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Excitons in quantum-dot quantum-well nanoparticles

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A variational calculation is presented for the ground-state properties of excitons confined in spherical core-shell quantum-dot quantum-well (QDQW) nanoparticles. The relationship between the exciton states and structure parameters of QDQW nanoparticles is investigated, in which both the heavy-hole and the light-hole exciton states are considered. The results show that the confinement energies of the electron and hole states and the exciton binding energies depend sensitively on the well width and core radius of the QDQW structure. A detailed comparison between the heavy-hole and light-hole exciton states is given. Excellent agreement is found between experimental results and our calculated $1s_e$–$1s_h$ transition energies.

Keywords: excitons, quantum-dot quantum-well, nanoparticle
PACC: 7135

1. Introduction

During the past few years semiconductor quantum-dot quantum-well (QDQW) nanoparticles have attracted much attention due to their interesting physics and possible electronic and optical applications.[1−9] The so-called QDQW nanoparticle is typically a spherical core-shell three-layer heterostructure composed of two different semiconductor materials, in which the material with the smaller bulk bandgap is embedded between a core and an outer shell made of the larger bandgap material (see Fig.1).[1,2] The QDQW nanoparticle can also be regarded as a complicated semiconductor quantum-dot (QD) structure with a smaller bandgap layer in its core acting as an internal well. In a QDQW, the introduction of the smaller bandgap shell layer gives rise to a significant redistribution of the electron and hole wavefunctions and can be expected to bring about a certain radial separation of the electron and hole wavefunctions,[3,4] which is different from that in a simple QD structure.[10−12] The QDQW nanoparticles provide the flexibility to tailor the electron and hole wavefunctions in a QD by changing the core diameter, the thicknesses of the well and of the outermost shell, which amounts to a three-dimensional example of wavefunction engineering. The electron transition energies can also be tuned. The radial separation of the electron and hole wavefunctions in a QDQW is expected to lead to a long lifetime exciton with a large dipole moment, thus enhancing nonlinear optical properties of QDQW nanoparticles.[4] All these unique properties of QDQW nanoparticles have stimulated intensive theoretical and experimental research in recent years.

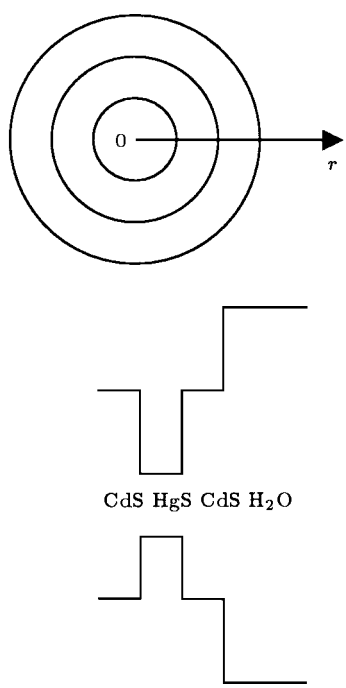


Fig.1. A schematic drawing of a CdS/HgS/CdS QDQW nanoparticle in dielectric water.

The first example of a successful synthesis of QDQW nanoparticles used a CdS/HgS/CdS material

system with a size-quantized CdS particle with a diameter of 4.7 nm acting as a core and a complete layer of HgS on the surface of this core followed by, again, CdS as the outermost shell embedded in water as the dielectric environment (shown in Fig.1).[1,2] This work paved the way for further theoretical and experimental investigations of QDQW nanoparticle physics. To date, most theoretical works have used the effective mass approximation and have neglected the mixing of heavy-hole (hh) and light-hole (lh) states.[2−6,8] Within the framework of the effective mass approximation, Mews *et al*[2] investigated the $1s_e$–$1s_h$ electronic transition energy in CdS/HgS/CdS particles, in which the Coulomb interaction between the electron and hole was ignored. Haus *et al*[3] studied the electron and hole wavefunctions, the shift of bandgap energy, and the overlap of wavefunctions using the infinite barrier approximation at the QDQW nanoparticle boundary. Chang and Xia[4] investigated the electronic structure, the overlap of the electron and hole wavefunctions and the exciton states of semiconductor QDQW nanoparticles using a numerical diagonalization method and adopting an infinite barrier approximation at the nanoparticle boundary. In Refs.[3] and [4], the interesting radial separation between the electron and hole wavefunctions in QDQW structures were investigated in detail. Schooss *et al*[5] further investigated, both theoretically and experimentally, the Coulomb interaction energy between the hole and electron and the $1s_e$–$1s_h$ electronic transition energy, considering the finite barrier effect at the nanoparticle boundary. Bryant[6] gave a configuration interaction calculation of exciton states in CdS/HgS/CdS QDQW nanoparticles. In Refs.[2]–[6], the heavy-hole states were not considered. Quite recently, a multi-band calculation of electron and hole states in QDQW nanoparticles has also been developed.[7] Good agreement between experiment and the effective mass theory shows that the envelope function approximation is suitable for describing the electron and hole states in QDQW nanoparticles containing layers as thin as one monolayer, as pointed out in Refs.[2]–[8] and [13], and thus it has been widely adopted, for example in Refs.[2]–[8]. The valence band mixing effect, as stated by Chang and Xia,[4] is weak for QDQW nanoparticles, less than 10 nm in diameter, and also strongly supported by the cluster band structure calculations.[14−16] Hence, the valence band mixing effect has been neglected in the investigations of the exciton states in QDQW nanoparticles in Refs.[2]–[6].

It is well known that one of the most interesting novel features of a QDQW nanoparticle is the electronic transition between the electron and hole states localized in its internal well layer. This transition gives rise to a new bandgap observed experimentally, referred to as the 1s–1s transition in Refs.[2]–[5]. So far, all of the reported experimental results have concentrated on the 1s–1s electronic transition energy in QDQW nanoparticles with a narrow internal well layer less than three monolayers in thickness.[2,5], Thus, in this paper we concentrate on the 1s state with the main quantum number $n = 1$ and the angular momentum quantum number $l = 0$. This state is significant due to the localization of the electron and hole wavefunctions in the quantum well (QW) layer, leading to a large optical matrix element and strong absorption for the 1s–1s transition in QDQW nanoparticles.[2−5] Furthermore, in commonly used QDQW samples with narrow internal well layers, the 1s state is the only confined state in the internal well layer.

In this paper, we present a variational calculation for the ground-state properties of excitons confined in a spherical QDQW nanoparticle. In our theory, both the finite value of the quantum confinement potential and the different effective electron and hole masses of the QDQW nanoparticle are explicitly taken into account. Moreover, the heavy-hole states, which have not been investigated in Refs.[2]–[6], are also included in this calculation. For simplicity, we use the effective mass envelope function approximation and neglect the valence band mixing effect, as has been done in Refs.[2]–[6]. We concentrate on the confinement energies of the electron and hole states, the $1s_e$–$1s_h$ transition energy and the exciton binding energy in CdS/HgS/CdS QDQW nanoparticles.

This paper is organized as follows. Our theory describing the electron (hole) states and variational calculation of exciton states in QDQW nanoparticles is outlined in section 2. Numerical results for electron and hole states, exciton binding energies, and a detailed comparison of the experimentally and theoretically determined $1s_e$–$1s_h$ transition energies are given in section 3. Finally, in section 4, we summarize the main conclusions obtained in this work.

2. Theory

2.1. Electron and hole states

We consider a spherical QDQW nanoparticle embedded in water used as the dielectric environment (see Fig.1). Within the framework of the effective mass envelope function approximation, the wavefunction of the electron (hole) states confined in a QDQW nanoparticle has the following general form

$$\psi_j(r,\theta,\phi) = R_j(r)Y_{lm}(\theta,\phi), \tag{1}$$

where $Y_{lm}(\theta,\phi)$ are spherical harmonics. $R_j(r) \equiv \chi_j(r)/r$ is the radial wavefunction, and $\chi_j(r)$ satisfies the following radial wave equation

$$\frac{\mathrm{d}^2}{\mathrm{d}r^2}\chi_j(r) + \left[\frac{2m_j(r)}{\hbar^2}(E_j - v_j(r)) - \frac{l(l+1)}{r^2}\right]\chi_j(r) = 0,$$

$$\chi_j(r) \overset{r\to 0}{\longrightarrow} 0, \tag{2}$$

where $m_j(r)$ is the electron (hole) band mass given by

$$m_j(r) = \begin{cases} m_{1j}, & 0 < r < r_1, \\ m_{2j}, & r_1 < r < r_2, \\ m_{3j}, & r_2 < r < r_3, \\ m_{4j}, & r > r_3. \end{cases} \tag{3}$$

The confinement potential $v_j(r)$ is given as

$$v_j(r) = \begin{cases} v_{1j}, & 0 < r < r_1, \\ v_{2j}(=0), & r_1 < r < r_2, \\ v_{3j}, & r_2 < r < r_3, \\ v_{4j}, & r > r_3, \end{cases} \tag{4}$$

where the subscripts $j =$ e, hh, lh denote the electron, heavy hole or light hole, respectively.

We have pointed out in section 1 that the 1s state in QDQW nanoparticles is the most important state, especially when the QDQW nanoparticle contains a narrow QW layer, as common in experiments. We will thus restrict the calculations to the 1s state, as has been done in Refs.[1]–[7]. For the 1s state with $l = m = 0$, the spherical harmonic $Y_{00}(\theta,\phi)$ yields only a constant factor of $1/\sqrt{4\pi}$. The solution of Eq.(2) for the 1s state takes the following form

$$\chi_j(r) = \begin{cases} C_{1j}\sinh(k_{1j}r), & 0 < r < r_1, \\ C_{2j}\sin k_{2j}(r - r_1) + C_{3j}\cos k_{2j}(r - r_1), & r_1 < r < r_2, \\ C_{4j}\mathrm{e}^{k_{3j}(r-r_2)} + C_{5j}\mathrm{e}^{-k_{3j}(r-r_2)}, & r_2 < r < r_3, \\ C_{6j}\mathrm{e}^{-k_{4j}(r-r_3)}, & r > r_3, \end{cases} \tag{5}$$

where k_{ij} is defined as

$$k_{ij} = \sqrt{\frac{2m_{ij}}{\hbar^2}|v_{ij} - E_j|}, \quad i = 1,2,3,4 \ \text{ and } \ j = e, \mathrm{hh}, \mathrm{lh}. \tag{6}$$

We use the boundary condition that $\dfrac{1}{m_{ij}}\left(\dfrac{\mathrm{d}\ln\chi_j(r)}{\mathrm{d}r} - \dfrac{1}{r}\right)$ is continuous at the interfaces $r = r_1, r_2, r_3$. This is equivalent to taking both $R_j(r)$ and $\dfrac{1}{m_{ij}}\dfrac{\mathrm{d}R_j(r)}{\mathrm{d}r}$ as continuous.[2,3,5] We then obtain

$$\begin{aligned} & m_{3j}(f_3 + f_4)[(k_{2j}r_2 f_1 - f_2)\cos k_{2j}(r_2 - r_1) \\ & - (f_1 + k_{2j}r_2 f_2)\sin k_{2j}(r_2 - r_1)] \\ & + m_{2j}\left[(1 - k_{3j}r_2)f_3 + (1 + k_{3j}r_2)f_4\right] \\ & \cdot [f_1\sin k_{2j}(r_2 - r_1) + f_2\cos k_{2j}(r_2 - r_1)] = 0. \end{aligned} \tag{7}$$

This equation determines the ground-state confinement energy E_j of the electron or hole in the QDQW potential Eq.(4). Using Eq.(7) is more convenient for numerical calculations in investigating electron transitions and optical absorption than previously.[3–5] The quantity f_i $(i = 1,2,3,4)$ in Eq.(7) is defined as

$$\begin{aligned} f_1 &= \frac{m_{2j}}{m_{1j}}k_{1j}r_1 + \left(1 - \frac{m_{2j}}{m_{1j}}\right)\tanh(k_{1j}r_1), \\ f_2 &= k_{2j}r_1\tanh(k_{1j}r_1), \\ f_3 &= \left[(1 - \frac{k_{4j}}{k_{3j}}\frac{m_{3j}}{m_{4j}})k_{3j}r_3 + (1 - \frac{m_{3j}}{m_{4j}})\right]\mathrm{e}^{-2k_{3j}r_3}, \\ f_4 &= \left[(1 + \frac{k_{4j}}{k_{3j}}\frac{m_{3j}}{m_{4j}})k_{3j}r_3 - (1 - \frac{m_{3j}}{m_{4j}})\right]\mathrm{e}^{-2k_{3j}r_2}. \end{aligned} \tag{8}$$

The function $\chi_j(r)$ can be normalized as follows:

$$\int_0^\infty \chi_j^2(r)\mathrm{d}r = 1. \tag{9}$$

2.2. Variational calculation of the exciton states

In order to investigate the ground-state properties of excitons confined in a spherical QDQW nanopar-

ticle, it is convenient to use triangular coordinates (r_e, r_h, r_{eh}) defined by[17–19]

$$r_e = |\boldsymbol{r}_e|, \quad r_h = |\boldsymbol{r}_h|, \quad r_{eh} = |\boldsymbol{r}_e - \boldsymbol{r}_h|, \tag{10}$$

where $\boldsymbol{r}_e$ ($\boldsymbol{r}_h$) is the position vector of the electron (hole) with the origin at the centre of the QDQW nanoparticle.

Within the framework of the effective mass approximation, the Hamiltonian of excitons confined in a spherical QDQW nanoparticle can be written as[19]

$$\begin{aligned}\hat{H} =& -\frac{\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial r_e^2} + \frac{2}{r_e}\frac{\partial}{\partial r_e} + \frac{r_e^2 - r_h^2 + r_{eh}^2}{r_e r_{eh}}\frac{\partial^2}{\partial r_e \partial r_{eh}}\right) \\ & - \frac{\hbar^2}{2m_h}\left(\frac{\partial^2}{\partial r_h^2} + \frac{2}{r_h}\frac{\partial}{\partial r_h} + \frac{r_h^2 - r_e^2 + r_{eh}^2}{r_h r_{eh}}\frac{\partial^2}{\partial r_h \partial r_{eh}}\right) \\ & - \frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r_{eh}^2} + \frac{2}{r_{eh}}\frac{\partial}{\partial r_{eh}}\right) \\ & + v_e(r_e) + v_h(r_h) - \frac{e^2}{4\pi\varepsilon_0\bar{\varepsilon} r_{eh}},\end{aligned} \tag{11}$$

where $\mu = \left(\frac{1}{m_e} + \frac{1}{m_h}\right)^{-1}$ is the reduced mass of the exciton, ε_0 is the permittivity of free space and $\bar{\varepsilon}$ is the effective mean relative dielectric constant of the embedding material between the electron and hole.[5–7]

As we have analysed in section 1, in commonly used QDQW samples with narrow internal well layers, the 1s state is the only confined state in the well. In experimental studies of QDQW nanoparticles, the most interesting electronic transition is the $1s_e$–$1s_h$ transition between the electron 1s state and the hole 1s state with the angular momentum quantum number $l = 0$. Thus, when we build a trial wavefunction for the exciton ground state confined in QDQW nanoparticles, the angular correlation between the electron and hole will be ignored, which has also been confirmed by Ref.[6]. Moreover, we know that the QDQW nanoparticle can also be regarded as a complicated QD structure with a smaller bandgap layer in its core acting as an internal well. Both the QDQW and the QD structures have a spherically symmetric potential. Hence the exciton trial wavefunction in QDQW nanoparticles can be built from the corresponding trial wavefunction in QD structures. Considering the above two factors, we have chosen the exciton trial wavefunction in a QDQW nanoparticle to have the following form

$$\psi(r_e, r_h, r_{eh}) = e^{-\lambda r_{eh}} R_e(r_e) R_h(r_h), \tag{12}$$

where λ is the variational parameter, and the functions $R_e(r_e)$ and $R_h(r_h)$ are the radial eigenfunctions of the electron and the hole, respectively. The variational wavefunction (12) can be regarded as an extension of the formalism of Refs.[18] and [20] in a simple QD structure. As a trial function, Eq.(12) has the advantage of having a simple form. It was also shown that it can give a good description for the exciton states confined in QD structures.[18,20] Our numerical calculations (see Fig.2) clearly show that the $1s_e$–$1s_h$ electronic transition energies calculated using Eq.(12) are in excellent agreement with the experimental results, confirming that the chosen trial wavefunction (12) describes accurately the exciton states confined in spherical QDQW nanoparticles.

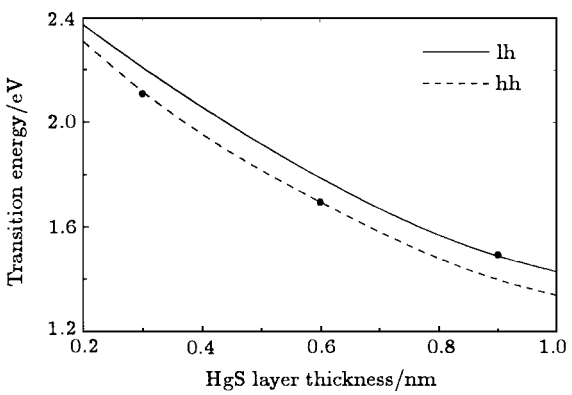


Fig.2. The calculated $1s_e$–$1s_h$ transition energy in CdS/HgS/CdS QDQW nanoparticles, with the CdS core diameter of 4.7 nm and the outermost CdS shell thickness of 0.6 nm as a function of the HgS layer thickness. Experimental results taken from Ref.[2] are shown as black dots (•).

The ground-state energy of an interacting electron–hole pair is computed from the expectation value of the Hamiltonian (11) with the trial wavefunction (12). After a lengthy calculation, we obtain the energy of an exciton confined in QDQW nanoparticles as follows

$$\begin{aligned}E_{\text{exciton}} =& \min_{\lambda}\left[\frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle}\right] \\ =& E_e + E_h + \min_{\lambda}\left[\hbar^2\lambda^2 \cdot I(\lambda)\right],\end{aligned} \tag{13}$$

where E_e (E_h) is the electron (hole) confinement energy and can be directly obtained by solving Eq.(7) numerically. The exciton binding energy is obtained from

$$E^B = E_e + E_h - E_{\text{exciton}} = -\min_{\lambda}\left[\hbar^2\lambda^2 \cdot I(\lambda)\right]. \tag{14}$$

The function $I(\lambda)$ in Eqs.(13) and (14) is defined

as

$$I(\lambda)=\frac{\int_0^\infty \mathrm{d}r_\mathrm{e}\int_0^\infty \mathrm{d}r_\mathrm{h} S_1(r_\mathrm{e},r_\mathrm{h};\lambda)}{\int_0^\infty \mathrm{d}r_\mathrm{e}\int_0^\infty \mathrm{d}r_\mathrm{h} S_2(r_\mathrm{e},r_\mathrm{h};\lambda)}, \quad (15)$$

where

$$\begin{aligned} &S_1(r_\mathrm{e},r_\mathrm{h};\lambda)\\ =&R_\mathrm{e}(r_\mathrm{e})R_\mathrm{h}(r_\mathrm{h})\{r_\mathrm{e}r_\mathrm{h}R_\mathrm{e}(r_\mathrm{e})R_\mathrm{h}(r_\mathrm{h})\\ &\times[L_1(r_\mathrm{e}+r_\mathrm{h})-L_1(|r_\mathrm{e}-r_\mathrm{h}|)]\\ &-(r_\mathrm{e}^2-r_\mathrm{h}^2)\left(\mathrm{e}^{-2\lambda(r_\mathrm{e}+r_\mathrm{h})}-\mathrm{e}^{-2\lambda|r_\mathrm{e}-r_\mathrm{h}|}\right)L_-\\ &-\frac{1}{2\lambda^2}L_+\left[L_2(r_\mathrm{e}+r_\mathrm{h})-L_2(|r_\mathrm{e}-r_\mathrm{h}|)\right]\}, \end{aligned} \quad (16)$$

and

$$\begin{aligned} &S_2(r_\mathrm{e},r_\mathrm{h};\lambda)\\ =&r_\mathrm{e}r_\mathrm{h}R_\mathrm{e}^2(r_\mathrm{e})R_\mathrm{h}^2(r_\mathrm{h})\left[L_3(|r_\mathrm{e}-r_\mathrm{h}|)-L_3(r_\mathrm{e}+r_\mathrm{h})\right]. \end{aligned} \quad (17)$$

The functions of $L_1(x)$, $L_2(x)$ and $L_\pm$ in Eq.(16) and $L_3(x)$ in Eq.(17) are defined as

$$\begin{aligned} L_1(x)&=\mathrm{e}^{-2\lambda x}\left(\frac{e^2}{2\pi\varepsilon_0\lambda\hbar^2\bar{\varepsilon}}+\frac{1}{\mu}\lambda x-\frac{3}{2\mu}\right),\\ L_2(x)&=\mathrm{e}^{-2\lambda x}\left[2\lambda x(\lambda x+1)+1\right],\\ L_\pm&=\frac{1}{m_\mathrm{e}}r_\mathrm{h}\frac{\mathrm{d}R_\mathrm{e}(r_\mathrm{e})}{\mathrm{d}r_\mathrm{e}}R_\mathrm{h}(r_\mathrm{h})\pm\frac{1}{m_\mathrm{h}}r_\mathrm{e}\frac{\mathrm{d}R_\mathrm{h}(r_\mathrm{h})}{\mathrm{d}r_\mathrm{h}}R_\mathrm{e}(r_\mathrm{e}),\\ L_3(x)&=\mathrm{e}^{-2\lambda x}(2\lambda x+1). \end{aligned} \quad (18)$$

The $1s_e$–$1s_h$ transition energy can be calculated as follows

$$E_{1s-1s}=E_\mathrm{e}+E_\mathrm{h}+E_\mathrm{g}-E^\mathrm{B}=E_\mathrm{exciton}+E_\mathrm{g}, \quad (19)$$

where the energy E_g is the bandgap energy of the well layer material in QDQW nanoparticles.

The average relative distance $\bar{r}_\mathrm{eh}$ between the electron and hole can be defined as

$$\bar{r}_\mathrm{eh}\equiv\frac{\langle\psi|r_\mathrm{eh}|\psi\rangle}{\langle\psi|\psi\rangle}=\frac{1}{\lambda}\frac{\int_0^\infty \mathrm{d}r_\mathrm{e}\int_0^\infty \mathrm{d}r_\mathrm{h} S_3(r_\mathrm{e},r_\mathrm{h};\lambda)}{\int_0^\infty \mathrm{d}r_\mathrm{e}\int_0^\infty \mathrm{d}r_\mathrm{h} S_2(r_\mathrm{e},r_\mathrm{h};\lambda)}, \quad (20)$$

where

$$\begin{aligned} &S_3(r_\mathrm{e},r_\mathrm{h};\lambda)\\ =&r_\mathrm{e}r_\mathrm{h}R_\mathrm{e}^2(r_\mathrm{e})R_\mathrm{h}^2(r_\mathrm{h})[L_2(|r_\mathrm{e}-r_\mathrm{h}|)-L_2(r_\mathrm{e}+r_\mathrm{h})]. \end{aligned} \quad (21)$$

The parameter λ in Eq.(20) can be determined by the variational calculation from Eq.(14).

It is worth pointing out that the above theory can easily be extended to more complicated QDQW structures with a larger number of layers.

3. Numerical results and discussion

We have performed numerical calculations for the exciton states confined in the CdS/HgS/CdS QDQW nanoparticles embedded in water used as the dielectric environment by employing the above theory. The material parameters used in the calculation are listed in Table 1.

Table 1. The material parameters used in this work. m_e, m_lh and m_hh are the effective masses of electrons, light holes and heavy holes in units of the free electron mass; ε is the dielectric constant; E_g is the bandgap; and V_CB and V_VB are the conduction and the valence band offsets, respectively.

Material	m_e	m_lh	m_hh	ε	E_g/eV	V_CB/eV	V_VB/eV
CdS	0.2[2,4–6]	0.7[2,4–7]	5.0[7]	5.5[4–6]	2.5[2,4–7]	1.35[2,4,6]	0.65[2,4]
HgS	0.036[2,4–6]	0.044[2,5,6]	0.31[7]	11.36[4–6]	0.5[2,4–6]		
H_2O	1[7]	1[7]	1[7]	1.78[4–6]	8[7]	3.75[7]	3.75[7]

* The number(s) in the bracket refers to the reference number

For the chosen seven CdS/HgS/CdS QDQW structures, the calculated confinement energies for the electron, light hole and heavy hole are shown in Table 2. Table 3 summarizes our calculated results for the $1s_e$–$1s_h$ transition energies. For the purpose of comparison, some theoretical and experimental results are also shown in Table 3. We can see from Table 3 that our variational calculation results for the light-hole exciton $1s_e$–$1s_h$ transition energies are in good agreement with the previous theoretical calculations of Refs.[4] and [5], indicating that our variational wavefunction (12) is suitable for the exciton states confined in QDQW nanoparticles. Moreover, Table 3 suggests that the experimental results for the $1s_e$–$1s_h$ electronic transition energies for samples 1–3 can be explained as due to heavy-hole exciton transitions. The corresponding results for samples 4–7 are attributed to the light-hole exciton $1s_e$–$1s_h$ transition. Table 3 clearly

shows that the previous theoretical results in Refs.[4] and [5] have also been significantly improved by our variational calculations. For example, the experimental result for the $1s_e$–$1s_h$ transition energy for sample 1 is 2.10 eV, while our calculation gives 2.17 eV with an error of 3.3%. The corresponding value calculated in Ref.[5] is 2.27 eV with an error of 8.1%. Reference [4] gives an even higher transition energy of 2.31 eV with an error of 10%.

Table 2. The CdS/HgS/CdS QDQW sample parameters and the corresponding confinement energies for the electron (E_e), light hole (E_{lh}) and heavy hole (E_{hh}).

Sample	CdS core diameter/nm	HgS layer thickness/nm	CdS layer thickness/nm	E_e/meV	E_{lh}/meV	E_{hh}/meV
1	4.7	0.3	0.3	1238.77	609.51	509.26
2	4.7	0.3	1.0	1202.62	541.83	469.16
3	4.7	0.3	1.5	1195.76	536.54	468.30
4	4.7	0.6	0.3	937.68	442.49	325.41
5	4.7	0.9	0.3	732.03	337.92	229.45
6	4.7	0.9	1.5	745.38	307.24	219.28
7	4.7	0.9	2.2	745.51	307.18	219.28

Table 3. The $1s_e$–$1s_h$ transition energies for the chosen seven CdS/HgS/CdS QDQW samples given in Table 2. Columns 2 (lh) and 3 (hh) show the present calculated transition energies. The previous theoretical results are given in column 4. The experimental results are shown in column 5. All of the transition energies are given in units of eV.

Sample	$1s_e$–$1s_h$ (lh)	$1s_e$–$1s_h$ (hh)	$1s_e$–$1s_h$ (Theor.)	$1s_e$–$1s_h$ (Expt.)
1	2.27	2.17	2.31[4], 2.27[5]	2.10[5]
2	2.17	2.11	2.16[5]	1.96[5]
3	2.16	2.10	2.15[5]	1.94[5]
4	1.81	1.70	1.9[4], 1.83[5]	1.76[5]
5	1.51	1.40	1.72[4], 1.53[5]	1.60[5]
6	1.50	1.40	1.50[5]	1.55[5]
7	1.50	1.40	1.50[5]	1.54[5]

Figure 2 shows the $1s_e$–$1s_h$ electron transition energy as a function of thickness of the HgS internal well layer in CdS/HgS/CdS QDQW nanoparticles with the CdS core diameter of 4.7 nm and the outermost CdS shell thickness of 0.6 nm. The calculations were carried out for the heavy-hole and light-hole excitons, separately. We can see from Fig.2 that the $1s_e$–$1s_h$ transition energy decreases monotonically with increasing HgS well layer thickness. This is because the confinement energies of the electron and hole states decrease if the well width is increased. Figure 2 also clearly indicates that the transition energy of the heavy-hole exciton is smaller than that of the light-hole exciton. The reason is that the heavy-hole state is more strongly localized in the well than the light-hole state due to the larger effective mass of the heavy hole. Moreover, Fig.2 shows that our numerical results are in excellent agreement with the experimental results of Ref.[2]. This further confirms that the variational wavefunction (12) is an excellent choice for the exciton wavefunction in QDQW nanoparticles. According to Fig.2, the experimental transition energies for the well widths 0.3 and 0.6 nm are due to the heavy-hole exciton transition; in contrast, the corresponding result for the well width 0.9 nm is attributed to the light-hole exciton transition. This result is different from that in Fig.3 of Ref.[6]. Furthermore, the results of Fig.2 also show that the mixing effect of the heavy-hole and light-hole states is weak if the QDQW nanoparticles are smaller than 10 nm in diameter, confirming that the assertion of Refs.[4] and [14]–[16] is reliable. Surprisingly, the effective mass envelope function approximation gives a good description of the electron and hole states confined in the QDQW nanoparticles containing layers as thin as one monolayer, which has also been confirmed by Refs.[2]–[8] and [13].

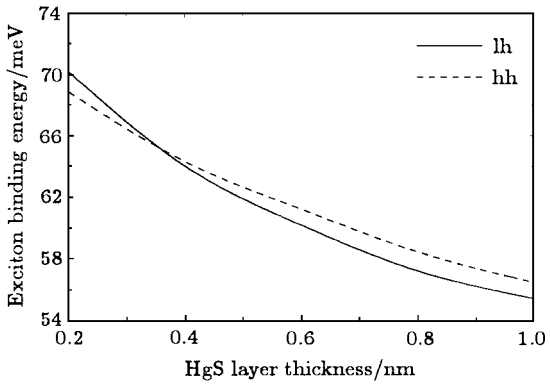


Fig.3. The ground-state exciton binding energy as a function of the HgS well layer thickness in the same CdS/HgS/CdS QDQW structures as in Fig.2.

The results of our calculations of the ground-state exciton binding energy as a function of the HgS well layer thickness are plotted in Fig.3 for the heavy-hole and light-hole excitons in the same CdS/HgS/CdS QDQW nanoparticles as in Fig.2. Figure 3 clearly shows that the exciton binding energy decreases monotonically with increasing HgS layer thickness or, equivalently, the total radius of QDQW nanoparticles, similar to that in simple QD structures.[18,20] In order to understand the results shown in Fig.3, we further calculate the average relative distance $\bar{r}_{\rm eh}$ between the electron and the hole in Fig.4, which determines directly the exciton binding energy. Figure 4 indicates that $\bar{r}_{\rm eh}$ increases with increasing HgS layer thickness or the total radius of the CdS/HgS/CdS QDQW nanoparticles. At the same time, the absolute value of the Coulomb interaction energy between the electron and the hole is reduced. Thus, the exciton binding energy decreases with increasing HgS layer thickness or the radius of the QDQW nanoparticles. The results shown in Fig.3 are also confirmed by Refs.[4] and [6]. Moreover, Fig.3 shows that the binding energy of the heavy-hole exciton becomes larger than that of the light-hole exciton if the well width is larger than 0.3 nm. This can be completely understood on the basis of calculations of the average distance $\bar{r}_{\rm eh}$. Figure 4 indicates that the distance $\bar{r}_{\rm eh}$ between the electron and heavy hole is smaller than that between the electron and light hole if the well width is larger than 0.3 nm. Thus, the exciton binding energy of the heavy hole is larger than that of the light-hole exciton, as shown in Fig.3.

Figures 2–4 show that the electron, hole and exciton states in CdS/HgS/CdS QDQW nanoparticles depend sensitively on the HgS well layer thickness. We have further investigated the relationship between the exciton states and the CdS core size. Our calculations show that the exciton binding energy decreases continuously with increasing CdS core radius in structures with the HgS well layer thickness of 0.6 nm and the outermost CdS shell thickness of 1.0 nm. This is due to an increase in the average distance $\bar{r}_{\rm eh}$ between the electron and hole. When the CdS core radius increases, the confinement energies of the electron and hole are reduced, while the Coulomb interaction between the electron and hole becomes weaker, and thus the $1s_e$–$1s_h$ transition energy remains almost unchanged.

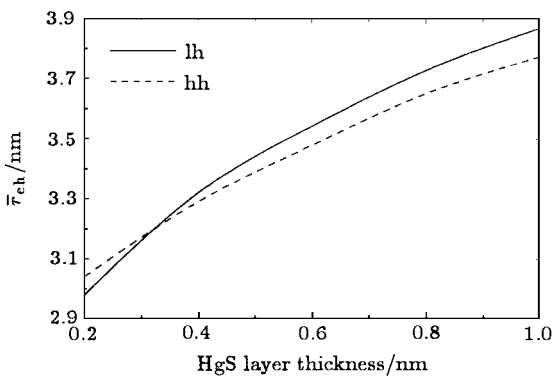


Fig.4. The average relative distance $\bar{r}_{\rm eh}$ between the electron and hole as a function of the HgS well layer thickness in the same CdS/ HgS/ CdS QDQW nanoparticles as in Fig.2.

When the CdS outermost shell thickness is increased, our calculations show that the exciton binding energy is reduced. The $1s_e$–$1s_h$ transition energy is also reduced if the CdS outermost shell thickness $d_{\rm CdS}$ is less than 1.0 nm and can be approximately regarded as a constant if $d_{\rm CdS}$ is larger than 1.0 nm, which has also been confirmed by experiments.[5]

4. Conclusion

In this paper, the Schrödinger equation of the electron (hole) confined in a spherical QDQW nanoparticle has been solved exactly within the framework of the effective mass theory for the most important ground state. An analytical solution has been obtained, which is more convenient for investigating the electron transition and optical absorption than the previous means.[3–5] A variational calculation is presented for the properties of the excitons confined in a spherical QDQW nanoparticle. In our variational calculations, both the heavy-hole and the light-hole states are included. The finite value of the quantum confinement potential and different effective electron

and hole masses of the QDQW nanoparticle are also considered explicitly. Numerical results are given for the CdS/HgS/CdS QDQW nanoparticles. The difference between the heavy-hole and light-hole exciton states is discussed in detail. The average relative distance $\bar{r}_{\rm eh}$ between the electron and hole is calculated. Our calculations show that the electron and hole states depend sensitively on the core radius, the well width and the outermost shell thickness of QDQW nanoparticles. With increasing radius of the core or the shell thickness, or, equivalently, the entire radius of QDQW nanoparticles, the exciton binding energy is reduced and the average relative distance $\bar{r}_{\rm eh}$ between the electron and hole is increased. The exciton binding energy of the heavy hole becomes larger than that of the light-hole exciton for larger well widths (>0.3 nm).

The $1s_e$–$1s_h$ transition energy is calculated variationally. A detailed comparison with some theoretical and experimental results is given. Our results are in excellent agreement with the experimental results. According to the present work, some experimental results can be explained as heavy-hole exciton transitions, and others are interpreted as light-hole exciton transitions. The present theoretical framework can also easily be extended to much more complicated QDQW structures with several layers. This work thus offers a theoretical basis for further investigation of the exciton states in general QDQW nanoparticles. The present calculations also strongly support the fact that the effective mass envelope function approximation is an adequate means to describe the electron and hole states confined in QDQW nanoparticles with layers as thin as one monolayer. The valence band mixing effect is weak for QDQW nanoparticles with a diameter of less than 10 nm. We hope that the present theory may motivate further theoretical and experimental investigations of QDQW nanoparticle physics.

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