Accurate optical spectra of solids from pure time-dependent density-functional theory

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We present accurate optical spectra of semiconductors and insulators within a pure Kohn-Sham time-dependent density-functional approach. In particular, we show that the onset of the absorption is well reproduced when comparing to experiment. No empirical information nor a theory beyond Kohn-Sham density-functional theory, such as GW, is invoked to correct the Kohn-Sham gap. Our approach relies on the link between the exchange-correlation kernel of time-dependent density functional theory and the derivative discontinuity of ground-state density-functional theory. We show explicitly how to relate these two quantities. We illustrate the accuracy and simplicity of our approach by applying it to a semiconductor and a wide-gap insulator.

Time-dependent-density functional theory (TDDFT) [1] has become, over the years, one of the few well-established first-principles' approaches to describe time-dependent phenomena for a large variety of systems, both in the linear-response regime and beyond (see, e.g., Refs [2, 3] and references therein). In the last two decades TDDFT has been increasingly applied to solids, and in particular to the calculation of the optical absorption spectra. Optical experiments in general are very useful tools to investigate and characterize condensed-matter systems; it is hence desirable to develop efficient and reliable theoretical approaches to complement experiment.

Within TDDFT the description of optical spectra depends crucially on the exchange-correlation (xc) kernel f_{xc} which relates the response of the Kohn-Sham system to a small perturbation to the response of the true system. Thanks to the numerical efficiency of TDDFT, it is desirable that a simple but accurate xc kernel is available for the calculation of optical spectra. It is well-known that traditional xc kernels, such as the random-phase approximation (RPA), i.e., $f_{xc} = 0$, and the adiabatic local-density approximation (ALDA) [4], fail to describe two important features of optical spectra: 1) excitonic effects and 2) the absorption onset. While excitonic effects can nowadays be described accurately with a variety of xc kernels [5–10], the correct description of the absorption onset within TDDFT remains an unsolved problem.

The starting point for a TDDFT calculation is the Kohn-Sham band structure. As is well known, the Kohn-Sham band gap is, in general, estimated to be much smaller than the fundamental gap, i.e., the difference between the ionization potential and the electron affinity. [11–13]. Therefore, since TDDFT should give the exact absorption spectra, the TDDFT xc kernel has the difficult task to ensure that there is no absorption below the optical gap even though transitions between Kohn-Sham valence and conduction bands are available. Indeed, optical spectra obtained with all currently avail-able xc kernels show absorption at energies close to the Kohn-Sham band gap, thereby severely underestimating the absorption onset.

The standard approach to circumvent this problem is to add a scissors operator [14] to the Kohn-Sham Hamiltonian. The shift parameter is either obtained from experiment or from a method that goes beyond KS-DFT, such as GW [15–19], or generalised KS-DFT with a hybrid functional, such as those based on a screened Coulomb interaction [20–23]. Unfortunately these approaches have a significantly larger computational cost than pure KS-DFT.

In this work we will present an expression for the xc kernel within a pure KS approach that correctly describes the absorption onset in optical spectra. We will combine it with an approach that accurately includes the excitonic effects [8], thereby obtaining spectra comparable to those obtained in experiment.

The TDDFT xc kernel f_{xc} can be written exactly as [24]

$$f_{xc}(1,2) = \underbrace{\chi_{\mathrm{KS}}^{-1}(1,2) - \chi_0^{-1}(1,2)}_{f_{xc}^{(1)}}$$
$$\underbrace{-i \int d345 \chi_0^{-1}(1,5) G(5,3) G(4,5) \frac{\delta\Sigma(3,4)}{\delta\rho(2)}}_{f_{xc}^{(2)}} \quad (1)$$

where χ_{KS} and $\chi_0 = -iGG$ are the Kohn-Sham and independent quasiparticle polarizability, respectively, and $G(1,2)$ and $\Sigma(1,2)$ are the one-body Green function and the self-energy, respectively. The collective index $(1) = (\mathbf{x}, t) = (\mathbf{r}, s, t)$ contains the space, spin and time coordinates. The xc kernel written in Eq. (1) clearly exhibits two distinct parts. The first part $f_{xc}^{(1)} = \chi_{\mathrm{KS}}^{-1} - \chi_0^{-1}$ only involves independent (quasi-)particles, and, therefore, is responsible for the shift of the Kohn-Sham band gap to the fundamental gap, while the second part, $f_{xc}^{(2)}$, which includes the electron-hole interaction, accounts for

the excitonic effects. In general, both terms are required to guarantee a correct onset of the absorption, unless the exciton binding energy is small, in which case $f_{xc}^{(1)}$ is sufficient. Although Eq. (1) clearly distinguishes these two parts it is not useful in practical applications since it would require the calculation of G. From the above discussion one would expect a link between $f_{xc}^{(1)}$ and the derivative discontinuity of ground-state DFT [25, 26], which is defined as the difference between the fundamental gap and the Kohn-Sham gap. One of the goals of this work is to make this link explicit.

In order to obtain an expression for $f_{xc}^{(1)}$ that can be applied in practice, we first generalize the two-point KS polarizability to four points: [27]

$$^4\chi_{\mathrm{KS}}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \mathbf{x}_4, \omega) = \sum_{i,j}(f_j - f_i)$$
$$\times \frac{\phi_i(\mathbf{x}_1)\phi_j(\mathbf{x}_2)\phi_j^*(\mathbf{x}_3)\phi_i^*(\mathbf{x}_4)}{\omega - (\epsilon_i - \epsilon_j) + i\eta}, \quad (2)$$

where ϕ_i is a KS spinorbital, ϵ_i its energy, f_i its occupation (0 and 1 for unoccupied and occupied orbitals, respectively), and η is a positive infinitesimal that ensures causality. For the solids we study here i and j are multi-indices composed of a band index (comprising the spin) and a Bloch vector, $\mathbf{k}$ and $\mathbf{k}'$, respectively. We note that, although the final goal is the description of optical absorption for which $\mathbf{k}' \to \mathbf{k}$, the discussion below is completely general, i.e., $\mathbf{k} \neq \mathbf{k}'$. The usual two-point KS polarizability is retrieved from $\chi_{\mathrm{KS}}^{(4)}$ by the following contraction,

$$\chi_{\mathrm{KS}}(\mathbf{x}_1, \mathbf{x}_2, \omega) = {}^4\chi_{\mathrm{KS}}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_1, \mathbf{x}_2, \omega). \quad (3)$$

We can express $\chi_{\mathrm{KS}}^{(4)}$ in the Kohn-Sham basis by using the following basis transformation

$$\chi_{KS[n_1 n_3]}^{[n_4 n_2]}(\omega) = \int d\mathbf{x}_1\mathbf{x}_2\mathbf{x}_3\mathbf{x}_4\, {}^4\chi_{\mathrm{KS}}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \mathbf{x}_4, \omega)$$
$$\times \phi_{n_1}^*(\mathbf{x}_1)\phi_{n_2}^*(\mathbf{x}_2)\phi_{n_3}(\mathbf{x}_3)\phi_{n_4}(\mathbf{x}_4). \quad (4)$$

This yields a $2M \times 2M$ diagonal matrix with M the number of KS excitations. It is schematically given by [28]

$$\chi_{\mathrm{KS}}(\omega) = \begin{pmatrix} \frac{1}{\omega - \omega_1} & & & & & \\ & \ddots & & & & \\ & & \frac{1}{\omega - \omega_M} & & & \\ & & & -\frac{1}{\omega + \omega_1} & & \\ & & & & \ddots & \\ & & & & & -\frac{1}{\omega + \omega_M} \end{pmatrix} \quad (5)$$

where ω_i is a KS excitation energy, i.e., a pole of $\chi_{\mathrm{KS}}(\omega)$, and the matrix elements are arranged in order of increasing excitation energy, i.e., $\omega_1 \geq \omega_2 \geq \omega_3$, etc. In particular, the lowest KS excitation energy is given by $\omega_1 = \epsilon_{\mathrm{CBM}} - \epsilon_{\mathrm{VBM}}$, with ϵ_{CBM} and ϵ_{VBM} the KS energy of the conduction band minimum (CBM) and the KS energy of the valence band maximum (VBM), respectively.

We now assume that also χ_0 is diagonal in the Kohn-Sham basis. This is in accordance with many practical calculations, in particular those based on the GW method, in which χ_0 is built with KS orbitals [17, 29]. We can thus write

$$\chi_0(\omega) = \begin{pmatrix} \frac{1}{\omega - \Omega_1} & & & & & \\ & \ddots & & & & \\ & & \frac{1}{\omega - \Omega_M} & & & \\ & & & -\frac{1}{\omega + \Omega_1} & & \\ & & & & \ddots & \\ & & & & & -\frac{1}{\omega + \Omega_M} \end{pmatrix} \quad (6)$$

where Ω_i are quasiparticle energy differences, i.e., differences of ionization potentials and electron affinities. In particular, the lowest excitation energy is given by $\Omega_1 = I - A$, where I is the first ionization potential and A is the first electron affinity. Here we assume that the ordering of the excitation energies is the same as that of the KS system. We thus obtain a frequency-independent xc kernel, $f_{xc}^{(1)} = \chi_{\mathrm{KS}}^{-1} - \chi_0^{-1}$,

$$f_{xc}^{(1)} = \begin{pmatrix} \Omega_1 - \omega_1 & & & & & \\ & \ddots & & & & \\ & & \Omega_M - \omega_M & & & \\ & & & \Omega_1 - \omega_1 & & \\ & & & & \ddots & \\ & & & & & \Omega_M - \omega_M \end{pmatrix}. \quad (7)$$

We note that $f_{xc}^{(1)}$ contains two equivalent blocks. The absorption onset is determined by the head of the matrix $f_{xc,11}^{(1)}$. It is given by

$$f_{xc,11}^{(1)} = I - A - (\epsilon_{\mathrm{CBM}} - \epsilon_{\mathrm{VBM}}) \quad (8)$$

It can be shown that the ionization potential is exactly equal to minus the KS energy at the VBM, i.e., $I = -\epsilon_{\mathrm{VBM}}$ [30–32]. Since an equivalent relation holds for the $N+1$ system, i.e., the system with one additional electron, and the fact that A should be equal to the first ionization potential of the $N+1$ system, one can deduce that $A = -\epsilon_{\mathrm{VBM}}^{N+1}$, where $\epsilon_{\mathrm{VBM}}^{N+1}$ is the KS energy at the VBM of $N+1$ system. Therefore, we can rewrite Eq. (8) as

$$f_{xc,11}^{(1)} = \epsilon_{\mathrm{VBM}}^{N+1} - \epsilon_{\mathrm{CBM}}. \quad (9)$$

Although Eq. (9) seems a simple expression, it is not easy to calculate in practice. The problem arises from the fact that $\epsilon_{\mathrm{VBM}}^{N+1}$ is difficult to evaluate in solids since they

are usually described within the thermodynamic limit, which implies an infinite number of electrons from the outset. However, $\epsilon_{\mathrm{VBM}}^{N+1} - \epsilon_{\mathrm{CBM}}$ is equal to the difference between the fundamental gap E_g and the KS gap E_{KS} [26, 32, 33]. This difference is also known as derivative discontinuity Δ [25, 26]. Therefore we arrive at the following relation,

$$f_{xc,11}^{(1)} = \Delta. \tag{10}$$

This is one of the main results of this work.

As first proposed by Kuisma $et\ al.$ [34] and further discussed by Baerends [32], the derivative discontinuity can be approximated in terms of simple ground-state KS-DFT quantities according to

$$\Delta = K_{xc} \sum_{i=1}^{N} \left[\sqrt{\epsilon_{\mathrm{CBM}} - \epsilon_i} - \sqrt{\epsilon_{\mathrm{VBM}} - \epsilon_i} \right]$$
$$\times \langle \phi_{\mathrm{CBM}} | \frac{|\phi_i|^2}{\rho_0} | \phi_{\mathrm{CBM}} \rangle \tag{11}$$

where ϕ_{CBM} is the KS spinorbital corresponding to the CBM, ρ_0 is the ground-state density and $K_{xc} = \frac{8\sqrt{2}}{3\pi^2} \approx 0.382$.

The expression in Eq. (11) can be obtained from the GLLB approximation to the ground-state xc potential [35]. The GLLB functional is an approximation to the exact exchange optimized effective potential. A detailed derivation of Eq. (11) is given by Baerends [32]. The constant K_{xc} ensures that the GLLB functional yields the exact ground-state energy of the uniform electron gas. Fundamental gaps calculated using the derivative discontinuity in Eq. (11) have been reported for a large number of solids. [32, 34, 36–38]. In general, the results are excellent.

We can include the effect of $f_{xc}^{(1)}$ on the spectra by introducing a modified Kohn-Sham polarizability $\chi_{KS}^{(1)}(\omega)$ defined by

$$[\chi_{\mathrm{KS}}^{(1)}]^{-1}(\omega) = [\chi_{\mathrm{KS}}]^{-1}(\omega) - f_{xc,11}^{(1)} = \omega - \omega_1 - \Delta. \tag{12}$$

Using the inverse of the basis set transformation in Eq. (4), and using a similar contraction as in Eq. (3) we obtain the following expression for the modified two-point KS polarizability $\chi_{KS}^{(1)}$,

$$\chi_{\mathrm{KS}}^{(1)}(\mathbf{x}_1, \mathbf{x}_2) = \sum_{i,j} (f_j - f_i) \frac{\phi_i(\mathbf{x}_1)\phi_j(\mathbf{x}_2)\phi_j^*(\mathbf{x}_1)\phi_i^*(\mathbf{x}_2)}{\omega - (\epsilon_i - \epsilon_j) - \Delta + i\eta}. \tag{13}$$

The modified KS polarizability $\chi_{\mathrm{KS}}^{(1)}$ will account for the correct absorption onset of the spectra. The true response function can then be written in terms of $\chi_{\mathrm{KS}}^{(1)}$ as

$$\chi(\omega) = \chi_{\mathrm{KS}}^{(1)}(\omega) + \chi_{\mathrm{KS}}^{(1)}(\omega) \left[v_c + f_{xc}^{(2)}(\omega) \right] \chi(\omega), \tag{14}$$
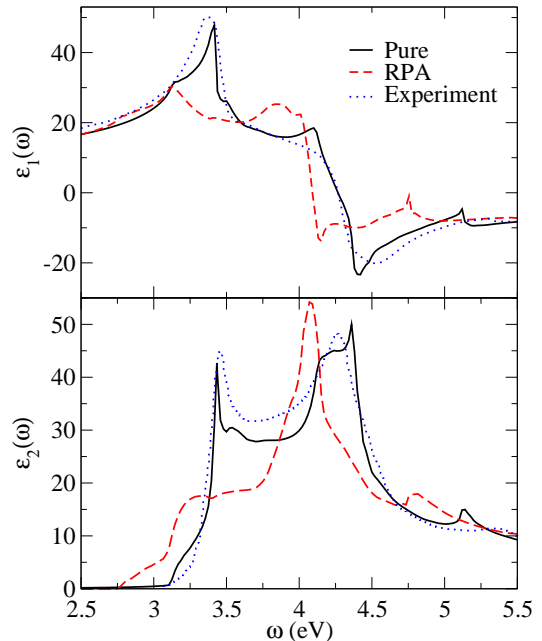

FIG. 1: (Color online) The optical absorption spectra of bulk silicon. Solid line (black): polarization functional (PF); Dashed line (red): RPA; Dotted line (blue): experiment from Ref. [48].

with v_c the Coulomb potential. From $\chi(\omega)$ one can readily obtain the dielectric function $\varepsilon(\omega) = 1 + v_c\chi(\omega)$. The optical spectra are obtained from the imaginary part of $\epsilon^M(\omega)$, the macroscopic part of $\epsilon(\omega)$:

$$\varepsilon^M(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega). \tag{15}$$

In practice, we use a slight generalization of TDDFT, namely TD-current-DFT (TDCDFT) [39–42]. The practical details of how we solve the KS equations within TDCDFT can be found elsewhere [43–47]. We approximate $f_{xc}^{(2)}$ with the polarization functional (PF) of Ref. [8] which accurately describes the excitonic effects. We will refer to the full kernel, i.e., $f_{xc}^{(1,GLLB)} + f_{xc}^{(2,PF)}$, as the Pure kernel to highlight the fact that it is based on pure Kohn-Sham theory.

We implemented our approach in a modified version of the Amsterdam Density Functional (ADF) code [49–51]. We use the TZ2P (triple-ζ + 2 polarization functions) and QZ4P (quadruple-ζ + 4 polarization functions) basis sets provided by ADF for bulk silicon and solid argon, respectively. The **k**-space integrals are done analytically using a Lehmann-Taut tetrahedron scheme [52]. The ground-state calculations are done within the GLLB-SC xc potential [32, 34, 35], which is based on the PBEsol [53] correlation potential and uses the GLLB approximation to the exchange optimized effective potential. The GLLB-SC values we obtained for Δ are 0.38 eV and 4.65 eV for silicon and solid argon, respectively.

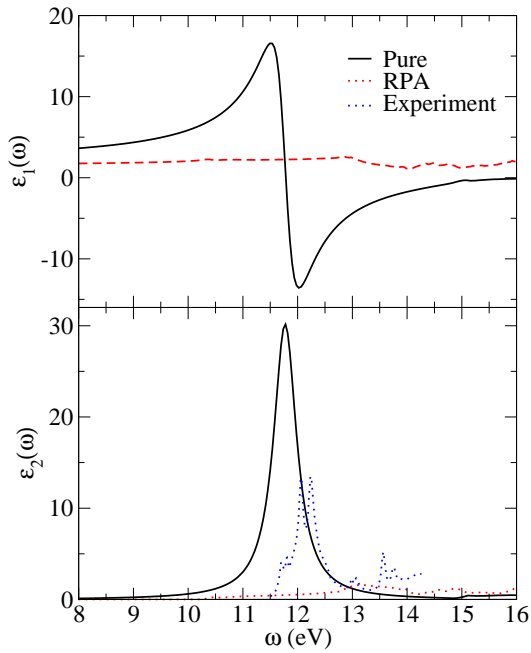We will now illustrate our approach by applying it to

FIG. 2: The optical absorption spectra of solid Argon. Solid line (black): polarization functional (PF); Dashed line (red): RPA; Dotted line (blue): experiment from Ref. [54].

the calculation of the optical spectra of two very different types of solids, Silicon and solid Argon, which are typical examples of a standard semiconductor and a wide-gap insulator, respectively.

In Fig. 1 we report the dielectric function of bulk silicon calculated with the Pure functional at 0 Kelvin and compare it to the RPA spectrum as well as to the experimental spectrum obtained at 30 Kelvin. The Pure kernel yields an absorption spectrum that is in excellent agreement with the experimental measurements. In particular, the absorption onset and the excitonic effects in $\epsilon_2(\omega)$ are well reproduced. Also, the real part of the dielectric function obtained with the Pure kernel compares well to the experiment. Instead, the RPA spectrum exhibits the well-known shortcomings mentioned before, i.e., the underestimation of the absorption onset and the absence of excitonic effects. We note that the theoretical spectra have more structure than the experimental spectrum because it is calculated at 0 Kelvin and no broadening parameter is used to simulate temperature effects.

In Fig. 2 we show the dielectric function of solid Argon calculated with the Pure kernel at 0 Kelvin and compare it to the RPA spectrum as well as to the experimental spectrum. We see that the onset of the absorption is well-reproduced as is the full spectrum, except for an overestimation of the first peak, i.e., the absorption related to the bound exciton. Unfortunately, to the best of our knowledge, there is no experimental data of $\epsilon_1(\omega)$.

In conclusion, we have made explicit the link between the derivative discontinuity of ground-state DFT and the xc kernel of TDDFT. Using this link we proposed the Pure kernel, which combines the derivative discontinuity and the polarization functional, to describe optical spectra. We showed that it yields optical spectra in good agreement with experiment for typical examples of a semiconductor and a wide-gap insulator. The central issue here is that these results were obtained within a pure KS approach without resorting to empirical data or approaches that go beyond TDDFT.

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