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Incomplete confinement of electrons and holes in microcrystals

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A simple variational calculation is presented for the ground-state energy of an electron-hole system confined in a microcrystal with finite potential barriers. It is shown that the effect of penetration of the wave function outside the microcrystal is quite large in the strong-confinement region and is consistent with the relatively small blueshift of the excitation energy observed in CdS microcrystals.

Recently, much attention has been focused upon the quantum size effects of semiconductor microcrystals. The motional state of the Wannier exciton is strongly modified by three-dimensional confinement[1,2] and this causes significant changes in the linear[3] as well as in the nonlinear[4] optical properties of the microcrystals from those of the bulk crystals.

In previous papers,[5,6] one of the present authors carried out a theoretical investigation of the quantum size effects of microcrystals within a simple model, which assumes the effective-mass approximation for the electron and the hole confined in a sphere with infinite potential barriers. The theory bridges the two extreme situations,[1] namely, the weak-confinement limit (the exciton-confinement regime) and the strong-confinement limit (the individual-particle-confinement regime). It was shown that the transition between the above two regimes occurs around parameter region $2 \lesssim R/a_B^* \lesssim 4$, where R is the radius of the microsphere and a_B^* is the effective Bohr radius of the exciton. It has been reported that the theoretical prediction of the blueshift of the ground-state energy of an exciton agrees fairly well with experimentally observed values in the intermediate region of CdTe microcrystals.[7]

In the case of strong confinement, however, the quantitative agreement becomes poor. For $R/a_B^* \lesssim 1$, theory predicts that the ground-state energy E of the electron-hole system is given by the asymptotic formula[2,5]

$$E = E_g^{(1)} + \frac{\hbar^2}{2\mu}\left(\frac{\pi}{R}\right)^2 - 3.572\left(\frac{a_B^*}{R}\right)E_{\rm Ry}^* - 0.248E_{\rm Ry}^* , \tag{1}$$

where $E_g^{(1)}$ is the band-gap energy of the bulk crystal, $E_{\rm Ry}^*$ is the effective Rydberg energy of the bulk exciton, and $\mu \equiv 1/(m_e^{-1}+m_h^{-1})$ is the reduced mass for the effective masses of the electron m_e and the hole m_h. Experimental observations carried out extensively for CdS_xSe_{1-x} and CdS microcrystals embedded in glass matrices have revealed that the high-energy shift in real materials is generally much smaller than the theoretical prediction in this region.[8–10] The discrepancy becomes salient, especially for R as small as 10–20 Å.[8] The same tendency also has been observed in the PbI_2 microcrystals incorporated into zeolite cages.[11]

One should note that the boundary constraint of the infinite barrier model is too artificial for such a small size of microcrystals: Formula (1) diverges in the limit $R \rightarrow 0$, while in real systems E should be bounded by the band-gap energy of a matrix material. It may well be expected that the main reason for the discrepancy is the unrealistic boundary constraint, although other possibilities, such as the nonparabolicity of the energy band, should also be examined.

The importance of the incompleteness of the confinement has been pointed out by Brus.[2] Grabovskis *et al.*[12] observed the photoionization of CdS microcrystals in glass. They estimated the height of the potential barrier for the electron as 2.3–2.5 eV. The penetration of the wave function outside the microcrystals also plays an essential role in the photochemical reactions in aqueous solutions.[2,13]

In this work, we report the results of a variational calculation of the ground-state energy of the electron-hole system confined in a microsphere by finite potential barriers and show that the effect of the incompleteness of a confinement is, in fact, quite large. Consider an electron and a hole in a dielectric sphere embedded in a continuum matrix. We neglect the difference in effective masses between the microcrystal and the matrix. This is not too bad, since most of the population density of the electron and the hole is still confined in the microcrystal for sizes of practical interest, as shown below. We also neglect the difference in the dielectric constant ϵ.

By adopting the Hylleraas coordinate system $r_e \equiv |\mathbf{r}_e|$, $r_h \equiv |\mathbf{r}_h|$, $r_{e\text{-}h} \equiv |\mathbf{r}_e - \mathbf{r}_h|$ defined for the coordinates of electron $\mathbf{r}_e$ and hole $\mathbf{r}_h$, the Hamiltonian is

$$H = E_g^{(1)} - \frac{\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial r_e^2} + \frac{2}{r_e}\frac{\partial}{\partial r_e} + \frac{r_e^2 - r_h^2 + r_{e\text{-}h}^2}{r_e r_{e\text{-}h}}\frac{\partial^2}{\partial r_e \partial r_{e\text{-}h}}\right) - \frac{\hbar^2}{2m_h}\left(\frac{\partial^2}{\partial r_h^2} + \frac{2}{r_h}\frac{\partial}{\partial r_h} + \frac{r_h^2 - r_e^2 + r_{e\text{-}h}^2}{r_h r_{e\text{-}h}}\frac{\partial^2}{\partial r_h \partial r_{e\text{-}h}}\right)$$
$$- \frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r_{e\text{-}h}^2} + \frac{2}{r_{e\text{-}h}}\frac{\partial}{\partial r_{e\text{-}h}}\right) - \frac{e^2}{\epsilon r_{e\text{-}h}} + V_e(r_e) + V_h(r_h) , \tag{2}$$

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where

$$V_i(r_i)=\begin{cases}0, & r_i \le R\\ \bar{V}_i, & r_i > R,\ i=e,h\ .\end{cases} \quad (3)$$

The confining potential $\bar{V}_i$ satisfies $E_g^{(1)}+\bar{V}_e+\bar{V}_h=E_g^{(2)}$, where $E_g^{(2)}$ is the band-gap energy of the matrix.

The trial wave function is chosen as

$$\Psi(r_e,r_h,r_{e\text{-}h})=A\phi_e(r_e)\phi_h(r_h)\chi(r_{e\text{-}h})\ , \quad (4)$$

where

$$\phi_i(r_i)=\begin{cases}\sin(\beta_i r_i)/r_i, & r_i \le R\\ B_i\exp(-\xi_i r_i)/r_i, & r_i > R,\ i=e,h\ ,\end{cases} \quad (5)$$

$$\chi(r_{e\text{-}h})=\exp(-r_{e\text{-}h}/\alpha)\ , \quad (6)$$

and A is the normalization constant. The variational parameters α, β_e, and β_h are varied so as to minimize the expectation value of energy E. The parameters B_i and ξ_i are given as functions of β_i and R by the condition that the wave function is smoothly connected at $r_i=R(i=e,h)$. Function (5) reproduces the result of the single-parameter theory[5] in the limit $\bar{V}_e\to\infty$, $\bar{V}_h\to\infty$.

In Fig. 1, an example of the calculated high-energy shift $\Delta E\equiv E-E_{ex}$ is plotted against $(a_B^*/R)^2$ where $E_{ex}\equiv E_g^{(1)}-E_{Ry}^*$ is an exciton energy of the bulk semiconductor. The values of the parameters $(\bar{V}_e,\bar{V}_h)$ are shown in Fig. 1 in units of E_{Ry}^*. The result of the infinite barrier model is also shown in the uppermost curve. As can be seen, the reduction of ΔE is relatively small in the weak-confinement region. Since the electron and hole behave as a tightly bound quasiparticle (exciton) in this region, the degree of penetration outside the quantum well is limited by that of the heavier particle, i.e., the hole, as long as $\bar{V}_e$ and $\bar{V}_h$ are not so different. As we go into a strong-confinement region, the amount of ΔE reduction becomes quite large. It depends sensitively on the mass ratio m_h/m_e. Since the main contribution to the high-energy shift comes from the lighter particle in this region, the reduction is larger for larger values of m_h/m_e for fixed values of $(\bar{V}_e,\bar{V}_h)$.

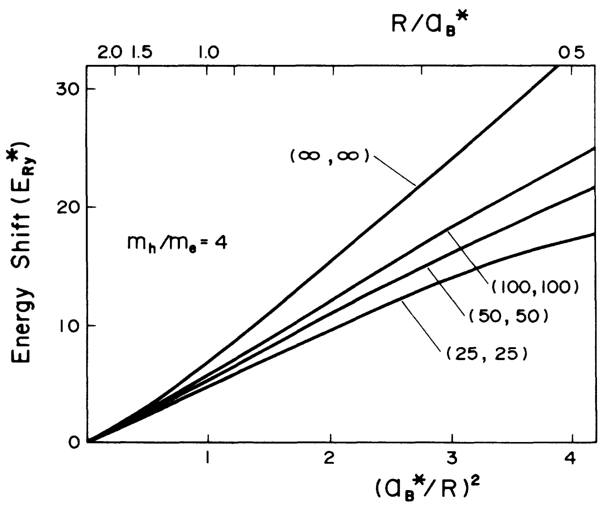

FIG. 1. Calculated high-energy shifts of the electron-hole system for $m_h/m_e=4$. The parameter values $(\bar{V}_e,\bar{V}_h)$ are indicated in the unit of E_{Ry}^*.

In order to analyze the experimental data, we need to know not only the band-gap energies $E_g^{(1)}$, $E_g^{(2)}$, but also the relative position of the bands. Moreover, the gap energy $E_g^{(2)}$ itself has some ambiguities in the case of glass. We tentatively assume the value $E_g^{(2)}=7$ eV roughly estimated from the optical data for sodium silicate glasses.[14] In Fig. 2, the calculated ground-state energy of an electron-hole system in CdS microcrystals in silicate glass is shown against R^{-2}. We adopted the parameter values $E_g^{(1)}=2.58$ eV, $E_{Ry}^*=30$ meV, $m_h/m_e=4$, and $a_B^*=30$ Å for CdS.[15] The centers of the band gaps of the semiconductor and the glass are assumed to coincide so that $\bar{V}_e=\bar{V}_h=2.21$ eV. In Fig. 2, the origin of the ordinate is chosen at $E_g^{(1)}$. The calculated ground-state energy is plotted by the bold solid line together with its decomposition into kinetic energy $\langle K\rangle$, Coulomb energy $\langle C\rangle$, and potential energy $\langle P\rangle$, due to the penetration into the glass matrix. The corresponding quantities calculated for the infinite barrier model are also shown by dashed lines.

Figure 2 clearly shows the mechanism of a high-energy shift reduction by the relaxation of the boundary constraint. Just like the case of the one-body problem, the reduction in the kinetic energy balances the increase in the potential energy to minimize the total energy. An important point here is that the gain in the Coulomb energy due to the strong overlapping of the electron and hole wave function does not decrease as much, even in the case of incomplete confinement. This is partly due to the long-range character of the Coulomb interaction. In the case $R=12$ Å, the existence probability of the electron in the microsphere is 0.92 and that of the hole is 0.99.

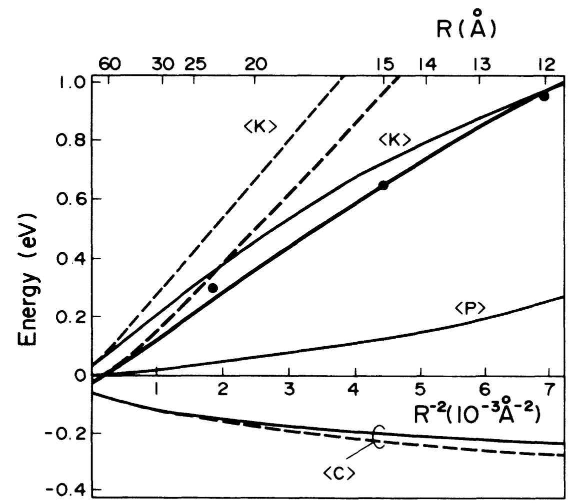

FIG. 2. Calculated ground-state energy of the electron-hole system in CdS microcrystal embedded in silicate glass. The bold line is the total energy. The expectation values of the kinetic energy $\langle K\rangle$, the Coulomb energy $\langle C\rangle$, and the potential energy $\langle P\rangle$ are also shown. The corresponding quantities calculated in the infinite barrier model are shown by the dashed lines. The origin of the energy is chosen at the band-gap energy of CdS. The experimental peak positions of the absorption spectra are plotted by the small circles.

In Fig. 2, the experimental values of the peak positions of the absorption spectra due to Ekimov, Efros, and Onuschenko[8] are also plotted by solid circles. Since the effective-mass approximation may not be fully justified for such a small size of microcrystals and since there are uncertainties in the choice of the parameter values, the excellence of the agreement would be somewhat fortuitous. What has been shown here, however, is that the effect of the incompleteness of the confinement *does* exist and *is* important in analyzing the experimental data.

In this work, we have restricted ourselves to the case where confining potentials $\bar{V}_e$ and $\bar{V}_h$ are both positive and so strong that the extrapolation from the complete-confinement limit works fairly well. As an extension, one may imagine a number of interesting situations according to the relative signs and magnitudes of $\bar{V}_e$ and $\bar{V}_h$. For example, when $\bar{V}_e < 0$ and $\bar{V}_h > 0$, the exciton wave function will have a peculiar structure localized around the surface of the microsphere with separated charge distribution. It will be worthwhile to apply sophisticated techniques of microfabrication to this field in order to provide well-controlled systems of microcrystals and to study optical properties of those exotic new materials.

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