Simulating Pump–Probe Photoelectron and Absorption Spectroscopy on the Attosecond Timescale with Time-Dependent Density Functional Theory

Umberto De Giovannini,*[a] Gustavo Brunetto,[a, d] Alberto Castro,*[c] Jessica Walkenhorst,[a] and Angel Rubio*[a, b]

1. Introduction

Pump–probe experiments are the preferred technique to study the dynamic behavior of atoms and molecules: the dynamics triggered by the pump pulse can be monitored by the time-dependent reaction of the system to the probe pulse; a reaction that can be measured in terms of, for example, the absorption of the pulse intensity or of the emission of electrons.[1] The time resolution of these experiments is mainly limited by the duration of the pulses, although it is also limited by the ability of the experimenter to ascertain the relative time delay and shape. To precisely fix this delay, the two pulses are coherently synchronized, in fact, they have the same origin, or one of them is used to generate the other, so that the delay is gauged by an optical path difference.[2] The electron dynamics has a natural timescale in the range of attoseconds, and therefore, could not be studied by pump–probe spectroscopy until the advent of attosecond-pulse laser sources one decade ago.[3, 4] Nowadays, time-resolved spectroscopy can be utilized to monitor electron dynamics in real time, giving rise to the field of attosecond physics.[5, 6]

A wealth of possibilities exists, depending on the frequencies, durations, and intensities of the two pulses. A common setup in attosecond physics employs an extreme ultraviolet (XUV) attosecond pulse and the relatively more intense near-infrared (NIR) or visible longer (a few femtoseconds) pulse used for its generation. Combining two XUV attosecond pulses is, in principle, possible (and has been theoretically analyzed[7]), but unfortunately the low outputs of current XUV attosecond pulses lead to signals that are much too weak. Another choice to make is the final observable, that is, what kind of system reaction is to be measured as a function of the time delay. Herein, we focus on two common choices. First, observing the emission of electrons (energies, angular distribution, or total yield) from the pumped system due to the probe pulse. This can be called time-resolved photoelectron spectroscopy (TRPES). Second, observing the optical absorption of the probe signal, which can be called time-resolved absorption spectroscopy, or transient absorption spectroscopy (TAS).

Both techniques can, of course, be used to look at longer time resolutions, and there is already a substantial body of literature describing such experiments. If we look at molecular reactions on the scale of tens or hundreds of femtoseconds, the atomic structure will have time to rearrange. These techniques are thus mainly employed to observe modification, creation, or destruction of bonds; a field now named femtochemistry.[8]

Molecular absorption and photoelectron spectra can be efficiently predicted with real-time time-dependent density functional theory. We show herein how these techniques can be easily extended to study time-resolved pump–probe experiments, in which a system response (absorption or electron emission) to a probe pulse is measured in an excited state. This simulation tool helps with the interpretation of fast-evolving attosecond time-resolved spectroscopic experiments, in which electronic motion must be followed at its natural timescale. We show how the extra degrees of freedom (pump-pulse duration, intensity, frequency, and time delay), which are absent in a conventional steady-state experiment, provide additional information about electronic structure and dynamics that improve characterization of a system. As an extension of this approach, time-dependent 2D spectroscopy can also be simulated, in principle, for large-scale structures and extended systems.
TAS, for example, has been successfully employed to watch the first photosynthetic events in chlorophylls and carotenoids,[26] which transform the energy gained by light absorption into molecular rearrangements. A review describing the essentials of this technique has been published.[10] Note, however, that, in addition to following chemical reactions, femtosecond-long pulses may also be used, for example, for characterizing the final electronic quantum state of ionized atoms.[31]

In TRPES, the probe pulse generates free electrons through photoionization and one measures their energy or angular distribution as a function of time. If this time is on the femtosecond scale, one can follow molecular dynamics in the gas phase, as demonstrated in the mid 1990s,[12, 13] although this technique had already been employed to follow electronic dynamics on surfaces.[14] This methodology is well documented in recent articles.[15–19]

If the goal—as in this work—is to study the electronic dynamics only, disentangling them from the vibronic degrees of freedom, then one must move down these spectroscopic methods to the attosecond regime.[20] In this regime, both TAS and TRPES have recently been demonstrated. Regarding TAS, we may cite, as a prototypical example, the recent experiment of Holler et al., in which the transient absorption of an attosecond pulse train (created by high harmonic generation) by a helium gas target was studied in the presence of an intense IR pulse.[21] The absorption was observed to oscillate as a function of the time delay of pump and probe. Another example is the real-time observation of valence-electron motion reported by Goulielmakis et al.[22]

Several cases of the use of TRPES with attosecond pulses have also been recently reported. For example, Ulbracker et al. could observe, in real time, the light-induced electron tunneling provoked by a strong NIR pulse, demonstrating how this electron tunneling could be used to probe short-lived electronic states.[23] Smirnova et al. also studied the ionization of an atom by an attosecond XUV pulse in the presence of an intense laser pulse, as a function of the time delay between both.[24] Johnsson et al. employed attosecond pulse trains and a helium target,[25] and attosecond photoelectron spectroscopy was also demonstrated to yield useful information for condensed matter systems.[26]

All these advances demand appropriate theoretical modeling. The use of more than one pulse of light intrinsically requires going beyond any “linear spectroscopy” technique, although if the pulses are weak then a perturbative treatment may still be in order. This nonlinear behavior provides much more information about the system at the cost of increasingly difficult analysis. The use of two (or more) coherent pulses of light, with fine control over their shape (sometimes called “multidimensional analysis”), permits deeper characterization. This fact was already acknowledged in the field of nuclear magnetic resonance, or later in femtochemistry, see, for example, references [27] and [28] for theoretical treatments of these cases.

A recent theoretical analysis of attosecond TAS based on perturbation theory was given by Baggesen et al.[27] Gaarde et al. presented a study of relatively weak pumping IR pulses in combination with XUV ultrafast probes, for helium targets and based on the single-active electron approximation (SAE).[29] Recently, experiments reported by Ott et al.,[30] in which ultrafast TAS of helium displayed characteristic beyond-SAE features, were theoretically analyzed in ref. [31], utilizing an exact solution of the time-dependent Schrödinger equation. This cannot however be easily extended to larger systems. Finally, the above-mentioned experiment of Goulielmakis et al.[22] was analyzed with the model described in ref. [32], which treated the pump IR pulse nonperturbatively.

Indeed, it would be desirable to analyze these processes with a theory that is simultaneously non-perturbative (since at least one of the pulses is usually very intense), and capable of going beyond the SAE, accounting for many-electron interaction effects. This last fact is relevant because attosecond time resolution obtained in this type of experiment is able to unveil fast dynamic electron–electron interaction effects. The SAE, which essentially assumes that only one electron actively responds to the laser pulse, has been successfully used to interpret many strong-field processes. However, its range of validity is limited and roughly speaking it is expected to fail whenever the energies of multielectron excitations become comparable to the laser frequencies or single-electron excitations.[30]

Time-dependent density functional theory (TDDFT)[34] in principle, meets all requirements: it may be used nonperturbatively, it includes electron–electron interactions, and can handle out-of-equilibrium situations. It has been routinely used in recent decades to study the electron dynamics in condensed matter in equilibrium. By this we mean that, usually, one computes the linear or nonlinear response properties of systems in the ground state (or at thermal equilibrium). In pump–probe experiments, however, one must compute the response of a system being driven out of equilibrium by an initial pulse. Herein, we explore the usability of TDDFT for this purpose and show how, at least for TAS and TRPES, the extension is straightforward.

2. Theory

DFT[35] establishes a one-to-one correspondence between the ground-state density and the external potential of a many-electron system. This implies that any system property is, in principle, a ground-state density functional. The computation of the ground-state density usually follows the Kohn–Sham (KS) scheme, in which one utilizes a fictitious system of noninteracting electrons that has the same ground-state density. For excited-state properties, however, or to simulate the behavior of the system in time-dependent external fields, one must use its time-dependent version, TDDFT.[34,37,38]

In the case of TDDFT, a one-to-one correspondence also exists between the time-dependent densities and potentials. One also uses an auxiliary fictitious system of noninteracting electrons that produces the same time-dependent density. This substitution is the source of great computational simplification because a noninteracting system of electrons can, in general, be represented by a single Slater determinant formed by a set of “Kohn–Sham” orbitals, \( \psi_i \), for \( i = 1, \ldots, N/2 \). We assume a spin-
compensated system of $N$ electrons doubly occupying $N/2$ spatial orbitals. If the real system is irradiated with an external field characterized by a scalar potential $v(r,t)$ (the extension to vector potentials is also possible), the “time-dependent Kohn–Sham” (TDKS) equations that characterize the evolution of the fictitious system are (atomic units are used hereafter) given by Equations (1) and (2):

$$\frac{\partial}{\partial t} \psi_i(r, t) = -\frac{1}{2} \nabla^2 \psi_i(r, t) + v_{KS}[n](r, t) \psi_i(r, t)$$  

$$n(r, t) = \sum_{i=1}^{N/2} |\psi_i(r, t)|^2$$  

The time-dependent density, $n(r,t)$, is the central object and is identical for the real and KS systems. The KS potential, $v_{KS}$, is a functional of this density and is defined by Equation (3):

$$v_{KS}[n](r, t) = v_H(r) + v_{\text{xc}}[n](r, t) + v_{\text{et}}[n](r, t)$$  

in which the Hartree potential, $v_H$, corresponds to a classical electrostatic term [Eq. (4):

$$v_{\text{et}}[n](r, t) = \int d\mathbf{r'} \frac{n(\mathbf{r'}, t)}{|\mathbf{r} - \mathbf{r'}|}$$  

$v_H(r)$ is the static external potential that characterizes the system in its ground state (in a molecule, originated by a set of nuclei) and the “exchange and correlation” potential is $v_{\text{xc}}[n]$. The exchange correlation potential is also a functional of the density and accounts for all the intricate many-electron effects. It is in practice unknown and must be approximated.\[34,39]

The TDKS equations can be utilized, either directly or in an appropriately transformed manner, to compute the response of a many-electron system to a perturbation, weak or strong. In the perturbative regime, ideally one wishes to obtain the response functions (hyper)polarizabilities, optical and magnetic susceptibilities, ...], since 1) these objects then permit any re- action to be predicted in the appropriate order and 2) experiments typically provide spectra that are directly related to the response functions, for example, the optical absorption cross section of a gas is proportional to the imaginary part of the dipole–dipole molecular polarizability. In contrast, in the strong-field regime, where perturbative treatments become cumbersome, one normally computes the particular response of the system to the perturbation of interest by directly propagating the TDKS equations in real time.

The vast majority of TDDFT applications have addressed the first-order response of the ground-state system to weak electric fields, which can provide the absorption spectrum, the optically allowed excitation energies and oscillator strengths, and so forth. This can be performed by linearizing the TDKS equations in the frequency domain and casting the result into the matrix-eigenvalue form or by propagating the same equations in real time by applying a sufficiently weak dipole perturbation. In any case, the response function computed in this manner will be that of the ground state. If we want to analyze a TAS experiment, the objective is to obtain the response of the excited states visited by the system as it is driven by the pump pulse (i.e. the response function of a system out of equilibrium). This extension is treated in Section 2.1.

Likewise, TDDFT can be used to compute strong-field nonlinear photoelectron spectra of atoms and molecules, for example, with the method recently developed by some of us.\[40] These spectra, however, are also characteristic of the ground state, although, as shown in Section 2.2, the methodology can be easily extended to tackle the pump–probe case (time-resolved photoelectron spectroscopy\[19]).

2.1. Attosecond TAS

When an electromagnetic pulse passes through a gas sample, the molecules polarize and this polarization modifies the otherwise free propagation of light; one of the consequences is its partial absorption. In a dilute gas, assuming the electric dipole approximation and a sufficiently weak pulse, the dipole–dipole linear dynamic polarizability entirely determines the polarization of the medium, and therefore, the amount of absorption. This is usually understood at equilibrium: the gas is formed by molecules at thermal equilibrium (perhaps at sufficiently low temperature that they can all be considered to be in their ground state) and the only light pulse present is that with the absorption we want to measure.

In the pump–probe situation discussed herein, however, one wishes to compute the absorption of a probe pulse by a set of molecules that is also irradiated by a pump, either simultaneously or with a given delay. The task is therefore to compute the response of the electric dipole with and without the probe pulse—the difference is the excess of polarization, which is responsible for the absorption of the probe. We assume, as is often the case, that the pump pulse is intense, whereas the probe is weak and can be treated in first-order perturbation theory.

This situation is amenable to a generalized definition of response functions, such as that given in the appendix of ref.\[41] and also discussed in detail in ref.\[42]. We review herein this definition, adapting it to the pump–probe situation. Let us depart from a Hamiltonian in the form (we only treat the electric part, neglecting the magnetic term of the electromagnetic field) given in Equation (5):

$$\hat{H}(t) = \hat{H}_0 + \mathcal{E}(t) \hat{V}$$  

in which $\hat{H}_0$ is the static Hamiltonian that defines the system itself, and $\mathcal{E}(t) \hat{V}$ is the coupling to the “pump” laser pulse. This is the “unperturbed” Hamiltonian, which contains only the pump pulse; the full Hamiltonian results of the addition of the probe pulse $f(t) \hat{V}$ are given by Equation (6):

$$\hat{H}(t) = \hat{H}_0 + \mathcal{E}(t) \hat{V} + f(t) \hat{V}$$
The evolution of the system is given by Equation (7):

$$i \frac{\partial}{\partial t} \rho(t) = [\hat{H}(t), \rho(t)]$$  \hspace{1cm} (7)$$

and initially (t = 0) some time before the arrival of both pump or probe, the system is at equilibrium [Eq. (8)]:

$$[\hat{H}, \rho_0] = 0$$  \hspace{1cm} (8)$$

For a fixed pump \( \delta \), we may assume the system evolution to be a functional of the probe shape: \( \rho = \hat{\rho}[f] \), and we may expand \( \hat{\rho} \) in a Taylor series (in the functional sense) around \( f = 0 \), resulting in Equation (9):

$$\hat{\rho}[f] = \sum_{n=0}^{\infty} \rho_n[f]$$  \hspace{1cm} (9)$$

where \( \rho_0 \) is the unperturbed system (i.e. the evolution of the system in the presence of the pump only: \( f = 0 \)), and \( \rho_n \) is the nth order in the perturbation: \( \hat{\rho}[f] = \lambda^n \rho[f] \). The system response to this perturbation is measured in terms of the expectation value of an observable \( \hat{\mathcal{A}} \), which can likewise be expanded to give Equation (10):

$$\mathcal{A}(t) = \text{Tr}[\hat{\rho}(t) \hat{\mathcal{A}}] = \sum_{n=0}^{\infty} A_n(t)$$  \hspace{1cm} (10)$$

where \( A_n(t) \) is given by Equation (11):

$$A_n(t) = \text{Tr}[\rho_n(t) \hat{\mathcal{A}}]$$  \hspace{1cm} (11)$$

For sufficiently weak probes, we are only interested in the first term [Eq. (12)]:

$$\Delta \mathcal{A}(t) = \mathcal{A}(t) - \mathcal{A}_0(t) \approx A_1(t) = \text{Tr}[\hat{\rho}_1(t) \hat{\mathcal{A}}]$$  \hspace{1cm} (12)$$

which is linearly related to \( f \) through a pump-probe dependent response function given by Equation (13):

$$A_1(t) = \int_{-\infty}^{\infty} df(t') \chi_{\mathcal{A}\mathcal{V}}[\delta](t,t')$$  \hspace{1cm} (13)$$

The response function is given by Equation (14):

$$\chi_{\mathcal{A}\mathcal{V}}[\delta](t,t') = i \theta(t - t') \text{Tr}[\hat{\rho}_1[\mathcal{A}_0[\delta](t), \hat{\mathcal{V}}_n[\delta](t')]]$$  \hspace{1cm} (14)$$

Inside the commutator, the operators appear in the Heisenberg representation given in Equation (15):

$$\mathcal{O}_n[\delta](t) = \mathcal{U}[\delta](t_0,t) \hat{\mathcal{O}} \mathcal{U}[\delta](t_0,t)$$  \hspace{1cm} (15)$$

where \( \mathcal{U}[\delta] \) is the time propagation operator in the presence of the pump only; hence, the functional dependence on \( \delta \). We keep this functional dependence explicit in the notation for \( \chi_{\mathcal{A}\mathcal{V}}[\delta](t,t') \) to stress that it is a property of both the system defined by the static Hamiltonian, \( \mathcal{H} \) and of the pump shape, \( \delta \), as opposed to the conventional response functions, which are only system dependent. Note also its dependence on two times \( t \) and \( t' \), which cannot be reduced to one by making use of time-translational invariance, which is customary when working at equilibrium.

The response itself, \( \delta \mathcal{A}(t) \), is a functional of both pump and probe pulses. If we take its Fourier transform we may write it as Equation (16):

$$\delta \mathcal{A}[(\delta, f)](\omega) = \int_{-\infty}^{\infty} dt' f(t') \chi_{\mathcal{A}\mathcal{V}}[(\delta, f)](\omega, t')$$  \hspace{1cm} (16)$$

To compute the response function, one can use as a probe a delta perturbation, that is, \( f(t) = \lambda \delta(t - t) \), which permits Equation (17):

$$\chi_{\mathcal{A}\mathcal{V}}[(\delta, f)](\omega, t) = \frac{1}{\mathcal{A}} \delta \mathcal{A}[(\delta, f)](\omega, t)$$  \hspace{1cm} (17)$$

The action of such a delta perturbation applied at instant \( t \) to the system is given by Equation (18):

$$\Phi(t \to t') = e^{-i \omega t} \chi_{\mathcal{A}\mathcal{V}}[(\delta, f)](\omega, t')$$  \hspace{1cm} (18)$$

From now on we restrict the discussion to pure states because ensembles are not needed for the results shown below. However, the discussion can easily be extended to general ensembles. We also restrict the discussion to a specific response function: the dipole–dipole polarizability \( \alpha[(\delta, f)](t,t') = \chi_{\mathcal{A}\mathcal{V}}[(\delta, f)](t,t') \), in which both \( \mathcal{A} \) and \( \mathcal{V} \) are the atomic or molecular dipole operator \( \hat{\mathcal{D}} \), when taking into account that, for the frequencies that we are dealing with, the dipole of interest is that of the electrons and the clamped nuclei approximation can be used. Moreover, we choose to work with light polarized in the \( x \) direction, so that we obtain Equation (19):

$$\hat{\mathcal{D}} = -\sum_{i=1}^{N} \hat{x}_i$$  \hspace{1cm} (19)$$

in which \( N \) is the number of electrons. The expectation value of this electronic dipole is an explicit functional of the time-dependent density, and so is its variation [Eq. (20)]:

$$\delta \mathcal{D}[(\delta, f)](\omega) = -\int d^d\mathbf{r} \delta(\mathbf{r}, \omega) x$$  \hspace{1cm} (20)$$

in which \( \delta(\mathbf{r}, \omega) \) is the Fourier-transformed difference between the electronic densities obtained with and without the probe pulse. This straightforward formula [Eq. (20)] in terms of the density is what makes TDDFT particularly suited for these computations: we may safely utilize the Kohn–Sham system of noninteracting electrons. The delta perturbation [Eq. (18)] must be applied to each of the Kohn–Sham orbitals, and takes the form of Equation (21):
The absorption of a particular probe pulse, $f$, is determined by the induced polarization, given by $\delta D(r, f)$. We compute the dynamic polarizability, $\alpha(\omega, \mathbf{r})$, which is the polarization induced by a delta perturbation [Eq. (22)]:

$$\alpha(\omega, \mathbf{r}) = \frac{1}{2} \delta D(\omega, \mathbf{r}, \delta \mathbf{r})$$

because it allows any particular response to be computed through the integration of Equation (16), as long as the probe is weak. In particular, we look at the imaginary part of $\alpha(\omega, \mathbf{r})$, which is the part responsible for absorption. Note, finally, that in a 3D situation the polarizability is not a scalar but a tensor, since there are three possible light polarization directions and three components for the system dipole moment. In most cases, one is interested in the trace of this tensor, which is an averaged quantity that corresponds to the absorption of a randomly oriented sample of molecules.

### 2.2. Time-Resolved Photoelectron Spectroscopy

The photoelectron spectra presented herein were produced within TDDFT by using the recently introduced Mask Method. In this method, we look at the imaginary part of the space partition implemented by the mask technique [see Figure 1(a) for a complete description] and demonstrate how it can be straightforwardly applied to the nonequilibrium situation required by pump–probe experiments.

In photoemission processes, a light source focused on a sample transfers energy to the system. Depending on the light intensity, electrons can absorb one or more photons and escape from the sample due to the photoelectric effect. In experiments, electrons are detected and their momentum is measured. By repeating measurements on similarly prepared samples, it is possible to estimate the probability of measuring an electron with a given momentum. From a computational point of view, the description of such processes for complex systems is a challenging problem. The main difficulty arises from the necessity of properly describing electrons in the continuum.

In typical experimental setups, detectors are situated far away from the sample and electrons overcoming the ionization barrier travel a long way before being detected. The distances that electrons travel are usually orders of magnitude larger than the typical interaction length scales in the sample. During their journey towards the detector, and far away from the parent system, they practically evolve as free particles driven by an external field. The solution of the Schrödinger equation for free electrons in a time-dependent external field is known analytically in terms of plane waves as Volkov states. It seems therefore a waste of resources to solve the Schrödinger equation numerically in the whole space if a considerable part of the wavefunction can be described analytically.

To take advantage of previous observations, we partitioned the space according to Figure 1(b). The space is divided into two regions, A and B. The inner region, A, containing the system with enough surrounding empty space, is where electrons are allowed to interact with each other and with the system, and region B, defined as the complement of A, is where electrons are noninteracting and freely propagating. Every KS orbital, $\varphi_i(\mathbf{r})$, can be decomposed accordingly, with $\varphi_i(\mathbf{r}) = \varphi^{\text{A}}(\mathbf{r}) + \varphi^{\text{B}}(\mathbf{r})$, so that $\varphi^{\text{A}}(\mathbf{r})$ resides mainly in region A and $\varphi^{\text{B}}(\mathbf{r})$ mainly in region B.

The geometrical partition is implemented by a smooth mask function, $M(r)$, defined to be one deep in the interior of A and zero outside [Eqs. (23) and (24); see Figure 1(a)]:

$$\varphi^{\text{A}}(\mathbf{r}) = M(r)\varphi_i(\mathbf{r})$$

$$\varphi^{\text{B}}(\mathbf{r}) = [1-M(r)]\varphi_i(\mathbf{r})$$

The mask function takes care of the boundary conditions in A by forcing every function to be zero at the border. To give a good description of functions extending over the whole space, it is convenient to represent $\varphi_i^B(\mathbf{r})$ orbitals in momentum space $\tilde{\varphi}_i^B(\mathbf{p})$.

A mixed real and momentum-space time evolution scheme can then be easily derived following geometrical splitting. Given a set of orbitals at time $t$, their value at a successive time $t + \Delta t$ is provided by Equation (25):

$$\varphi(t, t + \Delta t) = e^{i\mathcal{H}\Delta t}\varphi_i(t)$$

where $\mathcal{H}$ is the Hamiltonian of the system.
\[
\begin{align*}
\psi^i_a(t + \Delta t) &= M(r)e^{-i\hbar\Delta t}\psi^i_a(t) \\
\tilde{\psi}^i_b(p, t + \Delta t) &= e^{-i\hbar\Delta t}\tilde{\psi}^i_b(p, t) + \tilde{\psi}^i_b(p, t + \Delta t)
\end{align*}
\] (25)

in which the \(\hat{H}\) is the effective single-particle TDDFT Hamiltonian, \(A(t)\) is the total external time-dependent vector potential (the coupling with the external field is conveniently expressed in the velocity gauge), and \(\tilde{\psi}^i_b(p, t + \Delta t)\) is given by Equation (26), which constitutes the portion of electrons leaving the system at time \(t + \Delta t\).

\[
\tilde{\psi}^i_b(p, t + \Delta t) = \frac{1}{(2\pi)^{3/2}} \int dr (1 - M(r)) e^{-i\hbar\Delta t} \psi^i_a(r, t)e^{ip\cdot r} \quad (26)
\]

For each iteration in the evolution, the outgoing components of \(\psi^i_a(r)\) are suppressed in the interaction region by multiplication with \(M(r)\), while being collected as plane waves in \(\tilde{\psi}^i_b(p)\) via \(\tilde{\psi}^i_b(p)\). The resulting momentum space wavefunctions are then evolved analytically simply by phase multiplication.

The advantage of using such an approach resides in the fact that we can conveniently store the wavefunctions on a spatial grid inside A, while treating wavefunctions in B (and therefore the tails extend to infinity) as free electrons in momentum space. Moreover, the mask function introduces region C, where the wavefunctions in A and B overlap (see Figure 1), which acts as a matching layer. In spite of the fact that, from a theoretical point of view, having a whole region to perform matching is more stable and less influenced by different choices of spatial grids.

From the momentum components of the orbitals in B, it is possible to evaluate the momentum-resolved photoelectron probability distribution as a sum over the occupied orbitals [Eq. (27)]:

\[
P(p) \approx \lim_{t \to \infty} \sum_{i=1}^{m} |\tilde{\psi}^i_b(p, t)|^2 \quad (27)
\]

in which the limit \(t \to \infty\) ensures that all of the ionized components are collected. This scheme is entirely nonperturbative: in a pump–probe setup it does not assume linearity in either the pump or the probe. Therefore, it can be applied in the same manner when two pulses are present as that with only one pulse, as shown in ref. [40]. Similar to Section 3.1, we can generalize the previous derivation to address transient photoelectron spectroscopy (spin-, angle-, and energy-resolved) in practice by employing a pump–probe scheme and by performing numerical simulations with two time-delayed external pulses. A TRPES map is then generated by performing a computation for each time delay.

From \(P(p)\), several relevant quantities can be calculated. The energy-resolved photoelectron probability, \(P(E)\), which is usually referred to as a photoelectron spectrum (PES), can be obtained by integrating \(P(p)\) over solid angles [Eq. (28)]:

\[
P(E = p^2/2) = \int d\Omega_p P(p) \quad (28)
\]

The angular- and energy-resolved photoelectron probability, \(P(\theta, \phi, E)\) or photoelectron angular distribution (PAD), can easily be evaluated by expressing \(P(p)\) in polar coordinates with respect to a given azimuth axis.

It is noteworthy that during the evolution defined in Equation (25) the part of the density contained in A that is transferred to B is not allowed to return. Clearly, in cases in which the external field is strong enough to produce electron orbits crossing the boundary of A and backscattering to the core, the mask method provides a poor approximation. In these cases, a bigger region A or a more refined scheme must be employed. [46] The laser fields employed in this work are weak enough that we can safely assume that region A is always sufficiently large enough to contain all of the relevant electron trajectories.

3. Results

The theory described in the Section 2 was implemented in the octopus code. [44] We refer the reader to refs. [45] and [46] for a description of the essential points of the numerical methodology.

3.1. One-Dimensional Model Helium

For the first example we studied the absorption spectrum of an excited 1D soft-Coulomb helium atom. This is an exactly solvable model that provides a useful benchmark for testing different approximations. We first discuss the exact solution and later apply TDDFT. A more realistic 3D model is presented in Section 3.2.

The 1D model of the helium atom is defined by the Hamiltonian given in Equation (29):

\[
H(t) = T + V_{\text{ext}}(t) + V_{\text{ee}} \quad (29)
\]

in which the external potential is given by Equation (30):

\[
V_{\text{ext}} = -\frac{2}{\sqrt{1 + x_1^2}} - \frac{2}{\sqrt{1 + x_2^2}} + \delta(t)(x_1 + x_2) \quad (30)
\]

the electron Coulomb interaction \(1/|x|\) is softened to \(1/\sqrt{1 + x^2}\). Coupling with the external time-dependent field \(\delta(t)\) is expressed in length gauge, and electrons are confined to move along the \(x\) direction only. Finally, the kinetic energy is given by Equation (31):

\[
T = -\frac{1}{2}(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2}) \quad (31)
\]
and the electron–electron interaction is given by Equation (32):

\[
V_{ee} = \frac{1}{\sqrt{1 + (x_1 - x_2)^2}} \quad (32)
\]

This model is numerically solvable given the exact mapping discussed in refs. [47,48], in which it is proved that the many-body problem of \(N\) electrons in one dimension is equivalent to that of one electron in \(N\) dimensions. The wavefunctions and other necessary functions are represented on a real-space regular grid; a square (linear for 1D TD-DFT) box of \(L = 200\) a.u. and a spacing of \(\Delta x = 0.2\) a.u. was employed in all of the calculations.

To illustrate how an external field can modify the optical properties of the system shown in Figure 2, we show a scan of the nonequilibrium absorption spectrum generated by a 45 cycle \(\sin^2\) envelope pulse with intensity \(I = 5.26 \times 10^{11}\) W cm\(^{-2}\) at different carrier frequencies and then probed right after. The maximal response is observed for frequencies close to the first optical transition \(\omega_0 = 0.533\) a.u.

Figure 2. The out-of-equilibrium absorption spectrum as function of the pump laser frequency for 1D helium is shown. The system is driven out of equilibrium by 45 cycle \(\sin^2\) envelope laser pulses of intensity \(I = 5.26 \times 10^{11}\) W cm\(^{-2}\) at different angular frequencies of 0.51 a.u. \(\leq \omega_p \leq 0.59\) a.u. The plot displays \(\text{Im}(\alpha(\mathbf{q}, \omega)|\omega|\alpha(\mathbf{q}, \omega))\) when choosing \(\tau\) right at the end of the pump pulse.

It can be seen how the absorption around the first excitation frequency, 0.533 a.u., is strongly diminished when the frequency of the pump resonates with that frequency. In that situation, absorption peak also appears at around the excitation frequency corresponding to the transition from the first to the second excited state, in our case at 0.076 a.u. This behavior is a direct consequence of the fact that the laser pumps the system to the first excited state and this process is more efficient for a field tuned to the excitation energy. The absorption spectrum is therefore a mixture of the one corresponding to the unperturbed ground state and that of the first excited state.

To analyze this point further, a cross-section at the resonant frequency is displayed in the lower (blue) curves of Figure 3. The filled curve represents the spectrum obtained from the system in its ground state, whereas the solid line corresponds to the spectra of the system excited by a laser pulse with a frequency resonant with the first optical transition and probed after the perturbation. By direct comparison of the two spectra, it is easy to discriminate the peaks associated with the ground-state absorption from those characterizing the absorption from the excited state. In particular, peaks related to the ground-state absorption are located at energies of \(\omega_{g,i} = e_1 - e_0 = 0.533\) a.u., which corresponds to the transition from the ground \((\omega_0 = -2.238\) a.u.) to the first excited state \((e_1 = -1.705)\), and \(\omega_{g,3} = e_3 - e_0 = 0.672\) a.u., which corresponds to the third excited state \((e_3 = -1.566\) a.u.)—direct excitation of the second excited state is forbidden by symmetry. The solid curves show fingerprints of the population of the first excited state, namely, peaks corresponding to transitions from that first excited state to others: in particular, the peak appearing at a low energy of \(\omega_{1,2} = e_2 - e_1 = 0.076\) a.u. is associated with the transition from the first excited state, \(e_2\), to the second one \(e_2 = -1.629\) a.u.

These spectra contain information that is not contained in equilibrium ones. For example, let us consider the spectra that would be produced by each single eigenstate, given by the state-dependent dynamic polarizabilities, which may be written in the sum-over-states form [Eq. (33)]:

\[
\alpha^{(i)}(\omega) = \sum_{j=1}^{N} \left[ \frac{|\langle \Psi_i | D_{ij} | \Psi_j \rangle|^2}{\omega - (e_j - e_i) + i0^+} - \frac{|\langle \Psi_i | D_{ij} | \Psi_j \rangle|^2}{\omega + (e_j - e_i) + i0^+} \right] \quad (33)
\]

The poles of this function provide us with the eigenvalue differences, \(e_j - e_i\); if this value is positive, the corresponding term is associated with a photon absorption process; if it is negative, with a stimulated emission term. The weight associ-
ated with each one of these poles provides us with the dipole coupling matrix elements \( \langle \psi_f | D | \psi_i \rangle \).

During the time evolution, the wavefunction can be expanded on the basis of eigenstates of the unperturbed system, \( \psi(t) = \sum \eta_i(t) \psi_i \). When the system is probed at a certain time, \( t \), the resulting spectrum can be thought of as a linear combination of the spectra produced by each individual eigenstate. Analysis of the transient spectrum may therefore provide information about the mixing weights, \( \eta_i \), and about excitation energies and dipole couplings between excited states; this information is absent in the equilibrium ground-state linear response.

In our case, we found, by direct projection of the time-dependent wavefunction onto the eigenstates, that the system after the pulse was composed mainly of the ground and first excited state with weights \( |\eta_0|^2 = \langle \psi_0 | \psi(t) \rangle^2 = 0.7120 \) and \( |\eta_1|^2 = \langle \psi_1 | \psi(t) \rangle^2 = 0.2876 \). The same information can be recovered by comparing the perturbed and unperturbed spectra at \( E_\omega \). At this energy, we only have the contribution from \( \psi_0 \rightarrow \psi_1 \), and its inverse \( \psi_1 \rightarrow \psi_0 \). The peak height of the perturbed spectrum after the laser pulse, \( h_0 \), is therefore a combination of the heights associated with the ground, \( h_0 \), and the excited, \( h_1 \), states: \( h_0 = \frac{|\eta_0|^2}{h_0} \hat{n}_0 + |\eta_1|^2 \hat{n}_1 \). At this energy \( \alpha = \frac{h_0}{h_0} = \frac{|\eta_0|^2}{|\eta_1|^2} = 0.4258 \) thus gives direct information about the difference of the mixing weights. Complementing this information with a two-level system assumption, \( |\eta_0|^2 + |\eta_1|^2 = 1 \), we obtained \( |\eta_0|^2 = (1 + \alpha)/2 = 0.7129 \) and \( |\eta_1|^2 = (1 - \alpha)/2 = 0.2871 \), which was in good agreement with the results calculated by direct projection of the wavefunction.

In Figure 4, we display the population weights for two different laser pulses. The red lines correspond to the same laser pulse as that in Figure 3, whereas the blue lines pertain to a laser that is four times longer with the same parameters (intensity, envelope shape, and carrier frequency) and 180 optical cycles. For both lasers, the populations of both the ground and first excited states at each time almost sum to one, indicating essential two-level dynamics. In the case of the long pulse, we observe a maximum (minimum) of the population over the excited (ground) state at \( t = 30.62 \) fs. This behavior can be understood in terms of Rabi oscillations.

A Rabi oscillation is a fluctuation behavior of states occupation occurring due to the interaction of an oscillatory optical field in resonance with a two-level system. The occupation probability alternates with the Rabi frequency \( \Omega(t) = f(t) \mu_{\omega_1 \rightarrow \omega_2} \), in which \( \mu_{\omega_1 \rightarrow \omega_2} \) is the dipole transition matrix element between the states and \( f(t) \) is the electric field envelope. Extreme points of the populations should be located at times where the pulse area, \( \Theta(t) = \int_{-\infty}^{t} |f(t)| \mu_{\omega_1 \rightarrow \omega_2} \), is an integer multiple of \( \pi \), \( \Theta(t) = n \pi \). With the numerically calculated matrix element \( \mu_{\omega_1 \rightarrow \omega_2} = 1.11 \) a.u., the first maximal population of the excited state is expected at \( t = 30.65 \) fs; this is in good agreement with what is observed. The absorption spectrum at this time, as shown in Figure 3 (dashed blue line), displays a considerable enhancement at \( \omega_{\omega_1 \rightarrow \omega_2} \) and a negative emission peak at \( \omega_{\omega_2 \rightarrow \omega_1} \) as expected from a pure excited state.

It is interesting to study the same model with TDDFT instead of with an exact treatment to address the performance of available (mainly static) exchange-correlation (xc) functionals. In Figure 3 we display results obtained with TDDFT, employing two different xc functional approximations: EXX in red and 1D LDA in green. The calculations were performed in the adiabatic approximation by using the same parameters as those in the exact case. The laser frequency was tuned to match the first optical transition appearing at \( \omega_{\omega_1 \rightarrow \omega_2} = 0.549 \) a.u. for EXX and \( \omega_{\omega_2 \rightarrow \omega_1} = 0.475 \) a.u. for LDA.

The unperturbed spectrum (Figure 3, solid curve) provided by EXX is in good agreement with the exact calculation, and the perturbed one qualitatively reproduces the exact result. In particular, the new peak appearing at low energy associated with the transition \( 1 \rightarrow 2 \) is well represented. In contrast, LDA is only capable of reproducing one peak for the perturbed and unperturbed cases. This is due to the known problem of asymptotic exponential decay of the functional that, in this 1D example, supports only a single bound excited state.

A common feature of both approximations is constituted by the presence of negative values in the perturbed spectra. This can be tracked down to the lack of memory in the adiabatic xc-functional approximation.[32] The lack or wrong memory dependence in the functional results in slightly displaced absorption and emission peaks associated with the same transition. This fact, analyzed in the light of Equation (33), results, at the transition energy, in a sum of two Lorentzian curves with different sign and slightly different centers. This explains why we get two inverted peaks where we should have only a single one going from positive to negative strength as we populate the excited state, as shown by the exact (blue) curves in Figure 3.

![Figure 4. Exact population on the ground, \( |\eta_0(t)|^2 = \langle \psi_0 | \psi(t) \rangle^2 \) (solid lines), and first excited, \( |\eta_1(t)|^2 = \langle \psi_1 | \psi(t) \rangle^2 \) (dashed lines), states as a function of time for different laser pulses. In red a 45 cycle pulse with parameters, as in Figure 3, and in blue a longer 180 cycle pulse with the same parameters.](image)

### 3.2. Helium Atom in 3D

In this section we describe a study of the real helium atom. We employed the EXX functional and discretized TDDFT equa-
tions on a spherical box of radius $R = 14$ a.u., spacing $\Delta r = 0.4$ a.u., and absorbing boundaries $2$ a.u. wide.

We began by investigating the changes in absorption of He under the influence of an external UV laser field driving the system with the frequency of the first dipole-allowed excitation. To this end, we used a 45 cycle $\sin^2$ laser pulse in velocity gauge with carrier $\omega_p = 0.79$ a.u. resonant with the $1s^2 \rightarrow 1s2p$ transition of intensity $I = 2.6 \times 10^{12}$ W cm$^{-2}$ polarized along the $x$ axis.

In Figure 5 we show a comparison of the absorption spectrum for the unperturbed atom (filled curve) and the perturbed one probed with a delta perturbation right after the pump pulse at $\tau = 8.68$ fs (dashed line). The comparison presents many traits similar to the ones discussed in Section 3.1 for the 1D helium model. In particular, fingerprints of the population of the first excited state can be observed in the appearance of a peak in the gap at $\omega = 0.079$ a.u. associated with the transition $1s2p \rightarrow 1s3s$. The second peak, associated with the transition $1s^2 \rightarrow 1s2p$, presents height changes correlated with the former one. We also obtained small artifacts, such as energy shifts and negative values attributed to the xc-kernel memory dependence discussed previously.

Additional details on the excitation process can be acquired by expanding the time dimension of the absorption spectrum. The TAS map, which was produced by probing the system at different time delays, is displayed in Figure 6. As the delay increased, we observed the build up of the peak associated with the state being pumped by the laser pulse at $\omega_{2p\rightarrow 3s}$. These changes are reflected in the oscillations of the ground-state first optical peak at $\omega_{1s\rightarrow 2p}$. In TDDFT, the knowledge of the wavefunction is lost in favor of the density, which does not allow us to do a population analysis based on simple wavefunction projection. The transient absorption spectrum, on the other hand, is an explicit density functional and its computation with TDDFT may help us to understand the evolution of the state populations.

The peak appearing in the gap presents a maximum at $\tau = 5.39$ fs that emerges before the end of the pump pulse ($\tau = 8.68$ fs). This peak is associated only with the transition from $1s2p \rightarrow 1s3s$, and therefore, its height is proportional to population of the $2p$ excited state. The oscillation can then be interpreted in terms of Rabi physics, as discussed in Section 3.1.

Further insight can be achieved by investigating the photoemission properties of the system. The TRPES map, as calculated in a pump–probe setup, is shown in Figure 7. Photoelectrons are calculated with the technique outlined in Section 2.2. The pump pulse is the same as the one employed for TAS. The probe is a 40 cycle trapezoidal laser pulse (8 cycle ramp) with a carrier frequency of $\omega_p = 1.8$ a.u., an intensity of $I = 5.4 \times 10^9$ W cm$^{-2}$, polarized along the $x$ axis, and is weak enough to discard nonlinear effects. We performed a scan for different
time delays, measuring each delay as the difference from the probe center to the beginning of the pump. Negative delays correspond to the situation where the probe precedes the pump. Moreover, to include all of the relevant trajectories, a spherical box of \( R = 30 \text{ a.u.} \) was employed and photoelectrons were recorded only during the up time of the probe pulse.

The TRPES map in Figure 7 shows three main features at \( E_1 = 0.66 \text{ a.u.}, E_2 = 0.88 \text{ a.u.}, \) and \( E_3 = 1.67 \text{ a.u.} \). In our case, the probe pulse is weak and photoelectrons escaping the system undergo photoelectric-effect energy conservation. A bound electron can absorb a single photon and escape from the atom with a maximum kinetic energy of \( E = \omega_p - E_0 \) in which \( \omega_p \) is the probe carrier frequency and \( E_0 \) is the field-free ionization energy. The ionization potential can be evaluated in DFT as the negative energy of the highest occupied KS orbital (HOMO) \( E_0 = 0.92 \text{ a.u.} \). Thus, the peak appearing at \( E_1 \) is energetically compatible with photoelectrons emitted from the 2s level: \( E_1 = \omega_p - E_0 \). This peak is the only one consistently appearing at negative delays where the pulses do not overlap. Moreover, the peak strength varies weakly with the delay while slightly shifting towards lower values of around 3 fs in accordance with TAS findings. At about the same delay time the peak at \( E_3 \) begins to emerge. This peak corresponds to emission from the pump-excited 2p state, \( E_3 = \omega_p + \omega_p - E_0 \). It is a process in which the atom, initially in the ground state, absorbs a photon from the pump and gets excited to the 2p bound state. The subsequent absorption of a probe photon frees the electron into the continuum. The peak at \( E_1 \) is understood in terms of pump photons only: \( E_1 = 2 \omega_p - E_0 \). The ionization mechanism shares the first step with the \( E_1 \) process, namely, \( 2s \rightarrow 2p \) excitation produced by the absorption of a \( \omega_p \) photon. In the second step, the electron is directly excited to a continuum state by the absorption of a second \( \omega_p \) photon. In the linear regime, the direct photoionization cross-section decays exponentially with energy.\(^{28}\) For this reason, and due to the disparity in intensity between pump and probe, this ionization channel is by far the most favorable one.

In direct photoemission processes, the photoelectron angular distribution (PAD) contains information about the electronic configuration of the ionized state.\(^{104}\) To support the energetic arguments, PADs \( P(\theta, \phi, E) \) at \( E = 8.99 \text{ fs} \) are presented in Figure 8a, b, d together with cuts on a TRPES map at \( E = 0 \) and 8.99 fs (c). For each energy marked in Figure 8c, we performed spherical cuts of the photoionization probability on energy shells at \( E = E_1, E_2, E_3 \). Each cut was then plotted in polar coordinates, in which \( \theta \) was the angle from the z axis and \( \phi \) was the angle in the \( xy \) plane measured from the x axis. Intersections of the polarization axis of the lasers with the sphere are marked with a white cross.

Figure 8 shows clearly that photoelectrons at \( E_1 \) (a) and \( E_3 \) (d) are of similar nature in agreement with the energy analysis. Electrons emerging with a kinetic energy of \( E_2 \) are emitted from a 2s state and the symmetry of the orbital is imprinted in the angular distribution of the photoelectrons. To understand the PAD features, it must be taken into account that 2s electrons are perturbed by a laser with a specific polarization direction that breaks the rotational symmetry. The laser transfers maximal kinetic energy along the direction parallel to that of polarization and minimal kinetic energy along the perpendicular plane and, if nonlinear effects can be discarded, it induces a geometrical factor of the form \( |A \cdot \vec{p}| \), in which \( A \) is the polarization direction and \( \vec{p} \) is the electron momentum. For this reason, electrons emitted along \( \phi = 90 \) and 270° are strongly suppressed, and Figure 8b is compatible with the spherical symmetry of a 2s state.

In Figure 8a, electrons are excited to a p state and then ejected into the continuum by the absorption of two pump photons. The PAD displays marked emission maxima for the direction aligned with the laser polarization (indicated by white crosses). The extension in \( \theta \) is consistently narrower than that of the 2s emission in Figure 8b with ionization from a p orbital. Of the three degenerate p orbitals, \( \vec{p}_3 \) is the one producing the strongest response. The signatures of the \( \vec{p}_1 \) and \( \vec{p}_2 \) responses can be identified in the nonvanishing PAD on the yz plane around \( \phi = 90 \) and 270°. Such a perpendicular response indicates a degree of nonlinearity induced by the pump. Similar considerations hold for Figure 8b, in which the p state excited by the pump is probed with \( \omega_p \). As before, the emission is mainly from a p orbital.

### 3.3. Ethylene Molecule

In this section, we discuss an extension of our calculations to the treatment of \( \text{C}_2\text{H}_4 \) and show how these techniques permit the study of the time dependence of molecular electronic states. In particular, we report on the clear observation of a strong \( \pi - \pi^* \) transition.

To obtain a good description of states close to the ionization threshold, we employed the asymptotically correct LB94 xc
We chose the molecular plane to be in the xy plane with carbon atoms at coordinates (±1.26517,0,0) a.u. and hydrogen atoms at (±2.33230,1.75518,0) and (±2.33230,—1.75518,0) a.u. The ion positions were fixed during the time evolution. Norm-conserving Trouiller–Martin pseudo-potentials were employed to describe core electrons of carbon. Moreover TDDFT equations were numerically integrated on a spherical grid with a spacing of Δr = 0.3 a.u., a radius of R = 16, and 2 a.u. wide absorbing boundaries.

We perturbed the system with a 15 cycle (3 cycle ramp) trapezoidal laser pulse with a carrier frequency of ωp = 0.297 a.u. and an intensity of I = 1.38 × 1011 W cm−2 polarized in the x axis. The laser frequency and polarization direction are suited for the excitation of mainly the molecular π−π* transition. The absorption spectrum of the excited molecule probed after the pulse is shown in Figure 9. The emergence of a peak associ-

![Figure 9. Comparison of the absorption spectra of unperturbed (filled curve) and perturbed ethylene (solid line) below the ionization threshold. The molecule is excited by a 45 cycle sin² envelope laser pulse polarized along the x axis with carrier ωp = 0.297 a.u. of intensity I = 1.38 × 1011 W cm⁻².](image)

The absorption spectrum of the excited molecule probed after the pulse is shown in Figure 9. The emergence of a peak associ-

![Figure 10. TAS of the ethylene molecule. The pump laser pictured in the upper panel is the same as that given in Figure 5.](image)

![Figure 11. Logarithmic scale TRPES for C2H4. The molecule is probed at different delays with a 40 cycle trapezoidal laser pulse with an 8 cycle ramp, ωp = 1.8 a.u., and I = 5.4 × 10¹⁰ W cm⁻² polarized along the z axis perpendicular with the pump. The pump laser (upper panel) is the same as that given in Figure 10.](image)
indicates concentration along the C–C bond axis, and minima for \( \phi = 0 \) and 360° consistent with a depletion in the direction of each carbon atom.

Separated by a probe photon \( \omega_p \) at \( E_1 = \omega_p + \omega_p - E_s = 1.67 \) a.u., we find photoelectrons ejected from the \( \pi^* \) state. The intensity of the peak steadily increases with time according to what is observed with TAS. Compared with \( \pi \), the \( \pi^* \) orbital presents additional nodes on the plane perpendicular to the molecular bond and a field polarized along \( z \) is sensitive to this kind of geometry. The PAD \( P(\theta, \phi, E) \) in Figure 12e displays strong suppression of electrons along the \( yz \) plane at \( \phi = 90,270^\circ \), and therefore, presents a clear manifestation of photoemission from a \( \pi^* \) state.

Slow electrons ejected at \( E_1 = 2\omega_p - E_s = 0.16 \) a.u. gradually increase and become the predominant ionization channel. The emergence in time of multiphoton peaks separated by \( \omega_p \) indicates that the pump is strong enough to trigger nonlinear effects. These electrons are ejected after the simultaneous absorption of pump photons. Electrons at \( E_1 \) reach the continuum with an \( \omega_p \) photon after the molecule has been excited to a \( \pi^* \) state by another \( \omega_p \) photon. PAD should therefore again carry signs of \( \pi^* \) symmetry. It must be noted that, in this case, \( \pi^* \) electrons are probed with the pump itself, and therefore, the laser polarization is along \( x \). As already discussed in the previous section, laser polarization carries a geometrical factor of the form \( A \cdot \mathbf{p} \) with \( A = A_x \), which introduces suppression along the \( yz \) plane (\( \phi = 90,270^\circ \)). Unfortunately, this plane is precisely where the \( \pi^* \) photoemission minima should lie. For this reason, PAD \( P(\theta, \phi, E) \) in Figure 12b is not suited for use to clearly discern \( \pi \) from \( \pi^* \) symmetry and suppression for \( \theta = 0^\circ \) along the \( xy \) plane is compatible with both structures.

4. Conclusions

We studied the problem of describing ultrafast (atto-second scale) time-resolved absorption and photoemission in finite systems with TDDFT. We presented the theory and discussed how it could be implemented, such that TDDFT could be successfully employed in the task of describing the dynamics of electronic excited states in atoms and molecules. We illustrated the theory with three applications: the 1D helium model, a 3D helium atom, and an ethylene molecule.

We studied the 1D helium atom perturbed by an external time-dependent field exactly by solving the time-dependent Schrödinger equation (TDSE). We showed how it was possible to recover information about state populations through a comparison of perturbed and unperturbed absorption cross-sections and that the population evolution in time could be described in terms of Rabi physics. We then performed TDDFT calculations on the same model and we may conclude that the results obtained with the EXX potential were in good agreement with the exact solution, although small artifacts appeared due to the wrong description of functional memory dependence.

Furthermore, we investigated the helium atom in a more realistic 3D treatment using the EXX functional. We performed resonant pump–probe calculations by monitoring both absorption and photoemission properties of the excited atom. TAS was a sensible tool to monitor the build up of the excited state, allowing Rabi oscillations to be observed as a function of the time delay between pump and probe. TRPES also allowed the characterization of the excitation process with time. However, due to a dominant ionization channel associated with sequential two-photon (pump) absorption, information about excited-state population was less apparent. Nonetheless, PAD, which is an observable that is sensitive to the geometrical arrangement of the ionized state, is a useful tool to discern the nature of each photoelectron peak. As a final example, we considered the case of the ethylene molecule to study the time evolution of a \( \pi \rightarrow \pi^* \) transition. PAD for ejected electrons offered clear evidence that the states taking part in the process were indeed \( \pi \) and \( \pi^* \) nature.

Figure 12. Angular- and energy-resolved photoelectron spectra for \( \text{C}_2\text{H}_4 \) at two fixed delay times. a) Geometry of the process: \( \mathbf{p} \) indicates photoelectron direction, \( \mathbf{A} \) is the pump polarization vector, and \( \mathbf{A}_p \) the probe one. d) Logarithmic scale PES \( P(\theta) \) for \( \tau = -1.69 \) (green) and 3.63 fs (red). Normalized PADs \( P(\theta, \phi, E) \) at \( \tau = 3.63 \) fs and energies marked in (d) are shown for b) \( E_1 = 0.16 \) a.u., c) \( E_2 = 1.37 \) a.u., and e) \( E_3 = 1.67 \) a.u. White marks indicate the position of the probe polarization vector (c and e, at the corners) and the pump one (b) on the sphere.
The theoretical framework we have developed is a useful tool to understand and control nonequilibrium electronic dynamic processes in nanostructures and extended systems. New emergent properties of matter in the strong-coupling regime could appear that might give rise to new technological developments. Furthermore, monitoring electron and ion dynamics provides fundamental insights into structure (i.e. time-resolved crystallography) and chemical processes in biology and materials science (e.g. for energy applications). There is plenty of room for new and fascinating discoveries about the behavior of matter under out-of-equilibrium conditions.

Still, from the fundamental point of view, there is a clear need for the development of nonadiabatic exchange and correlation functionals able to provide a reliable description of nonequilibrium processes and strong light–matter interactions. Clearly, the methods presented herein will automatically benefit from any theoretical advance in this direction. Conversely, the developers of new functionals may take into account the correct description of pump–probe experiments as a useful quality test.

Acknowledgements

We acknowledge financial support from the European Research Council Advanced Grant DYNano (ERC-2010-AdG-Proposal No. 267374); Spanish Grants (FIS2011-65702-C02-01 and PIB2010US00652); ACI-Promociona (ACI2009-1036), Grupos Consolidados UPV/EHU del Gobierno Vasco (IT-319-07); European Commission projects CRONOS (280879-2 CRONOS CP-FP7) and THEMA (FP7-Council Advanced Grant DYNamo (ERC-2010-AdG-Proposal No. 228539)); the CAPES Foundation, and Minis-

Keywords: ab initio calculations · attosecond dynamics · laser spectroscopy · single-molecule studies · time-resolved spectroscopy

[1] In the first pump probe experiment performed by A. Toepfer [P. Krehl, S. Engemann, Shock Waves 1995, 5, 1], already in the 19th century, the probe was in fact used to photograph sound waves initiated by the pump.

[2] The use of two pulses derived from the same spark of light was already in the 19th century, the theoretical framework we have developed is a useful description of pump–probe experiments as a useful quality test.

[3] In the pump–probe experiment performed by A. Toepler [P. Krehl, S. Engemann, Shock Waves 1995, 5, 1], already in the 19th century, the probe was in fact used to photograph sound waves initiated by the pump.

[4] The two use of two pulses derived from the same spark of light was already invented as early as in 1899 (M. M. Abraham, J. Lemoine, Compt. Rend. 1899, 129, 206).


[6] The use of two pulses derived from the same spark of light was already in the 19th century, the theoretical framework we have developed is a useful description of pump–probe experiments as a useful quality test.


[8] The use of two pulses derived from the same spark of light was already in the 19th century, the theoretical framework we have developed is a useful description of pump–probe experiments as a useful quality test.


Received: December 3, 2012
Published online on 2013

These are not the final page numbers!
**Pulse by pulse:** Molecular absorption and photoelectron spectra can be efficiently predicted with real-time time-dependent density functional theory. This simulation tool helps with the interpretation of fast-evolving attosecond time-resolved spectroscopic experiments, in which electronic motion must be followed at its natural timescale (see picture).