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Ground state of excitons in quantum-dot quantum-well nanoparticles: stochastic variational method*

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Within the framework of effective mass approximation, the ground state of excitons confined in spherical core-shell quantum-dot quantum-well (QDQW) nanoparticles is solved by using the stochastic variational method, in which the finite band offset and the heavy (light) hole exciton states are considered. The calculated $1s_e$–$1s_h$ transition energies for the chosen CdS/HgS/CdS QDQW samples are in good agreement with the experimental measurements. Moreover, some previous theoretical results are improved.

Keywords: excitons, CdS/HgS/CdS quantum-dot quantum-well nanoparticles, stochastic variational method

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1. Introduction

Semiconductor quantum dots (QDs) are quantum semiconductor nanostructures, in which charge carriers are confined in a three-dimensional (3D) space. The discrete electron states in QDs can be tailored so as to enhance their optical properties. In recent years, a new type of complicated QD, called quantum-dot quantum-wells (QDQWs) with inhomogeneous internal structures, has attracted much attention due to their interesting physics and potential device applications.[1−12] In the general case, the QDQWs are composed of two different semiconductor materials of which the one with the small bulk band gap is embedded between a core and an outermost shell of the material with the large bulk band gap. The small band gap layer can be regarded as an internal well, which can cause a significant redistribution of the electron and hole wavefunctions, which is different from that in a simple QD structure.[13−15] The transition energy (new band gap[4]) can thus be tuned by the core diameter, the thicknesses of the internal well layer and of the outermost shell. It has been found that the linear absorption of QDQWs differs significantly from that of simple QDs. The characteristics and some linear and nonlinear optical properties of QDQWs have recently been reported.[1−7]

Based on the effective mass envelope function approximation, some theoretical investigations[1,5−7,9−11] have been concluded successively in recent years. Haus *et al*[7] developed a recursive method to calculate the electronic structure of QDQW nanoparticles, in which the Coulomb interaction between the electrons and holes is neglected. 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 outermost boundary of the QDQWs. Schooss *et al*[5] considered a more complicated model, in which the effects of finite band offset at the edge and the Coulomb interaction between the electrons and holes were taken into account. Moreover, Bryant[6] investigated the influence of pair correlation on the electronic structure of QDQW nanoparticles. Recently, Jaskólski and Bryant[9] developed a multiband theory to calculate the electron, hole and exciton states confined in QDQWs. Following Ref.[9], Xie and Bryant[10] fur-

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ther studied the optical excitonic gaps by incorporating the Coulomb and the exchange interactions into an empirical tight-binding model. Quite recently, Shi[11] investigated the light-hole and the heavy-hole exciton states confined in QDQWs. The remarkable effects of the internal well on the electron (hole) and the exciton states in a QDQW nanoparticle have been confirmed in the above-mentioned papers.[1,5−7,9−11]

In this paper, we present a calculation of the ground state of excitons confined in spherical onion-like QDQW nanoparticles by using the stochastic variational method (SVM)[16] with correlated Gaussian bases, in which the Coulomb interaction between the electrons and holes, the finite quantum confinement potential and the different light-hole and heavy-hole masses are all taken into account. The SVM has been widely used in quantum-mechanical few-body problems, especially in the case of simple QDs.[17−20] It has been shown that the SVM provides accurate solutions to some problems.[16] To the best of our knowledge, the present article is the first one to apply the SVM to solve the exciton states in QDQW nanoparticles.

This paper is organized as follows. In Section 2, we give the Hamiltonian of the system and present the SVM solution of the exciton states in a QDQW nanoparticle. In Section 3, numerical results are given and compared with the available experimental measurements and with some previous theoretical calculations. Good agreement with experiments is in evidence. The main conclusions are summarized in Section 4.

2. Theory

2.1. Stochastic variational method

The Hamiltonian describing an exciton confined in a spherical QDQW nanoparticle can be written as

$$H = T_{\rm e} + T_{\rm h} + V_{\rm e} + V_{\rm h} + V_{\rm C}, \tag{1}$$

where $T_i = \mathbf{p}_i^2/2m_i$ is the kinetic operator of the ith particle with the effective mass m_i for the electron ($i = e$) and the hole (i=h), and $V_{\rm e}$ ($V_{\rm h}$) is the quantum well confinement potential of the electron (hole),

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

In Eq.(1), $V_{\rm C}$ is the electron–hole Coulomb interaction potential,

$$V_{\rm C} = -\frac{e^2}{4\pi\varepsilon_0\overline{\varepsilon}}\frac{1}{|\boldsymbol{r}_{\rm e} - \boldsymbol{r}_{\rm h}|}, \tag{3}$$

where $\boldsymbol{r}_{\rm e}$ ($\boldsymbol{r}_{\rm h}$) is the position vector of the electron (hole), e is the electron charge, ε_0 is the permittivity of free space and $\overline{\varepsilon}$ is the effective mean relative dielectric constant of the embedding material between the electron and hole.

In order to solve the Hamiltonian (1), the exciton trial wavefunction in a QDQW nanoparticle can be expanded in terms of correlated Gaussian bases,

$$\psi(\boldsymbol{r}_{\rm e}, \boldsymbol{r}_{\rm h}) = \sum_{n=1}^{K} c_n \varphi_n(\boldsymbol{r}_{\rm e}, \boldsymbol{r}_{\rm h}), \tag{4}$$

where

$$\varphi_n(\boldsymbol{r}_{\rm e}, \boldsymbol{r}_{\rm h}) = \exp\left[-\frac{1}{2}\tilde{R}A_nR\right]. \tag{5}$$

Here the dimension of the basis, K, is increased until the energy is sufficiently accurate. In Eq.(5), the variational parameter A_n is a 2×2 symmetric matrix and is defined as

$$A_n \equiv \begin{pmatrix} A_{11n}, A_{12n} \\ A_{21n}, A_{22n} \end{pmatrix}, \tag{6}$$

and R is a 2×1 matrix,

$$R \equiv \begin{pmatrix} \boldsymbol{r}_{\rm e} \\ \boldsymbol{r}_{\rm h} \end{pmatrix}. \tag{7}$$

In Eq.(5), $\tilde{R}$ is the transpose matrix of R.

The energy E of the system can be obtained by solving the following generalized eigenvalue problem,

$$\sum_{j=1}^{K}(H_{ij} - EO_{ij})c_j = 0, \quad (i = 1, 2, \ldots, K), \tag{8}$$

where the matrix elements H_{ij} and O_{ij} are, respectively, defined as

$$\begin{aligned} H_{ij} &= <\varphi_i|H|\varphi_j>, \\ O_{ij} &= <\varphi_i|\varphi_j>. \end{aligned} \tag{9}$$

The eigenvalues E_1, E_2, ..., which crucially depends on the variational parameters, are variational upper bounds of the energies of the ground and first, second, ... excited states, and can be determined by using the following steps:

2.1.1. Select the first basis function $\varphi_1(\boldsymbol{r}_{\rm e}, \boldsymbol{r}_{\rm h})$

Let N sets of variational parameters $A_1^{(i)}$ (i = 1, 2, ..., N) be generated randomly and the one giving the lowest energy is chosen as the parameter of the

first basis function $\varphi_1(\boldsymbol{r}_\mathrm{e}, \boldsymbol{r}_\mathrm{h})$.

2.1.2. Increase the dimensions of the subspace from $(k-1)$D $(k \geq 2)$ to kD

Suppose the eigenvalue problem in the $(k-1)$D subspace has been solved and the corresponding basis functions φ_i $(i = 1, 2, \ldots, k-1)$ have been obtained. Again, N different sets of variational parameters $A_k^{(i)}$ $(i = 1, 2, \ldots, N)$ are generated randomly. By solving the eigenvalue problem in kD subspace using Eqs.(8) and (9), the corresponding energies $E_k^{(i)}$ $(i = 1, 2, \ldots, N)$ can be obtained. The one that gives the lowest energy is selected as the parameter of the kth basis function $\varphi_k(\boldsymbol{r}_\mathrm{e}, \boldsymbol{r}_\mathrm{h})$. The dimension of the basis, k, is increased until the energy is sufficiently accurate.

2.1.3. Refine the selected basis functions

Basis parameters are optimized by selecting new parameters in the vicinity of the existing ones. In our calculations, this step is implemented by requiring the new random parameters to be in a small interval, for example $[0.8\alpha, 1.2\alpha]$ $(\alpha = A_{11k}, A_{12k}, A_{21k}, A_{22k})$.[21] The step is executed one time when a new parameter set is selected.

2.2. Calculations of the matrix elements

One of the main advantages using the correlated Gaussian bases is that their matrix elements can be calculated analytically. Let us now calculate these matrix elements explicitly. First, the overlap integral between the two correlated Gaussian bases can be calculated as follows,:

$$\langle\varphi_A|\varphi_{A'}\rangle = \left[\frac{(2\pi)^2}{\det(A+A')}\right]^{3/2}. \tag{10}$$

The matrix element of the kinetic energy operator between the two correlated Gaussian bases can be derived as

$$\begin{aligned}&\langle\varphi_A|T_\mathrm{e}+T_\mathrm{h}|\varphi_{A'}\rangle\\ =&\langle\varphi_A|\varphi_{A'}\rangle\left[3\mathrm{Tr}(\Lambda A') - 3\mathrm{Tr}(A+A')^{-1}(A\Lambda A')\right],\end{aligned} \tag{11}$$

where Λ is a 2×2 diagonal matrix, and is defined as,

$$\Lambda = \begin{pmatrix} \dfrac{\hbar^2}{2m_\mathrm{e}} & 0 \\ 0 & \dfrac{\hbar^2}{2m_\mathrm{h}} \end{pmatrix}. \tag{12}$$

Moreover, the electron-hole Coulomb interaction potential can be written as

$$V_\mathrm{C}(\boldsymbol{r}_\mathrm{e}-\boldsymbol{r}_\mathrm{h}) = V_\mathrm{C}(BR) = \int \mathrm{d}\boldsymbol{r} V_\mathrm{C}(\boldsymbol{r})\delta(BR-\boldsymbol{r}). \tag{13}$$

Here B is a 1×2 matrix and is defined as

$$B = (\ 1, \quad -1\ ). \tag{14}$$

The matrix element of the Coulomb interaction potential can thus be obtained from the following calculation:

$$\begin{aligned}&\langle\varphi_A|V_\mathrm{C}(\boldsymbol{r}_\mathrm{e}-\boldsymbol{r}_\mathrm{h})|\varphi_{A'}\rangle\\ =&\langle\varphi_A|\varphi_{A'}\rangle\left(\frac{1}{2\pi p}\right)^{3/2}\int \mathrm{d}\boldsymbol{r} V_\mathrm{C}(\boldsymbol{r})\mathrm{e}^{-\frac{r^2}{2p}},\end{aligned} \tag{15}$$

where $p \equiv B(A+A')\tilde{B}$ with $\tilde{B}$ the transpose matrix of B.

3. Numerical results and discussion

Based on our theory given in Section 2, we have performed a SVM calculation for the ground state of an exciton confined in CdS/HgS/CdS QDQW nanoparticles embedded in water as the dielectric environment. The material parameters used in our calculations are the same as in Ref.[11]. Moreover, we choose the average dielectric constant between the electron and hole $\overline{\varepsilon} = 6.0$.[10]

We consider seven CdS/HgS/CdS QDQW samples with the same size of the CdS core and various thicknesses of the internal HgS well layer and of the outermost CdS shell. The structural parameters of these samples are listed in Table 1. Our numerical results for the $1s_\mathrm{e}$–$1s_\mathrm{h}$ transition energies are summarized in Table 2. We can see from Table 2 that our results are in good agreement with the experimental measurements.[5] According to Table 2, the experimental results for the $1s_\mathrm{e}$–$1s_\mathrm{h}$ transition energies for samples $1-3$ can be explained as due to the heavy-hole exciton transitions. The corresponding results for samples $4-7$ are attributed to the light-hole exciton $1s_\mathrm{e}$–$1s_\mathrm{h}$ transitions, as pointed out by Shi in Ref.[11]. Moreover, some previous theoretical results in Refs.[4,5,10,11] were evidently improved by our calculations. For example, compared with experimental measurement and with previous theoretical calculations performed for sample 3, our calculation for the $1s_\mathrm{e}$–$1s_\mathrm{h}$ transition energy gives satisfying result with an error of 0.5%. The corresponding values calculated in Refs.[5], [10] and [11] have errors 10.8%, 3.6% and 8.2%, respectively. Furthermore, our calculations for all of the chosen seven CdS/HgS/CdS samples have errors less than 4%, which clearly indicates that the SVM is a suitable method for solving QDQW systems

with internal well thickness ranging from one to several monolayers. For the other QDQWs, our calculations show that the $1s_e$–$1s_h$ transition energy is reduced if the thicknesses of HgS layer and of CdS outermost shell are increased. The transition energies have a weak dependence on the CdS core radius, which has also been confirmed by Chang[4] and Shi.[11]

Table 1. Structural parameters for chosen CdS/HgS/CdS samples.

Sample	CdS core diameter/nm	HgS layer thickness/nm	CdS layer thickness/nm
1	4.7	0.3	0.3
2	4.7	0.3	1.0
3	4.7	0.3	1.5
4	4.7	0.6	0.3
5	4.7	0.9	0.3
6	4.7	0.9	1.5
7	4.7	0.9	2.2

Table 2. The $1s_e$–$1s_h$ transition energies for the chosen CdS/HgS/CdS QDQW samples (see Table 1). Here lh (hh) denotes light-hole (heave-hole) exciton transition. Column 2 shows the present calculation results. The previous theoretical results are given in columns 3 and 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/hh	$1s_e$–$1s_h$ lh/hh	$1s_e$–$1s_h$ Theor.	$1s_e$–$1s_h$ Expt.
1	2.15/2.07	2.27/2.17[11]	2.31[4], 2.27[5], 2.11[10]	2.10[5]
2	2.05/1.94	2.17/2.11[11]	2.16[5], 2.01[10]	1.96[5]
3	2.04/1.93	2.16/2.10[11]	2.15[5], 2.01[10]	1.94[5]
4	1.78/1.65	1.81/1.70[11]	1.9[4], 1.83[5]	1.76[5]
5	1.54/1.42	1.51/1.40[11]	1.72[4], 1.53[5]	1.60[5]
6	1.50/1.35	1.50/1.40[11]	1.50[5]	1.55[5]
7	1.48/1.34	1.50/1.40[11]	1.50[5]	1.54[5]

4. Conclusion

In the present paper, the exciton states confined in spherical CdS/HgS/CdS core-shell QDQW nanoparticles are solved by means of the SVM. The $1s_e$–$1s_h$ transition energies are calculated. In our calculations, the finite value of confinement potential, the different electron and hole effective masses and the Coulomb interaction between the electrons and holes are taken into account. Within the framework of effective mass approximation, the heavy-hole and the light-hole exciton states are investigated separately. Numerical results are presented together with some previous theoretical calculations and with available experimental measurements. It has been found that our results are in good agreement with the experimental measurements and the previous theoretical calculations are improved obviously. The SVM is a suitable method to solve the exciton states in complicated QDs. We believe that the SVM used in the present work can also be extended to three or more charge carriers (charged excitons and biexcitons) confined in much more complicated QDQWs with several layers.

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