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Quantum Size Effects on Effective Mass and Band gap of Semiconductor Quantum Dots

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Abstract

In this research we calculate the band gap of ZnS nano particle and show that it increases with decreasing its size. The simplest way for discussing this phenomenon and finding the band gap for different sizes is effective mass approximation. We show, this method isn't accurate for particles smaller than 2.5 nm. This is due to the fact that the effective mass of particles at this size is dependent of size. To calculate the band gap of small size ZnS, the density functional theory was used. This theory has also used to determine the effective mass for various particle sizes. Our calculation indicates the appearance of blue shift by decreasing the size of particle.

Keywords: Density functional theory, band gap, effective mass, density of states.

Introduction

In recent years, various semiconductor nanocrystals have been synthesized and it has been found that their electrical and optical properties are dramatically different from their bulk counterparts[1-2]. A typical semiconductor nanocrystal with 1–10 nm diameters consists of about 100– 10000 atoms. These small colloidal nanocrystal as promising advanced functional materials can be found in many different applications, ranging from lasers[3-4], solar cells[5], to single-electron transistors[6]. One example of these nanocrystal applications is to incorporate them into biological systems[7-8]. CdSe quantum dots (QDs) permit *in vivo* cancer cell targeting and imaging in living mice [9]. Many of these applications are related to the size-dependence of the nanocrystal optical properties. In a semiconductor, the optical properties are related to the edge transitions of the electronic band gaps. Thus, studying the size dependence of the electron band gap and the related exciton energy is one of the most important topics in semiconductor nanocrystal research.

Among the nano material the ZnS nano particle is of more importance in industry because of its ability to produce the white color. For studying the optical specification of these substances, the energy levels must become calculated. To calculate the energy gap of ZnS nano particle, we benefit from the "effective mass approximation"[10] Calculation shows that this technique has a good speed and accuracy for particles larger than (2.5 nm) but there is a vast difference between the experimental and approximental results for smaller particles. This difference comes from ignoring the nano effective mass changes. To fix this error and for measuring the energy gap of smaller sizes, the density functional theory provided[11]. By this we have become able to measure the ZnS nano particle effective mass.

Methodology

Effective Mass Approximation (EMA) for nano particles: Hamiltonian of a nano particle would be like this through usage of effective mass approximation[12].

$$H = \left[\frac{-\hbar^2}{2m_e^*}\nabla_e^2 - \frac{\hbar^2}{2m_h^*}\nabla_h^2 - \frac{e^2}{\varepsilon_0 |r_e - r_h|} \right] + polarzation \quad terms \qquad (1)$$

For an accurate calculation of columbic interaction the produced amounts of "two polar substances" in between the nano particle surface and the inscribed substance must calculated. For this reason polarization terms have been brought to the equation. By solving eigenvalue for Hamiltonian results would be like this.

$$E(QD) = E_g(bulk) + \frac{\pi^2 \hbar^2}{2\mu R^2} - 1.786 \frac{e^2}{\varepsilon R} - 0.248\, E_{RY}^* \qquad (2)$$

Where

$$\frac{1}{\mu} = \frac{1}{m_e^*} + \frac{1}{m_h^*}$$

m_e^* And m_h^* are electron's and hole's effective masses, respectively, and '*R*' is the radius of QD, μ is the reduced mass, 'ε' is the permittivity of the vacuum and E_{RY}^* is the effective Rydberg energy. The first term on the right hand side represents the band gap of bulk materials, which is characteristic of the material: for example, 2.53 eV for CdS, 1.74 eV for CdSe and 1.50 ev for CdTe. The second additive term of the equation represents the additional energy due to quantum confinement having a $1/R^2$ dependence on band gap energy, Eg(QD). R (sphere radius) is associated to particle size. The third subtractive term stands for the columbic interaction energy of

exciton having 1*/R* dependence; often neglected due to high dielectric constant of the material. Witch the constant (1.8) has obtained from numerical solving of the nearest neighbors of columbic interaction[10] and ignoring atoms at away distance. As you see E (QD) would decrease with R^{-1} ratio and the quantum size effect would cause the increasing that energy with R^{-2} Ratio. So the energy gap of nano particle will always increase with decreasing of diameter. This variation the energy gap would cause a transition of red absorption wave length into blue witch called "blue shift". And as discussed it is the result of the "quantum size effect". In this paper we have used below numerical amounts to perform calculations of the energy gap [13].

$E_g = 3.84$; $m_e^* = 0.4m_e$; $m_h^* = 0.61m_h$; $\varepsilon = 5.2$

The obtained results from these calculations have been compared with experimental results[14] and they have shown in figure -1. The last subtractive term, stands for spatial correlation effect (independent of radius), and significant only in case of semiconductor materials with low dielectric constant.

For nano particles within (2.5-4 nm) increasing of the energy gap are related with experimental results but for smaller ones, the increasing rate expands with it, which would cause a vast difference between numerical and experimental results.

This disagreement comes from the choose amounts for electron and hole mass which were only suitable for bulk substances and because the effective mass contains all of the existing interaction on excited electron , so by decreasing the particles diameter, the amount of the effective mass must also changes with these variation. There is not a huge difference between the theory and experiment because the changes are not big for nano particle with diameter larger than 2.5nm. But these differences are clear for smaller particles and they must be calculated. There for the effective mass approximation method would not predict the ways of how effective mass variation and it's not usable for smaller dimensions. In the next chapter we have suggested another method not only usable to determine the energy gap variation but also suitable to calculate the how of effective mass variations.

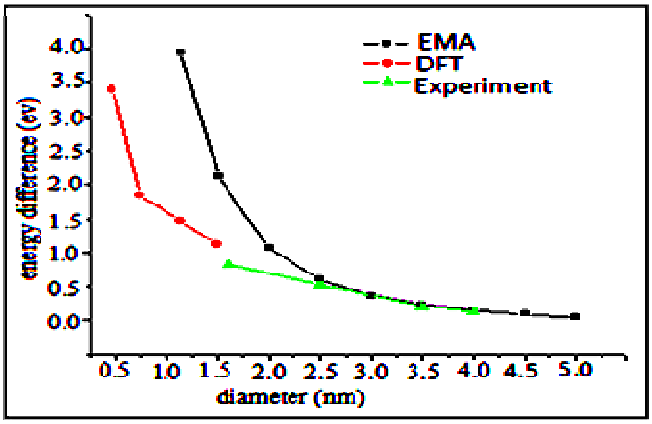

Figure -1
Comparison of the difference energy gap ZnS QDs and its bulk ($E_{QD} - B_{bulk}$) Between experiment , "DFT" and EMA calculations. Experimental data are from Ref [14]

Density Functional Theory(DFT) For Nano Particles: For a hamiltonic solving of nano particles we have used density functional theory[11]. For this we built a super-cell and then we made a vacuum around its 3 dimensions. So we did this instead of using the density functional theory, however is still one problem and it is dangling band issue, which it's the result of making a vacuum around the particle. To fix this we attach (H) to the sided atoms, (H) is a light weight element a won't cause problems during calculations[15]. For solving the (kohn-sham) equations the semi-potential software"PWscf" have been used. The cut wave function energy and the charge density are 30Ry and 140Ry.

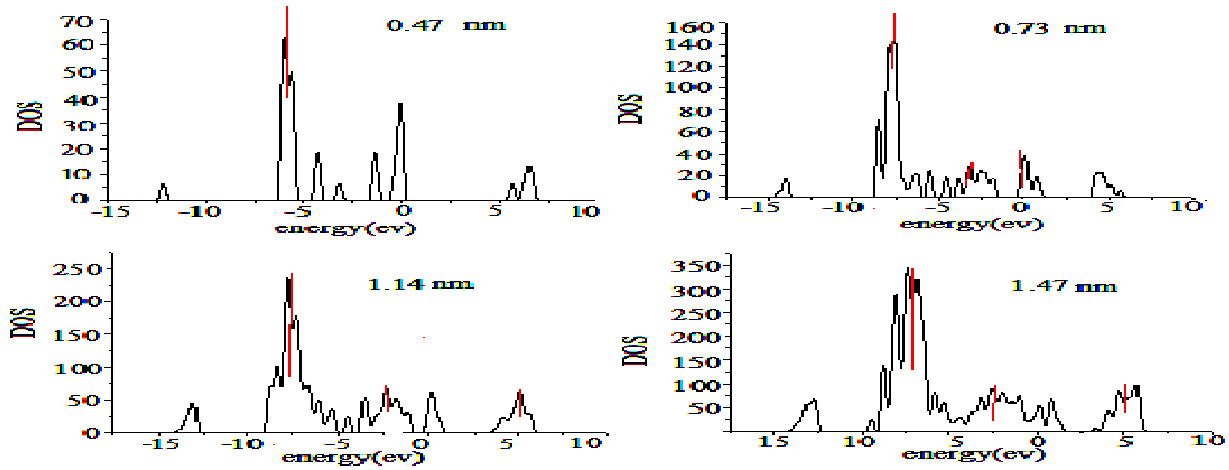

Figure-2
The calculated density of states (DOS) ZnS QDs with different size

Density of state (DOS) ZnS nano particle for these dimensions (0.47nm, 0.73nm, 1047nm) is presented in figure-2. Figure-3 shows the compared amounts of 0.47 nm ZnS nano particle density state the bulk substance ones. As you can see the density of state nano particle forms are so sharp that says the energy bands are quantized. Also decreasing particle size would result increase of energy gap. These increments are results of the nano particle size and show the blue-shift. The figure -1 shows comparison of this method to the experimental results.

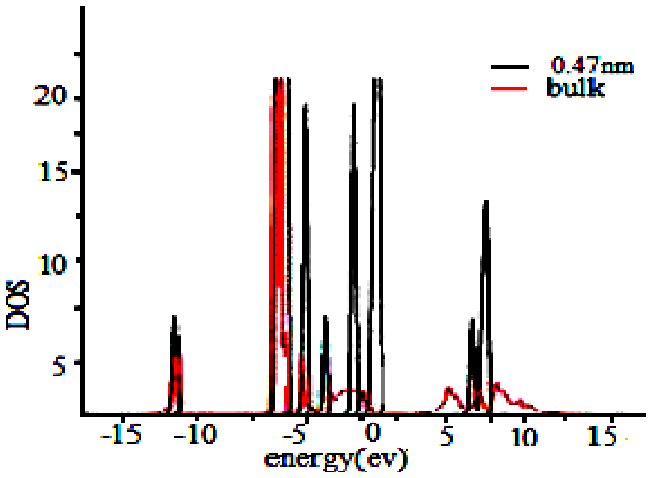

Figure-3
Comparison density of states ZnS QDs of 0.47 nm with its bulk

As you can see amounts of the density functional theory calculations are pretty matched to the reality for smaller particles, and this is the results obtained from figure-2 with substances band width, differences between nano particle band width and bulk substance, have been calculated and reported in table -1.

Table-1
Differences between nano particle band width with its bulk and calculation the effective mass variation with size

Dimension(nm)	ΔE (eV)	μ
bulk	0	$0.21\, m_e$
1.47	0.81	$0.46\, m_e$
1.14	1.15	$0.57\, m_e$
0.73	1.52	$0.97\, m_e$
0.47	3.08	$1.3\, m_e$

By using the results obtained from density functional method and also usage of number 2 equation, the effective mass variation per dimensions' of first particle have been reported in figure-4 as you can see in figure-4 the decreasing of particle size would increase the effective mass. It was also predictable because the smaller the particle size, much influence will gain from sided neighbor. By fitting of extracted data from the curve which is shown in figure-4 this equation is obtained.

$$\frac{\mu}{m_e} = 0.21 + 2.39 \exp(-\frac{R}{5.59})$$

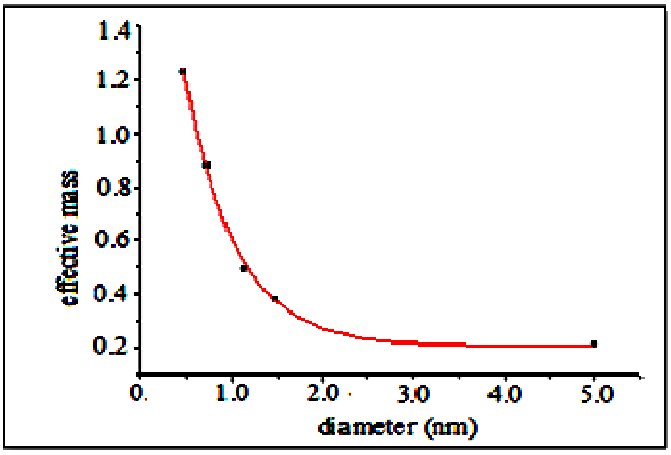

Figure-4
Variation of effective mass with diameter of nano particles

This equation is a damping one, which increasing of R will results in moving the "eve" towards to 21, which is the effective mass of the bulk substance ZnS. As you can see it's obvious that for bigger dimension (bigger than 2.5nm) the effective mass changes are very low. This is the cause of obtaining acceptable results by replacing amounts of bulk substance instead of smaller ones into the effective mass formula. But for minor sizes these variation would be huge and highly influence on obtained results. Through the processed equation the ZnS nano particle effective mass has obtained and the energy gap variation reproduced for various amount of size by putting results from the equation in number 2 equation.

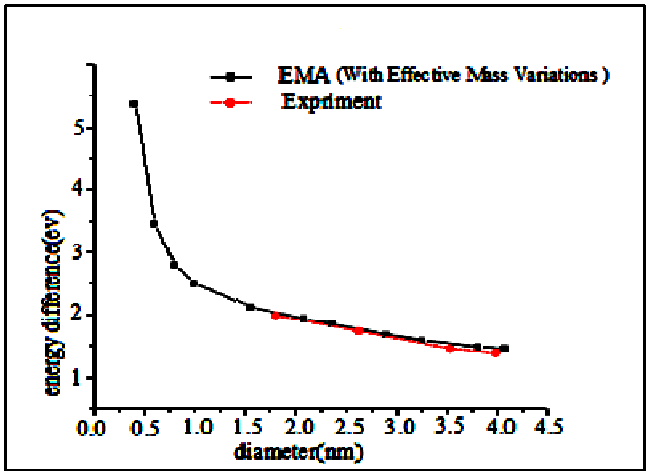

Figure-5
Comparison the mass effective variation with nanoparticle diameter by applying effective mass variations

By applying effective mass variations, there is no difference between calculative and experimental results for particles smaller than 2.5nm.

Results and Discussion

We assumed that the ZnS QDs have a wurtzite crystal structure. The parameters used in this paper are as follows: bulk lattice constants a=3.83 Å, c=6.25 Å; E_g =5.7eV. We first calculated difference energy gap ZnS QDs and its bulk between experiment effective mass approximation (EMA) shown in figure -1. Difference energy gap disagree with experimental for smaller dimensions because effective mass dependence of size of nano particles, there for the effective mass approximation method would not predict the ways of how effective mass variation and it's not usable for smaller dimensions. For solving this problem we have used density functional theory (DFT). for solving the (kohn-sham) equations the semi-potential software"PWscf" have been used. For this we built a super-cell and then we made a vacuum around its 3 dimensions. But it is one problem and it is dangling band issue, which it's the result of making a vacuum around the particle. To remove the dangling band we have used the Surface passivation.The surface of an unpassivated nanocrystal consists of dangling bonds, which will introduce band gap states. The purpose of a good passivation is to remove these band gap states. One way to do so is to pair the unbonded dangling bond electron with other electrons. If a surface atom has m valence electrons, this atom will provide m/4 electrons to each of its four bonds in a tetrahedral crystal. To pair these m/4 electrons in each dangling bond, a passivating agent should provide (8−m(/4 additional electrons. To keep the system locally neutral, there must be a positive (8−m) /4 nuclear charge nearby. Thus, the simplest passivation agent can be a hydrogenlike atom with (8−m) /4 electrons and a nuclear charge Z= (8−m) /4. For III-V and II-VI systems, the resulting atoms have a noninteger Z, thus a pseudohydrogen atom. These artificial pseudohydrogen atoms do describe the essence of a good passivation agent, and thus can serve as simplified models for the real passivation situations. This pseudohydrogen model has been used successfully in our previous studies.

By using density functional theory difference energy gap ZnS QDs and its bulk agreement with experiment shown in figure-1. This method not only usable to determine the energy gap variation but also suitable to calculate the how of effective mass variations. By applying effective mass variations for effective mass approximation, there is no difference between calculative and experimental results for particles smaller than 2.5nm according figure -5.

Conclusion

In this paper we have shown two methods for measuring the energy gap of ZnS nano particle and also we shown that the first method is not usable for smaller sizes (except) we calculated the effective mass variations. By using the density functional theory not only we determined the effective mass variation per particle size, also we showed that by using these variations it is possible to use the effective mass approximation for smaller sizes.

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