Electron linewidths of wide–gap insulators: excitonic effects in LiF

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Based on a recent exchange-correlation kernel developed within Time–Dependent–Density–Functional Theory we derive a practical and general expression for the three–point vertex function. We show that excitonic effects in LiF strongly modify the low–energy electron linewidths leading to linear scaling with quasiparticle energy. We also prove that, in contrast to previous results for the electron gas, simple metals and semiconductors, vertex corrections in the self–energy and in the screening function do not compensate each other.

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The experimental quasiparticle band structure of bulk metal and semiconductor systems has been successfully explained by the GW self–energy scheme $^{[1,2,3]}$ in its simplest non self–consistent $G_0W_0$ implementation. Similarly, the quasiparticle linewidths of simple and noble metals have been studied extensively $^{[4]}$, but a first–principles description of the electronic contribution to the electron/hole linewidths in semiconductor and insulators is not yet available. The reason is that the low–energy quasiparticle dynamics in semiconductors tends to be dominated by inelastic phonon scattering, the electronic contribution playing a minor role. However this scenario changes drastically when the quasiparticle energy is larger than the minimum energy required to excite an electron–hole pair. Above this threshold (that is zero in metals and approximatively twice the band gap in insulators) the rapidly increase in density of electron–hole pairs dominates the quasiparticle damping, resulting in a mainly electronic contribution to the lifetime. It is well known that in insulators, at difference with metals, the attractive interaction between electrons and holes can lead to the formation of a bosonic–like excitonic state $^{[3]}$. Excitons modify remarkably the optical and energy-loss spectra and, consequently, the microscopical mechanisms responsible for the quasiparticle damping. This effect is stronger in wide–gap insulators like LiF.

In this communication we tackle the problem of evaluating the impact of the excitonic effects on the quasiparticle(QP) dynamics of LiF, using a simplified vertex function in the electronic self–energy. An efficient approximation for the three–point many–body vertex function is given in terms of the two–point exchange–correlation kernel $f_{xc}$ $^{[5]}$, recently developed in the framework of Time–Dependent–Density–Functional Theory (TDDFT) $^{[6]}$. As result we show that the electronic linewidths of LiF display a linear dependence as function of the QP energy, that can be traced back to the incipient excitonic effects induced by $f_{xc}$ $^{[5]}$. Understanding the inelastic mechanism which dominates the phase coherence time is crucial to the field of quantum transport in mesoscopic and nanostructured materials. Thus this work is the first steps toward a full first–principles description of the quasiparticle dynamics of semiconductor and insulators.

In the usual one–shot $G_0W_0$ self–energy scheme, it is assumed that a basic Density–Functional–Theory (DFT) calculation $^{[1]}$ provides good approximation for QP wavefunctions and electronic screening (dominated by collective excitations, plasmons build from independent electron–hole transitions, i.e. excitonic effects in the screened Coulomb potential $W_0$ are neglected). The QP lifetime $\tau_i$ can be calculated with the Fermi golden–rule, using this non interacting $W_0$ as scattering potential: $\tau_i^{-1} = -2 \sum_0 \Omega_{ij}^2 \text{Im} [ W_0 (E_i - E_f) ]$, where $|i\rangle$, $|f\rangle$ are the initial and final state, with $W_0$ matrix elements $\Omega_{ij}$, and energies $E_i$ $E_f$ such that $E_i - E_f > 0$. This scattering scheme, also known as “on–mass shell” approximation to the $G_0W_0$ linewidths, provides valuable insight into the electron/hole linewidths of metals $^{[5]}$. Therefore, in Fig. 1 we estimate the electronic line widths of LiF (boxes) within this approximation. As $W_0$ is calculated in terms of non–interacting electron–hole pairs $\tau_i^{-1} = 0$ when $E_i - E_f < E_{gap}$ ($E_{gap}$ the DFT gap); quasiparticle states with energy $E_i < 2E_{gap}$ have zero line width (infinite lifetime). These states are indicated by the dashed area in Fig. 1 Above this region a quadratic energy dependence of the line width is recovered, as in metals $^{[5]}$.

As the short–range screened Coulomb repulsion modifies drastically the polarization function in LiF, one is tempted to apply the previous “on–mass shell” scheme to analyze the role of excitonic effects on the quasiparticle dynamics. This would correspond to replace $W_0$ by the screened coulomb potential $W$ obtained from the many–body Bethe–Salpeter equation (BSE) $^{[5,7,8]}$. In practice, the BSE sums all the possible binary collisions between electrons and holes, providing a consistent and successful framework for the calculation of the interacting polarization function. However, the BSE is computationally very demanding and it becomes unpractical when the microscopical dielectric matrix $\hat{\epsilon}(\mathbf{q}, \omega)$ much be calculated for a large set of transfer momenta $\mathbf{q}$ and frequencies $\omega$, as
it is the case for the calculation of linewidths \[4\]. To bypass this difficulty we compute $\hat{\epsilon}(\mathbf{q}, \omega)$ within a TDDFT framework, using an $f_{xc}$ kernel \[2\] that mimics well the BSE results \[1\]. This performance is illustrated in Fig. 2 for the loss function $\hat{\epsilon}^{-1}(\mathbf{q}, \omega)$, that is the relevant quantity to build the screened Coulomb potential $W$. From Ref. \[2\] we know that TDDFT reproduces the experimental loss function, therefore comparing the TDDFT and random phase approximation (RPA) results of Fig. 2 we see that RPA misses the strong weight of the loss spectra just above the band–gap. Consequently the inclusion of excitonic effects in this $G_0W$ calculation translates into a drastic change of the quasiparticle decaying rates (red circles in Fig. 1) compared to the RPA results (blue boxes).

![FIG. 1:](Color on-line) Left panel: calculated DFT bandstructure of LiF (here $E_{CBM}$ and $E_{gap}$ stand for the DFT conduction band minimum energy and the energy gap). Right panel: Electron linewidths calculated “on mass–shell” as function of the single–particle energy. Boxes: RPA $G_0W_0$. Circles: TDDFT–based vertex correction to the self–energy, i.e. a $G_0W^{[3]}_{\text{TDDFT}}$ approach that turn out to be very close to a simpler $G_0W$ calculation (see text). The dashed area denotes the forbidden energy region for quasiparticle decay into electron–hole pairs. Error bars represent the theoretical uncertain due to the “zero–broadening” extrapolation \[1\].

This simple scattering approach, though appealing, lacks of theoretical consistency. Exchange–correlation effects have been included only in the polarization function, while, in the spirit of the original work of Hedin \[1\], they should be included in the self–energy as well. However we will show below that the results obtained within a proper treatment of self–energy and polarization effects do not deviate appreciably from the previous $G_0W$ results. We start the derivation from the definition of the self–energy operator $\Sigma (1, 2)$, given by \[1\]

$$
\Sigma (1, 2) = i \int d34 W (1^+, 3) G (1, 4) \tilde{\Gamma} (4, 2; 3)
$$

(1)

Here $G(1, 2)$ is the interacting Green’s function and $\tilde{\Gamma} (1, 2; 3)$ the irreducible vertex function (numbers stands for space, time and spin coordinates). The screened Coulomb interaction $W$ is: $W (1, 2) = v (1, 2) + \int d34 v (1, 3) \tilde{\chi} (3, 4) W (4, 2)$ where $v (1, 2)$ is the bare Coulomb interaction and $\tilde{\chi}$ the irreducible polarization function:

$$
\tilde{\chi} (1, 2) = -i \int d34 G (1, 3) G (4, 1) \tilde{\Gamma} (3, 4; 2)
$$

(2)

Thus, given an approximation for $\tilde{\Gamma}$ the self–energy is completely defined trough Eqs. \[1\] plus the Dyson equation for $G$. Electron–hole effects are embodied in the vertex function $\tilde{\Gamma}$ that appears in the self–energy directly, in Eq. \[1\], and trough the polarization function, Eq. \[2\]. The interplay between those two effects has been strongly debated in the last years, using different approximations for $\tilde{\Gamma}$, and different levels of self–consistency in the solution of Dyson equation. However all the systems analyzed in the past are characterized by moderate, if not absent, excitonic effects in the polarization function. Thus even if the use of two–point DFT–based \[12, 13, 14\] or finite order vertex functions $\tilde{\Gamma}$ \[15\] can be justified in the case of the homogeneous electron gas or simple semiconductors, they will be inadequate in the case of wide–gap insulators (e.g. LiF), as well as in the case of other strongly correlated systems. Next we derive a TDDFT approximation to the vertex function $\tilde{\Gamma}$ following the spirit of Ref. \[2\] to reproduce the diagrammatic expansion of $\tilde{\Gamma}$ obtained within Many–body perturbation theory.

![FIG. 2:](Calculated loss function of LiF for momentum transfer $q$ along the direction $\Gamma U$. Continuous line: TDDFT calculation with an $f_{xc}$ kernel that mimics excitonic effects \[2\]. Dashed line: RPA.)

In the non self–consistent scheme the BSE expresses $\tilde{\Gamma}$ in terms of the independent particle $W_0$ (calculated using Eq. \[2\] assuming $\tilde{\Gamma} (1, 2; 3) = \delta (1, 2) \delta (1, 3)$) and the bare DFT Green’s function $G_0$ as:

$$
\tilde{\Gamma} (1, 2; 3) = \delta (1, 2) \delta (1, 3) + iW_0 (1, 2) \int d67 G_0 (1, 6) G_0 (7, 2) \tilde{\Gamma} (6, 7; 3)
$$

(3)
When this vertex \( \tilde{\Gamma} \) is inserted in Eq. (2), the correspond-
ing equation for \( \chi \) correctly describes excitonic effects in
the polarization function at the BSE level \( \Sigma \). Even if \( \Gamma \n\)
is an highly non–local, three–point function, it has been
recently shown that, as long as we are interested in the
two–point polarization function \( \chi \), Eq. (2) can be cast in
terms of the two–point exchange–correlation kernel \( f_{xc} \)
of TDDFT \( \Sigma \) \( \Gamma \):

\[
\chi (1, 2) = \chi_0 (1, 2) + \int d34 \chi_0 (1, 3) f_{xc} (3, 4) \chi (4, 2) .
\]

(4)

Here \( \chi_0 (1, 2) = -ig_0 (1, 2) G_0 (2, 1) \) gives the DFT polar-
ization function. At this point if we take the exchange–
correlation potential corresponding to \( f_{xc} \) as a local ap-
proximation to the self–energy, then the vertex function
can be easily contracted into a two–point function:

\[
\tilde{\Gamma}_{loc} (1, 2) = \left[ \delta (1, 2) - \int d3 f_{xc} (1, 3) \chi_0 (3, 2) \right]^{-1} .
\]

(5)

Thus Eq. (1) gives \( \Sigma (1, 2) = \int dW^{\text{TDDFT}} (1, 2) G_0 (1, 2) \), in terms of the
TDDFT effective potential \( W^{\text{TDDFT}} (1, 2) = \int d3 v (1, 3) \left[ \delta (3, 2) - \int d4 (v (3, 4) + f_{xc} (3, 4)) \chi_0 (4, 2) \right]^{-1} . \)

From this self–energy the lifetime of a generic conduction
state \( c \) with momentum \( k \) is given by

\[
\tau_{ck}^{-1} = -2\Omega^{-1} \sum_{G_1, G_2} \sum_{q, e \neq 0} \rho_{loc} (kqG_1) \rho_{loc} (kqG_2) \]
\[
\times \text{Im} \left[ W^{\text{TDDFT}} (q, \epsilon_{ck} - \epsilon_{c'k' - q}) \right] ,
\]

(6)

with \( \rho_{loc} (kqG) = \langle nk | e^{i(q + G) \cdot r'} | n'k - q \rangle \). \( G \) is a reciprocal
space vector and \( \Omega \) the crystal volume. Different expres-
sions for \( \tilde{\Gamma}_{loc} \) based either on local–field factor of the ho-
homogeneous electron gas \( \Sigma \) or on time–dependent local–
density approximation (TDLDA) \( \tilde{\Gamma} \) have shown that
inclusion of local vertex corrections in both \( \Sigma \) and \( \chi \n\)
almost cancel out, i.e., \( \tilde{\Gamma}_{loc} / \Sigma \) undresses the exchange–
correlation effects included in the polarization function \( \chi \). How-
ever such approximations for \( f_{xc} \) produce optical spectra very similar to RPA, in disagreement with ex-
periments. This important drawback of a TDLDA \( f_{xc} \) has
been recently related to the long–range nature of the ker-
nel, \( f_{xc} (r, r'; \omega) \sim -\alpha (\omega)/|r - r'| \) that partially con-
tracts the repulsive Hartree contribution \( \delta \). The stron-
ger the electron–hole effects are, the larger is the cor-
rection embodied in \( \alpha \). In the case of wide–gap insu-
lators like LiF there is a large region of frequencies and
transfer momenta \( q \) where \( f_{xc} \) is stronger than the
Hartree term (i.e. \( \alpha > 1 \)). This leads to unphysical
linewidths: for a large energy range \( \text{Im} \Sigma \), and hence
\( \tau^{-1} \), has a wrong sign! This result is visualized by notic-
ing that with respect to a \( G_0 W_0 \) calculation a change of
sign of \( \tau^{-1} \) is controlled by the sign \( (v + f_{xc}) \), that is pro-
portional to \( (1 - \alpha (\omega)) \). A similar result was obtained in Ref. \( \tilde{\Gamma} \) looking at the high \( q \) limit of the TDLDA kernel that goes as \( f_{xc} \sim q^2 \). The reason for this im-
portant failure of a two–point vertex function is connected
to the imposed reduction of the non–locality from the
original, three–point vertex function. In physical terms
\( \tilde{\Gamma}_{loc} \) overestimates the intensity of the vertex correction
because two incoming particles (entering in 1 and 2 in the
exact vertex function \( \Gamma \) are supposed to coexist at the
same time–space point. To overcome this difficulty we
decided to release the constrain on the spatial locality
and define a TDDFT vertex function \( \tilde{\Gamma}_{TDDFT} (1, 2; 3) \)
such that, for a given \( f_{xc} (1, 2) \), \( \tilde{\Gamma}_{TDDFT} \) is consistent with Eqs. (2-4). To this end we recall that in Ref. \( \tilde{\Gamma} \) we
derived a diagrammatic expression for \( f_{xc} \) in terms of the
screened coulomb potential \( W_0 \), that to first order reads:

\[
f_{xc} = \chi_0^{-1} \chi^{(1)} \chi_0^{-1} , \text{ with } \chi^{(1)} \text{ the first order expansion of Eq. (2) in } W_0 \text{[17]. From this } f_{xc} \text{ we get an approxi-
mation for the vertex function } \tilde{\Gamma}_{TDDFT} (1, 2; 3) \text{ im-
ing that once plugged in Eq. (2) it reproduces Eq. (4) for } \chi . \text{ By insp} \]

(7)

It is crucial to observe that \( \tilde{\Gamma}_{TDDFT} \) is not a first or-
der order vertex, as \( \tilde{\Gamma}_{loc} \) sums an infinite number of diagrams. Eq. (7) can be easily generalized to give higher order ap-
proximations for \( \tilde{\Gamma} \), consistent with the high order cor-
rections to \( f_{xc} \) of Ref. \( \tilde{\Gamma} \). As it is commonly done we
neglect dynamical effects in the BSE \( \tilde{\Gamma} \), i.e. we assume
\( W_0 (1, 2) \approx W_0 (r_1, r_2; \omega) = 0 \) in Eq. (7). This approxi-
mation is motivated in the present case, as we are in-
terested in the low–energy electronic linewidths neglect-
ing self–consistency effects. We have verified numerically
that for LiF, Si, diamond and SiO\(_2\) \( \tilde{\Gamma}_{TDDFT} (1, 2; 3) \) is an
excellent approximation to the “true” BSE vertex function
\( \Gamma \).

Now we can study the quasielectron lifetime in this
approximation for the vertex function and for the elec-
tronic self–energy. To do so, we use as above the “on
mass–shell” approximation, i.e., the lifetime is given by
the imaginary part of \( \Sigma = G_0 W^{\text{TDDFT}} (1) \) evaluated at
the DFT energies:

\[
\tau_{ck}^{-1} = -\text{Im} \left[ \langle c | \Sigma (r, r'; \epsilon_{ck}) + \tilde{\Sigma} (r, r'; \epsilon_{ck}) | c \rangle \right] .
\]

(8)

Here the linewidths are computed as an average of the
“left” and “right” self–energies, \( \Sigma \) and \( \tilde{\Sigma} \), in order to re-
store the proper \( r, r' \) symmetry of the self–energy. Using
Eq. (4) \( \tau_{ck}^{-1} \) can be simplified by performing the energy
integration in the complex plane and exploiting the pole
structure of $\Gamma^{(1)}_{TDDFT}$:

$$\tau_{ck}^{-1} = \tau_{ck,0}^{-1} - 2\Omega^{-1} \sum_{G_1, G_2, q, \omega} \text{Im} \left[ W^{TDDFT}_{G_1, G_2} \langle \omega, \epsilon_k - \epsilon_{c/(k-q)} \rangle \right]$$

$$\text{Re} \left[ \left( \Gamma^{cc}_{cc} (kqG_1) + \Gamma^{vc}_{cc} (kqG_1) \right) \rho^{cc}_{cc} (kqG_2) \right], \quad (9)$$

where $\tau_{ck,0}$ corresponds to the standard $G_0W$ approximation, and

$$\Gamma^{cc}_{cc} (kqG) = \Omega^{-1} \sum_{G_1, G_2, q, \omega} \rho^{cc}_{cc} (kqG_1) \left[ W_0 (Q) \right]_{G_1, G_2}$$

$$\rho^{cc}_{cc} (kqG_2) \rho^{cc}_{cc} (kqG)$$

$$\left( \epsilon_{ck} - \epsilon_{c/k-q} - \epsilon_{c/k-q} + \epsilon_{v2k-q} \right)^{-1}, \quad (10)$$

$$\Gamma^{vc}_{cc} (kqG) = \Omega^{-1} \sum_{G_1, G_2, q, \omega} \rho^{cc}_{v2} (kqG_1) \left[ W_0 (Q) \right]_{G_1, G_2}$$

$$\rho^{cc}_{v2} (k - QG_2) \rho^{cc}_{v2} (k - QG)$$

$$\left( \epsilon_{ck} - \epsilon_{c/k-q} - \epsilon_{c/k-q} + \epsilon_{v2k-q} \right)^{-1}. \quad (11)$$

Eq. (9) constitutes the main basic result of this communication, and can be easily extended to the quasihole linewidths. Eq. (10) must be compared with Eq. (9). In the case of weakly interacting systems the two equations with a TDLDA $f_{xc}$ give very similar quasiparticle corrections to the gap and electron linewidths [12 13 14]. But, as short–range correlations become important Eq. (10) tends to give non–sensible results (negative linewidths) because of the wrong sign of $W^{TDDFT}$. In Eq. (9), instead, the term $\left( \Gamma^{cc}_{cc} + \Gamma^{vc}_{cc} \right)$ reflects the spatial non–locality of $\Gamma^{(1)}_{TDDFT}$ strongly reducing the weight of $W^{TDDFT}$. Consequently the final expression for $\tau_{ck}^{-1}$ is given by $\tau_{ck,0}^{-1}$ plus a small vertex correction that does not change appreciably the results of a simpler $G_0W$ calculation. The fundamental practical result of this work corresponds to the solution of Eq. (9) for LiF, shown in Fig. 1. The overall effect of excitons in the linewidths is huge [15]: the linewidths up to 3eV above the forbidden region display a linear dependence with energy while the RPA are almost zero because of the slow rise of the RPA loss function (see Fig. 2). A similar energy dependence has been observed in highly correlated materials [15]. Instead the present linear dependence of the linewidths is due to the combination of an almost constant density–of–states close to the conduction band minimum and to a “step–like” energy dependence of loss function (see Fig. 2). Furthermore, the quasiparticle linewidths are not exactly zero in a small energy window of 0.5eV in the forbidden region. This effect can be traced back to the excitonic–induced transfer of oscillator strength in the dynamical dielectric function $\varepsilon_{kk}$ below the gap. This result is consistent with the fact that exciton dynamics is dictated by vertex–correction to the self–energy, therefore an interpretation of the quasiparticle scattering based only on independent–particle processes loses meaning. The results of the present work allow for the systematic analysis of the role of excitons in quasiparticle excitations and response functions of extended and low dimensional systems, where the standard $G_0W_0$ approximation fails [2 3].

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