Weakly correlated exciton pair states in large quantum dots

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We present a calculation of the two-exciton states in semiconductor quantum dots much larger in size than the exciton Bohr radius, and identify a weakly correlated exciton pair state that has a large oscillator strength, increasing proportionately to the volume of the quantum dot. This state is shown to be responsible for the saturation of the size dependence of the resonant excitonic optical nonlinearity. It also provides a satisfactory understanding of the blueshift of the excited-state absorption in quantum dots. These results and the biexciton binding energy and oscillator strength are in good agreement with reported experimental results on CuCl. [S0163-1829(96)51616-4]

Semiconductor microcrystallites, often referred to as quantum dots (QD's), have potential as novel nonlinear optical materials as well as prototype systems for studying the basic physics of spatially confined electrons and holes.[1] Theoretically, considerable progress has been achieved in the description of the single-particle electronic structure providing a satisfactory framework for describing the optical response of QD's of radius comparable to or smaller than the bulk exciton Bohr radius ($a_{\rm ex}$).[2] In larger crystallites, the Coulomb interaction between the electrons and the holes crucially determines the nature of the excitations and excitonic and biexcitonic states dominate the optical response. It is in this size range that many recent experiments on CuCl QD's have revealed distinctly nonbulklike features including enhanced nonlinear optical susceptibility with an intriguing size dependence,[3] very large gain for biexcitonic lasing,[4] and a blueshift of the excitonic absorption under a strong pump beam.[5] While reliable theoretical calculations of the excitonic states exist,[6–8] the biexciton calculations[9,10] so far have been restricted to QD's whose radius (R) is smaller than a few times $a_{\rm ex}$, due to the numerical complexity of the problem when $R \gg a_{\rm ex}$. In this paper, we present a theory of the biexciton states in QD's with radii up to $10a_{\rm ex}$ using a novel approach based on an exciton-exciton product state basis. We identify an excited exciton pair state with a large oscillator strength, which provides important insights into the experimental observations mentioned above. We obtain the biexciton binding energy and oscillator strengths in reasonable agreement with experimental results. We also show the importance of including the electron-hole exchange interaction for the proper understanding of the experimentally measured biexciton binding energy and the biexciton states in general.

The success of our calculation is based on avoiding the use of a single-particle product basis for the calculation of the exciton and biexciton states, as this is numerically prohibitive, especially for the four-particle biexcitonic states. Instead, we use an exciton-exciton product basis for the biexciton calculation. Working within the effective mass approximation (EMA) we first calculate a number of the low-energy exciton states using a correlated basis set used earlier by Kayanuma[7] for the $L=0$ excitons, where L is the angular momentum of the exciton envelope function. Although only the $L=0$ excitonic states are optically active, the $L>0$ states also need to be calculated to construct a reasonably complete exciton-exciton product state basis. We extend Kayanuma's approach to $L=1$ states by noting that, for two particles, any odd-parity $L=1$ state can be expressed in the form

$$\phi_X^{i1M}(\mathbf{r}_e,\mathbf{r}_h)=f_e^i(r_e,r_h,r_{eh})Y_{1M}(\Omega_e) + f_h^i(r_e,r_h,r_{eh})Y_{1M}(\Omega_h), \qquad (1)$$

where i denotes the radial quantum numbers, $r_{e(h)}$ is the electron (hole) radial coordinate, $r_{eh}=|\mathbf{r}_e-\mathbf{r}_h|$, and Y_{1M} denotes the spherical harmonic of order 1. This allows us to describe the $L=1$ states in terms of two functions, f_e and f_h, of the Hylleraas coordinates, and the same basis set used for the $L=0$ case can be used to expand f_e and f_h.

For $L>1$ states, no such simple form appears to exist so that the standard expansion into spherical harmonics using Clebsch-Gordan coefficients needs to be used. In the present calculation we consider only the $L\leqslant 2$ states. Although a general two-particle state of angular momentum L can have either parity, we consider only those states with parity $(-1)^L$ as all the low-energy states in relatively large QD's would have this parity.

As all the optically excited states have a vanishing angular momentum ($L=0$) for the envelope function, we consider only such biexciton states. Biexciton states with $L=0$ may be expanded into the exciton-exciton product states of the form $G_{XX}^{ijL}=\Sigma_{M=-L}^{L}\phi_X^{iLM}(\mathbf{r}_{e1},\mathbf{r}_{h1})\phi_X^{jLM*}(\mathbf{r}_{e2},\mathbf{r}_{h2})$ and a similar product with the hole coordinates interchanged. Here i,j denote the radial quantum numbers of the exciton eigenstates. For the largest QD, we use four $L=0$, three $L=1$, and two $L=2$ states giving a total of 58 product states forming a nonorthogonal basis.

In Fig. 1, we plot a few low-lying energy levels of the exciton and the biexciton. The results presented, though given scaled by the exciton Rydberg (E_R), correspond to an electron-hole mass ratio $m_e/m_h=0.28$ appropriate for CuCl with $m_e=0.5$ and $m_h=1.8$.[11] We note that, in CuCl with crystallographic point group T_d, the conduction band is of Γ_6 ($s=1/2$) symmetry while the topmost valence band is of Γ_7 ($j=1/2$) symmetry. Each fourfold degenerate $L=0$ exciton state arising from these two bands is split by the electron-

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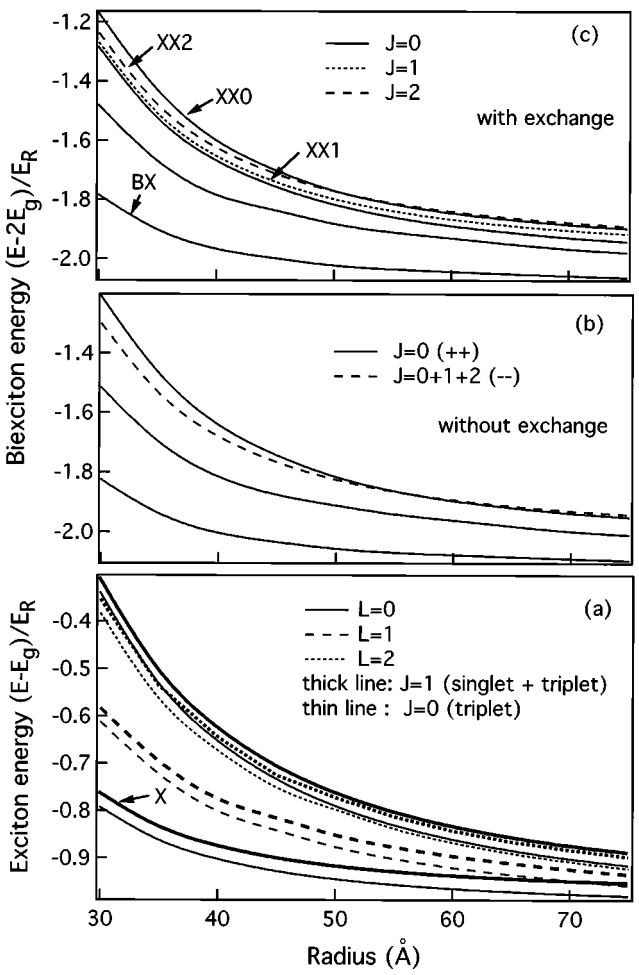

FIG. 1. Calculated energy levels of semiconductor QD's: (a) the exciton states, (b) and (c) the biexciton states, respectively, without and with the electron-hole exchange interaction included. E_R is the exciton Rydberg and E_g is the bulk band-gap energy. X, BX, $XX0$, $XX1$, and $XX2$, respectively, denote the singlet exciton ground state, the biexciton ground state, and the weakly correlated exciton pair states with $J=0,1,2$.

hole exchange interaction into two states, one with Γ_2 ($J=0$) symmetry and the other with Γ_5 ($J=1$) symmetry. The former is unaffected by the exchange interaction, while the latter, which contains the spin singlet, is shifted upwards in energy. This effect is included in the exciton energy levels shown in Fig. 1(a). Within EMA, the total angular momentum (J) is a good quantum number and we label all the states by their J value.

Although the effect of the electron-hole exchange interaction on the biexciton states has been studied in the past,[12] we reformulate the problem in a form suited to application to QD's, within the EMA. We find that the $J=0$ biexciton states may be expressed as

$$\Psi^0_{XX}=\Phi^{++}_{XX}(\mathbf{r}_{e1},\mathbf{r}_{h1},\mathbf{r}_{e2},\mathbf{r}_{h2})\chi_0 + \Phi^{--}_{XX}(\mathbf{r}_{e1},\mathbf{r}_{h1},\mathbf{r}_{e2},\mathbf{r}_{h2})\chi_1 . \quad (2)$$

Here χ_0 and χ_1 are products of the electron and hole Bloch functions with the total angular momentum equal to zero, such that the former has both the total electron spin and the total hole angular momentum vanishing while the latter has both these quantities equal to 1. $\Phi^{++(--)}_{XX}$ is symmetric (antisymmetric) under the interchange of the two electron or the two hole coordinates. We obtain a pair of coupled EMA equations satisfied by Φ^{++}_{XX} and Φ^{--}_{XX} and solve it by expanding these envelope functions into the exciton-exciton product states as described earlier.

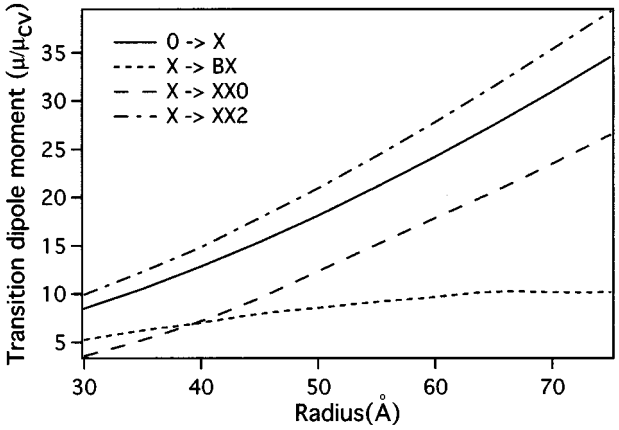

FIG. 2. Transition dipole moment for the excitation of the lowest exciton state and for the transitions from the lowest exciton to the biexcitonic states. The states involved in the transitions are indicated by the energy level labels used in Fig. 1. 0 denotes the ground state of the QD.

The resulting biexciton states are plotted in Fig. 1(c). The electron-hole exchange interaction mixes states of equal J and also lifts the degeneracy of the antisymmetric states [labeled $--$ in Fig. 1(b)] consisting of $J=0,1,2$.[13] For the largest size considered (75 Å), we find that the biexciton energy is increased by about $1.3\Delta E^{\rm ex}_{\rm exch}$, while in bulk CuCl, the exchange correction is quoted to be $1.6\Delta E^{\rm ex}_{\rm exch}$, obtained as a first-order perturbative estimate using a variational wave function, by Bassani *et al.*[12] Here $\Delta E^{\rm ex}_{\rm exch}$ is the exciton exchange splitting energy in the bulk material. We use $\Delta E^{\rm ex}_{\rm exch}=4.4$ meV for CuCl.[14]

The biexciton binding energy in CuCl QD's was recently measured by Masumoto *et al.*[15] As the radius of the QD increases from 30 Å to 75 Å, we find that the biexciton binding energy decreases from $0.257E_R$ (49 meV) to $0.156E_R$ (29.6 meV), while the experimental result in the same size range varies from $0.335E_R$ (64 meV) to $0.22E_R$ (42 meV), which is somewhat larger than the calculated result. This discrepancy may be partly attributed to the fact that the experimental sample contains somewhat flattened (platelet-shaped) crystallites[16] compared to the spherical shape that we consider.

The physical nature of the biexcitonic states and their relevance to optical response becomes clearer on considering the oscillator strengths for their excitation from the excitonic states. Taking the light polarization to be along the z axis, only the $J=1$, $M_J=0$ exciton states can be excited by one-photon absorption from the ground state, while only the $J=0$, $M_J=0$ and $J=2$, $M_J=0$ biexciton states can be excited by a subsequent one-photon absorption. In Fig. 2 we plot the calculated values of the dipole moments (μ_{XX}) for a few strong transitions from the $J=1$ exciton ground state to the biexciton states. μ_{XX} is given in units of μ_{cv}, which is

the dipole matrix element between the Γ_7 valence-band Bloch function and the Γ_6 conduction-band Bloch function summed over the spin degrees of freedom. Also shown is the dipole moment for excitation of the $J=1$ exciton ground state. The dipole moment for the biexciton ground state to the exciton transition, commonly referred to as the M-line emission, increases with the radius of the QD at small sizes, but saturates towards the bulk value at larger sizes. For $R=75$ Å, the M-line dipole moment of $10.2\mu_{cv}$ corresponds to an oscillator strength of $\approx 1900 f_{Z_3}$ for CuCl, which may be compared with the measured bulk value of $2500 f_{Z_3}$.[17] Here f_{Z_3} is the oscillator strength per unit cell of the bulk exciton.

The most interesting result of the present calculation is the existence of two nearly degenerate excited biexciton states [labeled $XX0$ and $XX2$ in Fig. 1(c)] with a large oscillator strength as is evident from Fig. 2. These states have oscillator strengths increasing proportional to the QD volume, and the sum of their oscillator strengths approximately equals twice that of the exciton, especially at large sizes. For linearly polarized excitation, the states that share such a large oscillator strength have $J=0$ or $J=2$, $M_J=0$. Interestingly, we find that the wave functions of these states are well approximated by a product of two independent ground-state exciton states, especially at larger sizes.

This situation is most easily understood by considering creation of a second exciton in a QD much larger in size than the exciton. Such a process will be most efficient when the second exciton is created uncorrelated with the first one, as it then would have an oscillator strength of the same order as that of creating a single exciton. Such an uncorrelated exciton pair would be an approximate eigenstate of large QD's because the exciton-exciton interaction is short ranged, unlike the electron-hole interaction in an exciton. We could, in fact, create two such excited states with almost the same energy,

$$\Phi_{XX}^{\pm\pm}=(1/\sqrt{2})[\phi_X^g(\mathbf{r}_{e1},\mathbf{r}_{h1})\phi_X^g(\mathbf{r}_{e2},\mathbf{r}_{h2}) \pm \phi_X^g(\mathbf{r}_{e1},\mathbf{r}_{h2})\phi_X^g(\mathbf{r}_{e2},\mathbf{r}_{h1})], \quad (3)$$

where ϕ_X^g is the envelope function of the exciton ground state. In the limit of large R these two states will have a combined oscillator strength of twice that of the exciton ground state. The exchange interaction splits these into four states, two with $J=0$, and one each with $J=1$ and $J=2$. Only two of these [$J=0$ and $J=2$, labeled $XX0$ and $XX2$ in Fig. 1(c)] are excited by multistep excitation via the $J=1$ exciton ground state. At finite R, the exciton-exciton interaction would modify this picture, but our numerical results agree with the above description, to a good approximation, especially at larger sizes. Thus, the two nearly degenerate states with large oscillator strengths have an energy very close to twice that of the $J=1$ exciton as can be seen from Fig. 1. The factor of 2 in the oscillator strength can also be understood as the bosonic enhancement factor corresponding to the creation of a second identical exciton.

As the size of the QD is reduced, the two excitons overlap with each other, the state corresponding to Φ_{XX}^{--} acquiring a repulsive energy as is well known with the case of the antibonding product state of the hydrogen molecule. On the other hand, the Φ_{XX}^{++} state gets more and more mixed with and repelled by the biexciton ground state. The net effect of this size-dependent evolution of the weakly correlated exciton pair state is a weakening of its oscillator strength as well as a blueshift of the corresponding exciton-biexciton transition, as the QD size is reduced.

Because of the large oscillator strength, these states would dominate the excited state absorption spectrum and we argue that the experimentally observed blueshift of the probe absorption in the presence of a strong pump beam[5] involves excitation of such exciton pair states. In this experiment, the pump beam creates electron-hole pairs above the band gap, which would relax and populate the three sublevels of the $J=1$ exciton. Therefore, unlike the coherent multistep excitation of the exciton pair state considered above, the probe absorption from such a mixed one-exciton state would be enhanced by a factor smaller than 2. Our calculation shows two nearly degenerate strong transitions from the $J=1$ exciton ground state to exciton pair states with $J=0,2$ ($XX0$, $XX2$) blueshifted from the ground-state absorption peak by 17.5 meV and 15.7 meV for $R=45$ Å and 11.4 meV, 11.5 meV for $R=50$ Å. The combined oscillator strength for these transitions is about 1.3 times that of the exciton ground state. These results agree very well with the experimentally observed excited state absorption peak, slightly broadened and blueshifted by about 10 meV for $R\approx 45$ Å.

The weakly correlated exciton pair state would also play a crucial role in the third-order nonlinear optical susceptibility ($\chi^{(3)}$) of QD's. To see this, we note that in a three-level model, appropriate in the present case with the ground state, the lowest exciton state and the two-exciton state forming the three levels, there are two competing contributions to $\chi^{(3)}$.[18] These two contributions exactly cancel when the doubly excited state has its energy and oscillator strength double that of the singly excited state, a situation to which the QD level structure is found to approach as R increases.

In fact, the resonant excitonic $\chi^{(3)}$ of CuCl QD's has been observed[3] to exhibit an interesting size dependence with $\chi^{(3)}$ increasing with radius to values much larger than in the bulk, but saturating at $R\approx 50$ Å (at 77 K) and then abruptly falling with further increase in R. The physical reason for this behavior becomes clear in the light of the above discussion. In Fig. 3 we plot the size dependence of the maximum value of $|\chi^{(3)}/\alpha|$, where α is the absorption coefficient, calculated for CuCl QD's using our calculated energy spectrum of one- and two-exciton states. We show the results for several values of the homogeneous broadening (γ_h) and the inhomogeneous broadening (γ_{ih}) of the exciton. For the size dependence of γ_h and of the exciton population decay rate, we follow the measurements reported in Ref. 3, and the values of γ_h indicated in Fig. 3 correspond to the largest radius (75 Å). We assume the same homogeneous width for all the transitions. We find that at the radius for which γ_h becomes comparable to the blueshift of the excited state absorption (i.e., the difference between the energy of the weakly correlated exciton pair state and twice the energy of the exciton ground state), the size dependence of $\chi^{(3)}$ tends to saturate and $\chi^{(3)}$ rapidly decreases with further increase in R. This mechanism responsible for the saturation of $\chi^{(3)}$ is of quite general nature and would apply to QD's of semiconductors other than CuCl as well.

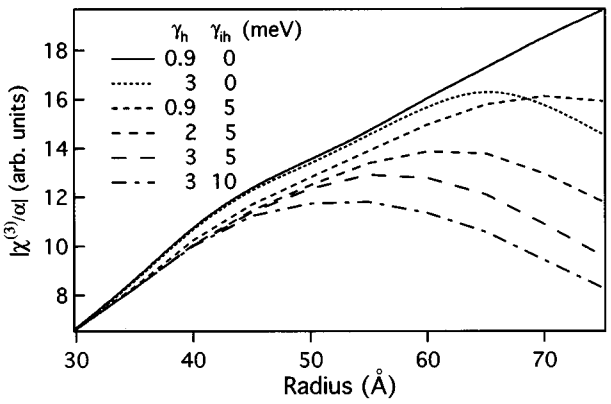

FIG. 3. Calculated size dependence of the peak value of $|\chi^{(3)}/\alpha|$ near the exciton resonance in CuCl QD's. All the curves are scaled to the same value at $R=30$ Å. The hump seen at $R\approx 45$ Å arises from the assumed size dependence of γ_h and has no special physical significance.

Increasing the inhomogeneous width also causes the saturation radius to shift to lower values. This is illustrated by the results shown in Fig. 3, obtained using a simple phenomenological Gaussian inhomogeneous broadening of all the transition energies. A detailed analysis would, however, need more information on the dephasing rates of the biexcitonic states as well as on the inhomogeneous broadening of the absorption spectrum.[19]

To conclude, we have presented a calculation of the excitonic and biexcitonic states in semiconductor QD's of radii up to 10 times the exciton Bohr radius. Our results show the presence of an excited state of the biexciton that is well approximated by a weakly correlated exciton pair, and it is shown to play a crucial role in determining the nonlinear optical response of such large QD's. This result provides a satisfactory understanding of the experimentally observed blueshift of the excitonic absorption in the presence of a strong pump beam as well as the size dependence of resonant $\chi^{(3)}$. We note that such weakly correlated exciton pair states would exist in other semiconductor structures such as quantum wells and wires also, and it would be interesting to investigate their effect on the optical response.

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