Quantum Optimal Control of High-Harmonic Generation from Molecular Systems

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## Contents

1 **Introduction**  
  1.1 Femtosecond and Attosecond Scale .......................... 1  
  1.2 Exploring Attosecond Scale: Need for Ultrafast Lasers .......... 2  
  1.3 Sources for Ultrafast Lasers ................................ 3  
  1.4 Challenges and goals ........................................... 5  
  1.5 Towards Realization .............................................. 5  
  \hspace{0.4cm} 1.5.1 Experimentalists: Adaptive Control .................. 6  
  \hspace{0.4cm} 1.5.2 Theoretical Side ........................................ 7  
  1.6 Our Work ......................................................... 8  

2 **HIGH-HARMONIC GENERATION**  
  2.1 Strong Lasers ................................................... 10  
  2.2 Physical model: Single-atom response ........................ 11  
  2.3 Harmonic spectrum .............................................. 15  
  2.4 Coherence ........................................................ 17  

3 **Theory of Quantum Optimal Control**  
  3.1 Controllabilty .................................................. 20  
  3.2 Writing Functionals for Optimization ........................ 21  
  3.3 The Control Equation from Variation of J ..................... 22  
  \hspace{0.4cm} 3.3.1 Variation with respect to the wavefunction $\Psi$ ....... 23  
  \hspace{0.4cm} 3.3.2 Variation with respect to the Lagrange multiplier $\chi$ 24  
  \hspace{0.4cm} 3.3.3 Variation with respect to the field ...................... 24  
  \hspace{0.4cm} 3.3.4 Control equations ....................................... 24  
  \hspace{0.4cm} 3.3.5 Solving The Control Equations .......................... 25  
  3.4 Direct Optimization .............................................. 28  
  \hspace{0.4cm} 3.4.1 Fixed fluence ........................................... 29  
  \hspace{0.4cm} 3.4.2 Optimization Algorithms ............................... 30
3.5 Comparison of Two Approaches of QOCT ........................................ 32
3.6 High Harmonic Generation Optimization with Direct Optimization Method .......................................................................................................................... 32

4 Results ........................................................................................................... 34
  4.1 Model Systems .............................................................................................. 34
  4.2 Initial Spectrum and Frequency of the incident laser .................................. 35
  4.3 Results for Hydrogen Atom ......................................................................... 35
  4.4 Results for Hydrogen Molecule ................................................................... 37
  4.5 Discussion .................................................................................................... 38
# List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Different targets for high-harmonic spectra: extension of the cutoff energy, increase in the efficiency of the high-harmonic conversion process, and the selection of single harmonics or range of harmonics.</td>
<td>5</td>
</tr>
<tr>
<td>1.2</td>
<td>Working principle of adaptive control. The incoming laser pulse is first shaped in a laser pulse shaper and is then used to perform the experiment in the quantum system. The experimental signal is analyzed and a fitness is assigned to the corresponding laser pulse. Utilizing this ranking, the evolutionary algorithm can automatically and iteratively find the optimum laser pulse shape.</td>
<td>7</td>
</tr>
<tr>
<td>2.1</td>
<td>Illustration of the three-step model for high-harmonic generation: (1) tunnel ionization of the electron, (2) acceleration in the laser electric field, and (3) recombination and emission of a high-energy photon. The energy of the emitted photon depends on the ionization potential of the atom and on the kinetic energy of the electron upon its return to its parent ion.</td>
<td>11</td>
</tr>
<tr>
<td>2.2</td>
<td>Different classes of electron trajectories during the propagation phase of high-harmonic generation, plotted in the position-velocity plane: The trajectories start at the atom located at (0,0). Depending on the phase $\phi$ of the electric field at the instant of ionization, they can return to the core at position 0 with different kinetic energies, visualized by the intersection with the velocity axis. The traces $a$ ($\phi = 45^\circ$) and $c$ ($\phi = 3^\circ$) correspond to the short and long trajectory, respectively, leading to the same final energy. Class $b$ ($\phi = 17^\circ$) is a cutoff trajectory with the highest kinetic energy (3.17$U_\text{p}$), $d$ ($\phi = 0^\circ$) starts at the peak of the electric field where most electrons are produced but returns to the core with zero kinetic energy. Trajectory $e$ ($\phi = -45^\circ$) never returns to its parent atom.</td>
<td>14</td>
</tr>
</tbody>
</table>
2.3 Typical high-harmonic spectrum (vertical axis in logarithmic scale). The spectrum can be divided into three parts which have been exaggerated in this schematic diagram for clarity: the perturbative regime at low orders, the plateau for intermediate orders, and the cutoff at the highest orders. ................................. 16

3.1 a) external potential of the asymmetric double well (Eq. (3.31)) (black curve), ground state (red) and excited state (green). b) Initial (red) and target states (green) and the final propagated state corresponding to the last iteration field (blue). .................................................. 27

4.1 The electric field of initial driving laser applied on Hydrogen atom versus time (in atomic units). The intensity of the laser $I$ is equal to $2 \times 10^{13}$, $T = 2.2 fms$. The total time is $20T$. ............................... 36

4.2 High-harmonic spectrum of Hydrogen atom generated with the laser in Fig. ?? versus harmonics of the incident laser frequency. ....................... 37

4.3 Optimization of high-harmonic generation of the Hydrogen with different merit functions for the 15th harmonics of the laser frequency. Optimization with the merit function in equation (3.52) (red curve) and with the merit function in equation (3.53) (green curve). Initial HHG is shown with blue. ................................. 38

4.4 Optimized lasers for Optimizing high-harmonic generation of the Hydrogen with different functions for the 15th harmonic of the incident laser frequency. Optimization with the function in equations (3.52) and (red curve) (3.53) gives the same result (red curve). Initial HHG is shown with green. ................................. 39

4.5 The electric field of initial driving laser applied on the Hydrogen molecule versus time (in atomic units). The intensity of the laser $I$ is equal to $2 \times 10^{13}$, $T = 2.2 fms$. The total time is $10T$. .............................. 40

4.6 High-harmonic spectrum of the Hydrogen molecule generated with the laser in Fig. 4.5 versus harmonics of the driving laser frequency. ........ 41

4.7 Optimization of high-harmonic generation of the Hydrogen molecule with functions in equation (3.53) the 15th harmonics of the incident laser frequency. Optimized HHG spectrum (red curve) and initial HHG spectrum (green curve). .................................................. 42

4.8 Optimized laser for Optimizing high-harmonic generation of the Hydrogen molecule for the 15th harmonics of the driving laser frequency. Optimization with the function in equation (3.53) (red curve). Initial laser shown in green. ................................. 43
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Abstract

Every scale needs right tools and devices to enable researchers to study and even control phenomena in that area. Given the fact that many fundamental phenomena in condensed matter physics and chemistry, such as chemical bonding or charge transfer, are happening on attosecond scale has encouraged researchers to look for essential tools for inspecting this region. At the present time, high-harmonic generation offers an attractive source of coherent radiation in the extreme-ultraviolet and soft-x-ray regions of the spectrum, allowing the production of single pulses or pulse trains. Hence, it provides sources that can be applied as our devices in attosecond studies. Here we summarize attempts and techniques has been made to generate attosecond lasers by experimentalists. Then we focus on high-harmonic generation as the best candidate, describing its physics in more details. At this point, we choose our target to be the selective high harmonic generation for a single or ranges of high harmonics. Since the total Hamiltonian of a system determines the dynamics of the system, this means that we can control the system by applying the correct electric field e.g., of a laser, yielding our target. To find this optimal field, we take our way towards the quantum optimal control of the system through direct optimization rather than the standard approach due to its limitation to deal with a many-body system (even though we describe it to see why we adopt another way). Finally, we present the result for hydrogen atom and hydrogen molecule in one dimension (soft coulomb potential used rather than pure coulomb potential).
Chapter 1

Introduction

1.1 Femtosecond and Attosecond Scale

Every scale in physics demands different tools and techniques which enable us to investigate, measure and manipulate phenomena in that region. Finding these new tools is, generally speaking, a difficult task which requires new ideas. This is especially true for things happening at a very small scale in which quantum mechanics plays a key role such as charge transfer within molecules or bond creation. It would be appealing if we manage to find the right instruments to control over these really interesting and challenging phenomena. Let us first review two interesting scales, mainly femtosecond ($10^{-15}$s) and attosecond ($10^{-18}$s). On femtosecond area we can mention:

1. A few femtoseconds is the typical time step for a molecular dynamics simulation,
2. 1.3 femtoseconds: cycle time for 390 nanometre light, transition from visible light to ultraviolet,
3. 2.57 femtoseconds: cycle time for 770 nanometre light, transition from visible light to near-infrared,
4. 200 femtoseconds: the swiftest chemical reactions, such as the reaction of pigments in an eye to light,
5. 300 femtoseconds: the duration of a vibration of the atoms in an iodine molecule,

and for attosecond scale there are:
6. 1 attosecond is the time it takes for light to travel
the length of three hydrogen atoms,
(2) 1 attosecond (1 as): estimated time it takes for an atomic nucleus to recoil,
(3) 24 attoseconds: the time taken for an electron to travel
from one side of a hydrogen atom to the other,
(4) about 200 attoseconds: half-life of beryllium-8, maximum time available for
the triple-alpha process for the synthesis of carbon and heavier elements in stars,
(5) 150 attoseconds is the time it takes for an electron to circle
the nucleus of an atom,
(6) 320 attoseconds: estimated time it takes electrons to hop between atoms.

Then, these two areas include a vast range of interesting phenomena and natural
desire would be to investigate them. Fortunately, the situation nowadays in femto-
second scale is relatively well-developed and we have necessary tools to not only
study but also to control over that region. On the other hand for attosecond scale,
although there are a few attempts to use existing technology to apply main focus
has been on how to build and improve required tools more efficiently and of course
economically viable.

1.2 Exploring Attosecond Scale: Need for Ultra-
fast Lasers

The advent of laser by T. H. Maiman in 1960 (1), has inspired physicists and chemists
to utilize it as such a tool. Capability of laser lies in having an intense focused electro-
magnetic fields that in principle can be used to coherently control quantum systems.
Of course, depending on what is the final goal we want to reach, we should find the
essential characteristics of the laser, such as intensity and the shape of the pulse. It
may be that there is not any laser available for our purpose or we find the required
laser that could do the task it is not viable due to technological reasons. As such
an example, we mention the first attempt to break a certain bond in a molecule (2).
In that work, they applied a laser which has been tuned on resonance to initiate a
resonance catastrophe. It did not succeed to fulfill the task. The molecule inter-
ernally converted the energy too quickly, so that the specific bond did not break but
instead the whole molecule was heated (3). To overcome this internal vibrational
relaxation (IVR) a smarter excitation strategy and further technological improve-
ments were necessary. With the emergence of femtosecond laser pulses in the 1980s
and technological progress in sophisticated pulse shaping (4) finally the object of
controlling complex chemical reactions with coherent light was finally achieved: for
example, in 1998 Assion et al (5) showed that the product ratio CpFeCOCl+/FeCl+ of the organo-metallic compound (CpFe(CO)2Cl) can be either maximized or minimized by a specially tailored light pulse; or in 2001, Levis et al (6) demonstrated a rearrangement of molecular fragments.

Nowadays, femtosecond lasers may apply to study and visualize atomic motion in real time (7; 8; 9) and to control molecular processes (5; 6; 15; 16; 17) with tailored femtosecond laser pulses. Despite these great achievements, there are still number of phenomena we desire to explore and manage but the realization of them is beyond the scope outlined by femtosecond lasers technology. The fact is that the period of the oscillations of atoms in molecules reside in the range of tens to hundreds of femtoseconds. Hence, with applying laser pulses with durations of this order of magnitude can efficiently measure and control molecular dynamics. However, if we want to follow or control electrons we must notice that the natural time scale of electrons falls into the subfemtosecond or attosecond regime. Consequently, important electronic processes, which they usually consist of charge transfer after excitation or atomic inner-shell transitions, require to develop new light sources for investigating the motion of electrons. Energies of these light sources should lie in the extreme-ultraviolet (XUV) region and have pulse time of the attosecond order to enable us to have a direct access to core-level electrons easily with one-photon transitions.

### 1.3 Sources for Ultrafast Lasers

Naturally, the question is how to generate laser with such a short wavelength. Several techniques can be used to reach this wavelength range. Laser-produced plasmas LPP are created by the interaction of a high-intensity laser pulse with high-density materials, leading to the emission of both bremsstrahlung and characteristic line radiation (18; 19). This radiation has time scale from the subpicosecond to femtosecond scale and is intrinsically synchronized to the external laser source that generated the plasma. As a drawback, the radiation is incoherent and is emitted into a large solid angle. LPP driven x-ray laser can yield spatially and coherent emission at selected wavelengths in the soft x-ray range (for an extensive review look at (20)).

As an alternative, it is possible to reach this range with undulator-based free electron lasers where the buildup of the x-ray pulses is coherent, leading to much higher fluxes in the forward direction (21). The state-of-art free electron lasers can now reach to 32 nm 38.8 eV (22). The main disadvantage in this method is that it requires very large facilities (of course too expensive as well).

To push this limitation and move from femtosecond lasers towards attosecond ones a different approach should be taken. One promising idea is to manipulate highly
nonlinear effects created with a high-power femtosecond laser. This means that the system will respond to this very strong laser by generating high-order harmonics of the driving laser, emitting coherent light in the soft-x-ray range \((23; 24; 25)\).

At the present time, the situation in femtosecond lasers is in such a way that we can afford to reach a very high peak power with pulse time less than 10 fs. It is then encouraging to use them to profit from nonlinear effects created with such intense energy. As a result, these nonlinear phenomena convert or modify the characteristics of the driving laser, such as frequency, polarization, pulse time, wavelength. Hence, by smart employing of a strong laser it is possible to modify its features with the desired ones that does not exit or difficult to generate.

Actually this idea is not new and it traces back to the early days of laser when in 1961 Franken was first to observe a second harmonic generation of the red ruby laser (694.3 nm) \((26)\). Consequently, with a strong laser applied to a medium, polarization in the medium contribute not only at the original frequency but terms of second, third, or higher order in the driving electric field appear. This will lead us to a method for generating high harmonics of the incident laser. As we mentioned above, regarding technological advances in femtosecond lasers these highly nonlinear responses may very well be exploited to render a preferred high-harmonic generation. It is worth to mention that this high generation first observed accidentally \((23; 27)\). Therefore, high-harmonic generation is a powerful alternative of ultrashort coherent radiation in the XUV and soft-xray range that the feaiblity of producing it on a laboratory scale attracts much attention.

Lately, experimentalists have successfully demonestrated creation of attosecond laser by high-harmonic generation (Antoine et al., \((28)\); Christov et al., \((29)\); Drescher et al., \((30)\); Hentschel et al., \((31)\); Paul et al., \((32)\); Mairesse et al., \((33)\)). At the same time several groups have exploited the unique temporal properties ofthis new radiation to examine electronic dynamics, for example, the Auger decay of innershell electrons (Nugent-Glandorf et al., \((34)\); Drescher et al., \((35)\); Kienberger et al., \((36; 37)\); Scrinzi et al., \((38)\)).

This will certainly open possibility of research on attosecond phenomena since now we are equipped with the right tool for that aim. Along the same lines that have been said before, the natural desire would be not only to study this scale but also to control over it. This is an open path that has been done a little on it and so this is up to us how to use this new tool to explore it.
Figure 1.1: Different targets for high-harmonic spectra: extension of the cutoff energy, increase in the efficiency of the high-harmonic conversion process, and the selection of single harmonics or range of harmonics.

1.4 Challenges and goals

As we mentioned before, the goal is to inspect phenomena occurring at attosecond scale. Then, femtosecond or attosecond time-resolved XUV or soft-x-ray spectroscopy, that they serve as our tools in that scale, poses several challenges as illustrated in Fig.1.1. The upper left panel shows the starting situation of unoptimized high-harmonic spectra. The other panels each demonstrates one specific optimization goal. For instance, in order to be able to investigate the time-dependent shifts of absorption edges the harmonic cutoff, which determines the highest energies possible, must be extended to shorter wavelengths (10). For any kind of nonlinear optics in the XUV range, a large number of harmonic photons is desirable, therefore the efficiency of HHG should still be increased to make the whole range of methods of pump probe technology available to the XUV domain (11). Moreover, for both spectroscopic applications and the optimization of attosecond pulse durations the selection of single harmonics or ranges of consecutive harmonics is necessary (12; 13).

1.5 Towards Realization

In return and for answering the demands mentioned in previous section, we should find an optimal driving laser that creates the desired attosecond laser through high-harmonic generation. Here, we briefly explain what is the current situation in theo-
1.5. Towards Realization

retical and experimental side.

1.5.1 Experimentalists: Adaptive Control

In order to shape high harmonics according to user defined targets, it is convenient and effective to employ adaptive control schemes. This provides a powerful method to guide quantum-mechanical processes by applying an optimal light field. The main experimental tool for achieving these goals is spectral phase shaping of femtosecond laser pulses combination with evolutionary-algorithm-based experimental feedback loops (15).

However, a direct transfer of pulse shaping techniques developed in the optical wavelength range to the soft-x-ray regime is not feasible. Existing devices require either spectral dispersion e.g., liquid crystal or deformable mirrors which because of small diffraction efficiencies for spectral dispersion and high absorption coefficients it prevents their applicability in the soft-x-ray spectral range. It then appears more desirable to directly generate a shaped soft-x-ray pulse, for instance, by shaping the fundamental laser pulse prior to the conversion process than after its production. By shaping the ultrashort driving laser pulse it is possible to control the high-harmonic spectrum in a comprehensive way, far beyond earlier results on the control of particular spectral properties such as conversion efficiency and line width (39).

The problem of finding this electric field can be solved by applying different pulse shapes in a closed-loop optimization setup as proposed by Judson and Rabitz (15), which we also employed for the adaptive control of high-harmonic generation in this work. Laser pulses are automatically tailored in a temporal or spatial pulse shaper according to user-defined optimization goals. The basic working principle is depicted in Fig. 1.2. It relies on an evolutionary algorithm (14) that finds an optimal electric field. In brief, the incoming laser pulses are shaped in some sort of pulse shaper. The modulated laser pulses in Fig. 1.2 a temporally shaped laser pulse is shown are then used to perform the experiment in the quantum system. The experimental signal is analyzed and a fitness is assigned to the corresponding laser pulse. Utilizing this ranking, the evolutionary algorithm can automatically find the optimum laser pulse. The applied algorithm is based on the evolutionary principle of survival of the fittest (14). A fitness measure for each shaped laser pulse is derived from the high-harmonic spectrum. This measure, also termed fitness function, maps the shape of the complete high-harmonic spectrum onto a single number. In this way it is possible to rank the performance of different laser pulse shapes according to how well it produced the desired harmonic spectrum or spectral feature. Each pulse shape termed an individual is characterized by a number of genes, e.g., the 19 high voltage
levels applied to the deformable mirror electrodes. These voltage parameters defining the pulse shape can therefore be regarded as the genetic elements of an individual laser pulse. Fifty different individuals represent a generation. The first generation consists of individuals each possessing randomly chosen genes voltages with values throughout the suitable voltage range. After applying those pulses in the harmonic generation experiment, their fitness is determined and the selection of the fittest is carried out. The evolutionary algorithm uses the ranking by the fitness function to keep the best-performing laser pulses for the next generation. The rest is dismissed or transferred to the next generation by mutation some genetic elements are randomly changed or crossover two individuals of the old generation each pass on a part of their genetic elements to their offspring until a population size of fifty is reached again. The members of the new generation are now tested for their performance in order to build the following generation, and the closed-loop optimization iteratively converges towards a maximum fitness value by gradually improving the laser pulse shapes from one generation to the next.

1.5.2 Theoretical Side

In principle, the total Hamiltonian of a system determines the potential energy surfaces and the dynamics of the system and the control of this quantum system is possible by applying the correct electric field e.g., of a laser. The great difficulty is
to determine the exact electric field that is needed to lead a quantum-mechanical reaction towards the desired output.

Any attempts for solving this problem will face two sources of difficulties. These are related to the fact that we are dealing not only with a many-body system but also we seek to control over its highly nonlinear respond.

At the present time and on the theoretical side, there is a standard approach called quantum optimal control (QOCT) which meant to give us the ability to control over the system. Despite this, in practice this method can not help because it needs the wave function of the system. So, the method is limited to very small systems. Therefore, it still remains a great challenge which it must be addressed.

1.6 Our Work

The main purpose of this work is the selective high harmonic generation for a single or group of high harmonics.

Regarding to the difficulties mentioned in previous section and our goal, we adopt another path rather than the standard approach of QOCT. This method is based on direct minimization of the target-dependent functional of the system (we will discuss it in Sec. 3.2).

In comparison with standard QOCT, there is a great advantage for using it due to the fact that the necessary functional for optimization of high-harmonic generation depends directly on the density of the system (equation \((3.50)\)). So, it opens the possibility of using time-dependent density functional theory (TDDFT), implying that we do not need the wave function of the interacting many-body system and all we need is its density. In principle, it is valid for every functional because after all, the wave function can be determined by knowledge of the density and so the functional as well. Unfortunately, this will not help us in practice unless that the optimization functional is known in terms of the density.

Nonetheless, due to open questions over validity of existing functionals in TDDFT for such highly nonlinear situations the problem is not completely solved. Hence, it is vital to propose new functionals that are able to deal in this area (we will not discuss this through this work).

For this reason, we choose systems that we can solve them numerically exact to make sure that artificial effects are present in optimization. Our model systems are hydrogen atom and hydrogen molecule in one dimension that we replace coulomb potential \((1/x)\) with soft coulomb potential\((1/(1 + x^2)^{1/2})\)(pure coulomb potential leads to divergence of wave function in one dimension or in the worst case it can split
the corresponding one-particle quantum systems at the origin into two completely decoupled subsystems (41; 42)).
Chapter 2

HIGH-HARMONIC GENERATION

As opposed to low-order nonlinear frequency conversion processes such as second-harmonic generation where moderate laser intensities are sufficient, high-order harmonics result from the highly nonlinear interaction of high-intensity laser pulses with typically a gaseous medium. Laser radiation is converted into large integer multiples of the original laser frequency, which reaches down to the XUV extreme ultraviolet and soft-x-ray range (for a very interesting work look at (1) in which they reached 300 times of the driving laser frequency). In this chapter we describe high-harmonic generation in more detail.

2.1 Strong Lasers

Let us first explain what we define exactly as a strong laser. Suppose that we consider the hydrogen atom in its classic picture, turning around the nucleus. Now we calculate the electric field at the classical distance of the electron from the core (Bohr radius) which it gives

\[ E = \frac{1}{4\pi\epsilon_0} \frac{e}{a_0^2} = 5.1 \times 10^9 \text{V/cm}. \]  

(2.1)

Consequently if a laser with this electric filed applied on the system, its intensity is

\[ I = \frac{1}{2} \epsilon_0 c E^2 = 3.51 \times 10^{16} \text{W/cm}^{-2}. \]  

(2.2)
2.2 Physical model: Single-atom response

The basic generation mechanism for high-order harmonics can be explained using the semiclassical so-called three-step model by Corkum (43) and Kulander et al. (44). In Fig. 2.1 we presented the essence of the theory. In the strong field of ultrashort high-intensity laser pulses, bound electrons from atoms or molecules are ionized close to the maximum of the laser field and set free with zero initial velocity. They are then accelerated away from their parent ions by the same electric field and move on classical electron trajectories in a laser field. In this semiclassical model the electron is treated quantum mechanically while it tunnels from the parent atom and its subsequent dynamics are treated with classically.

The average quiver energy of the electron in the laser field is called the ponderomotive energy $U_p$ and is directly proportional to the intensity $I$ of the driving laser and the square of the fundamental wavelength $\lambda$

$$U_p = \frac{e^2 E_L^2}{4m_e \omega_L^2} \propto I \lambda^2$$  \hspace{1cm} (2.3)
where $e$ and $m_e$ are the charge and the mass of the electron, and $E_L$ is the electric field strength of the laser with the angular frequency $\omega_L$ (or wavelength $\lambda$).

As soon as the electric field reverses, electrons are first decelerated and then accelerated back towards their parent ions. On the way back towards the ions several processes can happen.

*High-harmonic generation (HHG).* The electron can recombine with its parent ion with a certain probability, leading to the emission of a broadband extreme ultraviolet XUV photon. One photon per electron is emitted carrying the sum of the electrons kinetic energy plus the ionization potential $I_p$.

*(High order) above-threshold ionization (ATI).* In this process an atom may absorb many hundred more photons than it is necessary to get ionized and when it reaches to the ions it scatters elastically. Hence, in return an electron with very high energy will be ejected ($45; 46$).

A typical photoelectron spectrum shows a characteristic plateau of electron peaks, separated by one fundamental photon energy and rolling off at a cutoff of $10U_p$ ($47; 48$). The position of the ATI peaks can be shifted by the ponderomotive potential or even be suppressed, depending on the pulse duration of the driving laser ($46$).

*Nonsequential double ionization (NSDI).* Another possible scenario will happen when an inelastic collision of the electron with the ion occurs, ejecting another electron. Then, in the end the atom is doubly ionized ($49; 50$). Inelastic collision processes are the dominant, but not the only mechanism for NSDI, other processes, e.g., shakeup, are known to play a role ($51$).

Regarding the scope of our work, we are only interested in high-harmonic generation and the control of their spectral.

Before going further we should mention one important aspect of HHG related to the polarization of the incident laser. The semiclassical model shows that HHG will only occur if the driving laser field is linearly polarized. Ellipticity on the laser beam causes the returning electron to miss the parent nucleus. Quantum mechanically, the overlap of the returning electron wavepacket with the nuclear wavepacket is reduced. This has been observed experimentally, where the intensity of harmonics decreases rapidly with increasing ellipticity ($52$).

The energy of the photon that is emitted upon recollision of the accelerated electron with the ion core is determined by the sum of the ionization potential $I_p$ and the momentary kinetic energy $W_{kin}$ of the electron:

$$\hbar \omega = I_p + W_{kin}(\phi).$$  \hspace{1cm} (2.4)

The kinetic energy depends on the phase $\phi$ of the electric field at the moment of ionization. The maximum photon energy cutoff energy that can be achieved in this
process can be calculated using classical \((43)\), quantum mechanics \((58)\) and is given by

\[ E_{\text{cutoff}} = \hbar \omega_{\text{max}} = I_p + 3.17 U_p, \tag{2.5} \]

where \(\omega\) is the (angular) frequency of this photon and \(h\) is Planck's constant. The right-hand side of Eq. (2.5) is composed of the ionization potential \(I_p\) of the atom the binding energy of the electron and the maximum kinetic energy of the electron upon its return to the core: \(3.17 U_p\). This happens for a phase of \(\phi \approx 17^\circ\) close to the maximum of the electric field where also the ionization rate is highest.

To visualize the laser intensities needed for a sizable ponderomotive potential \(U_p\), Eq. (2.3) can be reformulated:

\[ U_p(\text{eV}) = 0.93 \times 10^{-13} I(W\text{cm}^{-2}) \lambda^2(\mu\text{m}^2). \tag{2.6} \]

Perturbation theory can usually capture essential physics for describing generation of low order harmonics. It predicts a decrease of harmonic intensities towards higher orders following an \(I^q\) power law where \(q\) is the number of the corresponding harmonic. As we are using very strong lasers that their electric fields approach the inneratomic electric field, perturbation theory breaks electric field. Despite this, it is possible to use this power law but with the effective exponential \(p\) is smaller than \(q\) \((53)\). Intermediate harmonic orders show a plateau in intensity \((24)\) which ends at the cutoff energy for the highest harmonic orders Fig. 2.1, upper panel.

According to Eq. (2.3), the cutoff can be extended to higher energies by using a longer-wavelength driving field. On the other hand, the efficiency of high-harmonic generation is increased for shorter-wavelength pulses due to the reduced wave packet spreading of the electron during its excursion time. Also, since the oscillation amplitude of the electron in the laser field scales as \(\lambda^2\), the electron spends more time in the vicinity of the atom for the shorter-wavelength driver and, therefore, has a larger probability of emitting a harmonic photon per unit time.

Of course, using a higher intensity driving laser pulse increases the cutoff, provided that plasma effects such as dephasing and defocusing are properly controlled and not all atoms will be ionized in the leading edge of the pulse. This can be achieved by using few cycle laser pulses, reducing the ionization probability prior to the maximum field strength in the center of the pulse. Consequently, it minimizes ground state depletion and plasma effects \((54)\). On the other hand, increasing intensity can not continue too much since relativistic effects start appearing. In high intensity laser fields electrons may gain velocities of the order of the velocity of light. So in this regime magnetic field forces become comparable to electric-field forces. The electron follows a figure eight trajectory due to the contribution of the \(v \times B\) terms
Figure 2.2: Different classes of electron trajectories during the propagation phase of high-harmonic generation, plotted in the position-velocity plane: The trajectories start at the atom located at (0,0). Depending on the phase $\phi$ of the electric field at the instant of ionization, they can return to the core at position 0 with different kinetic energies, visualized by the intersection with the velocity axis. The traces $a$ ($\phi = 45^\circ$) and $c$ ($\phi = 3^\circ$) correspond to the short and long trajectory, respectively, leading to the same final energy. Class $b$ ($\phi = 17^\circ$) is a cutoff trajectory with the highest kinetic energy ($3.17U_p$). $d$ ($\phi = 0^\circ$) starts at the peak of the electric field where most electrons are produced but returns to the core with zero kinetic energy. Trajectory $e$ ($\phi = -45^\circ$) never returns to its parent atom.

induced by the strong magnetic-field components which leads to a significant motion of the electron in the propagation direction of the laser field. As a consequence, there is less interaction with the nucleus and very few harmonics can be found in the radiation spectrum (55). Also, relativistic mass effects prevent the acceleration of the electron to even higher energies necessary for the extension of the cutoff.

Figure 2.2 shows a plot of different classes of electron trajectories during propagation in the electric field of the driving laser. Electrons start from the nucleus located at (0,0). Depending on the phase $\phi$ of the electric field at the instant of
ionization, they can return to the core at position 0. The intersection with the velocity axis determines their final kinetic energies at the moment of recombination. The electron along the cutoff trajectory $b$ was ionized at a phase of $\phi = 17^\circ$ and has the highest kinetic energy $(3.17U_p)$ upon its return to the core. Electrons are most likely produced at the peak of the electric field ($\phi = 0^\circ$) but they return to the core with zero kinetic energy ($d$). Most electrons, however, are produced at unfavorable phases of the electric field and never return to the core $e$. In the plateau region of high-harmonic spectra, there are typically two electron trajectories that give dominant contributions to high harmonic emission, which interfere with each other (56). The first short trajectory corresponds to a short return time $(a)$, the second long trajectory $(c)$ has a return time close to one period, which causes a strong intensity dependence of the phase. This can result in strong spectral broadening, leading to an overlap of neighboring peaks (57). The phase of the harmonic emission can be determined using a quantum-mechanical formulation, the so-called Lewenstein model (56; 58). This theory rephrases the classical models by Corkum and Kulander (43; 44) in a fully quantum theory. It is valid in the single-active-electron approximation (SAE) in a low-frequency, high-intensity limit $U_p \geq I_p$, and for high harmonics with energies greater than the ionization potential. As an alternative approach, Saliáres applied Feynman’s path integral formalism, (59), and expressed the probability amplitude for high-harmonic generation as a coherent superposition of contributions of all possible spatiotemporal paths that connect the initial and the final state of the system (quantum orbits). The weight of each path is a complex number whose phase is equal to the classical action $S$ along this path. In general, only the first two quantum orbits with travel times of less than one or two periods of the laser field contribute noticeably. For harmonics in the cutoff region, there is only one relevant trajectory whereas for plateau harmonics two trajectories are needed for an accurate description. They showed experimentally existence of these quantum orbits through the coherence properties of high harmonics and phase-matching techniques. We will discuss the coherence properties on a separate section.

### 2.3 Harmonic spectrum

Half-cycle after ionisation the electron will reverse direction as the electric field changes and accelerate back towards the parent nucleus. Hence, the generation of high-harmonic radiation is repeated every half-cycle of the electric field of the laser pulse. This translates itself into HHG spectrum that consists of only the odd harmonics of the fundamental laser frequency as it illustrated in Fig. 2.3.

Each half-cycle of the driving laser pulse gives rise to a short subfemtosecond burst
of XUV radiation. Therefore a driving pulse consisting of multiple cycles produces a
train of subfemtosecond XUV bursts, separated in time by half the oscillation period
of the driving laser attosecond pulse train. This periodicity of $T/2$ where $T$ is the
laser period is responsible for the observation of the harmonic spacing of $2\omega$. This
structure of HHG spectrum will be best understood by using Fourier transform of a
function that is periodic every $T/2$ in time domain as below

$$F(\omega) = \int_{-\infty}^{\infty} e^{-i\omega t} f(t) \, dt = \int_{-\infty}^{\infty} e^{-i\omega(t + T/2)} f(t) \, dt = e^{-i\omega T/2} F(\omega)$$

and therefore

$$\omega = 2n \omega_0$$

where $\omega_0$ is the laser frequency (here we assumed that the laser is a periodic continuous field).

Also, since bursts result from sequence of collisions from different directions, the
corresponding spectral components have the same spectral amplitude but differ in
sign. This results in, assuming spatial symmetry, destructive spectral interference for even-order harmonics $\omega = 2m \omega_L$, while constructive interference occurs for odd harmonics $\omega = (2m + 1) \omega_L$.

However, if the symmetry is broken, even-order harmonics can be generated. The symmetry can be broken both on the level of the laser pulses and on the level of the medium properties. For laser pulse durations approaching the single-cycle regime (54), even-order harmonics can be generated near the cutoff until the high-energy part of the harmonic spectrum merges into a continuum (?). This results from a loss of the strict periodicity of electric-field oscillations within a laser pulse for pulse durations of less than 10 fs. In this case, the pulses consist of only a few optical cycles, breaking the symmetry between consecutive oscillations.

Similarly, using oriented asymmetric molecules introduces a difference between consecutive half-cycles. The anisotropy of such a medium makes the contributions from the upper and the lower half-cycle of the laser oscillations different even for multicycle laser pulses, thus generating even-order harmonics. However, alignment alone is not sufficient because the symmetry is not broken (60).

### 2.4 Coherence

Another interesting aspect of HHG is related to its coherent property. The question is if emission of HHG is coherent or it generates bursts of random phases.

The first direct measurements of the temporal coherence of high-order harmonics were reported by Ditmire et al. 1996 (61) and complemented by Bellini et al. 1998 and Lyngå et al. 1999 (62; 63). In the reported work, the authors measured the fringe visibility of the interference pattern in the far field of two spatially separated sources of harmonic radiation that were delayed in time with respect to each other. Whereas in general the coherence times are comparable to the expected pulse durations, the interference pattern exhibits two well-separated spatial regions concentric rings with significantly different coherence times for some harmonics: the intense inner part has a long coherence time while the outer region displays a much shorter coherence time.

From the semiclassical interpretation of high-harmonic generation Sec. 2.2 there are actually two main trajectories that the electron can take during the excursion time between ionization and recombination. The first short trajectory has a phase that does not vary much with laser intensity (56). Consequently, the emitted radiation has a long coherence time and is well collimated. The dipole phase of the second long trajectory, however, varies rapidly with laser intensity leading to a strong curvature of the phase front due to the dependence of the intensity on the radial coordinate and therefore to a strongly divergent angular emission (64).
The spatial coherence of the high-harmonic light can be measured through the double-pinhole or double-slit interference technique. The modulation depth of the interference fringes after passing a beam through a pinhole pair is a direct measure for the degree of coherence across the spatial wave-front phase profile. If the phase difference between the two sampled points is constant, the fringe visibility will be unity whereas it is less than 1 if random phase variations exist. Such a two-pinhole setup has been used to verify full spatial coherence of high-harmonic radiation generated in a phase-matched hollow-fiber geometry (65). The first measurement of the spatial coherence of high-order harmonic radiation in the soft-x-ray region was performed by Ditmire et al. 1996 (61). They executed a series of Youngs two-slit experiments to find that the harmonics generated in a gas plume exhibit good fringe visibility and high spatial coherence. At high intensities the coherence is degraded due to the rapid production of free electrons, which imparts a rapidly varying phase on the harmonic, lowering the degree of coherence.

From a classical viewpoint, high-harmonic generation driven by coherent light is an inherently coherent process. However, the degree of coherence is degraded by mechanisms such as plasma refraction and the time-varying index of refraction. Also, as mentioned above, at least two trajectories with different phase behavior contribute to high-harmonic generation.

Gaarde et al. (66) followed the experiments by Bellini et al. (62) and devised a spatiotemporal analysis of high-harmonic radiation. By doing so, he managed to separate two quantum path components. Based on the numerical integration of the time-dependent Schrödinger equation, they determined the dipole moment $\mu_q(I)$ of the $q$th harmonic as a function of the intensity $I$ of the laser field:

$$\mu_q(I) = A(I) e^{i\Phi(I)}.$$  \hfill (2.9)

The dipole moment consists of several contributions with phases of the form

$$\Phi_k(r, z, t) = -\alpha_k I(r, z, t),$$  \hfill (2.10)

representing the different quantum paths, labeled by the index $k$. $I(r, z, t)$ is the space- and time-dependent intensity of the driving laser field, and $\alpha_k$ is the corresponding proportionality constant or slope of the phase function. By performing the equivalent of a time-frequency analysis using a window function for a range of intensities, the authors determined the spectrum of $\alpha_k$. The result showed that the separation into different quantum path components is indeed justified. As representative values, they found the following numbers for $\alpha_k$ for the 15th harmonic in argon: $\alpha_1 \approx 1 \text{ cm}^2/\text{W}$, $\alpha_2 \approx 27 \text{ cm}^2/\text{W}$. The value for the long trajectory is much larger than for the short trajectory.
Time-dependent intensity $I(t)$ causes a frequency chirp $\Delta \omega_k(t) = \frac{\partial \Phi_k(t)}{\partial t}$, leading to spectral broadening. This time dependency of the intensity along with the large value of $\alpha_k$ for the long trajectory cause that the radiation arising from this trajectory has a very short coherence time and a broad bandwidth (the harmonic pulse is strongly chirped).

In the same way, the radial variation of the intensity $I(r)$ introduces a curvature of the phase front, causing the beam to diverge, depending on the values of $\alpha$ and $I$. We can estimate the influence on both the curvature of the phase front and the chirp for both components. Using the values for $\alpha_k$ from above we find the ratios of the spectral widths $\Delta \omega_k$ and of the divergence angles $\theta_k$ in a geometrical-optics approximation as $\Delta \omega_2/\Delta \omega_1 \approx \theta_1/\theta_2 \approx 27$. Since the spectrum of the long trajectory is dominated by the dipole chirp whereas the spectral width of the short trajectory is determined by its Fouriertransform-limited broadening, this ratio reduces to values between 10 and 20 but is still very large for the two quantum paths.

Due to the spatially differing behavior (divergence angles) of radiation originating from the two trajectories, it is possible to macroscopically select only the short quantum path by placing an appropriate aperture in the harmonic beam, resulting in spatially and temporally highly coherent radiation. The separation of the two fields can also be achieved by introducing proper phase-matching conditions for the selection of one or the other contribution.
Chapter 3

Theory of Quantum Optimal Control

In this chapter, we briefly explain the basics of optimal control theory applied to quantum mechanics. Let us consider an electron in an external potential $V(r)$ under the influence of a laser field propagating in the z-direction. Given an initial state $\Psi(r,0) = \phi(r)$, the time evolution of the electron is described by the time-dependent Schrödinger equation with the laser field modelled in the dipole approximation (length gauge):

\[
i \frac{\partial \Psi(r,t)}{\partial t} = \hat{H} \Psi(r,t), \quad (3.1)
\]
\[
\hat{H} = \hat{H}_0 - \hat{\mu} \epsilon(t), \quad (3.2)
\]
\[
\hat{H}_0 = \hat{T} + \hat{V}, \quad (3.3)
\]

(atomic units are used $\hbar = m = e = 1$). Here, $\hat{\mu} = (\mu_x, \mu_y)$ is the dipole operator and $\epsilon(t) = (\epsilon_x(t), \epsilon_y(t))$ is the time-dependent electric field. The kinetic energy operator is $\hat{T} = -\frac{1}{2} \nabla^2$.

3.1 Controllabilty

Before trying to find an optimal control for a given target and quantum system we raise the question if the given control target can be reached at all with the given controller, here the controller is the laser field $\hat{H}_1 = -\hat{\mu} \epsilon(t)$. In the following, we want to summarize some of the rigorous results on controllability that exist in the literature. The most powerful and easy-to-use statements are available for N-level systems (67; 68; 69). We start with a definition of the term complete controllability
and then discuss the results from (68).

Definition (69): A quantum system

\[ \hat{H} = \hat{H}_0 + \hat{H}_I, \]  

\[ \hat{H} = \sum_{n=1}^{N} \epsilon_n |n><n|, \quad \hat{H}_I = \sum_{m=1}^{M} f_m(t) \hat{H}_m, \]  

is completely controllable if every unitary operator \( \hat{U} \) is accessible from the identity operator \( \hat{I} \) via a path \( \hat{\gamma}(t) = \hat{U}(t, t_0) \) that satisfies

\[ i\partial_t \hat{U}(t, t_0) = (\hat{H}_0 + \hat{H}_I) \hat{U}(t, t_0). \]  

Theorem (68): A necessary and sufficient condition for complete controllability of a quantum system defined by equations (3.4) and (3.5) is that the Lie algebra \( L_0 \) has dimension \( N^2 \).

A further statement in (68) guarantees that complete controllability can also be achieved under external constraints on the strength of the controller. We can therefore check the controllability of an \( N \)-level system by constructing its Lie algebra \( L_0 \) which is generated by \( \hat{H}_0, ..., \hat{H}_M \) and then calculate the rank of the algebra. An algorithm for this task has been suggested in (69).

Note that the definitions of controllability in the theorems stated above are quite strict. For all practical purposes, i.e., the optimization of expectation values or occupation numbers, it is sufficient that the path lies within \( su(N) \) which has dimension \( N^2 - 1 \) (68; 69).

The extension of such controllability theorems to an infinite-dimensional Hilbert space and the inclusion of unbound operators like \( r \) or \( \nabla_r \) turns out to be non-trivial as shown in (67). The conditions of controllability are only valid for quantum systems with a non-degenerate and discrete spectrum and do not include external constraints on the strength of the control functions.

3.2 Writing Functionals for Optimization

Let us consider the following quantum mechanical control problem:

Our goal is to find a laser pulse \( \epsilon(t) \) which drives a quantum system from its initial state \( \Psi(0) \) to a state \( \Psi(T) \) in such a way that the expectation value of an operator \( \hat{O} \) is maximized at the end of the laser interaction:

\[ \max_{\epsilon(t)} \quad \text{with} \quad J_1[\Psi] = \langle \Psi(T)| \hat{O} |\Psi(T)\rangle \]  

(3.7)
At this point we keep the operator $\hat{O}$ as general as possible. The only restriction on $\hat{O}$ is that it has to be a Hermitian operator. In addition to the maximization of $J_1[^{\Psi}]$, we require that the fluence of the laser field be as small as possible which gives rise to the following mathematical form:

$$J_2[^{\epsilon}] = -\sum_j \int_0^T dt \alpha_j \epsilon_j^2(t), \quad j = x, y.$$  \hspace{1cm} (3.8)

where $\epsilon_x(t)$ and $\epsilon_y(t)$ are the components of the laser field perpendicular to the propagation direction. The positive constants $\alpha_j$ play the role of penalty factors: the higher the laser fluence the more negative the expression, the smaller the sum $J_1 + J_2$. As pointed out in (70), the penalty factor can be extended to a time-dependent function $\alpha_j(t)$ to enforce a given time-dependent shape of the laser pulse, e.g. a Gaussian or sinusoidal envelope.

Besides these two constraints, there is another one which is merely saying the electronic wavefunction evolve in time through the time-dependent Schrödinger equation (TDSE). It is also possible to cast it into a functional form and expressed it as below

$$J_3[^{\epsilon, \Psi, \chi}] = -2\text{Im} \int_0^T \langle \chi(t) | i \partial_t - \hat{H}(t) | \Psi(t) \rangle$$  \hspace{1cm} (3.9)

where we have introduced the Lagrange multiplier $\chi(t)$. Since we require the TDSE to be fulfilled by the complex conjugate of the wavefunction as well, we obtain the imaginary part of the functional.

Then, The total Lagrange functional can be written by using either $J_1 + J_2 + J_3$ or $J_1 + J_2$ and enforcing TDSE as a constraint. In two following sections, we describe both possibilities respectively but main focus will be on the latter form.

### 3.3 The Control Equation from Variation of J

In this section, the functional is defined with

$$J[^{\chi, \Psi, \epsilon}] = J_1[^{\Psi}] + J_2[^{\epsilon}] + J_3[^{\epsilon, \Psi, \chi}].$$  \hspace{1cm} (3.10)

To find the optimal laser field from the functional in equation (3.10) we perform a total variation. Since the variables $\Psi, \epsilon$ and $\chi$ are linearly independent we can write

$$\delta J = \int_0^T d\tau \int dr \left\{ \frac{\delta J}{\delta \Psi(r, \tau)} \delta \Psi(r, \tau) + \frac{\delta J}{\delta \chi(r, \tau)} \chi(r, \tau) \right\} + \sum_{k=x,y} \int_0^T d\tau \frac{\delta J}{\delta \epsilon_k(\tau)} \delta \epsilon_k(\tau)

= \delta \Psi J + \delta \chi J + \sum_{k=x,y} \delta \epsilon_k J,$$  \hspace{1cm} (3.11)
where we have omitted the derivations with respect to the complex conjugate of the wavefunction $\Psi^*(t)$ and the Lagrange multiplier $\chi(t)$, since the functional derivative will result in the complex conjugate equations for these variations.

Since we are looking for a maximum of $J$, the necessary condition is

$$
\delta \psi J = 0, \quad \delta \chi J = 0, \quad \delta \epsilon_k = 0.
$$

\hfill (3.12)

### 3.3.1 Variation with respect to the wavefunction $\Psi$

First, let us consider the functional derivative of $J$ with respect to $\Psi$:

\[
\frac{\delta J_1}{\Psi(r', \tau)} = \hat{O}\Psi^*(r', \tau)\delta(T - \tau),
\]

\[
\frac{\delta J_2}{\Psi(r', \tau)} = 0,
\]

\[
\frac{\delta J_3}{\Psi(r', \tau)} = -i(i\partial_\tau + \hat{H}(\tau))\chi^*(r', \tau) - [\chi^*(r', \tau)\delta(t - \tau)]^T_0.
\]

For the last functional derivative we have used the following partial integration:

\[
\int_0^T dt \langle \chi(t)|i\partial_t - \hat{H}(t)|\Psi(t)\rangle = i\langle \chi(t)|\Psi(t)\rangle^T_0 - \int_0^T dt \langle \partial_t \chi(t)|\Psi(t)\rangle - \int_0^T dt \langle \hat{H}(t)\chi(t)|\Psi(t)\rangle
\]

\[
= i\langle \chi(t)|\Psi(t)\rangle^T_0 + \int_0^T dt \langle (i\partial_t - \hat{H}(t))\chi(t)|\Psi(t)\rangle
\]

\hfill (3.14)

We find for the variation with respect to $\Psi$:

\[
\delta \psi J = \langle \hat{H}(\tau)\Psi(t)|\hat{O}|\Psi(t)\rangle + i \int_0^T d\tau \langle (i\partial_\tau - \hat{H}(\tau))\chi(t)|\Psi(t)\rangle
\]

\[
- \langle \chi(T)|\delta\Psi(T)\rangle + \langle \chi(0)|\delta\Psi(0)\rangle.
\]

\hfill (3.15)

However, the last term in equation (3.15) vanishes because we have a fixed initial condition, $\Psi(0) = \phi$ and then $\delta\Psi(0) = 0$. 
3.3.2 Variation with respect to the Lagrange multiplier $\chi$

Now we do the same steps for $\delta J_1$ with respect to $\chi$

$$\delta J_1 = \frac{\delta J_1}{\chi(r', \tau)} = 0,$$

$$\delta J_2 = \frac{\delta J_2}{\chi(r', \tau)} = 0,$$

$$\delta J_3 = \frac{\delta J_3}{\chi(r', \tau)} = i(\hat{\chi} + \hat{H}(\tau))\Psi^*(r', \tau).$$  \hfill (3.16)

In contrast to the variation with respect to $\Psi$ there is no boundary term here. The variation of $J$ with respect to $\chi$ yields

$$\delta \chi J = i \int_0^T d\tau \langle i\partial_t - \hat{H}(\tau) \rangle \Psi(t) \chi(t) \rangle$$  \hfill (3.17)

3.3.3 Variation with respect to the field

The functional derivative with respect to $\epsilon_k(t)$ is

$$\delta J_1 = \frac{\delta J_1}{\epsilon_k(\tau)} = 0,$$

$$\delta J_2 = \frac{\delta J_2}{\epsilon_k(\tau)} = -2\alpha \epsilon_k(\tau),$$  \hfill (3.18)

$$\delta J_3 = \frac{\delta J_3}{\epsilon_k(\tau)} = -2\mathfrak{Re} \langle \chi(\tau) | \hat{m}u_k | \Psi(\tau) \rangle \quad k = x, y.$$  \hfill (3.19)

Hence, the variation with respect to $\epsilon_k(t)$ yields

$$\delta \alpha_k J = \int_0^T d\tau \left\{ -2\mathfrak{Re} \langle \chi(\tau) | \hat{m}u_k | \Psi(\tau) \rangle - 2\alpha \epsilon_k(\tau) \right\} \delta \epsilon_k.$$  \hfill (3.20)

3.3.4 Control equations

Setting each of the variations independently to zero results in the desired control equations. From $\delta \epsilon_k J = 0$ (equation (3.20)) it follows

$$\alpha_k \epsilon_k(t) = -2\mathfrak{Re} \langle \chi(\tau) | \hat{m}u_k | \Psi(\tau) \rangle \quad k = x, y.$$  \hfill (3.21)

The laser field $\epsilon_k(t)$ is calculated from the wavefunction $\Psi(t)$ and the Lagrange multiplier $\chi(t)$ at the same point in time. The variation $\delta \chi J$ in equation (3.17) yields a time-dependent Schrödinger equation for $\Psi(t)$ with a fixed initial state $\phi$,

$$(i\partial_t - \hat{H}(\tau)) \Psi(r, t) = 0, \quad \Psi(r, 0) = \phi(r).$$  \hfill (3.22)
3.3. The Control Equation from Variation of \( J \)

Note that this equation also depends on the laser field \( \epsilon(t) \) via the Hamiltonian.

The variation with respect to the wavefunction \( \delta \Psi J \) in equation (3.15) results in

\[
(i\partial_t - \hat{H}(t))\chi(r, t) = i(\chi(r, t) - \hat{O}\Psi(t))\delta(t - T).
\]

(3.23)

If we require the Lagrange multiplier \( \chi(t) \) to be continuous at \( t = T \), we can solve the following two equations instead of equation (3.23):

\[
(i\partial_t - \hat{H}(t))\chi(r, t) = 0,
\]

(3.24)

\[
\chi(r, T) = \hat{O}\Psi(T).
\]

(3.25)

To show this we integrate over equation (3.23):

\[
\lim_{k \to 0} \int_{T-k}^{T+k} dt \left[ (i\partial_t - \hat{H}(t))\chi(r, t) \right]
\]

\[
\lim_{k \to 0} \int_{T-k}^{T+k} dt \ i(\chi(r, t) - \hat{O}\Psi(t))\delta(t - T).
\]

(3.26)

The left-hand side of equation (3.26) vanishes because the integrand is a continuous function. It follows that also the right-hand side must vanish, which implies equation (3.25). From equations (3.25) and (3.23) then follows equation (3.24). Hence, the Lagrange multiplier \( \chi(t) \) satisfies a time-dependent Schrödinger equation with an initial condition at \( t = T \). The set of equations that we need to solve is now complete: (3.21), (3.22), (3.24), and (3.25).

This set of equations can be solved iteratively (71) which means that we should solve the time-dependent Schrödinger equation more than once and therefore, its solution gives an optimal field \( \epsilon(t) \).

### 3.3.5 Solving The Control Equations

The control equations (3.21), (3.22) (3.24) and (3.25) can be solved as follows (71). The scheme starts with propagating \( \Psi^{(0)}(0) = \phi \) forward in time. For the initial propagation we have to guess the laser field \( \epsilon^{(0)}(t) \).

Usually, the trivial initial guess \( \epsilon^{(0)}(t) = 0 \) is sufficient. However, if the algorithm does not work with this initial field replacing it with \( \epsilon^{(0)}(t) = \text{const} \) often helps. After the initial propagation we determine the final state for the Lagrange multiplier wavefunction \( \chi^{(0)}(T) \) by applying the target operator to the final state of
the wavefunction, $\hat{O}\Psi^{(0)}(T)$. The laser field for the backward propagation for $\chi^{(0)}(t)$, $\tilde{\epsilon}^{(0)}(t)$ is determined by

$$\tilde{\epsilon}^{(k)}_j(t) = -\frac{1}{\alpha_j} \Im \left( \langle \chi^{(k)}(t)|\hat{\mu}_j|\Psi^{(k)}(t) \rangle \right), \quad j = x, y. \quad (3.27)$$

The propagation from $\chi^{(0)}(T)$ to $\chi^{(0)}(T - dt)$ is done with the field $\tilde{\epsilon}^{(0)}(T)$, where we use $\chi^{(0)}(T)$ and $\Psi^{(0)}(T)$ in equation (3.27). The error introduced here can be reduced by choosing a sufficiently small time step. At the same time, we propagate $\Psi^{(0)}(T)$ backward with the previous field $\epsilon^{(0)}(t)$. This additional parallel propagation is only necessary if the storage of $\Psi^{(0)}(t)$ in the memory is not possible. For the next propagation step from $\chi^{(0)}(T - dt)$ to $\chi^{(0)}(T - 2dt)$ we use $\Psi^{(0)}(T - dt)$ and $\chi^{(0)}(T - dt)$ in equation (3.27). We repeat these steps until $\chi^{(0)}(0)$ is reached. To check the reliability of the parallel propagation we project $\Psi^{(0)}(0)$ onto $\phi$ and compare with 1. We summarize the whole iteration step by step $k$:

$$\text{step } k \quad \begin{array}{c} \Psi^{(0)}(T) \\
\hat{O}\Psi^{(k)}(T) = \chi^{(0)}(T) \\
\end{array} \quad \begin{array}{c} \epsilon^{(k)}(t) \\
\epsilon^{(k)}(t) \quad \chi^{(0)}(0). \\
\end{array} \quad (3.28)$$

The last part of the zeroth iteration step consists in setting $\Psi^{(1)}(0) = \phi$ and propagating $\Psi^{(1)}(0)$ forward with the field $\epsilon^{(1)}(t)$ determined by

$$\tilde{\epsilon}^{(k+1)}_j(t) = -\frac{1}{\alpha_j} \Im \left( \langle \chi^{(k)}(t)|\hat{\mu}_j|\Psi^{(k+1)}(t) \rangle \right), \quad j = x, y, \quad (3.29)$$

which requires the input of $\chi^{(0)}(0)$. Again, we have to use the saved values from the backward propagation or propagate from $\chi^{(0)}(0)$ to $\chi^{(0)}(T)$ in parallel using the previously calculated field $\tilde{\epsilon}^{(0)}(t)$. We end up having calculated $\epsilon^{(1)}(t)$ and $\Psi^{(1)}(T)$ which can be expressed by

$$\phi = \Psi^{(k+1)}(T) \quad \begin{array}{c} \tilde{\epsilon}^{(k)}(t) \\
\epsilon^{(k+1)}(t) \quad \chi^{(0)}(T). \\
\end{array} \quad (3.30)$$

This completes the zeroth iteration step. The loop is closed by continuing with equation (3.28), i.e., propagating $\hat{O}\Psi^{(1)}(T) = \chi^{(1)}(T)$ with $\epsilon^{(k)}(t)$ (equation (3.27)) backwards to $\chi^{(1)}(0)$.

If the initial guess for the laser field is appropriate the algorithm starts converging very rapidly and in a monotonic way, meaning that the value for the functional $J$ in equation (3.10) is increasing at each iteration step. The monotonic convergence
3.3. The Control Equation from Variation of $J$

Figure 3.1: a) external potential of the asymmetric double well (Eq. (3.31)) (black curve), ground state (red) and excited state (green). b) Initial (red) and target states (green) and the final propagated state corresponding to the last iteration field (blue).

can be proven analytically (71). In the proof an infinitely accurate solution of the time-dependent Schrödinger equation is assumed. Since this is not possible in practice, it may happen that the functional decreases in the numerical scheme, e.g., when absorbing boundaries are employed. This sensitivity provides an additional check on the accuracy of the propagation.

An example: Asymmetric Double Well

Suppose our aim is to find an optimized pulse which drives the system from the initial state $\Psi(0)$ to the desired target state $\phi_f$ up to a global phase factor $e^{i\gamma}$. This can be done if $\hat{O}$ is defined with $\hat{O} = |\phi_f\rangle\langle\phi_f|$ (projection operator).

Now, we solve the control equations, for a transition from the ground state of a given system, to the first excited state. Here, the system that we have chosen is a one-dimensional asymmetric double well, characterized by the potential:

$$V(x) = \frac{\omega_0^4}{64B}x^4 - \frac{\omega_0^2}{4}x^2 + \beta x^2,$$

(3.31)

where $\omega_0$ to the classical frequency at the bottom of the well and the parameter $B$ adjusting the barrier height. We put the parameter values to $\omega_0 = B = 1$ and $\beta = \frac{1}{256}$.

By the end of iteration procedure, the value of $J_1[\Psi]$ in equation (3.7) becomes $|\langle\Psi(T)|\Psi_t\rangle|^2 = 0.93931$, almost fulfilling our goal. The result is shown in Fig. 3.1.
3.4 Direct Optimization

Regarding to our purpose in this work, we assume a Hamiltonian in the general form of
\[ \hat{H}(t) = \hat{H}_0 + f(t) \cos(\omega_0 t)\hat{V}. \] (3.32)

The object to be optimized is the function \( f \). This form for the external control is suitable for a typical case: a laser field characterized by a “carrier” frequency \( \omega_0 \), modulated by a smoother “envelope”, \( f \). We wish to optimize the form of the envelope. Note, however, that this assumption does not imply any loss of generality, since the usual case in which the “full” field \( \epsilon(t) = f(t) \cos(\omega_0 t) \) is the object to be optimized is retrieved by setting \( \omega_0 = 0 \).

Instead of working directly in real-time, we now represent the function \( f \) in any alternative basis set, \( \{g_n\}_{n=1}^N \):
\[ f(t) = \sum_{n=1}^{N} f_n g_n(t). \] (3.33)

Hence, the problem transforms to finding \( f_n \).

The fluence of a given field \( \epsilon(t) = f(t) \cos(\omega_0 t) \), \( F[\epsilon] = \int_0^T \epsilon(t)^2 \) d(\( t \)) \( \epsilon \), can be rewritten in terms of these components as:
\[ F[\epsilon] = f^\dagger S f, \] (3.34)

where the matrix \( S \) is defined as:
\[ S_{mn} = \int_0^T dt g_m(t)g_n(t) \cos^2(\omega_0 t). \] (3.35)

Now to fit our needs for this work, we choose a sine-Fourier series as our basis set with the form of:
\[ g_n(t) = \sqrt{2/T} \sin(\omega_n t), \quad \omega_n = \frac{\pi}{T} n. \] (3.36)

This basis set is convenient because:

- It imposes, by construction, a natural cut-off frequency to the search space for \( f \):
\[ \omega_{\text{max}} = \omega_N = \frac{\pi}{T} N. \] (3.37)
3.4. Direct Optimization

- It is orthonormal:

\[
\langle g_n | g_m \rangle = \int_0^T dt g_n(t) g_m(t) = \delta_{nm}.
\] (3.38)

- It imposes zero boundary conditions (as it simulates switching on and off the field at initial and final time):

\[
f(0) = f(T) = 0.
\] (3.39)

Given \(f(t)\), we can calculate its components \(f_n\) as:

\[
f_n = \langle g_n | f \rangle = \int_0^T dt g_n(t) f(t).
\] (3.40)

Assuming a given initial condition \(|\Psi(t = 0)\rangle = |\Psi_0\rangle\), we will call \(|\Psi[f](t)\rangle\) to the solution of Schrödinger’s equation whenever the external control function is determined by the function \(f\):

\[
i \frac{d}{dt} |\Psi[f](t)\rangle = \left[\hat{H}_0 + f(t) \cos(\omega_0 t) \hat{V}\right] |\Psi[f](t)\rangle.
\] (3.41)

Since this function can also be represented by its vector of components in the previous basis set, \(\mathbf{f}\), we can also denote this solution \(|\Psi[f](t)\rangle\).

We can now define an \(N\)-dimensional “merit” function, \(G\), acting on the vector \(\mathbf{f}\). Its precise form will depend on what kind of target we wish to achieve; for example, if we attempt to maximize, at final time, the expectation value of some operator \(\hat{O}\), we can have:

\[
G(\mathbf{f}) = \langle \Psi[f](T) | \hat{O} | \Psi[f](T) \rangle - \alpha f^\dagger S \mathbf{f},
\] (3.42)

The last term (where the \(\alpha > 0\) is a fixed constant) imposes a “penalty” on the magnitude of the fluence of the field (otherwise, the previous function may not be bounded, or it may happen that the optimization procedure leads to unrealistically large fields).

3.4.1 Fixed fluence

It may happen that we want to constrain the search space to solutions whose fluence is fixed from the beginning:

\[
F[\mathbf{f}] = \mathbf{f}^\dagger S \mathbf{f} = F_0.
\] (3.43)
In this case, it is possible to enforce this constraint with a change of coordinates, in the following way: Let $\mathbf{U}$ be the unitary matrix that diagonalizes $\mathbf{S}$:

$$\mathbf{S}' = \mathbf{U}^{\dagger} \mathbf{S} \mathbf{U},$$

(3.44)

where $\mathbf{S}'$ is a diagonal matrix: $\mathbf{S} = \text{diag}[s_1, \ldots, s_N]$. We define the change of coordinates

$$\mathbf{f}' = \mathbf{U} \text{diag}[s_1^{-1/2}, \ldots, s_N^{-1/2}] \mathbf{f},$$

(3.45)

It can then be shown that:

$$\mathbf{f}'^\dagger \mathbf{f}' = \sum_{n=1}^{N} f_n'^2 = \mathbf{f}^\dagger \mathbf{S} \mathbf{f}. $$

(3.46)

The fixed-fluence condition can now be written as:

$$\sum_{n=1}^{N} f_n'^2 = F_0. $$

(3.47)

This suggests the use of hyperspherical coordinates, $\{r, \theta_1, \ldots, \theta_{N-1}\}$:

$$f_1 = r \cos(\theta_1),$$
$$f_2 = r \sin(\theta_1) \cos(\theta_2),$$
$$f_3 = r \sin(\theta_1) \sin(\theta_2) \cos(\theta_3),$$
$$\ldots \ldots \ldots$$
$$f_{N-1} = r \sin(\theta_1) \ldots \sin(\theta_{N-2}) \cos(\theta_{N-1}),$$
$$f_n = r \sin(\theta_1) \ldots \sin(\theta_{N-2}) \sin(\theta_{N-1}),$$

(3.48)

If we fix $r = F_0^{1/2}$, we ensure the fixed-fluence condition, and we can work with the set of $N - 1$ variables, $\Theta$. Therefore, optimization function can be defined simply as:

$$G(\Theta) = \langle \Psi(\Theta)(T)|\hat{O}|\Psi(\Theta)(T) \rangle,$$

(3.49)

if the problem is to maximize the expectation value of some operator $\hat{O}$ at the end of the propagation (in general it is still a function of $\Theta$).

### 3.4.2 Optimization Algorithms

It remains to specify the algorithms that perform the maximization of function $G(\mathbf{x})$ (the vector $\mathbf{x}$ being $\mathbf{f}$ or $\Theta$). The key point is that we cannot calculate the gradient $\nabla G$. Therefore, we must use gradient-free algorithms. Two possibilities are the following:
• **The Nelder-Mead simplex method** (72; 73):
  
The method uses the concept of a simplex, which is a polytope of $N + 1$ vertices in $N$ dimensions; a line segment on a line, a triangle on a plane, a tetrahedron in three-dimensional space and so forth. The method approximately finds a locally optimal solution to a problem with $N$ variables when the objective function varies smoothly. For example, a suspension bridge engineer has to choose how thick each strut, cable, and pier must be. Clearly these all link together, but it is not easy to visualize the impact of changing any specific element. The engineer can use the Nelder-Mead method to generate trial designs which are then tested on a large computer model. As each run of the simulation is expensive, it is important to make good decisions about where to look. Nelder-Mead generates a new test position by extrapolating the behavior of the objective function measured at each test point arranged as a simplex. The algorithm then chooses to replace one of these test points with the new test point and so the algorithm progresses.

  The simplest step is to replace the worst point with a point reflected through the centroid of the remaining $N$ points. If this point is better than the best current point, then we can try stretching exponentially out along this line. On the other hand, if this new point isn’t much better than the previous value, then we are stepping across a valley, so we shrink the simplex towards the best point.

  Like all general purpose multidimensional optimization algorithms, Nelder-Mead occasionally gets stuck in a rut. The standard approach to handle this is to restart the algorithm with a new simplex starting at the current best value. This can be extended in a similar way to simulated annealing to escape small local minima.

  Many variations exist depending on the actual nature of problem being solved. The most common, perhaps, is to use a constant size small simplex that climbs local gradients to local maxima. Visualize a small triangle on an elevation map flip flopping its way up a hill to a local peak. This, however, tends to perform poorly against the method described in this article because it makes small, unnecessary steps in areas of little interest.

  This method is also known as the Flexible Polyhedron Method

• **The unconstrained optimization algorithm scheme**
  
  This is a more complicated algorithm than the previous one by M. J. D. Powell (for more information about the method look at (74)).
3.5 Comparison of Two Approaches of QOCT

As an apparent disadvantage, the wave function of the system comes directly in equations (3.21), (3.22), (3.24), and (3.25), preventing it for application to real systems with many particles. On the other hand, it seems that we are facing the same problem in direct optimization as well. However, this difficulty can be remedied since the wave function of the system in principle is a functional of the time-dependent density, implying the target-dependent functional is a functional of the time-dependent density as well. Therefore, this allows to use time-dependent density functional theory (TDDFT) for direct optimization. Of course in practice this can be applied if the target-dependent functional is either known or estimated by a functional of the time-dependent density and in parallel, if existing functionals can be used safely for our target.

In next section, we will try to use this method for optimizing high-harmonic generation which the functional for this target is explicitly known in terms of the time-dependent density.

Finally we add that if for a system the standard QOCT is applicable usually it will be faster than direct optimization.

3.6 High Harmonic Generation Optimization with Direct Optimization Method

Suppose that we want to optimize the harmonic yield emitted by a system, especially maximizing the emission at $K$-th order of harmonic generation; that is, the harmonic emission at frequency $K\omega_0$ ($\omega_0$ is the carrier frequency). The harmonic emission spectrum can be approximated as:

$$H[\Theta](\omega) = \left| \int_0^T dt \ e^{i\omega t} \ \frac{d}{dt^2} \ \langle \Psi[\Theta](t)|\hat{D}|\Psi[\Theta](t) \rangle \right|^2,$$

(3.50)

where $\hat{D} = -\sum_{i=1}^N \hat{r}$ is the dipole operator (in atomic units). Therefore, the term inside integral in equation (3.50) simplifies to

$$\frac{d}{dt^2} \ \langle \Psi[\Theta](t)|\hat{D}|\Psi[\Theta](t) \rangle = -\frac{d}{dt^2} \ \int r \rho(r, t) \ dr,$$

(3.51)

where $\rho(r, t)$ is the density of the system, showing that $G(\Theta)$ is a functional of density.

A naive approach for optimization would be simply to define the merit function $G$ in the following way:

$$G(\Theta) = H[\Theta](K\omega_0).$$

(3.52)
3.6. High Harmonic Generation Optimization with Direct Optimization Method

But of course, this can be done in a more sophisticated way; e.g. we may choose a merit function with the form:

\[ G(\Theta) = \int d\omega \alpha(\omega) \log H[\Theta](\omega) . \]  

(3.53)

The log function form could be convenient due to the large differences in the values of the harmonic yield (sometimes order of magnitudes) at different frequencies. Naturally, one could define the merit function \textit{without} the log function.

The definition of the function \( \alpha \) is the key: it decides what is to be optimized. For example, if we want to maximize the \( K \)-th harmonic, but at the same time minimize the neighbors we could think of the following:

\[ \alpha(\omega) = \sum_{L=1}^{M} \alpha_L \delta_a(\omega - L\omega_0) . \]  

(3.54)

where \( \alpha_K = 1 \) and \( \alpha = -1 \) otherwise (or \( \alpha = 0 \), or whatever), and \( \delta_a \) is some finite representation of Dirac’s \( \delta \) function \( (\lim_{a \to 0} \delta_a = \delta) \). For example, the simple choice

\[ \delta_a(x) = \frac{1}{a} \top (\frac{x}{a}) , \]  

(3.55)

where \( \top \) is the rectangular function:

\[ \top (x) = \begin{cases} 1 & : \ |x| < \frac{1}{2} \\ 0 & : \ \text{elsewhere.} \end{cases} \]  

(3.56)

This choice for \( \alpha \) leads to the following expression for \( G \):

\[ G(\Theta) = \sum_{L=1}^{M} \frac{\alpha_L}{a} \int_{L\omega_0-a/2}^{L\omega_0+a/2} d\omega \log H[\Theta](\omega) . \]  

(3.57)

In the limit \( a \to 0 \),

\[ G(\Theta) = \sum_{L=1}^{M} \alpha_L \log H[\Theta](L\omega_0) \]  

(3.58)

This kind of definition would very closely follow the experimental set-up described in (39).

In the next chapter we will use these different possibilities to optimize high-harmonic generation.
Chapter 4

Results

In previous chapter, we described methods for optimization and now we use direct optimization for optimizing high-harmonic generation of the system. To achieve this, we use the OCTOPUS code (? ), implementing this method inside it.

4.1 Model Systems

First model is the simplest model in one dimension that is hydrogen atom but with soft coulomb potential instead of pure coulomb (since the wave function diverges at the origin). Its time-independent Hamiltonian is (in atomic units)

\[ \hat{H} = -\frac{1}{2} \frac{\partial^2}{\partial x^2} - \frac{1}{(1 + x^2)^{1/2}}. \] (4.1)

The next model will be the hydrogen molecule in one dimension which has two electrons. Instead of describing two electrons in one dimension it is possible to replace it with one electron in two dimensions. All calculations in this case are done by an exact numerical solution of the Schrödinger equation, reminding that this is not exact solution of the Hydrogen molecule since it is a one-dimensional model by soft coulomb potential. Calling \( x \) and \( y \), the coordinates of the two electrons, the Hamiltonian would be

\[ \hat{H} = -\frac{1}{2} \frac{\partial^2}{\partial x^2} - \frac{1}{2} \frac{\partial^2}{\partial y^2} - \frac{1}{(1 + (x - a)^2)^{1/2}} - \frac{1}{(1 + (x + a)^2)^{1/2}} - \frac{1}{(1 + (y - a)^2)^{1/2}} - \frac{1}{(1 + (y + a)^2)^{1/2}} + \frac{1}{(1 + (x - y)^2)^{1/2}}, \] (4.2)
where $a$ is the inter-atomic distance of the two hydrogen atoms.

As we said above, instead of describing two electrons in one dimension, we may think of one electron in two dimensions, subject to an external potential with the form given by:

$$V_{\text{ind-ext}} = -\frac{1}{(1 + (x-a)^2)^{1/2}} - \frac{1}{(1 + (x+a)^2)^{1/2}} - \frac{1}{(1 + (y-a)^2)^{1/2}} - \frac{1}{(1 + (y+a)^2)^{1/2}} + \frac{1}{(1 + (x-y)^2)^{1/2}}. \quad (4.3)$$

Since the Hamiltonian is identical, we must get the same result. Whether we regard $x$ and $y$ as the coordinates of two different particles in one dimension or as the coordinates of the same particle along the two axes in two dimensions is entirely up to us. Since it is usually easier to treat only one particle, we will solve the one-dimensional the Hydrogen atom in two dimensions.

### 4.2 Initial Spectrum and Frequency of the incident laser

In all calculations we used as an initial laser, a laser with the form of

$$\epsilon_{\text{initial}}(t) = F_0 \cos\left(\frac{\pi}{2} \left( \frac{t - 2\tau_0 - t_0}{\tau_0} \right) \right) \cos(\omega_0 t), \quad (4.4)$$

where $t_0$ and $\tau_0$ are the peak time and the width of the laser respectively. We set the peak time equal to half of time that laser applied to the system, implying that laser reaches to its peak at half time. Of course, this is an unoptimized laser and used only for calculating its initial high-harmonic-generation spectrum and after that we try to optimize it. Finally, since experimentalist are using femtosecond lasers for optimizing high-harmonic generation of the system, in this work we choose (arbitrarily) a femtosecond laser with (carrier) frequency $2.856 \times 10^{15}$ or the period time of $2.2 fms$.

### 4.3 Results for Hydrogen Atom

Here, we use a laser with an intensity of $2 \times 10^{13}$, shining on the system for $T_{\text{total}} = 20T = 44 fms$. The laser and HHG generated by it has been shown in Figures (??)
4.3. Results for Hydrogen Atom

Figure 4.1: The electric field of initial driving laser applied on Hydrogen atom versus time (in atomic units). The intensity of the laser $I$ is equal to $2 \times 10^{13}$, $T = 2.2 \text{fms}$. The total time is $20T$.

and (4.2). Now we set our target to optimize for its 15th harmonics. To achieve this, we use both merit functions in equations (3.52) and (3.53). The results are presented in figures (4.3) and (4.4).

The final result in both cases are practically the same. Although figure (4.3) shows a clear increase in HHG for the 15th harmonics at the same it shows an increase in the all rest as well.
4.4 Results for Hydrogen Molecule

A laser with an intensity of $2 \times 10^{13}$ shines on the system for $T_{total} = 10T = 22\, ms$. The laser and HHG generated by it has been shown in Figures (4.5) and (4.6). Again we demand to optimize for its 15th harmonics of the driving laser frequency. To reach this, we use only the merit function in equation (3.53) as it is likely to give us better results. The results are presented in figures (4.7) and (4.8).

Here, we see the same behaviour in the result as in the case of Hydrogen atom all the HHG spectrum has increased and not only the 15th.

Figure 4.2: High-harmonic spectrum of Hydrogen atom generated with the laser in Fig. ?? versus harmonics of the incident laser frequency.
Figure 4.3: Optimization of high-harmonic generation of the Hydrogen with different merit functions for the 15th harmonics of the laser frequency. Optimization with the merit function in equation (3.52) (red curve) and with the merit function in equation (3.53) (green curve). Initial HHG is shown with blue.
4.4. Results for Hydrogen Molecule

Figure 4.4: Optimized lasers for Optimizing high-harmonic generation of the Hydrogen with different functions for the 15th harmonic of the incident laser frequency. Optimization with the function in equations (3.52) and (red curve) (3.53) gives the same result (red curve). Initial HHG is shown with green.
Figure 4.5: The electric field of initial driving laser applied on the Hydrogen molecule versus time (in atomic units). The intensity of the laser $I$ is equal to $2 \times 10^{13}$, $T = 2.2 \text{ fm}$. The total time is $10T$. 
4.4. Results for Hydrogen Molecule

Figure 4.6: High-harmonic spectrum of the Hydrogen molecule generated with the laser in Fig. 4.5 versus harmonics of the driving laser frequency.
Figure 4.7: Optimization of high-harmonic generation of the Hydrogen molecule with functions in equation (3.53) the 15th harmonics of the incident laser frequency. Optimized HHG spectrum (red curve) and intial HHG spectrum (green curve).
Figure 4.8: Optimized laser for Optimizing high-harmonic generation of the Hydrogen molecule for the 15th harmonics of the driving laser frequency. Optimization with the function in equation (3.53) (red curve). Initial laser shown in green.
Chapter 5

Conclusion

In previous chapters we discussed about importance of high-harmonic generation and its implications for other applications such as nonlinear optics in the XUV range (11) or spectroscopic applications (12; 13). Due to growing interest in this field we therefore encouraged to study the problem of controlling quantum systems to answer demands and challenges in this area. Especially we focused on selective high-harmonic generation. To achieve our goal we used direct optimization method that it can be utilized, in principle, for many-body systems. Although the results in the last chapter were moving towards increasing the selected harmonics we could not control completely over the system, resulting in almost all harmonics increased as well. In the text, we only presented two results but some other calculations on the two models of the last chapter were showing the same behaviour, meaning always all harmonics has been increased not the target harmonics.

This can be due to some factors. First, we only applied our method on two artificial models that they were in one dimension. The other possible reason is related to the fact that our description of the laser is not completely according to experimental setup. Experimentalists introduce a time-dependent phase into carrier part of the electric field of laser, namely

\[ \epsilon(t) = f(t) \cos(\omega_0 t + \phi(t)), \]  

(5.1)

and when they optimize the field, they will use this phase as another parameter. At the worst case, it may possible that the direct optimization algorithm is not completely suitable to our need but this does not seem likely.

Hence, These points suggest a future path to take in the hope of fulfilling our aim.
Bibliography


