
Many-body perturbation theory using the density-functional concept

Fabien Bruneval,^a Francesco Sottile,^{ac} Valerio Olevano,^{ad} Rodolfo Del Sole,^b
and Lucia Reining^a

^a*Laboratoire des Solides Irradiés, UMR 7642 CNRS/CEA,
École Polytechnique, 91128 Palaiseau, France*

^b*Istituto Nazionale per la Fisica della Materia
e Dipartimento di Fisica dell'Università di Roma "Tor Vergata",
Via della Ricerca Scientifica, 00133 Roma, Italy*

^c*present address: Donostia International Physics Center (DIPC),
20018 Donostia/San Sebastian, Spain*

^d*present address: Laboratoire d'Études des Propriétés Électroniques des Solides,
UPR 11, CNRS, F-38042, Grenoble, France*

Abstract

Many-body perturbation theory (MBPT) offers a convenient framework for the calculation of electronic excitations. In principle, all kinds of electronic excitations (i.e., neutral or involving a change in particle number) are accessible, and the physics that has to be included is relatively well understood. Also time-dependent density-functional theory (TDDFT) allows one in principle to describe excitations, at a *a priori* lower computational cost. However, in that case it is more difficult to design good approximations for the exchange-correlation contribution, since one does not work in the physically intuitive quasi-particle picture. Moreover, only neutral excitations are accessible. In order to combine the advantages of both approaches, we propose an alternative formulation of many-body perturbation theory that uses the density-functional concept. Variations of many-body quantities upon excitation are expressed through variations with respect to the density. In this way, instead of the usual four-point integral equation for the polarizability (namely, the Bethe-Salpeter equation), we obtain a two-point one (i.e., like in TDDFT), that leads to excellent optical absorption and energy loss spectra. The corresponding three-point vertex function and self-energy are then simply calculated via an integration, for any level of approximation. Moreover, we show the direct impact of this formulation on the time-dependent density-functional theory. With the help of numerical results, we discuss the consequences of exchange-correlation contributions to the response for optical spectra and for the band gap of bulk silicon and solid argon.

1 Introduction

The electronic structure of materials and its response to an external perturbation are key quantities for the interpretation of many experimental results or for the design of technological devices. Electronic excitations enter a wealth of scientific questions or daily-life problems, ranging e.g. from the deformation of molecules upon absorption of radiation in cancer research, to defect creation in nuclear waste, to photosynthesis or to the design of more efficient solar cells. It is therefore highly desirable to be able to describe, understand, and even predict electronic excitations and their consequences.

In this context, *ab initio* electronic structure calculations have become a tool of choice. In the community of solid-state physicists the widely used Kohn-Sham (KS) framework of the density-functional theory (DFT) [1] is a convenient starting point. Although DFT is in principle a ground state theory and KS eigenvalues are not meant to represent measurable electron addition and removal energies, the KS band structure already yields much useful information, and occupied bands are often in quite reasonable agreement with, e.g., photoemission results. In order to describe the response to an external perturbation, such as it is measured for example in optical absorption experiments, one can then construct a response function using an independent particle Fermi's golden rule, eventually including the self-consistent variations of the Hartree potential (which is equivalent to the Random Phase Approximation (RPA) including crystal local-field effects).

Beyond this, one should try to improve the description of exchange-correlation effects, both in the band structure and in the self-consistent variation of the corresponding potential. State-of-the-art calculations for solids are based on the many-body perturbation theory (MBPT). Concerning the band structure, in that case, quasi-particle (QP) energies are obtained from the solution of an equation similar to the Kohn-Sham one, but with the KS exchange-correlation (xc) potential v_{xc} replaced by the electron self-energy Σ . The last quantity is most often calculated in Hedin's GW approximation [2], where Σ is equal to the product of the one-particle Green's function G and the screened Coulomb interaction W calculated in the RPA. The resulting band structures, and in particular the band gap, are generally much closer to the measured ones than the KS results [3]. In order to include the self-consistent variation of Σ (which is the corresponding xc "potential") upon excitation, and hence to get improved response functions, one can then add the so-called "vertex corrections" beyond the RPA. This is done in practice by solving the four-point Bethe-Salpeter equation (BSE) for the polarizability P ; the kernel of this integral equation expresses the electron-hole interaction (whereas electron and hole are non-interacting when the RPA is adopted and local-field effects are neglected). The BSE leads in general to excellent absorption and electron energy-loss spectra [4]. In particular, one correctly describes the important excitonic effects.

Unfortunately, calculations of vertex corrections are cumbersome essentially because of the four-point (electron-hole scattering) nature of the BSE (see e.g. [4]). Calculations of the response functions in this framework have therefore been limited to relatively simple systems. Moreover, attempts to go beyond the GW approximation through vertex corrections (see e.g. [6, 7, 8, 9]) are rare and restricted to relatively simple systems, even though it is well known that the precision of the standard GW approximation is limited, and that the approximation often fails

for moderately to strongly correlated materials (see e.g. [10]). Again, this lack of examples is essentially due to the above-mentioned computational difficulties.

However, at least concerning response functions, it is known that *in principle* one could obtain the polarizability directly from a two-point equation: this is the case when one works in the framework of time-dependent DFT (TDDFT) [11], since one propagates the density (a function that is local in time and space) instead of the one-particle Green's function (which is non-local both in time and in space). TDDFT could therefore clearly be a prominent computational alternative to the BSE for the calculation of P . The drawback resides in the fact that up to recently, and contrary to the MBPT framework, reliable approximations for the xc potential $v_{xc}(\mathbf{r}, t)$ and its first density-variation, the xc kernel $f_{xc}(\mathbf{r}, \mathbf{r}', t, t')$, were missing in particular concerning absorption spectra of solids. Several attempts were therefore made to derive the unknown, but two-point, xc kernel of the TDDFT linear response equation for P from the known, but four-point, BSE, in order to combine the precision of the latter with the computational advantages of TDDFT [12, 13, 14]. Various different approaches have lead to quite similar expressions that, tested for real materials, have turned out to be extremely successful in reproducing the underlying BSE via a TDDFT-like equation. While recalling below some of these recent results, we will however focus on some more general questions that, we believe, are answered by the present work. These are (i) a physical explanation for the unexpected success of these approaches, (ii) a prescription of how one can use this MBPT-TDDFT combination in order to get response functions beyond the approximations that are currently made for the BSE, and (iii) the use of the TDDFT concept within MBPT (instead of the use of MBPT quantities within TDDFT). In fact, since TDDFT is not designed to access one-QP properties, like the band structure, this enlarges significantly the range of problems that can be addressed by such a combination.

The ultimate goal of this line of research can be summarized as the hope to combine the density-functional and the QP concepts in such a way that systematic and efficient improvements to the spectroscopic quantities of interest could be obtained. We believe that this work shows how this goal can be reached [15].

2 Many-body perturbation theory and time-dependent density-functional theory: two approaches, in part to the same problem

2.1 Hedin's equations

In the field of electronic excitations, it is convenient to work with Green's functions. The time-ordered one-particle Green's function is defined

$$G(1, 2) = -i\langle\Phi_0|T[\hat{\psi}(1)\hat{\psi}^\dagger(2)]|\Phi_0\rangle, \quad (1)$$

where $|\Phi_0\rangle$ is the many-body N-particle ground state, $\hat{\psi}(1)$ ($\hat{\psi}^\dagger(1)$) is the annihilation (creation) operator of an electron, T is the time-ordering operator and 1 stands for the set of the real space and time coordinates plus the spin degree of freedom, $1 = \mathbf{r}_1, t_1, \sigma_1$. The Green's function G has poles that correspond to electron addition and removal energies. Since the many-body

ground state $|\Phi_0\rangle$ is another unknown of the problem, the calculation of this quantity is not straightforward. One has to search either for a diagrammatic expansion or for a set of equations governing G that eventually may be somehow approximated. Here we adopt the second line, developed in its present form by Lars Hedin [2]. For the sake of comprehension of all our subsequent developments, we estimate useful to summarize it in the following.

The main idea is that one starts by writing the equation of motion for the one-particle Green's function G via its time derivative. It is not astonishing to find that this gives rise to an expression involving a two-particle Green's function $G^{(2)}$: the particle propagating in the system polarizes the system. This polarization corresponds to the creation of electron-hole pairs, hence two particles. The problem of calculating the one-particle Green's functions is then translated into the problem of calculating the two-particle Green's function which, in its turn, would imply an higher order Green's function, and so on. In order to obtain a closed description, one introduces a potential-like operator that is however nonlocal in time and space, namely the self-energy Σ . By definition, G and Σ are linked through the Dyson equation

$$G^{-1}(1, 2) = G_0^{-1}(1, 2) - V(1)\delta(1, 2) - \Sigma(1, 2) \quad (2)$$

where G_0 is the free-particle Green's function, and $V(1) = U(1) + V_H(1)$, the total classical potential, (U is an external potential and V_H is the Hartree potential). Now, one wishes to introduce the above-mentioned two-particle Green's function $G^{(2)}$ via some known quantity. Since $G^{(2)}$ is responsible for the response to a perturbation, one can in fact also create it by applying an external potential. To this purpose in Hedin's approach a small time-dependent contribution is added to the external potential. The resulting U is constructed such that it goes to the static physical potential $V_{ext}(\mathbf{r})$ at times $\pm\infty$; its fictious time-dependent part will be made vanishing at the end of the derivation. One can then express the self-energy in terms of variations of the Green's function with respect to the external potential, $\Sigma = -ivG\delta G^{-1}/\delta U$ [2], or

$$\Sigma(1, 2) = iG(1, 4)\Gamma(4, 2; 5)\frac{\delta V(5)}{\delta U(3)}v(3, 1^+), \quad (3)$$

with the irreducible vertex function

$$\Gamma(1, 2; 3) = -\frac{\delta G^{-1}(1, 2)}{\delta V(3)} = \delta(1, 3)\delta(2, 3) + \frac{\delta \Sigma(1, 2)}{\delta V(3)} \quad (4)$$

and v the bare Coulomb interaction (integration over indices not present on the left is implicit throughout the equations).

The derivative $\delta\Sigma/\delta V$ is then usually replaced by the chain rule $(\delta\Sigma/\delta G)(\delta G/\delta V)$. Using the relation $(\delta G/\delta V) = -G(\delta G^{-1}/\delta V)G$, Eq. (4) is transformed into an integral equation

$$\Gamma(1, 2; 3) = \delta(1, 2)\delta(1, 3) + \int d4567 \frac{\delta \Sigma(1, 2)}{\delta G(4, 5)}G(4, 6)G(7, 5)\Gamma(6, 7; 3). \quad (5)$$

In the same way one obtains the remaining Hedin's equations

$$\Sigma(1, 2) = i \int d34 G(1, 3)\Gamma(3, 2; 4)W(4, 1) \quad (6)$$

$$W(1, 2) = v(1, 2) + \int d34 v(1, 3)P(3, 4)W(4, 2) \quad (7)$$

$$P(1, 2) = -i \int d34 G(1, 3)G(4, 1)\Gamma(3, 4; 2) \quad (8)$$

in terms of the time-ordered polarization operator $P(1, 2)$, and the dynamical screened interaction $W(1, 2) = \delta V(1)/\delta U(3)v(3, 2)$.

Disregarding Σ on the right-hand side of Eq. (4) would yield the GW approximation,

$$\Gamma(1, 2; 3) = \delta(1, 2)\delta(1, 3) \quad \Longrightarrow \quad \Sigma(1, 2) = iG(1, 2)W(2, 1) \quad (9)$$

Equation (5), or an equivalent form, with its four-point kernel dominated by $\delta\Sigma(1, 2)/\delta G(3, 4)$, has to be solved in order to get the irreducible polarizability $P = -iGG\Gamma$ ³ and an improved self-energy from Eq. (6). Equation (5) is the main obstacle on the way to a calculation of polarizabilities or self-energies beyond the RPA.

2.2 Response functions in Time-dependent density-functional theory

As pointed out above, in principle also TDDFT allows one to calculate the excitation energies and transition probabilities of a many-body system, for constant particle number. In the time-dependent approach, one studies how the system behaves when subject to a time-dependent external perturbation that gives rise to density variations. In this case, the system's response is directly related to the N -particle excited states of an N -particle system, in a similar manner that the one-particle Green's function is related to the $(N + 1)$ - and $(N - 1)$ -particle excited states of the same system.

In TDDFT, the linear density response of an interacting many-electron system [16]

$$\chi(\mathbf{r}, t, \mathbf{r}', t') = \frac{\delta\rho(\mathbf{r}, t)}{\delta U(\mathbf{r}', t')} \quad (10)$$

is obtained from the non-interacting Kohn-Sham response to a change in the total Kohn-Sham potential v_{KS}

$$\chi_0(\mathbf{r}, t, \mathbf{r}', t') = \frac{\delta\rho(\mathbf{r}, t)}{\delta v_{KS}(\mathbf{r}', t')}. \quad (11)$$

via

$$\chi(\mathbf{r}, \mathbf{r}'; \omega) = \chi_0(\mathbf{r}, \mathbf{r}'; \omega) + \int d\mathbf{r}_1 d\mathbf{r}_2 \chi_0(\mathbf{r}, \mathbf{r}_1; \omega) K(\mathbf{r}_1, \mathbf{r}_2, \omega) \chi(\mathbf{r}_2, \mathbf{r}'; \omega), \quad (12)$$

where the kernel K has been introduced as

$$K(\mathbf{r}_1, \mathbf{r}_2, \omega) = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + f_{xc}(\mathbf{r}_1, \mathbf{r}_2, \omega). \quad (13)$$

with the exchange-correlation contribution

$$f_{xc}(\mathbf{r}, t, \mathbf{r}', t') = \frac{\delta v_{xc}[\rho](\mathbf{r}, t)}{\delta\rho(\mathbf{r}', t')}. \quad (14)$$

³The irreducible polarizability P defined in this work is a time-ordered quantity. From the time-ordered P one can then obtain a physical (causal) response function with the usual conversion rules. It should be noted that in the following we do not make a distinction between time-ordered and causal quantities. However, one has to be careful because this apparent “subtlety” could cause severe errors in practice when not properly accounted for. One possible way is represented by the Keldysh formalism. In this scheme all the quantities are consistently defined on the Keldysh contour and pseudo-time-ordered. At the end, projecting from the pseudo-time to the physical time, causal physical response functions are restored.

The exact time-dependent exchange-correlation kernel is of course unknown, and practical calculations must rely on some approximation. The most commonly used, due to its simplicity but also its success mostly in finite systems, is the adiabatic local-density approximation also called time-dependent LDA (TDLDA), where $f_{xc}(\mathbf{r}_1, \mathbf{r}_2, \omega)$ is approximated with the (ω -independent) functional derivative of the LDA exchange-correlation potential:

$$f_{xc}^{\text{TDLDA}}(\mathbf{r}_1, \mathbf{r}_2, \omega) = \delta(\mathbf{r}_1 - \mathbf{r}_2) \frac{dv_{xc}^{\text{LDA}}(\rho(\mathbf{r}_1))}{d\rho(\mathbf{r}_1)}. \quad (15)$$

Apart from this approximation for f_{xc} , another approximation has to be done in practical calculations: the static Kohn-Sham orbitals and eigenvalues used to construct χ_0 are in fact calculated with an approximate exchange-correlation potential v_{xc} , typically the same as the one used in ground state calculations.

If all quantities were evaluated exactly, the retarded version of the time-ordered P calculated via Eq. (8) should yield the retarded response function χ (Eq. (12) via $\chi = P + Pv\chi$). However, whereas it has turned out that the commonly used GW approximation for Σ *together with* its variation ($\delta\Sigma/\delta G$) are successful in describing response functions (via the today standard Bethe-Salpeter equation), TDLDA often does not properly account for excitations. In particular absorption spectra in solids are badly described, even though LDA usually yields satisfactory ground state properties. Moreover, important quantities such as the measurable bandstructure are not accessible through TDDFT (at least not considering closed systems). For all these reasons, the idea consisting in keeping the substantial accuracy of MBPT while at the same time introducing the density degree of freedom concept, could lead to a more convenient framework where the computational advantages of density-functional play a fundamental role. Further on this route, indications on how to improve upon the well established many-body approximations, could constitute an important subproduct of this derivation.

3 MBPT and TDDFT: a successful combination

3.1 MBPT quantities in TDDFT: a summary of some previous works

During the last years, the scientific community has made a major effort trying to find reliable approximations for the exchange-correlation kernel of TDDFT. One important line of research has been the attempt to use MBPT as a starting point. This is in a sense, the opposite direction of the present work (where we aim at using TDDFT to improve within MBPT), but the two are of course tightly linked. We will therefore very briefly summarize some of the MBPT-TDDFT work that is of direct importance for the present approach.

Already in the eighties Streitenberger has suggested [5] to exploit the very fact that both TDDFT and MBPT should yield, at least in principle, the same (exact) polarizability, in order to define an effective xc-kernel for the homogeneous electron gas. Later on, the inclusion of approximate vertex functions in the self energy has been addressed by Mahan and Sernelius [6] for the homogeneous electron gas and, in the mid nineties, by Del Sole, Reining and Godby for silicon [7].

More recent work has focused on the extraction of an effective TDDFT xc-kernel by comparison

with the macroscopic dielectric function resulting from BSE calculations [17]. This yields some information on the analytic structure of the xc correlation kernel in extended systems, for instance about its long range behavior in real space, but does not avoid the cumbersome solution of the BSE. Very recently, approaches have been developed by a few groups to this aim. In one case, a perturbative expansion in W of the xc kernel obtained from the equality of the two macroscopic dielectric functions, namely the one calculated with the Bethe-Salpeter equation and the one calculated with the TDDFT screening equation, has yielded a result that already in first order turned out to yield excellent optical spectra in solids [13]. Another approach is based on the formal replacement of TDDFT kernel matrix elements taken in a basis of Kohn-Sham transitions with Bethe-Salpeter matrix elements, and arrives to the same formula and of course to numerical results of similar quality [12]. Finally, by recognizing that the same physics should be represented by the MBPT and the TDDFT equations, Stubner, Tokatly and Pankratov have developed a diagrammatic approach to the derivation of improved exchange-correlation kernels [14]. Again the same result for the effective xc kernel is obtained.

A final point to notice is that the xc correlation kernel derived above has a long range ($1/r$) tail in real space, and hence a small- q behavior of type α/q^2 , clearly visible from the equations. Hence it is possible to avoid the cumbersome calculation of α , that is of the kernel itself, looking instead for the α values which yield the best optical spectra. Even this very simple approach works well, and leads to good optical spectra using α values ranging from -0.2 for semiconductors to -1 for insulators. It is found that these values are roughly inversely proportional to the dielectric constant [18].

In conclusion, at present, at least three seemingly completely different approaches have hence led independently to the same expression for the effective xc correlation kernel, Eq. (27), which yields optical and energy loss spectra very close to those derived within the BSE approach. The present work sheds light on the deep reasons for their coincidence and success.

3.2 Density variations in MBPT: the idea and the equations

In the way TDDFT and MBPT are hence usually presented, self-consistent linear response in TDDFT is determined by variations of the potential with respect to the *density*, whereas in MBPT variations with respect to the one-particle *Green's function* are the key ingredient. However, in both cases it is a local external potential that actually creates these variations. Therefore, we have suggested that also in the case of MBPT one might rely on the fact that *density variations determine the physics* when the system is polarized. In practice, this means that one can use the Runge-Gross theorem of TDDFT [11] in order to rewrite $\delta\Sigma/\delta V$ in Eq. (4). The one-to-one relation between time-dependent densities and external potentials, or consequently between the densities and the classical potentials V , allows one then to use an alternative chain rule to express $\delta\Sigma/\delta V$, namely $(\delta\Sigma/\delta\rho)(\delta\rho/\delta V)$.

Equation (4) hence becomes

$$\Gamma(1, 2; 3) = \delta(1, 3)\delta(2, 3) + \frac{\delta\Sigma(1, 2)}{\delta\rho(4)}P(4, 3), \quad (16)$$

where $P = \delta\rho/\delta V$ is the irreducible polarizability that, as explained above, is usually calculated by solving the vertex equation. However, by integrating Eq. (16) with two Green's functions G ,

one directly obtains

$$P(1, 2) = P_0(1, 2) + P_0(1, 3)f_{xc}^{\text{eff}}(3, 4)P(4, 2), \quad (17)$$

with $P_0(1, 2) = -iG(1, 2)G(2, 1)$ and the two-point kernel

$$f_{xc}^{\text{eff}}(3, 4) = -iP_0^{-1}(3, 6)G(6, 5)G(5', 6)\frac{\delta\Sigma(5, 5')}{\delta\rho(4)}. \quad (18)$$

In other words, *one can now first determine the two-point irreducible polarizability P from the integral Eq. (17), and subsequently the three-point vertex Γ via the integration of Eq. (16)*. From P , the reducible polarizability P^{red} is obtained via $P^{\text{red}} = P + PvP^{\text{red}}$.

Finally, the self-energy becomes

$$\Sigma(1, 2) = iG(1, 2)W^{\text{TC-TC}}(2, 1) + iG(1, 4)\frac{\delta\Sigma(4, 2)}{\delta\rho(5)}P^{\text{red}}(5, 3)v(3, 1^+). \quad (19)$$

The first term has the GW form, but with the testcharge-testcharge (TC-TC) screened Coulomb interaction $W^{\text{TC-TC}} = (1 + vP^{\text{red}})v$, instead of the RPA one. In this expression, the term $vP^{\text{red}}v$ creates the induced Hartree potential felt by a classical charge. The additional term $(\delta\Sigma/\delta\rho)P^{\text{red}}$ in Eq. (19) is responsible for the missing induced xc potentials that act on an electron or hole. It is therefore useful to reformulate Eq. (16) as

$$\Gamma(1, 2; 3) = \delta(1, 3)\delta(2, 3) + \delta(1, 2)f_{xc}^{\text{eff}}(1, 4)P(4, 3) + \Delta\Gamma(1, 2; 3) \quad (20)$$

where

$$\Delta\Gamma(1, 2; 3) = \left(\frac{\delta\Sigma(1, 2)}{\delta\rho(4)} - \delta(1, 2)f_{xc}^{\text{eff}}(1, 4) \right) P(4, 3). \quad (21)$$

The “non-locality correction” $\Delta\Gamma$ has no effect on P , as one can see by integrating Eq. (21) with two Green’s functions and using Eq. (18). In the self-energy of Eq. (19), the inclusion of the two first terms of Eq. (20) (called $\Gamma^{(2)}$) leads to $\Sigma = iG\tilde{W}$ with a modified screened Coulomb interaction $\tilde{W} = (1 + (v + f_{xc}^{\text{eff}})P^{\text{red}})v$. This is a testcharge-testelectron (TC-TE) screened Coulomb interaction instead of $W^{\text{TC-TC}}$; this expresses the fact that an additional electron or hole in the system cannot be described as a classical charge. $\Delta\Gamma$ yields then in Σ a non-vanishing correction term. One can understand this by the fact that, contrary to the polarizability P that contains the response of the (quantum) system to an external (classical) perturbation, Γ has to contain the information that the screening in Σ has to act on an electron or hole. Hence, the screened object “feels” an exchange-correlation induced potential. Since we are talking about quasi-particles, this potential is necessarily non-local.

Equation (17) is a two-point equation for the polarizability, like in TDDFT; it is however involving the “polarizability” P_0 of independent quasi-particles. It is hence not a TDDFT, but a sort of hybrid equation. The advantage over TDDFT is that the set of equations still leaves accessible the observables of the original equations like QP energies, whereas this would not be the case in pure TDDFT.

3.3 The link to TDDFT

The link with TDDFT can be made by the fact that the diagonal of G yields the exact time-dependent density $-iG(1, 1^+) = \rho(1)$ [19]. $\delta G/\delta\rho = -G(\delta G^{-1}/\delta\rho)G$ leads to

$$iG(1, 3)G(4, 1^+)\frac{\delta G^{-1}(3, 4)}{\delta\rho(2)} = \delta(1, 2). \quad (22)$$

Since the same exact density, and hence the same Hartree potential, should also be obtained from the Kohn-Sham potential $v_{KS} = V + v_{xc}$ we can write

$$G^{-1}(1, 2) = G_0^{-1}(1, 2) - \delta(1, 2) [v_{KS}(1) - v_{xc}(1)] - \Sigma(1, 2). \quad (23)$$

As $\delta G_0^{-1}/\delta\rho = 0$, Eq. (22) becomes

$$P_0(1, 3)\chi_0^{-1}(3, 2) - iG(1, 3)G(4, 1^+)\frac{\delta\Sigma(3, 4)}{\delta\rho(2)} - P_0(1, 3)f_{xc}(3, 2) = \delta(1, 2), \quad (24)$$

where $\chi_0(12) = \delta\rho(1)/\delta v_{KS}(2)$ is the KS independent particle polarizability and $f_{xc}(1, 2) = \delta v_{xc}(1)/\delta\rho(2)$ is the xc kernel of TDDFT. This kernel turns out to consist of two terms, namely $f_{xc}^{(1)}$ and $f_{xc}^{(2)}$, with $f_{xc}^{(2)}$ exactly equal to the f_{xc}^{eff} arising from our previous approach and

$$f_{xc}^{(1)}(1, 2) = \chi_0^{-1}(1, 2) - P_0^{-1}(1, 2). \quad (25)$$

$f_{xc}^{(1)}$ has the effect to change the KS response function into the independent QP one, in particular, to solve the so-called band gap problem. $f_{xc}^{(2)}$ accounts for the electron-hole interaction. This splitting [14] is physically intuitive. Altogether, TDDFT yields then for the irreducible polarizability P ,

$$P = \chi_0 + \chi_0(\chi_0^{-1} - P_0^{-1} + f_{xc}^{\text{eff}})P. \quad (26)$$

This is equivalent to Eq. (17).

3.4 Approximations in practice

Of course, in spite of this apparent simplification, one stills faces an unsolvable problem, unless approximations are made. The big advantage of writing the formula in the present form is in fact that they suggest rather straightforward approximations. In particular, in order to get an explicit expression for f_{xc}^{eff} , we choose a starting approximation for the self-energy, and consistent approximations for the functional derivative of Σ and for G , on the right side of Eqs. (18) and (19). A simple choice could be to take Σ , G and P_0 as derived from a *local* and *adiabatic* xc potential, e.g. the LDA one. This leads of course to the TDLDA and the GWT approach of Ref. [7]. A better choice is to start from the GW approximation for Σ , taking W as a screened (e.g. static RPA) Coulomb interaction. For the functional derivative, one can now fully use the experience made using the BSE; in particular, this suggests to neglect also in the present framework the derivative of W with respect to ρ . One still has to find a good approximation for the term $\delta G/\delta\rho$. If one would choose a starting Σ obtained from a self-consistent GW calculation, one would have to evaluate $\delta G/\delta\rho = -G(\delta G^{-1}/\delta\rho)G = G(P^{-1} + (\delta\Sigma/\delta\rho))G$: one would again end up with an integral equation now for $\delta\Sigma/\delta\rho$, similar to the one depicted in Fig. 2(b) of Ref. [14]. However, again based on previous experience in MBPT calculations, one can suppose the Green's function on $\Sigma = iGW$ to be obtained from a suitable local potential, preferably with eigenvalues close to the GW ones. This leads approximately to $\delta G/\delta\rho = GP_0^{-1}G$.

We obtain hence from Eq. (18)

$$f_{xc}^{\text{eff}}(3, 4) = P_0^{-1}(3, 6)G(6, 5)G(5', 6)W(5, 5')G(5, 7)G(7, 5')P_0^{-1}(7, 4). \quad (27)$$

The present derivation is not the first attempt that leads to Eq. (27) [12, 13, 14]. Below, we will show results that we have obtained previously using this formula. However, we believe that the approach outlined here sheds light on the question *why* the former derivations had led to such (unexpectedly) good results: *the physics of the variation of the self-energy upon excitation, which gives rise to the electron-hole interaction, can be captured in terms of density variations only*. This is very important, since it encourages the use of the present scheme also for cases where one wishes to go beyond the above approximations. In particular, it is now clear how any improvement made on the approximations with respect to standard Bethe-Salpeter calculations can be straightforwardly extrapolated to the kernel Eq. (18).

4 Numerical results

Results using the approximation of Eq. (27) or similar approximations have been published by ourselves and by other authors concerning absorption and loss spectra [12, 13], and QP lifetimes [9]. Here we give some of our illustrations.

4.1 Optical spectra

It is instructive to apply Eq. (27) to the calculation of optical spectra of realistic materials, to understand the role of the two parts $f_{xc}^{(1)}$ and $f_{xc}^{(2)}$ of the TDDFT kernel. Figure 1 provides calculations of optical absorption spectrum of bulk silicon using the three highest valence bands and the three lowest conduction bands, a regular grid of 512 slightly shifted k-points in the full Brillouin zone, and an imaginary part in the energy denominators $\eta = 0.1$ eV.

As the figure shows, the TDLDA approach fails to reproduce the optical absorption, since both the band gap and the oscillator strengths of the main peaks are wrong. On the contrary, following our comparison between TDDFT and Green's functions, we have to evaluate the two contributions to the TDDFT kernel. The first term $f_{xc}^{(1)}$ accounts for the one-quasiparticle xc effects. It transforms the KS response function χ_0 into the GW independent quasiparticle P_0 . The corresponding curve in figure 1 gives the correct band gap. At this level, electron-hole interaction xc effects are still absent, as it is evident in the remaining blue shift of the spectrum and the underestimation in the oscillator strength of the first excitonic peak. The second term $f_{xc}^{(2)}$ accounts for the two-particle xc effects. If the same technical approximations as in BSE are used (use of a static W , neglect of the derivative of W with respect to G), the corresponding curve closely reproduces the solution of BSE, which is the current state-of-the-art concerning calculations of optical absorption.

The same considerations also apply to the example of another system, silicon carbide, whose optical absorption is shown in Fig. 2.

4.2 Quasiparticle energies

It is also interesting to see what one obtains when using this scheme to go beyond the GW approximation for the calculation of band gaps in semiconductors and insulators. Since systematic

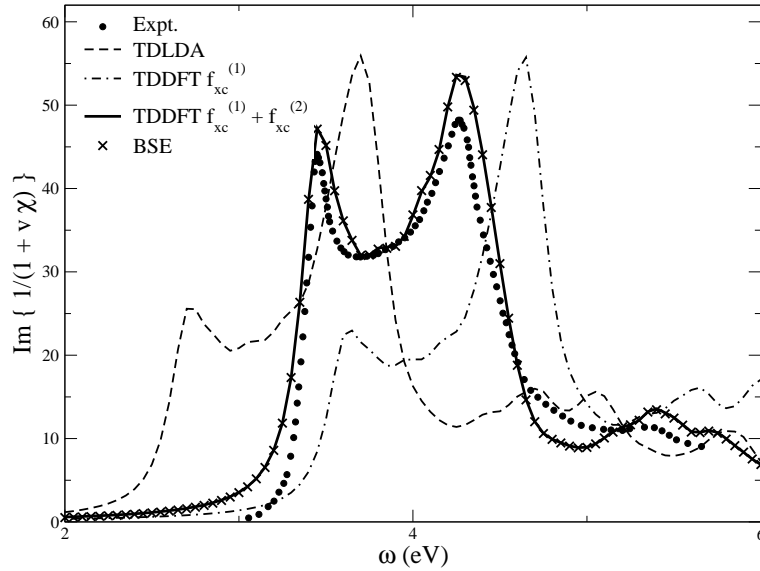


Figure 1: Optical absorption spectrum of bulk silicon calculated within different approximations and compared to experimental data of Ref. [20]. The dashed line represents the TDLDA curve, the dot-dashed line the TDDFT kernel using $f_{xc}^{(1)}$ of the text only, the full line the full TDDFT kernel of the text. The Bethe-Salpeter equation's solution (crosses) and the experimental curve (full circles) are given for comparison.

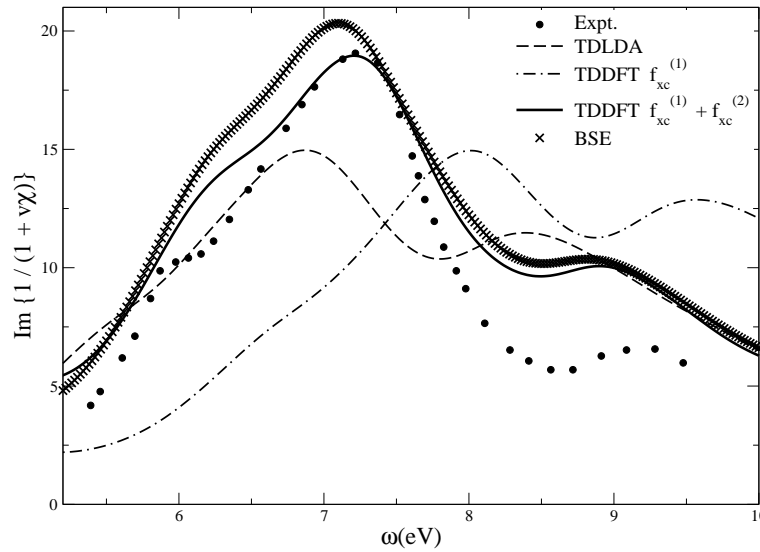


Figure 2: Optical absorption spectrum of bulk silicon carbide calculated within different approximations and compared to experimental data of Ref. [21]. The dashed line represents the TDLDA curve, the dot-dashed line the TDDFT kernel using $f_{xc}^{(1)}$ of the text only, the full line the full TDDFT kernel of the text. The Bethe-Salpeter equation's solution (crosses) and the experimental curve (full circles) are given for comparison.

GWT studies in literature are available only for a short-range (LDA) kernel [7], we provide here a discussion on the influence of a *long-range* contribution on QP energies.

For illustration, we present in Tables 2 and 3 results on bulk silicon and solid argon (obviously,

the effect of a long-range contribution is particularly interesting in a solid, and silicon and argon represent two extreme cases, the first one with strong screening and continuum excitons, the second one with almost no screening and strongly bound electron-hole pairs).

The first series of results, presented in Table 2, uses LDA as starting approximation for the right-hand side of Eq. (19), whereas the second series in Table 3 uses the static but nonlocal “Coulomb-hole-plus-screened exchange” (COHSEX) approximation to GW [2]. In the latter case, we use the kernel f_{xc}^{eff} given by Eq. (27) which, although approximate, has the correct long-range behavior [12, 13, 22]. Furthermore, LDA wavefunctions are used throughout: we suppose them to be similar to the COHSEX QP ones.

The two tables show the band gap at Γ for both materials under study. The first column gives the band gap that is obtained from the respective starting approximation (i.e. LDA or COHSEX). The second column uses this band structure, and provides the subsequent standard non-self-consistent GW^{RPA} . Columns 3 and 4 show the band gap for the approximations to the self-energy derived in this work, using either $W^{\text{TC-TC}}$ (first part of Eq. (19)) or \tilde{W} (neglect of only $\Delta\Gamma$). Finally, the experimental value is given in the last column [23]. Both materials show similar tendencies. In particular, there is a significant influence of the single-particle energies on the GW^{RPA} (second columns). The choice of COHSEX energies in W simulates the effect of the contribution $f_{xc}^{(1)}$ of Eq. (25). In most cases, the electron-hole vertex correction $f_{xc}^{\text{eff}} = f_{xc}^{(2)}$ in $W^{\text{TC-TC}}$ closes the gap (third columns) with respect to RPA. When f_{xc}^{eff} is included according to Eq. (19) in order to evaluate the explicit vertex in $\Sigma = iGW^{\text{TC-TC}}\Gamma^{(2)} = iG\tilde{W}$ (fourth columns), there is a strong opening of the gap. Our most complete result is hence determined by a series of cancellations. The overall behavior of both kernels under study (arising from LDA or the non-local COHSEX scheme) is very similar, even though the LDA kernel does not have the crucial, correct long-range contribution [22]. These results roughly justify calculations using the RPA GW form constructed with QP energies instead of KS ones. The $GW\Gamma$ gap turns out to be slightly bigger than the experimental value. In order to obtain improved agreement, one should of course avoid some of the above approximations; in particular we expect the non-locality correction to decrease the gap, since the neglected term should reduce the effect of the external vertex. Those and other more sophisticated numerical calculations (including, e.g., self-consistency in the wavefunctions) are however beyond the scope of this illustration.

5 Conclusions

In conclusion, using the concept of the density as crucial quantity we have derived a complete new set of equations for the many-body vertex, polarizability and self-energy. This approach does not require the solution of integral equations containing a four-point kernel. In particular, the polarizability is directly obtained from a two-point equation, containing a two-point many-body kernel f_{xc}^{eff} , which completely changes the way e.g. excitonic effects can be calculated. The exchange-correlation kernel of TDDFT turns out to differ from f_{xc}^{eff} by a term that is essentially responsible for the gap correction. Our approach explains the success of previously published approximations for the kernel and allows one to go beyond in a systematic way. On top of this progress concerning TDDFT, the approach also opens the way for better approximations to the

	LDA	GW^{RPA}	GW^{TC-TC}	$G\tilde{W}$	Expt.
Si	2.53	3.17	3.08	3.18	3.40
Ar	8.18	12.95	12.64	12.75	14.2

Table 2: Direct gap (in eV) at Γ in bulk silicon and solid argon, calculated using a local approximation (LDA) for the starting self-energy (see text).

	COHSEX	GW^{RPA}	GW^{TC-TC}	$G\tilde{W}$	Expt.
Si	3.64	3.30	3.18	3.32	3.40
Ar	14.85	14.00	14.16	14.76	14.2

Table 3: Same as Table 2, but based on a non-local approximation (COHSEX) for the starting self-energy.

self-energy and other many-body quantities.

These steps forward could be achieved by combining two fundamentally different frameworks. We think that this might be a nice illustration for the strength of a network like Ψ_k , that tries to bring together different communities of people working on similar problems. The present work has in fact benefitted from many formal and informal meetings; in particular, we are grateful for discussions with C.-O. Almbladh, U. von Barth, J. F. Dobson, A. Marini, A. Rubio, G. Stefanucci, R. van Leeuwen, and N. Vast. We also acknowledge support from the the EU's 6th Framework Programme through the NANOQUANTA Network of Excellence (NMP4-CT-2004-500198), and computer time from IDRIS (project 544).

References

- [1] P. Hohenberg and W. Kohn, Phys. Rev. **136** B864 (1964); W. Kohn and L. J. Sham, Phys. Rev. **140** A1133 (1965).
- [2] L. Hedin, Phys. Rev. **139**, A796 (1965); G. Strinati, Riv. Nuovo Cimento **11**, 1 (1988).
- [3] W. G. Aulbur, L. Jonsson, and J. W. Wilkins, Solid State Physics **54**, 1 (1999), and references therein.
- [4] G. Onida, L. Reining, and A. Rubio, Rev. Mod. Phys. **74**, 601 (2002), and references therein.
- [5] P. Streitenberger, Phys. Status Solidi. B **125**, 681 (1984); P. Streitenberger, Phys. Lett. A **106**, 57 (1984).
- [6] G. D. Mahan and B. E. Sernelius, Phys. Rev. Lett. **62**, 2718 (1989).
- [7] R. Del Sole, L. Reining, and R. W. Godby, Phys. Rev. B **49**, 8024 (1994).
- [8] E. L. Shirley and R. M. Martin, Phys. Rev. B **47**, 15404 (1993); R. T. M. Ummels, P. A. Bobbert, and W. van Haeringen, Phys. Rev. B **57**, 11962 (1998).

- [9] A. Marini and A. Rubio, Phys. Rev. B **70**, 081103(R) (2004).
- [10] F. Aryasetiawan, Phys. Rev. B **46**, 13051 (1992).
- [11] E. Runge and E. K. U. Gross, Phys. Rev. Lett. **52**, 997 (1984).
- [12] L. Reining *et al.*, Phys. Rev. Lett. **88**, 066404 (2002); F. Sottile, V. Olevano, and L. Reining, Phys. Rev. Lett. **91**, 056402 (2003).
- [13] G. Adragna, R. Del Sole, and A. Marini, Phys. Rev. B **68**, 165108 (2003); A. Marini, R. Del Sole, and A. Rubio, Phys. Rev. Lett. **91**, 256402 (2003).
- [14] I. V. Tokatly and O. Pankratov Phys. Rev. Lett. **86**, 2078-2081 (2001); R. Stubner, I. V. Tokatly, and O. Pankratov, Phys. Rev. B **70**, 245119 (2004).
- [15] F. Bruneval, F. Sottile, V. Olevano, R. Del Sole, and L. Reining, Phys. Rev. Lett. **96**, 186402 (2005).
- [16] E. K. U. Gross and W. Kohn, Phys. Rev. Lett. **55**, 2850 (1985).
- [17] R. Del Sole, G. Adragna, V. Olevano and L. Reining, Phys. Rev. B **67**, 045207 (2003).
- [18] S. Botti, F. Sottile, N. Vast, V. Olevano, H.-C. Weissker, L. Reining, G. Onida, A. Rubio, R. W. Godby, and R. Del Sole, Phys. Rev. B **69**, 155112 (2004).
- [19] R. van Leeuwen, Phys. Rev. Lett. **76**, 3610 (1996).
- [20] P. Lautenschlager, M. Garriga, L. Vina, and M. Cardona, Phys. Rev. B **36**, 4821 (1987).
- [21] S. Logothetidis and J. Petalas, J. Appl. Phys. **80**, 1768 (1996).
- [22] Ph. Ghosez, X. Gonze, and R. W. Godby, Phys. Rev. B **56**, 12811 (1997).
- [23] R. R. L. Zucca and Y. R. Shen, Phys. Rev. B **1**, 2668 (1970); R. Haensel, Phys. Rev. Lett. **23**, 1160 (1969).