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THEORETICAL STUDY OF THE QUANTUM CONFINEMENT EFFECTS ON QUANTUM DOTS USING PARTICLE IN A BOX MODEL

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Using particle in a box model, we have studied the quantum confinement effects on quantum dots (QDs). A mathematical equation for the confinement energy and energy gap for the quantum dot crystal was obtained and used to calculate such energies specifically for CdSe, ZnS and GaAs quantum dots. The box size was adjusted to fit the real life dot crystals that are geometrically spherical in shape rather than square and the dot particles assumed their effective masses in the periodic lattice. Results showed that discrete electronic states arose at conduction and valence bands. Therefore optical spectra of QDs showed a blue shift in the transition energy. Also, energy gap became size dependent and decreased with increasing size (radius). Thus, energy gap could be fine tuned by changing the size of QDs, which played a fundamental role in optical and electronic properties of QDs. In addition, our results indicate that confinement energy was inversely proportional to the square of QDs size. Our simple model accurately predicts QD energy gap at any radius. Among the QDs considered, CdSe quantum dot possessed distinctive optical properties that could be utilized for photonics applications owing to its size-dependent luminescence colours which spanned nearly the visible and near infra red spectra.

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1. Introduction

The science of semiconductor quantum dots (QDs) has, in recent time, attracted strong interest among researchers owing to the unique properties and potential applications that arise when the dimensions of a material become nanometric. These properties include size tunable optical and electronic properties that are not seen in the bulk counterparts of same materials.

Systems of confined electrons are seen in nature in the form of atoms where the orbiting electrons are confined by the Coulomb force. Researches on nanomaterials have found alternative ways of confining electrons with the help of artificial potential barriers as in the case of QDs. Thus, confined systems of electrons in QDs represent a unique opportunity to study fundamental quantum theories in a controllable atomic-like setup [1].

Quantum dots as well as quantum wires or quantum wells show properties of standard atomic physics, as a result of the restriction of the motion of conduction band electrons and valence band holes to a confined region of space of nanometric size [2]. The quantum dots have achieved great confinement that has not been seen in the bulk semiconductors and other quantum structures [3]. The quantum size effect characterized by a blue shift in the optical spectra has been observed in QDs due to the increase of their charge carrier confinement energy [4].

Quantum dots are semiconductors with core-shell structures and diameter that typically ranges from 2 to 10nm [5]. The core of QDs is usually composed of elements from groups II-IV, such as CdSe or CdS, groups III-V, such as InP or InAs and groups IV-VI, such as PbSe [6]. The shell is usually composed of ZnS [7]. Quantum dots are essentially zero dimensional nanocrystals of semiconductor materials in which the size of particles is comparable to the natural

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characteristics separation of electron-hole pair otherwise known as the exciton Bohr radius of the material [8].

In this limit, regarded as the strong confinement regime, the electron and hole wave functions experience three dimensional quantum confinement due to the dot boundary [9]. The unique optical properties of quantum dots are now known to be attributed to the quantum confinement effect[10]. The discrete energy levels of QDs relate them more closely to atoms rather than bulk materials [11], and have resulted in QDs being nicknamed “artificial atoms” [12]. The energy values within the QDs are inversely proportional to the square of QDs size [13] .

In this research, we used particle in a box model to develop theoretical models which were used to study confined systems of electrons in QDs with emphasis on the quantum confinement effect on CdSe, ZnS and GaAs QDs

2. Theoretical models

Particle in box model explains a particle free to move in a limited space surrounded by impassable barrier. The simplest model is that of a one dimensional system in which a single particle of mass m is confined in a box of length, L from which it cannot escape [14]. This quantum mechanical system that corresponds to particle in a box enables students of physics to apply quantum mechanics to solve real life problems. Here, the Schrodinger equation is solved to obtain the wavefunction and energy levels of a particle trapped in one dimensional box without approximations. The energy of confinement of particle in the one dimensional box is given as:

$$E_n = \frac{n^2 \pi \hbar^2}{2mL^2} = \frac{n^2 h^2}{8mL^2} \tag{1}$$

where m is mass of the particle, L is length of the box and n is the quantum number. The above equation shows that energy of the particle is quantized as a result of the need to fulfill the boundary conditions imposed on the system. However, the lowest amount of energy of the particle is at n=1, which implies that the lowest amount of energy of the particle is never zero but corresponds to:

$$E_n = \frac{h^2}{8mL^2} \tag{2}$$

In QDs, the electron and hole are confined such that they move freely within the dot but cannot go out, just like the particle in a box. Hence, QDs are real life particle in a box. We therefore used the particle in a model to study the effect of quantum confinement on the properties of QDs owing to their similarities. However, we have made some adjustments to compensate for their discrepancies. Firstly, there are two particles within the quantum dots (electron and hole) rather than one as seen in the particle in a box. Secondly, QDs are geometrically spherical in shape rather than square, hence the length of the box L is interchanged with radius R and thirdly, the masses of the electron and hole are replaced by their effective masses due to their interaction with the crystal lattice.

The confinement energy of the electrons in QDs thus becomes:

$$E = \frac{nh^2}{8m_e^* R^2} + \frac{nh^2}{8m_h^* R^2} \tag{3}$$

The ground state confinement energy of the electrons in QDs becomes:

$$\mathrm{E} = \frac{h^2}{8m_e^* R^2} + \frac{h^2}{8m_h^* R^2} \tag{4}$$

However, electrons in QDs do not move in a vacuum in contrast to the particle in a box, rather inside bulk semiconductor crystals. Therefore, energy gap of the bulk accounts for the baseline energy of the system. The energy gap of QDs is thus the energy gap of the bulk semiconductor and the confinement energy of both electrons and holes as shown below:

$$E_{g(qd)} = E_{g(bulk)} + \frac{h^2}{8R^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) \tag{5}$$

where $E_{g(bulk)}$ is the energy gap of the bulk, h is the Planck's constant, R is the radius of the QD,m_e^* is the effective mass of electron and m_h^* effective mass of hole. The electrons and holes are treated independently, as the coulomb interaction between them is not strong enough to form a bound exciton at nano sizes [15]. The simple models above show that discrete electronic states arise at conduction and valence bands and the energy gap of QDs becomes size dependent and larger with decreasing size due to the confinement of electrons and holes within the QDs. This is called quantum confinement effect and is thereby observed when the QD material size is close to the exciton Bohr radius.

3. Results

The results obtained in the computation of the confinement energy and energy gap of various sizes for CdSe, ZnS and GaAs QDs using the obtained model of equation 5 were as shown in the Fig. 1 and Fig. 2 respectively. In arriving at the results, several parameters that varied for CdSe, ZnS and GaAs, were as shown in the Table 1 and Table 2.

Table 1. The Material parameters used for the study[16].

Quantum dots	M_e^*	M_h^*	$E_{g(bulk)}$ at 300K	Bohr radius
CdSe	$0.13m_o$	$0.45m_o$	1.74Ev	6nm
ZnS	$0.34m_o$	$0.23m_o$	3.68eV	5nm
GaAs	$0.06m_o$	$0.51m_o$	1.42eV	10nm

Table 2. The radii used for the study

	Radii (nm)								
CdSe	0.90	1.20	1.44	1.92	2.40	2.96	3.50	4.20	4.80
ZnS	0.75	1.25	1.75	2.25	2.75	3.25	3.75	4.00	4.50
GaAs	1.50	2.00	2.50	4.00	5.50	6.60	7.00	7.50	8.00

4. Discussions

The graphs of confinement energy against dot radius for CdSe, ZnS and GaAs semiconductor QDs in Fig. 1 show an inverse square dependence of confinement energy on the size (radius) of the QDs. As the dot radius increases, the confinement energy decreased but never gets to zero for the different QDs considered. Thus, the ground state confinement of electrons in QDs is not zero, which implies that electrons in QDs are not stationary, but possess kinetic energy in a manner analogous to the particle in a box.

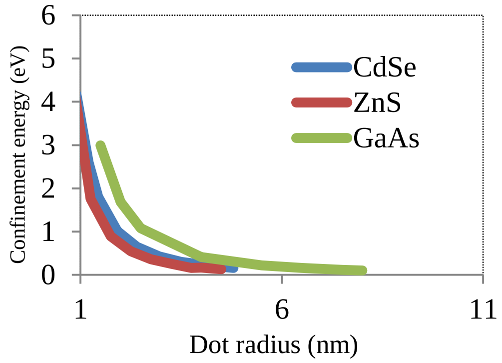

Fig. 1: Confinement energy vs dot radius for CdSe, ZnS and GaAs QDs

The results show that discrete electronic states arise at the conduction and valence bands, as the energy levels now have small and finite separations due to confinement of electrons and hence results to blue shift in the transition energy. Confinement energy of electrons within the QDs increases significantly with decreasing size, indicating a strong quantum size effect. Results also show that after 4–6nm the effect of the size of QDs on confinement energy is less for different QDs hence they are said to be in the weak confinement regime.

The graphs of energy gap against dot radius for CdSe, ZnS and GaAs QDs in Figure 2 show that energy gap of Quantum dot is consistence with confinement principles of potential well. Thus, energy gap of Quantum dot is inversely proportional to the dot size (radius), as one decrease the dot size, the energy gap increases significantly due to confinement of electrons. It means the biggest QDs produce the shortest energy gap (reddish spectrum) and smallest QDs make a longer energy gap (bluish spectrum). It also shows that electronic and optical properties which correspond to the energy gap of QDs can be fine tuned by changing the size of QDs, which plays a fundamental role in photonics and optoelectronics. The photoluminescence spectra of CdSe QD demonstrate a size-dependent luminescence colours.

Harbold [13] determined experimentally using transmission electron microscopy, the average radius of CdSe quantum dot corresponding to the different colours (energy gap) of the visible spectrum and obtained results as shown in the Table 3.

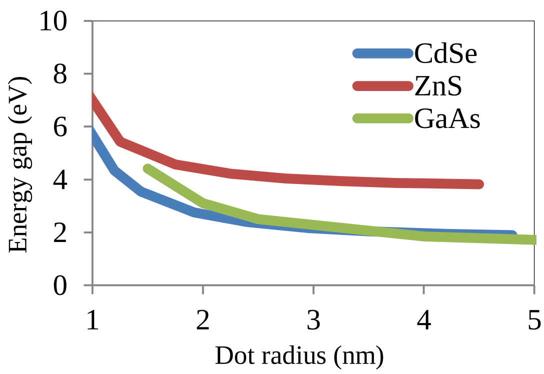

Fig. 2. Energy gap vs dot radius for CdSe, ZnS and GaAs quantum dots

Table 3. Radius and colour for CdSe quantum dot [13]

Radius (nm)	Colour	Energy gap (eV)
2.15	Green	2.18 – 2.51
2.60	Yellow	2.11 – 2.18
3.18	Orange	2.01 – 2.11
3.44	Red	1.66 – 2.01

The computed results, for the size and colours, for CdSe using simple model of the equation 5 are as shown in the Table 4.

Table 4. Computed size and colours for CdSe using our simple model

Radius (nm)	Colour	Computed energy gap (eV)
2.15	Green	2.54
2.60	Yellow	2.29
3.18	Orange	2.10
3.44	Red	2.06

However, the computed energy gaps for the different radius from our simple model correspond to the higher threshold of the experimental energy gap. The slight deviation between the experimentally obtained data[13] and the simple model proposed is attributed to the following:

Effective mass approximation assumption that the effective masses of electron and hole in the quantum dot are the same as in the bulk semiconductor. The weak coulomb interaction between the electron and hole that was neglected. The radius given by the transmission electron microscopy was an average value.

Other researchers show that capping a core quantum dot with a semiconductor material of a wider energy gap reduces the non-radiative recombination and results in brighter fluorescence emission. Therefore, CdSe quantum dots should be capped with ZnS in order to increase their emission efficiency and photostability.

5. Conclusions

We applied particle in a box model to study the effect of quantum confinement on CdSe, ZnS and GaAs QDs. It was found that discrete electronic states arose at the conduction and valance bands.Also the energy gap becomes size dependent and larger with decreasing size. Also, result obtained using our simple model was in substantial agreement with the experimentally observed data. In addition, our results indicated that as the dot radius increased the confinement energy decreased, but never got to zero. Thus, the ground state confinement energy of electrons within the quantum QDs was not zero. Result also showed that CdSe quantum dot possesses distinctive optical properties that could be utilized for photonics applications owing to its size-dependent luminescence colours which span nearly the visible and near infra red spectra**.**

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