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Finite Difference Calculation of Electron States in CdTe-CdS Core-Shell Quantum Dots

(Pengiraan Perbezaan Terhingga bagi Keadaan Elektron dalam Titik Kuantum Teras-Petala Cdte-Cds)

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ABSTRACT

We determined theoretically the confined electron states in a colloidal core-shell CdTe-CdS quantum dot system with CdTe as the core material with electron effective mass 0.095 m_e, CdS as barrier material of electron effective mass 0.25 m_e and having conduction band offset of 0.265 eV. Based on the one band effective mass approximation, the Schrödinger equation of this system with BenDaniel-Duke Hamiltonian is numerically solved using the finite difference method to obtain the energy level and wave function of the electron confined states. These electronic parameters are obtained by diagonalising the resultant N×N Hamiltonian matrix for principal quantum number n=l – 3, orbital quantum number l=0 – 3 and dot size r=10 – 100 Å. For comparison, we also analytically solve the Schrödinger equation with classical Hamiltonian and similar input parameters to determine the electronic properties. There is good agreement in the results of these two computational methods, where specifically their energy levels differ by less than 15%.

Keywords: BenDaniel-Duke Hamiltonian; core-shell; electron state; quantum dot; Schrödinger equation

ABSTRAK

Kami menentukan secara teori keadaan elektron terkurung dalam sistem titik kuantum teras-petala CdTe-CdS berkoloid dengan CdTe sebagai bahan teras dengan jisim berkesan elektron 0.095 m_e, CdS sebagai bahan sawar dengan jisim berkesan elektron 0.25 m_e dan mempunyai ofset jalur konduksi 0.265 eV. Berdasarkan penghampiran jisim berkesan satu jalur, persamaan Schrödinger bagi sistem ini dengan Hamiltonan BenDaniel-Duke telah diselesaikan secara berangka dengan menggunakan kaedah perbezaan terhingga untuk mendapatkan aras tenaga dan fungsi gelombang bagi elektron yang terkurung. Parameter-parameter elektronik ini telah diperoleh dengan memenjurukan matriks Hamiltonan N × N bagi nombor kuantum prinsipal n=l – 3, nombor kuantum orbit l=0 – 3 dan saiz titik r=10 – 100 Å. Sebagai perbandingan, kami juga menyelesaikan persamaan Schrödinger secara analitik dengan Hamiltonan klasik dan parameter input serupa untuk menentukan sifat-sifat elektronik itu. Terdapat persetujuan yang baik antara dua kaedah komputasi ini dan secara khusus aras tenaga berbeza dengan kurang daripada 15%.

Kata kunci: Hamilton BenDaniel-Duke; keadaan elektron; persamaan Schrödinger; teras-petala; titik kuantum

INTRODUCTION

Recently, semiconductor quantum dots, especially in the form of nanocrystals, have attracted considerable attention and interest. Research involving quantum dots has exploded since wet chemistry techniques were developed to produce colloidal nanoparticles of the desired radius with narrow size distribution (Alivisatos 1996; Klimov et al. 2000). Among II-VI semiconductor material quantum dots, cadmium telluride (CdTe) is one of the compounds providing very high photoluminescence quantum efficiency and could be synthesized in aqueous solution with simplicity and high reproducibility. Due to the tunability of the electro-optical properties of the II-VI materials, their electronic band gaps may be optimized for laser applications and biolabeling as well as in the improvement of solar cells (Schaller & Klimov 2004). Other successful systems of core-shell nanocomposites include PbSe-PbS and CdSe-ZnS. These II-VI materials differ in the fundamental semiconductor properties of dielectric constant, lattice constant, band offset and the most important quantity of effective mass. The BenDaniel-Duke boundary condition, derived in the earlier works of Conley et al. (1966) and BenDaniel and Duke (1966), have been applied to solve the Schrödinger equation for the electronic envelope function and predict the electronic properties of quantum dots. In this study, we determine the energy levels and wave functions of an electron confined in a core-shell CdTe-CdS quantum dot system by solving its Schrödinger equation using finite difference and BenDaniel-Duke Hamiltonian. We then compare these results with those obtained analytically using classical Hamiltonian.

METHODS

The envelope function for an electron in a core-shell quantum dot system is given by the Schrödinger equation,

$H\Psi = E\Psi$. In this one band effective mass approximation, H is the Hamiltonian operator, E is the eigen energy, and $\Psi = \Psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$ the eigenfunction; where $R(r)$ is the radial component and $Y(\theta,\phi)$ is the angular component of spherical harmonics. For this spherically symmetric system, the solutions of Ψ are only dependent on radial distance r; and the solution of Ψ thus reduces to the one-dimensional form of $R(r)$ (Banyai & Koch 1993; Schiff 1968). In our study, the spherical core-shell quantum dot system contains a CdTe core or well material of electron effective mass m_1, radius r_a and potential $V_a = 0$; and a CdS shell or barrier material of electron effective mass m_2, thickness $r_s = r_b - r_a$ and potential $V_b = V_o > 0$. This core-shell quantum dot is immersed in a medium of infinite potential, $V(r > r_b) = \infty$ with $r_b = r_a + r_s$, resulting in a standalone or isolated quantum dot system (Figure 1(a)-(b)). The conduction band offset of the system is $V_b - V_a = V_o$.

The BenDaniel-Duke form of the Hamiltonian, $H = -\hbar^2/2\,[\tilde{N}(m^{-1}\tilde{N})] + V(r)$, was introduced for the Schrödinger equation to resolve the issue of mass discontinuity in a system with position dependent mass, $m = m(r)$ (BenDaniel & Duke 1966; Conley et al. 1996). The Schrödinger equation with the BenDaniel-Duke Hamiltonian then could be numerically solved by the finite difference method. Specifically, the central difference of the finite difference method approximates the continuous Schrödinger equation with a discrete form:

$$-\frac{h^2}{b^2}\left(\frac{1}{m_i + m_{i+1}}\right)R_{i-1} + \left[\frac{h^2}{b^2}\left(\frac{1}{m_i + m_{i-1}} + \frac{1}{m_{i+1} + m_i} + \frac{b^2 l(l+1)}{m_i r_i^2}\right) + V_i\right]$$

$$R_i - \frac{h^2}{b^2}\left(\frac{1}{m_{i+1} + m_i}\right)R_{i+1} = E_{nl}R_i, \qquad (1)$$

where the radial domain of $r \in [0, r_b]$ is divided into N regions of grid size $b = r_b/N$. At the i-th nodal point with $i = 0, 1, 2, ..., N$, the local values of the position, effective mass, potential and wave function are r_i, $m_i(r)$, $V_i(r)$ and $R_i(r) = R_{nl,i}(r)$, respectively. By applying the BenDaniel-Duke (1966) boundary condition, i.e. continuity of $(dR_i/dr)/m_i$ and R_i, at r_a; and the fixed boundary condition of $R_{N+1} = 0$ at r_b, we construct an $N \times N$ Hamiltonian matrix and solve for eigenvalues E_{nl} and eigenfunctions $R_{nl,i}$. We have performed this computational procedure using N=100, principal quantum number n = 1 to 3 and orbital quantum number l = 0 to 3 for the core-shell CdTe-CdS quantum dot system of core radius r_a = 10 to 100 Å and shell thickness $r_s = r_a$.

To verify the finite difference computed results of the BenDaniel-Duke Hamiltonian, we analytically solved the Schrödinger equation with classical Hamiltonian, $H = -\hbar^2\tilde{N}^2/2m + V(r)$, for this quantum dot system of similar parameters, except that $r_s = \infty$. The radial functions for this classical Hamiltonian with finite potential and position dependent mass are of Hankel type I (Schiff 1968; Schwabl 1992),

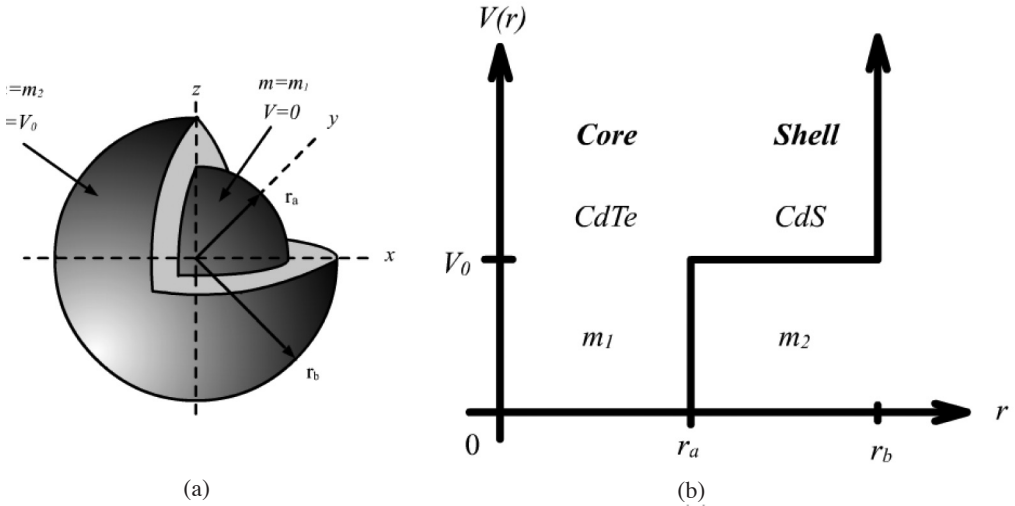
$$R_{nl}(\rho) = (-\rho)^l\left(\frac{1}{\rho}\frac{d}{d\rho}\right)^l\frac{\sin\rho}{\rho} - i(-\rho)^l\frac{\cos\rho}{\rho}$$

$$\text{with } \rho = \sqrt{\frac{2m(E_{nl} - V)}{\hbar^2}}\,r. \qquad (2)$$

In the analytical method we also use the BenDaniel-Duke boundary condition of $(dR_1(r_a^-)/dr)/m_1 = (dR_2(r_a^+)/dr)/m_2$ and $R_1(r_a^-) = R_2(r_a^+)$ at the interface point of $r = r_a$. Then, the energies E_{nl} and eigenfunctions R_{nl} for the classical Hamiltonian were obtained by finding the roots of the transcendental equation (Eq. 2).

Results and Discussion

In the simulations, we use the respective electron effective masses of 0.095 m_e and 0.25 m_e for CdTe and CdS; and the conduction band offset of 0.265 eV (Kuhaimi 2000; Madelung 2004). Figure 2(a) illustrates the normalized electron radial wavefunction, R_{nl}, produced by the finite difference calculation for the BenDaniel-Duke Hamiltonian



(a) (b)

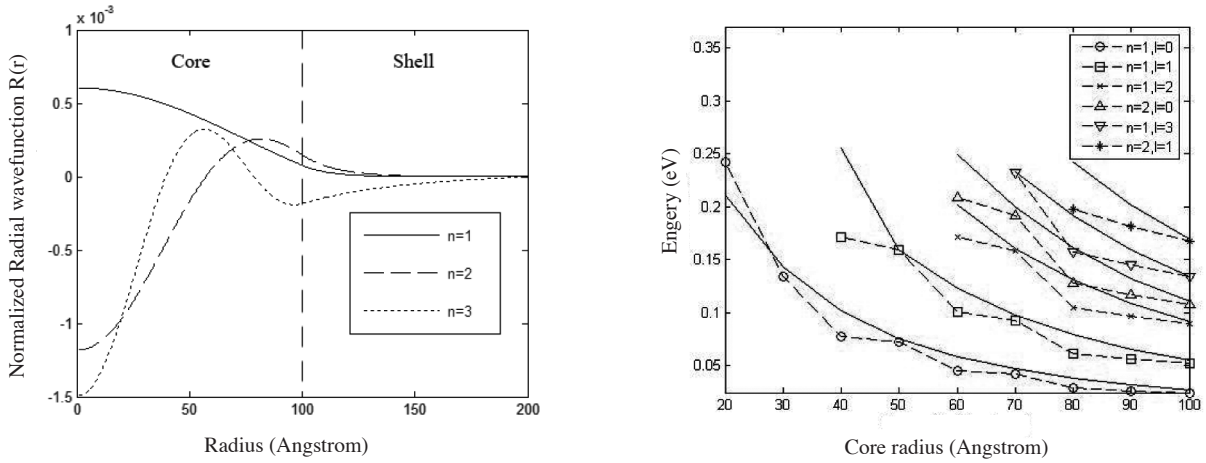
FIGURE 1. Core-shell CdTe-CdS quantum dot system showing (a) core and shell layers; and (b) layer potential profile

in the core-shell CdTe-CdS quantum dot system with core radius equal to shell thickness, $r_a = r_s$ =100 Å, and thus r_b = 200 Å. It shows that only the first three lowest states are confined for this system. Figure 2(b) shows the variation of energy level, E_{nl}, for the lowest six states when the dot sizes are $r_a = r_s$ = 20 – 100 Å with quantum numbers $n = l$ - 2, l = 0 – 3; for both the BenDaniel-Duke Hamiltonian with finite difference (BDDH-FD) and classical Hamiltonian with analytical (CH-AN) approaches. By sorting the calculated results, the energy level of a confined state is found to be inversely proportional to the dot radius as expected for a simplified picture of a particle-in-a-box model.

Table 1 shows that the percent difference in confined energy levels derived from the BenDaniel-Duke Hamiltonian and classical Hamiltonian is less than 15%; and that the percent error decreases with increasing energy level. In addition, Table 1 gives an idea about the transition energies of electrons in core-shell CdTe-CdS quantum dots. For example, electrons of CdTe-CdS quantum dots of radius 50 Å will be excited if we provide 87.3 meV of energy. This unique property may lead to sensor or application that emits photons of energy 80 - 90 meV. Thus, we also present the electron transition energy in Table 2 which follows the selection rule that principal quantum number n is always greater than orbital quantum number l and electron transition from orbital 2p to 1s is not allowed. Table 2 only shows transition energies from 60 to 100 Å, as electrons in quantum dots of radius 10 - 50 Å are not confined.

Conclusion

From our finite difference numerical solution of the Schrödinger equation using the BenDaniel-Duke Hamiltonian, we are able to estimate the few lowest electron states for core-shell CdTe-CdS quantum dots with



(a) (b)

FIGURE 2. Calculated results of core-shell CdTe-CdS quantum dot system for (a) normalized electron radial wavefunction, R_{nl}, with dot size $r_a = r_s$ =100 Å and quantum numbers $n = l$ – 3 and l = 0; for the finite difference calculation of of the BenDaniel-Duke Hamiltonian (BDDH-FD); and (b) energy level, E_{nl}, versus dot size, $r_a = r_s$, for the six lowest electron confined states of the BDDH-CH and CH-AN (classical Hamiltonian with analytical solution) methods. Here, the symbols with dashed lines are for BDDH-FD and the lines are for CH-AN

TABLE 1. Calculated electron confined energies, E_{nl}, in core-shell CdTe-CdS quantum dots of sizes $r_a = r_s$ = 20 - 50 Å obtained by finite difference calculation of BenDaniel-Duke Hamiltonian (BDDH-FD); and analytic solution for classical Hamiltonian (CH-AN). Here, ΔE% is the percentage difference in energies of the two computational methods

E_{nl} (meV)	20 Å			50 Å			100 Å		
	BDDH-FD	CH-AN	ΔE%	BDDH-FD	CH-AN	ΔE%	BDDH-FD	CH-AN	ΔE%
E_{10}	242	212	14	72	76	5	25	27	7
E_{11}	-	-	-	159	159	0	53	55	4
E_{12}	-	-	-	-	-	-	90	91	1
E_{20}	-	-	-	-	-	-	108	111	3
E_{21}	-	-	-	-	-	-	168	169	1
E_{22}	-	-	-	-	-	-	235	233	1
E_{30}	-	-	-	-	-	-	236	251	1

TABLE 2. Transition energies in core-shell CdTe-CdS quantum dots for dot sizes of $r_a = r_s = 60$ - 100 Å derived from the finite difference calculation of the BenDaniel-Duke Hamiltonian

E_{nl} (meV)	60 Å	70 Å	80 Å	90 Å	100 Å
E_{20}-E_{10}	163	149	99	91	83
E_{21}-E_{20}	-	-	70	65	60
E_{30}-E_{20}	-	-	-	137	45

core radii and shell thicknesses of 10 to 100 Å. Compared to the analytical solution of the Schrödinger equation using classical Hamiltonian, the energy level values for the few lowest states differ by < 15%. Wave functions and transition energies of electrons in this quantum dot system could also be determined using the finite difference method.

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