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Correlated electronic–nuclear dynamics in strong laser fields

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Declaration

I hereby certify that the work presented in this thesis is my own unless stated otherwise.

Lukas Medišauskas

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Abstract

This thesis investigates how atoms and molecules behave once a coherent electronic dynamics is excited by a high frequency attosecond pulse, via single photon ionization, low frequency IR pulse, via multiphoton ionization, or a combination of both. In particular, the focus is made on the role of vibrational dynamics and how the correlation between the vibrational and electronic dynamics influences the outcomes of induced processes.

First, the role of electronic coherence in modifying the optical properties of atoms is investigated in the context of circularly polarized harmonic generation. Next, we move to simple molecular systems and study the coupling between such electronic coherence and vibrational dynamics after photoionization of H_2 molecules where we focus on the formation of photoionization lineshapes. It is further shown how the initial electronic coherence can modify long-term vibrational dynamics of a molecule by studying dissociative ionization of N_2 molecule in an attosecond-XUV+IR pump-probe experiment.

Both numerical and analytical approaches are used in this thesis. The numerical approaches involve solving the time-dependent Schrödinger equation for the electron wavepacket in atomic potential or the vibrational wavepacket on molecular potential energy curves. The numerical calculations are aided by analytical analysis based on strong field approximation and semiclassical methods.

The phase-lock between excited electronic wavepackets and the time synchronization between the electronic and vibrational dynamics is established as the central object of molecular attosecond science, which allows one to achieve attosecond precision in measurements and coherent control.

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List of Abbreviations

AI - autoionization

BO - Born–Oppenheimer

CEP - carrier envelope phase

CDR - charge directed reactivity

HHG - high harmonic generation

HOMO - highest occupied molecular orbital

IR - infrared

KER - kinetic energy release

NSDI - non sequential double ionisation

PES - potential energy surface

PEC - potential energy curve

RABBITT - reconstruction of attosecond beating by interference of two-photon transitions

RESI - recollision excitation and subsequent ionization

TDSE - time dependent Schrodinger equation

XUV - extreme ultraviolet

Atomic units

The text make a heavy use of the system of atomic units. Below, a list of the constants used in the text to define the system of atomic units is presented.

$\hbar$ - Reduced Plancks constant

a_0 - Bohr radius (also “bohr”)

E_h - Hartree energy (also “hartree”)

m_e - Electron mass

Atomic units for common physical quantities

physical quantity	dimensions in atomic units
time	$\hbar/E_h$
energy	E_h
distance	a_0
electric field	E_h/ea_0
electron charge	e
angular frequency	$\text{rad } E_h/\hbar$
mass	m_e
momentum	$\hbar/a_0$

Some unit conversions

$$\text{Time: } 41.34 \hbar/E_h = 1 \text{ fs}$$

$$\text{Energy: } 1 E_h = 27.211 \text{ eV}$$

The relation between intensity and electric field

E - electric field in atomic units (E_h/ea_0); I - intensity in W/cm^2 :

$$E = \left(\frac{I}{3.51 \times 10^{16}} \right)^{1/2}.$$

Chapter 1

Introduction

When atoms and molecules are exposed to a laser electric field that has a strength comparable to the potential that binds the electrons with the core, a qualitatively new regime of *Strong Field Physics* is achieved [1–3]. It is manifested by the non-perturbative nature of the interaction with the electric field of the laser light, when matter can absorb many more photons than is strictly required to reach the excitation or ionization threshold. The two quintessential effects underlying many of the strong field physics phenomena are the Above Threshold Ionization (ATI), when photoelectrons absorb many more photons than required to reach the ionization threshold, and the High Harmonic Generation (HHG) [4, 5], when tens or even hundreds non-perturbative harmonics of a driving high intensity and low frequency field are produced in gaseous media. Partly due to the simplicity and the conceptual appeal of the three step model [6] that was introduced to phenomenologically explain HHG, ATI and related phenomena, numerous applications of these effects were developed. Among them, the attosecond nature of the pulses produced in HHG was demonstrated using the RABBIT (reconstruction of attosecond beating by interference of two photon transitions) measurement technique [7–10] and was followed by the generation of isolated attosecond pulses [11–14]. Furthermore, the control of continuum electron dynamics with strong low frequency laser fields and consequently HHG allowed to achieve, among others, tomographic reconstruction of molecular orbitals [15] and even demonstrate laser-induced electron holography [16]. Simultaneously, spectroscopy with attosecond pulses allowed one to achieve an unprecedented time resolution in pump-probe experiments such as measurements of ultrafast electronic dynamics in atoms [17] and measurements of the electron-correlation induced delays in the photoionization process, as small as few tens of attoseconds [18].

Despite the rapid development of tools and methods of strong field physics and attosecond science, their application to study the molecular dynamics is still limited [19]. Nevertheless, the prospect of probing or even manipulating the electronic dynamics during the formation and destruction of molecular bonds, thus taking control of the chemical reactions at an unprecedented level, stimulates the progress in molecular attosecond physics.

This thesis addresses a fundamental aspect of ultrafast — subfemtosecond to femtosecond — processes induced by strong laser fields and/or ultrashort (attosecond) pulses, both in molecules and in atoms. Specifically, it focuses on the role of coherence, correlation and entanglement between the electron removed by ionization and the ion left behind, and how this electron-ion correlation can manifest during the coupling of the electronic and nuclear dynamics in molecules.

1.1 Coupled electronic–vibrational dynamics in molecules

In both atoms and molecules, interaction with an attosecond pulse leads to ultrafast ionization, leaving the ion in a variety of electronic states allowed by the energy conservation law. Large bandwidth of the attosecond ionizing pulse, which easily covers between ten and several tens of electron-volts (eV), ensures that the multiple ionic states are populated coherently, creating a multi-electron wavepacket in the ion.

Coherent population of multiple ionic states can also be achieved upon multi-photon ionization with an intense, few cycle visible or near-infrared pulse. On the onset of strong field ionization, the laser field tends to liberate an electron from the highest occupied orbital, i.e. leave the ion in its ground state. However, as the laser intensity increases, electrons can be removed from deeper orbitals, leaving significant population in the lower excited ionic states [20]. Although in strong field ionization, the spectral bandwidth of the ionizing laser pulse may be smaller than the energy difference between the ionic states, the high non-linearity of the process enhances the effective spectral bandwidth and leads to significant coherence of the remaining hole [17].

According to the “three step model” that describes HHG process, the electron that is liberated from the molecule via tunnel ionization is accelerated in the continuum by the laser field. Once the sign of the electric field changes, the electron is driven back and can recombine with the ion, emitting a burst of high frequency radiation. Due to the delay between the time of ionization and the time of recombination, the emitted radiation carries information about the continuum electron dynamics. Moreover, due to intrinsic synchronization between the dynamics of the continuum electron and the residual ion, both of which are triggered by the photoionization, the coherent electronic and vibrational dynamics in the ion after ionization is also reflected in the emitted radiation [20–23].

The coherent population transfer between different molecular ionization continua correlated to different electronic states of the ion, as well as the vibrational dynamics of the ion, both taking place between ionization and recombination, impact the properties of the emitted harmonic radiation [24]. Hence, the harmonics record the intrinsic correlation between the dynamics of the ion and the continuum electron [21] and therefore provide insight into the properties of molecules. One possible example is the molecular chirality-dependent multielectron dynamics in the residual ion driven by the laser electric field with small ellipticity, which influences the harmonic radiation and provides a sensitive probe of chiral identification of molecules [25].

This thesis further explores the impact of electron-ion correlation on the properties of the radiation emitted when the electron recombines with the hole. It considers an atomic state consisting of two degenerate orbitals with $m=\pm 1$ quantum number, e.g., a 2p state of an atom. The dynamics of the electron in the continuum after ionization is correlated with an electronic hole in either $m=+1$ or $m=-1$ orbital of the residual ion, which is reflected in a correlated wavefunction after ionization

$$|\Psi_i(t)\rangle = |e^+\rangle|\text{ion}^+\rangle + |e^-\rangle|\text{ion}^-\rangle. \quad (1.1)$$

Here, $|e^\pm\rangle$ and $|\text{ion}^\pm\rangle$ correspond to the wavefunctions of the liberated electron and the residual ion after ionization from initial state with $m = \pm 1$ magnetic quantum number. Hence, the emitted radiation will depend on the coherent sum of the contributions of the “+” and “−” continua. Chapter 3 explores the situation when a tailored laser field used for HHG creates conditions where the contribution from “+” and “−” orbitals are asymmetric and their interference leads to ellipticity of the total harmonic radiation.

So far, our discussion has been mostly general and applied to both atoms and molecules. However, the ultrafast dynamics induced by ionization of molecules is distinct from atoms in two essential ways:

- I. The electronic states (which form the potential energy surfaces) in molecules are typically much denser than electronic states in atoms. This is particularly true in molecular ions, where a rich spectrum of electronic excitations often lies within a few electron-volts from the ground ionic state. Consequently, a strong IR field can induce very efficient transitions between these electronic states in molecules, while broadband attosecond pulses inevitably excite very rich superpositions of electronic states [26].

The dynamics of an electronic excitation in the ion after ionization can be conveniently described as a motion of a hole in electronic density created by ionization [27–29]. Such a hole can migrate across the ion on ultrafast timescales, faster than any nuclear dynamics. It was speculated by Weinkauff et. al. [30] that once localized, it can selectively break a chemical bond at a specific site, opening a way for the control of chemical reactivity via the electronic coherence. Therefore, studies of hole dynamics gained significant interest following the success of attosecond control schemes in atoms, and is often suggested as the mechanism that would allow to control chemical reactivity on an ultrafast timescale [31].

However, while the existence of electron correlation-driven hole migration was theoretically predicted for a number of molecules, the role of vibrational degrees of freedom in this process has been largely unexplored so far. Nevertheless, considering such coupling is absolutely necessary in order to understand the role of hole dynamics in chemical reactivity.

Furthermore, it is normally considered that the hole dynamics is initiated by ionization with a sub-femtosecond laser pulse, and modelled by simply removing a bound electron from a multielectron wavefunction. However, this simplification hardly corresponds to the actual excitation caused by an attosecond pulse [26]. Crucially, all the previous studies ignored the role of the photoelectron — in the standard approach, it is deleted from the wavefunction and is instantly forgotten. However, its correlation with the ion will determine the coherence of the hole and therefore its migration through the molecule and any coherently driven reactivity that could follow. In the thesis, we explore how this coherence/correlation between the hole and the departed electron can affect the dynamics triggered in the ion.

- II. Molecules exhibit vibrational degrees of freedom, and the dynamics along them can be strongly coupled to the electronic dynamics. Let us briefly discuss how this coupling could be affected by the removed electron.

The wavefunction that describes correlated electronic and vibrational wavepackets, after ionization by a strong IR field and/or attosecond pulse leads to the excitation of multiple electronic states, is

$$|\Psi\rangle = |\text{el}_1\rangle |\text{vib}_1\rangle |\text{BO}_1\rangle + |\text{el}_2\rangle |\text{vib}_2\rangle |\text{BO}_2\rangle. \quad (1.2)$$

Here, in the simple case of only two ionic states, the electronic wavepackets $|\text{el}_{1,2}\rangle$ describe the dynamics of the photoelectron in the continuum, while the vibrational wavepackets $|\text{vib}_{1,2}\rangle$ correspond to different Born–Oppenheimer ionic states $|\text{BO}_{1,2}\rangle$ in the molecular ion. Equation (1.2) immediately allows one to see why and how the continuum electronic wavepackets, which may be completely detached from a molecule, could be relevant for the coupled electronic–vibrational dynamics in the ion. Indeed, if we were to perform a measurement on the molecular ion, e.g., by using a projector $\hat{P}_{vib}$, the outcome of this measurement will also depend on the overlap of continuum

electron wavepackets:

$$\begin{aligned} \langle \Psi | (\hat{I}_{el} \otimes \hat{P}_{vib}) | \Psi \rangle = \\ \sum_{i=1,2} \langle el_i | el_i \rangle \langle BO_i | \langle vib_i | \hat{P}_{vib} | vib_i \rangle | BO_i \rangle \\ + \langle el_1 | el_2 \rangle \langle BO_1 | \langle vib_1 | \hat{P}_{vib} | vib_2 \rangle | BO_2 \rangle + c.c. \end{aligned} \quad (1.3)$$

and thus influence the coherence of the coupled electronic and vibrational dynamics in the ion. This overlap depends on the properties of the ionizing laser field: its intensity, spectral bandwidth and carrier wavelength, and on the ionization regime [17, 32].

Generally, the nuclear degrees of freedom are often viewed as an environment for the coherent motion of electronic wavepackets, leading to the decoherence of the system. It is therefore not clear under what circumstances a coherent superposition of wavepackets in different electronic states may lead to anything more than a statistical mixture of the resulting products. However, experimental and theoretical studies [26, 33, 34] hint at the possibility that the vibrational dynamics can be influenced by the coherent motion of the electronic wavepackets. This leads to the emergence of electronic timescale in nuclear dynamics, which underlies the molecular attosecond science. However, the general extent of these processes is far from clear. This thesis considers several relevant scenarios.

The coherence of the vibrational wavepackets correlated to different electronic states underlies all experiments that demonstrate attosecond time-scale in molecular dynamics, and distinguishes attosecond spectroscopy in molecules from methods attributed to femtosecond physics. Nevertheless, the attosecond timescale can emerge even when the characteristic timescale of underlying dynamics is much longer, i.e. femtoseconds and tens of femtoseconds, and does not necessarily require attosecond pulses. This is demonstrated in chapter 4, where the emergence of the attosecond timescale is the result of the coupling of a coherently prepared electronic wavepacket to the vibrational dynamics of a molecule.

The importance of the liberated electron for the dynamics of the residual molecular ion left behind opens new opportunities for coherent control of this dynamics. One such possibility is the control over continuum dynamics with a short (attosecond) XUV pulse, which nearly instantaneously ionizes the molecule and creates the electronic wavepackets $|el_{1,2}\rangle$. We will show that their overlap can be influenced by changing the parameters of the ionizing laser pulse and allows one to control the coherence between different ionization channels and thus affect any outcome of the coupled electronic–nuclear dynamics in the molecular ion that is

sensitive to the electronic coherence. In chapter 5 we will study how this coherence, once created, can indeed affect the outcome of the coupled electronic–vibrational dynamics that takes place in a molecule long after ionization.

1.2 Structure of the thesis

First, a short review of a selection of strong field phenomena that are particularly pertinent to the dynamics studied in this thesis will be presented (chapter 2). These include the role of nuclear dynamics in high harmonic generation and instantaneous polarization of the electronic states of the molecule by the laser field, which leads to additional sub-cycle modulation of ionization probability and time-dependent modification of the vibrational dynamics of the molecule. Furthermore, an overview of the progress in molecular attosecond science will be provided by using the example of the electron localization dynamics in the dissociating H_2^+ (D_2^+) molecule. This process has been studied using the main experimental approaches underlying strong field and attosecond science. Therefore, electron localization dynamics allows one to both review the development of experimental methods and to develop the main theoretical principles underlying the description of the attosecond dynamics in molecules, using a single physical system.

The original contributions by the author of this thesis starts with the study of high harmonic generation in two-colour counter-rotating fields (chapter 3), which illustrates the importance of coherence between different electronic states in strong field dynamics. In the following chapters, the vibrational dynamics is introduced to the problem and three distinct scenarios that illustrate the role of electronic coherence in coupled electron–vibrational dynamics are presented. The physical phenomena under study include autoionization of the H_2 molecule (chapter 4) and dissociation of the N_2^+ molecule after excitation with attosecond XUV+IR pulse (chapter 5). These scenarios differ in the relative timescales between the nuclear and the electronic dynamics. However, in all these cases, control of the coherence (the phase relation) between electronic and vibrational wavepackets determines the underlying dynamics.

1.3 Publications arising from the work presented in this thesis

Chapter 3

Medišauskas, Lukas, et al. “Generating Isolated Elliptically Polarized Attosecond Pulses Using Bichromatic Counterrotating Circularly Polarized Laser Fields.” *Physical Review Letters* 115.15 (2015): 153001.

Chapter 4

Medišauskas, Lukas, et al. “Signatures of attosecond electronic–nuclear dynamics in the one-photon ionization of molecular hydrogen: analytical model versus ab initio calculations.” *New Journal of Physics* 17.5 (2015): 053011.

Medišauskas, Lukas, et al. “A molecular clock: tracing autoionization dynamics in the H_2^+ bound wavepacket.” (In preparation).

Chapter 5

Medišauskas, Lukas, et al. “Initial electronic coherence in molecular dissociation induced by an attosecond pulse.” *Physical Review A* 92.5 (2015): 053403.

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Chapter 2

Attosecond physics with molecules

[illegible]

The electronic states of H_2 and H_2^+ are shown in figure 2.1. The dynamics after the H_2 molecule is ionized can be well described by the two lowest electronic states of H_2^+ . The first one is the bonding σ_g ground state, which has ionization potential of ~ 15.4 eV. The second is the antibonding σ_u first excited state, which is 15-20 eV higher at the Franck-Condon internuclear distance, near the equilibrium of H_2 . Both σ_g and σ_u states converge to the first dissociation threshold, which is

located at ~ 18 eV above the energy of the ground electronic state of the neutral at its equilibrium internuclear distance. There are many more electronic states in H_2^+ that are higher in energy and that converge to the higher dissociation limits. However, due to much higher energy and lower ionization cross sections usually they are not required to understand the dynamics induced by IR laser field, or by the pair of an attosecond XUV and the IR fields. Therefore, in the following, only the σ_g and σ_u states are considered.

In addition to the σ_g and σ_u states of H_2^+ , H_2 aligned parallel to the laser polarization can also be excited into the Q_1 band of doubly excited states that converge to the σ_u state of H_2^+ and is located ~ 2 eV below the σ_u state. The Q_1 band can be well approximated by a single electronic state that is most prominent in the photodynamics. It has a lifetime of just a couple of femtoseconds and after excitation decays into the σ_g state of H_2^+ by emitting an electron. Consequently, it interferes with the direct ionization channels into the σ_g continuum creating distinctive spectral features in both the photoelectron and the H^+ fragment spectra. In perpendicular alignment, H_2 molecule can be excited to the Q_2 band of doubly excited states (see figure 2.1). However, its dynamics is not required for the discussion that follow, while a more detailed description can be found in, e.g., [4].

After ionization of the H_2 molecule, the H_2^+ ion can dissociate via 3 main channels. The first channel is direct dissociation after ionization into the σ_u state. Once a vibrational wavepacket is created on the anti-bonding σ_u state potential curve, it rapidly dissociates creating H^+ and H fragments with kinetic energy of about 5-8 eV. The second important channel is the excitation of the Q_1 state. The autoionization decay of this state takes the vibrational wavepacket into the bound σ_g state. However, this vibrational wavepacket can gain enough kinetic energy while on the steep potential of the Q_1 state to dissociate, creating fragments with kinetic energy of about 1-5 eV. Finally, the σ_g state potential forms a deep well so that only a very small fraction of population dissociates directly. Nevertheless, in the presence of a strong IR field there can be a significant dissociation from this state due to the so-called bond-softening effect [2, 5–7], which will be discussed in more detail in section 2.2.2 below. Note, that for a range of photoelectron energies, the discussed dissociation channels are indistinguishable and therefore lead to interference effects in both photoelectron and H^+ fragment spectra, see e.g. [8]. These effects will be discussed in more detail in section 2.3.1 in the framework of electron localization.

Finally, a bound vibrational wavepacket created in σ_g electronic state oscillates with a period of ~ 15 fs. The corresponding vibrational spectra consists of broad progression of vibrational lines with highest intensity centred around $\nu = 2$

vibrational state.

2.2 Molecules in strong laser fields

Many attosecond experiments in molecules are performed in the presence of a strong IR laser field, which itself can induce non-perturbative dynamics. Hence, such effects will be discussed before moving to the review of approaches to measure and control the correlated electronic-nuclear dynamics of molecules.

2.2.1 High harmonic generation

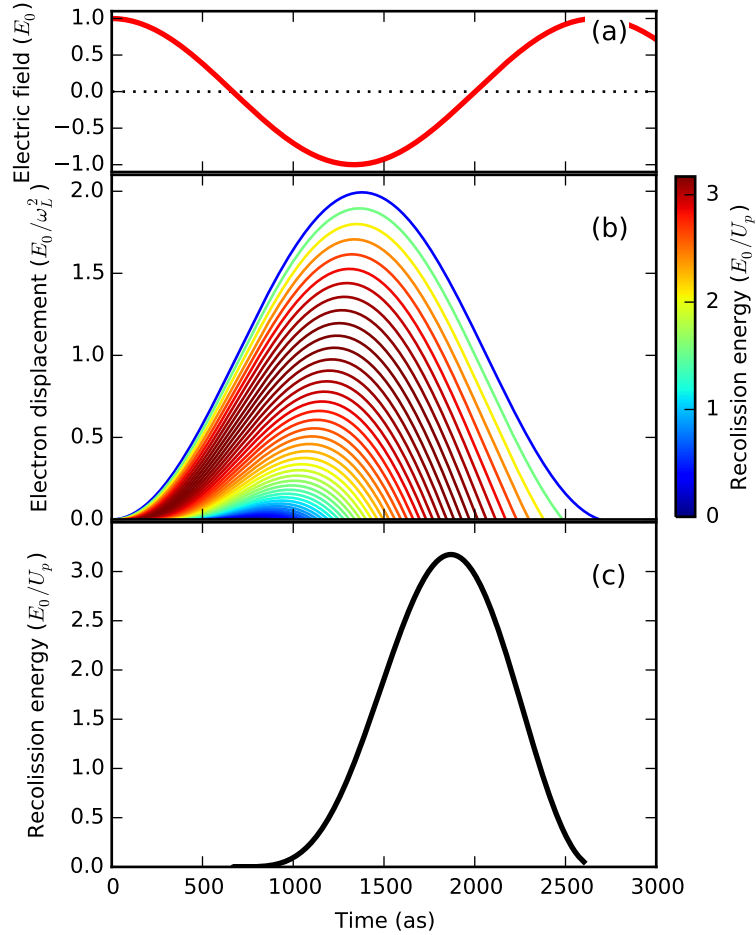


Figure 2.2: The spatio-temporal representation of returning electron trajectories (b) and impact energies (c) for a laser electric field shown in (a). The colour in (b) encodes the energy of the electron upon return.

High harmonic generation (HHG) is a parametric process that up-converts low frequency and high intensity laser radiation into higher frequencies, ranging from UV to XUV. HHG relies on highly non-perturbative response of a generating

medium, usually, but not limited to, atomic or molecular gas. According to the semi-classical 3-step model [9], HHG occurs when an electron is ionized via tunnel ionization from an atom or molecule by a strong laser field, accelerated in the continuum and, once the sign of the laser field changes, driven back to the parent ion. The radiative recombination of the electron and the parent ion leads to an attosecond burst of radiation – a sequence that is repeated every half-cycle of the driving laser field and therefore leads to odd harmonics of the driving field in a medium with inversion symmetry. HHG is usually treated in the S-matrix formalism adopted for this purpose by Lewenstein et. al. [10]. Analysing the arising expressions shows that the time-dependent dipole generating the HHG radiation can be described as a product of three amplitudes [11]

$$D(t_{rec}) = \sum a(t_{rec}) a_{prop}(t_i \rightarrow t_{rec}) a_i(t_i) \quad (2.1)$$

describing tunnel-ionization (a_i) at a time t_i , propagation of both the continuum electron and the ion (a_{prop}) between the time of ionization t_i and the time of recombination t_{rec} and recombination of the continuum electron with the parent ion (a_{rec}) at time t_{rec} . Within the Lewenstein et. al. formalism, the dynamics of the liberated electron in the continuum can thus be described using so-called quantum trajectories with each trajectory characterized by a well defined ionization and recombination times (see, e.g., [12] and [13]). Furthermore, each quantum trajectory also has a well defined kinetic energy of the electron upon return, as illustrated in figure 2.2. This energy plus the ionization potential is converted into the energy of the harmonic photon once the electron recombines with the atom or molecule. Furthermore, for each harmonic energy, a long and a short trajectory contribute, see figure 2.2b. However, due to different phase matching conditions, long trajectories are usually suppressed in HHG experiments (unless the experiment is designed to observe their effect [14–16]). Consequently, the harmonic spectrum provides a time energy mapping – each harmonic energy is directly related to a unique ionization and recombination time of the continuum electron [11, 17]. The attosecond radiation bursts, that are emitted during the HHG, are therefore chirped, with high frequency components generated later during the driving IR field period [17].

The role of nuclear dynamics in high harmonic generation

When HHG is performed in molecules, during the propagation of the electron in the continuum between the ionization and recombination, a vibrational wavepacket that is launched by ionization propagates in the parent ion. The vibrational dynamics

in the cation can be included into the Lewenstein formalism [18] and using the Born–Oppenheimer approximation leading to

$$D(t_{rec}, R) = \sum a(t_{rec}, R) \chi^*(t_i \rightarrow t_{rec}, R) a_{prop}(t_i \rightarrow t_{rec}, R) \times a_i(t_i, R) \chi_0(R) \quad (2.2)$$

where $\chi_0(R)$ is the initial vibrational wavepacket in the neutral ground state before ionization and $\chi(t_i \rightarrow t_{rec}, R)$ accounts for the vibrational dynamics in the cation between ionization and recombination of the continuum electron. The strong field ionization probability $a_i(t_i, R)$ is often very sensitive to the internuclear separation R , which is due to the change of ionization potential as a function of R . Hence, we can define

$$\chi(R, t_i) = \chi_0(R) M(R) \quad (2.3)$$

$$M(R) = \frac{a_i(t_i, R)}{a_i(t_i, R_{eq})} \quad (2.4)$$

where $\chi(t_i, R)$ is the vibrational wavepacket in the cation right after the ionization. $M(R)$ is the ionization mask that accounts for the modification of the initial vibrational wavepacket $\chi_0(R)$ after the strong field ionization [2, 19, 20]. If the R dependence of a_{prop} and a_{rec} is assumed to be small and therefore can be ignored, which is usually justified, the full harmonic dipole can be expressed as

$$D(t_{rec}) = \sum C(\tau) a(t_{rec}) a_{prop}(t_i \rightarrow t_{rec}) a_i(t_i, R_{eq}) \quad (2.5)$$

which is analogous to the HHG dipole for atoms in (2.1), except for the nuclear autocorrelation function

$$C(\tau) = \int dR \chi^*(R, \tau) \chi_0(R) \quad (2.6)$$

where $\tau = t_{rec} - t_i$ is the time between ionization and recombination of the continuum electron and where $\chi(R, \tau)$ is the vibrational wavepacket created in the cation at t_i and propagated till t_{rec} . Consequently, the intensity of the generated harmonics depends on the short time dynamics of vibrational wavepacket on the ionic potential surface after ionization [21].

The time-frequency mapping of the individual harmonics can be used as a single-shot pump-probe measurement, that allows one to reconstruct the movement of the vibrational wavepacket after ionization. In [22], it was achieved by comparing the relative intensity of harmonics generated in H_2 and D_2 molecules. The same

approach has also been used to study sub-femtosecond dynamics in CH_4^+ and CD_4^+ molecules [22]. On the longer timescales, the molecular vibrations that are induced by, e.g., a pump laser pulse, can also be reflected as modulation of the harmonic yield [23]. It is important to note that, in the experiments described above, the dependence of the harmonic spectra on the intrinsic nuclear dynamics could only be achieved because the electron dynamics in the continuum, which was driven by a strong laser field, was coherent with the simultaneous vibrational dynamics of the ion.

The role of electronic dynamics in the cation in high harmonic generation

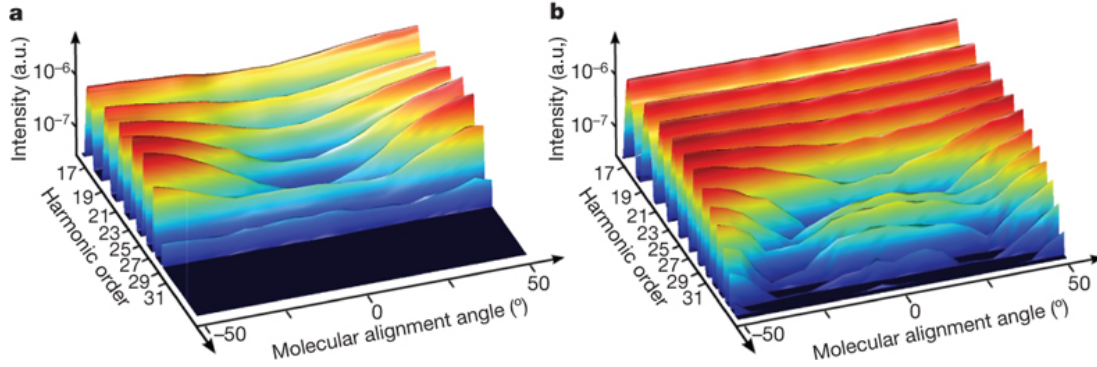


Figure 2.3: Harmonic spectra generated from CO_2 molecule as a function of the molecular angle for two different intensities: $\sim 1.1 \times 10^{14} \text{ W/cm}^2$ (a) and $\sim 1.8 \times 10^{14} \text{ W/cm}^2$ (b). Reprinted by permission from Macmillan Publishers Ltd: Nature [24], copyright 2009.

The probability of tunnel ionization P depends exponentially on the ionization potential I_p as $P \propto \exp(-2/3 (2I_p)^{3/2}/E)$ where E is the laser electric field. Therefore, in multi-electron systems and in the Hartree–Fock picture, the ionization is dominated by the removal of the electron from the highest occupied orbital. Strictly speaking, ionization leaves the ion in the ground electronic state. Ionization from the deeper lying orbitals is suppressed. Furthermore, the total HHG dipole (see (2.1) and (2.5)) depends on the recombination amplitude, which is quantified by the recombination dipoles. The latter are complex-conjugate to the one-photo ionization dipoles of a molecule or an atom. Hence, the HHG process is strongly related to photoionization and can therefore reveal the electronic structure of an atom or a molecule through the intensity, phase and ellipticity of the generated harmonics [25–27]. Moreover, if a pump pulse is used prior to HHG that initiates structural rearrangement in a molecule, than this rearrangement can be tracked by HHG-probe [28–30].

In molecules, lower orbitals are often just a couple of eV below the highest occupied molecular orbital (HOMO). Therefore, in spite of the exponential dependence of ionization probability on the binding energy, even a moderately strong IR field can lead to significant ionization of multiple orbitals, accessing many electronic states in the ion [31, 32]. Furthermore, the nodal structure of the molecular orbitals leads to a strong dependence of tunnel ionization probability on molecular alignment [33] helping deeper orbitals to compete with the HOMO in the HHG signal. The harmonic radiation produced in each HHG channel, associated with different ionization continuum (different orbitals), will have different channel-specific intensity, phase, ellipticity and alignment-dependence. Their interference creates regions of constructive and destructive minima and maxima in the harmonic spectra [24, 26, 34, 35], see figure 2.3. Such interference is possible because in HHG all the channels start and end at the same state - the ground state of the neutral molecule, making them quantum mechanically indistinguishable. They are different only by their intermediate ionic states.

The laser field can also induce transitions between the electronic states in the cation between the ionization and recombination steps of HHG. Therefore, once the electron returns to the parent ion, it can recombine into a different electronic state than the one it has been liberated from, creating *cross-channels* in HHG [35].

The position of the destructive interference minima in the harmonic spectra depend on the driving field intensity and the molecular orientation. This dependence allows one to reconstruct the phase relation between the different electronic states in the cation right after tunnel-ionization and this way reconstruct the shape and the dynamics of the initial electronic excitation [24, 35].

2.2.2 Instantaneous polarization of molecules by a strong IR field

A strong electric field leads to a significant modification of the potential energy surfaces (PES) of a molecule due the laser-induced coupling of different electronic states in the molecule. In frequency domain, the modification of PES can be interpreted using the Floquet picture, where additional PES are introduced that correspond to absorption or emission of laser field photons, including avoided crossings between different PES induced by the field [2, 7]. In a time-dependent picture, which is better suited for describing interaction at high laser field intensities and low laser frequencies, the field-free electronic states can be replaced by effective field-dressed or “quasi-static” electronic states that follow the instantaneous laser electric field $F(t)$, with time t treated as a parameter. For a two-level system

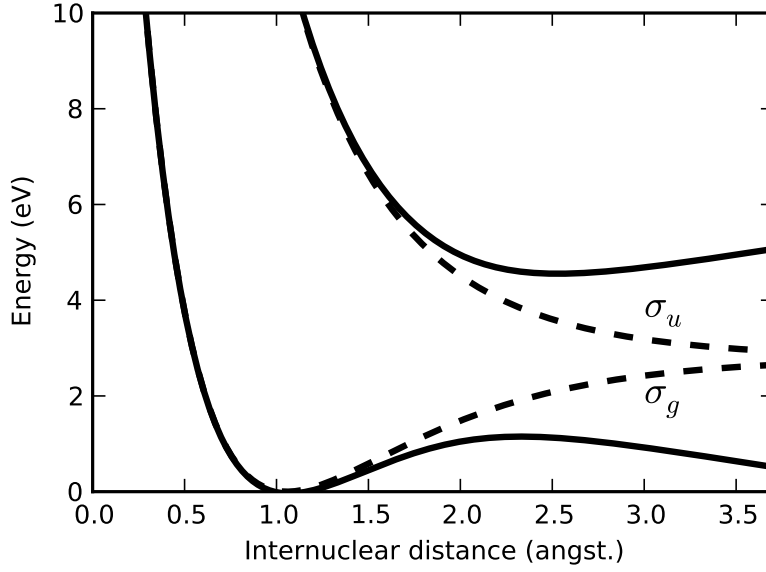


Figure 2.4: Field free (dashed lines) and field dressed (full lines) σ_g and σ_u potential curves of H_2^+ molecule for $2 \times 10^{13} \text{ W/cm}^2$ intensity dressing field. The field dressed states show the reduction of barrier for dissociation from σ_g state.

with eigenstate energies equal to E_1 and E_2 the time-dependent energies of such quasi-static states $E_{\pm}$ are

$$E_{\pm} = \frac{E_1 + E_2}{2} \pm \sqrt{\frac{(E_1 - E_2)^2}{4} + \left(d F(t)\right)^2} \quad (2.7)$$

where d is the transition dipole matrix element (also see appendix A for an extended discussion).

The vibrational dynamics on such effective field-dressed potentials might be very different from the corresponding field-free dynamics. In the H_2^+ molecular ion, the laser-induced coupling of σ_g and σ_u states leads to a strong energy shift of the field dressed potentials that reduces the potential barrier for dissociation in the σ_g ground electronic state and therefore also reduces the number of bound vibrational states [2, 5]. This effect, so called *bond softening*, opens up an additional dissociation channel for the H_2^+ molecular ion in its σ_g ground electronic state, when the ion is exposed to a strong (10^{13} – 10^{14} W/cm^2) laser field, and leads to low-energy ($< 2 \text{ eV KER}$) H^+ dissociation fragments [6]. Note also, that low energy fragments are also released from the process of *bond hardening*, which can be revealed by varying the pulse full time [36].

The oscillations of the laser electric field can in principle be synchronized with the motion of the vibrational wavepacket in a bound potential of a molecule. In such case, a laser pulse can be constructed in a way, that it lowers the dissociation barrier for the vibrational wavepacket exactly at the moment when the latter

reaches the outer turning point of the potential, thus allowing the wavepacket to escape [37, 38]. This, however, requires that the ionization step, which launches the vibrational wavepacket, is well timed within the oscillations of the control field, e.g., the ionization window is much shorter than the period of the control field. In [37], it was achieved by constructing an IR pulse with a single high intensity peak, which ionizes H_2 molecule and a modulated trailing end, which controls the barrier opening. Alternatively, in [38] the desired timing between the ionization step and the control pulse was achieved by ionizing the molecule with an attosecond pulse that precedes the IR control laser field with a controllable time delay.

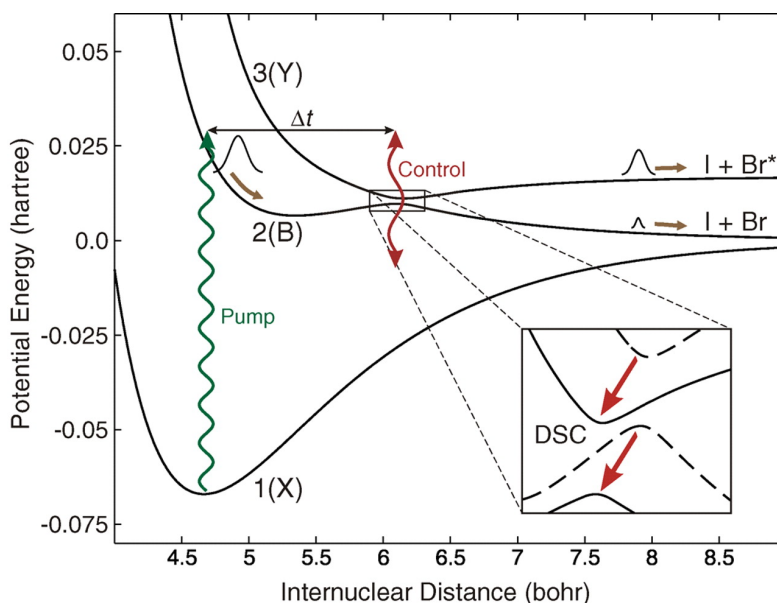


Figure 2.5: Dynamical Stark Control of dissociation of IBr molecule. An wavepacket created in the excited state traversed a nonadiabatic crossing, which is correlated to two different dissociation limits. A delayed IR field modifies the adiabatic potential barrier (inset) via the Stark effect, changing the outcome of the reaction. Reprinted from [39] with permission from AAAS.

In general, an oscillating laser electric field leads to the AC Stark Effect. The latter has sub-cycle dependence [40, 41] and it therefore shifts the energy of electronic states in a time-dependent manner in any molecule. When averaged over cycle, the size of the energy shift is proportional to the instantaneous intensity of the dressing field. However, the strength of this effect in general depends on the electronic state [42]. Crucially, however, it allows one to modify the effective field-dressed potentials on which the vibrational dynamics is taking place. In [39] a pump pulse was used to excite IBr molecules to a dissociative state. A control IR pulse was then applied with a variable time delay, modifying via the dynamical Stark effect the height of the potential barrier at an avoided crossing of two potential energy curves correlated to different dissociation products, as

illustrated in figure 2.5. The time delay between the pump and the control pulses allowed one to change the intensity of the control field and thus the height of the barrier at the avoided crossing once it is reached by the vibrational wavepacket moving towards dissociation. Since the probability for the wavepacket to either stay on the lower adiabatic state or to make a transition to the upper adiabatic state is very sensitive to the barrier height, the control of the probability of non-adiabatic passage can be achieved, as shown in [39].

2.2.3 Attosecond control of ionization probability

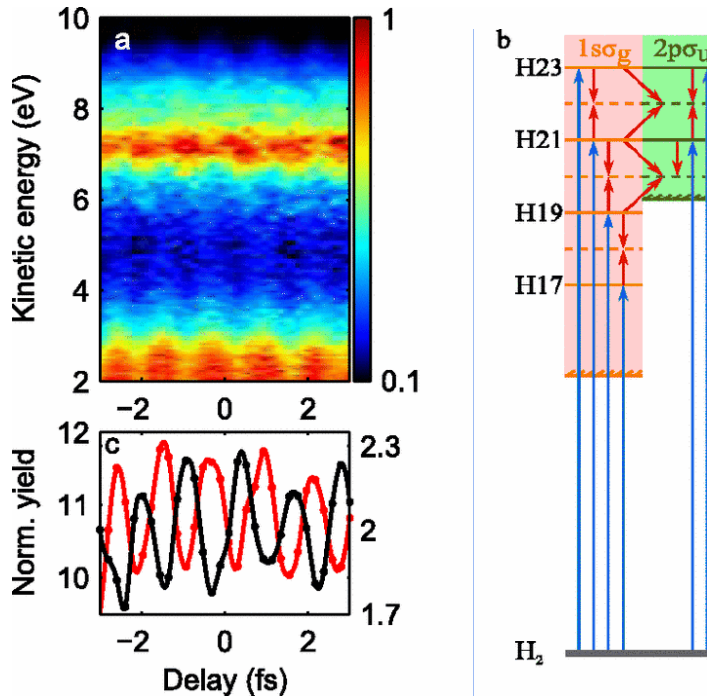


Figure 2.6: (a) D^+ fragment kinetic energy release spectrum as a function of delay between the attosecond pulse train (APT) and the IR pulse for fragments ejected parallel to the IR polarization. Panel (c) shows the ion yields as a function of delay for fragments centred at 7 eV (black) and 3 eV (red) normalized to the APT only yield at that energy. (b) Illustration of ionization of H_2 molecule at equilibrium internuclear distance with two colour APT+IR laser field. Blue arrows represent ionization by the XUV photon from the odd harmonics of the APT, red arrows represent transitions due to absorption or emission of an IR photon, which can take place within the same ionization channel (vertical arrow) or couple the σ_g and σ_u ionization continua (diagonal arrows). Reprinted figure with permission from [43]. Copyright 2011 by the American Physical Society.

When an atom is ionized by overlapping XUV and IR laser pulses with frequencies Ω and ω respectively, the photoelectron liberated by the XUV field can further absorb or emit an IR photon creating sidebands $\Omega \pm \omega$ of the main photoelectron

peak. If the XUV radiation is obtained by HHG process and therefore consists of odd harmonics of the driving IR field $\Omega_{2N\pm1} = (2N \pm 1)\omega$, than the sidebands of adjacent harmonics overlap, $\Omega_{2N-1} + \omega = \Omega_{2N+1} - \omega$. Their interference creates a beating of the photoelectron spectral amplitude $A \sim \cos(2\omega\Delta t + \phi)$ with changing time-delay Δt between the overlapping XUV and IR pulses and with a phase ϕ that depends on the two-colour ionization dipole and the phase difference between adjacent $2N + 1$ and $2N - 1$ harmonics. Hence, if the phase of the ionization dipole is known, the relative phase between different harmonics can be retrieved from the phases ϕ of adjacent sidebands in what is known as the RABBITT (Reconstruction of Attosecond Beating By Interference of Two-photon Transitions) measurement [17, 44–46]. Alternatively, given that the harmonic phases are known, the RABBITT measurement can be used to reconstruct the photoionization dipole phase [25, 47, 48]. Furthermore, in a RABBITT measurement in molecules both the main harmonic lines and sidebands show a vibrational progression originating from the electronic state accessed by XUV ionization. In analogy to atoms, the oscillation of the sidebands with XUV–IR time delay allows one to study short lived resonant states [49].

In the conventional RABBITT measurement, the IR photon is absorbed by the photoelectron that makes a transition between two continuum states within the same ionization channel. Hence, the total probability of ionization into a particular channel is not modulated [50].

In contrast, in molecules, close spacing between different electronic states in the cation inevitably leads to the IR induced coupling of different ionization continua. Consequently, the IR photon can be absorbed not only by the photoelectron changing its continuum state, but also by the ionic core changing the state of the ion and thus the ionization channel.

An experiment by Kelkensberg et. al. [43] demonstrated such “molecular RABBITT” for dissociative ionization of H_2 molecule due to an attosecond XUV pulse train and an overlapping IR field. In the experiment, the yield of H^+ fragments measured as a function of time delay between the XUV and IR pulses, which is directly related to the population in the σ_u state of H_2^+ after ionization, shows modulation with the half-period of the driving IR pulse (see figure 2.6a). It can be attributed to the interference of sidebands from different harmonics, similarly to the atomic RABBITT case. However, in the experiment of Kelkensberg et. al., the absorption of an IR photon changes the electronic state of the H_2^+ ion after XUV ionization. Hence, a RABBITT-like modulation is due to the interference of $+\omega$ and $-\omega$ ionization pathways that include different intermediate ionization channels (electronic states in the molecule), as illustrated in figure 2.6b. Unlike the atomic

RABBITT, such interference of ionization continua leads to the redistribution of the total wavefunction between different ionization continua and therefore modulates the ionization probability in a particular channel. Note also that in the experiment by Kelkensberg et. al., the modulations of the fragment spectra with the time delay at lower energies, where the doubly excited Q_1 state is expected to contribute, are shifted in phase compared to the higher fragment energies, as can be seen in figure 2.6c, which, however, was never explained.

During the two-colour XUV+IR ionization of a molecule, the IR field may not only induce transitions between the electronic states in the ion as discussed above, but it can also couple the states in the neutral molecule prior to absorption of an XUV photon. The ground electronic state of the neutral molecule is normally energetically well separated from the excited states by an energy gap, which is much bigger than the IR photon energy. Therefore, no real transitions between the electronic state of the neutral molecule are induced. However, the IR field can cause polarization of the molecule with the electronic cloud adjusting to the instantaneous IR electric field. When such polarized molecule is ionized by an attosecond XUV pulse, the ionization probability follows the instantaneous IR electric field [51]. Note, however, that formally it is not trivial to distinguish the polarization of the neutral molecule from the polarization of the ion in the ionization process.

2.3 Coherent electronic–nuclear dynamics in molecules: from electron localization to hole migration

As has been discussed in the previous sections, ionization of molecules may populate multiple electronic states of the cation and hence can induce coherent electron dynamics. The most basic molecule where such an excitation can be studied is H_2^+ , with coherent electronic dynamics induced by creating a coherent superposition of its ground and first excited states. Below, a review of attempts to create, measure and manipulate such a superposition will be presented. It allows us to introduce main experimental methods and theoretical concepts underlying the attosecond physics in molecules while using the same model system. Later, the ideas will be extended to bigger molecules in the context of hole migration and charge directed reactivity.

2.3.1 Electron localization

Left-right states

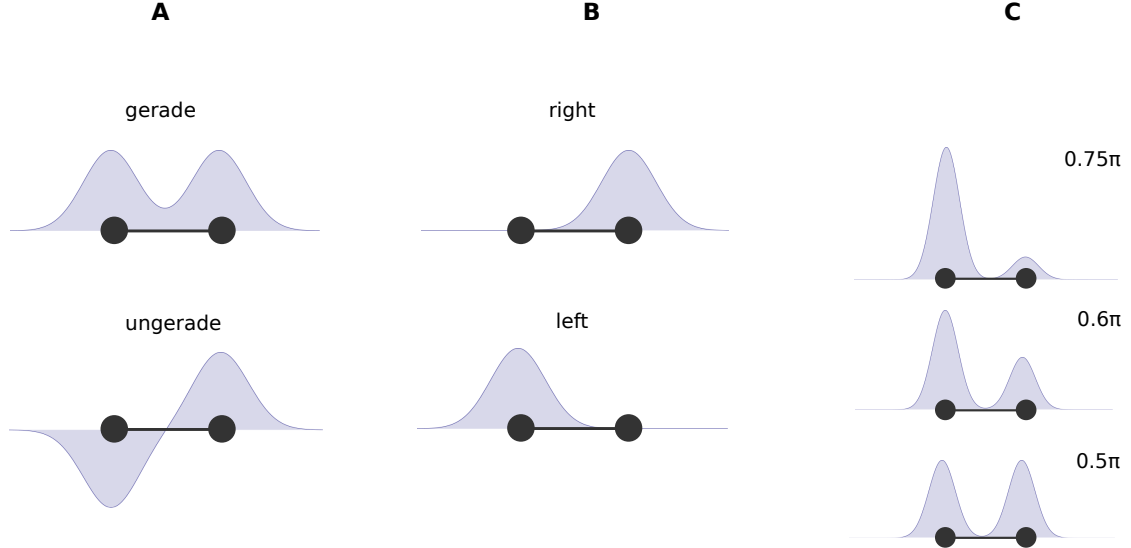


Figure 2.7: Schematic representation of the *gerade-ungerade* (A) and left-right (B) basis of the electronic states of a diatomic molecule. (C) illustrates the electron asymmetry due to the coherent sum of *gerade* and *ungerade* states with different relative phases between them.

Consider two electronic states in a diatomic homonuclear molecule that have opposite *gerade* and *ungerade* parity. An example, which will be considered below, is the σ_g and σ_u states of H_2^+ molecular ion. A coherent superposition of these states with equal weights leads to a localized state where the electron probability density is either on the left or on the right of the two atoms (where the “left” and “right” direction is arbitrary and could as well be “top” and “bottom”) (see figure 2.7)

$$\psi_{\text{left}}(R) = (\sigma_g(R) + \sigma_u(R))/\sqrt{2} \quad (2.8a)$$

$$\psi_{\text{right}}(R) = (\sigma_g(R) - \sigma_u(R))/\sqrt{2}. \quad (2.8b)$$

Localized electronic states can be easily understood from the molecular structure theory, where in the first order approximation molecular orbitals are constructed as bonding and antibonding combinations of atomic orbitals, i.e. $\sigma_{g,u} = 1s_1 \pm 1s_2$. The population in ψ_{left} and ψ_{right} states indicates the probability to find the electron on either the left or the right atom of the molecule. Electron localization on one of the protons of H_2^+ can thus be controlled by changing the relative phase or the amplitudes of the σ_g and σ_u states (see figure 2.7c).

If only σ_g or σ_u state is populated, then the relative population of ψ_{left} and

ψ_{right} states will be equal and hence the probability to find the electron on any of the two atoms will be equal. A coherent superposition of σ_g or σ_u leads to different population in the ψ_{left} and ψ_{right} and hence preferential electron localization. In [8], single photon ionization was used to create a coherent superposition of σ_g and σ_u states of the H_2^+ molecular ion. Since both electronic states converge to the same dissociation limit, they are indistinguishable in the case of dissociative ionization of the molecule. Consequently, asymmetry in the angular distribution of photoelectrons was observed due to the interference of photoelectrons correlated to dissociation channels converging to the σ_g and σ_u states, thus breaking of the inversion symmetry of the system. Note, however, that the left-right asymmetry is created in the molecular frame of reference and is not necessarily observed in the laboratory frame of reference. Hence, a measurement in the molecular reference frame has to be performed. This can be achieved by measuring both the photoelectrons and dissociation fragments in coincidence [8, 52]. Alternatively, a strong laser field can be used, that drives the dynamics of molecules in a particular direction in the laboratory frame and hence leads to laboratory frame asymmetry. Both of these methods will be discussed in more details below.

The role of vibrational dynamics in the formation of electron localization

A laser electric field can effectively couple the σ_g and σ_u electronic states of the H_2^+ molecule and coherently drive the population between them, especially when the energy separation between the states is close to one-photon or three-photon resonance [53, 54]. For a 800 nm wavelength laser light, which is typically used in strong-field experiments, the one- and three- photon resonant energy spacing between the σ_g and σ_u states is attained only at large internuclear distances, far away from the Franck-Condon (FC) position. Consequently, vibrational dynamics in the molecular ion is required to establish coherent superposition of σ_g and σ_u states by an IR laser field. If such superposition is established, a left-right asymmetry in the number of detected protons after dissociation can develop.

The development of the left-right asymmetry during the dissociation of H_2^+ ion is illustrated in figure 2.8. Once a vibrational wavepacket is created on the dissociative σ_u electronic state potential, after about 4 fs it reaches a region (green area) where the σ_g and σ_u states are strongly coupled by the 800 nm IR field (see figure 2.8c). During the time the wavepacket propagates in this region, the asymmetry between the left and right states is established (see figure 2.8d). However, when approximately 7 fs after ionization the vibrational wavepacket reaches the internuclear distance for which the σ_g and σ_u states are degenerate (red area). Then, the transitions between the left-right state stops and the electron

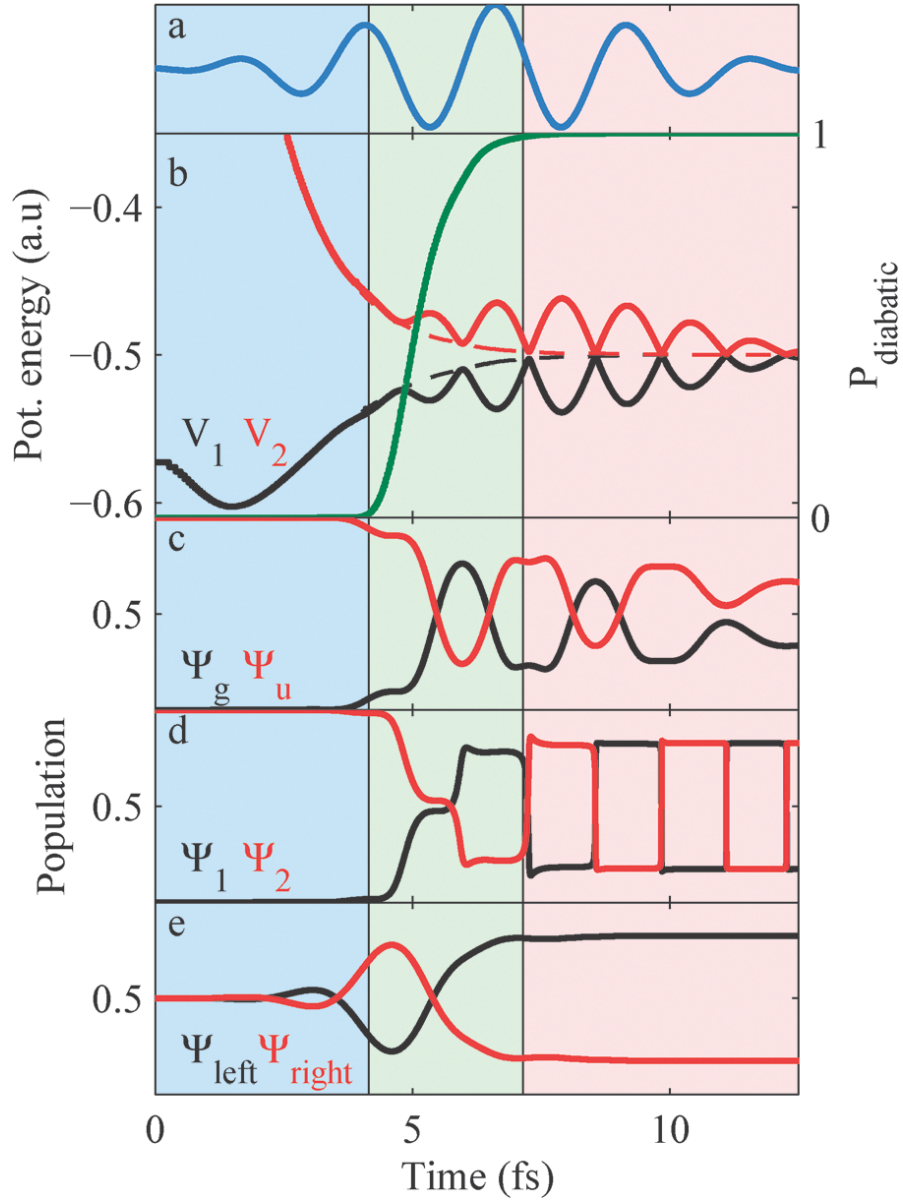


Figure 2.8: Comparison of H_2^+ dissociation dynamics in different bases. Picture (a) shows the laser field; picture (b) shows the field free (dashed) and quasi-static (full lines) electronic states and the Landau–Zener transition probability is represented as a green line; pictures (c,d,e) show the time-dependent population in different electronic state representations: *gerade* and *ungerade* (c), adiabatic states (d) and left-right localized states (e). Reproduced from [55] with permission of the PCCP Owner Societies.

is trapped on one of the two atoms. Note that in the adiabatic (field-dressed) state picture this corresponds to full population transfer between upper and lower adiabatic states at each zero-crossing of the laser electric field (see figure 2.8d). It signifies the breakdown of the adiabatic approximation, when the non-adiabatic couplings go to infinity. The region, where the left-right state mixing is strongest, can be identified by evaluating the Landau–Zener transition probability between the adiabatic (field dressed) electronic states (green line in figure 2.8b, also see appendix A). The mixing is strongest when the transition probability is significant but less than unity.

From figure 2.8 it is also clear how the electron localization can be controlled by the laser field. The shape of the electric field waveform when the vibrational wavepacket is in the strong mixing region determines the population dynamics between the σ_g and σ_u states. Once the H_2^+ molecular ion dissociates into an H atom and a H^+ ion (proton), the relative population and coherence of σ_g and σ_u states will determine the left–right localization of the electron on either of the departing atom (proton). It can be measured by detecting the charged ions in the left–right direction and is a sensitive probe for the coherent vibrational-electronic dynamics before dissociation. Crucially, it can be controlled using the electric field waveform and its synchronisation to the nuclear dynamics in the molecular ion.

2.3.2 Experimental observation and control of electron localization

Experiments that measure and control electron localization in molecules during the fragmentation process were among the first to demonstrate the control of electronic dynamics on sub-femtosecond timescale that is coherently coupled to the nuclear dynamics. Due to relatively simple theoretical description of electron localization and the simplicity of the electronic structure of the H_2^+ molecular ion, which leads to robustness of the effect, electron localization in dissociating H_2^+ molecules became a benchmark used to test many experimental techniques that later became widely used. Therefore, the review of experiments on electron localization also reflects the development of experimental approaches used to conduct attosecond and strong-field physics in molecules.

First demonstration of the control of electron localization

The development of the strong-field physics is closely related to the development of sources of strong and low-frequency (IR to visible) laser radiation. The ability to reduce the duration of these pulses to just a few oscillations of the electric field and

in particular the ability to control the carrier envelope phase (CEP), which is the phase of the electric field within the pulse envelope, allowed for the development of novel spectroscopic techniques with a sub-femtosecond time resolution that rely on the control of the laser field waveform.

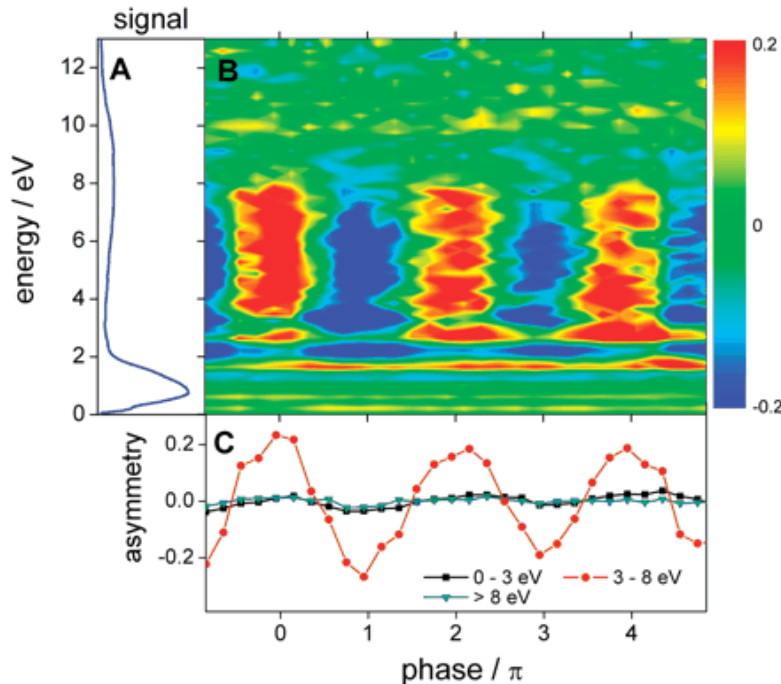


Figure 2.9: (A) kinetic energy release spectrum of D⁺ fragments for 5 fs, 10^{14} W/cm² laser pulses without phase stabilization. (B) The dependence of the asymmetry parameter on the fragment kinetic energy release and carrier envelope phase ϕ . (C) Asymmetry, integrated over selected energy ranges as a function of carrier envelope phase. From [56]. Reprinted with permission from AAAS.

Precise control of the electric field waveform of CEP stabilized short IR pulses provides the possibility to control the underlying coherent dynamics, such as electron localization, on sub-cycle level. It was demonstrated by Kling et. al. [56] in the dissociative ionization of D₂ molecules, which was initiated by an intense (10^{14} W/cm²) and short (5 fs FWHM) IR (750 nm wavelength) CEP stable pulse. In analogy to the three-step model in atoms, when a molecule is ionized by the IR field, the electron promoted to the continuum is accelerated by the laser field and is driven back to the parent ion. Simultaneously with the dynamics of the continuum electron, a vibrational wavepacket is created and evolves in the σ_g electronic ground state of the molecular ion. Previous works [57] have demonstrated that, once the continuum electron comes back, it can excite the parent ion to the dissociative σ_u electronic state with significant probability, leading to dissociation of D₂⁺ into D atoms and D⁺ ion. Importantly, the electron impact excitation is most likely at the moment of the return of the most energetic electrons, which happens around

the zeros of the driving IR field [58]. Therefore, the excitation by the returning electrons is automatically locked to the driving field waveform.

In the experiment by Kling et. al. [56], the D_2^+ molecules were also excited to the dissociative σ_u state by the impact of the returning electron. However, once the dissociating vibrational wavepacket in the σ_u state reached larger internuclear distance, the electric field that was still present due to the trailing end of the IR pulses coupled σ_g and σ_u electronic states creating their coherent superposition and led to the laboratory frame electron localization. It was measured as the asymmetry in the number N of D^+ fragments in opposite directions (left and right) along the laser polarization

$$A = \frac{N_{left} - N_{right}}{N_{left} + N_{right}} = \frac{|\Psi_{left}|^2 - |\Psi_{right}|^2}{|\Psi_{left}|^2 + |\Psi_{right}|^2} \quad (2.9)$$

and is displayed in figure 2.9. Crucially, the control of the CEP phase of the laser pulse allows one to control the asymmetry. Values from zero (no asymmetry) to a ± 0.2 were attained in the experiment.

The excitation of the D_2^+ molecular ions was predominantly caused by the impact of the highest energy electrons that are created around the peak of the laser electric field and return to the parent ion after about 3/4 of a laser period [58]. Consequently, the vibrational dynamics of the molecular ion after ionization, the excitation to the dissociative σ_u state and subsequent fragmentation of the molecular ion are synchronized with the electric field waveform as well. For a nearly single cycle IR pulse the strong-field ionization can be limited to a single half-cycle of the pulse. The change of the CEP phase by π changes the laser half-cycle, during which the electrons that lead to the excitation of the molecular ion to the dissociative σ_u state, are created [59]. This reverses the electric field waveform during the dissociation and thus the direction of electron localization. Such control is only possible due to the intrinsic synchronization of the IR driven electron dynamics in the continuum and the vibrational dynamics in the molecule.

Bond softening pathway

In the experiment by Kling et. al. [56], the dissociation of the molecule was initiated by electron recollision. Consequently, the dissociating wavepacket was created on a steep potential curve of the σ_u state resulting in large, up to 8 eV, Kinetic Energy Release of the D^+ fragments. A H_2^+ or D_2^+ molecular ion can also dissociate directly from its σ_g ground electronic state, due to the process known as *bond softening* [6], see section 2.2.2 for a more extended discussion. When a vibrational wavepacket is created in the σ_g ground electronic state of the molecular ion at Franck–Condon

internuclear distance, it starts travelling outwards. Once it reaches the outer turning point of the potential curve, where the energy spacing between the σ_g and σ_u is almost resonant with the IR field, the laser field strongly couples the two electronic states and promotes the wavepacket on the dissociating curve, leading to dissociation with fragment energies < 2 eV. This dissociation channel is analogous to the process of “bond softening” in which the vibrational wavepacket from the ground electronic state of H_2^+ ion escapes due to the suppression of dissociation barrier by the AC Stark effect.

Electron localization in the dissociation via bond-softening was demonstrated in [60]. Here, a short, 6 fs FWHM laser pulse guaranteed that the ionization of the molecule was taking place predominantly within a single half-cycle of the laser pulse. Hence, once the vibrational wavepacket reached the outer turning point of the potential, the control of the CEP phase allowed one to change the electric field profile at the tail of the pulse and thus the coupling between the σ_g and σ_u states, influencing the electron localization dynamics similarly to the experiment by Kling et.al.

We can see that the CEP control of short laser pulses and thus the ability to control the laser electric field waveform opens a way to manipulate coherent superposition of electronic states and thus the electron localization dynamics. Such control goes beyond the schemes that rely on the dynamical AC Stark effect, which were discussed in section 2.2.2. While the latter generally change the vibrational dynamics by modifying the PES, the experiments on electron localization extend the control to electronic wavepackets on their natural (electronic) timescale.

Further experiments

In the experiments described so far, the control of electron localization by the CEP of an IR pulse relied on short laser pulses, for which the ionization and recollision excitation are either limited to a single half-cycle of the laser pulse or a single half-cycle is prevalent. If the adjacent half-cycles contribute equally, two dissociating vibrational wavepackets are created during opposite phases of the IR field. This leads to opposite electron localization asymmetry for the two wavepackets, cancelling out the effect altogether [61].

Nevertheless, control of electron localization with a much longer 40 fs laser pulses was demonstrated in [62]. In this experiment, an IR laser field is combined with a weaker second harmonic field to produce an electric field waveform for which one half-cycle within the oscillation period is more intense than the other half-cycle. It effectively leads to a single dominating ionization event per driving IR field period. Hence, the lack of the inversion symmetry in the ionization process allows

one to achieve a preferential electron localization direction [61]. Note that a similar technique is used to produce even harmonics during high harmonic generation in atoms [63].

An attempt to achieve the control of electron localization in more complicated molecules was made for the CO molecule [64, 65] using 8 fs 760–800 nm wavelength and an $6\text{--}8 \times 10^{13}$ W/cm² intensity CEP controllable pulses. However, additional electronic states that were participating in the dynamics led to weaker electron localization and a more narrow range of KER energies, where the electron localization was observed. Indeed, using a simple scheme where only the CEP of the laser pulse is controlled does not give enough control freedom to prevent the decoherence of both the electronic and vibrational wavefunctions due to the couplings with other electronic states, both during the ionization of the molecule and propagation on the dressed potentials.

Low efficiency of the control of electron localization in bigger molecules reflects a general issue of the coherent control of quantum dynamics. Namely, if additional degrees of freedom are present, coupling between them induces the decoherence of the quantum wavepacket. In the limit of infinitely many degrees of freedom, this process can be described as coupling between the system and its environment (bath). This is particularly pertinent to big molecules, where the dynamics of interest are often limited to just a few degrees of freedom, while many other degrees of freedom are the environment that leads to decoherence.

A beautiful generalization of the electron localization mechanism to a coherent superposition of vibrational modes was demonstrated by Alnaser et. al. [66]. In the experiment, ionization of C₂H₂ molecule by a strong near single cycle IR laser pulse led to a coherent superposition of symmetric and antisymmetric stretching modes in the C₂H₂⁺ ion. The phase difference between the modes was determined by the CEP of the laser field, because only the anti-symmetric stretching mode can couple to the IR laser electric field. When the photoelectron was driven back and recollided with the C₂H₂⁺ parent ion, it further ionized the ion into the first excited state of C₂H₂⁺⁺. The coherent superposition of symmetric and antisymmetric stretching modes was then projected onto the C₂H₂⁺⁺ excited state potential energy surface. The phase difference between the modes determined which direction the newly created vibrational wavepacket will move in. Hence, the control of the laser CEP and thus the sign of the superposition of the vibrational modes allowed one to steer the vibrational wavepacket in C₂H₂⁺⁺ molecular ion towards either the left or the right dissociation limit, controlling the deprotonation process of the C₂H₂⁺⁺ ion.

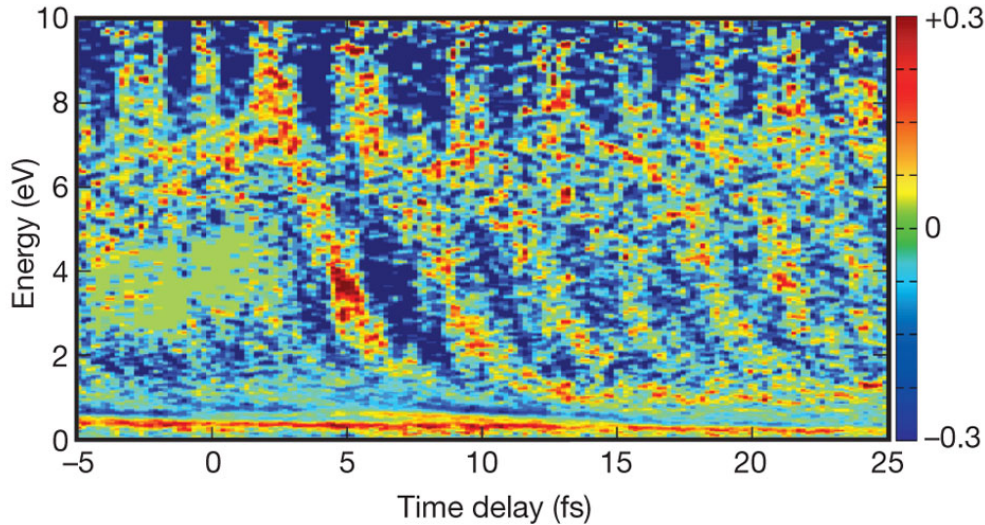


Figure 2.10: The dependence of the asymmetry parameter on the D^+ fragment kinetic energy release and the XUV-IR time delay. The asymmetry oscillates as a function of the XUV-IR delay and strongly depends on the kinetic energy release. Reprinted by permission from Macmillan Publishers Ltd: Nature [67], copyright 2010.

Attosecond XUV pump – IR probe measurements

The key goal of attosecond pump–probe spectroscopy is to use attosecond pulses as both pump and probe. This would not only allow to achieve an attosecond time resolution, but would also allow to observe field-free dynamics of the system not perturbed by the IR field between the pump and the probe pulses. Although attosecond pulses have already been demonstrated and used in experiments [68–71], due to the low efficiency of the generation process, the intensity of attosecond pulses is not yet sufficient for attosecond pump - attosecond probe measurements. Nevertheless, the intrinsic coherence between the driving IR pulse and the attosecond XUV pulse obtained from it using HHG allows one to perform pump-probe measurements with attosecond time resolution using the combination of attosecond XUV and femtosecond IR pulses.

Measurement and control of electron localization using an attosecond XUV pump - IR probe scheme was demonstrated by Sansone et. al. in [67]. In this experiment, H_2 (and D_2) molecules were first ionized by an attosecond XUV pump pulse, which directly populates the dissociative σ_u state. The electron localization is controlled using a delayed short IR pulse, see figure 2.10. Since replicas of the same IR pulse is used to both generate the attosecond XUV pulse via the HHG process and as the control field, near-perfect phase lock between the XUV and the IR fields within a small fraction of the IR laser cycle was guaranteed.

In the experiments described so far, the synchronization between the ionization

time and the control field waveform has been guaranteed by the high non-linearity of the strong field ionization process that creates a narrow ionization time window around the peak of the electric field waveform. In the experiment of Sansone et. al., due to the short duration of the attosecond pump pulse of just a fraction of IR field period, the synchronization between ionization and control fields is achieved naturally. The vibrational dynamics that is initiated by ionization starts at a well defined phase of the control IR field. This phase can be easily manipulated by changing the time-delay between the pump and the control pulses and therefore is not limited to the peaks of the IR field. This allows a fine control of the mixing between the σ_g and σ_u states during dissociation and therefore the electron localization dynamics that follows.

The coupled electron-nuclear dynamics during electron localization that has been discussed so far did not include doubly excited electronic states. However, in the experiment by Sansone et. al. [67], it was found that the Q_1 autoionizing doubly excited state of H_2 molecule provides a new and different mechanism to achieve electron localization. The Q_1 state, once populated by the attosecond pulse, decays into the σ_g ground electronic states of the H_2^+ molecular ion by emitting an electron, with a characteristic decay time of a couple of fs [4]. Part of the population that is created in the σ_g state due to autoionization dissociates. The vibrational wavepackets that are created by the resonant (via the Q_1 state) and direct (to the σ_u state) ionization dissociate along the σ_g and σ_u potential energy curves. Their interference in the dissociation continuum leads to electron localization in the laboratory frame.

Electron localization in the laboratory frame can be created only if the continuum electrons associated with the two interfering electronic states in the molecular ion have the same angular momentum $l_{g,u}$. Otherwise the two states are mutually orthogonal and do not interfere. In the case of two-electron (denoted by 1 and 2) wavefunction of a singly ionized H_2 molecule

$$\begin{aligned} \Psi = & c_1[1s\sigma_g(1)\epsilon l_g(2)]_g + c_2[1s\sigma_g(1)\epsilon l_u(2)]_u \\ & + c_3[1s\sigma_u(1)\epsilon l_u(2)]_g + c_4[1s\sigma_u(1)\epsilon l_g(2)]_u \end{aligned} \quad (2.10)$$

a mixed-parity superposition of the $\sigma_g(1)$ and $\sigma_u(1)$ states, which leads to electron localization, corresponds to the interference of the first and fourth or the second and third terms in (2.10). Since single photon XUV ionization leads to $c_2, c_4 \neq 0$ and $c_1, c_3 = 0$, no electron localization in the laboratory frame can be observed. (Nevertheless, it leads to structures in the angular distribution of photoelectron spectra as discussed in [8].) If an IR field is present during the ionization process,

an additional IR photon can be absorbed by either the photoelectron or the residual ion. Both cases lead to a change of the parity of the total wavefunction ($c_1, c_3 \neq 0$) and allow one to observe electron localization in the laboratory frame. This is exactly the case observed in the experiment by Sansone et. al., where a broadband attosecond XUV pulse coherently populates both the σ_u and Q_1 electronic states, while the IR laser field, that is present during ionization, additionally mixes the two electronic states during ionization.

The Q_1 dissociation channel is different from other channels discussed so far in an important way. In the previously discussed channels, the coherent superposition between the σ_g and σ_u states is established after the ionization event, and is set by the IR field-induced coupling at large internuclear distances. Hence, it is mediated by the vibrational dynamics of the cation. In contrast, in the Q_1 channel, the coherent superposition between the σ_g and σ_u electronic states is determined at the moment of ionization and hence prior to any nuclear motion.

Coincidence measurements of electron localization asymmetry in the molecular frame

The idea that coherent electron dynamics (electron localization) can be determined at the moment of ionization and persist till the dissociation of the molecule was emphasized by Fischer et. al. [72]. In this experiment, a broadband XUV pulse from HHG was used to ionize H_2 molecules, populating the ground σ_g electronic state, the first excited σ_u electronic state of H_2^+ and the doubly excited Q_1 state of the H_2 molecule. The kinetic energy release spectra of the charged H^+ fragments arising from the dissociation of H_2^+ molecular ions and the correlated spectra of photoelectrons were measured in coincidence. Since single photon ionization by a train of ultrashort pulses was used, the coherent superposition of states that led to electron localization dynamics could be established only at the moment of ionization. Nevertheless, it was observed after the molecule dissociated, in the distribution of the H^+ fragments. Note, that IR field was not used here, in contrast to the experiments discussed previously.

As discussed above, due to the absence of an IR pulse, it is not possible to establish a laboratory frame coordinate along which electron localization asymmetry can be measured and hence a *molecular frame measurement* has to be performed. Such measurement was demonstrated by Fischer et. al. using the COLTRIMS technique, which allows one to detect the energy and emission angle of all charged particles produced in the photoionization of a molecule [73] and to reconstruct the molecular frame picture of the reaction.

In the case of *molecular frame measurement*, the associated asymmetry param-

eter has to be redefined in the molecular frame for the correlated photoelectron-nuclear wavefunction [72]. It is done by introducing a basis

$$\begin{aligned} |\phi_{\rightleftharpoons}\rangle &= |p_{\rightarrow}\rangle \otimes |e_{\leftarrow}\rangle, & |\phi_{\leftrightsquigarrow}\rangle &= |p_{\leftarrow}\rangle \otimes |e_{\rightarrow}\rangle, \\ |\phi_{\rightarrow}\rangle &= |p_{\rightarrow}\rangle \otimes |e_{\rightarrow}\rangle, & |\phi_{\leftarrow}\rangle &= |p_{\leftarrow}\rangle \otimes |e_{\leftarrow}\rangle. \end{aligned} \quad (2.11)$$

for co- ($\rightleftharpoons$ and $\leftrightsquigarrow$) and counter- ($\leftrightsquigarrow$ and $\rightleftharpoons$) propagating photoelectron $|e\rangle$ and proton $|p\rangle$, where the normalization factors are omitted. In the new basis the asymmetry parameter becomes

$$A = \frac{(n_{\rightleftharpoons} + n_{\leftrightsquigarrow}) - (n_{\leftrightsquigarrow} + n_{\rightleftharpoons})}{(n_{\rightleftharpoons} + n_{\leftrightsquigarrow}) + (n_{\leftrightsquigarrow} + n_{\rightleftharpoons})} \quad (2.12)$$

where $n_{\rightleftharpoons} = \langle \phi_{\rightleftharpoons} | \phi_{\rightleftharpoons} \rangle$ and likewise for others. Hence, the localization asymmetry can be unambiguously defined in the molecular frame using a coincidence measurement of photoelectrons and photodissociation products. The electron localization manifests itself as a correlation between the direction of emission of the photoelectron relative to the direction of emission of the charged dissociation fragment.

Molecular frame asymmetry, measured in the experiment by Fischer et. al. [72] clearly demonstrates that the process of electron localization is the result of interference between two dissociation pathways that are indistinguishable even in a measurement that fully resolves all of the particles. It relies on the coherent superposition of multiple electronic states created in the ion by ionization. The relative population and phase of the superposition of states is determined by the photoionization matrix elements, that are very sensitive to the photon energy. Hence, the value of the asymmetry changes as a function of photon energy.

Coherent control in the single photon limit

In the experiment by Fischer et. al. [72] and other similar experiments that rely on a single photon process, the outcome of the experiment is completely determined by the properties of the system, and no coherent control of the outcome is possible in such linear regime [74]. Indeed, the probability of any single photon process can always be expressed as:

$$P(\epsilon) = |F(\Omega)|^2 |D(\epsilon = \Omega)|^2 \quad (2.13)$$

where ϵ is the energy of the final state, $F(\Omega)$ is the spectral density of the laser pulse and $D(\epsilon)$ is the matrix element between the initial and the final state. Hence,

the probability does not depend on the phase of the laser pulse, but only on its spectral content and the value of the matrix element at the corresponding energies. Therefore no coherent (phase) control is possible. Likewise, in the experiment by Fischer et. al., the direction and value of electron localization asymmetry was determined by the photoionization matrix elements. The laser field could determine only the photon energy at which the observations were made.

It is well known that coherent phase control of observables of an isolated system by a single photon process is not possible [74]. Hence, a single attosecond pulse, that normally leads to a single photon absorption, cannot be used alone to control an outcome of a chemical reaction. Nevertheless, this restriction does not apply to open quantum systems, where the environment plays an active role in the subsequent dynamics [75]. The dynamics in a molecule of a reasonable size can often be limited to a few most important modes, while other degrees of freedom act as an environment. However, such “control by decoherence” in open quantum systems is still an elusive topic [76].

2.3.3 Hole migration and charge directed reactivity

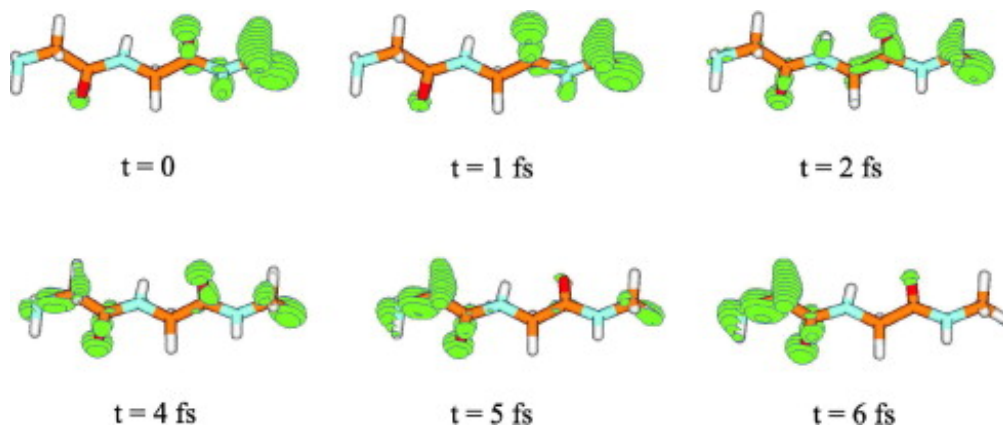


Figure 2.11: The evolution of the hole density following ionization of the GlyGlyN-HCH3 molecule. Reprinted from [77], with permission from Elsevier.

As was demonstrated by the experiments on electron localization, the relative phase between the electronic state in their coherent superposition determines the directionality of the electron dynamics in the residual ion. The possibility to control this phase during the ultrafast ionization of the molecule would allow one to control the electronic dynamics and subsequent reactivity of the residual molecule. This idea underlies the concept of Charged Directed Reactivity [78] (see also [79, 80] and references therein) and has recently received a lot of attention (see e.g. a recent discussion in review papers [81, 82]).

Traditionally it was thought that the fastest process that takes place after the absorption of a photon is the distribution of the excess energy between the vibrational modes. However, it was pointed out by Weinkauff et. al. [78], that the number of vibrational degrees of freedom rises rapidly with the size of a molecule. Hence, even modestly sized molecules have hundreds vibrational degrees of freedom $s \sim 10^2$. The probability that a fraction E_0 of excess energy E that is required to break a bond is localized at the appropriate vibrational mode is ¹

$$P \propto ((E - E_0)/E)^{s-1} \approx \exp(-E_0/E (s - 1)) \quad (2.14)$$

and decreases dramatically with the increase of the number of vibrational degrees of freedom s . Hence, due to high density of vibrational states, the rate of dissociation of even small peptides would be too small to observe any dissociation in an experiment. This led Weinkauff et. al. [78] to propose the mechanism of Charge Directed Reactivity (CDR) where the electronic dynamics after excitation or ionization of the molecule precedes the nuclear dynamics. In this model, an electronic excitation first propagates in the molecule with small or even no dissipation, till it reaches the molecular site where a weak bond can be broken. Only then the excitation energy is transferred to the vibrational degrees of freedom and the bond is broken.

The CDR concept was stimulated by compelling experiments [77, 83] studying the photodissociation of small peptide molecules. In these works, linear aromatic peptide molecules were first selectively ionized at the chromophore site, which has a lower ionization potential than other functional groups in the peptide. The ionization was followed by the breaking off of the NH_2 group, which is located at the opposite end of the peptide molecule than the ionization site. Hence, a conclusion had to be made that the electronic excitation has to propagate through the backbone of the molecule to induce the dissociation. Further experiments demonstrated, that the rate of fragmentation of the molecule and even the bond that is broken can be controlled by the choice of the functional group between the ionization site (chromophore) and bond-breaking site (the NH_2 group), further supporting the idea of CDR.

The work on CDR sparked significant theoretical efforts that were first focused on the development of a theoretical framework to describe the migration of holes in electronic density of a molecule created by photoionization in realistic systems [84–86]. Further work demonstrated [79] that a hole created by attosecond ionization, which was simulated by removing an electron from one of the molecular orbitals of the neutral molecule and projecting the resulting $(N-1)$ -electron wavefunction on

¹ $((E - E_0)/E)^{s-1} = \exp((s - 1) \ln(1 - E_0/E)) \approx \exp(-E_0/E (s - 1))$ for $E_0/E \ll 1$

the stationary states of the cation, leads to a superposition of a large number of excited states. The electronic excitation can be described as a “hole” wavepacket that oscillates between different sites of the peptide on a few femtosecond timescale – much faster than any nuclear dynamics in these molecules (however, see [87] for the description of unphysical artefacts such theoretical approach might lead to). These theoretical observations were found to be quite general and apply for different peptides and for ionization from both inner and outer valance orbitals [77, 88] including the PENNA molecule [88] for which time-resolved pump-probe experimental studies found evidence for the delayed fragmentation [89], see figure 2.11 for a graphical illustration.

The *ab initio* calculations of the hole migration confirmed that an electronic excitation that is created by the sudden removal of an electron leads to a “hole” in the electronic density that propagates across the molecule and can reach the site where the bond-breaking is expected to occur on an ultrafast timescale. However, due to the complexity of the full problem, nuclei were always considered to be fixed in these calculations. Nevertheless, the dynamics of the “hole” was found to be sensitive to the changes in nuclear configurations [80]. It was therefore proposed, that once the nuclear dynamics is initiated by ionization, it can suppress the oscillation of the “hole” density and trap the “hole” in a particular site, where the molecular bond would be weakened initiating the fragmentation of the molecule.

Further evidence of the role of vibrational dynamics were provided by studies of Benzene and PEA protein using the Ehrenfest method [90]. In this approach, the electronic wavefunction is obtained by solving the time-dependent Schrödinger equation and allows one to determine the potential for each nuclear configuration. The nuclear geometry follows a trajectory determined by the classical dynamics, making the problem computationally tractable. The Ehrenfest calculations of coupled electronic-nuclear dynamics showed, that although the nuclear dynamics can have a significant effect, migration of the charge across the whole molecule is still possible.

Direct evidence of ultrafast hole migration was finally found in a recent experiment by Calegari et. al. [91], where phenylalanine molecules were first ionized by an isolated attosecond (< 300 as) XUV (15–35 eV) pulse. A delayed short (4 fs) VIS/NIR (1.77 eV) probe pulse then produced doubly charged fragments by further ionizing the molecular ion. The measurement of the yield of one of the fragments as a function of time delay between the pump and the probe pulses showed an oscillation with a period of less than 4.5 fs. Such a short period of oscillations could only be attributed to coherent charge dynamics in the molecular ion.

In the theoretical calculations of charge migration dynamics, the ionization was

usually modelled by removing (“deleting”) an electron from specific configurations of the neutral species. However, the experiment by Calegari et. al. [91] and the supporting theoretical calculations revealed that electronic excitation created by an ultrashort pulse is extremely different from what was modelled in previous work. Namely, the broad bandwidth of the attosecond pulse leads to a coherent superposition of a huge number of excited electronic states in the molecular ion. This does not lead to a localized hole density, but rather creates a beating of the electronic wavepacket over the whole molecule. Surprisingly, it was found that a small number of dominating frequencies can be identified, that correspond to some of the many energy differences between the excited electronic states in the ion. One of these frequencies was found to agree very well to the frequency of the oscillations of the fragment yield observed in the experiment [91].

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Chapter 3

Controlling high harmonic
radiation properties by the
interfering contributions of
different ionization continua

In strong and/or high frequency laser fields, when the ionization of a molecule or an atom takes place, the correlation between the departing photoelectron and the residual ion often determines the coherence of the system. Hence, it provides a way for coherent control via the photoionization process and the electron dynamics in the continuum.

In this chapter, we consider the role of correlation between High Harmonic Generation (HHG) and the initial state of the system. In a multielectron system, this translates into the correlation between the continuum electron and the hole left in the cation. In the simple case of an atom considered here, the shape and the dynamics of this hole, which is determined by the interplay of two mutually coherent ionization channels, leads to unique properties of HHG radiation.

3.1 Introduction

The microscopic optical response of an atom in a laser field, which is the basic quantity in HHG, is described by the time dependent dipole $D(t)$, which is obtained by calculating the expectation value of the dipole operator $\hat{d}$. If the full wavefunction of the system $\Psi(t)$ is separated into a (usually small) part that is excited by the laser field Ψ_i and a (usually much larger) part that stays in the ground state Ψ_0 , then the time dependent dipole can be expressed as

$$|\Psi(t)\rangle \approx |\Psi_0(t)\rangle + |\Psi_i(t)\rangle \quad (3.1a)$$

$$D(t) = 2 \operatorname{Re} \left[\langle \Psi_i(t) | \hat{d} | \Psi_0(t) \rangle \right]. \quad (3.1b)$$

In this Chapter we consider an atomic state that has two degenerate orbitals with $l=1$ and $m=\pm 1$ quantum numbers, e.g., a 2p state of an atom. The ionization of this state can promote an electron into two continua that correspond to an electronic hole in either $m=+1$ or $m=-1$ orbital of the residual ion, which are degenerate if no spin-orbit interactions are considered. Hence, the ionized part of the wavefunction, up to anti-symmetrization, can be expressed as

$$\begin{aligned} |\Psi_i(t)\rangle &= |e^+\rangle |\text{ion}^+\rangle + |e^-\rangle |\text{ion}^-\rangle \\ &= |\Psi^+\rangle + |\Psi^-\rangle \end{aligned} \quad (3.2)$$

where it is factorized into the photoelectron $|e^\pm\rangle$ and the corresponding ionic parts

$|\text{ion}^\pm\rangle$. The time-dependent dipole becomes

$$D(t) \approx 2 \operatorname{Re} \left[\langle \Psi^+(t) | \hat{d} | \Psi_0(t) \rangle \right] + 2 \operatorname{Re} \left[\langle \Psi^-(t) | \hat{d} | \Psi_0(t) \rangle \right] \quad (3.3a)$$

$$= D^+(t) + D^-(t) \quad (3.3b)$$

and hence, the emitted radiation will depend on the coherent sum of the contributions of the $+$ and $-$ continua. In the above, the terms $\langle \Psi^\pm(t) | \hat{d} | \Psi^\mp(t) \rangle$ were neglected because $\| \Psi_0 \| \gg \| \Psi^\pm \|$. If both of the corresponding orbitals are occupied, which is the case for the closed shell system studied here, the cross terms $\langle \Psi^+(t) | \hat{d} | \Psi^-(t) \rangle$ are forbidden by the Pauli exclusion principle. Nevertheless, if only one of the orbitals is initially occupied by photoionization, the population can be driven into the unoccupied orbital by, e.g., laser coupling or spin orbit interactions, creating coherent ionic dynamics that would be reflected in the generated harmonics [1, 2].

Below, it will be demonstrated how the use of a tailored laser field allows one to control the coherent contributions of the $+$ and $-$ ionization continua to the total harmonic spectra. Thus, eventually it allows one to control the ellipticity of the generated radiation.

3.2 State of the art

The generation of circular or highly elliptic high harmonics and/or attosecond XUV pulses is very important in order to extend the applicability of HHG as a table-top source of bright, coherent, ultrashort pulses [3–6]. Indeed, circular or highly elliptic high harmonics would find numerous applications, e.g. in chiral-sensitive light-matter interactions such as chiral recognition via photoelectron circular dichroism (PECD) (see e.g. [7–9]), study of ultrafast chiral-specific dynamics in molecules (e.g. [10, 11]), and X-ray Magnetic Circular Dichroism (XMCD) spectroscopy (e.g. [12–18]), including time-resolved imaging of magnetic structures (e.g. [12–16]). Table-top sources of sub-100 fs, or even attosecond, chiral pulses would be a real breakthrough for laboratory-scale ultrafast studies. Not surprisingly, search for schemes enabling the generation of short, coherent XUV pulses with tunable polarization is a very active area of research, see e.g. [10, 19–33].

Importantly, the control over polarization is desired not only for individual harmonics, where it has just been demonstrated [29, 30], but also for individual attosecond pulses, both isolated and in a train, where a robust and practical scheme is still lacking. In this chapter, we show a way to solve this problem, proposing a practical scheme for the generation of highly elliptic attosecond pulses, both single

and in a train.

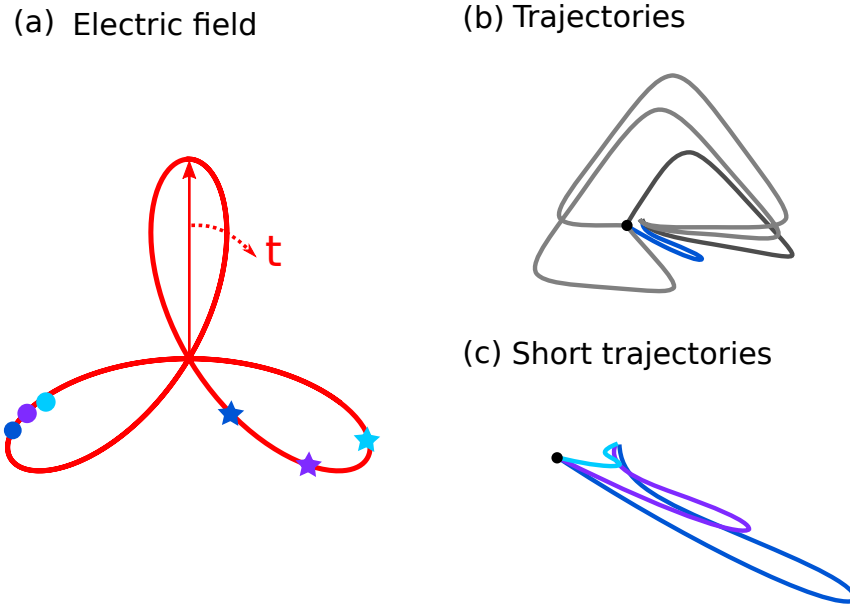


Figure 3.1: Laser electric field created by a circularly polarized driving field and its second harmonic field with opposite polarization and equal intensity (a); family of returning trajectories that start within the same $1/3$ of driving laser period and return to the parent ion at different times (b); a zoom of the shortest returning trajectories for different ionization times (c); the ionization times and the corresponding return times are indicated by colour-coded circles and stars in (a). The trajectories in (b) and (c) reprinted with permission from [22]. Copyright (2000) by the American Physical Society.

An elegant solution to generating individual high harmonics with circular polarization has been found by W. Becker and coworkers [22, 23, 25, 26]. It relies on combining a circularly polarized fundamental field with a counter-rotating second harmonic. The resulting electric field peaks three times within one cycle of the fundamental, producing three ionization bursts, see figure 3.1a. The electron promoted to the continuum near the peak of the instantaneous field can successfully revisit the parent ion within about half-cycle, emitting an attosecond radiation burst [22, 23], see figure 3.1b and 3.1c.

This approach has now been very successfully used in [29, 30], demonstrating the generation of bright, phase matched high harmonic radiation. Importantly, tuning the ellipticity of one of the fields allows to tune the ellipticity of the generated high harmonics from linear to circular [29]. While the theoretical interpretation of this control is a matter of debate [27, 29], the approach is very promising. However, until now the possibility of extending this scheme from controlling the polarization of individual harmonics to controlling the polarization of isolated attosecond pulses looked far from straightforward.

Indeed, the driving field dictates that the direction of electron return rotates by 120° three times per cycle, see figure 3.1a. Consequently, recombination with an s-state yields three *linearly* polarized attosecond bursts per cycle, with polarization rotating by 120° from burst to burst [23]. Hence, the superposition of these bursts creates a spectra formed out of harmonics that are *circularly* polarized. However, in turn this means that the superposition of all harmonics creates a train of linearly polarized attosecond pulses.

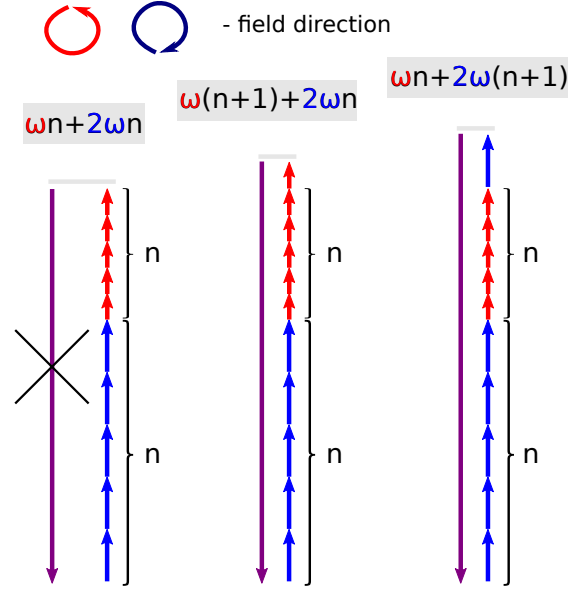


Figure 3.2: Energy diagram illustrating selection rules for circularly polarized harmonics. In a centrally symmetric medium, the harmonic photons with energies $\Omega = n\omega + 2n\omega = 3n\omega$ are parity forbidden since an even net number of photons has been absorbed. The harmonics that result from absorbing an extra photon from the low-frequency (ω) driving field ($\Omega = (3n + 1)\omega$), which here correspond to counter-clockwise circular polarization, have the same helicity as the low-frequency driver. Likewise, the harmonics that result from absorbing an extra photon from the high-frequency (2ω) driving field ($\Omega = (3n + 2)\omega$) have the same helicity as the high-frequency driver and have a clockwise circular polarization.

This can also be seen in the frequency domain. The harmonic lines are at energies $(n + 1)\omega + 2n\omega = (3n + 1)\omega$ and $n\omega + (n + 1)2\omega = (3n + 2)\omega$. In a centrally symmetric medium, and for circularly polarized driving fields, the selection rules dictate that the $\Omega = (3n + 1)\omega$ line has the same circularity as the fundamental while the $\Omega = (3n + 2)\omega$ line has the same circularity as the second harmonic, ($\Omega = n\omega + 2n\omega = 3n\omega$ is parity forbidden) [25, 26, 29, 30, 34, 35], see figure 3.2. Thus, the harmonics have alternating helicity. Adding harmonics of alternating helicity with equal intensity yields an attosecond pulse train where each subsequent pulse has linear polarization rotated by 120° , in concert with the time domain picture.

Suppressing every second allowed harmonic line, e.g. $\Omega^{(3n+2)} = (3n+2)\omega$, would solve the problem of generating individual attosecond pulses with circular polarization. O. Kfir et. al. [30] suggested that such suppression can be achieved by optimizing the phase-matching conditions in a gas-filled hollow fiber and reported substantial suppression of the lines $\Omega^{(3n+2)} = (3n+2)\omega$ in the experiment.

In this chapter, we show that relative intensities of the counter-rotating harmonic lines strongly depend on the orbital momentum of the initial state. For an initial p-state (as for a Neon, Argon, or Krypton gas), the harmonics co-rotating with the fundamental field can be much stronger than those co-rotating with the second harmonic. The effect is found with the contribution of both degenerate orbitals, $2p_+$ ($n=2, l=1, m=+1$) and $2p_-$ ($n=2, l=1, m=-1$), included in the calculation. As a result, circularly polarized attosecond pulses are generated already at the microscopic, single-atom level, see figure 3.3. Additional help from phase-matching is a bonus, but not necessary.

We also extend the scheme to generation of isolated attosecond pulses. We show that when the counter-rotating driving pulses become relatively short, e.g. 7-8 fs for the 800 nm driver and its second harmonic, one can generate an isolated attosecond pulse, or a controllable train with 2 or 3 pulses, by tuning the time delay between the fundamental and the second harmonic.

3.3 Details of the calculations

To demonstrate these effects, we numerically solve the time dependent Schrödinger equation (TDSE) for a 2D Neon-like model atom, for counter-clockwise (+) polarized fundamental and clockwise (−) polarized second harmonic. We show that the harmonics generated from orbitals with $m = \pm 1$ differ from those generated from s orbitals in two important ways. Firstly, the height of the adjacent left- and right-circularly polarized harmonics can differ by an order of magnitude, with the $m = 1$ state favouring harmonics co-rotating with fundamental and the $m = -1$ state favouring harmonics co-rotating with 2ω field. Secondly, once the two contributions are added coherently, + polarization dominates in a broad spectral range, leading to highly elliptic circularly polarized attosecond pulse train already at the single-atom level. Our findings are in accord with [30] (see Ne spectra in figure 3 of [30]), where such disparity was attributed to phase matching.

3.3.1 Correspondence between the multielectron and single electron systems in High Harmonic Generation

The calculations presented in this Chapter are performed within the single active electron approximation. Therefore electron correlation and exchange effects are omitted and electron spin is not considered. Nevertheless, this approach allows one to include the effect of multiple ionization channels pertinent to a multielectron atom.

Consider expanding the N -electron ground state wavefunction $|\Psi_{1,\dots,N}^g\rangle$ of the neutral atom in the basis of $(N-1)$ -electron ionic states $|\Psi_{1,\dots,N-1}^i\rangle$ [36, 37]

$$|\Psi_{1,\dots,N}^g\rangle = \sum_i |\Psi_N^{i,D}\rangle |\Psi_{1,\dots,N-1}^i\rangle \quad (3.4)$$

where i indicates the ionization channel and $1, \dots, N$ indicate the coordinates of the electrons, i.e., $\Psi_g(r_1, \dots, r_N) = \langle r | \Psi_{1,\dots,N}^g \rangle$. $|\Psi_N^{i,D}\rangle$ are the single electron Dyson orbitals associated with the i -th ionization channel and the N -th electron

$$|\Psi_N^{i,D}\rangle = \langle \Psi_{1,\dots,N-1}^i | \Psi_{1,\dots,N}^g \rangle \quad (3.5)$$

The Dyson orbitals can be propagated in laser field using standard single-electron TDSE approaches (see, e.g., [38, 39] for more examples and extended discussion). If we introduce the time-dependent single electron wavefunction $|\phi_N^i(t)\rangle$ that is obtained by propagating the corresponding Dyson orbital in the strong laser field then the time dependent dipole associated with radiation from the i -th channel can be calculated as

$$D_i(t) = \langle \Psi_N^{i,D} | \hat{d} | \phi_N^i(t) \rangle. \quad (3.6)$$

Hence, we replace the propagation of a multielectron ground state wavefunction $\Psi_g(r_1, \dots, r_N) = \langle r | \Psi_{1,\dots,N}^g \rangle$ with a single-electron Dyson orbital associated with a single ionization channel. In this formulation, i.e. neglecting electron exchange, the HHG from a multichannel many-electron system corresponds to the coherent sum of radiation from each individual ionization channel. In the case studied here, the single-electron p_+ and p_- initial orbitals used in the propagation are analogous to the Dyson orbitals for ionic states where the $2p_+$ or $2p_-$ electron is removed from the full multielectron wavefunction.

3.3.2 Details of the numerical propagation

We solve the TDSE in the length gauge (atomic units are used throughout unless stated otherwise):

$$i \frac{\partial}{\partial t} \Phi(t, r) = \left[\hat{T} + V(r) + \mathbf{r} \cdot \mathbf{E}(t) \right] \Phi(t, r). \quad (3.7)$$

The 2D model potential is taken from [40]

$$V(r) = -\frac{Z(r)}{\sqrt{r^2 + a}} \quad (3.8)$$

where $Z(r) = 1 + 9 \exp(-r^2)$ and $a = 2.88172 a_0^2$ to obtain the ionization potential of Ne atom $I_p = 0.793$ hartree for the 2p orbitals. The 1s state has an energy $E_{1s} = -2.952$ hartree and the 2s energy is $E_{2s} = -0.217$ hartree. For reference calculations we use 1s as the initial state but keep the same ionization potential taking $Z(r) = 1$ and $a = 0.1195 a_0^2$. The laser electric field is

$$\begin{aligned} E(t) = & E_{ir} f(t) (\cos[\omega t] + \cos[2\omega t]) \hat{x} \\ & + E_{ir} f(t) (\sin[\omega t] - \sin[2\omega t]) \hat{y} \end{aligned} \quad (3.9)$$

where $f(t)$ is the trapezoidal envelope with a 2 cycle rising and falling edges and a 5 cycle plateau (in units of fundamental). The ω -field rotates counter-clockwise (+). The second harmonic rotates clockwise (-).

The TDSE is propagated on a 2D Cartesian grid using Taylor-series propagator with expansion up to 8th order [41], also see appendix E. A complex absorbing potential

$$V_c(x) = \eta (x - x_0)^n \quad (3.10)$$

with $\eta = 5 \times 10^{-4}$ hartree and $n = 3$ is used to avoid non-physical reflections from the boundary. Other simulation parameters are summarized in table 3.1.

Convergence was tested with respect to the absorbing potential, the time step and the spatial grid. Note, that HHG in bicircular fields is dominated by very short trajectories [22].

The initial wavefunctions were obtained using imaginary time propagation filtering out the ground state wavefunction to obtain p_x and p_y orbitals. The $p_{\pm}$ states are defined as $p_{\pm} = p_x \pm i p_y$. The laser intensity was kept such as not to exceed 5% ionization and to avoid strong shifts and mixing of the degenerate atomic orbitals described in [40]. The spectra were obtained by performing the Fourier transform of the time-dependent dipole acceleration, evaluated at every 0.5

laser frequency	ω	0.05	$\text{rad } E_h/\hbar$	$(\lambda = 911 \text{ nm})$
laser electric field	E_{ir}	0.05	E_h/ea_0	$(I = 0.88 \times 10^{14} \text{ W/cm}^2)$
grid step size	dr	0.2	a_0	
time step size	dt	0.005	$\hbar/E_h$	
propagation time	T	1250	$\hbar/E_h$	(30.2 fs)
maximal grid extent	X_{max}	± 60	a_0	
absorbing boundary	x_0	± 36	a_0	

Table 3.1: Parameters of the calculations in atomic units unless stated otherwise.

a.u.

The time-dependent dipole was calculated along the x and y Cartesian coordinates. When required, it was converted to the left- and right- circular polarized basis by

$$D_{\pm}(t) = \frac{D_x(t) \pm iD_y(t)}{\sqrt{2}}. \quad (3.11)$$

The circularity of the emitted radiation can be conveniently estimated by calculating the ratio between the 0-th and the 3-rd Stokes parameters:

$$s = \frac{S_3}{S_0} = \frac{|D_+(t)|^2 - |D_-(t)|^2}{|D_+(t)|^2 + |D_-(t)|^2}. \quad (3.12)$$

However, this quantity is not equal to the ellipticity (the ratio between the major and minor axes of polarization ellipse), but has a non-trivial relation to it. Nevertheless, the proper ellipticity ϵ can be calculated from the ratio of the Stokes parameters s by using [42]

$$s = \sin(2\alpha) \quad (3.13a)$$

$$\epsilon = \tan(\alpha) \quad (3.13b)$$

where α is an intermediate dummy variable.

The results are robust with the variation of the pulse length, the shape and length of its rising and falling edges, laser intensity, and wavelength: we performed calculations from $\lambda = 600 \text{ nm}$ up to $\lambda = 1200 \text{ nm}$.

3.4 Calculation results

3.4.1 Asymmetric generation of harmonics with opposite helicity

Figure 3.3a shows reference spectra obtained for 1s initial state of the model potential with I_p of Neon. It agrees well with previously published results [22, 26,

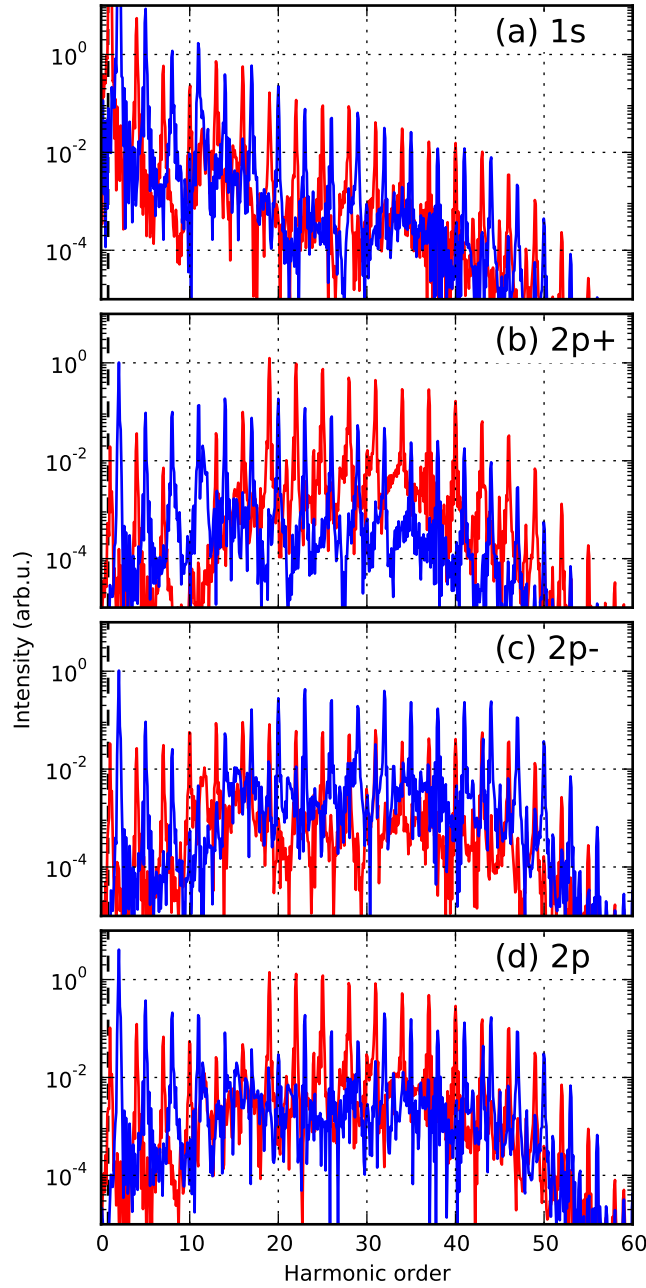


Figure 3.3: Spectra of circularly polarized harmonics for (a) 1s, (b) $2p_+$, (c) $2p_-$ initial states and (d) equal mixture of $2p_+$ and $2p_-$ states. Colours mark harmonics co-rotating (red) and counter-rotating (blue) with the ω field.

29, 30], the harmonics come in pairs $(n+1)\omega + n2\omega = (3n+1)\omega$ and $n\omega + (n+1)2\omega = (3n+2)\omega$ of similar heights. The left harmonic in the pair has the same polarization as the fundamental field, the right harmonic follows the 2ω driver. The harmonics $3n\omega$ are parity forbidden.

Figures 3.3b and 3.3c show spectra for the p_+ and p_- initial states. For the p_+ initial state, the harmonics that have the same polarization as the driving IR field are preferred. For the p_- initial state, the harmonics with the same polarization as the 2ω driver are stronger. There are additional spectral variations in the plateau region, different for p_+ and p_- orbitals. There is also a qualitative difference between the below-threshold ($<I_p$) and above-threshold ($>I_p$) harmonics, showing that the evolution of the photoelectron in the continuum is critical for the observed propensity in the harmonic strengths. A similar result was obtained in Strong-Field Approximation (SFA) calculations of HHG for Ne atom in two-colour bi-circular field reported in [43]. In this work, 3D orbitals with $l=1$, $m= \pm 1$ orbital and magnetic quantum numbers were used to calculate the harmonic spectra. The intensity of harmonics of opposite helicity differ by up to two orders of magnitude with harmonics of positive (negative) helicity preferred for $m= +1$ ($m= -1$) orbital.

Figure 3.3d shows the spectra obtained from adding the contributions from the p_+ and p_- orbitals coherently, as required. In the plateau region, harmonics with the same polarization as the driving IR field dominate over those with opposite polarization. Note, however, that this effect was not reported in the SFA calculations in [43].

The sub-cycle dynamics of the emission process was analysed using the Gabor Transform (GT) [44] of the time-dependent acceleration dipoles $a(t)$:

$$GT[\Omega, t_0] = \frac{1}{2\pi} \int dt a(t) e^{-i\Omega t} e^{-(t-t_0)^2/(2T^2)} \quad (3.14)$$

where we have chosen $T = 1/3\omega$. The reference spectrograms for the 1s initial state in figures 3.4a and 3.4b show the time-dependent intensity (a) and ellipticity (b) for time-resolved spectra, in the regions where spectral amplitudes are significant. As expected, there are 3 radiation bursts per ω cycle with linear polarization, as predicted in [22, 23, 26]. Note, that here the ellipticity ϵ is defined as both positive and negative, with the sign corresponding to the helicity h of the emitted radiation $\epsilon = |\epsilon| \text{sign}(h)$.

Figures 3.4c and 3.4d show the same spectrogram for the 2p state, i.e. the coherent superposition of the radiation from p_+ and p_- states. Although the signal strength in the spectrogram is similar to the s orbital, the helicity and ellipticity of the emitted radiation is very different. Three distinct regions can be identified:

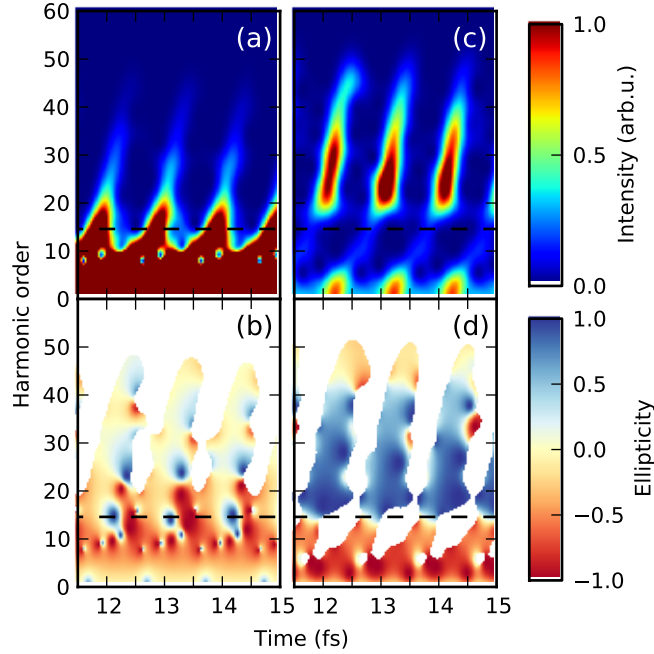


Figure 3.4: Time-resolved XUV emission intensity and ellipticity from 1s (a and b) and 2p (c and d) orbitals. Colour in (b) and (d) indicates the ellipticity of the spectral components in the regions where the amplitude of the spectrogram is significant. The horizontal dashed lines mark the ionization potential I_p .

(i) the below-threshold region, where the helicity is mostly negative, i.e. the XUV field counter-rotates with respect to the fundamental driver; (ii) the middle region, where the helicity is high and positive, i.e. the XUV field co-rotates with the fundamental driver and (iii) the near cutoff region where the emitted radiation is mostly linear. The energy region (ii) of the spectrogram coincides with the spectral window in figure 3.3d where the difference between clockwise and counter-clockwise harmonics is the greatest.

3.4.2 Generation of isolated elliptically polarized attosecond pulses

Application of bi-circular fields can be extended from the generation of an attosecond pulse train to the generation of an isolated attosecond pulse. The key idea is to use few cycle driving pulses and change the time delay between them. Indeed, the harmonic emission driven by circular fields is only possible when the two counter-rotating circular pulses overlap. Given the high nonlinearity of the overall process (including ionization), it will be limited to the temporal window where the two driving pulses overlap with high intensity of the both fields. This idea is tested in figure 3.5, which shows time-resolved spectrograms and ellipticity of the emitted light for $\lambda = 800$ nm and 400 nm counter-rotating drivers with full

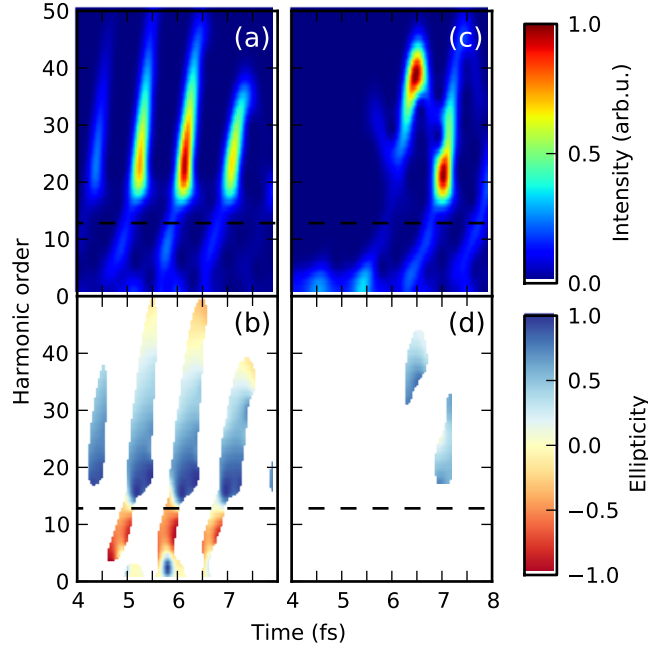


Figure 3.5: Time-resolved XUV emission from a 2p orbital, using two circularly polarized 800 nm and 400 nm pulses both 4 fs full width half maximum. (a) Spectral intensity and (b) time-dependent ellipticity for perfect overlap of the two-pulses. (c) Spectral intensity and (d) time-dependent ellipticity for the two-pulse delay of 2.6 fs. Spectra in (c) is multiplied by a factor of 2 to enhance the contrast. Colour in (b) and (d) indicates the ellipticity of the spectral components in the regions where the amplitude of the spectrogram is significant. The horizontal dashed lines mark the ionization potential I_p .

width half maximum duration of 4 fs and $\sin^2$ envelope with $I = 1.7 \times 10^{14} \text{ W/cm}^2$ peak intensity, for two time delays. In case of perfect overlap, 3 attosecond pulses are generated. Delaying the low-frequency pulse by 2.6 fs (full period of 800 nm field) yields two attosecond pulses with strong ellipticity, that are well separated in energy. An isolated pulse would be obtained by filtering the lower or higher energy pulse. When a shorter driving pulse with full width half maximum duration of 2.6 fs and $\sin^2$ envelope (3ω field cycles) is used and delaying the low-frequency driving pulse by 2 fs ($\frac{3}{4}$ of ω field period) yields a single attosecond pulse with highly elliptic polarization (see figure 3.6).

3.5 Discussion and conclusions

The physical origin of the HHG sensitivity to the angular momentum of the initial state can be explained as follows. The energy and angular momenta that the electron accumulates from the laser field while propagating in the continuum is transferred to the harmonic photon upon recombination. The matrix elements

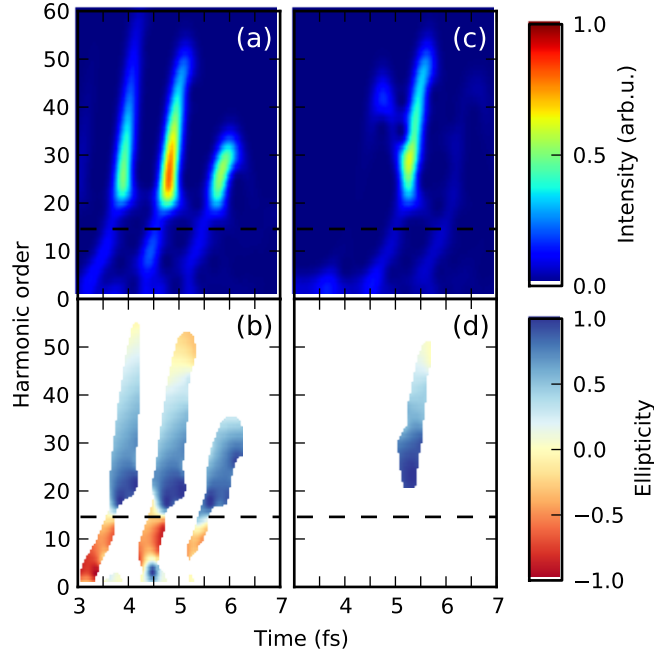


Figure 3.6: Time-resolved XUV emission from a 2p orbital, using two circularly polarized 800 nm and 400 nm pulses both 2.6 fs full width half maximum. (a) Spectral intensity and (b) time-dependent ellipticity for the perfect overlap of the two-pulses. (c) Spectral intensity and (d) time-dependent ellipticity for the two-pulse delay of 2 fs shows that a single, highly elliptic attosecond pulse is generated. Colour indicates the ellipticity of the spectral components in the regions of the spectrogram where the amplitude of the spectra is significant. The horizontal dashed lines mark the ionization potential I_p .

associated with recombination are the complex conjugate of the photoionization matrix elements. In 2D, one photon ionization with the field co-rotating with the initial state is much more likely than with counter-rotating field. This is a direct analogue of Bethe-Fano propensity rules [45] and is also the case for Rydberg states co-rotating and counter-rotating with the field [46, 47]. The propensity rules arise directly from the dipole matrix elements between a bound and a continuum electronic state of an atom. The ionization channel that increases the total angular momenta has in general a larger transition dipole matrix element as compared to an ionization channel that decreases total angular momentum of the system. Hence, in case of single photon ionization, an atom that is initially in a p state is more likely to be ionized into the d ionization continuum rather than into the s ionization continuum.

Consider the harmonic spectra from p_+ orbital. The right circularly polarized harmonics result from the $(n + 1)\omega + n2\omega$ pathway. The recombination step is conjugated to photo-ionization from p_+ state with a co-rotating field, favoured by the propensity rules. The left-circularly polarized harmonics result from the

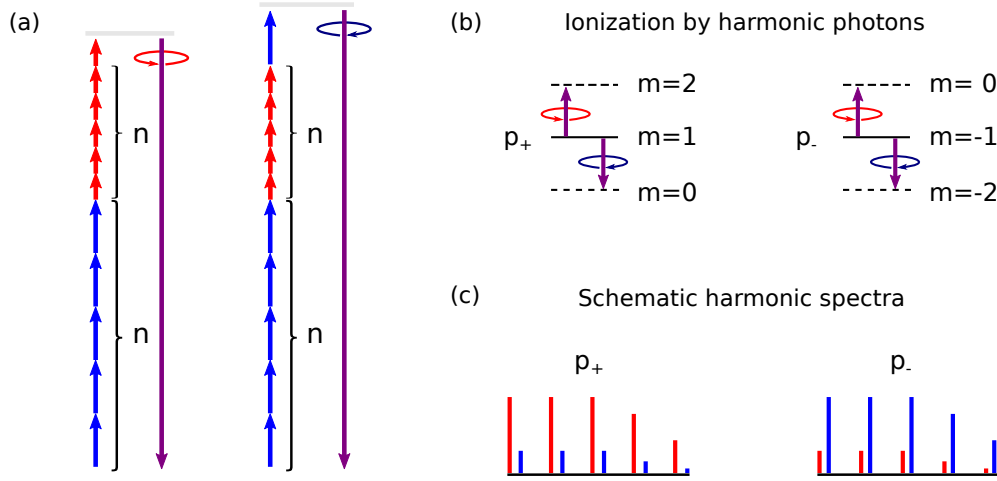


Figure 3.7: Energy diagrams for the generation of harmonics co- and counter-rotating with the low frequency driving field (a); schematic representation of ionization of $p_{\pm}$ states by the harmonic photons (b); schematic illustration of the harmonic spectra predicted from p_+ and p_- orbitals by the Bethe-Fano propensity rules for photoionization (c). The counter-clockwise polarized harmonic field increases (decreases) the total angular momenta of the system after ionization of p_+ (p_-) orbital, therefore the harmonics with counter-clockwise (clockwise) polarization are enhanced (suppressed).

$n\omega + (n+1)2\omega$ pathway. The recombination step is conjugated to photo-ionization from p_+ state with a counter-rotating field, dis-favoured by the propensity rules, see figure 3.7. This explains the relative heights of the harmonic pairs for the p_+ initial state. The same analysis explains why harmonics co-rotating with 2ω field are preferred for the p_- initial state.

The analysis above does not explain why the radiation from the p_+ orbital dominates over the radiation from the p_- orbital. The reason lies in the strong “chiral” effect of the lower-frequency (counter-clockwise) field on the continuum electron. This effect leads to higher population of the continuum states with positive than with negative angular momentum. The more probable recombination from such states is to the p_+ state, by emitting light with counter-clockwise polarization.

The carrier-envelope phase (CEP) stabilization will allow one to control the polarization ellipse of the attosecond pulse (but is not needed to make a short pulse). Indeed, as long as the relative phase between the two pulses, ω and 2ω , is locked, changing the CEP will only rotate the polarization ellipse of the attosecond pulse but will not alter its high ellipticity. This property, in combination with the possibility of using relatively routine durations of the two driving pulses, makes the scheme attractive for practical implementation.

Finally, we comment on the difference between the 2D model presented here

and a 3D system. Since the harmonic dipole for the $m=0$ orbital is negligible due to the nodal plane that coincides with the polarization plane of the driving field, the only expected difference is the spreading of the continuum electron wavepacket, which is different in 2D and 3D. However, it will not change the relative intensity of harmonics from p_+ and p_- orbitals, because for both of them the spreading is identical. Consequently, the ellipticity of the attosecond pulses is expected to be the same in both 2D and 3D.

Contributions

The project presented in this chapter was led by the author including planning, code development, running of the simulations, analysis and interpretation of the results. The development of numerical code for the TDSE solver was supervised by Prof. Hugo van der Hart and Jack Wrag from the Queens University Belfast.

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Chapter 4

Clocking the autoionization decay using molecular vibrations in H₂

In the previous chapter, we have looked at how the correlation between the hole and the continuum electron manifests in the non-linear response of an atom. We now move to ultrafast dynamics of autoionization, where electron-electron correlation plays the main role. Crucially, this time nuclear motion will be taken into account to demonstrate how the electron-nuclei coupling affects the autoionization dynamics of the two interacting electrons. We use the H_2 molecule as an example and study the photoelectron spectra created by single-photon ionization.

4.1 Introduction

An XUV pulse interacting with an H_2 molecule may not only ionize the molecule, but also promote it to a doubly-excited electronic state. The most prominent excitation in this case is to the lowest electronic state of the autoionizing Q_1 series, see figure 4.1. This state quickly, in just a few femtoseconds, will decay to the ground state of H_2^+ ion. The few-femtosecond timescale of this decay is comparable to the timescale of the nuclear motion of light protons in the strongly repulsive Q_1 state, leading to strong interaction between the dynamics along the electronic and nuclear degrees of freedom.

The presence of ultra fast nuclear motion that is correlated to the electronic decay means that the photoelectron lineshapes associated with the Q_1 state are very different from the atomic case. Moreover, the electronic decay cannot be factored out of the overall molecular dynamics. The goal of this chapter is to demonstrate a way to exploit electron-nuclei coupling as a tool to image ultrafast correlated two-electron dynamics, which leads to the electronic decay of the Q_1 state. It is demonstrated that if the pure vibrational dynamics in the final electronic state of the cation can be reliably evaluated, it can be used as a clock to trace and reconstruct the ultra-fast electronic decay. Furthermore, it reveals how the attosecond timescale in a molecule can arise due to the phase lock (synchronization) between the electronic and vibrational degrees of freedom, where the phase reference is provided by the absorption of an XUV photon. Interestingly, although the technique that is demonstrated in this chapter allows to achieve attosecond time resolution, it does not require the use of attosecond laser pulses.

4.2 State of the art

Fano interference [1] associated with autoionization is an ubiquitous feature in the photoionisation spectra of atoms. It appears whenever the same continuum state can be reached by direct ionisation or through an intermediate doubly excited

resonant state, with energy above the ionisation continuum and which decays via autoionization (AI). The interference of the direct and resonant ionisation pathways leads to an asymmetric spectral lineshape, which is well understood and can be used to obtain information on the properties of the resonant state, in particular its energy and the AI lifetime.

Autoionization resonances also exist in molecules [2], where the presence of molecular vibrations is of prime importance. In some cases, e.g., in N_2 , continuum resonances can be observed in the total ionization cross section and have the canonical Fano-type lineshape. In other cases, e.g. in molecular hydrogen, the presence of continuum resonances leads to complicated lineshapes that do not resemble the atomic ones. Moreover, these lineshapes can only be seen in the vibrationally resolved cross section.

AI in molecular hydrogen has been extensively studied both theoretically (see, e.g., [2–6], with an exact numerical solution obtained in [7]) and experimentally (see, e.g., [4, 8, 9]). Most experimental studies were focused on the dissociative ionization channel that corresponds to dissociation of H_2^+ ions formed after AI. Due to the energy correlation between the photoelectron and the H^+ fragment, the formation of the interference pattern due to the AI decay can also be investigated in the kinetic energy spectra of the fragments. Recently, a theoretical description was proposed which could describe the H^+ fragment spectral features analytically, using a semiclassical approach [10].

However, the dissociative photoionization channel is by no means dominant in molecular hydrogen. Photoionization leading to the formation of bound H_2^+ cation is substantially stronger. In other molecules, the relative contribution of the dissociative ionization channel is generally even weaker than in H_2 . This makes the analysis of the resonant features in the photoionization spectra that also resolves the final bound vibrational states very interesting.

Measurements of vibrationally resolved electron spectra in molecular hydrogen have recently been performed by means of photoelectron [11] and electron scattering [12] spectroscopy. They are also available for more complex diatomic and triatomic molecules, see, e.g., [13–16] and references therein. Although the experimental efforts were not aimed at a detailed study of the decay of doubly excited states, the published spectra do show resonant features (which, however, were mostly ignored so far).

In terms of theoretical approaches, *ab initio* numerical calculations of vibrationally resolved photoelectron spectra for the non-dissociative channel of molecular hydrogen showed [17] that the spectral features close to the energy of the resonance are much broader and have different shape than in the atomic case, supporting the

assumption that the nuclear motion should play a profound role in the process. However, to the best of our knowledge, there are no simple models that explain these observations in non-dissociative ionization. Developing, both numerically and analytically, a qualitative understanding of the lineshapes appearing in the differential photoionization cross section of molecules is the key aim of this chapter. Although the theory is presented for the H_2 molecule, for which high accuracy *ab initio* data is available, it can be extended to any molecular system.

The AI decay and the associated spectral lineshapes in molecules are strongly modified or even washed out by the nuclear motion. Its coupling to the electronic decay will be reflected in the final spectra, which will therefore encode the information not only on the electronic but also on the vibrational dynamics. Access to physically transparent yet quantitative description of the associated process should therefore hold the keys to unravelling the coupled electronic and vibrational dynamics.

In atoms, characterization of the Fano lineshapes opened up the possibility to infer properties of resonant states from the photoionization spectra. Here, we develop an analytical description for molecules, which allows one to perform similar analysis for the electronic AI decay strongly coupled to the vibrational motion. Our analytical description is based on a time-dependent semiclassical approach. We first verify its applicability using the example of the Q_1 band of doubly excited states of H_2 (see figure 4.1) that converge to the energy of the first σ_u excited state of H_2^+ molecular ion. Subsequently, we use our semiclassical approach to show how the interplay between the timescales of the nuclear motion and the electronic decay determine the final lineshapes obtained in the differential photoelectron spectra. Finally, we demonstrate how vibrational dynamics in the molecular ion can be used to reconstruct the electronic decay of the resonant state.

This chapter is structured as follows. Section 4.3 introduces numerical and analytical methods used to simulate and interpret the signatures of the AI decay in molecules. Section 4.4 presents the calculation results and demonstrates that the vibrationally resolved measurement of AI spectra can be reproduced using simplified numerical calculations. Section 4.5 contains a discussion on the formation of the molecular autoionization lines for low vibrational bound states, the role of the nuclear motion, and the transition to the atomic limit. Finally, section 4.7 shows how this interference can be used to reconstruct the time evolution of the autoionization decay.

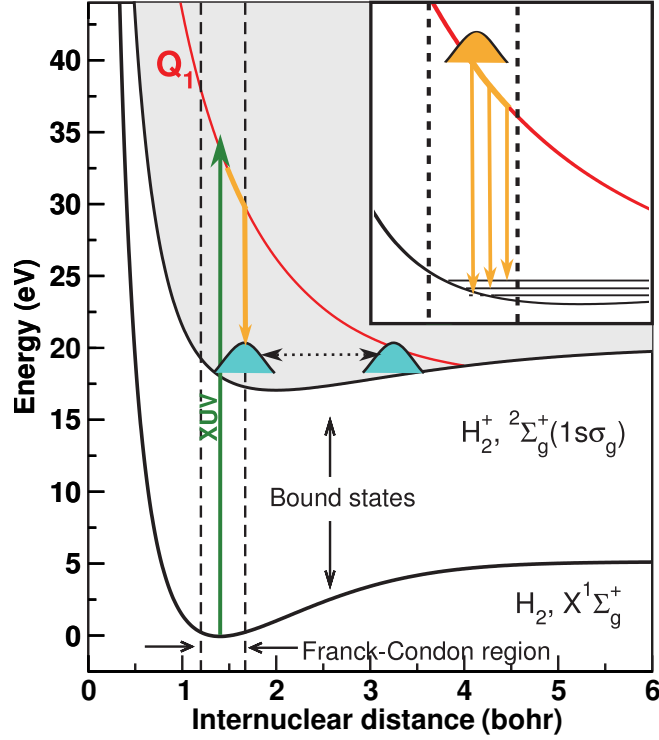


Figure 4.1: Illustration of autoionization decay of the Q_1 doubly excited state of H_2 molecule into the ground state of H_2^+ molecule. The decay into bound final states (inset) takes place right after excitation, while the vibrational wavepacket on the Q_1 doubly excited state potential energy curve is still in the vicinity of the inner classical turning point. At later times, as the wavepacket accelerates, the autoionization decay leads to a dissociating wavepacket.

4.3 Methodology

In this section we develop an analytical approach to describe the AI decay in molecules and compare it with the solution of a full dimensional calculation solving the time-dependent Schrödinger equation (TDSE) for the H_2 molecule, which was developed in [18–20].

In the TDSE calculation, the time-dependent wave function is expanded in a basis set of Born–Oppenheimer (BO) eigenstates of the isolated molecule, i.e., the products of H_2 electronic and vibrational states. Because we are using the eigenstates, the ionization amplitudes are directly given by the time-dependent coefficients of the expansion as long as the asymptotic limit is reached. In this approach, the molecular structure is computed using a Feshbach-like method that projects the total Hamiltonian in two separated half-spaces (P and Q). The subspaces are built such that, in the single ionization continuum, the Q subspace will hold the doubly excited states, while the P subspace holds the background continua. This approach allows an intuitive analysis of the autoionization decay

from the Q states into the P states. A detailed description of the method is given elsewhere [18–20] and therefore we will not describe it here.

Alongside the TDSE calculation, we also introduce a truncated calculation, which will be referred here as the “3-state model”. It uses a minimal basis of the BO states that are essential to describe the AI decay. Specifically, it reduces the basis to a single electronic BO curve for the initial, intermediate and final states and a single electronic continuum correlated to the ground electronic state of H_2^+ . We then numerically solve the TDSE within this restricted basis of electronic states, i.e. it is a hybrid representation where the vibrational wavepacket is propagated on a coordinate grid while the electronic continuum is expanded in the spectral basis. This method is described in section 4.3.1.

Finally, we derive our analytical approximation, the semiclassical method, and use it to calculate the vibrational wavepacket dynamics associated to the intermediate doubly excited electronic state prior to its decay. In this method, the quantum wavepacket dynamics is guided by the classical nuclear trajectories. Its results allow to describe the final photoelectron spectra while keeping clear physical connection to the classical trajectories that guide the wavepacket. Moreover, the comparison with both the *ab initio* and the 3-state model calculations confirm the validity of the analytical approach. The method is described in section 4.3.2.

4.3.1 3-state model

The 3-state model is constructed by selecting only those states from the full manifold of states of H_2 system, that significantly contribute to the autoionization dynamics studied here. The selection is based on energetic arguments, i.e., the σ_u state of H_2^+ ion is too high in energy to be significantly populated by the XUV pulses used in this analysis. Further selection follows the analysis of dipole coupling matrix elements, i.e., σ_u state and all higher states of H_2^+ ion have much smaller ionization dipoles compared to the σ_g state and therefore can be disregarded. In addition, of the Q_1 manifold of the autoionizing states only a single state has a short lifetime and a large matrix element to couple to the H_2 ground state. Hence, this is the only state from the whole Q_1 manifold that contributes significantly.

We start by introducing the following ansatz for the wavefunction:

$$\begin{aligned} \Psi(r, R, t) = & \chi_g(R, t)\phi_g(r, R) + \chi_a(R, t)\phi_a(r, R) \\ & + \int d\hat{k} \chi_k(R, t)\phi_k(r, R) \end{aligned} \quad (4.1)$$

where ϕ_g and ϕ_a are electronic wavefunctions for the ground and doubly excited

state of H_2 respectively. The latter is the intermediate state that decays due to AI into the ground state of H_2^+ molecule. ϕ_k is the final state wavefunction representing one electron with momenta $\hbar k$ in the continuum plus a bound electron. $\chi(R)$ are the corresponding vibrational wavepackets. The time dependent Schrödinger equation then reads (atomic units are used everywhere)

$$i\frac{\partial\Psi}{\partial t} = [T_N(R) + H_{el}(r, R) + V_{XUV}(r, R, t) + V_{ee}(r, R)] \Psi(r, R, t) \quad (4.2)$$

where $T_N(R)$ is the nuclear kinetic energy, $H_{el}(r, R)$ includes the electronic kinetic energy and the electron-nuclei interaction, $V_{ee}(r, R)$ is the electron-electron interaction and $V_{XUV}(r, R, t)$ is the interaction with the electromagnetic field. The latter can be expressed as $V_{XUV}(r, R, t) = -d(r, R) F(t)$, where $d(r, R)$ is the dipole and $F(t)$ is the laser electric field.

By applying the adiabatic approximation, i.e. omitting the electronic transitions due to the nuclear kinetic energy term ($\langle\phi_{g,a,k}(r, R)|\hat{T}_N(R)|\phi_{g,a,k}(r, R)\rangle = 0$), we obtain three coupled equations for the vibrational wavepackets:

$$i\frac{\partial}{\partial t}\chi_g(t) = [T_N + V_g]\chi_g(t) + F(t) D_{ga} \chi_a(t) - F(t) \int dk D_{gk} \chi_k(t) \quad (4.3a)$$

$$i\frac{\partial}{\partial t}\chi_a(t) = [T_N + V_a]\chi_a(t) + F(t) D_{ag} \chi_g(t) + \int dk V_{ak} \chi_k(t) \quad (4.3b)$$

$$i\frac{\partial}{\partial t}\chi_k(t) = \left[T_N + V_{ion} + \frac{k^2}{2}\right]\chi_k(t) + F(t) D_{kg} \chi_g(t) + V_{ka} \chi_a(t) \quad (4.3c)$$

where the dependence on R is implicit for all functions except $F(t)$. $V_g(R)$ and $V_a(R)$ are the ground and Q_1 Born–Oppenheimer (BO) potentials of H_2 molecule and $V_{ion}(R)$ is the σ_g ground state BO potential of the H_2^+ molecular ion. Finally,

$$D_{ga}(R) = \int dr \phi_g(r, R)^* d(r, R) \phi_a(r, R) \quad (4.4)$$

are the dipole-coupling matrix element between the corresponding electronic states and

$$V_{ak}(R) = \int dr \phi_a(r, R)^* V_{ee}(r, R) \phi_k(r, R) \quad (4.5)$$

are the electron–electron coupling matrix element that are responsible for the AI decay, and analogously for others.

This 3-state model is very similar to the full *ab initio* calculation. Approx-

imations are made by keeping a single ionization channel ($l=1$) and employing the adiabatic approximation which neglects non-BO effects during the nuclear motion along the Q_1 state. The model excludes first excited σ_u and all other higher energy states of the H_2^+ (D_2^+) ion. On the other hand, exact matrix elements for the electronic couplings (both dipole and electron–electron) extracted from the *ab initio* calculations are used. Finally, the Q_1 series of doubly excited states of H_2 molecule consists of many closely spaced doubly excited states. Here, it is limited to a single lowest energy state that has the largest ionization cross section.

The final vibrational population and the photoelectron spectra can be extracted from $\chi_k(R, t)$. Note that the χ_k part is calculated for every continuum state, leading to a mixed spectral-grid representation of the photoelectron-vibrational wavefunction.

4.3.2 Analytical model

In order to treat the problem analytically we first simplify (4.3) by adiabatically eliminating the continuum from (4.3b) for the wavepacket in the bound Q_1 part of the autoionizing state. This approximation is known to give adequate results when applied to autoionization of H_2 , see, e.g., [2–4, 21] for the detailed discussion and [22–24] for derivations and discussions in time-dependent picture. The derivation of the adiabatic approximation is also provided in appendix B. In short, by introducing the decay width

$$\Gamma(R) = 2\pi \left| \int dr \phi_k(r, R)^* V_{ee}(r, R) \phi_a(r, R) \right|^2 \quad (4.6)$$

we can approximate (4.3b) and (4.3c) as:

$$\begin{aligned} i \frac{\partial}{\partial t} \chi_a(t) &= [T_N + V_a] \chi_a(t) - i \frac{\Gamma}{2} \chi_a(t) \\ &\quad - F(t) D_{ag} \chi_g(t) - F(t) \int dk D_{kg} V_{ak} \chi_g(t) \end{aligned} \quad (4.7a)$$

$$i \frac{\partial}{\partial t} \chi_k(t) = \left[T_N + V_{ion} + \frac{k^2}{2} \right] \chi_k(t) + \sqrt{\frac{\Gamma}{2\pi}} \chi_a(t) - F(t) D_{kg} \chi_g(t) \quad (4.7b)$$

where the dependence on R is again implicit. The above set of equations implies that the Q_1 state BO potential acquires a complex component $V_a(R) \longrightarrow V_a(R) - i \frac{\Gamma(R)}{2}$. Note, that the last term in (4.7a) describes the excitation of the Q_1 state by the laser field through the ionization continuum. Although it is a second-order process, as will become clear later, it is significant in the case at hand.

The adiabatic approximation relies on two essential assumptions. First, that the electron–electron coupling matrix elements and the ionization dipoles are

smooth functions of photoelectron energy in the vicinity of the doubly excited state. Secondly, that the doubly excited state is far away from the ionization threshold. Both assumptions are reasonable for the particular case studied here — the Q_1 doubly excited state resonance of H_2 molecule.

Equation for the direct channel

We assume that the laser field is weak so it does not perturb the H_2 ground state, which can then be described by the vibrational eigenfunction:

$$\chi_g(R, t) = \chi_0(R) e^{-iE_g t} \quad (4.8)$$

where E_g is its vibronic energy.

We expand the vibrational wavepacket $\chi_k(R, t)$ in (4.3c) into a basis of vibrational eigenstates of H_2^+ ground state potential:

$$\chi_k(R, t) = \sum_v a_{k,v}(t) \chi_v(R) e^{-i(E_v + \epsilon)t} \quad (4.9)$$

where $\epsilon = k^2/2$ is the photoelectron energy and where the vibrational eigenfunctions $\chi_v(R)$ satisfy the time-independent Schrödinger equation

$$[T_N + V_{ion}(R)] \chi_v(R) = E_v \chi_v(R). \quad (4.10)$$

Using (4.8) together with (4.9) and (4.10) the final state population in (4.7b) can be written as

$$i \frac{\partial}{\partial t} a_{k,v}(t) = \int dR \chi_v^*(R) e^{i(E_v + \epsilon)t} \sqrt{\frac{\Gamma(R)}{2\pi}} \chi_a(R, t) - F(t) e^{-i(E_g - E_v - \epsilon)t} D_{k,v}; \quad (4.11)$$

where the first term on the right hand side of (4.11) corresponds to the resonant contribution while the second term corresponds to the direct contribution. $D_{k,v}$ is the matrix element describing the direct photoionization from the H_2 vibrational ground state that creates a photoelectron with energy $\epsilon = k^2/2$ and leaves the H_2^+ ion in the ground electronic state and v vibrational eigenstate:

$$D_{k,v} = \int dR \chi_v^*(R) D_{kg}(R) \chi_0(R) \quad (4.12)$$

Equation for the resonant channel

Let us define a wavepacket $\Psi_q(R, t)$ that satisfies the following TDSE

$$i \frac{\partial}{\partial t} \Psi_q(R, t) = [T_N + V_a] \Psi_q(R, t) - i \frac{\Gamma}{2} \Psi_q(R, t) \quad (4.13)$$

with the initial condition

$$\Psi_q(R, t = t_0) = \chi_0(R). \quad (4.14)$$

Equation (4.13) above can be easily solved using numerical methods. Additionally, a semiclassical method to evaluate it analytically will be proposed in the next section.

In the case of one-photon ionization, (4.7a) for the dynamics of the vibrational wavepacket in the resonant state can be solved formally using the time-dependent wavepacket $\Psi_q(R, t)$ in (4.13) together with the expression for $\chi_g(R, T)$ in (4.8):

$$\chi_a(R, t) = -i \int^t dt' \Psi_q(R, t \leftarrow t_0 = t') (-F(t')) D_q e^{-iE_g t'}, \quad (4.15)$$

where $\Psi_q(R, t \leftarrow t_0 = t')$ corresponds to the wavepacket satisfying (4.13) and where Ψ_q was created at time $t_0 = t'$ and was propagated for $\Delta t = t - t'$. D_q is the dipole matrix element from the H_2 vibrational ground state to the resonant state, averaged over the distribution of the initial vibrational wavepacket:

$$D_q = D_q^{(0)} + D_q^{(1)} \quad (4.16a)$$

$$D_q^{(0)} = \int dR \chi_0(R)^* D_{ag}(R) \chi_0(R) \quad (4.16b)$$

$$D_q^{(1)} = \int dk \int dR \chi_0(R)^* V_{ak}(R) D_{kg}(R) \chi_0(R) \quad (4.16c)$$

It has two contributions - direct excitation dipole $D^{(0)}$ from the ground state of H_2 molecule to the resonant state, which is real, and indirect contribution $D_q^{(1)}$ via the ionization continuum, which is in general complex.

The adiabatic approximation, which was used to arrive at (4.6) and (4.7), can be applied to evaluate the integral over the photoelectron states k in (4.16c). With this approximation, the $D_q^{(1)}$ dipole becomes

$$D_q^{(1)} = -i\pi \int dR \chi_0(R)^* \sqrt{\frac{\Gamma(R)}{2\pi}} D_k(R) \quad (4.17a)$$

$$D_k(R) = D_{kg}(R) \Big|_{k=k_{res}} \quad (4.17b)$$

and where $D_k(R)$ is the vibrationally unresolved matrix element for direct ionization from the ground state of H_2 molecule to the ground state of H_2^+ ion. $D_k(R)$ is evaluated at photoelectron energy $\epsilon = k_{res}^2/2 \sim 15$ eV, i.e. such that the total energy of photoelectron+ H_2^+ ion in σ_g state (~ 30 eV) would be in resonance with the Q_1 state in the Franck–Condon region.

The evaluation of the first and second order matrix elements $D_q^{(0)}$ and $D_q^{(1)}$ showed, that they lead to approximately equal contribution to the total population in the Q_1 state created by the laser pulse. This is the case, because the small magnitude of the electron-electron coupling element Γ is compensated by large direct ionization matrix element $D_k(R)$. Hence, the total D_q matrix element up to a good approximation can be expressed as simply

$$D_q \approx D_q^{(0)} (1 - i) = D_q^{(0)} \sqrt{2} e^{-i\pi/4}. \quad (4.18)$$

Note, that the matrix element $D_q^{(0)}$ describing the direct excitation of the Q_1 state is strictly real, because it corresponds to a bound-bound transition. Nevertheless, the additional second-order term $D_q^{(1)}$ that describes the excitation of the Q_1 state via the ionization continuum, leads to a complex “effective” matrix element D_q for the excitation of the Q_1 state.

Final state population

Inserting the solution for $\chi_a(R, t)$ in (4.15) into (4.11), the final state amplitude $a_{k,v}(t)$ can be defined by the expression

$$\begin{aligned} i \frac{\partial}{\partial t} a_{k,v}(t) = & -F(t) e^{-i(E_g - E_v - \epsilon)t} D_{k,v} + e^{-i(E_g - E_v - \epsilon)t} D_q \\ & \times i \int_{t-t_0}^0 d[-\Delta t] F(t - \Delta t) e^{iE_g \Delta t} \\ & \times \int dR \chi_v^*(R) \sqrt{\frac{\Gamma(R)}{2\pi}} \Psi_q(R, t \leftarrow t - \Delta t) \end{aligned} \quad (4.19)$$

where $\Delta t = t - t'$ was used. Expanding the laser field into its Fourier components

$$F(t) = \frac{1}{\sqrt{2\pi}} \int d\Omega \tilde{F}(\Omega) e^{-i\Omega t} \quad (4.20)$$

allows one to rewrite (4.19) as

$$i \frac{\partial}{\partial t} a_{k,v}(t) = - \frac{1}{\sqrt{2\pi}} \int d\Omega \tilde{F}(\Omega) e^{-i(E_g + \Omega - E_v - \epsilon)t} \times \left(D_{k,v} - D_q i \int_{t-t_0}^0 d[-\Delta t] e^{i(E_g + \Omega)\Delta t} V(\Delta t) \right) \quad (4.21)$$

where

$$V_v(\Delta t) = \int dR \chi_v^*(R) \sqrt{\frac{\Gamma(R)}{2\pi}} \Psi_q(R, t \leftarrow t - \Delta t) \quad (4.22)$$

Atomic limit

Let us first consider the atomic limit, where

$$V_v(R, \Delta t) \rightarrow V(\Delta t) = \sqrt{\Gamma_0/2\pi} e^{-iE_q\Delta t - \Gamma_0/2\Delta t} \quad (4.23)$$

and E_q is the energy of the resonant state and all dependences on the internuclear distance R are dropped, i.e. a single point along R is considered. The integral over Δt in (4.21) becomes

$$i \int_{t-t_0}^0 d[-\Delta t] e^{i(E_g + \Omega)\Delta t} V(\Delta t) \rightarrow i \int_{t-t_0}^0 d[-\Delta t] \sqrt{\Gamma_0/2\pi} e^{i(E_g + \Omega - E_q)\Delta t} e^{-\Gamma_0/2\Delta t} = \quad (4.24a)$$

$$- \sqrt{\frac{\Gamma_0}{2\pi}} \frac{1}{E_g + \Omega - E_q + i\Gamma_0/2} \quad (4.24b)$$

and (4.21) reduces to

$$i \frac{\partial}{\partial t} a_{k,v}(t) = - \frac{1}{\sqrt{2\pi}} \int d\Omega \tilde{F}(\Omega) e^{-i(E_g + \Omega - E_v - \epsilon)t} \times \left(D_{k,v} + D_q \sqrt{\frac{\Gamma_0}{2\pi}} \frac{1}{E_g + \Omega - E_q + i\Gamma_0/2} \right). \quad (4.25)$$

which can be formally integrated yielding

$$a_v(\epsilon) = \frac{i}{\sqrt{2\pi}} \int d\Omega \left(\int dt' e^{-i(E_g + \Omega - E_v - \epsilon)t'} \right) \tilde{F}(\Omega) \tilde{D}_v(\Omega, \epsilon) \\ = \sqrt{2\pi} i \tilde{F}(\Omega = E_v + \epsilon - E_g) \tilde{D}_v(\Omega = E_v + \epsilon - E_g, \epsilon) \quad (4.26)$$

with

$$\tilde{D}_v(\Omega, \epsilon) = D_{k,v} + D_q \sqrt{\frac{\Gamma_0}{2\pi}} \frac{1}{E_g + \Omega - E_q + i\Gamma_0/2} \quad (4.27)$$

and where D_q is defined in (4.16) and (4.17). Also note, that the definition of Dirac delta function

$$\delta(x - a) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i(x-a)t} dt \quad (4.28)$$

was used to arrive at (4.26). It can be shown (see appendix C), that the expression for the ionization dipole in (4.26) is the same as the one derived by Fano in [1].

Molecular case

In the molecular case, the final state amplitude can also be expressed similarly as in (4.26), where, however, the dipole $\tilde{D}_v(\Omega, \epsilon)$ has to be replaced with

$$\tilde{D}_v(\Omega = E_v + \epsilon - E_g, \epsilon) = D_{k,v} - D_q i \int_0^{\infty} dt e^{i(E_v + \epsilon)t} V_v(t) \quad (4.29)$$

and $V_v(t)$ is defined in (4.22). To arrive at the expression above, Δt was relabelled into t . The integration limit was also changed to $t_0 \rightarrow -\infty$, which does not affect the final value of the integral because the function $V_v(t)$ decays to zero rather quickly due to quickly decaying overlap between the vibrational wavepacket $\Psi(R, t)$ accelerating on the dissociative Q_1 state potential energy curve and the stationary vibrational eigenstates $\chi_v(R)$ of the final σ_g electronic state.

We see that the key part of the analytical description is the dynamics of the vibrational wavepacket dissociating on the Q_1 state potential curve. We now proceed to deriving the analytical description of this dynamics.

4.3.3 Analytical solution for a vibrational wavepacket on the resonant state

The essential aspect of the analytical semiclassical description is the need to start the vibrational wavepacket with zero velocity, which is where the standard WKB approximation breaks down. We overcome this limit by solving the problem in the time domain directly. Hence, our model does not suffer from the standard WKB constraint and thus can be applied to describe the wavepacket close to the classical turning points, e.g., where the AI decay into the final bound vibrational states happens (see figure 4.1).

First, we neglect the decay of the *vibrational* wavepacket propagating along the

$V_a(R)$ potential energy curve (PEC) of Q_1 state and write it as

$$\chi(R, t) = B(t) e^{iS(R, t)} \quad (4.30)$$

where $B(t)$ normalizes the wavepacket to unity. The decay can be accounted for in the overall amplitude later. A Gaussian wavepacket is a good approximation for the ground vibrational state of most molecules. Moreover, the shape of the vibrational wavepacket will be preserved after excitation by a short laser pulse in the sudden excitation limit.

We now substitute the ansatz into the time dependent Schrödinger equation for the vibrational motion along the $V_a(R)$ potential. This leads to the Hamilton-Jacobi equation for the phase $S(t)$:

$$-\frac{\partial S}{\partial t} = \frac{1}{2\mu} \left(\frac{\partial S}{\partial R} \right)^2 + V_a(R) \quad (4.31)$$

where μ is the reduced mass of the nuclei and, as usual for the WKB method, the second-order derivative of $S(R)$ is neglected. Let $R_{cl}(t)$ be the classical trajectory that starts at the centre of the initial wavepacket with zero initial momentum and moves along the potential $V_a(R)$ following the usual Newton's equations. We now expand the $V_a(R)$ potential energy curve in a Taylor series up to the 2nd order around this classical trajectory $R_{cl}(t)$:

$$V_a(R) \approx V_a(R_{cl}) + V'_a(R - R_{cl}) + \frac{1}{2} V''_a(R - R_{cl})^2 + \dots \quad (4.32)$$

Accordingly, we look for a solution for $S(t)$ in a polynomial form, up to the 2nd order in powers of R_{cl} :

$$S(R, t) = S_{cl}(t) + P_{cl}(t)(R - R_{cl}) - \frac{1}{2} \sigma(t)(R - R_{cl})^2. \quad (4.33)$$

Here, the momentum $P_{cl}(t)$ is conjugated to the coordinate $R_{cl}(t)$ and corresponds to the solution of Newton's equations of motion on the potential energy surface $V_a(R)$. The action $S_{cl}(t)$ is the classical action accumulated along the trajectory $R_{cl}(t)$ and $\sigma(t)$ is the time dependent width of the wavepacket. The above polynomial expansion implies that the initially Gaussian wavepacket, created by photo-absorption into the Q_1 state, maintains its approximately Gaussian shape while acquiring a time- and R -dependent phase profile. This approximation proved quite accurate, especially during the initial stage of propagation. For H_2 on the very steep Q_1 surface this corresponds to times $\lesssim 1fs$, which we found to be sufficient for the AI decay into the bound vibrational states to occur.

Using (4.31) to (4.33)) we obtain the following expression for the time-dependent wavepacket:

$$\begin{aligned} \chi_Q(R, t) = & \left[\frac{\text{Re}[\sigma(t)]}{\pi} \right]^{\frac{1}{4}} \exp \left[i S_{cl}(t) + i \left(R - R_{cl}(t) \right) P_{cl}(t) \right] \\ & \times \exp \left[-\frac{1}{2} \left(R - R_{cl}(t) \right)^2 \sigma(t) \right] \end{aligned} \quad (4.34)$$

where $\sigma(t)$ is

$$\sigma(t) = \sqrt{\mu \alpha(t)} \frac{1 + C \exp \left(-i 2 \sqrt{\frac{\alpha(t)}{\mu}} t \right)}{1 - C \exp \left(-i 2 \sqrt{\frac{\alpha(t)}{\mu}} t \right)} \quad (4.35)$$

expressed via the parameter C

$$C = \frac{1 - \sqrt{\mu \alpha(t)} X_0^2}{1 + \sqrt{\mu \alpha(t)} X_0^2} \quad (4.36)$$

and the curvature of the potential $\alpha(t) = \alpha(R_{cl}(t))$, i.e. the second derivative of the potential at $R_{cl}(t)$. Finally, X_0 is a parameter related to the initial width of the wavepacket:

$$\sigma(t=0) = \frac{1}{X_0^2}. \quad (4.37)$$

In the presence of AI decay, $V_a(R)$ acquires a complex component $-i\Gamma(R)/2$. Including it in the 0-th order into (4.32) introduces an additional term

$$\chi_Q(R, t) \rightarrow \chi_{\Gamma, Q}(R, t) = \chi_Q(R, t) \exp \left(-\frac{1}{2} \int_0^t \Gamma(R_{cl}(t')) dt' \right). \quad (4.38)$$

With the analytical description of the vibrational dynamics on the Q_1 curve in place, we will now proceed to compute the photoelectron spectra and the associated lineshapes correlated to different vibrational states of the H_2^+ ion. Then the spectra will be compared with the results of numerical simulations and also reconstruction of the AI dynamics from the photoelectron spectra will be developed.

4.3.4 Computational details

The time propagation of the vibrational wavepacket associated to the coupled PECs described by (4.3) was performed in the length gauge using a Crank-Nicholson scheme. Some of the parameters used in the calculation are summarized in table 4.1. The maximum propagation time, 4 fs, ensures that the asymptotic limit is reached for both dissociative and non-dissociative ionization components. The H_2 ground state potential was obtained from [25] and used to calculate the initial vibrational

wavepacket $\chi_g(R, t_0)$ by solving the one-dimensional vibrational eigenvalue problem in a B-spline basis set. We use as discretized electronic continua a set of potential energy curves that are parallel and equidistant in electron momentum with respect to the ground state of H_2^+ . The former has been accurately calculated using Power's OEDM (one-electron diatomic molecule) code [26, 27]. The potentials $V_{g,a,ion}(R)$ and electronic couplings between the electronic states at different values of R are extracted from the *ab initio* calculations [18, 20].

The analytical solution from our model, as described in section 4.3.2, was evaluated by first calculating a classical trajectory along the $V_a(R)$ surface starting at the H_2 equilibrium internuclear distance R_0 to obtain $S_{cl}(t)$, $R_{cl}(t)$ and $P_{cl}(t)$. They were then used in (4.34) to (4.37) to evaluate $\chi_Q(R, t)$ and subsequently $\chi_{Q,\Gamma}(R, t)$. The decay width $\Gamma(R)$ was extracted from the full electrostatic couplings $V_{ee}(R, \epsilon)$ as described in [3].

The vibrational eigenvalues $\chi_v(R)$ and vibronic energies E_v were calculated using $V_{ion}(R)$ PEC. The integrals over R and t in (4.26) and (4.29) were performed numerically, where the $F(t)$ and dipole couplings between PECs were the same as in the 3-state model calculation.

The ionization probability $P(E)$ as a function of photoelectron energy E was obtained by multiplying the populations a_n^E of the discrete continuum states by the density of states ρ_n^E :

$$P(E) = |a_n^E|^2 \rho_n^E = \frac{2 |a_n^E|^2}{E_{n+1} - E_{n-1}}. \quad (4.39)$$

Additionally, probabilities that are independent on the laser field parameters were obtained by dividing the probability $P(E)$ by the square of the amplitude of the laser pulse spectra $|F(\Omega)|^2$ at the frequency $\Omega = E$

$$|D(\epsilon)|^2 \sim P(E) / |F(\Omega = \epsilon)|^2 \quad (4.40)$$

where

$$F(\Omega) = \frac{1}{2\pi} \int dt F(t) e^{-i\Omega t} \quad (4.41)$$

as described in detail in [28].

4.4 Calculation results

The vibrationally resolved photoionization probabilities obtained from the full and truncated calculations, as introduced in section 4.3, are plotted in figure 4.2 and compared with results from the semiclassical model. The calculations were carried

Table 4.1: Summary of parameters used in the calculations.

propagation time, t_{max}	165.4	$\hbar/E_h$	(4 fs)
time step, Δt	0.031	$\hbar/E_h$	(0.75 as)
internuclear distance grid length, R	25	a_0	
internuclear distance grid spacing, dR	0.01	a_0	
number of continuum states, N	99		
maximum continuum energy, ϵ	1442	E_h	(53 eV)
H ₂ reduced mass, μ	918.58	m_e	
H ₂ equilibrium internuclear distance, R_0	1.4325	a_0	
initial width, X_0	0.2364	a_0	

out with a single attosecond XUV pulse. The pulse had a duration of 400 as (appreciably shorter than the autoionization lifetimes for H₂ [10, 17]) and a central photon energy of 30 eV, which is in resonance with the first doubly excited state of the Q₁ series. The laser intensity was set to $I=10^9$ W/cm², which is low enough to ensure a perturbative regime. This gives a direct correspondence between the total cross sections and ionization probability for any photon energy within the bandwidth of our pulse [28].

The transition probabilities obtained using the *ab initio* approach are presented in figure 4.2a. They match the equivalent results obtained using the time-independent approach reported in [17]. The effect of the resonance can be clearly seen as a modulation of the transition probability which spans a much broader photon energy range and has a smaller amplitude than those found in the atomic ionization cross section close to a resonance (see, e.g., reference [29]). Note, however, that due to a systematic shift of the modulation pattern in photoelectron energy for different ν 's, no resonance traces would be observed for vibrationally unresolved spectra. In general, the full atomic photoionization probability and the differential molecular probabilities presented here are qualitatively very different. The origin of these differences will be the focus of section 4.5 of this thesis.

The results obtained using the “3-state model” (figure 4.2b) are in an excellent agreement with the *ab initio* reference results. It shows that a reduced dimensionality model calculation for the time-dependent dynamics allows one to quantitatively reproduce the results of a more sophisticated *ab initio* TDSE calculation. Of course, this implies that the same electrostatic dipole matrix elements are used in both cases. Importantly, it shows that the autoionization dynamics in the H₂ molecule at this energy range can be successfully described by the 3 PECs, validating the 3-state truncation used en route to deriving the analytical model (see section 4.3.2).

Good agreement between the “3-state model” and the *ab initio* calculation shows

that it is possible to simplify the analysis of correlated electron-nuclear dynamics by performing time-dependent propagation for relevant coupled potential energy surfaces. This is important for more complex molecules, where the evaluation of the exact coupling-matrix elements may not be feasible. However, it may still be possible to use reduced dimensionality TDSE calculations and infer the correct coupling elements by comparing with experimental data.

The probabilities obtained using the analytical approach are shown in figure 4.2c. They are in good agreement with both the *ab initio* and the 3-state model results. The exact details, e.g., such as the exact positions of minima and maxima for different vibrational states differ slightly compared to those of the more sophisticated models. In particular, the analytical calculation over-estimates the modulation of the ionization probabilities close to the resonance. However, considering the simplicity of the approach, the qualitative agreement is excellent and captures all relevant physical effect governing the AI dynamics in the H_2 molecule.

A possible reason for the disagreement between the TDSE calculations and the analytical results is the non-negligible influence of the ionization threshold. It is not taken into consideration in the analytical calculations due to the application of the adiabatic approximation (see appendix B). However as can be seen from figure 4.2 the modulation of the ionization probability due to the interference of direct and resonant contributions is still non-negligible at the ionization threshold, suggesting that the adiabatic approximation might induce large errors.

The effects of the interference between the direct and resonant ionization channels become more clear upon inspecting the final ionization probability as a function of both the final vibrational state energy and the photoelectron energy. Such spectra, presented in figure 4.3, allow one to identify the key spectral features and the correlations between different vibrational states more easily. Note, that unlike the previous data, the spectra in figure 4.3 are not divided by the laser spectral density and therefore depend on the laser pulse parameters.

Comparison of the results obtained using different methods shows a similar trend to that seen in figure 4.2. The 3-state calculations are in excellent agreement with the *ab initio* results, while the analytical spectra provide a qualitatively similar picture, correctly capturing all spectral features but over-estimating the modulations.

The effect of the interference between the direct and the AI pathways is revealed most clearly by looking at the difference spectra obtained with and without including the AI decay, see figures 4.3e-f. The interference pattern resembling a Fano profile can be identified although, as it will be clear later, its origin is very different. A minimum due to destructive interference can be seen for photoelectron energies

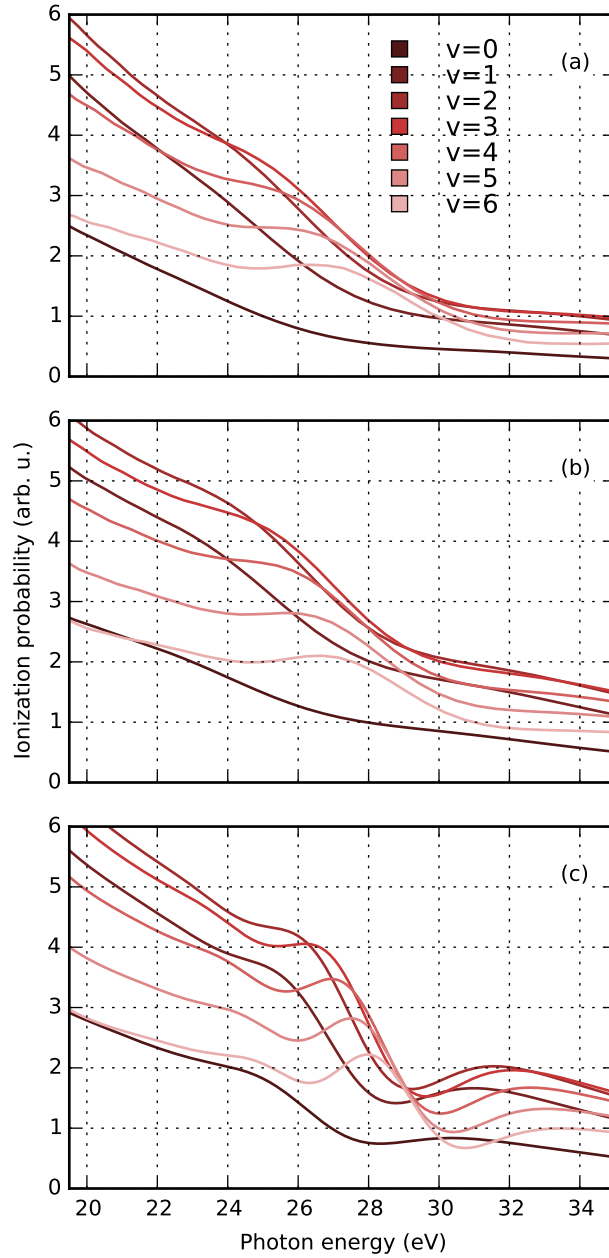


Figure 4.2: Vibrationally resolved photoionization probability demonstrating the traces for AI decay calculated using (a) *ab initio* numerical method, (b) the reduced 3-state model and (c) and the analytical treatment.

between 10-15 eV, while a maximum due to constructive interference appears around 8-10 eV. For each individual vibrational state, the maximum is shifted to lower photoelectron energies compared to the 'direct only' channel. Finally, the interference minima and maxima for higher vibrational energies shift to higher photoelectron energies, creating a tilted shape of the overall spectra. These features are present in the *ab initio* results (figure 4.3e), the 3-state model (not shown), and in the analytical calculation (figure 4.3f).

To summarize, the semiclassical analytical model of molecular photoionization in the presence of a continuum resonance proved capable of reproducing all essential qualitative features of the full spectrum, resolved both on the photoelectron energy and the vibrational eigenstate of the cation. The model works for steep potentials in good agreement with previous more standard WKB methods. Moreover, it also yields no difficulties when starting the wavepacket motion at the turning point of the classical trajectory (where application of standard time-dependent WKB methods requires extra care), and works well for describing transitions to the bound vibrational states on the σ_g surface with high $\nu \gg 1$ ('semiclassical region') and the states with low $\nu = 0, 1$ ('quantum region'). In the following section this analytical model will be used to explain the origin of the observed spectral features.

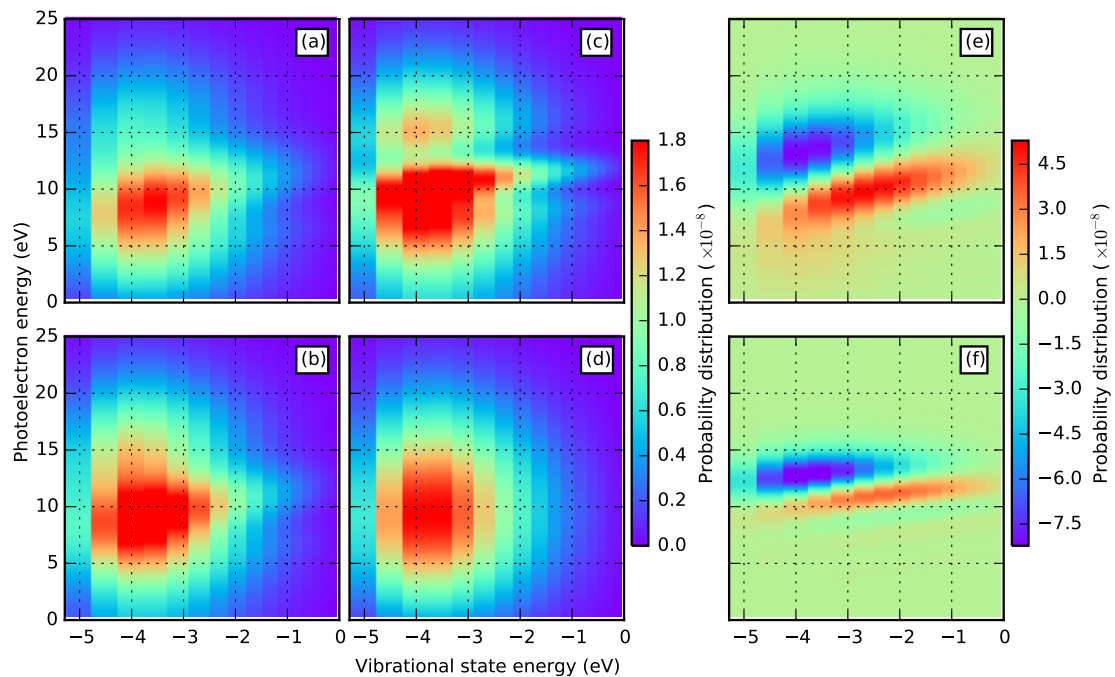


Figure 4.3: Differential photoionization probabilities (differential in vibrational and photoelectron energies) for a 400 as pulse centred around 30 eV photon energy obtained using *ab initio* (a), reduced 3-state (b) and analytical (c) approaches. The probability distribution of the direct only channel, which is indistinguishable for different models, is plotted in (d). The difference between the *ab initio* (a) and direct-only (d) probabilities is plotted in (e). (f) shows the same difference spectra for the analytical calculation. Plots (e) and (f) have a shifted colour scale than the rest to accommodate negative (blue) and positive (red) values. Note, that the discontinuities in the plotted probability distribution arise because a discrete spectra of bound vibrational states is represented on the horizontal axis.

4.5 Formation of lineshapes

The disappearance of Fano-like interferences in the AI decay of H_2 molecule was previously discussed by Palacios et. al. [10] for the dissociative spectra of H^+ fragments. It was shown that the interference patterns are dominated by the phase difference accumulated by the vibrational wavepackets propagating along the direct channel (σ_g surface) and the AI dissociation channels (the Q_1 surface) up to a transition point R_i , masking the atomic-like Fano interference.

The method used in [10] is based on the time-independent WKB approach and is not suitable for the non-dissociative channel. Its direct application meets with technical difficulties when applying it to the dynamics involving low vibrational states, especially in the vicinity of the classical turning points of the potential. In particular, in the semiclassical treatment the transition from the AI state potential curve to the σ_g curve takes place at the point R_i of the classical trajectory where the classical momenta associated with vibrational motion on the two potential curves become equal [5, 6, 10]. In other words, both energy and momentum at the transition point are conserved. In contrast to the dissociative vibrational continuum, bound vibrational states carry low momentum and should therefore be populated while the vibrational wavepacket on the AI surface is still close to the classical turning point, where the time-independent WKB method is not applicable. Moreover, as we will see later, for the lowest vibrational states the condition of equal momenta at the transition point R_i is never satisfied for any real value of R_i .

To illustrate this point further, we examine the time dependence of the AI decay into final vibrational states with low ($\nu=0$) and high ($\nu=10$) quantum numbers. These represent respectively “quantum” and “semiclassical” final states. The transition probability is obtained by evaluating the time dependent dipole matrix element $\int dR \chi_v^*(R) \sqrt{\Gamma(R)/2\pi} \chi_Q(R, t)$ between the Q_1 and σ_g states used in the (4.29). Its value as a function of time for the two different final vibrational bound states is plotted in figure 4.4a. We can clearly see that while the transition probability into $\nu=10$ final vibrational state is peaked at a certain time, the equivalent probability into $\nu=0$ final state decreases monotonically with time, and is therefore not clearly associated with a specific transition point R_i .

The difference between the curves in figure 4.4a can be understood from the dynamics of the vibrational wavepacket on the $W_a(R)$ surface in the Wigner phase space representation. It is shown in figure 4.4b for three values of time: before, after and at the most likely AI decay time for the $\nu=10$ final state. During this time the wavepacket does not move significantly along the position coordinate R . However, its evolution along the momentum axis is substantial. Hence, the time dependence

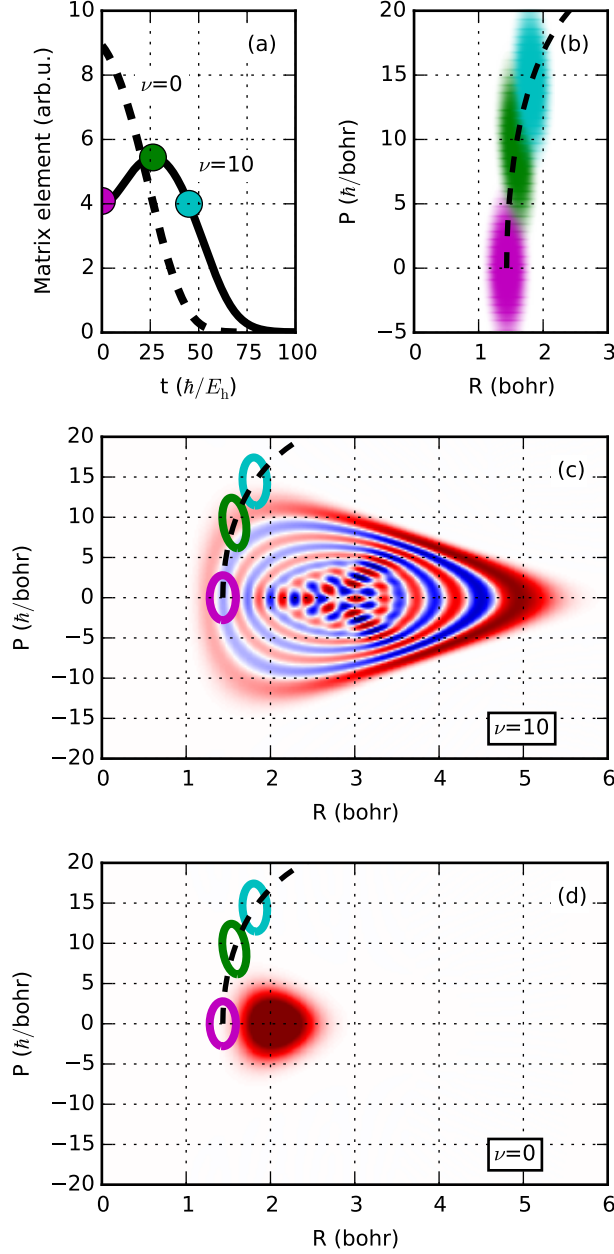


Figure 4.4: (a) The Franck–Condon overlap of vibrational wavepacket on the Q_1 state with the $\nu=0$ and $\nu=10$ final bound vibrational states of the H_2^+ σ_g state potential as a function of time; (b) the Wigner representation of the vibrational wavepacket on the Q_1 surface at 3 different times marked in (a) where the dashed line shows the classical trajectory; the same data is represented in (c) and (d) as contour lines where they are overlapped with the phase-space representation of the $\nu=10$ (c) and $\nu=0$ (d) vibrational state distributions.

of the AI decay probability into a specific bound vibrational states is determined not by the motion of a vibrational wavepacket on the resonant state potential, but by the much more rapid evolution of its momentum. We can conclude that acceleration of the wavepacket when it is created on a steep potential curve creates a phase mask which determines the overlap with the final vibrational bound state it decays into.

The time evolution of the transition probability can be better understood by examining the phase space distributions of the vibrational wavepacket on the $V_a(R)$ curve with the final bound state eigenfunction $\chi_v(R)$ shown in figures 4.4c-d. We note in passing that the overlap between two wavefunctions in the Wigner representation can be expressed as $|\int dx \Psi_1(x)^* \Psi_2(x)|^2 \sim \int dx dp W_1(x, p) W_2(x, p)$. For $\nu=10$ final state the transition probability is small when the wavepacket on the $V_a(R)$ curve is at internuclear distance, where the $\nu=10$ vibrational eigenstate is highly oscillatory. The maximum of the transition probability is reached when the wavepacket on the $V_a(R)$ curve passes the internuclear distance at which the $\nu=10$ vibrational eigenstate has its last anti-node, which is relatively smooth and broad. For the $\nu=0$ vibrational state, on the other hand, the wavepacket on $V_a(R)$ surface starts away from the maxima of the final state distribution and never crosses it. As a result, the AI decay probability into this state decays monotonically with time. This is why no clear 'classical' transition point R_i can be defined. We note again that in both $\nu=0$ and $\nu=10$ cases the evolution predominantly takes place along the momentum and not the position axis.

An intuitive way to understand the connection between the shape of spectral lines and the dipole response function in a time domain picture was presented by Ott et.al. [30]. There it was demonstrated that a short laser pulse can give a "kick" to the time-dependent dipole response of an atomic system, which introduces an additional phase shift. The latter translates into the modification of the Fano spectral lineshape. A similar interpretation can be applied to molecules, where a "kick" by a laser pulse is replaced by the momentum evolution of the vibrational motion. However, in this case, the momentum evolution leads not to a uniform phase-shift, but to a phase profile across the vibrational wavepacket, which determines the appearance of the spectral lines.

4.6 Atomic vs. molecular lineshapes

We now focus our attention on the difference between the atomic and molecular spectra at resonance. For atoms, the lineshape corresponds to the well known Fano profile [1]. We will now analyse how the shape of the vibrationally resolved molecular

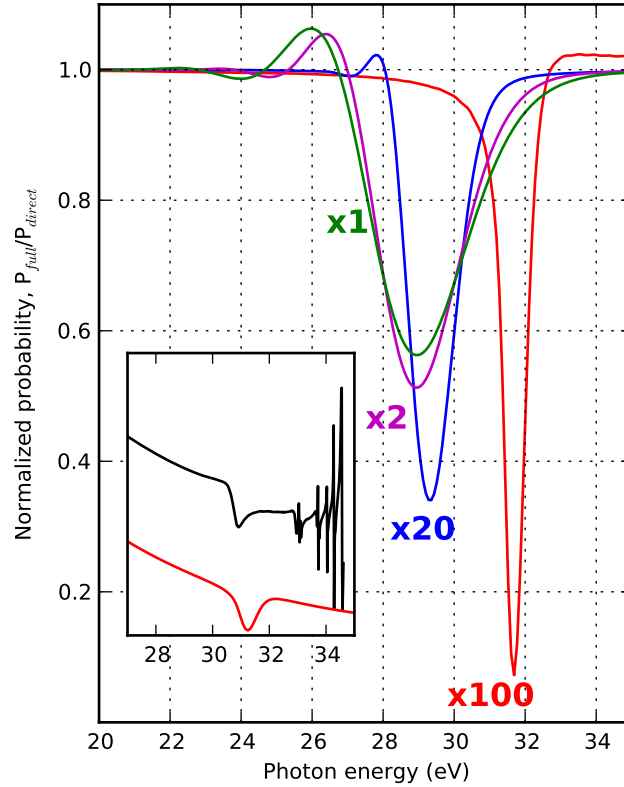


Figure 4.5: The dependence of the lineshape on the reduced mass of the nuclei for masses that are 1, 2, 20 and 100 times bigger than the mass of H_2 . The lineshapes correspond to $\nu=2$ vibrational eigenstate. The inset shows comparison between the ionisation cross section obtained from the TDSE calculation where the mass of the nuclei was increased by a factor of 100 (red line) and the *ab initio* results in the fixed nuclei approximation (black line).

photoionization spectra is modified by the interplay between the electronic decay, characterized by the $\Gamma(R)$ width, and the nuclear motion. Specifically, we shall look at the spectral lineshapes defined as the ratio between the full ionization probability and the probability associated with the direct channel only, P_{full}/P_{direct} . This allows one to deconvolve the spectra from the laser pulse parameters and the cross section of direct ionization, and focus on the effect of the interference between the direct and resonant contributions.

To examine the role of the nuclear motion, we begin by gradually increasing the reduced mass of the nuclei while at the same time leaving the electronic system intact. This corresponds to dihydrogen isotopes, deuterium and tritium, as well as fictitious systems with heavier nuclei. The lineshapes for different masses are plotted in figure 4.5. As the mass is gradually increased, the lineshapes get narrower and deeper while the position of minima and maxima shift towards higher energies. The infinite mass limit obtained in our calculation agrees well with the *ab initio* calculations performed for the hydrogen molecule in the fixed nuclei approximation,

which is described in [29] (see the inset of figure 4.5).

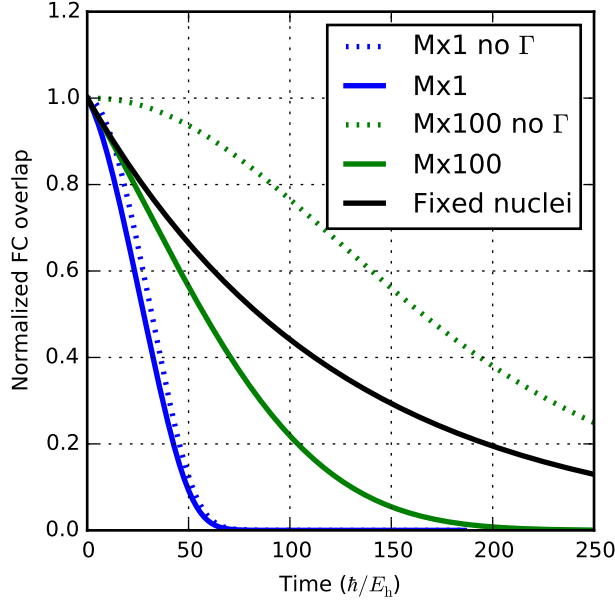


Figure 4.6: Franck–Condon overlap time-dependence for $\nu=2$ with (solid lines) and without (dotted lines) electronic decay $\Gamma(R)$ for different nuclear masses. The black solid curve shows purely electronic decay without nuclear motion.

The transformation of the spectra in figure 4.5 can be understood by analysing the time-dependence of the transition probability for different masses. Approximating the decay width with its value at the equilibrium internuclear distance $\Gamma(R) \approx \Gamma(R_{eq}) = \Gamma_0$ we can rewrite the time-dependent transition dipole as

$$\left[\int dR \chi_v(R)^* \sqrt{\frac{\Gamma(R)}{2\pi}} \chi_{\Gamma,Q}(R, t) \right] \sim \left[\int dR \chi_v(R)^* \chi_Q(R, t) \right] \exp\left(-\frac{\Gamma_0}{2}t\right). \quad (4.42)$$

Hence, the AI transition probability is determined by two timescales. The first is due to the electronic decay governed by the term Γ_0 . It yields an exponential decay of the resonant state population, exactly as in the atomic case. The vibrational dynamics of a molecule leads to the second timescale due to the time-dependent Franck–Condon overlap $\langle \chi_v(R) | \chi_Q(R, t) \rangle_R$ between the wavepacket in the resonant state and the final vibrational eigenstate.

The interplay between these two timescales, for different masses of the system, is illustrated in figure 4.6. For small masses and hence rapid nuclear evolution, which is the case for the H_2 molecule, the decay of the FC overlap is much faster than the electronic decay determined by Γ_0 . As a result, the time dependence of the transition probability into a particular final vibrational state ν is governed by the Franck–Condon overlap — once the wavepacket on the $V_a(R)$ curve starts moving

and the FC overlap decays, the transition probability vanishes. Importantly, the FC overlap into a particular vibrational state vanishes much faster than the time the nuclei take to move any appreciable distance (see figure 4.4).

Thus, for light molecules the observed lineshapes are governed by the nuclear motion in the momentum space. As the mass increases, the *vibrational* dynamics slows down and the FC time window increases. As it becomes longer, the electronic decay due to Γ_0 acquires a larger influence on the overall time dependence of the decay. For a mass 100 times bigger than the original mass of H_2 , the decay into a bound vibrational state is dominated by the timescale of the electronic decay and the vibrationally resolved lineshape starts resembling the atomic case. Also note that the decay probability as a function of time transforms from a non-exponential decay for small mass to a pure exponential decay for a big mass.

One may ask the question, whether it is possible to predict the relative importance of the electronic decay versus nuclear dynamics in the formation of resonances for a specific molecule of interest. Although, it is possible to estimate the speed of nuclear dynamics from the mass of the system relatively well, the lifetimes of the resonant states can vary significantly not only between different molecules, but also for different resonances states of the same molecule. Hence, some molecular resonances may look very similar to atomic resonances in the photoelectron spectra. On the other hand, for other resonances of the same molecule, which have a lifetime comparable to the timescale of nuclear motion, treatment presented in this chapter might be required. It should also be stressed, that resonances that are strongly perturbed by the nuclear motion might be only visible in the vibrationally resolved photoionization spectra, as discussed at the beginning of this chapter.

With the qualitative and quantitative understanding of the formation of the photoelectron lineshapes and underlying dynamics, we can now move to the next task of reconstructing these dynamics from the photoelectron spectra.

4.7 Reconstruction of the decay of Q_1 transient state

The interference between the reference vibrational wavepacket created in the H_2^+ ground state and the signal vibrational wavepacket created via autoionization decay records the relative phases between the two channels by mapping them into amplitude modulations in the population of vibrational states shown in figure 4.2. This leads to a time-energy mapping illustrated in the inset of figure 4.1, when the decay from the autoionizing Q_1 state populates higher final vibrational states of

the H_2^+ ion at later times after the XUV excitation, see, e.g., figure 4.4a. Hence, it acts as a pump-probe measurement, where the excitation by the XUV pulse is the pump while the autoionization of the Q_1 state is the probe. It is conceptually similar to the core hole spectroscopy, see, e.g., [31], where the lifetime of the core hole of an atom acts as the internal clock. Here, however, the vibrations of the molecule act as the internal clock.

Below, the full vibrationally resolved photoionization spectra obtained using *ab initio* calculations will be considered as a “numerical experiment”. The unperturbed photoionization spectra that accounts only for the direct ionization channel and do not include the contribution from the Q_1 resonant state will act as the reference. The overall final lineshape is the interference of the “signal” wavepacket and the “reference” wavepacket, whose dynamics is assumed to be known. Hence, we will use a partial knowledge of the system - the direct ionization channel, and attempt to extract the “unknown” dynamics of the wavepacket on the Q_1 PEC.

Finally note, that while *ab initio* calculation includes the dynamics of H_2 molecule in the laser field fully, it does not account for all of the features of an experiment in the laboratory. For example, the *ab initio* calculation considers a perfectly aligned molecule and a laser field with a well defined energy and intensity. In a laboratory experiment, a certain degree of averaging over alignment angles and intensities is normally inevitable.

4.7.1 The reconstruction procedure

As was formally demonstrated in section 4.3.2, the probability of single photon ionization into a selected final vibrational state can be expressed as the coherent sum of contributions from the direct and the resonant channels

$$S_v(\epsilon) \propto |D_v^{full}(\epsilon)|^2 = |D_v(\epsilon) + Q_v(\epsilon)|^2 \quad (4.43)$$

where $D_v^{full}(\epsilon)$ is explicitly expressed in (4.29). D_v and $Q_v = -iD_q$ are respectively the contributions from the direct and resonant ionization channels. Hence, the full spectra records the interference between the two ionization paths

$$S_v(\epsilon) = |D_v(\epsilon)|^2 + |Q_v(\epsilon)|^2 + 2\text{Re}[D_v(\epsilon) Q_v(\epsilon)] \quad (4.44a)$$

$$= |D_v(\epsilon)|^2 + |Q_v(\epsilon)|^2 + |D_v(\epsilon)||Q_v(\epsilon)| \cos(\phi_D(\epsilon) - \phi_Q(\epsilon)). \quad (4.44b)$$

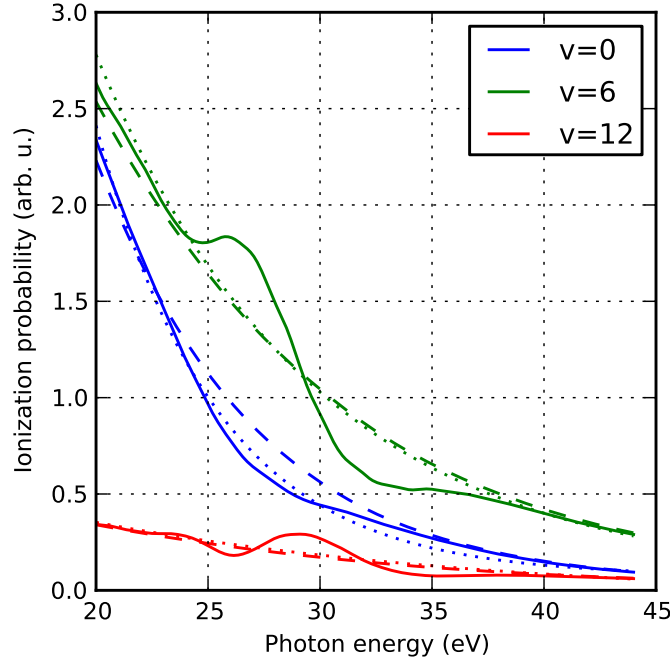


Figure 4.7: Vibrationally resolved ionization probabilities for the selected vibrational states together with direct-only photoionization channel that does not include the contribution from the resonant state (dashed lines). Both spectra are obtained using *ab initio* numerical calculations.

If the direct path contribution $D_v(\epsilon)$ is known, the resonant path contribution can be expressed as

$$\text{Re}[Q_v(\epsilon)] \approx (S_v(\epsilon) - |D_v(\epsilon)|^2) / 2\text{Re}[D_v(\epsilon)] \quad (4.45)$$

where it was assumed that $|Q_v(\epsilon)|^2 / |D_v(\epsilon)|^2 \ll 1$ and $\text{Im}[D_v(\epsilon)] \approx 0$, both of which are good approximations in the particular case of H_2 ionization close to the Q_1 resonance. In a more general case, when these approximations do not apply, it may still be possible to retrieve the resonant contribution, however a more involved procedure would be required.

The connection between the dynamics in the Q_1 state and the photoelectron spectra

Let us now consider only the resonant channel contribution. Its dipole

$$\tilde{D}_v(\epsilon) = D_q \int_0^\infty dt e^{i(E_v + \epsilon)t} V_v(t), \quad (4.46)$$

which is also expressed in (4.29), closely resembles a Fourier transform. Therefore, it can be concluded that the photoelectron spectra of the resonant channel is the energy representation of the time-dependent Franck–Condon overlap

$$V_v(t) = \frac{1}{\sqrt{2\pi}} \int dR \chi_v^*(R) \sqrt{\Gamma(R)} \Psi_q(R, t)$$

between the wavepacket Ψ_q moving on the Q_1 state, the final vibrational eigenfunction χ_v (together with the electron-electron coupling Γ responsible for the autoionization decay). Consequently, if the resonant channel contribution can be extracted from the photo-electron spectra, a Fourier Transform can be used to obtain $V_v(t)$

$$\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} d\epsilon e^{-i\epsilon t} \text{Re}[Q(\epsilon)] = \frac{1}{2} \sqrt{2\pi} (e^{iE_v t} V_v(t) + e^{iE_v t} V_v^*(-t)) \quad (4.47)$$

and hence the dynamics of the wavepacket in the Q_1 resonant state.

4.7.2 Reconstruction results and discussion

In order to demonstrate the reconstruction of the dynamics of the Q_1 state decay, three vibrational states $\nu=0, 6$ and 12 (see figures 4.2 and 4.7) are selected that represent low, middle and high energy states of the vibrational progression of H_2^+ ground state. The real part of the resonant channel contribution, plotted in figure 4.8a, is then obtained by evaluating the right hand side of (4.45). The direct channel is obtained from *ab initio* calculations (see figure 4.8a). Additionally, an analogous quantity obtained by using the analytical semiclassical model presented in sections 4.3.2 and 4.3.3 is plotted in figure 4.8b for the case when the “dressing” of the Q_1 state by the ionization continuum is on (full lines) and off (dashed lines). This corresponds to including only the direct excitation of the Q_1 state ($D_q \equiv D_q^{(0)}$) or both the direct and continuum excitation channels ($D_q \equiv D_q^{(0)} + D_q^{(1)}$), see section 4.3.2 for the discussion.

Overall, the spectra obtained using the *ab initio* calculations and the semiclassical approach are in good agreement. The minima and maxima of the curves match well for $\nu=6$ and $\nu=12$ cases. However, for the $\nu=0$ final vibrational state the agreement is less satisfactory. A systematic shift of the modulations to higher photon energies is present in the analytically calculated spectra, as compared to the *ab initio* result.

The lineshapes of the vibrationally resolved photoionization spectra shown in figure 4.8 are determined by the phase accumulated due to the vibrational dynamics on the Q_1 state, as discussed above. Nevertheless, the electronic phase

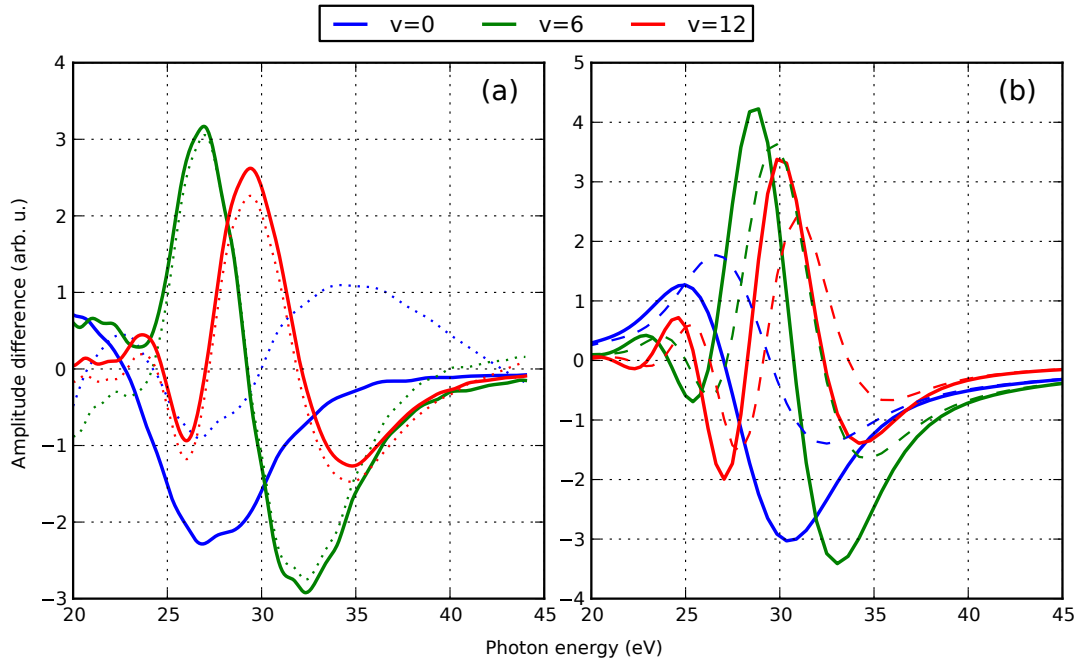


Figure 4.8: (a) The difference between the full spectra and the direct-only contribution for the selected vibrational states. The direct channel is obtained using *ab initio* numerical calculation (full lines) and by a fitting procedure (dotted lines), see text for details. (b) The real part of the resonant channel ionization dipole into selected final vibrational states obtained using the semiclassical model. The real part of the full dipole (full lines) and the dipole omitting the “dressing” of the Q_1 state by the ionization continuum (broken lines) are shown.

acquired during the excitation of the Q_1 state introduces an additional overall shift of the lineshapes in the photoelectron energies without significantly modifying their structure, as is evident from figure 4.8b. This shift does not depend on the vibrational dynamics of the molecule, but it is proportional to the electron–electron interaction strength, e.g., the square root of Γ , and therefore is a signature of a purely electronic phase. Hence, while the overall photoionization lineshape is determined mainly by the phase accumulated due to the vibrational dynamics, as was discussed earlier, the position of these lineshapes along the energy axis is proportional to the strength of the decay width Γ . Hence, the two spectral features — the lineshape and their energetic position — give almost independent parameters characterizing either vibrational or electronic dynamics of the resonant state.

Reconstruction of the time-dependent decay of the Q_1 state

Performing the Fourier transform of the curves in figure 4.8a and taking the modulus-squared of the transformed spectra allows one to retrieve the time-dependent population transfer rates from the Q_1 state to each of the final vibrational states

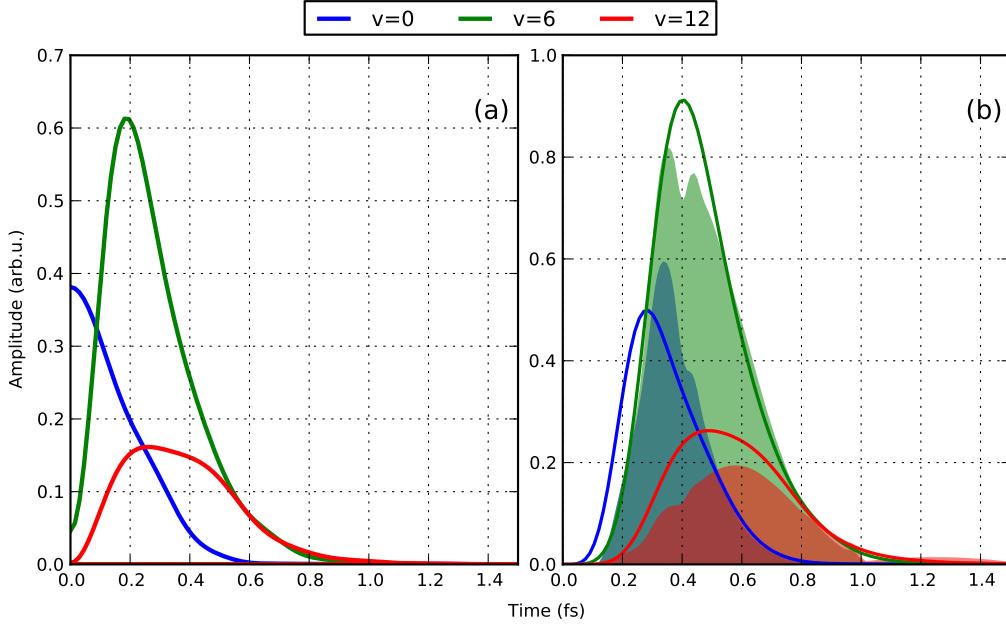


Figure 4.9: (a) Reconstructed population transfer into the selected vibrational states as a function of time after ionization using *ab initio* direct channel. (b) Time-dependent population transfer into selected final vibrational states obtained using numerical calculation where only the resonant channel was included (shaded area) and reconstruction result convoluted with the laser field envelope (full lines).

(see figure 4.9a). They are compared in figure 4.9b with the rate calculated numerically using the *ab initio* method, where the Q_1 state is fully included, but the direct ionization dipole matrix elements between H_2 ground state and the ground state of H_2^+ are set to zero. It allows one to single-out the resonant channel contribution to the final vibrational state populations and thus, to retrieve the rate of population transfer from the Q_1 state to the H_2^+ ground electronic state as a function of time (shaded area in figure 4.9b). Finally, in order to directly compare the rates extracted from the time-dependent *ab initio* calculation with the reconstructed rates in figure 4.9a, the latter were convoluted with the envelope of the laser pulse used in the *ab initio* calculations (full lines in figure 4.9b).

The reconstructed and numerically calculated population transfer rates in figure 4.9a and figure 4.9b reveal the time-energy mapping discussed above and illustrated in the inset of figure 4.1. Namely, each final vibrational state is populated during a short time window of a fraction of femtosecond and centred around a specific time after ionization. Furthermore, this time is increasing for higher vibrational numbers v . Hence, each final vibrational state captures a “time-frame” of the decay of the Q_1 doubly excited state. Since the decay into bound vibrational states finishes in under 1 fs, the time resolution between the different “frames” is just a fraction of a femtosecond providing an intrinsic attosecond clock. Furthermore,

the attosecond time resolution is compatible with excellent spectral resolution that can be achieved due to the single-photon nature of the process.

4.7.3 Fitting of the direct channel contribution

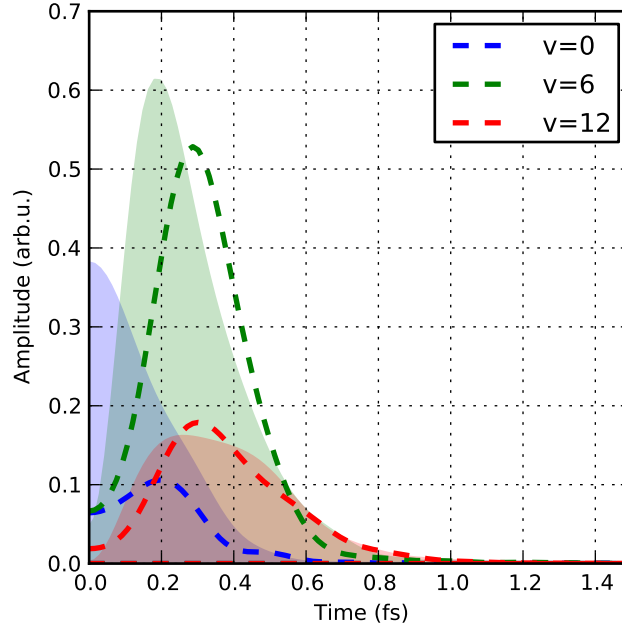


Figure 4.10: Reconstructed population transfer into the selected vibrational states as a function of time after ionization using fitted direct channel (broken lines). The reconstructed rates using the *ab initio* direct channel data, the same as in figure 4.9a, are also displayed as filled area for direct comparison.

v	0	6	12
a	5.17	3.67	0.44
b	0.184	0.102	0.055
c	0.072	0.048	-0.049
I_p (eV)	15.7	17.1	18.

Table 4.2: Fit parameter values.

The reconstruction procedure introduced above relies on the knowledge of the direct photoionization contribution. Here, the *ab initio* calculation where the Q_1 doubly excited states are artificially removed is used. Although, in many cases, the direct channel can be reliably calculated, this may not always be the case and an estimate of the direct channel may not be available. Hence, to address such circumstances we additionally estimate the direct-only transition spectra by performing a standard least-square fit of the full photoelectron spectra using the

guess function

$$f(\omega) = a e^{-b(\omega - I_p)} + c \quad (4.48)$$

where a , b and c are fit parameters, ω is the photon energy and I_p is the ionization potential of H_2 into a particular vibrational state. An additional constraint is introduced requiring that the guess function must match exactly the fitted spectra at $\omega > 40$ eV, i.e., where the Q_1 resonant state does not contribute. The values obtained for the fit parameters are summarized in table 4.2. The difference spectra obtained using the fitted direct channel is plotted as dotted lines in figure 4.8a. We can see that the fitting procedure gives a reasonable agreement with the exact *ab initio* results for higher vibrational states $\nu=6$ and $\nu=12$ while for $\nu=0$ the agreement is rather poor. Consequently, the decay rate reconstructed using the fitted direct channel, which is plotted in figure 4.10, matches the rates reconstructed using the *ab initio* data for the direct channel rather well for $\nu=6$ and $\nu=12$ states. However, the match is poor for $\nu=0$ state.

4.8 Conclusions

We have demonstrated an analytical approach that is able to describe the decay of autoionizing states into the final bound vibrational eigenstates of molecules. The method is based on the time-dependent semiclassical approximation and accurately describes vibrational dynamics in the regions of the potential energy surfaces where the wavefunction nature of the vibrational wavepackets is important and therefore the time-independent semiclassical approximations (WKB) encounter difficulties. Comparison with *ab initio* calculations for the Hydrogen molecule shows that our model provides a faithful description of the underlying dynamics.

Employing the developed methodology we showed that the lineshapes arising in vibrationally resolved one-photon ionization of molecular hydrogen close to the energy of the Q_1 resonance are very sensitive to nuclear dynamics in the resonant state. Importantly, it is not the motion along the internuclear coordinate of the wavepacket but the additional phase mask it acquires due to the momentum evolution on the dissociating surface that is the determining factor in the formation of the spectrum. Finally, we showed how the final spectral lineshape can change from molecular-like to atomic-like with increasing molecular mass because of the interplay between timescales arising due to the nuclear motion, through the Franck-Condon overlap, and due to the electronic decay, through the decay width Γ .

The maximum of the FC overlap of the resonant state with different final vibrational states is obtained at different times after ionization. Consequently, the

lineshape correlated with each final vibrational state reflects a snapshot of the dynamics on the resonant state within a different time window. Therefore, the photoelectron spectra associated with each final vibrational state captures a different time instance of electronic decay encoding information on both the vibrational motion on the transient state and the decay rate. They can be extracted from the experimentally measured photoelectron spectrum when the direct ionization contribution not perturbed by the electronic decay is available. Moreover, it is possible to obtain reliable results using a straightforward fit of the experimental data.

In the case of H_2 photoionization studied here, the molecular clock provides a time-resolution which is a fraction of a femtosecond and is able to time-resolve the ultrafast AI decay. Importantly, the probe is provided by the intrinsic electronic and vibrational dynamics of the molecule and therefore is always perfectly synchronized to the pump pulse. This allows to combine excellent spectral resolution with a sub-femtosecond time resolution.

This work uses the H_2 molecule as a reference system because highly accurate *ab initio* calculations, potential energy surfaces and dipole coupling are available, allowing one to test the validity of our methodology. Nevertheless, it can be used as a “recipe” to study other molecular systems. Moreover, the description is not limited to doubly excited electronic states embedded into the ionization continuum but could in principle be applied to any transient state that decays by emitting an electron. For example, the Resonant Auger Decay, where nuclear motion in the core excited states has a strong influence on the final Auger electron spectra, can be a possible target of studies, see [32, 33] and the references therein.

Finally, the atomic Fano resonances have recently become an active field of study in the ultrafast physics community, with direct time-dependent spectroscopic approaches used to trace the decay of resonant states [34, 35]. The prime goal of these experiments was to test and refine the tools of ultrafast pump-probe spectroscopy for studying correlated electronic dynamics. Doubly excited states of atoms provided an excellent test bed for such studies. The analysis of coupled electronic and nuclear dynamics on the 1-fs time-scale in molecules appears to be a natural and interesting extension of such experiments. We believe that the time-dependent approach developed here will provides a recipe to interpret ultrafast time-resolved experiments in molecular systems.

Contributions

The work presented in this chapter is based on the initial ideas by Prof. Olga Smirnova from Max–Born institute and also Dr. Alicia Palacios from Universidad Autónoma de Madrid who developed the idea independently. However, the project was led by the author and all the result presented in this chapter except the *ab initio* calculations are the work of the author. These include the development of the theory for photoionization of molecule, the calculation and interpretation of lineshapes and the development of the reconstruction procedure. The *ab initio* calculations were performed by Roger Bello, Dr. Alicia Palacios, Prof. Fernando Martín from Universidad Autónoma de Madrid. The development of numerical code for the 3-state model was performed by the author and was also supported by Dr. Felipe Morales from Max–Born Institute. The development of the analytical model for the semiclassical propagation of quantum wavepacket is based on the ideas by Prof. Misha Ivanov and Dr. Lev Plimak from Max–Born Institute.

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Chapter 5

**Attosecond-XUV+IR
pump-probe spectroscopy of
dissociative ionization of N₂
molecule**

We have just discussed the impact of coupled electron–nuclei motion excited by an ultrashort (attosecond) pulse on the photoelectron spectra. Furthermore, we looked at the manifestation of coherence between two ionization pathways and the vibrational motion. We now move to the analysis of how such coherence can affect the fragmentation dynamics on a much longer timescale. We will focus on the coherent attosecond excitation of several electronic states in the molecular ion, and on the correlated continuum wavepackets associated with these electronic states. Furthermore, we will consider the attosecond XUV pump – IR probe setup using as an example the photodissociation of the N₂ molecule.

5.1 Introduction

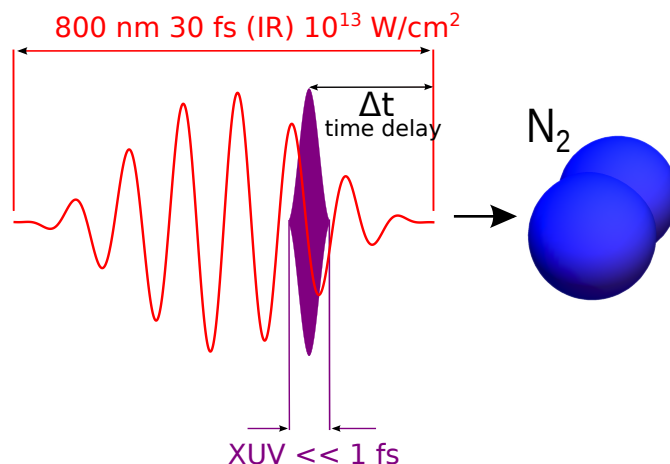


Figure 5.1: Illustration of the XUV-IR pump–probe photoionization of the nitrogen molecule. The attosecond XUV pump is phase locked with the oscillations of the IR laser field with a controllable time delay, allowing one to achieve attosecond time resolution.

A scheme where an attosecond XUV pulse or a pulse train is used in combination with a coherent IR pulse has become a “standard” in attosecond spectroscopy [1]. In this pump–probe scheme, attosecond time resolution is achieved even though the IR pulse can be many tens of femtoseconds long. It is possible due to the microscopic mechanism of HHG that guarantees intrinsic phase locking between the XUV pulse envelope and the waveform of the generating IR field (see section 2.2.1 for more details). Between other things, this scheme has been used to resolve the lifetime of Auger decay [2] and has allowed one to measure the electron–correlation induced delays in the photoionization process as small as few tens of attoseconds [3].

While this approach has been extremely successful in atoms, the interpretation of such pump–probe experiments in molecules is a lot more challenging due to much

more complicated electronic structure and the presence of the additional, nuclear, degrees of freedom. On the other hand, it is precisely for this type of system that the coupling of electronic and nuclear degrees of freedom, as well as the effects of the correlation between the continuum electron and the ionic dynamics, can be anticipated.

Here we study the dissociative ionization of a nitrogen molecule by an attosecond extreme ultraviolet (XUV) pulse in the presence of a weak, few tens of femtoseconds long infrared (IR) pulse, as illustrated in figure 5.1. Thus, we consider the typical attosecond pump-probe setup where the XUV pulse acts as a pump and the oscillations of the IR pulse act as a probe, with the position of the XUV pulse controlled relative to the oscillations of the IR field.

The main result of this chapter is to show that the kinetic energy spectrum of the fragment ions is sensitive to the correlation between the molecular ion and the electron removed by the XUV pulse. Therefore, the initial electronic coherence created in the N₂⁺ ion by XUV ionization on the attosecond timescale can influence dissociation of N₂⁺ that takes $\sim 10^2$ fs. Crucially, the correlation between the departing photoelectron and the parent ion is key in determining the coherence and dynamics of electronic excitation created by ionization. However, up till now this correlation was largely ignored in most works that study coherent dynamics of atoms and molecules after their ultrafast ionization.

5.2 State of the art

Attosecond photoionization naturally creates coherent population of several electronic states. Such electronic wavepacket corresponds to the occurrence of a hole moving across a molecule. The possible impact of hole motion (migration) across a molecule [4] on the longer-term nuclear dynamics has been theoretically discussed by Kuleff et. al. [5] in the context of the hypothesis of charge-directed reactivity, first suggested by Weinkauff et. al. [6, 7]. In [8] the predicted influence of small changes in the nuclear configuration of the glycine molecule on hole dynamics suggested that the interplay between the electronic and nuclear degrees of freedom could indeed influence fragmentation patterns. Mendive-Tapia et. al. [9] showed how this influence can be systematically studied using the Ehrenfest dynamics approach, where the electronic dynamics is treated quantum-mechanically and the nuclear dynamics is treated classically.

Thus, one can envision control of the fragmentation pattern by controlling the initial sub-femtosecond to few-femtosecond hole dynamics. Theoretically such control has been first studied by Dietrich et. al. [10] for HCl molecule and

by Thachuk et. al. [11, 12] for dissociative ionization of H₂, where the sub-femtosecond modulation of potential energy surface (PES) was considered as the control mechanism. In both works, the modulations of the PES were driven by the oscillations of the strong IR laser field, leading to the concept of the time-dependent Born–Oppenheimer surfaces [13]. The control of their modification on a sub-cycle timescale using the carrier-envelope phase of an ultrashort laser pulse was predicted by Haljan et.al. [14].

Experimentally, the possibility to influence molecular fragmentation patterns on the sub-femtosecond timescale using a strong IR field was demonstrated by Kling et. al. for the case of dissociative ionization of D₂⁺ molecules into D⁺ [15]. Electrons were steered by the IR field during the dissociation of molecular ion, along the repulsive $2p\sigma_u$ state, resulting in control of electron localization onto one of the two fragments. A similar observation was made in two-colour XUV+IR pump–probe experiment on H₂ where an isolated attosecond pulse was used to launch a dissociative wavepacket on the $2p\sigma_u$ state [16].

A recent experiments on H₂ [17] using a combination of an attosecond pulse train and a co-propagating IR laser demonstrated the sensitivity of H⁺ fragment kinetic energy spectra on the the time delay between XUV and IR pulses, which were temporally overlapped. The explanation of this experiment showed some similarities to the RABBITT (Reconstruction of Attosecond Beating By Interference of Two-photon Transitions) technique used to characterize the attosecond pulse trains [18]. However, in this case the attosecond XUV pulses ionized the H₂ molecules into the $1s\sigma_g$ continuum whereas the two-colour XUV±IR ionized the molecules into the $2p\sigma_u$ continuum. The interference of the two-photon transitions resulted in the modulation of the ionization probability into the $2p\sigma_u$ continuum as a function of XUV–IR time-delay. The dissociation of the H₂⁺ ions created in the repulsive $2p\sigma_u$ electronic state in turn led to the oscillation in the H⁺ fragment yield.

A more recent experiment by Ranitovic et. al. [19] showed the possibility of coherent control of photodissociation dynamics of H₂ molecules. In this work, an XUV+IR pump together with a time-delayed IR probe were used. It was demonstrated that both the total ionization yield and the H⁺ dissociation fragment yield depend on the XUV frequency and pump–probe time delay which also implied the control of coupled electron–nuclear dynamics on the attosecond time scale.

In this chapter, we discuss a mechanism that relies on the interplay between attosecond electronic coherence, which is established by the XUV ionisation, the coherence due to femtosecond nuclear motion on different, coherently populated PES, and the liberated electron wavepackets correlated to these ionic channels. Both the initial electronic coherence and the coherence between vibrational wavepackets

on different coherently populated PES play a crucial role in determining the final fragment kinetic energy spectra. We will consider the example of N₂. However, the mechanism we will present is general and it will arise in any pump–probe experiment that involves an isolated attosecond pump pulse or a train of attosecond pulses and an IR probe pulse phase locked to the XUV pump.

In general, the overlaps of the continuum electron wavepackets correlated to different ionic states are crucial for observing coherent electronic dynamics in the molecular and atomic ions. Here we demonstrate how these overlaps can influence vibrational dynamics on femtosecond time scales. Thus, the interference of vibrational wavepackets is affected by the coherence of the continuum electronic wavepackets entangled with the cation. Specifically, this interference is controlled by the photoionization (half-scattering) phases in different photoionization channels. The fragmentation outcome is controlled by the electronic coherence even for an uncorrelated measurement, which does not specify any of the properties of the photoelectrons, i.e., which integrates over the continuum electronic wavefunction.

5.3 Theoretical background

To see how initial electronic coherence may impact molecular dissociation, we consider ionization by a sub-femtosecond laser pulse. Due to a broad bandwidth of the pulse multiple coherent vibrational wavepackets are created on different electronic PES of the ion. With each of these electronic states comes a continuum electron wavepacket, correlated to the vibrational wavepacket in energy, momentum and symmetry. The full wavefunction of the system after the end of the XUV laser pulse is:

$$|\Psi(t)\rangle = \sum_i |\phi_i(t)\rangle |\Psi_i(t)\rangle \quad (5.1)$$

where $|\Psi_i(t)\rangle$ are the vibronic states of the ion associated with ionization into the ion electronic eigenstate $|i\rangle$. With each of these vibronic states comes a continuum electron wavepacket $|\phi_i(t)\rangle = \int dE a_i^E(t) |\phi^E\rangle$, correlated to the vibronic wavepacket in channel i in energy, momentum and symmetry. The index i sums over all coherently excited electronic states of the ion. $|\phi^E\rangle$ is an energy-resolved asymptotic continuum eigenstate, which for the i -th ionization channel has an amplitude $a_i^E(t)$.

Consider a measurement which resolves the vibrational continuum states of the molecular ion but which integrates over the states of the photoelectron $|\phi^E\rangle$. Moreover, the measurement of the ionic fragments may or may not discriminate the fragment's exact electronic states.

An illustrative example is the dissociative ionization of $\text{H}_2 \rightarrow \text{H}_2^+ + e^- \rightarrow \text{H} + \text{H}^+ + e^-$, for which the control of electron localization was demonstrated. The two lowest electronic states of H_2^+ , the gerade and ungerade states σ_g and σ_u , become degenerate as the internuclear distance $R \rightarrow \infty$. A practical measurement may not distinguish between the two but will be able to detect an H^+ fragment moving in a particular direction, say, towards a “left” detector, measuring localization of the bound electron on the H atom moving in the opposite direction, i.e. to the “right” detector (see e.g. [15, 16, 20]). The measurement basis associated with left and right localized electronic states is $|n_{\pm}\rangle = 1/(\sqrt{2})|\sigma_g \pm \sigma_u\rangle$. Thus, electronic degeneracy upon dissociation may lead to a measurement basis that is different from the electronic states produced near the equilibrium geometry (also see section 2.3.1 for a detailed discussion).

Let us now specify a measurement basis for the electronic states of the ionic fragments $|n\rangle$. This basis is not necessarily coincident with the electronic eigenstates that are adiabatically connected to the states $|i\rangle$ of the molecular ion near the equilibrium configuration. This way we also naturally include processes such as autoionization and non-adiabatic transitions, where the different initial electronic states $|i\rangle$ initially populated by the laser pulse converge to the same final electronic state $|n\rangle$. In the illustrative example of H_2 this means, for example, excitation of a Q_1 autoionizing series followed by autoionization and dissociation in the $|\sigma_g\rangle$ continuum. In this case, even a measurement that selects the $|\sigma_g\rangle$ state will not be able to distinguish the two pathways leading to the same fragments, resulting in an interference, see Sansone et. al. [16] for detailed experimental and theoretical discussion.

The probability amplitude associated with a measurement on (5.1) detecting the continuum electron in a state $|\phi\rangle$, the ion in a state $|n\rangle$ and projecting the vibrational wavepacket on a state $|\chi\rangle$ is

$$A_n(\phi, \chi, t) = \langle n | \langle \phi | \langle \chi | \Psi(t) \rangle \quad (5.2)$$

The probability $W_n(\chi, t) = |A_n(\chi, t)|^2$, integrated over all final states $|\phi^E\rangle$ of the continuum electron,

$$\begin{aligned} W_n(\chi, t) &= \int d\phi^E |A_n(\chi, t)|^2 = \sum_i |\langle n\chi | \Psi_i(t) \rangle|^2 \\ &+ \sum_{i \neq j} \langle \Psi_j(t) | n\chi \rangle \langle n\chi | \Psi_i(t) \rangle \times \langle \phi_j(t) | \phi_i(t) \rangle. \end{aligned} \quad (5.3)$$

is a sum of contributions from each individual ionization channel i plus the inter-

ference term between the channels. Importantly, the interference terms include the overlaps $\langle \phi_j(t) | \phi_i(t) \rangle = \int dE (a_j^E)^* a_i^E$, i.e. the overlaps of the continuum electron wavepacket $\phi_{i,j}$ correlated to different ionization thresholds i and j . This term must be non-zero for the coherence to affect the dissociation fragment spectra. Therefore (i) a wavepackets initially created in different electronic eigenstates $|i\rangle$ and $|j\rangle$ must contribute to the same final eigenstate $|n\rangle$ and (ii) the overlap $\langle \phi_j(t) | \phi_i(t) \rangle = \int dE (a_j^E)^* a_i^E$ of the photoelectron wavepackets $\phi_{i,j}$ must be significant.

5.4 Photodissociation of N₂ molecule in two-colour XUV+IR laser fields

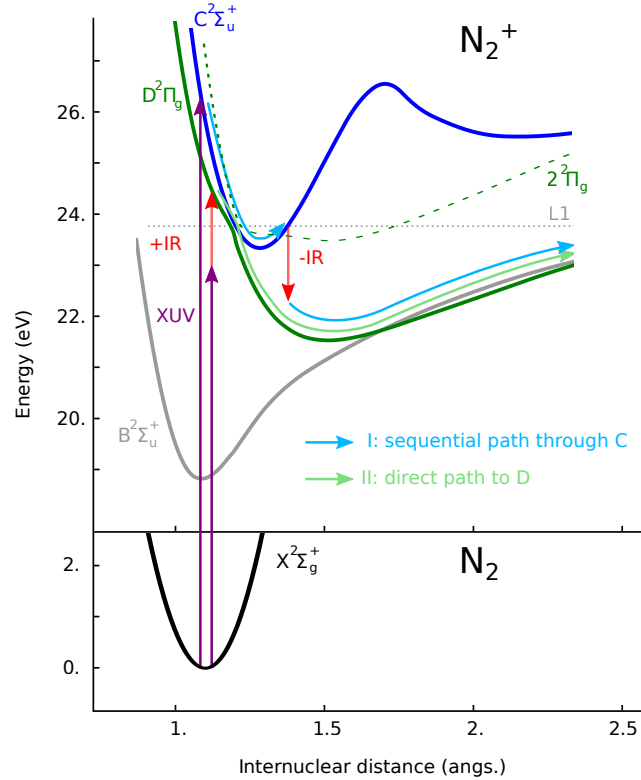


Figure 5.2: Sequential XUV–IR (I) and direct XUV+IR (II) dissociation pathways leading to low energy N⁺ fragments and the relevant potential energy curves (see text for further explanation). 2²Π_g is the upper adiabatic branch of the D²Π_g state, which for simplicity is not included in the calculation. The horizontal dotted line indicates the dissociation limit. The bandwidth of a 500 as (FWHM) pulse spans an energy range of ~7 eV.

In what follows, we investigate the case of the N₂ molecule exposed to an XUV+IR laser field. After ionization, the N₂⁺ molecular ion dissociates, and a

detector measures the kinetic energy release (KER) spectrum of N⁺ fragments. We consider two fragmentation pathways, enabled by XUV photoionization in the presence of an IR dressing field, leading to the low energy fragments [21] (figure 5.2).

The first pathway, labelled XUV–IR (I), describes the sequential transition that consists of the following two steps. The first step is attosecond XUV-induced photoionization into the bound C²Σ_u state of N₂⁺. This leads to the formation of a coherent superposition of vibrational states of the C²Σ_u potential, each with a well-defined energy. The second step is the de-excitation of the wavepacket by the IR field into the dissociative D²Π_g state, after propagating on the C²Σ_u surface for some time. Within the validity region of Franck–Condon approximation, i.e., where the electronic potential energy curves are well separated and dipole coupling matrix elements are smooth, which is also the case here, the laser wavelength determines the internuclear distance where the second step occurs. For an IR wavelength λ = 800 nm, which was used in this work, the one photon de-excitation occurs near the outer turning point of the vibrational motion at the point of one-photon resonance.

The second pathway, labelled XUV+IR (II), describes the direct two-photon transition that reaches the dissociative D²Π_g state after absorbing both an XUV photon (from the attosecond XUV pulse) and an IR photon.

For the aforementioned pathways to interfere there must be an overlap of the photoelectron wavepackets produced after ionization in each path. For the XUV+IR pathway the ionization leads directly to the D²Π_g state, while for the XUV–IR case it leads to the C²Σ_u state. In the latter case the sequential transition due to IR field takes place in the ion therefore it does not affect the photoelectron wavepacket. Indeed, it takes about ≈ 7 fs for the vibrational wavepacket in the C²Σ_u state to reach the outer turning point. This time is enough for the photoelectron to depart far away from the ion, where the short range part of the ionic potential is negligible. Hence, at the time of sequential transition in the ion the photoelectron will feel only the long-range part of the ionic potential, which does not depend on the electronic state of the ion.

Given the strengths and the energetics of the XUV-induced transitions, the main contributing intermediate virtual state for the XUV+IR transition is the B²Σ_u⁺ state. The X²Σ_g state, which has a strong single-photon ionization dipole, does not couple with the D²Π_g state by the IR field due to the symmetry considerations. Furthermore, the dipole matrix element between the A²Π_u electronic state and the D²Π_g state is significantly smaller than that between the B²Σ_u⁺ and the D²Π_g state. All other possible intermediate states have much smaller single-photon ionization dipoles and are therefore not considered here.

Photoionization into the $C^2\Sigma_u^+$ state is much weaker than into the $B^2\Sigma_u^+$ state and therefore a direct XUV–IR pathway via the $C^2\Sigma_u^+$ state into the $D^2\Pi_g$ state is much weaker. On the other hand, while the strength of the direct transition is proportional to the IR pulse intensity at the moment of arrival of the XUV pulse, the sequential transition is proportional to the square of the integral over the IR pulse from the time of arrival of the XUV pulse to the end of the IR pulse, see appendix D. Hence, for sufficiently long IR pulses the sequential pathway allows plenty of time for the resonant IR transition, compensating for the relatively low probability of one-photon ionization into the $C^2\Sigma_u^+$ state. Therefore, the sequential XUV–IR pathway can efficiently compete with the direct XUV+IR pathway. Finally, the sequential XUV+IR transition via the $B^2\Sigma_u^+$ state is much less likely due to the very low probability of the off-resonant IR coupling.

5.5 Estimate of coherence between ionization channels of N₂ molecule

A significant degree of coherence between the ionization channels i and j , which is expressed by the overlaps $\langle\phi_j(t)|\phi_i(t)\rangle$ in section 5.3, is of key importance to observe any dependence of vibrational dynamics in the molecular ion on the photoionization (scattering) phase. Such coherence is expected to occur after ultrafast ionization by an ultrashort laser pulse [22, 23] and has been observed in studies of electron localization [16, 24]. Here we evaluate it for the special case at hand.

We are considering two photoionization channels: the channel I that represents one-photon ionization into the $C^2\Sigma_u^+$ state and the channel II that represents two-photon XUV+IR ionization into the $D^2\Pi_g$ state of N₂⁺ molecule. Hence, the wavefunction after photoionization is

$$|\Psi\rangle = |\Psi_D\rangle|\phi_D\rangle + |\Psi_C\rangle|\phi_C\rangle \quad (5.4)$$

where $|\Psi_C\rangle$ and $|\Psi_D\rangle$ are the target eigenstates of the N₂⁺ ion and $|\phi_{C,D}\rangle$ are the corresponding photoelectron wavepackets.

The coherence between different photoionization channels is directly related to the off diagonal elements of the density matrix. It is defined as

$$\rho = \langle\epsilon|\langle\Psi_{C,D}|\Psi\rangle\langle\Psi|\Psi_{C,D}\rangle|\epsilon\rangle \quad (5.5)$$

and where the photoelectrons are traced out. In the above, $|\epsilon\rangle$ is a photoelectron (single electron) eigenstate with an asymptotic energy ϵ . In addition, $|\Psi_C\rangle$ and

$|\Psi_D\rangle$ are assumed to be orthonormal.

The amount of coherence g between the $|\Psi_C\rangle$ and the $|\Psi_D\rangle$ ionization channels can be quantified using the off-diagonal elements of the reduced density matrix ρ

$$g = \frac{\rho_{CD}}{\sqrt{\rho_A \rho_D}} = \int d\epsilon \frac{\langle \epsilon | \phi_D \rangle \langle \phi_C | \epsilon \rangle}{\sqrt{|\phi_D|^2 |\phi_C|^2}} = \frac{\langle \phi_C | \phi_D \rangle}{\sqrt{|\phi_D|^2 |\phi_C|^2}} \quad (5.6)$$

and is directly related to the overlap of photoelectron wavepackets correlated to each channel.

perpendicular		parallel	
channel (l, m)	coherence $ g_{l,m} $	channel (l, m)	coherence $ g_{l,m} $
(2,1)	0.77 (0.97)	(2,0)	0.89 (0.93)
(4,1)	0.46 (0.68)	(0,0)	0.45 (0.73)
(4,3)	0.51 (0.74)	(4,0)	0.76 (0.81)

Table 5.1: Amount of coherence between considered ionization channels for each partial wave for an XUV field oriented perpendicular and parallel to the molecular axis. The channels are arranged in an order of decreasing strength. The values in brackets are for dipoles with removed continuum resonances.

Let us assume that in the XUV+IR photoionization channel II, the XUV photon is absorbed by the photoelectron while the IR photon is absorbed by the residual ion. Hence, this channel can be described by the photoionization dipole for the B²Σ_u⁺ target state while the IR photon transfers the population from the B²Σ_u⁺ state into the D²Π_g state.

The R-matrix method [25] was used to obtain the one-photon ionization dipoles into the C²Σ_u⁺ and the B²Σ_u⁺ (intermediate) states, which are resolved in final energy and (l, m)-partial wave channel (see figure 5.3):

$$d^{C,B}(\epsilon, l, m) = \sum_{l,m} a_{l,m}^{C,B}(\epsilon) Y_{l,m} \quad (5.7)$$

where $Y_{l,m}$ are spherical harmonic functions (see ref. [25] for more details). The dipoles are calculated for equilibrium internuclear distance. Also note, that the ionization dipoles in figure 5.3 contain a lot of sharp structures originating from the doubly excited states. However, the R-matrix code does not provide accurate representation of these states and therefore the continuum resonances might be inaccurate. Hence, the coherence is also evaluated when the resonances are removed from the dipoles. This is done by simply applying a Gaussian filter of width 0.07 hartree to the full dipoles.

In the R-matrix code, the dipoles are calculated between the N₂ ground state

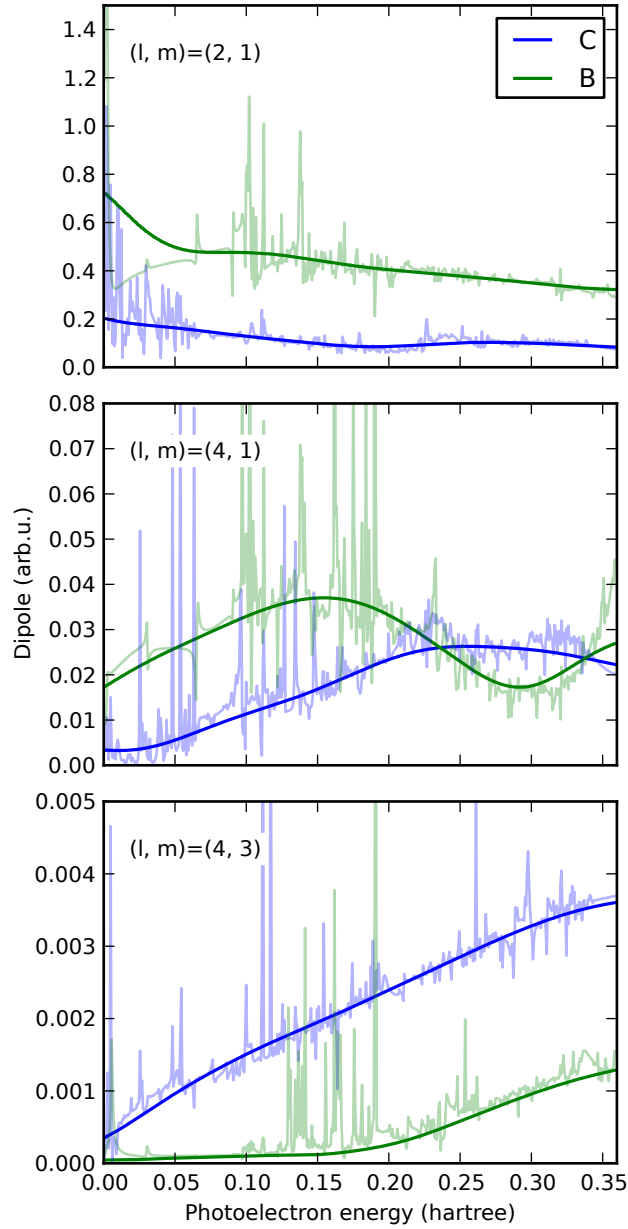


Figure 5.3: Dipoles for one-photon ionization into the $C^2\Sigma_u^+$ (blue) and $B^2\Sigma_u^+$ (green) target states of the N_2^+ ion and for different final (l, m) partial waves for laser polarization perpendicular to the molecular axis. Sharp peaks present in the dipoles, which are due to the continuum resonances, are removed by a Gaussian filter of width 0.07 hartree (bold lines).

and outgoing scattering states $|\phi^- \rangle$, in which case (5.6) becomes

$$g = \frac{\rho_{CD}}{\sqrt{\rho_A \rho_D}} = \iint d\epsilon_{C,D} \frac{\langle \phi_C^- | \epsilon_C \rangle \langle \epsilon_C | \epsilon_D \rangle \langle \epsilon_D | \phi_D^- \rangle}{\sqrt{|\phi_D^-|^2 |\phi_C^-|^2}} \approx \int d\epsilon \frac{\langle \phi_C^- | \epsilon_C \rangle \langle \epsilon_D | \phi_D^- \rangle}{\sqrt{|\phi_D^-|^2 |\phi_C^-|^2}} \quad (5.8)$$

where we assume that $\langle \epsilon_C | \epsilon_D \rangle = \delta(\epsilon_C - \epsilon_D)$ which in general is not true, since the scattering potentials for B and D ionization channels are different. For low values of ϵ , the amount of the coherence, estimated below, gives an upper bound. The approximation $\langle \epsilon_C | \epsilon_D \rangle = \delta(\epsilon_C - \epsilon_D)$ improves for high photoelectron energies ϵ . Note also, that the approximation above does not influence the accuracy of the dipoles, but only the estimate of the coherence between the photoionization channels.

Using the dipoles in (5.7), (5.8) for each final (l,m) partial wave can be written as

$$g_{l,m} = \sum_{\epsilon} (a_{l,m,\epsilon}^B)^* a_{l,m,\epsilon}^C / \sqrt{\sum_{\epsilon} |a_{l,m,\epsilon}^B|^2 \sum_{\epsilon} |a_{l,m,\epsilon}^C|^2}. \quad (5.9)$$

Note, that, as mentioned earlier, the dipoles for one-photon ionization into the B²Σ_u⁺ state are used to quantify the two-photon ionization into the D²Π_g state.

For one-photon ionization into the B²Σ_u⁺ and C²Σ_u⁺ final target states and for a XUV field oriented perpendicular to the molecular axis only 3 channels contribute significantly. The amount of coherence obtained from (5.9) for these channels is summarized in table 5.1. The estimate suggests that the amount of coherence created between the I and II photoionization channels can be quite large.

The high level of coherence between the two photoionization channels can be understood by inspecting the cosine of their phase difference $\delta_{l,m}(\epsilon)$ as a function of energy

$$\cos(\delta_{l,m}(\epsilon)) = \frac{(a_{l,m,\epsilon}^B)^* a_{l,m,\epsilon}^C + \text{c.c.}}{2|a_{l,m,\epsilon}^B||a_{l,m,\epsilon}^C|}, \quad (5.10)$$

which is plotted in figure 5.4. Despite sharp jumps in the phase, the average phase difference over a small energy region is approximately constant and changes only slowly with photoelectron energy. This means that, when contributions to all the photoelectron energies are summed up, the phase variation does not wash-out the interferences.

In an experiment, the photoelectron energy is determined by the laser frequency and bandwidth. From figure 5.4 it can be seen that by changing the laser frequency and thus the photoelectron energy it is possible to control the photionization phase difference between the channels.

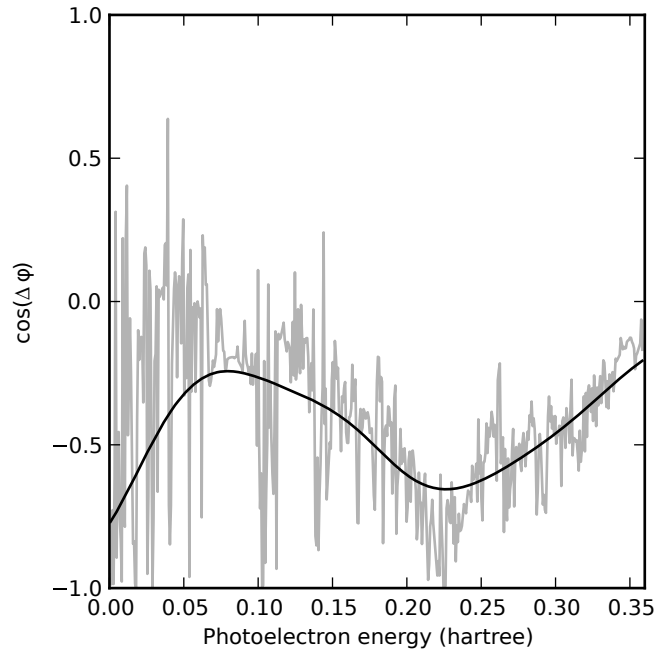


Figure 5.4: Cosine of the phase difference between the dipoles for photoionization into the $C^2\Sigma_u^+$ and $B^2\Sigma_u^+$ states as a function of photoelectron energy. The phase is shown for the dominant $(l,m)=(2,1)$ partial wave and for the XUV field perpendicular to the molecular axis. The phase difference for dipoles that include the continuum resonances (gray line) and without the continuum resonances (black line) are shown.

5.6 Effect of the photoionization phase on the N⁺ fragment spectra

The overlap of photoelectron wavepackets $\phi(t)$ originating from the photoionization channels I and II will allow the vibronic wavepackets $\Psi(t)$, originating from paths I and II, to interfere on the detector. Within the Born–Oppenheimer approximation, the latter can be described in terms of vibrational wavepackets $\chi(R,t)$ moving on electronic potential curves of the ion. The final KER spectra will depend both on the phase of the photoelectron wavepacket $\phi(t)$, accumulated during the ionization, and the phase of the vibrational wavepacket $\chi(t)$, accumulated during propagation along the paths I and II towards dissociation.

Control of the XUV and IR pulse parameters allows one to manipulate the interference between paths I and II. First, the relative strength between the sequential XUV–IR (I) and direct XUV+IR (II) transitions can be tuned by changing the duration of the XUV and IR pulses: the probability of the sequential pathway increases when increasing the IR pulse duration.

The interference of the dissociating pathways also depends on the relative phases accumulated in the vibrational continuum on the way towards the final

state $|n\rangle|\chi\rangle$. The phase accumulated by the vibrational wavepacket depends on the potential on which the wavepacket is moving. Hence, the vibrational phases can be controlled by a dressing laser field both by modifying the potential energy surfaces in a time-dependent manner [26] via non-resonant Stark shifts, and also by inducing real transitions between the electronic states. In the former case, the same potential is modified adiabatically by the strong laser field. In the later case, the potential is switched altogether due to the laser field induced transition.

5.6.1 Calculation details

We now turn to study the role of electronic coherence created upon ionization on the nuclear dynamics in the molecular ion by solving the Time-Dependent Schrödinger Equation (TDSE) for the vibrational wavepackets $\chi(R, t)$ in the N₂⁺ ion in the IR laser field. We consider two limiting cases: no coherence and perfect coherence between ionization channels. In section 5.3 it corresponds to respectively $\langle\phi_j(t)|\phi_i(t)\rangle = 0$ and $e^{-i\delta}$, where we additionally consider two different values of the scattering phase difference δ .

We employ a combined XUV and IR laser field, with parameters similar to those in [16, 17, 27]. The IR pulse has a wavelength $\lambda = 800$ nm and 30 fs full width half-maximum (FWHM) long, with a peak intensity of 10^{13} W/cm². It is polarized perpendicular to the molecular axis. The XUV field is taken to be an isolated attosecond pulse sufficiently short (FWHM = 0.5 fs) compared to the IR laser half-cycle and the nuclear dynamics. Hence, photoionization can be described by a vertical Franck–Condon transition onto the cationic electronic states assuming the sudden ionization approximation, i.e. that the vibrational distribution after ionization is the same as that of N₂ ground state vibrational wavepacket. The XUV carrier frequency is $\Omega \simeq 25$ eV, which predominantly leads to the formation of the X²Σ_g⁺, A²Π_u, and B²Σ_u⁺ bound ionic states, and low-lying vibrational levels of the C²Σ_u⁺ state [21, 28]. The latter predissociate into the B²Σ_u⁺ state creating a well known vibrational structure [29] in the low energy N⁺ KER. However, the predissociation takes place on nanosecond timescales and is therefore independent of XUV-IR time delay.

The wavepackets were propagated on the B²Σ_u⁺, C²Σ_u⁺ and D²Π_g PES of N₂⁺ coupled by the IR field. Spectroscopically, the D²Π_g state of N₂⁺ is known to arise from the strongly-interacting pair of ²Π_g states [28]. For simplicity, we chose to include only the lower adiabatic branch of this pair in our simulations. It is responsible for the de-excitation step of the sequential path, and is therefore sufficient to reproduce qualitative features of the I and II dissociation paths.

The XUV ionization cross sections for the $B^2\Sigma_u^+$ and the $C^2\Sigma_u^+$ channels were obtained from the literature [28]. The PES and transition dipoles between the PES were calculated with the GAMESS-US package [30], using aug-cc-pVTZ basis set. The MRCI wavefunctions included all single excitations from CAS(9,8), which was optimized for the $D^2\Pi_g$ state. In addition to the states shown in figure 5.2, a large number of electronic surfaces are present in the cation. However, due to ionization dipole selection rules, energetic positions and weaker couplings to the $C^2\Sigma_u^+$ and $B^2\Sigma_u^+$ states they are less significant for the studied dynamics.

The propagation on the PES coupled by the IR field was performed by a standard split-operator method (see appendix F for more details). The final KER spectrum from the dissociation continuum of the $D^2\Pi_g$ state was extracted by projecting the wavefunction on the continuum vibrational eigenstates of the $D^2\Pi_g$ potential.

5.6.2 Calculation results

Both the initial phase difference and the amplitude of pathways I and II depend on the time delay between the XUV and the IR pulses. To explore the influence of only the initial phase, a set of reference spectra were calculated (figure 5.5), where the contributions from both channels were set to be equal for every time delay. In this calculation, a Franck–Condon (FC) wavepacket corresponding to the ground vibrational state of N₂ was placed on either the $C^2\Sigma_u^+$ or the $D^2\Pi_g$ states of the N₂⁺ ion and propagated in the presence of the IR pulse. The obtained wavefunctions were renormalized such that the dissociating part would be equal for both pathways. Finally, the spectra of their incoherent and coherent sums were obtained for four different arbitrary initial phase difference values. This allowed us to isolate the ionization step from the propagation in the ion and investigate the effect of the initial attosecond phase acquired during the ionization on the final KER spectrum.

The spectrum of the two incoherently added wavepackets (figure 5.5a) shows peaks corresponding to higher vibrational states with $v \geq 10$ of the $C^2\Sigma_u^+$ potential due to de-excitation of the wavepacket from the $C^2\Sigma_u^+$ to the $D^2\Pi_g$ potential surface (pathway I). They are overlapping with a broad nearly Gaussian shape background that is due to a direct two-photon transition to the $D^2\Pi_g$ state, which is repulsive at the FC point (pathway II). The lower vibrational peaks of the $C^2\Sigma_u^+$ potential are not visible because they are de-excited by the IR into the bound part of the $D^2\Pi_g$ state potential and do not dissociate. The fraction of population resonantly transferred from the $C^2\Sigma_u^+$ to the $D^2\Pi_g$ state in a sequential process is small.

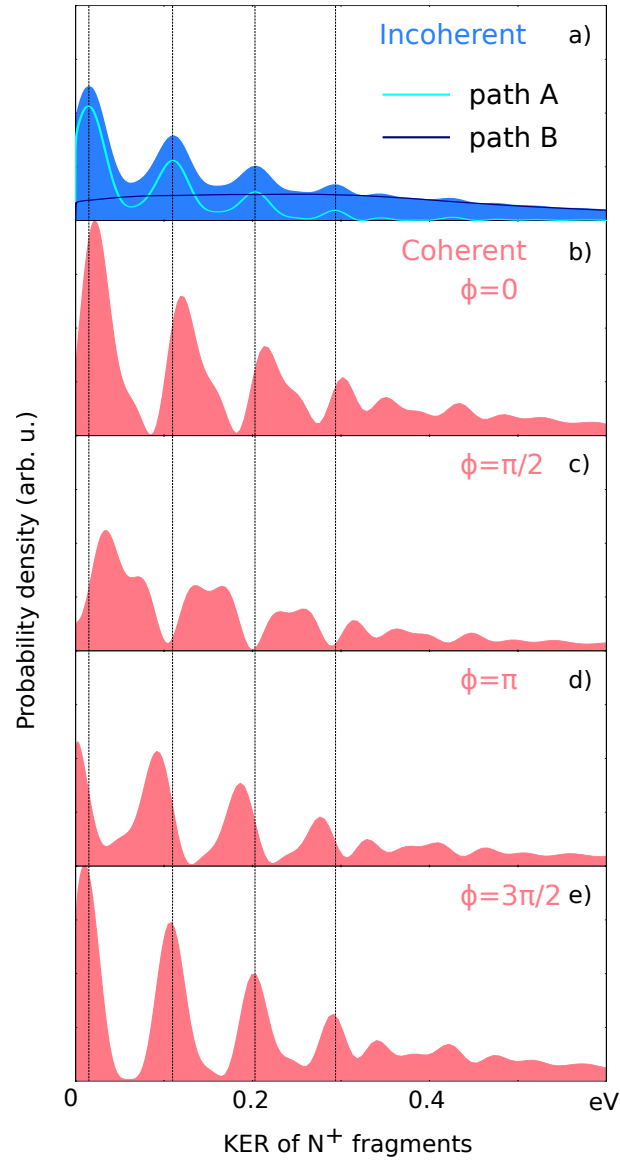


Figure 5.5: The Kinetic Energy Release (KER) spectrum of N⁺ fragments for the case of incoherent (a) and coherent (b, c, d, e) interference of direct and sequential dissociation channels. The coherent spectrum is obtained for 4 different assumed values of initial phase difference δ between the A and B dissociation pathways. Vertical lines mark the position of vibrational peaks resolved in the incoherent spectrum.

Therefore, the broadening of the vibrational lines reflects the bandwidth of the IR pulse, as there are no other decay mechanisms present in the calculation. Finally note, that small computational inaccuracies in the vibrational progression of the C²Σ_u⁺ state are amplified in the KER spectra because the high lying vibrational states have a KER which is close to zero. An additional shift appears because the transition matrix elements for the vibrational states strongly depend on the energy.

The spectra of the coherently added wavepackets (figures 5.5b-e) also show a

peaked structure that can be associated with the vibrational bands. However, the modulation depth is much greater and, as a result, the low-intensity peaks at the higher energy are much more pronounced. Crucially, not only the strength and the shape but also the positions of the peaks change significantly depending on the value of the relative phase between the two dissociative channels determined by photoionization. We remind the reader that these phases can be controlled by the XUV-IR time delay.

The initial phase for each of the channels corresponds to the half-scattering phase of the outgoing photoelectron after the ionization event. It is accumulated due to the interaction of the outgoing photoelectron with the short range core potential of the ion in the presence of the IR field. The value of the scattering phase depends on the particular electronic state of the ion, intermediate resonances the photoelectron may encounter on the way, as well as the properties of dressing laser field.

The interference between the vibrational wavepackets is a result of the interplay between the electronic and vibrational degrees of freedom. No interference can occur due to ionization alone and without the propagation of the nuclear wavepackets, because they are created on separate molecular PES and the vibrational dynamics of the molecular ion is required to bring them to the same electronic state ($\langle \Psi_j(t) | n\chi \rangle \langle n\chi | \Psi_i(t) \rangle \neq 0$ in (5.3)). Also, no interference would be observed in the fragment kinetic energy spectra if the electronic wavepackets would not overlap ($\langle \phi_j(t) | \phi_i(t) \rangle \neq 0$ in (5.3)). It is only the fulfillment of both conditions - overlap of both electronic and vibrational wavepackets, that allows the interference to happen. While one of the conditions is set at the moment of ionization purely due to the electronic coherence, the second is fulfilled only after tens of femtoseconds by the IR field-induced transition between the two PES.

5.6.3 The N⁺ fragment spectra dependence on the time-delay between the XUV and IR pulses

We now turn to a simulation of a time-delay scan that takes into account the relative strength of the two dissociating pathways and their dependence on the time overlap between the XUV and IR pulses. The ionic wavepackets were created as a FC projection of the N₂ ground state vibrational wavepacket at different times during the IR pulse corresponding to the arrival time of the attosecond XUV pulse. One-photon ionization to the C²Σ_u⁺ state (pathway I) was simulated by placing a FC wavepacket in the corresponding state. The direct two-photon XUV+IR ionization (pathway II) was simulated by preparing a FC wavepacket in the B²Σ_u⁺

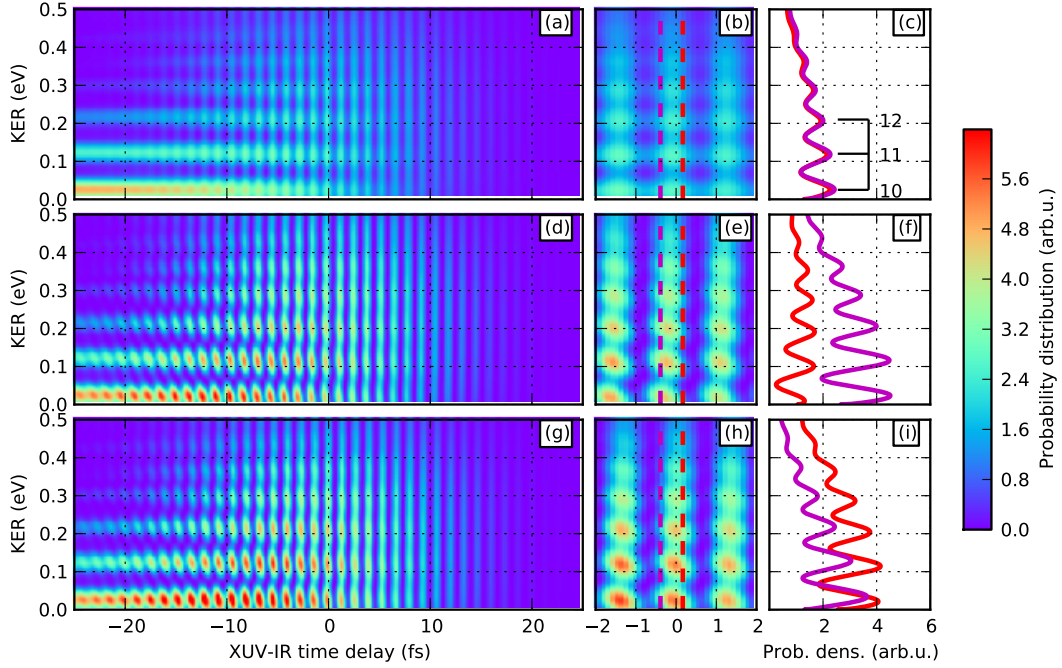


Figure 5.6: Calculated N⁺ KER spectrum as a function of XUV and IR pump-probe time delay for the case of incoherent (a) and coherent (d) and (g) summation between the direct (path II) and sequential (path I) dissociation channels (see section 5.6.3). The KER spectra shown in (d) and (g) were obtained for scattering phase set to $\pi/2$ and 0, respectively. A zoom of the spectra is shown in (b), (e) and (h). Vertical lines show two selected time delays at which the spectra are plotted in (c), (f) and (i). Negative time delay corresponds to the XUV pulse arriving before the IR pulse.

state. The coupling between the $B^2\Sigma_u^+$ and $D^2\Pi_g$ states by the IR field ensured inclusion of the direct transition between the two states as well as the effects of the envelope and the XUV-IR delay-dependent phase of the IR field.

Clear differences can be seen between the time delay spectra when the channels are added up incoherently (figures 5.6a-c) and coherently (figures 5.6d-f and figures 5.6g-i). Although both spectra show a modulation with twice the IR laser field frequency, their origin is different for the coherent and incoherent cases. In the case of incoherent addition, the modulation is entirely due to the sub-cycle dependence of the direct two-photon transition (pathway II) which follows the instantaneous IR electric field intensity at the moment of ionization. This is very similar to what was seen in the experiment by Kelkensberg et. al [17], where it was demonstrated how the coupling of different ionization continua by an IR field may lead to a periodic modulation of ionization probability. As a result, the modulation depth is biggest around the time delay $\Delta t = 0$. In this case, the vibrational bands originating from the sequential pathway I are not modulated. However, they become weaker as one moves from negative to positive time delays, because the sequential path requires

time for the transition from the $C^2\Sigma_u^+$ to the $D^2\Pi_g$ state.

In the case of coherent addition, (figures 5.6d-f and figures 5.6g-i) the main source of modulation is the interference between the sequential and the direct pathways. Consequently, the modulation is enhanced and the maximum modulation depth is shifted to negative time delays ($\Delta t \sim -7$ fs) when the XUV pulse precedes the peak of the IR pulse and the contributions from both pathways are equal.

Another important difference between the spectra resulting from the coherent and incoherent addition of dissociation channels is the phase of the oscillation with respect to $\Delta t = 0$ time delay. For the incoherent case (figures 5.6a-b), the maximum of oscillation exactly matches the IR electric field maximum/minimum, which for the cosine-pulse used in the calculation is at $\Delta t = 0$, i.e. the oscillations are in phase with the IR field. In contrast, in the spectrum obtained by coherent addition of the dissociation channels (figures 5.6d-e and figures 5.6g-h) the maximum does not match the maximum/minimum of the IR electric field but is, e.g., at $\Delta t \sim 200$ as for the scattering phase of $\delta = \pi/2$ (figures 5.6d-e). For an oscillation with a periodicity of 1.33 fs this corresponds to 54° phase shift. This value, however, strongly depends on the initial phase difference, as can be seen by the shift of the spectra in figures 5.6g-h. The phase difference in turn is determined by the electron-electron correlations at the moment of ionization.

The observed beating in figures 5.6d-e and figures 5.6g-h is due to the interference of XUV+IR and XUV-IR dissociation channels. Indeed, let the attosecond XUV pulse be centred around $t = 0$ and the oscillations of the IR pulse be delayed by τ relative to the XUV peak. As long as the time-delay is short compared to the IR pulse duration, so that changes in the IR intensity envelope can be ignored, second-order perturbation theory for the two-photon transitions XUV+IR (amplitude $a_+(\tau)$) and XUV-IR (amplitude $a_-(\tau)$) immediately shows that:

$$a_+(\tau) = a_+ e^{-i\omega\tau} \quad (5.11a)$$

$$a_-(\tau) = a_- e^{+i\omega\tau + i\varphi} \quad (5.11b)$$

$$|a_-(\tau) + a_+(\tau)|^2 = |a_-|^2 + |a_+|^2 + 2|a_- a_+| \cos(2\omega\tau + \varphi) \quad (5.11c)$$

where $a_\pm \equiv a_\pm(\tau = 0)$ and φ is the phase difference between the complex amplitudes $a_\pm$. Mathematically, the origin of this modulation is similar to the one in the RABBITT-type characterization of attosecond laser pulses [18]. However, in our case, the oscillation is not due to the modulation of continuum population and free-free transitions induced by the IR, as in [17, 31], but it differs in two important aspects. First, ionization creates population in different ionization continua, which are coupled by a time-delayed IR field. Hence, the IR field leads to sequential

transitions between the molecular PES. Second, the phase difference between the two channels is determined not only by the relative phase of the laser pulses, but also by the difference of scattering phases associated with each ionisation continua and the phases accumulated due to propagation on different molecular PES. Therefore, such *molecular RABBITT* is sensitive to both the scattering properties of the molecule and the dissociation dynamics.

5.6.4 Separation of direct and sequential transitions

The $C^2\Sigma_u^+$ and the $D^2\Pi_g$ potentials of N_2^+ are energetically very close to each other at the FC internuclear distance of N_2 molecule. This is, however, not an avoided crossing as the two potential curves have different symmetries. The coupling of the $C^2\Sigma_u^+$ and the $D^2\Pi_g$ states by the IR field at this point induces noticeable two-photon XUV–IR direct transition to the $D^2\Pi_g$ state where the $C^2\Sigma_u^+$ state acts as an intermediate virtual state. The strength of this transition depends on the energy difference between the $C^2\Sigma_u^+$ and the $D^2\Pi_g$ potential curves, which in turn is sensitive to the accuracy of the PEC. Moreover, as the energy of the $C^2\Sigma_u^+$ and the $D^2\Pi_g$ states become almost degenerate, the strength of this channel scales nonlinearly with the IR field intensity. Finally note, that this pathway was not considered up till now.

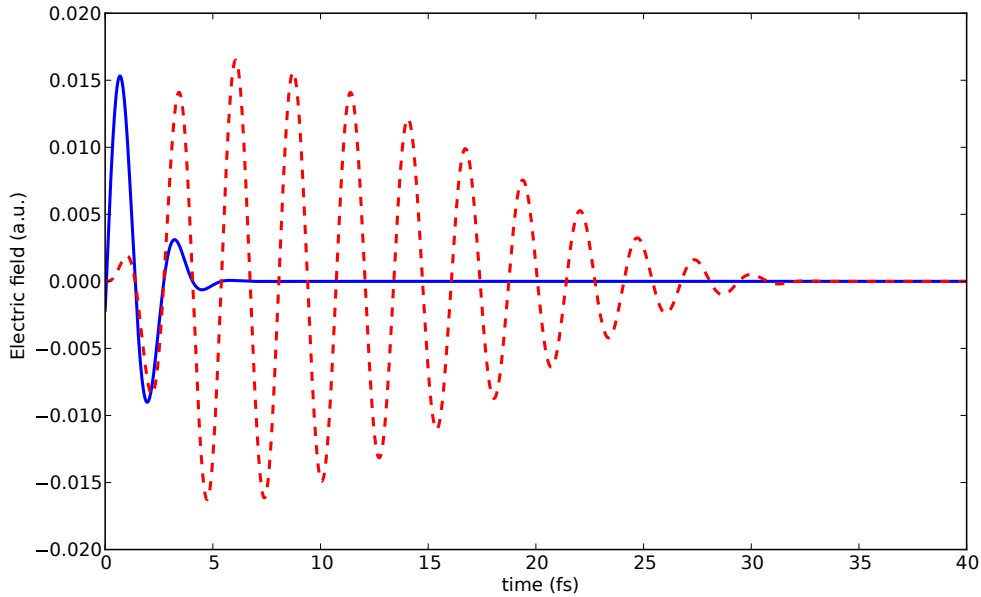


Figure 5.7: Laser pulse splitting to separate the direct (blue full line) from the sequential (red dashed line) transitions; $t=0$ corresponds to the chosen arrival time of the XUV pulse.

We have calculated the contribution from the direct transition from the $C^2\Sigma_u^+$ to the $D^2\Pi_g$ state and evaluated its influence on the final KER spectra as a function of time-delay between the XUV and the IR pulses. In order to separate the direct and the sequential transitions that both start in the $C^2\Sigma_u^+$ state and end in the $D^2\Pi_g$ state we split the IR laser pulse into two parts: (i) the leading edge, that induces only direct transitions and (ii) the trailing edge, that induces only sequential transitions (figure 5.7). The splitting was performed by multiplying the laser electric field with $\exp(-t^2/\tau^2)$ mask function. The optimal value of the parameter τ was found empirically, so as to minimize the modulation of the direct-only channel as a function of XUV-IR time delay, and was set to $\tau = 100 \hbar/E_h$.

KER from the $D^2\Pi_g$ state was then calculated using (i) only the direct $B^2\Sigma_u^+$ to $D^2\Pi_g$ and sequential $C^2\Sigma_u^+$ to $D^2\Pi_g$ channels (figure 5.6) as before and (ii) with the new direct $C^2\Sigma_u^+$ to $D^2\Pi_g$ channel included (figure 5.8). It was found that the direct $C^2\Sigma_u^+$ to $D^2\Pi_g$ transition changes the N⁺ KER spectra insignificantly. It affects the modulation depth of the spectra in a time delay scan. Note, that the time delay at which the panels (c, f and i) in figure 5.8 are plotted were also adjusted to this phase shift. Importantly, the sensitivity of the N⁺ fragment KER spectra and vibrational peak position on the scattering phase and the XUV-IR time delay, which are the main findings of the work, remain. Moreover, quantitative corrections due to the direct $C^2\Sigma_u^+$ to $D^2\Pi_g$ transition are small.

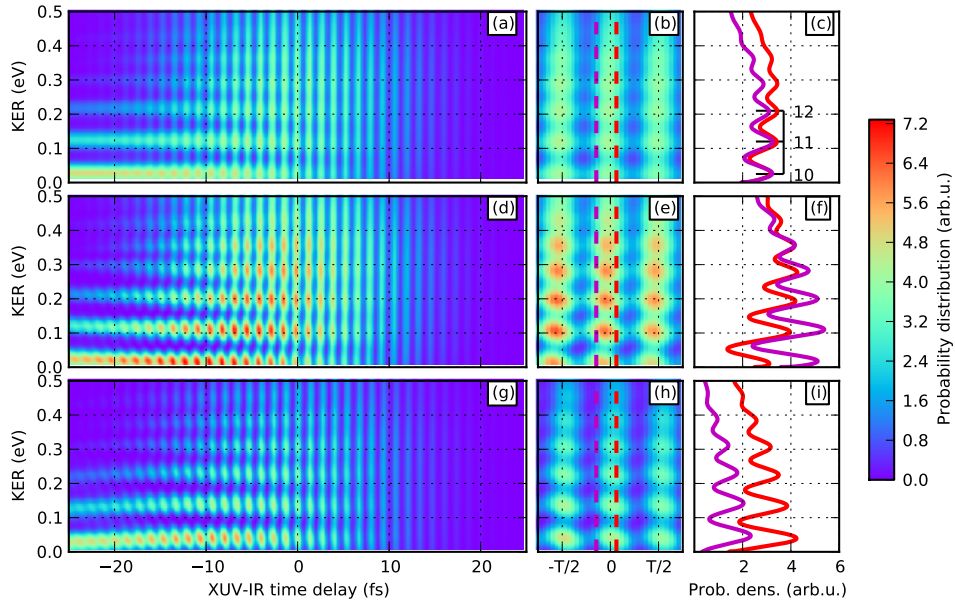


Figure 5.8: N⁺ KER spectra for direct $B^2\Sigma_u^+$ to $D^2\Pi_g$, direct $C^2\Sigma_u^+$ to $D^2\Pi_g$ and sequential $C^2\Sigma_u^+$ to $D^2\Pi_g$ transitions; see text for the explanation of the panels.

5.7 Extension to attosecond pulse trains

The experimental techniques used to generate isolated attosecond pulses normally rely on the use of few cycle IR pulses that also act as a phase-locked pump or probe fields. Therefore, the combination of an isolated attosecond pulse that is phase-locked to a many cycle IR pulse considered in this work is not straightforward to achieve in an experiment. Nevertheless, here it will be demonstrated that if an attosecond pulse train characteristic of HHG is used, the effects of the initial electronic coherence on nuclear dynamics, which were discussed till now, remain valid and can be observed.

5.7.1 Numerical approach to the photodissociation by an attosecond pulse train

The Schrödinger equation in the integral form describing one-photon ionization in the perturbative regime and the consecutive dynamics is

$$\begin{aligned} \Psi(R, q, t) = & -i \int_{t_0}^t dt' e^{-i\frac{q^2}{2}(t-t')} \sum_{i,N} d_i(R, q) e^{-i\delta_{q,i}} \\ & \times c_N f(t' - t_N) e^{-i\Omega_{XUV}t'} e^{-iE_g(t'-t)} U_{ion}(t, t') \Phi(R, t') \end{aligned} \quad (5.12)$$

where the index i indicates the target ionic state for the XUV, index N sums over attosecond pulses in the pulse train and q is the asymptotic continuum electron momentum. $d_i(R, q)$ is the amplitude of the (complex) ionization dipole into the target ionic state i with a phase $\delta_{q,i}$. c_N is the intensity of N -th pulse in the pulse train, $f(t' - t_N)$ is the envelope of a single attosecond pulse in the train, which is centred around time t_N . $U_{ion}(t, t')$ is the propagator for the vibronic wavepacket $|\Phi(R, t')\rangle$ created in the ion by the ionization. The expression above is written for a specific final photoelectron momentum q .

The ionic propagator is split into two parts

$$U_{ion}(t, t') = U_{ion}(t, t_N) U_{ion}(t_N, t'). \quad (5.13)$$

from time t' to the centre of N -th attosecond pulse t_N and from t_N to the final time t . Further, it is assumed that no nuclear dynamics takes place near the peak of attosecond pulse t_N

$$U_{ion}(t_N - t') \Phi(R, t') \simeq e^{-iE_i(R)(t_N-t')} \Phi(R, t_N). \quad (5.14)$$

where $E_i(R)$ is the R -dependent potential energy of the target electronic states.

Such assumption is justified as the integral over t' is bounded by the envelope of the attosecond pulse $f(t' - t_N)$, which is much shorter than the timescale of nuclear dynamics. Choosing a Gaussian shape for the envelope of the attosecond pulses $f(t - t_N)$

$$f(t' - t_N) = e^{-\frac{(t' - t_N)^2}{\lambda}} \quad (5.15)$$

(5.12) becomes

$$\begin{aligned} \Psi(R, q, t) = & -i e^{-i\frac{q^2}{2}t + iE_g(R)t_0} \sum_i d_i(R, q) e^{-i\delta_{q,i}} \sqrt{\pi\lambda} e^{-\left(\frac{\sqrt{\lambda}\Delta(q,R)}{2}\right)^2} \\ & \times \sum_N c_N U_{ion}(t, t_N) \Phi(R, t_N) e^{i\left(\frac{q^2}{2} - \Omega_{XUV} - E_g(R)\right)t_N} \end{aligned} \quad (5.16)$$

where

$$\Delta(q, R) = \frac{q^2}{2} + E_i(R) - \Omega_{XUV} - E_g(R) \quad (5.17)$$

is the detuning from the resonance energy. The term $\exp\left(-\left(\frac{\sqrt{\lambda}\Delta(q,R)}{2}\right)^2\right)$ accounts for the bandwidth of the attosecond pulse. It will determine the envelope of the harmonic comb, after performing the summation over attosecond bursts N . The phase Ω_{IR} due to the IR field and the electronic phase due to the propagation in the final ionic state $E_i(R)$ are accounted for by the ionic propagator $U_{ion}(t, t_N)$ acting on $|\Phi(R, t_N)\rangle$, which is done numerically.

Different detuning $\Delta(q, R)$ must be used for the direct and sequential photodissociation channels. For the direct two-photon transition the detuning term corresponds to the final ionic state (after two XUV+IR photon absorption) while for the sequential transition - to the initial ionic state (after XUV photon absorption). Therefore, the contributions from the direct and sequential channels must be used separately in (5.16). However, a “clean” separation is possible only for a large energy spacing between the target state populated by the XUV pulse and other ionic states that are populated due to the IR field. This is indeed the case for the transition from the $B^2\Sigma_u^+$ to the $D^2\Pi_g$ state. However, it is not true for a direct transition from the $C^2\Sigma_u^+$ to the $D^2\Pi_g$ state (at around equilibrium internuclear distance).

Below an algorithm is proposed, that allows one to sum contributions from individual numerical calculations for photodissociation due to an isolated attosecond pulse and obtain fragment and photoelectron spectra due to an APT:

1. For each time delay between the XUV and IR pulses the IR laser field is split into two parts: short first part (direct transitions only) and long second part (sequential transitions only), as discussed in section 5.6.4.

2. A separate numerical propagation is performed for each time delay and for each of the two parts of the split IR field.
3. A summation is performed over attosecond pulses in the pulse train separately for direct and sequential transitions using (5.16).
4. The contributions from the direct and from the sequential transitions are added up coherently for each photoelectron momentum.
5. The final KER spectra are obtained by summing over different photoelectron energies incoherently, i.e. integrating over the final photoelectron momentum.

5.7.2 Dissociation spectra due to ionization by an attosecond pulse train

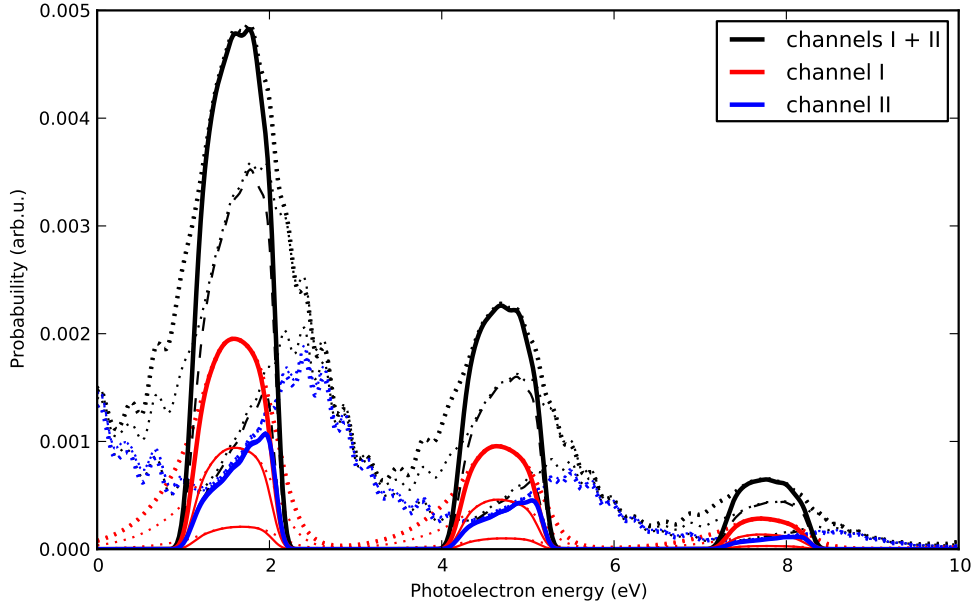


Figure 5.9: Photoelectron spectra obtained for direct (red), sequential (blue) dissociation channels and their coherent sum (black) for 3 different time delays — 0, $\pi/6\omega_{ir}$ and $\pi/3\omega_{ir}$, where 0 corresponds to the optimal overlap of the attosecond pulse train and the IR pulse. Only part of the spectra contribute to KER < 0.5 (full lines), while the remaining part of the spectra is due to population trapped in the bound part of the D²Π_g state potential (dotted lines). Note, that the photoelectron spectra is calculated only for the two photon XUV±IR channels.

First, the photoelectron spectra due to the photodissociation by an attosecond pulse train and an applied IR field is investigated. It is obtained by calculating the norm of the vibrational wavepacket after photoionization (both bound and

dissociating part) for each photoelectron energy in the final $^2\Pi_g$ ionic state. Thus, the photoelectron spectra correspond only to two-photon $XUV \pm IR$ transitions. In reality, the photoelectron spectra will be dominated by the contribution from the direct XUV-only ionization. Also, no dependence of the photoionization probability or phase on the photoelectron energy is assumed. However, if available, they can be trivially included by using the photoelectron energy (and possibly angle) dependent dipole $d_i(R, q)$ in (5.16). Therefore, a realistic scattering phase value can be trivially included into the analysis.

An ATP with 300 as FWHM attosecond bursts is assumed with a $\sin^2$ shaped 15 fs FWHM envelope of the pulse train. The central frequency of the XUV pulse is chosen to be equal to the 15-th harmonic of 800 nm driving IR field.

The obtained photoelectron spectra are shown in figure 5.9. The spectra are replicated for different harmonics that are above the ionization threshold. For the direct channel II, which starts by XUV ionization into the state $B^2\Sigma_u^+$, the lowest contributing harmonic of the IR driving field is the H15. For the sequential channel I, which starts by ionization into the $C^2\Sigma_u^+$ state, it is the harmonic H17.

The spectra that corresponds only to the part of the vibrational wavepacket that dissociates with $KER < 0.5$ is shown with full lines in figure 5.9. In addition, a large contribution to the full spectra (dotted lines) is due to the part of the vibrational wavepacket that stays trapped in the bound part of the $D^2\Pi_g$ state potential (dotted lines). This is particularly prominent in the case of the sequential channel II.

The spectra in figure 5.9 are shown for the case when the maxima of the APT envelope matches the maxima of the IR field envelope (thick lines) as well as for 3 different time delays that are separated by $1/12$ of the IR period (lines of decreasing thickness). The dependence of the spectra on the XUV-IR time delay demonstrates that the direct channel II strongly depends on the IR sub-cycle time-delay, as discussed previously, while the sequential channel I does not depend on this delay.

Finally, the delay-dependent KER spectra due to APT+IR photodissociation with parameters described above is shown in figure 5.10. The differences from the spectra obtained using an isolated attosecond pulse (figure 5.6) are minor and limited to slight intensity variations of different energy regions of the spectra.

High-harmonic radiation is much easier to produce in laboratory conditions than an isolated attosecond pulse. In addition, it is challenging to achieve an isolated attosecond pulse synchronized with a long IR pulse. Hence, the fact that an isolated attosecond pulse can be replaced by an APT promises that an experimental studies of the physical mechanism described here and the impact of the continuum photoelectron on the long term coupled electron–nuclear dynamics

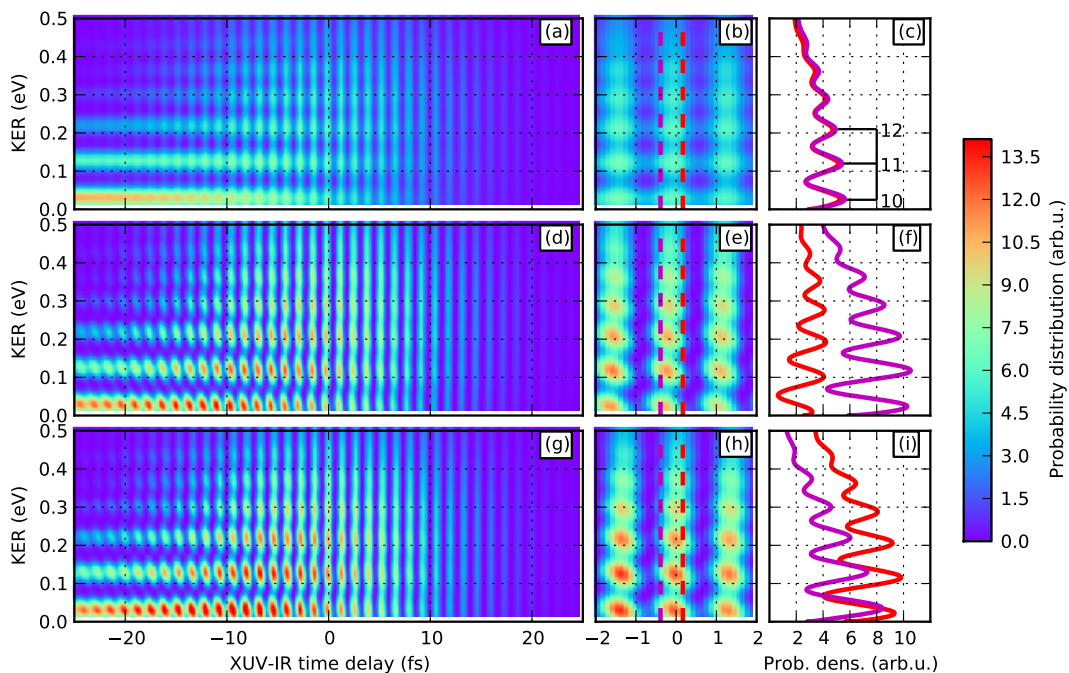


Figure 5.10: Calculated N⁺ KER spectrum as a function of APT and IR pump-probe time delay for the case of incoherent (a) and coherent (d) and (g) summation between direct (path II) and sequential (path I) dissociation channels. The meaning of panes is as before.

in the molecular ion after ionization are much more accessible.

5.8 Conclusions

We have demonstrated how attosecond electronic coherence can influence the outcome of a simple photochemical reaction that evolves during tens of femtoseconds. Using the N₂⁺ molecule as a model system we have shown how electronic coherence created by an ultrashort pulse can influence the interference of vibrational wavepackets and can non-trivially modify the observed vibrationally resolved dissociation spectrum. Its precise appearance depends on the interplay of the attosecond electronic dynamics during ionization and the femtosecond vibrational dynamics that lead to the fragmentation of the molecule. A scan of time delays between ionizing and dressing laser pulses allows one to observe a RABBITT-like interference pattern in the spectra of dissociation products that is sensitive to the phases of the underlying correlated electronic-nuclear dynamics. The effects can be observed with isolated attosecond pulses or an attosecond pulse train.

The connection between electronic and vibrational coherence and its effect on the vibrational dynamics is central to the concept of attochemistry [32]. The idea that the outcome of a chemical reaction can be determined by electronic coherence

on an attosecond time scale leads to the question of how exactly such coherence affects the nuclear dynamics that follows. This work suggests that the coherence of continuum electronic wavepackets can translate into the coherence of different paths for the coupled electron-vibrational dynamics and, upon the interference of these paths, to a modification of the fragmentation dynamics of the molecule. This principle is universal and has to be taken into account whenever the role of electronic coherence in nuclear dynamics is considered.

Contributions

The work presented in this Chapter was partly inspired by experimental work performed by Christian Neidel, Jesse Klei, Dr. Arnoud Rauzeé at Max-Born Institute. The potential energy curves and dipole coupling elements used in this work are the courtesy of Dr. Alex Harvey and Dr. Serguei Patchkovskii from Max-Born Institute. One-photon ionization dipoles were calculated by Alex Harvey. Otherwise, all the work presented in this Chapter was led and performed by the author. This includes the development of numerical code to propagate vibrational wavepackets and obtain the spectra, evaluation of the coherence between the ionization channels using the provided ionization dipole elements, analysis and interpretation of the data.

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Appendix A

Time-dependent dynamics of a coupled two-level system in the adiabatic basis

Two potential energy curves (PEC), dressed by a laser field, can be analytically exactly transformed into a field-dressed basis of adiabatic states. Let us consider two states σ_g and σ_u with eigenenergies $E_g(R)$ and $E_u(R)$ that parametrically depend on the coordinate R . Moreover, the two states are coupled by a laser field $V_l(t)$ with the strength of the coupling given by the matrix-element $d(R) = \langle \sigma_g(R) | \hat{d} | \sigma_u(R) \rangle$. The Hamiltonian of the system in matrix form is

$$H = \begin{pmatrix} E_g(R) & d(R) V_l(t) \\ d(R) V_l(t) & E_u(R) \end{pmatrix}. \quad (\text{A.1})$$

It can be diagonalized to obtain the quasi-static adiabatic states

$$\psi_1(R, t) = \cos(\Theta(R, t)) \sigma_g(R) + \sin(\Theta(R, t)) \sigma_u(R) \quad (\text{A.2a})$$

$$\psi_2(R, t) = -\sin(\Theta(R, t)) \sigma_g(R) + \cos(\Theta(R, t)) \sigma_u(R) \quad (\text{A.2b})$$

where the mixing angle $\Theta(R, t)$ depends on the coordinate R and t . The angle is defined by the relation

$$\tan(2\Theta) = -\frac{2d(R)V_l(t)}{\omega_0(R)}, \quad (\text{A.3})$$

where $\omega_0(R) = E_u(R) - E_g(R)$ is the energy difference between the diabatic states σ_g and σ_u . The time-dependent eigenenergies of the adiabatic states $\Psi_{1,2}(R, t)$ are

$$E_{1,2}(R, t) = \frac{E_g(R) + E_u(R)}{2} \pm \sqrt{\frac{\omega_0^2}{4} + (d(R)V_l(t))^2}. \quad (\text{A.4})$$

APPENDIX A. TIME-DEPENDENT DYNAMICS OF A COUPLED TWO-LEVEL SYSTEM IN THE ADIABATIC BASIS

Inserting the amplitudes of the adiabatic states in A.2 into the time-dependent Schrödinger equation (TDSE) will lead to the equations

$$i\dot{\psi}_1(R, t) = E_1(R, t)\psi_1(R, t) + i\dot{\Theta}(R, t)\psi_2(R, t) \quad (\text{A.5a})$$

$$i\dot{\psi}_2(R, t) = E_2(R, t)\psi_2(R, t) - i\dot{\Theta}(R, t)\psi_1(R, t). \quad (\text{A.5b})$$

The time-dependence of the mixing angle $\Theta(R, t)$ leads to the coupling term

$$\dot{\Theta}(R, t) = -\frac{\dot{V}_l(t)d(R)\omega_0(R)}{\omega_0(R)^2 + 4d(R)^2V_l(t)^2} \quad (\text{A.6})$$

that is proportional to the time-derivative of the laser potential $\dot{V}_l(t)$.

The coupling is due to the breakdown of the adiabatic approximation. If the laser field is constant, the non-adiabatic coupling $\dot{\Theta}(R, t) = 0$ and the $\psi_{1,2}$ are the exact eigenstates of the dressed system. Since the laser coupling is time-dependent, $\psi_{1,2}$ are not the instantaneous eigenstates of the system and are therefore coupled by non-adiabatic coupling $\dot{\Theta}(R, t)$.

The non-adiabatic coupling $\dot{\Theta}(R, t)$ is inversely proportional to the laser field $V_l(t)$ and directly proportional to its time-derivative $\dot{V}_l(t)$. As a result, it peaks around the zero-crossings of the laser. Its time-width becomes narrower as the laser fields becomes stronger (see figure A.1c). Hence, it results in a step-like population transfer between the adiabatic states.

The figure A.1b shows how the eigenenergies $E_{1,2}$ of the states $\psi_{1,2}$ form an avoided crossing at the zero-crossing of the laser field. In this case, the transition probability can be expressed by the Landau-Zener relation, which, for a laser field

$$\hat{V}_l(t) = f(t) \cos(\omega_l t + \phi), \quad (\text{A.7})$$

is

$$P(R, t) = \exp\left(-\frac{\pi\omega_0(R)^2}{4\omega_l d(R)f(t)}\right). \quad (\text{A.8})$$

Equation (A.8) describes the overall probability of transition between the adiabatic states during a single zero-crossing of the field. The time-dependence of this probability comes from the laser field envelope function $f(t)$, which is considered to be a slow-varying function.

Finally, if the spacing between the diabatic states becomes zero ($\omega_0 \rightarrow 0$ in (A.8)) then the non-adiabatic transition probability $P(R, t) \rightarrow 1$. Hence, a full population transfer takes place between the adiabatic states at each zero-crossing of the field.

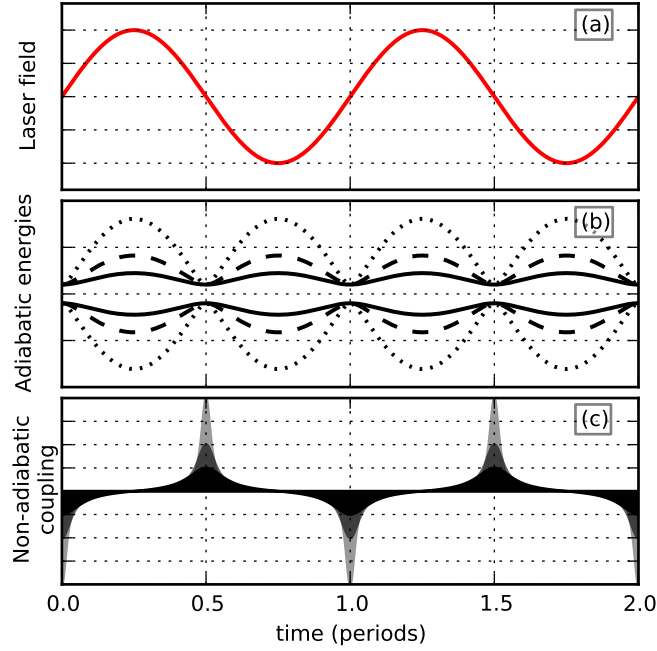


Figure A.1: Laser electric field (a) together with the adiabatic state energies $E_{1,2}(R, t)$ (b) and the non-adiabatic couplings $\dot{\Theta}(R, t)$ (c) for different laser electric field strengths. The energies of the adiabatic states are time-dependent and have an avoided crossing at the zeros of the field. The non-adiabatic couplings are strongly peaked at the time of the avoided crossings.

Appendix B

Adiabatic elimination of ionization continuum

In this appendix the adiabatic approximation is presented. It allows to eliminate the ionization continuum from the time-dependent Schödinger equation (TDSE) governing the dynamics of the autoionizing (AI) state. Hence, it allows to decouple the system of equations (4.3) and hence obtain analytical results.

Firs, let us start with the coupled system of equations (4.3) that describes the decay of an AI state

$$i \frac{\partial}{\partial t} \chi_g(t) = [T_N + V_g] \chi_g(t) + \\ - F(t) D_{ga} \chi_a(t) - F(t) \int dk D_{gk} \chi_k(t) \quad (\text{B.1a})$$

$$i \frac{\partial}{\partial t} \chi_a(t) = [T_N + V_a] \chi_a(t) + \\ - F(t) D_{ag} \chi_g(t) + \int dk V_{ak} \chi_k(t) \quad (\text{B.1b})$$

$$i \frac{\partial}{\partial t} \chi_k(t) = \left[T_N + V_{ion} + \frac{k^2}{2} \right] \chi_k(t) + \\ + V_{ka} \chi_a(t) - F(t) D_{kg} \chi_g(t) \quad (\text{B.1c})$$

where

$$D_{ga} = \langle \phi_g(r) | \hat{d}(r) | \phi_a(r) \rangle \quad (\text{B.2})$$

are the dipole-coupling matrix element between the corresponding electronic states and

$$V_{ak} = \langle \phi_a(r) | V_{ee}(r) | \phi_k(r) \rangle \quad (\text{B.3})$$

are the electron-electron coupling matrix element that are responsible for the AI decay, and analogously for others.

The adiabatic approximation is performed only on the electronic degree of freedom. Hence, the derivation below is performed for each internuclear distance R separately. Since the vibrational dynamics is not considered, in the following the nuclear kinetic energy terms T_N are dropped.

We define a new set of time-dependent coefficients $\tilde{\chi}_{g,k,a}(t)$ for which the fast-oscillating phase term is removed

$$\chi_{g,k,a}(t) = \tilde{\chi}_{g,k,a}(t)e^{-iE_{g,k,a}t} \quad (\text{B.4})$$

and where

$$E_k = V_{ion} + \frac{k^2}{2} \quad (\text{B.5})$$

is the combined energy of the final state of the ion and the photoelectron with momenta $\hbar k$.

With the new coefficients and without the nuclear motion (B.1c) can be rewritten as

$$i\dot{\tilde{\chi}}_k = -F(t)D_{kg}\tilde{\chi}_g e^{-i(E_g-E_k)t} + V_{ka}\tilde{\chi}_a e^{-i(E_a-E_k)t} \quad (\text{B.6})$$

and can be formally integrated yielding

$$\tilde{\chi}_k = i \int^t dt' F(t') D_{kg} \tilde{\chi}_g e^{-i(E_g-E_k)t'} \quad (\text{B.7a})$$

$$-i \int^t dt' V_{ka} \tilde{\chi}_a e^{-i(E_a-E_k)t'}. \quad (\text{B.7b})$$

Inserting solution (B.7) into equation (B.1b) for $\tilde{\chi}_a(t)$ we obtain

$$i\dot{\tilde{\chi}}_a = -F(t)D_{ag}e^{-i(E_g-E_a)t} + \quad (\text{B.8a})$$

$$+ i \int dt' \int dk F(t') V_{ak} e^{-i(E_k-E_a)t} D_{kg} \tilde{\chi}_g e^{-i(E_g-E_k)t'} \quad (\text{B.8b})$$

$$- i \int dt' \int dk V_{ak} e^{-i(E_k-E_a)t} V_{ka} \tilde{\chi}_a e^{-i(E_a-E_k)t'}. \quad (\text{B.8c})$$

The main goal of the adiabatic approximation is to evaluate the integrals over dt' and dk in (B.8b) and (B.8c).

The decay term

We shall start from the term (B.8c). Here, it is loosely referred to as the “decay term”, because it leads to term that determines the lifetime of the AI state, as will become clear later.

Rearranging term in (B.8c) such that

$$I = -i \int^t dt' \tilde{\chi}_a(t') \int dk V_{ak} V_{ka} e^{-i(E_a - E_k)(t - t')} \quad (\text{B.9})$$

noting that

$$V_{ak} V_{ka} = |V_{ak}|^2 \quad (\text{B.10})$$

and introducing new variables

$$E_k = E_a + \epsilon \quad (\text{B.11a})$$

$$t - t' = \tau \quad (\text{B.11b})$$

the integral (B.9) can be written as

$$I = -i \int_0^\infty d\tau \tilde{\chi}_a(t - \tau) \int_{-\epsilon_{lim}}^{\epsilon_{lim}} d\epsilon |V_{ak}|^2 e^{-i\epsilon\tau}. \quad (\text{B.12})$$

If we assume that the term $|V_{ak}|^2$ does not vary significantly in the region, where the integral over $d\epsilon$ is accumulated (i.e. $\epsilon = 0$), then we can take $|V_{ak}|^2$ out of the energy integral. Integrating the remaining exponent leads to

$$I = -i \int_0^\infty d\tau \tilde{\chi}_a(t - \tau) \left| V_{ak}^{(0)} \right|^2 \frac{2 \sin(\epsilon_{lim} \tau)}{\tau}. \quad (\text{B.13})$$

If ϵ_{lim} is large than the function $\sin(\epsilon_{lim} \tau)/\tau$ is sharply peaked around $\tau = 0$ value. If the characteristic width of this function is much smaller than that of $\tilde{\chi}_a(t - \tau)$ around $\tau = 0$ we can regard the latter as fixed ($\tilde{\chi}_a(t - \tau) \rightarrow \tilde{\chi}_a(t)$) for the purpose of integration over $d\tau$. Hence, this integration can be performed analytically

$$I \approx -i \tilde{\chi}_a(t) \left| V_{ak}^{(0)} \right|^2 \int_0^\infty d\tau \frac{2 \sin(\epsilon_{lim} \tau)}{\tau} \quad (\text{B.14a})$$

$$\approx -i \pi \tilde{\chi}_a(t) \left| V_{ak}^{(0)} \right|^2 \quad (\text{B.14b})$$

$$= -i \frac{\Gamma}{2} \tilde{\chi}_a(t) \quad (\text{B.14c})$$

where the definition of the decay width

$$\Gamma = 2\pi \left| V_{ak}^{(0)} \right|^2 \quad (\text{B.15})$$

was introduced in the last line of (B.14). Note that Γ must be evaluated at each internuclear distance R by taking the matrix element $\left| V_{ak} \right|^2$ at such k value, that $E_k(R) = E_a(R)$.

In the above, three main approximations were made:

1. The electron-electron coupling matrix element $|V_{ak}|^2$ does not vary significantly close to the energy of the autoionizing state E_a . In general, this means that the ionization continuum is “flat” close to the resonance energy E_a and there are no other physical mechanisms that could lead to big changes of ionization probability.
2. The limit ϵ_{lim} for the integral over $d\epsilon$ is large so that the sinc function $\sin(\epsilon_{lim}\tau)/\tau$ is close to a delta function. In this case the upper limit of the integral can safely be set to ∞ because the atomic continuum spectra is not bound from above. Hence, the limiting factor is the lower integration limit, which is usually determined by the ionization threshold. Hence, the approximation is good as long as the energy of the AI state is not close to the threshold.
3. The rate of change of coefficients $\tilde{\chi}_a(t)$ is much slower than that of $\sin(\epsilon_{lim}\tau)/\tau$ function. This is almost always the case for atomic or molecular systems. Exceptions may arise if there are other decay channels that are more efficient than the AI decay or if the AI state is coherently coupled with some other state.

The polarization term

Now we will deal with the term (B.8b). It is loosely termed the “polarization term”, because it induces an energy and phase shift of the AI state due to the coupling to the continuum that is only present when the laser field is on. Nevertheless, the derivation below involves analogous approximations as in dealing with the “decay term”.

First, the laser field is split

$$F(t) = f(t)e^{-i\Omega t} \quad (\text{B.16})$$

into the envelope $f(t)$ and the carrier frequency term $e^{-i\Omega t}$. Furthermore, we assume that the depletion and polarization of the neutral ground state is negligible, thus setting

$$\tilde{\chi}_g(t) \equiv 1. \quad (\text{B.17})$$

The integral (B.8b) becomes

$$I = i \int_0^t dt' e^{iE_a t'} e^{-i(E_g + \Omega)t'} f(t') \int dk V_{ak} D_{kg} e^{-iE_k(t-t')}. \quad (\text{B.18})$$

APPENDIX B. ADIABATIC ELIMINATION OF IONIZATION CONTINUUM

Defining the energy of the center of the spectral line

$$E_g + \Omega - E_k^{(0)} = 0 \quad (\text{B.19a})$$

$$E_k = E_k^{(0)} + \epsilon \quad (\text{B.19b})$$

the integral above can be rewritten as

$$I = i \int^t dt' e^{iE_a t} e^{-i(E_g + \Omega)t'} f(t') e^{-iE_k^{(0)}(t-t')} \int_{-\epsilon_{lim}}^{\epsilon_{lim}} d\epsilon V_{ak} D_{kg} e^{-i\epsilon(t-t')} \quad (\text{B.20a})$$

$$= i \int^t dt' e^{iE_a t} e^{-i(E_g + \Omega)t'} f(t') e^{-iE_k^{(0)}(t-t')} [V_{ak} D_{kg}]^{(0)} \frac{2 \sin(\epsilon_{lim}(t-t'))}{t-t'} \quad (\text{B.20b})$$

where it was assumed that $V_{ak} D_{kg}$ does not vary significantly close to the AI state energy E_a , as done previously. $[V_{ak} D_{kg}]^{(0)}$ corresponds to the value of the matrix elements for a value of k that corresponds the center of the spectral line.

Introducing new variable for time

$$t - t' = \tau \quad (\text{B.21})$$

the integral above becomes

$$\begin{aligned} I &= -ie^{iE_a t} e^{-i(E_g + \Omega)t} [V_{ak} D_{kg}]^{(0)} \int_0^\infty d\tau f(t - \tau) e^{-i(E_k^{(0)} - E_g - \Omega)\tau} \frac{2 \sin(\epsilon_{lim}\tau)}{\tau} \\ &= -ie^{iE_a t} e^{-i(E_g + \Omega)t} [V_{ak} D_{kg}]^{(0)} \int_0^\infty d\tau f(t - \tau) \frac{2 \sin(\epsilon_{lim}\tau)}{\tau} \end{aligned} \quad (\text{B.22})$$

where the definition of the spectral line center in (B.19a) was used to arrive at the second line. Finally, assuming that the integration limits ϵ_{lim} can be extended sufficiently far and taking $f(t - \tau)$ at $\tau = 0$ as before the integral over τ can be performed analytically

$$\begin{aligned} I &= i\pi e^{-i(E_g + \Omega - E_a)t} [V_{ak} D_{kg}]^{(0)} f(t) \\ &= i\pi e^{-i(E_g - E_a)t} [V_{ak} D_{kg}]^{(0)} F(t). \end{aligned} \quad (\text{B.23})$$

Note, that in order to perform the integration over τ we formally require that the rate of change of the laser field envelope function $f(t)$ is much slower than the rate of change of the sinc function $\sin(\epsilon_{lim}\tau)/\tau$. This might not be the case for ultrashort attosecond laser pulses. Nevertheless, this limitation can be avoided by expanding the laser field $F(t)$ into spectral components.

Appendix C

Derivation of the parametrized Fano lineshape relation

We shall start from the relation for the atomic dipole for ionization close to a resonant state in (4.27):

$$\tilde{D}_v(\Omega, \epsilon) = D_v + D_q \sqrt{\frac{\Gamma_0}{2\pi}} \frac{1}{E_g + \Omega - E_q + i\Gamma_0/2}. \quad (\text{C.1})$$

Using D_q given by (4.16) and (4.17) and adapted for the atomic limit by dropping the dependence on the internuclear distance R :

$$D_q = D_q^{(0)} - i\pi \sqrt{\frac{\Gamma_0}{2\pi}} D_v. \quad (\text{C.2})$$

the ionization dipole can be written as

$$\tilde{D}_v = D_v \left[1 + \frac{D_q^{(0)}}{D_v} \left(1 - i\pi \sqrt{\frac{\Gamma_0}{2\pi}} \frac{D_v}{D_q^{(0)}} \right) \frac{\sqrt{\Gamma_0/2\pi}}{E_g + \Omega - E_q + i\Gamma_0/2} \right] = \quad (\text{C.3a})$$

$$= D_v \left[1 + \left(1 - i\pi \sqrt{\frac{\Gamma_0}{2\pi}} \frac{D_v}{D_q^{(0)}} \right) \left(\frac{D_q^{(0)}}{D_v} \middle/ \sqrt{\frac{\Gamma_0}{2\pi}} \pi \right) \middle/ \left(\frac{E_g + \Omega - E_q}{\Gamma_0/2} + i \right) \right]. \quad (\text{C.3b})$$

APPENDIX C. DERIVATION OF THE PARAMETRIZED FANO LINESHAPE RELATION

Introducing dimensionless variables for the energy (ϵ) and the coupling strength (q) as follows:

$$\epsilon = \frac{E_g + \Omega - E_q}{\Gamma_0/2} \quad (\text{C.4a})$$

$$q = \frac{D_q^{(0)}}{\pi \sqrt{\frac{\Gamma_0}{2\pi}} D_v} \quad (\text{C.4b})$$

and substituting the variables q and ϵ into (C.3b) we obtain

$$\tilde{D}_v = D_v \left(1 + \left(1 - \frac{i}{q} \right) \frac{1}{\epsilon + i} q \right) \quad (\text{C.5a})$$

$$= D_v \left(1 + \frac{q - i}{\epsilon + i} \right) \quad (\text{C.5b})$$

$$= D_v \frac{\epsilon + q}{\epsilon + i}. \quad (\text{C.5c})$$

Taking the modulus squared we get

$$|\tilde{D}_v|^2 = |D_v|^2 \frac{(\epsilon + q)^2}{\epsilon^2 + 1} \quad (\text{C.6})$$

which is exactly the relation originally derived by H. Fano.

Appendix D

Estimation of the relative strength of direct and sequential two-photon transitions

Here, an estimate will be provided for the relative strength of direct and sequential two photon XUV+IR transition. The estimate is made by using the 1st order perturbation theory and employing the integral form of the time-dependent Schrödinger equation

$$\Psi(t) \propto \int_{t_0}^t dt_1 \int_{t_1}^t dt_2 e^{-i\hat{H}_f(t-t_2)} \hat{V}_2(t_2) e^{-i\hat{H}_i(t-t_1)} \hat{V}_1(t_1) e^{-i\hat{H}_g(t_1-t_0)} \Psi_g(t_0). \quad (\text{D.1})$$

The expression above describes a system that evolves in its ground state Ψ_g from the initial time t_0 till time t_1 , where the ground state evolution is governed by the time-independent Hamiltonian $\hat{H}_g$. At time t_1 the system is promoted to an intermediate state (i) by the interaction $\hat{V}_1$. At time t_2 the system is promoted to the final state (f) by interaction $\hat{V}_2$. Furthermore, it is assumed that $t_2 > t_1$ (time ordering).

In the following, we will assume that the ground, intermediate and the final states are the eigenstates of the respective Hamiltonians with eigenenergies $E_{g,i,f}$. The interaction is assumed to be laser dipole coupling of the form

$$\hat{V}_j(t)\Psi(t) = d_j f_j(t) e^{-i\omega_j t} \Psi(t) \quad (\text{D.2})$$

where d_j is the dipole matrix element, $f_j(t)$ is the envelope function and ω_j is the laser frequency. Note, that the rotating wave approximation is used. The interaction $\hat{V}_1$ will be taken to be an XUV laser field with $\omega_1 \equiv \Omega_x$ and the interaction $\hat{V}_2$ will be taken to be the IR field with $\omega_2 \equiv \omega_{ir}$. With these definitions

APPENDIX D. ESTIMATION OF THE RELATIVE STRENGTH OF DIRECT AND SEQUENTIAL TWO-PHOTON TRANSITIONS

equation D.1 becomes

$$\begin{aligned} \Psi(t) = & \int_{t_0}^t dt_1 \int_{t_1}^t dt_2 e^{-iE_f(t-t_2)} d_{ir} f_{ir}(t_2) e^{-i\omega_{ir}t_2} \\ & \times e^{-iE_i(t-t_1)} d_x f_x(t_1) e^{-i\Omega_x t_1} e^{-iE_g(t_1-t_0)} \Psi_g(t_0). \end{aligned} \quad (\text{D.3})$$

Sequential transition

The sequential transition is important when both the XUV and the IR fields are resonant. Hence, applying the conditions

$$E_i - E_g - \Omega_x = 0 \quad (\text{D.4a})$$

$$E_f - E_i - \omega_{ir} = 0 \quad (\text{D.4b})$$

to the equation D.3, it reduces to

$$\Psi(t) = d_x d_{ir} \int_{t_0}^t dt_1 f_x(t_1) \times \int_{t_1}^t dt_2 f_{ir}(t_2) \Psi_g(t_0). \quad (\text{D.5})$$

If we consider that the XUV pulse is much shorter than a single period of the IR field and denote the t_x as the time when the XUV pulse envelope peaks, then for long times t the equation above can be approximated as

$$\Psi(t) \approx d_x d_{ir} I_x I_{ir}^S(t_x) \Psi_g(t_0) \quad (\text{D.6a})$$

$$I_x = \int_{-\infty}^{\infty} dt_1 f_x(t_1) \quad (\text{D.6b})$$

$$I_{ir}^S(t_x) = \int_{t_x}^{\infty} dt_2 f_{ir}(t_2) \quad (\text{D.6c})$$

Direct transition

The direct transition is important when the combined XUV+IR field is resonant with the final state, i.e.

$$E_g + \Omega_x + \omega_{ir} - E_f = 0. \quad (\text{D.7})$$

With this condition equation D.3 can also be written as

$$\Psi(t) \approx d_x d_{ir} I_x I_{ir}^D(t_x) \Psi_g(t_0) \quad (\text{D.8a})$$

$$I_x = \int_{-\infty}^{\infty} dt_1 f_x(t_1), \quad (\text{D.8b})$$

APPENDIX D. ESTIMATION OF THE RELATIVE STRENGTH OF DIRECT AND SEQUENTIAL TWO-PHOTON TRANSITIONS

where, however,

$$I_{ir}^D(t_x) = \int_{t_x}^{\infty} dt_2 e^{-i(E_i + \omega_{ir} - E_f)t_2} f_{ir}(t_2) \quad (\text{D.9a})$$

$$\approx -\frac{f_{ir}(t_x)}{i(E_i + \omega_{ir} - E_f)}. \quad (\text{D.9b})$$

The last line was obtained by assuming that $f_{ir}(t)$ is a slow varying function.

Relative strength

From the results above it is evident that :

- the probability of the sequential transition is proportional to the integral of the IR pulse envelope from the time of arrival of an XUV pulse;
- the probability of the direct transition does not depend on the length of the IR pulse, but is proportional to the instantaneous intensity of the IR pulse at the time of arrival of the XUV pulse;
- the strength of the direct transition is inversely proportional to the detuning of the IR laser field from the transition between the intermediate and the final states.

In summary:

$$\frac{P_{sequential}}{P_{direct}} = \left| \int_{t_x}^{\infty} dt_2 f_{ir}(t_2) \right|^2 \bigg/ \frac{|f_{ir}(t_x)|^2}{(E_i + \omega_{ir} - E_f)^2} \quad (\text{D.10})$$

where t_x is the time of arrival of the XUV pulse.

Appendix E

Taylor propagator for quantum wavepacket

In the propagation by a Taylor expansion propagator, at each time step the exponent of the Hamiltonian is expanded in the Taylor series

$$\exp[-i\hat{H}\Delta t] \approx 1 - i\hat{H}\Delta t - \frac{1}{2}\hat{H}^2(\Delta t)^2 + \dots \quad (\text{E.1})$$

where the order of expansion is chosen high enough to ensure the convergence of the calculation. In practise, it was found that expansion of up to 4-th order already provided physical results while expansion of up to 8-th order was enough to reach numerical double precision accuracy.

The wavefunction at each time step is evaluated by repeatedly applying the Hamiltonian and adding the result to the previously obtained wavefunction, such that, for the expansion of the Hamiltonian up to the 3rd order, we would calculate

$$\begin{aligned} & [1 - i\hat{H}\Delta t - \frac{1}{2}\hat{H}^2(\Delta t)^2 + i\frac{1}{6}\hat{H}^3(\Delta t)^3] \times \Psi_0 = \\ & [-i\hat{H}\Delta t] \left(\frac{1}{2}[-i\hat{H}\Delta t] \left(\frac{1}{3}[-i\hat{H}\Delta t]\Psi_0 + \Psi_0 \right) + \Psi_0 \right) + \Psi_0. \end{aligned} \quad (\text{E.2})$$

The Taylor series propagator requires the use of a rather small time step and hence require a longer propagation than more sophisticated methods. Moreover, the propagation “blows up” very quickly if non-converged parameters, namely time-step and grid-step size, are used. Nevertheless, this property makes it easy to troubleshoot any convergence issues.

The Taylor propagator is easy and straightforward to implement numerically to utilize parallel computation capabilities. This is especially true if the derivative operator in the Hamiltonian is described using high-order finite difference scheme.

APPENDIX E. TAYLOR PROPAGATOR FOR QUANTUM WAVEPACKET

Then the grid can be divided into sectors, each of which is calculated by a different processor. The edges of these sectors overlap to allow to evaluate the derivative at the boundary points. The overlapping regions are then communicated between the different processors after each update of the wavefunction.

Appendix F

Numerical propagator for vibrational wavepacket on coupled potential energy curves

The Split-Operator Fast Fourier Transform method for propagating a quantum wavefunction is based on two ideas.

First, at each time step the propagator for the full Hamiltonian is split into the propagators for the kinetic and potential parts

$$\begin{aligned}\exp[-i\hat{H}(t)\Delta t] &= \exp[-i(\hat{K} + \hat{V}(t))\Delta t] \\ &\approx \exp[-i\hat{K}\Delta t] \exp[-i\hat{V}(t)\Delta t]\end{aligned}\tag{F.1}$$

where $\hat{K}$ and $\hat{V}$ are the operators for the kinetic and potential energy respectively. This splitting is accurate up to the order $(\Delta t)^2$ in time step, where the error is due to the non-vanishing commutator between $\hat{K}$ and $\hat{V}$.

Second, the kinetic energy propagator is evaluated in the frequency domain, where the kinetic energy operator is diagonal, by employing the Fast Fourier Transform (FFT)

$$\exp[-i\hat{K}\Delta t]\Phi(t) = \text{iFFT} \times \tilde{\Phi}(p) \times \exp[-i\frac{p^2}{2}\Delta t] \times \text{FFT} \times \Phi(t)\tag{F.2}$$

where p corresponds to the momentum and FFT corresponds to the transformation to the frequency domain by performing FFT. In turn, the potential energy is evaluated in the real space, where it is a diagonal operator.

Calculating the coupling between the potential energy curves

When the propagation of vibrational wavepackets takes place on multiple coupled potential energy curves, the coupling can be accounted for in the potential energy operator matrix $V(t)$. The associated propagator for a single time-step is then

$$\Phi(t + \Delta t) = \exp(-iV(t)\Delta t) \Phi(t) \quad (\text{F.3})$$

where $V(t)$ is the time-dependent potential matrix

$$V(t) = V_0 + D f(t). \quad (\text{F.4})$$

Here, V_0 is a diagonal matrix containing the energies of the electronic states, $f(t)$ is the laser electric field.

Assuming that the collection of vibrational wavefunction on the i -th potential energy curve (PEC), described by ϕ_i , are stored in a vector as

$$\Phi = \begin{pmatrix} \phi_1 \\ \phi_2 \\ \vdots \\ \phi_i \end{pmatrix}, \quad (\text{F.5})$$

the dipole coupling matrix $D(t)$ is written as

$$D = \begin{pmatrix} 0 & d_{1,2} & d_{1,3} & \dots & d_{1,i} \\ d_{2,1} & 0 & d_{2,3} & \dots & d_{2,i} \\ \vdots & \vdots & \vdots & & \vdots \\ d_{i,1} & d_{i,2} & d_{i,3} & \dots & 0 \end{pmatrix} \quad (\text{F.6})$$

where $d_{i,j}$ is the dipole matrix element between the i -th and the j -th PECs. The matrix D can be formally diagonalized

$$D = S^{-1} \lambda S \quad (\text{F.7})$$

where I is a unit matrix and λ is a vector of eigenvalues of D ; S is the unitary transformation matrix.

Using relation in (F.7) above, the propagator for a time step in (F.3) can be

APPENDIX F. NUMERICAL PROPAGATOR FOR VIBRATIONAL WAVEPACKET ON COUPLED POTENTIAL ENERGY CURVES

written as

$$\Phi(t + \Delta t) = \exp(-iV(t)\Delta t) \Phi(t) \quad (\text{F.8a})$$

$$= \exp(-iV_0\Delta t) \exp(-if(t)D\Delta t) \Phi(t) = \quad (\text{F.8b})$$

$$= \exp(-iV_0\Delta t) S^{-1} \exp(-if(t)\lambda\Delta t) S \Phi(t). \quad (\text{F.8c})$$

Hence, the costly calculation of the exponential of a matrix at each time step by evaluating $\exp(-iV(t)\Delta t)$ is substituted with the multiplication of two (sparse) matrices S^{-1} and S and a vector $\exp(-if(t)\lambda\Delta t)$, which is very efficient numerically.

The propagation scheme described above requires the unitary matrices S^{-1} and S and the eigenvalue vector λ . They are calculated once by numerically diagonalizing the D matrix before the time dependent propagator and used throughout the propagation. Moreover, they can be reused for different calculations as long as the spacial grid and the number of the potential energy curves is kept unchanged.

Appendix G

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