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Simulation of quantum dots (QDs) in the confinement regime

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Abstract: The ground state confinement energy and its associated wavelength as a function of radius for three different semiconductor quantum dots (QDs) were calculated using the Brus equation. The experimental observation of the size dependence on the band gap energy is in good agreement with the theoretical models for the semiconductor nanocrystals considered. The confinement of electrons in semiconductor quantum dots increases dramatically with decrease in its size (radius) and shows exponential dependence on wavelength of light emitted.

Keywords: Quantum dots, exciton, Brus equation, confinement.

1. Introduction

Semiconductor nano-particles often referred as quantum dot's (QD's) are semiconductor particles with physical dimensions smaller than the exciton Bohr radius and are confined in three spatial directions. It is one of the most prospective and rapidly developing zero-dimensional nano-size structures, representing the utmost challenge and opportunity to achieve fascinating novel device (Hasaneen et al, 2004) in semiconductor technology.

The promising properties and potential applications cannot be overemphasized. Owing to their quantum size effects and surface effects, quantum dot (QD) can display novel optical, electronic, magnetic, chemical and structural properties (Jana *et al*, 2009) that might find many important technological applications, ranging from antireflecting coatings to bioelectronics and light emitting devices.

In the foreseeable future, they have emerged as the carriers of a wide range of new applications, example as sources for a semiconductor laser or single photon in quantum optics (Martyniuk and Rogalski, 2008; Lagatsky et al, 2010), as qubits for quantum information processing (Dirk et al, 2009), as single electron transistors in electronics or as artificial flourophores for intra-operative detection of tumors (Jana *et al*, 2009), biological imaging or cell studies (Kumar, 2007). Thus a close theoretical investigation on their behavior and resources as a quantum object seems to be justified.

The electronic and optical properties of materials are affected by size and shape. Well established technical achievements including QD were derived from size manipulation and investigation for their theoretical corroboration on quantum confinement effect (Norris, 1995). The major part of the theory is the behavior of the exciton ensembles more like an atom as its surrounding space shortens. A rather good approximation of an exciton's behavior is the three-dimensional model of a particle-in-a-box (Brus, 1983). Shown in figure 1.1 is the change in electron energy level and band gap energy between nanomaterial and its bulk state.

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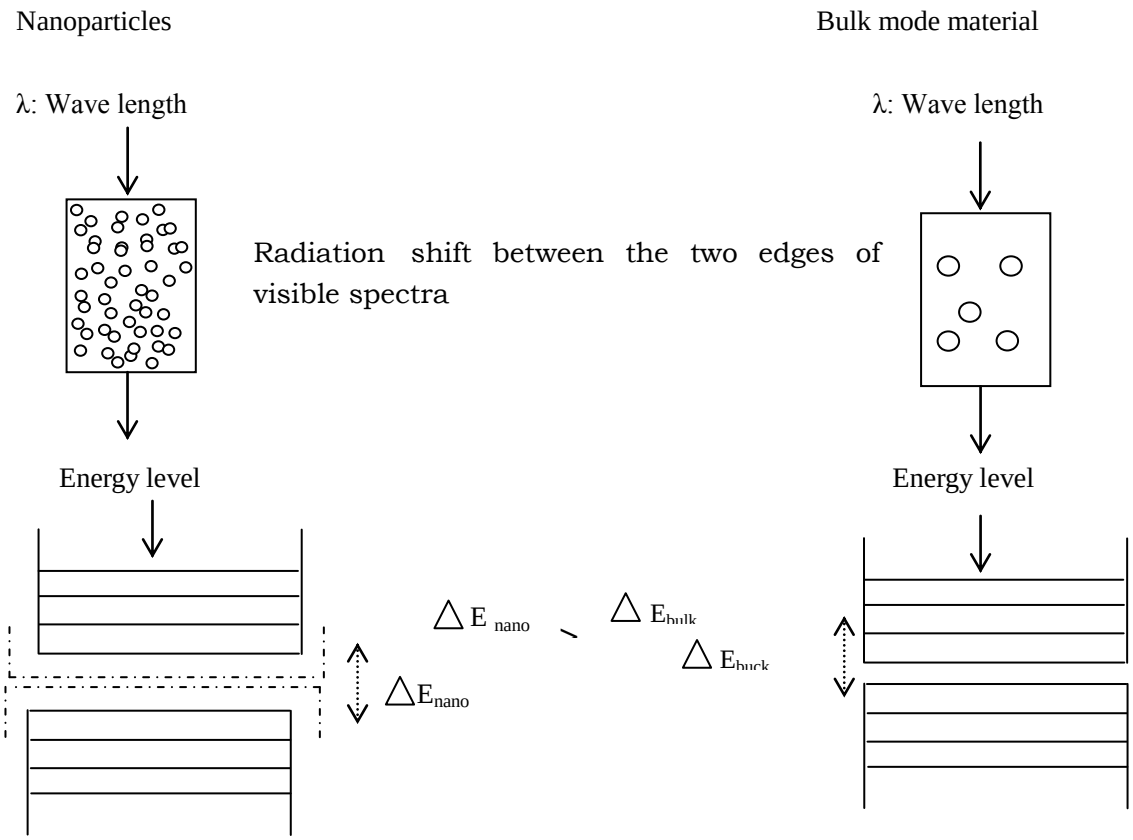

Figure 1.1: Quantum confinement is responsible for the increase of energy difference between energy states and bandgap (Chukwuocha et al, 2012.)

In the bulk semiconductor material (several times bigger than 10nm), charge carriers can have a range of energies. These energies are so close together, that they can be described as continuous (see fig 1.1). There is a certain forbidden range of energies called band gap. Almost all carriers naturally occupy the energy levels below the band gap (valence band) and only very few of them are in the conduction band (above the band gap).

They can jump to the conduction band when they get additional energy from outside (heat, radiation, etc.,) and they leave a hole in the valence band. This electron-hole pair is called an exciton which is the true nature of a charged dot and has a lot of properties similar to the hydrogen atom (Sinclair and Dagotto, 2009). There is an average distance between the exciton called the exciton Bohr radius $a_{B,}$

This length is material dependent and when the size of the material becomes comparable to this value, the energy spectrum is no longer continuous and has to be treated as discrete (fig 1.1). Confinement is therefore said to have occurred, carriers are thus confined inside the dot, similar to an atom.

If the size of the dot is 3-10 times the exciton bohr radius the dot is said to be in the weak confinement regime, but if it is smaller the dot is in strong confinement regime (Sinclair and Dagotto, 2009). Confinement in quantum dots can also arise from electrostatic potentials generated by external electrodes, doping, strain or impurities (Michler, 2003).

Table 1.1: Exciton bohr radius of some semiconductors (Sinclair and Dagotto, 2009)

Semiconductor	Classification	Exciton bohr radius (nm)	Bandgap energy (eV)
Si	IV	4.3	1.11
Ge	III- V	25	0.66
GaAs	II-VI	10	1.424
CdS	II-VI	2.8	2.583
CdSe	II-VI	6	1.74
ZnS	II-VI	5	3.68
PbS	IV-VI	20	0.41

The width of the quantum dot band gap depends on its size and chemical composition, making it easy to tune absorption and emission spectra, what is impossible for atoms, but desirable for optical properties (Wang *et al*, 2001).

In this research, we try to look how the Brus equation can be used to obtain the emission energy, confinement energy, and the wavelength associated with quantum dot of a given radius. The wavelength obtained will be compared to that of the colours that make up the visible spectrum. Also the model to predict the emission energy of quantum dot given the radius is established and compared with known experimentally observed data.

2. Theoretical Framework

Brus (1984) gave the first theoretical calculation for semiconductor nanoparticles (using CdS and CdSe as examples) based on "effective mass approximation" (EMA). In this approximation, an exciton is considered to be confined to a spherical volume of the crystallite and the mass of electron and hole is replaced with effective masses (m_e and m_h) to define the wave function.

$$\mathbf{E_{g(qd)}} = \mathbf{E_{bulk+}}\frac{h^2}{8R^2}\left(\frac{1}{m_e^*}+\frac{1}{m_h^*}\right)-\frac{1.786e^2}{4\pi\varepsilon_o\varepsilon_r R^2} \qquad (2.1)$$

Where,

$\mathbf{E_{g(qd)}}$ = band gap energy of quantum dot

E_g(bulk) = band gap energy of bulk semiconductor

R = radius of quantum dot

m^*_e = effective mass of excited electron

m*h = effective mass of excited hole

h = Planck's constant

Kayanuma (1988) accounted for the electron-hole spatial correlation effect and modified the Brus equation. Based on the modified equation, the size dependence on the band gap energy of quantum dots can be quantified as follows:

$$E_{g(qd)} = E_{bulk} + \frac{h^2}{8R^2}\left(\frac{1}{m_e^*} + \frac{1}{m_e^*}\right) - \frac{1.786e^2}{4\pi\varepsilon_o\varepsilon_r R^2} - 248E^*_{Ry} \quad (2.2)$$

Where,

h = Planck constant

m^*_e = effective mass of excited electron

m^*_h = effective mass of excited hole

R = radius of quantum dot

e = electronic charge

ε_o = permittivity of vacuum

ε_r =relative permittivity

E^*_{Ry} = Rydberg energy

The first term in the right hand side of equation (2.2) represents the band gap energy of bulk materials, which is characteristic of the material. The second additive term of the equation represents the additional energy due to quantum confinement having R^{-2} dependence on the band gap energy. It can indeed be thought of as the infinite square-well contribution to the band gap. The third subtractive term stands for the columbic interaction energy exciton having $\mathbf{R^{-1}}$ dependence (often neglected due to high dielectric constant of semiconductor material). The numerical factor in this term originates from calculations of wave function overlap integrals and its value may vary slightly from material to material. The last subtractive term, stands for spatial correlation effect (independent of radius) and significant only in case of semiconductor materials with low dielectric constant.

However equation 2.2 is only approximated and is expected to fail. In assuming the effective mass approximation he noted that due to the significant number of the electronic wave functions inside the nanocrystal which have wave function overlapping with the edge of the crystal (where the potential landscape is no longer periodic). As a result, equation (2.2) is expected to fail for very small nanocrystals (pan *et al*, 1995).

If we assume that the nanocrystal is Spherical. Decoupling of the Schrodinger equation into a radial part (depending on r) and a spherical harmonic part (depending on the angles Θ *and* $\emptyset$) is possible. This significantly reduces the difficulty of calculating the energy states because the wave functions involved are now products of the two separate wave functions:
$\Psi_{Elm}(r) = R_{Elm}(r) \times Y_{lm}(\Theta, \emptyset)$. This approximation is often quite good since most chemically synthesized nanocrystals have aspect ratios (defined as the ratio between the longest and shortest axes) smaller than 1.1. High aspect ratio nanocrystals can also be synthesized (Kippeny *et al*, 2002) and for such nanocrystals this approximation indeed breaks down.

In the Infinite potential barrier**,** the true potential-step at the surface of a nanocrystal is not infinite. A typical value for this barrier is in the order of 1 to 3 eV (due to the work function of the semiconductor). This value is quite large compared to typical electron and hole energies. As a result, only a small fraction of the electron and hole wave functions will 'leak' out of the nanocrystal. This can result in tunnel conductivity from the nanocrystal to its surroundings (i.e. other nanocrystals or a conducting substrate) and an overestimation of the semiconductor band gap based on equation (2.2). The exact nature, form and

magnitude of the surface potential will only become important in very small nanocrystals or for nanocrystals with an exceptionally low work function. This infinite potential barrier approximation also implies that $E_g(R)$ is insensitive to an externally applied potential and to the surroundings of the nanocrystal. The effect of the surroundings will indeed probably be very small, but the effect of an externally applied potential can be quite significant. Therefore, this approximation is expected to fail when the externally applied potential becomes too large. The Brus equation can be used to describe the emission energy of quantum dot semiconductor nanocrystal in terms of the band gap energy (E_g), Planck's constant (h), the radius of the quantum dot(r), the mass of the excited electron (m^*_e), and the mass of the electron hole (m^*_h) (Kippeny *et a*l, 2002).The radius of the quantum dot affects the wavelength of the emitted light due to quantum confinement, and this describes the effect of changing radius of the quantum dot on the wavelength emitted ($\Delta E = \frac{hc}{\lambda}$ where c = speed of light in m/s).

The overall Brus equation for calculating the emission energy is given as:

$$\Delta E(R) = E_g(R) + \frac{h^2}{8R^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) \qquad (2.3)$$

Where ΔE = the emission energy

3. Results

The parameters used in this research and the results obtained with the dimensionless and physical quantities are presented below (see table 3.1). In this research we will calculate the ground state confinement energy and its associated wavelength as a function of radius for three different semiconductor quantum dots. In arriving at the results, several parameters were used, for Cadmium Selenide, Zinc Sulphid and Gallium arsenide as shown on table 3.1 below.

Table 3.1: showing material parameter used for the computation of the confinement energies at various radii which is less than the Bohr radius a_B (Sinclair and Dagotto, 2009).

QDs	m^*_e	m^*_h	E_{bulk} at 300k	a_B (Bohr radius)
CdSe	$0.13m_o$	$0.45m_o$	1.7 eV	6 nm
ZnS	$0.34m_o$	$0.23m_0$	3.68 eV	5nm
GaAs	$0.063m_o$	$0.51m_o$	1.424 eV	10nm

Table 3.1 shows the material parameter that were used for the computation of the confinement energies with the dot radii for CdSe, ZnS, and GaAs, taken from Chukwuocha et al, 2012. The ground state confinement energies (E_{CF}), the emission energies and wave length at various dot radii were computed using Equation (2.3). Also the columbic term is ignored in the equation.

4. Discussion of Results

4.1 Effect of size on ground state confinement energy

The results obtained for the three QD's under studies shows that the ground state confinement energy is

size dependent. Thus, as one increases the radius (size), the confinement energy decreases, but never reaches zero. i.e., the lowest possible energy for the quantum dot sample is not zero Chukwuocha et al, 2012.

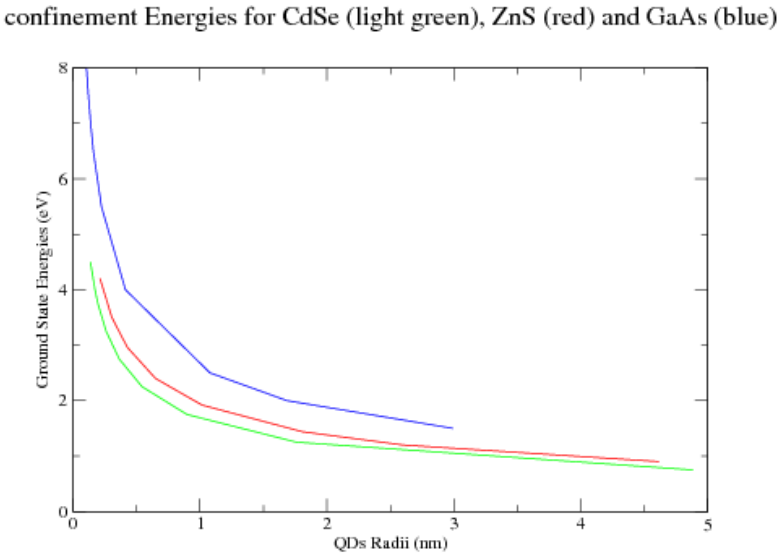

Figure 3.1: showing the ground state energies for CdSe, ZnS and GaAs

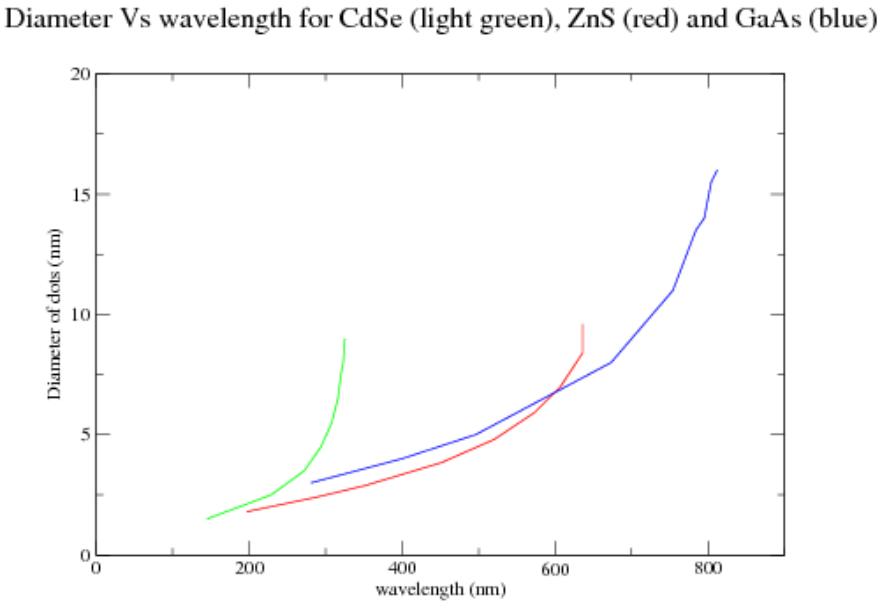

Figure 3.2: Showing the Sizing of the dots versus wavelength

The confinement energy is observed in quantum dots through an increase in the energy of the band gap. Confinement begins when radius of the quantum dot sample is comparable or of the order of the exciton bohr radius, a_B (6 nm for cadmium selenide, 10nm for gallium arsenide, and 5nm for zinc sulphide). In order words when the size is comparable to $2a_B$ (doubles the exciton bohr radius). The confinement energy increases as the size of the quantum dot is gradually reduced until the cluster and magic number limit for the particular crystal is reached. At this limit, Brus equation no longer holds, and the crystal losses its

stability (Brus, 1983). The energy spectrum is discrete rather than continuous in the confinement regime. Thus, only certain energies are allowed for a quantum dot of a given size. The density of states gets peaked at these energies. Experimentally, this can be observed in the absorption spectrum of the given quantum dot (Harbold and Monica, 2008). The confinement region is subdivided into strong confinement regime and weak confinement regime (Harbold, 2005). It must however be noted that in the weak confinement regime, the energy levels form a near continuum. In Figure (3.1), sharp increase in confinement energy begins at a dot radius of about 1.92nm. Thus, the limit of strong confinement for cadmium selenide is at 3.84nm, which corresponds to confinement energy of about 1.015eV. Beyond this limit, the discrete nature of the energy spectrum becomes more apparent until one gets to the cluster and magic number limit. A closely look at the confinement nature of GaAs shows that a sharp increase in confinement energy begins from radius of 4 nm up to the cluster and magic number limit. Thus, the limit or threshold for strong confinement corresponds to energy of about 0.421eV. Similarly, for ZnS the strong confinement limit is observed when the size is scaled down to about 4.50nm (radius of 2.25nm). This corresponds to confinement energy of about 0.543 eV.

4.2 Effect of size on wavelength

The sizing (diameter vs wavelength) curves plotted (Fig.3.2) for the three different semiconductors show an exponential dependence of wavelength of light emitted on size of quantum dot. One can conclude that the larger the dot, the redder (lower energy) its fluorescence spectrum would be. Conversely, smaller dots emit bluer (higher energy) light. The coloration is directly related to the energy levels of the quantum dot. Quantitatively speaking, the band gap energy that determines the energy (and hence colour) of the fluorescent light is inversely proportional to the size of the quantum dot. Larger quantum dots have more energy levels which are also more closely spaced. i.e., the energy levels form a near continuum (weak confinement regime). Van Driel (2005) showed that the lifetime of fluorescence is determined by the size of the quantum dot. Larger dots have more closely spaced energy levels in which the electron-hole pair can be trapped. Therefore, electron-hole pairs in larger dots live longer causing larger dots to show a longer lifetime. Harbold and Monica (2008) determined experimentally using transmission electron microscopy, the average radius of cadmium selenide quantum dot corresponding to the different colours (wavelength) of the visible spectrum and obtained results as follows:

Table 4.1: Showinh the radius (size) and colour for CdSe quantum dot obtained experimentally by Harbold and Monica (2008) and our computed wavelengths.

Radius(nm)	colour	Experimental observed wavelength(nm)	Computed wavelength(nm)
2.15	Green	495-570	488
2.60	Yellow	570-590	542
3.18	Orange	590-620	589
3.44	Red	620-750	605

However, our simulation results of wavelengths form the different radii and that of our simple model give slightly different values corresponding to lower threshold of the wavelength. This slight deviation between

the experimentally observed data (after Harbold and Monica) and the simple model proposed is attributed to the following:

1. Spherical shape assumption-in reality, quantum dots of shapes such as cones, pyramids, domes, disks, ellipsoids etc. exist.
2. The weak columbic interactions that were ignored though should be considered at very small radius (size).
3. Ground state was considered in our model, while peak emission energy was considered by Harbold and Monica.
4. The radius given by the transmission electron microscopy (TEM) was an average value

5. Conclusions

The consequence of the confinement can be seen clearly like that of a particle-in-a-box model. The simple models obtained for the three different semiconductor nanocrystals exhibit the size dependence predicted by the particle –in-a-box model. The experimental observation of the size dependence on the band gap energy is in good agreement with the theoretical models for the semiconductor nanocrystals considered. The confinement of electrons in semiconductor quantum dots increases dramatically with decrease in its size (radius). The larger the exciton Bohr radius the wider the range of tunability. Also the continuum observed in the conduction band and valence band in the case of bulk materials is replaced with discrete atomic like energy levels as the particle size decreases. The degree of confinement among the three nanocrystals considered is found to be strongest in cadmium selenide, followed by zinc sulphide and then gallium arsenide. Effort should be made to develop a single model that can predict the size, shape, composition, and surface density of quantum dot given growth parameters and material parameters.

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