Exciton and Bi-exciton Binding Energy Calculation in a Core Shell Quantum Dot

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Abstract. We report the effect of shell thickness on exciton and biexciton binding energy calculation for a CdSe/ZnSe core shell quantum dot. Wentzel Kramers Brillouin approximation help us to create proper wave function for the system. It incorporates core shell boundary effect correctly. For excitons, the binding energy is affected by the Columbic confinement potentials and during biexciton binding energy calculation, the exchange and correlation effects were taken into account. It is observed that the excitonic binding energy shows an initial increase with increasing shell thickness but saturates for thick shell while it always gives a negative value for bi-excitonic binding energy. This confirms the existence of antibonding states for biexcitons.

Keywords: Core Shell quantum dot, Band gap, Exciton, Bi-exciton, Binding energy

1. Introduction:

The rapid progress in semiconductor nanoscience and technology can be envisaged from its reach technological applications and its incredible growth. The semiconductor quantum dots (QDs), due to its great demand for encouraging the miniaturization of modern technological devices, are studied well. Depending on their tunable optical properties, QDs have been widely used for numerous optoelectronic devices from detectors to QD Lasers source for different wavelength ranges or in nano-spintronic devices [1-8]. A new type of nanostructures, commonly recognized as core shell quantum dots (CSQDs), where the carrier particles (i.e. electrons and holes) are confined within the size of the core material having lower band gap and surrounded by another higher band gap shell material. It has been reported, introducing a shell layer externally on the surface of a bare QD enhances its optical properties. This external shell layer enhances the localization probability of the charge carriers along with the passivation of surface nonradiative recombination sites. These interesting materials are under intense investigation due to its high photoluminescence (PL) efficiency, optical amplification, spectral tunability etc. Some well-known examples of CSQDs are CdSe/ZnS, ZnS/CdS, CdSe/CdS, ZnSe/ZnS, etc. [4, 7, 9]. CdSe QDs are considered as one of the most proficient material in visible spectral range because of its emission wavelength can precisely be adjusted from blue to red region. Moreover, the ZnS shell in CdSe/ZnSe CSQD, can be excited by UV light, to use it as fluorescent biological labelling [10]. The possibility to tunnel out from the core for the carriers is always high as the built-in potential well is not high enough to block carriers (electrons and holes) inside CdSe core in a CdSe/ZnSe CSQDs. Due to that, in presence of
ZnSe shell CdSe nanocrystals exhibit very high PL efficiency. Recent results by Shen et al. [11] and Moon et al. [12] reports that the PL efficiency in these CSQDs are enhancing around 20% (approximate) due to the presence of shell which makes them a correct choice for promising light source development or to utilize them in color display applications.

In the present paper, our aim is to investigate the effect of shell creation, on exciton, bi-exciton binding energy and on the transition energy for ground-to-exciton state ($\omega_{0e}$) in a CdSe/ZnSe CSQD. Theoretical formulations interpreted in terms of a model, which includes Wentzel-Kramers-Brillouin (WKB) wave functions in such a way that, the core shell boundary effect may incorporate properly during calculations.

The final result shows that with increasing shell thickness, the exciton binding energy increases while the calculated energy shows negative values which confirms the presence of antibonding states and the ground-to-exciton state transition energy ($\sim \omega_{0e}$) shows a decreasing trend in a CdSe/ZnSe CSQD, as the external ZnSe shell continues to grow on CdSe core.

2. Theoretical Formulation:

The conduction and valence band (CB and VB) alignments for core and shell materials classifies CSQDs into 2 types. Type-I CSQD, where both career particles are strongly confined inside the core region only; and Type-II CSQD are those in which one of the particle (electron/hole) is restricted in the core region and the other may extend to the shell [3, 4, 9]. Fig. 1 shows the geometry of CdSe/ZnSe CSQD used for calculation. Here $a$ and $b$ are the radii of the core and total CSQD, respectively. Thus, the shell thickness is $|b - a| = d$. The confinement potential of the charge carriers is considered as parabolic in nature and given as [3]

$$V_c(r) = \frac{V_c}{a^2} (r^2 - a^2)$$

and

$$V_h(r) = \frac{V_h}{a^2} (r^2 - a^2)$$

$V_c$ and $V_h$ denote CB and VB offsets, respectively. A strong confinement potential experienced by carriers, inside the core due to the existence of ZnS shell layer, as detailed in Ref. [3, 4]. The WKB wave functions for single particles, under such condition are [3, 4]

$$\phi_j(a, b) = \begin{cases} \frac{A_j}{\kappa j} \exp \left( \int_{-b}^{-a} \kappa j \, dr \right) & \text{for } -b < r < -a \\ \frac{A_j}{\kappa j} \exp \left( \int_{-a}^{a} \kappa j \, dr + \frac{\pi}{4} \right) & \text{for } -a < r < a \\ \frac{A_j}{\kappa j} \exp \left( -\int_{a}^{b} \kappa j \, dr \right) & \text{for } a < r < b \end{cases}$$

Here, the subscript $j$ represents individual electron (e) or hole (h) particles. Details of normalization constant $A_C$ and $A_S$ are already explained in Ref [3, 4]. The parameter $k_j$ can be explained mathematically as [3]
The running parameter $r$ for bare QD is in the range $-a \leq r \leq a$. The effect for inclusion of shell in the structure, taken into account for calculations by considering $r$ as $-b \leq r \leq -a$ and $a \leq r \leq b$. Eq. (3) represents the WKB wave functions which are the single particle envelope functions with proper consideration of the energy and effective mass of the carriers. The total wave functions for electron ($\psi_e$) and for hole ($\psi_h$) may described as\[3]\]

\[\psi_e(a, b, r_e) = \phi_e(a, b) \cdot u_e(r_e) \quad \text{(5a)}\]

and

\[\psi_h(a, b, r_h) = \phi_h(a, b) \cdot u_h(r_h) \quad \text{(5b)}\]

Here we are considering the concept of effective mass approximation (EMA). The product of the envelope function, as described above, with the Bloch functions ($u_e, u_h$) helps to complete the total wave functions in such nanostructures under EMA approximation. $r_e$ and $r_h$ represents the positions of different career particles like electron and hole of the core shell system, respectively. The optical properties of semiconductor QDs are determined by the paired electron-hole ($e$-$h$) states popular as exciton. Coulombic influence comes into the picture for any small QD to form e-$h$ pair or exciton. Complete exciton wave function ($\psi_X$) in ground state with Hartree approximation is\[13]\]

\[\psi_X(a, b, r_e, r_h) = \phi_e(a, b) u_e(r_e) \cdot \phi_h(a, b) u_h(r_h), \quad \text{(6)}\]

and the exciton binding energy $\Delta_X$ is\[3, 4]\]

\[\Delta_X(a, b) = \langle \psi_X(a, b, r_e, r_h) \mid V + \frac{e^2}{4\pi\epsilon_0} \mid \psi_X(a, b, r_e, r_h) \rangle + \langle \psi_X(a, b, r_e, r_h) \mid V_h + \frac{e^2}{4\pi\epsilon_0} \mid \psi_X(a, b, r_e, r_h) \rangle \quad \text{(7)}\]

### 3. Results and Discussions:

The band gap energy for CdSe and ZnSe are 1.716 eV\[14]\] and 2.8 eV\[15]\], respectively. In CdSe/ZnSe CSQD, ZnSe offers strong confinements to the carriers due to its higher band gap energy. The CB off set for electrons and VB off set for holes in CdSe/ZnSe is 0.735 eV and 0.135 eV, respectively\[16]\]. We are using these parameters for our calculation of binding energy.

![Figure 2](image.png)

**Figure 2:** (a) Exciton binding energy ($\Delta_X$) as a function of CdSe QD radius (b) Change in exciton binding energy ($|\Delta_X|$) with increasing shell thickness in a CdSe/ZnSe CSQD.

Fig. 2 (a) depicts the effect of increasing dot dimension on the exciton binding energy for a bare CdSe QD. The theoretical results suggest bigger QDs leads to a decreasing exciton binding energy. Fig. 2 (b)
shows the effect of the shell structure on the binding energy of excitons ($\Delta_x$).

The calculation is applied to two different CSQDs of core radii 2.5 and 2.0 nm. For each core, the shell thickness is varied up to 8nm. It is evident from the figures that the exciton binding energy increases up to a thickness of the shell. The exciton binding energy starts saturating after a certain thickness for the shell for CdSe/ZnSe CSQD. According to Talapin et al. [10] there is a remarkable improvement in PL quantum efficiency ZnSe shell around CdSe core structure. They also confirmed a clear red shift in absorption wavelength spectra in such structures. A comparative study clearly confirms the external shell is the reason of such observation in any CSQD. The observed red shift confirms the fact that ZnSe shell fails to support with enough strong barrier potential to avoid the outflow of the carrier particles from core to the shell. So, we can conclude that the increment in the exciton binding energy attributed to the spreading of single particle wave function into the shell region. The observed red shift in transition energy can explain using the Eq. (8) below,

$$\hbar \omega_{ee} = \left[ \epsilon_g - |\Delta_x(a,b)| \right]$$

Fig. 3, shows the change in ground ($|0\rangle$) to exciton ($|e\rangle$) state transition energy with increasing shell thickness. As the exciton binding energy i.e. $|\Delta_x(a,b)|$ increases with increasing shell thickness (Fig.3), from Eq.(8) it is confirmed that the ground-to-exciton level transition frequency $\omega_{ee}$ reduces, causing a red-shift in transition energy with increasing shell thickness. We further investigated the effect of shell formation on bi-exciton binding energy in the same CdSe/ZnSe CSQD. A well-established mathematical formula to calculate bi-exciton binding energy $\Delta_{XX}(a, b)$ is [3, 4]

$$\Delta_{XX}(a, b) = \left( \psi_x(a, b, r_c) \left( \epsilon_g + \frac{\epsilon^a}{\epsilon_{op}} \right) \psi_x(a, b, r_c) - \left( \psi_x(a, b, r_0) \left( \epsilon_g + \frac{\epsilon^a}{\epsilon_{op}} \right) \psi_x(a, b, r_0) \right) + \left( \psi_x(a, b, r_0) \left( \epsilon_g + \frac{\epsilon^a}{\epsilon_{op}} \right) \psi_x(a, b, r_0) \right) - \left( \psi_x(a, b, r_c) \left( \epsilon_g + \frac{\epsilon^a}{\epsilon_{op}} \right) \psi_x(a, b, r_c) \right) + \left( \psi_x(a, b, r_0) \left( \epsilon_g + \frac{\epsilon^a}{\epsilon_{op}} \right) \psi_x(a, b, r_0) \right) \right)$$

Fig. 4 (a) shows increase in the bi-exciton binding energy ($\Delta_{XX}(a, b)$) for varying dot radius in a bare CdSe QD. Fig. 4 (b) illustrates the same due to the growth of ZnSe shell on CdSe core. The similar experimental findings by Sarkar et al. [17] report about the bi-exciton binding energy and on the fine structure splitting in case of a single self-assembled InAs/AlAs QD, further validate our theoretical prediction for CdSe/ZnSe CSQD. The increase in the binding energy indicates the possibility to attain the antibonding state. The biexciton binding energy (plotted as $\Delta_{XX}(a, b)$ with shell thickness in Fig. 4(b)) drops down suddenly with growing shell thickness. The negative value for bi-exciton binding energy indicates the presence of antibonding states which appears due to the stronger carrier confinement from external ZnSe shell in CdSe/ZnSe CSQD. These leads to an enhancement in the interaction between the
carriers represented in Eq. (9). The strong interaction reveals an escalation in the repulsive force activating antibonding of bi-excitons.

Figure 4: (a) bi-exciton binding energy ($\Delta_{\text{XX}}$) with dot radius in a bare CdSe QD. (b) Variation in $\Delta_{\text{XX}}$ with growing shell thickness in a CdSe/ZnSe core shell quantum dot.

4. Conclusion:

In conclusion, theoretical analysis of the exciton, bi-exciton binding energy and transition frequency of a CdSe/ZnSe CSQD has been presented in this paper using WKB wave function to include the exact surface effect near core-shell boundary during calculation. The influence of QD radius on binding energy and the impact of externally grown ZnSe shell on CdSe core has also been calculated and compared with bare CdSe QD. The study is helpful to understand the experimentally observed red shifted nature in absorption and PL spectra. This can be explained using Eq. (7) and Eq. (8), which shows that as the exciton binding energy increases, the transition energy reduces, and this leads to the red shift during the investigation of optical properties. The theory effectively explains the tendency to attain the antibonding states for biexcitons in a CSQD.

5. References:

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