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Many-Particle Effects in the Optical Excitations of a Semiconductor

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We present (a) a general formulation of the electron-hole interaction which takes into account both screened electron-hole attraction and its exchange counterpart, giving rise to the excitonic and local-field effects, respectively; (b) a quantitative calculation of absorption and modulation spectrum in Si, which demonstrates the dominant role played by the continuum-exciton effect on the main optical absorption of a covalent semiconductor; and (c) a model analysis of the continuum-excitonic effect on the optical excitations of semiconductors in general.

It is well established by now[1-5] that the optical absorption spectrum of solids derived from non-interacting electron-hole pairs is modified by interaction effects. They consist primarily of the attraction between the electron and the hole and its exchange counterpart, which gives rise to the local-field effect. Ample evidence for the importance of these many-particle effects can be found among the optical data of a wide class of insulators[1,3] and semiconductors.[1-6] A typical example is silicon, where the single-particle treatment gives the oscillator strength for the E_1 peak about one-half of the observed value and that of the E_2 peak somewhat too large.[7]

Recently, much effort has been made to clarify the role of the local-field effect on the electronic excitations in semiconductors and insulators.[7-11] Usually, only the local-field effect in the random-phase approximation (RPA) is considered which takes the electron and its hole as noninteracting. In a recent Letter[7] this RPA local-field effect has been shown in Si to shift absorption strength to higher energies as compared to the one-particle calculation. In the main absorption region this behavior increases the discrepancy between the calculated absorption and experiment. It has also been found in recent work on insulators, independent of whether a pseudopotential representation[7,9] or the local-orbital scheme, which we have developed,[8] was used.[8,10,11] On the other hand, following an empirical treatment by Phillips,[3] saddle excitons have been considered as the cause of the discrepancy in the effective-mass approximation (EMA),[12,13] or in a short-range Slater-Koster model[6,14,15] for the electron-hole attraction.

On the basis of a very general formulation of the electron-hole interaction, employing the local-orbital method, also in vogue recently for the impurity problem,[16,17] we present here (a) a numerical investigation for Si which demonstrates that the combined effect of exciton interaction and its exchange increases the intensity of the E_1 peak by about a factor of 2 and shifts the peak position by 0.2 eV to lower energies compared to the single-particle interband transi-

tions; (b) arguments that the significant deviations of the one-particle spectra of group-IV semiconductors and III-V and II-VI semiconductor compounds from experiment can similarly be explained.

The dielectric response, from which the observed spectrum can be calculated is given by the two-particle Green's functions S.[8,18] Our starting point is the equation of motion for this two-particle Green's function, known as the Bethe-Salpeter equation,[18] an integral equation, of the form

$$S = S^0 + S^0 I S, \tag{1}$$

where S^0 is the noninteracting electron-hole pair, including however, all the band-structure effects and the many-body effects on the one-electron energy and wave function, and I is the interaction. This interaction term I is taken to include the screened electron-hole attraction, $-V^s$, and the unscreened exchange term V. Thus, Eq. (1) includes the overall band effect, the exciton effect, and the exchange correction. It is solved by expressing it in terms of local orbitals, thus converting it to a matrix equation, with S given by

$$S = S^0[1 - (V - V^s)S^0]^{-1}. \tag{2}$$

Here S^0 is the single-particle polarization in the local representation.[8] If the electron-hole attraction, $-V^s$, is omitted the Bethe-Salpeter equation with just the unscreened exciton exchange V reduces to the usual RPA. V is given by

$$V_{\lambda\lambda'} = \sum_m \int\int d^3r\, d^3r'\, \varphi_\mu^*(\vec{r} - \vec{R}_l - \vec{R}_m)\varphi_\nu(\vec{r} - \vec{R}_m) v(\vec{r} - \vec{r}')\varphi_{\nu'}^*(\vec{r}')\varphi_{\mu'}(\vec{r}' - \vec{R}_{l'}), \tag{3}$$

where $\lambda = (l, \nu, \mu)$ and the symbols are the same as in Ref. 8. $\varphi_\mu(\vec{r} - \vec{R}_l)\varphi_\nu(\vec{r})$ is the charge density of an electron-hold pair with "dipole moment" $\vec{R}_l$. The fact that in a periodic crystal one needs to consider the interaction of "dipoles" excited in a screening process having structure on an atomic scale reflects the physical intuition of the microscopic or local-field effects. V in Eq. (3) corresponds to a transition where an electron-hole pair at site $\vec{R} = 0$ induces a new electron-hole pair on a site $\vec{R}^m$ and destroys itself, thus the excitation can move around the crystal. The dipole-dipole interaction between Frenkel excitons,[20] the splitting of longitudinal and transverse excitons,[21] and the interference of continuous x-ray edges in simple metals[22] have been recognized as consequences of this exciton exchange.[19] However, in all these investigations the exciton exchange has been studied by neglecting the k dependence of the Bloch functions which generate the exciton states in consideration. Thus, V in Eq. (3) represents a general form of electron-hole exchange.

The electron-hole attraction is described by

$$-V^s = -\tfrac{1}{2}\sum_m \int\int d^3r\, d^3r'\, \varphi_\mu^*(\vec{r} - \vec{R}_l - \vec{R}_m)\varphi_\nu(\vec{r}' - \vec{R}_m) v_s(\vec{r}, \vec{r}')\varphi_{\nu'}^*(\vec{r}')\varphi_{\mu'}(\vec{r} - \vec{R}_{l'}). \tag{4}$$

If all orbitals generating $-V^s$ are well localized, then the $\vec{R}_m$'s entering the summation in Eq. (4) as well as $\vec{R}_l$ and $\vec{R}_{l'}$ are limited to the same shells of first neighbors. In particular, if $\vec{R}_l = \vec{R}_{l'}$, we have the short-range attraction between an electron-hold pair of dipole moment $\vec{R}_l$, which determines the central-cell corrections in the excitonic picture.

The matrix inversion of Eq. (2) becomes impractical when (i) the exciton radius ($\boldsymbol{R}_l$) becomes large, as near the fundamental gap, in which case, one has to resort to EMA or (ii) the wave functions are free-electron–like, in which case, the plane-wave representation should be used, as will be discussed below.

The nonlocal electron-hole interaction $v_s(\vec{r}, \vec{r}')$ in Eq. (4) has been discussed in the most general form by Sham and Rice.[18] In Ref. 8 we considered a short-range approximation to it, which is the electron-hole interaction in the "same bond". The Coulomb interaction in a crystal medium is subjected to screening by the dynamic dielectric function which we want to calculate.[18,23] In the following we keep local, static screening in the interaction V^s.

In our explicit calculation of $\epsilon(\omega)$ for Si we used an "experimental" band structure[24] which was fitted with a third–nearest-neighbor overlap model of bonding and antibonding sp^3 orbitals. The adjustment of energies to optical experiment is justified, since the many-particle corrections to the one-electron critical points are small ($\lesssim 0.2$ eV, see below) and within the error range of our approximate band-structure determination. The s and p local orbitals are expanded in Gaussians with the parameters optimized with respect to a simultaneous adjustment both to the density profiles[25] and to the current-conservation criterion.[8] The local screening $\epsilon^{-1}(\vec{r} - \vec{r}')$

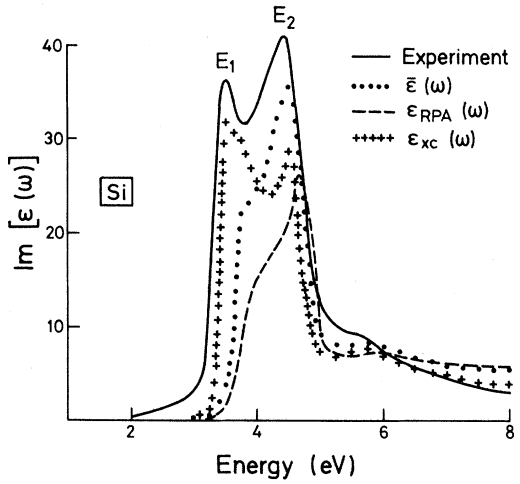

FIG. 1. Imaginary part of the dielectric constant vs energy; experimental data from Ref. 27; $\bar{\epsilon}$ gives the single-particle calculation, ϵ_{RPA} the calculation within RPA with local-field correction, and ϵ_{xc} the calculation including screened electron-hole attraction and local-field correction.

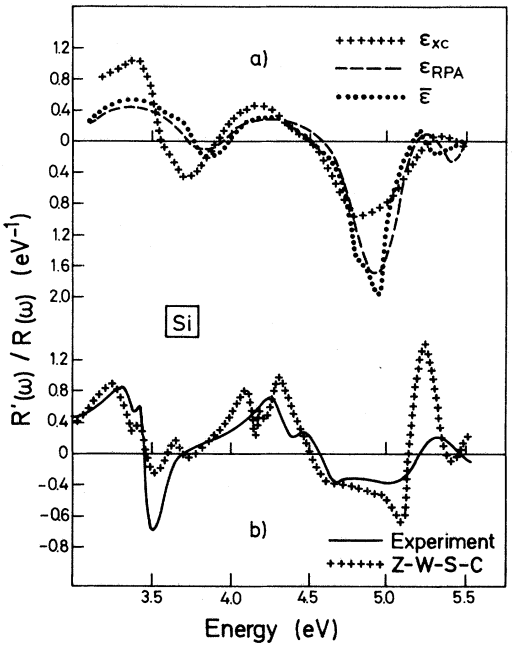

FIG. 2. A comparison of theoretical and experimental modulated reflectivity for Si. For legend see also Fig. 1. Experimental and single-particle pseudopotential data (*Z–W–S–C*) are taken from Ref. 28.

in the electron-hole attraction also is fitted in terms of Gaussians to the Fourier-transformed dielectric function of Walter and Cohen.[26] We include only nearest-neighbor overlap of wave functions φ_v, having found the higher-order contributions negligible within the error range of our approximate band structure and wave functions. The dimension of the screening matrix S in Eq. (2) is then 28.

The results for the imaginary part of $\epsilon(\omega)$ are plotted in Fig. 1 and compared with experiment. The single-particle calculation [$S = S^0$ in Eq. (2), which is denoted by $\bar{\epsilon}(\omega)$ in Fig. 1], just indicates structure around the E_1 position. Local-field effects within the RPA [$\epsilon_{RPA}(\omega)$ corresponding to the screening denominator $(1 - VS^0)$ in Eq. (2)] reduce the oscillator strength on the low-energy side contrary to what is required to reconcile theory with experiment. This result shows the same general trend as our previous diamond calculation[8] and is also in rough agreement with other Si RPA treatments.[7,10] Inclusion of screened electron-hole interaction [$(V - V^s)$ in Eq. (2)] gives rise to electron-hole attraction. This continuum-exciton effect in $\epsilon_{xc}(\omega)$ almost doubles the intensity of the E_1 peak and shifts the position by about 0.2 eV to lower energies. Thus, the excitonic interaction in Si slightly modifies the critical-point structure derived from the underlying single-particle band structure.

This is also reflected in Fig. 2 for the modulation spectrum $R^{-1}(\omega)dR(\omega)/d\omega$ in Si, where $R(\omega)$ is the reflectivity. With our coarse grid evaluation of S^0, we only want to examine the overall line shape connected with the E_1 and E_2 peaks and the interaction effects thereupon.

Single-particle calculations are given in Fig. 2(a) and 2(b). Both the local-orbital calculation derived from $\bar{\epsilon}$ in Fig. 1 and a pseudopotential calculation, which has the principal gaps fitted to experiment, give the negative modulation strength around 3.5 eV too small by about a factor of 2 in comparison with experiment.[28] This is connected with the slope between E_1 and E_2 peaks: Quite generally, *whatever* energy and wave-function description is used in $\bar{\epsilon}$, it does not reproduce the experimental low-energy absorption line shape (see also Refs. 7, 10). Inclusion of RPA local-field effects in Fig. 2(a) makes both positive and negative values of $R^{-1}(\omega)dR/d\omega$ around E_1 point smaller, thus furthering the discrepancy with experiment. The continuum-exciton effect significantly improves overall agreement with experiment, in particular in the main-adsorption region between 3.5 and 4 eV. It also shifts peak structure to lower energies as compared in the single-particle calculation.

The E_1 peak comes from a sizable region of nearly parallel conduction and valence bands,

near the L and Γ points. Thus, the EMA would be inappropriate. We have found in our calculation of Si that the dominant effect of the screened interaction is given by the almost unscreened terms in Eq. (4) with all the orbitals on the same site $\vec{R}=0$. This "electron-hole attraction in the same bond" approximation which we used for diamond[8] is thus justified, in contrast to a discussion given in Ref. 10.

In order to get a simple understanding of our findings on the many-particle corrections from a different point of view and to generalize the results to semiconductors with free-electron–like wave functions, let us finally consider a plane-wave model. Here the E_2 peak can be calculated in a two-plane-wave model, and the E_1 peak by a model of two parallel bands along $\langle 111\rangle$ direction.[4] The sum of the two contributions yields S^0, now in a plane-wave basis rather than in the local-orbital basis. The excitonic effect due to the screened Coulomb interaction is qualitatively of the form as in Eq. (2), with V put to zero, since for extended wave functions the local-field effect is negligible. Because the E_2 peak has an inverse-square-root singularity, by the Kramers-Kronig relation the real part of $(1+V^sS^0)$ in the same energy range is always larger than unity. Therefore, the excitonic effect reduces the strength of the E_2 absorption peak as is also shown in the local-orbital results in Fig. 1. Since the model E_1 peak has a step-function discontinuity, Kramers-Kronig analysis yields the real part of $(1+V^sS^0)$ in the E_1 energy range always reduced below unity. Hence the excitonic effect increases the strength of the E_1 peak.

Summarizing, the combined many-particle effects introduce a small shift of the low-energy absorption structure in Si by about 0.2 eV to lower energies and almost doubles its intensity compared to the one-particle spectrum. These main results are also reflected in the calculated modulation spectrum. It is expected that observed deviations from the one-particle picture in group-IV semiconductors and III-V and II-VI semiconductor compounds,[29] and also in the spin-orbit splitting of absorption data, in the temperature,[30] and in stress dependence[31] can be similarly accounted for.

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