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# EFFECT OF DIELECTRIC CONSTANT ON THE EXCITON GROUND STATE ENERGY OF CdSe QUANTUM DOTS

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The B-spline technique is used in the calculation of the exciton ground state energy based on the effective mass approximation (EMA) model. The exciton is confined in CdSe microspherical crystallites with a finite-height potential wall (dots). In this approach, (a) the wave function is allowed to penetrate to the outside of the dots; (b) the dielectric constants of the quantum dot and the surrounding material are considered to be different; and (c) the dielectric constant of the dots are size-dependent. The exciton energies as functions of radii of the dots in the range 0.5–3.5 nm are calculated and compared with experimental and previous theoretical data. The results show that: (1) The exciton energy is convergent as the radius of the dot becomes very small. (2) A good agreement with the experimental data better than other theoretical results is achieved. (3) The penetration (or leaking) of the wave function and the difference of the dielectric constants in different regions are necessary for correcting the Coulomb interaction energy and reproducing experimental data. (4) The EMA model with B-spline technique can describe the status of excition confined in quantum dot very well.

**Keywords:** dielectric constant, quantum dots, excitons, size-dependence
**PACC:** 7135

## I. INTRODUCTION

The quantum size effects in small semiconductor crystallitites have been widely studied experimentally.[1−6] One of the best-studied quantum dot systems is CdSe. Quasispherical CdSe crystallites with radius smaller than 3.0 nm have been synthesized by different methods, for example, by colloidal preparation,[5] by chemical deposition.[6] They are the subjects of detailed spectroscopic studies, thus offering the opportunity for detailed comparison between experiment and theory. The optical-absorption spectra of these crystallites exhibit a peak near the absorption threshold. This peak is assigned to the creation of electron-hole pairs in the crystallites. The location of the peak is size dependent and shifted to higher energy as the radius decreases. The states of the excitons are strongly modified by three-dimensional confinement, which causes a significant change in optical property of microcrystals from those of the bulk crystal.

Theoretically, many efforts have been devoted to account for the size dependency.[7−22] Several methods have been used in previous theoretical studies of the spectra of CdSe dots, such as the tight-binding method,[16] the effective mass approximation (EMA) model,[12] the plane-wave semiempirical pseudopotential method with nonlocal potential,[4] etc. There have been clear discrepancies between previous theoretical results and experimental data. For example, the energies of excitons in CdSe crystallites obtained by using a plane-wave semiempirical pseudopotential method[4] are not in good agreement with the experimental data. The recent calculated results by Marin *et al.*[12] based on the EMA are closer to the experimental data only for exciton radius $r_0 > 1.7$ nm, but differs obviously with experimental data in the strong-confinement regime. We believe that the discrepancies in EMA method[12] come from:(1) the trial wave function is too simple to describe the complex states of the excitons reasonably; (2) the penetration(or leaking) of the charge carriers to the outside of the dot is not considered. However, the effective Bohr radius is about 4.0 nm for the small effective masses of the electron and hole, the penetration should not be neglected; (3) the difference in dielectric constants between the inside and outside regions of the dot and the size-dependence of dielectric constant are neglected.

In this paper, we report the results of a variational calculation of the ground state energy of CdSe dots. We assume that the electron and hole confined in a sphere with a finite potential barrier. The penetration of the charge carriers to the outside of the dot and the difference in dielectric constant between the dots and the surrounding material are taken into consideration. Kinetic energy is treated by the EMA. The

radial wave function for the two-particle system is expanded by using finite B-spline bases, which have been recently applied to the calculation of atomic properties successfully.[23−30] To our knowledge, it is the first time to use the B-spline technique to describe the status of the confined excitons in dots.

## II. THE METHOD OF CALCULATION

The exciton consists of a conduction-band electron and a valence-band positive hole $h^+$. Let $m_1$ and $m_2$ be the effective masses of the electron and the hole. The effect of interaction of the electron and hole with the lattice is such that $m_1$ and $m_2$ are usually less than the free-electron mass $m_0$. The Hamiltonian for the system of exciton is

$$H = E_{\rm gap} - \frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 - \frac{e^2}{4\pi\varepsilon_0\varepsilon r_{12}} + V_1 + V_2, \tag{1}$$

where

$$\frac{1}{r_{12}} = \sum_{l=0}^{\infty}\frac{4\pi}{2l+1}\frac{r_<^l}{r_>^{l+1}}\sum_{m=-l}^{l}Y_{lm}^*(\hat{r}_1)Y_{lm}(\hat{r}_2). \tag{2}$$

In Eq(1), $\varepsilon$ is the dielectric constant, $\boldsymbol{r}_1, \boldsymbol{r}_2$ are the position vectors of the electron and hole relative to the center of the sphere, and $E_{\rm gap}$ is the bulk gap energy. Let $\varepsilon = \varepsilon_1$ for both $r_1$ and $r_2 < r_0$($r_0$ is the radius of the quantum dots), $\varepsilon = \varepsilon_2$ for both $r_1$ and $r_2 > r_0$, and $\varepsilon = (\varepsilon_1\varepsilon_2)^{1/2}$ is assumed to be the dielectric constant for $r_1 < r_0$ and $r_2 > r_0$ or $r_1 > r_0$ and $r_2 < r_0$. $V_1$ and $V_2$ are the barrier heights of the confining potential of the dot for the electron and hole, respectively. It is assumed that $V_1 = V_2 = V$ and $V$ be a square barrier; i.e., $V = 0$ if $r_i < r_0 (i = 1, 2)$, and $V = V_0$ if $r_i > r_0$. The polarized energy of the dot is very small,[7] and it is assumed to be included in $V_0$ in this paper. A trial wave function of the system can be introduced as

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \sum_{K_1K_2} C_{K_1K_2} f_{K_1}(r_1) f_{K_2}(r_2) \Theta_{l_1l_2}^{L0}(\hat{r}_1, \hat{r}_2), \tag{3}$$

where

$$\Theta_{l_1l_2}^{L0}(\hat{r}_1, \hat{r}_2) = \sum_{m_1m_2} C_{l_1m_1l_2m_2}^{L0} Y_{l_1m_1}(\hat{r}_1) Y_{l_2m_2}(\hat{r}_2), \tag{4}$$

$C_{l_1m_1l_2m_2}^{L0}$ is the Clebsch-Gordan coefficient. $Y_{l_im_i}(r_i)$ is the spherical harmonics. $L$ is the total orbital angular momentum. The radial basis function for the two particles is

$$f_K(r) = r^l \mathrm{e}^{-\beta r} B_{n,k}(r), \tag{5}$$

$K$ denotes the set $K = \{n, l\}$, and $B_{n,k}(r)$ are the B-spline function of order $k$. In Eq.(5), the two factors in front of $B_{n,k}(r)$ are necessary to describe the asymptotic behaviour; $\beta$ is an adjustable variational parameters. The characteristic of the B-spline function is that it is highly localized. Each B-spline function is only distributed in a specified region, which can be easily changed by adjusting the knot sequence. For a knot sequence on the $r$ axis $\{t_1 \le t_2 \le t_3 \le \cdots \le t_n \le t_{n+1}, \cdots, \le t_{N+k}\}$, B-spline function of order $k$ is defined as

$$B_{j,k}(r) = \frac{r - t_j}{t_{j+k-1} - t_j} B_{j,k-1}(r) + \frac{t_{j+k} - r}{t_{j+k} - t_{j+1}} B_{j+1,k-1}(r), \tag{6}$$

where $B_{j,k}(r)$ is a piecewise polynomial of degree $(k-1)$ that vanishes except in the interval $t_j \le r < t_{j+k}$, with $B_{j,1}(r) = 1$ for $t_j \le r < t_{j+1}$ and $B_{j,1}(r) = 0$ for $r < t_i$ or $r \ge t_{j+1}$. When a function is expanded by a set of splines, one can choose a suitable set of knots according to the distribution of the function. In this paper, the sequence of the knots is adopted as $\{0 = t_1 = t_2 = t_3 \cdots = t_k \le \cdots \le t_n \le t_{n+1} \cdots \le t_{n+k} = R\}$ in the interval between $r = 0$ and $r = R$, where the first $k$ knots overlap with each other. There are more knot points near the origin and less near the boundary $R$ of the wave function.

It has been believed that the dielectric constant depends on the size of the dot.[4] A simple formula for the size-dependent dielectric constant $\varepsilon^{\rm dot}(r_0)$ of the dot is

$$\frac{1}{\varepsilon^{\rm dot}(r_0)} = \frac{1}{\varepsilon_\infty^{\rm dot}(r_0)} - \chi(r_0) \cdot \left[\frac{1}{\varepsilon_\infty^{\rm dot}(r_0)} - \frac{1}{\varepsilon_\infty^{\rm dot}(r_0) + 3.5}\right], \tag{7}$$

where

$$\varepsilon_\infty^{\rm dot}(r_0) = 1 + (\varepsilon_\infty^{\rm bulk} - 1)/[1 + (0.375{\rm nm}/r_0)^{1.2}], \tag{8}$$

in which $\varepsilon_\infty^{\rm bulk}$=6.2 is the bulk dielectric constant for CdSe,[4] $\chi(r_0)$ indicates how much the ions have participlated in the exciton screening, for example, $\chi(r_0)$=0.348, 0.282, 0.212, and 0.139 for $r_0$=1.923 nm, 1.4625 nm, 1.032 nm, and 0.6395 nm, respectively.[4] By using Eqs.(7) and (8), the curves of $\varepsilon_\infty^{\rm dot}(r_0)$ and $\varepsilon_1 = \varepsilon^{\rm dot}(r_0)$ vs $r_0$ are plotted in Fig.1.

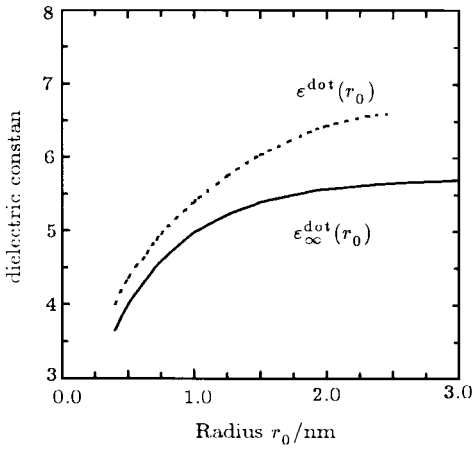



**Fig.1.** The size -dependent dielectric constant.

The Schrödinger equation in matrix form is

$$H\,C = E\,S\,C,$$

where $E$ and $C$ are eigenvalues and eigenvectors. $H$ and $S$ are the Hamiltonian matrix and the overlap matrix of the basis functions. We will obtain energy eigenvalues by diagonalizing the Hamiltonian matrix.

## Ⅲ. RESULTS AND DISCUSSION

We have calculated the exciton energies using a 312×312 matrix and made a comparison with the experimental data in Ref.[4]. The values of $m_1 = 0.135m_0$, $m_2 = 0.410m_0$, the same as in Ref.[12], have been chosen.

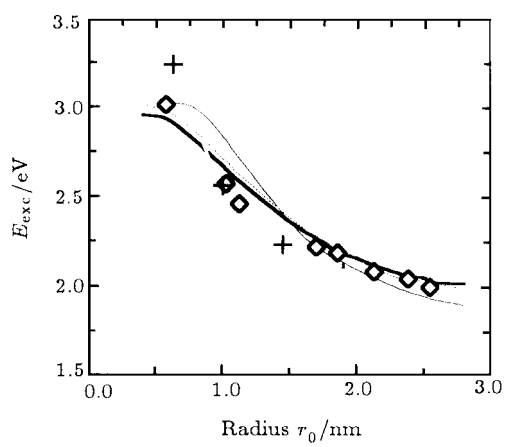



**Fig.2.** The exciton energy vs radius of the CdSe dots. The diamonds stand for experimental data in Ref.[4]. The pluses and the thin solid line stand for the calculated results in Refs.[4] and Ref.[12] and in this paper, respectively. The thick solid line and the dashed line stand for the calculated results in this paper.

Figure 2 shows the experimental values (diamonds) and theoretical predictions of the exciton ground state energies of the CdSe dots of various sizes. The thin solid line represents the theoretical prediction calculated based on the effective mass approximation (EMA)[12] with the set of parameters $V_1 = V_2 = V_0 = 1.30\,\text{eV}$, $m_1 = 0.13m_0$, and $m_2 = 0.41m_0$. The pluses represent the theoretical prediction calculated based on the plane-wave semiempirical pseudopotential method.[4] In the above two cases, the behaviors of the curves differ obviously with the experimental data. The thick solid line represent our theoretical prediction calculated by using the B-spline technique, corresponds to $\varepsilon_2 = 1.5$, and $E_{\text{gap}} = 1.74\text{eV}$.[5] In particular, the size-dependence given by Eq.(7) has been taken into acount. Keeping $m_1$, $m_2$, $\varepsilon_1$ (see Fig 1.), and $\varepsilon_2$ invariant in this calculation, we adjust the parameter $V_0$=0.68 eV so that the resulting energies are in better agreement with the experimental data for radius in the whole range of 0.5–3.0 nm. It turns out that, when the radius becomes very small, the exciton energy tends to an almost finite value (2.96 eV), and the slope of the thick solid curve in Fig.2 becomes almost zero. This indicates that the confining force decreases as radius $r_0 < 0.75\,\text{nm}$.

One might ask how serious is the effect of the size dependence of the dielectric constant $\varepsilon_1$. When we do not consider the size-dependence of dielectric constant and let $\varepsilon_1$=6.2 (bulk dielectric constant), the energies obtained (the dashed line in Fig.2) are different from the results of the thick solid line by about 0.05 eV in the region $r_0 < 1.0\,\text{nm}$. Thus we conclude that the size-dependence, as discussed by some authors, brings on an obvious change in exciton energy for small radius.

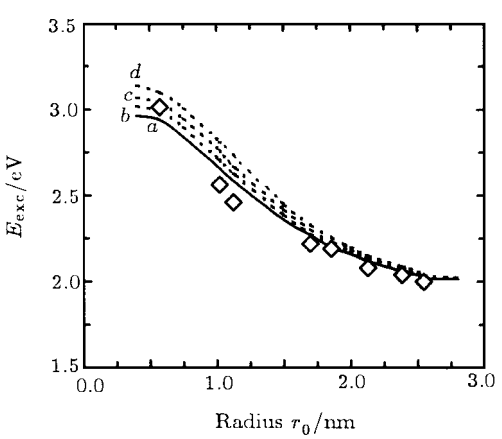



**Fig.3.** The exciton energy vs $\varepsilon_2$. The curves $a, b, c$ and $d$ correspond to $\varepsilon_2$=1.5, 3.0, 6.0 and 12.0, respectively.

Figure 3 shows the increase of energies as $\varepsilon_2$ increases. We see in Fig.3 that the energies are a little

more sensitive to $\varepsilon_2$ for small $\varepsilon_2$ that for large $\varepsilon_2$ in the region $r_0$ <1.5 nm.

Let us define the Coulomb interaction energy as

$$E_{\mathrm{C}} = \langle \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) | \frac{e^2}{4\pi\varepsilon_0\varepsilon r_{12}} | \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) \rangle.$$

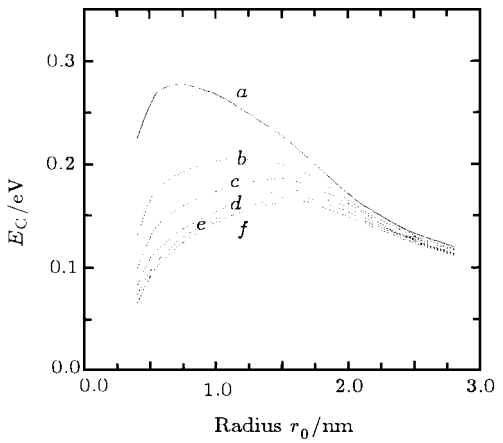



**Fig.4.** Coulomb interaction energy as a function of $\varepsilon_2$. The curves $a, b, c, d, e$ and $f$ correspond to $\varepsilon_2$=1.5, 3.0, 4.5, 6.0, 7.5 and 9.0, respectively.

It is shown in Fig.4 that $E_{\mathrm{C}}$ decreases as $\varepsilon_2$ increases, and the rate of decrease is fast for small $\varepsilon_2$, but becomes slow for large $\varepsilon_2$. We see that in region $r_0$ <0.75 nm, for example on curve $a$, the Coulomb interaction energies drop rapidly as $r_0$ becomes small. This indicates that the interaction of the two particles becomes weak.

## IV.SUMMARY

From the above results we can reach the following conclusion:

(1) The EMA model with the B-splines technique can describe the status of confined exciton very well. The calculated exciton energies are in good agreement with the experimental data with an error about 0.04 eV in the whole confinement regime. (2) The effect of penetration and distinction in dielectric constant in different regions are necessary to be taken into account in calculating the Coulomb interaction energy and reproducing experimental data. (3) The method with B-spline technique leads to accurate and convergent results of the excition energy, and can be used to study exited state also. (4) The size-dependence of dielectric constant is not a very important effect for this kind of systems.

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