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Biexciton binding in quantum boxes

Garnett W. Bryant
McDonnell Douglas Research Laboratories, P.O. Box 516, St. Louis, Missouri 63166-0516
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In ultrasmall quantum nanostructures the interparticle Coulomb energy is a small perturbation to single-particle confinement and kinetic energies. Third-order perturbation theory has been used to calculate energies of excitons and biexcitons confined in quantum box nanostructures. The confined biexciton is more stable than two independent excitons in ultrasmall structures. The confinement-induced enhancement in biexciton binding should be negligible for boxes larger than several exciton diameters. Results are presented as a function of electron-hole mass ratio to develop a qualitative model of exciton-exciton interactions in zero-dimensional systems.

The near-band-edge nonlinear optical response of a semiconductor structure is determined by multiexciton states. In a semiconductor structure with at least one degree of unconfined motion, i.e., in bulk, in a quantum well or in a quantum well wire, the two-exciton states are biexcitons, spatially localized by the exciton-exciton effective attraction. In a zero-dimensional quantum nanostructure, the confining potential localizes the two excitons to the same region. However, the exciton-exciton effective interaction still determines the energy of the confined biexciton (two interacting, confined excitons) relative to the energy of two independent confined excitons. The exciton and biexciton energies must be modeled accurately because the energy ordering of these states influences the line shape of the nonlinear optical response.[1]

A theoretical model for the energies and optical response of excitons confined in spherical microcrystallites[2-10] and in flat quantum boxes fabricated by nanolithography from narrow quantum wells[11] has been developed. The development of a theoretical model of biexcitons confined in zero-dimensional structures was just recently begun.[1,12,13] Banyai *et al.*[1] modeled biexcitons confined in microcrystallites for the intermediate size regime where the two electrons occupy the lowest-energy confinement state but the holes, assumed to have a heavier mass, are weakly perturbed by the confinement and move in the static potential of the two electrons. Banyai *et al.*[1] calculated the confined-biexciton energy to be greater than twice the energy of a confined exciton. The destabilization of the confined biexciton was attributed to the hole-hole repulsion which displaced the holes from the center of the structure thereby increasing the hole confinement energy. This destabilization of the biexciton when confined in all three dimensions is a surprising result because increasing confinement normally increases binding energies.[11,14]

The stability of the confined biexciton can be investigated by low-order perturbation theory. In a zero-dimensional structure the single-particle kinetic and confinement energy scales as $1/A^2$ and the Coulomb interaction scales as $1/A$, where A is the size of the structure. The Coulomb interaction is a small perturbation to the kinetic and confinement energy in very small structures. The zeroth- (kinetic and confinement energy) and first-order (Coulomb energy of the unperturbed ground state) contributions to the biexciton energy are exactly twice the zeroth- and first-order exciton energies. The stability of the biexciton relative to two independent excitons, when confined in a small structure, is determined by the size-independent second-order energies E_2^{bi} and E_2^{ex} for the biexciton and exciton. A straightforward evaluation of second-order perturbation theory[12,15] shows that

$$E_2^{\mathrm{bi}}-2E_2^{\mathrm{ex}}=\sum_{\substack{n>1\\ m>1}}|V_{nm}|^2\left(\frac{1}{E_{11}^e-E_{nm}^e}+\frac{1}{E_{11}^h-E_{nm}^h}+\frac{2}{E_{11}^{eh}-E_{nm}^{eh}}\right), \tag{1}$$

where $V_{nm}=\langle 11|U|nm\rangle$ is the two-particle interaction which scatters two particles from the ground state $|11\rangle$ to an excited state $|nm\rangle$ for two confined, noninteracting particles; E_{nm}^e, E_{nm}^h, and E_{nm}^{eh} are the confinement energies for two independent electrons, holes, and an electron and hole, respectively, and n is the quantum number for the discrete single-particle states. $E_2^{\mathrm{bi}}-2E_2^{\mathrm{ex}}$ is negative, independent of the form of the interaction U or confinement energy. Banyai[12] calculated upper and lower bounds for $E_2^{\mathrm{bi}}-2E_2^{\mathrm{ex}}$ and found enhancement of the biexciton binding in zero-dimensional structures in contrast to previous predictions of destablization.[1]

We have used third-order perturbation theory to develop a more complete model of biexciton binding in small structures. We evaluate the second-order energies (numerically) exactly to determine the enhancement of biexciton binding expected in very small structures. We calculate the third-order energies to estimate the range of structure sizes which provide enhanced biexciton binding. Takagahara[13] estimated the size dependence of biexciton binding by use of a variational approach. He predicted enhanced biexciton binding in large structures. However, in small structures the biexciton had a higher energy than two independent excitons, contrary to perturbation theory. The third-order results presented here should provide the best estimate to date of biexciton binding in very small structures.

We model biexcitons which are confined in zero-dimensional structures fabricated from narrow quantum wells by use of nanolithography to confine the lateral motion. The well width w is assumed to be much narrower than the lateral dimension A of the box (a square cross section is used for simplicity). The same model has been used to study confined excitons.[11] The electrons and holes are treated in the isotropic effective-mass approximation. The confining potential is assumed to be infinite. The dielectric mismatch between the well and the barrier is ignored so the interparticle interaction is the statically screened Coulomb interaction. The effects of the shape of the structure and of nonisotropic hole masses, as occurs in quantum wells, are considered in another publication.[15]

The stability of the biexciton is determined by the energy difference

$$\Delta = \Delta_2 + \Delta_3 = E_2^{bi} - 2E_2^{ex} + E_3^{bi} - 2E_3^{ex} . \quad (2)$$

E_2^{ex} and E_2^{bi} are calculated using expressions similar to Eq. (1). E_3^{ex} and E_3^{bi} are determined by a straightforward evaluation[15] of the third-order energy term. Typically, ten single-particle basis states for the lateral confinement in each direction were included to evaluate the energy sums accurately.[15] To reduce the number of transitions included in the sums we used an empirically accurate "conservation of momentum" approximation. In a confined system the basis states are standing waves, one component of the standing wave with wave vector k and the other with wave vector $-k$. In the conservation of momentum approximation we include only those transitions which couple two-particle initial and final states which have at least one standing-wave component with the same wave vector.

The exciton and biexciton energies depend on the material parameters for the well region—the electron and hole masses (m_e and m_h) and the dielectric constant ε. We present results for $m_h \geq m_e = 0.067$ and $\varepsilon = 13.1$. A fixed (independent of m_e/m_h) energy scale (the electron effective Rydberg $R_e = Rm_e/\varepsilon^2$, where R is the atomic Rydberg) and length scale (a_0, the atomic Bohr radius) are used. If the lengths were scaled by the electron effective Rydberg a_e ($a_e = \varepsilon a_0/m_e$) then the scaled energies as a function of scaled lengths would be independent of ε and m_e. The results presented here were calculated ignoring the effect of well width ($w=0$). The effect of finite well width is considered elsewhere.[15]

Third-order perturbation theory provides an accurate model for confined-exciton energies in small structures ($A \lesssim 5d_\mu$ where d_μ is the diameter of a two-dimensional unconfined exciton with reduced mass μ, $d_\mu = \sqrt{3/2}a_\mu = \sqrt{3/2}\varepsilon a_0/\mu$). Confined-exciton energies for $m_e/m_h = 0.75$ calculated by use of zeroth-, first-, second-, and third-order perturbation theory are compared with the energy obtained by use of a variational approach[11] in Fig. 1 (the band-gap energy has been ignored). The kinetic plus confinement energy E_0 is a good model for the exciton energy only if $A \ll d_\mu$. However, adding the direct Coulomb energy accounts for most of the binding when $A \lesssim d_\mu$. For $d_\mu \lesssim A \lesssim 5d_\mu$ the second-order (size independent) energy E_2^{ex} accounts for about half of the energy difference between E_{0+1}^{ex} and E_{var}, and E_3^{ex} accounts for most of the remaining energy difference. Third-order theory becomes less accurate as m_e/m_h decreases. However, the energies are still accurate for $A \lesssim 5d_\mu$. For $A \gtrsim 5d_\mu$ the exciton is weakly perturbed by confinement and E_{var} approaches the asymptotic energy expected for an unconfined exciton. The third-order perturbation theory is a good model for exciton energies for sizes up to the size regime when confinement effects are small.

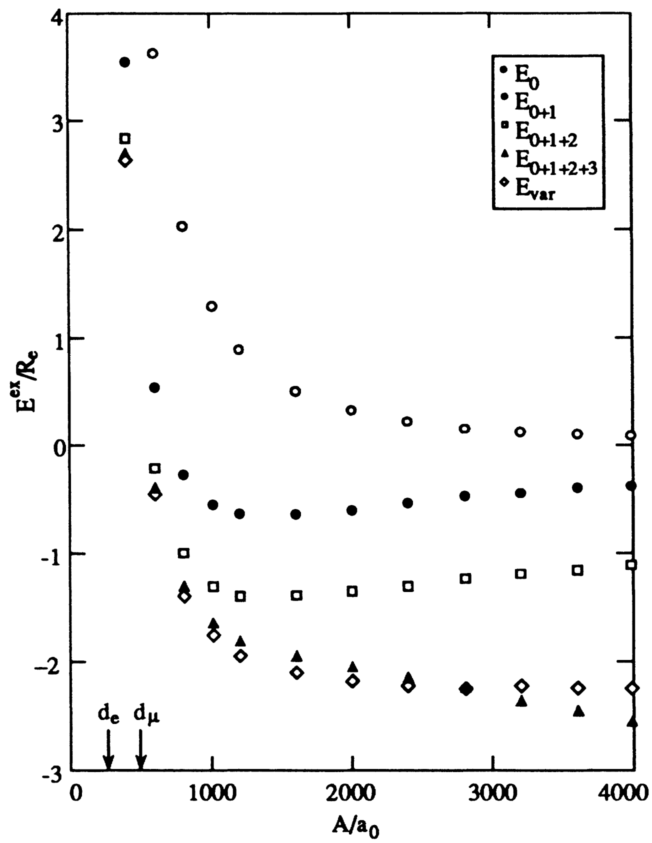

FIG. 1. Exciton energies calculated in zeroth-, first-, second-, and third-order perturbation theory. The energy obtained with a variational wave function is shown for comparison. The exciton is confined in a box with side A and narrow well width $w=0$; $m_e/m_h = 0.75$. The two-dimensional electron and exciton diameters are indicated ($m_e = 0.067$).

The lowest-order energy difference between the biexciton and two independent excitons occurs in second order. The mass dependences of E_2^{bi}, E_2^{ex}, and Δ_2 are shown in Fig. 2. The second-order energy shifts are negative, making the exciton and biexciton more stable. E_2^{bi} is 5–10 times larger in magnitude than E_2^{ex} indicating that the biexciton is more sensitive to the Coulomb interaction. The biexciton is stable relative to two independent excitons ($\Delta_2 < 0$) when confined in very small structures where the size independent term Δ_2 is the dominant contribution to the energy difference. The mass dependence of E_2^{bi}, E_2^{ex}, and Δ_2 are similar. An increase in magnitude proportional to $(m_e/m_h)^{-1}$ occurs as $m_e/m_h \rightarrow 0$ because hole excited states make the dominant contribution in this

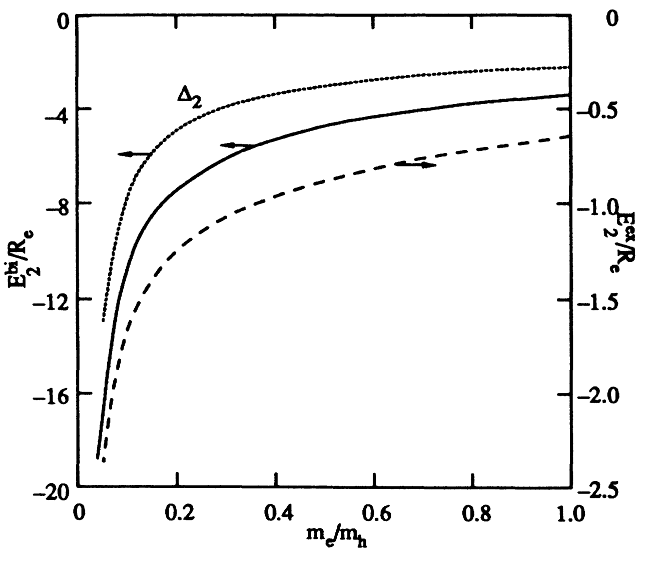

FIG. 2. Second-order, confined biexciton and exciton energies E_2^{bi} and E_2^{ex}, and the energy difference Δ_2. Note the different scale used for E_2^{ex}.

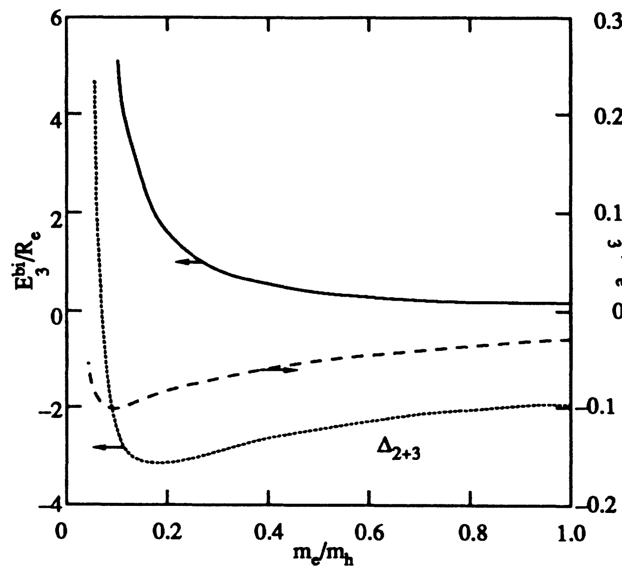

FIG. 3. Third-order confined biexciton and exciton energies E_3^{bi} and E_3^{ex} and the total energy difference $\Delta_{2+3}=\Delta_2+\Delta_3$. Results are shown for $A=100a_0$. Note the different scales for E_3^{bi} and E_3^{ex}.

limit.

Banyai *et al.*[1] predict that $\Delta > 0$ when $m_e/m_h \ll 1$ and the electrons are confined to their ground states. We have calculated Δ_2 using two approximations used in Banyai *et al.*[1] We first calculated Δ_2 by ignoring all contributions from the electron-electron interaction. We also calculated Δ_2 by ignoring any contribution from electrons in excited states. For both approximations and all ratios $m_e/m_h < 1$, we obtained $\Delta_2 < 0$. Thus the exact calculation and the two approximations predict that the biexciton confined in a very small structure is stable.

The third-order confined biexciton and exciton energy shifts are shown in Fig. 3. E_3^{bi} and E_3^{ex}, which are shown for $A=100a_0$, scale linearly with A. E_3^{bi} is positive while E_3^{ex} is an order of magnitude smaller and is negative except for $m_e/m_h \approx 0$. The third-order perturbation sums involve two intermediate states. The terms which make the largest contribution to E_3^{bi} are those terms for which at least one of the intermediate states has both electrons or both holes excited. These terms give a positive energy shift and destabilize the biexciton. These terms do not contribute to E_3^{ex}. Hole excited states make the dominant contribution as $m_e/m_h \rightarrow 0$ and the energy shifts are proportional to $(m_e/m_h)^{-2}$.

The biexciton-exciton stabilization energy $\Delta=\Delta_2+\Delta_3$ is shown in Fig. 4. The $A\rightarrow 0$ limit is Δ_2 and the linear change for $A>0$ is determined by Δ_3. The Δ_∞ are the stabilization energies expected as $A\rightarrow\infty$ as determined by Kleinman[14] for unconfined two-dimensional biexcitons. The biexciton stabilization energy is enhanced by a factor of 5 when an unconfined two-dimensional biexciton is confined in a very small structure.

The following qualitative model can be deduced from third-order perturbation theory. The confined biexciton binding is strongly enhanced in small structures. The binding is greater for biexcitons formed from heavier holes because Coulomb effects are more important for heavier holes. Δ is enhanced even when Δ is scaled by R_μ rather than R_e. The enhancement of Δ as a function of m_e/m_h is not just the change in energy scale expected because R_μ depends on m_e/m_h but is a result of the greater hole-hole correlation that is possible for heavier holes. The reduction in binding as A increases occurs most rapidly for small m_e/m_h. In fact, $\Delta_{2+3} > \Delta_\infty$ if $A \gtrsim d_\mu/2$ for

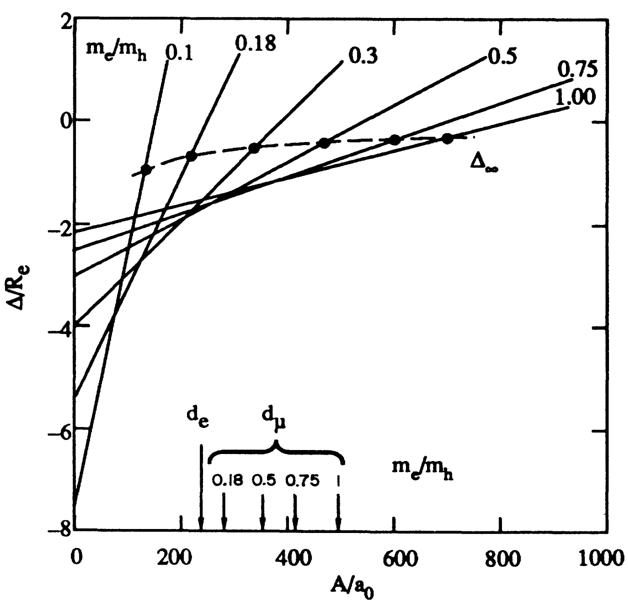

FIG. 4. Total biexciton-exciton energy difference $\Delta=\Delta_2+\Delta_3$ as a function of A for the indicated mass ratios. Δ_∞ is the biexciton binding energy for an unconfined, two-dimensional biexciton ($A\rightarrow\infty$) obtained from Ref. 14. Electron and exciton diameters are indicated.

$m_e/m_h \lesssim 0.1$ but $\Delta_{2+3} < \Delta_\infty$ if $A \lesssim 2d_\mu$ for $m_e/m_h = 1$. For $m_e/m_h \to 0$ the biexciton acts as two excitons, each tightly bound so exciton-exciton interactions are weak until confinement forces the two excitons to overlap ($A \lesssim d_\mu$). However, for $m_e/m_h \to 0$ Coulomb energies are large so enhanced binding occurs when the excitons are forced to overlap by confinement. For $m_e/m_h \to 1$, the excitons are less tightly bound so enhancements in binding energy as $A \to 0$ are smaller but the exciton-exciton interaction has a longer range and enhancement occurs for $A \lesssim 2d_\mu$.

In conclusion, a third-order perturbation theory has been used to develop a qualitative model for confined biexcitons. Biexcitons are stable in small structures. Higher-order perturbation theory would have to be used to determine exactly how Δ approaches Δ_∞ as A increases and whether $\Delta > 0$ for any m_e/m_h and A. If the biexciton is destabilized at some A_d then the biexciton must undergo a complicated transition from stability at small A to instability near A_d and back to stability for large A.

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