Quantum size effects in spherical semiconductor microcrystals

Selvakumar V. Nair, Sucharita Sinha, and K. C. Rustagi
Laser Division, Bhabha Atomic Research Centre, Bombay 400085, India
(Received 19 November 1986)

The size dependence of the lowest electron-hole state in semiconductor microcrystals is calculated using the variational principle with a three-parameter Hylleraas-type wave function. For very small particles the Coulomb interaction may be treated as a perturbation. For larger particles the size dependence of the energy is much sharper than that expected in previous work.

Wannier excitons in semiconductor microcrystals provide an interesting spectroscopic system for the study of size quantization effects. Recently, several groups[1-5] have studied this phenomenon in colloidal spherical particles of CdS and spherical microcrystals of CuCl, CdS, CdSe, and CdS_xSe_{1-x}, etc., in a glass matrix. Brus[1] has given a variational calculation for the size dependence of the electron-hole pair state while Efros and Efros[5] have calculated the spectra in some limiting cases. For a particle radius smaller than the Bohr radius a_0 of the exciton, the size quantization of the electron and hole band states dominates and the effect of the Coulomb attraction between the electron and hole can be treated as a perturbation. For very large particles, Efros and Efros[5] conclude that the lowest energy of the electron-hole pair in the microcrystal is larger than that in the bulk due to size quantization of the center-of-mass motion. The size dependence of the measured energy levels can thus yield a good estimate of the total mass m_1+m_2 of the electron-hole pair. From a semiconductor-physics point of view this would be especially interesting because the total mass is sensitive to the heavier-particle mass, usually the hole, while the reduced mass involved in the bulk exciton binding energy is sensitive to the lighter-particle mass, usually the electron. Experimental results[3] for CuCl particles give a total mass much smaller than that generally accepted. In this Brief Report we report an accurate variational calculation for the lowest electron-hole pair state. The dependence of the energy levels as well as the wave functions on the particle size are critically evaluated. Our calculations clearly indicate that the determination of the total mass by this method is not satisfactory.

In the effective-mass approximation the essential problem is to solve the Schrödinger equation for the envelope function ψ:

$$\left[-\frac{\hbar^2\nabla_1^2}{2m_1}-\frac{\hbar^2\nabla_2^2}{2m_2}-\frac{e^2}{4\pi\epsilon_0\epsilon r_{12}}+V_0\right]\psi(\mathbf{r}_1,\mathbf{r}_2) = E\psi(\mathbf{r}_1,\mathbf{r}_2)\ , \quad (1)$$

where m_1, m_2 and $\mathbf{r}_1, \mathbf{r}_2$ are the electron and hole masses and position vectors, respectively, and $r_{12}=|\mathbf{r}_1-\mathbf{r}_2|$. The confining potential V_0 is 0 inside the spherical crystallite of radius R and infinite outside this sphere, with the corresponding boundary condition

$$\psi(\mathbf{r}_1,\mathbf{r}_2)=0 \quad \text{for } r_1 \text{ or } r_2 \geq R\ . \quad (2)$$

For small particles the energy levels were calculated by treating the Coulomb interaction between the electron and hole as a perturbation. From single-particle wave functions[5] linear combinations corresponding to zero angular momentum were formed. Using a finite set of these as the basis set, the matrix representation for the Hamiltonian in Eq. (1) was obtained and diagonalized. While the unperturbed level spacings scale as $1/R^2$, the Coulomb term scales as $1/R$. Thus as particle size increases the perturbation theory requires a larger and larger matrix to be diagonalized. Using a 20×20 matrix we obtained satisfactory convergence for $R \leq 1.5a_0$. For larger particles, the lowest energy for the electron-hole pair states was obtained by a variational calculation. We used a trial wave function of the form

$$\psi(\mathbf{r}_1,\mathbf{r}_2)=\begin{cases} N\left[\dfrac{\sin(\pi r_1/R)}{r_1/R}\right]^{\alpha_1}\left[\dfrac{\sin(\pi r_2/R)}{r_2/R}\right]^{\alpha_2}\exp(-\beta r_{12}/R) & \text{for } r_1, r_2 \leq R \\ 0 & \text{outside,}\end{cases} \quad (3)$$

where N is the normalization constant and α_1, α_2, and β are the three variational parameters. This form of the trial wave function was chosen to satisfy the boundary condition (2) and other known limiting forms. For $\alpha_1=\alpha_2=1$ and $\beta=0$ we obtain the single-particle product states expected for small particles. For large particles, the expected ground-state wave function corresponding to the size quantization of the center-of-mass motion is

$$\psi \sim \frac{\sin(\pi r_{\text{c.m.}}/R)}{r_{\text{c.m.}}/R}e^{-r_{12}/a_0}\ , \quad (4)$$

where $r_{\text{c.m.}}$ is the center-of-mass coordinate. Strictly, this

function does not obey the boundary condition (2) and is not acceptable. However, because of the exponential dependence on r_{12} the limiting form $\alpha_1=\alpha_2=\frac{1}{2}$ and $\beta=R/a_0$ corresponds quite closely to this limit. Similarly the wave function corresponding to a free exciton at rest can be obtained in the limit $\alpha_1=\alpha_2=0$ and $\beta=R/a_0$ which, again, is not acceptable since it does not obey the boundary condition.

Using Hylleraas coordinates[6] r_1, r_2, and r_{12}, the additional angular variables needed to specify $\mathbf{r}_1$ and $\mathbf{r}_2$ are not required in the evaluation of the expectation value $\langle\psi|H|\psi\rangle/\langle\psi|\psi\rangle$. Further, since all distances have been scaled to the particle size R, the expectation values of the kinetic energy term and the potential energy term need to be evaluated for only one R for any given set of parameters α_1, α_2, and β. The kinetic energy term scales like R^{-2} and the potential energy term like R^{-1}. These were evaluated for several discrete values of α_1, α_2, and β. For intermediate values an interpolation method was used. The minimum energy was found by minimizing the expectation value successively with respect to α_1, α_2, and β till an absolute minimum was reached. It was verified to be independent of the order of α_1, α_2, and β. Figures 1 and 2 show the calculated energies for parameters appropriate to CuCl ($m_1/m_0=0.44$, $m_2/m_0=3.60$, $\epsilon=5.4$, and $a_0=7.286$ Å) and CdS ($m_1/m_0=0.205$, $m_2/m_0=1.020$, $\epsilon=8.46$, and $a_0=26.219$ Å) as a function of $(a_0/R)^2$. The values of corresponding parameters α_1, α_2, and β are shown in Table I for some representative cases. For CdS particles smaller than the exciton radius, the calculated energies are very close to those obtained by the perturbation calculation. However, even here the effect of Coulomb interaction is significant. For a CdS particle of radius $R=20$ Å, the calculated energy is 0.387 eV from variational calculation, 0.395 eV from perturbation calculation, and 0.551 eV when the Coulomb interaction is totally neglected. For CdS, even at $R=2a_0$, the lowest-energy eigenvalue is positive, i.e., above the band gap in the bulk material. For CuCl, the exciton radius is comparable with the lattice constant, and thus it is not physically meaningful to consider particle radii smaller than a_0.

When the particle size increases, the lowest excited-state energy decreases first rapidly and then slowly as it approaches the value of the free exciton in bulk. At $R=10a_0$, the calculated energy is within 2% of the limiting value. However, it is in this region that one could expect the exciton to behave like a single particle and exhibit the behavior depicted by the equation[5]

$$E(R)=E(\infty)+\frac{\hbar^2\pi^2}{2MR^2}\ , \tag{5}$$

where $M=m_1+m_2$ is the total mass of the exciton. The calculated energies in this region are only slightly above those given by Eq. (5). Nevertheless, the difference is significant in that the mass M obtained from the slope in this region is $1.8m_0$ and $0.75m_0$ for CuCl and CdS, respectively compared to the actual values $4.04m_0$ and $1.22m_0$. Even though a better variational trial function may give lower energy expectation values, there are at least two reasons to doubt the applicability of the idea of the center-of-mass confinement in this size range. First, we note that α_1 and α_2 have not reached the expected limiting value $\frac{1}{2}$ even for the largest particles in our calculation. In fact, for $\alpha_1=\alpha_2=\frac{1}{2}$ the expectation value of the kinetic energy diverges for all finite R. Thus α_1 and α_2 can tend to $\frac{1}{2}$ only as $R\to\infty$. More important, α_2 remains much larger than $\frac{1}{2}$ for CdS and CuCl. This is because when the electron and hole motion are strongly

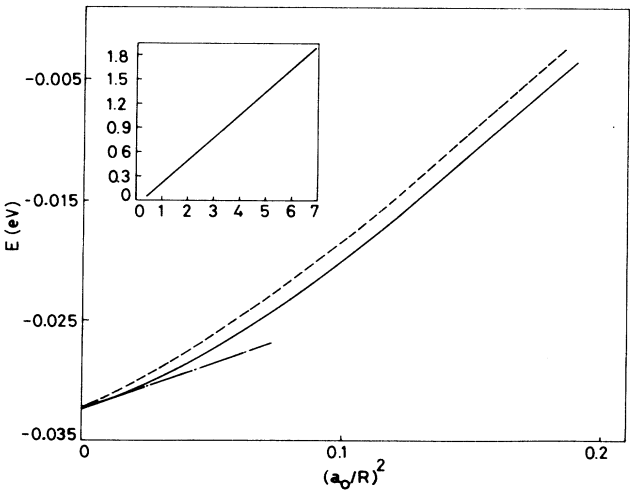

FIG. 1. Size dependence of the calculated lowest-energy eigenvalue of the electron-hole system for CdS. The solid line shows the results for a three-parameter variational calculation and the dashed curve for a one-parameter calculation. The dot-dashed line indicates the limiting slope. The inset gives the same curve for smaller CdS particles.

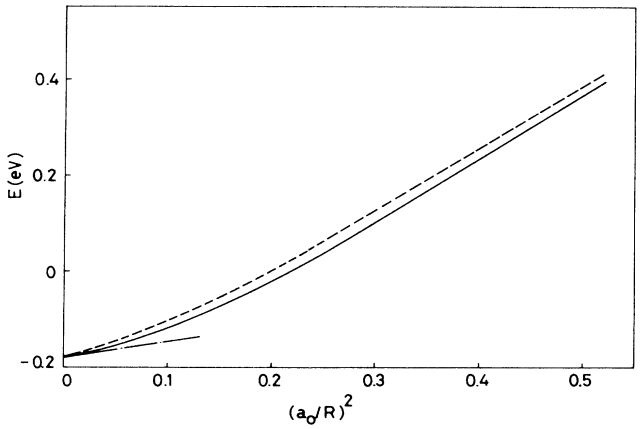

FIG. 2. Size dependence of the calculated lowest-energy eigenvalue of the electron-hole system for CuCl. Notation is the same as in Fig. 1.

TABLE I. The variational parameters β, α_1, and α_2 for some representative particle radii for CuCl and CdS.

	CuCl			CdS		
R (Å)	β	α_1	α_2	β	α_1	α_2
10	0.95	0.9	1.5	0.36	0.95	1.0
20	2.37	0.75	2.1	0.55	0.94	1.1
40	5.10	0.63	2.1	1.06	0.89	1.2
60	7.96	0.56	1.9	1.86	0.82	1.5
100	13.53	0.53	1.7	3.33	0.73	1.6
150	20.45	0.53	1.6	5.35	0.64	1.7
200	27.35	0.53	1.5	7.31	0.60	1.5
400				15.08	0.53	1.3

correlated the heavier hole cannot approach the boundary since it should remain closer to the center of mass. Indeed, we found that α_1 and α_2 can both approach closer to the limiting value of $\frac{1}{2}$ if the electron and hole masses are equal. Second, if we assume that the exciton is not a point particle but a rigid particle of effective radius, say $1.5a_0$, we should expect the center-of-mass motion to be confined to a sphere of radius $(R-1.5a_0)$. Plotting our calculated energy values against $(R-1.5a_0)^{-2}$ we find that a linear relationship obtains over a larger energy interval and the slope corresponds to a total exciton mass $2.9m_0$ for CuCl, closer to the actual value. For CuCl particles with $R \gtrsim 25$ Å our calculated values are in satisfactory agreement with the experimental data.[3] Noticeable discrepancy, however, exists for smaller particles. Since for $R \lesssim 15$ Å the variational results are in good agreement with those of the perturbation calculation, we conclude that the discrepancy indicates an inadequacy of the theoretical model. The most likely cause is that the potential well is of finite depth V_0 and this lowers the energy considerably[4,7] when $2mV_0a^2/\hbar^2$ reduces to values $\lesssim 10$.

Following Henry and Nassau[8] the oscillator strength f of a bound electron-hole pair is related to f_{ex}, that of the free Wannier exciton by

$$f/f_{ex}=\frac{\left|\int d^3r\psi(\mathbf{r},\mathbf{r})\right|^2}{|\psi_{ex}(0)|^2V^2}\frac{\omega_{ex}}{\omega_0}, \tag{6}$$

where ω_0 and ω_{ex} are the lowest transition frequencies for the bound and free excitons, ψ_{ex} is the free-exciton envelope function and V is the crystallite volume. The calculated oscillator strengths for various particle sizes is shown in Fig. 3. The small scatter of the calculated values indicates the accuracy of our calculation. The oscillator strength is large for smaller particles and for larger particles it decreases to $\sim 0.3f_{ex}$ instead of f_{ex}. This may be a restriction imposed by the limiting functional form. Since for larger particles the size quantization plays a negligible role, the trial wave function could include higher single-particle states too.

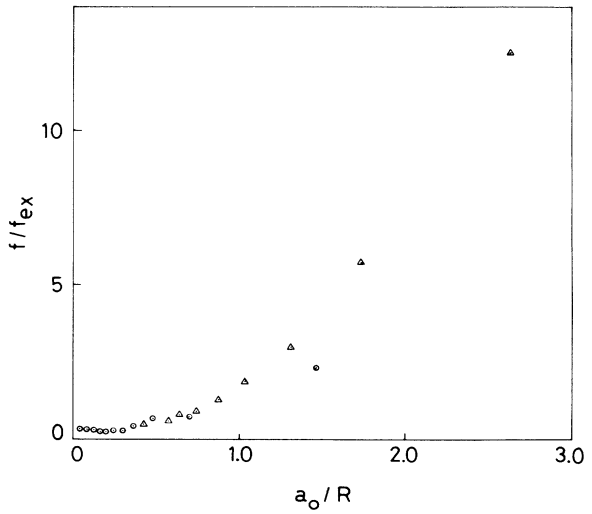

FIG. 3. Size dependence of the oscillator strength of the lowest electron-hole pair state for CdS (△) and CuCl (⊙).

Since completion of this work a recent paper has appeared where Kayanuma[9] reports an independent variational calculation of energy in the restricted function space described by $\alpha_1=\alpha_2=1$. Our own earlier results were also obtained using such a trial wave function and have been added in Figs. 1 and 2.

To summarize, we have calculated the lowest energy level of an electron-hole pair in semiconductor particles. For particles not larger than the exciton, the Coulomb interaction may be treated in perturbation theory. For much larger particles our calculated energy values show a much sharper dependence on particle radius than expected by Efros and Efros.[5] The electron-hole interaction tends to increase the confinement of the hole. The oscillator strength for the lowest electron-hole excited state is expected to increase substantially as the particle size is decreased.

We are grateful to Professor C. S. Warke for many useful comments.

[1]L. E. Brus, J. Chem. Phys. **80**, 4403 (1984).
[2]J. Warnock and D. D. Awschalom, Appl. Phys. Lett. **48**, 425 (1986).
[3]A. I. Ekimov, A. L. Efros, and A. A. Onushchenko, Solid State Commun. **56**, 921 (1985).
[4]H. Weller *et al.* Chem. Phys. Lett. **124**, 557 (1986).
[5]Al. L. Efros and A. L. Efros, Fiz. Tekh. Poluprovodn. **16**, 1209 (1982). [Sov. Phys.—Semicond. **16**, 772 (1982)].
[6]E. A. Hylleraas, Z. Phys. **54**, 347 (1929); H. A. Bethe, *Quantenmechanik der Ein—und Zwei—Elektronenprobleme, Handbuch der Physik* (Springer, Berlin, 1933), p. 354.
[7]L. I. Schiff, *Quantum Mechanics,* 3rd ed. (McGraw-Hill, Tokyo, 1968), p. 83.
[8]C. H. Henry and K. Nassau, Phys. Rev. B **1**, 1628 (1970).
[9]Y. Kayanuma, Solid State Commun. **59**, 405 (1986).