

Excitonic Effects in Solids Described by Time-Dependent Density-Functional Theory

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Starting from the many-body Bethe-Salpeter equation we derive an exchange-correlation kernel f_{xc} that reproduces excitonic effects in bulk materials within time-dependent density functional theory. The resulting f_{xc} accounts for both self-energy corrections and the electron-hole interaction. It is *static*, *non-local*, and has a long-range Coulomb tail. Taking the example of bulk silicon, we show that the $-\alpha/q^2$ divergency is crucial and can, in the case of continuum excitons, even be sufficient for reproducing the excitonic effects and yielding excellent agreement between the calculated and the experimental absorption spectrum.

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The calculation of electronic excitations has remained a major challenge in the field of solid state theory. In fact, whereas ground state properties can be computed today with good precision within density functional theory (DFT) [1], electronic excitations are accessible only through additional corrections. Within many-body perturbation theory, Hedin's *GW* corrections [2] are used to get electron addition and removal energies, and the Bethe-Salpeter equation (BSE) for neutral excitations as those measured, for example, in absorption or electron-energy-loss spectroscopy (EELS). In fact, for several years *ab initio* BSE calculations have yielded generally good agreement between the calculated and the experimental absorption spectra for both finite [3] and infinite systems [4–6]. However, these calculations are necessarily cumbersome, which has up to now prevented their application to very complex systems.

In recent years, an alternative approach has been developed which allows in principle the correct description of exchange-correlation effects in the neutral excited state, namely time-dependent density functional theory (TDDFT) [7,8]. As in the case of static DFT the main obstacle resides in finding a good approximation to the unknown exchange-correlation (xc) contribution. For the ground state properties of the majority of finite and infinite systems, the local density approximation (LDA) has turned out to yield surprisingly good results. In the case of the absorption and EELS spectra of finite systems, and of EELS spectra of solids, TDDFT has yielded good results using the adiabatic LDA approximation (TDLDA) for the xc kernel f_{xc} [8]. However, this is not true for the *absorption* spectra of *solids* [9]. In fact, it has turned out that the results for the latter obtained within TDLDA are extremely close to those obtained in a simple random phase approximation (RPA) calculation, where the xc kernel is completely neglected, and only local field effects (in other words, the contribution coming from the variation of the Hartree potential) are taken into account. It should be

pointed out that this similarity between RPA and TDLDA spectra to some extent also holds in the case of clusters and EELS spectra of solids, but the results are nevertheless satisfactory because in those cases already RPA spectra, including local field effects, are in good agreement with experiment.

On the other hand, it would be extremely desirable to obtain good absorption spectra of solids within TDDFT, since the equations to be solved are two-point ones, in contrast to the four-point BSE. The obstacle to be removed to this aim is hence the fact that a good approximation to the xc kernel must be found. In this context, extensive discussions can be found in literature about the need to include long-range nonlocal terms and dynamical (memory) effects in the kernel [8,10].

In this work, we show how a TDDFT equation for the macroscopic dielectric function can be derived from the Bethe-Salpeter equation. The derivation is exact in the sense that the resulting equation does yield the same spectra as the standard Bethe-Salpeter equation (with its own various approximations [4–6]). We demonstrate that the resulting xc kernel has a $1/q^2$ contribution, the strength of which is inversely proportional to the screening in the system. Finally, we calculate the absorption and the refraction index spectra of bulk silicon within TDDFT, using only this *static* long range tail as xc kernel, and obtain excellent agreement with experiment.

To start with it is useful to put the TDDFT equation and the Bethe-Salpeter equation for ε^{-1} on the same footing. In fact, both equations can be written schematically in the same Dyson-like form,

$$S = S^{(0)} + S^{(0)}KS. \quad (1)$$

Here, S can be either the two-point polarizability χ , from which we can obtain the inverse dielectric function $\varepsilon^{-1} = 1 + \nu\chi$, or $S = L$, the two-particle correlation function

which yields χ (and then ε^{-1}) by contracting two of its four indices

$$\chi(x_1, x_2) = L(x_1, x_1^+; x_2, x_2^+). \quad (2)$$

Here x stands for space, spin, and time coordinates. Of course, this holds only for what concerns the form, but not the specific details. First, quantities in the TDDFT equation are two-point ones, whereas in the BSE they are four-point ones. Second, in TDDFT $S^{(0)}$ is the independent-particle response function $\chi^{(0)}$ constructed with the Kohn Sham (KS) orbitals and eigenvalues, whereas in the BSE formalism $S^{(0)}$ stands for the independent quasiparticle response $L^{(0)}$, i.e., it is constructed using quasiparticle eigenvalues and eigenfunctions (e.g., obtained from a GW calculation). Finally, in the TDDFT case, the kernel K is defined as $K = v + F^{\text{TDDFT}}$, where v is the Coulomb potential and F^{TDDFT} stands for the f_{xc} kernel. In the case of the BSE, $K = v + F^{\text{BSE}}$, where v and F^{BSE} are the four-point functions $v(x_1, x_2, x_3, x_4) = \delta(x_1, x_2)\delta(x_3, x_4)v(x_1, x_3)$ and $F^{\text{BSE}}(x_1, x_2, x_3, x_4) = -\delta(x_2, x_4)\delta(x_1, x_3)W(x_1, x_2)$, where W is the screened interaction. In the case of TDDFT, one can also understand Eq. (1) as a four-point equation, but with $F^{\text{TDDFT}}(x_1, x_2, x_3, x_4) = \delta(x_1, x_2)\delta(x_3, x_4)f_{\text{xc}}(x_1, x_3)$ which implies that one can immediately contract the indices by pairs and reduce the equation to a two-point one.

If one performs a basis transformation of the form $x_l \rightarrow \psi_n(x_l)$, where the $\psi_n(x_l)$ are the one-particle orbitals which diagonalize the four-point $S^{(0)}$, Eq. (1) can be transformed to an effective two-particle Hamiltonian equation,

$$H_{(n_1 n_2)(n_3 n_4)}^{2p} \equiv (\epsilon_{n_2} - \epsilon_{n_1})\delta_{n_1 n_3}\delta_{n_2 n_4} + (f_{n_1} - f_{n_2})K_{(n_1 n_2)(n_3 n_4)}. \quad (3)$$

Here the indices n_i refer to the fact that matrix elements involve four eigenfunctions of the starting effective one-particle Hamiltonian with eigenvalue ϵ_{n_i} and occupation f_{n_i} . Defining the identity operator $I = \delta_{m_1 m_3}\delta_{m_2 m_4}$, S is directly obtained from H^{2p} as

$$S_{(n_1 n_2)(n_3 n_4)} = [H^{2p} - I\omega]_{(n_1 n_2)(n_3 n_4)}^{-1}(f_{n_4} - f_{n_3}). \quad (4)$$

H^{2p} can be diagonalized, and from its eigenvalues E_λ and eigenstates $A_\lambda^{n_1 n_2}$ the spectral representation of S can be constructed.

Since the $\psi_n(x_l)$ have to diagonalize $S^{(0)}$, they must be the KS orbitals for the TDDFT equation and the QP eigenfunctions for the BSE. If these functions are equal, and if the A_λ and E_λ are equal, the BSE and TDDFT spectra would be the same. For a static f_{xc} kernel, this implies that the matrix elements of the Hamiltonians H_{TDDFT}^{2p} and H_{BSE}^{2p} are equal. In this scenario, we can directly compare the BSE and TDDFT approaches. First, in the BSE the eigenvalues ϵ_n are quasiparticle energies (as obtained, for example, from a GW calculation), whereas in TDDFT they are the eigenvalues obtained from the KS equation

with the (in principle exact) xc potential. Second, for the BSE we have

$$F_{(n_1 n_2)(n_3 n_4)}^{\text{BSE}} = - \int d\mathbf{r} d\mathbf{r}' \Phi(n_1, n_3; \mathbf{r}) \times W(\mathbf{r}', \mathbf{r})\Phi^*(n_2, n_4; \mathbf{r}'),$$

with the matrices Φ defined according to

$$\Phi(n_1, n_2; \mathbf{r}) := \psi_{n_1}(\mathbf{r})\psi_{n_2}^*(\mathbf{r}), \quad (5)$$

whereas the exchange-correlation contribution to the TDDFT kernel reads

$$F_{(n_1 n_2)(n_3 n_4)}^{\text{TDDFT}} = \int d\mathbf{r} d\mathbf{r}' \Phi(n_1, n_2; \mathbf{r}) \times f_{\text{xc}}(\mathbf{r}, \mathbf{r}')\Phi^*(n_3, n_4; \mathbf{r}').$$

[The Hartree contribution $v_{(n_1 n_2)(n_3 n_4)}$ is of course equal in both cases.] A comparison of the two cases does hence immediately tell us that the BSE and TDDFT equations would yield the same spectrum if the static f_{xc} satisfies

$$(f_{n_1} - f_{n_2}) \int d\mathbf{r} d\mathbf{r}' \Phi(n_1, n_2; \mathbf{r})f_{\text{xc}}(\mathbf{r}, \mathbf{r}')\Phi^*(n_3, n_4; \mathbf{r}') = \mathcal{F}_{(n_1 n_2)(n_3 n_4)}, \quad (6)$$

where [11]

$$\mathcal{F}_{(n_1 n_2)(n_3 n_4)} = (\epsilon_{n_2}^{\text{QP}} - \epsilon_{n_1}^{\text{QP}} - \epsilon_{n_2}^{\text{DFT}} + \epsilon_{n_1}^{\text{DFT}})\delta_{n_1 n_3}\delta_{n_2 n_4} + (f_{n_1} - f_{n_2})F_{(n_1 n_2)(n_3 n_4)}^{\text{BSE}}. \quad (7)$$

It is clear that, if the transformation $x_l \rightarrow \psi_n(x_l)$ was complete in all four indices, Eq. (6) could never be satisfied. The reason is that the two operators, F^{TDDFT} and \mathcal{F} , cannot be equal because of the way the δ functions are put in real space. On the other hand, if the two operators cannot be made equal, then the spectrum can be equal only if at least one of the two operators (in that case, f_{xc}) is energy dependent [12]. This in principle correct, general statement, can be made less restrictive by realizing that in practice only a finite number of transitions contributes to the optical spectrum. This means that we can use an incomplete basis in transition space. In this reduced Hilbert space we can still find a static operator that satisfies the required equality in transition space in a particular energy range, even though the real-space operators are *not* equal [13]. In order to discuss this possibility, we rewrite Eq. (6) as

$$(f_{n_1} - f_{n_2}) \sum_{\mathbf{G}, \mathbf{G}'} \Phi(n_1, n_2; \mathbf{G})f_{\text{xc}}(\mathbf{q}, \mathbf{G}, \mathbf{G}')\Phi^*(n_3, n_4; \mathbf{G}') = \mathcal{F}_{(n_1 n_2)(n_3 n_4)}, \quad (8)$$

where $\mathbf{q} = \mathbf{k}_2 - \mathbf{k}_1 = \mathbf{k}_4 - \mathbf{k}_3$. Since for the particle-hole and hole-particle contributions of a nonmetal the factor $(f_{n_1} - f_{n_2})$ can never be zero, we could in principle obtain the matrix f_{xc} from Eq. (8) by inverting the matrices Φ :

$$f_{xc}(\mathbf{q}, \mathbf{G}, \mathbf{G}') = \sum_{n_1 n_2 n_3 n_4} \frac{1}{(f_{n_1} - f_{n_2})} \times \Phi^{-1}(n_1, n_2; \mathbf{G}) \mathcal{F}_{(n_1 n_2)(n_3 n_4)} \times (\Phi^*)^{-1}(n_3, n_4; \mathbf{G}'). \quad (9)$$

As pointed out above, the sum over the indices n_i is necessarily limited to some subspace of important transitions, because otherwise the inverse of Φ does not exist. In certain cases, a subspace which at the same time allows the matrix to be invertible and to reasonably reproduce the exciton spectrum cannot be found. One example is a two-band model with $\epsilon^{\text{DFT}} = \epsilon^{\text{QP}}$ consisting of plane wave states $\psi_{b\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{G}_b \cdot \mathbf{r}} e^{i\mathbf{k}\mathbf{r}}$, with $\mathbf{G}_b = \mathbf{G}_v$ or \mathbf{G}_c . In this case the matrices Φ are k independent, which means that all their rows are equal. In other words, the matrix F^{TDDFT} is k independent, whereas the matrix F^{BSE} goes as $1/(k - k')^2$, which is a clear contradiction. On the other hand, if a subspace where Φ is invertible can be

found, it is clear that the resulting kernel is *frequency independent*, as none of the quantities implied, F^{BSE} or Φ , are frequency dependent (if the kernel of the BSE is chosen to be frequency independent [12]). Moreover f_{xc} is necessarily *not local*, as the expression in Fourier space depends separately on \mathbf{G} and on \mathbf{G}' . In fact, its nonlocality is used as the degree of freedom which is necessary to fulfill equality (6).

On the other hand, one can try to look directly at S instead of focusing on f_{xc} . To do that we go back to the initial Eq. (1) which we can write in a symmetric way as

$$S = S^{(0)}[S^{(0)} - S^{(0)}KS^{(0)}]^{-1}S^{(0)}. \quad (10)$$

Since the independent particle polarizability is

$$\chi^{(0)}(\mathbf{r}, \mathbf{r}', \omega) = \sum_{n_1 n_2} (f_{n_1} - f_{n_2}) \times \frac{\Phi(n_1, n_2; \mathbf{r})\Phi^*(n_1, n_2; \mathbf{r}')}{\epsilon_{n_1}^{\text{DFT}} - \epsilon_{n_2}^{\text{DFT}} - \omega},$$

the equation for the two-point $S = \chi$ becomes

$$\chi(\mathbf{r}, \mathbf{r}', \omega) = \int d\mathbf{r}'' d\mathbf{r}''' \chi^{(0)}(\mathbf{r}, \mathbf{r}'', \omega) \cdot \left[\chi^{(0)}(\mathbf{r}_1, \mathbf{r}_2, \omega) - \int d\mathbf{r}_3 d\mathbf{r}_4 \chi^{(0)}(\mathbf{r}_1, \mathbf{r}_3, \omega) \nu(\mathbf{r}_3, \mathbf{r}_4) \chi^{(0)}(\mathbf{r}_4, \mathbf{r}_2, \omega) + \sum_{n_1 n_2 n_3 n_4} \frac{\Phi^*(n_1, n_2; \mathbf{r}_1)}{\epsilon_{n_2}^{\text{DFT}} - \epsilon_{n_1}^{\text{DFT}} - \omega} \mathcal{F}_{(n_1 n_2)(n_3 n_4)} \frac{\Phi(n_3, n_4; \mathbf{r}_2)(f_{n_4} - f_{n_3})}{\epsilon_{n_4}^{\text{DFT}} - \epsilon_{n_3}^{\text{DFT}} - \omega} \right]_{\mathbf{r}'', \mathbf{r}'''} \cdot \chi^{(0)}(\mathbf{r}''', \mathbf{r}', \omega), \quad (11)$$

where we have used $\Phi(n_1, n_2, \mathbf{r}) = \Phi^*(n_2, n_1, \mathbf{r})$, and substituted the term $\Phi f_{xc} \Phi^*$ using Eq. (6). In other words, *for those cases where the equality (6) can be fulfilled, i.e., in particular when a static kernel can be found*, we have succeeded in writing the two-point TDDFT equation in a way that exactly yields the BSE spectrum [14].

The explicit knowledge of the kernel is actually not needed. There is still a four-point quantity appearing, namely \mathcal{F} , however only in a matrix product instead of inversions and diagonalizations, which allows us to change space in a convenient way as it is also done in recursive inversions of BSE [5]. Despite this fact, in view of the ongoing discussions about the xc kernel it is interesting to examine some of its features, and in particular its long-range behavior. In fact, for valence (v, k) and conduction ($c, k + q$) states, $\Phi(v, \mathbf{k}, c, \mathbf{k} + \mathbf{q}; \mathbf{G} = 0)$ goes to zero as q for small q . Since $\mathcal{F}_{(v,c),(v,c)}$ in this limit behaves as a constant, an $f_{xc}(\mathbf{q}, \mathbf{G} = \mathbf{G}' = 0)$ obtained from Eq. (9) must behave as $1/q^2$. There is in fact a positive long-range contribution stemming from the QP shift of eigenvalues (as also predicted in Ref. [15]), and a negative one resulting from the electron-hole interaction, which is the main point of interest here.

Using the above results, one can also understand why the TDLDA approximation yields much worse results for the absorption than for the loss spectra of solids. In fact, energy-loss spectra are directly related to the inverse of the dielectric matrix $\epsilon^{-1} = 1 + \nu\chi$. For the calculation of χ , the kernel f_{xc} is then added to ν , which already contains a long-range contribution $\nu(\mathbf{G} = 0)$. So the presence or absence of the long range term in f_{xc} does not necessarily

show up. However, in the case of absorption spectra, one can show [16] that the macroscopic dielectric function is given by

$$\epsilon_M(\omega) = 1 - \lim_{\mathbf{q} \rightarrow 0} [\nu(\mathbf{q}) \bar{\chi}_{\mathbf{G}=\mathbf{G}'=0}(\mathbf{q}, \omega)], \quad (12)$$

where $\bar{\chi}$ has been calculated in a Dyson-like equation such as (1) using the same f_{xc} , but added to a coulombian $\bar{\nu}$ which does not contain the long range term, i.e., $\nu(\mathbf{G} = 0)$ is set to zero. Obviously in that case, a neglect of the divergence in f_{xc} makes an essential difference.

We can carry this discussion about the long-range electron-hole interaction term farther by (i) assuming that we absorb the first, positive contribution in the energy shift of our starting $\chi^{(0)}$ (since anyway we do not know the eigenvalues of the exact xc potential which would go along with the exact kernel) and (ii) supposing that we have a system where the long-range term is completely dominating the rest of the xc contribution, namely, where we can approximately write $f_{xc}(\mathbf{q}, \mathbf{G}, \mathbf{G}') = -\delta_{\mathbf{G}, \mathbf{G}'} \alpha / |\mathbf{q} + \mathbf{G}|^2$. In other words, the long-range electron-hole attraction part of f_{xc} reduces the Hartree part, which is reasonable since it stems from the exchange potential. This approximation works best for systems with weakly bound excitons. For a demonstration we have therefore performed a TDDFT calculation for bulk silicon, in the following way: First, we have determined the DFT-LDA electronic structure. Second, we have constructed $\chi^{(0)}$, but with the eigenvalues shifted to the GW ones, in order to simulate the first part of the kernel as explained above.

Third, we have used $f_{xc}(\mathbf{r}, \mathbf{r}') = -\alpha/4\pi|\mathbf{r} - \mathbf{r}'|$, with the empirical value $\alpha = 0.2$. The result of the TDDFT calculation for $\epsilon_M(\omega)$ is shown in Fig. 1. The dots are the experimental results for the absorption spectrum [$\text{Im}(\epsilon)$] measured by Lautenschlager *et al.* [17] and the refraction index [$\text{Re}(\epsilon)$] measured by Aspnes and Studna [18]. The dot-dashed curve is the result of a standard TDLDA calculation (i.e., using DFT-LDA eigenvalues and the static short-range LDA xc kernel). We find the well-known discrepancies with experiment. The dashed curve is the BSE result. Finally, the continuous curve is the result of our approximate TDDFT calculation: It fits almost perfectly all experimental features in both real and imaginary parts of ϵ . It turns hence out that this *static long-range* contribution to the kernel is sufficient to reproduce the strong excitonic effect in a material with weakly bound excitons such as silicon. Preliminary results on other materials such as GaAs or AlAs are showing a similar quality of agreement with experiment. We refer to a forthcoming manuscript [19] for details.

In conclusion, we have derived a TDDFT equation from the Bethe-Salpeter equation which should be particularly suitable for practical applications to the absorption spectra

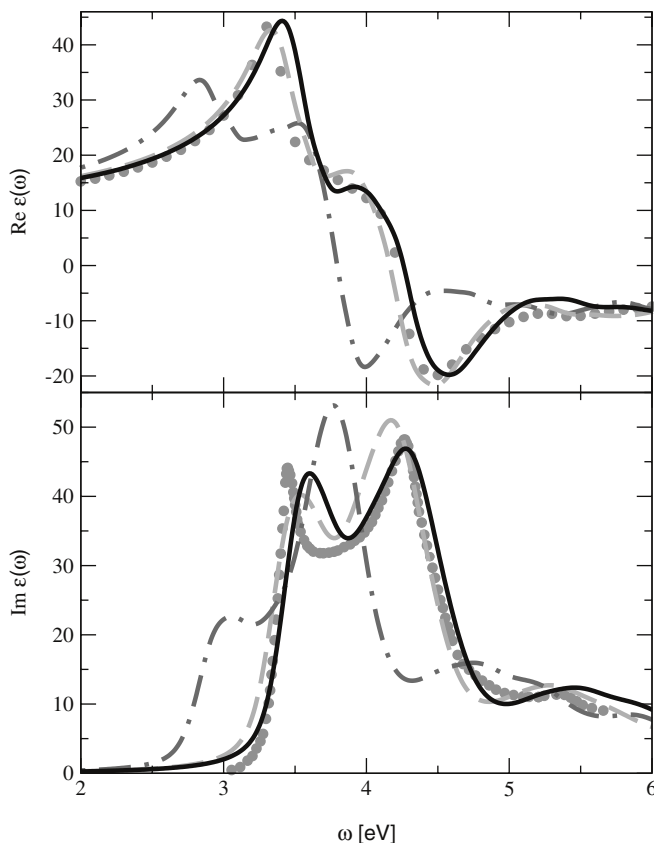


FIG. 1. Silicon, optical absorption (bottom), and refraction index (top panel) spectra. Dots: experiment. Dot-dashed curve: TDLDA result. Dashed curve: result obtained through the Bethe-Salpeter method. Continuous curve: TDDFT result using the long-range kernel derived in this work.

of solids. We have demonstrated that the static exchange-correlation kernel has a long-range contribution stemming from the electron-hole interaction. We have explained why this long-range contribution is particularly important for the absorption spectra of solids. At the example of bulk silicon, we have shown how a very simple approximation for the kernel can yield excellent agreement between the calculated TDDFT absorption spectrum and experiment.

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- [14] Note that in order to obtain this simple formula, we had to assume that KS orbitals and QP wave functions are equal. Otherwise, we could write, for example, the BSE in the KS basis, and we would get a complicated ω dependence instead of the simple $(\epsilon_{n_1} - \epsilon_{n_2} - \omega)$ diagonal part in Eq. (4).
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