, W_k(\rho, \sigma, t' + s - \sigma) \exp \left( i\mu \cdot [a_k(\sigma) - a_k(t' - \rho)] - i\frac{\mu^2}{2m}(\sigma - t') \right). \tag{2.75} \]
Inserting this expression into Eq. (2.64), we obtain
\[ \chi_k(r', t', s) = -\int_{t'}^{t'+s} d\sigma \int d\rho \, W_k(\rho, \sigma, t' + s - \sigma) \times \int \frac{d\mu}{(2\pi)^d} \exp \left( i\mu \cdot [a_k(r', \sigma) - a_k(t') - \rho] - i\frac{\mu^2}{2m}(\sigma - t') \right), \tag{2.76} \]
where we have introduced \( R_k(r', t', \sigma) \) based on Eq. (2.72). Here, we recognize that the integral over \( \mu \) is a Fresnel integral, and so it can be solved exactly (see, Appendix C). In doing so, we arrive at the following expression for the eikonal,
\[ \chi_k(r', t', s) = -e^{-id\pi/4} \int_{t'}^{t'+s} d\sigma \left( \frac{m}{2\pi(\sigma - t')} \right)^{d/2} \times \int d\rho \exp \left( \frac{im}{2(\sigma - t')} [R_k(r', t', \sigma) - \rho]^2 \right) W_k(\rho, \sigma, t' + s - \sigma). \tag{2.77} \]
For our further purpose, let us also represent it in terms of an effective potential \( V_{\text{eff}} \),
\[ \chi_k(r', t', s) = -\int_{t'}^{t'+s} d\sigma \, V_{\text{eff}}(R_k(r', t', \sigma), t', \sigma), \tag{2.78} \]
where
\[ V_{\text{eff}}(R_k(r', t', \sigma), t', \sigma) = e^{-id\pi/4} \left( \frac{m}{2\pi(\sigma - t')} \right)^{d/2} \times \int d\rho \exp \left( \frac{im}{2(\sigma - t')} [R_k(r', t', \sigma) - \rho]^2 \right) W_k(\rho, \sigma, t' + s - \sigma). \tag{2.79} \]

The effective potential \( V_{\text{eff}} \) can be also introduced into the definition of the propagator. In order to do so, we go back to Eq. (2.48). After performing there the integrals over \( \Omega \) and \( s \), one obtains the following integral representation of the retarded propagator in the velocity gauge,
\[ K_V(r, t; r', t') = \int \frac{dk}{(2\pi)^d} \exp \left[ ik \cdot (r - r') + i(t - t') \left( -\frac{k^2}{2m} + i\epsilon \right) \right. \]
\[ + i\Phi_k(t', t - t') + i\chi_k(r', t, t - t') \tag{2.80} \]
Here, $\Phi_k(t', s)$ is defined by Eq. (2.57) while $\chi_k(r', t', s)$ by Eq. (2.77). Now, let us consider Eqs. (2.57) and (2.72). It follows from these expressions that

$$\frac{k^2}{2m}(t - t') - \Phi_k(t', t - t') = \frac{m}{2} \int_{t'}^{t} d\sigma \left( \frac{\partial R_k(r', t', \sigma)}{\partial \sigma} \right)^2. \quad (2.81)$$

Hence, the retarded propagator describing an electron in the laser field $A(t)$ and in the potential $V(r, t)$, calculated in the velocity gauge, becomes

$$K_V(r, t; r', t') = \int \frac{dk}{(2\pi)^d} \exp \left\{ ik \cdot (r - r') - i \int_{t'}^{t} d\sigma \left[ \frac{m}{2} \left( \frac{\partial R_k(r', t', \sigma)}{\partial \sigma} \right)^2 + V_{\text{eff}}(R_k(r', t', \sigma), t', \sigma) \right] \right\}. \quad (2.82)$$

On the other hand, using the gauge transformation (2.45), the propagator (2.80) in the length gauge takes the form

$$K_L(r, t; r', t') = \int \frac{dk}{(2\pi)^d} \exp \left[ i(k - eA(t)) \cdot r - i(k - eA(t')) \cdot r' - i(t - t') \frac{k^2}{2m} \right. \right.$$

$$\left. + i\Phi_k(t', t - t') + i\chi_k(r', t', t - t') \right], \quad (2.83)$$

with the exact same functions $\Phi_k(t', s)$ and $\chi_k(r', t', s)$ as before. Note that

$$k - eA(t) = m \frac{\partial R_k(r', t', t)}{\partial t}, \quad (2.84)$$

$$k - eA(t') = -m \frac{\partial R_k(r', t', t)}{\partial t'}. \quad (2.85)$$

Therefore, the retarded propagator (2.83) in the length gauge can be written as

$$K_L(r, t; r', t') = \int \frac{dk}{(2\pi)^d} \exp \left\{ i\frac{m}{2} \left( \frac{\partial R_k(r', t', \sigma)}{\partial \sigma} \right)^2 + V_{\text{eff}}(R_k(r', t', \sigma), t', \sigma) \right\}. \quad (2.86)$$

Based on the above formulas, one can propose an iterative method of calculating the eikonal (2.78). Namely, in the first step,

$$W_k^{(1)}(r', t', s) = V(r', t'), \quad (2.87a)$$

$$V_{\text{eff}}^{(1)}(R_k(r', t', \sigma), t', \sigma) = e^{-id\pi/4} \left( \frac{m}{2\pi(\sigma - t')} \right)^{d/2} \right.$$

$$\times \int d\rho \exp \left( \frac{im}{2(\sigma - t')} \left[ R_k(r', t', \sigma) - \rho \right]^2 \right) W_k^{(1)}(\rho, \sigma, t' + s - \sigma), \quad (2.87b)$$

$$\chi_k^{(1)}(r', t', s) = - \int_{t'}^{t' + s} d\sigma V_{\text{eff}}^{(1)}(R_k(r', t', \sigma), t', \sigma). \quad (2.87c)$$
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The second iteration gives

\[
W_{k}^{(2)}(r', t', s) = V(r', t') + \frac{1}{2m} \left[ \nabla' \chi^{(1)}_k(r', t', s) \right]^2, \quad (2.88a)
\]

\[
V_{\text{eff}}^{(2)}(R_k(r', t'), t', \sigma) = e^{-i\pi/4} \left( \frac{m}{2\pi(\sigma - t')} \right)^{d/2} \times \int d\rho \exp \left( \frac{i m}{2(\sigma - t')} |R_k(r', t'), \sigma) - \rho|^2 \right) W_{k}^{(2)}(\rho, \sigma, t' + s - \sigma), \quad (2.88b)
\]

\[
\chi^{(2)}_k(r', t', s) = - \int_{t'}^{t+s} d\sigma V_{\text{eff}}^{(2)}(R_k(r', t'), t', \sigma), \quad (2.88c)
\]

and in the \(n\)-th step we have

\[
W_{k}^{(n)}(r', t', s) = V(r', t') + \frac{1}{2m} \left[ \nabla' \chi^{(n-1)}_k(r', t', s) \right]^2, \quad (2.89a)
\]

\[
V_{\text{eff}}^{(n)}(R_k(r', t'), t', \sigma) = e^{-i\pi/4} \left( \frac{m}{2\pi(\sigma - t')} \right)^{d/2} \times \int d\rho \exp \left( \frac{i m}{2(\sigma - t')} |R_k(r', t'), \sigma) - \rho|^2 \right) W_{k}^{(n)}(\rho, \sigma, t' + s - \sigma), \quad (2.89b)
\]

\[
\chi^{(n)}_k(r', t', s) = - \int_{t'}^{t+s} d\sigma V_{\text{eff}}^{(n)}(R_k(r', t'), t', \sigma). \quad (2.89c)
\]

These equations also define the retarded propagator in the respective iterative step, calculated either in the velocity

\[
K_{V}^{(n)}(r, t; r', t') = \int \frac{dk}{(2\pi)^d} \exp \left\{ i k \cdot (r - r') - i \int_{t'}^{t} d\sigma \left[ \frac{m}{2} \left( \frac{\partial R_k(r', t'), \sigma)}{\partial \sigma} \right)^2 + V_{\text{eff}}^{(n)}(R_k(r', t'), t', \sigma) \right] \right\}, \quad (2.90)
\]

or in the length gauge,

\[
K_{L}^{(n)}(r, t; r', t') = \int \frac{dk}{(2\pi)^d} \exp \left\{ \frac{i m}{2\pi(\sigma - t')} |R_k(r', t'), t) \cdot r + i m \frac{\partial R_k(r', t), t)}{\partial \sigma} \cdot r' \right\} \times \int_{t'}^{t} d\sigma \left[ \frac{m}{2} \left( \frac{\partial R_k(r', t), \sigma)}{\partial \sigma} \right)^2 + V_{\text{eff}}^{(n)}(R_k(r', t), t, \sigma) \right] \right\}, \quad (2.91)
\]

with \(V_{\text{eff}}^{(n)}\) defined by Eq. (2.89b).

Eqs. (2.87a), (2.87b), and (2.87c) are the essence of the generalized eikonal approximation. Since they arise from Eq. (2.63) as the approximation with respect to the potential, one can understand that the GEA holds if

\[
\frac{1}{2m} [\nabla' \chi_k(r', t', s)]^2 \ll |V(r', t')|, \quad (2.92)
\]

This results in calculating \(K_{V}^{(1)}(r, t; r', t')\) and \(K_{L}^{(1)}(r, t; r', t')\) under the GEA framework [Eqs. (2.29) and (2.31) for \(n = 1\)]. Note that the GEA as the first-order term of the eikonal perturbation theory was proposed in [18] for both the nonrelativistic Schrödinger and relativistic Klein-Gordon equations, and
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was applied to the free-free transitions. In this thesis we develop the GEA to treat the nonrelativistic ionization processes.

In order to calculate an expression for the generalized eikonal, let us write down Eq. (2.87b) explicitly,

\[ V_{\text{eff}}^{(1)}(R_k(r', t', \sigma), t', \sigma) = \frac{m}{2\pi i(\sigma - t')} \frac{d/2}{d} \int d\rho V(\rho, \sigma) \exp \left[ \frac{im}{2(\sigma - t')} \left( R_k(r', t', \sigma) - \rho \right)^2 \right], \]

(2.93)

where we understand that \( i^{-d/2} = e^{-i\pi d/4} \). Thus, according to Eq. (2.87c), the generalized eikonal takes the form

\[ \chi^{(1)}_k(r', t', s) = - \int_{t'}^{t' + s} d\sigma \left( \frac{m}{2\pi i(\sigma - t')} \right)^{d/2} \times \int d\rho V(\rho, \sigma) \exp \left[ \frac{im}{2(\sigma - t')} \left( R_k(r', t', \sigma) - \rho \right)^2 \right], \]

(2.94)

and it will be analyzed later for particular potentials \( V \).

At this point, let us investigate the limit of short-time intervals, i.e., when in Eq. (2.93) we have \( \sigma \approx t' \). In this context, the short-time interval limit is equivalent to the classical one, when \( \hbar \to 0 \). First, we start with Eq. (2.93) and make use of the following model of a \( d \)-dimensional Dirac delta function,

\[ \delta(r) = \lim_{\varepsilon \to 0} \frac{\exp \left( \frac{i \varepsilon^2}{2} \right)}{(2\pi)^{d/2} \varepsilon^d}, \]

(2.95)

where a small parameter \( \varepsilon \) corresponds to \( (\sigma - t') \). This leads us to \( \delta(R_k(r', t', \sigma) - \rho) \) under the integral in (2.93). Performing the remaining spatial integral we arrive at the conclusion that, in the limit when \( \sigma \approx t' \),

\[ V_{\text{eff}}^{(1)}(R_k(r', t', \sigma), \sigma) \approx V(R_k(r', t', \sigma), \sigma). \]

(2.96)

Going further, let us note that in this limit, we can approximate \( R_k(r', t', \sigma) \) as

\[ R_k(r', t', \sigma) \approx r' - \frac{e}{m} \int_{t'}^{\sigma} d\tau A(\tau), \]

(2.97)

which follows from Eq. (2.72). Hence, Eq. (2.96) becomes

\[ V_{\text{eff}}^{(1)}(R_k(r', t', \sigma), \sigma) \approx V \left( r' - \frac{e}{m} \int_{t'}^{\sigma} d\tau A(\tau), \sigma \right). \]

(2.98)

Thus, the propagator (2.82) under the generalized eikonal approximation and in the limit of short-time intervals becomes

\[ K_{V}^{(1)}(r, t; r', t') \approx \int \frac{dk}{(2\pi)^d} \exp \left[ i(t - t') \left( -\frac{k^2}{2m} + i\epsilon \right) + i\mathbf{k} \cdot \left( \mathbf{r} - \mathbf{r}' + \frac{e}{m} \int_{t'}^{t} d\tau A(\tau) \right) \right] - i \frac{e^2}{2m} \int_{t'}^{t} d\tau A^2(\tau) - i \int_{t'}^{t} d\tau V \left( r' - \frac{e}{m} \int_{t'}^{\tau} d\sigma A(\sigma), \sigma \right). \]

(2.99)
Performing here the integral over $k$, which is the Fresnel integral in an arbitrary number of dimensions $d$ (see, Appendix C), we obtain

$$K^{(1)}_V(r, t; r', t') \approx e^{-i\pi d/4} \left( \frac{m}{2\pi(t - t')} \right)^{d/2} \exp \left[ \frac{im}{2(t - t')} \left( r - r' + \frac{e}{m} \int_{t'}^t d\tau A(\tau) \right)^2 \right]$$

$$- \frac{e^2}{2m} \int_{t'}^t d\tau A^2(\tau) - i \int_{t'}^t d\tau V^2 \left( r' - \frac{e}{m} \int_{t'}^t d\sigma A(\sigma, \sigma) \right).$$  \hspace{1cm} (2.100)

This result is in agreement with the Dirac conjecture \[84, 85\] that in the short-time interval limit (and only in this limit, i.e., when the quantum spreading of the electron wave packet is negligible) the propagator is proportional to $e^{iS_{cl}}$, where $S_{cl}$ is the classical action (see, Appendix D). This afterward has led Feynman to the path integrals \[86\]. Note that in the current case $S_{cl} = S_V$, which is derived in Appendix D.3. As it follows from the gauge transformation defined by Eq. (2.36), in the considered limit, the propagator in the length gauge equals

$$K^{(1)}_L(r, t; r', t') \approx e^{-i\pi d/4} \left( \frac{m}{2\pi(t - t')} \right)^{d/2} \exp \left[ \frac{im}{2(t - t')} \left( r - r' + \frac{e}{m} \int_{t'}^t d\tau A(\tau) \right)^2 \right]$$

$$- ieA(t) \cdot r + ieA(t') \cdot r' - \frac{e^2}{2m} \int_{t'}^t d\tau A^2(\tau) - i \int_{t'}^t d\tau V^2 \left( r' - \frac{e}{m} \int_{t'}^t d\sigma A(\sigma, \sigma) \right).$$  \hspace{1cm} (2.101)

Here, again, we see that the propagator is proportional to $e^{iS_{cl}}$, where $S_{cl} = S_L$ is given by Eq. (D.28).

### 2.3 Original eikonal approximation (EA)

Before we proceed with derivations of the generalized eikonal for particular model potentials, let us work out the general formula for the original eikonal. In the EA, one neglects in Eq. (2.62) the term $\frac{1}{2m} \Delta' \chi_k(r', t', s)$ (see, for instance, Ref. [58]). This is due to the semiclassical nature of the original eikonal approximation [17], and the fact that $\frac{1}{2m} \Delta' \chi_k(r', t', s)$ is actually a higher order term in $\hbar$ than the remaining terms in (2.62). Now, following the derivations leading to our GEA, we find out that

$$\chi_{k,\text{original}}(r', t', s) = - \int_{t'}^{t+s} d\sigma \int d\rho W_k(\rho, \sigma, t' + s - \sigma) \int \frac{d\mu}{(2\pi)^d} \exp \left( i\mu \cdot [R_k(r', t', \sigma) - \rho] \right),$$  \hspace{1cm} (2.102)

which is analogous to Eq. (2.76) except that, in the exponent, it is missing the term proportional to $\mu^2$. This simplifies our treatment, as the last integral in Eq. (2.102) leads to a $d$-dimensional Dirac delta function, $\delta(R_k(r', t', \sigma) - \rho)$. Thus, the integral over $\rho$ becomes trivial, and finally we obtain

$$\chi_{k,\text{original}}(r', t', s) = - \int_{t'}^{t+s} d\sigma W_k(R_k(r', t', \sigma), \sigma, t' + s - \sigma),$$  \hspace{1cm} (2.103)

with the function $W_k$ defined by Eq. (2.63).
Eq. (2.103) can be treated by iterations, similar to what we have described in Sec. 2.2. From our point of view it is important that, when the condition (2.92) is satisfied, the originally used eikonal (2.103) becomes,

$$\chi_{k,\text{original}}(r', t', s) = - \int_{t'}^{t'+s} d\sigma V(R_k(r', t', \sigma), \sigma).$$  \hfill (2.104)

Thus, in the EA, the analog of the effective potential (2.87b) would be the potential calculated along the free electron trajectory in the laser field, i.e., $V(R_k(r', t', \sigma), \sigma)$. This means that the original eikonal follows as the short-time interval limit of our generalized eikonal [see, Eq. (2.96)]. This will be further discussed for various model potentials.

2.4 Generalized eikonal approximation for model potentials

So far, our analysis has been general in the sense that we have considered an arbitrary potential $V(r, t)$. In our case, however, it is an atomic potential which couples to the electron along with the laser field. We will model it as a static and spherically-symmetric potential, meaning that $V(r, t) = V(|r|) \equiv V(r)$. Unless otherwise stated, from now on we will be interested in the case when $d = 3$.

According to the GEA (2.93),

$$V^{(1)}_{\text{eff}}(R_k(r', t', \sigma), t', \sigma) = \left( \frac{m}{2\pi i(\sigma - t')} \right)^{3/2} \int d\rho V(\rho) \exp \left[ \frac{im}{2(\sigma - t')}(R_k(r', t', \sigma) - \rho)^2 \right],$$  \hfill (2.105)

where we have substituted $d = 3$. This integral can be performed for various model potentials. To simplify our notation, we introduce a parameter

$$\xi = \frac{m}{2(\sigma - t')},$$  \hfill (2.106)

where we keep in mind that $\xi > 0$. Hence, Eq. (2.105) takes the form

$$V^{(1)}_{\text{eff}}(R_k(r', t', \sigma), \xi) = \left( \frac{\xi}{1\pi} \right)^{3/2} \int d\rho V(\rho) \exp \left[ i\xi(R_k(r', t', \sigma) - \rho)^2 \right].$$  \hfill (2.107)

Introducing spherical coordinates here, we perform the integral over the solid angle $d\Omega_\rho$. The remaining integral is over the radial coordinate $\rho$,

$$V^{(1)}_{\text{eff}}(R_k(r', t', \sigma), \xi) = \sqrt{\frac{\xi}{1\pi}} \frac{1}{|R_k(r', t', \sigma)|} \int_0^\infty d\rho \rho V(\rho) \left[ e^{i\xi(|\rho - |R_k(r', t', \sigma)||^2} - e^{i\xi(|\rho + |R_k(r', t', \sigma)||^2} \right],$$  \hfill (2.108)

which we will calculate now for different model potentials, starting with the Coulomb potential.
2.4.1 Coulomb potential

For the Coulomb potential describing the interaction of an electron of charge \( e \) (\( e < 0 \)) and a nucleus of charge \(-Ze\), where \( Z = 1, 2, \ldots \) is the atomic number,

\[
V(r) = \frac{-Ze\alpha}{r}.
\]  
(2.109)

Here, \( \alpha = e^2/(4\pi\varepsilon_0c) \) is the fine structure constant. Note that in the atomic units, used in our numerical analysis, \( \alpha c = 1 \). For the Coulomb potential, \( V^{(1)}_{\text{eff}} \) defined by Eq. (2.108) becomes

\[
V^{(1)}_{\text{eff}}(R_k(r', t', \sigma), \xi) = \frac{Z\alpha c}{|R_k(r', t', \sigma)|} \int_0^\infty d\rho \left[ e^{i\xi(\rho + |R_k(r', t', \sigma)|)^2} - e^{i\xi(\rho - |R_k(r', t', \sigma)|)^2} \right].
\]  
(2.110)

After changing the integration variable in each term separately (namely, \( y = \rho + |R_k(r', t', \sigma)| \) in the first term and \( y = \rho - |R_k(r', t', \sigma)| \) in the second term), we simplify this expression such that

\[
V^{(1)}_{\text{eff}}(R_k(r', t', \sigma), \xi) = -\frac{\xi}{2\pi} \int_{|R_k(r', t', \sigma)|}^{R_k(r', t', \sigma)} dy \, e^{i\xi y^2}.
\]  
(2.111)

Now, we make use of the definition of the Fresnel’s integrals (Eqs. (7.2.7) and (7.2.8) in Ref. [87])

\[
S(z) = \int_0^z dt \sin\left(\frac{\pi t^2}{2}\right), \quad C(z) = \int_0^z dt \cos\left(\frac{\pi t^2}{2}\right),
\]  
(2.112)

and the fact that (Eq. (7.5.8) in Ref. [87])

\[
C(z) + iS(z) \equiv \int_0^z dt \, e^{i\pi t^2/2} = \frac{1 + i}{2} \, \text{erf}\left[\frac{\sqrt{\pi}}{2}(1 - i)z\right],
\]  
(2.113)

where \( \text{erf}(z) \) is the error function [87]. In order to be able to use the last result, we replace the integral in Eq. (2.111) by twice the integral over the interval from \( 0 \) to \( |R_k(r', t', \sigma)| \). After introducing a new variable \( y = t\sqrt{\frac{\pi}{2}} \), we derive the final form of \( V^{(1)}_{\text{eff}} \),

\[
V^{(1)}_{\text{eff}}(R_k(r', t', \sigma), \xi) = -\frac{Z\alpha c}{|R_k(r', t', \sigma)|} \, \text{erf}\left[\frac{e^{-i\pi/4}\sqrt{\xi}|R_k(r', t', \sigma)|}{1/2\xi}\right],
\]  
(2.114)

or, equivalently,

\[
V^{(1)}_{\text{eff}}(R_k(r', t', \sigma), t', \sigma) = -\frac{Z\alpha c}{|R_k(r', t', \sigma)|} \, \text{erf}\left[\frac{\sqrt{m}}{2i(\sigma - t')}|R_k(r', t', \sigma)|\right],
\]  
(2.115)

where we have substituted \( \xi \) according to Eq. (2.106), and where we understand that \( \sqrt{i} = e^{i\pi/4} \).

Based on this result and taking into account Eq. (2.94), we obtain that the generalized eikonal in the case when the electron-ion interaction is modeled as the Coulomb potential (2.109) equals

\[
\chi^{(1)}_k(r', t', s) = Z\alpha \int_{t'}^{t'+s} d\sigma \, \frac{d\sigma}{|R_k(r', t', \sigma)|} \, \text{erf}\left[\frac{\sqrt{m}}{2i(\sigma - t')}|R_k(r', t', \sigma)|\right].
\]  
(2.116)
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Now, it is important to analyze the properties of this expression.

Let us start with considering large values of the argument of the error function in (2.116). As it follows from Eqs. (7.2.2) and (7.12.1) in Ref. [87],

\[
\text{erf}(z) = 1 - \frac{e^{-z^2}}{\sqrt{\pi z}} \sum_{n=0}^{\infty} (-1)^n \frac{(2n - 1)!!}{(2z^2)^n},
\]  

(2.117)

when \( z \gg 1 \). In our case, it means that the aforementioned expansion holds if

\[
\sqrt{\frac{m}{2(\sigma - t')}} |\mathbf{R}_k(r', t', \sigma)| \gg 1.
\]  

(2.118)

This condition is automatically satisfied for short-time intervals (\( \sigma \approx t' \)) provided that the trajectory \( \mathbf{R}_k(r', t', \sigma) \) does not come back to the potential centre (i.e., \( |\mathbf{R}_k(r', t', \sigma)| \neq 0 \)). It follows from the expansion (2.117) that, in the short-time interval limit for which Eq. (2.118) is satisfied,

\[
\chi^{(1)}_k(r', t', s) \approx \chi_{k,original}(r', t', s) = Z\alpha c \int_{t'}^{t'+s} \frac{d\sigma}{|\mathbf{R}_k(r', t', \sigma)|},
\]  

(2.119)

where \( \chi_{k,original}(r', t', s) \) is the original eikonal derived in Sec. 2.3. Note that the original eikonal (2.119) does not follow from the generalized eikonal (2.116) when \( |\mathbf{R}_k(r', t', \sigma)| \to 0 \) for \( \sigma \neq t' \). Thus, even though we derive \( \chi_{k,original}(r', t', s) \) as the limiting case of the generalized eikonal \( \chi^{(1)}_k(r', t', s) \), when doing this we do not run into the problem noted by Popruzhenko and Bauer in [63]. Namely, that the original eikonal (2.119) is singular for those electron trajectories \( \mathbf{R}_k(r', t', \sigma) \) which may revisit the nucleus. This suggests that the GEA is applicable even for the returning electron trajectories, which are of crucial importance in the context of rescattering processes in ionization.

It is worth mentioning that the condition (2.118) is fulfilled for large distances from the Coulomb centre. This means that the original and generalized eikonals coincide with each other not only for short times, but also at distant points in space. Hence, if the electron wave packets or quantum trajectories are far away from the centre during the time evolution both approximations should give similar results. This is usually the case if the final kinetic energy of photoelectrons is much larger than \( 3U_p \), where \( U_p \) is the ponderomotive energy defined below [Eq. (2.192)]. This will be demonstrated numerically later on.

Another problem noted in [63] regarding the commonly used eikonal (2.119) is that it diverges logarithmically at the lower integration limit (\( \sigma \approx t' \)). Specifically, this happens when the electron trajectories approach the nucleus since for the most important of them, \( |r'| \approx 0 \) [63]. Note that the generalized eikonal (2.116) avoids this problem. While it is still defined as the improper integral with respect to the lower integration limit, its integrand contains an integrable singularity. In order to show this, we represent the electron trajectory (2.72) as \( \mathbf{R}_k(r', t', \sigma) \approx \mathbf{R}_k(0, t', \sigma) \approx [k - eA(\tilde{\tau})](\sigma - t') \), where \( \tilde{\tau} \) is an intermediate time which falls into the interval \( \tilde{\tau} \in (t', \sigma) \). Thus, it follows from Eq. (2.116) that the argument of the error function behaves as \( \sqrt{\sigma - t'} \), and it is small in the limit under considerations. Next, we apply in Eq. (2.116) the following series expansion (see, Eq. (7.6.1)
of Ref. [87]),
\[
\text{erf}(z) = \frac{2}{\sqrt{\pi}} \sum_{n=0}^{\infty} \frac{(-1)^n z^{2n+1}}{n!(2n+1)},
\]
which always converges. Hence, the generalized eikonal (2.116) becomes
\[
\chi_k^{(1)}(r', t', s) \approx \chi_k^{(1)}(0, t', s) \approx Z_\alpha c \sqrt{\frac{2m}{\pi}} \int_{\sigma}^{t'+s} \frac{d\sigma}{\sqrt{(\sigma - t')}} = Z_\alpha c \sqrt{\frac{8m\sigma}{\pi}}.
\]
As we see, in contrast to the original eikonal, the integrand here contains an integrable \((\sigma - t')^{-1/2}\) singularity. While its form was derived for \(|R_k(r', t', \sigma)| \to 0\) and \(\sigma \approx t'\), the integrand of \(\chi_k^{(1)}(r', t', s)\) will be exactly the same if \(|R_k(r', t', \sigma)| \to 0\) and \(\sigma \neq t'\). This coincides with our earlier conclusion that the generalized eikonal \(\chi_k^{(1)}(r', t', s)\) accounts for those electron trajectories which may return back to the origin of the Coulomb potential.

Note that similar close expressions for the eikonal \(\chi_k^{(1)}(r', t', s)\) can be also derived for other potentials such as Yukawa, exponential, or Gaussian potentials. This is presented below.

### 2.4.2 Yukawa potential

In many cases, the atomic potential can be modeled as a Yukawa or “screened-Coulomb” potential. Specifically, this concerns weakly bound atomic systems such as negative ions (see, for instance, Refs. [88, 89]). In this case, within the single-active-electron approximation, a negative ion can be described by the potential,
\[
V(r) = V_0 e^{-\beta r} ,
\]
where \(\beta^{-1} (\beta > 0)\) is a characteristic interaction length such that for \(r \gg \beta^{-1}\) the nuclear charge is screened by the charge of the remaining electrons, so the potential seen by the active electron decays exponentially at large distances from the potential origin. At small distances from the potential origin \((r \ll \beta^{-1})\), on the other hand, the Yukawa potential behaves in a similar manner to the Coulomb potential (2.109). In addition, \(V_0 < 0\) describes the interaction strength of the active electron with the remaining system. Let us also keep in mind that the pure Coulomb potential (2.109) is obtained from Eq. (2.122) in the limit when \(\beta \to 0\) and \(V_0 \to -Z_\alpha c\).

In order to obtain the expression for the effective potential (2.108), we plug there Eq. (2.122). As a result, we obtain
\[
V_{\text{eff}}^{(1)}(R_k(r', t', \sigma), \xi) = \sqrt{\frac{\xi}{1\pi}} \frac{V_0}{|R_k(r', t', \sigma)|} \times \int_{0}^{\infty} d\rho e^{-\beta \rho} \left[ e^{i\xi(\rho-|R_k(r', t', \sigma)|)^2} - e^{i\xi(\rho+|R_k(r', t', \sigma)|)^2} \right].
\]
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After changing the integration variable in each term separately, in the exact same way that it was done for the Coulomb potential, Eq. (2.123) becomes

\[
V^{(1)}_{\text{eff}}(R_k(r', t', \sigma), \xi) = \frac{V_0}{2|R_k(r', t', \sigma)|} \left\{ e^{-\beta |R_k(r', t', \sigma)|} \text{erfc}\left[ e^{-\frac{\xi}{2\sigma}} \sqrt{\xi} \left( |R_k(r', t', \sigma)| + \frac{\beta}{2\xi} \right) \right] ight. \\
- \left. e^{\beta |R_k(r', t', \sigma)|} \text{erfc}\left[ e^{-\frac{\xi}{2\sigma}} \sqrt{\xi} \left( |R_k(r', t', \sigma)| + \frac{\beta}{2\xi} \right) \right] \right\}. \tag{2.124}
\]

The remaining integrals can be again expressed in terms of the Fresnel integrals (2.112), which leads to

\[
V^{(1)}_{\text{eff}}(R_k(r', t', \sigma), \xi) = \frac{V_0 e^{i\beta/(4\xi)}}{2|R_k(r', t', \sigma)|} \left\{ e^{-\beta |R_k(r', t', \sigma)|} \text{erfc}\left[ e^{-\frac{\xi}{2\sigma}} \sqrt{\xi} \left( |R_k(r', t', \sigma)| + \frac{\beta}{2\xi} \right) \right] ight. \\
- \left. e^{\beta |R_k(r', t', \sigma)|} \text{erfc}\left[ e^{-\frac{\xi}{2\sigma}} \sqrt{\xi} \left( |R_k(r', t', \sigma)| + \frac{\beta}{2\xi} \right) \right] \right\}. \tag{2.125}
\]

Here, \( \text{erfc}(z) = 1 - \text{erf}(z) \) is the complementary error function (see, Eq. (7.2.2) in Ref. [87]). Note that in the limit when the Yukawa potential (2.122) turns into the Coulomb potential (2.109) (meaning that \( \beta \to 0 \) and \( V_0 \to -Z\alpha c \)), Eq. (2.125) becomes

\[
V^{(1)}_{\text{eff}}(R_k(r', t', \sigma), \xi) = \frac{Z\alpha c}{2|R_k(r', t', \sigma)|} \left\{ \text{erf}\left[ e^{-\frac{\xi}{2\sigma}} \sqrt{\xi} |R_k(r', t', \sigma)| \right] ight. \\
- \left. \text{erfc}\left[ e^{-\frac{\xi}{2\sigma}} \sqrt{\xi} |R_k(r', t', \sigma)| \right] \right\}. \tag{2.126}
\]

Using here the property that the error function is an odd function, meaning that \( \text{erf}(-z) = -\text{erf}(z) \) (Eq. (7.4.1) in Ref [87]), we reproduce Eq. (2.114) that we have derived for the Coulomb potential.

Finally, based on Eqs. (2.94) and (2.126), we find that the generalized eikonal \( \chi^{(1)}_k(r', t', s) \) in the case when the ionized electron moves in the Yukawa potential is

\[
\chi^{(1)}_k(r', t', s) = -\frac{V_0}{2} \int_{r'}^{r'+s} d\sigma \frac{e^{i\beta/(2m)}}{|R_k(r', t', \sigma)|} \left\{ e^{-\beta |R_k(r', t', \sigma)|} \text{erfc}\left[ \sqrt{\frac{m}{2i(\sigma - t')}} \left( |R_k(r', t', \sigma)| + \frac{\beta(\sigma - t')}{m} \right) \right] ight. \\
- \left. e^{\beta |R_k(r', t', \sigma)|} \text{erfc}\left[ \sqrt{\frac{m}{2i(\sigma - t')}} \left( |R_k(r', t', \sigma)| + \frac{\beta(\sigma - t')}{m} \right) \right] \right\}, \tag{2.127}
\]

where we understand that \( \sqrt{i} = e^{i\pi/4} \), and where we have explicitly written the value of \( \xi \) (2.106). Similar to the Coulomb case, this eikonal is defined by the integral which is improper with respect to the lower integration limit. Therefore, it is necessary to analyze this integral at short-time intervals.

We start by inspecting the behavior of the generalized eikonal (2.127) in the short-time interval limit, assuming that the electron trajectory does not come back to the origin of the potential (meaning
that $|\mathbf{R}_k(r',t',\sigma)| \neq 0$). In this case, we can write down that
\[
\chi_k^{(1)}(r',t',s) \approx -\frac{V_0}{2} \int_{t'}^{t'+s} \frac{d\sigma}{|\mathbf{R}_k(r',t',\sigma)|} \left\{ e^{-\beta|\mathbf{R}_k(r',t',\sigma)|} \text{erfc} \left[ -\sqrt{\frac{m}{2i(\sigma - t')}} |\mathbf{R}_k(r',t',\sigma)| \right] \right\}.
\]
(2.128)

Note that in the considered limit, the condition (2.118) is satisfied. Taking into account that for large arguments ($z \gg 1$) (Eqs. (7.12) in Ref. [87]),
\[
\text{erfc}(z) = e^{-z^2} \sqrt{\frac{\pi}{z}} \sum_{n=0}^{\infty} (-1)^n \frac{(2n - 1)!!}{(2z^2)^n},
\]
(2.129)
\[
\text{erfc}(-z) = 2 - e^{-z^2} \sqrt{\frac{\pi}{z}} \sum_{n=0}^{\infty} (-1)^n \frac{(2n - 1)!!}{(2z^2)^n},
\]
(2.130)
we find out that the generalized eikonal (2.127) in the short-time interval limit is
\[
\chi_k^{(1)}(r',t',s) \approx \chi_{k,\text{original}}(r',t',s) = -V_0 \int_{t'}^{t'+s} d\sigma \frac{e^{-\beta|\mathbf{R}_k(r',t',\sigma)|}}{|\mathbf{R}_k(r',t',\sigma)|}.
\]
(2.131)
Comparing this result with Eq. (2.104) one can see that we have recovered the original eikonal for the Yukawa potential. As indicated by the condition (2.118), this limit excludes the trajectories returning to the potential centre for $\sigma \neq t'$.

In the short-time interval limit ($\sigma \approx t'$) but for those electron trajectories which approach the potential centre, $|\mathbf{R}_k(r',t',\sigma)| \to 0$, the arguments of the complementary error functions in Eq. (2.127) behave like $\sqrt{\sigma - t'}$, representing a small argument. Thus, in the current limit, we can use the series expansion (2.120). As a result we obtain that, for returning electron trajectories and for short-time evolution, the generalized eikonal derived for the Yukawa potential behaves like
\[
\chi_k^{(1)}(r',t',s) \approx \chi_k^{(1)}(0,t',s) \approx -V_0 \int_{t'}^{t'+s} \frac{d\sigma}{\sqrt{(\sigma - t')}} = -V_0 \sqrt{\frac{8m\hbar^2}{i\pi}}.
\]
(2.132)
As we can see, it contains the same integrable singularity as the generalized eikonal for the Coulomb potential (2.121). We conclude, therefore, that the developed formalism is applicable for the returning trajectories also for the Yukawa potential.

### 2.4.3 Exponential potential

Another potential for which it is possible to derive the generalized eikonal (2.94) in a closed form is an exponential potential. We define it as
\[
V(r) = V_0 e^{-\beta r},
\]
(2.133)
where $V_0 < 0$ and $\beta > 0$ are the constants describing the strength and the range of atomic interaction, respectively.

The effective potential, according to Eq. (2.108), is given in this case as

\[
V_{\text{eff}}^{(1)}(\mathbf{R}_k(r', t', \sigma), \xi) = \sqrt{\frac{\xi}{1\pi}} \frac{V_0}{|\mathbf{R}_k(r', t', \sigma)|} \int_0^\infty d\rho e^{-\beta\rho} \left[ e^{i\xi(\rho-|\mathbf{R}_k(r', t', \sigma)|)} - e^{i\xi(\rho+|\mathbf{R}_k(r', t', \sigma)|)} \right].
\]

(2.134)

With the help of the same change of variables as in the previous two cases, we obtain that

\[
V_{\text{eff}}^{(1)}(\mathbf{R}_k(r', t', \sigma), \xi) = \sqrt{\frac{\xi}{1\pi}} \frac{V_0}{|\mathbf{R}_k(r', t', \sigma)|} \times \left[ e^{-\beta|\mathbf{R}_k(r', t', \sigma)|} \int_{-|\mathbf{R}_k(r', t', \sigma)|}^\infty dy (y + |\mathbf{R}_k(r', t', \sigma)|) e^{i\xi y - \beta y} - e^{\beta|\mathbf{R}_k(r', t', \sigma)|} \int_{|\mathbf{R}_k(r', t', \sigma)|}^\infty dy (y - |\mathbf{R}_k(r', t', \sigma)|) e^{i\xi y - \beta y} \right].
\]

(2.135)

Both terms which contain integrals $\int dy \, ye^{i\xi y - \beta y}$ cancel each other, leading to

\[
V_{\text{eff}}^{(1)}(\mathbf{R}_k(r', t', \sigma), \xi) = \sqrt{\frac{\xi}{1\pi}} \frac{V_0}{|\mathbf{R}_k(r', t', \sigma)|} e^{i\beta^2/(4\xi)} \left\{ e^{-\beta|\mathbf{R}_k(r', t', \sigma)|} \int_{-|\mathbf{R}_k(r', t', \sigma)|}^\infty dy \exp\left[ i\xi \left( y + \frac{\beta}{2\xi} \right)^2 \right] + e^{\beta|\mathbf{R}_k(r', t', \sigma)|} \int_{|\mathbf{R}_k(r', t', \sigma)|}^\infty dy \exp\left[ i\xi \left( y + \frac{\beta}{2\xi} \right)^2 \right] \right\}.
\]

(2.136)

This expression is very similar to the one derived for the Yukawa potential (2.124). Hence, we obtain

\[
V_{\text{eff}}^{(1)}(\mathbf{R}_k(r', t', \sigma), \xi) = \frac{V_0}{2} e^{i\beta^2/(4\xi)} \left\{ e^{-\beta|\mathbf{R}_k(r', t', \sigma)|} \text{erfc}\left[ e^{-\frac{1}{2\xi}} \sqrt{\xi \left( -|\mathbf{R}_k(r', t', \sigma)| + \frac{\beta}{2\xi} \right)} \right] + e^{\beta|\mathbf{R}_k(r', t', \sigma)|} \text{erfc}\left[ e^{-\frac{1}{2\xi}} \sqrt{\xi \left( |\mathbf{R}_k(r', t', \sigma)| + \frac{\beta}{2\xi} \right)} \right] \right\}.
\]

(2.137)

Note that in the limit when $\beta \to 0$, the above expression tends to $V_0$, in agreement with the result obtained directly from Eq. (2.93) for a constant potential, $V(\rho, \sigma) = V_0$.

The above formula allows us to define the generalized eikonal (2.94),

\[
\chi^{(1)}_k(r', t', s) = -\frac{V_0}{2} \int_{t'}^{t' + s} d\sigma e^{i\beta^2(\sigma-t')/(2m)} \times \left\{ e^{-\beta|\mathbf{R}_k(r', t', \sigma)|} \text{erfc}\left[ \sqrt{\frac{m}{2i(\sigma-t')}} \left( -|\mathbf{R}_k(r', t', \sigma)| + \frac{\beta(\sigma-t')}{m} \right) \right] + e^{\beta|\mathbf{R}_k(r', t', \sigma)|} \text{erfc}\left[ \sqrt{\frac{m}{2i(\sigma-t')}} \left( |\mathbf{R}_k(r', t', \sigma)| + \frac{\beta(\sigma-t')}{m} \right) \right] \right\}.
\]

(2.138)
where we have substituted the value of $\xi$ (2.106). In the short-time interval limit $\sigma \approx t'$, but excluding the returning electron trajectories for which $|R_k(r', t', \sigma)| \to 0$, we obtain from here that

$$\chi^{(1)}_k(r', t', s) \approx -\frac{V_0}{2} \int_{t'}^{t'+s} d\sigma \left\{ e^{-\beta|R_k(r', t', \sigma)|} \text{erfc} \left[ -\sqrt{\frac{m}{2i(\sigma - t')}} |R_k(r', t', \sigma)| \right] ight. \left. + e^{\beta|R_k(r', t', \sigma)|} \text{erfc} \left[ \sqrt{\frac{m}{2i(\sigma - t')}} |R_k(r', t', \sigma)| \right] \right\}. \quad (2.139)$$

Since in this limit the argument of the error function is large (2.118), we can use the equations (2.129) and (2.130). This leads to an approximate formula,

$$\chi^{(1)}_k(r', t', s) \approx \chi^{(1)}_{k,\text{original}}(r', t', s) = -V_0 \int_{t'}^{t'+s} d\sigma e^{-\beta|R_k(r', t', \sigma)|}, \quad (2.140)$$

which corresponds to the original eikonal (2.104) for the exponential potential (2.133). Note that for short-time intervals, Eq. (2.138) is not singular for the electron trajectories which come back to the potential origin.

### 2.4.4 Gaussian potential

As the final example, we consider the Gaussian potential,

$$V(r) = V_0 e^{-\beta r^2}, \quad (2.141)$$

where the real constants $V_0 < 0$ and $|\beta|$ define the strength and the range of atomic interaction, respectively. This time, $\beta$ can be either positive or negative. Since the respective spatial integrals for the Gaussian potential can be performed analytically in an arbitrary number of dimensions $d$, in contrast to the previous cases, we keep an arbitrary $d$.

For the Gaussian potential (2.141), $V^{(1)}_{\text{eff}}$ in a general $d$-dimensional case (2.93) takes the form

$$V^{(1)}_{\text{eff}}(R_k(r', t', \sigma), \xi) = V_0 \left( \frac{\xi}{1 - \beta^2} \right)^{d/2} \int d\rho \exp \left[ i \xi (\rho - R_k(r', t', \sigma))^2 - \beta^2 \rho^2 \right], \quad (2.142)$$

which can be calculated exactly, leading to

$$V^{(1)}_{\text{eff}}(R_k(r', t', \sigma), \xi) = V_0 \left( \frac{\xi}{\xi + i\beta^2} \right)^{d/2} \exp \left[ -\frac{\xi \beta^2}{\xi + i\beta^2} \right] \int d\rho \exp \left[ -\frac{\beta^2}{\xi + i\beta^2} R_k^2(r', t', \sigma) \right]. \quad (2.143)$$

According to Eq. (2.87c), the generalized eikonal for the Gaussian potential (2.141) is given by

$$\chi^{(1)}_k(r', t', s) = -V_0 \int_{t'}^{t'+s} d\sigma \left[ \frac{m}{m + 2i\beta^2(\sigma - t')} \right]^{d/2} \exp \left[ -\frac{m \beta^2 R_k^2(r', t', \sigma)}{m + 2i\beta^2(\sigma - t')} \right], \quad (2.144)$$
where we have introduced the explicit form of $\xi$ (2.106). Note that in the short-time interval limit, i.e., when $\sigma \approx t'$, Eq. (2.144) becomes,

$$\chi^{(1)}_k(r', t', s) \approx \chi^{(1)}_{k,\text{original}}(r', t', s) = -V_0 \int_{t'}^{t'+s} d\sigma e^{-\beta^2 R_k^2(r', t', \sigma)}.$$  (2.145)

This formula corresponds to the original eikonal (2.104) which, for the Gaussian potential, accounts for all electron trajectories.

Note that even though we have presented the analytical formulas for the generalized eikonal when the electron interacts with different potential models, the derivations and numerical calculations developed in the next Sections are devoted exclusively to the Coulomb case. However, the formulas presented above can be used to analyze the photoionization process of negative ions and other atomic systems under the GEA. Such analyses go beyond the scope of this thesis.

### 2.5 Probability amplitude of ionization

The goal of this Section is to derive the expression for the probability amplitude of ionization within the generalized eikonal approximation. We start, however, with more general considerations as presented below.

Consider a time-dependent problem described by the Hamiltonian $\hat{H}(t)$, which for our purposes we separate into two parts,

$$\hat{H}(t) = \hat{H}_0(t) + \hat{H}_I(t).$$  (2.146)

As introduced in Sec. 2.1, the time-evolution operator $\hat{U}(t, t')$ corresponding to the Hamiltonian $\hat{H}(t)$ satisfies the Schrödinger equation (2.5) with the initial condition (2.2). The solution to this problem is given by Eq. (2.7). Let us also introduce operators $\hat{U}_0(t, t')$ and $\hat{U}_I(t, t')$ which determine the time-evolution governed by the Hamiltonians $\hat{H}_0(t)$ and $\hat{H}_I(t)$, respectively. In other words, it happens that

$$i \frac{\partial \hat{U}_0(t, t')}{\partial t} = \hat{H}_0(t)\hat{U}_0(t, t'), \quad \hat{U}_0(t', t') = \hat{I}$$  (2.147)

and

$$\hat{U}_0(t, t') = \hat{T} \exp \left( -i \int_{t'}^{t} d\tau \hat{H}_0(\tau) \right),$$  (2.148)

and similar for $\hat{U}_I(t, t')$. It can be shown that the time-evolution operator $\hat{U}(t, t')$ fulfills the integral Lippmann-Schwinger equation such that

$$\hat{U}(t, t') = \hat{U}_0(t, t') - i \int_{t'}^{t} d\tau \hat{U}(t, \tau) \hat{H}_I(\tau) \hat{U}_0(\tau, t').$$  (2.149)

From now on, we will assume that the Hamiltonian $\hat{H}_0(t)$ is independent of time, $\hat{H}_0(t) \equiv \hat{H}_0$, whereas the Hamiltonian $\hat{H}_I(t)$ (sometimes called the interaction Hamiltonian) varies with time in
the interval when \( t \in [0, T] \) and is zero otherwise,
\[
\hat{H}_I(t) = 0 \quad \text{for} \quad t < 0 \quad \text{and} \quad t > T.
\]  
(2.150)

Our aim is to calculate the probability amplitude for a system governed by the Hamiltonian \( \hat{H}(t) \) to make a transition from the initial state \( |\psi_i\rangle \) to the final state \( |\psi_f\rangle \). We assume that these are stationary states of the Hamiltonian \( \hat{H}_0 \) which belong to the energies \( E_i \) and \( E_f \), respectively,
\[
\hat{H}_0|\psi_{f,i}\rangle = E_{f,i}|\psi_{f,i}\rangle.
\]  
(2.151)

We also assume that these states are orthogonal, meaning that
\[
\langle \psi_f | \psi_i \rangle = 0.
\]
For completeness, we note that their time-evolution is given by
\[
|\psi_{f,i}(t)\rangle = \hat{U}_0(t, 0)|\psi_{f,i}\rangle = e^{-iE_{f,i}t}|\psi_{f,i}\rangle.
\]  
(2.152)

The aforementioned probability amplitude calculated at time \( T \) is
\[
\mathcal{A}_{f,i}(T) = \langle \psi_f(T)|\hat{U}(T, 0)|\psi_i(0)\rangle.
\]  
(2.153)

It follows from Eq. (2.149) that this quantity can be rewritten as
\[
\mathcal{A}_{f,i}(T) = \langle \psi_f(T)|\psi_i(T)\rangle - i \int_0^T dt' \langle \psi_f(T)|\hat{U}(T, t')\hat{H}_I(t')|\psi_i(t')\rangle.
\]  
(2.154)

Since the first term vanishes due to the orthogonality of the initial and final states, this formula can be rewritten as
\[
\mathcal{A}_{f,i}(T) = -i \int_0^T dt' \langle \psi_f(T)|\hat{U}(T, t')\hat{H}_I(t')|\psi_i(t')\rangle.
\]  
(2.155)

This general framework can be conveniently applied to describe short-pulse ionization processes. For this purpose, let us specify that \( \hat{H}_0 \) is the atomic Hamiltonian in the single-active-electron approximation,
\[
\hat{H}_0 = \frac{\hat{p}^2}{2m} + V(\hat{r}),
\]  
(2.156)

whereas \( \hat{H}_I \) describes the coupling with the laser field in the length gauge,
\[
\hat{H}_I(t) = -e \mathbf{E}(t) \cdot \hat{r}.
\]  
(2.157)

At this point, we also specify that the vector potential \( \mathbf{A}(t) \), which describes a laser pulse, depends on time for \( t \in [0, T] \) and is zero otherwise. It is related to the electric field \( \mathbf{E}(t) \) such that \( \mathbf{A}(t) = -\int_0^t d\tau \mathbf{E}(\tau) \), which means that \( \int_0^T d\tau \mathbf{E}(\tau) = \mathbf{A}(0) - \mathbf{A}(T) = 0 \). Moreover, the initial state is the atomic ground state of energy \( E_0, \psi_0(\mathbf{r}) \), which evolves in time according to
\[
\langle \mathbf{r}|\psi_i(t)\rangle = e^{-iE_0t}\psi_0(\mathbf{r}).
\]  
(2.158)
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The final state is the scattering state $\psi_p^{(-)}(r)$ which describes a particle of momentum $p$,  

$$
\langle r | \psi_f(t) \rangle = \exp \left(-i \frac{p^2}{2m} t \right) \psi_p^{(-)}(r).
$$

(2.159)

With these definitions, the probability amplitude of ionization (2.155) becomes  

$$
\mathcal{A}(p) = -i \int_0^T dt' \exp \left(i \frac{p^2}{2m} T - iE_0 t' \right) \int dr \int dr' \psi_p^{(-)*}(r) K_L(r, T; r', t') (-e\mathbf{E}(t') \cdot \mathbf{r}') \psi_0(r'),
$$

(2.160)

where we have introduced the retarded propagator $K_L(r, T; r', t'$) [see, its general definition (2.16)]. In our case, this propagator describes an electron under a simultaneous action of the laser field and the external potential in the length gauge (2.83). As presented in the next Section, it allows us to calculate the probability amplitude of ionization under the generalized eikonal approximation.

### 2.5.1 Probability amplitude of ionization under the GEA

In the GEA, the ionization probability amplitude in the length gauge (2.160) equals  

$$
\mathcal{A}^{(1)}(p) = -i \int_0^T dt' \exp \left(i \frac{p^2}{2m} T - iE_0 t' \right) \int dr \int dr' \psi_p^{(-)*}(r) K_L^{(1)}(r, T; r', t') (-e\mathbf{E}(t') \cdot \mathbf{r}') \psi_0(r'),
$$

(2.161)

with  

$$
K_L^{(1)}(r, T; r', t') = \int \frac{dk}{2\pi^3} \exp \left[i \mathbf{k} \cdot \mathbf{r} - i(\mathbf{k} - e\mathbf{A}(t')) \cdot \mathbf{r}' - i(T - t') \frac{k^2}{2m} \right. 
+ \left. i\Phi_k(t', T - t') + i\chi_p^{(1)}(r', t', T - t') \right],
$$

(2.162)

where $\Phi_p(t', T - t')$ and $\chi_p^{(1)}(r', t', T - t')$ are defined by Eqs. (2.57) and (2.94). Having this in mind and performing the integral over $r$ in Eq. (2.161), we arrive at  

$$
\mathcal{A}^{(1)}(p) = -i \int_0^T dt' \exp \left(i \frac{p^2}{2m} T - iE_0 t' \right) \int dr' \int \frac{dk}{2\pi^3} \tilde{\psi}_p^{(-)*}(k) (-e\mathbf{E}(t') \cdot \mathbf{r}') \psi_0(r')
\times \exp \left[-i(\mathbf{k} - e\mathbf{A}(t')) \cdot \mathbf{r}' - i(T - t') \frac{k^2}{2m} + i\Phi_k(t', T - t') + i\chi_p^{(1)}(r', t', T - t') \right].
$$

(2.163)

In the following, we assume that the Fourier transform of the final scattering state, $\tilde{\psi}_p^{(-)}(k)$, is centred around $k \sim p$. Essentially, this corresponds to a plane wave approximation in the final electron state, which is the common approximation applied in strong-field physics. In other words $|\psi_p^{(-)*}(0)|$, which emerges under this approximation in Eq. (2.163), contributes only to the normalization of the plane wave. Therefore, we can disregard this multiplication factor remembering that the density of final electron states per unit volume equals $dp/(2\pi)^3$. This way, the probability amplitude of
ionization (2.163) becomes
\[
\mathcal{A}^{(1)}(p) = -i \int_0^T dt' \exp \left[ i \left( \frac{p^2}{2m} - E_0 \right) t' + i \Phi_p(t', T - t') \right] \times \int dr' \left( -e \mathbf{E}(t') \cdot \mathbf{r}' \right) \psi_0 \left( \mathbf{r}' \right) \exp \left[ -i \left( p - e \mathbf{A}(t') \right) \cdot \mathbf{r}' + i \chi^{(1)}_p(\mathbf{r}', t', T - t') \right].
\]

(2.164)

This result is the basis of our numerical illustrations presented in Sec. 2.6.

### 2.5.2 Probability amplitude of ionization under the Keldysh and the first order Born approximations

In the previous Section, we have derived the expression describing the probability amplitude of ionization under the GEA. The objective of this Section is to analyze and compare this result with other well-established theories of ionization. Such a comparison will help us to ensure validity and to explore the range of applicability of the present theory.

As it was pointed out at the beginning of this Chapter, the vastly used strong-field approximation completely neglects the Coulomb interaction during the electron excursion in the continuum, i.e., after ionization takes place. As we have already mentioned there, many efforts have been undertaken to include the Coulomb potential into the SFA. Here, let us relate to the improved strong-field approximation which arises when the interaction of the ionized electron with its parent ion is treated within the first Born approximation (for a development of the SFA-based theories, see, for instance the reviews [10, 90–93]). In this Section, the relation between the improved strong-field approximation and the generalized eikonal approximation is going to be studied.

Consider a system described by the Hamiltonian,
\[
\hat{H}_L(\hat{r}, \hat{p}, t) = \frac{\hat{p}^2}{2m} - e \mathbf{E}(t) \cdot \hat{r} + V(\hat{r}, t).
\]

(2.165)

In order to analyze the problem perturbatively, we separate this Hamiltonian according to Eq. (2.146). This time,
\[
\hat{H}_0 = \frac{\hat{p}^2}{2m} - e \mathbf{E}(t) \cdot \mathbf{r}
\]

(2.166)
describes the electron in a laser field, whereas
\[
\hat{H}_I = V(\hat{r}, t)
\]

(2.167)
relates to the external potential which, for the time being, we keep as general as possible. Note that, contrary to the factorization introduced in the previous Section, \( \hat{H}_0 \) depends explicitly on time. As it follows from Eq. (2.149), the time-evolution operator \( \hat{U}(t, t') \) satisfies in this case the following integral equation,
\[
\hat{U}(t, t') = \hat{U}_0(t, t') - i \int_{t'}^t d\tau \hat{U}(\tau, \tau)V(\hat{r}, \tau)\hat{U}_0(\tau, t').
\]

(2.168)
Here, \( \hat{U}_0(t, t') \) is the Volkov operator responsible for the time-evolution of the electron in the laser field only (see, Appendix B). Throughout the whole thesis we denote it as \( \hat{U}_L^{GV}(t, t') \equiv \hat{U}_L(t, t') \), where the subscript ' \( L \) ' acknowledges the fact that \( \hat{H}_0 \) is represented in the length gauge (2.166). The last equation can be rewritten in terms of the retarded propagators,

\[
K_L(r, t; r', t') = K_L^{GV}(r, t; r', t') - i \int_{t'}^t d\tau \int dy K_L(r, t; y, \tau)V(y, \tau)K_L^{GV}(y, \tau; r', t'),
\]

(2.169)

where \( K_L^{GV}(r, t; r', t') \) is given by Eq. (2.61).

Applying the last formula in the definition of the probability amplitude of ionization (2.160), we conclude that

\[
A(p) = A_K(p) + A_{resc}(p),
\]

(2.170)

where

\[
A_K(p) = -i \int_0^T dt' \exp \left( \frac{i p^2}{2m} T - i E_0 t' \right) \int dy \int dr' \psi_p^{(-)*}(r) K_L^{GV}(r, T; r', t')(-eE(t') \cdot r') \psi_0(r')
\]

(2.171)

can be recognized as the probability amplitude under the SFA [5]. It is known as the Keldysh amplitude. On the other hand,

\[
A_{resc}(p) = - \int_0^T dt' \exp \left( \frac{i p^2}{2m} T - i E_0 t' \right) \int_0^T d\tau \int dr' \psi_p^{(-)*}(r) \int dr' \int dy K_L(r, T; y, \tau)V(y, \tau)K_L^{GV}(y, \tau; r', t')(-eE(t') \cdot r') \psi_0(r') \]

(2.172)

is the exact rescattering amplitude. The latter can be expanded with respect to the potential \( V(r, t) \), leading to the so-called Born expansion. In the first order Born approximation, the exact propagator \( K_L(r, T; y, \tau) \) in Eq (2.172) is replaced by the Volkov propagator \( K_L^{GV}(r, T; y, \tau) \) [Eq. (2.61)]. As a result, we obtain

\[
A_{resc}^{(1)}(p) = - \int_0^T dt' \exp \left( \frac{i p^2}{2m} T - i E_0 t' \right) \int_0^T d\tau \int dr' \psi_p^{(-)*}(r) \int dr' \int dy K_L^{GV}(r, T; y, \tau)V(y, \tau)K_L^{GV}(y, \tau; r', t')(-eE(t') \cdot r') \psi_0(r').
\]

(2.173)

For ionization, i.e., when \( V(y, \tau) \) represents the atomic potential, this quantity will describe a single rescattering event of a photoelectron.

As before, we assume that the final scattering state is described by the plane wave of momentum \( p \), i.e., \( \psi_p^{(-)}(r) \approx e^{ip \cdot r} \). This makes it possible to perform explicitly the integrals over \( dr \) in
Eqs. (2.171) and (2.173). Namely,
\[
\int \! dr \psi_p^{(-)}(r) K_{L}^{GV}(r, T; r', t') = \int \! d\mathbf{r} e^{-ip \cdot \mathbf{r}} K_{L}^{GV}(r, T; r', t')
\]
\[
= \exp \left[ -i(p - eA(t')) \cdot \mathbf{r}' - i \int_{t'}^{T} \! d\sigma \frac{1}{2m} (p - eA(\sigma))^2 \right] = [\psi_{p,L}^{GV}(r', t')]^* \quad (2.174)
\]
is related to the Volkov solution of the Schrödinger equation in the length gauge [see, Eq. (B.8)].
Hence, the Keldysh amplitude, \( A_K(p) \), and the rescattering amplitude in the first Born approximation, \( A_{\text{resc}}^{(1)}(p) \), can be rewritten as
\[
A_K(p) = -i \int_{0}^{T} \! dt' \exp \left( \frac{iP^2}{2m} T - iE_0 t' \right) \int \! d\mathbf{r}' [\psi_{p,L}^{GV}(r', t')]^*(-eE(t') \cdot \mathbf{r}') \psi_0(\mathbf{r}') \quad (2.175)
\]
and
\[
A_{\text{resc}}^{(1)}(p) = -i \int_{0}^{T} \! dt' \exp \left( \frac{iP^2}{2m} T - iE_0 t' \right) \int \! d\mathbf{r}' \int_{t'}^{T} \! d\tau
\times \int \! d\mathbf{y}[\psi_{p,L}^{GV}(\mathbf{y}, \tau)]^* V(\mathbf{y}, \tau) K_{L}^{GV}(\mathbf{y}, \tau; r', t')(-eE(t') \cdot \mathbf{r}') \psi_0(\mathbf{r}'), \quad (2.176)
\]
respectively.

The last formula can be further simplified. For this purpose, let us rewrite the Volkov propagator (2.61) as
\[
K_{L}^{GV}(\mathbf{y}, \tau; r', t') = \exp \left[ i(\mathbf{p} - eA(\tau)) \cdot \mathbf{y} - i(\mathbf{p} - eA(t')) \cdot \mathbf{r}' - \frac{i}{2m} \int_{t'}^{T} \! d\sigma [\mathbf{p} - eA(\sigma)]^2 \right]
\times \int \frac{dk}{(2\pi)^3} \exp \left[ i(\mathbf{k} - \mathbf{p}) \cdot \mathbf{y} - i(\mathbf{k} - \mathbf{p}) \cdot \mathbf{r}' - \frac{i}{2m} \int_{t'}^{T} \! d\sigma [(\mathbf{k} - eA(\sigma))^2 - [\mathbf{p} - eA(\sigma)]^2] \right].
(2.177)
\]

Next, we change the integration variable such that \( \kappa = \mathbf{k} - \mathbf{p} \). This leads to
\[
K_{L}^{GV}(\mathbf{y}, \tau; r', t') = \exp \left[ i(\mathbf{p} - eA(\tau)) \cdot \mathbf{y} - i(\mathbf{p} - eA(t')) \cdot \mathbf{r}' - \frac{i}{2m} \int_{t'}^{T} \! d\sigma [\mathbf{p} - eA(\sigma)]^2 \right]
\times \int \frac{d\kappa}{(2\pi)^3} \exp \left[ -\frac{i(-\tau - t')}{2m} \kappa^2 - i\kappa \cdot (\mathbf{R}_p(r', t', \tau) - \mathbf{y}) \right], \quad (2.178)
\]
where we have introduced the electron free trajectory in the laser field, \( \mathbf{R}_p(r', t', \tau) \), defined by
\[^1\text{Note that } \psi_{p,L}^{GV}(r', t') \text{ defined in Eq. (2.174) differs from Eq. (B.8) by an irrelevant phase factor.}\]
Chapter 2. Generalized eikonal approximation in strong-field ionization

Eq. (2.72). Here, we recognize that the integral over \( \kappa \) can be performed analytically as the Fresnel integral (see, Appendix C). As a result, we obtain

\[
K_L^{GV}(y, \tau; r', t') = \exp \left[ i(p - eA(\tau)) \cdot y - i(p - eA(t')) \cdot r' - \frac{i}{2m} \int_{\nu}^{\tau} d\sigma [p - eA(\sigma)]^2 \right] 
\times \left( \frac{m}{2\pi i(\tau - t')} \right)^{3/2} \exp \left[ \frac{im}{2(\tau - t')} (R_p(r', t', \tau) - y)^2 \right]. \tag{2.179}
\]

Making use of Eq. (2.174), we conclude that the Volkov propagator in the length gauge (2.61) can be represented as

\[
K_L^{GV}(y, \tau; r', t') = \left[ \psi_{p,L}^{GV}(r', t') \right]^* \left( \frac{m}{2\pi i(\tau - t')} \right)^{3/2} \exp \left[ \frac{im}{2(\tau - t')} (R_p(r', t', \tau) - y)^2 \right]. \tag{2.180}
\]

Now, let us go back to Eq. (2.176). By plugging Eq. (2.180) into (2.176), we obtain

\[
A^{(1)}_{\text{resc}}(p) = -\int_0^T dt' \exp \left( \frac{iP^2}{2m} - iE_0 t' \right) \int dr' \left[ \psi_{p,L}^{GV}(r', t') \right]^* (-eE(t') \cdot r') \psi_0(r') \tag{2.181}
\times \int_{\nu}^{\tau} d\tau \left( \frac{m}{2\pi i(\tau - t')} \right)^{3/2} \int dy V(y, \tau) \exp \left[ \frac{im}{2(\tau - t')} (R_p(r', t', \tau) - y)^2 \right].
\]

Here, we recognize the generalized eikonal \( \chi^{(1)}_p(r', t', T - t') \) [see, Eq. (2.94)]. Therefore, the rescattering amplitude in the first-order Born approximation becomes

\[
A^{(1)}_{\text{resc}}(p) = \int_0^T dt' \exp \left( \frac{iP^2}{2m} - iE_0 t' \right) \tag{2.182}
\times \int dr' \left[ \psi_{p,L}^{GV}(r', t') \right]^* \chi^{(1)}_p(r', t', T - t') (-eE(t') \cdot r') \psi_0(r').
\]

Putting together Eqs. (2.175) and (2.182), we obtain that the total probability amplitude (2.170) in the first order Born approximation is given as

\[
A^{(1)}(p) = A_{K}(p) + A^{(1)}_{\text{resc}}(p). \tag{2.183}
\]

Note that the same expression is derived from the GEA, in the limit when \( |\chi^{(1)}_p(r', t', T - t')| \ll 1 \). In this case, in Eq. (2.164) we use the following Taylor expansion, \( e^{i\chi^{(1)}_p(r', t', T - t')} \approx 1 + i\chi^{(1)}_p(r', t', T - t') \). Such an agreement is not achievable within the EA. This shows that the first Born approximation, which has been extensively used in the analysis of rescattering processes in ionization [10], is the limiting case of the generalized eikonal series expansion. While our considerations in this Section were for an arbitrary potential \( V(r, t) \), they remain valid for static atomic potentials \( V(r, t) \equiv V(r) \).

In this Section, we have demonstrated that the GEA agrees with the well-known theories of strong-field ionization such as the Keldysh theory and the first order Born approximation. In the next Section, we shall use the GEA and the Keldysh approximation to analyze ionization by short laser pulses. More precisely, we will study how, by changing parameters of those pulses, one can control the signal of ionized electrons.
2.6 Application of the GEA and the Keldysh approximation to strong-field ionization

We will start our analysis by introducing a detailed description of the driving laser field. In order to interpret the results obtained from the GEA, a lot of space will be devoted to the results obtained within the Keldysh approach. This will be followed by a detailed analysis of the photoelectron energy spectra arising from the GEA.

2.6.1 Laser pulse and its characteristics

In the above formulation it was assumed that a finite laser pulse lasts for time $T$ and, therefore, it is described by the electric field $\mathcal{E}(t)$ which vanishes for $t < 0$ and $t > T$. The pulse duration $T$ defines the fundamental frequency of field oscillations, $\omega = 2\pi/T$. One can also introduce the field phase, $\phi = \omega t$, which can be used to rewrite the above condition such that $\mathcal{E}(\phi)$ vanishes for $\phi < 0$ and $\phi > 2\pi$. It is assumed that the driving pulse is linearly-polarized along the $z$-axis. In this case, we describe the laser field by the electric field vector

$$\mathcal{E}(\phi) = \mathcal{E}_0 f_E(\phi)e_z,$$  \hspace{1cm} (2.184)

where $\mathcal{E}_0$ is related to the amplitude of field oscillations. Here, the shape function $f_E(\phi)$ is adjusted such that $f_E(\phi) = 0$ for $\phi < 0$ and $\phi > 2\pi$, and it has to satisfy the condition \[10\]

$$\int_0^{2\pi} f_E(\phi)d\phi = 0.$$  \hspace{1cm} (2.185)

This condition is fulfilled provided that the shape function has the following Fourier decomposition,

$$f_E(\phi) = \sum'_{N=-N_0}^{N_0} \mathcal{E}_N e^{-iN\phi},$$  \hspace{1cm} (2.186)

where $\sum'$ means that the zeroth Fourier component is excluded from the sum, $N \neq 0$. Since $f_E(\phi)$ is a real function, it is also required that $\mathcal{E}_N^* = \mathcal{E}_{-N}$. This expansion can be used to define the average intensity carried out by the laser pulse,

$$I = \langle c\varepsilon_0\mathcal{E}^2 \rangle = \frac{1}{2\pi} \int_0^{2\pi} c\varepsilon_0\mathcal{E}^2(\phi)d\phi.$$  \hspace{1cm} (2.187)

Namely,

$$I = 2c\varepsilon_0\mathcal{E}_0^2 \sum_{N=1}^{N_0} |\mathcal{E}_N|^2.$$  \hspace{1cm} (2.188)

Note that this definition, even though derived for a finite laser pulse, is consistent with the monochromatic plane wave approximation. In the latter case, taking the electric field of the form $\mathcal{E}(\phi) = \mathcal{E}_0 e^{i\omega t}$, the average intensity is given by

$$I = \langle c\varepsilon_0\mathcal{E}^2 \rangle = \frac{c\varepsilon_0 E_0^2 \omega}{2\pi}.$$  \hspace{1cm} (2.189)
$E_0 \sin(\phi)e_z$, one has $E_{\pm 1} = \mp i/2$. Hence, it follows from Eq. (2.188) that the averaged intensity of the monochromatic plane wave equals $I = c\varepsilon_0 E_0^2/2$.

Let us now define the shape function for the vector potential $A(\phi)$,

$$f_A(\phi) = -\int_{0}^{\phi} f_\varepsilon(\varphi)d\varphi,$$  \hspace{1cm} (2.189)

which leads to

$$A(\phi) = \frac{E_0}{\omega} f_A(\phi)e_z.$$  \hspace{1cm} (2.190)

Using Eq. (2.186), one can derive the corresponding Fourier decomposition of the shape function $f_A(\phi)$ [Eq. (2.189)]

$$f_A(\phi) = A_0 + \sum_{N=-N_0}^{N_0} A_N e^{-iN\phi},$$  \hspace{1cm} (2.191)

where $A_0 = -2 \sum_{N=1}^{N_0} \text{Re}[A_N]$ and $A_N = -i\varepsilon_0 N/N$ assuming that $N \neq 0$. Since we have imposed the condition $A(0) = A(2\pi) = 0$, the vector potential has a constant and an oscillatory contributions, $A(\phi) = A_{\text{const}} + A_{\text{osc}}(\phi)$. It is the oscillatory contribution to the vector potential, $A_{\text{osc}}(\phi)$, which describes the quiver motion of free electrons in the laser field. The ponderomotive energy of such a motion can be defined as

$$U_p = \langle \frac{e^2 A_{\text{osc}}^2}{2m} \rangle = \frac{1}{2\pi} \int_{0}^{2\pi} \frac{e^2}{2m} A_{\text{osc}}^2(\phi)d\phi.$$  \hspace{1cm} (2.192)

Applying here the series expansion (2.191), we find out that

$$U_p = \frac{e^2 \varepsilon_0^2}{m\omega^2} \sum_{N=1}^{N_0} \frac{\varepsilon_0^2 N^2}{N^2}.$$  \hspace{1cm} (2.193)

Again, for the monochromatic plane wave, we obtain from Eq. (2.193) that $U_p = e^2 \varepsilon_0^2/(4m\omega^2)$. This is the well-known formula for the ponderomotive energy of a free electron driven by the monochromatic plane wave.

At this point, let us comment on the presence of a constant term $A_0$ in the vector potential $A(\phi)$. One can choose this term differently, by adding to $A_0$ an arbitrary constant $a_0$. This is equivalent to adding to $A(\phi)$ a constant vector $a = \varepsilon_0 a_0 e_z/\omega$. However, such a term can be eliminated from the Schrödinger equation by the gauge transformation (2.35), where $A(r,t) = a \cdot r$ for both the initial $\psi_0(r)$ and final $\psi_p^{-}(r)$ states, and by the corresponding transformation for the propagator (2.36). For more details on gauge transformations, see Sec. 2.1.2. This means that the ionization probability amplitude (2.160) is independent of $a$. The same applies to Eq. (2.164). While the probability distributions are invariant under such a transformation, for our choice of $A_0$ not only the electric field $\varepsilon(\phi)$ but also the vector potential $A(\phi)$ vanishes when $\phi < 0$ and $\phi > 2\pi$. This allows us to interpret $p$ in Eqs. (2.160) and (2.164) as the free electron momentum which is measured at the detector after the interaction with the laser field is finished.
For further purposes, we introduce the vector function

\[ \alpha(\phi) = \frac{E_0}{\omega^2} f_\alpha(\phi) e_z, \]  

(2.194)

where

\[ f_\alpha(\phi) = -\int_0^\phi f_A(\varphi) d\varphi. \]  

(2.195)

This expression can be separated into three different terms, namely

\[ f_\alpha(\phi) = f_{\alpha,0} + f_{\alpha,1}\phi + f_{\alpha,\text{osc}}(\phi), \]  

(2.196)

with

\[ f_{\alpha,0} = 2 \sum_{N=1}^{N_0} \frac{\text{Re}[E_N]}{N^2}, \]  

(2.197)

\[ f_{\alpha,1} = 2 \sum_{N=1}^{N_0} \frac{\text{Im}[E_N]}{N}, \]  

(2.198)

\[ f_{\alpha,\text{osc}}(\phi) = -\sum_{N=-N_0}^{N_0} \frac{E_N}{N^2} e^{-iN\phi}. \]  

(2.199)

This function will be used in Sec. 2.6.5.1.

We consider the laser field described by the shape function

\[ f_E(\phi) = \begin{cases} \sin^2\left(\frac{N_{\text{rep}}}{2}\phi\right) \sin(N_{\text{rep}}\phi), & \phi \in [0, 2\pi], \\ 0, & \text{otherwise.} \end{cases} \]  

(2.200)

Such a laser field consists of \(N_{\text{rep}}\) single-cycle pulses with no time delay in-between (where \(N_{\text{rep}} = 1, 2, 3, \ldots\)). Introducing the laser carrier frequency \(\omega_L = N_{\text{rep}} \omega\), we can represent Eq. (2.200) as

\[ f_E(t) = \begin{cases} \frac{1}{2} \sin(\omega_L t) - \frac{1}{2} \sin(2\omega_L t), & t \in [0, T], \\ 0, & \text{otherwise.} \end{cases} \]  

(2.201)

This clearly shows that the laser field (2.200) can be composed out of two harmonics, i.e., \(\omega_L\) and \(2\omega_L\). For our choice of the shape function, the only nonzero coefficients in its Fourier expansion (2.186) are \(E_{\pm N_{\text{rep}}} = \mp i/4\) and \(E_{\pm 2N_{\text{rep}}} = \pm i/8\). Therefore, according to Eq. (2.188), the averaged intensity carried out by the laser pulse (2.200) is

\[ I = \frac{5}{32} \epsilon_0 E_0^2. \]  

(2.202)
Moreover, it follows from Eq. (2.193) that the ponderomotive energy associated with the quiver motion of an electron in such a field equals

\[ U_p = \frac{17}{256} \frac{e^2 \xi_0^2}{m \omega_L^2}. \]  

(2.203)

Further we shall assume that \( \omega_L \) equals the frequency of the Ti-Sapphire laser, \( \omega_L = 1.55 \) eV, while the averaged intensity of the pulse is \( I = 3.125 \times 10^{13} \) W/cm\(^2\). Thus, the ponderomotive energy of the electron oscillating in the laser pulse (2.200) equals \( U_p = 1.024 \omega_L \).

Our motivation for choosing the laser field of the form (2.200) is twofold. Firstly, it contains only two harmonics which significantly reduces the number of saddle points and quantum trajectories discussed below. Secondly, each modulation of the field [defined for \( \phi \in (2\pi(\ell - 1)/N_{\text{rep}}, 2\pi\ell/N_{\text{rep}}) \) with \( \ell = 1, \ldots, N_{\text{rep}} \)] satisfies all necessary conditions imposed on a laser pulse: (i) the time-integral of the electric field is 0; (ii) the electric field and its first derivative are continuous; (iii) the electric field vanishes smoothly in the beginning and at the end of each modulation. Thus, one can conclude that Eq. (2.200) describes a finite train of identical pulses with each having the \( \sin^2 \) envelope. At the same time, it is the linear superposition of the first and the second harmonics [Eq. (2.201)] which makes it feasible to generate such a pulse train in laboratory settings (see, e.g., Ref. [94] for a particular realization of such a train).

Below, the energy spectra of photoelectrons ionized from a hydrogen-like atom by the laser field (2.200) with different \( N_{\text{rep}} \) will be analyzed. In general, while changing the number of pulse repetitions, \( N_{\text{rep}} \), the time duration of the entire sequence of pulses, \( T = 2\pi N_{\text{rep}}/\omega_L \), will change as well. First, the respective results based on the Keldysh theory are going to be presented.

### 2.6.2 Keldysh approximation

In the Keldysh approximation, the amplitude of ionization \( A_K(p) \) is given by Eq. (2.175). Substituting there Eq. (2.174), where we add and subtract the term \( iE_0T \) in the exponent, we arrive at

\[
\begin{align*}
A_K(p) &= -i \exp \left[ i \left( \frac{p^2}{2m} - E_0 \right) T \right] \int_0^T dt' \int d\mathbf{r}' \exp \left\{ -i(\mathbf{p} - eA(t')) \cdot \mathbf{r}' \right\} \\
&\quad - i \int_{\ell}^T d\sigma \left[ \frac{1}{2m} (\mathbf{p} - eA(\sigma))^2 - E_0 \right] \left\{ -e \mathbf{E}(t') \cdot \mathbf{r}' \right\} \psi_0(\mathbf{r}') \\
&\quad \times \int d\mathbf{r}' \exp \left\{ -i(\mathbf{p} - eA(t')) \cdot \mathbf{r}' + i \int_0^{t'} d\sigma \left[ \frac{1}{2m} (\mathbf{p} - eA(\sigma))^2 - E_0 \right] \right\} \left\{ -e \mathbf{E}(t') \cdot \mathbf{r}' \right\} \psi_0(\mathbf{r}').
\end{align*}
\]

(2.204)

This equation can be further rewritten as

\[
A_K(p) = -i \exp \left\{ i \left( \frac{p^2}{2m} - E_0 \right) T - i \int_0^T d\sigma \left[ \frac{1}{2m} (\mathbf{p} - eA(\sigma))^2 - E_0 \right] \right\} \int_0^T dt' \\
\times \int d\mathbf{r}' \exp \left\{ -i(\mathbf{p} - eA(t')) \cdot \mathbf{r}' + i \int_0^{t'} d\sigma \left[ \frac{1}{2m} (\mathbf{p} - eA(\sigma))^2 - E_0 \right] \right\} \left\{ -e \mathbf{E}(t') \cdot \mathbf{r}' \right\} \psi_0(\mathbf{r}').
\]

(2.205)
Here, let us introduce the phase of the laser pulse, \( \phi = \omega t \). We also denote as
\[
\Pi(\phi) = p - eA(\phi)
\] (2.206)

the kinetic momentum of the electron in the laser field. Introducing these abbreviations, we obtain the Keldysh amplitude in the form
\[
A_K(p) = -i \exp \left\{ i\left( \frac{p^2}{2m} - E_0 \right) T - i \int_0^{2\pi} d\phi \frac{\Pi^2(\phi)}{2m} - E_0 \right\}
\times \int_0^{2\pi} d\phi \int dr' \exp \left\{ -i\Pi(\phi) \cdot r' + i \int_0^{\phi} d\phi' \frac{\Pi^2(\phi')}{2m} - E_0 \right\} (-eE(\phi) \cdot r')\psi_0(r') .
\] (2.207)

For our further purpose, let us also introduce a function
\[
G(p, \phi) = \frac{1}{\omega} \int_0^{\phi} d\phi' \frac{\Pi^2(\phi')}{2m} - E_0 .
\] (2.208)

This helps us to rewrite Eq. (2.207) as
\[
A_K(p) = -i \exp \left\{ i\left( \frac{p^2}{2m} - E_0 \right) T - iG(p, 2\pi) \right\} \int_0^{2\pi} d\phi \frac{e^{iG(p, \phi)}}{\omega} \int dr' e^{-i\Pi(\phi) \cdot r'} (-eE(\phi) \cdot r')\psi_0(r') .
\] (2.209)

The exponential prefactor in Eq. (2.209), which does not depend on the \( r' \) or \( \phi \) variables, contributes to the global phase of the probability amplitude. From now on, we will denote it as
\[
\Phi_0(p) = \left( \frac{p^2}{2m} - E_0 \right) T - G(p, 2\pi) .
\] (2.210)

Thus, the probability amplitude of ionization in the Keldysh approximation becomes
\[
A_K(p) = -i \frac{e^{i\Phi_0(p)}}{\omega} \int_0^{2\pi} d\phi \frac{e^{iG(p, \phi)}}{\omega} \int dr' e^{-i\Pi(\phi) \cdot r'} (-eE(\phi) \cdot r')\psi_0(r') .
\] (2.211)

We consider the ionization from the ground state of a hydrogen-like atom. In this case,
\[
\psi_0(r) = \sqrt{\frac{\lambda}{\pi}} e^{-\lambda r}, \quad E_0 = -\frac{\lambda^2}{2m} ,
\] (2.212)
where \( \lambda = (Za_0)^{-1} \), \( a_0 \) is the Bohr radius, and \( Z \) represents the atomic number of the element. The integral over the position variable in Eq. (2.211) can be represented as
\[
\int dr' e^{-i\Pi(\phi) \cdot r'} (-eE(\phi) \cdot r')\psi_0(r') = -ieE(\phi) \cdot \nabla_\Pi \int dr' e^{-i\Pi(\phi) \cdot r'}\psi_0(r') ,
\] (2.213)
where \( \nabla_\Pi \) is the gradient taken over the variable \( \Pi \). Note that \( \psi_0(r') \) depends only on the distance \( |r'| = r' \) [Eq. (2.212)]. This allows us to perform the remaining angular integrals. To this end, we introduce the spherical coordinates such that the polar angle \( \theta \) is measured with respect to the direction
Performing the integral over the azimuthal angle, we arrive at
\[
\int \mathrm{d}r' e^{-i\Pi(\phi) \cdot r'}(-e E(\phi) \cdot r')\psi_0(r') = -2\pi i\lambda \sqrt{\frac{\lambda}{\pi}} e E(\phi) \cdot \nabla \Pi \int_0^\infty \mathrm{d}r' r'^2 \int_0^\pi \mathrm{d}\theta \sin \theta e^{-\lambda r' + i r' \Pi \cos \theta}.
\] (2.214)

It is straightforward to perform the integral over \(\theta\). The radial integral is done by parts, which leads to the following expression
\[
\int \mathrm{d}r' e^{-i\Pi(\phi) \cdot r'}(-e E(\phi) \cdot r')\psi_0(r') = 2\lambda \sqrt{\frac{\lambda}{\pi}} e E(\phi) \cdot \nabla \Pi \left[ \frac{1}{\Pi(\lambda + i\Pi)^2} - \frac{1}{\Pi(\lambda - i\Pi)^2} \right].
\] (2.215)

In the final step, we calculate the gradient of the expression in the brackets. As a result we obtain that the position integral in Eq. (2.211) equals
\[
\int \mathrm{d}r' e^{-i\Pi(\phi) \cdot r'}(-e E(\phi) \cdot r')\psi_0(r') = 32\pi i\lambda^2 \sqrt{\frac{\lambda}{\pi}} e E(\phi) \cdot \Pi(\phi)
\]
\[
\left( \lambda^2 + \Pi(\phi)^2 \right)^{\frac{3}{2}}.
\] (2.216)

Note that, according to Eq. (2.208), the first and the second derivatives of the function \(G(p, \phi)\) with respect to the variable \(\phi\) are given by
\[
G'(p, \phi) \equiv \frac{\partial}{\partial \phi} G(p, \phi) = \frac{1}{\omega} \left[ \frac{\Pi(\phi)^2}{2m} - E_0 \right] = \frac{1}{2m\omega} \left( \lambda^2 + \Pi(\phi)^2 \right)
\] (2.217)
and
\[
G''(p, \phi) \equiv \frac{\partial^2}{\partial \phi^2} G(p, \phi) = \frac{1}{m\omega^2} e E(\phi) \cdot \Pi(\phi),
\] (2.218)
where the relation \(\frac{\partial \Pi(\phi)}{\partial \phi} = -e \frac{\partial A(\phi)}{\partial \phi} = e \omega E(\phi)\) has been used. Employing expressions (2.217) and (2.218), the integral (2.216) becomes,
\[
\int \mathrm{d}r' e^{-i\Pi(\phi) \cdot r'}(-e E(\phi) \cdot r')\psi_0(r') = 4i\lambda^2 \sqrt{\frac{\lambda}{\pi}} m^2 \omega G''(p, \phi) \left[ G'(p, \phi) \right]^3.
\] (2.219)

Taking into account Eq. (2.211), the probability amplitude of ionization of a hydrogen-like atom from its ground state, within the framework of the Keldysh theory, equals
\[
\mathcal{A}_K(p) = 4\lambda^2 \sqrt{\frac{\lambda}{m^2\omega^2}} \int \mathrm{d}^2 \phi e^{i\Phi_0(p)} \int_0^{2\pi} \mathrm{d}\phi \frac{G''(p, \phi)}{\left[ G'(p, \phi) \right]^3} e^{iG(p, \phi)}.
\] (2.220)

The remaining integral can be performed numerically. However, for our further purpose, we also present below an approximate method of calculating it, which is by using the saddle-point method.
2.6.2.1 Keldysh approximation and the saddle-point method

The main contributions to the integral in Eq. (2.220) come from the saddle points (known also as the stationary points), \( \phi_s \), which are defined as the solutions of the equation,

\[ G'(p, \phi)|_{\phi=\phi_s} = 0. \] (2.221)

An ordinary saddle-point method (see, Appendix E.1) would consist in replacing in Eq. (2.220) the function \( G''(p, \phi) \) by its value at the saddle point \( \phi_s \) and, also, in replacing the argument of the exponent by the first nonvanishing term arising from the Taylor expansion of \( G(p, \phi) \) around \( \phi_s \). In the current case, this procedure would lead to a singularity and, for this reason, the ordinary saddle-point approach has to be modified. In Appendix E.2, we show how the integrand in Eq. (2.220) has to be modified in order for the saddle-point method to be applicable. By means of the so-called singular saddle-point technique we estimate the integral in Eq. (2.220) as

\[ I_3 = \int_0^{2\pi} d\phi G''(p, \phi) \left( \frac{G'(p, \phi)}{G''(p, \phi)} \right)^3 e^{iG(p, \phi)} \approx -\frac{\pi}{2} \sum_s e^{iG(p, \phi_s)} G''(p, \phi_s). \] (2.222)

This result has been derived in Appendix E.2 [Eq. (E.23) for \( \nu = 3 \)]. Note that the sum in (2.222) is carried out over all saddle points such that

\[ \text{Im}[G'(p, \phi_s)] > 0 \quad \text{and} \quad \text{Im}[G''(p, \phi_s)] > 0. \] (2.223)

As it will become clear shortly, these conditions are compatible with the requirement that \( \text{Im}(\phi_s) > 0 \). Note also that the most important contribution to the sum in (2.222) comes from the points with the smallest value of \( \text{Im}(\phi_s) \). Keeping this in mind, the Keldysh amplitude of photoionization from the ground state of a hydrogen-like atom and approximated according to the singular saddle-point method, \( A_K^{(\text{saddle})}(p) \), becomes

\[ A_K^{(\text{saddle})}(p) = -2\sqrt{\lambda} \left( \frac{\pi \lambda}{m \omega} \right)^2 e^{i\Phi_0(p)} \sum_s \frac{e^{iG(p, \phi_s)}}{G''(p, \phi_s)}. \] (2.224)

As one can understand, it is now crucial to analyze the saddle points.

2.6.2.2 Analysis of saddle points

We start by calculating the saddle points, which are the solutions of Eq. (2.221). The function \( G'(p, \phi) \) is given by Eq. (2.217), meaning that the saddle points are the roots of the following equation,

\[ [p - eA(\phi_s)]^2 = -\lambda^2. \] (2.225)

As the vector potential \( A(\phi) \) is obtained according to Eqs. (2.189) and (2.190), and the shape function
Figure 2.1 Positions of the saddle points $\phi_s$ as a function of the kinetic energy of electrons $E_p$, calculated from Eq. (2.227). Only these saddle points which satisfy (2.223) are plotted. The saddle points with the same imaginary part are marked either as solid or dashed lines. The parameters of the driving laser field [described by Eqs. (2.184) and (2.200)] are $\omega_L = 1.55$ eV, $N_{\text{rep}} = 3$, and $I = 3.125 \times 10^{15}$ W/cm$^2$. The final electrons are detected asymptotically at the polar angle $\theta_p = 0.2\pi$.

$f_{\mathcal{E}}(\phi)$ is given in Eq. (2.200), for the present pulse choice, the equation defining saddle points reads

$$\left[ p + \frac{e\mathcal{E}_0}{N_{\text{rep}}\omega} \sin^4 \left( \frac{N_{\text{rep}}\phi_s}{2} \right) e_z \right]^2 = -\lambda^2. \quad (2.226)$$

When solving this equation, one has to remember that $0 \leq \phi_s \leq 2\pi$. Due to the cylindrical symmetry of the problem, the positions of saddle points do not depend on the azimuthal angle of ionized electrons, just on their polar angle $\theta_p$. Therefore, the previous relation becomes

$$\left[ |p| \cos \theta_p + \frac{e\mathcal{E}_0}{N_{\text{rep}}\omega} \sin^4 \left( \frac{N_{\text{rep}}\phi_s}{2} \right) \right]^2 + p^2 \sin^2 \theta_p = -\lambda^2. \quad (2.227)$$

This equation has, in general, $8N_{\text{rep}}$ solutions but just half of them satisfy the relations (2.223). Among the remaining solutions, we can distinguish two groups of solutions ($2N_{\text{rep}}$ points each) with the exact same positive imaginary parts for $\phi_s$, $G(p, \phi_s)$, and $G''(p, \phi_s)$. To illustrate this, we consider a Ti:Sapphire laser ($\omega_L = 1.55$ eV) producing a field composed out of three single-cycle pulses ($N_{\text{rep}} = 3$), with the electric field described by Eqs. (2.184) and (2.200). We choose the averaged intensity of the laser field $I = 3.125 \times 10^{15}$ W/cm$^2$. For the present calculations we have chosen $\theta_p = 0.2\pi$. In Fig. 2.1, we plot the real (upper panel) and imaginary (lower panel) parts of the solutions to Eq. (2.227) which obey the conditions (2.223). For $N_{\text{rep}} = 3$, we observe 12 such saddle
Figure 2.2  Shows the shape function \( f_E(\phi) \) for a triple \((N_{\text{rep}} = 3)\) laser pulse defined by Eq (2.200). In the lower panels, the corresponding shape functions \( f_A(\phi) \) and \( f_\alpha(\phi) \) are displayed [Eqs. (2.189) and (2.195), respectively]. We have marked the real parts of saddle points, \( \text{Re}\phi_s \), as vertical lines. While the thin black lines correspond to the position of these saddle points which contribute very little to the probability amplitude of ionization (2.224), the major contribution there comes from the saddle points marked as the thick (both solid and dashed) lines. The positions of \( \text{Re}\phi_s \) are for \( E_p \approx 3U_p \) and \( \theta_p = 0.2\pi \).

In Figs. 2.2 and 2.3, we present the shape functions \( f_E(\phi) \), \( f_A(\phi) \), and \( f_\alpha(\phi) \) for \( N_{\text{rep}} = 3 \) and two different kinetic energies \((E_p = 3.13\omega_L \approx 3U_p \text{ in Fig. 2.2 and } E_p = 12.22\omega_L \approx 12U_p \text{ in Fig. 2.3})\). The vertical lines represent the real parts of saddle points, \( \text{Re}\phi_s \). The thin black lines correspond to those saddle points that do not contribute much to the probability amplitude of ionization (2.224). This is not surprising as their real parts correspond to the nearly zero value of the electric field. Contrary to this, the remaining vertical lines (thick solid and dashed lines) correspond to the saddle points that have to be accounted for in Eq. (2.224). We see that the important saddle points have their real parts which correspond to the nearly extreme values of the electric field. Note that we choose those particular values for the kinetic energy only for the illustration of a general behavior of \( \text{Re}\phi_s \). This behavior is qualitatively similar for all energies \( E_p \) from the interval \([0, 40\omega_L]\) considered in Fig. 2.1.
In Figs. 2.4 and 2.5, we draw the dependence of the functions $G(p, \phi_s)$ and $G''(p, \phi_s)$ on the kinetic energy of photoelectrons $E_p$ for those saddle points $\phi_s$ that contribute significantly to the probability amplitude of ionization (2.224). These saddle points were denoted in Fig. 2.1 by the solid lines. Among these points, we can distinguish between the ones that relate to the maxima (solid blue lines) and minima (dashed red lines) of the shape function $f_E(\phi)$ (see, Figs. 2.2 and 2.3). We denote these saddle points as $\phi_{N_{\text{rep}}}^{(\ell)}$ and $\tilde{\phi}_{N_{\text{rep}}}^{(\ell)}$, respectively, with $\ell = 1, 2, ..., N_{\text{rep}}$. They have the same positive imaginary part but their real parts differ such that

$$\text{Re}\phi_{N_{\text{rep}}}^{(\ell)} = \phi_0 + \frac{2\pi}{N_{\text{rep}}} (\ell - 1),$$

(2.228)

$$\text{Re}\tilde{\phi}_{N_{\text{rep}}}^{(\ell)} = -\phi_0 + \frac{2\pi}{N_{\text{rep}}} \ell.$$  

(2.229)

Here, $\phi_0$ denotes the real part of the first saddle point which gives a significant contribution to the probability amplitude. It can be anticipated from the upper panel of Fig. 2.4 that

$$\text{Re}[G(p, \phi_{N_{\text{rep}}}^{(\ell)})] = G_0(p) + 2\pi(\ell - 1)F(p),$$

(2.230)

$$\text{Re}[G(p, \tilde{\phi}_{N_{\text{rep}}}^{(\ell)})] = \tilde{G}_0(p) + 2\pi(\ell - 1)F(p).$$

(2.231)

Even though it is possible to derive the exact forms of functions $G_0(p), \tilde{G}_0(p)$, and $F(p)$, it is not of a particular interest. As we will show shortly, only the structure of the functions $\text{Re}[G(p, \phi_{N_{\text{rep}}}^{(\ell)})]$ and $\text{Re}[G(p, \tilde{\phi}_{N_{\text{rep}}}^{(\ell)})]$ is important for interpreting the resulting energy distributions of photoelectrons.
Figure 2.4 Shows the dependence of the real (upper panel) and imaginary (lower panel) parts of $G(p, \phi_s)$ [Eq. (2.208)] on the photoionized electron kinetic energy, $E_p$, calculated for the same parameters as in Fig. 2.1. Only these saddle points are accounted for which significantly contribute to the probability amplitude of ionization (2.224).

Moreover, it follows from the bottom panel of Fig. 2.4 that

$$\text{Im}[G(p, \phi^{(\ell)}_{N_{\text{rep}}})] = \text{Im}[G(p, \tilde{\phi}^{(\ell)}_{N_{\text{rep}}})] \equiv W(p) > 0.$$ (2.232)

Another important observation, based on Fig. 2.5, is that

$$\text{Re}[G''(p, \phi^{(\ell)}_{N_{\text{rep}}})] = - \text{Re}[G''(p, \tilde{\phi}^{(\ell)}_{N_{\text{rep}}})],$$ (2.233)

$$\text{Im}[G''(p, \phi^{(\ell)}_{N_{\text{rep}}})] = \text{Im}[G''(p, \tilde{\phi}^{(\ell)}_{N_{\text{rep}}})].$$ (2.234)

Having this in mind, we shall denote in the following:

$$G''_0(p) = |G''(p, \phi^{(\ell)}_{N_{\text{rep}}})| = |G''(p, \tilde{\phi}^{(\ell)}_{N_{\text{rep}}})|$$ (2.235)

and

$$\psi_{G''}(p) = \text{arg}[G''(p, \phi^{(\ell)}_{N_{\text{rep}}})] = \pi - \text{arg}[G''(p, \tilde{\phi}^{(\ell)}_{N_{\text{rep}}})].$$ (2.236)

This analysis will be used in the next Section to derive the so-called diffraction formula for ionization by a train of pulses defined by Eqs. (2.184) and (2.200).

### 2.6.2.3 Diffraction formula for strong-field ionization

Before we present numerical results for photoelectron energy spectra, let us analyze the structure of the formula defining the Keldysh probability amplitude $A^{(\text{saddle})}_K(p)$ [Eq. (2.224)]. With the
help of Eqs. (2.230), (2.231), and (2.232), the amplitude of ionization \( A^{(\text{saddle})}_K(p) \) can be written in a more revealing way,

\[
A^{(\text{saddle})}_K(p) = -2 \sqrt{\frac{\lambda}{\pi}} \frac{\pi \lambda}{m \omega} \frac{G''_{0}(p)}{G''_{0}(p)} e^{i\Phi_{0}(p)} \left( e^{i[G_{0}(p) - \psi_{G''}(p)]} + e^{i[\tilde{G}_{0}(p) - \pi + \psi_{G''}(p)]} \right) \sum_{\ell=1}^{N_{\text{rep}}} e^{i2\pi(\ell-1)F(p)} .
\]

(2.237)

Here, we accounted only for these saddle points which contribute significantly to \( A^{(\text{saddle})}_K(p) \). Next, we note that

\[
e^{i[G_{0}(p) - \psi_{G''}(p)]} + e^{i[\tilde{G}_{0}(p) - \pi + \psi_{G''}(p)]} = 2i \sin \left[ \frac{1}{2} G_{0}(p) - \frac{1}{2} \tilde{G}_{0}(p) - \psi_{G''}(p) \right] e^{i\left[ \frac{1}{2} G_{0}(p) + \frac{1}{2} \tilde{G}_{0}(p) \right]} .
\]

(2.238)

Using this formula, we rewrite the amplitude (2.237) as

\[
A^{(\text{saddle})}_K(p) = -i \sqrt{\frac{\lambda}{\pi}} \frac{2\pi \lambda}{m \omega} \frac{G''_{0}(p)}{G''_{0}(p)} e^{i[\Phi_{0}(p) + \frac{1}{2} G_{0}(p) + \frac{1}{2} \tilde{G}_{0}(p)]} \times \sin \left[ \frac{1}{2} G_{0}(p) - \frac{1}{2} \tilde{G}_{0}(p) - \psi_{G''}(p) \right] \sum_{\ell=1}^{N_{\text{rep}}} e^{i2\pi(\ell-1)F(p)} .
\]

(2.239)

The remaining sum can be performed as a finite geometric series, leading to

\[
\sum_{\ell=1}^{N_{\text{rep}}} e^{i2\pi(\ell-1)F(p)} = \frac{\sin \left[ \pi N_{\text{rep}} F(p) \right]}{\sin \left[ \pi F(p) \right]} e^{i\pi(N_{\text{rep}}-1)F(p)} .
\]

(2.240)
Hence, the Keldysh probability amplitude for ionization stimulated by interaction with a train of \(N_{\text{rep}}\) single-cycle pulses (2.200) takes the form

\[
A_K^{(\text{saddle})}(p) = -i \sqrt{\frac{\lambda}{\pi}} \left( \frac{2\pi\lambda}{m\omega} \right)^2 e^{i[\Phi_0(p) + \pi(N_{\text{rep}} - 1)F(p) + \frac{1}{2}G_0(p) + \frac{1}{2}\tilde{G}_0(p)]} \\
\times \frac{e^{-W(p)}}{G_0''(p)} \sin \left[ \frac{1}{2}G_0(p) - \frac{1}{2}\tilde{G}_0(p) - \psi_G'(p) \right] \frac{\sin[\pi N_{\text{rep}}F(p)]}{\sin[\pi F(p)]}. \tag{2.241}
\]

This equation has been factorized into three essential parts which describe the overall dynamics of the process. The term \(e^{-W(p)}/G_0''(p)\) is responsible for an exponential decay of the probability amplitude of ionization \(A_K^{(\text{saddle})}(p)\) while increasing the photoelectron energy. Another factor, \(\sin \left[ \frac{1}{2}G_0(p) - \frac{1}{2}\tilde{G}_0(p) - \psi_G'(p) \right]\), corresponds to slow modulations of the probability amplitude on the electron energy scale. This is in contrast to the term \(\sin[\pi N_{\text{rep}}F(p)]/\sin[\pi F(p)]\), which in optics is called the interference term [95]. As we will demonstrate shortly, this factor is the source of very sharp peaks in the energy spectrum of photoelectrons similar to the diffraction fringes observed in the experiment by Davisson and Germer [96].

### 2.6.3 Total probability and differential probability distribution of ionization

At this point, we define the total probability of ionization \(\mathcal{P}\). To calculate it, one has to integrate \(|A(p)|^2\) over the density of final states, \(\frac{dp}{(2\pi)^3}\). Therefore, we can write

\[
\mathcal{P} = \int \frac{dp}{(2\pi)^3} |A(p)|^2 = \frac{1}{(2\pi)^3} \int d\Omega_p |p|^2 |A(p)|^2, \tag{2.242}
\]

where \(d\Omega_p\) is the electron differential solid angle. Since the electron kinetic energy is \(E_p = p^2/(2m)\), the previous expression becomes

\[
\mathcal{P} = \frac{m}{(2\pi)^3} \int d\Omega_p \int dE_p |p||A(p)|^2. \tag{2.243}
\]

It implicitly defines the triply differential probability distribution of ionization, \(\frac{d\mathcal{P}}{d\Omega_p dE_p}\). Since

\[
\mathcal{P} = \int d\Omega_p \int dE_p \frac{d\mathcal{P}}{d\Omega_p dE_p}, \tag{2.244}
\]

thus

\[
\frac{d\mathcal{P}}{d\Omega_p dE_p} = \frac{m}{(2\pi)^3} |p||A(p)|^2. \tag{2.245}
\]

Even though we have kept here an arbitrary probability amplitude of ionization \(A(p)\), one needs to replace it by either \(A^{(1)}(p), A_K(p)\) or \(A_K^{(\text{saddle})}(p)\).
Chapter 2. Generalized eikonal approximation in strong-field ionization

2.6.4 Photoelectron energy spectra using the Keldysh approximation

We start by presenting the results calculated using the Keldysh approximation. This will allow us to test, at least partially, our numerical software. Specifically, in order to calculate $A_K(p)$ we will perform a direct integration in Eq. (2.220), and we will compare it with the results obtained using the saddle-point approach [Eq. (2.224)]. Thus, the portion of the numerical code calculating the saddle points, used later in the GEA calculations, will be tested. In addition, the Keldysh approximation will allow us to interpret our numerical results.

In the following, we consider ionization of a hydrogen atom by a train of identical one-cycle pulses which are linearly polarized, as described by Eqs. (2.184) and (2.200). We assume that the photon energy is $\omega_L = 1.55\text{eV}$ and the averaged intensity carried out by the train is $I = 3.125 \times 10^{13}\text{W/cm}^2$. There is no time delay in-between pulses which comprise the train, as illustrated in Fig. 2.2. While the corresponding spectra do not depend on the azimuthal detection angle of a photoelectron, we present the results for its polar detection angle equal to $\theta_p = 0.2\pi$. Let us note, however, that qualitatively the energy spectra of ionized electrons look the same for other angles $\theta_p$.

In Fig. 2.6, we plot $|p||A_K(p)|^2$ as a function of the electron energy. As it follows from Eq. (2.245) where $A(p)$ is replaced by $A_K(p)$, this quantity defines the triply differential probability distribution of ionized electrons in the Keldysh approximation. For a visual purpose, it has been multiplied by $e^{0.6E_p/\omega_L}$. In the upper frame, we present the exact results based on a direct numerical calculation of the integral in Eq. (2.220). The mirror-reflected curves, shown in the lower frame, have been calculated using the saddle-point method with respect to the aforementioned integral, i.e., based...
Figure 2.7 In the top panel, we show a portion of the energy spectrum presented in the upper frame of Fig. 2.6. Only the curve for $N_{\text{rep}} = 3$ is plotted, and the results are not divided by $N_{\text{rep}}^2$. Vertical lines mark the energies at which we observe the main maxima. The same but for $N_{\text{rep}} = 10$ is plotted in the middle panel. Note that in both cases the main maxima occur at the exact same energies of the final electron. At those energies the function $F(p)$, drawn in the bottom panel as the solid blue line, takes on integer values. Note that $F(p)$, in contrast to the dashed black line, is not a linear function of its argument. Therefore, the peaks in the energy distribution of photoelectrons are not equally spaced.

on Eq. (2.224). While spectra in both frames differ in magnitude, their actual patterns are the same. In each frame we present three curves. The solid black envelopes correspond to the case when the driving pulse is a single-cycle pulse ($N_{\text{rep}} = 1$). As it follows from the saddle-point treatment (2.241), in this case the interference term equals 1 and, therefore, only slow modulations of the spectra are manifested. As we have also checked, for more energetic photoelectrons we observe similar modulations which, however, decrease in magnitude. Such a behavior can be explained by the exponentially decaying term in Eq. (2.241). The dashed red line is for $N_{\text{rep}} = 2$, meaning that the driving field consists of two one-cycle pulses. Already in this case, an interference pattern is observed. We see very sharp peaks within the envelope. This happens for any $N_{\text{rep}} \geq 2$, in agreement with formula (2.241). For instance, for $N_{\text{rep}} = 3$, the corresponding sharp peaks are plotted with the solid blue line. Note
that each spectrum was divided by $N_{\text{rep}}^2$. This resulted in nearly the same heights of the peaks for different $N_{\text{rep}}$. While for energies $6\omega_L \lesssim E_p \lesssim 25\omega_L$, one can actually see that the scaled peaks have the same heights for different $N_{\text{rep}}$, for energies $3\omega_L \lesssim E_p \lesssim 6\omega_L$ this is not exactly the case. Such a behavior of the presented spectra can be explained using the derivation based on the saddle-point approximation (2.241). According to this formula, the sharp peaks appear at electron energies such that $F(p) = L$, where $L$ is integer. This behavior is distorted by the term $\sin\left[\frac{1}{2}G_0(p) - \frac{1}{2}\tilde{G}_0(p) - \psi_G^p(p)\right]$, which manifests strongly for $3\omega_L \lesssim E_p \lesssim 6\omega_L$. Let us also note that the spectra divided by $N_{\text{rep}}^2$ have contact points at such electron energies $E_p$ that the phase of the probability amplitude of ionization takes the same values regardless of $N_{\text{rep}}$ (as it is for other strong-field processes; see, for instance, Refs. [97, 98]).

In order to analyze the impact of the interference term and the influence of the function $F(p)$ on the ionization signal, we present Fig. 2.7. We plot there a portion of the spectrum presented in Fig. 2.6 for $N_{\text{rep}} = 3$ (top panel). The same but for $N_{\text{rep}} = 10$ is plotted in the middle panel. Note that in both cases we observe the enhancement of the spectra at the exact same electron energies, as indicated by the solid vertical lines. In the bottom panel, we show the function $F(p)$ (solid blue line). As expected, the main maxima in the upper panels occur at those photoelectron energies when $F(p)$ takes integer values. At these energies, the interference term in (2.241) tends to $N_{\text{rep}}$ and, hence, the respective probability distributions scale as $N_{\text{rep}}^2$. Since the major peaks become more narrow with increasing $N_{\text{rep}}$, the angle-resolved probability of ionization, when integrated over the electron energy, scales approximately as $N_{\text{rep}}$. Therefore, for the Keldysh theory it is meaningful to talk about the probability rate of ionization per one modulation of the laser pulse. Also, note that $F(p)$ is not a linear function of the photoelectron kinetic energy, which is in contrast to a straight line (dashed black line) shown in the bottom panel of Fig. 2.7. It means that, in general, the enhancement peaks are not equally spaced on the photoelectron energy scale. Another feature which can be observed in Figs. 2.6 and 2.7 is that with increasing $N_{\text{rep}}$, there appear $(N_{\text{rep}} - 2)$ additional maxima between any two consecutive main peaks. Their positions can be derived from Eq. (2.241), $F(p) = L + (M + 1/2)/N_{\text{rep}}$ where $M = 1, 2, \ldots, N_{\text{rep}} - 2$. These additional maxima are accompanied by zeroes in the energy spectra. For $N_{\text{rep}} \geq 2$, there are always $(N_{\text{rep}} - 1)$ zeroes which are observed when $F(p) = L + M/N_{\text{rep}}$ with $M = 1, 2, \ldots, N_{\text{rep}} - 1$.

The interference pattern in the photoelectron energy spectra is observed only when $N_{\text{rep}} \geq 2$, i.e., when the driving pulse train is composed of at least two modulations. Its features can be explained based on an approximate formula for the probability amplitude of ionization (2.241), which suggests a very intuitive interpretation of the observed pattern. Namely, the probability amplitudes from each modulation interfere constructively, leading to enhancements at certain electron energies. One can conclude, therefore, that each pulse from the train acts as a slit in the Young-type experiment of matter waves performed by Davisson and Germer [96]. Note that similar inter-pulse interferences can be observed in other strong-field processes as well, with the most recent examples in the area of strong-field quantum and classical electrodynamics [97–100] or in optics for electromagnetic waves passing through diffraction gratings [37].

It is clearly seen that the separation of the interference peaks in Figs. 2.6 and 2.7 is not equal to the carrier frequency $\omega_L$. Let us also note that these patterns are rather marginally modified for
Figure 2.8  Shape functions for the electric field, $f_E(\phi)$, and the vector potential, $f_A(\phi)$, for the $\sin^2$ envelope, Eq. (2.246), and for $N_{\text{rep}} = 3$ and $N_{\text{osc}} = 16$.

other emission angles $\theta_p$. The reason being that we have considered very short (one-cycle) pulses with the $\sin^2$ envelope [Eq. (2.200)]. However, for longer pulses the typical multiphoton structure of the photoelectron spectrum can be restored. To illustrate this, we consider the electric field (2.184) with the shape function

$$f_E(\phi) = \begin{cases} \sin^2\left(\frac{N_{\text{rep}} \phi}{2}\right) \cos(N_{\text{rep}}N_{\text{osc}} \phi), & 0 \leq \phi \leq 2\pi, \\ 0, & \text{otherwise} \end{cases}$$

(2.246)

where $N_{\text{rep}}$ still denotes the number of pulses constituting the train and $N_{\text{osc}}$ is the number of cycles in each pulse. While previously we kept $N_{\text{osc}} = 1$ [see, Eq. (2.200)], this time we allow $N_{\text{osc}}$ to have an arbitrary value. Specifically, in the numerical analysis presented below we take $N_{\text{osc}} = 16$. Note that in Eq. (2.246) the cosine carrier wave has been chosen. In this case, the constant term of the vector potential $A(\phi)$ is zero while the condition $A(0) = A(2\pi) = 0$ is still satisfied. As we have checked for the shape function (2.246) with the sine carrier wave, for which the vector potential has a nonzero constant component, the structure of the energy spectra of photoelectrons is qualitatively similar. This is not surprising as both cases differ by a carrier-envelope phase, which has a secondary effect on ionization when driven by long laser pulses. In Fig. 2.8, we plot the functions $f_E(\phi)$ and $f_A(\phi)$ for the parameters $N_{\text{rep}} = 3$ and $N_{\text{osc}} = 16$. As above, the carrier frequency $\omega_L$ is fixed. Therefore, the time duration of the train equals $T = 2\pi N_{\text{rep}}N_{\text{osc}}/\omega_L$ and $\omega = 2\pi/T = \omega_L/N_{\text{rep}}N_{\text{osc}}$.

For long driving pulses, one can expect the appearance of multiphoton peaks in the angular-resolved energy distribution of photoelectrons, separated by $\omega_L$. This is indeed the case for $N_{\text{rep}} = 1$, as presented in Fig. 2.9. Due to the finite time duration of the driving pulse, the major peaks in Fig. 2.9 are also broadened and small secondary peaks appear (note that for such long pulse, more saddle points contribute significantly to the probability amplitude leading to the appearance of such extra structures). However, for $N_{\text{rep}} = 2$ and 3 we observe the interference peaks whose maxima scale as $N_{\text{rep}}^2$. These interference peaks are not separated by $\omega_L$, but rather by $\omega_L/N_{\text{osc}}$. Hence, for longer pulses the denser distribution of interference peaks is observed (compare, for instance, Figs. 2.6 and 2.9). Note that the peak separation can be also controlled by introducing the time delay between
Figure 2.9 The energy spectra of photoelectrons \(2.245\) calculated within the Keldysh approximation \(2.220\) ionized by the train of pulses with the \(\sin^2\) envelope \(2.246\) for \(N_{\text{osc}} = 16\). The frequency of the laser field is taken \(\omega_L = 1.55\text{eV}\), its mean intensity is \(I = 10^{14}\text{W/cm}^2\), and the photoelectron emission angles are \(\theta_p = 0.2\pi\) with an arbitrary \(\varphi_p\). The envelope of the spectra (solid black line) corresponds to a 16-cycle driving pulse \((N_{\text{rep}} = 1)\). Other curves correspond to a sequence of either two 16-cycle \((N_{\text{rep}} = 2; \text{dashed red line})\) or three 16-cycle \((N_{\text{rep}} = 3; \text{solid blue line})\) driving pulses. All results have been divided by \(N_{\text{rep}}^2\). They have also been multiplied by \(eE_p/\omega_L\) to magnify the main features of the distributions. The results have been obtained by performing the integral in Eq. \(2.220\) exactly.

Pulses in the train, as it was demonstrated for Compton or Thomson scattering \([99]\). More precisely, the separation of the interference peaks decreases if the time duration between the consecutive pulses in the train increases, similarly to the interference of light by an equally spaced sequence of apertures.

### 2.6.5 Photoelectron energy spectra using the GEA

We have shown in the previous Section that interference patterns in the photoelectron energy spectra follow from the Keldysh theory. Since the Keldysh theory neglects the Coulomb interaction between the ejected electron and the residual ion, the question arises whether the similar patterns can be still observed if the Coulomb interaction between the two is taken into account. To answer this question we will use now the GEA.

The probability amplitude of ionization in the generalized eikonal approximation \(2.164\) contains the extra time- and space-dependent phase factor as compared to the Keldysh amplitude [see, Eq. \(2.204\)]. Namely, under the GEA,

\[
\mathcal{A}^{(1)}(p) = -i \int_0^T \! dt' \exp \left[ i \left( \frac{p^2}{2m} - E_0 \right) t' \right] \int \! dr' \exp \left[ -i (p - eA(t')) \cdot r' \right] \\
- \frac{1}{2m} \int_0^T \! d\sigma (p - eA(\sigma))^2 + i \chi_p^{(l)}(r', t', T - t') \left( -e\mathbf{E}(t') \cdot r' \right) \psi_0(r'),
\]

\(2.247\)
where in Eq. (2.164) we have explicitly put (2.57). This formula can be further modified such that
\[ A^{(1)}(p) = -i \exp \left\{ i \left( \frac{p^2}{2m} - E_0 \right) T - i \int_0^T \! \! \! d\sigma \left[ \frac{1}{2m} (p - eA(\sigma))^2 - E_0 \right] \right\} \int_0^T \! \! \! dt' \times \int \! \! \! dr' \exp \left\{ -i (p - eA(t')) \cdot r' + i \int_0^t' \! \! \! d\sigma \left[ \frac{1}{2m} (p - eA(\sigma))^2 - E_0 \right] + i \chi_p^{(1)}(r', t', T - t') \right\} \times (-eE(t') \cdot r') \psi_0(r') . \] (2.248)

By introducing here the laser phase, \( \phi = \omega t' \), and employing the definitions (2.206), (2.208), and (2.210), this expression becomes
\[ A^{(1)}(p) = -i \frac{e^{i \Phi_0(p)}}{\omega} \int_0^{2\pi} \! \! \! d\phi e^{iG(p, \phi)} \int \! \! \! dr' e^{-i\Pi(\phi) r'} + i \chi_p^{(1)}(r', \frac{\phi}{\omega}, \frac{2\pi \sigma}{\omega}) (-eE(\phi) \cdot r') \psi_0(r') , \] (2.249)
i.e., it differs from Eq. (2.211) by the eikonal phase.

The probability amplitude (2.249) can be reformulated in terms of classical complex trajectories [63, 73]. Let us denote as
\[ r_{cl}(\sigma; r', \phi, p) = R_p \left( r', \frac{\phi}{\omega}, \frac{\sigma}{\omega} \right) \] (2.250)
the real-time classical trajectory in the laser field, where \( R_p \) is defined by Eq. (2.72). In other words,
\[ r_{cl}(\sigma; r', \phi, p) = r' + \frac{1}{m\omega} \int_\phi^\sigma \! \! \! d\varphi |p - eA(\varphi)| . \]

Note that the eikonal phase (2.116) functionally depends on these trajectories, which we emphasize by introducing a new notation. More precisely, we rewrite Eq. (2.249) such that
\[ A^{(1)}(p) = -i \frac{e^{i \Phi_0(p)}}{\omega} \int_0^{2\pi} \! \! \! d\phi e^{iG(p, \phi)} \int \! \! \! dr' e^{-i\Pi(\phi) r'} - iU[r', \phi, p|r_{cl}] (-eE(\phi) \cdot r') \psi_0(r') , \] (2.252)
where, for the Coulomb potential,
\[ U[r', \phi, p|r_{cl}] = -\frac{Z\alpha c}{\omega} \int_\phi^{2\pi} \! \! \! d\sigma \frac{\tilde{r}_{cl}(\sigma; r', \phi, p)}{\left| \tilde{r}_{cl}(\sigma; r', \phi, p) \right|} \text{erf} \left[ \sqrt{\frac{m\omega}{2i(\sigma - \phi)}} \left| \tilde{r}_{cl}(\sigma; r', \phi, p) \right| \right] , \] (2.253)
which follows from Eq. (2.116). The notation \( U[r', \phi, p|r_{cl}] \) means that \( U \) being the function of \( r' \), \( \phi \), and \( p \), depends also functionally on the classical trajectory \( r_{cl} \). The same applies to the functionals \( W[\phi, p|r_{cl}] \) and \( S[\phi, r_{cl}] \), which we introduce below.

Note that the real-time classical trajectory \( r_{cl}(\sigma; r', \phi, p) \) depends on \( r' \) and \( p \) (here \( \sigma \) plays the role of time in units of \( 1/\omega \)) through the initial and final conditions,
\[ r_{cl}(\sigma; r', \phi, p)|_{\sigma = \phi} = r' , \] (2.254)
\[ \frac{\partial}{\partial \sigma} r_{cl}(\sigma; r', \phi, p)|_{\sigma = 2\pi} = \frac{p}{m\omega} . \] (2.255)
respectively. It is worth noting that, by following the standard procedure (see, e.g., Ref. [63]), the functional

\[ W[\phi, p|r_{cl}] = -G(p, 2\pi) + G(p, \phi) - U[r', \phi, p|r_{cl}] \]  

(2.256)
can be rewritten in the form

\[ W[\phi, p|r_{cl}] = S[\phi|r_{cl}] + m\omega r_{cl}(\phi) \cdot r'_{cl}(\phi) - p \cdot r_{cl}(2\pi), \]  

(2.257)

where we have used the abbreviation \( r_{cl}(\sigma) = r_{cl}(\sigma; r', \phi, p) \). Here, the ‘prime’ means the derivative over \( \sigma \) and

\[ S[\phi|r_{cl}] = \frac{1}{\omega} \int_{\phi}^{2\pi} d\sigma \mathcal{L}_{\text{eff}}(r_{cl}(\sigma), r'_{cl}(\sigma), \sigma) \]  

(2.258)
is the classical action with the effective Lagrangian,

\[ \mathcal{L}_{\text{eff}}(r_{cl}(\sigma), r'_{cl}(\sigma), \sigma) = \frac{m\omega^2}{2}[r'_{cl}(\sigma)]^2 + e\mathbf{E}(\sigma) \cdot \mathbf{r}_{cl}(\sigma) - V^{(1)}_{\text{eff}}(r_{cl}(\sigma), \sigma - \phi) + E_0. \]  

(2.259)

Here, the effective potential is defined by Eq. (2.115) with time in units of \( 1/\omega \). Since we deal with the static Coulomb potential, then \( V^{(1)}_{\text{eff}} \) depends only on the classical trajectory and the phase difference \( (\sigma - \phi) \). Finally, the probability amplitude (2.252) can be put in the form

\[ A^{(1)}(p) = -i \frac{e^{i\left(p^2/2m-E_0\right)t}}{\omega} \int_{0}^{2\pi} d\phi \int d\mathbf{r}' e^{-i\mathbf{M}(\phi) \cdot \mathbf{r}'} (-e\mathbf{E}(\phi) \cdot \mathbf{r}') \psi_0(\mathbf{r}') e^{iW[\phi, p|r_{cl}]}, \]  

(2.260)

which is suitable for the saddle-point and quantum trajectory analysis.

### 2.6.5.1 Quantum trajectories

The direct integration over the space variables, \( d\mathbf{r}' \), in (2.260) is very difficult to carry out as the effective potential oscillates rapidly. For this reason, it is very convenient to apply the saddle-point method. In our further analysis we use the simplest approximation, namely, in the effective potential we replace the classical real-time trajectory \( r_{cl}(\sigma) \) by its quantum analog (which is frequently called the complex-time trajectory [63]) being the solution of the free particle Newton equation in a laser field. This is in agreement with the assumption, which is commonly made in the strong-field approximation, that the binding potential rather marginally modifies the electron trajectory in the laser field.

The quantum trajectory is the solution of the classical Newton equation in the laser field,

\[ r''_{q}(\sigma; p, \phi_s) = \frac{e}{m\omega^2} \mathbf{E}(\sigma), \]  

(2.261)

where the ‘prime’ again means the derivative with respect to the phase \( \sigma \). These trajectories, however, have to fulfill the complex initial conditions for \( \sigma = \phi_s \),

\[ \text{Re}[r_q(\phi_s; p, \phi_s)] = 0, \quad [m\omega r'_q(\phi_s; p, \phi_s)]^2 = -\lambda^2, \]  

(2.262)
where \( \lambda \) relates to the binding energy of a hydrogen-like atom (2.212). Following Ref. [63], we can write down the quantum trajectories in the form

\[
r_q(\sigma; p, \phi_s) = \frac{p}{m\omega} [\sigma - \text{Re}(\phi_s)] + \frac{e}{m} \alpha(\sigma) - \frac{e}{m} \text{Re}[\alpha(\phi_s)],
\]

where \([\text{cf., Eq. (2.194)}]\)

\[
\alpha(\sigma) = -\frac{1}{\omega} \int_0^\sigma A(\phi) d\phi = \frac{E_0}{\omega^2 f_\alpha(\sigma)} e_z.
\]

These trajectories satisfy both conditions (2.262). The first condition in (2.262) states that the real part of the complex trajectory starts at the centre of the atom. The second condition defines the initial phase \( \phi_s \), which turns out to be the saddle-point solution of Eq. (2.221). In addition, the trajectories (2.263) are real in real phase \( \sigma \),

\[
\text{Im}[r_q(\text{Re }\sigma; p, \phi_s)] = 0.
\]

The same holds for the velocity,

\[
\text{Im}[r_q'(\text{Re }\sigma; p, \phi_s)] = 0.
\]

Since we deal with the Coulomb-free trajectories, if the laser pulse is switched off the photoelectron will carry the momentum \( p \). In other words,

\[
m\omega r_q'(2\pi; p, \phi_s) = p.
\]

This condition agrees with the assumption made above that the electron final state is approximated by the plane wave solution. It also agrees with the numerical analysis showing that the quantum trajectories at the end of sufficiently intense laser pulses (which is the case for the intensity considered in this thesis) are far away from the Coulomb centre. In other words, that the electron final momentum is rather marginally affected by the interaction with the residual ion.

Let us calculate now the complex trajectories defined by Eq. (2.263). As before, this will be done for the case when a train consisting of three \( (N_{\text{rep}} = 3) \) identical, linearly-polarized pulses [see Eqs. (2.184) and (2.200)] interacts with the hydrogen atom. The remaining laser field parameters are \( \omega_L = 1.55\text{eV} \) and \( I = 3.125 \times 10^{13}\text{W/cm}^2 \). The ionized electron is detected with the energy \( E_p = 3.13\text{eV} \approx 3U_p \) (Fig. 2.10) or \( E_p = 12.22\text{eV} \approx 12U_p \) (Fig. 2.11) at the polar angle \( \theta_p = 0.2\pi \). As before, the results are independent of the azimuthal angle \( \varphi_p \) of the electron. As discussed in Sec. 2.6.2.2, in the case under consideration, there are twelve important saddle points, i.e., the solutions to Eq. (2.227) which satisfy the conditions (2.223). However, as it follows from Fig. 2.1, six of them will contribute more significantly to the probability amplitude of ionization. Therefore, in Figs. 2.10 and 2.11 only the relevant quantum trajectories are presented. In these figures, we plot the real (solid blue lines) and imaginary (dashed red lines) parts of the quantum trajectories which originate from the essential saddle points. These saddle points relate either to the maximum or minimum of the electric field (solid blue and dashed red lines in Figs. 2.2 and 2.3, respectively). The trajectories starting at the former points are plotted in the left columns of Figs. 2.10 and 2.11, whereas the trajectories starting at the latter points are plotted in the right columns of Figs. 2.10 and 2.11. Note that these trajectories are parametrized by Cartesian coordinates \( x_q \) and \( z_q \). When comparing Figs. 2.10 and 2.11, note a significant difference of the scale of \( x_q \).
Figure 2.10  Real (solid blue line) and imaginary (dashed red line) parts of the quantum trajectories (in a.u.) as calculated from Eq. (2.263) for an electron with kinetic energy of $E_p = 3.13\text{eV}$ ionized by a train of three single-cycle pulses defined by Eqs. (2.184) and (2.200). The laser field parameters are $\omega_L = 1.55\text{eV}$ and $I = 3.125 \times 10^{13}\text{W/cm}^2$. Each panel represents a trajectory (2.263) starting at a different saddle point $\phi_s$. Only those saddle points are considered which are denoted in Fig. 2.2 by solid blue lines (left column) and dashed red lines (right column).

It can be seen in Fig. 2.10 that, for $E_p = 3.13\text{eV} \approx 3U_p$, the real part of some of the quantum trajectories approach the ion after the electron is ejected. This is shown in the top and middle panels of the left column. For $E_p = 12.22\text{eV} \approx 12U_p$ (Fig. 2.11), shortly after ionization, $x_q$ acquires large values and the electron never comes back near the potential centre. As it will be illustrated, the trajectories which come back to its origin lead to singularities in the formulation based on the original eikonal approximation. Our generalized eikonal approximation avoids this problem.

In the literature (see, e.g., Ref. [5]) two names for the method, quantum trajectories and complex-time trajectories, are frequently used. In light of our analysis and more thorough studies carried out, for instance, in Refs. [5, 63], the second name seems to be more appropriate, as the trajectory $r_q(\sigma; p, \phi_s)$ satisfies the Newton equation with the classical binding potential $V(r)$ but with the complex initial conditions. In such a formulation of the method, there are no quantum signatures in the definition of $r_q(\sigma; p, \phi_s)$. This approach, however, leads to some problems related to the Coulomb singularity at the origin. Our investigations show that this obstacle can be eliminated in the complex-time method. Indeed, the form of the effective Lagrangian (2.259) suggests to assume that the trajectories should fulfill the Newton equation of the form [cf., Eq. (2.261)],

$$m\omega^2 r_q''(\sigma; p, \phi_s) = e\mathcal{E}(\sigma) - \nabla V_{\text{eff}}^{(1)}(r_q(\sigma; p, \phi_s), \sigma - \phi_s),$$  \hspace{1cm} (2.268)
with suitable initial conditions. The effective potential $V_{\text{eff}}^{(1)}(r, \sigma)$, contrary to the classical one $V(r)$, is not singular at the origin for nonzero time and is smeared out by the ‘quantum diffusion’ represented by the Laplacian and the nonlinear term in Eqs. (2.56) or (2.62). In other words, it accounts for the spreading of the electron wave packet during the quantum time-evolution. The Laplacian introduces the Planck constant into the definition of the effective potential in the GEA. In other words, $V_{\text{eff}}^{(1)}(r, \sigma)$ differs from $V(r)$ by quantum corrections which vanish in the limit $\hbar \to 0$. This also means that $r_q(\sigma; p, \phi_s)$ does contain quantum corrections and, therefore, we should rather call those trajectories ‘complex-time quantum trajectories’.

### 2.6.5.2 Comparison between the GEA, the EA, and the Keldysh approximation

In this Section, we are going to compare the results obtained based on the original eikonal approximation, its generalization formulated in this thesis, as well as the Keldysh theory of strong-field ionization. The original eikonal takes the form,

$$
\chi_{q, \text{original}}(p, \phi_s) = \frac{Z\alpha c}{\omega} \int_{\phi_s}^{2\pi} d\sigma \frac{1}{|r_q(\sigma; p, \phi_s)|},
$$

(2.269)
whereas the generalized one is given by

$$\chi^{(1)}_{q}(p, \phi_s) = \frac{Z \alpha c}{\omega} \int_{\phi_s}^{2\pi} d\sigma \frac{1}{|r_q(\sigma; p, \phi_s)|} \text{erf}\left(\sqrt{\frac{m \omega}{2i(\sigma - \phi_s)}} |r_q(\sigma; p, \phi_s)| \right).$$  \hspace{1cm} (2.270)

Hence, the probability amplitude of ionization in the generalized eikonal approximation can be treated according to the saddle-point method described in the previous Sections. This leads to the formula

$$A_{saddle}^{(1)}(p) = -2 \sqrt{\frac{\lambda}{\pi}} \left(\frac{\pi \lambda}{m \omega}\right)^{2} e^{i \Phi_0(p)} \sum_s e^{iG(p, \phi_s) + i \chi^{(1)}_{q}(p, \phi_s)} G''(p, \phi_s).$$  \hspace{1cm} (2.271)

A similar expression for the amplitude of ionization is obtained for the EA by replacing \(\chi^{(1)}_{q}(p, \phi_s)\) by \(\chi_{q, original}(p, \phi_s)\). At this point, let us also mention Eq. (2.220) which defines the probability amplitude of ionization in the Keldysh approximation. These three approaches will be compared now for typical parameters used in this thesis.

In Fig. 2.12, we present the energy distributions of ionized electrons similar to Fig. 2.6. The difference is that, this time, the lower frame shows the spectra calculated within the GEA and saddle-point approximation (2.271). In this case, we account for the Coulomb interaction between ejected photoelectrons and their parent ions. As we see in the lower frame, the positions of peaks and zeroes in the spectra are almost identical as in the upper frame where we plot the spectra calculated based on the Keldysh approach (2.220). What is changed, however, when we account for the Coulomb interaction between the electrons and the residual ions, is a significant enhancement of the ionization signal. Also, we observe a partial loss of coherence since the distributions in the lower frame of Fig. 2.12 do not scale as \(N_{\text{rep}}^2\).

![Figure 2.12](image-url) The photoelectron energy distribution calculated according to the Keldysh theory by direct integration of Eq. (2.220) (upper frame) and according to the generalized eikonal approximation formulated via quantum trajectories (lower frame) [Eq. (2.271)]. The laser field parameters are the same as in Fig. 2.6. The results are for \(N_{\text{rep}} = 1\) (solid black line), \(N_{\text{rep}} = 2\) (dashed red line), and \(N_{\text{rep}} = 3\) (solid blue line). All results are divided by \(N_{\text{rep}}^2\) and multiplied by the factor \(e^{0.6E_p/\omega_L}\).
Figure 2.13  The thin black line represents the energy distribution of ionization according to the Keldysh theory [Eq. (2.224)], the thick blue line corresponds to the results obtained from the GEA [Eq. (2.271)], whereas the dashed red line to the ones obtained by the EA [Eqs. (2.271) and (2.269)]. The saddle-point method was used in order to calculate these results. The upper and the lower panels demonstrate the distributions for \( N_{\text{rep}} = 1 \) and \( 3 \), respectively. The remaining laser field parameters are \( \omega_L = 1.55 \text{eV} \) and \( I = 3.125 \times 10^{13} \text{W/cm}^2 \).

The enhancement of the ionization yield can create some doubts about the validity of our approach and the eikonal perturbation theory \([18]\) in general. Let us note, however, that the perturbation is carried out in the exponent. Therefore, for our approach to be justified, the eikonal term \( \chi^{(1)}(p, \phi_s) \) in Eq. (2.271) should be much smaller than \( G(p, \phi_s) \), for both the real and imaginary parts. This condition is very well fulfilled for the laser pulse parameters considered in this thesis.

In Fig. 2.13, the photoelectron energy spectra calculated under different approximations are plotted. The thin black line represents the results arising from the Keldysh theory [Eq. (2.220)]. While the dashed red line represents the results based on the original eikonal approximation [Eq. (2.269)], the thick blue line is for the GEA [Eq. (2.270)]. This time the factor \( e^{0.6E_p/\omega_L} \) is not included because the objective of such plots is to compare the overall difference between the three theories. The laser parameters are \( \omega_L = 1.55 \text{eV} \) and \( I = 3.125 \times 10^{13} \text{W/cm}^2 \).

The upper panel of Fig. 2.13 corresponds to ionization by a single-cycle pulse \((N_{\text{rep}} = 1)\). Here, we observe a rather marginal difference between the GEA and EA results, and a significant enhancement (by roughly one order of magnitude) of these distributions as compared to the Keldysh theory. Qualitatively, however, all three distributions look similar. The differences appear for longer train of pulses, when \( N_{\text{rep}} > 1 \). This is illustrated in the lower panel for \( N_{\text{rep}} = 3 \). For electron kinetic energy \( E_p \approx 3\omega_L \), the distributions for generalized and original eikonals differ significantly. However, for \( E_p > 5\omega_L \) both approaches again give nearly the same results. The wiggles observed for the EA distribution can be explained if we note that for the laser field parameters considered in this figure the ponderomotive energy is close to \( \omega_L \), which means that the structure appears for \( E_p \approx 3U_p \).
Chapter 2. Generalized eikonal approximation in strong-field ionization

As it was shown in Fig. 2.10, for such energetic photoelectrons some of the complex trajectories can return very close to the origin of the Coulomb potential. Since the original eikonal is singular for such trajectories, we observe the rapid change of $\chi_{q,\text{original}}(p, \phi_s)$ when the kinetic energy passes through the value $3U_p$ (in the considered case the real part of $\chi_{q,\text{original}}(p, \phi_s)$ exhibits the sharp peaks for these particular trajectories, as illustrated in Fig. 2.14). This results in wiggles observed in the lower panel of Fig. 2.13 for the EA. Such a behavior, however, is not observed for the GEA, as the generalized eikonal is not singular for trajectories returning to the potential origin (see, Fig. 2.15). If we compare the GEA with the Keldysh approach, we see the enhancement of ionization but again the distributions are qualitatively similar. In our opinion, the lack of spurious behavior of trajectories returning back to the vicinity of the parent ion and the fact that the first Born approximation is the limiting case of the GEA make the approach presented in this thesis an attractive tool for investigations of ionization, rescattering, and high-order harmonic generation by strong laser pulses. This includes also more complex systems such as diatomic molecules or fullerenes.

Figure 2.14 Imaginary and real parts of the original eikonal, $\chi_{q,\text{original}}(p, \phi_s)$, calculated according to Eq. (2.269), as a function of the electron energy. Solid blue lines represent trajectories starting at the essential saddle points which appear at the maximum of the electric field whereas the dashed red lines are for the essential saddle points which appear at the minimum of the electric field (see, Figs. 2.10 and 2.11). The laser field parameters are $\omega_L = 1.55\text{eV}$, $I = 3.125 \times 10^{13}\text{W/cm}^2$, and $N_{\text{rep}} = 3$. 
2.7 Summary

In this Chapter, we have developed the generalized eikonal approximation to describe the strong-field ionization driven by short laser pulses. We have applied it to different model potentials including the Coulomb, Yukawa, exponential, and Gaussian potentials. Our focus was, however, on the Coulomb potential which describes the ionization of neutral atoms. This was the case thoroughly studied in this Chapter.

A direct comparison of the photoelectron energy spectra obtained from the Keldysh theory, the generalized eikonal, and the original eikonal approximations was performed. We have shown that the original eikonal becomes singular for electron trajectories which come back to the potential centre. This, in turn, generates unphysical wiggles in the probability distribution of photoelectrons. The same does not happen when the GEA is employed, due to the absence of such singularities. This makes it promising to further apply the GEA in studies of rescattering and high-order harmonic generation by short and intense laser pulses.

We have shown numerically that the energy spectrum of photoelectrons exhibits a diffraction pattern depending on the parameters of the driving field. The spectral response obtained from the interaction of a hydrogen atom with a train of \( N_{\text{rep}} \) identical pulses presents well-localized peaks for \( N_{\text{rep}} \geq 2 \). This is a consequence of inter-pulse interferences arising when the driving field consists of at least two pulses. As we have shown, the intensity and width of such peaks can be controlled.
by varying the parameter $N_{\text{rep}}$; with increasing the number of pulses comprising the train, the energy spectrum of photoelectrons presents increasingly more intense and narrow peaks. Other parameters such as the time delay between pulses, the number of cycles within the individual pulse or its shape may alter the details of diffraction patterns. We believe, therefore, that the sensitivity of photoelectron energy distributions to the parameters of the driving laser field can be efficiently used to design new sources of electron beams.
Chapter 3

High-order harmonic generation

In recent years, high-order harmonic generation has been a very active research topic in the experimental and theoretical fields due to the new and interesting properties of nonlinear interaction between laser radiation and molecules or atoms. This process involves the transformation of multiple low-energy photons coming from the laser field into a single high-energy photon [101]. When an intense laser field interacts with a molecule or atom, coherent radiation of frequencies that are integer multiples of the original driving frequency are emitted [29]. A common feature of the HHG spectra is that the first harmonics decrease in intensity rapidly, followed by a plateau where the strength of the peaks is fairly constant. After the plateau, a sharp cutoff determines a new region where, again, the peaks start to decrease rapidly. Under the scope of the three step semiclassical model (see, Sec. 3.1) and for a monochromatic laser field, the maximum energy at the end of the plateau can be approximated by the formula [27, 29]

\[ E_{\text{cutoff}}^{\text{TSM}} = I_p + 3.17U_p, \]  

where \( I_p \) is the ionization potential and \( U_p \) is the ponderomotive energy of an electron oscillating in a laser field. For our further purposes, we define the position of the cutoff \( N_{\text{cutoff}}^{\text{TSM}} \) such that

\[ E_{\text{cutoff}}^{\text{TSM}} = N_{\text{cutoff}}^{\text{TSM}} \omega_L, \]  

where \( \omega_L \) is the laser carrier frequency. Even though the position of the cutoff is well approximated by this equation, the Lewenstein model predicts a slightly different relation [29]. We will address this problem in Sec. 3.2.2.

As high-order harmonic generation is a purely quantum-mechanical process, its most suitable treatment comes from the complete solution of the time-dependent Schrödinger equation (TDSE) (see, e.g. [28, 102]). Note, however, that to solve the TDSE is a challenging task already for two-electron systems. While it is time-consuming and requires a big amount of computational effort, it can be used to model the interaction of atoms and simple molecules with strong laser fields presenting, with good agreement with experiments, a plateau before the sharp cutoff [103]. With increasing the laser field intensity or the complexity of the molecule, solving the TDSE becomes prohibitive.
In this Chapter, we introduce the semiclassical and the quantum-mechanical descriptions of the HHG by means of the three step and the Lewenstein model, respectively. Note that, when the full quantum-mechanical treatment is considered, several approximations need to be done leading to an absence of gauge invariance in the calculations. Since the Lewenstein model is the main focus of this and the next Chapters, we will present it in the length and velocity gauges.

3.1 Three step model

As we mentioned in Chapter 1, the three step model [24–27] treats the HHG process as a sequence of three events: ionization, propagation, and recombination. After ionization has been completed, the electron is considered as a classical charged particle with negligible initial velocity. It accelerates in the continuum due to the action of the oscillating electric field, \( E(t) \). The corresponding electron trajectory can be directly calculated by solving the Newton equation of motion,

\[
m \ddot{r} = eE(t). \tag{3.3}
\]

We assume that the electron appears at the origin of coordinates at time \( t' \) with zero velocity, meaning that \( r(t') = 0 \) and \( \dot{r}(t') = 0 \). For a monochromatic plane wave field polarized along the \( z \)-axis, with the amplitude \( E_0 \),

\[
E(t) = E_0 e_z \cos(\omega_L t), \tag{3.4}
\]

the solution of Eq. (3.3), taking into account the initial conditions, shows that the electron propagates parallel to the laser field polarization direction. The corresponding classical trajectory is given by

\[
z(t) = -\frac{eE_0}{m\omega_L^2} [\cos(\omega_L t) - \cos(\omega_L t') + \omega_L (t - t') \sin(\omega_L t')], \tag{3.5}
\]

whereas the electron kinetic energy as a function of time equals

\[
E_p(t) = \frac{m\dot{z}^2(t)}{2} = \frac{e^2E_0^2}{2m\omega_L^2} [\sin(\omega_L t) - \sin(\omega_L t')]^2 = 2U_p [\sin(\omega_L t) - \sin(\omega_L t')]^2. \tag{3.6}
\]

It is clear that not all trajectories satisfying the above initial conditions contribute to HHG. It is crucial that the electron comes back and recombines with the parent ion at a certain time \( t'' \) in order to emit a high-energy photon. Thus, taking into account Eq. (3.5), the following condition must be imposed,

\[
\cos(\omega_L t'') - \cos(\omega_L t') + \omega_L (t'' - t') \sin(\omega_L t') = 0. \tag{3.7}
\]

Note that the emitted photon energy can be related to the kinetic energy of the electron at the moment of recollision by simple energy conservation considerations [29, 101, 104]. Namely,

\[
\Omega = E_p(t'') + I_p, \tag{3.8}
\]
where $\Omega$ is the frequency of the HHG photon. By solving numerically Eq. (3.7) for $t''$ and applying Eq. (3.6), one can relate each possible trajectory (3.5) to a given harmonic whose energy is determined by Eq. (3.8).

Note that the maximum instantaneous kinetic energy acquired by an electron that comes back to the parent ion is $3.17U_p$, which explains the position of the cutoff [27, 28]. For a given kinetic energy smaller than $3.17U_p$, Eqs. (3.6) and (3.7) allow for two different trajectories resulting in the same harmonic. The first trajectory, called a short trajectory, is characterized by a relatively short time spent by the electron in the continuum whereas the second one, called a long trajectory, corresponds to longer times [28]. For all other cases, when Eq. (3.7) is not fulfilled, electrons are ionized without emitting harmonics.

It has been shown [105], as well, that Eq. (3.5) subject to the condition (3.7) can accept more than one solution for certain initial times $t'$. This happens when the electron can revisit the nucleus several times before the recombination. This situation is recognized as multiple rescattering in HHG, which we do not address in this thesis.

### 3.2 Lewenstein model

Even though the three step model presented in the previous Section gives a very intuitive description of HHG and predicts accurately many of its features, the classical treatment during the propagation step leaves many quantum effects without consideration. To have a more detailed analysis of the process it is necessary to account for such factors like the quantum diffusion of wave packets and quantum interferences, that cannot be considered under the classical picture. The full quantum-mechanical model of the process was developed by Lewenstein et al. in Ref. [29] as a counterpart of the TSM under three basic assumptions:

1. The contribution of excited bound states can be neglected. Just the ground state contributes to the HHG process.
2. The depletion of the ground state can be neglected for intensities lower than the saturation intensity.
3. The atomic potential can be neglected during the propagation.

This model can be viewed in a similar way as the TSM, considering three steps: ionization, propagation, and recombination. The main difference between these two approaches is that the Lewenstein model considers the electron propagation quantum-mechanically. Namely, it establishes that the evolution in the continuum is described by the Volkov state, i.e., the electron is considered as a free particle interacting with an electromagnetic wave (for Volkov states, see Appendix B).
3.2.1 Lewenstein model for atomic systems in the length gauge

Consider the interaction of a strong electromagnetic wave described by the electric field $\mathbf{E}(t)$ and an atom centred at the origin of coordinates. In the length gauge, the Hamiltonian $\hat{H}_L$ describing the system is given by Eq. (2.165) with $V(r, t) \equiv V(r)$. It can be further separated into the atomic Hamiltonian $\hat{H}_0$, defined by Eq. (2.156), and the interaction Hamiltonian $\hat{H}_I$, defined by Eq. (2.157). Using the formulation introduced in Sec. 2.5, we can define the time-evolution operator $\hat{U}(t, t')$ that corresponds to the full Hamiltonian and it satisfies the Lippmann-Schwinger equation (2.149).

The time-dependent dipole moment due to the response of the atomic system, described using the SAE approximation, to the laser field is

$$d_L(t) = \langle \psi(t) | e \hat{\mathbf{r}} | \psi(t) \rangle ,$$

where the subindex ‘L’ indicates that it is calculated in the length gauge. Formally, taking into account that the electron is ionized from the ground state and recombines to the same state, the dipole moment takes the form

$$d_L(t) = \langle \psi_0(t') | \hat{U}(t', t) e \hat{\mathbf{r}} \hat{\mathbf{U}}(t, t'') | \psi_0(t'') \rangle .$$

Here, we have used Eq. (2.1) and we have written explicitly $|\psi_0(t)\rangle$ for the atomic ground state at time $t$. Applying now Eq. (2.149), we obtain that

$$d_L(t) = \langle \psi_0(t) | e \hat{\mathbf{r}} | \psi_0(t) \rangle - i \int_{t''}^{t} d\tau' \langle \psi_0(\tau) | e \hat{\mathbf{r}} \hat{\mathbf{U}}(\tau, \tau') \hat{H}_I(\tau') | \psi_0(\tau') \rangle$$

$$+ i \int_{t''}^{t} d\tau \langle \psi_0(\tau) | \hat{H}_I(\tau) \hat{U}(\tau, t) e \hat{\mathbf{r}} | \psi_0(t) \rangle$$

$$+ \int_{t''}^{t} d\tau \int_{t''}^{\tau} d\tau'' \langle \psi_0(\tau) | \hat{H}_I(\tau) \hat{U}(\tau, t'') e \hat{\mathbf{r}} \hat{\mathbf{U}}(t, \tau') \hat{H}_I(\tau') | \psi_0(\tau') \rangle .$$

Here $t', t'' \to -\infty$, in which case the state of the system corresponds to the unperturbed atomic ground state. Note that the first term does not contribute to the dipole moment if the considered potential is symmetric. The fourth term represents multiple interactions of the electron with the laser field and the atomic potential, and it is ignored in the first approximation. Finally, the dipole moment can be approximated as

$$d_L(t) = -i \int_{-\infty}^{t} d\tau \langle \psi_0(t) | e \hat{\mathbf{r}} \hat{\mathbf{U}}(t, \tau) \hat{H}_I(\tau) | \psi_0(\tau) \rangle + c.c. ,$$

where the complex conjugate ($c.c.$) guarantees that this quantity is real. According to the Lewenstein model, once the electron is ionized, it evolves in the continuum without the influence of the atomic potential. In this case, the time-evolution operator in Eq. (3.12) is substituted by the Volkov operator $\hat{U}_{L}^{GV}(t, t')$, given by Eq. (B.11).

Let us define the complex dipole moment $D_L(t)$,

$$D_L(t) = -i \int_{-\infty}^{t} dt' \langle \psi_0(t) | e \hat{\mathbf{r}} \hat{\mathbf{U}}_{L}^{GV}(t, t') \hat{H}_I(t') | \psi_0(t') \rangle ,$$

where the subindex ‘L’ indicates that it is calculated in the length gauge.
such that
\[ d_L(t) = D_L(t) + D_L^*(t) \, . \] (3.14)

Taking into account Eq. (B.11) and substituting the definition of the interaction Hamiltonian \( \hat{H}_I(t) \) [Eq. (2.157)] in Eq. (3.13), we obtain
\[
D_L(t) = \frac{ie^2}{(2\pi)^3} \int dp \int_{-\infty}^{t} dt' \exp \left( -i \int_{t'}^{t} \frac{d\tau}{2m} \left[ p - eA(\tau) \right]^2 \right) 
\times \langle \psi_0(t)| \hat{r}| p - eA(t) \rangle \langle p - eA(t')| \hat{r} \cdot \mathbf{E}(t')| \psi_0(t') \rangle . \] (3.15)

Since the atomic ground state of energy \( E_0 \) evolves in time according to Eq. (2.152), we can rewrite Eq. (3.15) as follows
\[
D_L(t) = \frac{ie^2}{(2\pi)^3} \int dp \int_{-\infty}^{t} dt' \exp \left( -i \int_{t'}^{t} \frac{d\tau}{2m} \left[ p - eA(\tau) \right]^2 + iE_0(t - t') \right) 
\times \langle \psi_0(t)| \hat{r}| p - eA(t) \rangle \langle p - eA(t')| \hat{r} \cdot \mathbf{E}(t')| \psi_0(t') \rangle . \] (3.16)

Note that the term in the exponent corresponds to the semiclassical action \( S(p, t, t') \) [29],
\[
S(p, t, t') = \int_{t'}^{t} d\sigma \left[ \frac{(p - eA(\sigma))^2}{2m} + I_p \right] , \] (3.17)

where the ionization potential is related to the ground state energy as \( I_p = -E_0 \).

In Eq. (3.16), we recognize that the expression \( e\langle p - eA(t')| \hat{r} \cdot \mathbf{E}(t')| \psi_0(t') \rangle \) represents the dipole moment caused by the transition of the electron from the atomic state to the continuum at time \( t' \). From now on, this expression will be referred to as the ionization matrix element (IME). On the other hand, the term \( e\langle \psi_0(t)| \hat{r}| p - eA(t) \rangle \) can be interpreted as the dipole moment caused by recombination at time \( t \) and, hence, it will be called the recombination matrix element (RME). Introducing the following notation,
\[
d_{\text{ion}}^L(p - eA(t)) = d_{\text{rec}}^L(p - eA(t)) = \frac{1}{(2\pi)^{3/2}} \langle p - eA(t)| \hat{r} \cdot \mathbf{E}(t')| \psi_0(t') \rangle , \] (3.18)

where we do not account for the electron charge, Eq. (3.16) can be written in a compact form as
\[
D_L(t) = ie^2 \int dp \int_{-\infty}^{t} dt' \exp [-iS(p, t, t')] |d_{\text{rec}}^L(p - eA(t))| \frac{d_{\text{ion}}^L(p - eA(t')) \cdot \mathbf{E}(t')}{|d_{\text{rec}}^L(p - eA(t))|} . \] (3.19)

Note that the integration over momentum in (3.19) is difficult to perform exactly as it requires a large amount of computational effort (see, for example, Ref. [106]). So, usually, one applies one more approximation. Taking into account the fact that the function \( \exp [-iS(p, t, t')] \) oscillates fast compared to other terms, the momentum integration can be performed using the saddle-point approximation (see, Appendix E for a detailed description of this method). The saddle point in momentum, \( p_s \), is calculated according to the equation
\[
\nabla_p S(p, t, t')|_{p_s} = 0 , \] (3.20)
which, for the semiclassical action defined in (3.17), gives

\[
p_s = \frac{e}{\tau} \int_{t-\tau}^{t} d\sigma A(\sigma).
\] (3.21)

The parameter \( \tau = t - t' \) is the so-called return time [29]. For each of the momentum components, the second derivative of the action gives

\[
\frac{\partial^2 S}{\partial p_i^2} = \frac{(t - t')/m}{m} = \tau/m,
\] (3.22)

where \( i = x, y, z \). Hence, \( D_L(t) \) given by Eq. (3.19) can be approximated as

\[
D_L(t) \approx ie^2 \int_{0}^{\infty} d\tau \left( \frac{2\pi i}{\epsilon + i\tau/m} \right) \frac{3/2}{3/2} \exp \left[ -i S(p_s, t, t - \tau) \right]
\times d_{rec}^L(p_s - eA(t)) \left[ d_{ion}^L(p - eA(t - \tau)) \cdot E(t - \tau) \right],
\] (3.23)

where \( \epsilon \) is an infinitesimal regularization constant [29]. According to Ref. [29], the term \( \left( \frac{2\pi i}{\epsilon + i\tau/m} \right) \frac{3/2}{3/2} \) takes into account the quantum-mechanical spreading of the electron wave packet during its excursion to the continuum (completely neglected in the semiclassical TSM), and diminishes the contribution of electrons with return times much larger than the laser period.

After the saddle-point method is used, it becomes intuitively clear that under the Lewenstein picture [see, Eq. (3.23)]: first, the electron is ionized at time \( t' = t - \tau \) and it propagates in the continuum from \( t' \) to \( t \). During this time interval, the electron wave packet acquires a phase \( \exp \left[ -i S(p_s, t, t') \right] \) and spreads according to \( \left( \frac{2\pi i}{\epsilon + i\tau/m} \right) \frac{3/2}{3/2} \). Finally, the electron recombines at time \( t \).

### 3.2.2 Interpretation of the Lewenstein model in terms of saddle points

Another way to study the spectral properties of the emitted radiation, which gives an interesting physical interpretation of the process, is to consider the complex dipole moment in frequency space [i.e., the Fourier transform of \( D_L(t) \)] [28, 29],

\[
\tilde{D}_L(\Omega) = ie^2 \int dt \int dp \int_{-\infty}^{\infty} dt' \exp \left[ -i S(p, t, t') + i\Omega t \right] d_{rec}^L(p - eA(t)) \left[ d_{ion}^L(p - eA(t')) \cdot E(t') \right].
\] (3.24)

The expression for \( \tilde{D}_L(\Omega) \) involves a multidimensional integral over \( t, t', \) and \( p \), and can be treated according to the saddle-point approximation for multiple variables. In doing so, we make use of the procedure developed in Ref. [107].

First, we apply the saddle-point method with respect to \( t' \) considering \( p \) and \( t \) as fixed parameters,

\[
\frac{d}{dt'} S(p, t, t') = \frac{\partial}{\partial t'} S(p, t, t') \bigg|_{t'} = 0.
\] (3.25)
This, according to Eq. (3.17), gives

$$\frac{1}{2m} [p - eA(t_s')]^2 + I_p = 0 .$$

(3.26)

To approximate the integral over momentum in (3.24), it is necessary to consider that $p$ depends on the variable $t'$ evaluated at the saddle point,

$$\frac{d}{dp_i} S(p, t, t') = \frac{\partial}{\partial p_i} S(p, t, t') + \frac{\partial}{\partial t_s'} S(p, t, t') \frac{dt_s'}{dp_i} ,$$

(3.27)

where $i = x, y, z$. According to Eq. (3.25), the last term vanishes and the saddle-point equation for momentum reads

$$\nabla \cdot S(p, t, t')|_{p_s} = 0 ,$$

(3.28)

with the solution defined by Eq. (3.21). Finally, to complete the approximation of the multidimensional integral, it is necessary to take into account that the variable $t$ depends on $p_s$ and $t_s'$. In this case, the derivative of the action with respect to time is given as

$$\frac{d}{dt} S(p_s, t, t_s') = \frac{\partial}{\partial t} S(p_s, t, t_s') + \nabla_{p_s} S(p_s, t, t_s') \cdot \frac{dp_s}{dt} + \frac{\partial}{\partial t_s'} S(p_s, t, t_s') \frac{dt_s'}{dt} .$$

(3.29)

According to Eqs. (3.25) and (3.28), the last two terms vanish. Hence, the saddle-point equation for $t$, which follows from the phase of the integrand in Eq. (3.24), reads

$$\frac{\partial}{\partial t} [S(p_s, t, t_s') - \Omega t] \bigg|_{t_s} = 0 .$$

(3.30)

This leads to

$$\frac{1}{2m} [p_s - eA(t_s')]^2 + I_p = \Omega .$$

(3.31)

Now, we have access to a set of three equations [Eqs. (3.21), (3.26), and (3.31)] which describe the behavior of the system and can explain the HHG mechanism with physical arguments. Eq. (3.21) can be rewritten in a more revealing way as

$$\frac{1}{m} \int_{t'}^{t} d\sigma [p_s - eA(\sigma)] = 0 .$$

(3.32)

The term inside the integral represents the kinetic momentum of the electron (2.206). For the purpose of this Chapter, we will explicitly write it as $\Pi(p_s, t)$. Its integral from $t'$ to $t$ divided by the mass defines the total displacement of the electron, with canonical momentum $p_s$, between ionization and recombination events. Eq. (3.32) implies, therefore, that the electron recombines at the same position where the ionization took place. In other words, that the electron which contributes to HHG is the one that returns to the nucleus. Based on Eq. (3.26) evaluated at the momentum saddle point, and on Eqs. (3.31) and (2.206), we can write that

$$\frac{1}{2m} [\Pi^2(p_s, t_s) - \Pi^2(p_s, t_s')] = \Omega ,$$

(3.33)
which is the energy conservation condition just before the recombination process occurs. It is worth noting that for the harmonic emission, which happens during recombination, the relation (3.31) holds, and that the radiated energy is equal to the kinetic energy at time $t_s$ plus $I_p$.

Finally, the dipole moment in Eq. (3.24) can be approximated as a sum over the saddle points $s$ (see, Appendix E),

$$
\tilde{D}_L(\Omega) \approx 2\pi e^2 \sum_s \left( \frac{2\pi}{\epsilon + i(t_s - t'_s)/m} \right)^{3/2} \frac{1}{\sqrt{\det S''(p_s, t_s, t'_s)}} \exp \left[ -iS(p_s, t_s, t'_s) + i\Omega t_s \right] \nonumber 
\times d^L_{\text{ion}}(p_s - eA(t_s)) \cdot d^L_{\text{rec}}(p_s - eA(t'_s)) \cdot \mathbf{E}(t'_s),
$$

which can be interpreted as a superposition of contributions coming from quantum trajectories starting at different saddle points (for quantum trajectories in the Lewenstein model, see Sec. 3.2.8). The term $\det S''(p, t, t')$, which arises when a multivariable approximation is developed, is given by [28, 107]

$$
\det S''(p, t, t') = \frac{\partial^2 S}{\partial t^2} \frac{\partial^2 S}{\partial t'^2} - \left( \frac{\partial^2 S}{\partial t \partial t'} \right)^2.
$$

Let us comment now on Eq. (3.26). If the ionization potential was zero, then the electron appears in the continuum with no kinetic energy, as it is assumed in the TSM. In real systems, $I_p$ is always positive. Thus, in order to fulfill Eq. (3.26), the kinetic energy has to be negative during the tunneling process. This implies the complex character of momentum and velocity during the ionization, which can be only accepted by considering $t'_s$ as a complex quantity [29] (see, also our discussion in Sec. 2.6.5). Actually, $t'_s$ is identified as the time at which the electron arrives at the potential barrier, just before being transferred to the continuum, and its real part is the exact moment when the electron appears on the other side of the barrier. The electron displacement during this process is, in general, complex. The evolution in the continuum now presents complex initial conditions (for the position and velocity) and it is governed by a complex time. Nevertheless, the complex time analysis requires the observable (in this case, the photon energy) to be real [107].

As it was mentioned before, there is a difference between the TSM and the Lewenstein model predictions concerning the exact position of the cutoff. The former approach predicts the position of the cutoff at $(I_p + 3.17U_p)/\omega_L$ whereas the numerical solution of Eqs. (3.21), (3.26), and (3.31), evaluated at the saddle points, leads to the relation [29, 107]

$$
N_{\text{cutoff}} = (1.32I_p + 3.17U_p)/\omega_L.
$$

This $0.32I_p$ additional energy is often related to the fact that, during the recombination, the electron suffers an additional acceleration between the tunneling barrier and the nucleus position [28, 29]. This process is completely neglected in the TSM by considering that the ionization and recombination always happens at the origin of coordinates.

In this Section, we have shown that the Lewenstein model can be interpreted by analyzing a set of three saddle-point equations [Eqs. (3.21), (3.26), and (3.31)]. Up to now, our analysis has been restricted to the case when the harmonic target is a single atom at the origin of coordinates.
In Sec. 3.2.4, after a brief introduction to the concept of linear combination of atomic orbitals in Sec. 3.2.3, we will show how the saddle-point equations are modified when multiple atomic centres are considered.

### 3.2.3 Linear combination of atomic orbitals (LCAO)

If the target contains multiple atoms, its ground state can be approximated by means of a linear combination of atomic orbitals (LCAO). A molecular orbital in such approximation is defined as a linear superposition of functions centred at the nuclei locations (which are considered static compared to the fast dynamics of the electrons),

\[
\psi_0(r) = \sum_{j=1}^{N} \sum_{\ell=0}^{n} C_\ell \phi_\ell(r - R_j).
\]  

(3.37)

Here, \(N\) is the total number of atoms constituting the molecule, \(n\) is the number of atomic orbitals, and \(\phi_\ell(r)\) is the wave function associated with a single atomic orbital centred at \(R_j\), which is the position of the \(j\)-th nucleus. The parameters \(C_\ell\) depend on the molecular structure and 'weight' of each atomic contribution. Usually, a superposition of Gaussian type functions is used to approximate the atomic orbitals. Namely, using Cartesian coordinates,

\[
\phi_\ell(r) = N_\ell \sum_{k=1}^{k_{\text{max}}} \eta_k x^a y^b z^c e^{-\alpha_k r^2} = N_\ell \sum_{k=1}^{k_{\text{max}}} \varphi_k^{(a,b,c)}(r),
\]  

(3.38)

where \(N_\ell\) is a normalization constant, \(\eta_k\) is a superposition coefficient, whereas \(a, b,\) and \(c\) are integers (more precisely, positive integers or zeroes) such that \(a + b + c = \ell\). In addition, \(k_{\text{max}}\) is the number of functions \(\varphi_k^{(a,b,c)}(r)\) necessary to model the orbital. \(\alpha_k\) is the so-called exponent, which is closely related to the ‘spreading’ of the particular Gaussian orbital in the molecule. For larger \(\alpha_k\) values, the atomic orbital shows a larger probability that the electron will be localized near the nucleus. The term

\[
\varphi_k^{(a,b,c)}(r) = \eta_k x^a y^b z^c e^{-\alpha_k r^2}
\]  

(3.39)

is called a Gaussian primitive (GP) and it constitutes the basic block of the molecular orbital construction. The function \(\phi_\ell(r)\) defined by Eq. (3.38) is called a Gaussian type orbital (GTO).

It is worth noting that the GTOs are merely mathematical functions used to approximate the real atomic orbitals. Initially, this approximation was obtained by using a more natural primitives in the so-called Slater type orbitals (STOs). The STO is a superposition of wave functions related to the electron states in a hydrogen-like atom [108]

\[
\varphi_{nlm}(r) = N_{nlm} r^{n-1} e^{-\xi_{lm} r} Y_m^l(\theta, \varphi).
\]  

(3.40)

Here, \(n, l, m\) are the principal, azimuthal, and magnetic quantum numbers of the particular orbital, \(N_{nlm}\) is a normalization constant, \(Y_m^l(\theta, \varphi)\) is the respective spherical harmonic, and \(\xi_{lm}\) is the so-called Slater orbital exponent. The use of STOs in quantum chemistry was rapidly overcome by the
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<table>
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Table 3.1 Gaussian primitives (3.39) corresponding to \(s\), \(p\), and \(d\) atomic orbitals, neglecting the normalization constants.

The use of GTOs due to several advantages such as faster computational time and easy implementation, with the disadvantage of losing part of the physical insight offered by the STOs [108].

In the GTOs, the principal and magnetic quantum numbers do not appear explicitly as they do in the STOs, but the integer \(\ell\) is closely related to the azimuthal quantum number. For example, for \(\ell = 0\) the GTO corresponds to an \(s\) type orbital, \(\ell = 1\) represents a \(p\) type orbital, whereas \(\ell = 2\) a \(d\) type orbital. The mathematical description of the \(s\), \(p\), and \(d\) Gaussian primitives (without the normalization constants) is shown in Table 3.1 [108].

3.2.4 Lewenstein model for molecular systems in the length gauge

Since in the length gauge, the ionization and recombination matrix elements are related through Eq. (3.18), in the following we analyze only the IME. It is expressed in terms of the kinetic momentum \(\Pi\) [Eq. (2.206)],

\[
d_{\text{ion}}^{L}(\Pi) = \frac{1}{(2\pi)^{3/2}} \int d\mathbf{r} e^{-i\Pi \cdot \mathbf{r}} \psi_0(\mathbf{r}) .
\]  

(3.41)

Taking into account the LCAO approximation [Eq. (3.37)], \(d_{\text{ion}}^{L}(\Pi)\) becomes a sum over dipole matrix elements centred at each nucleus,

\[
d_{\text{ion}}^{L}(\Pi) = \frac{1}{(2\pi)^{3/2}} \sum_{j=1}^{N} \sum_{\ell=0}^{n} C_{\ell} \int d\mathbf{r} e^{-i\Pi \cdot \mathbf{r}} \phi_{\ell}(\mathbf{r} - \mathbf{R}_j) .
\]  

(3.42)

As each atomic orbital is approximated as a superposition of GPs, the IME can be written as a sum of partial contributions arising from each primitive,

\[
d_{\text{ion}}^{L}(\Pi) = \frac{1}{(2\pi)^{3/2}} \sum_{j=1}^{N} \sum_{\ell=0}^{n} C_{\ell} N_{\ell} \sum_{k} \eta_{k} \sum_{a,b,c} \int d\mathbf{r} (x - x_j)^{a}(y - y_j)^{b}(z - z_j)^{c} e^{-\alpha_{k}(\mathbf{r} - \mathbf{R}_j)^2} \mathbf{r} e^{-i\Pi \cdot \mathbf{r}} .
\]  

(3.43)
The integrals in the above expression can be performed analytically for any Gaussian orbital. If we define the quantity

$$d^k(\Pi, \mathbf{R}_j) = \frac{1}{(2\pi)^{3/2}} \int \, d\mathbf{r} \left( x - x_j \right)^a \left( y - y_j \right)^b \left( z - z_j \right)^c e^{-\alpha_k (r-R_j)^2} e^{-i\Pi \cdot \mathbf{r}}, \quad (3.44)$$

then, for instance, for \( s \) and \( p \) type orbitals, we get

$$d^k_s(\Pi, \mathbf{R}_j) = \frac{1}{(2\alpha_k)^{5/2}} \left[ 2\alpha_k \mathbf{R}_j - i\Pi \right] e^{-\frac{n^2}{\alpha_k} - i\Pi \cdot \mathbf{R}_j}, \quad (3.45)$$

$$d^k_{ps}(\Pi, \mathbf{R}_j) = -\frac{1}{(2\alpha_k)^{7/2}} \left[ \Pi_x [\Pi + 2i\alpha_k \mathbf{R}_j] - 2\alpha_k e_x \right] e^{-\frac{n^2}{\alpha_k}} - i\Pi \cdot \mathbf{R}_j, \quad (3.46)$$

$$d^k_{ps}(\Pi, \mathbf{R}_j) = -\frac{1}{(2\alpha_k)^{7/2}} \left[ \Pi_y [\Pi + 2i\alpha_k \mathbf{R}_j] - 2\alpha_k e_y \right] e^{-\frac{n^2}{\alpha_k}} - i\Pi \cdot \mathbf{R}_j, \quad (3.47)$$

$$d^k_{ps}(\Pi, \mathbf{R}_j) = -\frac{1}{(2\alpha_k)^{7/2}} \left[ \Pi_z [\Pi + 2i\alpha_k \mathbf{R}_j] - 2\alpha_k e_z \right] e^{-\frac{n^2}{\alpha_k}} - i\Pi \cdot \mathbf{R}_j. \quad (3.48)$$

Hence, the total ionization matrix element (3.43) takes the form,

$$d^k_{ion}(\Pi) = \sum_{j=1}^{N} \sum_{\ell=0}^{n} C_{\ell} N_{\ell} \sum_{k} \eta_k \sum_{q} d^k(\Pi, \mathbf{R}_j), \quad (3.49)$$

where the sum over \( q \) includes the contribution of different type orbitals, depending on the value of \( \ell \).

As it follows from Eqs. (3.45) to (3.48), the multicentre structure of a molecule results in new oscillatory terms in the IME. The factor \( e^{-i\Pi \cdot \mathbf{R}_j} \) is common for all Gaussian orbitals and it is considered to be highly oscillating function of momentum for large values of \( \mathbf{R}_j \). This suggests to use in Eq. (3.19) the saddle-point method to calculate the integral over momentum.

If the saddle-point method is to be applied in Eq. (3.19), the oscillatory terms need to be grouped together in the action [109]. We define, therefore, a new quantity, the modified semiclassical action, which in the length gauge has the form

$$S_L(p, t, t', \mathbf{R}_i, \mathbf{R}_j) = \int_{t'}^{t} \, d\sigma \left[ \frac{(p - e A(\sigma))^2}{2m} + I_p \right] + [p - e A(t')] \cdot \mathbf{R}_j - [p - e A(t)] \cdot \mathbf{R}_i. \quad (3.50)$$

Here, the ionization and recombination oscillatory terms were added to the original semiclassical action (3.17) taking into account that both processes may occur at different atoms (\( \mathbf{R}_j \) and \( \mathbf{R}_i \)) and different times (\( t' \) and \( t \)). With this modification, we find the new saddle-point equation for momentum,

$$p_s = \frac{1}{t - t'} \left[ e \int_{t'}^{t} \, d\sigma A(\sigma) + m (\mathbf{R}_i - \mathbf{R}_j) \right]. \quad (3.51)$$

Rewriting it as

$$\frac{1}{m} \int_{t'}^{t} \, d\sigma \left[ p_s - e A(\sigma) \right] = \mathbf{R}_i - \mathbf{R}_j, \quad (3.52)$$
we recognize again that the term \((p_s - eA(t))\) corresponds to the kinetic momentum, whereas the integral from \(t'\) to \(t\) divided by the electron mass represents the total displacement between the ionization and recombination events. Therefore, Eq. (3.52) implies that the total displacement of an electron ionized at the atom position \(R_j\) and recombined at \(R_i\) is \((R_i - R_j)\). In this case, the electrons that contribute to the harmonic emission in multicentre systems are not just the ones that are emitted and recombined at the same location, but also those which are emitted at a certain atom and recombine at another. It is possible that the electron comes back to the parent nucleus (i.e., \(i = j\)), in which case the saddle-point equations are the same as in the case of a single atom. The harmonics generated by this process are called direct harmonics. In contrast, if the electron is recombined in a different location (i.e., \(i \neq j\)), the harmonics are called transfer harmonics [109].

In order to analyze the remaining saddle-point equations for \(t\) and \(t'\), one can use the analogous equation to (3.24) which would account for the multicentre structure of the molecule. In this case, the Fourier transform of the complex dipole moment is given by the relation,

\[
\tilde{D}_L(\Omega) = \sum_{i=1}^{N} \sum_{j=1}^{N} \tilde{D}_{i,j}^{L}(\Omega),
\]

(3.53)

where \(N\) is the number of atoms and

\[
\tilde{D}_{i,j}^{L}(\Omega) = i e^2 \int dt \int dp \int_{-\infty}^{t} dt' \exp \left[-iS_L(p, t, t', R_i, R_j) + i\Omega t\right] d_{rec}^{L}(p - eA(t), R_i)
\times \left[d_{ion}^{L}(p - eA(t'), R_j) \cdot \mathbf{E}(t')\right].
\]

(3.54)

While we incorporate the additional oscillatory terms into the modified semiclassical action, we also redefine the ionization and recombination matrix elements such that

\[
d_{ion}^{L}(p - eA(t), R_j) = d_{rec}^{L}(p - eA(t), R_j)
= \frac{1}{(2\pi)^{3/2}} \langle \mathbf{r} | \psi_0(R_j) \rangle \exp \left(i\langle \mathbf{p} - eA(t) | \mathbf{r} \rangle \right),
\]

(3.55)

Proceeding as in Sec. 3.2.2, we obtain the saddle-point equation for \(t'\),

\[
\frac{1}{2m} |\mathbf{p} - eA(t_s)|^2 + I_p - e\mathbf{E}(t_s) \cdot \mathbf{R}_j = 0,
\]

(3.56)

and for \(t\),

\[
\frac{1}{2m} |\mathbf{p} - eA(t)|^2 + I_p - e\mathbf{E}(t) \cdot \mathbf{R}_i = \Omega,
\]

(3.57)

where the fact that \(\mathbf{E}(t) = -\frac{\partial A(t)}{\partial t}\) has been used. In Eqs. (3.56) and (3.57), two new terms related to the multicentre structure of the molecule modify the saddle-point equations as compared to the case of a single atom [Eqs. (3.26) and (3.31)].

Having a closer look at Eq. (3.57), we notice that the frequency of the emitted photon increases monotonically with the internuclear distance [109]. This abnormal behavior is more pronounced for large internuclear distances and becomes less important for small molecules. In general, the HHG
signal from large molecules tends to present an unphysical extension of the plateau in the length
gauge \cite{109}. In order to determine the validity of calculations performed in the length gauge, let us
define the meaning of “large” and “small” molecules quantitatively. The value of the integral of the
vector potential in Eq. (3.51) can be estimated such that \cite{109}
\[ e \int_{t'}^{t} d\sigma A(\sigma) < 2\alpha_0 m , \quad (3.58) \]
where the quiver radius \( \alpha_0 \) is the amplitude of classical oscillations of an electron in the laser field,
\[ \alpha_0 = |e|E_0/(m\omega_L^2). \] If the atomic separation \( R \) is larger than \( 2\alpha_0 \), the unphysical
effects are stronger. This has been proven for diatomic molecules and extended to bigger systems \cite{101, 104, 109}. If a
molecule with large number of atoms is taken into consideration, we define a new parameter \( Q \),
\[ Q = \frac{R_{\text{max}}}{2\alpha_0} , \quad (3.59) \]
where \( R_{\text{max}} \) is the maximum distance between two atoms in the molecule. This parameter may
help to determine whether or not the length gauge calculations can be performed without introducing
unphysical effects (see, Ref. \cite{101}). For these effects not to be manifested: \( Q < 1 \).

Note that one of the most relevant features of the strong-field approximation in the Lewenstein
model is the absence of gauge invariance and, hence, many problems related to the gauge choice may
arise when multielectron systems are considered. Therefore, in the next Sections, the mathematical
description of the HHG process in the velocity gauge is provided.

### 3.2.5 Lewenstein model for atomic systems in the velocity gauge

Consider the interaction of an electron with an oscillating electric field and a static atomic po-
tential in the velocity gauge. The respective Hamiltonian is defined by Eq. (2.40). This Hamiltonian
can be separated into the atomic Hamiltonian \( \hat{H}_0 \) [Eq. (2.156)], which governs the evolution of the
electron in the atomic ground state, and the interaction Hamiltonian \( \hat{H}_I(t) \), which describes the inter-
action of the electron with the electromagnetic field. This time,
\[ \hat{H}_I(t) = -\frac{e}{m} \hat{p} \cdot \hat{A}(t) + \frac{e^2}{2m} \hat{A}^2(t) . \quad (3.60) \]
Proceeding in the same way as in Sec. 3.2.1, we find out that the time-dependent dipole moment in
the velocity gauge can be represented as
\[ d_V(t) = D_V(t) + D_V^*(t) , \quad (3.61) \]
where
\[ D_V(t) = -i \int_{-\infty}^{t} dt' \langle \psi_0(t)|e\hat{r}\hat{U}^{\text{GV}}(t,t')\hat{H}_I(t')|\psi_0(t') \rangle . \quad (3.62) \]
Using Eqs. (B.10) and (3.60), we obtain

\[ D_V(t) = \frac{ie^2}{m(2\pi)^3} \int dp \int_{-\infty}^{t} dt' \exp \left[ -iS(p, t, t') \right] \langle \psi_0 | r | p \rangle \langle p | \hat{p} \cdot A(t') - \frac{e}{2} A^2(t') | \psi_0 \rangle, \] (3.63)

where \( S(p, t, t') \) is the semiclassical action defined in Eq. (3.17). As one can understand from these formulas, the differences between the two gauges follow from the form of the interaction Hamiltonian and the fact that the Volkov propagator in the velocity gauge depends on the canonical momentum \( p \), not on the kinetic momentum \( \Pi \) as it happens in the length gauge. These differences cause important consequences for the calculations. First of all, the ionization matrix element is presented in a different way compared to the one in the length gauge [Eq. (3.18)]. Namely,

\[ d_{ion}^V(p, t) = \frac{1}{(2\pi)^{3/2}} \langle \psi_0 | r | p \rangle \langle p | \hat{p} - \frac{e}{2} A(t) | \psi_0 \rangle. \] (3.64)

The RME in the velocity gauge has a similar form as the one in the length gauge [Eq. (3.18)], except that the kinetic momentum is replaced by the canonical one,

\[ d_{rec}^V(p) = \frac{1}{(2\pi)^{3/2}} \langle \psi_0 | r | p \rangle. \] (3.65)

Taking into account the definitions (3.64) and (3.65), the complex vector \( D_V(t) \) can be rewritten as

\[ D_V(t) = \frac{ie^2}{m} \int dp \int_{-\infty}^{t} dt' \exp \left[ -iS(p, t, t') \right] d_{rec}^V(p) \left[ d_{ion}^V(p, t') \cdot A(t') \right]. \] (3.66)

Now, the integral over momentum in Eq. (3.66) is approximated according to the saddle-point method. In this case, the quantity \( D_V(t) \) takes the form

\[ D_V(t) \approx \frac{ie^2}{m} \int_0^{\infty} d\tau \left( \frac{2\pi}{\epsilon + i\tau/m} \right)^{3/2} \exp \left[ -iS(p_s, t, t - \tau) \right] d_{rec}^V(p_s) \left[ d_{ion}^V(p_s, t - \tau) \cdot A(t - \tau) \right], \] (3.67)

where \( \tau = t - t' \) is the return time, \( \epsilon \) is a small regularization parameter, and \( p_s \) is the saddle point in momentum given by Eq. (3.21). The integral over time in Eq. (3.67) can be calculated numerically.

3.2.6 Lewenstein model for molecular systems in the velocity gauge

In order to calculate the saddle-point equations for a multicentre system it is necessary to modify the semiclassical action, as it has been done for the length gauge in Sec. 3.2.4. Applying the concepts developed there, we derive the analytical expressions for the recombination and ionization matrix elements. The recombination one, under the LCAO approximation and taking into account the
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Gaussian primitives as basis functions (see, Sec. 3.2.4), can be written as
\[
d^{\ell}_{\text{rec}}(p) = \frac{1}{(2\pi)^{3/2}} \sum_{j=1}^{N} \sum_{\ell=0}^{n} C_{\ell} N_{\ell} \sum_{k} \eta_{k} \sum_{a,b,c} \int d\mathbf{r} (x-x_{j})^{a} (y-y_{j})^{b} (z-z_{j})^{c} e^{-\alpha_{k}(r-R_{j})^{2}} r e^{i p \cdot r}.
\]
(3.68)

We now define a quantity
\[
d^{k}_{\text{rec}}(p, R_{j}) = \frac{1}{(2\pi)^{3/2}} \int d\mathbf{r} (x-x_{j})^{a} (y-y_{j})^{b} (z-z_{j})^{c} e^{-\alpha_{k}(r-R_{j})^{2}} r e^{i p \cdot r},
\]
(3.69)

which for s and p type orbitals reads
\[
d^{k}_{\text{rec},a}(p, R_{j}) = \frac{1}{(2\alpha_{k})^{5/2}} \left[ 2\alpha_{k} R_{j} + i p \right] e^{\frac{p^{2}}{4\alpha_{k}} + i p \cdot R_{j}},
\]
(3.70)
\[
d^{k}_{\text{rec},p}(p, R_{j}) = -\frac{1}{(2\alpha_{k})^{7/2}} \left( p_{x} [p - 2i\alpha_{k} R_{j}] - 2\alpha_{k} e_{x} \right) e^{\frac{p^{2}}{4\alpha_{k}} + i p \cdot R_{j}},
\]
(3.71)
\[
d^{k}_{\text{rec},s}(p, R_{j}) = -\frac{1}{(2\alpha_{k})^{7/2}} \left( p_{y} [p - 2i\alpha_{k} R_{j}] - 2\alpha_{k} e_{y} \right) e^{\frac{p^{2}}{4\alpha_{k}} + i p \cdot R_{j}},
\]
(3.72)
\[
d^{k}_{\text{rec},c}(p, R_{j}) = -\frac{1}{(2\alpha_{k})^{7/2}} \left( p_{z} [p - 2i\alpha_{k} R_{j}] - 2\alpha_{k} e_{z} \right) e^{\frac{p^{2}}{4\alpha_{k}} + i p \cdot R_{j}}.
\]
(3.73)

According to these expressions, the recombination matrix element can be written as
\[
d^{\ell}_{\text{rec}}(p) = \sum_{j=1}^{N} \sum_{\ell=0}^{n} C_{\ell} N_{\ell} \sum_{k} \eta_{k} \sum_{q} d^{k}_{\text{rec},q}(p, R_{j}),
\]
(3.74)

where the sum over \( q \) includes contributions of different type orbitals. As we see, Eqs. (3.70) to (3.73) contain the oscillatory term \( e^{i p \cdot R_{j}} \), which can be factorized and absorbed into the semiclassical action.

The ionization matrix element can be expanded, under the same approximations, as follows
\[
d^{\ell}_{\text{ion}}(p, t) = \frac{1}{(2\pi)^{3/2}} \sum_{j=1}^{N} \sum_{\ell=0}^{n} C_{\ell} N_{\ell} \sum_{k} \eta_{k} \sum_{a,b,c} \int d\mathbf{r} e^{-i p \cdot r} \left[ -i \mathbf{\nabla} - \frac{e}{2} \mathbf{A}(t) \right] \times (x-x_{j})^{a} (y-y_{j})^{b} (z-z_{j})^{c} e^{-\alpha_{k}(r-R_{j})^{2}}.
\]
(3.75)

Now, the quantity of interest is
\[
d^{k}_{\text{ion}}(p, R_{j}, t) = \frac{1}{(2\pi)^{3/2}} \int d\mathbf{r} e^{-i p \cdot r} \left[ -i \mathbf{\nabla} - \frac{e}{2} \mathbf{A}(t) \right] (x-x_{j})^{a} (y-y_{j})^{b} (z-z_{j})^{c} e^{-\alpha_{k}(r-R_{j})^{2}}.
\]
(3.76)
The analytical expressions for the ionization matrix elements related to $s$ and $p$ GPs are given by

$$d_{ion,s}^k(p, R_j, t) = \frac{1}{(2\alpha_k)^{3/2}} \left[ p - \frac{e}{2} A(t) \right] e^{\frac{p^2}{4\alpha_k} - ip R_j}, \quad (3.77)$$

$$d_{ion,p_x}^k(p, R_j, t) = -\frac{i}{(2\alpha_k)^{5/2}} p_x \left[ p - \frac{e}{2} A(t) \right] e^{\frac{p^2}{4\alpha_k} - ip R_j}, \quad (3.78)$$

$$d_{ion,p_y}^k(p, R_j, t) = -\frac{i}{(2\alpha_k)^{5/2}} p_y \left[ p - \frac{e}{2} A(t) \right] e^{\frac{p^2}{4\alpha_k} - ip R_j}, \quad (3.79)$$

$$d_{ion,p_z}^k(p, R_j, t) = -\frac{i}{(2\alpha_k)^{5/2}} p_z \left[ p - \frac{e}{2} A(t) \right] e^{\frac{p^2}{4\alpha_k} - ip R_j}. \quad (3.80)$$

In this case, the total ionization matrix element takes the form,

$$d_{ion}^V(p, t) = \sum_{j=1}^N \sum_{t=0}^n C_t N_t \sum_k \sum_q d_{ion,q}^k(p, R_j, t). \quad (3.81)$$

The common oscillatory terms of the type $e^{-ip R_j}$, for each $R_j$ in Eq. (3.81), need to be grouped inside the modified semiclassical action before the saddle-point approximation in momentum is performed. In doing so, the modified semiclassical action in the velocity gauge becomes

$$S_V(p, t, t', R_i, R_j) = \int_{t'}^{t} d\sigma \left[ \frac{(p - e A(\sigma))^2}{2m} + I_p \right] + p \cdot R_j - p \cdot R_i. \quad (3.82)$$

The saddle points in momentum are given by Eq. (3.51). Thus, the vector $D_V(t)$ can be approximated as

$$D_V(t) \approx \frac{e^2}{m} \sum_{i=1}^N \sum_{j=1}^N \int_0^\infty d\tau \left( \frac{2\pi}{\epsilon + i\tau/m} \right)^{3/2} \exp \left[ -iS_V(p_s, t - \tau, R_i, R_j) \right] \times d_{ion2}^V(p_s, R_i) [d_{ion2}^V(p_s, R_j, t - \tau) \cdot A(t - \tau)], \quad (3.83)$$

where the modified ionization and recombination matrix elements are defined such that

$$d_{ion2}^V(p, R_j, t) = \frac{1}{(2\pi)^{3/2}} \langle p | \hat{\rho} - \frac{e}{2} A(t) | \psi_0(R_j) \rangle \exp (ip \cdot R_j), \quad (3.84)$$

$$d_{rec2}^V(p, R_j) = \frac{1}{(2\pi)^{3/2}} \langle \psi_0(R_j) | \hat{\rho} | p \rangle \exp (-ip \cdot R_j). \quad (3.85)$$

Taking the Fourier transform of the complex dipole moment $D_V(t)$ and applying the same procedures as before, we find out that the saddle-point equations for $t'$ and $t$ are

$$\frac{1}{2m} [p - e A(t')]^2 + I_p = 0, \quad (3.86)$$

$$\frac{1}{2m} [p - e A(t)]^2 + I_p = \Omega. \quad (3.87)$$

Now, comparing Eqs. (3.86) and (3.87) with (3.56) and (3.57) one can see that, under the Lewenstein
model in the velocity gauge, the terms \((-e\mathbf{E}(t) \cdot \mathbf{R}_i)\) and \((-e\mathbf{E}(t') \cdot \mathbf{R}_j)\) do not appear in the saddle-point equations. Having a look at Eqs. (3.26) and (3.31), we conclude that two of the saddle-point equations for a molecule in the velocity gauge are the same as for an atom in the length gauge. In this case, no unphysical extension of the plateau is expected. These results suggest that, when the Lewenstein model is applied to molecules with large internuclear distances and for low laser intensities [i.e., for large values of \(Q\); see, Eq. (3.59)], the velocity gauge would be the preferable one [109]. Nevertheless, according to Refs. [101, 104], the length gauge can be safely applied when the values of the parameter \(Q\) are reasonably small, with no evidence of an unphysical increment of the cutoff value. Finally, by comparing Eq. (3.51) for \(\mathbf{R}_i = \mathbf{R}_j = 0\) with Eq. (3.21), we notice that the saddle-point equations arising from the Lewenstein model are the same in the velocity and length gauges for the atomic case.

### 3.2.7 Spectral response

In the previous Sections we have shown that the Lewenstein model allows one to calculate the time-dependent dipole moment \(d(t)\) [either \(d_L(t)\) in the length gauge or \(d_V(t)\) in the velocity gauge] induced by the interaction of the laser field and the atomic or molecular target. As the harmonic signal is detected at distances much larger than the dimensions of the source, the power radiated by the oscillating dipole moment can be approximated according to the Larmor formula [80],

\[
P(t) = \frac{2}{3\pi c^3} \ddot{d}(t)^2 . \tag{3.88}
\]

It defines the spectral density of radiation emitted over all times,

\[
P(\Omega) = \frac{2}{3\pi c^3} |\tilde{d}(\Omega)|^2 , \tag{3.89}
\]

where \(\tilde{d}(\Omega)\) is the Fourier transform of the dipole moment \(d(t)\). For our further purposes, we define the harmonic spectral response polarized along a certain direction \(n\), where \(n^2 = 1\),

\[
\mathcal{I}_n(\Omega) = \frac{2\Omega^4}{3\pi c^3} |\mathbf{n} \cdot \tilde{d}(\Omega)|^2 . \tag{3.90}
\]

In this thesis, the spectral response \(\mathcal{I}_n(\Omega)\) is obtained by calculating the time-dependent dipole moment \(d(t)\) and performing the Fourier transform by numerical methods. No further approximations are used.

### 3.2.8 Quantum trajectories in the Lewenstein model

As it was pointed out in Sections 3.2.2, 3.2.4, and 3.2.6, many features of HHG can be understood by solving a set of three saddle-point equations. When the harmonic target is a single atom at the origin of coordinates, the saddle-point equations [Eqs. (3.21), (3.26), and (3.31)] are the same in the velocity and length gauges. Their numerical solution shows that, for each photon energy below
the cutoff, two roots \( t_s^{(1)} \) and \( t_s^{(2)} \) are obtained, with corresponding \( t_s^{(1)'} \) and \( t_s^{(2)'} \). This shows that, during the laser period, ionization and recombination processes can take place twice. In general, one of the recombination times corresponds to a longer electron excursion in the continuum, whereas the second root shows a shorter interval between ionization and recombination. As in the TSM, the first case corresponds to a long trajectory and the second one to a short trajectory [107]. Contrary to the semiclassical approach, the trajectories arising from the Lewenstein model are complex due to the complex initial conditions associated with Eq. (3.26).

Even though the analysis in Sec. 3.2.2 was carried out in the length gauge, the numerical solution of the saddle-point equations in the velocity gauge predicts, in a similar way, the presence of long and short trajectories. Next, we will show how the time-frequency analysis can be used to visualize the quantum trajectories.

### 3.2.8.1 Time-frequency analysis

As we have mentioned above, the interpretation of HHG under the scope of the Lewenstein model is easier by considering the electron quantum trajectories. The saddle-point approximation allows us to calculate such trajectories in a standard way, without many complications. When the spectral responses are calculated by solving TDSE, by other ab-initio calculations or by performing the time and momentum integrals in the Lewenstein model exactly, the physical intuition gets blurred. Fortunately, the time-frequency analysis allows one to visualize the electron trajectories for any harmonic spectrum, without relying on approximations. The aforementioned method consists of the systematic multiplication of the spectral response by a window in order to isolate the signal at specific frequencies. After that, the inverse Fourier transform is applied and the data is recovered in the time domain for the selected frequencies. The window (or wavelet) employed in the present calculations is a Gaussian function described by the equation

\[
W(\Omega_G, \Omega) = e^{-\frac{(\Omega-\Omega_G)^2}{2\sigma^2}}.
\]  

(3.91)

Here, \( \Omega \) is the harmonic frequency, \( \Omega_G \) is a parameter that runs from 0 up to the end of the harmonic spectrum and corresponds to the central peak of the Gaussian, \( \sigma \) determines the accuracy in frequency domain and it is related to the full width at half maximum (FWHM), \( \text{FWHM} = 2\sqrt{2\ln2} \sigma \). The last parameter has to be chosen carefully because, according to the uncertainty principle, the width of the temporal resolution is inversely proportional to the width of frequency resolution [110]. After the inverse Fourier transform is performed, the signal is obtained as a function of the selected harmonic frequency \( \Omega_G \) and the emission time,

\[
\text{Signal}_n(\Omega_G, t) = \frac{1}{2\pi} \left| \int d\Omega e^{-i\Omega t} W(\Omega_G, \Omega) \mathcal{I}_n(\Omega) \right|.
\]  

(3.92)

Here, \( \mathcal{I}_n(\Omega) \) is given by Eq. (3.90) and \( W(\Omega_G, \Omega) \) is the Gaussian wavelet defined above. The signal is plotted as a function of the selected harmonic order (\( \Omega_G/\omega_L \)) and laser cycle \( [\omega_L t/(2\pi)] \).
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Figure 3.1  The left panel is a graphical illustration of the time-frequency analysis. The right panel shows a typical color mapping of the HHG signal after performing the wavelet analysis, with the short trajectories visualized by a positive slope and the long ones by a negative slope. This particular time-frequency analysis does not correspond to the spectrum shown in the left panel but it has been chosen for illustrative purposes.

In the left panel of Fig. 3.1, we illustrate graphically the scheme of the applied wavelet analysis. The Gaussian function, centred at the frequency $\Omega_G$, selects certain frequencies to be analyzed. The FWHM determines the extension of the harmonic spectrum which is considered. In the right panel of the same figure, we show a typical time-frequency analysis of the HHG signal. The short trajectories, generally more intense, always appear with a positive slope, whereas the long ones are characterized by a negative slope [33]. In the next Chapter, the wavelet analysis is going to be used in order to visualize regions where different quantum trajectories may interfere.

3.3 Summary

In this Chapter, the high-order harmonic generation has been described using the semiclassical three step model and its quantum-mechanical counterpart, the Lewenstein model. The general characteristics of the harmonic response, which include a long plateau followed by a sharp cutoff located at photon energies of $3.17U_p + I_p$ (obtained under the scope of the semiclassical model [25–27]) or $3.17U_p + 1.32I_p$ (obtained from the quantum-mechanical treatment [29]), were introduced. The concepts of long and short, classical and quantum trajectories which contribute to the HHG have been recognized as important tools to understand the process.

In Sec. 3.2.1, the Lewenstein model was presented for a single atomic centre in the length gauge. The integrals over momentum were approximated according to the saddle-point technique and the HHG was analyzed with the help of the saddle-point equations in time. In Sec. 3.2.4, the model was modified in order to account for multicentre systems.

Finally, in Sec. 3.2.6, the modified Lewenstein model for molecules has been presented in the velocity gauge. It has been shown that the two gauges show differences in the semiclassical action and in the expressions for the ionization matrix elements. The calculations in the length gauge involve...
the kinetic momentum of the electron in the presence of a laser field, whereas in the velocity gauge they relate to the canonical momentum. We pointed out that the possible unphysical effects observed in [109], when the length gauge is applied to molecules, are less important for small values of the parameter $Q$ defined by Eq. (3.59).
Chapter 4

Application of the Lewenstein model to molecules

High-order harmonic generation from molecules is a much richer phenomenon compared to the atomic case. The new degrees of freedom and the possibility of molecular alignment make it feasible to develop new techniques to control the harmonic response from molecules [111]. Multicentre interference\(^1\) effects and the spatial distribution of the molecular wave function have proven to be fundamental for the analysis and control of HHG [112]. These properties are the basis of molecular orbital tomography, as proposed in Ref. [35]. In order to retrieve information about the system, it is necessary to achieve certain degree of molecular alignment. It has been shown that the interaction of strong linearly-polarized fields with linear molecules induces their sharp alignment along a specific direction, but the molecules are still free to rotate around the main axis (see, Ref. [113] and references therein). In contrast, the use of elliptically-polarized fields can fix the three Euler angles describing the position of polyatomic molecules [113, 114].

Multicentre interference from diatomic and small polyatomic molecules causes the reduction of certain harmonics intensities. As well, it has proven to have important effects on the phase and polarization of the harmonic signal, depending on the molecular orbital symmetry [112, 115–119]. Even though such effects play a fundamental role in understanding the harmonic response, another phenomenon, the interference of quantum trajectories, can generate extensive modulations in the spectrum, as it has been demonstrated theoretically and experimentally in Refs. [120–122].

HHG from small molecules has been extended to analyze larger carbon structures. For example, the \(C_{60}\) fullerene has attracted most attention due to its unique properties. First of all, its very symmetric structure avoids the problem of alignment in the medium that other less symmetric molecules require. Its large polarizability, large stability in the presence of strong laser fields, and a considerable increase of the saturation intensities compared to single atoms with the same ionization potential make this structure even more attractive when high laser intensities are involved [123]. As well, it

\(^1\)By multicentre interference we understand the interference originated from the recollision of the electron wave packet with more than one atomic centre. This takes place during recombination.
has been recognized that the harmonic response from the thin graphite layers can be controlled by modifying the polarization and intensity of the driving field [124].

It has been shown that multicentre interferences cause the pronounced modulations of the peak intensities in the harmonic response from large carbon, symmetric fullerenes. These interferences are directly related to the size and molecular symmetry of these structures [101, 104].

The intensity of a certain harmonic has a strong connection to the symmetry and structure of molecular orbitals, and to the particular arrangement of nuclei positions. Therefore, a detailed observation of the plateau, together with the cutoff location, could give important information about the molecule. As it will become clear in this Chapter, the modulations of the plateau constitute a fingerprint of the molecular structure and its symmetry. The polarization properties of the emitted harmonics are sensitive to the atom locations and the structure of molecular orbitals. Note that these observations could make it possible to differentiate between carbon clusters.

Even though we use the single-active-electron approximation in this thesis, it is worth noting that multielectron effects can play an important role in HHG. When the SAE approximation is used, important quantum-mechanical properties such as the indistinguishability of electrons are ignored [125, 126]. However, multielectron dynamics has to be accounted for in order to study the polarization and excitation of neutral atoms by the laser field, polarization and excitation of ions by the colliding electron wave packet, and electron exchange effects [127]. To account for the indistinguishability of electrons, new terms related to the transition dipole between the highest occupied molecular orbital (HOMO) and other bound molecular orbitals need to be added [125]. This is particularly important for molecular orbital tomography, as it has been pointed out in Refs. [125–127]. It has been shown that multielectron contributions can play an important role in calculations of the harmonic response from molecules with orbitals presenting similar ionization potential perpendicular to the molecular axis (see, [102] and references therein). Nevertheless, as the first approximation, we neglect such effects in this thesis.

The goal of the next Section is to analyze the relation between the geometric properties of different $C_{20}$ isomers and the spectral properties of harmonics under the SAE approximation. Modulations of the plateau peak intensities for symmetric and less symmetric molecular structures, together with the polarization properties of the emitted radiation (which we introduce as a new and very important parameter in the HHG analysis), are going to be explored in order to gain a better understanding of the process. Our numerical calculations are carried out under the modified Lewenstein model in order to include multicentre effects. We present results in both the velocity and length gauges. In the last Section, we study the harmonic ellipticity obtained from nitrogen molecules interacting with linearly-polarized fields.

### 4.1 $C_{20}$ isomers

Fullerenes are defined as closed graphitic structures with the chemical formula $C_n$, possessing exactly 12 pentagonal and $(n/2 - 10)$ hexagonal rings [128]. Their stability is directly related to
the number of carbon atoms $n$ and their distribution, which is due to the large strain generated by the vicinity of pentagons [129]. One of the most important criteria for the fullerenes stability is the so-called isolated pentagon rule, developed by Kroto [130], which establishes that the most stable fullerene is the one consisting of pentagons separated as far as possible from each other [128]. When the size of the structure is reduced, the proximity between pentagons makes it more reactive and unstable. Even though the smallest possible fullerene, the $C_{20}$, containing only 12 pentagons should be unstable, many theoretical studies predicted its stability together with at least two more isomers, the bowl (which can be considered as a $C_{60}$ fragment) and the monocyclic ring [129, 131]. The first evidence of the bowl and fullerene was presented in 2000 by Prinzbach et al., who obtained the two compounds by debromification of the corresponding halogenated structures [132].

In order to calculate the molecular orbitals for these structures, the Hartree-Fock methods included in the quantum chemistry package GAMESS [133] are used after a proper convergence is guaranteed. In order to model the atomic orbitals of each carbon atom, eleven GPs corresponding to $s$ orbitals and five GPs corresponding to $p$ orbitals are used. In the Pople’s notation [134, 135], the basis set used in our calculations is denoted as 6-311G.

The main goal of this Section is to analyze the three most important $C_{20}$ isomers: bowl, ring, and symmetric cage. In Fig. 4.1, the spatial molecular distribution of these structures, according to the Hartree-Fock calculations, is presented. It can be seen that the ring is a monocyclic structure of carbon atoms connected by double bonds. The bowl consists of a characteristic pentagon surrounded by 5 hexagons containing single and double bonds. The cage shows the expected 12 pentagons with single and double bonds between the carbon atoms.
Chapter 4. Application of the Lewenstein model to molecules

<table>
<thead>
<tr>
<th>$C_{20}$ Structure</th>
<th>$I_p^{\text{HOMO}}$ (a.u.)</th>
<th>$I_p^{\text{HOMO}-1}$ (a.u.)</th>
<th>$d_x$ (D)</th>
<th>$d_y$ (D)</th>
<th>$d_z$ (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ring</td>
<td>0.3209</td>
<td>0.3192</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Bowl</td>
<td>0.3658 *</td>
<td>0.3568 *</td>
<td>0.0</td>
<td>0.0</td>
<td>0.2048</td>
</tr>
<tr>
<td>Fullerene</td>
<td>0.3293</td>
<td>0.2782</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Table 4.1 Ionization potentials and static dipole moments for three stable $C_{20}$ isomers shown in Fig. 4.1. The data was obtained by the Hartree-Fock methods according to the quantum chemistry package GAMESS using the 6-311G basis set. The asterisk (*) denotes a two-fold degeneracy of the molecular orbital. Only ionization potentials of HOMO and HOMO-1 are presented, as they are the most important for the analysis developed in this Section.

Due to the symmetry exhibited by the fullerene and ring, no permanent dipole moment is observed for these structures. In contrast, the bowl has a permanent dipole moment along the $z$-direction, which is a consequence of the lack of an inversion centre. In Table 4.1, we present the values of the mentioned static dipole moments together with the calculated ionization potentials of the HOMO ($I_p^{\text{HOMO}}$) and HOMO-1 ($I_p^{\text{HOMO}-1}$). Note that the HOMO-N refers to the molecular orbital which, on the energy scale, is the N-th orbital below HOMO.

### 4.1.1 Calculations of HHG from $C_{20}$ isomers

In order to analyze the harmonic response from $C_{20}$ isomers, the Lewenstein model using the velocity and length gauge formalisms was applied. As the considered structures are multicentred, the expressions for the saddle point in momentum and for the semiclassical action were modified, as introduced in the previous Chapter, and the LCAO approximation using the expansion in terms of GPs was used to approximate the molecular orbitals. The parameters $C_l$, $\alpha_k$, and $\eta_k$ in Eqs. (3.37) and (3.38) were directly obtained from the Hartree-Fock calculations. The numerical analysis was carried out following the steps:

- The integration over momentum in the complex dipole moment $D(t)$ was approximated using the saddle-point method. The saddle points in momentum, as functions of $t$ and the return time $\tau$, were calculated according to Eq. (3.51) with $t' = t - \tau$.

- The modified semiclassical action was calculated according to either Eq. (3.50) or (3.82), depending on the gauge.

- Ionization and recombination matrix elements were calculated as sums over different orbital contributions $d^k_s$, $d^k_p_x$, $d^k_p_y$, and $d^k_p_z$ expressed by Eqs. (3.45) to (3.48) for the length gauge, and by Eqs. (3.70) to (3.73) and (3.77) to (3.80) for the velocity gauge. In general, homonuclear carbon molecules can be very well described by a linear combination of $s$ and $p$ orbitals.
The complex dipole moment was calculated in the length gauge according to the following expression,

$$D_L(t) = i e^2 \int_0^\infty d\tau \left( \frac{2\pi}{\epsilon + i\tau/m} \right)^{3/2} \sum_{i=1}^N \sum_{j=1}^N \exp[-iS_L(p_s, t, t - \tau, R_i, R_j)]$$

$$\times d_{\text{rec}}^L(p_s - eA(t), R_i) [d_{\text{ion}}^L(p_s - eA(t - \tau), R_j) \cdot \mathcal{E}(t - \tau)], \quad (4.1)$$

whereas, in the velocity gauge, according to

$$D_V(t) = \frac{i e^2}{m} \int_0^\infty d\tau \left( \frac{2\pi}{\epsilon + i\tau/m} \right)^{3/2} \sum_{i=1}^N \sum_{j=1}^N \exp[-iS_V(p_s, t, t - \tau, R_i, R_j)]$$

$$\times d_{\text{rec}}^V(p_s, R_i) [d_{\text{ion}}^V(p_s, R_j, t - \tau) \cdot A(t - \tau)]. \quad (4.2)$$

We performed numerically the integration over $\tau$ and no further approximations were assumed. See Chapter 3 for details concerning these formulas.

Once the time-dependent dipole moment $d(t) = D(t) + D^*(t)$ was obtained, the power spectrum of harmonics polarized in a certain direction was calculated using Eq. (3.90).

In order to reduce the influence of undesired frequency components, a standard Blackman window (see, Ref. [136]) was used to filter the data before performing the fast Fourier transform in (3.90).

### 4.1.2 Analysis of spectral modulations using the recombination matrix element

It has been shown that the harmonic response from molecules can exhibit strong modulations of the intensity along the plateau (see, e.g., Refs. [101, 104, 116]). In general, when the atomic case is considered, the returning electron wave packet collides with a unique centre whereas, in the molecular case, many atomic centres are present, leading to pronounced interference minima. The position and intensity of the suppressed harmonics depend strongly on the molecular orientation and orbital configuration [116]. As the interference effects are directly related to the distribution of atoms, a detailed analysis of the minima of peak intensities in the harmonic spectrum can provide valuable information about the molecule. It has been proven for other fullerenes and multiatomic systems that some of the modulations in the spectrum along the plateau are strongly related to the recombination matrix element, presenting minima in the region when the RME vanishes [101, 104]. Other type of spectral modulations is traditionally related to interferences between different quantum trajectories [29, 117].

As it follows from Chapter 3, the RMEs in the length and velocity gauges have the same form except that the kinetic momentum in the length gauge is replaced by the canonical momentum in the velocity gauge. For convenience of the reader, let us recall that the RME for the molecule is calculated...
according to the formula,

\[
d_{\text{rec}}(p) = \frac{1}{(2\pi)^{3/2}} \sum_{j=1}^{N} \sum_{\ell=0}^{n} C_{\ell} N_{\ell} \sum_{k \eta} \sum_{n,b,c} \int d\mathbf{r} (x-x_j)^a (y-y_j)^b (z-z_j)^c e^{-\alpha_k (r-R_j)^2} r^\ell e^{i\mathbf{p} \cdot \mathbf{r}}, \tag{4.3}
\]

where, depending on the gauge, one should substitute the respective momentum. Since the RME is a function of the electron momentum during the recombination and the harmonic response depends on the frequency of the emitted photon, it is possible to relate these two quantities. In doing so, we use the energy conservation relation [101, 104]

\[
\Omega = \frac{1}{2m} \mathbf{\Pi}^2 + I_p. \tag{4.4}
\]

This relation allows us to find the harmonic frequencies for which the RME vanishes. Since now on, we will express the frequency of emitted HHG radiation in terms of the driving field frequency [29]. That is we will use the notion of the harmonic order \( \mathcal{N} \) such that \( \Omega = \mathcal{N} \omega_L \).

As it has been pointed out before, when a multicentre system is considered, the saddle point in momentum has nonzero components in all directions [see, Eq. (3.51)], depending on the molecular geometry and orientation. If the internuclear distance is small enough (more precisely, if the parameter \( Q \) [Eq. (3.59)] is small enough), it is expected that the main component of the saddle point in momentum is parallel to the laser field polarization direction. The other components can be fairly large as well, especially for small values of \( \tau \). In the following, the RME is calculated as a function of the harmonic order \( \mathcal{N} \) by increasing the momentum (kinetic or canonical) in just one direction and setting the other components to zero. This gives an idea of the approximate behavior of the RME along the plateau, accounting for the three momentum components separately.

### 4.1.2.1 Spectral responses in the length gauge

In this Section, the properties of HHG signal from the \( C_{20} \) isomers are studied within the length gauge. We consider a semi-infinite and monochromatic plane wave laser field described by the electric vector,

\[
\mathbf{E}(t) = \begin{cases} 
\mathbf{E}_0 \mathbf{e}_j \sin(\omega_L t) & \text{if } t \geq 0, \\
0 & \text{if } t < 0.
\end{cases} \tag{4.5}
\]

The field is linearly polarized with the polarization vector \( \mathbf{e}_j \) (\( j = x, y, z \)). \( \mathbf{E}_0 \) is the field amplitude. We assume, similar to Chapter 2, that the field frequency is \( \omega_L = 1.55 \) eV (wavelength \( \lambda = 800 \) nm), which corresponds to the Ti-Sapphire laser. In order to study the spectral modulations of the HHG plateau, a relatively large intensity of \( 5 \times 10^{14} \) W/cm\(^2\) is chosen such that the cutoff is located beyond the 60th harmonic. It can be clearly seen in Table 4.2 that, for such laser parameters, the \( Q \) values are small enough, with the largest value equal to 0.21 for the ring. This suggests that the length gauge can be safely applied for all considered carbon systems.
### Table 4.2

The maximum distance between two atoms in the molecule and the corresponding parameter $Q$ [Eq. (3.59)] calculated for the laser field intensity $I = 5 \times 10^{14} \text{W/cm}^2$ and the wavelength $\lambda = 800 \text{nm}$.

<table>
<thead>
<tr>
<th>Structure</th>
<th>$R_{\text{max}}$ (a.u.)</th>
<th>$Q$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ring</td>
<td>15.6</td>
<td>0.21</td>
</tr>
<tr>
<td>Bowl</td>
<td>12.2</td>
<td>0.16</td>
</tr>
<tr>
<td>Fullerene</td>
<td>7.8</td>
<td>0.11</td>
</tr>
</tbody>
</table>

Note that a linearly-polarized laser field interacting with molecules can generate harmonic responses in directions perpendicular to the driving field polarization [109]. Thus, the complete study of the HHG should involve three different harmonic responses for each laser field polarization. In total, nine responses are calculated for each isomer. In order to distinguish between them, each response is going to be denoted as $d_{ij}$ ($i, j = x, y, z$), where the first index indicates the harmonic polarization whereas the second index relates to the driving field polarization direction. In other words, for a given polarization direction of the laser field $e_j$, there are three possible harmonic responses $I_{e_i}(\Omega)$ [Eq. (3.90)], which are denoted as $d_{ij}$.

In this Section, we show the harmonic responses obtained from the HOMO of each isomer, whereas in Sec. 4.1.2.2 we will analyze the contribution of HOMO-1 to the HHG spectrum. The results which account for contributions of other inner orbitals are presented in Appendix F.

**$C_{20}$ fullerene**

When the laser field polarized along the $x$-axis interacts with the cage (Fig. 4.1c), a strong harmonic response is observed in the $x$-direction, with a plateau characterized by multiple modulations in the peak intensity. The spectral response $d_{xx}$ as a function of the harmonic order is presented in Fig. 4.2b. The most visible minima are located between the 23rd and 27th, 31st and 39th, and 55th and 65th harmonic orders (HOs). In Fig. 4.2a, we present the modulus squared of the $x$-component of the recombination matrix element, calculated according to Eq. (4.3). As the present analysis is carried out in the length gauge, the RME depends on the kinetic momentum $\Pi$ which is not necessarily parallel to the laser field polarization direction. For this reason, we present three curves - each plotted by parameterizing the harmonic order $N$ with a certain component of the kinetic momentum $\Pi$: the solid blue line is for $\Pi_x$, the dashed red line is for $\Pi_y$, and the dashed-dotted green line is for $\Pi_z$. It is expected that, for systems characterized by small values of the parameter $Q$, the major contribution to the kinetic momentum (2.206) arising from the saddle points (3.51) should be parallel to the laser field polarization direction (solid blue line). It can be seen that the spectral minima from the 23rd to 27th and from the 55th to 65th harmonic orders (the most prominent modulations) match very well with the zeroes of the RME as a function of $\Pi_x$. The regions from the 19th to 21st (less pronounced) and from the 31st to 39th harmonics are located near the points where the RME vanishes as a function of $\Pi_y$ (dashed red line). The most pronounced minima agree with the zeroes of the RME and, therefore, one can attribute the corresponding modulations to interference effects arising from the multicentre structure of the molecule. Similar minima have been observed in other harmonic responses obtained from larger icosahedral fullerenes [101]. It is worth noting that when, for the given
Chapter 4. Application of the Lewenstein model to molecules

Figure 4.2  Panel a presents the modulus squared of the $x$-component of the recombination matrix element as a function of the harmonic order for the $C_{20}$ fullerene. The harmonic order $N$ is related to the kinetic momentum of the electron $\Pi$ through the relation $N = \omega L = \Pi^2/(2m) + I_p$. Therefore, to plot the dependence of the corresponding RME on $N$, we vary one component of $\Pi$ while the other two we set to zero. Thus, the solid blue line corresponds to the harmonic order expressed in terms of $\Pi_x$, the dashed red line is for $\Pi_y$, whereas the dashed-dotted green line is for $\Pi_z$. Panel b shows the harmonic response $d_{xx}$ as a function of $N$ calculated for the HOMO of the $C_{20}$ fullerene. The laser field is described by Eq. (4.5) and it is considered to be polarized along the $x$-direction, with the wavelength $\lambda = 800\text{nm}$ and the intensity $I = 5 \times 10^{14}\text{W/cm}^2$.

Figure 4.3  The left column presents the harmonic response from the HOMO of $C_{20}$ fullerene when the laser field is polarized along the $y$-direction ($d_{yy}$ harmonic response is presented in panel a and $d_{zy}$ response in panel c). The right column corresponds to a polarization of the driving field along the $z$-direction ($d_{yz}$ response is presented in panel b and $d_{zz}$ response in panel d). The remaining laser field parameters are the same as in Fig. 4.2.
Figure 4.4  Panel a presents the modulus squared of the \( x \)-component of the recombination matrix element as a function of the harmonic order parametrized by either \( \Pi_x \) (solid blue line) or \( \Pi_y \) (dashed red line) for the ring. \( |d_{\text{rec},x}|^2 \) vanishes as a function of \( \Pi_z \). Panel b shows the same but for the \( y \)-component of the RME. In panels c and d the harmonic responses \( d_{xx} \) and \( d_{yy} \) are shown, respectively. The laser field parameters are the same as in Fig. 4.2. Only the HOMO for the ring is taken into account in the calculations.

It can be seen from Fig. 4.3 that, in the plateau region, all spectra present smoother variations of the peak intensities as compared to the \( d_{xx} \) case (i.e., the envelope of the peaks shows less modulations). In all four cases, the \( y \)- and \( z \)-components of the RME vanish independently of the kinetic momentum direction. This can be considered as a consequence of the symmetry of the molecular orbitals. As we have checked, if any of the atoms is artificially displaced from its original position the RME presents strong oscillations, similar to the \( d_{xx} \) case. The very smooth modulations along the plateau are, as it will be shown later, consequences of interferences between quantum trajectories.
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Figure 4.5 HHG spectra generated from the HOMO orbital of the ring. The harmonic responses $d_{yx}$ and $d_{xy}$ are shown in panels a and b, respectively. The laser field parameters are the same as in Fig. 4.2.

C$_{20}$ ring

The ring (Fig. 4.1a) is an interesting C$_{20}$ isomer due to its planar configuration and its highly symmetric structure with respect to the z-axis. When the $d_{xx}$ and $d_{yy}$ responses are considered, strongly modulated harmonic plateaus are observed (panels c and d of Fig. 4.4). Similarly to the case of the C$_{20}$ fullerene, the modulations of the HHG spectra are related to oscillating components of the RME (with their modulus squared presented in panels a and b of the same figure). Some of the most pronounced minima (located from the 37th to 47th and from the 51st to 65th HOs) can be directly related to the zeroes of the RME components (solid blue line in panel a for $d_{xx}$ and dashed red line in panel b for $d_{yy}$). In panels c and d of Fig. 4.4, the peaks in the range between the 17th and 23rd harmonics present strong modulations. In this region the RME components reach zero at several points.

When the laser field is polarized along the x- or y-directions, two other harmonic responses are observed ($d_{yz}$ and $d_{xy}$), which are presented in Fig. 4.5. Due to the geometry of the molecule and, therefore, also the symmetry of the wave function in the xy-plane, one can expect to obtain similar results for both laser polarization along x- and y-directions. This is confirmed by our results, as one can see by comparing panels c and d in Fig. 4.4 and panels a and b in Fig. 4.5. There are relatively small differences in the intensity of some peaks, which are related to imperfect symmetry of the wave function introduced by the numerical error of ab-initio calculations using the GAMESS code. Nevertheless, the spectra are very similar.

When the driving field is polarized along the z-axis, just one harmonic response, $d_{zz}$, is observed (Fig. 4.14e). In this case, the z-component of the RME vanishes independently of the harmonic order and the resulting spectrum presents the characteristic smooth plateau.
Figure 4.6  HHG spectra generated from the HOMO orbital of the bowl. The laser field is polarized along the $x$-axis (top row), the $y$-axis (middle row), and the $z$-axis (bottom row). Harmonic responses are $a \ d_{yz}$, $b \ d_{zx}$, $c \ d_{xy}$, $d \ d_{zy}$, $e \ d_{xz}$, and $f \ d_{yz}$. The laser field parameters are the same as in Fig. 4.2.

$C_{20}$ bowl

The bowl (Fig. 4.1b) is the least symmetric of the studied $C_{20}$ isomers, which directly influences the harmonic spectrum. As demonstrated in Figs. 4.6 and 4.7, all nine harmonic responses (for different combinations of the laser field and harmonic polarizations) are nonzero. In addition, all of them exhibit several modulations along the plateau, being the least prominent for the $d_{zz}$ case (Fig. 4.7f).

In Fig. 4.7, the $d_{xx}$, $d_{yy}$, and $d_{zz}$ spectra are plotted together with the modulus squared of the three components of the RME as functions of the harmonic order parametrized by either $\Pi_x$ (solid blue line), $\Pi_y$ (dashed red line), or $\Pi_z$ (dashed-dotted green line). For this particular structure, due to the generally complicated shape of the plateau, a comparison between the RME zeroes and expected minima of the HHG envelope is not as clear as in the previous two cases. When analyzing the $d_{xx}$ response (Fig. 4.7d), a minimum can be found between the 21st and 35th harmonics, which coincides with minima of the solid blue and dashed red lines in Fig. 4.7a. We suspect that other modulations can be attributed to the oscillations of the RME as a function of all three components of $\Pi$. Interference between electron (short and long) trajectories starting at different atoms are also expected to influence modulations of the peak intensities in the HHG spectrum. What is certain is that the $x$-component of the RME as a function of $\Pi_x$ does not contribute to destructive interference due to the absence of zeroes in the plateau region (dotted-dashed green line in Fig. 4.7a). A similar analysis can be applied to the spectral response $d_{yy}$ shown in Fig. 4.7e. A general decrease of the HHG peaks is observed.
Figure 4.7  Panel a shows the modulus squared of the $x$-component of the RME as a function of the harmonic order parametrized by either $\Pi_x$ (solid blue line), $\Pi_y$ (dashed red line), or $\Pi_z$ (dashed-dotted green line) for the bowl isomer. Panel b shows the same but for the $y$-component of the RME, whereas panel c is for the $z$-component of the RME. Note that $|d_{rec,z}(\Pi_z)|^2$ vanishes for the considered harmonic orders. Panels d, e, and f present the harmonic responses $d_{xx}$, $d_{yy}$, and $d_{zz}$, respectively. The results have been obtained for the HOMO orbital of the bowl. The laser field parameters are the same as in Fig. 4.2.

between the 25th and 35th HOs, which corresponds to the minimum of $|d_{rec,y}|^2$ represented by the dashed red curve in Fig. 4.7b. The following peaks show lower intensities, which can be attributed to small values of the $y$-component of the RME.

The $d_{zz}$ spectrum (Fig. 4.7f) shows a different behavior. Even though we observe small modulations of the peaks comprising the plateau, the general trend is more uniform than in the previous two cases. It can be explained by the rapid decrease of $|d_{rec,z}|^2$ with increasing the harmonic order, as shown in Fig. 4.7c. While $|d_{rec,z}(\Pi_z)|^2$ is expected to have a strong influence on the spectrum, it vanishes at the considered range of HOs. Note that, in the absence of oscillations of the RME, the harmonic response presents a relatively smooth plateau.

Let us note that, in all spectra obtained from the bowl, peaks corresponding to even multiples of the driving frequency, in addition to the well-defined odd harmonics, are present. This feature is not observed for other two structures, which is a direct consequence of symmetry of the molecule. Even though the bowl has an axial symmetry, it is not symmetric with respect to the $xy$-plane. The appearance of even harmonics in the spectrum has been observed when the Lewenstein model is applied, in both length and velocity gauges, to atoms or molecules displaced from the origin of coordinates.
### Table 4.3

<table>
<thead>
<tr>
<th>Structure</th>
<th>(N_{\text{cutoff}}^{\text{HOMO-1}})</th>
<th>(N_{\text{cutoff}}^{\text{HOMO}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ring</td>
<td>69</td>
<td>69</td>
</tr>
<tr>
<td>Bowl</td>
<td>70</td>
<td>69</td>
</tr>
<tr>
<td>Fullerene</td>
<td>69</td>
<td>68</td>
</tr>
</tbody>
</table>

Table 4.3  Cutoff position of the HHG plateau for the HOMO and HOMO-1 calculated according to Eq. (3.36) and for the values of ionization potential taken from Table 4.1. The laser field intensity is \(I = 5 \times 10^{14}\) W/cm\(^2\) and the wavelength \(\lambda = 800\) nm.

[109]. The crucial point to observe the appearance of even harmonics is the absence of an inversion point of symmetry in the molecule.

It is worth noting that all harmonic responses from \(C_{20}\) isomers calculated in this Section have a very sharp cutoff at the positions described by the relation (3.36), with the numerical values presented in Table 4.3. In other words, no unphysical extension of the plateau is observed. This is expected due to small values of the parameter \(Q\). It also agrees with the observations presented in Refs. [101, 104].

#### 4.1.2.2 Multiorbital contributions: influence of HOMO-1

One of the challenges related to studying HHG from large molecules and nanostructures is that a large number of electrons makes it relatively easy to ionize the system. Note also that the ionization potentials for several valence orbitals can differ by less than one electronvolt. For this reason, one often needs to consider multiple molecular orbitals in the LCAO expansion and the contributions from

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Figure 4.8  The same as in Fig. 4.7 after including the contribution of the HOMO-1.
different orbitals can interfere. In this Section we present how, for the $C_{20}$ isomers, the contribution of HOMO-1 modifies the HHG spectra. The behavior of RMEs is expected to change as well. It is particularly important to include the HOMO-1 in calculations for the ring and bowl, due to the close values of ionization potentials of the HOMO and HOMO-1 reported in Table 4.1.

Fig. 4.8 shows the same as Fig. 4.7 but it includes the contributions from both orbitals, the HOMO and HOMO-1 of the bowl. Comparing these results, one can see a different behavior of the solid blue and dashed red curves which are related to $\Pi_x$ and $\Pi_y$, respectively. This is in contrast to the dashed-dotted green curve which does not show pronounced changes. The $d_{zz}$ harmonic responses (Figs. 4.7f and 4.8f) are almost identical meaning that, in this case, the contribution of HOMO-1 does not play an important role. For $d_{xx}$ and $d_{yy}$, the major differences appear between the 10th and 40th HOs, where the RMEs differ the most. Nevertheless, zeroes and minima of the modulus squared of the RME components are generally located at the same positions.

Fig. 4.9 shows the other harmonic responses obtained from the bowl after the contribution of HOMO-1 is included. Even though the general trend of the plateau in panels a - d is very similar to the case when just the HOMO is accounted for (Fig. 4.6), some of the peaks intensities are modified after the contribution of HOMO-1 is added. This is particularly true for the region between the 40th harmonic and the cutoff. As expected, the minima of the spectral envelopes in panels a - d of Figs. 4.6 and 4.9 seem to be maintained at roughly same locations. The most important changes are present in panels e and f. While the responses show a higher intensity, the plateau modulations become less pronounced.

Considering now the $C_{20}$ fullerene and comparing Figs. 4.2a and 4.10a, one can clearly see that no important modifications of the RME are observed after the contribution from the HOMO-1 is included.
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Figure 4.10 The same as in Fig. 4.2 after including the contribution of the HOMO-1.

Figure 4.11 Modulus squared of the $y$- (panel a) and the $z$-component (panel b) of the RME and harmonic responses obtained from the $C_{20}$ fullerene, taking into account the contributions from both the HOMO and HOMO-1. The laser field is polarized either along the $y$-direction (left column) or along the $z$-direction (right column). The harmonic responses $d_{yy}$, $d_{yz}$, $d_{zy}$, and $d_{zz}$ are presented in panels c, d, e, and f, respectively. In contrast to the case when only the HOMO is considered, the contribution from HOMO-1 results in nontrivial dependence of the $y$- and $z$-components of the RME on $\Pi_x$. The remaining RMEs vanish, as in the HOMO case. The laser field parameters are the same as in Fig. 4.2.
added. When looking at the dashed-dotted curves, a general increase of the RME values is observed, but the RME zeroes are located at the same positions. The resulting harmonic response $d_{xx}$, presented in Fig. 4.10b, is almost identical as compared to the purely HOMO case (Fig. 4.2b). In fact, one can see a small increase of the $d_{xx}$ peaks once the HOMO-1 is considered. This follows from the fact that $|d_{rec,x}|^2$ as a function of $\Pi_z$ (dashed-dotted curve) is enhanced in this case.

Other harmonic responses from the fullerene are shown in Fig. 4.11 (see also Fig. 4.3, where only the contribution from the HOMO is considered). When the HOMO-1 is included in the calculations, the $y$- and $z$-components of the RME as a function of $\Pi_x$ acquire nonzero values (panels a and b of Fig. 4.11). This can generate minor changes in the modulations of the plateau, as it can be seen by comparing Figs. 4.3 and 4.11. For example, the $d_{yz}$ harmonic response presents a more pronounced minimum at around the 45th harmonic for the combined contributions of HOMO and HOMO-1 (see, Figs. 4.3b and 4.11d).

Finally, the inclusion of the HOMO-1 in calculations for the ring seems to leave unchanged the RME (Fig. 4.12a and b as compared to Fig. 4.4a and b). Responses $d_{xx}$ and $d_{yy}$ (Fig. 4.12c and d) are identical to the pure HOMO case (Fig. 4.4c and d). The same concerns the crossed terms $d_{yx}$ and $d_{xy}$, as it follows from a comparison of Fig. 4.13 and Fig. 4.5.

When the $d_{zz}$ harmonic response from the ring includes the contribution of both the HOMO and HOMO-1, the $z$-component of the RME as a function of $\Pi_x$ and $\Pi_y$ acquire nonvanishing values (see, Fig. 4.14a). This is in contrast to the case when just the HOMO is considered, in which the $z$-component of the RME is always zero. Even though the RME which contributes the most to the present configuration $[d_{rec,z}(\Pi_z)]$ is zero, it is expected that the two other components change in a
Figure 4.13  The same as in Fig. 4.5 after including the contribution of the HOMO-1.

minor way the shape of the plateau. As it can be seen in Fig. 4.14, the harmonic response obtained by accounting for HOMO and HOMO-1 (panel b) presents a similar trend to the spectral response obtained from HOMO (panel c), with an increase in intensity. The difference between the modulations of the plateau for these two cases appears only in the low-energy portion of the plateau, where the $z$-component of the RME acquires nonzero values.

As we have shown in this Section, depending on the target under consideration, the inclusion of inner molecular orbitals may affect the harmonic responses. In order to obtain very precise harmonic responses, the inclusion of several molecular orbitals below the HOMO is sometimes necessary. For the sake of completeness, we present them in Appendix F.

Figure 4.14 Panel a presents the modulus squared of the $z$-component of the RME calculated for the ring when the contributions from both the HOMO and HOMO-1 are accounted for. The corresponding spectral response $d_{zz}$ is shown in panel b. In panel c, we present the harmonic response from the ring restricted to the contribution of the HOMO orbital, for which the corresponding $z$-component of the RME vanishes. The laser field parameters are the same as in Fig. 4.2.
4.1.2.3 Spectral responses in the velocity gauge

As it has been shown in the previous Chapter, the lack of gauge invariance related to the Lewenstein model has direct consequences on the predictions for HHG spectra from molecules, particularly when they are characterized by large internuclear distances. This Section is devoted to the analysis of the harmonic spectra from the $C_{20}$ fullerene calculated in the velocity gauge. The results will be compared with the ones obtained in the length gauge. We restrict our considerations to this particular structure because of its simple spectral responses in the length gauge. Our purpose is to analyze how they depend on both the RME and the IME.

In order to analyze the ionization matrix element for molecules in the velocity gauge, we start from its definition [Eq. (3.64)]. In the position representation and using the LCAO approximation (see, Secs. 3.2.3 and 3.2.6), the ionization matrix element can be written as

$$\begin{align*}
    d_{\text{ion}}^{V}(p,t) &= \frac{p - e^2 A(t)}{(2\pi)^{3/2}} \sum_{j=1}^{N} \sum_{\ell=0}^{n} C_{\ell N \ell} \sum_{k} \eta_k \sum_{a,b,c} \int \! d\mathbf{r} (x - x_j)^a (y - y_j)^b (z - z_j)^c \\
    & \quad \times e^{-\alpha_k (\mathbf{r} - \mathbf{R}_j)^2} e^{-ip \cdot \mathbf{r}}.
\end{align*}$$

(4.6)

In order to simplify the calculations, we introduce now the scalar ionization matrix element (scalar IME),

$$
    d_{\text{ion}}^{V}(p) = \frac{1}{(2\pi)^{3/2}} \sum_{j=1}^{N} \sum_{\ell=0}^{n} C_{\ell N \ell} \sum_{k} \eta_k \sum_{a,b,c} \int \! d\mathbf{r} (x - x_j)^a (y - y_j)^b (z - z_j)^c e^{-\alpha_k (\mathbf{r} - \mathbf{R}_j)^2} e^{-ip \cdot \mathbf{r}}
$$

(4.7)

such that

$$
    d_{\text{ion}}^{V}(p,t) = d_{\text{ion}}^{V}(p) \left[ p - e^2 A(t) \right].
$$

(4.8)

The zeroes of $d_{\text{ion}}^{V}(p)$ indicate the regions for which interference effects are expected. On the other hand, the recombination matrix element is calculated in the same way as in the length gauge [see, Eq. (4.3)], but its argument corresponds to the canonical momentum $p$, instead of the kinetic one, $\Pi$.

In order to illustrate the influence of the RME and the scalar IME on the spectral response, both quantities are calculated according to Eqs. (4.3) and (4.7) as functions of the canonical momentum $p$. For the very symmetric $C_{20}$ fullerene, the scalar IME behaves in the same way as a function of $p_x$, $p_y$, or $p_z$, so just one of the momentum components is chosen for the analysis. The harmonic frequency is related to the electron momentum according to the energy conservation relation [Eq. (4.4)]. As a first approximation, the kinetic momentum $\Pi$ is replaced by the canonical one $p$. This will generate a shift between the zeroes of the RME or the scalar IME and the minima in the HHG signal along the plateau. Nevertheless, one can still relate these zeroes to the modulations of the HHG plateau.

In Fig. 4.15a, we show the modulus squared of the $x$-component of the RME, calculated in the velocity gauge, as a function of the harmonic order parametrized by three components of the canonical momentum. The laser field is polarized along the $x$-axis whereas its remaining parameters are the same as in Fig. 4.2. This time, the electric field is described as the semi-infinite cosine function. As expected, the three curves behave exactly the same as if calculated in the length gauge (Fig. 4.2a).
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Figure 4.15 Panel a shows the modulus squared of the $x$-component of the RME [Eq. (4.3)] as a function of the harmonic order $N$ parametrized either by $p_x$ (solid blue line), $p_y$ (dashed red line), and $p_z$ (dashed-dotted green line), calculated for the HOMO orbital of $C_{20}$ fullerene. Panel b shows the modulus squared of the scalar IME calculated according to Eq. (4.7), with $p_x$ related to the harmonic order. Finally, panel c presents the $d_{xx}$ spectral response from the considered structure. The laser field parameters are the same as in Fig. 4.2.

Nevertheless, the spectrum shown in Fig. 4.15c exhibits clear differences compared to Fig. 4.2b. This time, one can see a fast decrease of the harmonic signal after the 15th harmonic, followed by a relatively smooth plateau. There are two pronounced minima along the spectrum which are located at the 19th harmonic and in the region between 47th and 59th HOs. Such a behavior cannot be fully explained by just taking into account the RME, but a complementary study of the scalar IME (Fig. 4.15b) has to be performed. The modulus squared of the scalar IME shows two minima along the spectrum. The first one is located in the range between the 13th and 17th HOs, whereas the second extends from the 39th up to the 47th HO. These observations suggest a shift by roughly 8 harmonic orders between zeroes of the scalar IME and the modulations of the plateau.

Even though the contribution from the scalar IME seems to be very important for the overall behavior of the HHG spectrum calculated in the velocity gauge, the influence of the RME can still be observed. The latter seems to have a smaller effect on the spectrum than in the length gauge. For example, the minimum in the spectral response envelope shown in Fig. 4.15c between the 5th and 9th harmonic orders coincides with the first zero of $|d_{rec,x}(p_x)|^2$. The soft modulation in peak intensities presented in the region of the 25th-39th harmonics can be related to minima in $|d_{rec,x}(p_y)|^2$.

Let us investigate now whether the zeroes of the scalar IME introduce modulations in other spectra from the fullerene. In Fig. 4.16, we show the harmonic response $d_{yy}$ (panel b) together with the modulus squared of the scalar IME (panel a). Note that the RME components vanish for this specific configuration. It can be seen that, contrary to the calculations performed in the length gauge (see, Fig. 4.3a), new modulations are found along the HHG spectrum. The minimum located at the
Figure 4.16  Panel a shows the modulus squared of the scalar IME as a function of the harmonic order (that is parametrized by $p_x$), calculated according to Eq. (4.7), for the HOMO orbital of $C_{20}$ fullerene. Panel b shows the spectral response $d_{yy}$ from this structure for the same laser field parameters as in Fig. 4.2.

Figure 4.17  The same as in Fig. 4.16 but for the $d_{zz}$ harmonic response (panel b) and its corresponding scalar IME (panel a).
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Figure 4.18  The same as in Fig. 4.16 but for the $d_{zy}$ (left column) and $d_{yz}$ (right column) harmonic responses.

15th harmonic was not observed in Fig. 4.3a but it clearly coincides with the zero of the scalar IME. A pronounced valley between the 31st and 61st harmonic orders is present in the spectrum. It can be related to the zero of the scalar IME located at roughly the 45th harmonic order. Note also that $|d_{ion}(p_x)|^2$ becomes very small towards the end of the spectrum, which leads to a decreasing intensity of HHG peaks.

Fig. 4.17b presents the $d_{zz}$ spectrum from the fullerene. The modulus squared of the scalar IME as a function of the harmonic order is shown in Fig. 4.17a. As before, the harmonic order is related to $p_x$. The first minimum appears between the fifth and the eleventh harmonic, which again is displaced by $6\omega_L$ to the left with respect to the first zero of the scalar IME. The decrease of the peaks strength can be observed at roughly the 19th harmonic, which is approximately 10 harmonic orders before $|d_{ion}(p_x)|^2$ starts to decrease rapidly. Another modulation starting at around $57\omega_L$ and extending towards the end of the plateau cannot be easily explained by analyzing the scalar IME as a function of just one component of momentum and keeping the other two components constant.

In Fig. 4.18, the harmonic responses $d_{zy}$ and $d_{yz}$ from the $C_{20}$ fullerene are plotted in panels c and d, respectively. The modulus squared of the scalar IME [see, Eq. (4.7)] related to the canonical momentum $p_x$ is shown in panels a and b, respectively. The general trend of the spectra is qualitatively similar, as it is in the case of $d_{yy}$ or $d_{xx}$. There are two major modulations: one at the beginning of the spectrum, located near the 9th harmonic order, and a broad valley between the 23rd and 59th harmonic orders. In these cases, the modulations seem to be shifted 6 harmonic orders to the left with respect to the zeroes of the scalar IME. There is another minimum around the 59th harmonic which cannot be related to any zero of the matrix element.

By comparing Figs. 4.15 to 4.18 with Figs. 4.2 and 4.3, we note that the length and velocity gauges predict the exact same position of the cutoff as anticipated by Eq. (3.36) (see also numerical values collected in Table 4.3). No unphysical extensions of the plateau are observed, neither in the length nor in the velocity gauge. With respect to the general characteristics of the spectra, it is clear that the velocity and length gauges predict different modulations in the peak intensities along the
plateau. This is due to a different behavior of the IME and the RME in terms of the kinetic and canonical momenta. The relatively smooth plateaus corresponding to the responses $d_{yy}$, $d_{yz}$, $d_{zy}$, and $d_{zz}$ calculated in the length gauge (Fig. 4.3) show stronger modulations when calculated in the velocity gauge. In the latter case, all spectra are characterized by an early minimum at around the 9th harmonic and a fast decrease after the 21st harmonic. The shift between zeroes of the scalar IME and the modulations of HHG peaks along the plateau follows from the fact that, instead of the kinetic momentum, the canonical momentum is used in the energy conservation relation. Nevertheless, the influence of the scalar IME on the general shape of the plateau can be analyzed within the present scope, remembering about the aforementioned shift.

4.1.3 Influence of the pulse shape on the HHG spectrum

Up to now, the results presented in this Chapter have been obtained by approximating the driving laser field as a semi-infinite, monochromatic plane wave. In order to describe the field more accurately, an envelope can be introduced. Similar to Chapter 2, we have chosen the envelope of the sine-squared type. Thus, using our current notation, we write the corresponding electric field as

$$E(t) = \begin{cases} E_0 e^{j\sin^2(\frac{\omega_L t}{2N_{\text{osc}}}) \sin(\omega_L t)} & \text{if } 0 \leq t \leq \frac{2\pi N_{\text{osc}}}{\omega_L}, \\ 0 & \text{if } t < 0 \text{ or } t > \frac{2\pi N_{\text{osc}}}{\omega_L}, \end{cases}$$

(4.9)

where $E_0$ relates to the intensity of the field, $e_j$ is the linear polarization vector of the laser field, $\omega_L$ represents its carrier frequency, whereas $N_{\text{osc}}$ denotes the number of field oscillations within the pulse. Now, the question is: How does the shape function modify the harmonic spectrum? As it follows from Chapter 2, the function $\sin^2$ adds new spectral components to the Fourier decomposition of the laser pulse and, hence, it may significantly alter the calculations. On the other hand, one expects that, for sufficiently long pulses (with many cycles $N_{\text{osc}}$), the predictions obtained for the pulse and for the plane wave should become similar. We will illustrate this for the $C_{20}$ fullerene.

In Fig. 4.19, we show harmonic responses $d_{xx}$ from the $C_{20}$ fullerene calculated in the length gauge for the electric field described by Eq. (4.9) with $N_{\text{osc}} = 5$ (blue line), $N_{\text{osc}} = 10$ (green line), and $N_{\text{osc}} = 15$ (red line). In order to compare these spectra with the corresponding results obtained for the semi-infinite plane wave [Eq. (4.5)], the response calculated for the latter is plotted as a black line. It can be seen that sharp, equidistant peaks in the HHG spectrum, calculated for the sinusoidal wave, become broader and not necessarily equally spaced when the electric field takes the form (4.9). This is particularly well seen for small values of $N_{\text{osc}}$. For example, the last part of the plateau for $N_{\text{osc}} = 5$ (between the 51st and 61st harmonics) is characterized by small oscillations instead of a series of peaks. The early and middle plateau present small broad peaks, which are difficult to relate to integer harmonics.

By increasing $N_{\text{osc}}$, the peaks in Fig. 4.19 become more narrow. For a 10-cycle pulse ($N_{\text{osc}} = 10$), one can observe very well-defined peaks (up to the 21st harmonic order) that resemble the results obtained for the semi-infinite plane wave. The middle and late plateau regions are characterized
Figure 4.19  HHG spectra from the HOMO of the $C_{20}$ fullerene corresponding to the $d_{zx}$ response calculated in the length gauge. The electric field is defined by Eq. (4.9) with $N_{osc} = 5$ (blue line), $N_{osc} = 10$ (green line), and $N_{osc} = 15$ (red line). The black line represents the results obtained for a semi-infinite plane wave (4.5). In each case, the carrier frequency $\omega_L = 1.55\text{eV}$ is related to the Ti-Sapphire laser and the peak intensity is $5 \times 10^{14}\text{W/cm}^2$. All spectra have been shifted vertically for visual purposes.

by low intensity and not very well-defined peaks which, in general, are not located at the odd harmonic positions. If the duration of the pulse is increased to 15 cycles, the peaks become considerably narrower and appear at the expected positions. The spectrum starts to resemble the corresponding spectrum generated by the semi-infinite plane wave. Even though the parameter $N_{osc}$ has a direct impact on the detailed structure of the HHG spectrum, qualitatively the spectra are similar. The same concerns spectra for the remaining isomers of $C_{20}$.

4.1.4 Quantum path interference

As it has been pointed out in Sec. 3.2.8, the time-frequency analysis is an important numerical tool to investigate the physical processes behind HHG. The direct visualization of quantum trajectories as well as the relation between time of emission of harmonics and their frequency can help to understand important features of the harmonic spectra. This will be demonstrated in this Section.

Up to now, the analysis of modulations of the peak intensities along the HHG plateau for three different $C_{20}$ structures has been based on the importance of the RME and IME. It is clear that these two quantities contain vital information about the molecular configuration and that they account for multicentre interference effects. As it will become clear in this Section, another quantity which provides substantial information about the process is the modified semiclassical action.

The fact that some minima in the harmonic response from diatomic molecules appear at the same frequencies as expected multicentre interference effects was initially observed by Lein et al. [116, 117]. However, interference features of a different nature, namely, the interference between quantum
Figure 4.20  Panel a shows the time-frequency analysis of the $d_{yy}$ harmonic response from the HOMO orbital of the $C_{20}$ fullerene. The spectral response $d_{yy}$ (Fig. 4.3a) is plotted again in panel c. The first vertical red line shows the starting point of the region where the interference between quantum trajectories starts to be evident. The second vertical line points at the region where the destructive interference is maximum. Panel b presents the time-frequency analysis of the $d_{zy}$ response, which is repeated in panel d from Fig. 4.3c. The vertical line points at the minimum of the harmonic spectrum envelope, which can be directly related to the QPI effects.

Trajectories (known as the quantum path interference, QPI) were ignored. QPI was originally proposed for a single atom [120], where multicentre effects play no role. Intuitively, it can be understood by analyzing the Lewenstein model: the electrons which contribute to HHG can follow two paths, one short and one long. During the excursion to the continuum the electron wave packet spreads and acquires a phase, given by the semiclassical action, which depends on the ionization and recombination times. When the recollision takes place, electrons with different phases interfere. This has direct consequences on the harmonic spectrum. The QPI effects in the analysis of HHG from diatomic molecules have been recently studied by Yang et al. (see, Ref. [122]) and have been found to significantly modify the general behavior of the harmonic plateau. New minima have been observed with no relation to the multicentre interference. They were unequivocally related to QPI processes, which followed from the time-frequency analysis. Such effects have shown to be important even for ultrashort driving pulses [122].

The QPI analysis in the atomic case, when just the long and short electron paths are considered, is straightforward. If a multicentre system is considered, the complexity of the problem increases with the number of atoms. It follows from Eq. (3.50) that the modified semiclassical action does not depend only on the ionization and recombination times, but it depends as well on the position of nuclei. In this sense, short and long trajectories are composed of direct and transfer trajectories which may interfere and generate very complex harmonic responses.
In Sec. 4.1.2.1, we have interpreted the modulations of peak intensities in the HHG spectra as multicentre interferences. However, some of such modulations could not be matched with minima of the RME. It has been proven that the harmonic responses related to oscillating RMEs exhibit heavily modulated plateaus and many of the minima match fairly good with the zeroes of the RME. The harmonic responses related to non-oscillating RMEs present smooth plateaus with soft modulations of the peak intensities (e.g., the $d_{yy}$, $d_{zy}$, $d_{yz}$, and $d_{zz}$ spectra from the fullerene shown in Fig. 4.3). In order to identify the nature of such soft variations, the time-frequency analysis has been performed for the four aforementioned responses. Again, the $C_{20}$ fullerene has been considered as the corresponding numerical results are the simplest to interpret. Together with the respective spectra, the time-frequency plots are presented in Figs. 4.20 and 4.21. In general, all plots show the well-defined long and short trajectories with distinctive interference regions. Interferences can be observed as bifurcations or interactions between the otherwise clear, well-defined, and independent paths. The vertical red lines identify the harmonics for which strong QPI effects can be observed. Starting with Fig. 4.20a, one can see that the $d_{yy}$ response exhibits interference features from around the 21st HO, where a decrease of the peak intensities can be observed. The most evident destructive interference effects are present between the 39th and 49th harmonic orders, where the minimum of the plateau is present (Fig. 4.20c). The $d_{zy}$ response shows the QPI effects starting from roughly the 31st harmonic, where the intensity of the peaks starts to decrease (see, panels b and d of Fig. 4.20). The most pronounced destructive interference effect (for both long and short trajectories) is clearly located between the 45th and 55th harmonic orders, which again coincides with the position of the minimum in the HHG spectrum.

When the laser field is polarized along the z-axis, fewer interference effects are observed. Particularly interesting is the time-frequency analysis of the $d_{yz}$ response (Fig. 4.21a). It exhibits very

Figure 4.21  The same as in Fig. 4.20 but the time-frequency analysis was performed for the $d_{yz}$ (panel a) and $d_{zz}$ (panel b) responses. The corresponding harmonic signals (Fig. 4.3 panels b and d) are plotted again in panels c and d. The vertical red lines point at the regions where the modulations in the spectral response coincide with interference of quantum trajectories.
well-defined short and long trajectories, except for the region of the 25th-41st harmonics. In this region, the long trajectories are clearly distorted and curved as a consequence of strong interference. This is the exact position of the spectral minima. Finally, the $d_{zz}$ case (Fig. 4.21b) presents relatively small QPI effects, being the most pronounced at around the 21st-35th harmonics. In this region, the two trajectories seem to interact the most and the minimum in the plateau is present. There are other destructive interferences near to the cutoff.

In closing this Section, it is worth noting that the smooth variations of the spectral response for the cases where the multicentre effects are less important can be directly related to QPI effects. This occurs due to the phase differences acquired by electrons following different quantum paths.

As it has been demonstrated in this Section, the high-order harmonics of a particular polarization are generated depending on the orientation and nature of the $C_{20}$ isomer. The complexity of the response makes it difficult to characterize properties of the observed harmonic radiation; in particular, its ellipticity. In order to analyze the ellipticity of the HHG signal, a much simpler diatomic molecule ($N_2$) has been chosen, as presented in the next Section.

### 4.2 $N_2$ molecule

The HHG spectrum from molecular nitrogen $N_2$ has been a subject of extensive studies due to the simplicity and large stability of this molecule. For instance, Itatani et al. [35] have proposed the idea of a tomographic imaging of molecular orbitals by analyzing the HHG spectrum and have illustrated this technique by imaging the HOMO of nitrogen molecule. Also, the strong elliptically-polarized harmonic response from $N_2$ interacting with a linearly-polarized laser field has been experimentally observed [137] and theoretically studied under the SFA framework [138], based on the time-dependent density functional theory (TDDFT) [102], and other numerical methods [119].

The idea of creating strong elliptically- or circularly-polarized ultrashort laser pulses and high-order harmonics in a table-top device has attracted a lot of attention due to multiple applications in ultrafast spectroscopy or in the analysis of ultrafast chiral dynamics in molecules (see, [139] and references therein). It is clear that if the harmonic target is completely symmetric, the HHG signal is expected to be polarized in the same direction as the driving field. If this symmetry is broken, the signal can have components parallel and perpendicular to the driving field polarization direction. Hence, the resulting harmonics are elliptically-polarized [138].

It has been shown in Ref. [138] that the application of the Lewenstein model to molecules, in its original formulation which does not include the oscillatory terms related to the atomic positions in the semiclassical action, predicts a linearly-polarized response parallel to the laser field polarization direction. It follows from Eq. (3.21) that the saddle point in momentum does not contain any components perpendicular to the vector potential. In such a case, the arguments of the ionization and recombination matrix elements in Eq. (3.23) are parallel to $A(t)$. The introduction of the oscillatory terms into the action induces a component in the saddle point in momentum, which is perpendicular to the vector potential and depends directly on the position of ionization and recombination centres.
according to the term $m(R_i - R_j)/\tau$ [see, Eq. (3.51)]. This term follows from the symmetry breaking in multicentre systems and assures that the electron trajectory starts at certain atom and ends at another. Even though this term is fundamental for an appropriate treatment of the ellipticity and polarization of the harmonic response, the electron configuration plays another very important role in calculations. It is expected that the ionization probability increases in regions of high electron density and vice versa. The molecular orbital, under the LCAO approximation, is defined as a linear combination of different Gaussian functions which contain different exponents $\alpha_k$ and the coefficients $\eta_k$, $C_\ell$, and $N_\ell$ [Eqs. (3.37) to (3.39)]. It is clear that these parameters influence considerably the values of the recombination and ionization matrix elements [see, Eqs. (3.43) to (3.49)] and, hence, the respective ellipticities. In Ref. [119], the importance of the molecular electron configuration has been illustrated for two orbitals with different symmetry (namely, $\sigma_g$ and $\sigma_u$ of the ion $H_2^+$). This has led to pronounced differences of the resulting harmonic ellipticities. Taking these observations into account, one has to properly choose a basis of atomic orbitals and include the oscillatory terms into the action.

In this Section, we focus on harmonics which are generated from the HOMO of the nitrogen diatomic molecule. For this purpose, the orbital was calculated by optimized Hartree-Fock methods included in the quantum chemistry package GAMESS [133]. In this case, twelve GPs corresponding to $s$ orbitals and six GPs corresponding to $p$ orbitals were used. In the Pople’s notation [134, 135], this basis set is denoted as 6-311G.

### 4.2.1 Harmonic ellipticity from the nitrogen molecule

The ellipticity and phase of the harmonic response from diatomic molecules can be calculated following Refs. [119] and [102], without making any assumptions about the nature of the harmonic radiation or its direction. We assume that the molecule is oriented along the $z$-direction. The laser field linear polarization is adjusted such that it makes an angle $\theta$ with the molecular axis. In this case, the $x$- and $z$-components of the time-dependent dipole moment $[d_x(t) \text{ and } d_z(t)]$ are nonzero, whereas the $y$-component vanishes. In what follows, $d_x(t)$ and $d_z(t)$ are calculated according to the Lewenstein model in the length and velocity gauges, in the exact same way as described for the $C_{2v}$ isomers. Hence, also the parallel $[d_\parallel(t)]$ and perpendicular $[d_\perp(t)]$ components (with respect to the laser polarization direction) of the time-dependent dipole moment can be obtained,

$$d_\parallel(t) = d_x(t) \sin \theta + d_z(t) \cos \theta,$$

$$d_\perp(t) = d_x(t) \cos \theta - d_z(t) \sin \theta,$$

(4.10)

(4.11)

together with their Fourier transforms, $\tilde{d}_\parallel(\Omega)$ and $\tilde{d}_\perp(\Omega)$. These Fourier transforms define the parallel and perpendicular harmonic responses, $I_\parallel(\Omega)$ and $I_\perp(\Omega)$. The latter can be calculated from Eq. (3.90) by setting $n = (\sin \theta, 0, \cos \theta)$ and $n = (\cos \theta, 0, -\sin \theta)$, respectively. As an illustration, in Fig. 4.22, we show the parallel and perpendicular harmonic responses obtained from a diatomic nitrogen molecule interacting with a semi-infinite and linearly-polarized sinusoidal laser field [Eq. (4.5)] in the length gauge (panels b, d, and f) and a semi-infinite cosine field in the velocity gauge (panels a, c, and e). The results are for the laser field intensity $I = 1 \times 10^{14}$ W/cm$^2$ and wavelength $\lambda = 800$ nm.
Figure 4.22  Parallel (black curve) and perpendicular (red curve) spectral responses $I_{\parallel}(\Omega)$ and $I_{\perp}(\Omega)$ calculated for the HOMO of the $N_2$ molecule. The laser field intensity is $I = 1 \times 10^{14}$ W/cm$^2$ and its wavelength equals $\lambda = 800$ nm. The results presented in panels a, c, and e correspond to axial angles of 40°, 50°, and 60°, respectively, and were obtained in the velocity gauge. Panels b, d, and f represent the same but in the length gauge. Calculations in the length gauge were performed for the driving field modeled as a semi-infinite sine wave [Eq. (4.5)] whereas the ones in the velocity gauge were done for a semi-infinite cosine wave.

The angle $\theta$ between the molecular axis and the laser field polarization direction corresponds to 40°, 50°, and 60°.

To calculate the ellipticity of the HHG signal, two parameters are necessary, i.e., the amplitude ratio, $r(\Omega)$, defined by the following equation,

$$r(\Omega) = \frac{|\tilde{d}_{\perp}(\Omega)|}{|\tilde{d}_{\parallel}(\Omega)|},$$  \hspace{1cm} (4.12)

and the harmonic phase difference, $\delta(\Omega)$, defined as

$$\delta(\Omega) = \arg[\tilde{d}_{\perp}(\Omega)] - \arg[\tilde{d}_{\parallel}(\Omega)].$$  \hspace{1cm} (4.13)

Finally, the ellipticity as a function of the harmonic frequency is calculated according to [102, 119]

$$\varepsilon(\Omega) = \sqrt{\frac{1 + r^2 - \sqrt{1 + 2r^2 \cos 2\delta + r^4}}{1 + r^2 + \sqrt{1 + 2r^2 \cos 2\delta + r^4}}}. $$  \hspace{1cm} (4.14)

The harmonic ellipticity (4.14) can range from 0 (in the case of linearly-polarized harmonics) to 1 (for circularly-polarized harmonics). \footnote{If the parallel and perpendicular responses are in phase, then $\delta = 0$ and the resulting polarization is linear. If $2\delta = \pi$ and the ratio $r = 1$, then the two dipoles oscillate with the same amplitude and a phase difference $\pi/2$, which corresponds to a circularly-polarized light and the ellipticity equal to 1 [119].} Fig. 4.23 illustrates the behavior of the ellipticity with respect to the ratio $r$ and the phase $\delta$. As it can be seen, in order to achieve a high ellipticity of the harmonic response it is necessary that the amplitudes of the parallel and perpendicular components of the dipole
Figure 4.23  Shows the ellipticity as a function of the phase difference, \( \delta \), and the amplitude ratio, \( r \), calculated from Eq. (4.14). It can be seen that the maximum value (\( \varepsilon = 1 \)) is obtained when the parallel and perpendicular components have the same amplitude (\( r = 1 \)) and differ in phase by \( \delta = \pm \pi/2 \).

moment are comparable and that the two dipoles oscillate with a phase difference \( \delta = \pm \pi/2 \). On the other hand, small ellipticities are obtain either for small or very large amplitude ratios. While in the former case the parallel harmonic response is dominant, in the latter case it is the perpendicular harmonic response. Note that small ellipticities are also achieved for phase differences \( -\pi, \pi \) or 0.

4.2.2 Amplitude ratio, phase difference, and the recombination model

As it has been pointed out, in order to obtain large values of the harmonic ellipticity it is necessary that the parallel and perpendicular responses have a similar amplitude and that the phase difference between them is around \( \pm \pi/2 \). In Ref. [119], Son et al. have developed an intuitive method to understand the intensity difference of the peaks along the plateau, which we describe below.

It is expected that the parallel component of the harmonic yield would exhibit a larger signal compared to the perpendicular one [138]. In the previous Sections, devoted to the analysis of the harmonic spectra from \( C_{20} \) isomers, it has been also demonstrated that certain modulations along the plateau can be directly related to multicentre interference effects. For the parallel component of the harmonic response from diatomic molecules, the positions of peak intensities minima can be estimated by means of the recombination model used in Refs. [117, 140]. In this model, the electron wave packet is approximated as a plane wave colliding with two interference centres. It has been shown that, in the velocity gauge, the destructive interference for a symmetric combination of atomic orbitals can be observed when the following relation holds [117, 138],

\[
R \cos \theta = \frac{(2n + 1)\lambda}{2}.
\]  

(4.15)

In this equation, \( R \) is the separation distance between nuclei, \( n \) is a positive integer or zero, \( \lambda = 2\pi/|p| \) is the de Broglie wavelength of the incoming electron, whereas \( \theta \) is the angle between the molecular
axis and the laser field polarization direction. The photon frequency is assumed to be equal to the kinetic energy of the electron just before the recollision, without including the ionization potential. In other words, it is assumed that the energy gained by the electron while approaching the Coulomb centre is approximately $I_p$ [117]. Under such conditions, the relation (4.15) becomes

$$N_{\text{sym}}^{\text{destr.}} = \frac{(2n + 1)^2 \pi^2}{2m \omega_L R^2 \cos^2 \theta}, \quad (4.16)$$

where $N_{\text{sym}}^{\text{destr.}}$ is the harmonic order at which one observes the destructive interference generated by a symmetric combination of atomic orbitals. On the other hand, constructive interference is expected when [117]

$$R \cos \theta = n\lambda. \quad (4.17)$$

For a given angle $\theta$,

$$N_{\text{sym}}^{\text{const.}} = \frac{2n^2 \pi^2}{m \omega_L R^2 \cos^2 \theta}, \quad (4.18)$$

is the harmonic order which corresponds to constructive interference.

The amplitude of the perpendicular harmonic response has to be calculated in a different way and it does not present the interference pattern expected from the recombination model [119]. Since the electric field in this direction is considered to be small, an estimate of $d_\perp$ can be obtained using the first order perturbation theory [119]. In this case, the dipole moment is proportional to the electric field acting in the same direction. Namely,

$$d_x(t) = \alpha_{xx} |\mathbf{E}(t)| \sin \theta, \quad (4.19)$$
$$d_z(t) = \alpha_{zz} |\mathbf{E}(t)| \cos \theta, \quad (4.20)$$

where $\alpha_{xx}$ and $\alpha_{zz}$ are two of the diagonal terms of the polarizability tensor. Taking this into account, the perpendicular component can be estimated from Eq. (4.11) as follows

$$d_\perp(t) \approx (\alpha_{xx} - \alpha_{zz}) |\mathbf{E}(t)| \cos \theta \sin \theta = \frac{\alpha_{xx} - \alpha_{zz}}{2} |\mathbf{E}(t)| \sin 2\theta. \quad (4.21)$$

Hence, it is expected that the perpendicular component of the dipole moment should vary smoothly with the angle $\theta$ for a given harmonic order, without presenting any pronounced peak. This also implies that the ratio $r$ is proportional to $\sin 2\theta$ and vanishes for angles $\theta = 0$ and $\theta = \pi/2$.  

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$R$(Å)</th>
<th>$I$(W/cm²)</th>
<th>$\omega_L$(a.u)</th>
<th>$Q$</th>
<th>$I_p$(a.u)</th>
<th>$N_{\text{cutoff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_2$</td>
<td>1.11</td>
<td>$1 \times 10^{14}$</td>
<td>0.057</td>
<td>0.018</td>
<td>0.390</td>
<td>21</td>
</tr>
</tbody>
</table>

Table 4.4 The laser field and molecular parameters used in numerical illustrations in Sec. 4.2.2. The ionization potential ($I_p$) and equilibrium nuclear distance ($R$) have been calculated with the quantum chemistry package GAMESS. The parameter $Q$ is obtained from Eq. (3.59) [note that, for diatomic molecules, $R_{\text{max}}$ present in Eq. (3.59) corresponds to the equilibrium nuclear distance]. $I$ represents the intensity of the laser field and $\omega_L$ its carrier frequency.
Now, by rewriting Eq. (4.16) as follows

\[ \cos \theta = \frac{(2n + 1)\pi}{R \sqrt{2N_{\text{sym}}^\text{destr} m\omega_L}}, \]  

(4.22)

it is clear that the parallel component of the dipole moment can exhibit interference minima if \((2n + 1)\pi/(R \sqrt{2N_{\text{sym}}^\text{destr} m\omega_L}) \leq 1\). Moreover, for angles which fulfill Eq. (4.22) and for which \(\sin 2\theta\) is close to 1, the amplitude ratios can be very large. In this case, a strongly polarized harmonic response can be obtained if the phase difference is around \(\pm \pi/2\). For \(N_2\) and for the laser field parameters used in our calculations (see, Table 4.4), we obtain that the relation (4.22) becomes

\[ \cos \theta = 4.437 \frac{(2n + 1)}{\sqrt{N_{\text{sym}}^\text{destr}}}. \]  

(4.23)

This equality is just fulfilled for \(n = 0\) when \(N_{\text{sym}}^\text{destr} \geq 21\), which is in the region of the cutoff and above. In this case, no destructive interference is predicted along the plateau. It is clear that, for \(n > 0\), Eq. (4.23) has no physical solutions in the studied spectral region.

It can be seen in the right column of Fig. 4.22, corresponding to the calculations in the length gauge, that the parallel and perpendicular harmonic responses become very similar at the 15th and 17th harmonics, before an almost complete overlap at the 19th and 21st HOs for 40°, 50°, and 60°. The following peaks are located beyond the cutoff and the predictions of the Lewenstein model start to fail. It is worth remembering that the minima in the HHG signal along the plateau, which are not a consequence of multicentre interference, follow from interference between different quantum trajectories [29, 117]. In the velocity gauge (left column of Fig. 4.22), the larger amplitude ratios are located mostly at the beginning of the spectrum. The fact that the parallel component is always larger than the perpendicular one in the middle- and high-energy plateau (except perhaps for the 17th HO at 60°) suggests that no important multicentre destructive interference occurs in these regions.

It is clear that the electron configuration of molecular orbitals affects the location of maxima and minima in the HHG spectrum. It has been shown in Ref. [119] that the condition (4.22) determines the interference minima in the HHG spectrum for a symmetric combination of atomic orbitals (e.g., \(\sigma_g\) orbital in the \(H_2^+\) ion), but it relates to constructive interference for an antisymmetric combination of atomic orbitals (the case of \(\sigma_u\) in \(H_2^+\)). If the wave function is antisymmetric, then the multicentre destructive interference is expected to happen when the condition (4.17) is satisfied [141]. In terms of the harmonic order, it can be written as

\[ N_{\text{destr}}^\text{antisym} = \frac{2n^2 \pi^2}{m\omega_L R^2 \cos^2 \theta}. \]  

(4.24)

By comparing Eq. (4.24) for \(n = 1\) and Eq. (4.16) for \(n = 0\), it becomes clear that the first destructive interference in the spectrum obtained for an antisymmetric wave function is located at four times the position of the first minima for a symmetric wave function. This implies that, in general, the minima from antisymmetric combination of atomic orbitals are going to be located after the cutoff, and only constructive interference is expected along the plateau. It is worth noting that the case of the \(N_2\) molecule is particularly interesting due to the contribution of both symmetric and antisymmetric
combination of atomic orbitals in the HOMO [119]. This, of course, makes the direct application of
the recombination model more difficult. Nevertheless, such model is an interesting tool to understand
the overall behavior of the phase difference, the amplitude ratios, and, therefore, the ellipticity of the
harmonic signal obtained from $N_2$.

It has been shown that the phase difference, which in general varies slowly with the orientation
angle $\theta$, changes smoothly but rapidly around $\pi$ at angles for which the multicentre destructive inter-
ference occurs [106, 117, 119]. This is mostly expected to happen along the plateau for symmetric
combination of atomic orbitals, as the destructive interference is more probable in this case. This
is presented in Ref. [119], where the parallel and perpendicular amplitudes together with the phase
differences have been analyzed for the ground (symmetric) and excited (antisymmetric) states of $H_2^+$. 
Thus, according to the work of Son et al. [119], it is also expected that a symmetric combination of
atomic orbitals for $N_2$ would lead to a large ellipticity of harmonic signal under the conditions when
the two-centre destructive interference takes place. On the other hand, the ellipticity of harmonics
generated from antisymmetric wave functions is expected to be considerably smaller due to the fact
that the destructive interference is less probable along the plateau.

In Fig. 4.24 the ellipticity, the phase difference, and amplitude ratios for the given harmonics
calculated from the HOMO of $N_2$ molecule are presented as a function of the angle $\theta$. The calcula-
tions were performed in the length gauge for the laser field modeled as a semi-infinite sinusoidal
plane wave [see, Eq. (4.5)] with parameters presented in Table 4.4. Different panels show the results
corresponding to harmonics between the 7th and 27th. Note that in this case the cutoff is located
at approximately the 21st HO. As the Lewenstein model describes very well the spectrum along the
plateau whereas its predictions are less accurate after the cutoff, the ellipticity values calculated in the
present approach are expected to exhibit larger errors beyond the 21st harmonic order. Nevertheless,
the analysis of the region above the cutoff can be done in order to illustrate important properties of
the ellipticity, the ratio, and phase differences, as it will become clear shortly.

It can be seen in panels i, j, and k of Fig. 4.24 that the amplitude ratios $r$ for the harmonics
below the 21st order do not present peaks and achieve maximum values between 40$^\circ$ (19th harmonic)
and 60$^\circ$ (7th harmonic). At 0$^\circ$ and 90$^\circ$, the ratio vanishes for all harmonic orders due to the large value
of the parallel dipole moment as compared to the perpendicular one. It follows from Eq. (4.21) that
the perpendicular dipole moment (and therefore $r$) should vanish at such angles independently of the
harmonic order, which is exactly the case. The general trend of the middle and late plateau shows that
the maximum ratio increases with the harmonic order, being the largest for the 21st harmonic at the
angle $\theta = 30^\circ$, where $r$ is approximately 1.2. It follows from Fig. 4.24 that after the 21st harmonic
the ratios achieve larger values and the general trend is changed, presenting peaks at certain angles $\theta$. 
For example, the ratio for the 25th harmonic exhibits a large peak ($r \approx 6$) for $\theta = 30^\circ$. To understand
this behavior it is necessary to analyze the parallel [$A_{\parallel}^{(N)}(\theta)$] and perpendicular [$A_{\perp}^{(N)}(\theta)$] harmonic
amplitudes, which we define as

$$A_{\parallel/\perp}^{(N)}(\theta) = 2\omega^2 L^2 \frac{1}{6\pi c^3} |\tilde{d}_{\parallel/\perp}(N\omega_L)|.$$  \hspace{1cm} (4.25)
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Figure 4.24 The ellipticity [Eq. (4.14)], the phase difference [Eq. (4.13)], and the amplitude ratio [Eq. (4.12)] of the given harmonics calculated from $N_2$ as functions of the angle $\theta$ formed between the molecular axis and the laser field polarization direction. The laser field and molecular parameters are shown in Table 4.4. The laser field is approximated as a semi-infinite sinusoidal plane wave [Eq. (4.5)]. The calculations have been performed from the 7th up to the 27th harmonic order. Note that the cutoff is located around the 21st HO.

Here, $\tilde{d}_{\|/\perp}(N \omega_L)$ is the Fourier transform of the parallel or perpendicular components of the time-dependent dipole moment [Eqs. (4.10) and (4.11)] for a certain harmonic order.

In Fig. 4.25, we present the amplitudes $A_{\|/\perp}^{(N)}(\theta)$, defined by Eq. (4.25), for $N = 9, 19, \text{ and } 27$. It can be seen that, for all presented harmonics, the amplitudes $A_{\perp}^{(N)}(\theta)$ behave similarly to the function $\sin 2\theta$, in agreement with Eq. (4.21). As expected, $A_{\perp}^{(N)}(0^\circ) = A_{\perp}^{(N)}(90^\circ) = 0$ and it has a maximum around $40^\circ - 50^\circ$. On the other hand, the parallel harmonic amplitude exhibits a different behavior, which strongly depends on the orientation angle $\theta$. In panel a, one can see that $A_{\|}^{(9)}(\theta) > A_{\perp}^{(9)}(\theta)$ for all angles, and that the minimum value of the parallel harmonic amplitude is at least twice the value of the perpendicular one, at the fixed angle. The situation changes for the 19th harmonic (panel b) where the two amplitudes acquire very close values at $40^\circ$ and $50^\circ$, but without any crossing between the two curves. For the 27th harmonic (panel c), $A_{\|}^{(27)}(\theta)$ exhibits a very pronounced minimum at $30^\circ - 40^\circ$. Note that, in this angular window, the perpendicular harmonic amplitude is considerably larger than the parallel one leading to large values of the amplitude ratio. The crossing of the two curves and the pronounced minimum of the parallel harmonic amplitude indicate the presence of multistate destructive interference, for which high ellipticity is expected. The same occurs already for the 25th
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**Figure 4.25** Parallel and perpendicular harmonic amplitudes [Eq. (4.25)] as functions of the angle $\theta$ calculated for the 9th, 19th, and 27th harmonics (panels a, b, and c, respectively). The calculations were performed in the length gauge and the laser field was modeled as a semi-infinite sinusoidal wave [Eq. (4.5)] with the parameters specified in Table 4.4. It can be seen that the perpendicular harmonic amplitudes behave similar to $\sin 2\theta$, whereas the parallel ones exhibit a more complex behavior.

harmonic for angles between $20^\circ$ and $30^\circ$. It is worth noting that the interference appears around 4 harmonic orders after the cutoff and that the predictions obtained from the Lewenstein model are not so accurate at such frequencies. In addition, the recollision model, as expressed by Eq. (4.23), works best in the region of the plateau [119].

Panels e, f, and g of Fig. 4.24 show the phase difference for harmonics up to the cutoff. All curves slowly vary with $\theta$ and are located around $\pm \pi$, which can explain relatively small ellipticity of the respective harmonics. For the 25th and 27th orders (panel h), one observes a change in phase by roughly $\pi$. This happens between $\theta = 20^\circ$ and $40^\circ$, which corresponds to the region where the maximum amplitude ratio is achieved. This observation corroborates the presence of an interference minimum for such harmonics. The ellipticities, calculated according to Eq. (4.14), are shown in panels a, b, and c for the plateau region. In general, their values are quite small, being the maximum for the 21st harmonic at $\theta = 10^\circ$ where $r \approx 2$ and $\delta \approx -\pi/2$. The ellipticity of the 25th and 27th harmonics at $\theta = 10^\circ$ and $20^\circ$ takes a medium value, which is due to the amplitude ratio $r > 1$ and phases which increase in absolute value before the jump. It is worth noting that Eq. (4.23) predicts a destructive interference for $N_{\text{sym destr.}} = 23$ at an angle $\theta = 22^\circ$, for $N_{\text{sym destr.}} = 25$ at $\theta = 27^\circ$, and for $N_{\text{sym destr.}} = 27$ at $\theta = 31^\circ$. These results roughly coincide with the angles for which the phase difference changes more abruptly and the intensity ratios are higher (see, panels h and l of Fig. 4.24). Such observation again corroborates the idea of strong multicentre interference at the mentioned angles and harmonic orders. The recollision model predicts, as well, interference effects for $N_{\text{sym destr.}} = 21$ at around $\theta = 14^\circ$, which correspond to the largest ellipticity for this harmonic order (see, panel c of Fig. 4.24). However, the typical changes of the ratio and phase difference accompanying multicentre destructive interference are not observed in this case.

Fig. 4.26 shows the ellipticity, the phase difference, and the amplitude ratios as functions of the angle $\theta$ but, this time, calculated for a semi-infinite cosine laser field in the velocity gauge. It can
be seen that the amplitude ratios are smaller than the ones calculated in the length gauge, except for the 17th harmonic. In this case, the amplitude ratio has a maximum at around $60^\circ$. The amplitude ratio for the 7th harmonic exhibits a change of the general trend (panel i) between $\theta = 30^\circ$ and $60^\circ$, where it becomes convex. All amplitude ratios obtained in the velocity gauge are smaller than the unity and none of them (perhaps except for the 7th and 17th harmonics) presents sharp peaks. This suggests that, in the current case, no interference minima should be present in the region between the 9th and 27th HOs. In order to prove this, in Fig. 4.27 we plot separately the parallel and perpendicular harmonic amplitudes for the 9th, 19th, and 27th HOs. It is clear that $A_{||}^{(9)}(\theta) > A_{\perp}^{(9)}(\theta)$ in all cases and that the amplitudes vary smoothly with the angle $\theta$. Note that $A_{||}^{(9)}(\theta)$ (red curve in panel a) increases with $\theta$ whereas $A_{\perp}^{(9)}(\theta)$ (black curve in panel a) reflects a deviation from the $\sin 2\theta$ tendency. The 19th and 27th harmonics (panels b and c) show a different behavior of their parallel and perpendicular amplitudes: while the former one decreases smoothly with the angle, the latter one follows the perturbative behavior [Eq. (4.21)]. As it has been checked for the 17th harmonic, the corresponding parallel and perpendicular amplitudes behave similar to the 27th harmonic. The difference is that, for the 17th HO, the parallel amplitude reaches its minimum when the perpendicular one is maximum. This produces the observed increase in the amplitude ratio at $\theta = 60^\circ$. No crossing between the curves is observed for this harmonic.

With respect to the phase difference (middle row in Fig. 4.26), there is no evidence of a sudden
change by $\pm \pi$ for any of the studied harmonics. All phases vary smoothly with the angle and, after the 17th harmonic, are close to $\pm \pi$. This suggests small harmonic ellipticities. The 7th, 13th, 15th, and 17th harmonics present relatively large ellipticities even though there is no evidence of multicentre interference. The actual maximum is found for the 15th harmonic and the angle $\theta = 50^\circ$, reaching the value $\varepsilon = 0.25$.

It is worth noting that the calculations performed in the velocity and length gauges predict small and medium values of ellipticity along the plateau for almost all HOs. Very large ellipticities are observed only between the 23rd and 27th harmonic orders in the length gauge, which is due to multicentre destructive interference. In the velocity gauge, only small values of the harmonic ellipticity are observed after the cutoff.

It is sometimes important to study how the ellipticity varies with respect to the harmonic order at a fixed angle. Some ab-initio calculations have shown that the harmonic response from a collection of perfectly aligned $N_2$ molecules exhibits very large ellipticities at $40^\circ$, $50^\circ$, and $60^\circ$ for harmonics ranging from the 15th to 19th orders [102]. The maximum values are roughly $\varepsilon \approx 0.6$ or $\varepsilon \approx 0.8$, depending on the angle [102]. For the sake of comparison, Figs. 4.28 and 4.29 illustrate the results for ellipticities (panels a), phase differences (panels b), and amplitude ratios (panels c) of the harmonic responses from $N_2$, calculated at fixed angles $30^\circ$, $40^\circ$, $50^\circ$, $60^\circ$, and $70^\circ$. The corresponding laser field parameters are presented in Table 4.4. While Fig. 4.28 shows the results calculated in the length gauge, Fig. 4.29 shows the same but in the velocity gauge. All phase differences are restricted to the interval $-\pi \leq \delta < \pi$.

It can be seen from Fig. 4.28 that the plateau region shows a maximum ellipticity for the 13th harmonic and all presented angles. Its largest value is for $\theta = 30^\circ$ and $40^\circ$ reaching $\varepsilon \approx 0.125$. The amplitude ratios for the harmonics before the cutoff are relatively small and do not present significant changes. This together with the fact that the phases are maintained at around $-\pi$ and do not approach the value $\pm \pi/2$ result in small ellipticities. After the cutoff, the amplitude ratio increases and so the ellipticity does. The phases are nearly constant up to the 23rd harmonic. Between the 23rd and the 27th harmonics, the phase difference at $\theta = 30^\circ$ grows from $-\pi$ up to $-0.2\pi$. Such a behavior of the
phase difference with respect to the harmonic order (a change close to $\pi$ at the constant angle) has been experimentally observed for other molecules [141].

By analyzing Fig. 4.29, it becomes clear that the velocity gauge leads to different predictions. In this case, the harmonic ellipticity can achieve values close to 0.25 for the 15th harmonic and the angles $\theta = 50^\circ$ and $60^\circ$. For these parameters, the amplitude ratios acquire relatively large values ($r \approx 0.4$) and the phase difference changes by roughly $\pi$. After the 19th harmonic, the ratios are relatively constant for all angles whereas the phases change between $-\pi$ to $\pi$. This results in smaller ellipticities (i.e., smaller than 0.05 in this region).

Comparing the results obtained from the Lewenstein model (Figs. 4.28 and 4.29) with the ones obtained from the TDDFT for a collection of perfectly aligned $N_2$ molecules (upper panel of Fig. 1, Ref. [102]), one can conclude that neither the length nor the velocity gauge manages to reproduce large ellipticities predicted in [102] (close to 0.8 for the 17th and 19th harmonic orders at $40^\circ$). The velocity gauge seems to compare qualitatively better with the TDDFT results than the length gauge. It is important to note that the ab-initio calculations performed in [102] show the importance of multi-electron contribution from the HOMO, HOMO-1, and HOMO-2, which can alter the general behavior of the harmonic ellipticity. In the present calculations, the SAE approximation and just the HOMO have been taken into account, which can be another source of discrepancies between the two methods. Moreover, according to [119] and references therein, it is also possible that the molecular orbitals of

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**Figure 4.28** Ellipticity [Eq. (4.14)], phase differences [Eq. (4.13)], and amplitude ratios [Eq. (4.12)], (panels a, b, and c, respectively) of the harmonics generated from the HOMO of $N_2$ for the laser field and molecular parameters shown in Table 4.4. The calculations are carried out in the length gauge by approximating the laser field as a semi-infinite sinusoidal plane wave [Eq. (4.5)]. All phase differences are restricted to the interval $-\pi \leq \delta < \pi$. 
Figure 4.29  The same as in Fig. 4.28 but calculated in the velocity gauge. The laser pulse is modeled as a semi-infinite plane wave of the cosine type.

$N_2$ exhibit a resonance between the HOMO and HOMO-1 for a laser pulse with wavelength near 800nm, which is exactly the case studied in this Section. In this situation, the contribution of HOMO-1 becomes even more important for the electron dynamics and the subsequent emission of the HHG radiation.

Note that a similar analysis of the modified Lewenstein model as the one presented here was published in [138]. The harmonic ellipticities from the HOMO of $N_2$ were calculated for more intense laser fields. One of the main differences between the two approaches is that the calculations developed in [138] take into consideration exclusively short electron trajectories, whereas in this thesis the full calculation has been performed. As it has been stated before, some of the spectral modulations that are not caused by the multicentre nature of the molecule are attributed to interference between short and long trajectories, which makes our analysis of the harmonic ellipticity much more rich. At the equilibrium internuclear spacing, the results of Ref. [138] show particularly low values of ellipticities at $\theta = 40^\circ$, $50^\circ$, and $60^\circ$. The largest ellipticity obtained in [138] is $\varepsilon \approx 0.025$, and it corresponds to the 27th harmonic and the angle $\theta = 60^\circ$. These calculations have shown rapid phase changes accompanied by a minimum in the parallel amplitude component, which suggests regions of destructive multicentre interference at the 17th and 27th harmonic orders.

As it was mentioned before, the analysis of harmonic ellipticity from diatomic molecules is important in light of potential applications of HHG. The possibility to generate an elliptically- and circularly-polarized harmonic radiation in table-top devices is particularly useful for the development of chiral-sensitive spectroscopic techniques [139].
4.3 Summary

The first part of this Chapter was devoted to the analysis of the harmonic response from three $C_{20}$ isomers (fullerene, ring, and bowl) interacting with a linearly-polarized laser field. The Lewenstein model in the length gauge was chosen to perform the calculations. Two main quantities were used to characterize the harmonic spectra: the RMEs as functions of three components of the electron momentum and the polarization properties of the harmonic response. We have shown that every spectrum presents a well-defined plateau with a sharp cutoff at the position given by Eq. (3.36). The harmonic response from each structure presents characteristic modulations of peak intensities along the plateau, which can be directly related to the RME zeroes. This has allowed us to conclude that such modulations are a consequence of multicentre interference effects. Also, the polarization of the harmonic signal characterizes the target, as it relates to the geometric distribution and electron configuration of the particular isomer.

It has been shown that, for certain laser field polarization directions, the RMEs for the fullerene vanish but the corresponding spectral responses exhibit relatively soft modulations in the spectral envelope along the plateau, which cannot be explained by considering multicentre interference effects. By means of the time-frequency analysis, we have related such modulations to quantum trajectories interferences.

After comparing the results obtained in the length and velocity gauges from the $C_{20}$ fullerene, we have shown that the position of the cutoff remains the same. Nevertheless, the spectral responses in both cases present different modulations of the envelope. It has turned out that the IME contributes importantly to the spectral response and, together with the RME, determines the modulations of the HHG spectrum in the velocity gauge.

In this Chapter, we have demonstrated that harmonic responses from $C_{20}$ isomers show characteristic modulations of peak intensities along the plateau. The polarization of harmonic radiation depends on the particular isomer and its orientation. The general shape of the harmonic spectrum and its polarization direction are related to the distribution of atoms in the molecule and to its symmetry. This fact can be used in the development of very simple spectroscopic techniques. Namely, by locating the position of the multicentre interference regions and determining the polarization of the harmonics, it would be possible to differentiate between harmonic targets consisting of a collection of aligned rings, bowls or randomly oriented fullerenes.

In the final part of this Chapter, we have analyzed the ellipticity of the harmonic response from a nitrogen diatomic molecule interacting with a linearly-polarized laser field, in the velocity and length gauges. This particular molecule has been chosen due to the relative simplicity of its harmonic response and it has been used to illustrate the general properties of the ellipticity of the HHG signal. Nevertheless, similar analyses can be done for multicentre harmonic targets (e.g., the $C_{20}$ structures), but the complexity of the responses makes it more difficult to understand the underlying physics of the process. With respect to the calculations for $N_2$, we have observed relatively large harmonic ellipticities when the Lewenstein model is applied. The largest values are obtained in the length gauge for angles and harmonic orders that admit multicentre interference effects. This is a consequence of the increase in the amplitude ratio and the change of the phase difference of harmonics by nearly $\pi$. 
Chapter 5

Conclusions and prospects

In this thesis, we have investigated two closely related phenomena which are stimulated and controlled by laser fields: strong-field ionization and high-order harmonic generation. The analysis of the former has been carried out according to the Keldysh theory, where the influence of an atomic potential on the ionized electron is neglected, and according to the generalized eikonal approximation, which accounts for this interaction. The high-order harmonic generation was treated according to the modified Lewenstein model for molecules and, as it is usually done in the SFA, the electron interactions with the parent ion were ignored between ionization and recombination events.

In the first part of the thesis, we have developed the generalized eikonal approximation to describe the strong-field ionization by finite laser pulses. We have proven that the inclusion of the Coulomb interaction via the GEA is very general and other theories, including the improved SFA [11–13] (which incorporates the electron interaction with the atomic potential by means of the first order Born approximation), can be derived as its limiting cases. In a similar way we have shown that, in the short-time interval limit, the GEA reduces to the original eikonal approximation provided that the electron does not revisit the potential centre.

The application of the GEA theory to photoionization by strong laser fields has many advantages as compared to the original eikonal approximation. We have shown that, contrary to the latter approximation, the GEA is not singular for electron trajectories that approach the nucleus. This makes it a very promising tool to study rescattering-related phenomena and high-order harmonic generation from atoms, molecules, and clusters. The calculation of the GEA for the Coulomb potential involves an integrand with integrable singularity and does not diverge logarithmically, as it happens in the case of the original eikonal [63].

The generalized eikonal has been calculated for other model potentials, like the exponential, Gaussian or Yukawa potentials. They can be used, for instance, to describe the photoionization process of weakly-bound atomic systems such as negative ions.

Using the GEA we have discussed the appearance of interference patterns in photoelectron energy spectra and their modifications induced by the interaction of photoelectrons with their parent ions. We have identified the conditions necessary to obtain such coherent patterns. If a pulse consists
of at least two modulations, each of these modulations acts as a slit in the Young-type experiment for matter waves resulting in a coherent enhancement of ionization signal at particular electron energies. As we have illustrated this numerically, if the number of modulations within a pulse is increased, the comb-like structures in the energy spectrum of photoelectrons become similar to the $\delta$-like structures. This is particularly interesting in the context of designing new sources of electron pulses, which is a topic to be studied in near future.

In the second part of this thesis, we have presented an analysis of harmonic responses from three different $C_{20}$ isomers (fullerene, ring, and bowl) interacting with intense laser fields. To the best our knowledge, such a comparative analysis has never been done for these structures. The modified Lewenstein model for the molecular case has been used in our calculations. Each harmonic response has proven to be sensitive to the geometry and electron arrangement of the molecule. We have shown that the most pronounced modulations along the HHG plateau are the consequence of interference effects. This is due to the multicentre nature of the systems, and coincide with the zeroes of the recombination matrix elements. Other less pronounced modulations are related to quantum path interference effects, as it is evident from the time-frequency analysis of the spectral responses. According to our calculations, the complete analysis of the HHG spectrum from molecules must also include an appropriate study of QPI effects. In this thesis, we have analyzed for first time the role that QPI effects play in the harmonic response from relatively large carbon structures.

In our analysis, in contrast to the previous works (see, for instance, [101, 104]), we have looked at the polarization properties of generated harmonics. We believe that this may help to identify the symmetry of the molecular target. The observation of such properties requires a certain degree of molecular alignment which, according to the available experimental techniques, is feasible for some of the studied isomers.

The respective calculations from the $C_{20}$ fullerene in the velocity gauge have shown different harmonic responses as compared to the length gauge. The ionization matrix element has turned out to play a very important role in determining the modulations along the HHG plateau. The minima have been observed very close to the regions where the scalar IME vanishes. Other modulations have been attributed to interference effects arising from the simultaneous contribution of the RME components and IME.

As we have shown in Chapter 4, the harmonic responses from $C_{20}$ isomers present two important characteristics directly related to the atomic and electronic configuration: strong modulations along the HHG plateau and a specific polarization direction of the harmonic signal. The observation of these two parameters can give an idea about the geometry of the molecule, which opens the door to simple spectroscopic techniques. Furthermore, the relation between the spatial atomic distribution, the molecular electron configuration, and the resulting harmonic response is fundamental in designing new targets to control HHG processes.

The last part of this thesis has been devoted to the analysis of the ellipticity of the harmonic response obtained from the nitrogen molecule. We have shown that the Lewenstein model analyzed according to the saddle-point equations, in its original form, predicts linearly-polarized responses from symmetric targets interacting with linearly-polarized laser fields. The modifications of this model, that
include the oscillatory terms into the semiclassical action and which are necessary for the analysis of HHG from molecules, make feasible the theoretical observation of relatively high ellipticities. We have calculated the amplitude ratios, phase differences, and ellipticities for different angles between the molecular axis of $N_2$ and the laser field polarization direction. The largest ellipticities have been obtained in the length gauge, when multicentre interferences take place.

In closing, let us note that the application of the GEA theory to the HHG is a very promising tool that would allow us to study the Coulomb effects in high-order harmonic generation. The fact that the rescattering (and multiple rescattering) events can be accounted for on quantum-mechanical footings using the GEA promises the raise of new features in the harmonic response from molecules and atoms. The inclusion of electron interactions with the atomic potential in the HHG via the generalized eikonal approximation is a potential topic of our further investigations.
Appendix A

Fourier transforms conventions

In this Appendix, we are going to establish the mathematical conventions used in this thesis.

A.1 Position and momentum transformations

If the quantum-mechanical state of the system is described by the wave function in position representation, \( \psi(r) \equiv \langle r | \psi \rangle \), its Fourier transform, according to the convention used in this thesis, is given in general as a \( d \)-dimensional integral,

\[
\tilde{\psi}(k) = \int dr e^{-ik \cdot r} \psi(r).
\]  
(A.1)

On the contrary, the inverse Fourier transform is given by

\[
\psi(r) = \int \frac{dk}{(2\pi)^d} e^{ik \cdot r} \tilde{\psi}(k),
\]  
(A.2)

where the term \( (2\pi)^{-d} \) is present. The position eigenvectors are normalized in the following way,

\[
\langle r | r' \rangle = \delta(r - r'),
\]  
(A.3)

and the closure relation for these vectors is

\[
\int dr |r\rangle \langle r| = \hat{I},
\]  
(A.4)

where \( \hat{I} \) is the identity operator. We have chosen the normalization of a plane wave such that

\[
\langle r | k \rangle = e^{ik \cdot r}.
\]  
(A.5)
With the help of the closure relation (A.4), we can write that for an arbitrary state, $|\psi\rangle$,

$$|\psi\rangle = \int \! d\mathbf{r} |\mathbf{r}\rangle \langle \mathbf{r}| \psi\rangle = \int \! d\mathbf{r} |\mathbf{r}\rangle \psi(\mathbf{r}) ,$$  \hspace{1cm} (A.6)

which, projected over the momentum eigenstate, gives

$$\langle \mathbf{k}|\psi\rangle = \int \! d\mathbf{r} \langle \mathbf{k}|\mathbf{r}\rangle \psi(\mathbf{r}) = \int \! d\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} \psi(\mathbf{r}) .$$  \hspace{1cm} (A.7)

Hence, we understand that $\tilde{\psi}(\mathbf{k}) = \langle \mathbf{k}|\psi\rangle$.

The normalization of momentum states can be easily calculated as follows,

$$\langle \mathbf{k'}|\mathbf{k}\rangle = \int \! d\mathbf{r} \langle \mathbf{k'}|\mathbf{r}\rangle \langle \mathbf{r}|\mathbf{k}\rangle = \int \! d\mathbf{r} e^{i(\mathbf{k}-\mathbf{k'})\cdot\mathbf{r}} = (2\pi)^d \delta(\mathbf{k'} - \mathbf{k}) ,$$  \hspace{1cm} (A.8)

and, in order to keep our notation consistent, the closure relation for momentum eigenstates has to be written as

$$\int \! \frac{d\mathbf{k}}{(2\pi)^d} |\mathbf{k}\rangle \langle \mathbf{k}| = \mathbf{I} .$$  \hspace{1cm} (A.9)

### A.2 Time and frequency transformations

As the Fourier transform relating position and momentum representations is defined by Eq. (A.1), the one that relates time and frequency, in our current notation, is given by

$$\tilde{f}(\omega) = \int \! dt \, e^{i\omega t} f(t) .$$  \hspace{1cm} (A.10)

The inverse Fourier transform is then written as

$$f(t) = \int \! \frac{d\omega}{2\pi} e^{-i\omega t} \tilde{f}(\omega) .$$  \hspace{1cm} (A.11)
Appendix B

Volkov states

The Volkov state (also known as the Gordon-Volkov state) represents the quantum-mechanical state of a charged particle with a defined asymptotic momentum $\mathbf{p}$ that interacts with an electromagnetic field. While these solutions can be derived beyond the dipole approximation in the relativistic theory, within the scope of this thesis we restrict ourselves to the dipole approximation only (Section 2.1.3). Thus, we are interested in deriving the solutions of the time-dependent Schrödinger equation for a charged particle (of a charge $e < 0$) in the presence of the electromagnetic field. To represent the field, we set the scalar potential $\phi(\mathbf{r}, t)$ to zero, so the vector potential $\mathbf{A}(t)$ fully describes the field.

Under the aforementioned assumptions, the time-dependent Schrödinger equation written in the velocity gauge has the form,

$$\frac{i}{\hbar} \frac{d}{dt} |\psi_V(t)\rangle = \frac{1}{2m} [\hat{\mathbf{p}} - e\mathbf{A}(t)]^2 |\psi_V(t)\rangle,$$

(B.1)

which can be easily solved in the momentum representation. If $\tilde{\psi}_V(\mathbf{p}, t)$ describes the particle state in the momentum representation, then it follows from (B.1) that

$$\frac{i}{\hbar} \frac{\partial}{\partial t} \tilde{\psi}_V(\mathbf{p}, t) = \frac{1}{2m} [\mathbf{p} - e\mathbf{A}(t)]^2 \tilde{\psi}_V(\mathbf{p}, t).$$

(B.2)

The solution to this equation is

$$\tilde{\psi}_V(\mathbf{p}, t) = Ne^{-i \frac{1}{\hbar m} \int^t d\tau [\mathbf{p} - e\mathbf{A}(\tau)]^2},$$

(B.3)

where $N$ is a suitably chosen normalization constant. In order to obtain the respective wave function in the position representation, one has to calculate the inverse Fourier transform following Eq. (A.2). Hence, we obtain that

$$\psi_V(\mathbf{r}, t) = N \int \frac{d\mathbf{p}}{(2\pi)^d} e^{i\mathbf{p} \cdot \mathbf{r} - i \frac{1}{\hbar m} \int^t d\tau [\mathbf{p} - e\mathbf{A}(\tau)]^2}.$$ 

(B.4)

This formula represents a wave packet which is a superposition of states with all possible momenta. An elementary wave in this superposition will be called the Volkov wave (or the Gordon-Volkov wave)
Volkov states

\[ \psi_{p,V}(r,t) = \exp \left[ i p \cdot r - \frac{i}{2m} \int_0^t d\tau (p - eA(\tau))^2 \right] . \]  

We can also write it down independently of the representation as

\[ |\psi_{p,V}(t)\rangle = |p\rangle e^{-\frac{i}{2m} \int_0^t d\tau (p - eA(\tau))^2} . \]  

These are the elementary solutions to Eq. (B.1) and they are labeled by \( p \). The latter has the meaning of an asymptotic momentum of the particle. It follows from Eq. (B.6) that the Volkov solutions are normalized such that

\[ \langle \psi_{p,V}(t)|\psi_{p',V}(t)\rangle = (2\pi)^d \delta(p - p') , \]  

where the property (A.8) has been used.

In order to derive an explicit formula for the Volkov solution in the length gauge, we perform the gauge transformation (2.35) with \( \Lambda(\hat{r}, t) = -A(t) \cdot \hat{r} \) [Eq. (2.41)]. In doing so, we find out that the Volkov state in the length gauge is given by

\[ \psi_{p,L}(r,t) = \exp \left[ i (p - eA(t)) \cdot r - \frac{i}{2m} \int_0^t d\tau (p - eA(\tau))^2 \right] . \]  

For completeness, we also write it irrespectively of the representation,

\[ |\psi_{p,L}(t)\rangle = |p - eA(t)\rangle e^{-\frac{i}{2m} \int_0^t d\tau (p - eA(\tau))^2} . \]  

The Volkov solutions, derived above in both the velocity and length gauges, allow us to define the corresponding time-evolution operator. We shall call it the Volkov (or, the Gordon-Volkov) operator. For the Hamiltonian implicitly defined in (B.1), it is given as

\[ \hat{U}^{GV}_{V}(t,t') = \int \frac{dp}{(2\pi)^d} |p\rangle \langle p| e^{-\frac{i}{2m} \int_0^t d\tau (p - eA(\tau))^2} . \]  

Equivalently, we can write it in the length gauge,

\[ \hat{U}^{GV}_{L}(t,t') = \int \frac{dp}{(2\pi)^d} |p - eA(t)\rangle \langle p - eA(t')| e^{-\frac{i}{2m} \int_0^t d\tau (p - eA(\tau))^2} . \]  

Hence, we also obtain the form of the retarded propagator (2.12) in both gauges. Namely, the retarded propagator in the velocity gauge,

\[ K^{GV}_{V}(r,t; r', t') = \int \frac{dp}{(2\pi)^d} \exp \left[ i (p - eA(t)) \cdot (r - r') - \frac{i}{2m} \int_{t'}^t d\tau (p - eA(\tau))^2 \right] , \]  

and in the length gauge,

\[ K^{GV}_{L}(r,t; r', t') = \int \frac{dp}{(2\pi)^d} \exp \left[ i (p - eA(t)) \cdot r - i (p - eA(t')) \cdot r' - \frac{i}{2m} \int_{t'}^t d\tau (p - eA(\tau))^2 \right] , \]  

where (A.8) has been used.
where we understand that the propagation is forward in time, i.e., $t > t'$. Note that these propagators are related through the gauge transformation (2.45).
Appendix C

Fresnel integral

In this Appendix, we are going to calculate a $d$-dimensional Fresnel-type integral,

$$\mathcal{I}_d = \int \frac{d\mu}{(2\pi)^d} e^{-i|a|\mu^2 + i b \cdot \mu}, \quad (C.1)$$

with arbitrary $a$ and $b$. By completing the squares in the exponent, the previous expression becomes

$$\mathcal{I}_d = e^{i b^2 4 a} \int \frac{d\mu}{(2\pi)^d} e^{-i a (\mu - \frac{b}{2a})^2}, \quad (C.2)$$

where one has to remember that $b$ and $\mu$ are $d$-dimensional vectors. Thus, the $d$-dimensional integral over independent variables $\mu_j$ (where $j = 1, 2, \ldots, d$) can be represented in the following way,

$$\mathcal{I}_d = e^{i b^2 4 a} \prod_{j=1}^{d} \int_{-\infty}^{\infty} \frac{d\mu_j}{2\pi} e^{-i a (\mu_j - \frac{b_j}{2a})^2}. \quad (C.3)$$

Each of these integrals (for $j = 1, 2, \ldots, d$) can be performed by deforming the integration path such that $\mu_j = \frac{b_j}{2a} + \rho_j e^{i \alpha_j}$, where $\rho_j$ is a real parameter and where we adjust $\alpha_j$ so it equals $\alpha_j \equiv \alpha = -\frac{\pi}{4} - \frac{1}{2} \arg(a)$. Hence, Eq. (C.3) becomes

$$\mathcal{I}_d = e^{i b^2 4 |a|} \prod_{j=1}^{d} \int_{-\infty}^{\infty} \frac{d\rho_j}{2\pi} e^{-|a|\rho_j^2}. \quad (C.4)$$

The remaining integrals are over real-valued Gaussian functions, so they can be calculated directly. This leads to

$$\mathcal{I}_d = \frac{e^{i b^2}}{(4\pi|a|)^{d/2}}, \quad (C.5)$$

or, equivalently, to

$$\mathcal{I}_d = \frac{e^{i b^2 - i \pi d/4}}{(4\pi|a|)^{d/2}} \equiv \frac{e^{i b^2}}{(4\pi|a|)^{d/2}}. \quad (C.6)$$

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Even though the above result has been derived for arbitrary $a$ and $b$, for the purpose of Eqs. (2.76) and (2.99) we have $a \in \mathbb{R}_+$. This result specifies that $\sqrt{i} = e^{i \pi/4}$. It also agrees with Eq. (7.5.8) from [87] which is cited in this thesis [see, Eq. (2.113)].
Appendix D

Classical action of a particle in an electromagnetic field

D.1 Classical action in the velocity gauge

We devote this Section to the classical analysis of a particle with mass $m$ and charge $e$ interacting with an electromagnetic field. The latter is described by the vector potential $A(t)$. In this case, the Lagrangian of the system in the velocity gauge is

$$L_V = \frac{m}{2} \dot{r}^2 + e \dot{r} \cdot A(t).$$  \hfill (D.1)

Hence,

$$\frac{\partial L_V}{\partial \dot{r}} = m \ddot{r} + e A(t), \quad \frac{\partial L_V}{\partial r} = 0. \quad \hfill (D.2)$$

Substituting these derivatives to the Euler-Lagrange equation,

$$\frac{d}{dt} \left( \frac{\partial L_V}{\partial \dot{r}} \right) - \frac{\partial L_V}{\partial r} = 0,$$  \hfill (D.3)

we obtain

$$m \ddot{r} + e \dot{A} = 0.$$  \hfill (D.4)

This equation can be integrated directly to obtain the classical trajectory of the particle moving in the electromagnetic field,

$$r(t) = -\frac{e}{m} \int_0^t d\tau A(\tau) + v_0 t + r_0,$$  \hfill (D.5)

where $v_0$ and $r_0$ are integration constants which can be determined from the initial conditions. These conditions are such that

$$r(t_1) = r_1,$$  \hfill (D.6)

$$r(t_2) = r_2.$$  \hfill (D.7)
Taking into account Eq. (D.5), one can write the expressions for \( r_1 \) and \( r_2 \),

\[
\begin{align*}
    r_1 &= -\frac{e}{m} \int_{t_0}^{t_1} d\tau A(\tau) + v_0 t_1 + r_0, \\
    r_2 &= -\frac{e}{m} \int_{t_0}^{t_2} d\tau A(\tau) + v_0 t_2 + r_0.
\end{align*}
\] (D.8)

By solving this system of equations we find out that

\[
\begin{align*}
    r_0 &= \frac{r_1 t_2 - r_2 t_1}{t_2 - t_1} + \frac{e}{m} \int_{t_1}^{t_1} d\tau A(\tau) - \frac{e t_1}{m(t_2 - t_1)} \int_{t_1}^{t_2} d\tau A(\tau), \\
    v_0 &= \frac{r_2 - r_1}{t_2 - t_1} + \frac{e}{m(t_2 - t_1)} \int_{t_1}^{t_2} d\tau A(\tau).
\end{align*}
\] (D.10)

Note that in the derivation below, the explicit form of \( r_0 \) is not used. Nevertheless, we present it for completeness.

The classical action is defined as the integral of the Lagrangian over time. In other words, in the velocity gauge, we have

\[
S_V = \int_{t_1}^{t_2} d\tau \mathcal{L}_V = \int_{t_1}^{t_2} d\tau \left( \frac{m}{2} \dot{r}^2 + e\dot{r} \cdot A(\tau) \right).
\] (D.12)

Substituting here the classical trajectory [Eq. (D.5)], with account for the definition (D.11), we obtain that the classical action of the charged particle in the electromagnetic field equals

\[
S_V = \frac{m}{2(t_2 - t_1)} \left( r_2 - r_1 + \frac{e}{m} \int_{t_1}^{t_2} d\tau A(\tau) \right)^2 - \frac{e^2}{2m} \int_{t_1}^{t_2} d\tau A^2(\tau).
\] (D.13)

This formula relates to the velocity gauge, as indicated by the subscript "V" present in \( S_V \).

### D.2 Classical action in the length gauge

Note that by performing a gauge transformation

\[
\mathcal{L}' = \mathcal{L} + e \frac{d}{dt} \Lambda(r, t),
\] (D.14)

where \( \Lambda(r, t) \) is an arbitrary function, we end up with the exact same equation defining the classical trajectory (D.4). Taking

\[
\Lambda(r, t) = -r \cdot A(t),
\] (D.15)

we can write down that the Lagrangian in the length gauge is

\[
\mathcal{L}_L = \mathcal{L}_V - e \frac{d}{dt} [r \cdot A(t)] = \frac{m}{2} \dot{r}^2 - e r \cdot \dot{A}(t),
\] (D.16)
where we have substituted the expression for $\mathcal{L}_V$ [Eq. (D.1)]. It follows directly from Eq. (D.16) that
\[
\frac{\partial \mathcal{L}_L}{\partial \dot{r}} = m \dot{r}, \quad \frac{\partial \mathcal{L}_L}{\partial r} = -e \dot{A}(t) .
\] (D.17)
Thus, we arrive at the same equation of motion (D.4), which can be solved exactly for an arbitrary $A(t)$ [see, Eqs. (D.5), (D.10), and (D.11)]. The classical action calculated in the length gauge, $S_L$, is
\[
S_L = \int_{t_1}^{t_2} d\tau \left( \mathcal{L}_V - e \frac{d}{d\tau} [\mathbf{r} \cdot \mathbf{A}(\tau)] \right) = S_V - e \mathbf{r}_2 \cdot \mathbf{A}(t_2) + e \mathbf{r}_1 \cdot \mathbf{A}(t_1) ,
\] (D.18)
where we have used the initial conditions [Eqs. (D.6) and (D.7)]. Finally, inserting here Eq. (D.13), we obtain that the classical action in the length gauge has the form,
\[
S_L = \frac{m}{2(t_2 - t_1)} \left( \mathbf{r}_2 - \mathbf{r}_1 + e \int_{t_1}^{t_2} d\tau \mathbf{A}(\tau) \right)^2 - \frac{e^2}{2m} \int_{t_1}^{t_2} d\tau \mathbf{A}^2(\tau) - e \mathbf{r}_2 \cdot \mathbf{A}(t_2) + e \mathbf{r}_1 \cdot \mathbf{A}(t_1) .
\] (D.19)

### D.3 Classical action in the presence of an external potential

Consider the case when, in addition to the electromagnetic field, $\mathbf{A}(t)$, an external potential acts on a charged particle. Let $V(\mathbf{r}, t)$ describe the respective potential energy. Using the velocity gauge as described in Appendix D.1, we can write down the corresponding Lagrangian,
\[
\mathcal{L}_V = \frac{m}{2} \dot{\mathbf{r}}^2 + e \dot{\mathbf{r}} \cdot \mathbf{A}(t) - V(\mathbf{r}, t) .
\] (D.20)
Its derivatives with respect to $\dot{\mathbf{r}}$ and $\mathbf{r}$ are
\[
\frac{\partial \mathcal{L}_V}{\partial \dot{\mathbf{r}}} = m \ddot{\mathbf{r}} + e \dot{\mathbf{A}}(t), \quad \frac{\partial \mathcal{L}_V}{\partial \mathbf{r}} = -\nabla V(\mathbf{r}, t) .
\] (D.21)
It follows from these relations and from Eq. (D.3) that the classical trajectory satisfies the equation
\[
m \ddot{\mathbf{r}} + e \ddot{\mathbf{A}}(t) + \nabla V(\mathbf{r}, t) = 0 .
\] (D.22)
If the electromagnetic field is much stronger than the interaction with the external potential, meaning that $|e \ddot{\mathbf{A}}(t)| \gg |\nabla V(\mathbf{r}, t)|$, Eq. (D.22) can be approximated as
\[
m \ddot{\mathbf{r}} + e \ddot{\mathbf{A}}(t) \approx 0 .
\] (D.23)
Note that this assumption is typical for strong-field phenomena involving a laser field and an atomic potential, which is exactly the case considered in this thesis. Based on this assumption, we proceed with deriving the classical action,
\[
S_V = \int_{t_1}^{t_2} d\tau \left( \frac{m}{2} \dot{\mathbf{r}}^2 + e \dot{\mathbf{r}} \cdot \mathbf{A}(\tau) - V(\mathbf{r}, \tau) \right) .
\] (D.24)
Similar as before, we impose the initial conditions (D.6) and (D.7) on the classical trajectories satisfying the equation (D.23). This means that the first two terms in the integrand in (D.24) are the same as in (D.13). This leads us to

\[ S_V = \frac{m}{2(t_2 - t_1)} \left( r_2 - r_1 + \frac{e}{m} \int_{t_1}^{t_2} d\tau A(\tau) \right)^2 - \frac{e^2}{2m} \int_{t_1}^{t_2} d\tau A^2(\tau) - \int_{t_1}^{t_2} d\tau V(r, \tau). \] (D.25)

It follows from Eqs. (D.5), (D.10), and (D.11) that in the short-time interval limit

\[ r(\tau) \approx r_1 - \frac{e}{m} \int_{t_1}^{\tau} d\sigma A(\sigma). \] (D.26)

After substituting this result in Eq. (D.25), we obtain that the classical action of a charged particle coupled to an electromagnetic field and to an external potential takes the form

\[ S_V \approx \frac{m}{2(t_2 - t_1)} \left( r_2 - r_1 + \frac{e}{m} \int_{t_1}^{t_2} d\tau A(\tau) \right)^2 - \frac{e^2}{2m} \int_{t_1}^{t_2} d\tau A^2(\tau) - \int_{t_1}^{t_2} d\tau V(r_1 - \frac{e}{m} \int_{t_1}^{\tau} d\sigma A(\sigma), \tau). \] (D.27)

which corresponds to the limit \( t_2 \approx t_1 \). The same but in the length gauge has the form,

\[ S_L \approx \frac{m}{2(t_2 - t_1)} \left( r_2 - r_1 + \frac{e}{m} \int_{t_1}^{t_2} d\tau A(\tau) \right)^2 - e r_2 \cdot A(t_2) + e r_1 \cdot A(t_1) - \frac{e^2}{2m} \int_{t_1}^{t_2} d\tau A^2(\tau) \]

\[ - \int_{t_1}^{t_2} d\tau V(\frac{e}{m} \int_{t_1}^{\tau} d\sigma A(\sigma), \tau). \] (D.28)
Appendix E

Saddle-point method

Sometimes, it is important to determine the asymptotic behavior of certain functions defined as integrals in the complex plane, e.g., the Gamma function, Bessel functions, etc., [144]. Therefore, a method to determine the approximate behavior of such integrals is important. In this Appendix, we are going to describe the so-called saddle-point method to approximate one-dimensional integrals (see, Refs. [144–147]), which will help us to treat some expressions in Chapter 2. The present approach can be extended to multidimensional integrals, which are going to be used in Chapter 3. Such extension becomes clear once the method for the one-dimensional case is formulated. The notation in this Appendix is the same as the one used in Chapter 2.

E.1 Ordinary saddle-point method

Let us consider the integral defined as

\[ I = \int_{a}^{b} d\phi F(\phi)e^{i\zeta G(\phi)}, \]  

(E.1)

where \( \zeta \) is a large, real, and positive parameter. The application of such integral to physical phenomena involves, in general, functions \( F(\phi) \) and \( G(\phi) \) bounded, and sufficiently regular for real \( \phi \). Due to these properties, the integral (E.1) is also finite. This can be shown by analyzing the inequality

\[ \left| \int_{a}^{b} d\phi F(\phi)e^{i\zeta G(\phi)} \right| < \int_{a}^{b} d\phi |F(\phi)| < M, \]  

(E.2)

which holds for an arbitrary large \( \zeta \). For physical applications, this large parameter depends on the characteristics of the theory and it can be absorbed into the function \( G(\phi) \) without modifying its mathematical properties. Because of the analyticity of the integrand, we can replace Eq. (E.1) by the complex contour integral,

\[ I = \int_{C} d\phi F(\phi)e^{i\zeta G(\phi)}, \]  

(E.3)
where the contour $C$ starts at the point $(a, 0)$ and ends at $(b, 0)$. Such contour can be modified in a way that it passes through all relevant saddle points, $\phi_s$, which are defined by the condition \cite{144}

$$G' (\phi_s) \equiv \frac{dG(\phi)}{d\phi} \bigg|_{\phi_s} = 0 . \quad (E.4)$$

Now, we expand the function $G(\phi)$ in the vicinity of the saddle point $\phi_s$,

$$G(\phi) \approx G(\phi_s) + \frac{dG(\phi)}{d\phi} \bigg|_{\phi_s} (\phi - \phi_s) + \frac{d^2G(\phi)}{d\phi^2} \bigg|_{\phi_s} \frac{(\phi - \phi_s)^2}{2} = G(\phi_s) + \frac{d^2G(\phi)}{d\phi^2} \bigg|_{\phi_s} \frac{(\phi - \phi_s)^2}{2} , \quad (E.5)$$

where the expansion has been carried on up to the second order and the condition (E.4) has been applied. We assume that $G''(\phi_s) \neq 0$. Using Eq. (E.5), we approximate the integral (E.1) as

$$\mathcal{I} \approx \sum_s e^{iG(\phi_s)} F(\phi_s) \int_C d\phi \ e^{iG''(\phi_s) \frac{(\phi - \phi_s)^2}{2}} , \quad (E.6)$$

where the summation is carried over all relevant saddle points and the function $F(\phi)$ has been evaluated at $\phi_s$. As it was discussed before, the integral $\mathcal{I}$ is finite, so the relation (E.6) requires that $\text{Im}[G''(\phi)] > 0$ (in order for the integral over $\phi$ to be convergent) and $\text{Im}[G(\phi)] > 0$ [in order to keep $e^{iG(\phi_s)}$ bounded for any parameter $\zeta$ in Eq. (E.1)]. We have also assumed that $F(\phi_s)$ is finite.

Next, we deform the path such that $\phi = \phi_s + \rho e^{i\varphi_s}$, where $\varphi_s = \frac{\pi}{4} - \frac{1}{2} \text{arg}[G''(\phi_s)]$ and $\rho$ is a real parameter in the interval $[\rho_s^{(1)}, \rho_s^{(2)}]$. The parameters $\rho_s^{(1)}$ and $\rho_s^{(2)}$ define the integration region along the complex path where the saddle point is located. In this case, Eq. (E.6) becomes

$$\mathcal{I} \approx \sum_s F(\phi_s) e^{iG(\phi_s) + i\varphi_s} \int_{\rho_s^{(1)}}^{\rho_s^{(2)}} d\rho \ e^{-\frac{1}{2} \zeta |G''(\phi_s)| \rho^2} . \quad (E.7)$$

As the main contribution to the integral in (E.7) comes from points such that $\rho \sim 0$, we can extend the integration limits from $-\infty$ to $+\infty$ for all saddle points. Hence,

$$\mathcal{I} \approx \sum_s F(\phi_s) e^{iG(\phi_s) + i\varphi_s} \int_{-\infty}^{\infty} d\rho \ e^{-\frac{1}{2} \zeta |G''(\phi_s)| \rho^2} . \quad (E.8)$$

This formula is valid assuming that the saddle points are not equal to the initial or final limits of the integration, $a$ or $b$. If that was the case, just half of the Gaussian function has to be accounted for.

The remaining integral in (E.8) is a real integral over the Gaussian function, which can be performed analytically,

$$\mathcal{I} \approx \sum_s \sqrt{\frac{2\pi}{|\zeta| G''(\phi_s)}} F(\phi_s) e^{iG(\phi_s) + i\varphi_s} = \sum_s \sqrt{\frac{2\pi}{\zeta G''(\phi_s)}} F(\phi_s) e^{iG(\phi_s) + i\pi/4} . \quad (E.9)$$

It follows from this expression that the relevant saddle points are those with the smallest positive $\text{Im}[G(\phi_s)]$. 

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\textbf{Appendix E. Saddle-point method}
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The extension of this approximation to the \(d\)-dimensional case is straightforward and we only present the final result,

\[
I_d \approx \sum_s \sqrt{\frac{(2\pi/\zeta)^d}{\det[G''_{i,j}(\phi_s)]}} F(\phi_s)e^{iG(\phi_s)+id\pi/4},
\] (E.10)

where \(\phi_s = (\phi_{s,1}, \phi_{s,2}, \ldots, \phi_{s,d})\) is a saddle point in the \(d\)-dimensional space and \(G''_{i,j}(\phi_s) = \frac{\partial^2 G(\phi_s)}{\partial \phi_{s,i} \partial \phi_{s,j}}\).

### E.2 Singular saddle-point method

If the function \(F(\phi)\) has a pole at the saddle point, the formulas derived in the previous Section cannot be applied. This concerns specifically the integral

\[
I_\nu = \int_0^{2\pi} d\phi \frac{H(\phi)}{[G'(\phi)]^\nu} e^{i\zeta G(\phi)},
\] (E.11)

which is important for derivations presented in Chapter 2.

Similar to the last Section, we replace Eq. (E.11) by a complex contour integral,

\[
I_\nu = \int_C d\phi \frac{H(\phi)}{[G'(\phi)]^\nu} e^{i\zeta G(\phi)},
\] (E.12)

where the contour \(C\) starts from the point \((0, 0)\) and ends at \((2\pi, 0)\). In order to avoid the singularity at the saddle point, we start by rewriting the denominator of the integrand in Eq. (E.11) with the help of the Gamma function (see, Eq. (5.2.1) in Ref. [87]),

\[
\frac{1}{[G'(\phi)]^\nu} = \frac{1}{\Gamma(\nu)} \int_0^\infty d\xi \xi^{\nu-1} e^{-G'(\phi)\xi}.
\] (E.13)

We assume that \(G'(\phi)\) is a positive function, as it is in Chapter 2. Taking into account Eq. (E.13), the integral (E.11) becomes,

\[
I_\nu = \frac{1}{\Gamma(\nu)} \int_0^\infty d\xi \xi^{\nu-1} \int_C d\phi H(\phi) \exp[-G'(\phi)\xi + iG(\phi)],
\] (E.14)

where the parameter \(\zeta\) has been incorporated into the definition of \(G(\phi)\). As in the previous Section, the contour has to be modified in order to include all relevant saddle points, which are determined by Eq. (E.4). Now, we represent the exponent in Eq. (E.14) in the vicinity of the saddle point, \(\phi_s\), as

\[
-G'(\phi)\xi + iG(\phi) \approx iG(\phi_s) + \frac{i}{2} G''(\phi_s)\xi^2 + \frac{i}{2} G''(\phi_s)(\phi - \phi_s + i\xi)^2,
\] (E.15)
where Eq. (E.4) has been used. According to this expansion and assuming that \(G''(\phi_s) \neq 0\), we approximate the integral (E.11) in the following way,

\[
\mathcal{I}_\nu \approx \sum_s \frac{H(\phi_s)}{\Gamma(\nu)} e^{G(\phi_s)} \int_0^\infty d\xi \xi^{\nu-1} e^{\frac{i\nu}{2} G''(\phi_s) \xi^2} \int_0^\infty d\rho e^{-\frac{i}{2} G''(\phi_s) \rho^2},
\]

(E.16)

where we have replaced \(H(\phi)\) by its value at the saddle point \(\phi_s\). This time, we deform the path such that \(\phi = \phi_s - i\xi + \rho e^{i\varphi_s}\), where \(\varphi_s = \frac{\pi}{4} - \frac{1}{2} \arg[G''(\phi_s)]\) and \(\rho\) extends from \(-\infty\) to \(\infty\). In this case, the integral \(\mathcal{I}_\nu\) is approximated as

\[
\mathcal{I}_\nu \approx \sum_s \frac{H(\phi_s)}{\Gamma(\nu)} e^{G(\phi_s)+i \varphi_s} \int_0^\infty d\xi \xi^{\nu-1} e^{\frac{i\nu}{2} G''(\phi_s) \xi^2} \int_0^\infty d\rho e^{-\frac{i}{2} G''(\phi_s) \rho^2}.
\]

(E.17)

Performing the Gaussian integral over \(\rho\), we arrive at

\[
\mathcal{I}_\nu \approx \sum_s \frac{H(\phi_s)}{\Gamma(\nu)} \sqrt{\frac{2\pi}{G''(\phi_s)}} e^{iG(\phi_s)+i \pi/4} \int_0^\infty d\xi \xi^{\nu-1} e^{\frac{i\nu}{2} G''(\phi_s) \xi^2}.
\]

(E.18)

Next, we rotate the integration contour by an angle \(\beta = \frac{\pi}{4} - \frac{1}{2} \arg[G''(\phi_s)]\). This means that we parametrize \(\xi\) such that \(\xi = \alpha e^{i\beta}\), where \(\alpha\) goes from 0 to infinity. Hence, we arrive at the expression

\[
\mathcal{I}_\nu \approx \sum_s \frac{H(\phi_s)}{\Gamma(\nu)} \sqrt{\frac{2\pi}{G''(\phi_s)}} e^{iG(\phi_s)+i \pi/4 + i \nu \beta} \int_0^\infty d\alpha \alpha^{\nu-1} e^{-\frac{i}{2} G''(\phi_s) |\alpha|^2}.
\]

(E.19)

Now, introducing a new variable \(x = \alpha^2 |G''(\phi_s)|/2\), we rewrite Eq. (E.19) as

\[
\mathcal{I}_\nu \approx \frac{1}{2} \sum_s \frac{H(\phi_s)}{\Gamma(\nu)} \left( \frac{2}{|G''(\phi_s)|} \right)^\nu/2 \sqrt{\frac{2\pi}{G''(\phi_s)}} e^{iG(\phi_s)+i \pi/4 + i \nu \beta} \int_0^\infty dx x^{\nu/2-1} e^{-x}.
\]

(E.20)

Finally, the integral \(\mathcal{I}_\nu\) can be approximated as

\[
\mathcal{I}_\nu \approx \frac{\Gamma(\nu/2)}{2\pi^{\nu/2} \Gamma(\nu)} \sum_s \left( \frac{2\pi}{G''(\phi_s)} \right)^{\nu+1} \frac{1}{\pi^{\nu+3/2}} H(\phi_s) e^{iG(\phi_s)+i(\nu+1) \pi/4}.
\]

(E.21)

In order to simplify this relation, we use the duplication formula (see, Eq. (5.5.5) in Ref. [87]),

\[
\Gamma \left( \frac{\nu}{2} \right) \Gamma \left( \frac{\nu + 1}{2} \right) = 2^{1-\nu} \sqrt{\pi} \Gamma(\nu).
\]

(E.22)

Taking into account this expression and Eq. (E.21), the integral \(\mathcal{I}_\nu\) defined by Eq. (E.11) and approximated by the singular saddle-point method becomes

\[
\mathcal{I}_\nu \approx \frac{\pi}{2^{\nu+1} \Gamma \left( \frac{\nu + 1}{2} \right)} \sum_s \left( \frac{2\pi}{G''(\phi_s)} \right)^{\nu+1} H(\phi_s) e^{iG(\phi_s)+i(\nu+1) \pi/4}.
\]

(E.23)

This expression is used in Section 2.6.2.1 for \(\nu = 3\).
Appendix F

Converged harmonic responses from the $C_{20}$ isomers

In Sec. 4.1.2.2, we have studied how the particular molecular orbitals contribute to the HHG spectrum. In this Appendix, the harmonic responses from the three $C_{20}$ isomers, after the total convergence is achieved (i.e., when the influence of inner orbitals starts to be negligible in the calculations), are presented. Each structure requires a different number of molecular orbitals to be accounted for in order to obtain the convergence. In Figs. F.1, F.2, and F.3, we present the results for the cage, ring, and bowl, respectively. In order to obtain the convergent results, seven molecular orbitals have been accounted for for the cage (from HOMO to HOMO-6), thirteen for the ring (from HOMO to HOMO-12), and eight for the bowl (from HOMO to HOMO-7).

Figure F.1 The converged harmonic responses for the cage. The laser field parameters are the same as in Figs. 4.2 and 4.3. Panels a, b, c, d, and e show the harmonic responses $d_{xx}$, $d_{yy}$, $d_{zy}$, $d_{yz}$, and $d_{zz}$, respectively. Seven molecular orbitals have been accounted for (from HOMO to HOMO-6) to assure proper convergence.
Appendix F. *Converged harmonic responses for the $C_{20}$ structures*

Figure F.2  The converged harmonic responses for the ring. The laser field parameters are the same as in Figs. 4.4 and 4.5. Panels a, b, c, d, and e show the harmonic responses $d_{xx}$, $d_{yx}$, $d_{xy}$, $d_{yy}$, and $d_{zz}$, respectively. In these calculations, thirteen molecular orbitals have been accounted for (from HOMO to HOMO-12) to assure the convergence.

Figure F.3  The converged harmonic responses for the bowl. The laser field parameters are the same as in Figs. 4.6 and 4.7. Panels a, b, and c show the harmonic responses obtained for the laser field polarized along the $x$-direction ($d_{xx}$, $d_{yx}$, and $d_{zx}$, respectively). The middle row corresponds to the responses $d_{xy}$, $d_{yy}$, and $d_{zy}$ (panels d, e, and f, respectively) and the bottom row to the responses $d_{xz}$, $d_{yz}$, and $d_{zz}$ (panels g, h, and i). In this case, eight molecular orbitals have been accounted for (from HOMO to HOMO-7) to assure the convergence.
In Sec. 4.1.2.1, it has been demonstrated that some of the modulations of the spectral envelope are directly related to zeroes of the RME. We have shown that the addition of inner molecular orbitals can modify the harmonic response together with the corresponding RME. However, the relation between envelope modulations and RME zeroes remains valid.
Bibliography


