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Biexcitons in one-dimensional systems with electron-hole exchange interactions

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Biexcitons in one-dimensional systems with electron-hole (e-h) exchange interactions are studied. By numerically diagonalizing a one-dimensional two-band tight-binding model, we found that the bound state (biexciton) of two triplet excitons or two singlet excitons is obtained as the strength of e-h exchange interactions is varied. Both biexcitons have strong optical nonlinearity, which gives information on the electronic structure of excited states, including single excitons as well as biexcitons. [S0163-1829(97)01419-7]

Recently, Kuwata-Gonokami *et al.*[1] reported experimental results on multiexciton states in one-dimensional charge-transfer insulators, which have opened up new possibilities to observe biexcitons in semiconductors with low-dimensional structures and/or strong electron-hole (e-h) interactions in which the radius of excitons is comparable to the lattice constant.[2,3]

When interactions between electrons and/or holes are strong, the effect of e-h exchange interactions on excitons is no longer negligible. For example, it is well known that in molecular crystals strong e-h exchange interactions cause a large energy splitting between singlet excitons and triplet excitons.[4] Although corresponding effects of e-h exchange interactions are expected for biexcitons, former studies[5] employed a continuum model in which electrons and holes are so weakly coupled that e-h exchange interactions play only a subsidiary role.[6]

It should be noted that we must consider two spin configurations for singlet states with four fermions: one is composed of two singlet pairs and the other is a composite of two triplet pairs. Corresponding to the energy splitting of singlet excitons and triplet excitons, the above two states with different spin configurations are affected by e-h exchange interactions in a different manner. This means that the lowest singlet state with two e-h pairs is not sufficient to study the effect of e-h exchange interactions, i.e., we should investigate not only the lowest biexciton, but also higher excited states with two e-h pairs of which the energy is comparable to twice the singlet exciton energy in order to make the effect of e-h exchange interactions on many-body excited states clearer.

In this paper we show how biexcitons in one-dimensional semiconductors and their optical nonlinearities are affected by strong e-h exchange interactions. Possible biexciton level structures in one-dimensional systems are shown comparing with the results of previous studies.[3,7] We employed a one-dimensional tight-binding model of which the Hamiltonian is described by

$$\mathcal{H}=-t_e\sum_{i\sigma}(a^\dagger_{i+1\sigma}a_{i\sigma}+a^\dagger_{i\sigma}a_{i-1\sigma})-t_h\sum_{i\sigma}(c^\dagger_{i+1\sigma}c_{i\sigma}$$

$$+c^\dagger_{i\sigma}c_{i-1\sigma})+U\sum_{i\sigma\sigma'}(a^\dagger_{i\sigma}a_{i\sigma}a^\dagger_{i\sigma'}a_{i\sigma'}+c^\dagger_{i\sigma}c_{i\sigma}c^\dagger_{i\sigma'}c_{i\sigma'}$$

$$-a^\dagger_{i\sigma}a_{i\sigma}c^\dagger_{i\sigma'}c_{i\sigma'})-J\sum_i \vec{s}^{\,e}_i\cdot\vec{s}^{\,h}_i, \qquad (1)$$

where $a_{i\sigma}$ and $c_{i\sigma}$ denote the annihilation operator of an electron and a hole with spin σ at site i, respectively. $\vec{s}^{\,e(h)}_i$ denotes the second-quantized spin operator of an electron (hole). Since low-lying biexcitons are considered, the typical energy relevant to the present study is twice the lowest exciton energy. As long-range Coulomb interactions between electrons and/or holes are irrelevant to the qualitative features of the lowest excitons,[3] they do not contribute to the biexciton properties of interest, and thus the direct interaction is taken to be short ranged. The values of the parameters are: $t_e=t_h=1$ and $U=8$. The relation between U and J is determined if the material under consideration is chosen. However, this relation is affected by the properties of the conduction and valence bands and hence there is no universal value for J/U. Furthermore, it is important to vary the value of J to investigate the effect of the e-h exchange interactions on biexcitons. Thus J is not fixed, but taken to be 0, 1, 2, and 3.

Both the singlet exciton and the triplet exciton in Hamiltonian (1) were obtained analytically, of which the energy dispersion is, for example, given by[3,8]

$$E_S(k)=-\sqrt{(U-3J/4)^2+4(t_e^2+t_h^2+2t_et_h\cos k)}, \qquad (2)$$

$$E_T(k)=-\sqrt{(U+J/4)^2+4(t_e^2+t_h^2+2t_et_h\cos k)}, \qquad (3)$$

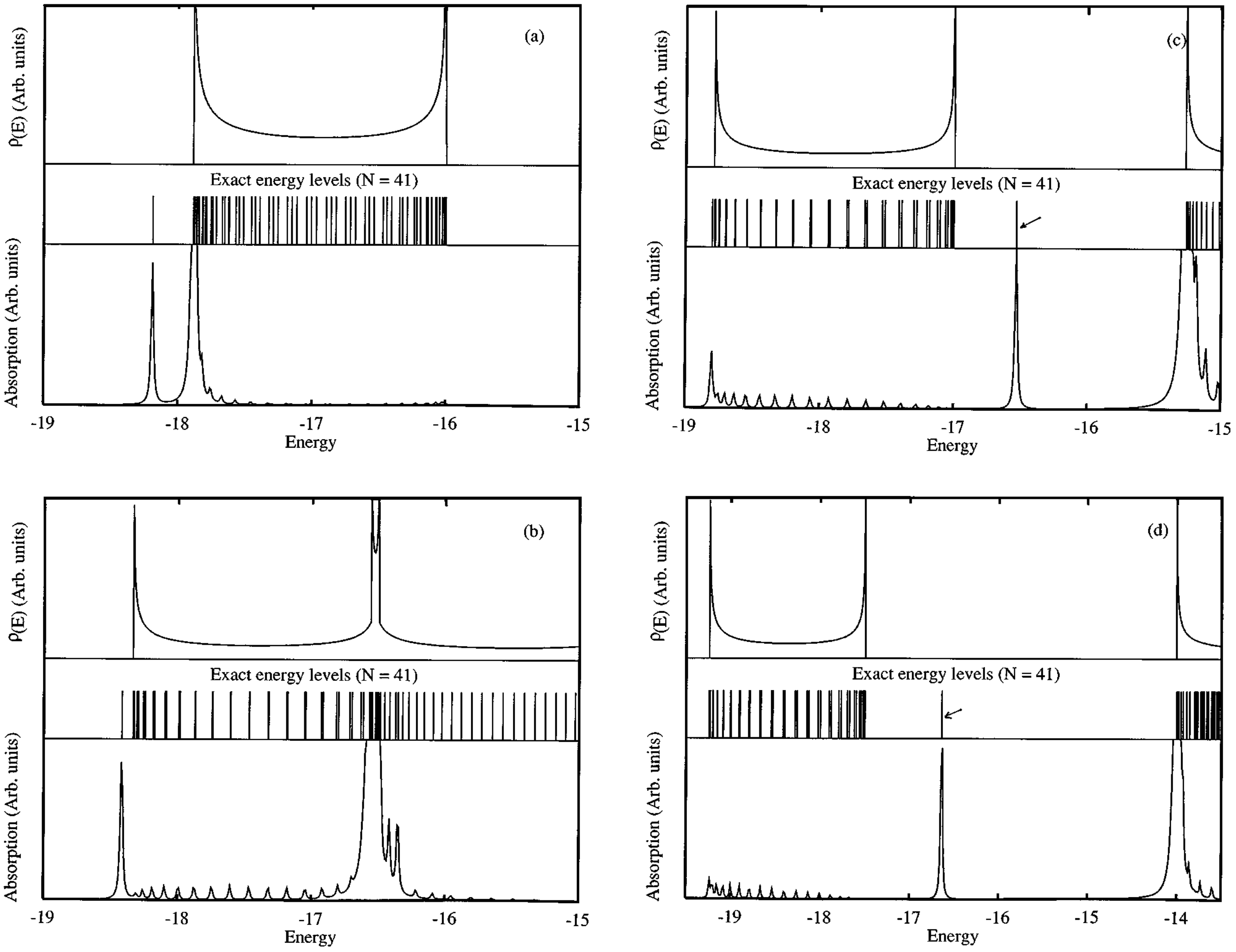

FIG. 1. $\rho(E)$, the joint density of states for excitons, the exact energy levels of the low-lying excited states (vertical bars), and the induced absorption spectra for (a) $J=0$, (b) $J=1$, (c) $J=2$, and (d) $J=3$.

where the lattice constant is taken to be unity.

To obtain the eigenstates with two e-h pairs, we numerically diagonalized Hamiltonian (1) on a chain with 41 sites in the subspace of two e-h pairs which form spin singlet states. Then it is necessary to find a method to distinguish bound states from unbound states of two excitons. Supposing there were two-exciton states (total momentum = 0) without ‘‘exciton-exciton interactions,’’ the energy levels of those states would be understood by joint density of states for excitons defined by

$$\begin{aligned}\rho(E)&=\frac{N}{2\pi}\int_{-\pi}^{\pi}\{\delta[E_T(k)+E_T(-k)-E]\\&\quad+\delta[E_S(k)+E_S(-k)-E]\}dk\\&=\frac{N}{8\pi}\left\{\frac{|E|\,\theta[E-2E_T(0)]\,\theta(2E_T(\pi)-E)}{\sqrt{[E^2-4E_T^2(0)][4E_T^2(\pi)-E^2]}}\right.\\&\quad\left.+\frac{|E|\,\theta[E-2E_S(0)]\,\theta[2E_S(\pi)-E]}{\sqrt{[E^2-4E_S^2(0)][4E_S^2(\pi)-E^2]}}\right\},\end{aligned}\tag{4}$$

where

$$\theta(x)=\begin{cases}0 & (x<0)\\ 1 & (x>0),\end{cases}\tag{5}$$

and N is the size of the system. In other words, Eq. (4) determines the two-exciton continuum in the present model. Equation (4) shows that there is an ‘‘energy gap’’ in $\rho(E)$ when the top of the triplet exciton band is below the bottom of the singlet exciton band, i.e., $E_T(\pi)<E_S(0)$. Deviation of the energy spectrum (density of states) of $\mathcal{H}$ from $\rho(E)$ typically shows the effect of ‘‘exciton-exciton interactions,’’ e.g., the existence of bound states (biexcitons).

Figures 1(a)–1(d) show $\rho(E)$, and the exact energy levels of the low-lying eigenstates (vertical bars) for $J=0$, 1, 2, and 3, respectively. We also calculated induced absorption (IA) spectra, in which one of the laser beams is tuned to the resonance of the transition between the ground state and the singlet exciton, and the results are shown in Figs. 1(a)–1(d). We note that the highest peak at $2E_S(0)$ corresponds to the double resonance by the singlet exciton, which is not directly related to our interest in the present study.

Those states which lie between $2E_T(0)$ and $2E_T(\pi)$ or between $2E_S(0)$ and $2E_S(\pi)$ correspond to unbound states of two excitons. On the other hand, Figs. 1(a)–1(c) show that

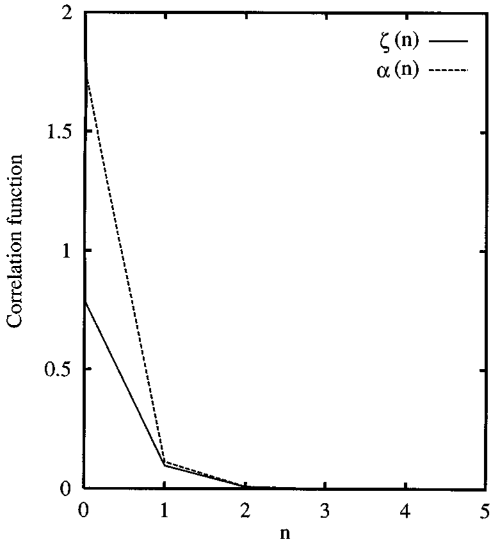

FIG. 2. The hole-hole correlation function $\zeta(n)$ and the electron-hole correlation function $\alpha(n)$ (Ref. 3) for the state in the middle of the energy gap pointed by an arrow in Fig. 1(d).

there is an eigenstate below $2E_T(0)$ which corresponds to a biexciton for $J=0$, 1, and 2. For $J=3$, no biexciton is obtained below $2E_T(0)$.

For $J=2$ and 3, we found a state in the middle of the energy gap in $\rho(E)$ which is pointed by an arrow in Figs. 1(c) and 1(d). This state is also a bound state of two e-h pairs, as shown below. In general the wave function of bound states is spatially localized which is typically shown by the hole-hole (h-h) correlation function[3] defined by

$$\zeta(n)=\sum_{i,\sigma,\sigma'} \langle c^{\dagger}_{i\sigma}c_{i\sigma}c^{\dagger}_{i+n\sigma'}c_{i+n\sigma'}\rangle. \tag{6}$$

$\zeta(n)$ corresponds to the biexciton wave function discussed in the former variational studies,[9] and is suitable for distinguishing bound states from unbound states. Figure 2 shows the h-h correlation function and the e-h correlation function[3] defined by

$$\alpha(n)=\sum_{i,\sigma,\sigma'} \langle a^{\dagger}_{i\sigma}a_{i\sigma}c^{\dagger}_{i+n\sigma'}c_{i+n\sigma'}\rangle \tag{7}$$

for the state in the middle of the energy gap in $\rho(E)$ for $J=3$. It is seen that two electrons and two holes are bound to each other, i.e., they are in a state similar to the biexciton in the usual sense.[9] We also found that the two holes (or excitons) are located so close to each other that the deformation of wave functions in forming a biexciton[3] is no longer negligible, and the spin configuration of the two e-h pairs is rearranged, and as a result is different both from a composite of two singlet excitons and from that of two triplet excitons. Hence the spin configurations are not appropriate to determine the character or the origin of the biexcitons. However, considering that, without e-h exchange interactions, the biexciton binding energy defined as energy difference between two excitons at infinite distance and a biexciton is $\lesssim 0.3$,[3] we will call this state *a biexciton of two singlet excitons* (B_S), while the biexciton which is defined as the lowest (bound) state of two e-h pairs shall be called *a biexciton of two triplet excitons* (B_T). The energy levels of the triplet exciton $[E_T(0)]$, the singlet exciton $[E_S(0)]$, and the biexcitons $[\varepsilon_{T(S)}$ for $B_{T(S)}]$ are summarized in Table I. This terminology is also justified if we consider the effect of J on the binding energy of biexcitons. First we define the binding energy of each biexciton by

TABLE I. Energy eigenvalues of the singlet exciton, the triplet exciton, and the biexcitons for $J=0$, 1, 2, and 3.

Exciton\ J	0	1	2	3
$E_T(0)$	-8.944 27	-9.168 56	-9.394 15	-9.620 94
$E_S(0)$	-8.944 27	-8.280 25	-7.632 17	-7.004 46
ε_T	-18.1910	-18.4167	-18.8013	
ε_S			-16.5305	-16.6386

$$E^B_{\mu}=2E_{\mu}(0)-\varepsilon_{\mu} \quad (\mu=T,S), \tag{8}$$

Figures 3(a) and 3(b) exemplify schematically the role of J on the exciton-exciton interaction. Although the spin configurations shown in the figures do not correspond to the exact singlet states, they are sufficient to understand the role of J.

When two *singlet* excitons are located close to each other [Fig. 3(a)], the e-h exchange interaction between the electron in exciton A and the hole in exciton B, for example, decreases the total energy of the whole system, and hence E^B_S should increase as a function of J. On the other hand, when there are two *triplet* excitons separated by a short distance [a lattice constant, for example; see Fig. 3(b)], the e-h exchange interaction between the electron in exciton A and the hole in exciton B increases the total energy of the whole system. Hence E^B_T should decrease as J increases. Figure 4, which shows E^B_S and E^B_T as a function of J, clearly indicates that E^B_S increases with J, and that E^B_T decreases as J increases, and hence the characterization of the two types of bound states is appropriate.

B_S appears when the energy gap in $\rho(E)$ is present, i.e., $E_T(\pi)<E_S(0)$. In the present case, the threshold value of J for the presence of the energy gap is $J_0=4(4-\sqrt{14})\sim 1.03$. Below this value, there is no bound state corresponding to B_S. In this case unbound states of two triplet excitons the energy of which is close to $2E_S(0)$, in-

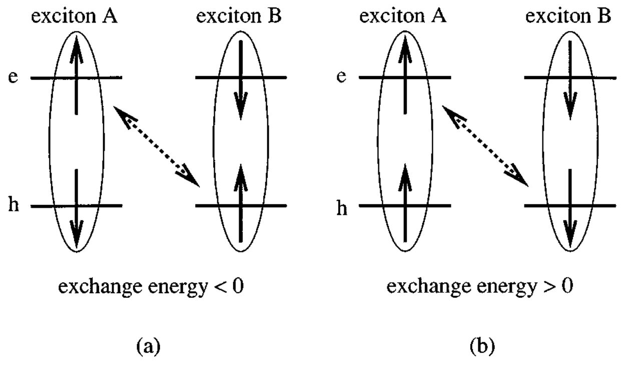

FIG. 3. Schematic view of the effect of e-h exchange interactions on biexcitons for (a) two singlet excitons and (b) two triplet excitons.

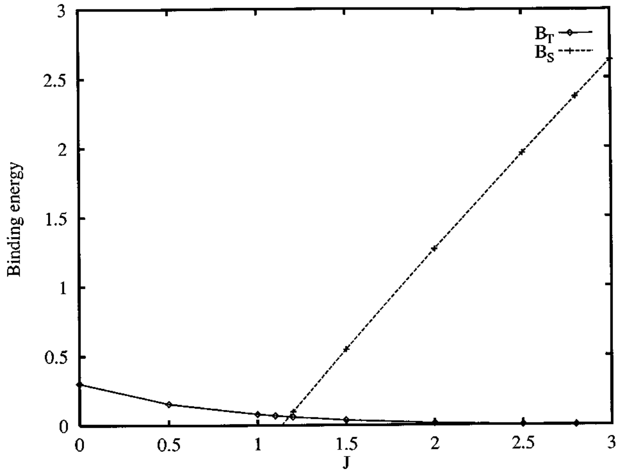

FIG. 4. Binding energy of B_S and B_T as a function of J. Solid and dotted lines are drawn as a guide for the eye.

terfere with the states with two singlet excitons, and such spatially extended states prevent them from forming a bound state. In other words, the energy gap in $\rho(E)$ separates the states with two triplet excitons from those with two singlet excitons, and hence we obtained a bound state B_S as an eigenstate of $\mathcal{H}$ for $J > J_0$.

The IA spectra show that both types of biexcitons have strong optical response, i.e., peaks due to the transition between a singlet exciton and a biexciton appear prominently in each spectrum. In particular, a biexciton peak for B_T is present, although it is a bound state of two triplet excitons due to the rearrangement of spin configurations described above. Conversely, except for the two unbound excitons at the band edge of the two-singlet-exciton continuum, other states do not have measurable IA strength, and hence IA spectra look as if there were only one two-exciton continuum and two biexcitons B_S and B_T below the band edge.

For $J=3$, several peaks are observed at and slightly above $2E_T(0)$, although no biexciton (B_T) is obtained below $2E_T(0)$. This structure in the IA spectrum is reminiscent of the linear absorption spectra in one-dimensional semiconductors without exciton effects which directly reflect the joint density of states. When, however, excitons are taken into account, it was shown that the lowest exciton occupies most of the oscillator strength and thus the fundamental absorption edge is not observable.[10] This is characteristic of one-dimensional systems, and we can apply it to the present case; i.e., the IA intensity is weak at $2E_T(0)$ when B_T appears, while a certain structure is observed at $2E_T(0)$ when B_T is not obtained. Nevertheless, we note that those signals are weak compared to the peak for B_S, and hence this spectrum can be distinguished from the other cases shown in Figs. 1(a)–1(c).

IA spectra show us other properties regarding with excited states. First, when B_T is observed in IA spectra, half of its energy gives a lower bound of triplet exciton energy $E_T(0)$. Usually $E_T(0)$ is estimated by luminescence spectra, in which we should take into account the energy shift of excitons due to relaxation. However, any relaxation processes are not involved in IA spectra in principle, and hence $E_T(0)$ can be determined only with the ambiguity due to the binding energy of B_T ($\lesssim 0.3$).[3,11] Furthermore, the relaxation energy of the triplet exciton can be estimated by comparing IA spectra with luminescence spectra.

Another aspect of IA spectra is seen from Figs. 1(a)–1(d), i.e., IA spectra give information on exciton band structure. When B_S is observed in IA spectra, the top of the triplet exciton band is below the bottom of the singlet exciton band, which is given as the exciton peak energy in linear absorption spectra. Furthermore, when B_T is observed as well, it means that the bottom of the triplet exciton band $[E_T(0)]$ is above half of the peak energy in the IA spectra. Hence, when both biexcitons are observed [Fig. 1(b) or 1(c)], half of the energy difference between those of the two peaks gives the upper bound of the triplet exciton bandwidth, which cannot be measured by means of either linear optical spectra or luminescence spectra.

It has been shown that the 2 ^1A_g state in conjugated polymers is mainly composed of two triplet excitations.[12] Since the energy splitting between ^1B_u exciton and ^3B_u exciton is comparable to the Coulomb interactions between electrons,[13] the effective e-h exchange interactions is regarded to be strong in conjugated polymers. Hence the biexciton level structure is strongly affected by the e-h exchange interactions in those materials. However, the correspondence between biexcitons in the present model and those in the model of conjugated polymers, e.g., the Pariser-Parr-Pople model, is not clarified and is left for future study.

The e-h exchange interactions are neglected in many of the studies on biexcitons.[3,9] The present results show that B_T will be obtained if we perform perturbational calculations on the biexciton for $J=0$. In this context we conclude that B_S has a different nature from the biexcitons which has been discussed with continuum models.[9]

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