Fully parameter-free calculation of optical spectra for insulators, semiconductors and metals from a simple polarization functional

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We present the first fully parameter-free density-functional approach for the accurate description of optical absorption spectra of insulators, semiconductors and metals. We show that this can be achieved within time-dependent current-density-functional theory using a simple dynamical polarization functional. Our method is truly predictive because not a single parameter is used. In particular, we do not use an ad hoc material-dependent broadening parameter to compare theory to experiment as is usually done. Our approach is also numerically efficient; the cost of a calculation equals that of a calculation within the random-phase approximation.

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sequence knowledge of the induced density in the unit cell is not sufficient to calculate response properties of materials. However, response properties can be calculated by solving the TDDFT Dyson equation which relates the Kohn-Sham density-density response function to the true density-density response function. Unfortunately this makes calculations much more costly since the Kohn-Sham response function has to be explicitly calculated.

There is a more elegant and efficient alternative which is to switch to the current density as the fundamental quantity of a DFT for time-dependent phenomena since the perturbing potential is a unique functional of the periodic current density. This can be understood because the density and the current density are related through the continuity equation and the macroscopic polarization is related to the average current in a unit cell according to

$$\vec{P}_{\text{mac}}(\omega) = -\frac{i}{\omega V} \int d\vec{r} \hat{\vec{J}}(\vec{r}, \omega),$$

(1)

where $V$ is the volume of the unit cell. Therefore, TDDFT is the natural extension of DFT for extended systems described with PBC. Knowledge of the induced current density is sufficient to calculate response properties and the explicit calculation of Kohn-Sham response functions is not needed. The macroscopic polarization is induced by a macroscopic electric field $\vec{E}_{\text{mac}}(\omega)$ which comprises both the externally applied field and the macroscopic induced electric field. The latter represents the nonperiodic part of the Hartree potential due to the surface charges as well as the retarded contribution of the induced transverse current density $20$. The constant of proportionality is the electric susceptibility tensor $\chi^e(\omega)$:

$$\vec{P}_{\text{mac}}(\omega) = \chi^e(\omega) \cdot \vec{E}_{\text{mac}}(\omega).$$

(2)

The macroscopic dielectric tensor $\varepsilon_M(\omega)$ can be obtained from the electric susceptibility according to

$$\varepsilon_M(\omega) = 1 + 4\pi \chi^e(\omega).$$

(3)

Therefore, for a given $E_{\text{mac}}(\omega)$, knowledge of the induced current suffices to calculate $\varepsilon_M(\omega)$ from Eqs. (1)-(3).

Within Kohn-Sham linear response the current density is calculated according to $24$

$$\delta \vec{J}(\vec{r}, \omega) = -\frac{i}{\omega V} \int d\vec{r} \chi^{s, \delta J}(\vec{r}, \omega) [\vec{E}_{\text{mac}}(\omega) + \vec{E}_{\text{mac}}^{xc}(\omega)]$$

$$+ \int d\vec{r} \chi^{* s, \delta J}(\vec{r}, \omega) \delta \nu_{\text{mic}}^{xc}(\vec{r}, \omega),$$

(4)

where $\vec{E}_{\text{mac}}^{xc}(\omega)$ is the macroscopic part of the electric xc field, $\delta \nu_{\text{mic}}^{xc}(\vec{r}, \omega)$ is the microscopic part of the induced Hartree and xc scalar potentials and $\chi^{s, \delta J}(\omega)$ and $\chi^{* s, \delta J}(\omega)$ are the Kohn-Sham current-current and current-density response functions, respectively. We note that in practice these functions are never needed explicitly. Note that in Eq. (4) we neglect the microscopic part of the transverse electric xc field. The macroscopic electric xc field is related to the induced current through the TDDFT xc kernel $\int \delta \vec{J}(\omega)$:

$$\vec{E}_{\text{mac}}^{xc}(\omega) = \frac{i \omega}{V} \int d\vec{r} \int d\vec{r}^\prime \vec{J}^{\delta}(\vec{r}, \omega) \cdot \delta \vec{J}(\vec{r}^\prime, \omega).$$

(5)

Substitution of Eq. (4) into Eq. (5) reveals that $\vec{E}_{\text{mac}}^{xc}(\omega)$ is proportional to the Kohn-Sham electric field $\vec{E}_{\text{mac}}(\omega) + \vec{E}_{\text{mac}}^{xc}(\omega)$. Following Ref. $12$ we can define the auxiliary susceptibility $\chi^{e}_{\text{aux}}$ according to

$$\vec{P}_{\text{mac}}(\omega) = \chi^{e}_{\text{aux}}(\omega) \cdot \vec{E}_{\text{mac}}(\omega),$$

(6)

where $\chi^{e}_{\text{aux}}$ is the susceptibility obtained from a calculation with $\vec{E}_{\text{mac}}^{xc}(\omega) = 0$. Comparison of Eqs. (2) and (6) leads to the following relation between $\chi^e(\omega)$ and $\chi^{e}_{\text{aux}}(\omega)$

$$[\chi^e(\omega) - [\chi^{e}_{\text{aux}}(\omega)] \cdot \vec{P}_{\text{mac}}(\omega) = \vec{E}_{\text{mac}}^{xc}(\omega).$$

(7)

If one chooses $\vec{E}_{\text{mac}}^{xc}(\omega)$ equal to zero as is usually done we obtain $\chi^e(\omega) = \chi^{e}_{\text{aux}}(\omega)$. We will now go beyond this approximation.

To find a polarization functional for $\vec{E}_{\text{mac}}^{xc}(\omega)$ we start from Eq. (1) in which we substitute $\delta \vec{J}(\vec{r}, \omega)$ by its unit-cell average. We obtain

$$\vec{E}_{\text{mac}}^{xc}(\omega) = \vec{\alpha}(\omega) \cdot \vec{P}_{\text{mac}}(\omega)$$

(8)

where we used Eq. (1) and in which we defined

$$\vec{\alpha}(\omega) = -\frac{\omega^2}{V} \int d\vec{r} \int d\vec{r}^\prime \vec{J}^{\delta}(\vec{r}, \vec{r}^\prime, \omega).$$

(9)

Substitution of Eq. (8) into Eq. (7) leads to

$$[\chi^e(\omega) - [\chi^{e}_{\text{aux}}(\omega) - \vec{\alpha}(\omega)]$$

(10)

Therefore, for a given $\vec{\alpha}(\omega)$, we can simply calculate $\chi^e(\omega)$ from $\chi^{e}_{\text{aux}}(\omega)$. Here we will use the RPA ($\delta \nu_{\text{mic}}^{xc} = 0$) to calculate the latter, i.e., $\chi^e_{\text{aux}} = \chi^e_{\text{RPA}}$.

Since continuum excitons are underestimated and bound excitons and Drude tails are absent in RPA optical spectra these effects have to be included through $\alpha(\omega)$. We will now show how this can be efficiently done. To simplify our argumentation we will assume for the moment that $\chi^e(\omega)$, $\chi^e_{\text{RPA}}(\omega)$ and $\vec{\alpha}(\omega)$ are isotropic, i.e., $\alpha_{ij}(\omega) = \alpha(\omega) \delta_{ij}$, etc. Following similar arguments as put forward in Ref. $29$ one can show that the condition to have a bound exciton is $\text{Re} \left[ \alpha(\omega) \right] = 1/\text{Re} \left[ \chi^e_{\text{RPA}}(\omega) \right]$ (with $\text{Im} \left[ \alpha(\omega) \right]$ small) where $\omega$ corresponds to an energy below the band gap. Furthermore, from comparison to the BSE, it has been shown that when the long-range part of the TDDFT xc kernel is proportional to $[\nu_{\text{RPA}}(\omega)]^{-1}$ one has a correct description of continuum excitons $14$. $33$ A similar proportionality holds
for $\alpha(\omega)$. Since for systems with strongly bound excitons $[\chi_{c}\text{RP}A(\omega = 0)]^{-1}$ is typically slightly smaller than unity, this suggests that the following static kernel could describe both bound and continuum excitons,

$$\alpha = \frac{[\chi_{c}\text{RP}A(\omega = 0)]^{-1}}{\chi_{c}\text{RP}A(\omega = 0)}.$$  \hfill (11)

Here the denominator contains $\chi_{c}\text{RP}A(\omega = 0)$, which is in general slightly smaller than $\text{Re}\{\chi_{c}\text{RP}A(\omega)\}$ (for $\omega$ below the band gap), to compensate for the fact that the numerator is slightly smaller than unity for systems with strongly bound excitons. This guarantees that the condition necessary to describe bound excitons remains approximately satisfied. We note that Eq. (11) has a similar form as the heuristic bootstrap kernel \cite{22}, but that no self-consistent procedure is needed to calculate it.

However, since the above expression is static it does not describe memory effects and will therefore be unable to account for the finite width of bound excitons and Drude tails. For this reason we add to Eq. (11) $Y_{VK}(\omega)$, the long-range part of the dynamical Vignale-Kohn functional \cite{20} in which we replace the current density by its unit-cell average \cite{14}:

$$\bar{Y}_{VK}(\omega) = \frac{1}{V} \int d\vec{r} \left( \frac{\nabla \rho_{0}(\vec{r}) \cdot \nabla \rho_{0}(\vec{r})}{\rho_{0}^{2}(\vec{r})} \right) f_{xcT}(\bar{\rho}, \omega) \bar{Y}^{\alpha}$$

$$+ \frac{\nabla \rho_{0}(\vec{r}) \odot \nabla \rho_{0}(\vec{r})}{\rho_{0}^{2}(\vec{r})} \left[ f_{xcL}(\bar{\rho}, \omega) - f_{xcT}(\bar{\rho}, \omega) \frac{d^{2}e_{xc}}{d\rho^{2}} \right],$$  \hfill (12)

where $f_{xcL(T)}(\omega)$ is the longitudinal (transverse) xc kernel of the homogeneous electron gas, $e_{xc}$ is the xc energy per volume of the homogeneous electron gas, $\rho_{0}(\vec{r})$ is the ground-state density and $\bar{\rho}$ is its average in the unit cell. For $f_{xcL(T)}(\omega)$ we use the parametrization of Ref. \cite{31} in the QVA approximation \cite{21}. The Vignale-Kohn functional is the exact functional of a slightly inhomogeneous electron gas and hence describes correctly the optical spectra of metals \cite{21}. For this reason Eq. (12) is complementary to Eq. (11) which tends to zero for metallic systems. It will account for the Drude tails and finite width of bound excitons which are exactly the features that are absent in Eq. (11). We finally obtain the following approximation for $\bar{\alpha}(\omega)$,

$$\bar{\alpha}(\omega) = \frac{[\chi_{c}\text{RP}A(0)]^{-1}}{\chi_{c}\text{RP}A(0)} + \bar{Y}_{VK}(\omega)$$  \hfill (13)

where we generalized Eq. (11) to a tensor form. We note that it satisfies the Kramers-Kronig relations. Equation (13) is the main result of this work.

We will now demonstrate our approach by applying it to the calculation of the optical spectra of several materials. We briefly outline the full procedure. The ground-state calculations are done within the local-density approximation (LDA) \cite{32} and we use LDA lattice parameters in all calculations. We apply a scissor operator to shift the unoccupied bands and we modify the current operator accordingly to guarantee that exact constraints such as the continuity equation remain satisfied. The energy shift is calculated with the GW method \cite{10, 11} and is equal to the GW correction for the direct band gap at the $\Gamma$ point which we calculate using the Abinit code \cite{33}. We implemented the polarization functional in a modified version of the Amsterdam Density Functional (ADF) code \cite{34, 35}. We used the TZ2P (triple-$\zeta$ + 2 polarization functions) basis set provided by ADF. The $\vec{k}$-space integrals are done analytically using a Lehman-Taut tetrahedron scheme \cite{37}. Since we do not include effects due to electron-phonon coupling the spectra obtained with the above approach are predictions of the optical spectra at low temperature where electron-electron scattering dominates electron-phonon scattering. For this reason we will compare our calculated spectra with spectra measured at low temperature where available.

In Fig. 1 we report the optical absorption spectra of bulk silicon and GaP obtained with our polarization functional and compare it to the RPA spectra and to experimental results obtained at low temperature (15 Kelvin). Silicon and GaP are typical examples of materials for which the RPA strongly underestimates the first peak which appear in the experimental spectra around 3.4 eV (Si) and 3.8 eV (GaP). Our polarization functional solves this problem by including the necessary excitonic effects and the first peak compares well with experiment both in position and magnitude. Overall, the spectra are very close to experiment with the exception of the peak around 5.2 eV in the spectrum of GaP which is overestimated. We also note that the first peak in the silicon spectrum is not just a shoulder in the RPA, as is commonly reported in the literature, but a true peak. The appearance of this peak as a shoulder in many RPA spectra is an artefact due to an ad hoc broadening parameter.
In Fig. 2 we show the optical absorption spectra of solid argon and LiF obtained with the polarization functional and compare it to the RPA spectra and to experimental results. Solid argon and LiF are typical materials that exhibit strongly bound excitons. We see that these excitons which appear in the experimental spectra around 12.2 eV (Ar) and 12.6 eV (LiF) are completely absent in the RPA spectra. Our polarization functional describes these bound excitons and also reproduces their position accurately. We note that the experimental spectrum of solid argon is only known in arbitrary units which precludes a comparison of the peak heights. For LiF the calculated peak height is clearly overestimated with respect to experiment. This discrepancy is due to electron-phonon broadening in the experiment which was done at room temperature as well as to the fact that density-functional approaches tend to overestimate this peak \[23, 25\].

Finally, in Fig. 3 we report the optical absorption spectra of diamond and copper obtained with the polarization functional and compare it to the RPA spectra and to experimental results. Diamond is another typical test case since the RPA spectrum is quite different from the experimental spectrum. Due to the absence of excitonic effects the RPA spectrum has too much weight at high energy. With our polarization functional the spectral weight is shifted to lower energy and we obtain a very good agreement with experiment. While the RPA spectrum of copper accurately reproduces the part of the spectrum which is due to interband transitions, the Drude tail at low energy, which is due to intraband transitions, is completely absent. Our polarization functional accurately describes the Drude tail while maintaining the good agreement for the interband part.

In conclusion, we presented the first fully parameter-free density-functional approach that gives accurate optical spectra for insulators, semiconductors and metals alike. Our approach is therefore truly predictive and due to its numerical efficiency opens the way for the prediction of optical spectra of large systems.

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