X-ray Spectroscopy of Molecules Driven by Strong Infrared Fields

Freddy Fernandes Guimarães
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PAPER VI  V. C. Felicissimo, F. F. Guimarães, A. Cesar, F. Gel‘mukhanov, and H. Ågren, *Proton transfer mediated by vibronic coupling in oxygen core ionized states of glyoxalmonoxime studied by infrared–x-ray pump-probe spectroscopy*, In Manuscript

PAPER VII  F. F. Guimarães and F. Gel‘mukhanov, *Pump-probe spectroscopy of molecules driven by IR field in both ground and excited states*, In Manuscript

Other published papers not included in the thesis


Comments on my contributions in the papers included in the thesis

- I wrote the wave packet programs as well as the code for simulations of x-ray spectra with taking into account the spin-orbit interaction. These codes are used in all articles of my thesis.

- I was responsible for theory, calculations, writing and editing of manuscript in Papers I, II, III, VII and VIII.

- I participated in discussions and theoretical work, and I was responsible for a few calculations in Papers IV, V and VI.
ABSTRACT

The current thesis deals with one important branch of the physics of ultrafast processes, namely modeling of femtosecond nuclear dynamics. We suggest a new type of time resolved spectroscopy, the phase sensitive infrared–x-ray pump probe spectroscopy, which combines rich opportunities of IR laser techniques in quantum control of molecular systems with the site selectivity of x-rays. We have developed and applied a dynamical theory of x-ray pump-probe spectroscopy to study different molecular systems. Special attention is paid to design of the wave packets of desirable shape and spectral composition. Such a quantum control of the nuclear wave packet enables the study of molecular properties in regions that are unavailable by standard x-ray spectroscopies. The IR–x-ray pump probe spectroscopy is nicely suited to perform mapping of wave packet trajectories, to study revival phenomena, femtosecond chemical dynamics, and proton transfer, to mention a few examples.

Our simulations show that the phase of the infrared pulse strongly influences the trajectory of the nuclear wave packet, and hence, the x-ray spectrum. Such a dependence is caused by the transfer of the phase of the IR field to the wave packet through the interference of the one (x-ray) and two-photon (IR + x-ray) excitation channels. The time resolved x-ray spectra are sensitive to the shape, duration and delay time between the pulses. The phase of the IR pulse influences the molecular dynamics also when the Rabi period becomes comparable with the period of vibrations, breaking down the rotating wave approximation. We predict a phase memory effect which is a promising technique in studies of chemical dynamics on different time scales. It is shown that the final state interaction with the pump affects the probe spectrum when the pump and probe pulses overlap.

In a further step, we explore the electronic recoil effect in x-ray photoelectron spectroscopy, which has recently attracted attention of experimentalists due to its sensitivity to intramolecular interaction. We show that an IR field enhances the manifestation of the recoil effect through the formation of extensive vibrational wave packets. The theory of x-ray Raman scattering from molecules with strong spin-orbit coupling accompanied by electron-hole interaction is developed and applied to simulations of resonant x-ray Raman scattering of the HCl molecule. Special attention is paid to the theoretical methodologies to reduce the computational cost of our wave packet codes.
CHAPTER 1

Introduction

1.1 Time-resolved spectroscopy and quantum dynamics: Brief overview

Interaction of intense and short electromagnetic pulses with matter are attracting increasing interest due to its intrinsic potential to investigate the dynamics of quantum systems in real time scales and because of the possibility to manipulate quantum states. Time-resolved laser spectroscopies open new perspectives in the studies of dynamical processes in structural chemistry, biology and the physics of phase transitions. The coherent superpositions of quantum states, or wave packets, that can be created by electromagnetic fields, are recognized to be important in different branches of physics and modern technology.\textsuperscript{1-7} The laser is the ideal tool to control or even design the wave packet properties through the variation of the light parameters: frequency, shape, duration time and intensity. From this point of view, one can say that lasers are able to act as catalysts driving the target to the desirable transition states and final products.\textsuperscript{2,3}

Time dependent pump-probe spectroscopy turns out to be the adequate setup to study ultrafast quantum dynamics of electrons and nuclei, for example the fast motion of the nuclear wave packet in the potential energy surfaces. The wave packet is the natural concept and theoretical tool to describe the time evolution of quantum systems.

In the next section (1.2) some historical aspects of the quantum theory and spectroscopy will be briefly discussed. The experimental evolution in the development of short laser pulses and the new information that can be provide by the ultrashort laser pulses are presented in Sec. 1.3. Sec. 1.4 is dedicated to the quantum control of the atomic and molecular systems that leads to two major areas: (i) the reaction control and (ii) the quantum computation. Finally, the chapter ends up with Sec. 1.5 devoted to a
new phase sensitive time-resolved spectroscopy, which combines short infrared (IR) and synchrotron radiation pulses, to study ultrafast nuclear dynamics. Such kind of spectroscopy is a promising new experimental tool in studies of femto and subfemtosecond processes in molecular physics and chemistry.

1.2 Spectroscopy and quantum theory: Historical aspects

Historically, spectroscopy was the area where quantum mechanics was first successfully applied, and the physics behind the atomic and molecular spectral lines was for long the main aim of quantum mechanics. The Balmer-Rydberg equation,

\[ \frac{1}{\lambda} = R_y \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right), \]

(1.1)
can be considered as the first accurate empirical description of the positions of the atomic spectral lines depicted in Fig. 1.1. \( \lambda \) is the wavelength, \( n_i, n_f \) are integers and \( R_y \) is a universal constant. In the years of 1884 and 1885, Balmer, who indeed was not interested in science itself but actually in numerology, discovered a formula to compute the 19 lines of the Fraunhofer spectrum and all the lines in the visible region. In 1890 Rydberg rewrote the Balmer expression in terms of wavelengths, and he extended it to describe the series of the alkali metals, the alkaline earths and other elements introducing the parameter \( R_y \) (see Eq. (1.1)), which is known as the Rydberg constant.

![Bright line spectra](image)

FIG. 1.1: Bright line spectra.
1.3 Strong and intense ultrashort laser pulses

It is possible to recognize from Eq. (1.1) that the wavelengths of the spectral lines are always given as the difference between two quantities and that emission frequencies are determined by a single universal constant. The Bohr atomic model of 1913, which considered quantized momenta for the electrons in each electronic orbit, brought these facts together. The Bohr theory is able to correctly describe the hydrogen atom properties, producing the Balmer equation and an analytical expression for the Rydberg constant.

The Bohr description of the hydrogen atom is able to describe the position of the lines in the atomic spectra. However, this theory is unable to explain the distribution of intensities of the spectral lines. A general theory of spectral lines was built only after the creation of quantum mechanics [Wave Mechanics of E. Schrödinger and Matrix Mechanics of Born, Heisenberg and Jordan].

The development of the quantum theory and of the atomic model was an effort of many scientists. The ideas about the atoms, which started to be developed by the ancient Greek philosophers, achieved its quantized form in the beginning of the 20th century (Fig 1.2). Nowadays, we can say that the background of the quantum theory is well established. However, this cannot be considered as the end of research in quantum mechanics. Actually, the quantum theory shows that is possible to build many new exciting technological devices that were unconceivable from the classical theories. Some examples of recent developments are quantum teleportation and quantum computation. There are a lot of theoretical and experimental efforts in these areas but, so far, neither of them are yet practical. The great challenge of modern science is the physics of complex systems.

![The ancient Greek philosophers (first ideas) → D. H. D. (early 20th) → J. J. Thomson (1897) → E. Rutherford (1911) → N. Bohr (1913) → Schrödinger (1926)](image)

FIG. 1.2: Some key scientists and chronological evolution of the atomic model.

1.3 Strong and intense ultrashort laser pulses

Light Amplification by Stimulated Emission of Radiation, called LASER, is one of the greatest technological achievements of the 20th century. The first lasers were constructed in 1960. They use the process of stimulated emission (after Einstein) to amplify light waves in order to produce monochromatic light. The lasing starts from the pump of the
system which creates the inversion of populations. The spontaneous photon emitted by the atom stimulates the photon emission from the next atom, and so on. The optical resonators or mirrors are an important ingredient in laser generation.

Since the mid 80’s the generation of short and ultrashort laser pulses has received a considerable interest from the scientific community. The reason for this is that short and ultrashort laser pulses have increasing applications in many distinct branches of science like nonlinear optics, biophysics, modern information and communication technologies. The fast process, for instance, can be studied with the use of ultrashort laser pulses, yielding important insight into the underlying dynamics\textsuperscript{11} of quantum systems. Two-way laser communication in space has long been a goal for NASA because it would enable data transmission rates that are 10 to 1,000 times higher than traditional radio waves. While lasers and radio transmissions both travel at light-speed, lasers can pack more data. In biology and medicine the direct utilization of laser pulses includes propagation studies in scattering media with applications in optical mammography, dosimetry for photodynamic therapy and assessment of species concentration.\textsuperscript{12} Time-resolved studies of the physical-chemical processes of living organisms has become a hot topic in modern laser spectroscopy.

The generation of ultrashort laser pulses rely mainly on two advanced methods: colliding-pulse modelocking\textsuperscript{13} and high(-order) harmonic generation.\textsuperscript{14,15} The colliding-pulse modelocking technique enables the generation of femtosecond pulses from a dye laser. Ti-sapphire lasers (660 nm to 1180 nm), that use passive modelocking techniques, can produce pulses as short as 5 femtoseconds long. Although, 5 femtoseconds is already a very short duration time, the more advanced technique of high harmonic generation may be able to produce pulses even as short as 100 attoseconds (0.1 femtoseconds). A more detailed description of the techniques for generating, manipulating and detecting picosecond and sub-picosecond electromagnetic pulses are described in the literature in refs.\textsuperscript{16-18} The high(-order) harmonic generation\textsuperscript{15} is nowadays the only way to get sub-femtosecond x-ray pulses. The x-ray free-electron laser (XFEL) will produce brilliant but rather long pulses about 100-200 fs.\textsuperscript{19} The slicing technique allows to produce shorter x-ray pulses with lower intensity.\textsuperscript{20,21} Very recently, the first experiments with a VUV free-electron laser were performed at DESY.\textsuperscript{22}

New measurements techniques and data processing methods have been and are being developed for ultrafast measurements. In fact, they are indispensable for analyzing the detailed features of the real-time results delivered by high power lasers, wideband impulse radars and x-ray beamlines. Moreover, the developments in the pulse generation
have consequences for the instrumentation of measurements, as scientists endeavor to implement new methods and analytical approaches in the difficult challenge of modeling the dynamics of the ultrafast physical phenomena, which is one of the objectives of this thesis.

1.4 Quantum control

The term *quantum control* is used here in the sense to produce a specific Coherent Superposition of Quantum States (CSQS) or wave packet $\Psi(t)$ using the electromagnetic field. The intense short laser pulses coherently mix, or entangle, stationary quantum states of molecules $\psi_\nu$,

$$
\Psi(t) = \sum \nu a_\nu(t) \psi_\nu. \tag{1.2}
$$

The distinct CSQS are built by distinct laser pulses, that differ from each other in terms of their parameters, e.g., time duration, shape, intensity and frequency. The *quantum control* of the system (1.2) is the laser operation on the contributions of different stationary states $\psi_\nu$, through the coefficients $a_\nu(t)$.

1.4.1 Driving reactions

Since the first lasers were developed chemists have tried to use these special light sources to control the outcome of molecular reactions.\textsuperscript{23} The creation of the wave packet (WP) by laser pulses opens a new avenue of possibilities in the synthesis of chemical products. For instance, reactions can be driven to the unfavorable products due to the creation of an adequate CSQS. The experimental evidence that lasers are efficient tools for this purpose has begun to emerge in the last few years.\textsuperscript{4-6}

Beyond the general scenario of the mixture of quantum states, the inherent interferences in the CSQS play an important role in the reaction control. The induced constructive and destructive interferences in chemical reactants may allow obtaining products with high degrees of selectivity and yield. Such procedures are known nowadays as laser catalysis of reactions induced by quantum control via light interaction.\textsuperscript{2-7} In this area, there are a lot to be learned, just as chemists have done in developing reactions with traditional tools.
1.4.2 Performing quantum logic gates

Although much of the data in the world is now carried by light along optical fibers, the information processing and handling is usually still done after converting the signals into electrical currents, that are easily manipulated. The conversion of the signal slows down the whole process. A quantum computer, otherwise, could directly handle and process the information transmitted by the optical fibers. However, this is not the only advantage of the quantum computers. The quantum gates used in quantum computers are able to perform logical operations more efficiently than the Boolean ones, what would make the quantum computers much faster than the standard computers.

A brief history of quantum computing

The idea of a computational device based on quantum mechanics dates from 1970’s and early 1980’s, when scientists were pondering the fundamental limits of computation. If technology continued to abide by Moore’s Law with the continually shrinking size of circuitry packed onto silicon chips, when the individual elements becomes no larger than a few atoms, the properties of the circuit would no longer follow the classical mechanics. In the atomic scale the physical laws that govern the behavior and properties of the circuit are inherently quantized. From such kind of thinking the question if a computer could be based on the quantum mechanics principles started to rise.

Bits and qubits

Feynman gave an answer to this question producing an abstract model in 1982. The model showed that a quantum system, in principal, can be used to perform quantum logic gates. These quantum logical gates are analogous to the Boolean logic gates used in the standard computation. On one hand, the traditional computers manipulated bits via Boolean logic gates to produce an end result. On the other hand, the quantum computers, manipulate qubits via quantum logic gates. While the bits accept only two well defined values (0 or 1) the qubits are more flexible and powerful allowing the use of any linear combination of two quantum states e.g. the +1/2 and −1/2 spin of electrons.

Hardwares to perform quantum computation

A quantum computer can, in principal, be simulated by a classical computer. However, this does not improve its efficiency. The classical computer is incapable of performing
many tasks that a quantum computer could perform very easily, due the quantum laws like the entanglement that are behind a real quantum machinery.

The quantum computing hardware is still in its infancy. The most popular component in quantum hardware architecture nowadays is derived from the nuclear magnetic resonance (NMR) experiment. Despite of this the quantum controlled pump-probe spectroscopy, using ultrashort laser pulse technology and coherent beam interaction with matter, could be used alternatively. The realization of logical gates and quantum computing algorithms in atoms and molecules, especially using the feedback control methods can be found in the literature.\textsuperscript{24} The viability to use vibrational modes of molecules as qubits was demonstrated by Suzuki \textit{et. al.}\textsuperscript{25} and the connection between quantum computation and quantum control has been give by Shapiro \textit{et. al.}\textsuperscript{26,27} who recognized the importance of the fractional revivals of the vibrational wave packet to perform a logical gate.

1.5 Quantum controlled pump-probe spectroscopy

Pump-probe experiments in the IR and optical regions have been used during the last few years to measure properties of atomic and molecular systems.\textsuperscript{11} In this thesis we propose a setup that combines IR radiation and x-rays. The use of coherent IR fields as the pump radiation gives to this spectroscopy the status to be quantum controlled, because the properties of the system can be designed by the IR laser pulse generating a specific coherent superposition of vibrational states. The advantages of the use of x-rays rely on its site selectivity, which enables detailed studies in specific regions of large molecules. This means that such kind of a spectroscopic setup works as an experimental laboratory to rationalize the quantum control of large molecular systems that are beyond the current possibilities of a full \textit{ab-initio} theoretical description.

A qualitative illustration of IR–x-ray pump-probe spectroscopy is given in Fig. 1.3. In this spectroscopy, firstly the pump field in the IR region interacts with the initial stationary state (represented by the dashed line label A) generating a coherent dynamical state. The WP, represented in two different times by the continuous line labels B and C in the region near the turning points, where the velocity of the wave packet achieves its minimum and changes sign, moves back and forth in the Potential Energy Surfaces (PES) for long periods of time, due to the long life time of vibrations in comparison with the excited electronic states. The WP oscillations are probed by short x-ray pulses, displaying the sensitivity of x-ray absorption to the the WP localization and, hence, to
the time delay as can be seen from Fig. 1.3. The arrows in this figure mark the WP center of mass and the center of gravity of the spectrum. Since the spectral profile is sensitive to the WP position, one can expect a relationship between the trajectory of the wave packet and the center of gravity of the x-ray absorption.

![Graphs showing absorption and ionization probabilities](image)

**FIG. 1.3:** Qualitative illustration of the IR–x-ray pump-probe spectroscopy. The left and right panels are, respectively, the O(1s) x-ray absorption of the NO molecule and O(1s) x-ray photoelectron spectrum of the water dimer.

Time-resolved x-ray spectroscopy of the IR laser driven molecules constitutes the major part of the material presented in the following chapters, as well as, in the papers reprinted in the present thesis. The next chapters are organized as follow. The theoretical background is outlined in Chapter 2. In Chapter 3 we highlight the numerical methods used in the propagation of WPs. The physics of the phase sensitive IR–x-ray pump-probe spectroscopy is described in detail in Chapter 4. Chapter 5 is devoted to the dynamics of the formation of resonant x-ray Raman spectra of the HCl molecule near the Cl $L_{III}$ edge. The main results are summarized in Chapter 6.
CHAPTER 2

Theoretical background of x-ray interaction with molecules driven by strong IR pulses

2.1 General theory of IR–x-ray pump-probe spectroscopy

Let us begin with the general case of absorption of a probe x-ray pulse $E_X(t)$ by molecules driven by a strong IR field $E_L(t)$ in both ground and excited electronic states. These fields interact with the molecular dipole moment $d$

$$V(t) = V_X(t) + V_L(t), \quad V_n(t) = -(d \cdot E_n(t)) \cos(\omega_n t + \varphi_n), \quad n = L, X. \quad (2.1)$$

Atomic units are used everywhere unless otherwise stated. Here $\omega_n$ and $\varphi_n$ are the frequency and the phase of the $n$th field, respectively. We ignore the wave vectors of both fields $k_n$, although the small momentum of IR photon $k_L$ under certain conditions can influence the x-ray probe spectrum through the phase:

$$\varphi_L \rightarrow \varphi_L - k_L \cdot R_\alpha \quad (2.2)$$

where $R_\alpha$ is the coordinate of the molecular center of mass. The x-ray radiation mixes ground $\psi_0$ and core-excited $\psi_c$ electronic states

$$\Psi(t) = \psi_0 \Phi_0(R, t)e^{-iE_0t} + \psi_c \Phi_c(R, t)e^{-iE_c t}. \quad (2.3)$$

This electron-nuclear wave packet obeys the Schrödinger equation

$$i \left( \frac{\partial}{\partial t} + \hat{\Gamma} \right) \Psi(t) = H(t)\Psi, \quad H(t) = H - V(t) \quad (2.4)$$

Here, $H$ is the total molecular Hamiltonian; $\hat{\Gamma}$ is the matrix of relaxation (see below); $E_0 = U_0(R_0)$, and $E_c = U_c(R_c)$ are minimal energies of the ground and core-excited
potentials $U_0(R)$ and $U_c(R)$, respectively; $R$ is nuclear coordinates (bond distance in the case of diatomic molecules); $E_c$ is the dissociative limit $U_c(\infty)$ if the core-excited state is dissociative. The nuclear wave packets in ground ($\Phi_0$) and excited ($\Phi_c$) states satisfy the following coupled equations

$$i \left(\frac{\partial}{\partial t} + \hat{\Gamma}\right) \Phi = \hat{H} \Phi, \quad \hat{\Gamma} = \begin{pmatrix} 0 & 0 \\ 0 & \Gamma \end{pmatrix} \quad (2.5)$$

$$\Phi = \begin{pmatrix} \Phi_0 \\ \Phi_c \end{pmatrix}, \quad \hat{H} = \begin{pmatrix} h_0 + V_L^{00} & V_X^{0c} \\ V_X^{c0} & h_c + V_L^{cc} \end{pmatrix}$$

with the initial condition

$$\Phi(t = 0) = \begin{pmatrix} |0\rangle \\ 0 \end{pmatrix} \quad (2.6)$$

where $|0\rangle$ is the zero-point vibrational state of the ground electronic level. The decay matrix $\hat{\Gamma}$ takes into account only the decay rate of core excited state $\Gamma$ and ignores the decay rate of vibrational levels in the ground state $\Gamma_0$, because $\Gamma_0 \ll \Gamma$. The dynamics of the wave packets is defined by the nuclear Hamiltonians of ground ($h_0$) and excited ($h_c$) states

$$h_i = T + U_i(R) - E_i, \quad i = 0, c. \quad (2.7)$$

Here $T$ is the operator of kinetic energy of the nuclei. The interaction $V_L^{ii} = (\psi_i|V_L|\psi_i)$ of the nuclei with the IR field

$$V_L^{ii} = -(d_{ii} \cdot E_L(t)) \cos(\omega_L t + \varphi_L), \quad d_{ij} = d_{ij}(R) = \int \psi_i^*(\mathbf{r}, R) d_{ij}^*(\mathbf{r}, R) d\mathbf{r} \quad (2.8)$$

is different in ground and core-excited states due to the difference of the molecular dipole moments $d_{00}$ and $d_{cc}$. The $R$-dependence of these dipole moments is crucial for the interaction with the IR field, because vibrational transitions are absent if $d_{ii}(R) = \text{const}$. It is worthwhile to note that when $d_{ii}(R) = \text{const}$, the quadrupole interaction with the IR field becomes important.\textsuperscript{29} We treat the dipole interaction with a weak probe x-ray field in the framework of the rotating wave approximation

$$V_X^{c0} = V_X^{0c} = -\frac{1}{2}(\mathbf{E}_X(t) \cdot \mathbf{d}_{c0}) \Phi_0 e^{-i(\Omega t + \varphi_X)} \quad (2.9)$$

and introduce the detuning

$$\Omega = \omega_X - \omega_{c0} \quad (2.10)$$

of the carrier frequency $\omega_X$ of the x-ray field relative to the $\omega_{c0} = E_c - E_0$.

The coupled Schrödinger equations (2.5) with the initial condition (2.6) are solved numerically in Sec. 4.13. However, this numerical scheme is rather expensive, because to
get the spectrum we need to solve equations for each value of the photon frequency $\omega_X$ or photoelectron energy. As shown in Sec. 2.2, the numerical scheme is essentially simpler when the IR radiation interacts only with molecules in the ground electronic state.

### 2.1.1 X-ray probe spectrum

The instantaneous probability of x-ray absorption

$$P(t, \Omega) = 2 \Im \langle \Phi_c | V_x^{\Omega} | \Phi_0 \rangle = E_X(t) \Im \{ \langle \Phi_0 | d_0c(R) | \Phi_c \rangle \ e^{i(\Omega t + \varphi_X)} \}$$  \hspace{1cm} (2.11)

is nothing else than the rate of population of the core-excited state by the x-ray pulse

$$\left( \frac{\partial}{\partial t} + 2\Gamma \right) \rho_{cc}(t) = P(t, \Omega).$$  \hspace{1cm} (2.12)

The duration of standard x-ray measurements is longer than the pulse duration. This motivates us to use the integral probability which gives the spectrum of the probe signal

$$P(\Omega) = \int_{-\infty}^{\infty} P(t, \Omega) \ dt = 2\Gamma \int_{-\infty}^{\infty} \rho_{cc}(t) \ dt.$$  \hspace{1cm} (2.13)

Thus, according to Eq. (2.12), the x-ray probe spectrum can be computed using the instantaneous probability (2.11) or the population of the core excited state, $\rho_{cc}(t) = \langle \Phi_c | \Phi_c \rangle$.

We will see below (see Sec. 4.4) that the phase of the coherent IR radiation $\varphi_L$ affects strongly the x-ray absorption or photoionization when the duration of the x-ray pulse is shorter than the period of vibrations (Paper I). This happens because the IR induced WP dynamics depends strongly on $\varphi_L$. The absorption of the probe field does not depend on the phase of the x-ray pulse $\varphi_X$ except in the case of a time-dependent phase $\varphi_X(t)$.

### 2.2 Probe spectrum with x-ray pulse delayed relative to the IR pulse

The theory of pump-probe spectroscopy admits great simplification when the x-ray pulse is absorbed by molecules after the IR pulse has left the system. In this case the probe spectrum (Paper II)

$$P(\Omega) = \langle \phi_c(\Omega) | \phi_c(\Omega) \rangle, \quad \phi_c(\Omega) = \int_{-\infty}^{\infty} dt \ e^{-i\Omega t} \ E_X(t) \ |\phi_c(t)\rangle$$  \hspace{1cm} (2.14)
is simply the norm of the WP in the frequency domain, $|\phi_c(\Omega)|$. Here $|\phi_c(t)\rangle$ is the nuclear wave packet that evolves in core-excited potential energy surface,

$$|\phi_c(t)\rangle = e^{i\zeta t}|\phi(t)\rangle, \quad \zeta = \frac{1}{2}(d_{e0} \cdot e_X),$$

(2.15)

and, $e_X$ is the polarization vector of x-ray photon.

Contrary to $\Phi_c(t) \equiv \Phi_c(\omega_X, t)$ (2.5) the wave packet $\phi_c(t)$ (2.15) does not depend on the photon frequency $\omega_X$. Due to such an essential advantage we use $\phi_c(t)$ instead of $\Phi_c(t)$ in the numerical simulations of the probe signal with the delayed probe pulse. The calculation of $\phi_c(t)$ is performed along the contour (Fig. 2.1) where the ground state wave packet $\phi(t)$ evolves from the moment 0 up to $t$

$$i\frac{\partial}{\partial t}\phi(t) = [\hbar_0 - (d_{00} \cdot E_L(t)) \cos(\omega_L t + \varphi_L)] \phi$$

(2.16)

The x-ray field promotes $\phi(t)$ at the instant $t$ to the excited states where the newly formed wave packet $\phi_c(t)$ evolves in the inverse direction from moment $t$ up to 0. The dynamics in the inverse direction is seen from the fact that the wave packet $\phi_c(t) \equiv \phi_c(0, t)$ is the solution of the Schrödinger equation

$$i\frac{\partial}{\partial \tau}\phi_c(\tau, t) = \hbar_c \phi_c(\tau, t)$$

(2.17)

from $\tau = t$ till 0 with the initial condition $\phi_c(t, t) = \zeta \phi(t)$.

FIG. 2.1: Time loop used in the wave packet calculation.
CHAPTER 3

Wave packet propagation methods

Here, we outline implementation of three numerical techniques used in our computational simulations: The second order differencing (SOD) method, the Adams-Bashforth (ABM) method, and the short iterative Lanczos (SIL) propagation method.

3.1 Second order differencing scheme

The second order differencing (SOD) scheme is the simplest way to solve numerically first order differential equations. It consists in the discretization of the time dependent Schrödinger equation, where the derivative with respect to time is replaced by the finite difference expression\(^30\) given by

\[
|\psi(r, t + \Delta t)\rangle = |\psi(r, t - \Delta t)\rangle - \frac{2t\Delta t}{\hbar} H(t)|\psi(r, t)\rangle + \mathcal{O}[(\Delta t)^2].
\]

(3.1)

Here, \(H(t)\) is the Hamiltonian matrix, \(|\psi(r, t + \Delta t)\rangle\) is the WP in the coordinate domain and \(\Delta t\) is the time step. The biggest advantages of the SOD method are its simplicity, low memory usage, and fast computational time even when small time steps are used. The SOD method works very well in WP simulations with an ordinary real Hamiltonian which ignores the irreversible decay of quantum states. The SOD method is known to be unstable when an exponential decay is included. Therefore, it can not be used in problems where the relaxation is included directly in the Hamiltonian.

One of the main problems in the implementation of the SOD methods is related to the initial conditions, since the SOD method requires the knowledge of two initial conditions \(|\psi(r, 0)\rangle\) and \(|\psi(r, \Delta t)\rangle\). In general, the wave packet is known at the time, \(t = 0\); however, we do not know the WP at any future time. The way to solve this problem is to use a Taylor expansion

\[
|\psi(r, t + \Delta t)\rangle = \left(1 - \frac{i\Delta t}{\hbar} H(t)\right)|\psi(r, t)\rangle + \mathcal{O}[(\Delta t)]
\]

(3.2)
which needs only one initial value $|\psi(r, 0)|$.

The SOD technique (3.1) starts from $|\psi(r, 0)|$ and $|\psi(r, \Delta t/2)|$ computed making use the Taylor expansion (3.2). Then $|\psi(r, \Delta t)|$ is calculated using Eq. (3.1) in the instant $t = \Delta t/2$ with the step $\Delta t/2$. Thus, after the SOD scheme (3.1) is used to compute the wave packet for the future times. The SOD algorithm is shown schematically in Fig. 3.1. The symbols $v_t$ is the complex vector of a wave packet at the instant $t$ in different points of the coordinate space. In the eSPec program the Planck constant $\hbar$ is used in units of a.u./fs and the WP $|\psi(r, t)|$ has the euclidean $l^2$-norm equal to 1.

\vcenter{\begin{tabular}{|l|}
\hline
$v_{t=0}$ must be known and, $\Delta t$ is properly 
set to avoid numerical instabilities and errors
\hline
Initialization:
1. $v_{t=0.5\Delta t} = v_{t=0} - \left[i\Delta t/(2\hbar)\right] H v_{t=0}$;
2. $v_{t=\Delta t} = v_{t=0} - (i\Delta t/\hbar) H v_{t=0.5\Delta t}$;
\hline
Propagation:
for $k=1,2,\ldots$
3. $v_{t=(k+1)\Delta t} = v_{t=(k-1)\Delta t} - (2i\Delta t/\hbar) H v_{t=k\Delta t}$;
\hline
\end{tabular}}

FIG. 3.1: Implementation of the second order differencing propagation algorithm.

The SOD method was used to solve Eqs. (2.16) and (2.17) for different molecular systems (see Fig. 3.2). To avoid numerical errors we used the integration steps $\Delta t$ of the order of magnitude of $10^{-4}-10^{-5}$ fs. Such small time steps are able to keep constant the norm of the WP and conserve the average energy of the system for the time independent Hamiltonians.

### 3.2 Adams-Bashforth method

The Adams-Bashforth second-order formula is given by:

$$|\psi(r, t+\Delta t)| = |\psi(r, t)| - \frac{i\Delta t}{2\hbar} \left(3H(t)|\psi(r, t)| - H(t-\Delta t)|\psi(r, t-\Delta t)|\right) + O[(\Delta t)^2].$$

Due the second-order the Adams-Bashforth method (ABM) can be implemented in two distinct ways, since it requires the computation of $H(t-\Delta t)|\psi(r, t-\Delta t)|$. The first possible implementation, that will be called the fast computational algorithm (FCA), performs the calculations keeping in the computer memory the values of the matrix-vector multiplications $H(t)|\psi(r, t)|$ of the current step, which are used in the next step.
The second implementation, that we call low memory usage (LMU), consists of the direct computation of matrix-vector multiplication $H(t - \Delta t)|\psi(r, t - \Delta t)\rangle$ for each time step.

The two possible ABM implementations are shown in Fig. 3.3. The ABM must be initialized like the SOD method. This is done again using the Taylor expansion. The initialization is represented by steps 1, 2 and 3 in the FCA implementation and steps 1 and 2 in the LMU implementation. The propagation of the wave packet is done iteratively by steps 4, 5 and 6 and step 3 for FCA and LMU implementations, respectively.

In contrast to the SOD method, the Adams-Bashforth method has good stability properties. This means that errors are not amplified during the propagation. This allows to use slightly larger time steps in comparison with the SOD scheme, decreasing the computational time. Actually, the computational cost of the FCA implementation of the ABM is comparable with the SOD technique even for the same time step. The biggest advantage of the ABM is to solve Schrödinger equation including relaxation, like the finite life time of a core-excited state. The LMU implementation is not as fast as SOD or FCA-ABM; however, such implementations can be useful to solve multidimensional WP propagations, where the memory allocation is the key factor.

The FCA-ABM method is implemented in the eSPeC program (Fig. 3.2) for the solu-
$$v_{t=0} \text{ must be known and, } \Delta t \text{ is properly set to avoid numerical errors}$$

**Initialization:**

1. \( b = Hv_{t=0}; \)
2. \( v_{t=0.5\Delta t} = v_{t=0} - [i\Delta t/(2\hbar)] \ b; \)
3. \( v_{t=\Delta t} = v_{t=0.5\Delta t} - \frac{i\Delta t}{4\hbar} (3Hv_{t=0.5\Delta t} - p); \)

**Propagation:**

for \( k=1,2,\ldots \)

4. \( a = v_{t=k\Delta t} + \frac{i\Delta t}{2\hbar} b; \)
5. \( b = Hv_{t=k\Delta t}; \)
6. \( v_{t=(k+1)\Delta t} = a - \frac{i3\Delta t}{2\hbar} b; \)

FIG. 3.3: Two distinct implementations of Adams-Bashforth propagation algorithms. (a) is the FCA and (b) the LMU implementations.

...tion of the coupled Eqs. (2.5) with the constraint of the conservation of the total norm of the WP (but not partial norms).

### 3.3 Short iterative Lanczos propagation

The Short iterative Lanczos (SIL) propagation technique is the best method to simulate the multidimensional WP propagations. It consists of the Lanczos tridiagonalization procedure to obtain a tridiagonal matrix of reduced size. This method requires very low memory usage, because it has to allocate only \( 2n \) elements to tridiagonalize a Hermitian matrix with \( n \times n \) elements. The SIL method needs only one initial condition which is one of the advantages of this method comparing with the SOD and ABM techniques. Let us briefly outline the Lanczos tridiagonalization procedure and its implementation in the
3.3 Short iterative Lanczos propagation

3.3.1 Lanczos tridiagonalization procedure

The Lanczos tridiagonalization procedure starts from the orthogonal transformation

\[ L = Z^\dagger H(t)Z, \]  

(3.4)

of the Hamiltonian matrix \( H(t) \) to obtain the tridiagonal matrix \( L \) with elements,

\[
L = \begin{pmatrix}
\alpha_1 & \beta_1 & 0 & \ldots & 0 \\
\beta_1 & \alpha_2 & \beta_2 & \ddots & \vdots \\
0 & \beta_2 & \ddots & \ddots & 0 \\
\vdots & \ddots & \ddots & \ddots & \alpha_{n-1} \\
0 & \ldots & 0 & \beta_{n-1} & \alpha_n
\end{pmatrix}.
\]  

(3.5)

To compute the matrix elements \( \alpha_i \) and \( \beta_i \)

\[
\alpha_i = z_i^\dagger H(t)z_i, \quad \beta_{i-1} = z_{i-1}^\dagger H(t)z_i.
\]  

(3.6)

we need the vectors \( z_i \) which are the solutions of the following recursive equation

\[
z_{i+1} = H(t)z_i - \alpha_i z_i - \beta_{i-1}z_{i-1}.
\]  

(3.7)

One possible implementation of the Lanczos tridiagonalization algorithm is shown in Fig. 3.4. We see that the Lanczos technique begins with the initial guess of the vector \( z_1 \), which can be generated randomly. In many cases, as in the current thesis, a good initial guess for the vector \( z_1 \) is known explicitly.

3.3.2 SIL wave packet propagation

The Lanczos tridiagonalization procedure discussed in the previous subsection is well adapted for WP simulations, when the discretized form of the propagation operator,\(^8\)

\[
|\psi; t + \Delta t\rangle = e^{-iH(t)\Delta t/\hbar}|\psi; t\rangle,
\]  

(3.8)

is used. We want to point out that Eq. (3.8) is numerically correct even for time dependent Hamiltonians if the time step \( \Delta t \) is small enough to consider \( H(t) \) time independent on the interval \( \Delta t \).

When the \( L \) matrix is diagonalized the wave packet is computed as

\[
|\psi; t + \Delta t\rangle = (Z^\dagger)_{n \times p}(Q^\dagger)_{p \times p}e^{-i(D)_{p \times p}\Delta t/\hbar}(Q)_{p \times p}(Z)_{p \times n}|\psi; t\rangle.
\]  

(3.9)
1. \( z_1 \) is given;
2. \( k = 1; \)
3. \( \beta_1 = \sqrt{z_1^*z_1}; \)
4. \( k = k + 1; \)
4.1. \( q_k = z_{k-1}/\beta_{k-1}; \)
4.2. \( u_k = Hq_k; \)
4.3. \( z_k = u_k - \beta_{k-1}q_k; \)
4.4. \( \alpha_k = q_k^r; \)
4.5. \( z_k = z_k - \alpha_k q_k; \)
4.6. \( \beta_k = \sqrt{z_k^*z_k}; \)
5. If \( k > p \) finish;
6. If \( k < p \) go to 4;

**FIG. 3.4:** Lanczos algorithm for tridiagonalization of Hermitian matrices.

The diagonalization of the \( (L)_{p \times p} \) matrix results in the eigenvector \( (Q)_{p \times p} \) and eigenvalue \( (D)_{p \times p} \) which are equal approximately to the eigenvalues of \( H(t) \). Here the subscript is the matrix dimensionality. The SIL method is efficient because the number of recurrences \( p \) used in the Lanczos algorithm (Fig. 3.4) is much smaller than the number of rows \( n \) of the Hamiltonian.

The SIL algorithm is shown in Fig. 3.5. In the step 1 we compute the matrices \( Z \) and \( L \) using the algorithm shown in Fig. 3.4 and marked as \text{tridiag}. Matrices \( Q \) and \( D \) are obtained in the step 2 by diagonalization (\text{diag}) of the tridiagonal matrix \( L \). The algorithm is applied iteratively to compute the WP in the future times \( t \).

\[
\begin{align*}
\mathbf{v}_{t=0} \text{ must be known and, } & \Delta t \text{ is properly} \\
& \text{set to avoid numerical errors} \\
& \text{for } k=0,1,2,\ldots \\
1. & \mathbf{Z}_{t=k\Delta t}^{(p \times n)} \text{ and } \mathbf{L}_{t=k\Delta t}^{(p \times p)} \Rightarrow \text{tridiag} \left( \mathbf{H}_{t=k\Delta t} \right); \\
2. & \mathbf{Q}_{t=k\Delta t}^{(p \times p)} \text{ and } \mathbf{D}_{t=k\Delta t}^{(p \times p)} \Rightarrow \text{diag} \left( \mathbf{L}_{t=k\Delta t} \right); \\
3. & \mathbf{v}_{t=(k+1)\Delta t}^{(n)} = \mathbf{Z}_{t=k\Delta t}^d \mathbf{Q}_{t=k\Delta t}^d \exp \left( -i \mathbf{D}_{t=k\Delta t} \Delta t/\hbar \right) \mathbf{Q}_{t=k\Delta t}^d \mathbf{Z}_{t=k\Delta t}^d \mathbf{v}_{t=k\Delta t}.
\end{align*}
\]

**FIG. 3.5:** Algorithm of propagation SIL.
CHAPTER 4

Infrared–x-ray pump-probe spectroscopy

Let us turn our attention to the physics of x-ray absorption/photoionization of molecules driven by strong IR pulses. In this chapter, we focus mainly on the IR–x-ray pump-probe spectroscopy with the probe pulse delayed relative to the pump. Due to such delay the IR pulse interacts with the molecule only in the ground electronic state. We have to take into account the interaction of the pump radiation in both ground and core-excited states when the probe and pump pulses overlap (Sec. 4.13).

4.1 X-ray probe spectrum of molecules excited by incoherent light

The IR–x-ray pump-probe technique consists of two steps as illustrated in Fig. 1.3. In the first step a strong IR field excites vibrational levels \( \nu = 1, 2, \ldots \) of the ground electronic state with the amplitude of vibrational transitions

\[
\langle 0|d(R)|\nu\rangle \approx d'\langle 0|R - R_0|\nu\rangle.
\]

(4.1)

where \( R_0 \) is the equilibrium bond length. This equation shows that the IR transitions are allowed only when the molecular dipole moment depends on the bond length, \( R \). When the IR pulse leaves the system a short x-ray pulse promotes the vibrationally excited molecule to the core-excited or ionized state. The first important modification that takes place in the x-ray absorption profile is the appearance of hot bands. These hot bands origins in the x-ray transitions from the excited vibrational levels of ground electronic state \( \nu = 1, 2, \ldots \) to the vibrational levels of the final electronic state. Apparently, even incoherent IR pulses create hot bands. The shape of such hot bands strongly depends on the excited vibrational level of the ground electronic state, due to the strong sensitivity of the Franck-Condon (FC) distribution in relation to the initial vibrational state (see
Fig. 4.1). When the IR field is incoherent the only role of the IR field is to change the populations of the vibrational levels, $\rho_{\nu}$. In this case the spectrum is the sum of the partial probabilities, $P^{(\nu)}(\Omega)$, of the core excitation from a certain vibrational level, $|\nu\rangle$

$$P(\Omega) = \sum_{\nu} \rho_{\nu} P^{(\nu)}(\Omega).$$  \hspace{1cm} (4.2)

We must mention here that incoherent pump fields are unable to induce the quantum dynamics which is of crucial importance in different technological and scientific applications like reaction control, quantum computations, etc.

FIG. 4.1: The partial OK x-ray absorption profiles $P^{(\nu)}(\Omega)$ (4.2) of NO excited in ground state vibrational levels $\nu = 0, 1, 2$ for different core-excited states, $O1s \rightarrow 2\pi$: $2\Sigma^-, 2\Delta, 2\Sigma^+$. The total spectral profiles are shown by the thin solid lines. Narrow resonances display spectral distribution of the Franck-Condon factors for the $2\Sigma^-$ core-excited state.
4.2 Wave-packet dynamics

The physics changes drastically when the IR pulse is coherent with the fixed phase, $\varphi_L$. In this case the IR field mixes coherently vibrational states $|\nu\rangle$ and creates the wave packet

$$\phi(t) = \sum_{\nu} a_\nu(t) |\nu\rangle, \quad a_\nu(t) = c_\nu(t) e^{-i(\epsilon_\nu t + \nu \varphi_L)}$$  \hspace{1cm} (4.3)

which strongly depends on the phase $\varphi_L$ of the pump field. Here, $\epsilon_\nu$ is the energy of the $\nu$th vibrational level. The phase sensitivity of the nuclear dynamics is seen from the perturbative expansion of the wave packet’s square,

$$|\phi(t)|^2 \propto [1 + 2\sqrt{2}c_1(t)(R - R_0) \cos(\omega_{10} t + \varphi_L)] \exp\left(-\frac{(R - R_0)^2}{c_0^2}\right)$$  \hspace{1cm} (4.4)

where $c_1(t) \propto E_L(t)$ and $c_0$ are the size of the vibrational wave function (amplitude of vibrations). The WP dynamics is given by the second term at the right-hand side of this equation. This expression results in an important conclusion: The dynamics of the wave packet is absent if the IR field is incoherent. Indeed, the averaging over the random distribution of the IR phase cancels the time dependent term. The characteristic time of the WP propagation in the potential well is the period of vibrations, $2\pi/\omega_{10}$. The role of the phase can also be seen from Ehrenfest’s theorem. It shows that the mean force of the WP center of gravity is affected by the IR phase,

$$\langle F \rangle = \left\langle \phi(t) \left| \frac{d}{dR} E_L(t) \cdot d(R) \cos(\omega_L t + \varphi_L) \right| \phi(t) \right\rangle .$$  \hspace{1cm} (4.5)

and that the force changes sign when $\varphi_L \rightarrow \varphi_L + \pi$.

4.3 Quantum control of the system

We use here the term quantum control in a narrow sense, namely, the control of the shape and spectral composition of the nuclear wave packet. The WP strongly depends on the parameters of the IR pulse — the intensity $I_L(t)$, duration $\tau_L$, phase $\varphi_L$ and frequency $\omega_L$. The strong sensitivity of the populations of the vibrational levels to the laser parameters (Fig. 4.2) illustrates clearly that a proper choice of the IR pulse allows one to build the wave packet of the desirable shape (Fig. 1.3) and spectral composition. The inset in the plot (A) shows a weak modulation of the populations which is different for different laser phases $\varphi_L$. The origin of these oscillations is the breakdown of the rotating wave approximation (RWA). Contrary to the populations, the shape of the wave packet depends strongly on the IR phase (see below). The detailed description of the laser
parameters used in these simulations are described in Papers II and IV. The vibrational levels of the ground electronic state have long lifetimes which vary in broad region from \( ms \) in diatomic molecules up to \( ps \) in polyatomic molecules. Due to this fact the coherent superposition of vibrational levels created by the IR pulse has long lifetime: This wave packet exists even after the IR pulse leaves the system (see Fig. 4.2 and discussion below).

**FIG. 4.2:** Dynamics of populations of the vibrational levels on the ground electronic state of NO (A,B) and CO (C,D) molecules for different parameters of the IR pulse. The lowest panel in all figures display the amplitude of the IR pump field \( \zeta_L(t) = \mathcal{E}_L(t)/\mathcal{E}_L^{\max}(t) = \sqrt{\Phi_L(t-t_L)\cos(\omega_L t)} \) with the peak value normalized to one. \( I_L = 2.3 \times 10^{12} \text{ W/cm}^2 \) and \( I_L = 2.3 \times 10^{14} \text{ W/cm}^2 \) for NO and CO molecules, respectively. The inset in the panel A shows the cases \( \varphi_L = 0 \) (solid line) and \( \varphi_L = \pi/2 \) (dashed line).
4.4 Time-resolved x-ray probe spectra versus wave-packet dynamics

When the intensity of pump radiation is rather high one can see the modulation of populations with the Rabi period (Fig. 4.2 B,C,D)

\[ T_{\nu\nu'}^{(R)} = \frac{2\pi}{G_{\nu\nu'}^{(R)}}, \quad G_{\nu\nu'}^{(R)} = |E_L \cdot d_{\nu\nu'}|, \]

which becomes shorter than the duration of the IR pulse. The Rabi oscillations are absent if the IR pulse is shorter than the Rabi period (Fig. 4.2 A). Figs. 4.2 C, D display the decrease of the Rabi period for the higher vibrational levels. This effect is due to the increase of the transition dipole moment with the growth of \( \nu \):

\[ d_{\nu\nu'} = \delta_{\nu', \nu \pm 1} d_{\nu, \nu \pm 1}, \quad d_{\nu, \nu + 1} \approx d_{01} \sqrt{\nu + 1}. \]

Such a strong dependence of the Rabi period on the vibrational state gives the opportunity to obtain selective population of certain vibrational levels after the pulse leaves the system. First of all the vibrational levels with short Rabi periods (large \( \nu \)) comparing with the pulse duration \( \tau_L \) are depopulated adiabatically when the pulse leaves the system (\( \nu \geq 13 \) in Fig. 4.2 C and \( \nu \geq 7 \) in Fig. 4.2 D). We populated selectively the vibrational states with \( \tau_L \sim T_{\nu, \nu + 1}^{(R)} \) (7 \( \leq \nu \leq 12 \) in Fig. 4.2 C and 0 \( \leq \nu \leq 6 \) in Fig. 4.2 D). The vibrational levels with \( \tau_L < T_{\nu, \nu + 1}^{(R)} \) are also depopulated as one can see from Fig. 4.2 C (0 \( \leq \nu \leq 6 \)). One can control the populations and, hence, the shape of the WP changing the shape of the pulse. For example, the slow switching (switching time, \( \Delta T \), larger than the Rabi period) results in an adiabatic depopulation of the vibrational levels, while a fast switching freezes the system in the prepared state (see Fig. 4.2 A and B).

The vibrational subsystem keeps the information about parameters of the pump light for a long time. Fig. 4.3 shows that only amplitudes \( a_\nu(t) \) (4.3) of the excited vibrational states depend on the laser phase. As one can see from Eq. (4.3) the phase \( \nu \varphi_L \) of \( a_\nu(t) \) grows with increase of \( \nu \). The reason for this is that the molecule has to absorb \( \nu \) IR photons to reach the \( \nu \) vibrational state. This phenomenon, in principal, can be used to perform logical operations.

4.4 Time-resolved x-ray probe spectra versus wave-packet dynamics

Short x-ray pulses can be used to probe the dynamics of the nuclear wave packet created by the IR laser. The idea of such measurements was outlined earlier in Sec. 1.5. According to Fig. 1.3, one can expect a one-to-one correspondence between the time evolution of the wave packet and the x-ray spectrum. Let us check this idea comparing the trajectories
FIG. 4.3: The phase dependence of the contributions $a_\nu(t)$ (1.2) of different vibrational states ($\nu = 0, 1, 2, 3$) in the wave packet, $\phi(t)$: $\Delta a_\nu = a_\nu(t, \varphi_L = 0) - a_\nu(t, \varphi_L = \pi/2)$. The left and right panels show, respectively, the real and imaginary part of $\Delta a_\nu$. The vertical arrows show the instant where the IR intensity is decreased in two times.

of the center of gravities of the wave packet in the real space and of the x-ray spectrum in the energy domain:

$$
\langle r \rangle = \langle \phi(t)|r|\phi(t) \rangle, \quad \langle \Omega \rangle = \frac{\int d\Omega \Omega P(\Omega)}{\int d\Omega P(\Omega)},
$$

(4.8)

Fig. 4.4 shows that these trajectories coincide with high precision. The simulations displayed in this figure confirm our prediction (4.4) that the wave packet dynamics and, hence, the x-ray spectrum are sensitive to the phase of the light.

4.5 Role of the molecular orientation

The simulations shown in Fig. 4.4 correspond to oriented molecules. Usually, the molecules are randomly oriented and, due to this, the x-ray absorption$^{32}$ (XAS) or x-ray photoelectron$^{33}$ (XPS) spectra have to be averaged over molecular orientations. We will see below that such an averaging reduces the phase effect. It worthwhile mentioning that powerful techniques exist in x-ray spectroscopy which allow to get spectra of fixed-in-space molecules$^{34-36}$ even for randomly oriented samples. The measurement of x-ray absorption in ion yield mode is widely used in studies of x-ray spectra of fixed-in-space molecules, and this method is well adapted for observation of the discussed phase effect.
4.5 Role of the molecular orientation

FIG. 4.4: Trajectory of the WP and the center gravity of the OK x-ray absorption spectrum of NO (solid lines). The right panels display the phase sensitivity of the trajectory. Filled and dashed bands at the right-hand side display, respectively, the WP and the x-ray spectrum. \( \Delta t = t - t_L \) and \( \Delta t = t_X - t_L \) for \( \langle r \rangle \) and \( \langle \Omega \rangle \), respectively. \( \tau_X = 4 \) fs.

In the case of standard x-ray absorption measurements the x-ray probe spectrum has to be averaged over all molecular orientations. One can expect a strong suppression of the phase effect after this averaging. An analysis shows that the phase effect is suppressed mainly due to interference of the x-ray spectra of molecules with opposite orientation. Due to this we mimic the averaging procedure by a sum of x-ray spectra of molecules with \( \varphi_L \) and \( \varphi_L + \pi \) (see for details Paper II). Results of such an averaging are depicted in Fig. 4.6. Indeed it shows that the phase effect is smaller for disordered samples. The phase dependence grows with the increase of the IR intensity (compare A and B panels of Fig. 4.6). The explanation for this effect is as follows. When the IR field is rather weak the phase effect occurs due to the interference of one and two-photon channels (Fig. 4.5

FIG. 4.5: Qualitative picture of the phase effect. A) interference between one (x-ray) and two-photon (x-ray + IR) pathways. B) interference between one (x-ray) and three-photon (x-ray + 2xIR) pathways.
A). The orientational averaging quenches this term and, hence, deletes the phase effect

\[ P^{(1)}_{\text{int}}(t) \propto \Re \{ A_1 e^{-i\varphi_L} (d_{10} \cdot e_L) |D_{e0} \cdot e_X|^2 \} = 0. \]  

(4.9)

Stronger pump fields are able to populate the second vibrational level. In this case we have the interference of one- and three-photon channels (Fig. 4.5 B), which is not equal to zero after orientational averaging (Paper I)

\[ P^{(2)}_{\text{int}}(t) \propto \Re \{ A_2 e^{-2i\varphi_L} (d_{21} \cdot e_L) (d_{10} \cdot e_L) |D_{e0} \cdot e_X|^2 \} \neq 0, \]  

(4.10)

This term explain the growth of the phase effect with the increase of \( I_L \).

FIG. 4.6: Phase dependence of the probability of OK x-ray absorption of NO (2.14). The frequency of the IR field is tuned in resonance with the first vibrational level: \( \omega_L = \omega_{01} = 0.241 \text{ eV} \). The spectra averaged over molecular orientations are marked by \( \langle \varphi_L \rangle \) with \( \varphi_L = 0 \) and \( \pi/2 \). \( \tau_X = 3 \text{ fs} \). The delay time: \( \Delta t = 610 \text{ fs} \). \( \Omega = \omega - 531.3 \text{ eV} \). A) \( I_L = 1.5 \times 10^{12} \text{ W/cm}^2 \). B) \( I_L = 2.3 \times 10^{12} \text{ W/cm}^2 \).

To conclude this section, we would like to point out that the spectral profile of the x-ray pump-probe is sensitive to the phase of the IR field, delay time (\( \Delta t \)) and duration (\( \tau_X \)) of the x-ray pulse, as well as, to the orientation of the molecular system relative to the IR polarization vector. The spectra of randomly oriented molecules differ considerably from spectra of fixed-in-space molecules: The phase effect is larger for oriented molecules.

4.6 Role of the pulse duration on the phase effect

Let us discuss the phase dependence of the x-ray spectrum versus the duration of the x-ray pulse. Fig. 4.7 shows that the phase effect vanishes for either long and short pulses, as well as, the dependence of the phase effect in relation to the x-ray frequency. Apparently, a long x-ray pulse (\( \tau_X > 2\pi/\omega_{10} \)) is unable to detect the phase effect because it snapshots the nuclear wave packet in different points. As one can see from Fig. 4.4 the average
trajectories of the WP and of the spectrum do not depend on the IR phase. The phase effect also vanishes for small durations of the x-ray pulse. For short pulses the reason of the disappearance of the phase effect lies in the heart of the quantum mechanics: According to the uncertainty relation, $\Delta \omega \Delta t \sim 1$, the short x-ray pulse has many harmonics with different frequencies $\omega_X$. In this case the phase effect becomes invisible because of the broadening of the phase dependent x-ray spectrum, see Fig. 4.6.

![Graph showing probability of x-ray absorption](image)

**FIG. 4.7:** Probability of x-ray absorption ($O_1s \rightarrow 2\pi$) of NO versus duration of the x-ray pulse, $\tau_X$, for different phases (low panel). Upper panel displays the phase dependence for different $\Omega$. $I_L = 2.3 \times 10^{12}$ W/cm$^2$, delay time $\Delta t = 610$ fs. $\Omega = 0.4$ eV in lower panel.

### 4.7 2D wave packet dynamics

In previous sections we studied spectral manifestations of 1D dynamics of the wave packet. The wave packet dynamics in polyatomic molecules is essentially multi-dimensional. To give some insight in the role of the multi-dimensional dynamics let us consider the dynamics of the wave packet in the 2D potential surface of the core ionized water dimer molecule, which is the smallest water cluster that has a hydrogen bond between the molecules. The water dimer is formed by two chemically distinct water molecules possessing two non-equivalent oxygen atoms, the so-called donor $O_d$ and acceptor $O_a$ oxygens (Fig. 4.8).

![Equilibrium structure of the water dimer](image)

**FIG. 4.8:** Equilibrium structure of the water dimer.

We have chosen the two most important coordinates $r = r(O_d - H)$ and $R = R(O_d - O_a)$ to perform the WP simulations. The core ionization of the donor or acceptor oxygens of the dimer results in a drastic change of the potential (Fig. 4.9). Contrary to the ground
state, the global minimum is shifted to the proton transfer region when the core hole is created in the donor oxygen. In other words, the core ionization in the donor oxygen of the water dimer leads to a formation of a proton transferred state and consequently to a strengthening of the hydrogen bond. The map of the potential surface (Fig. 4.9) shows that the WP can reach the proton transfer region by two pathways: tunneling (or over-barrier) propagation and along the classical trajectory. The classical pathway starts from a slow approach of the heavy monomers followed by a quick transfer of the light proton along the \( r(O_d - H) \) coordinate. Our 2D WP simulations show that the propagation of the WP along the classical path is indeed very slow. The bottleneck here is the slow motion along \( O_d - O_a \) which takes approximately 28-34 fs. However, the dynamics of the proton transfer by the way of tunneling takes smaller time 8-16 fs, which actually is comparable with the lifetime of the core ionized state. As one can see from Fig. 4.9 a small part of the WP has time to approach the proton transfer region in the time 8 fs after the core ionization. The appearance of the wave packet in the proton transfer region can be detected making use of Auger or x-ray emission spectroscopies.\(^{28}\) The dynamics of the proton transfer is of importance in x-ray emission and Auger spectroscopic studies of liquid water, which were simulated recently in the framework of the molecular dynamics technique.\(^{37,38}\)

![Wave packet dynamics](image)

**FIG. 4.9:** 2D wave packet dynamics on the potential surface of the core ionized water dimmer molecule.
4.8 Wave packet revivals

The revival time is a well known phenomenon that is present in many branches of physics. Moreover, it is frequently observed in systems constituting coupled oscillators. Apparently, the first studies related with the revival time came from Poincare recurrences for a rotation map,\(^3\) where the revival is analyzed in classical systems. In quantum mechanics the earliest studies involving can be addressed to Schrödinger,\(^4\) while Paker and Stroud were the first to evidence the WP revival in numerical simulations of the dynamics of Rydberg states.\(^5,\!^6\) The wave packet revival, predicted in their numerical calculations, was experimentally confirmed a few years latter.\(^7\) Different mathematical and physical aspects of the revival phenomenon can be found in a recent review.\(^8\)

The quantum revival is essentially a coherent phenomenon related to the dynamics of coherent superposition of quantum states or the WP. The left hand-side panel in Fig. 4.4 and the middle plot in Fig. 4.10 show the low frequency modulation of the WP trajectory \(\langle r \rangle\) with period equal to the revival time

\[
T_R = \frac{2\pi}{\omega_{10} - \omega_{21}} = \frac{2\pi}{\omega_{10}x_e},
\]

where \(\omega_{10}x_e\) is the anharmonicity constant, \(\omega_{10}x_e = 0.0017\) eV for NO molecule. The revival period for the NO molecule is \(T_{rev} = 1210\) fs (Fig. 4.10).

![FIG. 4.10: The spread of the WP \(\Delta r(t)\) (panel a) versus the center of gravity of the OK x-ray absorption spectrum of NO \(\langle \Omega(\Delta t) \rangle\) (panels b and c). \(\varphi_L = \pi\). b) Short x-ray pulse, \(\tau_X = 4\) fs, c) Long x-ray pulse, \(\tau_X = 30\) fs.]

The wave packet revivals can be observed making use of x-ray absorption as is illustrated in Fig. 1.3. Indeed, the dynamics of the center of gravity of the x-ray spectrum follows one-to-one to the trajectory of the WP, Fig. 4.4. The observation of a slow dynamics of the center of gravity of the x-ray probe spectrum enables to measure the revival period and, hence, the anharmonicity constant. Here we thus face a somewhat paradoxical situation in that the short x-ray pulse allows to measure the fine structure of the molecular spectra. As a matter of fact, there is here no contradiction with the uncertainty relation because the anharmonicity is determined via long time measurements.

The revival phenomenon is caused by the coherence between adjacent vibrational levels and it is therefore very sensitive to decoherence due to vibrational quenching and due to intermolecular interaction. The detection of a slow “melting” of the revival pattern
caused by decoherence enables to study the intermolecular interactions (Paper III).

4.9 Wave packet squeezing

It is instructive to compare the trajectory of the WP $\langle r(t) \rangle$ or of the x-ray spectrum $\langle \Omega(\Delta t) \rangle$ with the spread of the WPs

$$\Delta r(t) = \sqrt{\langle r^2(t) \rangle - \langle r(t) \rangle^2}$$

(see Fig. 4.10 a and b). The regions with largest amplitude of oscillations of $\langle r(t) \rangle$ or $\langle \Omega(\Delta t) \rangle$ correspond to a highly coherent quasi-classical behavior with a well-localized, squeezed WP (small $\Delta r(t)$). The anharmonicity results in a quantum mechanical dephasing (suppression of amplitude of oscillations of $\langle r(t) \rangle$) and a spread of the WP. After the revival time $T_{\text{rev}} = 1210$ fs the coherence is restored and the WP localizes again. Our calculations show that both the WP and the x-ray spectrum restore the shape through the revival period and that the width of the x-ray spectrum $\Delta \Omega(\Delta t) = \sqrt{\langle \Omega^2(\Delta t) \rangle - \langle \Omega(\Delta t) \rangle^2}$ has almost the same time dependence as $\Delta r(t)$.

The squeezing of the WP in certain times is due to constructive interference which localizes the WP in a small region of the potential well. The WP squeezing is quite important from the point of view of reaction control. The constructive interference allows to increase the reaction rate and the efficiency of chemical reactions. The WP squeezing can be directly probed by the IR–x-ray pump-probe spectroscopy, making it a promising tool in control of reactions.

4.10 The breakdown of the rotating wave approximation in intense fields

Let us turn our attention to the mechanism of phase sensitive nuclear dynamics which occurs in a strong IR field. The origin of this phase dependence is the off-resonant interaction of the pump field with the molecule, which becomes important when the Rabi frequency $\ Gamma^{(R)}_{10}$ (4.6) approaches the frequency of the vibrational transition, $\omega_{10}$. In this case, the intensity of the pump pulse is strong enough to violate the RWA, which ignores the fast oscillating terms

$$\cos ((\omega_L + \omega_{10})t + 2\varphi_L)$$

in the dynamical equations (see Paper V). This is true when the resonant electromagnetic field is rather weak. In this case, only slow oscillations with frequency $\omega_{10} - \omega_L$ are kept,
while the fast oscillations with frequency $\omega_{10} + \omega_L$ are neglected.

FIG. 4.11: (A) The water dimer. (B) Phase dependence of the square of the wave packets of the ground and excited states at different times. The left panel shows the electric field of the pump pulse $E_L(t) = E_L(t) \cos(\omega_L t + \varphi_L)$. Solid and dashed lines correspond to $\varphi_L = 0$ and $\varphi_L = \pi/2$, respectively. Duration of the pump pulse $\tau_L = 50$ fs; the peak position corresponds to $t_L = 250$ fs; the peak intensity is $I_L = 10^{15}$ W/cm$^2$.

We consider now the resonant interaction of the IR field with the OH vibrational mode, $\omega_L \approx \omega_{10} = \omega_{OH}$ of the water dimer (Paper V), which is a prototype of a rather common case of molecules with both slow and fast vibrational motion. Both the zero-point energy and the energy of the next OH vibrational state depend on the OO distance (Fig. 4.11 (A)). We separate the fast OH and slow OO vibrational modes in the Born-Oppenheimer approximation, which is valid here because the reduced mass of the OH mode is much smaller than of the OO mode. The coherent IR radiation induces transitions between the two OH wells and creates wave packets in both, which perform oscillations along the OO bond.

Our simulations show that the populations of the ground ($\rho_g$) and the excited ($\rho_e$) states (Fig. 4.11 (A)) experience weak modulations with the double frequency of the laser field, which appear due to the non-RWA contribution (NRWA). The character of these weak oscillations is similar to the NRWA modulations in the NO molecule (see inset in Fig. 4.2 (A)). Contrary to populations $\rho_g$ and $\rho_e$, the dynamics of the wave packet is strongly influenced by the NRWA terms (Fig. 4.11(B)). The reason for this is that the breakdown of the RWA affects the spatial distribution of the nuclear wave packet much
stronger than such an integral characteristic as the population.

Snapshots of wave packets of the ground and excited states (Fig. 4.11(B)) show that the difference between wave packets induced by the pump field with a phase $\varphi_L = 0$ and $\pi/2$ is maximal when the intensity of the pump field and, hence, the Rabi frequency (4.6), reaches maximum (see left panel of Fig. 4.11(B)). We see that the wave packets depend on the doubled phase, $2\varphi_L$, due to the NRWA terms. Indeed, the simulations show that the wave packet does not change its shape when $2\varphi_L = 0 \rightarrow 2\pi$, contrary to the change of the phase $\varphi_L$ in $\pi/2$. The phase effect takes maximum value when $2\varphi_L = 0 \rightarrow \pi$.

### 4.11 Core hole hopping mediated by vibronic coupling in OK core ionized states of glyoxalmonoxime molecule

Let us apply the theory of x-ray pump-probe spectroscopy developed in previous sections to a more complex system. We study the core-hole induced intramolecular dynamics of proton transfer of glyoxalmonoxime (GM) (see Fig. 4.12) leading to the formation of the tautomer 2-nitrosoethanol (NE). The glyoxalmonoxime molecule contains two chemically non-equivalent oxygen atoms $O_1$ (oximic) and $O_2$ (keto) that possess distinct roles in the hydrogen bond: $O_1$ is a hydrogen donor while $O_2$ is a hydrogen acceptor. The ionization of the $1s$ electron of the donor or acceptor oxygens of GM leads to the formation of two $2A'$ core-ionized diabatic states which show a crossing (at $q = q_c$) of their potential curves ($q = q_c=2.18$ a.u.) along the OH stretching mode $q$ related to the intramolecular proton transfer channel (Fig. 4.13). The vibronic coupling (VC) of these states ($\psi_1(r, q)$ and $\psi_2(r, q)$) of the same symmetry

$$H_{12} = -H_{21} = -\frac{1}{2m_H} \left[ 2C_{12}(q) \frac{d}{dq} + \left( \frac{dC_{12}(q)}{dq} \right) \right], \quad C_{12}(q) = \langle \psi_1(r, q) \frac{d}{dq} | \psi_2(r, q) \rangle,$$

(4.14)

partially delocalizes the core holes and affects the dynamics of the proton transfer in the core-ionized state with the Hamiltonian

$$\mathcal{H} = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix}, \quad H_{nn} = -\frac{1}{2m_H} \frac{d^2}{dq^2} + E_n(q) - E_c.$$

(4.15)
4.11 Core hole hopping mediated by vibronic coupling in OK core ionized states of glyoxalmonoxime molecule

The proton transfer dynamics can be investigated using x-ray spectroscopy, like x-ray Raman scattering. A first impression is that the ordinary XPS technique is useless here because it maps the dynamics in a narrow Franck-Condon region near the equilibrium. However, we will see below that this is not true. When we explore the ordinary XPS spectra in addition to the XPS spectra of the GM molecule driven by an IR field. The coherent IR field changes the situation qualitatively. Indeed, due to the IR pump the molecule gains enough energy to promote the proton in the weakly bound proton transfer well which is about 0.9 eV higher in energy than the global minimum. Due to this fact the IR induced nuclear wave packet \( \phi(t) \) performs back and forth routes from the GM to the NE wells (Fig. 4.13). Now the probe x-ray pulse can excite the molecule in different regions of the core-ionized potential and thereby can monitor the dynamics of the proton transfer accompanied by the vibronic coupling.

The probability of core-ionization consists of two contributions

\[
P(\Omega) = \langle \varphi_c(\Omega) | \varphi_c(\Omega) \rangle = \langle \varphi_1(\Omega) | \varphi_1(\Omega) \rangle + \langle \varphi_2(\Omega) | \varphi_2(\Omega) \rangle. \tag{4.16}
\]

related to the two photoionization channels \( O_1(1s^{-1}) \) and \( O_2(1s^{-1}) \), respectively. Here

\[
|\varphi_n(\Omega)\rangle = \int_{-\infty}^{\infty} dt \ e^{-\Omega t} E_X(t) |\varphi_n(t)\rangle, \quad n = 1, 2. \tag{4.17}
\]

\[
\phi_c(t) = \begin{pmatrix} \phi_1(t) \\ \phi_2(t) \end{pmatrix} = e^{i\Omega t} \zeta \phi(t), \quad \zeta = \begin{pmatrix} \zeta_1 \\ \zeta_2 \end{pmatrix}, \quad \zeta_n = \frac{1}{2} (D_{n0} \cdot e_x), \tag{4.18}
\]

where \( \Omega = \text{BE} - I_{1s} \) is the relative binding energy (\( \text{BE} = \omega_X - \varepsilon \)), \( I_{1s} = E_c - E_0 \) is the smallest adiabatic core ionization potential (between the wells 1 and 2) and \( \varepsilon \) is the energy of the photoelectron. The nuclear wave packets (4.17) and (4.18) are natural generalization of the WPs introduced earlier in Sec. 2.2.

The VC operator (4.14) deserves a special comment. In the simulations we use the scalar form of the VC operator

\[
H_{12} = H_{21} = \lambda q \tag{4.19}
\]

because the HT representation is preferable from the numerical point of view.\(^{49}\) These representations differ from each other in the electronic wave functions which depend parametrically on the nuclear coordinates in the first case(4.14), while the electronic wave functions are taken at fixed nuclear geometry in the second case (4.19).\(^{49}\) Both approaches should give the same result if the total function is expanded over a complete electronic basis set.
FIG. 4.13: Potential energy curves of ground and core ionized states along a cartesian coordinate \( q \) related to the proton transfer channel. Dashed lines mark the adiabatic potentials \( E_\pm(q) \). Minimum of \( E_0(q) \) is situated at \( q_0=1.74 \) a.u.. The diabatic potentials (solid lines) cross each other in the point \( q_c=2.18 \) a.u.. The initial gaussian wave packet excited in the higher energy region performs back and forth routes from the GM to the NE wells.

Fig. 4.14 displays IR–x-ray pump-probe spectra of an oriented GM molecule (\( \mathbf{e}_L \parallel x \)) for different values of the vibronic coupling constant \( \lambda \) and different delay times \( \Delta t = t_X - t_L \) between the x-ray and IR pulses. Upper panels show XPS profiles for \( I_L=0 \), while the lower panels show the spectra of molecules driven by the IR field. The parameters of the IR pulse are \( I_L=2.3 \times 10^{14} \) W/cm\(^2\), \( t_L=200 \) fs, \( \tau_L=10 \) fs, \( \varphi_L=0.53 \) rad and \( \omega_L = \omega_{10}=0.33 \) eV. The duration of the x-ray pulse is \( \tau_X=4 \) fs. The dotted and dashed line are the partial photoionization probabilities \( P_1(\Omega) \) and \( P_2(\Omega) \), respectively. The vibrationally resolved XPS profile depicted in the left upper panel was calculated for a longer x-ray pulse, \( \tau_X = 15 \) fs.

Calculations show that the vibronic coupling, creating coherent superposition of local-
4.11 Core hole hopping mediated by vibronic coupling in OK core ionized states of glyoxalmonoxime molecule


ized states, influences the spectra even without an IR field (see upper panels in Fig. 4.14). Partial delocalization of the core holes leads to the suppression/enhancement of the newly formed bright/dark core-ionized states (Fig. 4.15). The origin of this effect is explained in detail in Paper VI. The XPS intensities $(d_+ / d)^2$ and $(d_- / d)^2$ (Fig. 4.15 A) display qualitatively different dependences on the coupling strength $\lambda_{qc}$ due to the constructive and destructive interference of localized core-hole states caused by VC. When $\lambda > 0$ one can see the quenching of the “dark” $\psi_-$ state and the enhancement of the XPS intensity of the “bright” state $\psi_+$ with the increase of $\lambda$. The dark and bright states are interchanged if the sign of the VC is inversed, $\lambda < 0$.

When the molecule is exposed by a strong IR pulse two new bands arise in the XPS profile. These bands origin in the core ionization from the region near the weakly bound well of the tautomer 2-nitrosoetanol. The laser induced nuclear wave packet moves in the ground state well, which makes the intensities of the newly formed XPS bands sensitive to the delay time between the x-ray and the IR pulses.

Referring to Fig. 4.16, one can realize the bottleneck of our study: We see that the wave packet is considerably delocalized. Such a delocalization restricts the spatial resolution of this technique, because it does not allow to excite the nuclear subsystem explicitly in a desired point $q$. This means that the shaping of the narrow nuclear wave packet deserves special attention, a problem well worth to consider. The main reason of delocalization of the wave packet in our case is known, namely its rather poor spectral composition. Indeed, the vibrational level $\nu = 4$ contributes almost 60% to $\phi(t)$
FIG. 4.15: A) XPS intensities \((d_+/d)^2\) versus the coupling strength, \(\zeta/2 = \lambda q/\Delta(q)\). \(\Delta(q_0) = 1.02\) eV. B) XPS spectra for positive and negative VC strengths (no IR field). Other parameters are the same as in Fig. 4.14.

(Paper VI). We got stronger localization of \(\phi(t)\) in the water dimer\(^{50}\) exciting simultaneously many vibrational levels.

To conclude this section one can say that a VC strength \(\lambda q_c\) larger than 0.1 eV is an apparent exaggeration for core ionization due to the small overlap of 1s functions localized on different oxygen atoms. However, we included in our analysis also large \(\lambda\) values keeping in mind the proton transfer which can occur also under photoionization of valence molecular orbitals where the coupling is stronger (see Paper VI).

FIG. 4.16: Squared wave packet \(|\phi(t)|^2\) and its trajectory, \(\langle \phi(t)|q|\phi(t)\rangle\) (solid line), versus time. Other parameters are the same as in Fig. 4.14.
4.12 Enhancement of the recoil effect

Let us consider x-ray photoionization of core levels with the photon frequency essentially larger than core ionization threshold. When a fast photoelectron is ejected, the molecule experiences a recoil. The momentum of the photoelectron \( \mathbf{p} \) is transferred both to the center of gravity, as well as, to the internal nuclear motion (vibrations). Because of this the vibrational profile starts to depend on the photon energy. However, to get a visible change of the vibrational profile, the energy of the photoelectron must be rather high (\( > 2 \) keV).\(^{51}\) Indeed, the recoil effect becomes large when the wavelength of the photoelectron becomes comparable with the size \( a \) of the initial vibrational state

\[
ap \sim 1
\]

This makes the measurements of the recoil effect very difficult.\(^{52}\) Recently, we recognized that the requirement (4.20) can be fulfilled for reasonable photoelectron energies if we increase the size of the ground state vibrational wave packet using a strong IR pulse (see Fig. 4.17 and Paper IV). Let begin with the physical picture of the IR induced enhancement of the recoil effect. The x-ray photoionization occurs mainly near the left (L) and the right (R) turning points of the IR induced WP, see Fig. 4.17. However, the photoelectron kicks the nuclei and makes the transition non-vertical (Fig. 4.18), implying that the left and right sidebands of the XPS spectrum experience shifts due to the recoil effect

\[
\Delta \omega = \frac{E_{\text{rec}}^{(i)}}{1 - F_0/F_c} \approx (\omega_X - I_{1s}) \frac{(m_B/m_A) \cos^2 \theta}{M(1 - F_0/F_c)}.
\]

Here \( m_A \) is the mass of the core-ionized atom A in the diatomic molecule AB, \( M = m_A + m_B \). Such a deformation of the XPS spectrum is seen clearly in Fig. 4.19. As one can see from Eq. (4.21) the spectral shift increases when the ratio of the gradients \( F_0/F_c \) of the potentials in ground and core-ionized states approaches unity. The IR pulse allows to make this ratio close to one. This results in an additional enhancement of the recoil effect (see Paper IV).
The results of our simulations are shown in Fig. 4.19. This calculations are based on the wave packet technique outlined in Sec. 2.2. The electronic recoil effect is taken into account by multiplying the transition dipole moment in Eq. (2.15) by the phase factor

\[ \mathbf{d}_{\epsilon_0} \rightarrow \mathbf{d}_{\epsilon_0} e^{-i\alpha \mathbf{p} \cdot \mathbf{R}} \]  

(4.22)

where \( \mathbf{R} \) is the internuclear radius vector and \( \alpha = m_B/(m_A + m_B) \). The momentum representation for the generalized FC amplitude

\[ \langle c, \nu | e^{-i\alpha \mathbf{p} \cdot \mathbf{R}} | 0, \nu_0 \rangle = e^{-i\alpha \mathbf{p} \cdot \mathbf{R}_0} \int_{-\infty}^{\infty} dk \phi_{c\nu}^*(k) \left( k + \frac{\alpha}{2} \mathbf{p} \cos \theta \right) \phi_{0\nu_0}(k) \]  

(4.23)

clearly exposes the momentum transfer from the photoelectron to the nuclei. Here \( \phi_{c\nu}(k) \) and \( \phi_{0\nu_0}(k) \) are the vibrational wave functions in the momentum space, \( k \) is the momentum of relative motion of the nuclei, \( R_0 \) is the equilibrium bond length and \( \theta \) is the angle between \( \mathbf{p} \) and \( \mathbf{R} \).

### 4.13 Pump-probe spectroscopy with overlapping pump and probe pulses. Role of the final state interaction.

In previous sections we focused our attention on pump-probe spectroscopy with delayed pump and probe pulses. In this case the IR pump field interacts with the molecule only in the ground electronic state. Here, we consider overlapping pump and probe fields (see Paper VII). Due to this the pump field interacts with the molecule in both ground and excited electronic states. The results analyzed in this section are based on the coupled equations (2.5) from Sec. 2.1.

Our simulations show that the detuning of the IR frequency allows to investigate separately the role of the pump radiation in the ground and ionized states as seen clearly in Fig. 4.20. The interaction of a strong IR field with the ionized molecule results in a Rabi splitting of the photoelectron lines, which one can see from comparison of Fig. 4.20 b, c, Fig. 4.20 d. One can also see that the effect of the Rabi splitting increases for higher vibrational levels. The growth of the Rabi frequency with increase of \( \nu \) is due to the increase of the transition dipole moment, Eq. (4.7). When the IR field is tuned with the ground state vibrational frequency the main effect is the appearance of hot bands (Fig. 4.20 a0). However, we do not see the Rabi splitting except in the high frequency region where the small splitting probably is due to the dynamical Stark effect. One
FIG. 4.18: Physical picture of Eqs. (4.21). A: Different potentials of the ground and core ionized states, $F_c \neq F_0$. B: The same potentials of the ground and core ionized states.

FIG. 4.19: CK XPS spectra driven by an IR field. The dotted line shows the XPS spectrum without taking into account the recoil effect.
The possible reason for such a qualitative difference between final (left panel) and ground (right panel) state interactions (Fig. 4.20) can be that the IR pulse has a duration which is comparable with the Rabi period. Due to this the populations of the vibrational levels of the excited electronic state do not display Rabi oscillations for the intensity $I_L = 5 \times 10^{12}$ W/cm² used in these simulations (see Paper VII).

FIG. 4.20: Photoelectron spectra $X^1\Sigma^+ \rightarrow X^2\Pi$ of carbon monoxide. The IR field is tuned in strict resonance with excited state vibrational frequency, $\omega_L=\omega_{01}^{(c)} = 0.193$ eV (left panel) and with the vibrational frequency of the ground state, $\omega_L=\omega_{01}^{(g)} = 0.269$ eV. $I_0=5 \times 10^{12}$ W/cm². $\tau_{X}=\tau_{L}=100$ fs The Rabi frequencies of IR transitions in the ground and excited states are $G_{01}^{(R)} = E\delta_{01} = 0.193$ eV and 0.269 eV, respectively. The IR field interacts with the molecule in both ground and excited states (panels c_e and c_0).
CHAPTER 5

Resonant $L_{II,III}$ Raman x-ray scattering of HCl

The molecule HCl has been widely used in investigations of dynamical effects accompanying x-ray excitation using the resonant Auger effect in the soft x-ray region\textsuperscript{53,54} and resonant x-ray Raman scattering\textsuperscript{53,55} (RXS) near the Cl K-edge.\textsuperscript{56,57} In this chapter we combine experiment and theory to study the Cl $L_{II,III}$ RXS spectrum of HCl (see Paper VIII). The scheme of scattering is depicted in Fig. 5.1. One of the major difficulties of the theory is that the Cl 2p$_{II,III}$ core excited state is simultaneously affected by spin-orbit (SO) and molecular-field interactions in the core shell as well as the Coulomb interaction between the core hole and valence electrons. The SO splitting, about 1.75 eV, can be comparable with the Coulomb interaction between core and vacant molecular orbitals (MO) involved in the scattering. Due to this we were forced to invoke the intermediate coupling scheme\textsuperscript{58} and to solve the corresponding equations explicitly.

We start from diagonalization of the non-relativistic many-electron molecular Hamiltonian $H$ and we get singlet and triplet core-excited states using the Multiconfigurational Self Consistent Field (MCSCF) method.\textsuperscript{59} Then we take into account the SO interaction $V_{SO}$ in the $L$ shell by diagonalizing the total Hamiltonian (Paper VIII)

$$\mathcal{H} = H + V_{SO}, \quad V_{SO} = A(r)L \cdot S. \quad (5.1)$$

This gives us the many electron wave functions $\Phi_{\lambda}$ and energies $E_{\lambda}$ of the core-excited states.

FIG. 5.1: Scheme of Raman transitions.
5.1 Cross section of x-ray Raman scattering

The amplitude of the resonant inelastic x-ray Raman scattering (RIXS) is given by the Kramers-Heisenberg formula (KH)

\[ F_f(q) = \sum_{\Lambda=1}^{12} \frac{\langle 0|(e \cdot D)|\Phi_\Lambda\rangle\langle \Phi_\Lambda|(e_1 \cdot D)|\Psi_f(q)\rangle}{\omega_1 - \omega_{\Lambda,f(q)} + i\Gamma}, \quad q = S, T, \]  

(5.2)

where \( \Gamma \) is the lifetime broadening of the core-excited state; \( \omega, e, \) and \( \omega_1, e_1 \) are the frequencies and polarization vectors of the incident and the scattered x-ray photons, respectively; \( \omega_{\Lambda,f(q)} = E_{\Lambda} - E_f(q) \) is the resonant frequency of emission transition from the core-excited to the final singlet (\( \Psi_f(q) = \Psi_f(S) \)) or triplet (\( \Psi_f(q) = \Psi_f^m(T) \)) states.

The RXS cross section includes scattering to singlet and triplet final states

\[ \sigma(\omega, \omega_1) = \sum_f \left[ |F_f(S)|^2 \Phi(\omega_1 - \omega + \omega_{f(S),0}; \gamma) + \sum_{m=1,0,-1} |F_f^m(T)|^2 \Phi(\omega_1 - \omega + \omega_{f(T),0}; \gamma) \right] \]

(5.3)

where \( \omega_{f(q),0} = E_f(q) - E_0 \) is the frequency of transition from ground to final singlet or triplet state. The spectral function of incident radiation is assumed to be a Gaussian with the half width at half maximum (HWHM) equal to \( \gamma \). The scattering to the final triplet state is allowed due to the SO interaction in the 2p-shell. Indeed, the wave function of the core excited state is a superposition of singlet and triplet states

\[ \Phi_\Lambda = a\Phi(S) + b\Phi(T) \]

(5.4)

because of the SO interaction in the core shell. Due to the admixture of the triplet state, emission is allowed also to the triplet final states.

The experiment was performed with gas phase molecules and with a fixed angle \( \chi = 0 \) between \( e \) and the wave vector of the emitted photon \( k_1 \). In this case, we have to use in Eq. (5.3) the partial contributions averaged over molecular orientations,

\[ |F_f(S)|^2 = \frac{2}{9} \sum_{\Lambda=1}^{12} \sum_{\Lambda_1=1}^{12} \frac{1}{(\omega_1 - \omega_{\Lambda_1,f(S)} + i\Gamma)(\omega_1 - \omega_{\Lambda_1,f(S)} - i\Gamma)} \times \left[ \{D^{(\Lambda)}(S) \cdot D^{(\Lambda_1)s}(S)\}\{D_f^{(\Lambda)}(S) \cdot D_f^{(\Lambda_1)}(S)\} \right. \\
+ \frac{3}{20}(1 - 3\cos^2 \chi) \times \left[ \{D^{(\Lambda)}(S) \cdot D_f^{(\Lambda)s}(S)\}\{D^{(\Lambda_1)s}(S) \cdot D_f^{(\Lambda_1)}(S)\} \right. \\
\left. \left. + \{D^{(\Lambda)}(S) \cdot D_f^{(\Lambda_1)}(S)\}\{D^{(\Lambda_1)s}(S) \cdot D_f^{(\Lambda)}(S)\} \right] \right] \
\]  

(5.5)
Here, we have introduced the scalar product of the complex vectors $a$ and $b$ without conventional complex conjugation of the bra vector $a$: $\{a \cdot b\} = \sum_{k=x,y,z} a_k b_k$. The dipole moments of absorption ($D^{(A)}(S)$) and emission ($D^{(A)}_f(T)$, $D^{(A)}_{fm}(T)$) transitions are computed using the eigenvectors of the total Hamiltonian (5.1) and the one-electron transition dipole moments (for more details see Paper VIII).

### 5.2 Cl $L_{II,III}$ x-ray absorption

Fig. 5.2 A shows the theoretical Cl $L-$ x-ray absorption spectrum calculated making use the following formula for the photoabsorption cross section

$$
\sigma(\omega) = \frac{2}{3} \sum_{\nu} \sum_{\Lambda=1}^{12} |D^{(A)}(S)|^2 \Delta (\omega - \omega_{\Lambda \nu \Gamma}), \quad \omega_{\Lambda \nu \Gamma} = E_\Lambda - E_\nu,$$

for the transitions $2p \rightarrow 6\sigma, 7\sigma, 8\sigma, 9\sigma$ and $2p \rightarrow 3\pi, 4\pi, 1\delta$. The relativistic calculations based on the four component STEX technique show rather similar intensities for the first spin-doublet ($6\sigma$), and it gives $\Delta_{SO} \approx 1.6$ eV (Fig. 5.2 C), which is close to the experimental spin-orbital splitting $\Delta_{SO} \approx 1.75$ eV. Both MCSCF and relativistic calculations show the fine structure of each component of the spin-doublet caused by the molecular orbital splitting of the core shell, as well as by the Coulomb interaction between the $L_{II,III}$ shell and the vacant MO. We see mainly triplet and doublet fine structure of the $6\sigma_{3/2}$ and $6\sigma_{1/2}$ bands, respectively. We label the core-excited state $|2p_{j-1}^{-1}\nu^1\rangle$ as $\nu_j$, with $j = 1/2, 3/2$. The accuracy of our simulations of $\sigma$ and $\pi$ subsystems is very sensitive to the CAS space. To get a better agreement with experiment, we shifted uniformly the $\pi$ spectrum (panel B) to lower energy region by 0.85 eV as shown in Fig. 5.2 A. A rather similar displacement of the $\pi$ levels relative to the $\sigma$ subsystem was observed earlier in calculations of XAS of the OCS molecule.
FIG. 5.2: Theoretical Cl $L_{II,III}$ x-ray absorption spectrum of HCl. Dashed lines in panel A show the XAS of the $\pi$ and $\delta$ subsystems (depicted in panel B) shifted by 0.85 eV. $\Gamma = 0.0465$ eV. Panel C shows the results of relativistic simulations of the first three peaks in the Cl $L_{II,III}$ XAS spectrum of HCl.

At the beginning we computed the first spin-doublet related to core excitation to the $6\sigma$ MO (marked in Fig. 5.2 as $6\sigma_{3/2}$ and $6\sigma_{1/2}$) taking into account only the lifetime broadening $\Gamma$. However, the transition to the $6\sigma$ MO experiences strong broadening because the first core-excited state is dissociative (Fig. 5.3). We simulated the dissociative broadening of the first spin-doublet using the wave packet technique.$^{62}$ The results of the calculations are shown in Fig. 5.2 A by the dotted-dashed line. Fig. 5.2 A reproduces all experimental features in the XAS spectrum (Fig. 5.4) after the above mentioned shift of the $\pi$ and $\delta$ resonances. However, the intensity ratio is far from being perfect. Due to this, we rescaled the transition dipole moments by fitting our theoretical profile to the experiment (Fig. 5.4). The whole theoretical XAS spectral profile, Fig. 5.2 A, is shifted to a lower energy region by 1.25 eV.

5.3 X-ray Raman scattering

Both experimental and theoretical RXS spectral profiles for different excitation energies are shown in Fig. 5.5. The $4\sigma$ band was shifted to a higher energy region comparing to the MCSCF calculation by 2.28 eV. The peaks $6\sigma_{3/2}$ and $6\sigma_{1/2}$ deserve a special comment. The origin of these resonances is the scattering through the dissociative core-excited state $2p^{-1}6\sigma$ (Fig. 5.3). Simulations show that the intensity of the $5\sigma$ band is much smaller than the intensity of the $4\sigma$ peak. Due to this, we focus our attention only on the analysis of the $4\sigma \rightarrow 2p$ fluorescence. The ground state nuclear wave packet is promoted to the potential of the core-excited state and moves from the point of the vertical transition
FIG. 5.3: Potential surfaces of the ground (GS), first core-excited \(^{2p^{-1}6\sigma}\) and final \(^{4\sigma-16\sigma}\) states. The dotted line displays the final \(^{4\sigma-16\sigma}\) state potential shifted in energy to show the parallel feature of the potentials.

FIG. 5.4: Comparison of the experimental \(L_{II,III}\) XAS spectrum of HCl (dotted line) with the theoretical simulations (solid line) based on the rescaling of transition dipole moments (see the text). Dashed lines show the partial contributions. \(\Gamma = 0.14\) eV for all states except for the dissociative \(6\sigma_{3/2}\) and \(6\sigma_{1/2}\) states with HWHM = 0.84 eV.

to the region of higher bond lengths. During the dissociation in the core-excited state, the molecules continuously decay to the final dissociative state \(|2p^{-1}4\sigma\rangle\) (Fig. 5.3). A previous study of the resonant Auger spectra of HCl suggest that the hydrogen atom has time to approach the region of dissociation.\(^{63}\) As is well known,\(^{53,62,64}\) the RXS profile in general consists of two qualitatively different bands. Decay transitions near the equilibrium geometry form the molecular band while decay transitions in the dissociative region (where the potentials of the core-excited and final states are parallel) result in so-called atomic peaks. Contrary to the molecular band the peak position of the atomic peak does not depend on the excitation energy \(\omega\) (except in the hard x-ray region\(^{57}\)). However, the final and core-excited state potentials in the studied case are parallel to each other along the whole pathway of the wave packet (Fig. 5.3). This means that the molecular and atomic bands coincide with each other and that they form a single non-dispersive atomic peak, as one can see clearly from our wave packet simulations of the RXS channels \(6\sigma_{3/2}\) and \(6\sigma_{1/2}\). The non-dispersive behavior of the corresponding experimental peaks confirms our simulations and interpretation. A detailed interpretation of the RXS spectra of the HCl molecule is given in Paper VIII.
FIG. 5.5: Experimental and theoretical RXS spectra of HCl for different excitation energies. The label below the excitation energy shows the corresponding resonant peak in the x-ray absorption, Fig. 5.4. The theoretical spectra were computed using the data from Fig. 5.4. The theoretical 4σ band is shifted to higher energy by 2.28 eV. The 5σ band is increased in intensity in 3 times for all excitation energies.
CHAPTER 6

Summary of results

• A new type of spectroscopy is proposed: The phase sensitive IR–x-ray pump-probe spectroscopy.

• A dynamical theory of phase sensitive IR–x-ray pump-probe spectroscopy is developed.

• The phase sensitivity of the x-ray spectra driven by strong IR fields depends strongly on the duration time of the pulses, the delay time between them, the shape of the IR radiation and on the orientational ordering of the sample.

• The x-ray absorption profile is the sum of partial contributions of core excitation from pumped vibrational levels in the case of incoherent IR pulses or long x-ray pulses.

• It is shown that the trajectory of the nuclear wave packet changes qualitatively upon change of the phase of the pump IR field.

• X-ray probe spectra display a phase memory effect: The wave packet keeps memory about the infrared phase after the pump field left the system when the IR field is switched off faster than the Rabi period.

• It is found that the center of gravity of the probe spectrum in the frequency domain follows the wave packet trajectory in coordinate space. This constitutes the physical background of phase sensitive IR–x-ray pump-probe spectroscopy.

• Variations of the phase, intensity and shape of the pump pulse allows the quantum control of the nuclear wave packet, which means the selective population of certain groups of vibrational levels and preparation of the wave packet of desirable shape.
• It is shown that the phase of the radiation affects the dynamics of the nuclear wave packet when the Rabi frequency approaches the resonant frequency, thus breaking down the rotating-wave approximation.

• Time resolved x-ray probe spectra display the revival phenomenon caused by the potential anharmonicity. The determination of the revival period allows measurements of the anharmonicity constant. Decay of the revival pattern gives information about intra and intermolecular interactions.

• It is shown that a strong coherent IR field enhances the electronic recoil effect in x-ray photoelectron spectra when the size of the wave packet is increased.

• An extra enhancement of the electronic recoil effect occurs when the gradients of the ground and core-ionized potentials are close to each other in the turning points of the wave packet.

• The two sidebands of the x-ray photoelectron band experience blue- and red-shifts, due to the different signs of the gradients in the right and left classical turning points of the potentials curves.

• Time resolved x-ray probe spectra map the IR induced wave packet dynamics in the ground electronic state in the case of delayed probe pulses relative to the pump pulse. The probe spectra are affected by the IR induced wave packet dynamics in both ground and core-excited states when pump and probe pulses overlap.

• IR–x-ray pump-probe spectroscopy is a proper tool to study light-induced chemical processes in molecular systems, e.g. proton transfer.

• Vibrations couple to intersecting core-ionized states in glyoxalmonoxтme resulting in partial delocalization of the core holes in the oxygen atoms. Vibronic coupling entangles the core holes and results in “bright” and “dark” spectral bands.

• We developed a general theory of L x-ray Raman spectra which takes into account the spin-orbit interaction, molecular orbital splitting and Coulomb interaction between core hole and valence electrons. Our theory explains the main spectral features of recently measured Cl $L_{II,III}$ spectra of the HCl molecule.
Bibliography


