Ab initio calculation of the exchange-correlation kernel in extended systems

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We develop a method to calculate the polarizability of a many-electron system within Green's function theory in a similar way as within time-dependent density functional theory and apply it to Si and GaAs. The method joins the computational simplicity of the latter with the accuracy of the former approach. The resulting exchange-correlation many-body kernel f_{xc}^{FQP} and optical spectra are in good agreement with those obtained by the solution of the Bethe-Salpeter equation.

It has been well known for two decades, after the pioneering work by Hanke and Sham,[1] that the inclusion of the electron-hole interaction is crucial to obtain absorption spectra of semiconductors in good agreement with experiments. However, the inclusion of this interaction in *ab initio* calculations is computationally so cumbersome that only very recently it could be considered for a number of systems, from small atomic clusters[2] to bulk crystals[3–5] to simple surfaces.[6] The difficulties arise from the fact that one has to solve the Bethe-Salpeter equation for the two-particle (electron and hole) Green's function, rather than a single-particle equation as in band theory. It would be highly desirable to develop a simpler method to deal with the electron-hole interaction.

A hint about how to reach this goal comes from time-dependent density functional theory (TDDFT),[7] where all many-body (MB) effects are embodied in the frequency-dependent exchange-correlation kernel $f_{xc}(\mathbf{r}_1,\mathbf{r}_2;\omega)$, which accounts for exchange-correlation (xc) in the linear response. Once it is known, the calculation of the polarizability and of the dielectric function proceeds in the Kohn-Sham (KS) scheme[8] as for independent electrons. The problem is that $f_{xc}(\mathbf{r}_1,\mathbf{r}_2;\omega)$ of TDDFT is not known and any approximation based on the homogeneous electron gas will miss important features of semiconductors and insulators.[9] In particular, it has been recently shown that $f_{xc}(\mathbf{r}_1,\mathbf{r}_2;\omega)$ has a long range component, of the form $\alpha(\omega)/|\mathbf{r}_1-\mathbf{r}_2|$, which cannot be derived from the homogeneous electron gas kernel but is essential to determine accurate optical spectra.[10,11]

In Ref. 10 a many-body xc kernel $f_{xc}^{FQP}(\omega)$ similar to that of TDDFT, was defined to be used with the independent-quasiparticle polarizability obtained within Green's function theory.[12] Its long-range component, which is very important to calculate optical properties, has been determined from the results of Bethe-Salpeter calculations of the macroscopic dielectric function of silicon and diamond and shown to be characterized by a frequency dependence much simpler than that of $f_{xc}(\omega)$. This approach, although yielding important information on the properties of $f_{xc}^{FQP}(\omega)$, does not allow a quick calculation of optical spectra, since it relies anyway on the solution of the Bethe-Salpeter equation. Very recently, an exchange-only calculation of the TDDFT kernel f_x has been carried out, which yields optical spectra agreeing well with

experiments only after an *ad hoc* truncation of the kernel in reciprocal space to account for correlation.[13,14] To summarize, the present situation is promising but not satisfactory; what is needed is a method for the direct (*ab initio*, without *ad hoc* adjustments and not based on the solution of the Bethe-Salpeter equation) calculation of the exchange–correlation kernel. This is the very purpose of this paper.

We present a suitable approximation for $f_{xc}^{FQP}(\omega)$, based on a first-order expansion in terms of the screened electron-hole interaction W, which allows its calculation *ab initio* without solving the Bethe-Salpeter equation. We apply this formulation to the optical spectra of Si and GaAs and find very good agreement with experiments. Moreover, in the case of Si we show that the calculated $f_{xc}^{FQP}(\omega)$ is in good agreement with that extracted from Bethe-Salpeter calculations. These results show that the present formulation, though approximate, account well for the electron-hole interaction in semiconductors.

The charge density induced by a time-dependent perturbation is described by the irreducible polarizability $P(\mathbf{r}_1,\mathbf{r}_2;t-t')$. Within TDDFT, its time Fourier transform $P(\mathbf{r}_1,\mathbf{r}_2;\omega)$ is given by

$$
\begin{aligned}
P(\mathbf{r}_1,\mathbf{r}_2;\omega) = {} & \chi_{KS}^{(0)}(\mathbf{r}_1,\mathbf{r}_2;\omega) \\
& + \int\int d\mathbf{r}_3\,d\mathbf{r}_4 \chi_{KS}^{(0)}(\mathbf{r}_1,\mathbf{r}_3;\omega) f_{xc}(\mathbf{r}_3,\mathbf{r}_4;\omega) \\
& \times P(\mathbf{r}_4,\mathbf{r}_2;\omega),
\end{aligned}
\tag{1}
$$

where $\chi_{KS}^{(0)}(\mathbf{r}_1,\mathbf{r}_2;\omega)$ is the independent-particle response function obtained within the KS scheme.

Equation (1) is relatively easy for numerical implementation, since it is a product of matrices whose indices are *single* space variables. The main obstacle is the poor knowledge of the xc kernel $f_{xc}(\mathbf{r}_1,\mathbf{r}_2;\omega)$ of real systems. The most widely used approximation is the adiabatic local-density approximation (LDA),[15] where the static xc kernel of the homogeneous electron gas with the local density is used at nonzero frequencies. Such an approximation fails to give a quantitative description of the optical properties of solids (see, in particular, Ref. 9 for Si).

A good quantitative description of the spectra of solids is instead obtained within MB theory, although at the expense of a huge computational effort. According to it, the KS states are dressed solving the Dyson equation containing a self-energy operator $\Sigma_{xc}(1,2)$. Consequently the independent-quasiparticle (independent-QP) polarizability is given by[16]

$$\chi^{(0)}(1,2) = -iG(1,2)G(2,1). \quad (2)$$

Here $G(1,2)$ is the one-particle Green's function, 1 (as well as 2, 3, etc) indicates space, time and spin coordinates $\mathbf{r}_1, t_1, \sigma_1$ altogether. The irreducible polarizability $P(1,2)$ differs from $\chi^{(0)}(1,2)$ for the presence of interactions among QP's

$$P(1,2) = -i \int \int d34 G(1,3)G(4,1)\Gamma(3,4;2)$$
$$:= \chi^{(0)}(1,2) + \delta P(1,2), \quad (3)$$

where $\delta P(1,2)$ is the change in the irreducible polarizability due to the excitonic effects and $\Gamma(1,2;3)$ is the irreducible vertex function. It is determined, following the Baym-Kadanoff scheme,[17] by solving the Bethe-Salpeter equation (BSE)

$$\Gamma(1,2;3) = \delta(1,2)\delta(1,3) + \int d(4567)\frac{\delta\Sigma_{xc}(1,2)}{\delta G(4,5)}$$
$$\times G(4,6)G(7,5)\Gamma(6,7;3). \quad (4)$$

The self-energy operator $\Sigma_{xc}(1,2)$ is usually evaluated according to the GW approximation[18] and $\delta\Sigma_{xc}/\delta G$ is calculated by neglecting terms of second order in W. As a consequence, it is given by the screened Coulomb interaction $W(1,2)$. An additional approximation is to neglect dynamical effects both in the self-energy and in W, which cancel each other to a good extent in semiconductors.[19] Calculations carried out in the past years by a few groups along these lines[2–6] have yielded spectra in quantitative agreement with experiments for many systems. However, they are computationally very demanding because one has to diagonalize an effective two-particle (electron-hole) Hamiltonian.[3]

In order to avoid this bottleneck, we have cast the MB linear-response theory in a form similar to the TDDFT linear response[10]

$$\hat{P}(\mathbf{q},\omega) = \hat{\chi}^{(0)}(\mathbf{q},\omega) + \delta\hat{P}(\mathbf{q},\omega)$$
$$:= \hat{\chi}^{(0)}(\mathbf{q},\omega) + \hat{\chi}^{(0)}(\mathbf{q},\omega)\hat{f}^{FQP}_{xc}(\mathbf{q},\omega)\hat{P}(\mathbf{q},\omega). \quad (5)$$

Here $\mathbf{q}$ is the transferred momentum and all quantities are matrices in the reciprocal space. Equation (5) defines the MB analog, $\hat{f}^{FQP}_{xc}(\mathbf{q},\omega)$, of the DFT xc kernel $\hat{f}_{xc}(\mathbf{q},\omega)$. $\hat{f}^{FQP}_{xc}$ can be found in terms of $\delta\hat{P}$ from Eq. (5), by inverting $\hat{\chi}^{(0)}$ and $\hat{P}$:

$$\hat{f}^{FQP}_{xc}(\mathbf{q},\omega) = [\hat{\chi}^{(0)}(\mathbf{q},\omega)]^{-1}\delta\hat{P}(\mathbf{q},\omega)\hat{P}^{-1}(\mathbf{q},\omega). \quad (6)$$

This is the very definition of the MB analog of the xc kernel of TDDFT. By expressing $\delta\hat{P}$ as $\hat{P} - \hat{\chi}^{(0)}$, Eq. (6) is easily seen to be equivalent to the form

$$\hat{f}^{FQP}_{xc}(\mathbf{q},\omega) = [\hat{\chi}^{(0)}(\mathbf{q},\omega)]^{-1} - \hat{P}^{-1}(\mathbf{q},\omega). \quad (7)$$

Similar work has been carried out by Streitenberger[20] for the homogeneous electron gas. The use of $\hat{f}^{FQP}_{xc}$ allows one to calculate the polarization similarly to the case of TDDFT, according to

$$\hat{P}(\mathbf{q},\omega) = (1 - \hat{\chi}^{(0)}_{KS}(\mathbf{q},\omega)\hat{f}_{xc}(\mathbf{q},\omega))^{-1}\hat{\chi}^{(0)}_{KS}(\mathbf{q},\omega)$$
$$= (1 - \hat{\chi}^{(0)}(\mathbf{q},\omega)\hat{f}^{FQP}_{xc}(\mathbf{q},\omega))^{-1}\hat{\chi}^{(0)}(\mathbf{q},\omega), \quad (8)$$

where the first equality is derived within TDDFT and the second within MB theory.

The problem is that $\hat{f}^{FQP}_{xc}$ itself is defined in Eq. (6) in terms of the (unknown) polarization $\hat{P}$. However, Eq. (6) allows us to make approximations on $\hat{f}^{FQP}_{xc}$. This is the TDDFT counterpart of the Bethe-Salpeter kernel, which is usually approximated to first order in $W(1,2)$. In the same spirit, we can approximate $\hat{f}^{FQP}_{xc}$, as given by Eq. (6), to the same order. As $\delta\hat{P}$ is of first order in W [see Eqs. (3) and (4)] it is sufficient to approximate $\hat{P}^{(-1)} \approx [\hat{\chi}^{(0)}]^{(-1)}$ in Eq. (6), yielding

$$\hat{f}^{FQP}_{xc}(\mathbf{q},\omega) \approx [\hat{\chi}^{(0)}(\mathbf{q},\omega)]^{-1}\hat{P}^{(1)}(\mathbf{q},\omega)[\hat{\chi}^{(0)}(\mathbf{q},\omega)]^{-1}, \quad (9)$$

where $\hat{P}^{(1)}$ is the expansion of $\delta\hat{P}$ to first order in W

$$P^{(1)}(1,2) = \int d(34) G(1,3)G(4,1)W(3,4)G(3,2)G(2,4). \quad (10)$$

As a result $\hat{f}^{FQP}_{xc}$ can be calculated by avoiding the solution of the BSE, the most computationally demanding part of the excitonic calculations. Indeed, after cumbersome, but straightforward algebra, we find

$$P^{(1)}_{\mathbf{G}_1\mathbf{G}_2}(\mathbf{q},\omega)$$
$$= 2\sum_{cc'vv'}\left[\frac{B_{cv}(-\mathbf{q}-\mathbf{G}_1)}{\omega - E_{cv} + i\delta}\right.$$
$$\times\left(\frac{B_{c'v'}(\mathbf{q}+\mathbf{G}_2)}{\omega + E_{c'v'} - i\delta}W_{vv'c'c} - \frac{B_{v'c'}(\mathbf{q}+\mathbf{G}_2)}{\omega - E_{c'v'} + i\delta}W_{vc'v'c}\right)$$
$$+ \frac{B_{vc}(-\mathbf{q}-\mathbf{G}_1)}{\omega + E_{cv} - i\delta}\left(\frac{B_{v'c'}(\mathbf{q}+\mathbf{G}_2)}{\omega - E_{c'v'} + i\delta}\right.$$
$$\left.\left.\times W_{cc'v'v} - \frac{B_{c'v'}(\mathbf{q}+\mathbf{G}_2)}{\omega + E_{c'v'} - i\delta}W_{cv'c'v}\right)\right], \quad (11)$$
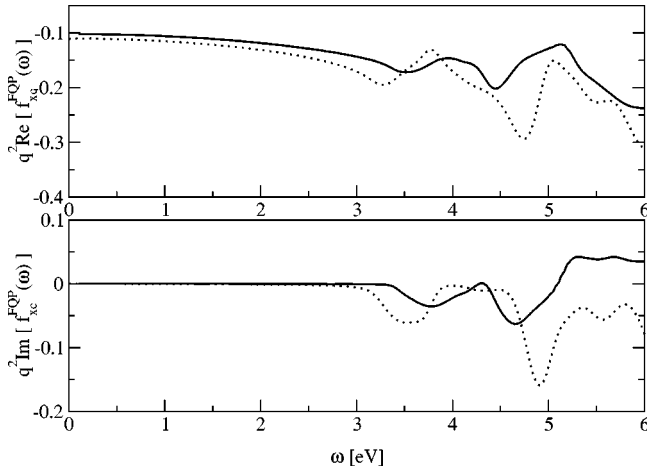
FIG. 1. Long-range component of the exchange-correlation kernel $[f_{xc}^{FQP}(\mathbf{q},\omega)]_{00}$ for $\mathbf{q}\rightarrow\mathbf{0}$ of Si. Dotted line: extracted from the Bethe-Salpeter equation approach, from Ref. 10. Full line: present work, Eq. (9).

where $\mathbf{q}$ is restricted to the first Brillouin Zone, v and v' label filled states, while c and c' label empty states (v, c, etc. include a band index n and wave vector $\mathbf{k}$). We have defined

$$W_{vv'c'c} := V^{-1} \int \int d\mathbf{r}_1 d\mathbf{r}_2 \psi_v^*(\mathbf{r}_1)\psi_{v'}^*(\mathbf{r}_2)$$
$$\times W(\mathbf{r}_1,\mathbf{r}_2)\psi_{c'}(\mathbf{r}_1)\psi_c(\mathbf{r}_2) \qquad (12)$$

and

$$B_{cv}(\mathbf{k}) := \int d\mathbf{r}\psi_c^*(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}\psi_v(\mathbf{r}), \qquad (13)$$

where $W(\mathbf{r}_1,\mathbf{r}_2)$ is the statically screened Coulomb interaction and V is the crystal volume. Equation (12) can be evaluated using the LDA wave functions, which well approximate QP ones.[21] $\hat{P}^{(1)}(\mathbf{q},\omega)$, $\hat{f}_{xc}^{FQP}(\mathbf{q},\omega)$ and $\hat{\chi}^{(0)}(\mathbf{q},\omega)$ are matrices indexed by $\mathbf{G}$ and $\mathbf{G}'$, whose products and inversions can be easily evaluated numerically.

The approximated expression for $\hat{f}_{xc}^{FQP}$ given in Eq. (9) can be improved in a systematic way, by inserting higher-order terms both in $\hat{\delta P}$ and $\hat{P}$ in Eq. (6).[22] We will show below that the first term, Eq. (9), already yields spectra in good agreement with experiments. It should be borne in mind that this approximation, although made in the spirit of the Bethe-Salpeter equation approach, is not fully equivalent to it; Eqation (6) is equivalent to the BSE approach, while Eq. (9) contains an additional expansion to first order in W.

Equation (9) is the most important result of this paper. It allows one to calculate the irreducible polarizability according to the second line of Eq. (8). This must be contrasted with the result obtained by simply expanding the irreducible polarizability to first order in W

$$\hat{P}(\mathbf{q},\omega) = \hat{\chi}^{(0)}(\mathbf{q},\omega) + \hat{P}^{(1)}(\mathbf{q},\omega). \qquad (14)$$
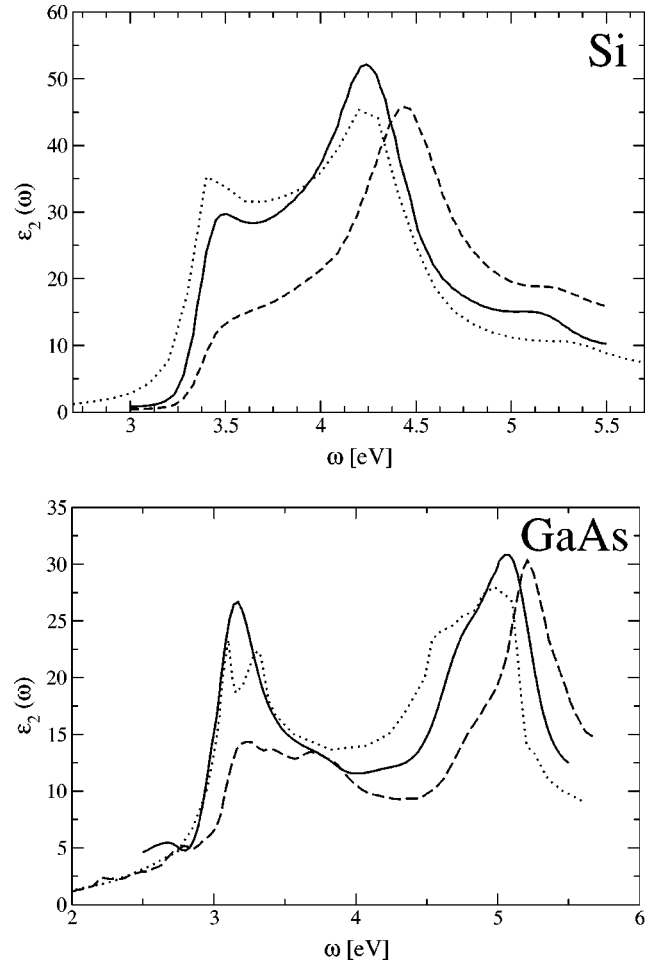

FIG. 2. Imaginary part of the dielectric function of Si (upper frame) and GaAs (lower frame). Long dashes: independent-quasiparticle spectrum. Full line: present work. For Si, dots: full BSE calculation, from Ref. 3. For GaAs, dots: experiment, from Ref. 26.

The two methods coincide to first order in W, but are different when higher-order terms are considered. Which of them is a better approximation can be decided only by comparing their results with experiments; however, it may be noticed soon that the former method may describe the formation of bound exciton states (and indeed it does[22]), corresponding to the vanishing of the denominator in the second line of Eq. (8), while the latter method, Eq. (14), cannot. We show below that the former method yields a good description of optical spectra of semiconductors, while Eq. (14) yields worse results, very close to those obtained within the independent-QP approximation.

Although similar equations for f_{xc} can be found in the literature,[23] we stress that Eq. (9) is for a different quantity, f_{xc}^{FQP}, which allows an efficient calculation of optical spectra in semiconductors and insulators.

We have first calculated the LDA-RPA (random phase approximation) absorption spectrum of Si and GaAs using several sets of $\mathbf{k}$ points including up to 2048 special $\mathbf{k}$ points in the whole Brillouin Zone and performing additional Monte Carlo integrations on 15 000 random $\mathbf{k}$ points to account for

the rapidly varying quantity $(\omega - E_{cv})^{-1}$. Self-energy corrections were included in the spectrum, for the sake of simplicity, in the form of a rigid upward shift (of 0.7 eV for Si and of 0.8 eV for GaAs) of the conduction bands [this is known to be a very good approximation in Si and GaAs (Ref. 24)]. To be consistent we used the same set of **k** points to calculate the quantity $\hat{P}^{(1)}(\mathbf{q}, \omega)$. Fifty bands were used for the RPA spectrum, while eight bands were seen to be sufficient to achieve a well converged $\hat{P}^{(1)}(\mathbf{q}, \omega)$ in the optical range. Local-field effects were included bringing the size of the dielectric matrix to 89×89. For more details, see Ref. 25.

It has already been shown[10,11] that only the long-range component of f_{xc}^{FQP}, i.e., with $\mathbf{G}, \mathbf{G}' = \mathbf{0}$ and **q** tending to zero, which diverges as $1/\mathbf{q}^2$, is important to determine optical properties in the frequency range of band-to-band transitions. This is shown in Fig. 1 as calculated for Si according to Eq. (9), and compared to that extracted from the Bethe-Salpeter approach in Ref. 10. In spite of the different approximations made in the two approaches, the agreement is very good up to 4.5 eV. The spectrum, calculated as in Ref. 10 by taking into account only the long-range component of the kernel, is compared in Fig. 2 (upper frame) with that obtained by solving the Bethe-Salpeter equation, and the agreement is very good. The approximate character of the present approach shows up only in a slight underestimation of the transfer of oscillator strength to low frequencies with respect to the Bethe-Salpeter approach. Even better results are obtained for the optical spectrum of GaAs, shown in Fig. 2 (lower frame). Optical spectra calculated for both materials according to a naive expansion of the irreducible polarizability to first order in W, Eq. (14), are much worse, very close to those obtained within the independent-quasiparticle approximation.

It is worth comparing the present results with those of Ref. 11. Our *ab initio* calculations confirm that the long-range component of $\hat{f}_{xc}^{FQP}$ is indeed frequency dependent, in agreement with the findings of Ref. 10, and at variance with the approach of Ref. 11. The static kernel of the latter work is recovered as a frequency-averaged value in the range of strong optical absorption. Finally, we compare our findings with the exchange-only approach of Refs. 13 and 14. Our Eq. (11) is equivalent to Eqs. (15) and (16) of Ref. 14, after substituting the bare with the screened Coulomb interaction. The other terms in Ref. 14 come from the QP corrections and are already embodied in our independent–QP polarizability. Although both approaches yield good optical spectra, we stress that ours is completely *ab initio*, while that of Refs. 13 and 14 has to use an *ad hoc* cutoff of the kernel in reciprocal space to account for correlation.

In conclusion, we propose a method for calculating *ab initio* the exchange correlation kernel of TDDFT, based on its expansion to first order in W, the screened electron-hole interaction. A similar method could be used to calculate f_{xc} of TDDFT, provided the true exchange-correlation potential is known. The calculation of optical spectra including excitonic and local-field effects according to the present method retains the computational simplicity of TDDFT. Calculations carried out for Si and GaAs yield very good agreement with experimental spectra. The kernel itself, as calculated for Si, compares very well with that extracted from the solution of the BSE, although the two approaches rely on different approximations. The present method is well promising to yield good optical spectra of complex systems, like surfaces or large clusters, where the Bethe-Salpeter approach is hardly applicable.

At the final stage of this work, we became aware of an apparently different approach,[27] based on the assumption of the equality of the four-point polarizabilities calculated within TDDFT and within the BSE approch, which yields the same result as ours [Eqs. (8), (9) and (11)] for optical spectra. While the convergence of both approaches to a common result is surely encouraging, the deep reason for it is still not understood.

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