Simulating pump-probe photo-electron and absorption spectroscopy on the attosecond time-scale with time-dependent density-functional theory

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Molecular absorption and photo-electron spectra can be efficiently predicted with real-time time-dependent density-functional theory (TDDFT). We show here 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 to interpret the fast evolving attosecond time-resolved spectroscopic experiments, where the electronic motion must be followed at its natural time-scale. 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 a system characterization. As an extension of this approach, time-dependent 2D spectroscopies can also be simulated, in principle, for large-scale structures and extended systems.

I. INTRODUCTION

Pump-probe experiments are the preferred technique to study the dynamical behaviour 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. 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 their relative time delay and shape. In order 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. The electron dynamics has a natural time-scale 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. Nowadays time-resolved spectroscopy can be utilized to monitor electron dynamics in real time, giving birth to the field of attosecond physics.

A wealth of possibilities exists, depending on the frequencies, durations and intensities of the two pulses. A common set-up in attosecond physics employs a XUV attosecond pulse and the relatively more intense NIR or visible longer (few femtoseconds) pulse used for its generation. Combining two XUV attosecond pulses is in principle possible (and has been theoretically analysed), but unfortunately the low outputs of current XUV attosecond pulses lead to much too weak signals. Another choice to make is the final observable, i.e. what kind of system reaction is to be measured as a function of the time delay. In this work we focus on two common choices. One, observing the emission of electrons (their energies, angular distribution, or total yield) from the pumped system due to the probe pulse. This can be called time-resolved photo-electron spectroscopy (TRPES). Two, 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 reaction 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.

TAS, for example, has been successfully employed to watch the first photo-synthetic events in chlorophylls and carotenoids that transform the energy gained by light absorption into molecular rearrangements. A review describing the essentials of this technique can be found in Ref.¹⁴ 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.

In TRPES, the probe pulse generates free electrons.
through photo-ionization, and one measures their energy or angular distribution as a function of time; if this time is in the femtosecond scale one can follow molecular dynamics in the gas phase, as demonstrated already in the mid 1990s[12,13] although this technique had already been employed to follow electronic dynamics on surfaces.[13] 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.[25] 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.[23] where, 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. 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 use of TRPES with attosecond pulses have also been recently reported. For example, Ubiker-acker et al.[23] could observe in real time the light induced electron tunneling provoked by a strong NIR pulse, demonstrating how this electron tunneling can be used to probe short lived electronic states. Smirnova et al.[24] 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. Jonnsson et al.[26] employed attosecond pulse trains and a Helium target, and attosecond photoelectron spectroscopy was also demonstrated to yield useful information for condensed matter systems.[26]

All these advances demand an appropriate theoretical modeling. The use of more than one pulse of light intrinsically requires to go beyond any “linear spectroscopy” technique—although if the pulses are weak a perturbative treatment may still be in order. This non-linear behavior, provides much more information about the system at the cost of a increasingly difficult analysis. The use of two (or more) coherent pulses of light, with fine control over their shape (sometimes called a “multidimensional analysis”), permits a deeper characterization. This fact was already acknowledged in the field of nuclear magnetic resonance, or later in femtochemistry—see for example Refs. [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.[29] presented a study for relatively weak pumping IR pulses in combination with XUV ultrafast probes, for Helium targets and based on the single active electron approximation (SAE). Very recently, the experiment reported by Ott et al.[30] in which the ultrafast TAS of Helium displayed characteristic beyond-SAE features, was theoretically analyzed in Ref. [31] utilizing an exact solution of the time-dependent Schrödinger equation, that 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. [22] which treated the pump IR pulse non-perturbatively.

Indeed, it would be desirable to analyze these processes with a non-perturbative theory (since at least one of the pulses is usually very intense), which at the same time is capable of going beyond the SAE and accounting for many-electron interaction effects. This last fact is relevant since the attosecond time resolution obtained in this type of experiments is able to unveil the fast dynamical 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 multi-electron excitations become comparable to the laser frequencies or the single electron excitations.[33]

Time-dependent density functional theory (TDDFT)[34] in principle meets all requirements: it may be used non-perturbatively, includes the electron-electron interaction and can handle out-of-equilibrium situations. It has been routinely used in the past decades to study the electron dynamics in condensed matter in equilibrium. By this we mean that, usually, one computes the linear or non-linear 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 that is being driven out of equilibrium by an initial pulse. In this work, we will explore the usability of TDDFT for this purpose, and show how, at least for the two cases of TAS and TRPES, the extension is straightforward.

II. THEORY

Density-functional theory[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)[36] scheme, in which one utilizes a fictitious system of non-interacting electrons that has the same ground state density. For excited states, properties, however, or in order to simulate the behavior of the system in time-dependent external fields, one must use its time-dependent version, TDDFT.[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 non-interacting electrons that produces the same time-dependent density. This substitution is the source of the great computational simplification, since a non-interacting system of electrons can in general be represented by a single Slater determinant formed by a set of “Kohn-Sham” orbitals, $\varphi_i (i = 1, \ldots, N/2)$. We will
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 $v(\vec{r}, t)$ (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 will be used hereafter):

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

(1)

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

(2)

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

$$v_{\text{KS}}[n](\vec{r}, t) = v_0(\vec{r}) + v_H[n](\vec{r}, t) + v_{\text{xc}}[n](\vec{r}, t),$$

(3)

where the Hartree potential $v_H$ corresponds to a classical electrostatic term

$$v_H[n](\vec{r}, t) = \int d^3 \vec{r}' \frac{n(\vec{r}', t)}{|\vec{r} - \vec{r}'|},$$

(4)

$v_0(\vec{r})$ 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.

The TDKS equations can be utilized, either directly or in 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 $\{\text{hyper-}\}$-polarizabilities, optical and magnetic susceptibilities, \ldots, since (i) these objects then permit to predict any reaction in the appropriate order, and (ii) experiments typically provide spectra that are directly related to the response functions – e.g. 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, etc. This can be performed by linearizing the TDKS equations in the frequency domain and casting the result into matrix-eigenvalue form, or by propagating the same equations in real time 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 that are 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 will be treated in Section II A.

Likewise, TDDFT can be used to compute strong field non-linear photo-electron spectra of atoms and molecules, for example with the method recently developed by some of us. These spectra, however, are also characteristic of the ground state, although, as it will be shown in Section II B the methodology can be easily extended to tackle the pump-probe case (time-resolved photoelectron spectroscopy).

A. Attosecond transient absorption spectroscopy

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 being the partial absorption of it. In a dilute gas, assuming the electric dipole approximation and a sufficiently weak pulse, the dipole-dipole linear dynamical 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 so that they all can be considered to be at their ground state), and the only light pulse present is that whose absorption we want to measure.

In the pump-probe situation discussed here, 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 being the excess of polarization, responsible for the absorption of the probe. We will assume, as it 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 the one given in the appendix of Ref. and also discussed in detail in Ref. We will review here 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):

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

(5)

where $\hat{H}$ 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, that contains only the pump pulse; the full Hamiltonian results of the addition of the probe pulse $f(t)\hat{V}$:

$$\hat{H}(t) = \hat{H} + \mathcal{E}(t)\hat{V} + f(t)\hat{V}.$$ (6)
The evolution of the system is given by:

$$i \frac{\partial}{\partial t} \hat{\rho}(t) = \left[ \hat{H}(t), \hat{\rho}(t) \right], \quad (7)$$

and initially \((t = t_0, \) some time before the arrival of both pump or probe), the system is at equilibrium:

$$\left[ \hat{H}, \hat{\rho}_{eq} \right] = 0. \quad (8)$$

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

$$\hat{\rho}[f] = \sum_{n=0}^{\infty} \hat{\rho}_n[f], \quad (9)$$

where \(\hat{\rho}_0\) is the unperturbed system evolution (i.e. the evolution of the system in the presence of the pump only: \(f = 0\)), and \(\hat{\rho}_n\) is \(n\)-th order in the perturbation: \(\hat{\rho}[\lambda f] = \lambda^n \hat{\rho}[f]\). The system response to this perturbation is measured in terms of the expectation value of an observable \(A\), which can likewise be expanded:

$$A(t) = \text{Tr} \left[ \hat{\rho}(t) \hat{A} \right] = \sum_{n=0}^{\infty} A_n(t), \quad (10)$$

where

$$A_n(t) = \text{Tr} \left[ \hat{\rho}_n(t) \hat{A} \right]. \quad (11)$$

For sufficiently weak probes, we are only interested in the first term:

$$\delta A(t) = A(t) - A_0(t) \approx A_1(t) = \text{Tr} \left[ \hat{\rho}_1(t) \hat{A} \right], \quad (12)$$

which is linearly related to \(f\) through a pump-dependent response function:

$$A_1(t) = \int_{-\infty}^{\infty} dt' f(t') \chi_{\hat{A},\hat{V}}[\mathcal{E}](t, t'). \quad (13)$$

The response function is given by:

$$\chi_{\hat{A},\hat{V}}[\mathcal{E}](t, t') = i \theta(t-t') \text{Tr} \left\{ \hat{\rho}_{eq} \left[ \hat{A}_{H}[\mathcal{E}](t), \hat{V}_{H}[\mathcal{E}](t') \right] \right\} \quad (14)$$

Inside the commutator, the operators appear in the Heisenberg representation:

$$\hat{O}_H[\mathcal{E}](t) = \hat{U}[\mathcal{E}](t_0, t) \hat{O} \hat{U}^*[\mathcal{E}](t, t_0), \quad (15)$$

where \(\hat{U}[\mathcal{E}]\) is the time propagation operator in the presence of the pump only—hence the functional dependence on \(\mathcal{E}\). We keep this functional dependence explicit in the notation for \(\chi_{\hat{A},\hat{V}}[\mathcal{E}](t, t')\), to stress that it is a property of both the system (defined by the static Hamiltonian \(\hat{H}\)) and of the pump shape \(\mathcal{E}\), 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 only one by making use of time-translation invariance, as it is customary when working at equilibrium.

The response itself, \(\delta A(t)\), will be a functional of both pump and probe pulses. If we take its Fourier transform we may write it as:

$$\delta A[\mathcal{E}, f](\omega) = \int_{-\infty}^{\infty} dt' f(t') \chi_{\hat{A},\hat{V}}[\mathcal{E}](\omega, t'). \quad (16)$$

In order to compute the response function, one can use as a probe a delta perturbation, i.e. \(f(t') = \lambda \delta(t' - \tau)\), which permits to identify:

$$\chi_{\hat{A},\hat{V}}[\mathcal{E}](\omega, \tau) = \frac{1}{\lambda} \delta A[\mathcal{E}, \lambda \delta_{\tau}](\omega). \quad (17)$$

The action of such a delta-perturbation applied at the instant \(\tau\) on the system is given by:

$$|\Phi(t \to \tau^+)\rangle = e^{-i\lambda V} |\Phi(\tau)\rangle. \quad (18)$$

From now on we will restrict the discussion to pure states, since ensembles are not needed for the results that will be shown below. However it can easily be extended to general ensembles. We also restrict the discussion to a specific response function: the dipole-dipole polarizability \(\alpha[\mathcal{E}](t, t') = \chi_{\hat{D},\hat{D}}[\mathcal{E}](t, t')\), where both \(\hat{A}\) and \(\hat{V}\) are the atomic or molecular dipole operator \(\hat{D}\)—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:

$$\hat{D} = -\sum_{i=1}^{N} \hat{x}_i, \quad (19)$$

where \(N\) 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:

$$\delta D[\mathcal{E}, f](\omega) = -\int d^3r \: \delta n(\vec{r}, \omega) x, \quad (20)$$

where \(\delta n(\vec{r}, \omega)\) is the Fourier-transformed difference between the electronic densities obtained with and without the probe pulse. This straightforward formula in terms of the density is what makes TDDFT specially suited for these computations: we may safely utilize the Kohn-Sham system of non-interacting electrons. The delta perturbation, Eq. [18], must be applied to each one of the Kohn-Sham orbitals, and takes the following form:

$$\varphi(\vec{r}, t \to \tau^+) = e^{i \lambda x} \varphi_1(\vec{r}, \tau). \quad (21)$$

The absorption of a particular probe pulse \(f\), is determined by the induced polarization, given by \(\delta D[\mathcal{E}, f](\omega)\).
We will compute the dynamical polarizability \( \alpha[\mathcal{E}](\omega, \tau) \), which is the polarization induced by a delta perturbation, i.e.:

\[
\alpha[\mathcal{E}](\omega, \tau) = \frac{1}{\lambda} \delta D[\mathcal{E}, \lambda\delta_r](\omega),
\]

since it allows to compute any particular response through the integration of Eq. (16), as long as the probe is weak. In particular, we will look at the imaginary part of \( \alpha[\mathcal{E}](\omega, \tau) \), 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, an averaged quantity that corresponds to the absorption of a randomly oriented sample of molecules.

**B. Time-resolved photoelectron spectroscopy**

The photoelectron spectra presented in this work are produced within TDDFT using the recently introduced Mask Method. This method is based on a geometrical partitioning and a mixed real- and momentum-space time evolution scheme. In the following, we summarize the main traits of the technique (we refer the reader to Ref. [40] for a complete description), and demonstrate how it can be straightforwardly applied to the non-equilibrium 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 to measure 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 describing properly 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 wave function can be described analytically.

In order to take advantage of the previous observations we partition the space according to the scheme in Fig. 1 (a): 

\[
\varphi^A(r) = M(r)\varphi_i(r),
\]

\[
\varphi^B(p) = (1 - M(r))\varphi_i(r).
\]

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

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

\[
\begin{align*}
\varphi^A_r(t + \Delta t) &= M(r)e^{-iH\Delta t}\varphi^A_r(t) \\
\tilde{\varphi}^B_p(t + \Delta t) &= e^{-i(p - A\xi_0)^2\Delta t}\tilde{\varphi}^B_p(t) + \tilde{\varphi}^A_r(t + \Delta t)
\end{align*}
\]

(b). The space is divided into two regions, \( A \) and \( B \); the inner region \( A \) containing the system with enough empty space around, 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 non-interacting and freely propagating. Every KS orbital \( \varphi_i(r) \) can be decomposed accordingly with \( \varphi_i(r) = \varphi^A_i(r) + \varphi^B_i(r) \), so that \( \varphi^A_i(r) \) resides mainly in region \( A \) and \( \varphi^B_i(r) \) 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 (see Fig. 1 (a)):

\[
\varphi^A(r) = M(r)\varphi_i(r),
\]

\[
\varphi^B(r) = (1 - M(r))\varphi_i(r).
\]

The solution of the Schrödinger equation numerically in the whole space if a considerable part of the wave function can be described analytically.
with \( \hat{H} \) being the effective single-particle TDDFT Hamiltonian, \( \mathbf{A}(t) \) the total external time dependent vector potential (the coupling with the external field is conveniently expressed in the velocity gauge), and

\[
\tilde{\varphi}_i^A(p, t+\Delta t) = \frac{1}{(2\pi)^{3/2}} \int dr (1-M(r)) e^{-i\hat{H}\Delta t} \varphi_i^A(r, t) e^{ip \cdot r},
\]

constituting the portion of electrons leaving the system at time \( t + \Delta t \). At each iteration in the evolution the outgoing components of \( \varphi_i^A(r) \) are suppressed in the interaction region by the multiplication with \( M(r) \) while being collected as plane waves in \( \tilde{\varphi}_i^B(p) \) via \( \varphi_i^A(p) \). The resulting momentum space wavefunctions are then evolved analytically simply by a 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 extending to infinity) as free-electrons in momentum space. Moreover the mask function introduces a region \( C \), where the wavefunctions in \( A \) and \( B \) overlap (see Fig. 1) and that acts as matching layer. In spite of the fact that, from a theoretical point of view, the matching between inner and outer region could be performed on a single surface, from a numerical point of view, having a whole region to perform the 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

\[
P(p) \approx \lim_{t \to \infty} \sum_{i=1}^{\text{occ}} |\tilde{\varphi}_i^B(p, t)|^2,
\]

the limit \( t \to \infty \) ensuring that all the ionized components are collected. This scheme is entirely non-perturbative; in a pump-probe setup, it does not assume linearity in either pump or probe. Therefore, it can be applied in the same manner when two pulses are present than with one pulse only, as it was shown in Ref. [40]. Like in Sec. II A 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 performing numerical simulations with two time delayed external pulses. A TRPES map is then generated by performing a computation for each different time delay.

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

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

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 Eq. (25) the part of the density contained in \( A \) transferred to \( B \) is not allowed to return. Clearly, in cases where 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 [47]. The laser fields employed in this work are weak enough that we can safely assume region \( A \) to always be sufficiently large to contain all the relevant electron trajectories.

### III. RESULTS

The theory described in the previous section has been implemented in the octopus code [44]; we refer the reader to Refs. [15] and [46] for the essential points of the numerical methodology.

In order to simplify the illustration of the results a clamped ion approximation has been used in the calculations for the molecular case. Further inclusion of the ionic motion could be done at the semi-classical level with Ehrenfest dynamics [45,47] – already implemented in the code – and without any essential modification to the theory presented.

#### A. One-dimensional model Helium

As first example we study the absorption spectrum of an excited one-dimensional soft-Coulomb Helium atom. This is an exactly solvable model that provides a useful benchmark to test different approximations. We will first discuss the exact solution, and later apply TDDFT. A more realistic 3D model will be presented in the next section.

The 1D model of the Helium atom is defined by the following Hamiltonian:

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

where

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

is the external potential: the electron Coulomb interaction \( 1/|x| \) is softened to \( 1/\sqrt{1+x^2} \). The coupling with the external time-dependent field \( \mathcal{E}(t) \) is expressed in length gauge, and electrons are confined to move along the \( x \) direction only. Finally,

\[
T = -\frac{1}{2} \left( \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} \right)
\]
is the kinetic energy, and the electron-electron interaction is

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

(32)

This model is numerically solvable given the exact mapping discussed in Refs. 48 and 49 where 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 wave functions and other necessary functions are represented on a real space regular grid; a squared (linear for one-dimensional TDDFT) box of size \( L = 200 \) a.u. and spacing \( \Delta x = 0.2 \) a.u. has been employed in all the calculations.

In order to illustrate how an external field can modify the optical properties of a system in Fig. 2 we show a scan of the non-equilibrium 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. Maximal response is observed for frequencies close to the first optical transition \( \omega_p = 0.533 \) a.u.

In order to analyze this point further, a cut at the resonant frequency is displayed in the lower (blue) curves of Fig. 3. The filled curve represents the spectrum obtained from the system in its ground state while the solid line corresponds to the spectra of the system excited by a laser as in Fig. 2 resonant with the first allowed optical transition: exact time-dependent Schrödinger equation \( \omega_p = 0.533 \) a.u. (in blue), EXX \( \omega_p = 0.549 \) a.u. (in red), and LDA \( \omega_p = 0.475 \) a.u. (in green). The dashed blue line is the absorption of the system perturbed by a 180 cycle laser and probed at \( t = 30.62 \) fs, where the population on the excited state is maximal. The lines have been shifted by a vertical constant to facilitate the comparison between results.
polarizabilities, which may be written in the sum-over-states form as:

$$\alpha^{(i)}(\omega) = \sum_{j \neq i} \left[ \frac{|\langle \Psi_i | \hat{D} | \Psi_j \rangle|^2}{\omega - (\epsilon_j - \epsilon_i) + i0^+} - \frac{|\langle \Psi_i | \hat{D} | \Psi_j \rangle|^2}{\omega + (\epsilon_j - \epsilon_i) + i0^+} \right]. \quad (33)$$

The poles of this function provide us with the eigenvalue differences $\epsilon_j - \epsilon_i$; 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 associated with each one of these poles provide us with the dipole coupling matrix elements $\langle \Psi_i | \hat{D} | \Psi_j \rangle$.

During the time evolution, the wavefunction can be expanded on the basis of eigenstates of the unperturbed system $\Psi(t) = \sum_j \eta_j(t) \Psi_j$. When the system is probed at a certain time $t$, the resulting spectrum can be thought as a linear combination of the spectra produced by each single eigenstate. An 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 – information that is absent in equilibrium ground-state linear response.

In our case, we find by direct projection of the time-dependent wave function onto the eigenstates, that the system after the pulse is composed mainly of the ground and the 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 the unperturbed spectrum at $E_{0 \rightarrow 1}$. At this energy we only have the contribution coming 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 $h_t$ is therefore a combination of the heights associated with the ground $h_0$ and the excited $h_1$ states: $h_t = |\eta_0|^2 h_0 + |\eta_1|^2 h_1$. At this energy $h_0 = -h_1$ due to the nature of the transition $1 \rightarrow 0$ the ratio $\alpha = h_1/h_0 = |\eta_0|^2/|\eta_1|^2 = 0.4258$ thus gives direct information on the difference of the mixing weights. Complementing this information with a two-level system assumption $|\eta_0|^2 + |\eta_1|^2 = 1$ we obtain $|\eta_0|^2 = (1 + \alpha)/2 = 0.7129$ and $|\eta_1|^2 = (1 - \alpha)/2 = 0.2871$ in good agreement with the results calculated by direct projection of the wavefunction.

In Fig. 4 we display the population weights for two different laser pulses. The red lines correspond to the same laser pulse as in Fig. 3 while the blue lines pertain to a four times longer laser 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 state at each time almost sum to one, indicating an 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 $\Omega(t) = f(t)\mu_{0 \rightarrow 1}$, where $\mu_{0 \rightarrow 1}$ is the dipole transition matrix element between the states and $f(t)$ is the electric field envelope. Extremal points of the populations should be located at times where the pulse area $\Theta(t) = \int_{-\infty}^{t} d\tau f(t)\mu_{0 \rightarrow 1}$ is an integer multiple of $\pi$, $\Theta(t) = n\pi$. With the numerically calculated matrix element $\mu_{0 \rightarrow 1} = 1.11$ a.u. the first maximal population of the excited state is expected at $t = 30.65$ fs, in good agreement with what is observed. The absorption spectrum at this time, as shown in Fig. 3 (dashed blue line), displays a considerable enhancement at $\omega_{1 \rightarrow 2}$ and a negative emission peak at $\omega_{0 \rightarrow 1}$ as expected from a pure excited state.

It is interesting to study the same model with TDDFT instead of with an exact treatment in order to address the performance of available (mainly static) xc-functionals. In Fig. 5 we display results obtained with TDDFT, employing two different exchange-correlation (xc) functional approximations: exact exchange (EXX) in red, and one-dimensional local density approximation (LDA) in green. The calculations were performed in the adiabatic approximation using the same parameters as in the exact case. The laser frequency was tuned to match the first optical transition appearing at: $\omega_P = 0.549$ a.u. for EXX, and $\omega_P = 0.475$ a.u. for LDA.

The unperturbed spectrum (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 both for the perturbed and unperturbed cases. This is due to the known problem of asymptotic exponential decay of the functional that in this one-dimensional 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. 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 Eq. 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 Fig. 5.

B. Helium atom in 3D

In this section we study the real Helium atom. We employed the EXX functional and discretized TDDFT equations 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 begin 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 Fig. 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 Sec. III A for the one-dimensional 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 $\omega_{2p\rightarrow 3s} = 0.079$ 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 obtain the small artifacts, such as the energy shifts and the 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. In Fig. 6 the time resolved absorption spectrum (TAS) map is displayed. The map was produced by probing the system at different time delays. As the delay is increased we observe the build-up of the peak associated with the state being pumped by the laser pulse at $\omega_{2p\rightarrow 3s}$. This 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 wave function 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 the $1s2p \rightarrow 1s3s$ and therefore its height is proportional to the $2p$ excited state population. The oscillation can then be interpreted in terms of Rabi physics as discussed in Sec. III A.
Further insight can be achieved investigating the photoemission properties of the system. In Fig. 7 we show the TRPES map, as calculated in a pump-probe set up. Photoelectrons are calculated with the technique outlined in Sec. III B. The pump pulse is the same as the one employed for TAS. The probe is a 40 cycles trapezoidal laser pulse (8 cycles ramp) with carrier frequency \( \omega_p = 1.8 \) a.u., intensity \( I = 5.4 \times 10^9 \) W/cm\(^2\), polarized along the \( x \)-axis and is weak enough to discard non-linear effects. We performed a scan for different time delays, measuring each delay as the difference from the up-time of the probe pulse. Negative delays correspond to the situation where the probe precedes the pump. Moreover, in order to include all the relevant trajectories a spherical box of \( R = 30 \) a.u. was employed, and photoelectrons were recorded only during the up-time of the probe pulse.

The TRPES map in Fig. 7 shows three main features at \( E_1 = 0.66 \) a.u., \( E_2 = 0.88 \) a.u. and \( E_3 = 1.67 \) 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 \( E = \omega_p - I_P \), where \( \omega_p \) is the probe carrier frequency and \( I_P \) 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) \( I_P = \varepsilon_{2s} = 0.92 \) a.u. Thus the peak appearing at \( E_2 \) is energetically compatible with photoelectrons emitted from the 2s level: \( E_2 = \omega_p - I_P \). Consistently, this peak is the only one appearing at negative delays where the pulses do not overlap. Moreover, the peak strength is weakly varying with the delay while slightly shifting towards lower values 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 \( E_3 = \omega_p + \omega_p - I_P \). It is a process where 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: \( E_3 = 2\omega_p - I_P \). The ionization mechanism shares the first step with the \( E_3 \) process, namely a \( 2s \rightarrow 2p \) 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. 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. In order to support the energetic arguments, PADS \( P(\theta, \phi, E) \) at \( \tau = 8.99 \) fs are presented in Fig. 8 (a), (b), (d) together with cuts on TRPES map at \( \tau = 0 \) fs and \( \tau = 8.99 \) fs (b). For each energy marked in Fig. 8 (c) we perform spherical cuts of the photoemission probability on energy shells at \( E = E_1, E_2, E_3 \). Each cut is then plotted in polar coordinates with \( \theta \) being the angle from the \( z \)-axis and \( \phi \) the angle in the \( xy \)-plane measured from the \( x \)-axis. Intersection of the lasers polarization axis with the sphere are marked with a white cross.

Fig 8 shows clearly that photoelectrons at \( E_1 \) (a) and...
$E_3$ (d) have similar nature compared to $E_2$ (b), in agreement with the energy analysis. Electrons emerging with a kinetic energy of $E_2$ are emitted from a $2s$ state, and symmetry of the orbital is imprinted in the photoelectrons angular distribution. In order 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 directions parallel with the polarization and minimal along the perpendicular plane and, if non-linear effects can be discarded, it induces a geometrical factor of the form $|\mathbf{A} \cdot \mathbf{p}|$ where $\mathbf{A}$ is the polarization direction and $\mathbf{p}$ the electron momentum. For this reason electron emitted along $\phi = 90^\circ$, and $270^\circ$ are strongly suppressed, and panel (b) is compatible with the spherical symmetry of a 2s state.

In panel (a) 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 narrower compared with the 2s emission in panel (b) consistently with ionization from a $p_z$ orbital. Of the three degenerate $p$ orbitals the $p_x$ is the one producing the strongest response. Signatures of $p_y$ and $p_z$ response can be identified in the non vanishing PAD on the $yz$-plane around $\phi = 90^\circ, 270^\circ$. Such perpendicular response indicates a degree of non-linearity induced by the pump. Similar considerations hold for panel (b) where the $p$ state excited by the pump is probed with $\omega_p$. As before the emission is mainly from a $p_x$ state.

C. Ethylene molecule

In this section we extend our calculations to the treatment of the Ethylene molecule (C$_2$H$_4$) and show how these techniques permit to study the time-dependence of molecular electronic states. In particular we report on the clear observation of a strong $\pi \rightarrow \pi^*$ transition.

In order to have a good description of states close to the ionization threshold we employed the asymptotically correct LB94 xc-functional in the adiabatic approximation. We choose the molecular plane to be in the $xy$-plane with carbon atoms at coordinates $(\pm 1.26517, 0, 0)$ a.u. and hydrogens at $(\pm 2.33230, 1.75518, 0)$ a.u., $(\pm 2.33230, -1.75518, 0)$ a.u.. The ion positions are held fixed during the time evolution. Norm-conserving Trouiller-Martin pseudopotentials are employed to describe core electrons of Carbon. Moreover TDDFT equations are numerically integrated on a spherical grid with spacing $\Delta r = 0.3$ a.u., radius $R = 16$ a.u. and 2 a.u. wide absorbing boundaries.

We perturb the system with a 15 cycles (3 cycles ramp) trapezoidal laser pulse having carrier frequency $\omega_p = 0.297$ a.u. and intensity $I = 1.38 \times 10^{11}$ W/cm$^2$ polarized in the $x$-axis. The laser frequency and the polarization direction are suited to excite mainly the molecular $\pi \rightarrow \pi^*$ transition. The absorption spectrum of the excited molecule probed after the pulse Fig. 9 shows the emergence of a peak associated with a population of the $\pi^*$ state. Optical transitions from this excited state to high lying bound states occur at energies lower than the HOMO-LUMO gap as illustrated by the scheme in Fig. 9. Effects of the lack of memory in our xc-potential can be observed in the shifts of the peaks with respect to the known excitations of the unperturbed system. The characteristic excitations of a many-body system should not depend on the perturbation, unless we are in a strong light-matter coupling regime.

The build up of the transient spectrum as a function of time is shown in Fig. 10. In comparison with the case of He discussed in Sec. III B the TAS map does not display any maxima during the pump time lapse due to the env-
loped area not crossing $\pi$ by the end of the pulse. A pulse with larger area would reveal the first Rabi oscillation.

The TRPES map is presented in Fig. 11. Calculations were performed in a box of radius $R = 30$ a.u. and the probe pulse is equal to the one used for the Helium atom in Sec. III B, namely a 40 cycles (8 cycles ramp) trapezoidal pump at $\omega_p = 1.8$ a.u. and $I = 5.4 \times 10^9$ W/cm$^2$, but polarized along the $z$-axis. The choice of the polarization direction is important since, as we shall show, the spectra may reveal geometrical features that depend on it.

The TRPES displays a behavior similar to the one discussed in Sec. III B. A set of constant crests can be observed in the energy range from 0.8 a.u. to 1.5 a.u. These are the peaks associated with electrons residing in the ground-state and ejected by the probe pulse. In particular the peak at $E_2 = 1.37$ a.u. corresponds to emission from the HOMO $E_2 = \omega_p - \epsilon_x$, with $\epsilon_x = 0.43$ a.u. The $\pi$ orbital is localized on the Carbon atoms with two density lobes lying in the $xz$-plane and nodes in the $xy$-plane (refer to Fig. 12 (a) for geometrical visualization). A probe laser orientation along $y$ should suppress electrons on $xy$-plane perpendicular to its polarization and therefore PAD $P(\theta, \phi, E_2)$ in Fig. 12 (c) for $\theta = 0^\circ$ is diminished also due to geometrical reasons. Signature of a $\pi$ symmetry can be clearly observed in the oscillations with $\phi$ presenting maxima at $\phi = 90^\circ$, and $270^\circ$ along the plane perpendicular to $x$ that indicates a concentration along the $C - C$ bond axis, and minima for $\phi = 0^\circ$, $360^\circ$ consistent with a depletion in direction of each carbon atom.

Separated by a probe photon $\omega_p$ at $E_3 = \omega_p + \omega_p - \epsilon_x = 1.67$ a.u. we find photoelectrons ejected from the $\pi^*$ state. The intensity of the peak steadily increases in time accordingly 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 sensible to this kind of geometry. The PAD $P(\theta, \phi, E_3)$ in Fig. 12 (e) displays strong suppression of electrons along the $yz$-plane at $\phi = 90^\circ$, $270^\circ$ and therefore presents a clear manifestation of photoemission from a $\pi^*$ state.

Slow electrons ejected at $E_1 = 2\omega_p - \epsilon_p = 0.16$ a.u. gradually increase and become the predominant ionization channel. The emergence in time of multi-photon peaks separated by $\omega_p$ indicates that the pump is strong enough to trigger non-linear 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 carry again 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, the laser polar-

FIG. 11. Logarithmic scale TRPES for C$_2$H$_4$. The molecule is probed at different delays with is a 40 cycles trapezoidal laser pulse with 8 cycles ramp, $\omega_p = 1.8$ a.u., $I = 5.4 \times 10^9$ W/cm$^2$ polarized along the $z$-axis perpendicular with the pump. Pump laser (upper panel) is the same as in Fig. 10.

FIG. 12. Angular- and energy-resolved photoelectron spectra for C$_2$H$_4$ at two fixed delay times. Panel (a) geometry of the process: $p$ indicates photoelectron direction, $A$ is the pump polarization vector, and $A_p$ the probe one. Panel (d), logarithmic scale PES $P(E)$ for $\tau = -1.69$ fs (red) and $\tau = 3.63$ fs (green). Other panels depict normalized PADS $P(\theta, \phi, E)$ at $\tau = 3.63$ fs and energies marked in (d): (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), (e) (at the corners) and the pump one in (b) on the sphere.
ization carries a geometrical factor of the form $\mathbf{A} \cdot \mathbf{p}$ with $\mathbf{A} = \mathbf{A}(\phi)$, that introduces a suppression along the $yz$-plane ($\phi = 90^\circ, 270^\circ$). Unfortunately, this plane is precisely where the $\pi^*$ photoemission minima should lay. For this reason PAD $P(\theta, \phi, E_3)$ in Fig. 12(b) is not suited to clearly discern a $\pi$ from a $\pi^*$ symmetry, and the suppression for $\theta = 0^\circ$ along the $xy$-plane is compatible with both structures.

IV. CONCLUSIONS

In this work we studied the problem of describing ultrafast (attosecond scale) time-resolved absorption and photoemission in finite systems with TDDFT. We presented the theory and discussed how it can be implemented, such that TDDFT can 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: one-dimensional Helium model, three-dimensional Helium atom, and Ethylene molecule.

We studied the one-dimensional Helium atom perturbed by an external time dependent field exactly, by solving TDSE. We showed how it is possible to recover information about state populations through a comparison of the perturbed and unperturbed absorption cross-sections, and that the population evolution in time can 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 are in good agreement with the exact solution, although small artifacts appear due to the wrong description of the functional memory dependence.

Furthermore we investigated the Helium atom in a more realistic three-dimensional treatment using the EXX functional. We performed resonant pump-probe calculations monitoring both absorption and photoemission properties of the excited atom. TAS turned out to be a sensible tool to monitor the build-up of the excited state, allowing to observe Rabi oscillations as a function of the time delay between pump and probe. TRPES also allowed the characterization of the excitation process in time. However, due to a dominant ionization channel associated with sequential two (pump) photons absorption, the information about the excited state population was less apparent. Nonetheless PAD, being an observable 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 of $\pi$ and $\pi^*$ nature.

The theoretical framework that we have developed is a useful tool to understand and control non-equilibrium electronic dynamical 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 non-adiabatic exchange and correlation functionals able to provide a reliable description of non-equilibrium processes and strong-light-matter interaction. Clearly, the methods presented here 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.

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

2The use of two pulses derived from the same spark of light was already invented as early as in 1899 [M. M. Abraham and J. Lemoine, Compte Rendus 129, 206 (1899)].

3M. Hentschel, R. Kienberger, C. Spielmann, G. A. Reider, N. Miklosevic, T. Brabec, P. Corkum, U. Heinzmann, M. Drescher, and F. Krausz, Nature 414, 509 (2001).

4R. Kienberger, E. Goulielmakis, M. Uberacker, A. Baltuska, V. Yakovlev, F. Bammer, A. Scrinzi, T. Westerwalbesloh, U. Kleineberg, U. Heinze, et al., Nature 427, 817 (2004).

5F. Krausz and M. Ivanov, Rev. Mod. Phys. 81, 163 (2009).

6A. Scrinzi, M. Y. Ivanov, R. Kienberger, and D. M. Villeneuve, Journal of Physics B: Atomic, Molecular and Optical Physics 39, R1 (2006).

7J. C. Baggesen, E. Lindroth, and L. B. Madsen, Phys. Rev. A 85, 013415 (2012).

8A. Zewail, J. Phys. Chem. A 104, 5660 (2000).

9R. Berera, R. van Grondelle, and J. T. M. Kennis, Photosynth. Res. 101, 101 (2009).

10F. Foggi, L. Bussotti, and F. V. R. Neuwahl, International Journal of Photoenergy pp. 103–109 (2001).

11Z.-H. Loh, M. Khalil, R. Correa, R. Santra, C. Buth, and S. Leone, Physical Review Letters 98, 143601 (2007).

12T. Baumert, R. Thalweiser, and G. Gerber, Chemical Physics Letters 209, 29 (1993).
13A. Assion, M. Geisler, J. Helbing, V. Seyfried, and T. Baumert, Phys. Rev. A 54, R4605 (1996).
14H. Haight, J. Bokor, J. Stark, R. H. Storz, R. R. Freeman, and P. H. Bucksbaum, Phys. Rev. Lett. 54, 1302 (1985).
15A. Stolow, International Reviews in Physical Chemistry 22, 377 (2003).
16A. Stolow, A. E. Bragg, and D. M. Neumark, Chemical Reviews 104, 1719 (2004).
17M. Bauer, Journal of Physics D: Applied Physics 38, R253 (2005).
18T. Suzuki, Annual Review of Physical Chemistry 57, 555 (2006).
19G. Wu, P. Hockett, and A. Stolow, Phys. Chem. Chem. Phys. 13, 18447 (2011).
20T. Pfeifer, M. J. Abel, P. M. Nagel, A. Jullien, Z.-H. Loh, M. J. Bell, D. M. Neumark, and S. R. Leone, Chemical Physics Letters 463, 11 (2008).
21M. Holler, F. Schapper, L. Gallmann, and U. Keller, Phys. Rev. Lett. 106, 123601 (2011).
22E. Goulielmakis, Z.-H. Loh, A. Wirth, R. Santra, N. Rohringer, V. S. Yakovlev, S. Zherebtsov, T. Pfeifer, A. M. Azzeer, M. F. Kling, et al., Nature 466, 739 (2010).
23M. Uiberacker, T. Uphues, M. Schultz, A. J. Verhoef, V. Yakovlev, M. F. Kling, J. Rauschenberger, N. M. Kabachnik, H. Schroder, M. Lezius, et al., Nature 446, 627 (2007).
24O. Smirnova, M. Spanner, and M. Y. Ivanov, Journal of Physics B: Atomic, Molecular and Optical Physics 39, S323 (2006).
25P. Johnsson, J. Mauritsson, T. Remetter, A. L’Huillier, and K. J. Schafer, Phys. Rev. Lett. 99, 233001 (2007).
26A. L. Cavalieri, N. Muller, T. Uphues, V. S. Yakovlev, A. Baltuska, B. Horvath, B. Schmidt, L. Blumel, R. Holzwarth, S. Hendel, et al., Nature 449, 1029 (2007).
27S. Mukamel and D. Abramavicius, Chemical Reviews 104, 2073 (2004).
28W. Pollard, S. Lee, and R. Mathies, The Journal of chemical physics 92, 4012 (1990).
29M. B. Gaarde, C. Buth, J. L. Tate, and K. J. Schafer, Phys. Rev. A 83, 013419 (2011).
30C. Ott, A. Kaldun, P. Raith, K. Meyer, M. Laux, Y. Zhang, S. Hagstotz, T. Ding, R. Heck, and T. Pfeifer, arXiv:1205.0519v1.
31L. Argenti, C. Ott, T. Pfeifer, and F. Martin, arXiv:1211.2566v1.
32R. Santra, V. S. Yakovlev, T. Pfeifer, and Z.-H. Loh, Phys. Rev. A 83, 033405 (2011).
33M. Lezius, V. Blanchet, D. M. Rayner, D. M. Villeneuve, A. Stolow, and M. Y. Ivanov, Phys. Rev. Lett. 86, 51 (2001).
34M. A. L. Marques, N. T. Maitra, F. M. S. Nogueira, E. K. U. Gross, and A. Rubio, eds., Fundamentals of Time-Dependent Density Functional Theory, vol. 837 of Lecture Notes in Physics (Springer, Berlin Heidelberg, 2012).
35W. Kohn, Rev. Mod. Phys. 71, 1253 (1999).
36W. Kohn and L. J. Sham, Physical Review 140, 1133 (1965).
37E. Runge and E. Gross, Physical Review Letters 52, 997 (1984).
38R. Baer, L. Kronik, and S. Kimmel, eds., Open problems and new solutions in time dependent density functional theory, vol. 391 of Chemical Physics (Elsevier, 2011).
39M. A. Marques, M. J. Oliveira, and T. Burnas, Computer Physics Communications 183, 2272 (2012).
40U. De Giovannini, D.Varsano, M. A. L. Marques, H. Appel, E. K. U. Gross, and A. Rubio, Physical Review A 85, 062515 (2012).
41A. Castro and I. V. Tokatly, Phys. Rev. A 84, 033410 (2011).
42S. Mukamel, Principles of Nonlinear Optical Spectroscopy (Oxford University Press, USA, 1999).
43S. Chelkowski, C. Foisy, and A. Bandrauk, Physical Review A 57, 1176 (1998).
44The code can be freely downloaded from [http://www.tddft.org/programs/octopus](http://www.tddft.org/programs/octopus).
45M. A. Marques, A. Castro, G. F. Bertsch, and A. Rubio, Computer Physics Communications 151, 60 (2003).
46A. Castro, H. Appel, M. Oliveira, C. A. Rozzi, X. Andrade, P. Lorenzen, M. A. L. Marques, E. K. U. Gross, and A. Rubio, physica status solidi (b) 243, 2465 (2006).
47J. Alonso, X. Andrade, P. Echenique, F. Falceto, D. Prada-Gracia, and A. Rubio, Physical Review Letters 101, 096403 (2008).
48N. Helbig, J. I. Fuks, I. V. Tokatly, H. Appel, E. K. U. Gross, and A. Rubio, Chemical Physics 391, 1 (2011).
49N. Helbig, J. Fuks, M. Casula, M. Verstraete, M. Marques, I. Tokatly, and A. Rubio, Physical Review A 83, 032503 (2011).
50L. Allen and J. H. Eberly, Optical Resonance and Two-level Atoms (Wiley, 1975).
51S. Kimmel and J. Perdew, Physical Review B 68 (2003).
52M. Casula, S. Sorella, and G. Senatore, Physical Review B 74, 245427 (2006).
53J. Fuks, N. Helbig, I. Tokatly, and A. Rubio, Physical Review B 84, 075107 (2011).
54O. Fojo´n, A. Palacios, J. Fern´andez, R. Rivarola, and F. Martín, Physics Letters A 350, 371 (2006).
55P. Puschnig, S. Berkebile, A. J. Fleming, G. Koller, K. Emteev, T. Seyller, J. D. Riley, C. Ambrosch-Draxl, F. P. Netzer, and M. G. Ramsey, Science 326, 702 (2009).
56R. van Leeuwen and E. J. Baerends, Physical Review A 49, 2421 (1994).