Electronic structures of CdSe quantum dots embedded in ZnSe

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ABSTRACT

The electronic structures and optical matrix elements of CdSe semiconductor quantum dots of near cubical, hemispherical and cylindrical shape embedded in ZnSe were calculated. Bulk Hamiltonian matrices were obtained using the empirical tight binding method including spin-orbital coupling and relativistic effects. All quantum dots were simulated in reciprocal space and the number of atoms in each quantum dot was kept nearly equal for the comparison purpose. An adjacency matrix was produced which indicates the adjacencies of unit cells and the bulk Hamiltonian was included for each adjacency point in order to obtain the quantum dot Hamiltonians. The strain effects, valence band offset and spin orbital coupling were included in the calculations. The quantum dot Hamiltonian was solved to obtain the highest and lowest eigenvalues from which the electronic structure was obtained. Then eigenvalues near integers ranging from the lowest eigenvalue to highest eigenvalue was generated for the $\Gamma$ point.

Keywords: Quantum dot, LCAO method, adjacency matrix, strain effects, valence band offset, folded spectrum method, optical matrix elements, Sparse matrices

1. INTRODUCTION

By the end of the nineteen eighties, a decent understanding of quantum wells and superlattices was achieved and the attention shifted towards systems of further reduced dimensionality, quantum wires (QWr) of one dimension (1D) and zero dimensional (0D)
objects known as quantum dots (QDs). Evolution of the density of states (DOS) as the dimensionality of the system is reduced from a bulk (3D) to a quantum well (2D), further to a quantum wire (1D) and ultimately to a quantum dot (0D) is shown in Figure 1. The QDs were discovered at the beginning of nineteen eighties by Ekimov in a glass matrix [1] and Brus in colloidal solutions [2]. Semiconductor QDs are tiny particles formed in semiconductor materials in nanometer scale and due to their small size, they exhibit unique optical and electronic properties compared to bulk materials such as discrete energy levels, permitting them to be called as “artificial atoms”. In contrast to real atoms, QDs are tuneable and represent a unique model system, in which quantum mechanical effects can be explored. Completely new physics not observable at all in their atomistic counterparts can arise in QDs due to the interplay with their solid state environment.

![Figure 1. Evolution of the density of states (DOS) with dimensionality of the system](image)

The energy levels are quantized in QDs due to the three dimensional spatial confinement of electrons. Changing the size of quantum dots will vary the band structure producing QDs of different properties even with the same material. This property is used to optimise the optoelectronic devices. Quantum dots have been engineered to absorb a specific wavelength of light, to optimise photovoltaic cells and to produce LEDs and white light emitting devices. They are used as efficient and brighter lasers since photon energies can be controlled by selecting the appropriate size of the quantum dot. These are also used in the industry of quantum computing, data storage, developing high resolution television screens and monitoring cancer cells [3]. For all kinds of new applications the detailed understanding of the electronic structure is of essential importance, since this provides the link between the structural and optical properties of these systems. Research in QDs formed from wide band gap II-VI semiconductors CdSe/ZnSe are attractive for optoelectronic applications in the blue-green spectral regions [4] and can be grown with excellent optical quality.

Different approaches are used to calculate the electronic structure of quantum dots. Some are first principle studies while the others are empirical studies. Density functional theory (DFT) and local density approximation (LDA) are used in ab initio calculations. However the requirement of large calculations has reduced the usage of these methods. Due to these drawbacks, empirical models such as pseudo potential model, $k.p$ method and tight
binding model are widely used. The tight binding or linear combination of atomic orbitals (LCAO), originally proposed by Bloch in 1928 [5] was simplified in 1954 by Slater and Koster [6] using an orthogonal set of atomic orbitals (Lowdin functions) which removes the unnecessary integrals. Empirical tight binding method (ETB) was implemented to study electronic structures of QDs [7, 8] and by Schulz [9] to calculate the electronic structures and optical properties of truncated pyramidal and lens shaped quantum dots. As the dot size is reduced, the electronic energy is increased due to the increased kinetic energy [9]. ETB methods represent computationally affordable models capable of describing even large quantum dots up to 25 nm size, without restricting atomic-scale variations on the wave functions considerably [10].

In this study of electronic structure of CdSe QD embedded in ZnSe, the bulk band structure of CdSe and ZnSe zinc blende materials were obtained using the empirical tight binding method. The Bulk Hamiltonian with the spin-orbital coupling and relativistic effects was used as a building block to prepare the quantum dot Hamiltonians including the strain effects and the valence band offset of the QDs. CdSe QDs of near cubical shape of dimensions $7a\times7a\times6a$ with 294 unit cells, hemispherical shape of radius $5a$ with 298 unit cells and cylindrical shape of radius $4a$ and height of 6 unit cells with 294 unit cells embedded in a ZnSe super cell of dimensions $18a\times18a\times18a$ unit cells (46656 atoms) with a wetting layer (WL) of a thickness of one lattice constant $a = 5.668\AA$ of the bulk ZnSe were simulated. The matrices including the data about adjacency atoms of the super cell were produced indicating the adjacencies of unit cells. The bulk Hamiltonian was included for each adjacency point in order to obtain the quantum dot Hamiltonians. This was carried out for all three different shapes. The quantum dot Hamiltonian was solved to obtain the highest valence band and lowest conduction band eigenvalues from which the electronic structure was obtained. Then eigenvalues near integers ranging from the lowest eigenvalue to highest eigenvalue was generated for the $\Gamma$ point. The optical matrix elements were obtained for these three different shapes.

2. BULK BAND STRUCTURES

CdSe and ZnSe are II-VI Semiconductors with zinc-blende structure forming tetrahedrally directed covalent bonds from hybridized $s$ and $p$ atomic orbitals. In an elementary unit cell containing one anion and a cation, the diatomic basis contains a cation at $(0,0,0)$ and the anion at $(1,1,1)a/4$ relative to the lattice point (Figure 2).

![Figure 2. Tetrahedral bonding (sp³-bonding). Small spheres indicate the anions, large black spheres the cations.](image)
The eight valence electrons are distributed among the \( s \) and three \( p \) orbitals. The atomic orbitals \( s, p_x, p_y, p_z \) denoted by \( \beta(\beta = s, x, y, z) \) with spin \( \sigma (\sigma = \uparrow, \downarrow) \) are set up on each of the two types of atomic orbitals \( \eta (\eta = a \text{ for anion and } \eta = c \text{ for cation}) \). The atomic wave function of the atomic orbital centered on \( R_j \) are denoted by \( \phi_\mu(r - R_j) \) with \( \mu = \beta, \eta, \sigma \).

Because of the large iconicity of the II-VI semiconductors Lowdin orbitals are expected to be similar to atomic orbitals and the orthonormalized Lowdin functions \( \psi_\mu(r - R_j) \) can be constructed from atomic functions \( \phi_\mu(r - R_j) \). The orthonormal set of wave functions \( \chi_{\mu k}(r) \) for an electron in a crystal for the wave vector \( k \) is given by [11]:

\[
\chi_{\mu k}(r) = N^{-1} \sum_j e^{ik(R_j + \tau_\eta)} \psi_\mu(r - R_j - \tau_\eta)
\]

\( N \) is the total number of lattice points. \( \tau_\eta \) specifies the position of the anion or cation \( \eta \) relative to the origin of the cell \( R_j \). If one takes \( \tau_\eta = \delta_{\eta,a} (r_0/4)(1,1,1) \) where \( r_0 \) is the cubic lattice constant, then the cation will be at the origin.

Near heavier nuclei, the potential is very strong and consequently, the kinetic energy of the electrons is very large. So the velocity of electrons is comparable to the velocity of light. Therefore in order to obtain accurate results for the bulk band structures, the relativistic effects of the electrons have to be considered. Spin orbit coupling arise due to the interaction of the electron spin magnetic moment with the magnetic field seen by the electron. Spin orbit energy can be added to the bulk Hamiltonian:

\[
H_{\text{bulk}} = h_0 = h + h^s
\]

\( h \) includes the kinetic energy, potential energy and spin independent relativistic correction while \( h^s \) contain the spin-orbit interaction. The matrix elements of \( h_0 \) is given by:

\[
E'_{\mu k,\mu'k'} = \left\langle \chi_{\mu k} | h_0 | \chi_{\mu'k'} \right\rangle = \delta_{\sigma,\sigma'} \delta_{k,k'} \sum_{l,m,n} e^{ik(R_j + \tau_\eta - \tau_\eta')} E'_{\alpha l,\alpha m,\alpha n}(l,m,n)
\]

Here \( E'_{\alpha l,\alpha m,\alpha n}(l,m,n) \) are the Slater-Koster parameters. \( (R_j + \tau_\eta - \tau_\eta) \) can be written as \((a/4)(li + mj + nk)\) where \( l, m, n \) are integers and \( i, j, k \) are unit vectors along Cartesian directions.

Since spin-orbit interactions are short ranged, only the interaction on one atom is considered and \( h^s \) is taken as that of an isolated atom. Therefore only nonzero elements will be the elements linking different \( p \)-orbitals on the same atom as \( s \) state with \( l = 0 \) is not split, since the angular part is constant. Spin orbit coupling can be given by [9]:

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\[ \langle x \uparrow \downarrow | h^s | z \downarrow \uparrow \rangle = \pm \lambda \]
\[ \langle x \uparrow \downarrow | h^s | y \uparrow \downarrow \rangle = \mp i\lambda \]
\[ \langle y \uparrow \downarrow | h^s | z \downarrow \uparrow \rangle = -i\lambda \]

The bulk Hamiltonian can be represented by:

\[
H^0 = \begin{bmatrix}
    h_{aa} + h^s_{aa} (\uparrow \uparrow) & h_{ac} & h^s_{aa} (\uparrow \downarrow) & 0 \\
    h_{ca} & h_{cc} + h^s_{cc} (\uparrow \uparrow) & 0 & h^s_{cc} (\uparrow \downarrow) \\
    h^s_{aa} (\downarrow \uparrow) & 0 & h_{aa} + h^s_{aa} (\downarrow \downarrow) & h_{ac} \\
    0 & h^s_{cc} (\downarrow \uparrow) & h_{ca} & h_{cc} + h^s_{cc} (\downarrow \downarrow)
\end{bmatrix}
\]

Both \( h_{\eta \eta'} \) and \( h^s_{\eta \eta'} \) are 4\times4 matrices.

A somewhat simplified version of the tight binding model, the empirical bond orbital model (EBOM) introduced by Chang [12] was initially applied to superlattices. In polar semiconductors such as ZnSe and CdSe, the valence bands originate primarily from the anion, and the conduction band from the cation. From the perspective of atomic orbitals near the \( \Gamma \) point, the valence bands originate from the valence p orbitals while the conduction band arises from the s orbitals [12]. To minimize the computational cost, one s-like antibonding orbital for the conduction band and three p-like bonding orbital for the valence band can be considered. For the study of the optical properties of CdSe and ZnSe semiconductor materials with a direct band gap, as the electronic properties in the region near the \( \Gamma \)-point is needed, a smaller s\(_c\)p\(_c^1\) tight binding basis is sufficient for a proper description of the electronic structure of these systems [12]. This approach requires only eight independent parameters and allows for the investigation of larger nanostructures. Hence the dimensions of the quantum dot Hamiltonian which is about 80000\times80000 will be reduced to 46656\times46656. The bulk Hamiltonian matrix has the form:

\[
H_{\text{bulk}} = \begin{bmatrix}
    |a_{px} \uparrow\rangle & |a_{px} \downarrow\rangle & |a_{py} \uparrow\rangle & |a_{py} \downarrow\rangle & |a_{pc} \uparrow\rangle & |a_{pc} \downarrow\rangle & |c_r \uparrow\rangle & |c_r \downarrow\rangle \\
    |a_{px} \downarrow\rangle & 0 & E_{sx} & 0 & E_{sy} - i\lambda & 0 & E_{sz} & \lambda & E_{sx} & 0 \\
    |a_{py} \uparrow\rangle & 0 & E_{sx} & 0 & E_{sy} + i\lambda & -\lambda & E_{sz} & 0 & E_{sx} \\
    |a_{py} \downarrow\rangle & 0 & E_{sx} & 0 & E_{sy} & -i\lambda & E_{sz} & 0 & E_{sx} \\
    |a_{pc} \uparrow\rangle & E_{sx} & -\lambda & E_{sy} & i\lambda & E_{sz} & 0 & E_{sz} & 0 \\
    |a_{pc} \downarrow\rangle & \lambda & E_{sx} & i\lambda & E_{sy} & 0 & E_{sz} & 0 & E_{sx} \\
    |c_r \uparrow\rangle & E_{sx} & 0 & E_{sx}^* & 0 & E_{sy}^* & 0 & E_{sz}^* & 0 \\
    |c_r \downarrow\rangle & 0 & E_{sx}^* & 0 & E_{sy}^* & 0 & E_{sz}^* & 0 & E_{sx}^* 
\end{bmatrix}
\]
Here

\[ E_{aa} = E(0,0,0)_{aa} + 4E_{xx} (110)_{aa} \cos \left( \frac{k_x a}{2} \right) \left[ \cos \left( \frac{k_y a}{2} \right) + \cos \left( \frac{k_z a}{2} \right) \right] + 4E_{xx} (011)_{aa} \cos \left( \frac{k_y a}{2} \right) \]

\[ E_{ss} = E(0,0,0)_{cc} + 4E_{xx} (110)_{cc} \left[ \cos \left( \frac{k_x a}{2} \right) \cos \left( \frac{k_y a}{2} \right) + \cos \left( \frac{k_x a}{2} \right) \cos \left( \frac{k_z a}{2} \right) \right] \]

\[ E_{as} = 4E_{xx} \left( \frac{1}{2} \frac{1}{2} \frac{1}{2} \right)_{ca} \left[ \cos \left( \frac{k_x a}{4} \right) \sin \left( \frac{k_y a}{4} \right) \sin \left( \frac{k_z a}{4} \right) - i \sin \left( \frac{k_x a}{4} \right) \cos \left( \frac{k_y a}{4} \right) \cos \left( \frac{k_z a}{4} \right) \right] \]

\[ E_{ab} = -4E_{xy} (110)_{aa} \sin \left( \frac{k_x a}{2} \right) \sin \left( \frac{k_y a}{2} \right) \]

and the indices \( \{ \alpha, \beta, \gamma \} \in \{ x, y, z \} \) are pair-wise unequal. The ‘*’ indicate the complex conjugate elements.

For CdSe and ZnSe the \( sp^3 \) tight binding Slater-Koster parameters [6] are given in Table 1. The bulk band structures of CdSe and ZnSe obtained from this 8×8 with spin-orbit coupling are presented in figure 3(a) and 3(b) respectively for \( \Delta \) and \( \Lambda \) directions of the Brillouin zone for the second nearest neighbour interactions. CdSe has a band gap of 1.74 eV and ZnSe a band gap of 2.82 eV at the \( \Gamma \) point. Literature values for the energy gap of zinc blende CdSe at 300 K vary from 1.66 to 1.74 eV [7]. The characteristic properties of the band structure in the region of the \( \Gamma \) point were sufficient and satisfactory as compared to the bulk bands obtained from 16×16 Hamiltonian given in equation 5.

**Table 1.** Tight binding parameters of CdSe and ZnSe with spin orbit coupling for second nearest neighbours [7]

<table>
<thead>
<tr>
<th></th>
<th>CdSe</th>
<th>ZnSe</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_{xx} (000)_{aa} )</td>
<td>-1.2738</td>
<td>-1.7277</td>
</tr>
<tr>
<td>( E_{ss} (000)_{cc} )</td>
<td>3.6697</td>
<td>7.0462</td>
</tr>
<tr>
<td>( E_{sx} (\frac{1}{2} \frac{1}{2} \frac{1}{2})_{ca} )</td>
<td>1.1396</td>
<td>1.1581</td>
</tr>
<tr>
<td>( E_{xx} (110)_{aa} )</td>
<td>0.1512</td>
<td>0.1044</td>
</tr>
<tr>
<td>( E_{xx} (011)_{aa} )</td>
<td>0.1738</td>
<td>0.1874</td>
</tr>
<tr>
<td>( E_{xy} (110)_{aa} )</td>
<td>0.1512</td>
<td>0.3143</td>
</tr>
<tr>
<td>( E_{ss} (011)_{cc} )</td>
<td>-0.1608</td>
<td>-0.3522</td>
</tr>
<tr>
<td>( \lambda )</td>
<td>0.1367</td>
<td>0.1433</td>
</tr>
</tbody>
</table>
3. CdSe QUANTUM DOTS EMBEDDED IN ZnSe

In forming CdSe quantum dot (QD) in ZnSe, since different band gaps of these semiconductors are combined, the valence band offset $\Delta E_v$ and conduction band offset $\Delta E_c$ have to be considered. These are determined by the electron affinities of the materials [11]. The valence band offset $\Delta E_v$ between the two materials is considered by shifting the diagonal matrix elements of the dot material [7]. If $R$ denotes the particular unit cell, then the Hamiltonian when $(R, \beta)$ and $(R', \beta')$ are in the region of the QD material can be written as:

$$H_{lR,mR}^{QD} = H_{lR,mR}^{bulkQD} + \Delta E_v \delta_{lR',mR}$$  \hspace{1cm} (6)

where $l = \beta', \eta', \sigma'$ and $m = \beta, \eta, \sigma$.

The embedded quantum dots are formed due to the strain introduced by lattice mismatch between two materials. This strain energy is distributed in the whole quantum dot introducing deformations to the quantum dot lattice. These atomic displacements can be included in the tight binding method. If bulk matrix elements without taking strain into account are denoted by $H_{lR,mR}^0$, then the Hamiltonian with strain effect is given by for $R \neq R'$

$$H_{lR,mR} = H_{lR,mR}^0 \left( \frac{d_{R-R}}{d_{R''-R}} \right)^2$$  \hspace{1cm} (7)
where \( d_{R-R}^0 \) and \( d_{R-R} \) denote the relative atomic positions before and after the strained displacements respectively. The strain tensor \( \varepsilon \) is related to the strain dependent relative atom positions \( d_{R-R} \) by [7]:
\[
d_{R-R} = (I + \varepsilon)d_{R-R}^0
\]
where \( I \) is the unit matrix and the element of the matrix \( \varepsilon \) are given by \( \varepsilon_{ij} = \delta_{ij} \) in the absence of a shear strain the elements of equation 8:
\[
\begin{bmatrix}
dx \\
dy \\
dz 
\end{bmatrix} = \begin{bmatrix}
1 + \tilde{\eta}_{xx} & 0 & 0 \\
0 & 1 + \tilde{\eta}_{yy} & 0 \\
0 & 0 & 1 + \tilde{\eta}_{zz}
\end{bmatrix}
\begin{bmatrix}
dx^0 \\
dy^0 \\
dz^0
\end{bmatrix}
\]
where \( (d_{R-R}^2)^2 = dx^2 + dy^2 + dz^2 \) and \( (d_{R-R}^0)^2 = dx^{02} + dy^{02} + dz^{02} \).

As lattice mismatch semiconductor is grown on a substrate, the overlayer has a built in strain which has an effect on the electronic and optoelectronic properties of the material. For an overlayer with lattice constant \( a_L \) grown on a substrate with lattice constant \( a_S \), the strain between the two materials is defined as:
\[
\varepsilon = \frac{a_S - a_L}{a_L}
\]

If the strain is small, the lattice constant of the epitaxial layer in the direction parallel to the interface is equal to the lattice constant of the substrate. The lattice constant of the epitaxial perpendicular to substrate will change by Poisson effect. For layer by layer growth, the epitaxial layer is biaxially strained in the plane of the substrate by an amount \( \varepsilon_{\parallel} \) and uniaxially strained in the perpendicular direction by an amount \( \varepsilon_{\perp} \). To determine the strain tensor far away from the embedded quantum dot the wetting layer is treated as a quantum well. For a thick substrate of a coherently grown film, the strain components in-plane of the strain is:
\[
\varepsilon_{\parallel} = \varepsilon_{xx} = \varepsilon_{yy} = \frac{a_S - a_L}{a_L} = \varepsilon
\]

Since the layer is not subject to any stress in the perpendicular direction, perpendicular strain \( \varepsilon_{\perp} \) is proportional to \( \varepsilon_{\parallel} \)
\[
\varepsilon_{\perp} = \varepsilon_{zz} = \frac{\varepsilon_{\parallel}}{\sigma} = \frac{C_{12}}{C_{11}} \varepsilon_{\parallel}
\]
$C_{11}$ and $C_{12}$ are elastic constants and $\sigma$ is the Poisson ratio [12]. The strain effects inside the quantum dots are given in the reciprocal space.

$$e_{ij} = \varepsilon_{ij} X_{QD}(\varepsilon) \left[ \delta_{ij} - \frac{3C_{12} + 2C_{44}}{C_{12} + 2C_{44}} \frac{\varepsilon_i \varepsilon_j}{\varepsilon^2} \right]$$

(13)

where $i$ and $j$ represent $(x, y, z)$. Due to the strain introduced into quantum dots the atoms are shifted from their original positions leading to polarizations.

To model a CdSe quantum dot (QD) embedded in a ZnSe material a sufficiently large supercell must be chosen with a crystal lattice so that the numerical artifacts in the localized QD states are avoided. Therefore a cubical box of dimensions $18a \times 18a \times 18a$ unit cells (46656 atoms) was considered. Figure 4 shows a supercell of a CdSe spherical quantum dot (red spheres) embedded in ZnSe (green spheres) simulated in $k$-space, each sphere representing a unit cell of dimension $\left(\frac{2\pi}{a}\right)(1 \times 1 \times 1)$. In this box, a CdSe wetting layer (WL) (blue spheres) of a thickness of one lattice constant $a = 5.668 \text{Å}$ of the bulk ZnSe was considered. To study CdSe quantum dot embedded in ZnSe, the Löwdin basis states can be used as they depend on the neighbouring atoms. The embedded quantum dot and the nanocrystal were modeled on an atomistic level from the bulk tight-binding (TB) parameters.

**Figure 4.** Spherical quantum dot embedded in a matrix material
The matrix elements for each lattice site were set according to the occupying atom. For the matrix elements we use the TB parameters of the corresponding bulk materials. At the interfaces averages of the tight binding parameters are used to take into account that the selenium atoms are not explicitly attributed to one of the constituting materials. For the treatment of the surfaces of the nanocrystal or of the boundaries of the supercell, fixed boundary conditions were used in order to reduce the number of non-zero matrix elements. As the numbers of nonzero elements present when compared with all elements of the matrices were small, sparse matrices were used to store the matrix data, the indices and the values of nonzero elements.

The dimension of the Hamiltonian matrix includes all the atoms of the supercell. The nearest neighbour terms in the matrix are computed using the Slater-Koster overlap integrals. The bulk Hamiltonians were included in the adjacency matrices to obtain the quantum dot Hamiltonians. For the adjacency points of ZnSe, bulk Hamiltonian was included without any perturbations as strain effects are not present in matrix material. To account for the valence band offset between two materials CdSe and ZnSe the diagonal elements of CdSe bulk Hamiltonian are shifted before including in the adjacency points. For each adjacency point 8×8 bulk Hamiltonian was included and the strain tensor elements were calculated.

These were used in equation 9 to calculate the differences in atomic positions d_{RR} due to the strain introduced by lattice mismatch of two materials. The Hamiltonian with strain effect was obtained using differences in atomic positions with and without strain was calculated using equation 7.

Then the strain effects were included in the bulk Hamiltonians and for quantum dot adjacency points. For the adjacency points in the wetting layer strain is assumed to be zero. For these calculations wetting layer right below the quantum dot is assumed as part of the quantum dot. Hamiltonian for the adjacency points between two materials are also calculated including strain effects. Strain effect for the adjacency points between wetting layer and matrix material were calculated using the equations 11 and 12 [11]. Piezoelectric effect is less important for CdSe and ZnSe zinc blend structured materials [7]. To build the matrix, we iterate through the adjacency lists and place the overlap matrix block into the Hamiltonian for each connected pair of atoms.

The single-particle Hamiltonian of the whole supercell corresponds to a very large matrix. For the electronic structure and optical properties of a nanostructure, the electronic states near the band gap are the states that are of particular interest. If valence and conduction band would decouple, the states of interest would be the eigenfunctions with the largest and smallest eigenvalues in valence and conduction bands respectively. Schrödinger equation can be solved as an interior eigenvalue problem to compute only a few eigenvalues near the band gap region. For this purpose the folded spectrum method is employed. In the original eigenvalue problem

\[ H |\psi_i\rangle = \epsilon_i |\psi_i\rangle \quad (13) \]

the expectation value \( \langle \psi_i | H | \psi_i \rangle \) is maximized to obtain the lowest energy eigenstate. In order to find the eigenvalues near conduction and valence bands, a reference value has to be computed. This is accomplished by converting equation 13 to an equation which has the same solutions [7]:

\[ |\phi_i\rangle = \frac{1}{\langle \psi_i | H | \psi_i \rangle} |\psi_i\rangle \]
\( (H - \varepsilon_{ref})^2 |\psi_i\rangle = (\varepsilon_i - \varepsilon_{ref})^2 |\psi_i\rangle \)  \( (14) \)

Figure 5 illustrates how the eigenvalues near a reference value, near the valence band maximum and those near conduction band minimum are obtained in the folded spectrum method. Properties of the CdSe and ZnSe band structures. The lattice constants are given by 6.077 Å and 5.668 Å, respectively. Eg denotes the band gap, \( \Delta s \) the spin-orbit coupling and \( m_e \) the effective electron mass. \( C_{ij} \) are the elements of the elastic stiffness tensor.

**Table 2. Parameters for CdSe and ZnSe**

<table>
<thead>
<tr>
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<th>CdSe</th>
<th>ZnSe</th>
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<tbody>
<tr>
<td>( a ) [Å]</td>
<td>6.077</td>
<td>5.668</td>
</tr>
<tr>
<td>( E_g ) [eV]</td>
<td>1.74</td>
<td>2.82</td>
</tr>
<tr>
<td>( m_e )</td>
<td>0.12</td>
<td>0.147</td>
</tr>
<tr>
<td>( C_{12} ) [GPa]</td>
<td>46.3</td>
<td>50.6</td>
</tr>
<tr>
<td>( C_{11} ) [GPa]</td>
<td>66.7</td>
<td>85.9</td>
</tr>
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</table>

**Figure 5.** Folded spectrum method [6]
4. NEAR CUBICAL QUANTUM DOT

For a near cubical quantum dot the strain effects are given by

\[ X_{QD}(\varepsilon) = \frac{8}{\varepsilon_1 \varepsilon_2 \varepsilon_3} \sin \left( \frac{\varepsilon_1 a_1}{2} \right) \sin \left( \frac{\varepsilon_2 a_2}{2} \right) \sin \left( \frac{\varepsilon_3 a_3}{2} \right) \]  

(15)

where \( a_1, a_2 \) and \( a_3 \) are the dimensions of the quantum dot and origin of the coordinates are at the centre of the quantum dot. In the super cell of dimensions \( 18a \times 18a \times 18a \) unit cells (46656 atoms) The near cubical quantum dot of CdSe with dimensions \( 7a \times 7a \times 6a \) (2352 atoms) with 294 unit cells (red spheres) embedded in ZnSe atoms (green spheres) is shown in Figure 6. The blue layer is the wetting layer of CdSe atoms. By checking adjacent atoms, adjacency matrices were produced and for this near cubical quantum dot it is presented in Figure 7.

![Figure 6. Near cubical quantum dot](image)

Figures 8 include the places of nonzero elements of the quantum dot Hamiltonians. Adjacencies of ZnSe matrix material atoms are the green points, while the red points are the adjacencies of CdSe quantum dot material. Points shown in blue correspond to the adjacencies between two materials. The \( k_z \) axis was chosen to go through the centres of the quantum dots. The highest and lowest eigenvalues corresponding to the specified \( k_z \) - space points were found by solving the Hamiltonian. These are shown in figure 9. The largest energy gap of 129.57 MeV occurs for \((0, 0, 2\pi/2)\) point and the lowest of 43.59 MeV at \( \Gamma \) -point \((0, 0, 0)\). So in order to identify the lower limit of conduction band and higher limit of valence band energy values were obtained near every integer at \( \Gamma \) -point. These are shown in Figure 10.
Figure 7. Adjacency matrix for near cubical quantum dot

Figure 8. Hamiltonian matrix for near cubic
Figure 9. The highest and lowest energy eigenvalues for near cubic quantum dot at 
\( a (0,0,\pm n\pi / a)(n = 0,5) \)

Figure 10. Energy levels near integers at point (0, 0, 0) in k space for near cubic quantum dot
5. HEMISPHERICAL QUANTUM DOT

For hemispherical quantum dot the strain effects are given by

\[ X_{QD}(\varepsilon) = \frac{1}{2} X_{QD}^{\text{sphere}}(\varepsilon) + \frac{2\pi i}{\varepsilon_3} \left[ \frac{R}{\varepsilon} J_1(R\varepsilon_\|) - R^2 I_0(R\varepsilon_3, R\varepsilon_\|) \right] \]  

(16)

where \( R \) is the radius of the hemisphere and \( \varepsilon_\| = \sqrt{\varepsilon_1^2 + \varepsilon_2^2} \) and the Bessel functions \( J_1 \) and \( I_{j_0} \) are given by:

\[ J_1(x) = \frac{x}{2} + \frac{x^3}{16} + \frac{x^5}{384} \]  

(17)

\[ I_{j_0}(\alpha, \beta) = \int_0^1 x \cos(\alpha - 1 - x^2) J_0(\beta x) dx \]

and \( J_0(x) \) is

\[ J_0(x) = \frac{1}{2} - \frac{x^2}{16} + \frac{x^4}{384}. \]

The strain effect of a spherical quantum dot is:

\[ X_{QD}^{\text{sphere}}(\varepsilon) = \frac{4\pi}{\varepsilon} \left[ \frac{\sin(\varepsilon R)}{\varepsilon \varepsilon^2} - \frac{R \cos(\varepsilon R)}{\varepsilon} \right] \]  

(18)

where \( \varepsilon = \sqrt{\varepsilon_1^2 + \varepsilon_2^2 + \varepsilon_3^2} \) and \( R \) is the radius of the sphere.

A super cell of dimensions 18a×18a×18a unit cells was simulated in k-space, each sphere representing a unit cell of dimension \((2\pi/a)(1\times1\times1)\). The hemispherical CdSe quantum dot (red spheres) of radius 5 unit cells with 298 unit cells embedded in ZnSe atoms (green spheres) is shown in Figure 11. The blue layer is the wetting layer of CdSe atoms. Figures 12 shows the places of nonzero elements of the quantum dot Hamiltonians. The green points indicates the adjacencies of ZnSe matrix material atoms, the red points the adjacencies of CdSe quantum dot material atoms and blue points correspond to the adjacencies between two materials. The highest and lowest eigenvalues corresponding to the specified k-space points were found by solving the Hamiltonian are shown in Figure 13. The largest energy gap of 130.05 MeV occurs for \((0,0,2\pi/a)\) point and lowest gap of 33.45 at \( \Gamma \) point point \((0,0,0)\).
Figure 11. Hemispherical quantum dot

Figure 12. Hamiltonian for hemispherical quantum dot
Figure 13. The highest and lowest energy eigenvalues for hemispherical quantum dot at 
$(0,0,\pm n\pi/a)(n = 0, 5)$

The energy values were obtained near every integer at $\Gamma$-point is shown in Figure 14.

Figure 14. Energy levels near integers at point $(0, 0, 0)$ in $k$ space for hemispherical quantum dot
6. CYLINDRICAL QUANTUM DOT

For cylindrical quantum dot, the strain effects are given by

\[
X_{QD}(\varepsilon) = \frac{1}{2} X_{QD}^{\text{sphere}}(\varepsilon) + \frac{2\pi d}{\varepsilon s} \sin\left(\frac{\varepsilon_s h}{2}\right) J_1\left(\frac{d\varepsilon_s}{2}\right)
\]

(18)

where \(d\) and \(h\) are the diameter and the height of the cylindrical quantum dot. The Bessel function in equation 17.

The same super cell of dimensions \(18a \times 18a \times 18a\) unit cells dots was simulated in \(k\)-space, each sphere representing a unit cell of dimensions \((2\pi/a)(1\times1\times1)\). The cylindrical CdSe quantum dot with across sectional radius of 4 unit cells and a height of 6 unit cells with a total of 294 unit cells in red embedded in green ZnSe atoms is shown in Figure 15. Figures 16 shows the places of nonzero elements of the quantum dot Hamiltonians. The green points indicates the adjacencies of ZnSe matrix material atoms, the red points the adjacencies of CdSe quantum dot material atoms and blue points correspond to the adjacencies between two materials. The highest and lowest eigenvalues corresponding to the specified \(k\)-space points were found by solving the Hamiltonian are shown in Figure 17. The largest energy gap of 129.37 occurs for \((0,0,4\pi/a)\) point and and lowest gap of 44.61 at \(\Gamma\) point point \((0, 0, 0)\).

The energy values were obtained near every integer at \(\Gamma\)-point is shown in Figure 18.

![Figure 15. Cylindrical quantum dot](image)
Figure 16. Hamiltonian for cylindrical quantum dot

Figure 17. The highest and lowest energy eigenvalues for cylindrical quantum dot at $(0, 0, \pm n\pi / a)(n = 0, 5)$
Figure 18. Energy levels near integers at point (0, 0, 0) in k space for cylindrical quantum dot

7. CONCLUSIONS

To study the electronic and optical properties of CdSe/ZnSe semiconductor quantum dots, a theoretical model of empirical tight binding approach, limiting the local degrees of freedom only to a small basis set $s_c p_a^3$ was used to take into account the atomistic structure of the QDs. The predictions of the model for QD structures are dependent on the choice of the material parameters for the bulk semiconductors. In the simplified and restricted tight binding $s_c p_a^3$ basis set the s orbitals at the anions (Se) are not taken into account. Therefore, the surface states formed by the dangling bonds of unsaturated Se at the nanocrystal surface states are removed and we do not obtain any indications of quasimetallic behavior. The data obtained for the three different shapes has slight differences. So there is an effect of the shape to the electronic structure of quantum dots. According to the data obtained in this research project effect due to the shape is very small, which can’t be used for any controversial application. However this slight effect can be used to optimize highly sensitive applications.

References


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