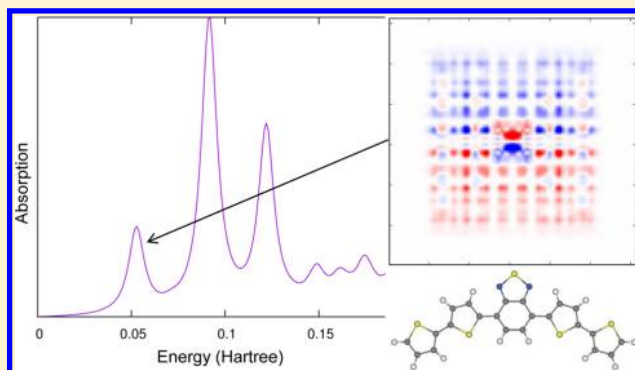


The Particle–Hole Map: A Computational Tool To Visualize Electronic Excitations

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ABSTRACT: We introduce the particle–hole map (PHM), which is a visualization tool to analyze electronic excitations in molecules in the time or frequency domain, to be used in conjunction with time-dependent density-functional theory (TDDFT) or other *ab initio* methods. The purpose of the PHM is to give detailed insight into electronic excitation processes that is not obtainable from local visualization methods, such as transition densities, density differences, or natural transition orbitals. The PHM is defined as a nonlocal function of two spatial variables and provides information about the origins, destinations, and connections of charge fluctuations during an excitation process; it is particularly valuable to analyze charge-transfer excitonic processes. In contrast with the transition density matrix, the PHM has a statistical interpretation involving joint probabilities of individual states and their transitions; it satisfies several sum rules and exact conditions, and it is easier to read and interpret. We discuss and illustrate the properties of the PHM and give several examples and applications to excitations in one-dimensional model systems, in a hydrogen chain, and in a benzothiadiazole (BT)-based molecule.



1. INTRODUCTION

The first-principles calculation of electronic excitation energies and excited-state properties is among the most important tasks in quantum chemistry and many other areas of science. Time-dependent density-functional theory (TDDFT)^{1–3} has achieved much popularity for calculating excitation energies and for simulating electron dynamics in real time, thanks to its favorable balance of accuracy and computational efficiency. TDDFT yields excited-state properties such as transition frequencies, oscillator strengths, or excited-state forces and geometries that are of similar quality as results obtained in ground-state density functional theory (DFT).^{4,5}

Within a single-particle picture such as that given in TDDFT, molecular electronic excitations can be analyzed to determine which single-particle transition is dominant; at times, several single-particle transitions contribute significantly to the excitation of the many-body system. However, it is often desirable to gain additional insight into the nature of an electronic transition, and to analyze the change in the many-body wave function for specific patterns in the rearrangement of the electronic configuration. This is very useful, for instance, in the treatment of charge-transfer (CT) excitations, or for conjugated donor–acceptor molecules. There exist various tools for the analysis of electronic transitions, as reviewed by Dreuw and Head-Gordon.⁶ First of all, one can simply inspect the relevant molecular orbitals close to the highest occupied and lowest unoccupied molecular orbital (HOMO–1, HOMO, LUMO, LUMO+1, etc.).^{7,8} If one transition, for example,

HOMO–LUMO, is dominant, such analysis will be straightforward. Similarly, the density difference between the excited state and the ground state often provides useful insights.^{9,10} Other widely used tools to analyze electronic excitations in molecules are transition densities^{11,12} and natural transition orbitals.^{13–16}

The analysis tools mentioned so far all have in common that they are local (i.e., they are dependent on a single position vector, *r*). However, there are important aspects of electronic excitations that cannot be described using a local quantity, but are intrinsically nonlocal (i.e., they are dependent on two position vectors, *r* and *r'*). For instance, an exciton is a bound electron–hole pair, and one should ask about the position of both the electron and the hole. Or, for a CT excitation process, one might want to know which parts of the system act as donors of charge, and to where that charge is transferred: in other words, one would like a map that indicates the origins and destinations of CT in a molecule or molecular complex, and which donor and acceptor regions are connected. The density difference or the transition density do not contain enough information to answer these questions.

The transition density matrix (TDM)¹⁷ is a well-known concept in quantum chemistry, which has been widely used as a nonlocal visualization tool to map excitonic effects and electron–hole pair coherences for molecular excitations.^{18–31} The TDM is defined as the density matrix connecting the

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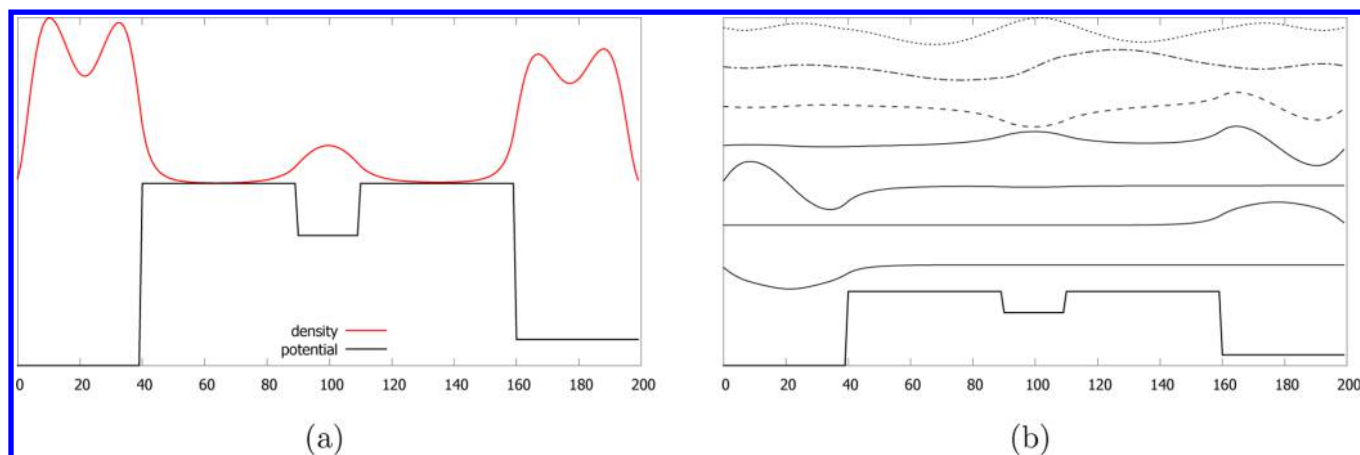


Figure 1. One-dimensional (1D) model with eight electrons confined in a triple potential well: (a) ground-state density and potential wells, and (b) the seven lowest single-particle wave functions.

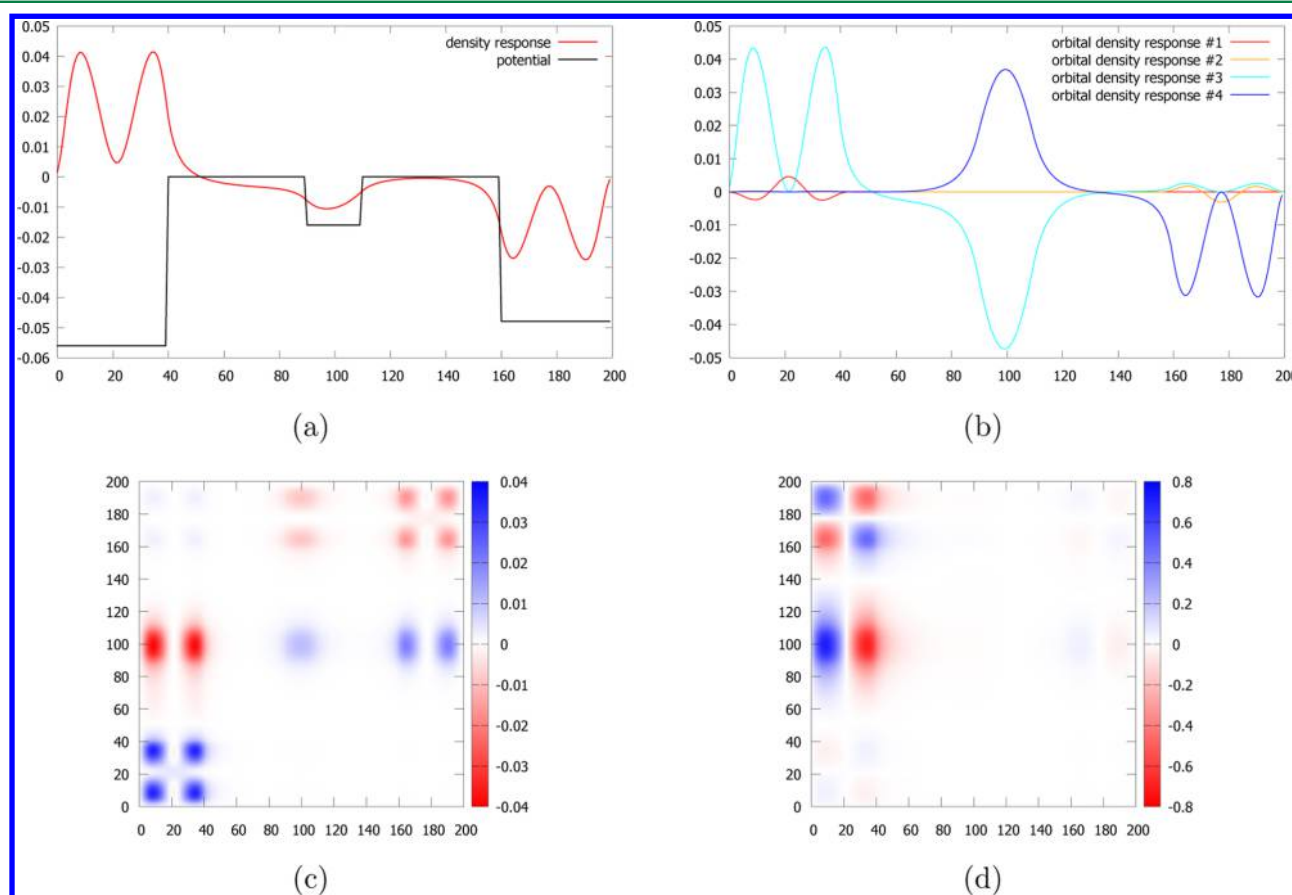


Figure 2. (a) Density response associated with the first excitation; (b) individual density responses of the four occupied orbitals; (c) associated particle–hole map (PHM); and (d) the associated transition density matrix (TDM).

molecular ground state and a particular excited state (the precise definition will be given below in section 3.4). However, despite its popularity, the TDM suffers from various shortcomings, as we will make clear in the following. The purpose of this paper is to introduce an alternative to it: the particle–hole map (PHM).

Before giving precise definitions of the PHM and the TDM (see section 3), we will provide some motivation via a simple illustration. We consider a one-dimensional (1D) model, described by the Kohn–Sham equation,

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{e^2}{4\pi\epsilon_0} \int \frac{n(x') dx'}{\sqrt{(x-x')^2 + \alpha^2}} + v_{\text{ext}}(x) \right] \varphi_i(x) = \epsilon_i \varphi_i(x) \quad (1)$$

Here, α is a parameter used to regularize the one-dimensional (1D) Coulomb interaction, and $v_{\text{ext}}(x)$ is the external confining potential; for simplicity, we only include the Hartree potential and set the exchange–correlation (xc) potential to zero. The occupied and unoccupied Kohn–Sham eigenfunctions $\varphi_i(x)$ serve as input to a TDDFT calculation to obtain the excitation

spectrum and the PHM or TDM corresponding to the n th excitation.

We discretize eq 1 on an equidistant lattice with 200 points in a box with a length of 10 a.u. and infinite walls. As the left panel of Figure 1 shows, $v_{\text{ext}}(x)$ is slightly asymmetric: the left well is slightly deeper than the right one. The system has eight electrons and, hence, four doubly occupied orbitals. The ground-state density indicates that the electrons mainly remain in the left and right wells. Figure 1 also plots the first seven single-particle eigenstates; clearly, the confinement from the wells becomes less important for higher levels.

Figure 2 shows the total density response, the orbital density responses, and the PHM and TDM for the lowest excitation. The density response indicates an electron transfer between the left and right wells. However, the individual orbital density responses reveal that the smaller well in the middle of the system plays a very important role: the responses of the third and fourth orbital have a very large peak in the middle, which is cancelled out in the total response. Thus, even in a simple 1D system such as this one, the problem of identifying the internal motion of the individual charges during an excitation process is not straightforward.

Unfortunately, the TDM does not provide much help in the analysis of the excitation process, but instead leads to a rather distorted picture. As the lower right panel of Figure 2 shows, the TDM does give a hint of the importance of the small well in the middle, but it also produces an asymmetric picture that is rather misleading, since it seems to suggest that the left well hardly participates in the excitation process (as we shall see below, the TDM is to be read with respect to the diagonal).

Instead, the PHM (lower left panel of Figure 2) provides a very clear picture of the charge redistribution during the excitation process: its horizontal axis indicates where charges are coming from, and the vertical axis tells us where they are going to; red and blue indicate electrons and holes, respectively. One can see very nicely that the CT from left to right proceeds via the middle well. We will justify this interpretation of the PHM below, and will outline a set of simple rules about how to construct it and how to read it.

The remainder of this paper is organized as follows. In section 2, we give a brief summary of the basic elements of TDDFT, which will be needed later in this study. Section 3 contains the definition of the PHM in the time domain and in the linear-response frequency domain, as well as a comparison with the TDM. Section 4 contains examples and discussions: in section 4.1, we return to our 1D model system, and in sections 4.4 and 4.5 we discuss application to a hydrogen chain and a benzothiadiazole (BT)-based molecule. Section 5 gives our conclusions.

2. A BRIEF SUMMARY OF TIME-DEPENDENT DENSITY FUNCTIONAL THEORY (TDDFT)

In this section, we briefly summarize the essentials of TDDFT that will be needed for the later discussion. More details on the formal framework of TDDFT can be found elsewhere.^{2,3}

In the following, we will consider N -electron systems that are not magnetic or spin-polarized, so that we can ignore the spin index. The systems are initially in the ground state, described by the static Kohn–Sham equation,

$$\left[-\frac{\hbar^2 \nabla^2}{2m} + v_{\text{nuc}}(\mathbf{r}) + \frac{e^2}{4\pi\epsilon_0} \int d^3r' \frac{n_0(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{\text{xc}}^{(0)}[n_0](\mathbf{r}) \right] \varphi_j^{(0)}(\mathbf{r}) = \epsilon_j \varphi_j^{(0)}(\mathbf{r}) \quad (2)$$

Here, $v_{\text{nuc}}(\mathbf{r})$ is the electrostatic potential caused by fixed classical nuclei (we make the Born–Oppenheimer approximation), and $v_{\text{xc}}^{(0)}[n_0](\mathbf{r})$ is the exchange correlation potential of ground-state DFT, which is a functional of the ground-state density:

$$n_0(\mathbf{r}) = \sum_{j=1}^N |\varphi_j^{(0)}(\mathbf{r})|^2 \quad (3)$$

Equation 2 is solved self-consistently, using a suitable approximation for $v_{\text{xc}}^{(0)}[n_0](\mathbf{r})$.

The majority of applications of TDDFT fall into two categories: propagation in real time under arbitrary external perturbations, or calculation of the frequency-dependent linear-response, which allows one to extract, among other things, the excitation spectrum of the system. In this paper, we will consider both situations.

The time-dependent Kohn–Sham equation, which is given by

$$\left[-\frac{\hbar^2 \nabla^2}{2m} + v_{\text{nuc}}(\mathbf{r}) + v_{\text{ext}}(\mathbf{r}, t) + \frac{e^2}{4\pi\epsilon_0} \int d^3r' \frac{n(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} + v_{\text{xc}}[n](\mathbf{r}, t) \right] \varphi_j(\mathbf{r}, t) = i\hbar \frac{\partial}{\partial t} \varphi_j(\mathbf{r}, t) \quad (4)$$

propagates a set of N Kohn–Sham orbitals forward in time, under the influence of an arbitrary time-dependent external potential $v_{\text{ext}}(\mathbf{r}, t)$ that is switched on at the initial time t_0 . Similar to ground-state DFT, the time-dependent exchange–correlation potential $v_{\text{xc}}[n](\mathbf{r}, t)$ is a functional of the time-dependent density,

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

and must be approximated in practice. Most commonly used is the adiabatic approximation,

$$v_{\text{xc}}^{\text{adia}}[n](\mathbf{r}, t) = v_{\text{xc}}^{(0)}[\tilde{n}](\mathbf{r}) \Big|_{\tilde{n}=n(\mathbf{r}, t)}$$

The time-dependent Kohn–Sham equation given as eq 4 is an initial value problem, where

$$\varphi_j(\mathbf{r}, t) = \varphi_j^{(0)}(\mathbf{r})$$

From the time-dependent density $n(\mathbf{r}, t)$, one then calculates the physical observables of interest, such as the dipole moment $\mathbf{d}(t)$ ($\mathbf{d}(t) = \int d^3r \mathbf{r} n(\mathbf{r}, t)$) and the spectral properties following from it. In this way, one can calculate the optical spectra of molecules, following a pulsed excitation and subsequent free time propagation.³²

A more widely used approach for calculating excitation energies and excited-state properties of molecules is via the frequency-dependent linear response. The idea is that an electronic excitation corresponds to an eigenmode of the electronic density, which can oscillate without any driving force, similar to the normal modes of a classical system of coupled

oscillators. These electronic eigenmodes are found via solution of the so-called “Casida equation”:³³

$$\begin{pmatrix} \mathbf{A} & \mathbf{K} \\ \mathbf{K} & \mathbf{A} \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \Omega \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} \quad (6)$$

where the elements of the matrices \mathbf{A} and \mathbf{K} are given by

$$A_{ia,i'a'}(\omega) = \delta_{ii'}\delta_{aa'}\omega_{ai} + K_{ia,i'a'}(\omega) \quad (7)$$

$$K_{ia,i'a'}(\omega) = \int d^3r \int d^3r' \varphi_i^{(0)*}(\mathbf{r}) \varphi_a^{(0)}(\mathbf{r}) \times \left[\frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{xc}(\mathbf{r}, \mathbf{r}', \omega) \right] \varphi_{i'}^{(0)}(\mathbf{r}') \varphi_{a'}^{(0)*}(\mathbf{r}') \quad (8)$$

and i, i' and a, a' run over occupied and unoccupied Kohn–Sham orbitals, respectively. The exchange–correlation kernel $f_{xc}(\mathbf{r}, \mathbf{r}', \omega)$ is defined via the Fourier transform of

$$f_{xc}(\mathbf{r}, t, \mathbf{r}', t') = \frac{\delta v_{xc}[n](\mathbf{r}, t)}{\delta n(\mathbf{r}', t')} \bigg|_{n_0(\mathbf{r})} \quad (9)$$

Almost all commonly used expressions for f_{xc} are constructed within the adiabatic approximation, wherein the frequency dependence is ignored.

Solution of eq 6 gives, in principle, the exact excitation energies of the n th excited state Ω_n . The eigenvectors \mathbf{X} and \mathbf{Y} can be used to calculate the related oscillator strengths, as well as the transition densities,

$$n_1(\mathbf{r}, \Omega_n) = \sum_{ia} [\varphi_i^{(0)}(\mathbf{r}) \varphi_a^{(0)*}(\mathbf{r}) X_{ia}(\Omega_n) + \varphi_i^{(0)*}(\mathbf{r}) \varphi_a^{(0)}(\mathbf{r}) Y_{ia}(\Omega_n)] \quad (10)$$

i.e., the density fluctuations associated with the n th electronic eigenmode.

For real orbitals, the Casida equation (eq 6) can be recast into the simpler form:

$$\mathbf{CZ} = \Omega^2 \mathbf{Z} \quad (11)$$

where $\mathbf{C} = (\mathbf{A} - \mathbf{B})^{1/2}(\mathbf{A} + \mathbf{B})$, $(\mathbf{A} - \mathbf{B})^{1/2}$ and $\mathbf{Z} = (\mathbf{A} - \mathbf{B})^{1/2}(\mathbf{X} - \mathbf{Y})$. The transition densities then become

$$n_1(\mathbf{r}, \Omega_n) = \sum_{ia} \varphi_i^{(0)}(\mathbf{r}) \varphi_a^{(0)}(\mathbf{r}) \omega_{ia}^{1/2} Z_{ia}(\Omega_n) \quad (12)$$

3. DEFINITION AND PROPERTIES OF THE PARTICLE–HOLE MAP (PHM)

3.1. Densities and Orbital Densities and Their First-Order Responses. Let us consider an N -electron system, starting at time t_0 from the Kohn–Sham ground state, and evolving in time under the influence of an external time-dependent potential. The time-dependent Kohn–Sham orbitals can be written as

$$\varphi_i(\mathbf{r}, t) = \varphi_i^{(0)}(\mathbf{r}) e^{-i\epsilon_i t/\hbar} + \delta\varphi_i(\mathbf{r}, t) e^{-i\epsilon_i t/\hbar} \quad i = 1, \dots, N \quad (13)$$

where $t \geq t_0$ and $\delta\varphi_i(\mathbf{r}, t)$ denotes the deviation of the i th Kohn–Sham orbital from its initial form, which can be expanded as

$$\delta\varphi_i(\mathbf{r}, t) = \sum_{k=1}^{\infty} C_{ik}(t) \varphi_k^{(0)}(\mathbf{r}) e^{i\omega_{ik} t} \quad (14)$$

where $\omega_{ik} = (\epsilon_i - \epsilon_k)/\hbar$. The expansion coefficients can be calculated using standard time-dependent perturbation theory: to first order, one finds

$$C_{ik}^{(1)}(t) = \frac{1}{i\hbar} \int_{t_0}^t H'_{ki}(t') e^{i\omega_{ki} t'} dt' \quad (15)$$

where $H'_{ki}(t)$ is the matrix element of the time-dependent Kohn–Sham potential between the states $\varphi_k^{(0)}(\mathbf{r})$ and $\varphi_i^{(0)}(\mathbf{r})$. In the following, we assume that all Kohn–Sham ground-state orbitals are real.

The expansion given by eq 14 involves a sum over occupied and unoccupied Kohn–Sham orbitals, and we can split it up as $\delta\varphi_i(\mathbf{r}, t) = \delta\varphi_{i,o}(\mathbf{r}, t) + \delta\varphi_{i,u}(\mathbf{r}, t)$, where

$$\begin{aligned} \delta\varphi_{i,o}(\mathbf{r}, t) &= \sum_{j=1}^N C_{ij}(t) \varphi_j^{(0)}(\mathbf{r}) e^{i\omega_{ij} t} \\ \delta\varphi_{i,u}(\mathbf{r}, t) &= \sum_{a=N+1}^{\infty} C_{ia}(t) \varphi_a^{(0)}(\mathbf{r}) e^{i\omega_{ia} t} \end{aligned} \quad (16)$$

We can also obtain $\delta\varphi_{i,u}(\mathbf{r}, t)$ by projection as

$$\delta\varphi_{i,u}(\mathbf{r}, t) = \varphi_i(\mathbf{r}, t) - \sum_{j=1}^N \varphi_j^{(0)}(\mathbf{r}) \int d^3r' \varphi_i(\mathbf{r}', t) \varphi_j^{(0)}(\mathbf{r}') \quad (17)$$

The time-dependent density is given by

$$n(\mathbf{r}, t) = \sum_{i=1}^N |\varphi_i(\mathbf{r}, t)|^2 = \sum_{i=1}^N n_i(\mathbf{r}, t) \quad (18)$$

which defines the orbital densities $n_i(\mathbf{r}, t)$. From the perturbation expansion of the orbitals, we obtain the first-order orbital densities as

$$n_i^{(1)}(\mathbf{r}, t) = n_{i,o}^{(1)}(\mathbf{r}, t) + n_{i,u}^{(1)}(\mathbf{r}, t) \quad (19)$$

where

$$n_{i,o}^{(1)}(\mathbf{r}, t) = \sum_{j=1}^N \varphi_i^{(0)}(\mathbf{r}) \varphi_j^{(0)}(\mathbf{r}) [e^{i\omega_{ij} t} C_{ij}^{(1)}(t) + e^{i\omega_{ji} t} C_{ij}^{(1)*}(t)] \quad (20)$$

and

$$\begin{aligned} n_{i,u}^{(1)}(\mathbf{r}, t) &= \sum_{a=N+1}^{\infty} \varphi_i^{(0)}(\mathbf{r}) \varphi_a^{(0)}(\mathbf{r}) [e^{i\omega_{ia} t} C_{ia}^{(1)}(t) \\ &+ e^{i\omega_{ai} t} C_{ia}^{(1)*}(t)] \end{aligned} \quad (21)$$

It is straightforward to see that the total first-order density response is given by

$$n_1(\mathbf{r}, t) = \sum_{i=1}^N n_{i,u}^{(1)}(\mathbf{r}, t) \quad (22)$$

and all contributions from $n_{i,o}^{(1)}(\mathbf{r}, t)$ sum up to zero. In other words, the total density response only comes from transitions to unoccupied orbitals, as expected. Rotations within the space of occupied Kohn–Sham orbitals are not reflected in the total density response, but they do contribute to the orbital density responses via $n_{i,o}^{(1)}(\mathbf{r}, t)$. These contributions can be significant, and they will be discarded in constructing the PHM.

3.2. The Time-Dependent Particle–Hole Map (PHM). Let us consider the following object:

$$P(\mathbf{r}, \mathbf{r}', t) = \sum_{i=1}^N \{|\varphi_i(\mathbf{r}', t)|^2 - |\varphi_i^{(0)}(\mathbf{r}')|^2\} |\varphi_i^{(0)}(\mathbf{r})|^2 \quad (23)$$

This expression has a straightforward interpretation: it is the sum of the density fluctuations of each time-evolving Kohn–Sham orbital, $|\varphi_i(\mathbf{r}', t)|^2 - |\varphi_i^{(0)}(\mathbf{r}')|^2$, weighted by the density of the i th ground-state orbital $|\varphi_i^{(0)}(\mathbf{r})|^2$. Each term in the sum has the form of a difference of joint probabilities: it is the product of the probability density of the i th ground-state Kohn–Sham orbital at position \mathbf{r} , with the probability density fluctuation, relative to the ground state, of the i th orbital at time t and position \mathbf{r}' .

Let us now assume that the time-dependent perturbation is sufficiently small, so that we can neglect terms of order δ^2 . We then obtain

$$\begin{aligned} |\varphi_i(\mathbf{r}', t)|^2 - |\varphi_i^{(0)}(\mathbf{r}')|^2 &= \varphi_i^{(0)}(\mathbf{r}') \delta\varphi_i(\mathbf{r}', t) + \text{c.c.} \\ &= \varphi_i^{(0)}(\mathbf{r}') \delta\varphi_{i,u}(\mathbf{r}', t) + \varphi_i^{(0)}(\mathbf{r}') \delta\varphi_{i,v}(\mathbf{r}', t) \\ &\quad + \text{c.c.} \end{aligned} \quad (24)$$

We now define the PHM as follows:

$$\Xi(\mathbf{r}, \mathbf{r}', t) = \sum_{i=1}^N \{ \varphi_i^{(0)}(\mathbf{r}') \delta\varphi_{i,u}(\mathbf{r}', t) + \text{c.c.} \} |\varphi_i^{(0)}(\mathbf{r})|^2 \quad (25)$$

The PHM thus involves only those orbital density fluctuations that result from transitions into initially unoccupied Kohn–Sham states. In other words, $\Xi(\mathbf{r}, \mathbf{r}', t)$ is the sum of joint probabilities that a particle originates at position \mathbf{r} and moves, during the excitation process, to position \mathbf{r}' . We will illustrate this later with several examples.

Note that $\Xi(\mathbf{r}, \mathbf{r}', t)$ is expressed in terms of the Kohn–Sham orbitals, which in and by themselves do not have a rigorous physical meaning (it is possible, in principle, to construct a PHM using time-dependent natural orbitals,^{34–36} which may have some formal advantages). Thus, “particle” and “hole” are to be understood as referring to Kohn–Sham particles and holes (or superpositions thereof), rather than to the quasi-particles defined rigorously within many-body theory. As the examples will show, the particles and holes are identified as negative and positive charge distributions with varying degrees of localization.

The time-dependent PHM has several exact properties. First of all, it vanishes at the initial time, $\Xi(\mathbf{r}, \mathbf{r}', t_0) = 0$, and it also vanishes for $t > t_0$ if $v_{\text{ext}}(\mathbf{r}, t)$ is constant (of course, provided that the system starts from the ground state). In addition to these rather obvious requirements, the PHM satisfies two important sum rules:

$$\int \Xi(\mathbf{r}, \mathbf{r}', t) d^3r' = 0 \quad (26)$$

and

$$\int \Xi(\mathbf{r}, \mathbf{r}', t) d^3r = n_1(\mathbf{r}', t) \quad (27)$$

Equation 26 is due to norm conservation; in the present context, it expresses the fact that if during the excitation process an electron is emitted from position \mathbf{r} , a hole of equal and opposite charge remains behind, so that the overall charge of the system does not change. Equation 27, on the other hand, shows that if we integrate over all the “origins”, the PHM

simply delivers the linear density response $n_1(\mathbf{r}', t)$, which is obtained in principle exactly from TDDFT.

3.3. The Frequency-Dependent Particle–Hole Map.

The time-dependent PHM, described by eq 25, provides a real-time visualization of the particle–hole dynamics of electronic excitations, following the solution of the time-dependent Kohn–Sham equation, eq 4. However, most applications of TDDFT are in the frequency-dependent linear-response regime. Let us derive the associated frequency-dependent PHM, which targets a specific excitation with energy Ω_n .

Inserting the expansion given by eqs 16 into eq 25, we obtain

$$\begin{aligned} \Xi(\mathbf{r}, \mathbf{r}', t) &= \sum_{i=1}^N \sum_{a=N+1}^{\infty} \{ C_{ia}(t) e^{i\omega_{ia}t} \varphi_i^{(0)*}(\mathbf{r}') \varphi_a^{(0)}(\mathbf{r}) \\ &\quad + \text{c.c.} \} |\varphi_i^{(0)}(\mathbf{r})|^2 \end{aligned} \quad (28)$$

To identify the coefficients $C_{ia}(t)$, we consider the linear-response case and make use of the sum rule given by eq 27. If the system is in an electronic eigenmode corresponding to the n th excited state, then the linear density response is given by

$$n_1(\mathbf{r}, t) = e^{-i\Omega_n t} n_1(\mathbf{r}, \Omega_n) \quad (29)$$

However, the frequency-dependent density response follows from the Casida equation (see eq 10), and comparison suggests that the frequency-dependent PHM is given by³⁷

$$\begin{aligned} \Xi(\mathbf{r}, \mathbf{r}', \Omega_n) &= \sum_{ia} \{ \varphi_i^{(0)}(\mathbf{r}') \varphi_a^{(0)*}(\mathbf{r}') X_{ia}(\Omega_n) \\ &\quad + \varphi_i^{(0)*}(\mathbf{r}') \varphi_a^{(0)}(\mathbf{r}') Y_{ia}(\Omega_n) \} |\varphi_i^{(0)}(\mathbf{r})|^2 \end{aligned} \quad (30)$$

For the case of real orbitals (see eqs 11 and 12), this expression simplifies to

$$\Xi(\mathbf{r}, \mathbf{r}', \Omega_n) = \sum_{ia} |\varphi_i^{(0)}(\mathbf{r})|^2 \varphi_i^{(0)}(\mathbf{r}') \varphi_a^{(0)}(\mathbf{r}') \omega_{ia}^{1/2} Z_{ia}(\Omega_n) \quad (31)$$

Thus, the frequency-dependent PHM can be obtained in a straightforward manner from the solutions of the Casida equation. It is easy to see that it satisfies the sum rules

$$\begin{aligned} \int \Xi(\mathbf{r}, \mathbf{r}', \Omega_n) d^3r' &= 0 \\ \int \Xi(\mathbf{r}, \mathbf{r}', \Omega_n) d^3r &= n_1(\mathbf{r}', \Omega_n) \end{aligned} \quad (32)$$

in analogy with the sum rules for the time-dependent PHM (see eqs 26 and 27).

In the following, we use the abbreviations PHM_ω and PHM_t for the frequency-dependent and time-dependent particle–hole maps, respectively.

Before we conclude this section, let us add one more comment. In this paper, we focus on applications of the PHM_t in the linear regime, restricting the calculations to weak and essentially monochromatic external fields in order to demonstrate that the time- and frequency-dependent PHMs are consistent. However, the PHM_t is suitable for arbitrary time-dependent potentials, as long as one remains in the linear regime; this opens up a wide field of application in the area of ultrafast dynamics.

To go beyond the linear regime, one could attempt to generalize the definition of the PHM_t and include terms of order δ^2 . However, in the nonlinear regime, it is no longer justified to discard the contributions of the initially occupied

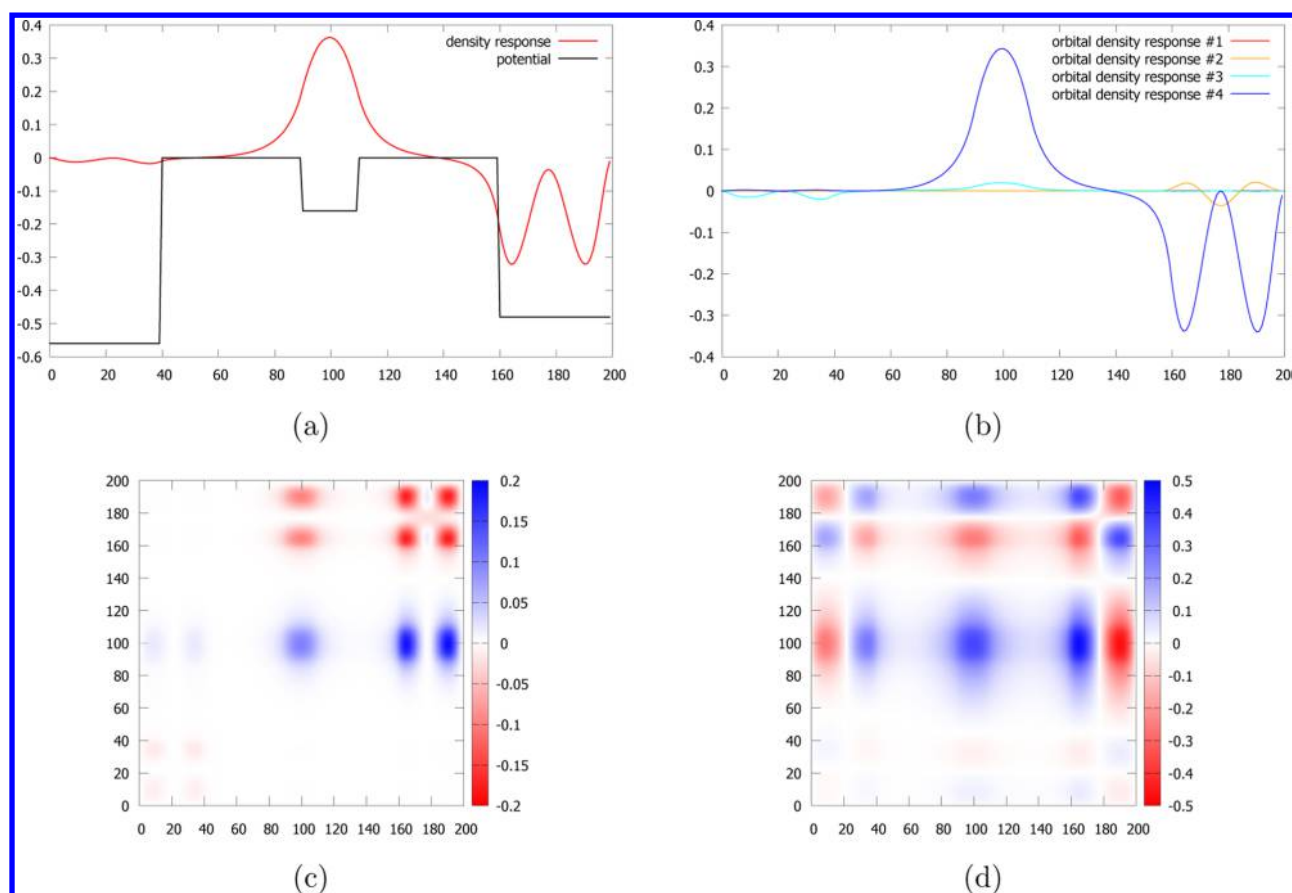


Figure 3. (a) Density response associated with the second excitation; (b) individual density responses of the four occupied orbitals; (c) the associated PHM_ω; and (d) the associated TDM.

orbitals in the induced change $\delta\varphi_i(\mathbf{r},t)$ of the i th Kohn–Sham orbital. In that case, it will be preferable to work directly with the joint probability $P(\mathbf{r},\mathbf{r}',t)$ of eq 23.

3.4. Comparison with the Transition Density Matrix (TDM). The TDM associated with an electronic transition between the many-body ground state Ψ_0 and the n th excited state Ψ_n is defined as^{17,20,38}

$$\Gamma_n(\mathbf{r}, \mathbf{r}') = \langle \Psi_n | \hat{\rho}(\mathbf{r}, \mathbf{r}') | \Psi_0 \rangle \quad (33)$$

where $\hat{\rho}(\mathbf{r},\mathbf{r}')$ is the reduced one-particle density matrix operator. The TDM can be obtained from the solutions of eq 6, as follows:³⁸

$$\Gamma_n(\mathbf{r}, \mathbf{r}') = \sum_{ia} \{ \varphi_i^{(0)}(\mathbf{r}') \varphi_a^{(0)*}(\mathbf{r}) X_{ia}(\Omega_n) + \varphi_i^{(0)*}(\mathbf{r}) \varphi_a^{(0)}(\mathbf{r}') Y_{ia}(\Omega_n) \} \quad (34)$$

For real orbitals (see eqs 11 and 12), this becomes

$$\Gamma_n(\mathbf{r}, \mathbf{r}') = \frac{1}{2} \sum_{ia} \{ \varphi_i^{(0)}(\mathbf{r}') \varphi_a^{(0)}(\mathbf{r}) (\omega_{ai}^{1/2} + \omega_{ai}^{-1/2}) + \varphi_i^{(0)}(\mathbf{r}) \varphi_a^{(0)}(\mathbf{r}') (\omega_{ai}^{1/2} - \omega_{ai}^{-1/2}) \} Z_{ia}(\Omega_n) \quad (35)$$

The diagonal of the TDM is equal to the transition density, i.e., $\Gamma_n(\mathbf{r},\mathbf{r}) = n_1(\mathbf{r},\Omega_n)$.

In an earlier paper, we defined the time-dependent TDM as³⁹

$$\Gamma(\mathbf{r}, \mathbf{r}', t) = \langle \Psi(t) | \hat{\rho}(\mathbf{r}, \mathbf{r}') | \Psi_0 e^{-iE_0 t} \rangle \quad (36)$$

where $\Psi(t)$ is the time-dependent many-body wave function that evolves from the ground state Ψ_0 . In TDDFT, the exact wave function is not available, but it can be approximated by the time-dependent Kohn–Sham Slater determinant. The time-dependent TDM can then be expressed in terms of the time-dependent Kohn–Sham orbitals. One can then plot the difference of the absolute squares of the time-dependent TDM and the ground-state Kohn–Sham density matrix, $|\Gamma^{\text{KS}}(\mathbf{r},\mathbf{r}',t)|^2 - |\Gamma_0^{\text{KS}}(\mathbf{r},\mathbf{r}')|^2$.

4. IMPLEMENTATION AND EXAMPLES

4.1. One-Dimensional (1D) Model System Revisited:

How To Read the PHM. The PHM produces a map that illustrates the charge motion and redistribution during an excitation process. There are various ways in which such a map can be realized in practice. For example, in our 1D triple-well model introduced in Section 1, the full PHM_ω, $\Xi(x,x',\Omega_n)$, has 200×200 pixels (corresponding to the 200 grid points). The horizontal label (the x -axis) indicates where an electron or hole is originating from, and the vertical label (the x' -axis) indicates where it is going. Each pixel contains the associated joint probability fluctuation, according to the definition given by eq 25. This can be a positive or a negative number: we associate a positive number with the probability of an electron (here, color-coded as blue) and a negative number with the probability of a hole (represented as red). Any signature in the PHM that is located near the diagonal indicates that the origin and destination coincide, so there is no transfer.

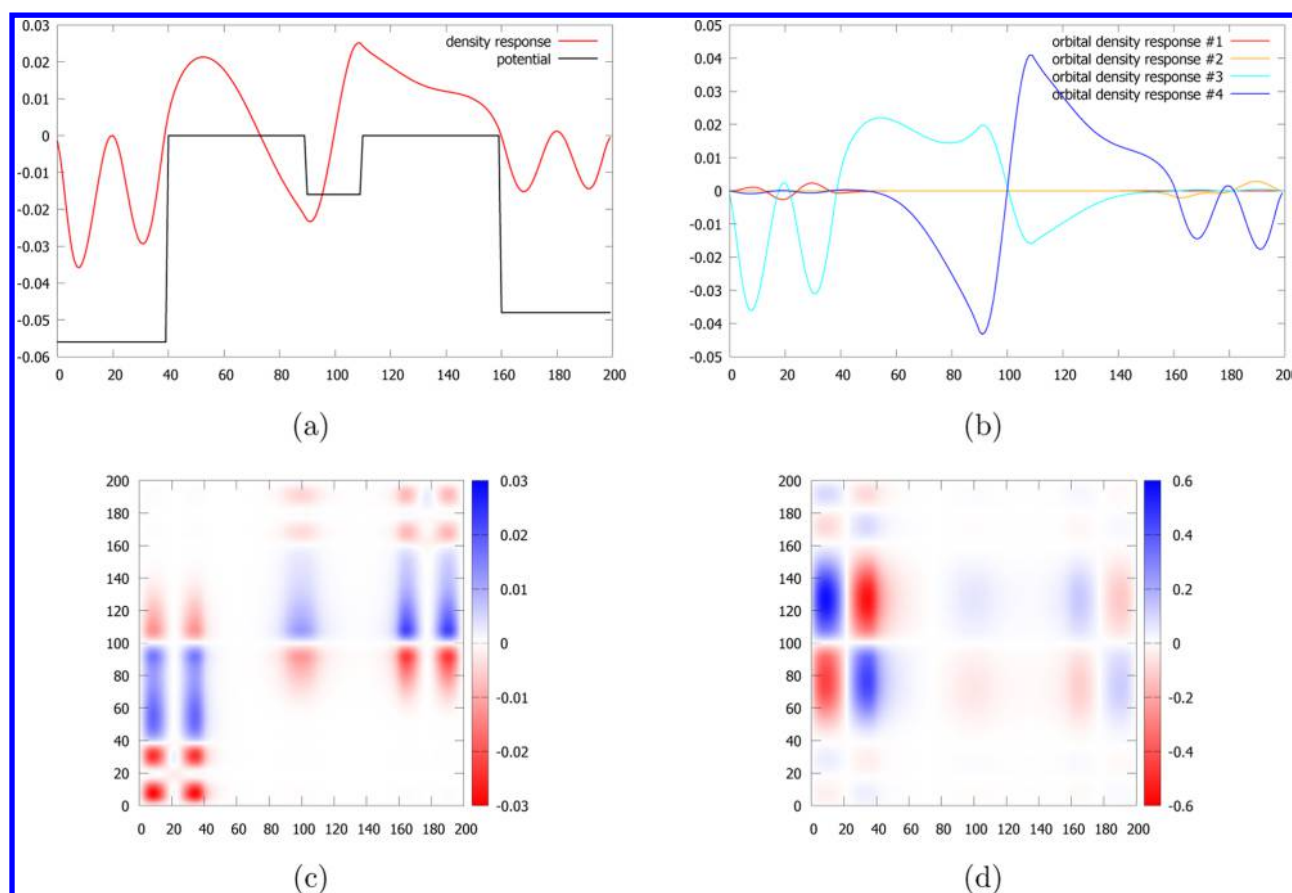


Figure 4. (a) Density response associated with the third excitation; (b) individual density responses of the four occupied orbitals; (c) the associated PHM_ω ; and (d) the associated TDM.

Let us now give a more-detailed explanation of the PHM_ω shown in Figure 2. From the orbital density response, we can see that there are two major contributions in the first excitation: the left-middle CT and the right-middle CT. Columns 1–40 contain the information on left-middle CT, since they describe the excitations *from* the left well. The four blue patches indicate an electron staying in the left quantum well while a hole goes to the middle well. The detailed structure is related to the double peaks of the ground-state density on the left and on the right.

From the vertical band around column 100, we see that an electron is left in the middle well and the hole goes to the right well. Similarly, we can read the vertical band between columns 160–200 as representing an electron transfer to the middle well and a corresponding hole left behind. The horizontal rows represent how the final density response is a superposition of different CT processes. For example, the horizontal band in the middle of the map shows how the hole from the right well is neutralized by the electron from center and right wells. For each point in the system, summing over all the electron and hole probabilities coming from the entire system leads to the total density response.

By contrast, the TDM is difficult to interpret. The diagonal, which is the density response, is relatively small, compared to the left top block. Mathematically, it is due to the fact that orbital 3 and orbital 5 contain almost no common nonzero part. On this level, one does not see a clear explanation of the observed pattern, and one cannot derive any useful information from it. It is also difficult to apply the delocalization length and

the coherence length concept to the plot, since this is not a large molecular chain system.²⁰

In Figure 3, which illustrates the second excitation, the PHM_ω and the TDM are not so drastically different. From the PHM_ω , we see that the upper right block (columns 80–200) is similar to what was seen for the first excitation. It shows that this excitation only involves charge fluctuations within the right part of the system. The TDM gives a similar message, but one must reckon with respect to the diagonal, which is not so intuitive.

For the third excitation (see Figure 4), the charge redistributions are no longer confined to the wells but also appear on top of the barriers. The PHM_ω shows that the charge fluctuation on the left barrier comes from the left well only, while the charge on the right barrier comes from the middle and right wells. The signatures on the barriers are rather diffuse. As previously noted in Figure 2, the TDM suffers from a lack of clarity along the diagonal.

4.2. One-Dimensional (1D) Model System Revisited: PHM_ω versus PHM_r . Another simple 1D example is given in Figure 5. The potential has several barriers and wells that are intended to represent a 1D molecule-like system with seven doubly occupied Kohn–Sham orbitals. We see that the first excitation is dominated by a single orbital density response with a strong peak around column 60. There are clear features in the PHM_ω around column 60 and row 60. By contrast, the TDM does not allow one to extract any useful information.

The second excitation, shown in Figure 6, is selected because it is dominated by two orbital density responses, which makes it

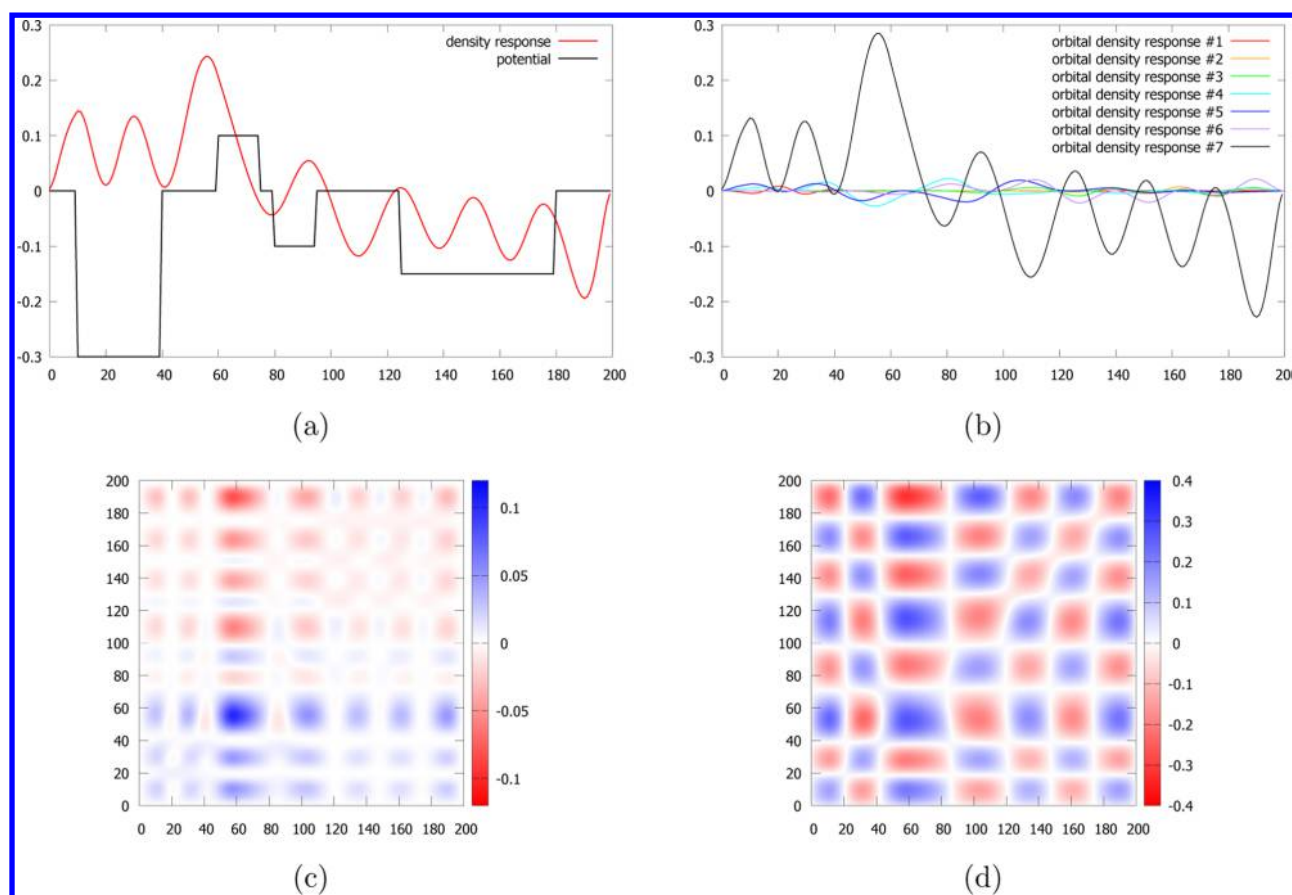


Figure 5. (a) Density response associated with the first excitation in a 1D system; (b) individual density responses of the seven occupied orbitals; (c) the associated PHM_ω ; and (d) the associated TDM.

a more interesting case. We will use it as an example to compare the PHM_ω and the PHM_t .

We solve the time-dependent Kohn–Sham equation with an external potential of the form

$$v_{\text{ext}}(x, t) = \begin{cases} V_0(x)A \sin^2\left(\frac{\pi}{w}t\right) \sin(\omega t) & 0 < t < w \\ 0 & t > w \end{cases} \quad (37)$$

Here, the term $A \sin^2[(\pi/w)t]$ defines the time envelope of the field. The width w of the envelope is selected to include 30 cycles of the oscillation, and the frequency ω is chosen as the second excitation energy. We found that $V_0(x)$, which is the spatial shape of the external field, only has a very minor influence on the density response. The scaled time-dependent density fluctuation agrees with the linear response very well, as shown in the left panel of Figure 7. The right panel of Figure 7 shows the PHM_t . We observe a very nice agreement of the time-dependent snapshot with the frequency-dependent map PHM_ω of Figure 6.

4.3. Representations for Three-Dimensional (3D) Systems. For real systems such as molecules and solids, Ξ is a complicated function of six spatial coordinates. To extract any visual information from the PHM, simplification and reduction to lower dimensionality is necessary. This can be done in various ways, depending on the system under consideration and on the computational approach.

For instance, one can plot $\Xi(\mathbf{r}_0, \mathbf{r}', t)$ or $\Xi(\mathbf{r}_0, \mathbf{r}', \Omega_n)$ as a function of \mathbf{r}' in a given plane cutting through a molecule or

solid, where both \mathbf{r}_0 and \mathbf{r}' are restricted to lie in the plane and \mathbf{r}_0 is a fixed reference point. This produces a direct 2D image of the PHM, analogous to the way in which exciton wave functions and electron–hole distributions in periodic systems are typically plotted.^{40–42} A disadvantage of this way of representing the PHM is that this limits the information one can extract to one origin, \mathbf{r}_0 , at a time.

Alternatively, one can reduce the complexity of Ξ by spatial averaging or coarse-graining procedures. For instance, the Kohn–Sham molecular orbitals are often expressed on an atom-centered basis:

$$\varphi_j(\mathbf{r}, t) = \sum_{l=1}^{N_A} \sum_{k=1}^{M_l} \zeta_{jk}^l(t) \eta_k^l(\mathbf{r}) \quad (38)$$

where N_A is the number of atoms in the molecule and M_l is the number of basis functions in the l th atom. If this expansion is inserted into eqs 25, 30, or 31, a complication arises because the Kohn–Sham orbitals enter quadratically, which leads to cross-terms between basis functions belonging to different atoms. To eliminate these terms, one can make the approximation of zero overlap, $\eta_k^l(\mathbf{r})\eta_{k'}^{l'}(\mathbf{r}) \approx 0$ for $l \neq l'$. This allows one to represent the time- and frequency-dependent PHMs as $\Xi_{lm}(t)$ and $\Xi_{lm}(\Omega_n)$, respectively, where the indices l and m run over all atomic origins and destinations of particles and holes. The result is a two-dimensional array that is analogous to the TDMs found in the literature.^{18–28}

Instead of using basis sets, some codes solve the Kohn–Sham equations on a real-space grid, in which case it is convenient to work with a real-space partitioning scheme. We

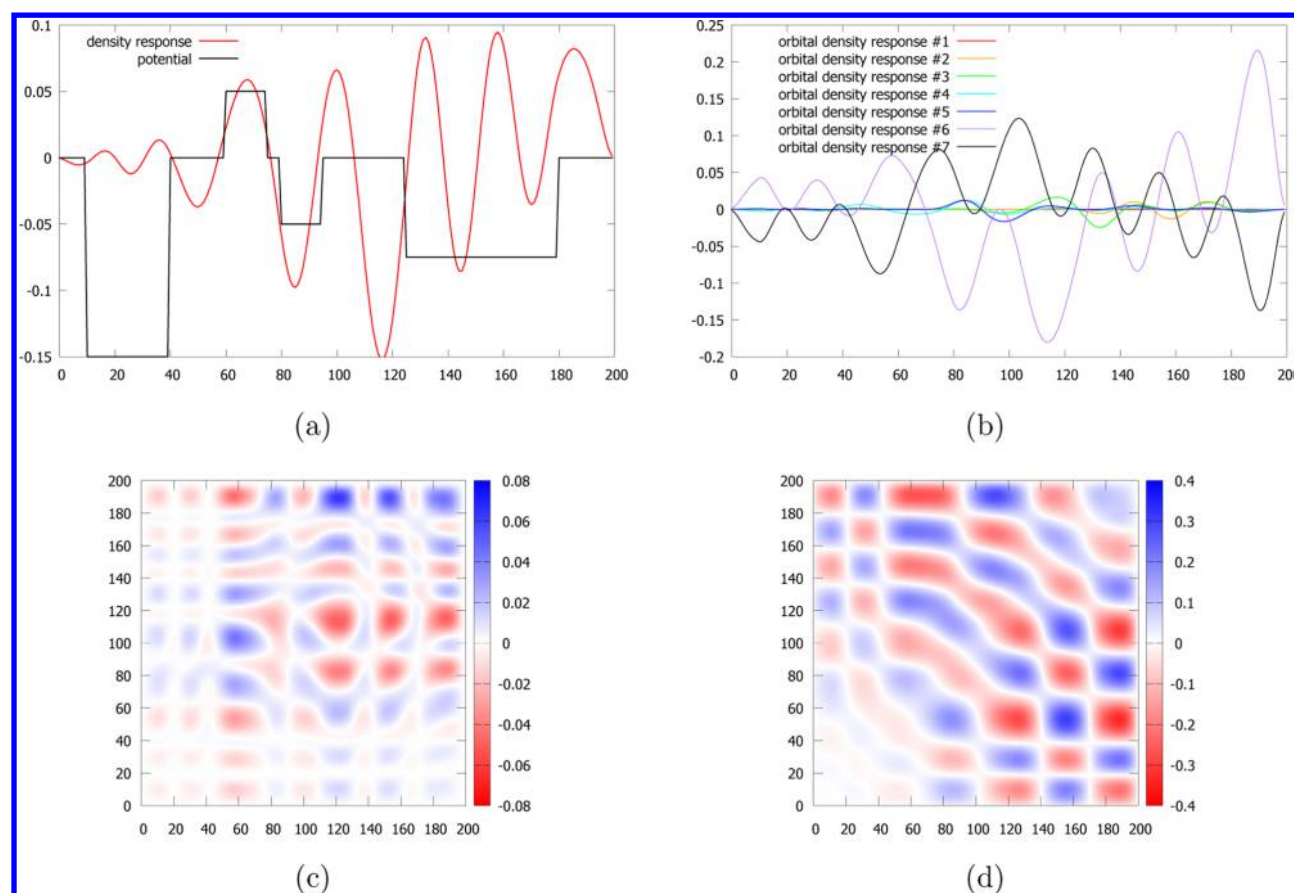


Figure 6. (a) Density response associated with the second excitation in a 1D system; (b) individual density responses of the seven occupied orbitals; (c) the associated PHM_o; and (d) the associated TDM.

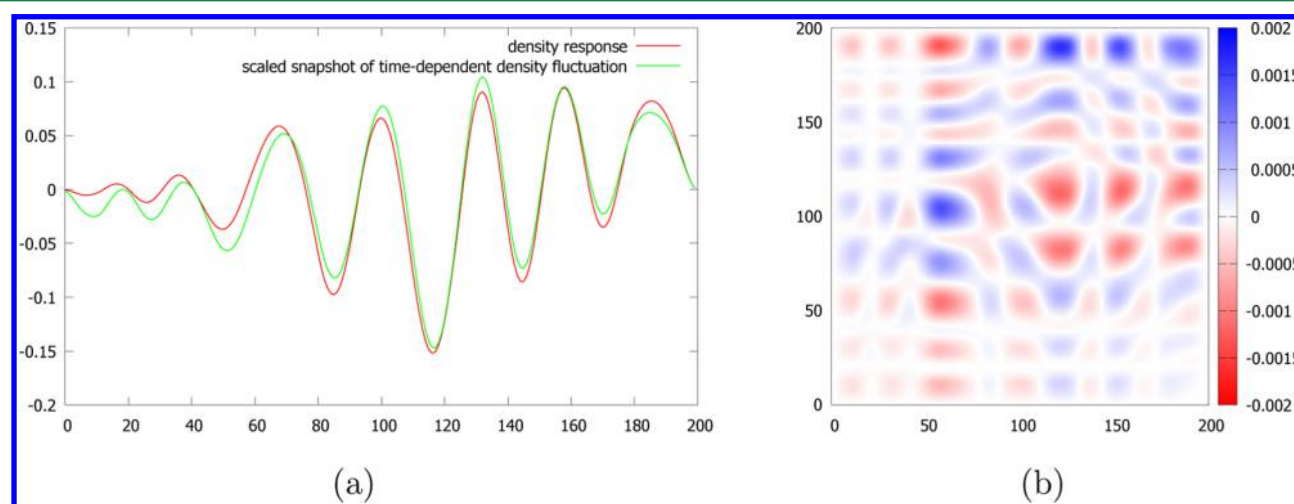


Figure 7. (a) Comparison of the total density fluctuation for the second excitation obtained from frequency-dependent linear response and from time propagation (the snapshot is taken after the external field vanished); (b) the associated PHM_r.

have implemented such a scheme for the octopus code,⁴³ as we will now discuss.

Any spatial partitioning can be defined in terms of a set of weight functions, where different weights are assigned to different spatial locations. Consider a function $f(\mathbf{r})$ that is defined over all space; we define a partitioning operator \hat{P}_q acting on $f(\mathbf{r})$ as

$$\hat{P}_q[f(\mathbf{r})] = \int d^3r w_q(\mathbf{r})f(\mathbf{r}) \quad (39)$$

We assume the weight function $w_q(\mathbf{r})$ to be 1 if \mathbf{r} lies within the q th bin; otherwise, $w_q(\mathbf{r}) = 0$. Hence, \hat{P}_q simply performs an average of $f(\mathbf{r})$ over the q th bin. The weight functions are assumed to seamlessly cover all space, $\sum_{q=1}^{N_B} w_q(\mathbf{r}) = 1$, where N_B is the number of bins.

Figure 8 shows examples of spatial partitioning for a linear molecule. The first two examples, shown in Figures 8a and 8b, show a partitioning into equally sized boxes, but with different degrees of coarse graining; this division of space is particularly

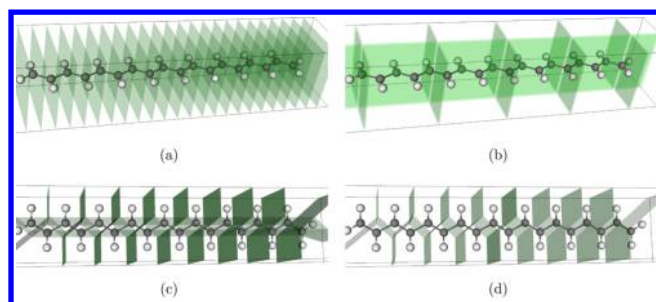


Figure 8. Schematic illustrations of spatial partitioning schemes for molecules: (a, b) box partitioning, (c) atom-centered partitioning, and (d) atom-centered partitioning with hydrogen ignored.

simple, and yields a straightforward connection between molecular geometry and spatial map. Clearly, this type of box partitioning is most useful for molecules with a linear structure and may become less practical for molecules of a more general (i.e., nonlinear) shape.

Having bins with identical sizes and shapes is conceptually straightforward but by no means necessary. A spatial partitioning method with more flexibility, the atom-centered partitioning, is shown in Figures 8c and 8d. Here, we define the q th bin as that region in space that is closer to the q th atom than to any other atom; this method is similar to the definition of the Wigner–Seitz unit cell in a solid.

4.4. The PHMs for a Hydrogen Chain. Let us consider a simple hydrogen chain with eight H atoms. This is not a particularly interesting system, as far as the charge dynamics during excitation processes is concerned, but it is simple and useful as a proof of concept to illustrate our approach. We calculate the linear response and the time-dependent propagation using the adiabatic local-density approximation (ALDA) for the exchange-correlation potential and the exchange-correlation kernel. The 3D objects are reduced by using the box partitioning scheme, as discussed above (see Figures 8a and 8b).

In Figure 9, the excitation spectrum and the PHM_ω associated with the first three excitation frequencies are shown. The first and the second excitation produce similar maps, with a significant accumulation of electron and hole charges at the opposite ends of the chains. The third excitation is somewhat more confined to the interior of the chain. Because of the delocalized nature of the molecular orbitals, the maps appear rather uniform, with no outstanding CT features (as expected).

Figure 10 shows four snapshots taken during the time propagation of the H_8 chain, subject to a laser pulse at the first excitation frequency. The pattern is very similar to the corresponding PHM_ω (Figure 9b), with a time periodicity associated with the density response. There is a periodic

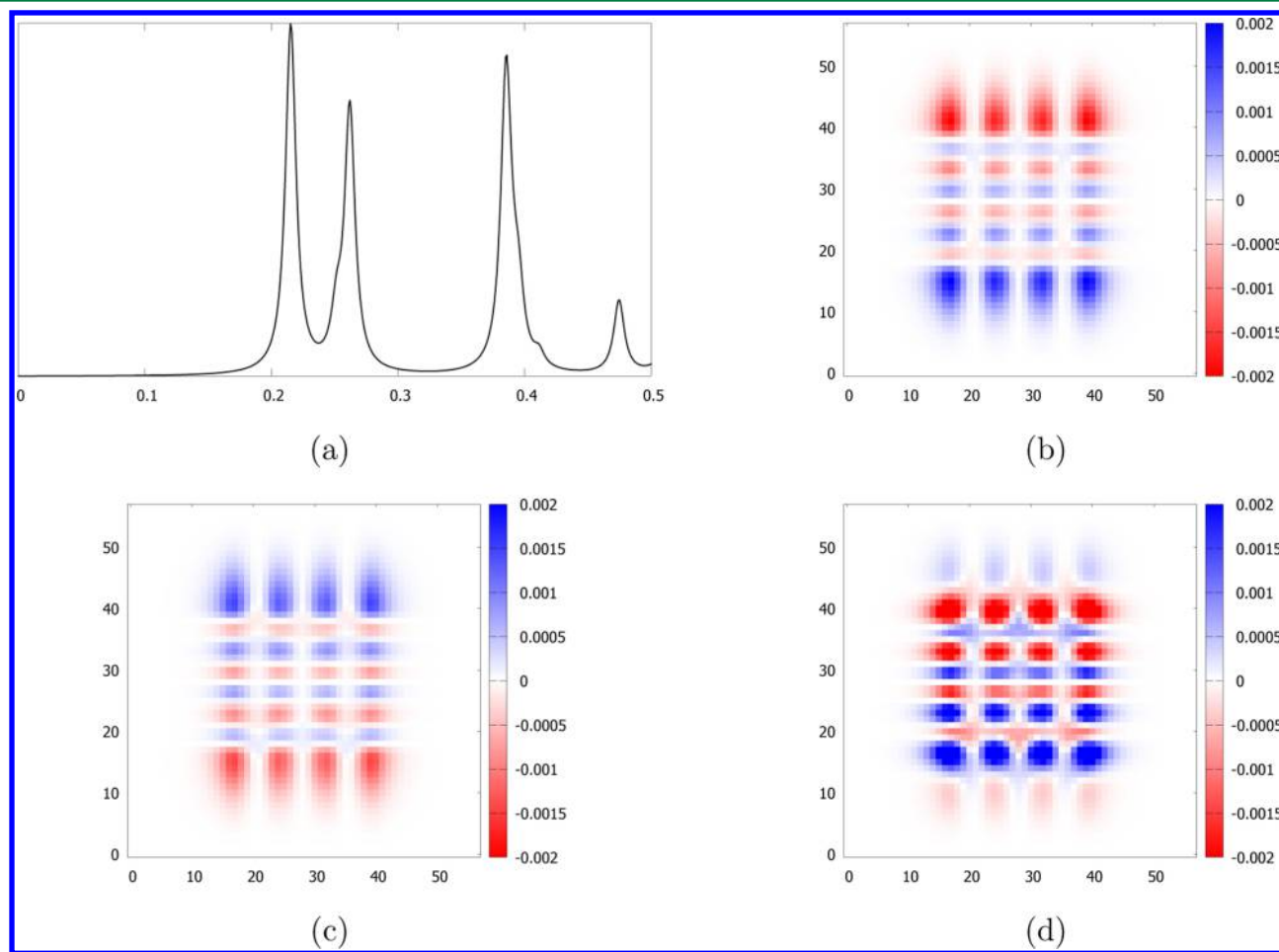


Figure 9. (a) Excitation spectrum of an H_8 linear chain, obtained using linear response with ALDA; (b) PHM_ω for the first excitation peak; (c) PHM_ω for the second excitation peak; (d) PHM_ω for the third excitation peak.

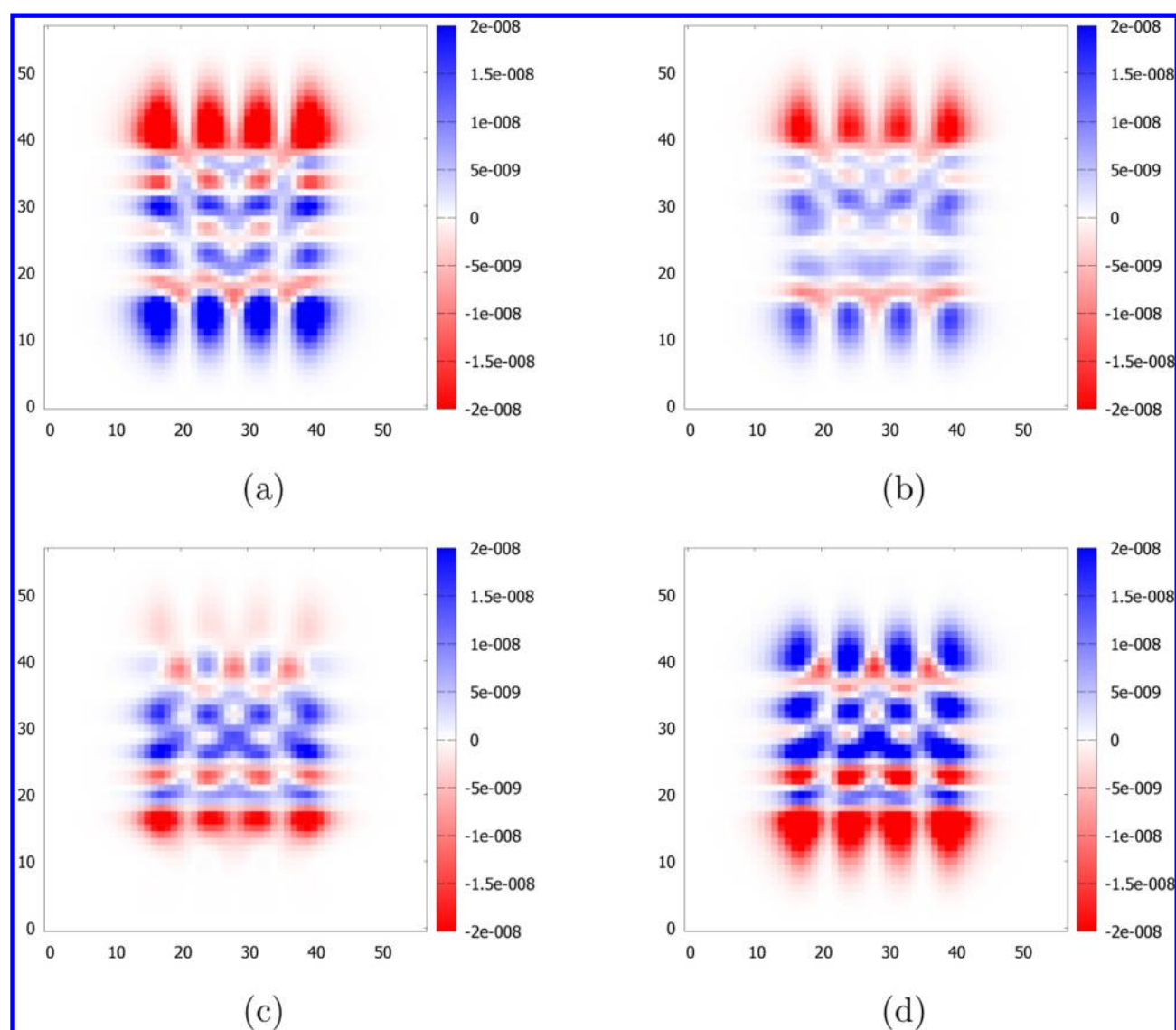


Figure 10. Series of snapshots of the PHM_t in an early stage of the simulation. The time-dependent potential is in resonance with the first excitation of H_8 . The snapshots start at 2.36 fs (panel a) and end at 2.47 fs (panel d).

oscillation of charge density back and forth along the chain, with a spatial modulation imprinted by the individual H atoms.

In this example, the driving external potential was chosen to be monochromatic and on resonance with a given excitation energy, with a rather small amplitude and with a slowly changing pulse envelope, in order to allow a comparison with the PHM_ω coming from frequency-dependent linear response theory. However, generally, no such restriction is necessary: the PHM_t can be calculated for arbitrary time-dependent fields, as long as they are sufficiently weak, so that the dynamics remains in the linear regime.

4.5. The PHM_ω for a Benzothiadiazole (BT)-Based Molecule. We now apply the PHM_ω concept to a benzothiadiazole (BT)-based donor–acceptor–donor (DAD) molecule, illustrated in Figure 11. This system belongs to a class of organic molecules that have been well-studied for years, since they are known as promising materials for photovoltaic applications.⁴⁶ The BT DAD system is well-suited for our purposes, because it will allow us to illustrate how the PHM works for intramolecular CT processes.

Figure 11 shows the structure of BT, including two thiophene units on each side (which are expected to act as donors); in practice, systems of this form may include side chains of various types, which we have neglected here. We also show the most important molecular orbitals, from HOMO–2 to LUMO+3, calculated using the B3LYP hybrid functional.⁴⁷ The excited states were then calculated using ALDA. Clearly, the orbitals extend over the entire system without concentration to any particular thiophene or the BT unit.

The solution of the TDDFT linear-response, eq 6, yields the optical spectrum given in Figure 12a. The figure shows that there are three significant peaks at low energies; the associated transition densities are also given. The transition densities hint at a pronounced polarization behavior along the entire system, as well as between neighboring units; let us now see whether the PHM_ω will give us more insight into the nature of the excitations. The PHM_ω values are shown in Figure 13. They were again calculated using a simple partitioning scheme obtained by slicing along the x -direction (see Figures 8a and 8b).

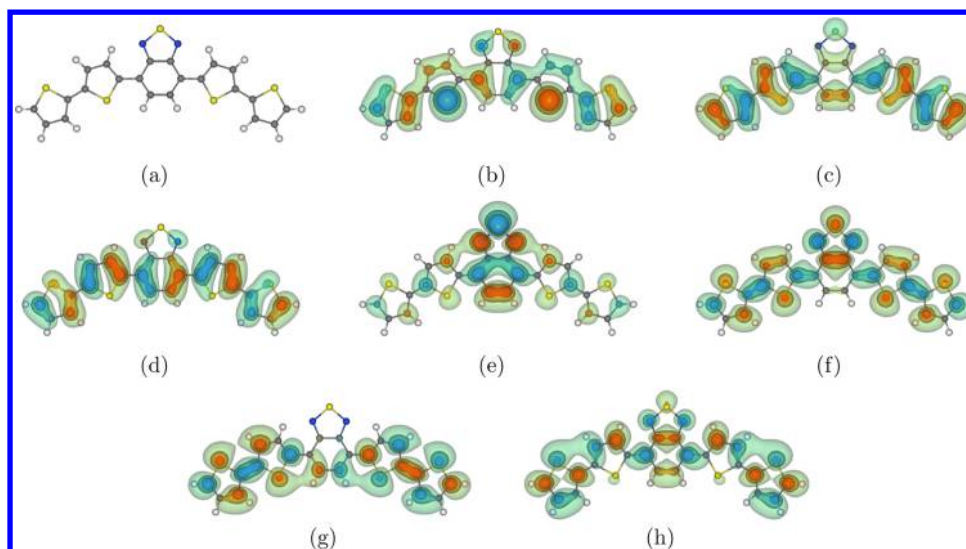


Figure 11. (a) Structure of benzothiadiazole (BT); (b) HOMO-2; (c) HOMO-1; (d) HOMO; (e) LUMO; (f) LUMO+1; (g) LUMO+2; and (h) LUMO+3.

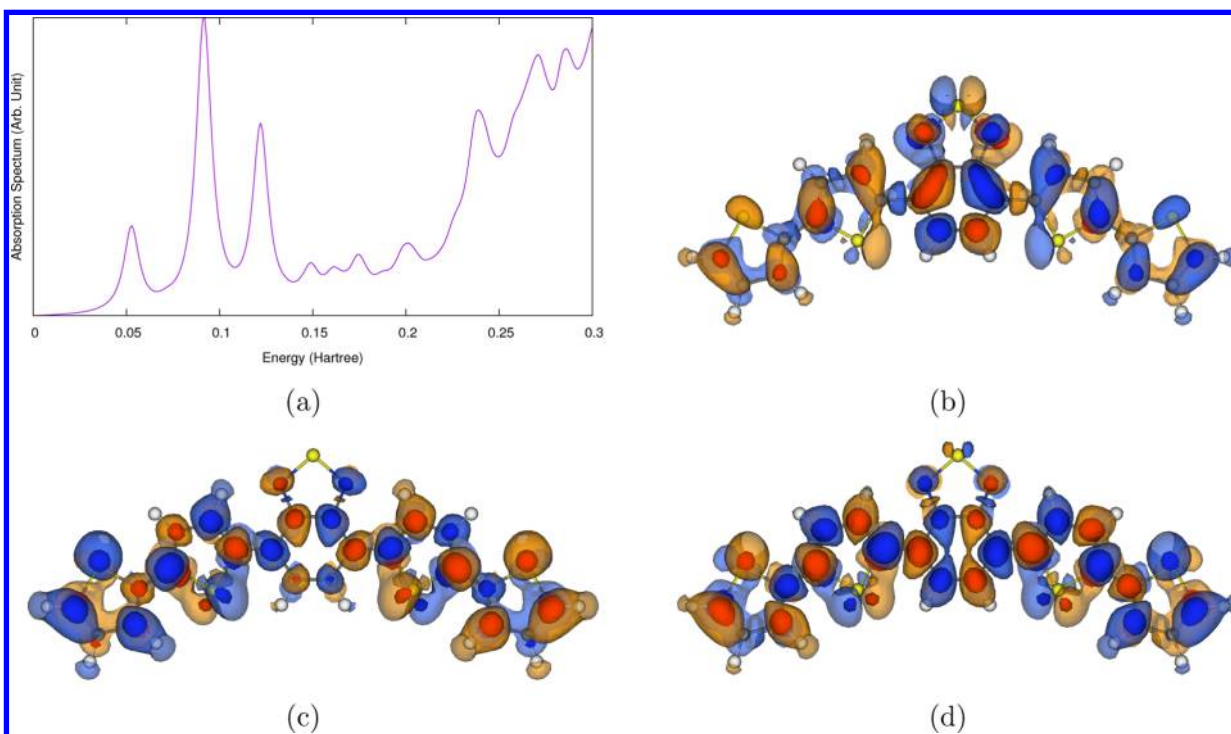


Figure 12. (a) Absorption spectrum of BT; (b–d) transition densities associated with the peaks located at 0.0527, 0.0915 and 0.122 hartree, respectively (red features represent density depletion, and blue features represent density accumulation.)

The PHM_w values for the first three excitations show intricate patterns of charge redistribution, and they indicate that the BT central unit and the thiophene side units play very different roles. For the lowest excitation (Figure 13b), we see that there appears to be a rather uniformly polarized background, but the central part shows the reverse behavior. The vertical columns around 20–30 and 90–100 suggest that the leftmost and rightmost thiophene units contribute uniformly to the polarization of the system. However, the other two thiophene units (columns 40–50 and 75–85) are strongly influenced by the proximity to BT and transfer a significant amount of electron and hole probability to the BT unit.

The PHM_w values for the second and third excitations can be analyzed along similar lines. In the second excitations, the left and right thiophene units are not strongly involved and play a rather passive role; by contrast, the two central thiophenes and the BT unit give rise to a significant electron–hole redistribution. The third excitation is even more complex, but again the BT unit stands out.

Overall, the PHM_w values that are shown in Figure 13 do not exhibit a very strong intramolecular CT character; this would, for instance, be the case if a vertical column starting at one end of the molecule would only end up at the middle, rather than extend over the entire length of the molecule. A possible reason for the rather-delocalized nature of the excitations that we

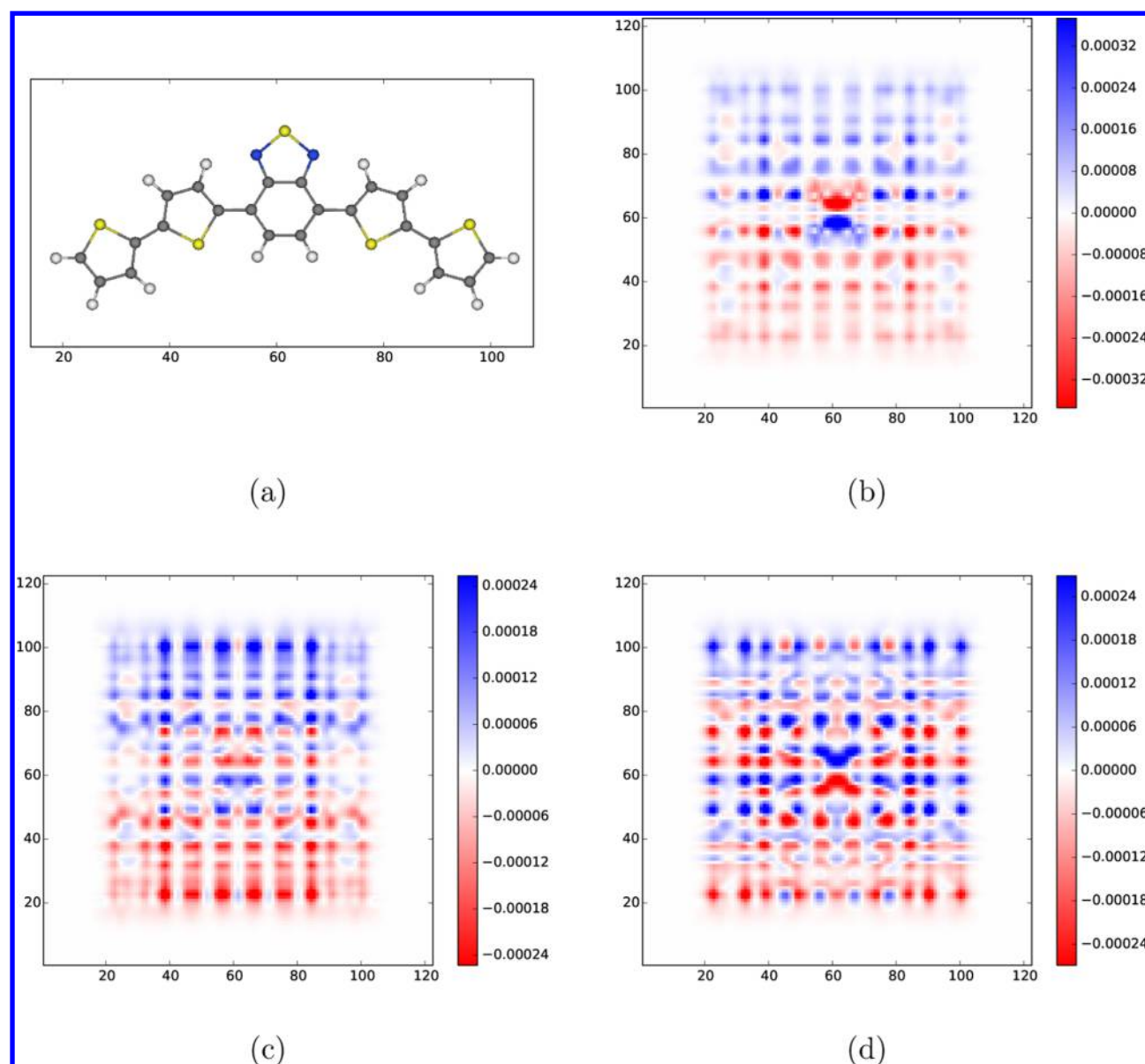


Figure 13. (a) Coordinates for the PHM box partitioning (horizontal label defines the slicing along the x -direction); (b–d) PHM_ω for the first three excitations.

observe here is that the TDDFT calculations were performed with the ALDA. Other, more-sophisticated exchange-correlation functionals (for instance, certain classes of hybrid functionals) are known to better capture CT excitations. Further tests will be required to ascertain this.

5. CONCLUSION

In this paper, we have proposed a new computational tool, the Particle–Hole Map (PHM), which can be used to visualize not only the charge redistribution, but the detailed origins and destinations of electrons and holes during an excitation process. Hence, it is ideally suited to identify and characterize charge-transfer (CT) excitonic effects. The method is applicable to a wide range of materials, from molecules to solids.

We have defined the PHM both in the frequency and in the time domain, to be applied as a post-processing tool, following a time-dependent density functional theory (TDDFT) calculation. The parameters PHM_ω and PHM_t are defined in

terms of Kohn–Sham orbital densities; this means that they are not formally rigorous observables in terms of the density, but they rely on giving physical meaning to individual Kohn–Sham orbitals. This may be questioned, from a formal point of view, but there is a general consensus that the Kohn–Sham orbitals are more than just auxiliary quantities and, indeed, have a considerable degree of physical significance,⁴⁴ particularly if they have been obtained with high-quality exchange-correlation functionals.

The main appeal of the PHM_ω and PHM_t is their interpretation in terms of joint probabilities of ground-state orbital densities and excited-state density fluctuations. In view of this, we can simply say that the PHM tells us where electrons and holes are coming from and where they are going during an excitation process. No other nonlocal visualization tool (such as the transition density matrix (TDM)) has such a simple interpretation. In addition, the PHMs satisfy physically important sum rules.

We have illustrated the PHMs with various examples. Simple one-dimensional (1D) model systems teach us the rules regarding how to read the PHMs, and show us that the parameters PHM_o and PHM_t are consistent with each other. In three-dimensional (3D) systems, a dimensional reduction is necessary; we have given several such schemes, depending on the particular mode of calculation. The majority of numerical calculations in molecules are carried out with atom-centered basis sets, and it is straightforward to construct the PHMs in this case. Here, we carried out calculations using the grid-based octopus code, and, for this purpose, we introduced spatial partitioning schemes that amount to simple binning. Applications to linear H_8 chains and to benzothiadiazole (BT)-based donor–acceptor–donor (DAD) systems illustrated the viability and usefulness of the approach. More applications to other types of molecules and to periodic extended systems are currently underway and will be reported elsewhere.

Other future applications of the PHM may involve the motion of the nuclei (for instance, using Ehrenfest dynamics). Lattice relaxation plays an important role in many optical processes and is absolutely crucial for charge separation in photovoltaics.⁴⁵ It should be straightforward to implement the PHM_t in systems with moving nuclei. Extensions to magnetic systems, involving a spin-dependent PHM, are also possible.

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Notes

The authors declare no competing financial interest.

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