Electron-Hole Excitations in Semiconductors and Insulators

Michael Rohlfing and Steven G. Louie
Department of Physics, University of California, Berkeley, California 94720-7300,
and Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720

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We present a new *ab initio* approach to calculate the interaction between electrons and holes in periodic crystals and to evaluate the resulting coupled electron-hole excitations. This involves a novel interpolation scheme in reciprocal space in solving the Bethe-Salpeter equation for the two-particle Green's function. We apply this approach to the calculation of the entire optical absorption spectrum, as well as of the energies and wave functions of bound exciton states in GaAs and LiF. Very good agreement with experiment is observed. [S0031-9007(98)07068-9]

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The interaction of the excited electrons and holes plays a central role in the optical properties of condensed matter [1–3]. For many materials and systems, the behavior of the isolated excited electrons and holes is well understood, and very reliable *ab initio* methods have been developed to calculate these quasiparticle states [4]. However, when optical properties are computed from such quasiparticle band structures, one encounters some systematic shortcomings. On the one hand, the overall shape of the absorption spectrum of a semiconductor is not correctly described by free electron-hole transitions. The calculations typically underestimate the absorption strength at low energies and overestimate it at high energies (see, e.g., the dashed curve in Fig. 1 for the case of GaAs). On the other hand, bound exciton states are completely missing from the spectra. Both shortcomings have long been identified to originate from the missing electron-hole interaction, but attempts to overcome these failures have been limited to relatively simple situations, such as the effective-mass approximation to bound excitons or the empirical tight-binding approach of Hanke and Sham [2] to the continuous spectrum. The theoretical study of optical excitations in electronic systems so far is thus limited and incomplete. The goal of our present work is to develop a unified *ab initio* approach that can handle all aspects of quasiparticle self-energy, electron-hole interaction, and optical excitations on equal footing. In particular, such an *ab initio* method would be most useful for predicting the optical properties of new materials or materials under novel conditions, such as in reduced dimensions, confined geometries, or under pressure.

In this paper, we go beyond the free-quasiparticle picture and study electron-hole excitations including their interaction. To this end, we solve the Bethe-Salpeter equation (BSE) for the two-particle Green's function of electron-hole pairs. The BSE is expressed in terms of the wave functions and energies that are obtained from an *ab initio* quasiparticle calculation within the *GW* approximation for the electron self-energy [6,7]. In a recent paper, we have applied this general approach to small semiconductor clusters [6]. Here we extend the technique to bulk crystals by introducing a novel interpolation scheme in **k** space for the electron-hole interaction. Using different methods, several studies on excitonic effects have already been performed for bulk insulators and semiconductors. Albrecht *et al.* [8] calculated the lowest-energy exciton in Li_2O, as well as the optical spectrum of Si. Benedict *et al.* [9] presented a different approach that allows for the calculation of the optical absorption spectrum, but the method does not focus on individual excitations. In this paper, we present an approach that allows one to calculate the entire excitation spectrum of a periodic system, as well as to analyze the properties of individual excitations (e.g., discrete bound levels) that contribute to the spectrum.

A natural basis for describing optical excitation processes is given by free quasielectron-quasihole pairs $|vc\mathbf{k}\rangle := \hat{a}^{\dagger}_{v\mathbf{k}}\hat{b}^{\dagger}_{c,\mathbf{k}+\mathbf{Q}}|0\rangle$, where $\hat{a}^{\dagger}_{v\mathbf{k}}$ and $\hat{b}^{\dagger}_{c,\mathbf{k}+\mathbf{Q}}$ are quasihole and quasielectron creation operators and $\mathbf{Q}$ is the momentum of the absorbed photon. $|0\rangle$ is the ground state of

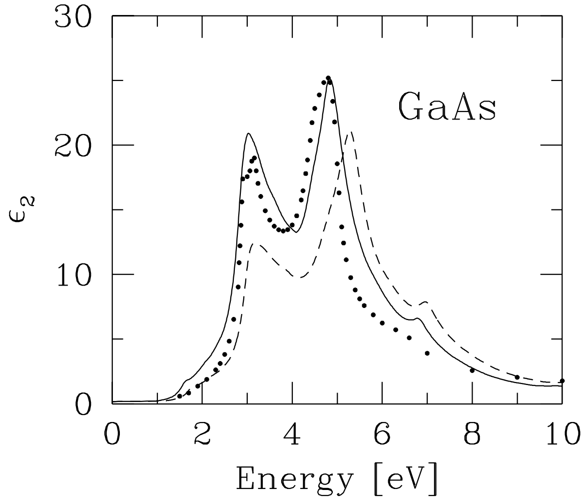

FIG. 1. Calculated optical absorption spectrum of GaAs with (solid lines) and without (dashed lines) electron-hole interaction, using three valence bands, six conduction bands, 500 **k** points to the Brillouin zone (BZ), and an artificial broadening of 0.15 eV. The dots denote experimental data [5].

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the system. Because of the electron-hole interaction, the pair configurations are coupled, and the resulting excitations $|S\rangle$ are given by [10]

$$|S\rangle = \sum_{\mathbf{k}} \sum_{v}^{\text{hole}} \sum_{c}^{\text{elec}} A^S_{vc\mathbf{k}} \hat{a}^\dagger_{v\mathbf{k}} \hat{b}^\dagger_{c,\mathbf{k}+\mathbf{Q}} |0\rangle . \qquad (1)$$

The electron-hole amplitudes $A^S_{vc\mathbf{k}}$ and the corresponding excitation energies Ω_S are determined by the BSE [3]:

$$(\epsilon^{\text{QP}}_{c,\mathbf{k}+\mathbf{Q}} - \epsilon^{\text{QP}}_{v\mathbf{k}}) A^S_{vc\mathbf{k}} + \sum_{v',c',\mathbf{k}'} \langle vc\mathbf{k}|K^{eh}|v'c'\mathbf{k}'\rangle A^S_{v'c'\mathbf{k}'} = \Omega_S A^S_{vc\mathbf{k}} , \qquad (2)$$

where K^{eh} is the electron-hole interaction. The energies and the optical transition matrix elements of the excitations S finally determine the imaginary part $\epsilon_2(\omega)$ of the macroscopic dielectric function, i.e., the optical absorption spectrum.

Because of the two-particle nature of the problem, the computational effort of solving the BSE is enormous. Combinations of several occupied and unoccupied bands at several hundred wave vectors, i.e., up to 10^4 basis functions, have to be taken into account in Eqs. (1) and (2). The determination of the 10^8 matrix elements $\langle vc\mathbf{k}|K_{eh}|v'c'\mathbf{k}'\rangle$ of the electron-hole interaction forms the bottleneck of such calculations. A key component of our present approach is a radical reduction of this computational demand by more than 2 orders of magnitude. We achieve this by calculating the interaction explicitly for only a few wave vectors and interpolating in between, which requires a new method of very careful handling of the wave functions and phases of the one-particle states.

Within the usual approximations [3,7], the electron-hole interaction K^{eh} consists of a direct, screened interaction term K^d and an exchange term K^x. If we neglect dynamic screening effects [11], the direct term is given by

$$\langle vc\mathbf{k}|K^d|v'c'\mathbf{k}'\rangle = \int dx\, dx' \psi^*_{c,\mathbf{k}+\mathbf{Q}}(x) \psi_{c',\mathbf{k}'+\mathbf{Q}}(x) \times W(\mathbf{r},\mathbf{r}') \psi_{v\mathbf{k}}(x') \psi^*_{v'\mathbf{k}'}(x') , \qquad (3)$$

where W is the statically screened Coulomb interaction. The variable $x = (\mathbf{r}, \sigma)$ comprises position and spin. To develop a numerical evaluation of Eq. (3), it is most convenient to write W as

$$W(\mathbf{r},\mathbf{r}') = \sum_{\mathbf{q}\mathbf{G}\mathbf{G}'} e^{-i(\mathbf{q}+\mathbf{G})\mathbf{r}} \frac{\epsilon^{-1}_{\mathbf{G},\mathbf{G}'}(\mathbf{q})}{|\mathbf{q}+\mathbf{G}|\,|\mathbf{q}+\mathbf{G}'|} e^{i(\mathbf{q}+\mathbf{G}')\mathbf{r}'} , \qquad (4)$$

where ϵ^{-1} is the static inverse dielectric matrix. Only the $\mathbf{q} = \mathbf{k}' - \mathbf{k}$ terms in Eq. (4) contribute to Eq. (3).

Solving the BSE requires the knowledge of K^d and K^x on a very fine grid $\{\mathbf{k}\}$ in the Brillouin zone. The matrix elements of K^d depend very sensitively on the reciprocal distance $\mathbf{q}$, in particular, when $\mathbf{q}$ is small. An interpolation scheme for K^d itself would thus be very unstable. An interpolation scheme can, nevertheless, be obtained in the following way. From Eqs. (3) and (4), the matrix elements of K^d are given by double sums over $\mathbf{G}$ and $\mathbf{G}'$. For small $\mathbf{q}$, the "head" ($\mathbf{G} = \mathbf{G}' = 0$) and "wings" ($\mathbf{G} = 0$ or $\mathbf{G}' = 0$) of W behave as $1/\epsilon_0(q)q^2$ and $1/q$, respectively, whereas all other components of $W_{\mathbf{G},\mathbf{G}'}(\mathbf{q})$ (the "body") remain finite. Correspondingly, the matrix elements of K^d can be written as

$$\langle vc\mathbf{k}|K^d|v'c'\mathbf{k}'\rangle = \frac{a_{vc\mathbf{k},v'c'\mathbf{k}'}}{\epsilon_0(\mathbf{q})q^2} + \frac{b_{vc\mathbf{k},v'c'\mathbf{k}'}}{q} + c_{vc\mathbf{k},v'c'\mathbf{k}'} \qquad (5)$$

with $\mathbf{q} = \mathbf{k}' - \mathbf{k}$. a, b, and c vary weakly with respect to $\mathbf{k}$ and $\mathbf{k}'$. We calculate a, b, and c for a coarse grid $\{\tilde{\mathbf{k}}\}$ of points in the Brillouin zone. Based on $(\tilde{\mathbf{k}}, \tilde{\mathbf{k}}')$, a matrix element of a (or b, c) at $(\mathbf{k}, \mathbf{k}')$ on the fine grid required for the BSE is then approximately given by

$$a_{vc\mathbf{k},v'c'\mathbf{k}'} = \sum_{\tilde{v}\tilde{c}\tilde{v}'\tilde{c}'} d^{\tilde{v}\tilde{\mathbf{k}}}_{v\mathbf{k}} d^{\tilde{c}\tilde{\mathbf{k}}^*}_{c\mathbf{k}} d^{\tilde{v}'\tilde{\mathbf{k}}'^*}_{v'\mathbf{k}'} d^{\tilde{c}'\tilde{\mathbf{k}}'}_{c'\mathbf{k}'} a_{\tilde{v}\tilde{c}\tilde{\mathbf{k}},\tilde{v}'\tilde{c}'\tilde{\mathbf{k}}'} \qquad (6)$$

with

$$d^{\tilde{\nu}\tilde{\mathbf{k}}}_{\nu\mathbf{k}} = \int \psi^*_{\tilde{\nu}\tilde{\mathbf{k}}}(x) e^{i(\tilde{\mathbf{k}}-\mathbf{k})\mathbf{r}} \psi_{\nu\mathbf{k}}(x)\, dx . \qquad (7)$$

The points $\tilde{\mathbf{k}}$ and $\tilde{\mathbf{k}}'$ should be chosen close to $\mathbf{k}$ and $\mathbf{k}'$. The integrals $d_{\nu\mathbf{k},\tilde{\nu}\tilde{\mathbf{k}}}$ account for the change of the wave functions when going from $\tilde{\mathbf{k}}$ to $\mathbf{k}$.

In the following, as illustrations, we discuss electron-hole excitations in GaAs and LiF. Figure 1 shows the optical spectrum of GaAs, calculated with (solid lines) and without (dashed lines) electron-hole interaction. The spectrum resulting from the free-quasiparticle transitions shows systematic deviations from experiment. At low energies (2–5 eV) the absorption strength is much lower than in experiment while it is too high for energies above 5 eV. When we include the electron-hole interaction, the peaks at 3 and at 5 eV are strongly enhanced; in addition, the peak structure at 5 eV is effectively shifted to lower energies. The spectrum including the interaction is in much better agreement with the measured data. The same type of improvement has been observed by Benedict *et al.* [9].

The modifications of the spectrum do not result from a negative shift of the transition energies, as one might naively expect from the attractive nature of the interaction. In fact, we find that the joint density of states of the electron-hole transitions remains nearly unchanged by the interaction (except for the formation of bound excitons; see below). The changes in the optical spectrum originate mainly from the *coupling* of the electron-hole configurations in the excited-state wave function, which leads to a constructive coherent superposition of the oscillator strengths for transitions at lower energies and to a destructive superposition at energies above 5 eV. Such modifications of the spectrum occur also in other semi-conductors [2,8,9,12].

Figure 1 does not exhibit bound exciton states because of the limited resolution (~0.15 eV) arising from the finite set of 500 $\mathbf{k}$ points in the BZ used. To describe the discrete exciton states, we have to increase the $\mathbf{k}$-point grid density to 10^8 $\mathbf{k}$ points in the Brillouin zone.

TABLE I. Calculated binding energies of excitons in GaAs (cf. Fig. 2), compared with data from optical absorption [13] and from two-photon absorption [14] measurements.

	This work [meV]	Exp. [meV]
E_{1s}	4.0	4.2[a]
E_{2s}	0.9	1.05[a]
E_{2p}	0.2–0.7	~0.1[b]

[a] Reference [13].

[b] Reference [14].

Fortunately, the use of about 1000 of these **k** points near the position of the band extrema allows already for a converged representation of the $1s$, $2s$, and $2p$ excitons. The exciton spectrum is given in Table I and in Fig. 2. The lower panel displays the exciton levels and their degeneracy from our *ab initio* calculation. The first two peaks at -4.0 and -2.5 meV below E_g are given by the $1s$ excitons. The states at -4.0 meV are composed of mixed (due to spin-orbit interaction) triplet and singlet excitonic states. The splitting of 1.5 meV between these states and the next one, which can be identified as a longitudinal exciton, is caused by the exchange part of the electron-hole interaction [15]. The $2s$ excitons at -0.9 and -0.7 meV form a similar multiplet. Between -0.7 and -0.2 meV we observe the $2p$ excitons. The splitting among these states and the energy difference to the $2s$ level are caused by the anisotropy of the valence bands [16]. Our calculated binding energies agree well with available experimental data (see Table I). Because of the finite **k**-point sampling used, the higher transitions, which are more extended in real space, do not form accurately a hydrogenlike series in our spectrum. This problem may be overcome with a denser **k**-point grid or a nonuniform grid near the band minimum. In the upper panel of Fig. 2 we display the corresponding dipole oscillator strengths of the exciton states. Because of the selection rules, only the transverse s states have a nonvanishing dipole matrix element and are observable in optical experiments [15]. The ratio I_{2s}/I_{1s} of the strengths of the $2s$ and the $1s$ exciton is 0.1, which is close to the ideal ratio of $1/8$ for hydrogenlike envelope functions.

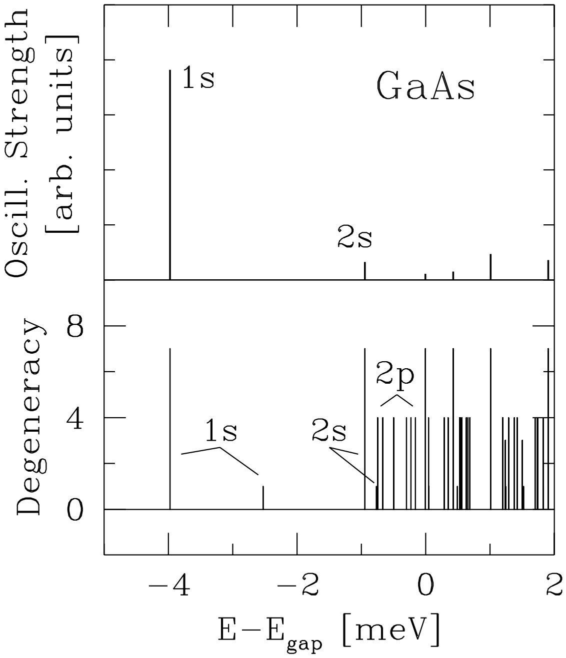

FIG. 2. Calculated exciton spectrum of GaAs relative to the fundamental gap energy, showing the oscillator strength (upper panel) and the degeneracy (lower panel) of the exciton states. Two valence bands, one conduction band, and 1000 **k** points ($|\mathbf{k}| < 0.015$ a.u.) near the Γ point were used. The band structure includes spin-orbit interaction.

Of course, all these structures and effects are well known for GaAs. A simple effective-mass approach with adjustable parameters can reproduce the experimental features. The novelty here is that the present approach yields the same results without any assumptions on the dispersion and wave functions of the bands and on the electron-hole interaction. Our scheme can thus directly be applied to situations in which simple empirical techniques do not hold.

Now we discuss a much different system, LiF. Compared to GaAs, the electron-hole interaction is much stronger, and the corresponding modifications of the optical absorption spectrum (shown in Fig. 3) are much more pronounced. In fact, the spectrum is completely altered from the noninteracting case. Again, the spectrum including the interaction is in much better agreement with experiment. The most pronounced feature in the calculated spectrum is the occurrence of two strongly bound singlet excitons at 12.8 eV (transverse excitons). In addition, a longitudinal singlet exciton, which is not visible in the optical spectrum, is found at 13.3 eV.

Our approach further allows us to explicitly calculate the real-space electron-hole amplitude

$$\chi_S(\mathbf{r}_h, \mathbf{r}_e) = \sum_{\mathbf{k}} \overset{\text{hole}}{\sum_{v}} \overset{\text{elec}}{\sum_{c}} A^S_{vc\mathbf{k}} \psi^*_{v\mathbf{k}}(\mathbf{r}_h) \psi_{c,\mathbf{k}+\mathbf{Q}}(\mathbf{r}_e) \quad (8)$$

of each excitation. $\mathbf{r}_h$ ($\mathbf{r}_e$) refers to the coordinates of the hole (electron). As an example, we discuss the lowest

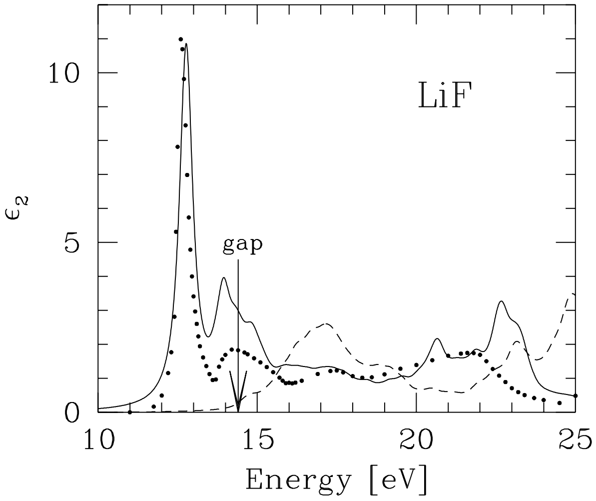

FIG. 3. Same as Fig. 1, but for LiF. A broadening of 0.25 eV is included. The experimental data are from Ref. [17].

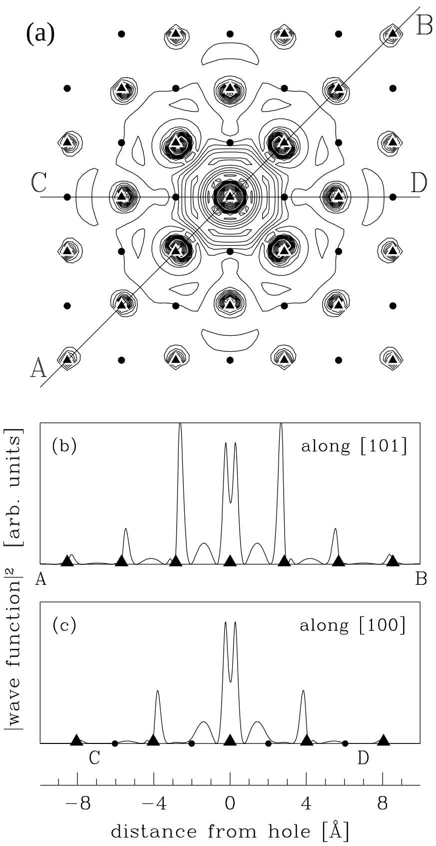

FIG. 4. (a) Real-space distribution $|\chi_S(\mathbf{r}_h, \mathbf{r}_e)|^2$ of the electron ($\mathbf{r}_e$) with respect to the hole ($\mathbf{r}_h$) for the lowest-energy exciton in LiF (at 12.8 eV), in the (010) plane. Dots (triangles) denote Li (F) atoms. The hole ($\mathbf{r}_h$) is fixed at the central F atom. (b),(c) The same quantity, along the lines *AB* and *CD* indicated in panel (a).

exciton in LiF. In Fig. 4(a) we show the distribution of the electron relative to the hole, which we fix at an F atom, in the (010) plane. The envelope function is s-like, with slight modifications due to the anisotropy of the cubic crystal, and has a mean radius of slightly over 4 Å or one lattice constant. Figures 4(b) and 4(c) show the same quantity as a line plot along the [101], as well as along the [100] direction [indicated as lines *AB* and *CD*, respectively, in panel (a)]. The figures exhibit several interesting features. First, the charge density of the electron is very low at the Li atoms. From an extreme Frenkel excitonlike picture, one might have expected that the electron hops from the central F atom to the nearest-neighbor Li atoms. Instead, it partly remains on the central F atom and partly hops to the first- and second-nearest F atoms and even farther away. Second, the electron distribution on these neighbor F atoms is not isotropic but is highly polarized towards the central F atom. This results from the correlation of the quasielectron to the effective positive charge of the quasihole on the central F atom.

In conclusion, we have presented an approach for including the interaction between quasielectrons and quasiholes in *ab initio* electronic structure and optical properties calculations for periodic systems. By using an interpolation scheme in reciprocal space, the matrix elements of the interaction are obtained with very modest computational effort. We have discussed the results of applications to GaAs and LiF. Very good agreement with experiment is obtained—both for the entire absorption spectrum and for the low-energy absorption threshold due to discrete bound excitons. Furthermore, we have presented the details of the two-particle wave function of the lowest exciton in LiF in real space.

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