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Theoretical Study of Quantum Confinement Effect and Optical Absorption Coefficient of Zinc Blende Quantum Dot

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Abstract. In this paper, the effect of quantum confinement on the energy band structure and the absorption coefficient of the spherical quantum dot has been investigated. The quantum dot chosen from the zinc blende materials such as ZnS, ZnSe and ZnTe. The approximation of the effective mass and the degenerate valence energy band at the center of the first Brillion region are considered in our calculations. Our theoretical calculations included dispersion relation of the bulk and the effect of quantum confinement on the energy band gap, joint density of states and absorption coefficient of quantum dot. We will display the curves of ZnS only, because the curves of other zinc blende materials are in the same behavior. All results show a good agreement between our theoretical calculations and experimental evidence from the literature.

INTRODUCTION

The amount of space freedom permitted for electron mobility is proportional to the degree of confinement. The spatial restriction of motion of charge carrier in metals or semiconductors was achieved by reducing the physical dimension of matter to the nanoscale range. As a result, the continuous energy levels of bands are convert into discrete energy levels. Then, the band gap energy increased, which can be explained by the quantum confinement effect [1-4]. These two effects can be seen in the emission spectra and electronic absorption of semiconductor quantum dots with a direct band gap.

Many features of semiconductor nanomaterials are reliant on their physical dimension, such as dielectric constant and absorption cross section [5]. Quantum confinement size has an impact on all of these features. In ref.[6], the effects of incident light polarization, alloy mole fraction, quantum dot diameters, and doping were explored, and it was discovered that in-plane polarized light absorption is greater than perpendicularly polarized light absorption. A lower energy gap and a longer absorption wavelength result from increasing the mole fraction of the strain controlling layer. Surprisingly, changes in the dot diameter are very sensitive to changes in the absorption wavelength, but changes in the dot height are practically insensitive. The sensitivity analysis of several parameters that affect the optical transition energy explains this unexpected result.

Many studies has focused on the strong nonlinear optical behavior of low-dimensional materials such as quantum dots and core-shell quantum dots. Quantum dots could be beneficial in photoelectronics, photovoltaic nonlinear optics, light-emitting diode manufacture, and laser protections because their emission can be controlled by changing their size. Quantum dots increased nonlinear optical capabilities are defined by variations in core and shell shape and size, as well as chemical composition [7-9]. In ref.[10,] certain particular nonlinear optical features of CdTe and CdSe quantum dots (QDs), such as nonlinear refraction, optical limiting, saturable absorption, reverse saturated absorption, as well as core-shell QDs and their applications, were evaluated. Semiconductor materials are used to create quantum dots (from groups III-V and II-VI such as CdSe, CdS, InP, ZnS, ZnSe, ZnTe and PbTe). The electrical and optical properties of semiconductor materials are largely determined by their band gap energy.

The compound semiconductors of groups III-V and II-VI are usually found in two crystal forms: Zinc-Blende (ZB) and Wurtzite (W), the relative energy positions of the bands and the composition of the radial parts of the wave functions associated with an energy band are affected by the crystal structure. The cell radial section of the

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conduction band (CB) wave function exhibits atomic s orbital, i.e. at the Brillion zone center (crystal momentum k=0).

MODEL CALCULATION

The Effective Mass Model (EMM) has been successfully applied to understanding optical phenomena of bulk semiconductor. The behavior of the electron around conduction and valence band edges likes the behavior of free electrons [11]. For the direct-gap semiconductors (zinc – blende II – VII), the conduction band edge is spherical shape, at the center of Brillion zone (k=0). So, the conduction band energy is defined by:

$$E_{CB} = E_g + \frac{\hbar^2 k^2}{2m_e^*} \tag{1}$$

The valence bands degenerate three times towards the edge (heavy hole (HH), light hole (LH) bands degenerate in the core, and a band split off (SO) by spin-orbit splitting, Δ_{SO}) given by:

$$E_{VB}(HH) = -\frac{\hbar^2 k^2}{2m_{HH}^*} \tag{2}$$

$$E_{VB}(LH) = -\frac{\hbar^2 k^2}{2m_{LH}^*} \tag{3}$$

$$E_{VB}(SO) = -\Delta_{SO} - \frac{\hbar^2 k^2}{2m_{SO}^*} \tag{4}$$

- m_e^* : The electron effective mass.
- $m_{HH,LH,SO}^*$ is the holes effective masses.

The quantum confinement effects are strongly affecting optical properties of semiconductor quantum dots by changing their sizes. The absorption edge of the large dots is mostly similar to that of bulk. In the spectra of the small dots, the quantum – sized oscillations concerned with the optical transitions are usually observed between the discrete quantum confinement levels [12]. The energy band gap of the quantum dots, which made from the semiconductors that have a direct band gap, takes the following form [13-17]:

$$E_{g(QD)} = E_g + \frac{\hbar^2 \pi^2}{2R^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - \frac{1.786e^2}{4\pi\epsilon R} \tag{5}$$

E_g and R are the energy gap of the corresponding bulk semiconductor and radius of spherical quantum dot respectively. $m_e^*(m_h^*)$ is electron (hole) effective mass, e is electron charge and ϵ represents the dielectric constant.

In the effective mass approximation, the effective masses of carriers in quantum dots are the same as in a bulk semiconductor. The second term of eq.5 represents the additional energy due to confinement. The Coulomb interaction energy is the third term.

In addition to increasing the band gap energy and splitting the electronic states, the quantum confinement effect also increases the density of states (DOS) and modifies the joint density of states [18]. The difference in density of states between the bulk and low dimensional structures plays an important role in many physical properties and potential applications [19]. The number of dimensions enabling free transit of an electron gas is described by the dimensionality of the system. Lower-dimensional systems (quantum dots, nanocrystallines, clusters, nanoparticles, colloids, and so on) have more discrete density of states as dimensionality reduces, resulting in greater optical absorption coefficients [20].

In quantum dot, because the particles are confined in all directions (i.e. no dispersion curves), thus the density of states depends only on the number of certain levels. For isolated quantum dot there are two (spin-degenerate) states of each confined energy levels, and the relation between the density of states and energy could be a delta function, similar to those seen in atomic physics. The density of states is described as [21]:

$$DOS^{0D}(E) = 2\delta(E - E_C) \tag{6}$$

The density of states for more than one quantum state, is given by [22, 23]:

$$DOS^{0D} = 2\sum_{n} \delta(E - E_C) \tag{7}$$

δ : The Dirac delta function. It is zero everywhere except when its argument $(E - E_C)$ equals to zero, will be infinity. The DOS is further applied to both bands (V.B and C.B) of a material to obtain the joint density of states JDOS. The JDOS supplies a measure of the number of allowed optical transitions between occupied electronic states in the valence band and unoccupied electronic states in the conduction band that are separated by photon energy $\hbar\omega$, giving an understanding about optical and electronic features. The JDOS of the quantum dot is described by the following equation [23]:

$$JDOS^{0D} = 2\delta\left(E - E_{g(QD)}\right) \tag{8}$$

The electronic and optical behavior of semiconductors can be studied throughout the energy band gap and refractive index n_r. As well as, the dielectric constant ϵ depends on the refractive index which can be calculated from the knowledge of the energy band gap [24]:

$$n_r = \sqrt{\epsilon} \tag{9}$$

There are many of the empirical relations indicate the relation between these correlated quantities (E_g and n_r). The general relation between the refractive index and energy band gap [24, 25] is:

$$n_r^4 = \frac{95eV}{E_g} \tag{10}$$

Ravindra et.al. [26, 27] introduced a relation of refractive index for the semiconductors:

$$n_r = 4.084 + \beta E_g \quad , \quad \beta = -0.62eV^{-1} \tag{11}$$

Herve and Vandamme [28] showed the following relation:

$$n_r^2 = 1 + \left(\frac{A}{E_g + B}\right)^2 \quad , \quad A = 13.6eV \;\; and \;\; B = 3.47eV \tag{12}$$

Reddy *et al.* [29] have proposed an empirical relation:

$$n_r^2 = \frac{12.417}{\left(E_g - 0.365)\right)} \tag{13}$$

Anani *et al.* [30] obtained the following relation:

$$n_r^4 = 1 + \frac{A}{E_g^2} \quad , \quad A = 40.8eV \tag{14}$$

Kumar and Singh [31] obtained the following relation:

$$n_r = KE_g^C \quad , \quad K = 3.3668eV^{-1} \quad , C = -0.32234 \tag{15}$$

In our calculations, it had been choose the nearest values to the experimental data [32] of the refractive index.

The optoelectronic devices are based on the optical absorption spectrum, the optical response of a semiconductor is described by the spectral dependence on the optical absorption coefficient. The optical absorption coefficient, $\alpha\ (\omega)$, is written as:

$$\alpha(\omega) = \frac{1}{V}\frac{4\pi^2 e^2}{m_e^2 \epsilon_0 \omega n_r c}|\rho_{cv}|^2 JDOS^{0D} \tag{16}$$

c and ω are the light speed and frequency respectively. V is the volume of the quantum dot and ρ_{cv} is the momentum matrix element between V.B and C.B, the squared absolute value of the momentum matrix element is described [33,34]:

$$|\rho_{cv}|^2 = \frac{3m_0^2 E_{gQD}\left(E_{gQD} + \Delta_{so}\right)}{2\left(3E_{gQD} + 2\Delta_{so}\right)}\left(\frac{1}{m_e^*} - \frac{1}{m_0}\right) \tag{17}$$

$JDOS^{0D}$ is joint density of states of quantum dot and ϵ_0 is the permittivity constant.

RESULTS AND DISCUSSION

In our calculations, we used the following data according to the local density approximation (LDA) in [100] direction [10]: $m_e^* = 0.150\, m_0$, $m_{HH}^* = 0.775\, m_0$, $m_{LH}^* = 0.224\, m_0$, $m_{SO}^* = 0.385\, m_0$ with m_0 the free electron mass; $E_g = 1.8516$ eV , $\Delta_{so}= 0.0642$, $\epsilon = 7.1629$, $n_r = 2.6764$. We used eqs.(1-4) to plot electronic band structure for bulk of ZnS semiconductor around the first Brillion zone. In fig.1, the valance bands depend on the total angular momentum J and can be classified to the sum of orbital angular momentum and spin angular momentum. However, combining the orbital angular momentum l and the angular momentum $(1/2)$ of the spin is giving a four-fold degenerate valance band with the total angular momentum $= \frac{3}{2} m_J$, $m_J = \pm\frac{3}{2};\pm\frac{1}{2}$, and 2-fold degenerate valance band with $J = \pm 1$. At $k = 0$, the two bands $J = \frac{3}{2}$ and $J = \frac{1}{2}$ are split in energy with the separation given by spin – orbit coupling constant Δ_{so}.

Table 1. indicates the refractive index and dielectric constant for several components ZnS, $ZnSe$ and $ZnTe$. The calculated energy gap and corresponding absorption coefficient $\alpha(\omega)$ for ZnS spherical quantum dot depending on QD radius for [110] and [111] directions and its comparison with [100] direction as shown in the table 2. Clearly that the best shown values are the values that go back to the [100] direction of the ZnS quantum dots. Therefore, the other interest was raised, that is to examine the energy gap and absorpsion coefficient as a function of the radius of other zinc-blende quantum dots such as ZnSe and ZnTe for the same [100] direction. From table 2 and for certain value of quantum dot radius, although the different values of band gap energy, the value of absorption coefficient be similar in three directions [10]. In this calculations, we use the following data for $ZnSe$: $m_e^* = 0.077\, m_0$, $m_{HH}^* = 0.564\, m_0$, $E_g = 0.9484$ eV, $\Delta_{so}= 0.3925\, eV$, $\epsilon = 6.8088$, and n_r =2.6094. While, for $ZnTe$: $m_e^* = 0.064\, m_0$, $m_{HH}^* = 0.775\, m_0$, $E_g = 0.7715$ eV, $\Delta_{so}= 0.8966\, eV$, $\epsilon = 8.3395$, and $n_r = 2.8878$ [6]. So, table 3 shows that the quantum dots of ZnTe semiconductor gives largest values of the energy gap and absorption coefficient.

Figure(2) explains that the energy gap $E_{g(QD)}$ (red stars) increases with decreasing the radius of spherical quantum dot, as pointed in eq.(5) that shows the dependence of the energy gap $E_{g(QD)}$ upon quantum dots radius. The opened blue circles represents the bulk energy band gap. However, by decreasing quantum dot size (radius) we actually increasing the energy of particle that leads to adsorbing light at shorter wavelengths.

Figure(3) represents the joint density of states of the spherical quantum dot as a function of energy band gap for single quantum state which have the shape of Dirac-delta function.

Figure(4) represents the relation between absorption coefficient and energy band gap. We see that the larger value of the absorption coefficient corresponds the smaller size of quantum dot because the energy gap be larger too. Consequently, the absorption coefficient increasing with decreasing the quantum dot size (radius). In addition, absorption coefficient proportional to the JDOS, i.e. the absorption coefficient and joint density of states are proportional to each other.

TABLE 1. Dielectric constant (eq.9) and corresponding refractive index for ZnS, ZnSe and ZnTe.

Materials	**Quan-tity**	n_r **experi.**	**eq.10**	**eq.11**	**eq.12**	**eq.13**	**eq.14**	**eq.15**
ZnS	n_r	2.27	2.6764	2.9360	2.7761	2.8901	1.8952	2.7604
$E_g = 1.8516$ eV	ϵ	-------	7.1629	8.6201	7.7065	8.3526	3.5917	7.6200
$ZnSe$	n_r	2.43	3.1636	3.4960	3.2836	4.6134	2.6094	3.4248
$E_g = 0.9484$ eV	ϵ	-------	10.0084	12.2220	10.7818	21.2839	6.8088	11.7292
$ZnTe$	n_r	2.70	3.3312	3.6057	3.4101	5.5269	2.8878	3.6604
$E_g = 0.7715$ eV	ϵ	-------	11.0967	13.0009	11.6290	30.5461	8.3395	13.3988

TABLE 2. Energy gap ($E_{g(QD)}$) and corresponding absorption coefficient as a function of the radius in [100], [110] and [111] directions for ZnS.

$\boldsymbol{R(nm)}$	$\boldsymbol{E_{g(QD)}}$ **[100]** $\boldsymbol{m_e^* = 0.150\, m_0}$ $\boldsymbol{m_{HH}^* = 0.755 m_0}$ $\boldsymbol{m_{SO}^* = 0.385\, m_0}$	$\boldsymbol{E_{g(QD)}}$ **[110]** $\boldsymbol{m_e^* = 0.150\, m_0}$ $\boldsymbol{m_{HH}^* = 1.766 m_0}$ $\boldsymbol{m_{SO}^* = 0.355\, m_0}$	$\boldsymbol{E_{g(QD)}}$ **[111]** $\boldsymbol{m_e^* = 0.150\, m_0}$ $\boldsymbol{m_{HH}^* = 2.755 m_0}$ $\boldsymbol{m_{SO}^* = 0.365\, m_0}$	$\boldsymbol{\alpha_{100}(\omega) \times 10^8}$	$\boldsymbol{\alpha_{110}(\omega) \times 10^8}$	$\boldsymbol{\alpha_{111}(\omega) \times 10^8}$
0.5	76.5713	69.7719	67.8631	5.5774	5.5776	5.5776
1.0	20.5315	18.8317	18.3545	0.6977	0.6978	0.6978
1.5	10.1538	9.3983	9.1862	0.2069	0.2070	0.2070
2.0	6.5216	6.0966	5.9773	0.0874	0.0874	0.0874
2.5	4.8404	4.5684	4.4921	0.0448	0.0448	0.0448
3.0	3.9271	3.7383	3.6853	0.0260	0.0260	0.0260
3.5	3.3765	3.2377	3.1988	0.0164	0.0164	0.0164
4.0	3.0191	2.9129	2.8830	0.0110	0.0110	0.0110
4.5	2.7741	2.6901	2.6666	0.0077	0.0077	0.0077
5.0	2.5988	2.5308	2.5117	0.0056	0.0056	0.0056

TABLE 3. Energy gap ($E_{g(QD)}$) and corresponding absorption coefficient as a function of the radius in [100] direction for ZnSe and ZnTe.

$\boldsymbol{R(nm)}$	$\boldsymbol{E_{g(QD)}\ (ZnSe)}$ **[100]**	$\boldsymbol{E_{g(QD)}\ (ZnTe)}$ **[100]**	$\boldsymbol{\alpha_{(ZnSe)}(\omega) \times 10^9}$	$\boldsymbol{\alpha_{(ZnTe)}(\omega) \times 10^9}$
0.5	139.5520	172.1440	1.2109	1.3360
1.0	35.5993	43.6146	0.1518	0.1678
1.5	16.3488	19.8129	0.0452	0.0501
2.0	9.6111	11.4823	0.0192	0.0214
2.5	6.4925	7.6264	0.0099	0.0111
3.0	4.7985	5.5318	0.0057	0.0065
3.5	3.7770	4.2689	0.0036	0.0041
4.0	3.1141	3.4492	0.0025	0.0028
4.5	2.6596	2.8872	0.0017	0.0020
5.0	2.3344	2.4852	0.0013	0.0015

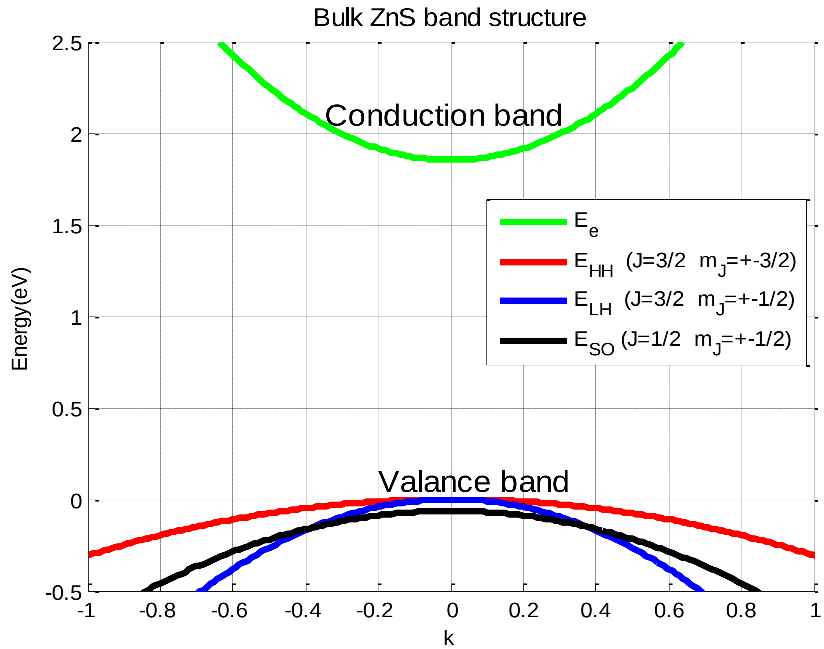

FIGURE 1. The electronic band structure in the center of the Brillion zone.

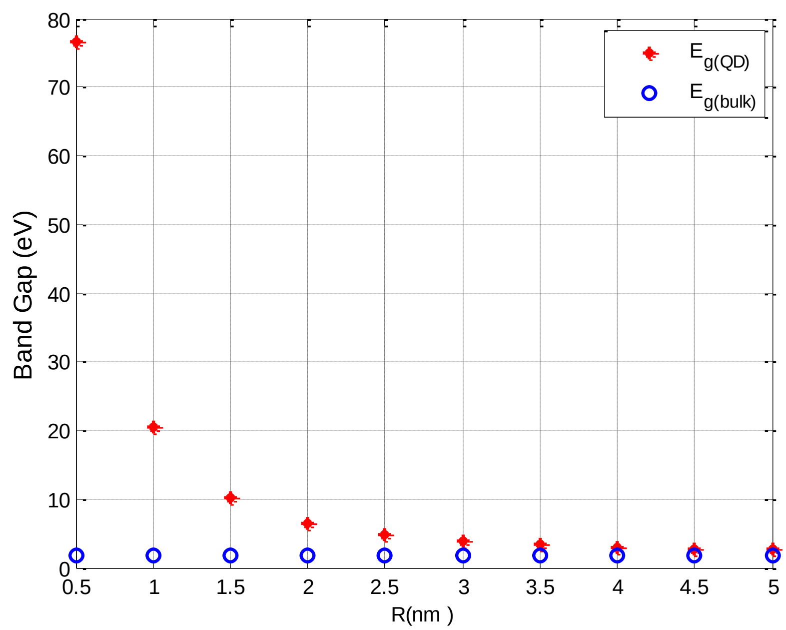

FIGURE 2. Energy band gap as a function of radius.

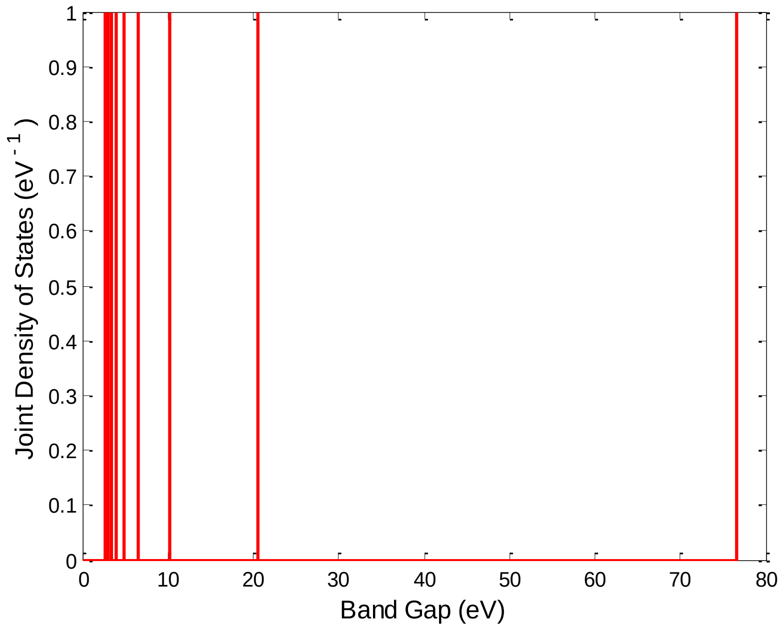

FIGURE 3. The JDOS as a function of energy gap of single quantum state for ZnS QD.

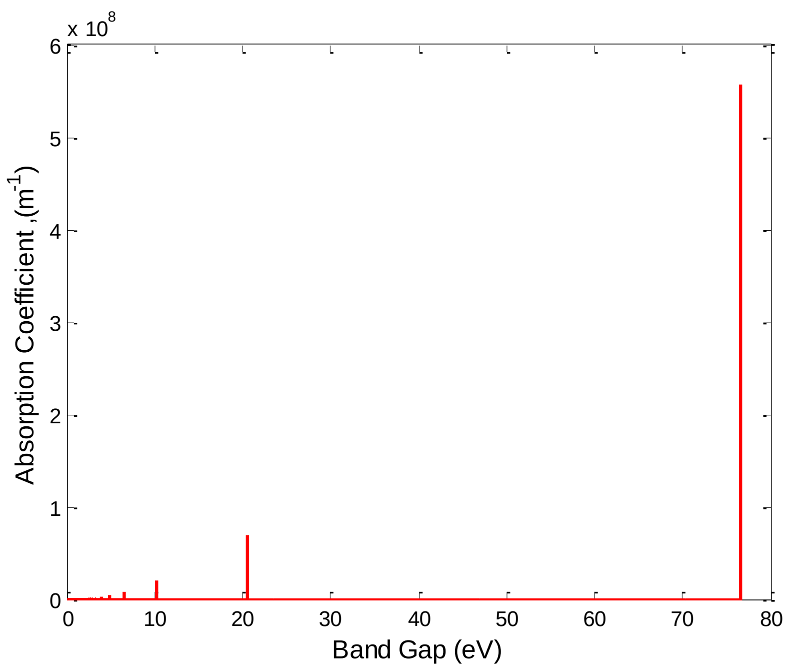

FIGURE 4. Shows the absorption coefficient as a function of energy gap for ZnS QD.

CONCLUSION

The aim of this work is that how quantum confinement affects the energy gap and absorption coefficient of zinc-blende semiconductors like ZnS, ZnSe, and ZnTe. The charge carriers' effective mass, spherical conduction band, and three-fold valance band (HH, LH, and SO) were all considered. Because it is inversely proportional to R^2, confinement characterizes by reducing quantum dot size and producing an expansion of the band gap, while the material conserves semiconductor features. As the energy gap widens, the electronic states split, causing the density of states (DOS) to change into modified joint density of states (JDOS). The absorption coefficient rises as the quantum dot size (radius=R) decreases, and it is proportional to JDOS. The smaller the quantum dot, the higher the absorption coefficient value. The comparison of the [110], [100] and [111] orientations for one zinc blende semiconductor ZnS, the [100] crystallography gives satisfactory results for the energy gap and absorption coefficient. By comparing the results of the same crystallographic direction [100] for other quantum dots of zinc blende materials, ZnSe and ZnTe, one may conclude that the bigger energy gap and absorption coefficient values be with a smaller radius R.

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