Pump-probe photoemission simulated in real time: Revealing many-particle signatures

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We simulate the photoemission from an electronically excited system by computing the escape of electron density in real space using time-dependent density functional theory in real time. We show that for a oneelectron system, the angular resolved photoemission after an initial excitation can be interpreted as the mapping of a previously unoccupied orbital. For the molecule perylene-3,4,9,10-tetracarboxylic dianhydride, the angular resolved photoemission (ARPES) calculated after a preceding pump pulse reveals signatures of the many-particle character of the first electronic excitation: The photoemission results from more than one time-dependent orbital, and comparing the ARPES pattern to a particle-hole analysis of the first electronic excitation confirms that the excitation does not just correspond to one electron having been moved into a previously empty orbital, but is a superposition of several single-particle excitations.

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I. INTRODUCTION: PROBING ELECTRONIC STRUCTURE BY PHOTOEMISSION

Photoemission spectroscopy is one of the important techniques for obtaining insight into the electronic structure of condensed matter. For the simplest case of an atom or molecule in the gas phase, its basic principle is conveyed by the equation

$$E_{\rm kin} = \frac{\boldsymbol{p}^2}{2m} = \frac{\hbar^2 \boldsymbol{k}^2}{2m} = \hbar\omega - |E_{\rm B}| \tag{1}$$

that expresses the measured kinetic energy E_{kin} of the emitted electron as the difference between the known energy of the exciting photon of frequency ω and the initially unknown electron binding energy $E_{\rm B}$. Here, \hbar is Planck's constant, m is the electron mass, and p denotes the electron's momentum. In practice, photoemission experiments are often interpreted by relating the photoemission peaks to single-particle eigenvalues and orbitals. This amounts to identifying $E_{\rm B}$ with a single-particle eigenvalue. In the context of Hartree-Fock theory, this approach rests on Koopman's theorem [1]. In density functional theory (DFT), the question of the physical interpretability of the Kohn-Sham or generalized Kohn-Sham eigenvalues can depend strongly on the chosen exchange-correlation approximation [2–6]. Yet, the DFT-based single-particle interpretation of photoemission experiments has been very successful, especially for organic semiconductors [7-22].

Not withstanding this success, it is well known that the physical interpretation of the density of states from single-particle theories is intrinsically of approximative nature [23,24], as condensed matter systems consist of interacting particles. Many-body interaction (W) effects can be taken into account, e.g., by Green's function (G) methods [25]. The GW method [26] in different variants [27–29], specifically quasiparticle self-consistent GW [30], is widely used to calculate photoemission observables. Green's function approaches that go beyond the GW approximation have also been demonstrated to capture exciton physics and allow one to calculate time-resolved and angle-resolved photoemission [31].

The Dyson orbital is a formally exact quantity related to photoemission. Signatures of the differences between molecular orbitals and Dyson orbitals have been found even for otherwise benevolent organic semiconductor molecules such as perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) [32]. The question in how far photoemission can be interpreted in terms of single-particle concepts, and when many-particle effects are so prominent that they cannot be ignored, is therefore not only of interest from a theoretical point of view, but is also of importance for the proper interpretation of experimental data. The present paper aims at contributing to this understanding from the perspective of time-dependent density functional theory (TDDFT).

The particular focus of our work is on photoemission in a pump-probe setup, i.e., a photoemission process in which a system is excited by a first electromagnetic pulse that does not lead to ionization, and then by a second pulse, which leads to ionization. Experimentally this situation has been realized in different ways, and we refer to Refs. [33–35] for just a few exemplary references for solid state, atomic, and molecular realizations, respectively. Different approaches, often using model Hamiltonians, have been developed to theoretically describe this situation; Refs. [36,37] serve to point out again just two well-known examples from a vast range of publications.

Our work here is about the first-principles simulation of such processes using TDDFT in the real-time approach. Real-time simulations of photoemission are attractive because no fitting of model parameters to experimental data is required, i.e., the approach is first principles and thus has predictive power. At the same time, real-time TDDFT

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can be made computationally efficient [38–53] so that simulations for systems with many electrons are possible. Different methods have been proposed to simulate photoemission with TDDFT [42,54–60] and have revealed, e.g., that such calculations can accurately predict even difficult observables such as circular dichroism signals [61], which are of increasing interest experimentally [62]. In the present paper we use real-time TDDFT to simulate photoemission from excited systems in the above-mentioned pump-probe scenario.

In Sec. II, we explain our simulation method. Section III is devoted to a proof of principle. By solving the time-dependent Schrödinger equation for a one-electron system we demonstrate that the real-time ARPES simulation allows us to map excited states. In Sec. IV, we then compute pump-probe photoemission from the PTCDA molecule, a frequently studied model organic semiconductor. We show that here, photoemission from the excited molecule shows signatures of more than one molecular orbital. This is in line with interpreting the many-particle excitation as a superposition of several singleparticle contributions. The result demonstrates that the notion of one electron being emitted from one orbital has its limits, that TDDFT in real time allows us to go beyond this singleparticle interpretation of photoemission, and that ARPES can reveal such features. We offer conclusions in Sec. V.

II. REAL-TIME TDDFT SETUP FOR SIMULATING PHOTOEMISSION FROM ELECTRONICALLY EXCITED SYSTEMS

We calculate photoemission as a dynamical process in real time. The key elements of the process are captured in a single calculation that simulates the excitation and ionization dynamics that eventually lead to the emission and angle-resolved detection of the photoelectrons.

First, we calculate the ground state of the *N*-electron system self-consistently. Starting from that ground state, we solve the time-dependent Kohn-Sham (KS) equations in real time, i.e., we find the solutions of the equations

$$i\hbar\frac{\partial}{\partial t}\varphi_j(\mathbf{r},t) = \left[-\frac{\hbar^2}{2m}\nabla^2 + v_{\rm KS}(\mathbf{r},t)\right]\varphi_j(\mathbf{r},t) \qquad (2)$$

by numerical propagation for j = 1, ..., N. Here, φ_j denotes the *j*th KS orbital, *i* the imaginary number, and $v_{\text{KS}}(\mathbf{r}, t)$ the local KS potential

$$v_{\rm KS}(\boldsymbol{r},t) = v_{\rm H}(\boldsymbol{r},t) + v_{\rm xc}(\boldsymbol{r},t) + v_{\rm ext}(\boldsymbol{r}) + v_{\rm dip}(\boldsymbol{r},t)$$
(3)

that consists of the Hartree $v_{\rm H}$, exchange correlation (XC) $v_{\rm xc}$, and the external potential. For clarity, we split the latter in the contribution from the nuclei $v_{\rm ext}$, which we assume to be static, and the time-dependent potential $v_{\rm dip}$ that represents the light field in the dipole approximation. Direct ionization out of the ground state can be simulated using one electric field represented by the potential

$$v_{\rm dip}(\mathbf{r},t) = e\sin(\omega t)f(t)\mathbf{E}_0 \cdot \mathbf{r}.$$
 (4)

Here, e denotes the elementary charge, E_0 is the (constant) laser polarization, ω is the frequency of the radiation, and f(t)describes the temporal pulse shape, which in our simulations was chosen as detailed in Appendix B, Eq. (B1). One obtains the time-dependent density $n(\mathbf{r}, t)$ from the sum

$$n(\mathbf{r},t) = \sum_{j=1}^{N} |\varphi_j(\mathbf{r},t)|^2.$$
(5)

From the time-dependent orbitals one can compute the approximate probability of finding a photoelectron at a specific point in space, denoted as the detection point \mathbf{R}_D . This approach has first been put forward pragmatically [55]. In later work, it has been justified in more detail [57–59]. As the previous derivations differ to some extent, we shortly summarize our view of the theory in the following.

Under the action of the time-dependent potential v_{dip} , an occupied orbital $\varphi_j(\mathbf{r}, t)$ of Eq. (2) can evolve such that parts of it become an outgoing wave packet. At a point \mathbf{R}_D that is far away from the system's center, one can write this wave packet as a superposition of plane waves

$$\varphi_j(\boldsymbol{R}_D, t) = \int c_j(\boldsymbol{k}) e^{i(\boldsymbol{k}\cdot\boldsymbol{R}_D - \omega_k t)} d^3 k.$$
 (6)

The plane wave expansion is valid under the assumption that the ionizing dipole field has either been switched off by the time that the wave packet arrives at \mathbf{R}_D , or that the field strength is negligibly small. In this case, k and ω_k are related by the dispersion relation for free particles,

$$\omega_k = \frac{\hbar}{2m}k^2. \tag{7}$$

As the plane waves are the eigenstates of the momentum operator, $|c_j(\mathbf{k})|^2$ is the probability of detecting the momentum $\hbar \mathbf{k}$ in the outgoing wave packet. For obtaining the coefficient $c_j(\mathbf{k})$ one performs a Fourier transform of $\varphi_j(\mathbf{R}_D, t)$ to the frequency domain:

$$\varphi_{j}(\boldsymbol{R}_{D},\omega) = \int_{-\infty}^{\infty} e^{i\omega t} dt \int c_{j}(\boldsymbol{k}) e^{i(\boldsymbol{k}\cdot\boldsymbol{R}_{D}-\omega_{k}t)} d^{3}k$$
$$= \int c_{j}(\boldsymbol{k}) e^{i\boldsymbol{k}\cdot\boldsymbol{R}_{D}} d^{3}k \int_{-\infty}^{\infty} e^{i(\omega-\omega_{k})t} dt$$
$$= 2\pi \int c_{j}(\boldsymbol{k}) e^{i\boldsymbol{k}\cdot\boldsymbol{R}_{D}} \delta(\omega-\omega_{k}) d^{3}k.$$
(8)

The Dirac δ on the right-hand side indicates that only one specific value of ω_k contributes to the wave packet at \mathbf{R}_D . Via the dispersion relation Eq. (7) this relates to one unique value of k > 0. Furthermore, far from the system's center the plane waves will be purely outgoing in the radial direction, i.e., the direction of \mathbf{k} is fixed by the direction of the detection point $\mathbf{R}_D, \mathbf{k}/k = \mathbf{R}_D/R_D$. The vector \mathbf{k} is thus uniquely specified.

This analysis of Eq. (8) shows that $\varphi_j(\mathbf{R}_D, \omega)$ is proportional to $c_j(\mathbf{k}_{\omega})$, with $k_{\omega} = \sqrt{2m\omega/\hbar}$. One can convert the probability from frequency to kinetic energy units via

$$|\varphi_j(\boldsymbol{R}_D, \omega)|^2 = |\varphi_j(\boldsymbol{R}_D, E_{\rm kin}/\hbar)|^2.$$
(9)

Under the assumption that Kohn-Sham particles can be identified with electrons, the total probability for detecting an electron with momentum $\hbar k$ at the point R_D is given by summing up the probabilities for all outgoing wave packets, i.e., summing the contributions from all occupied Kohn-Sham orbitals. Therefore, a measure for the total probability $I(\mathbf{R}_D, E_{kin})$ of finding a photoelectron with kinetic energy E_{kin} at \mathbf{R}_D is

$$I(\boldsymbol{R}_D, E_{\rm kin}) \propto \sum_{j=1}^{N} |\varphi_j(\boldsymbol{R}_D, E_{\rm kin}/\hbar)|^2.$$
(10)

Before we proceed to discuss how Eq. (10) is used in practice, we discuss its theoretical foundations. Interpreting the occupied Kohn-Sham orbitals is an approximation, but one that can well be justified: Chong et al. [2] have shown that the occupied Kohn-Sham eigenvalues resulting from an accurate XC potential are very good approximations to ionization potentials. It has further been argued that for systematic reasons [11,63], DFT eigenvalues can well approximate relaxed ionization energies. For molecules with a complicated electronic structure, e.g., orbitals localized on different length scales, this may require advanced functional approximations [4,14]. (For our study here, we explain further down why our XC approximations are justified.) It has also been argued on general grounds that DFT orbitals can approximate Dyson orbitals [32,64], and photoemission experiments have confirmed such interpretations [9]. Thus, the DFT-based interpretation of photoemission is an approximate but nevertheless powerful point of view that complements the perspective of traditional quasiparticle theory. Practical implementations of the latter, e.g., in the form of the GW approximation, come with their own set of approximations, leading to different variants of GW with potentially differing results [26-29,65-67]. The common basis and unifying perspective can be seen in the Dyson equation. Especially the generalized Kohn-Sham formalism, which for orbital-dependent XC functionals leads to a nonmultiplicative potential, establishes a formal similarity to the nonlocal self-energy of traditional many-particle theory (see, e.g., Refs. [6,14] for recent overviews focusing on molecules and organic semiconductors).

Equation (10) is our basis for computing ARPES spectra and their relative intensities. The molecule of interest is subjected to a time-dependent dipole field that liberates some density. Numerically, we assure that this liberation is possible by representing the time-dependent orbitals on large numerical grids in real space. The time-dependent Kohn-Sham orbitals are recorded as functions of time on a set of spatially fixed detection points $\{R_D\}$ placed on a hemisphere around the system's center. Carefully tailored absorbing boundaries make sure that reflections at the grid boundaries are minimized (see Appendix B) and thus do not contribute noticeably to the recorded signals. The recorded values of $\varphi_j(R_D, t)$ are numerically Fourier transformed into the frequency domain and the photoemission intensity at each point R_D on the hemisphere is calculated via Eq. (10).

In the present study we want to simulate photoemission from an excited system, and therefore extend the abovedescribed scheme in the following way. We first determine the dipole-allowed electronic excitation energies of the system that we want to study in a separate, initial linear response calculation. Any linear response technique can be used here, e.g., one could resort to the well-known Casida [68] or Sternheimer [69,70] TDDFT methods. In this work, we stay with the real-time approach also for this task and use the well-established boost excitation [38]. The resulting linearresponse signal is evaluated with the advanced technique that has been described in full detail in Ref. [51]. From it we obtain the excitation energies and the corresponding transition dipole moments and transition densities accurately.

We then start the actual simulation of the pump-probe photoemission process by exciting the system, which initially is in its ground state, with a first potential

$$v_{\text{pump}}(\boldsymbol{r},t) = e\sin(\omega_{\text{L},1}t)f_1(t)\boldsymbol{E}_{0,1}\cdot\boldsymbol{r}.$$
 (11)

The frequency $\hbar\omega_{L,1}$ is chosen such that it corresponds to the first dipole allowed excitation energy of the system. This models the pump excitation. We are using low enough intensities so that the plane-wave approximation of Eq. (6) is well justified [57]. After a waiting time, which we realize via a delayed ramp-up function $f_2(t)$ we turn on a second potential

$$v_{\text{probe}}(\boldsymbol{r},t) = e\sin(\omega_{\text{L},2}t) f_2(t) \boldsymbol{E}_{0,2} \cdot \boldsymbol{r}.$$
 (12)

We deliberately chose a frequency $\omega_{L,2}$ that only allows the ionization from the excited system, i.e., we chose $\hbar\omega_{L,2} < |\varepsilon_{HOMO}|$, where ε_{HOMO} is the energy of the highest occupied ground state orbital φ_{HOMO} . Thus, the total time-dependent external field is given by (see Appendix B for details and a plot)

$$v_{\rm dip}(\boldsymbol{r},t) = v_{\rm pump}(\boldsymbol{r},t) + v_{\rm probe}(\boldsymbol{r},t), \qquad (13)$$

and we then record and evaluate the propagated Kohn-Sham orbitals with angular resolution as described above, cf. Eq. (10).

This is the general setup for the pump-probe TDDFT simulations. The approach can be realized with different numerical implementations of the real-time Kohn-Sham equations. For the calculations in this paper we used the real-space real-time technique of the BTDFT program package that has been detailed in Ref. [51]. It is numerically efficient and parallelizes well so that large grids can be used. Appendix B gives an overview of related numerical details.

Regarding the evaluation of the photoemission signals we note that on the one hand summing Eq. (10) over all detection points R_D yields the total kinetic energy spectrum (KES) of the photoemission process, as shown, e.g., in Fig. 1. In such



FIG. 1. KES of a one-electron Na atom in the pseudopotential approximation. The intensity weighted mean peak position $E_{\rm kin} = (0.93 \pm 0.03) \,\text{eV}$ is indicated by the vertical black line. The theoretically expected peak position is $E_{\rm kin} = \hbar \omega_{\rm L,2} - |\varepsilon_p| = 4.00 \,\text{eV} - 3.08 \,\text{eV} = 0.92 \,\text{eV}$. See main text for details.



FIG. 2. Intensity momentum map for photoemission from the one-electron pseudoatom obtained from two different approaches. Left (a): Real-time simulation in the pump-probe setup with $\hbar\omega_{L,1} = 2.23 \text{ eV}$ and $\hbar\omega_{L,2} = 4.00 \text{ eV}$ as described in the main text. The map corresponds to the angle-resolved evaluation for the kinetic photoelectron energy interval of $E_{\text{kin}} \in [0.82, 1.04] \text{ eV}$ centered around the main peak of the respective KES of Fig. 1. Right (b): Map for the p_1 orbital as obtained from Fermi's golden rule with a planewave final state and a photon energy of $\hbar\omega = 4.00 \text{ eV}$ and a kinetic energy $E_{\text{kin}} = 0.92 \text{ eV}$. Intensities have been normalized to ease the comparison.

spectra we determine the mean peak position by weighting the energy with the intensity. The uncertainty in this mean value is estimated by choosing different energy intervals that all include the main peak, see Appendix B for a detailed explanation of this weighting procedure and for comments on further numerical details, e.g., regarding the background intensity.

On the other hand, we visualize ARPES spectra in the form of intensity maps for the photoelectron's momentum $p = \hbar k$, where k is the wave vector, as shown, e.g., in Fig. 2. In order to obtain these maps, we proceed in the following way. For evaluating the ARPES signal that corresponds to a certain single peak in the KES, one could in principle evaluate the spectrum at the kinetic energy that corresponds to the peak maximum. In practice, we evaluate Eq. (10) in an energy window around that peak, i.e., for a certain interval of frequencies, in order to increase the accuracy, cf. Appendix **B**. For a given frequency the magnitude of the momentum $|\mathbf{p}|$ can be calculated from Eq. (1) via $|\mathbf{p}| = \sqrt{2mE_{\text{kin}}}$. The vectorial components of \mathbf{p} are directly determined by the photoelectron emission angle, which can be inferred from the detection point's position. This means that each position $R_{\rm D}$ relates to a specific emission direction $(\mathbf{p}/|\mathbf{p}|)$. Thus, the (relative) intensity of finding $\mathbf{p}(E_{\text{kin}})$ is revealed by the kinetic energy spectrum $I(\mathbf{R}_D, E_{kin})$ at the respective individual detection point R_D . This evaluation is repeated for each kinetic energy in the aforesaid interval and the signals are then summed up over the interval. In Appendix B we elaborate on the more technical details of this real-time ARPES detection scheme and explain it in detail.

III. VERIFYING THE REAL-TIME PUMP-PROBE SCHEME: ONE-ELECTRON TEST CASE

We first demonstrate the general concept of the real-time pump probe scheme and its suitability for calculating photoemission from excited states in a proof-of-concept calculation for a transparent model system. In choosing the model, we are guided by two considerations. First, in order to eliminate uncertainties due to the exchange-correlation approximation, we chose a one-electron system. Second, for clarity of the analysis it is advantageous to look at a system in which transitions between well-specified states can be triggered. For the latter reason we chose the Na atom in the pseudopotential approximation. The latter also offers the third advantage that it can be conveniently represented on a real-space grid.

We would like to stress that the aim of this section is just a one-electron proof-of-principle calculation that the real-time, grid-based detection point scheme works for the pump-probe setup. Such a calculation could have been done with any one-electron potential. The Na pseudoatom is just a choice that can be conveniently realized in the grid-based code and that is numerically transparent. As we are looking at a one electron system, Eq. (2) can be turned into the time-dependent Schrödinger equation by setting the Hartree and XC potential to zero. The pseudopotential then just serves as the external potential of this one-electron system.

For this one-electron system we then follow the procedure described in Sec. II. First, we compute the ground state $\varphi_s(\mathbf{r})$ of the one-electron pseudoatom. It is of *s* type and the ground state eigenvalue is $\varepsilon_s = -5.31 \text{ eV}$. Here and in all the following cases, bound states have negative eigenvalues. We also calculate the lowest unoccupied orbitals $\varphi_{p_k}(\mathbf{r})$. They are of *p* type, threefold (k = 1, 2, 3) degenerate orthonormal and with eigenvalues $\varepsilon_p = -3.08 \text{ eV}$. Due to our numerical setup on a Cartesian grid with a finite spacing, the *p*-type orbitals preferentially align along specific spatial directions, as detailed below.

Next, we calculate the dipole-allowed excitation energies. The first excitation occurs at an energy of $E_{\text{exc}} = 2.23 \text{ eV}$, which accurately relates to the eigenvalue difference $\Delta \varepsilon = \varepsilon_p - \varepsilon_s$, and thus, to the dipole-active transition $s \rightarrow p$.

We then solve the one-electron Schrödinger equation with the ground state as the initial state and the potential $v_{dip}(\mathbf{r}, t)$ of Eq. (13) with the parameters $\hbar\omega_{L,1} = E_{exc}$ and $\hbar\omega_{L,2} =$ 4.00 eV. The latter choice ensures that the *p* states can be ionized, but that there is no direct ionization from the ground state, since $|\varepsilon_p| < \hbar\omega_{L,2} < |\varepsilon_s|$. By judiciously choosing the polarization $\mathbf{E}_{0,l}$ of both the pump and probe lasers to match the orientation of one of the *p* orbitals, we can predominantly excite to and ionize from one specific *p* orbital. In the following discussion we focus on p_1 , which is oriented in the (1,1,1) direction, i.e., the space diagonal of the Cartesian grid.

Figure 1 depicts the thus obtained KES, i.e., it results from the time evolution of what initially was the *s* orbital. The spectrum shows one clear peak at $E_{kin} = (0.93 \pm 0.03) \text{ eV}$ (vertical black line in Fig. 1). The peak value matches Eq. (1), corresponding to a theoretical kinetic energy $E_{kin} = \hbar \omega_{L,2} - |\varepsilon_p| = 0.92 \text{ eV}$ for the ionization from the excited *p* state. This is the first confirmation that our simulation captures the desired pump-probe process $s \rightarrow p \rightarrow$ continuum.

A second and more detailed confirmation that our simulation correctly describes the pump-probe photoemission is seen in Fig. 2. Figure 2(a) shows the ARPES intensity momentum map $I(k_x, k_y)$ corresponding to the kinetic energy interval of [0.82, 1.04] eV that encompasses the peak from Fig. 1. The map features two intensity spots, which are centered around $(k_x, k_y) \approx \pm (0.3, 0.3) \text{ Å}^{-1}$. In order to demonstrate that this intensity map correctly reflects photoemission from the p_1 orbital, we also compute $I(k_x, k_y)$ for photoemission from the p_1 orbital in an independent, second approach using perturbation theory and Fermi's golden rule. For an electromagnetic field in the dipole approximation and under the assumption that the emitted electron's final state is a plane wave, the ARPES intensity *I* is given [9,32] by the Fourier transform of the initial orbital $\tilde{\varphi}_{in}(\mathbf{k})$ from which the electron is emitted, evaluated at the value

$$|\mathbf{k}| = \sqrt{2m(\hbar\omega - |E_{\rm B}|)}/\hbar \tag{14}$$

determined by the energy conservation Eq. (1), i.e.,

$$I(k_x, k_y) \propto |\mathbf{A} \cdot \mathbf{k}|^2 |\tilde{\varphi}_{in}(\mathbf{k})|_{k=\text{const}}^2 .$$
(15)

The vector potential A describes the electromagnetic field corresponding to the photon energy $\hbar\omega$ and k is the wave vector of the plane-wave final state. This line of thinking leads to the famous "visualization of orbital densities in reciprocal space" interpretation of ARPES patterns [9].

The ARPES intensity momentum map from the golden rule Eq. (15) can be compared to the one obtained from the real-time simulation along the following lines: When one substitutes the Fourier transform $\tilde{\varphi}_{p_1}(\mathbf{k})$ and binding energy ε_p of the respective p_1 state into Eq. (14) and Eq. (15), and ensures that the vector potential \mathbf{A} and photon energy $\hbar\omega$ correspond to the polarization ($\mathbf{E}_{0,2}$) and energy of the probe laser ($\hbar\omega_{\mathrm{L},2}$) of the real-time simulation (where $\mathbf{E} = -\partial \mathbf{A}/\partial t$), then the two momentum maps should show the same relative intensity pattern if the real-time simulation describes photoemission from the p_1 orbital.

The right panel, Fig. 2(b), shows the intensity map that one obtains by evaluating Eq. (15) for the p_1 orbital as just described. When comparing Figs. 2(a) and 2(b), one can see small differences, e.g., evaluating Eq. (15) leads to slightly higher intensity towards the *k*-space origin. Small deviations are to be expected, e.g., because the real-time simulation goes beyond the plane-wave final state approximation [61]. However, it is very reassuring to see that overall the two intensity maps are very similar and feature the same characteristic bright spots at $(k_x, k_y) \approx \pm (0.3, 0.3) \text{ Å}^{-1}$. For completeness we mention that we repeated this procedure for the other two p_k orbitals (k = 2, 3) in separate calculations. This leads to identical findings.

Finally, as a further test, we also calculated the direct ionization from the *s* ground state. To this end, we repeated the calculations using only one laser ($\hbar\omega_L = 6.23 \text{ eV} > |\epsilon_s|$). Figure 3 shows that the resulting ARPES intensity momentum map clearly differs from the one seen in Fig. 2, i.e., emission from the *s* and the *p* orbitals can clearly be distinguished from each other. Furthermore, comparing the left and the right panel in Fig. 3 shows that again the signal from the time-dependent calculation (evaluated around the main peak at 0.92 eV in the interval [0.82, 1.04] eV) on the one hand, and from Fermi's golden rule evaluated at the same energy on the other, are very similar and correspond to the emission that one expects from an *s* ground state. We also note that we verified explicitly that using LDA and ALDA in these calculations does not change the figures noticeably. This proof-of-principle study



FIG. 3. Intensity momentum map for for direct photoemission from the *s*-orbital ground state of the one-electron pseudoatom. Left (a): Real-time simulation using a single probe laser with energy $\hbar\omega_{\rm L} = 6.23$ eV evaluated around the main peak at 0.92 eV. Right (b): Map for the *s* orbital as obtained from Fermi's golden rule with a photon energy of $\hbar\omega = 6.23$ eV at the kinetic energy $E_{\rm kin} = 0.92$ eV.

thus shows that our setup allows us to simulate the pumpprobe process and to visualize the excited state.

IV. MANY-PARTICLE SIGNATURES IN THE PHOTOEMISSION FROM PTCDA

We proceed by studying the PTCDA molecule, which is of interest because it is a model organic semiconductor that forms well-defined films on, e.g., silver surfaces, and photoemission signals can be obtained with high accuracy. It has frequently been studied both experimentally and theoretically [7,11-15,17-20,61,71-75].

Being a many-electron system, the question of which XC approximation to use now becomes relevant. For our study, we benefit from previous work in which the electronic structure of PTCDA and how its depends on the XC approximation has been analyzed in great detail [4,6,7,11,12,76]. The finding that is decisive in the present context is that the molecular orbitals of PTCDA can be divided into two groups: Ones that are delocalized over the entire molecule and others that are more localized on the side groups. An overall correct description of, e.g., the orbital ordering, can only be reached with advanced functionals such as, e.g., the optimized effective potential self-interaction correction. The delocalized orbitals, however, are reasonably well described even by inexpensive approximations such as the LDA. As we point out in the following and also discuss in Appendix A, the process that we study here involves predominantly delocalized orbitals, and we can therefore reach a qualitatively correct description with the LDA.

Our study proceeds in the same way as in the previous section, with the only difference that we are now investigating a molecule with 140 valence electrons instead of a one electron system. We first calculate the ground state with LDA. The corresponding frontier eigenvalues are listed in Table I. Next, we calculate the dipole-allowed excitation energies with the adiabatic LDA (ALDA) and find the first at $E_{\rm exc} = 2.14 \, {\rm eV}$, with a transition dipole moment in the direction of the long molecular axis. Experimentally, the optical gap is $E_{\rm exc} = 2.6 \, {\rm eV}$ [72]. Thus, ALDA quantitatively underestimates the first excitation energy. However, we calculated the first excitation also with

TABLE I. Eigenvalues for the two lowest-unoccupied (l) and eleven highest-occupied (h) KS eigenvalues from an LDA DFT ground state calculation, in eV.

φ_{l+3}	φ_{l+2}	φ_{l+1}	$arphi_{ m l}$	$arphi_{ m h}$	$arphi_{ ext{h-1}}$	$\varphi_{\text{h-2}}$	$\varphi_{\text{h-3}}$	$arphi_{ ext{h-4}}$	$arphi_{ ext{h-5}}$	$arphi_{ ext{h-6}}$	$arphi_{ ext{h-7}}$	$arphi_{ ext{h-8}}$	$arphi_{ ext{h-9}}$	$\varphi_{\text{h-10}}$
-3.17	-3.66	-3.71	-5.08	-6.57	-7.16	-7.17	-7.70	-7.71	-7.83	-8.03	-8.04	-8.09	-8.64	-8.71

the hybrid functional B3LYP [77,78], which has been shown to yield an eigenvalue spectrum that compares well to the photoemission experiment [7]. We compared the character of the first excitation that we find with the ALDA to the one from the B3LYP functional, see Appendix A for details. This comparison shows that both functionals describe the structure of the first excitation very similarly. In both cases, the excitation is dominated by a transition from the highest-occupied molecular orbital (HOMO) to the lowest-unoccupied molecular orbital (LUMO), but also shows contributions from other orbitals. Also the difference between the density of the first excitation and the ground state density is extremely similar in the ALDA and the B3LYP calculation. Thus, although ALDA underestimates the first excitation energy, it correctly captures the main character of the first electronic excitation of PTCDA. Therefore, we can proceed with the ALDA, which can efficiently be evaluated on the large real-space grids that are needed for the real-time calculation of the photoemission.

Following our pump-probe photoemission protocol, we start a real-time propagation from the ground state and subject the molecule to a first excitation with a frequency that we chose to match the first excitation energy, i.e., $\hbar\omega_{L,1} = E_{exc}$. After 10 fs we switch on the second pulse that triggers the photoemission and chose $\hbar\omega_{L,2} = 6.00 \text{ eV}$. This choice prevents direct ionization from the ground state HOMO ($\varepsilon_h = -6.57 \text{ eV}$). The laser polarization direction $E_{0,l}/|E_{0,l}|$ is chosen along the long molecular axis, i.e., in the direction of the above-mentioned transition dipole moment.

Figure 4 depicts the KES that results from the detection of the 11 highest-occupied KS orbitals; with lower orbitals not contributing noticeably to the emission. We focus on the kinetic energies between approximately 1 eV and 3.5 eV, since our numerical setup is designed to represent this part of the spectrum. There is a dominant peak around $E_{kin} =$ (1.54 ± 0.04) eV, followed by some smaller intensity structures. An orbital-by-orbital analysis of the signal reveals that the main peak results not just from one orbital, but from the contributions of two orbitals, the time-dependent HOMO and the time-dependent HOMO-9. This is intriguing, because as discussed in Sec. I, in the standard interpretation of PES from organic semiconductor molecules, one peak is typically associated with one orbital. Furthermore, in previous TDDFT simulations of the direct photoemission from PTCDA, i.e., emission from the ground state, there was a one-to-one correspondence between peaks and orbitals [61]. We note that direct photoemission out of HOMO-9 to the continuum is energetically not possible even if the energy of both lasers was absorbed at once, since $E_{kin} = \hbar \omega_{L,1} + \hbar \omega_{L,2} + \varepsilon_{h-9} < 0$, cf. Appendix A.

In order to elucidate the situation further, we analyzed the emission in the form of an ARPES intensity momentum map $I(k_x, k_y)$ according to Eq. (10). Figure 5(a) shows the result. It depicts the total momentum distribution corresponding to the kinetic energy interval [1.44, 1.64] eV, i.e., to the main peak seen in Fig. 4. Figure 4(b) shows the contribution from the time-dependent HOMO and Fig. 4(c) the one from the



FIG. 4. KES of PTCDA obtained from the real-time pump-probe simulation. The spectrum corresponds to a pump and probe photon energy of $\hbar\omega_{L,1} = 2.14 \text{ eV}$ and $\hbar\omega_{L,2} = 6.00 \text{ eV}$, respectively. The total signal is computed from the detection of the eleven highest occupied time-dependent KS orbitals. The intensity weighted mean position of the main peak $E_{\text{kin}} = (1.54 \pm 0.04) \text{ eV}$ is indicated by the vertical black line. The main peak predominantly results from the detection of the HOMO and HOMO-9 orbitals.



FIG. 5. Intensity momentum map of PTCDA calculated for a pump-probe scenario as explained in the main text. The long molecular axis of PTCDA coincides with the *x* axis. Left (a): Total signal from the real-time detection of the eleven highest occupied KS orbitals. Top right (b): Signal from the time-dependent HOMO. Bottom right (c): Signal from the time-dependent HOMO-9. Intensities are in arbitrary units and normalized to the intensity maximum 0.0021 of (a).



FIG. 6. (a) Fourier transform of the LUMO, (b) LUMO + 1, (c) and the LUMO + 3 evaluated at 1.54 eV. See main text for discussion.

time-dependent HOMO-9 according to Eq. (9). Comparing the left- and the right-hand sides shows that a superposition of the signatures from the two time-dependent orbitals on the right can explain the dominant features of the total signal seen on the left. Thus, the real-time simulation of the ARPES process after an initial excitation shows without doubt that more than one time-dependent orbital is involved.

It is highly instructive to look at these results also from another perspective. The first excitation of PTCDA out of which the photoemission takes place after the second pulse can also be analyzed using Casida's formulation of linearresponse TDDFT based on perturbation theory [79,80]. From the point of view of the Casida formalism, a many-particle excitation is a superposition of one-electron excitations that go from occupied to unoccupied (virtual) single-particle orbitals that are the eigenstates of the time-independent, ground state Hamiltonian. The percentage with which each of the electron-hole pair excitations contributes to the true, manyparticle system excitation can readily be computed. We found, cf. Appendix A, that in the ALDA the HOMO to LUMO transition contributes 96.4% to the first dipole-allowed excitation, but there are also contributions from other electron-hole pairs. The second and third highest contribution stem from the pair HOMO-8 to LUMO + 1 and HOMO-5 to LUMO + 3, respectively.

Thus, if one thinks about pump-probe ARPES in the perturbation theory picture, then the first pulse leads to an excitation that can predominantly be understood as a superposition of LUMO, LUMO + 1, and LUMO + 3, and the second pulse then leads to emission from this superposition. Figure 6shows the Fourier transform of the LDA LUMO [Fig. 6(a)], LUMO + 1 [Fig. 6(b)], and LUMO + 3 [Fig. 6(c)] evaluated at 1.54 eV. In the straightforward interpretation of ARPES signals based on the single-particle picture and a plane-wave final state [9,32], one expects that the ARPES signal after the second pulse be dominated by these signatures. Since we do not know whether the different virtual orbitals will react differently to the second, ionizing pulse, we cannot predict how strongly each of these virtual orbitals contributes to the ARPES signal. Yet in any case, comparing Fig. 6 to Fig. 5(a) shows that, qualitatively, also this interpretation is in agreement with the ARPES signal that the real-time pump-probe simulation shows. We note, e.g., that the superposition of Fig. 6(b) and Fig. 6(c) reveals features that are seen in panel Fig. 5(c), e.g., the vertical intensity lines at $\approx k_x = \pm 0.3 \text{ Å}^{-1}$.

V. CONCLUSION

In this paper we demonstrated that one can simulate photoemission from an excited system quantitatively with real-time TDDFT. Our approach unites the key elements of the process—excitation, ionization, and detection—in a single calculation.

We first studied a one electron system as a proof of concept. In our simulation, an electron is excited from the ground state by a first pulse and the system is then ionized with a second pulse. For this one-electron case, the ARPES pattern closely corresponds to the pattern that one expects for an electron emitted out of the first excited orbital, i.e., out of the orbital that is the LUMO or one of the LUMOs, respectively, in the ground state calculation.

Then we investigated the same situation for the PTCDA molecule, which is a paradigm test system for photoemission and a many-particle system with 140 valence electrons. Our calculations rely on the ALDA to ease the numerical burden, which is high due to the need for large real-space grids to numerically capture the emission process far away from the molecule's center. Using the ALDA somewhat limits the accuracy of our calculations, but we have carefully evaluated its trust range and confirmed its reliability for the observables that we report here.

We subjected the PTCDA molecule to a first pulse whose frequency was chosen to match the energy difference between the ground state and the first excitation. A second pulse then leads to the emission of electrons. The resulting ARPES signal clearly shows contributions from two time-dependent orbitals, the time-dependent HOMO and the time-dependent HOMO-9. This means that the total electronic process cannot be understood as a single electron being excited to an unoccupied orbital and then ionized by the second pulse. Instead, the process must be considered as a many-electron process. We have verified this by repeating the analysis from the complementary perspective of first-order perturbation theory in the Casida linear-response formalism. From this point of view, the first excitation is dominantly a superposition of three electronhole pairs, one involving the LUMO and the others the LUMO + 1 and LUMO + 3, respectively. Correspondingly, the ARPES signal can also be interpreted as a superposition of the signals from the time-independent LUMO, LUMO + 1and LUMO + 3 orbitals. Thus, our calculations have demonstrated that real-time propagation and linear-response theory offer complementary views of the same physical reality. In both cases, the photoemission from PTCDA after an initial excitation shows clear signatures of the many-particle character of the first excitation and cannot be interpreted in a simple one-orbital picture. Extending the simulations to surface situations, e.g., by including parts of the substrate in addition to the active molecule, is a worthwhile task for future work. Time-dependent simulations of the type that we presented here can help to understand time-dependent experiments, e.g., of the type that was recently presented in Ref. [81].

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APPENDIX A: DETAILED ANALYSIS OF THE ELECTRONIC EXCITATION OF PTCDA

In this Appendix we give additional information about the calculations for PTCDA. First, we report in Table I the LDA ground state eigenvalues from the real-space grid calculation. We have also checked the character of the orbitals. The orbitals that contribute decisively to the physics that we discuss in the main text, i.e., HOMO, HOMO-9, LUMO, LUMO + 1, and LUMO + 3, are all delocalized and, therefore [4], represented qualitatively correct in the LDA calculation.

Second, we report details about the explicitly linearized TDDFT calculations in the Casida formalism [79,80]. In the latter, excitations energies are computed by solving a matrix equation that is defined in the basis of KS electron-hole pairs. Hence, the contributions of the latter to the many-particle excitation are obtained straightforwardly. For these calculations we used the TURBOMOLE [82] code and the def2-TZVP basis set.

First, we employed the ALDA. It yields the first dipoleallowed excitation (optical gap) at $E_{\text{exc}}^{\text{LR}} = 2.16 \text{ eV}$. This confirms the real-space excitation energy, and the small difference of $\pm 0.02 \,\text{eV}$ is within the range that one expects due to numerical differences such as basis set limitations. The Casida coefficients for the ALDA electron hole pairs are listed in the left half of Table II. From these coefficients we see that the LUMO, LUMO + 1, and the LUMO + 3 orbitals contribute the strongest to the first excitation energy. The next lower electron-hole contributions are 0.1% or less, and are therefore neglected. We did a corresponding calculation with the B3LYP [77,78] functional, which was successfully used in previous studies of PTCDA [7]. Our result $E_{\text{exc}}^{\text{LR}} = 2.38 \text{ eV}$ is close to the optical gap reported in Ref. [14], with a difference of only $\pm 0.03 \text{ eV}$). The right-hand side of Table II reports the Casida coefficients for the B3LYP calculation.

We further confirm the many-particle nature of the first excitation energy by an analysis of the transition density. The transition density of an excitation of a many-particle system

TABLE II. Casida linear response first excitation energy in eV (first column) and electron-hole pair contributions from HOMO- $j \rightarrow$ LUMO+k, notated as j,k., in percent, for the first three electron-hole pairs that contribute most, for two different XC approximations.

LDA	(0,0)	(8,1)	(5,3)	B3LYP	(0,0)	(6,1)	(1,3)
2.16	96.4	2.5	0.5	2.38	98.1	0.9	0.4



FIG. 7. Left (a): Transition density of the first dipole-allowed excitation ($E_{\rm exc} = 2.14 \, {\rm eV}$) of PTCDA obtained from a real-time TDDFT calculation with ALDA. Right (b): Transition density of the single-particle KS transition HOMO \rightarrow LUMO calculated from the corresponding stationary orbitals via $\rho_{\rm HOMO}^{\rm LUMO}(\mathbf{r}) = \langle \varphi_{\rm LUMO} | \hat{n} | \varphi_{\rm HOMO} \rangle$ with LDA. Blue and orange colors correspond to positive and negative values, respectively.

can directly be obtained accurately in a real-time calculation [51]. For an excitation that is purely of one-electron character going from one occupied to one unoccupied orbital, the transition density would be just the product of the occupied and the unoccupied orbital. We calculated the single-particle KS transition densities $\varphi_i^k(\mathbf{r}) = \langle \varphi_k | \hat{n} | \varphi_j \rangle$ for the 11 highest-occupied and 15 lowest-unoccupied stationary orbitals, where \hat{n} denotes the density operator. The transition density of the single-particle transition HOMO \rightarrow LUMO shows the largest similarity to the many particle transition density. However, Fig. 7 shows that there are differences between the full transition density $\rho(\mathbf{r}; E_{exc})$ [Fig. 7(a), left] and the single-particle $\rho_{\text{HOMO}}^{\text{LUMO}}(\mathbf{r})$ [Fig. 7(b), right]. These plots, as well as the ones shown in Fig. 8 and Fig. 9, used an isovalue of 0.0001 a_0^{-3} . Thus, the transition density analysis confirms the conclusion from the Casida coefficients, i.e., the first excitation of PTCDA, although dominated by the HOMO-LUMO transition, differs noticeably from a single-particle excitation.

This conclusion can be further confirmed also in other ways. One can compare the density that corresponds to the first excitation $n(\mathbf{r}; E_{\text{exc}})$ (as output by TURBOMOLE) to the density that is associated with the single-particle transition HOMO \rightarrow LUMO. The latter can be calculated straightforwardly as $n_{\text{HOMO}}^{\text{LUMO}} = n_0 - |\varphi_{\text{HOMO}}|^2 + |\varphi_{\text{LUMO}}|^2$, where $n_0(\mathbf{r})$ is the ground state density of PTCDA. The difference between



FIG. 8. Difference between the density of the first excitation (with ALDA) and the excited state density that corresponds to the single-particle transition from the ground state HOMO to the LUMO (LDA) of PTCDA. See text for details.



FIG. 9. Difference density of the first excitation and the ground state of PTCDA with (a) ALDA and (b) B3LYP. See main text for discussion.

 $n(\mathbf{r}; E_{\text{exc}})$ (ALDA) and $n_{\text{HOMO}}^{\text{LUMO}}(\mathbf{r})$ (LDA) is shown in Fig. 8. The notable differences again confirm that the first excitation of PTCDA cannot be explained solely by the dominant single-particle transition of HOMO \rightarrow LUMO.

In order to check whether the ALDA represents the decisive features of the density of the first excitation faithfully we have calculated the difference density of the first excitation and the ground state with both the ALDA and the B3LYP functional. The results are shown in Fig. 9. The difference density from the ALDA [Fig. 9(a), left] and from B3LYP [Fig. 9(b), right] are in very good qualitative agreement.

Finally, we computed the direct ARPES from the ground state of the PTCDA molecule in the gas phase with the ALDA as a crosscheck and reference for the pump-probe results discussed in the main text. We used a single ionizing pulse with $\hbar\omega_{\rm L} = 8.14 \,{\rm eV} > |\epsilon_h| = 6.57 \,{\rm eV}$ and with the same polarization E_0 along the long molecular axis as in the pump-probe scenario. Figure 10 shows the corresponding KES. Each peak results from the (real-time) detection of either one or several KS orbitals. In contrast to the pump-probe process in Sec. IV, however, the multiple contributions here are simply due to the (quasi)degeneracy of the corresponding orbitals in the initial state, cf. Table I. This can be seen from the peak positions of the individual orbital signals in Fig. 10, as they correspond to a direct ionization from the corresponding ground state orbitals, i.e., the peak positions

$$E_{\mathrm{kin},\,i} = \hbar\omega_{\mathrm{L}} - |\varepsilon_i|\,,\tag{A1}$$

can be explained from the occupied KS eigenvalues, cf. Table I.

It is instructive to compare the ARPES pattern due to emission from the HOMO in the direct process here to the emission from the HOMO in the pump-probe process of Sec. IV. The peak at $E_{kin} \approx 1.57$ eV in Fig. 10(a) results from the detection of only the HOMO. Other lines and Fig. 10(b) depict other orbital contributions. Figure 11 shows the HOMO contribution to the ARPES intensity momentum map in the direct photoemission from the ground state of PTCDA. The map corresponds to a kinetic energy interval $E_{kin} \in [1.44, 1.64]$ that encompasses the peak in Fig. 10(a) that results from the HOMO detection. The comparison of Fig. 5 and Fig. 11 shows significant differences, and thus confirms that in the pump-probe process one does not just see the initial ground state.



FIG. 10. KES of the direct ARPES of PTCDA. The spectrum results from the detection of the eleven highest occupied time-dependent KS orbitals. For better visualization, (a) shows the significantly contributing orbitals HOMO, HOMO-1, and HOMO-2 to the total spectrum and (b) separately shows the contributions of HOMO-3, HOMO-4, and HOMO-8. See main text for details.

APPENDIX B: NUMERICAL DETAILS

We used the real-space and real-time code BT-TDDFT [51], whose implementation of pseudopotentials originated in the PARESC code [83]. In the calculations for this paper we used an



FIG. 11. Intensity momentum map of PTCDA obtained from a real-time TDDFT ARPES simulation using a single ionizing pulse with energy $\hbar\omega_{\rm L} = 8.14 \,{\rm eV}$. The map results from the detection of the KS HOMO and corresponds to the angle-resolved evaluation for the kinetic photoelectron energy interval of $E_{\rm kin} \in [1.44, 1.64] \,{\rm eV}$ that encompasses the KES peak from the HOMO contribution at $\approx 1.57 \,{\rm eV}$ shown in Fig. 10.



FIG. 12. The pulse profile $f_j(t) \sin[\omega_{L,j}(t - t_{0,j})]$ used for the PTCDA calculation (pump: $\hbar \omega_{L,1} = 2.14 \text{ eV}$, $t_{0,1} = 0$, probe: $\hbar \omega_{L,2} = 6.00 \text{ eV}$, $t_{0,2} = 10 \text{ fs}$) for the first 20 fs. The delay of 10 fs between the pump and probe pulse is indicated by the vertical black line. After the ramp-up phase of 0.5 fs, both the pump and probe pulse keep oscillating with $\sin[\omega_{L,j}(t - t_{0,j})]$. See main text for details.

equidistant grid with a spherical boundary. The grid spacing was $\Delta r = 0.5 a_0$ and $\Delta r = 0.38 a_0$, and the boundary sphere radius was $R = 55 a_0$ and $R = 60 a_0$, for the calculations in Sec. III and Sec. IV, respectively. The atomic cores were described by norm-conserving Troullier-Martins [84] pseudopotentials with the following cutoff radii: H 1.39 a_0 (s), C 1.09 a_0 (s and p), O 1.10 a_0 (s and p), and Na 3.09 a_0 (s, p, and d). Considering only the valence electrons explicitly is well justified as the excitation energies in our simulations fall in the regime of VIS (pump laser) and UV-B up to UV-C (probe laser), respectively, and thus do not liberate core electrons.

The time evolution of the KS orbitals, cf. Eq. (2), was done with a Crank-Nicolson [51,85,86] propagator, a time step of $\Delta t = 0.002$ fs and a total propagation time of T = 50 fs. We used the following pulse shape $f_j(t)$ (j = 1, 2) in all ARPES simulations:

$$f_j(t) = \begin{cases} 0, & t < t_{0,j} \\ (t - t_{0,j})/t_{\rm r}, & t_{0,j} \leq t < t_{0,j} + t_{\rm r}, \\ 1, & t \ge t_{0,j} + t_{\rm r} \end{cases}$$
(B1)

where $t_{0,j}$ specifies the time at which the pulse is switched on and t_r is the duration of the linear ramp up. The functions $f_j(t)$ in the classical dipole fields of Eqs. (11) and (12) were chosen to ramp up within $t_r = 0.5$ fs to a constant intensity I_0 , cf. Eq. (B1). In the pump-probe simulations, we chose a delay of 10 fs between the pump and probe pulse, i.e., $t_{0,1} = 0$ and $t_{0,2} = 10$ fs. Figure 12 shows the pulse profile used in the pump-probe simulation of PTCDA.

The magnitude of the laser polarization $|E_0|$ and intensity I_0 are related via $I_0 = \frac{\epsilon_0 c}{2} |E_0|^2$; c is the speed of light in vacuum and ϵ_0 the vacuum permittivity. We use a laser intensity of 5×10^8 W/cm² for both the pump and the probe laser in Sec. III, and an intensity of 5×10^9 W/cm² for the calculations for PTCDA. If one wants to model a specific experiment, one can choose for the simulation the same intensity as in the experiment. In the absence of experiments, it is prudent to choose the intensity according to the following guidelines:

On the one hand, low intensities are beneficial for the reasons mentioned in the context of Eq. (6) in Sec. II, for keeping higher-order effects small, and a low rate of density escape avoids overstraining the absorbing boundary. On the other hand, higher intensities lead to higher density emission and thus increase the numerical accuracy of the observation-pointbased ARPES detection scheme. In practice, our experience is that the decisive ARPES features are rather robust. As an example we mention the small peak around 2.14 eV in Fig. 4, which is related to numerical noise at the frequency of the pump pulse (which was long in our simulation to get clear orbital signatures), and which does not interfere with accurately evaluating the main peak signal.

In Sec. III, we utilize the laser polarization $\hat{e}_{0,i} =$ $E_{0,(i)}/|E_{0,(i)}|$ to control which of the degenerate p_k (k = 1, 2, 3) orbitals is accessed in the process $s \rightarrow p_k \rightarrow p_k$ continuum. We maximize the excitation and ionization to one of the p_k orbitals by choosing the laser polarization direction of both the pump and probe laser such that it coincides with the fictitious line that connects the centers of the dumbbells of that orbital. We calculate that direction $\hat{\boldsymbol{e}}_0(p_k)$ from $\boldsymbol{d}_{p_k} = \int \boldsymbol{r} \varphi_{p_k}(\boldsymbol{r}) d^3 \boldsymbol{r}$, which reveals the centers of the dumbbells of the stationary orbital φ_{p_k} . In our Cartesian grid setup the directions are p_1 : $\hat{\boldsymbol{e}}_{0,1}(p_1) = \hat{\boldsymbol{e}}_{0,2}(p_1) \approx (0.5904, 0.5746, 0.5668); p_2$: $\hat{\boldsymbol{e}}_{0,1} = \hat{\boldsymbol{e}}_{0,2} \approx (-0.7894, 0.5575, 0.2571); \ p_3: \ \hat{\boldsymbol{e}}_{0,1} = \hat{\boldsymbol{e}}_{0,2} \approx$ (0.1682, 0.5992, -0.7827). In the calculations for PTCDA, the polarization direction of the pulses always coincides with the long molecular axis of PTCDA, which is oriented along the x axis in our coordinate system.

In our angle-resolved real-time detection scheme we use a set of N_D equally distributed points $\{\mathbf{R}_D\}_{D=1,...,N_D}$ on a hemisphere with radius $\mathbf{R}_D = |\mathbf{R}_D|$. \mathbf{R}_D must be sufficiently large so that the interaction between the emitted density and the remaining ionized system is negligible at \mathbf{R}_D . $\mathbf{R}_D = 40 a_0$ and $N_d = 6400$ in all calculations shown in this paper, with the initial system being in the coordinate system's center. Recording photoemission signals on the upper hemisphere is sufficient in this study due to the symmetry of the one-electron system and the planar PTCDA molecule, respectively.

The vectorial components of the photoelectron's momentum $p = \hbar k$ can be written as $(E_{kin} = \frac{\hbar^2 k^2}{2m})$

$$\hbar k_x = \sqrt{2mE_{\rm kin}}\cos\phi\sin\theta \tag{B2}$$

$$\hbar k_y = \sqrt{2mE_{\rm kin}}\sin\phi\sin\theta \tag{B3}$$

$$\hbar k_z = \sqrt{2mE_{\rm kin}\cos\theta} \tag{B4}$$

using spherical coordinates for the description of the photoelectron's emission angles (ϕ, θ) . We derive the latter from the angular position of the detection point at which the wave packet is recorded. The resolution of the intensity momentum maps $I(\mathbf{p}(E_{\text{kin}}))$ that we construct depends on the surface density of the detection points $\{\mathbf{R}_D\}$.

We determine the momentum intensity maps not only for a single kinetic energy, but for an energy interval via

$$I(\boldsymbol{p}; [E_{\min}, E_{\max}]) = \int_{E_{\min}}^{E_{\max}} I(\boldsymbol{p}(E_{\min})) \, dE_{\min}.$$
(B5)

peak. For overlapping peaks or closely spaced signatures, the interval is chosen to be narrower, approximately between the full width at half-maximum and these latter minima, to reduce interfering signals. In the numerical implementation using a discrete-time fast Fourier transform \mathcal{FT} for calculating $\mathcal{FT}\{\varphi_j(t; \mathbf{R}_D)\}$, the interval $[E_{\min}, E_{\max}]$ is a discontinuous sequence and consequently, the integral in Eq. (B5) becomes a sum. We express the ARPES intensity maps in terms of the components \mathbf{k} as $I(k_x, k_y)$ of the wave vector evaluated in the above-mentioned energy interval $([E_{\min}, E_{\max}])$. Specifying (k_x, k_y) also determines k_z , which is positive due to the detection of outgoing wave packets,

$$k_z = \sqrt{\frac{2mE_{\rm kin}}{\hbar^2} - k_x^2 - k_y^2} \,. \tag{B6}$$

The ARPES detection scheme is numerically demanding. Figure 1 nicely exemplifies some of the consequences. There are small kinetic energy signals before and after the main peak, e.g., around $E_{\rm kin} \approx 1.45 \, {\rm eV}$, which we consider to be numerical noise. These can result from our ground state and real-time calculations being subject to finite convergence criteria, such as the discrete grid spacing and the finite numerical accuracy with which the ground state orbitals are computed. The latter limitation can be more noticeable in the propagation than in usual ground state calculations because we need to use large grids in order to be able to place the detection points far away from the ionized molecule's center. The exponential decay of the ground state orbitals leads to very small numerical values

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on far outlying grid points, which are difficult to represent numerically accurately. Under propagation with an ionizing pulse, numerical limitations can lead to noticeable numerical noise intensity at low kinetic energies.

After the angle-resolved detection, we absorb the outgoing density to prevent reflections at the numerical boundaries. This is achieved with a complex potential as described in Refs. [87–89] and in the form, which has been explicitly detailed in Eq. (1) in the Supplemental Material of Ref. [61]. For both the one electron and the PTCDA calculations the onset of that potential is at $R_{\rm S} = 40 a_0$ and a shift of $\Delta = 3 a_0$ relocates the singularity of the potential outside of the numerical sphere.

Finally, we list the details for the propagation calculations with which we determine the transition energies and densities of the initial, neutral systems. Following the procedure described in Ref. [51], we calculate the dipole-allowed electronic excitation energies and transition densities by fitting the data from the numerical propagation to the analytical form of the electronic dipole response to a dipolelike boost excitation applied to the system's ground state. All calculations are performed on a spherical grid with an equidistant grid spacing. For calculating the dipole spectrum in Sec. III we use a time step of $\Delta t = 0.01$ fs, a total propagation time of T = 50 fs and a boost strength of 0.0001 Ry. We choose a spherical grid radius of $R = 30 a_0$ with a spacing of $\Delta r = 0.5 a_0$. For PTCDA we used a time step of $\Delta t = 0.01$ fs, a total propagation time of T = 50 fs and a boost strength of 0.0001 Ry in combination with a grid radius $R = 40 a_0$ and grid spacing $\Delta r = 0.38 a_0$. After determining the energetic position of the first excitation in the dipole spectrum of PTCDA, we obtain the transition density of the former from a separate calculation employing the same numerical setup.

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