Parameter-Free Calculation of Response Functions in Time-Dependent Density-Functional Theory

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We have established and implemented a fully *ab initio* method which allows one to calculate optical absorption spectra, including excitonic effects, without solving the cumbersome Bethe-Salpeter equation, but obtaining results of the same precision. This breakthrough has been achieved in the framework of time-dependent density-functional theory, using new exchange-correlation kernels f_{xc} that are free of any empirical parameter. We show that the same excitonic effects in the optical spectra can be reproduced through different f_{xc}'s, ranging from frequency-dependent ones to a static one, by varying the kernel's spatial degrees of freedom. This indicates that the key quantity is not f_{xc}, but f_{xc} combined with a response function. We present results for the optical absorption of bulk Si and SiC in good agreement with experiment, almost indistinguishable from those of the Bethe-Salpeter approach.

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The theoretical description of electronic excitations in the framework of many-body perturbation theory (MBPT) [1] has undergone a rapid development since new approaches and the increase of computer power made numerical calculations feasible for real systems. Within MBPT one can calculate with a good precision charged excitations (i.e., electron addition and removal energies) using, e.g., the GW approximation for the electron self-energy [2,3]. In the same framework, neutral excitations (e.g., optical and energy-loss spectra) are also well described today through the solution of the Bethe-Salpeter equation (BSE) [3,4]. However, the intrinsic two-particle nature of the BSE makes the calculations very cumbersome, since a four-point equation has to be solved. Therefore, in spite of the excellent results obtained with the BSE for moderately simple systems, the efficient description of electron-hole excited states in realistic materials is still considered to be an unsolved problem in condensed matter theory [3]. Time-dependent density-functional theory (TDDFT) [5] might be an advantageous alternative [6] to the BSE formalism because, as in the case of the very successful static density-functional theory (DFT), this theory relies on the (now time-dependent) electron density ρ instead of the one-particle Green's function. Two-point response functions are involved in the formalism instead of the four-point ones required in the BSE approach. However, one has to find good approximations for the time-dependent exchange-correlation (xc) potential v_{xc} as well as its density variation (to first order in linear response), the xc kernel $f_{xc} = \delta v_{xc}/\delta\rho$. The widely used adiabatic local-density approximation [5,7] (TDLDA) for f_{xc} does not systematically improve optical spectra of solids with respect to the random phase approximation (RPA) where $f_{xc} = 0$ [3].

Recently, there have been several attempts [8–12] to go beyond the TDLDA in practical calculations of absorption spectra of solids. Reference [8] is situated in the framework of current-density functional theory [13]. An effective long-range kernel is proposed that improves the RPA and TDLDA results for the optical spectra of various materials, including silicon and diamond. In Ref. [14] an "exact exchange-only" (EXX) kernel is presented as the first order term of an expansion in the framework of the adiabatic-connection perturbation theory [15]. In Ref. [9] this kernel and the EXX potential are used to calculate the optical absorption spectrum of bulk silicon and again, the result is considerably improved with respect to the TDLDA. In Ref. [10] an analytical expression for f_{xc} is found from a comparison with MBPT, using the successful approximations of the latter, namely, the GW form for the self-energy [2] and a static electron-hole interaction in the BSE. Only the long-range limit (vanishing wave vector q) of the resulting $f_{xc}(\mathbf{q})$ is then explicitly studied, which is sufficient to demonstrate that a $1/q^2$ divergence of f_{xc} is, to a certain extent, able to reproduce excitonic effects in the optical spectra of bulk silicon.

However, none of the above numerical calculations are truly *ab initio*: empirical parameters, corrections, or cutoffs are used in all cases to fit the results to experiment. In Ref. [8], material-dependent rigid shifts of the spectra and an empirical prefactor to adjust intensity ratios are used. In Ref. [9] finite, non-negligible terms in the expression of the kernel are cut off to avoid the otherwise occurring "collapse" of the resulting spectra, and to fit the result to the experiment. Finally, in Ref. [10] the weight of the $1/q^2$ divergence is not explicitly evaluated but again fitted to experiment, even though later (in Ref. [11]) its material dependence with respect to the screening has been elucidated. Only one parameter-free calculation of the frequency dependence of the long-range contribution to f_{xc} has been published so far in a bulk material (namely for silicon and diamond) [12], but at the price of fully solving the BSE, which is of course not of immediate practical interest.

A suggestion of how excitonic effects might be obtained without solving the BSE, and without using adjustable parameters, is given in Ref. [10]. However, it has never been shown how well this approach would work in practice, and its success is *a priori* far from obvious.

In the present Letter we show that the approach proposed in Ref. [10] *is* in fact one possible *solution* for the long-standing problem of calculating *parameter-free* optical spectra, including excitonic effects, in the framework of TDDFT and *without solving the BSE.* We generalize the kernel given in that reference to a class of dynamical ones, and show that a static f_{xc}, when it exists, is just one of many possibilities which yield a correct spectrum. We demonstrate, taking silicon and SiC as examples, that formula (11) of Ref. [10] yields virtually the same results as a BSE calculation.

We work in reciprocal space and start from a symmetric form of the matrix equation for the response function χ (from which the inverse dielectric matrix ε^{-1} is obtained via $\varepsilon^{-1} = 1 + v\chi$) that reads schematically

$$\chi = \chi^{(0)}(\chi^{(0)} - \chi^{(0)} v \chi^{(0)} - T)^{-1}\chi^{(0)}. \tag{1}$$

v is the bare Coulomb interaction, $\chi^{(0)}$ is the independent particle Kohn-Sham (KS) response function, and $T = \chi^{(0)} f_{xc} \chi^{(0)}$. From the BSE calculations it is known [3] that for the systems studied here it is a good approximation to use only the resonant part of the response function, and to employ a static electron-hole interaction and LDA-KS wave functions. In the following, we make use of these approximations. For vanishing momentum transfer (vertical transitions $t = \{vc\mathbf{k}\}$ from valence $v\mathbf{k}$ to conduction $c\mathbf{k}$ states), $T_{\mathbf{G}\mathbf{G}'}(\omega)$ can be rewritten as

$$T = \frac{2}{N_k}\sum_{tt'} \frac{\Phi^*(t;\mathbf{G})}{\epsilon^{\mathrm{KS}}_{c\mathbf{k}} - \epsilon^{\mathrm{KS}}_{v\mathbf{k}} - \omega} F^{\mathrm{TDDFT}}_{tt'} \frac{\Phi(t';\mathbf{G}')}{\epsilon^{\mathrm{KS}}_{c'\mathbf{k}'} - \epsilon^{\mathrm{KS}}_{v'\mathbf{k}'} - \omega},$$

where ϵ^{KS} are KS eigenvalues, $\Phi(t;\mathbf{G})$ is the Fourier transform of a pair $(v\mathbf{k}, c\mathbf{k})$ of KS eigenfunctions, and $F^{\mathrm{TDDFT}}_{tt'}$ are matrix elements of f_{xc} in the basis of the Φ's. In the spirit of Ref. [10], we choose the latter equal to the sum of the matrix elements of the self-energy correction and of the electron-hole interaction in the BSE. This yields $T = T_1 + T_2$ with

$$T_1 = \frac{2}{N_k}\sum_{t} \frac{\Phi^*(t;\mathbf{G})\Phi(t;\mathbf{G}')}{(\epsilon^{\mathrm{KS}}_{c\mathbf{k}} - \epsilon^{\mathrm{KS}}_{v\mathbf{k}} - \omega)^2}[\Delta\epsilon^{\mathrm{GW}}_{c\mathbf{k}} - \Delta\epsilon^{\mathrm{GW}}_{v\mathbf{k}}] \tag{2}$$

and

$$T_2 = \frac{2}{N_k^2}\sum_{tt'} \frac{\Phi^*(t;\mathbf{G})}{\epsilon^{\mathrm{KS}}_{c\mathbf{k}} - \epsilon^{\mathrm{KS}}_{v\mathbf{k}} - \omega} F^{\mathrm{BSE}}_{tt'} \frac{\Phi(t';\mathbf{G}')}{\epsilon^{\mathrm{KS}}_{c'\mathbf{k}'} - \epsilon^{\mathrm{KS}}_{v'\mathbf{k}'} - \omega}. \tag{3}$$

$\Delta\epsilon^{\mathrm{GW}}$ are GW corrections to the KS eigenvalues and

$$F^{\mathrm{BSE}}_{tt'} = -\int d\mathbf{r}d\mathbf{r}'\,\Phi(v\mathbf{k}, v'\mathbf{k}';\mathbf{r})W(\mathbf{r}',\mathbf{r})\Phi^*(c\mathbf{k}, c'\mathbf{k}';\mathbf{r}')$$

are matrix elements of the screened Coulomb interaction. Spin has already been summed over. This result is equal to Eq. (11) of Ref. [10]; however, the present derivation is more general since it does not use Eq. (9) of Ref. [10]: *it does not require* Φ *to be invertible and* f_{xc} *to be static.*

In order to elucidate this important point, and to assess the validity of both approaches, it is crucial to analyze the behavior of the different terms. We will do this looking at the macroscopic dielectric function $1/\varepsilon^{-1}_{00}(\mathbf{q} \to 0, \omega)$ of bulk silicon, that has been studied in previous publications [8–10]. To start with, we note that in Ref. [10] the Φ's were considered as elements $(vc\mathbf{k};\mathbf{G})$ of an invertible matrix. For a fixed number of reciprocal lattice vectors $\mathbf{G}$, this necessarily implies a fixed number of k-points, hence a discretization of the Brillouin zone. It is easier to understand some important relations using a coarse sampling. We therefore use first only two special k-points in the irreducible Brillouin zone, and six (three valence and three conduction) bands in order to illustrate the validity of Eqs. (2) and (3).

In the upper panel of Fig. 1 we have shown the result of a standard DFT-LDA RPA calculation [i.e., $T = 0$ in Eq. (1): dotted curve], a GW-RPA result (where LDA-KS eigenvalues have been replaced by quasiparticle ones in a $\chi^{(0)}_{\mathrm{GW}}$, but still T is neglected: dashed curve), and the result of a BSE calculation (continuous curve). We have then again used LDA-KS eigenvalues in $\chi^{(0)}$, but considered the contribution T_1. The resulting curve (circles) yields results that are indistinguishable from the GW-RPA ones: *the contribution* T_1 *correctly acts here as an effective self-energy shift.* Finally, the squares show the result *when both* T_1 *and* T_2 *are included: the spectrum is now identical to the BSE result.* In the following, we concentrate on the electron-hole contribution T_2, since including the self-energy correction via T_1 is of no practical interest (it does not avoid the calculation of $\Delta\epsilon^{\mathrm{GW}}$) and even worsens the overall behavior; hence we use $\chi^{(0)}_{\mathrm{GW}}$ and ϵ^{GW} instead of $\chi^{(0)}$ and ϵ^{KS}, and do not consider T_1. To further investigate T_2, we study $f^{\mathrm{e-h}}_{xc}(\omega) = \chi^{(0)-1}_{\mathrm{GW}}(\omega)T_2(\omega)\chi^{(0)-1}_{\mathrm{GW}}(\omega)$. The lower panel of Fig. 1 shows several results for $q^2\Re f^{\mathrm{e-h}}_{xc}(\mathbf{q}, \mathbf{G} = \mathbf{G}' = 0, \omega)$ for vanishing momentum transfer $\mathbf{q}$. Other wing and body elements ($\mathbf{G} \neq 0$) behave similarly, and are therefore not shown here. The different curves have been obtained by varying the dimension N_G of the matrices $\chi^{(0)}_{GW}$ and T_2. If we use $N_G = 1$, the resulting kernel (dotted line) has a very sharp pole-like frequency dependence. With increasing N_G, this feature moves to higher energy, leaving behind an essentially flat $f^{\mathrm{e-h}}_{xc}$. At $N_G = 169$, $f^{\mathrm{e-h}}_{xc}$ is completely static in the optical range. In fact, only when N_G approaches the number of transitions N_t that are considered (288 in our example), the hypothesis of invertibility of the matrices Φ, made in the derivation

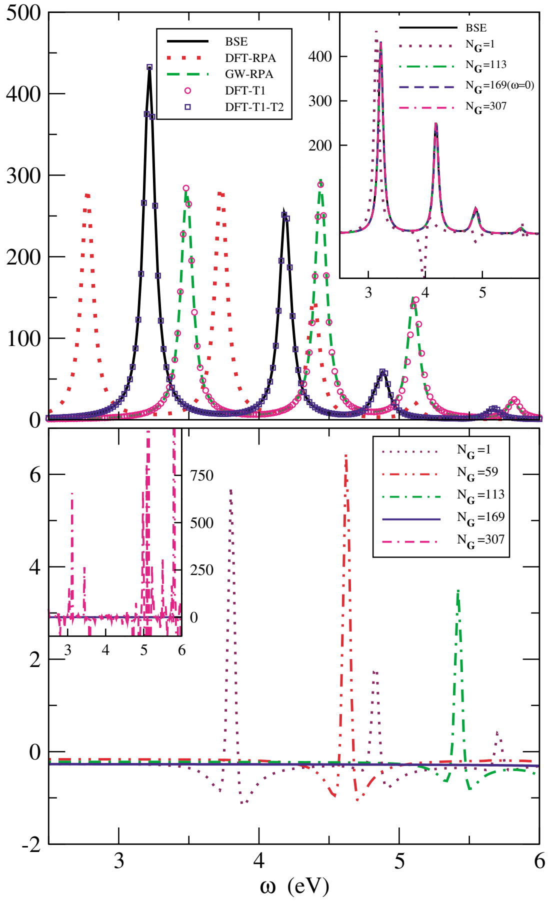

FIG. 1 (color online). Upper panel: Imaginary part of the macroscopic dielectric function of Si calculated using 2 k-points in the irreducible Brillouin zone. Dotted line: RPA calculation using DFT-KS eigenvalues; dashed line: RPA using GW energies; solid line: BSE result; circles: obtained using Eq. (1) including T_1 (*not* T_2); squares: same but including both T_1 and T_2. In the inset: solid line: BSE result; dotted line: obtained using $f_{xc}^{\mathrm{e-h}}$ calculated with $N_G = 1$ (see text); dot-dashed line: same but $N_G = 113$; dashed line: $N_G = 169$, and adiabatic approximation $f_{xc}^{\mathrm{e-h}}(\omega = 0)$; doubledash-dotted line: $N_G = 307$. Lower panel: Real part of $\lim_{\mathbf{q}\to 0} q^2 f_{xc}^{\mathrm{e-h}}(\mathbf{q}, \omega)$, using several matrix dimensions N_G. In the inset, out of scale, result for $N_G = 307$.

of a static kernel in Ref. [10], can be valid. However, as explained above, using the present derivation this condition can be dropped. In fact, the inset in the upper panel of Fig. 1 shows the spectra that are obtained using $N_G = 1$, 113, 169, and 307. Besides the clearly wrong result obtained in the first case, leading even to negative absorption, all other results are equally virtually perfect. This set of results includes the one shown already in the main part of the panel, which had been obtained with $N_G = 113$, the result for $N_G = 169$ corresponding to a static kernel (note that the static limit $f_{xc}^{\mathrm{e-h}}(\omega = 0)$ has been used to produce the absorption curve for this value), and is even true for $N_G = 307$. Now $N_G > N_t$, and $\chi_{\mathrm{GW}}^{(0)}$ has several eigenvalues close to zero. Therefore $f_{xc}^{\mathrm{e-h}}$ is scattered and out of the vertical range of Fig. 1 (see the out of scale inset), but since this meaningless kernel is finally used in a multiplication with $\chi_{\mathrm{GW}}^{(0)}$, the result remains so surprisingly excellent [16].

These findings are not only promising, but also of potential practical interest since, if one does not require the Φ's to be invertible and the kernel to be static, the basis size N_G can be chosen to be much smaller than N_t (basis size of the BSE). It remains to check how things work out in a realistic calculation. Therefore, we have shown in Fig. 2 the spectra of bulk silicon calculated with the same number of bands, but a converged set of 256 shifted k-points in the Brillouin zone. The result (solid line), obtained with $N_G = 307 \ll N_t = 2304$, is again practically coincident with the BSE calculation (dashed line), which is in turn as usual in good agreement with the experiment (dots) [18]. The present parameter-free *ab initio* result is clearly closer to the BSE result than was the fitted result of Ref. [10] (doubledot-dashed line). Concerning the relation between N_t and N_G, one should also note that, with increasingly dense Brillouin zone sampling, one can find more nontrivial eigenvalues of $\chi_{\mathrm{GW}}^{(0)}$ close to zero for N_G well below N_t: it happens for $N_G = 387 \ll N_t = 2304$ in the present calculation of silicon [19]. An immediate consequence for the calculation using the denser k-point sampling is the fact that, although we find an excellent spectrum, the kernel starts to be scattered at relatively low N_G, so that the limit of a completely static kernel is never reached.

Finally, we have decided to expose the method to a more severe test, by applying it to cubic silicon carbide. SiC is in fact a large-gap material with half the dielectric

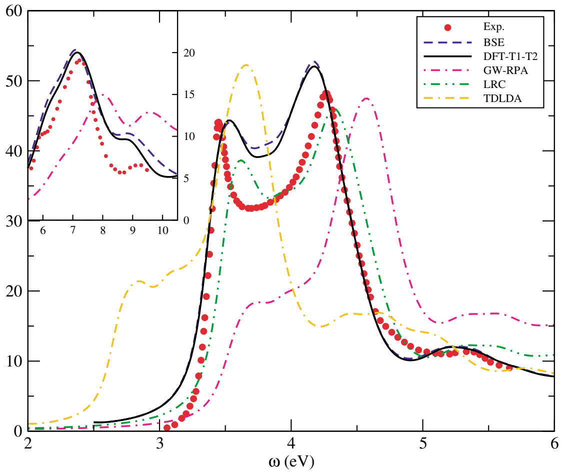

FIG. 2 (color online). Imaginary part of the macroscopic dielectric function of Si. Doubledash-dotted line: TDLDA result; dot-dashed line: RPA result using GW energies; dashed line: BSE result; solid line: calculated using Eq. (1); doubledot-dashed line: calculated using only the long-range contribution to the xc kernel, Ref. [10]; dots: experiment [18]. In the inset: imaginary part of the macroscopic dielectric function of SiC.

constant of silicon (hence twice the electron-hole interaction) which requires a considerably higher number of plane waves to describe the wave functions with respect to silicon. One might hence suspect that, contrary to the case of silicon, a well-converged spectrum cannot be obtained before N_G passes some critical value leading to absurd results. In fact, we have found that also in the case of SiC, calculated with three valence and three conduction bands, and using 256 shifted k-points as in silicon, strong fluctuations in $\chi_{\mathrm{GW}}^{(0)-1}$ show up when N_G is chosen to be bigger than 387. However, in that range a reasonably converged spectrum, shown by the solid line in the inset of Fig. 2, is already in very good agreement with the result of the BSE calculation (dashed line), and hence corrects most of the error of the GW-RPA result (dot-dashed line) with respect to experiment (dots) [20].

The present formulation allows one a straightforward comparison to the EXX kernel studied by Kim and Görling [9]: if in Ref. [9] one supposes that EXX-KS and Hartree-Fock wave functions are equal, the second term of their kernel should correspond to a shift from EXX to Hartree-Fock eigenvalues, i.e., a term analogous to our self-energy shift term T_1, but for the *unscreened* exchange. Analogously, their first term contains the bare Coulomb interaction in the same way as our excitonic T_2 treats the *screened* one. The empirical cutoff in Ref. [9] can therefore be seen as a way to simulate the missing screening, which should be contained in the further correlation terms of their expansion.

This stresses a big advantage of our formulation: in contrast to other approaches, here it is straightforward to use all achievements made in the framework of MBPT (including, as pointed out, the correct use of screening, which makes our method parameter-free). A second advantage of this generalized TDDFT is that, as in the corresponding BSE calculations, we can in practice often use the simple LDA ground state KS potential instead of the more complicated one of which our f_{xc} would be the functional derivative (although this approximation is of course expected to lead to the corresponding violation of sum rules [21]). Finally, we never have to explicitly calculate f_{xc}, besides the mostly academic discussions above: as we have shown, the calculation of a spectrum is in fact much less critical, and the results much more stable, than the calculation of f_{xc}. This explains the excellent results that we have shown above, and suggests that the approach we have presented may open the way to a precise but efficient calculation of electronic spectra for even complex systems [22].

In conclusion, we have solved the long-standing problem of how to calculate *ab initio* realistic absorption spectra of materials without solving the BSE, by combining the knowledge gained from the latter with the advantages of TDDFT. We have obtained a generalization and further insight by showing that the *same* spectra can be obtained using very different kernels, ranging from static to frequency dependent ones.

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Note added.—A different derivation of Eq. (3) and similar results for silicon have been brought to our attention [23].

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