Dynamical excitonic effects in metals and semiconductors

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The dynamics of an electron–hole pair induced by the time–dependent screened Coulomb interaction is discussed. In contrast to the case where the static electron–hole interaction is considered we demonstrate the occurrence of important dynamical excitonic effects in the solution of the Bethe–Salpeter equation. This is illustrated in the calculated absorption spectra of noble metals (copper and silver) and silicon. Dynamical corrections strongly affect the spectra, partially canceling dynamical self–energy effects and leading to good agreement with experiment.

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The standard approach to account for the electron–hole interaction in optical spectra is based on the solution of the Bethe–Salpeter equation (BSE) [1, 8] for the two–particle Green’s function. An important ingredient of the BSE is the electron–hole interaction, described by the screened, time–dependent Coulomb interaction $W(r, r'; t − t')$. However, the BSE with a time–dependent interaction is hardly solvable and, as common practice, the electron–hole interaction is assumed to be instantaneous; this is equivalent to approximating the time Fourier transform of $W$ with its static value, $W(r_1, r_2, \omega = 0)$. This approximation is verified a posteriori through the comparison with the experimental and physically corresponds to the assumption that the electron–hole scattering time is much longer than the characteristic screening time of the system (roughly speaking, the inverse of the plasma frequency). Indeed, the static approximation is expected to work well for transition energies much smaller than the plasma frequency [2]. However, the most striking examples of systems that do not fulfill this condition are silver and copper. The well–known sharp plasmon of silver, which dominates the electron–energy–loss spectra (EELS) [6, 7], is located just above the interband gap (∼3.9 eV). Similarly, the EELS of copper shows strong, broad peaks in the optical range [2].

In this letter we prove that dynamical excitonic effects in copper and silver are possible when the BSE is solved with a time–dependent electron–hole interaction. Their experimental optical spectra are correctly explained only thanks to a delicate interplay between dynamical excitonic and self–energy effects. In order to clarify the relation between the present approach and the previous results obtained within the static approximation [2], we show that the optical spectrum of silicon can be obtained without using the approximations commonly employed in the static approach, that is without neglecting quasiparticle renormalization factors and dynamical electron–hole interaction effects.

The absorption spectrum is given by the imaginary part of the dielectric function $\epsilon(\omega) \equiv 1 − 8\pi\Lambda^\dagger P(\omega)\Lambda$, where $P(\omega)$ is the matrix representation of the polarization function in the non–interacting electron–hole basis and $\Lambda$ is a vector embodying the corresponding optical oscillators. The single–particle states are calculated by means of density–functional–theory (DFT) in the local–density–approximation (LDA) [10], while quasiparticle (QP) corrections are added on top of the DFT–LDA band structure following the implementation of the GW method [11] described in Ref. [12]. The polarization function is obtained by solving the BSE, an integral
the electron–hole interaction is approximated as "practically unsolvable" [14]) and this reason the BSE is considered hardly solvable (if not practically unsolvable) in all cases. Hence, we look for a solution of equation (1) without the two major approximations employed in the SBSE, i.e. keeping the Z’s smaller than 1 and W frequency dependent. To this end we expand \( L(t_1, t_2; t_1, t_2) = \tilde{W}(t_1 - t_2) L(t_1, t_2; t_1, t_2) \) and using generalized indexes \( \mathbf{K} := (c v \mathbf{k}) \) the first order term of this expansion, \( P^{(1)}(t_1, t_2) \), is given by:

\[
P^{(1)}_{\mathbf{K}_1, \mathbf{K}_2}(t) = \int \, dt_1 \, dt_2 \, \delta(t_1 - t_2) \left[ L^{(0)}_{\mathbf{K}_1}(t, t_2; t_1, t_1) \tilde{W}_{\mathbf{K}_1, \mathbf{K}_2} (t_1 - t_2) L^{(0)}_{\mathbf{K}_2}(t_1, 0; t_2, 0) + L^{(0)}_{\mathbf{K}_1}(t, t_1; t_2, t_2) \tilde{W}_{\mathbf{K}_1, \mathbf{K}_2} (t_2 - t_1) L^{(0)}_{\mathbf{K}_2}(t_2, 0; t_1, 0) \right].
\]

From Eq. 2 it is straightforward to see that:

\[
P^{(0)}_{\mathbf{K}_1}(t, t_2; t_1, t_1) = i \left[ P^{(0)}_{\mathbf{K}_1}(t - t_1) e^{i E_{\mathbf{k}_1}(t_1 - t_2)} \delta(t_1 - t_2) + P^{(0)}_{\mathbf{K}_1}(t - t_2) e^{-i E_{\mathbf{k}_1}(t_1 - t_2)} \delta(t_2 - t_1) \right],
\]

\[
P^{(0)}_{\mathbf{K}_2}(t_1, 0; t_2, 0) = i \left[ P^{(0)}_{\mathbf{K}_2}(t_2) e^{-i E_{\mathbf{k}_2}(t_2 - t_1)} \delta(t_1 - t_2) + P^{(0)}_{\mathbf{K}_2}(t_1) e^{i E_{\mathbf{k}_2}(t_2 - t_1)} \delta(t_2 - t_1) \right],
\]

that inserted in Eq. 4, casts \( P^{(1)}(t) \) as a time convolution of three terms (as shown diagrammatically in Fig. 1 left diagram).

Because of the time dependent term \( \tilde{W}(t_1 - t_2) \), Eq. 1 cannot be rewritten in terms of \( P(t) \) only. For this reason the BSE is considered hardly solvable (if not "practically unsolvable" [14]) and for computational convenience the electron–hole interaction is approximated as static, \( \tilde{W}(t) \approx \tilde{W}(\omega = 0) \delta(t) \). Thus Eq. 1 can be formally solved by means of a Fourier transform:

\[
P(\omega) = P^{(0)}(\omega) - P^{(0)}(\omega) \left( \mathbf{V} + \tilde{W} \right) P(\omega).
\]

As a consequence, in the frequency domain \( P^{(1)}(\omega) \) has the form:

\[
P^{(1)}(\omega) = -P^{(0)}(\omega) \left[ \Pi^{(a)}(\omega) + \Pi^{(b)}(\omega) \right] P^{(0)}(\omega),
\]

where the BSE kernel is decomposed into a sum of the first order term of this expansion, \( P^{(1)}(t) \) for \( t_1 > t_2 \), left diagram) and second \( P^{(2,a)}(t) \), right diagram) order contributions to the polarization function \( P(t) \) according to the BSE (see text). Crosses indicate the time points where the incoming and outgoing non–interacting Green’s functions are “cut” according to Eqs. 6 and 7.
with \( \Pi^{(a)}_{K_{1}K_{2}}(\omega) = \tilde{W}^{(+)}_{K_{1}K_{2}}(\omega + E_{v_{1}k_{1}} - E_{c_{2}k_{2}}) \) and \( \Pi^{(b)}_{K_{1}K_{2}}(\omega) = \tilde{W}^{(+)}_{K_{1}K_{2}}(\omega + E_{v_{2}k_{2}} - E_{c_{1}k_{1}}) \), \( \tilde{W}^{(+)}(\omega) \) being the Laplace transform of \( W(t) \). The two terms denoted by (a) and (b) correspond to the two possible time orderings of the interaction ends \( (t_{1} > t_{2} \text{ for term (a), shown in Fig.1; } t_{2} > t_{1} \text{ for term (b), not shown}) \). Eq. (8) can be thought of as the first order expansion of \( P(\omega) \) in the frequency–dependent interaction \( \Pi(\omega) = \Pi^{(a)}(\omega) + \Pi^{(b)}(\omega) \), which replaces \( W \) of the SBSE. Thus a partial summation of the BSE can be performed writing:

\[
P(\omega) = P^{(0)}(\omega) - P^{(0)}(\omega) [V + \Pi(\omega)] P(\omega).
\] (8)

This is the Dynamical Bethe–Salpeter equation (DBSE), the central result of this work. The diagrams summed up in Eq. (8) are those containing the ladder series of repeated electron–hole interactions with non overlapping (in time) interaction lines. The poles of \( P(\omega), \Theta_{\lambda} \), will be given by the solution of the equation \( [P^{(0)}(\Theta_{\lambda})]^{-1} + V + \Pi(\Theta_{\lambda}) = 0 \). In contrast to the kernel of the SBSE, \( \Pi(\Theta_{\lambda}) \) is not hermitian and, accordingly, \( \Theta_{\lambda} \) is in general complex. Its imaginary part gives the inverse excitonic lifetime. Thus the interacting electron–hole states are actually dressed excitons, or quasiexcitons. This agrees with what has been already found in the core exciton limit and emphasizes the analogy between the DBSE and the Dyson equation. Consequently, as in the single–particle problem, we expect to find similar renormalization effects on the quasiexcitonic Green's function. To develop further this aspect we expand linearly the smooth function \( \tilde{W}^{(+)}(\omega) \) around the non–interacting electron–hole energies, obtaining

\[
\Pi^{(et)}_{K_{1}K_{2}}(\omega) = \Pi^{(et)}_{K_{1}K_{2}}(\omega)_{\omega=E_{c_{2}k_{2}}-E_{v_{2}k_{2}}} = \text{the static limit of the dynamical Bethe–Salpeter kernel which turns out to be quite similar to the kernel of the SBSE.} \]

\[
\Theta_{K_{1}K_{2}} = \frac{\partial \Pi^{(et)}_{K_{1}K_{2}}(\omega)}{\partial \omega |_{\omega=E_{c_{2}k_{2}}-E_{v_{2}k_{2}}} \text{are the excitonic dynamical-renormalization factors. Thus Eq. (8) can be strongly simplified in the case of noble metals where the effect of } \Pi^{(et)} + V \text{ is very small. The corresponding polarization function } P(\omega) \text{ is approximatively given by:}
\]

\[
P^{(et)}_{K_{1}K_{2}}(\omega) \approx \left[ \left( Z^{eh}_{K_{1}K_{2}} \right)^{-1} + \Theta_{K_{1}K_{2}} \right]_{K_{1}K_{2}}
\] (9)

with \( Z^{eh}_{K_{1}K_{2}} = Z_{c_{1}k_{1}}Z_{v_{1}k_{1}}\delta_{K_{1}K_{2}} \). The connection between dynamical excitonic and self–energy effects is now clear. \( Z^{eh}_{K_{1}K_{2}} = 1 - \beta_{nk} \), where the negative factor \( \beta_{nk} \), the frequency derivative of the self–energy, is the weight lost by the QP because of the coupling with the excitations of \( W(\omega) \). The excitonic factors \( \Theta_{\lambda} \), instead, are due to the modification of such coupling as a consequence of the electron–hole interaction. Those two effects tend to cancel each other but the cancellation is, in general, not complete, as exemplified in Fig.2 for copper and silver.

The SBSE calculation (dotted line), with \( Z_{nk} = 1 \) and \( \Theta = 0 \), overestimates the experimental intensity (circles), while the inclusion of the \( Z^{eh} \) factors (dashed line) underestimates it (full line). In the DBSE (full line), obtained solving Eq. (8), the dynamical \( \Theta \) factors partially compensate for the \( Z^{eh} \) factors yielding a spectral intensity in good agreement with experiment.

FIG. 2: Absorption spectrum of bulk copper, silver, and silicon. Dotted line: SBSE without renormalization factors. Dashed line: SBSE including the QP renormalization factors. Full line: result of the dynamical Bethe–Salpeter equation including dynamical QP and excitonic effects. Circles: experimental spectra (Ref. [17] for Cu and Ag and Ref. [18] for Si).
order contributions in order to reproduce correctly the experimental optical spectrum. The main effect of the first order kernel $\Pi(\omega)$ is indeed to balance the reduction of optical strengths due to self-energy renormalization factors, as suggested by Bechstedt et al. [12]. However, the renormalized QP weights also imply a reduction of the statically screened electron–hole of almost $\sim 30\%$, which is the reason for the wrong relative intensities of the two peaks in the SBSE result. This shortcoming is fixed by the second-order diagrams, as discussed below. One of the two second order diagrams, $P^{(2,a)}(t)$, is shown in Fig.1 right diagram. In the other second-order diagram ($P^{(2,b)}(t)$, not shown), the interaction lines are ordered according to $t > t_2 > t_4 > t_1 > t_3 > 0$. Using Eqs. (10) we can isolate the external non–interacting terms, as schematically shown in Fig.1 by the crosses corresponding to the time points $t_1$ and $t_4$. Consequently $P^{(2,a)}(t)$ can be Fourier transformed to yield $P^{(2,a)}(\omega) = -P^{(0)}(\omega) \Pi^{(2,a)}(\omega) + \Pi^{(2,a)}(\omega) = \Theta^{(a)} Z^{eh} \Pi^{(a)}(\omega)$. Together with the contribution from diagram $P^{(2,b)}$, we obtain the total second–order kernel,

\[ \Pi^{(2)}(\omega) = \Pi(\omega) + \sum_{s=a,b} \Theta^{(a)} Z^{eh} \Pi^{(s)}(\omega). \] (10)

The solution of the DBSE with the kernel given by Eq. (10) is equivalent to summing all diagrams of the original BSE with up to two overlapping interaction lines. While the first-order term ($\Pi(\omega)$) partially restores the optical-strength intensities, the second-order correction ($\Theta^{(a)} Z^{eh} \Pi^{(a)}(\omega)$) reduces the screening of the electron–hole pair, thus enhancing their interaction. In the case of silicon this effect improves considerably the relative intensity of the two main peaks, as shown in Fig.1 (continuous line). Higher-order contributions can also be included in the DBSE kernel, although these terms contain either higher powers of $\Theta$ or higher order energy derivatives of $\Pi(\omega)$ that are negligible in the cases studied in this work.

Thus, in the case of copper and silver the BSE must be solved using a time–dependent electron–hole interaction to obtain good agreement with the experiment. The DBSE result in the case of silicon is similar to the case when, in the SBSE, the QP renormalization factors are neglected. We understand this result as follows: the electron–hole pair, being a neutral excitation, is less efficient than the electron and the hole alone in exciting virtual plasmons, which is the main process leading to QP renormalization. Only when dynamical effects are coherently included both in the self energy and in the electron–hole interaction, this (physically expected) result emerges from the bundle of many-body equations.

This confirms the SBSE results but not the separate approximations involved therein. Even though the plasma frequency of silicon is at $\sim 16\text{eV}$ (far above the optical energy range), the DBSE kernel needs a second order contribution to balance the self–energy dynamical factors.

In conclusion, we have shown that, in contrast to common belief, dynamical excitonic effects in metals do exist and are crucial for reproducing the experimental optical absorption. We have demonstrated that dynamical excitonic and self–energy effects must be included together in the calculation of the response functions as they do not completely cancel each other. The good agreement with experiment obtained using a static BSE kernel for semiconductors is confirmed by the present, more general approach.

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