

Many-body perturbation theory combined with time dependent DFT: A new method for the calculation of the dielectric function of solids

Rodolfo Del Sole^{*1}, Olivia Pulci¹, Valerio Olevano², and Andrea Marini¹

¹ European Theoretical Spectroscopy Facility (ETSF) and CNR-INFM, Department of Physics, University of Rome “Tor Vergata”, Via della Ricerca Scientifica 1, 00133 Roma, Italy

² European Theoretical Spectroscopy Facility (ETSF) and Laboratoire d’Études des Propriétés Électroniques des Solides, UPR 11, CNRS, 38042 Grenoble, France

Received 13 July 2005, revised 26 August 2005, accepted 2 September 2005

Published online 11 October 2005

PACS 71.15.Qe, 78.20.Bh

We show an approximate 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 (TDDFT). The basic idea is to join the computational simplicity of the latter with the accuracy of the former. We apply this approach to a prototype system, LiF. For comparison, we also show results obtained within other approximated TDDFT-based methods.

© 2005 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

1 Introduction

The inclusion of the electron–hole (e–h) interaction is crucial to calculate absorption spectra of semiconductors in good agreement with experiments [1]. This occurs because electron wavefunctions are strongly affected by the electron–hole interaction even in the energy range of band-to-band transitions. However, the inclusion of this interaction in *ab initio* calculations is computationally very cumbersome. So far it has been considered for a number of (simple) systems, from small atomic clusters [2] to bulk crystals [3–5] to surfaces [6–9]. Its application to more complex systems, like surfaces with complex reconstructions or biological systems, is still hampered by computational limitations. These 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 (for a short review, see the paper by Pulci et al. in this volume). It would be highly desirable to develop a simpler method to deal with the e–h interaction.

A hint about how to reach this goal comes from time-dependent density functional theory (TDDFT) [10], where all many-body (MB) effects are embodied in the frequency-dependent exchange–correlation kernel $f_{xc}(\mathbf{r}, \mathbf{r}'; \omega)$, 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 scheme [11] as for independent electrons. The problem is that $f_{xc}(\mathbf{r}, \mathbf{r}'; \omega)$ of TDDFT is not known and any approximation to it based on the homogeneous electron gas will miss important features of semiconductors and insulators [12].

Following this suggestion, a many-body xc kernel similar to that of TDDFT has been defined [13–15], to be used with the independent-quasiparticle polarizability obtained within Green’s function

* Corresponding author: e-mail: rodolfo.delsolo@roma2.infn.it

theory [16]. It is defined in terms of the so-called vertex function, $\Gamma(1, 2; 3)$. A suitable approximation has been found for it, by comparison with the excitonic hamiltonian of the BSE approach. However, in the TDDFT case the excitonic hamiltonian does not need to be diagonalized, which speeds up the calculations in a substantial way. It is quite surprising to notice that two seemingly different approaches, as that of Refs. [13, 14] and that of Ref. [15], yield the same formula for $f_{xc}(\mathbf{r}, \mathbf{r}'; \omega)$ to first order in the screened Coulomb interaction W . A rationale for this surprising result has been found very recently, by reformulating Many Body Perturbation Theory using the density functional concept [17].

In this paper we review in some detail the main steps which lead to determine the exchange correlation kernel, following the approach of Refs. [13, 14]. The resulting kernel, $f_{xc}(\mathbf{r}, \mathbf{r}'; \omega)$, clearly shows up a long range tail of the type $-\alpha/|\mathbf{r} - \mathbf{r}'|$, which is the key ingredient to describe excitonic effects in extended systems. Exploiting this property, a simplified approach had been developed in Ref. [18] to speed up calculations, where the value of α was chosen to reproduce the BSE optical spectrum. Such a simplified approach has been applied to many bulk semiconductors, yielding good results [19].

In order to show how these approaches work in the case of insulators, we consider here LiF, a wide gap insulator, as a test case. This is a severe test, since strongly bound excitons occur [20]. The approach based on the ab-initio $f_{xc}(\mathbf{r}, \mathbf{r}'; \omega)$ and the BSE yield mostly the same results. The simplified approach mentioned above, instead, can well describe the bound exciton with a suitable value of α , but the remaining part of the spectrum is not well described. Hence, in the case of LiF, any ω -independent xc kernel is not sufficient to produce good optical spectra.

2 Theoretical background

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

$$P(\mathbf{r}, \mathbf{r}'; \omega) = \chi_0(\mathbf{r}, \mathbf{r}'; \omega) + \int d^3\mathbf{r}'' \int d^3\mathbf{r}''' \chi_0(\mathbf{r}, \mathbf{r}''; \omega) f_{xc}(\mathbf{r}'', \mathbf{r}'''; \omega) P(\mathbf{r}''', \mathbf{r}'; \omega), \quad (1)$$

where $\chi_0(\mathbf{r}, \mathbf{r}'; \omega)$ is the independent-particle response function obtained within the Kohn–Sham (KS) scheme, and $f_{xc}(\mathbf{r}, \mathbf{r}'; \omega)$ is the time Fourier-transform of the exchange-correlation (xc) kernel

$$f_{xc}(\mathbf{r}, \mathbf{r}'; t - t') = \frac{\delta V_{xc}(\mathbf{r}; t)}{\delta n(\mathbf{r}'; t')}. \quad (2)$$

Equation (1) looks relatively easy for numerical implementation, since it is a product of matrices whose indices are *single* space variables. This must be contrasted with the calculations carried out within many-body (MB) theory, where the solution of the Bethe–Salpeter equation implies matrices whose indices are *pairs* of space variables. The main obstacle to its application in realistic calculations is the poor knowledge of the xc kernel $f_{xc}(\mathbf{r}, \mathbf{r}'; \omega)$ of real systems. The most widely used approximation is the Adiabatic Local-Density Approximation (ALDA, or TDLDA) [21], where the *static* xc kernel of the homogeneous electron gas with the local density is used at nonzero frequencies (see Section 2.1). Such an approximation, although surprisingly successful in atoms, molecules and small clusters [21], fails to give a quantitative description of the optical properties of solids (see, in particular, Ref. [12] 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 irreducible polarizability is given by [22]

$$P(1, 2) = P_{\text{QP}}(1, 2) + \delta P(1, 2), \quad (3)$$

where

$$P_{\text{QP}}(1, 2) = -iG(1, 2) G(2, 1) \quad (4)$$

is calculated within the independent-quasiparticle (independent-QP) approximation, and $\delta P(1,2)$ accounts for the interactions among QPs:

$$\delta P(1, 2) = -i \int d(345678) G(1, 3) G(4, 1) \frac{\delta \Sigma_{xc}(3, 4)}{\delta G(5, 6)} G(5, 7) G(8, 6) \Gamma(7, 8; 2). \quad (5)$$

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, Σ_{xc} is the exchange-correlation (xc) self-energy, and $\Gamma(7, 8; 2)$ is the vertex function, which can be obtained solving the equation:

$$\Gamma(1, 2; 3) = \Gamma_0(1, 2; 3) + \int d(4567) \frac{\delta \Sigma_{xc}(1, 2)}{\delta G(4, 5)} G(4, 6) G(7, 5) \Gamma(6, 7; 3), \quad (6)$$

with

$$\Gamma_0(1, 2; 3) = \delta(1, 2) \delta(1, 3). \quad (7)$$

One can solve Eq. (6) by defining the four-variable kernel $\Omega(1, 2; 3, 4)$:

$$\Omega(1, 2; 3, 4) = \int d(56) \frac{\delta \Sigma_{xc}(1, 2)}{\delta G(5, 6)} G(5, 3) G(4, 6); \quad (8)$$

then Γ is obtained by inverting $1 - \Omega$ in (6), and finally one finds for δP :

$$\delta P(1, 2) = -i \int d(345678) G(1, 3) G(4, 1) \Omega(3, 4; 5, 6) [1 - \Omega]^{-1}(5, 6; 7, 8) \Gamma_0(7, 8; 2). \quad (9)$$

Ab-initio calculations of this type are carried out solving a Bethe–Salpeter equation equivalent to (6), using the GW approximation for Σ_{xc} :

$$\Sigma_{xc}(1, 2) = iG(1, 2) W(1, 2), \quad (10)$$

($W(1, 2)$ is the screened Coulomb interaction), and approximating its functional derivative with respect to G as

$$\frac{\delta \Sigma_{xc}(1, 2)}{\delta G(3, 4)} = i\delta(1, 3) \delta(2, 4) W(1, 2), \quad (11)$$

that is, by neglecting $G \delta W / \delta G$ in calculating the functional derivative in (11).

An additional approximation is to neglect dynamical effects both in the self-energy and in W , which cancel each other almost completely [23]. Calculations carried out since 1998 by a few groups along these lines [2–9] have yielded spectra in quantitative agreement with experiments for many systems. However, they are computationally very demanding because one has to invert the four-variable kernel $1 - \Omega$.

In the present work we cast the many-body (MB) linear-response theory in a form similar to the TDDFT linear response. To this aim, we equate the TDDFT Eq. (1) to the MB Eq. (3):

$$P = \chi_0 + \chi_0 f_{xc} P = P_{IQP} + \delta P = P_{IQP} + P_{IQP} \tilde{f}_{xc} P. \quad (12)$$

Here all quantities are matrices with single-variable indices, as $P(1, 2)$ and $\delta P(1, 2)$; the last equality defines the MB analogue, \tilde{f}_{xc} , of the DFT xc kernel f_{xc} . It is worth noticing that, while P is the same in both approaches, the RPA approximations χ_0 , obtained within the independent-particle Kohn–Sham scheme, and P_{IQP} , obtained within the MB independent-QP approximation, are different. As a matter of fact, KS energies and wavefunctions enter χ_0 , while QP energies and wavefunctions enter P_{IQP} . As a consequence, also f_{xc} and \tilde{f}_{xc} are different.

\tilde{f}_{xc} can be found in terms of δP from Eq. (12), by inverting P_{IQP} and P :

$$\tilde{f}_{xc} = P_{\text{IQP}}^{-1} \delta P P^{-1}. \quad (13)$$

This is the very definition of the MB analogue of the xc kernel of TDDFT. By expressing δP as $P - P_{\text{IQP}}$, Eq. (13) is easily seen to be equivalent to the form

$$\tilde{f}_{xc} = P_{\text{IQP}}^{-1} - P^{-1}. \quad (14)$$

Similar work has been carried out by Streitenberger [24] in the context of the homogeneous electron gas. The use of \tilde{f}_{xc} allows to calculate the polarization similarly to the case of TDDFT, according to:

$$P = (1 - \chi_0 f_{xc})^{-1} \chi_0 = (1 - P_{\text{IQP}} \tilde{f}_{xc})^{-1} P_{\text{IQP}}, \quad (15)$$

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

The problem is that \tilde{f}_{xc} itself is defined in (13) in terms of the (unknown) polarization P . However, Eq. (13) allows us to make approximations on \tilde{f}_{xc} , which is, in a sense, a small quantity. It is small since it accounts for the electron–hole interaction, whose effects are somehow minor in semiconductors: their experimental spectra (which include its effects), indeed, are qualitatively similar to those calculated within the independent-QP approximation (which do not include them). By exploiting the fact that \tilde{f}_{xc} is small, we can approximate it, as given by (13), to first order in W :

$$\tilde{f}_{xc} \simeq P_{\text{IQP}}^{-1} P^{(1)} P_{\text{IQP}}^{-1}, \quad (16)$$

where $P^{(1)}$ is the expansion of Eq. (9) to first order in Ω , that is by approximating $(1 - \Omega)^{-1}$ with 1 therein. As a result, \tilde{f}_{xc} can be calculated by avoiding the inversion of the four-variable kernel $(1 - \Omega)$, that is the most computationally demanding part of the excitonic calculations. This approximation can be improved in a systematic way, by inserting higher-order terms both in δP and P [14]. We will show below that the first term, Eq. (16), already yields spectra in good agreement with experiments.

Equation (16) is the most important result of this approach [13, 14] and coincides with that derived, starting from different assumptions in Ref. [15, 17]. It allows to calculate the irreducible polarizability as:

$$P = (1 - P^{(1)} P_{\text{IQP}}^{-1})^{-1} P_{\text{IQP}}. \quad (17)$$

This must be contrasted with the result obtained by simply expanding P to first order in Ω in Eq. (3):

$$P \simeq P_{\text{IQP}} + P^{(1)}. \quad (18)$$

Equations (17) and (18) coincide to first order in $P^{(1)}$, 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 Eq. (17) may describe the formation of bound exciton states at the energies where the denominator vanishes, while Eq. (18) cannot. Extensive work carried out in the last three years has shown that Eq. (17) is definitely better than Eq. (18) [13–15].

Applying the usual approximations (10) and (11) for the self energy and for its functional derivative, we obtain for $P^{(1)}$:

$$P^{(1)}(1, 2) = \int d(34) G(1, 3) G(4, 1) W(3, 4) G(3, 2) G(2, 4). \quad (19)$$

It can be calculated from QP wavefunctions and the screened interaction. We neglect, as usual, dynamical effects on the Green's functions and on the screened interaction. Since we are here interested in

bulk crystals, we evaluate its space and time Fourier transform; after cumbersome, but straightforward algebra, we find:

$$\begin{aligned}
 P^{(1)}(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}'; \omega) = \sum_{cc'v'v} \left\{ \frac{B_{cv}(-\mathbf{q} - \mathbf{G})}{\omega - E_{cv} + i\delta} \left[\frac{B_{c'v'}(\mathbf{q} + \mathbf{G}')}{\omega + E_{c'v'} - i\delta} \langle vv' | W | c'c \rangle \right. \right. \\
 \left. \left. - \frac{B_{v'c'}(\mathbf{q} + \mathbf{G}')}{\omega - E_{c'v'} + i\delta} \langle vc' | W | v'c \rangle \right] \right. \\
 \left. + \frac{B_{vc}(-\mathbf{q} - \mathbf{G})}{\omega + E_{cv} - i\delta} \left[\frac{B_{v'c'}(\mathbf{q} + \mathbf{G}')}{\omega - E_{c'v'} + i\delta} \langle cc' | W | v'v \rangle \right. \right. \\
 \left. \left. - \frac{B_{c'v'}(\mathbf{q} + \mathbf{G}')}{\omega + E_{c'v'} - i\delta} \langle cv' | W | c'v \rangle \right] \right\}, \quad (20)
 \end{aligned}$$

where \mathbf{G} and \mathbf{G}' are reciprocal-lattice vectors, \mathbf{q} is restricted to the first Brillouin zone, v and v' label filled states, while c and c' label empty states. We have defined

$$\langle vv' | W | c'c \rangle = \int d^3 \mathbf{r}_1 \int d^3 \mathbf{r}_2 \psi_v^*(\mathbf{r}_1) \psi_{v'}^*(\mathbf{r}_2) W(\mathbf{r}_1, \mathbf{r}_2) \psi_{c'}(\mathbf{r}_2) \psi_c(\mathbf{r}_1) \quad (21)$$

and

$$B_{cv}(\mathbf{k}) = \int d^3 x \psi_c^*(\mathbf{x}) e^{i\mathbf{k}\mathbf{x}} \psi_v(\mathbf{x}). \quad (22)$$

$W(\mathbf{r}_1, \mathbf{r}_2)$ is the statically screened Coulomb interaction, and the Bloch wavevectors \mathbf{k} are embodied in c, v , etc.

Equation (20) can be evaluated using the LDA wavefunctions, which well approximate QP ones [25]. $P^{(1)}$, f_{xc} and P_{IQP} are matrices indexed by \mathbf{G} and \mathbf{G}' , whose products and inversions can be evaluated numerically.

Once we have calculated the irreducible polarizability $P(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}'; \omega)$, we get the microscopic dielectric function $\varepsilon = 1 - vP$, and its macroscopic component ε_M [26] which describes optical spectra:

$$\varepsilon_M(\omega) = \lim_{q \rightarrow 0} \frac{1}{(\varepsilon(q, \omega))_{G=0, G'=0}^{-1}}. \quad (23)$$

2.1 Other approximated methods

So far we have described a way to approximate the exchange and correlation kernel within a perturbative Many-Body approach. Actually, simpler approximations are nowadays largely in use, especially in the chemistry community, based on the so called Adiabatic Local Density Approximation (ALDA). It is in fact well known that one of the most used and successful scheme for calculating ground state properties of complex systems within DFT is the Local Density Approximation, that is based on the replacement of the (unknown) exact exchange and correlation energy E_{xc} of a system of interacting electrons with the functional form of the exchange and correlation energy of an homogenous electron gas (heg) of density $n(\mathbf{r})$:

$$E_{xc}[n] = \int d\mathbf{r} n(\mathbf{r}) \varepsilon_{xc}^{heg}(n(\mathbf{r})). \quad (24)$$

The LDA approximation is known to work very well even in systems far from being homogenous, and is at the basis of the huge success DFT has had in the last decades. It is hence natural to try to apply the

same scheme also in the case of Time-Dependent Density Functional Theory, by approximating the kernel $f_{xc}(\mathbf{r}, \mathbf{r}', \omega)$ by the ω independent functional derivative of the LDA exchange-correlation potential:

$$f_{xc}(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') \frac{\delta V_{xc}^{LDA}(n(\mathbf{r}), \mathbf{r})}{\delta n(\mathbf{r})}. \quad (25)$$

Many calculations have been performed within the ALDA scheme, and some successes have been obtained [27]. Unfortunately, the successful applications are limited to *finite* systems (atoms, molecules, small clusters), whereas no good agreement with experiments is found for *infinite* systems (bulks, surfaces, and so on). The reason for that was found in the fact that the full TDDFT kernel $v - f_{xc}$ accounts, through to the term v (bare Coulomb interaction), of the local field effects, that are very important in clusters (since clusters are highly non-homogeneous systems, being described as matter surrounded by a lot of vacuum). The term v alone is often able to correct most of the discrepancies found between RPA-LDA and experiments in clusters, and in some cases a static and local f_{xc} kernel (as the LDA one) is able to account for the remaining excitonic effects. On the other hand, in bulks and surfaces local fields effects are not very important, hence the details of the exact f_{xc} may become essential. In particular, the long range tail of f_{xc} should be proportional to $-1/q^2$ for small q [18]. This observation was at the basis of a very interesting approximation for f_{xc} for infinite system, known as RORO kernel: this approximated kernel, based on the comparison between the exact TDDFT one and the BSE one, consists of a contribution arising from the energy shift between the DFT-LDA and GW eigenvalues, and a second one which describes the electron hole interaction. Absorbing the first, positive contribution in an energy shift of χ_0 (that is, starting from P_{IQP} , built up using GW eigenvalues), part of the excitonic effects can be obtained using a static, long range kernel $f_{xc}(\mathbf{q}, \mathbf{G}, \mathbf{G}') = -\delta_{\mathbf{G}, \mathbf{G}'} \alpha / |\mathbf{q} + \mathbf{G}|^2$ [18]. The constant (energy independent) α depends on the material considered and there is no simple recipe to calculate it. For semiconductors with weak excitonic effects it has been shown [19] that α is related to the inverse dielectric function:

$$\alpha = 4.615 \varepsilon_{\infty}^{-1} - 0.213, \quad (26)$$

but this formula does not work in case of bound excitons.

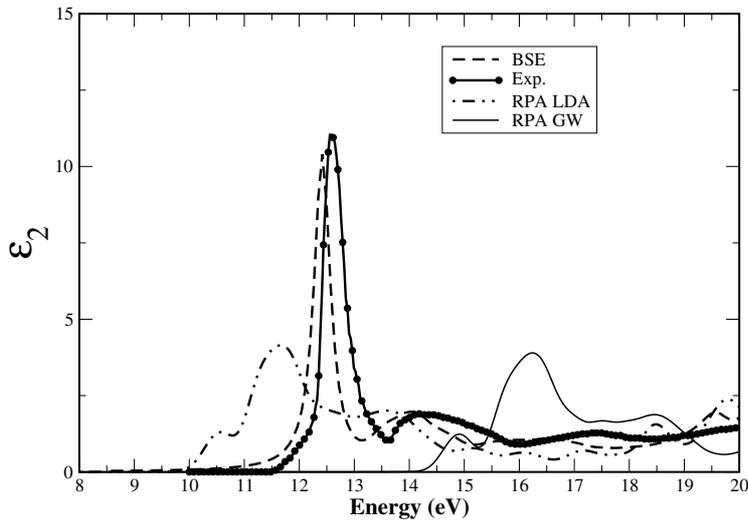


Fig. 1 Single particle approach (LDA-RPA), single quasi-particle approach (GW-RPA) and two-quasiparticle approach (BSE) calculations for the dielectric function of LiF. Experimental data from [30] are also shown.

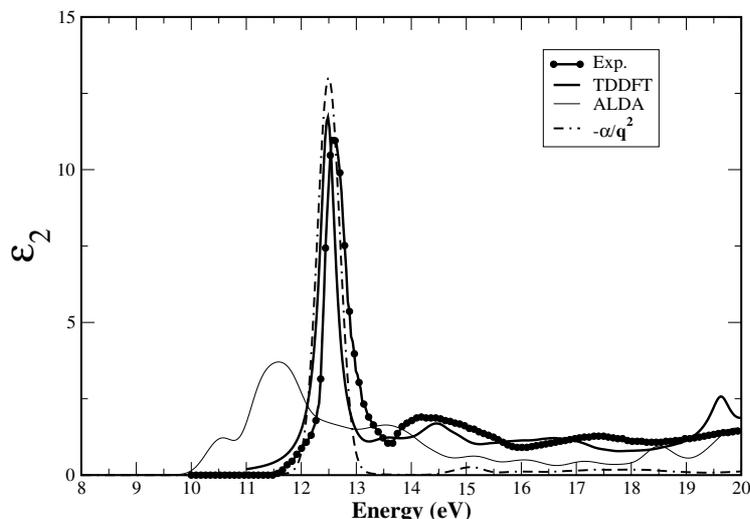


Fig. 2 Dielectric function of LiF calculated within the three TDDFT-based approaches, and comparison with experiment [30].

3 Results

As already mentioned, LiF is a prototype system for bound excitons since it presents a strong excitonic peak at 12.9 eV, with a binding energy of 1.4 eV. Some theoretical studies about the optical properties of LiF with the inclusion of excitonic effects have already appeared in the literature [14, 28, 29]. We show in Fig. 1 the absorption spectrum of LiF within the independent single particle approaches (DFT-RPA and GW-RPA): the DFT calculation gives, as usual, a redshifted spectrum when compared to the experiment. The GW spectrum, obtained within a single particle scheme using GW eigenenergies, shifts the spectrum towards high energies without improving the agreement. The Bethe–Salpeter approach, instead, well reproduces the bound exciton below the gap and also the spectrum at higher energies, thus confirming to be the state of the art technique for a proper description of optical properties with the inclusion of excitonic effects.

In order to test the validity of the approximated TDDFT approaches described in the previous section, we have now to apply the three schemes described (f_{xc} from MBPT, from ALDA and $f_{xc} = -\alpha/q^2$) to the calculation of the dielectric function of LiF and compare the results with the experiments. This is done in Fig. 2. The ALDA spectrum is almost identical to the LDA-RPA ones, thus showing the inadequacy of such approximation in infinite systems. On the other hand, the $-\alpha/q^2$ (calculated for a ‘best’ $\alpha = 5.5$) reproduces the bound exciton at 12.9 eV but not the higher energy part of the spectrum. Just the MBPT-TDDFT approach (Eq. (20)) is able to reproduce, in the full energy range, the dielectric function of LiF, thus confirming a-posteriori the validity of the approximations done.

4 Conclusions

In conclusion, we discuss a method for calculating the polarizability within MB theory, which retains the computational simplicity of TDDFT. Calculations carried out for LiF yield very good agreement with the experimental spectrum. On the other hand, simple approximations for the exchange and correlation kernel, based on the ALDA approach, shows no improvement with respect to the RPA. Finally, the use of the simplified static kernel $-\alpha/q^2$ allows, for one choice of the parameter α , a good representation of the excitonic peak but not of the remaining part of the spectrum.

Acknowledgements This work has been supported by the INFM PAIS project “CELEX”, MIUR-COFIN 2002 and by the EU’s 6th Framework Programme through the Network of Excellence ‘NANOQUANTA’ (NMP4-CT-2004-500198). We gratefully acknowledge CINECA CPU time granted by INFM.

References

- [1] W. Hanke and L. J. Sham, Phys. Rev. Lett. **43**, 387 (1979); Phys. Rev. B **21**, 4656 (1980).
- [2] G. Onida, L. Reining, R. W. Godby, R. Del Sole, and W. Andreoni, Phys. Rev. Lett. **75**, 818 (1995).
- [3] S. Albrecht, L. Reining, R. Del Sole, and G. Onida, Phys. Rev. Lett. **80**, 4510 (1998).
- [4] L. X. Benedict, E. L. Shirley, and R. B. Bohn, Phys. Rev. B **57**, R9385 (1998).
- [5] M. Rohlfing and S. G. Louie, Phys. Rev. Lett. **81**, 2312 (1998).
- [6] M. Rohlfing and S. G. Louie, Phys. Rev. Lett. **83**, 856 (1999).
- [7] P. H. Hahn, W. G. Schmidt, and F. Bechstedt, Phys. Rev. Lett. **88**, 016402 (2002).
- [8] M. Palummo et al., J. Phys.: Condens. Matter **16**, S4313 (2004).
- [9] M. Palummo et al., Phys. Rev. Lett. **94**, 087404 (2005).
- [10] E. Runge and E. K. U. Gross, Phys. Rev. Lett. **52**, 997 (1984).
- [11] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
- [12] V. Olevano, M. Palummo, G. Onida, and R. Del Sole, Phys. Rev. B **60**, 14224 (1999).
- [13] G. Adragna, R. Del Sole, and A. Marini, Phys. Rev. B **68**, 165108 (2003).
- [14] A. Marini, R. Del Sole, and A. Rubio, Phys. Rev. Lett. **91**, 256402 (2003).
- [15] F. Sottile, V. Olevano, and L. Reining, Phys. Rev. Lett. **91**, 056402 (2003).
- [16] L. Hedin and S. Lundquist, in: Solid State Physics, edited by H. Ehrenreich, F. Seitz and D. Turnbull (Academic Press, New York, 1969), Vol. 23, p. 1.
- [17] F. Bruneval, F. Sottile, V. Olevano, R. Del Sole, and L. Reining, Phys. Rev. Lett. **96**, 186402 (2005).
- [18] L. Reining, V. Olevano, A. Rubio, and G. Onida, Phys. Rev. Lett. **88**, 066404 (2002).
- [19] 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).
- [20] The electron–hole interaction is, in the case of LiF, very strong, so that it is not obvious that the perturbative approach (in W), which works very well in semiconductors, is appropriate also in this case.
- [21] I. Vasiliev, S. Ogut, and R. Chelikowsky, Phys. Rev. Lett. **82**, 1919 (1999).
- [22] R. Del Sole, L. Reining, and R. W. Godby, Phys. Rev. B **49**, 8024 (1994).
- [23] F. Bechstedt, K. Tenelsen, B. Adolph, and R. Del Sole, Phys. Rev. Lett. **78**, 1528 (1997).
A. Marini and R. Del Sole, Phys. Rev. Lett. **91**, 176402 (2003).
- [24] P. Streitenberger, phys. stat. sol. (b) **125**, 681 (1984).
- [25] M. S. Hybertsen and S. G. Louie, Phys. Rev. B **34**, 5390 (1986).
- [26] S. L. Adler, Phys. Rev. **126**, 413 (1962).
N. Wisser, Phys. Rev. **129**, 62 (1963).
- [27] J. R. Chelikowsky, L. Kronik, and I. Vasiliev, J. Phys.: Condens. Matter **15**, R1517 (2003).
- [28] M. Rohlfing and S. Louie, Phys. Rev. B **62**, 4927 (2000).
- [29] A. Marini and A. Rubio, Phys. Rev. B **70**, R081103 (2004).
- [30] D. M. Roessler and W. C. Waljer, J. Opt. Soc. Am. **57**, 835 (1967).