Excitonic Effects on the Silicon Plasmon Resonance

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We present an *ab initio* calculation of the electron energy loss spectrum of silicon including local-field, self-energy, and excitonic effects. When self-energy corrections are added to the standard random phase approximation (RPA) the line shape of the plasmon resonance worsens. The electron-hole interaction cancels this correction and improves the result both compared to the RPA and to the self-energy one, yielding very good agreement between theory and experiment provided that the mixing of interband transitions of both positive and negative frequencies is included.

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In a classical description of an extended system of charged particles, as in Drude's model, a plasmon is a collective excitation of the electrons which oscillate on a background of positively charged ions. Plasmons can be measured, for example, as resonances in electron energy loss spectra (EELS) at characteristic frequencies where the transfer of energy to the system is favored. However, the interpretation of EELS is not simple, because besides the structures associated to collective excitations there are those due to electron-hole interband transitions, or even to a coupled superposition of both. Nevertheless, if there are no significantly strong interband transitions in the plasmon energy region, the plasmon concept still retains its validity as a damped collective excitation. Moreover, looking at excitations with long wavelength (small transferred momentum q), the collective character of the modes dominates.

The classical free-electron model gives the relation $E_p = (4\pi ne^2/m)^{1/2}$ between the plasmon energy E_p and the average electron density n of the system. Indeed this relation gives a first indication for the position of plasmon resonances and can even be a good approximation in materials like simple metals at low electron density. In other materials, however, it yields only a rough estimate. In fact, it is crucial to include information about the band structure of the solid. This affects both the peak positions and the line shape of plasmon resonances. We therefore have to calculate the energy loss function (ELF) of the system, a quantity that completely characterizes the EELS. It is defined as $-\mathrm{Im}[\varepsilon^{-1}(\mathbf{q}, \omega)]$, where ε is the dielectric function. Essentially, the peaks of the ELF corresponding to collective excitations are zeros of the real part of the dielectric function. As a first step, the calculation of the ELF can be done in the independent-particle scheme of the random phase approximation (RPA), where the so called exchange-correlation effects (the effects due to the many-body interactions among the electrons of the system) are still neglected, but the band structure of the solid is now taken into account.

If one has to deal with inhomogeneous electron systems also the so called local-field (LF) effects should be considered. They are related to the fluctuation of the polarization of the system on the atomic scale. Thus the response to an external perturbation includes, besides the wavelengths of the perturbation, also wavelengths of the order of the lattice spacing, that is, Bragg diffracted components. The LF effects are described by the off-diagonal elements of the dielectric matrix $\varepsilon_{\mathbf{G},\mathbf{G}'}(\mathbf{q}, \omega)$, where $\mathbf{G}$ is a reciprocal lattice vector. The LF effects become stronger as the momentum transfer q increases, since then the wavelength of the excitation becomes smaller and one samples the local inhomogeneities of the electronic system under consideration.

The RPA with local-field effects is often a good approximation for the description of the EELS spectra. For silicon, to our knowledge the first work giving the RPA ELF by a band structure calculation is the one of Louie *et al.* [1] who indeed found good agreement with experiment concerning the position of the plasmon resonance. Later Daling, van Haeringen, and Farid [2] calculated the plasmon-resonance line shape in silicon at $q \rightarrow 0$ including both local-field effects, and exchange-correlation corrections in the framework of the time-dependent density-functional theory in the adiabatic local-density approximation (TD-LDA) [3]. This is an approximate way to include many-particle effects based on ingredients taken from the homogeneous electron gas. This approach is today widely used, as, for example, in a recent work on diamond by Waidmann *et al.* [4]. It is however a common finding that the inclusion of exchange-correlation corrections in the scheme of TD-LDA beyond the RPA approximation has a small effect [4] or even worsens [2] the agreement with experiment. The authors of Ref. [4] have instead pointed out the need to include the many-body effects more properly and, in particular, to treat excitonic effects explicitly.

Today it is hence a challenge to consider alternative, more precise ways to include many-body effects. A good level of approximation could be Hedin's *GW* approximation [5], in the framework of many-body quantum field theory. Using this approach one can calculate electron addition and removal (quasiparticle) energies through self-energy corrections to the density-functional theory

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local-density approximation (DFT-LDA) Kohn-Sham (KS) eigenvalues, taking hence properly into account the electron-electron interaction. When the response functions are then constructed using these eigenvalues instead of the DFT-LDA Kohn-Sham ones (*GW* approach), the loss function might be considerably altered. In fact, an estimate of this effect can be found in the work of Gavrilenko and Bechstedt [6], where the authors add *GW* corrections to the TD-LDA result using a simplified *GW* scheme, and it will certainly be interesting to verify the effect of *full GW* corrections to the ELF. Nevertheless, even when doing so, the effects related to the interaction between an excited electron and its associated hole (the so called excitonic effects) are still neglected, which is an inconsistent approximation.

In order to take into account also the excitonic effects, we have to consider vertex corrections to the *GW* expressions for the polarizability. In the calculation of $\mathrm{Im}(\varepsilon)$, hence, for example, in absorption spectra, from a large number of publications electron-hole interaction effects are known to be significant, even for silicon [7–9], and we can expect that this should also influence the EELS.

The aim of this work is to calculate the plasmon resonance in the EELS spectrum of silicon including local-field effects and many-body, up to excitonic, effects. The scheme we use is based on the one described by one of us [8,10], however going beyond an important approximation made in that and similar [9,11] works. Recently Caliebe *et al.* [12], still using the original scheme [9], have performed an excitonic calculation of the dynamic structure factor of diamond and LiF (measured in inelastic x-ray scattering spectroscopy experiments), which is directly related to the ELF $-\Im[\varepsilon^{-1}(\mathbf{q},\omega)]$. That work, however, deals with $q \neq 0$, while here we are interested in the limit $q \to 0$, that is, in the response of the system to a longitudinal perturbation with vanishing momentum transfer. In this range the loss function is dominated by the collective excitations of the electron system, i.e., the plasmons. Moreover, in this limit of large wavelength the local-field effects are smaller and do not mask the many-body effects we are interested in. In fact, as mentioned above, it turns out that we have to make an important extension to the approach used in Refs. [8] and [12], in order to describe these effects correctly. Therefore we briefly summarize the scheme of Ref. [8], concentrating on the modifications which are necessary in the case of the calculation of EELS spectra.

We compute the macroscopic dielectric function ε from the two-particle correlation function S, which is directly related to the polarizability χ of the system. The two-particle correlation function is calculated solving the Bethe-Salpeter equation through the introduction of an effective excitonic Hamiltonian containing unperturbed quasiparticle transition energies and the matrix elements of an interaction kernel Ξ taken between pairs of occupied/empty quasiparticle states (v, c). The excitonic Hamiltonian is diagonalized; its eigenvalues E_λ are the transition energies of the system. The eigenvectors A_λ^{vc} mix the independent-particle transitions $v \to c$ of the RPA (in fact, A_λ^{vc} would be a δ function in RPA without LF). To be precise, the general form of the excitonic Hamiltonian is

$$H = \begin{pmatrix} R & C \\ -C^* & -R^* \end{pmatrix}, \tag{1}$$

where $R = R^\dagger$ and $-R^*$ are, respectively, the resonant part, containing the $v \to c$ transitions of positive frequency, and the antiresonant part, containing the $c \to v$ transitions of negative frequency. $C = C^{\mathrm{T}}$ and $-C^*$, the off-diagonal parts, are the coupling elements between transitions of positive and negative frequencies. The coupling terms are in general smaller than the resonant and antiresonant terms (the influence of the coupling terms on exciton energies has been discussed in Ref. [13]). In fact, they can be neglected in the calculation of the optical properties (at least of silicon), as was done in Ref. [8]. On the contrary, and this is the main difference to the approach used for all *ab initio* calculations of absorption spectra up to now, in the case of the calculation of the energy loss function we *cannot* neglect them. This is of course intimately linked to the importance of the *real* part of ε which, via the Kramers-Kronig relation, contains transitions of positive and negative frequencies.

This fact is illustrated in Fig. 1 which shows the ELF calculated at a reduced number of k points ($N_k = 32$) in the Brillouin zone (BZ). There is a significant difference between the solid (inclusion of the coupling) and the dotted

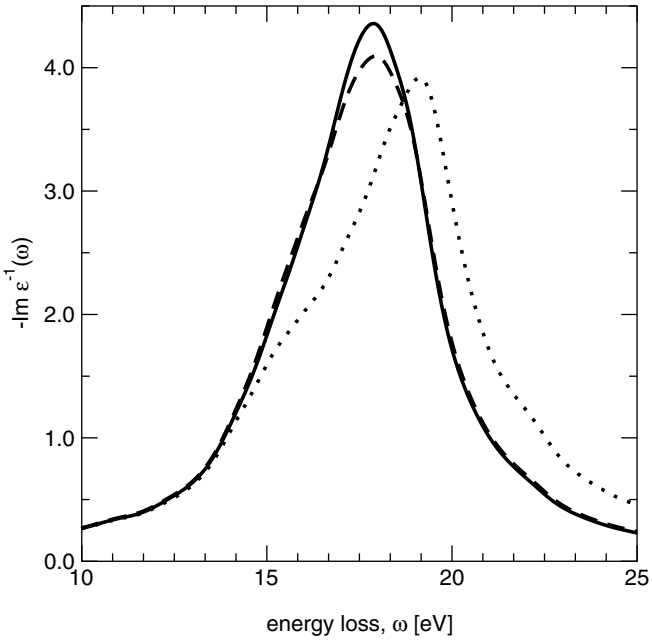

FIG. 1. Silicon, ELF calculated with only 32 k-points in the BZ: solid line, coupling fully included; dotted line, coupling neglected; dashed line, coupling included in first-order perturbation theory.

curve (neglect of the coupling). Hence, in the present case, we have to diagonalize the full non-Hermitian excitonic Hamiltonian, a task that is not easily accomplished even on the more powerful computers today.

Since the coupling terms are, however, much smaller than the resonant and antiresonant terms, we can try to include them in first-order perturbation theory, considering as the zero-order Hamiltonian $H^{(0)}$ and as perturbation $H^{(1)}$ the operators

$$H^{(0)} = \begin{pmatrix} R & 0 \\ 0 & -R^* \end{pmatrix}, \qquad H^{(1)} = \begin{pmatrix} 0 & C \\ -C^* & 0 \end{pmatrix}. \quad (2)$$

The result we obtain is the one shown by the dashed curve in Fig. 1. With respect to the solid curve where the coupling is accounted for to all orders, there is a relatively small residual error (i.e., an error much smaller than the effects we are studying), which is acceptable. It should be pointed out that, although the non-Hermitian Hamiltonian could, in principle, have imaginary eigenvalues, this is not the case here. In particular, first-order perturbation theory does not change the eigenvalues at all, but affects only the eigenvectors. In fact, as in the case of the absorption spectra, even the shifts of the peak positions are due to changes in the eigenvectors, and not to shifts of transition energies.

The ground state DFT-LDA calculation [14] was performed using norm-conserving pseudopotentials [15], an energy cutoff of 18 Ry, and 256 special MP k-points [16] in the BZ. In this way we obtain the KS electronic structure which is used to calculate the RPA spectra and which also form the input for the further calculations. Next we calculate the *GW* corrections to the KS band structure following the approach of Ref. [17]. The quite smooth *GW* corrections calculated at the special MP k-points are interpolated to obtain the *GW* corrections at the shifted 256 MP k-points needed for the calculation of the macroscopic dielectric function. The *GW* band structure is then used to calculate the *GW* spectra and serves as an input for the excitonic ELF calculation. For the latter we use $N_v = 4$ valence bands and $N_c = 13$ conduction bands, which is much more than the $4 + 3$ bands needed for an optical spectrum, since the ELF spreads over a larger energy range. With these parameters convergence is achieved within 5%, the main error remaining on the peak height.

The results are shown in Fig. 2. The dots are the electron energy loss experimental data of Stiebling [18]. The most visible feature in the case of the EELS spectrum of silicon at q close to 0 is the volume plasmon resonance located at about 16.8 eV. The dashed line is the RPA calculation, including local-field effects. We remark, as already stated in the previous works [1,2], the overall satisfactory agreement of the RPA curve with respect to the experiment, especially concerning the position of the plasmon resonance. The plasmon resonance line shape, however, exhibits several secondary structures stemming from band structure effects, which cannot be seen in the experiment, and it is too

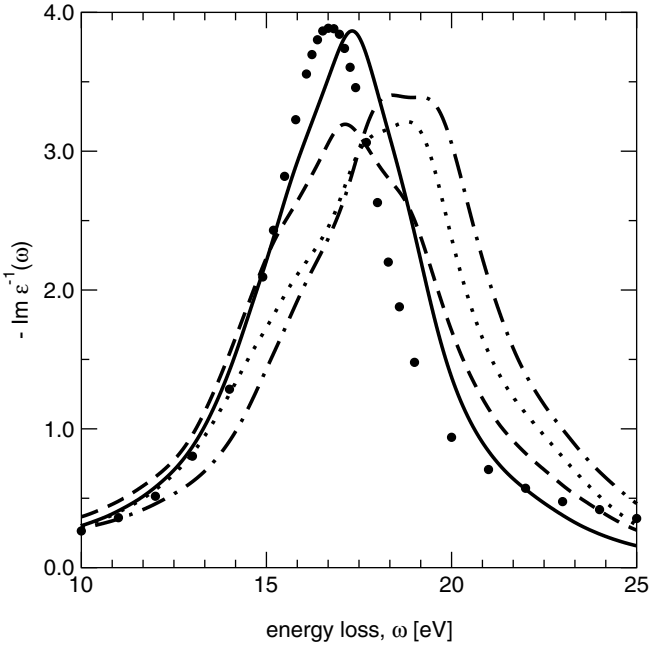

FIG. 2. Silicon, EELS spectrum: dots, experimental points by Stiebling (Ref. [18]); dashed line: RPA; dot-dashed line: *GW* corrections are added to the KS eigenvalues; solid line: *GW* corrections plus excitonic effects; dotted line: same as the solid line but neglecting the coupling. All the calculated results include local-field effects.

broad on the high energy side. The *GW* result, including local-field effects (dot-dashed curve), shows a large shift to higher energies. In fact, we have to realize that when we begin to include many-body effects via *GW*, hence still neglecting the vertex (electron-hole) corrections, the result clearly worsens with respect to the RPA one, concerning the position of the plasmon resonance, while also the line shape does not improve. This result nicely illustrates the usual difficulty to establish the "best" level of approximation in the framework of many-body perturbation theory.

Finally, the continuous curve has been obtained by including also the effects of the electron-hole interaction. The result clearly improves: we see that both the position of the plasmon resonance and the line shape are now in better agreement with experiment, with respect to the *GW* calculation, but also with respect to the RPA one. In fact, the remaining discrepancy with experiment is of the same order of magnitude as the error bar which we have to assume due to the first-order perturbation treatment of the coupling, and the convergence of the calculation.

As pointed out above, the behavior of the real part of ε dominates the EELS. In Fig. 3 we have plotted the real and imaginary parts of ε in the region of the plasmon resonance. We see that the main difference between the RPA (dashed curve), *GW* (dot-dashed curve), and excitonic (solid curve) calculations is directly related to the shift of the zero of $\Re(\varepsilon)$.

We stress the fact that the big improvement has been achieved only through the inclusion of the coupling terms,

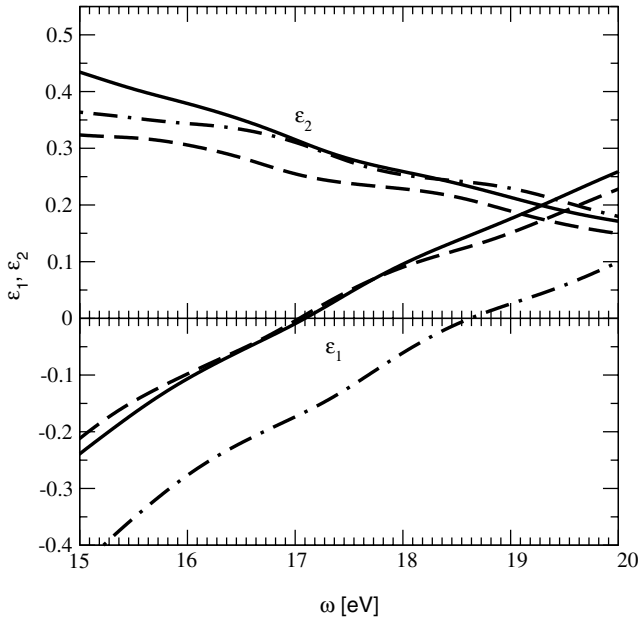

FIG. 3. Silicon, real ε_1 and imaginary ε_2 parts of the dielectric function: solid lines, excitonic calculation; dot-dashed lines, *GW* approach; dashed lines, RPA calculation.

which are generally completely omitted in the absorption spectra. The result we obtain if we neglect the coupling terms is the one shown by the dotted curve in Fig. 2, which represents an excitonic calculation with only the resonant and antiresonant terms. Clearly this result does not show the effect of the electron-hole interaction as it does not improve at all with respect to *GW*.

Finally, it would be interesting to compare at least qualitatively the results of the excitonic calculation to the TD-LDA ones found in literature [2,6,19,]. This is, however, not obvious: when exchange-correlation effects are included, in Ref. [2] a shift towards higher energies and a slight reduction of the broadening were obtained, while Ref. [6], on the contrary, shows a shift towards lower energies and a slight increase of the broadening. In Ref. [19] one of us has found an intermediate result, i.e., a shift towards lower energies and a slight reduction of the broadening. This last result indicates that also TD-LDA can yield an improvement with respect to RPA, although the improvement on the line shape is more evident in the present excitonic calculation than in all the published TD-LDA results.

In conclusion, we have calculated the EELS spectrum of silicon including local-field effects, *GW* corrections, and excitonic effects. We find that the inclusion of excitonic effects improves the results with respect to both the RPA, and more drastically, with respect to the *GW* calculations. The correct result can be obtained only by taking into account the coupling between transitions at positive and negative frequency, which are generally neglected in calculations of optical spectra.

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