CHAPTER III
EFFECTS OF STRAIN ON THE BAND ALIGNMENT AND THE OPTICAL GAIN OF A CdTe/ZnTe QUANTUM DOT

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3.1 Abstract

The band lineups at the strained layer interfaces, in \( \text{Zn}_x\text{Cd}_{1-x}\text{Te}/\text{ZnTe} \) quantum dot nanostructure for various Zn alloy content, are computed using model solid theory with an example of CdTe/ZnTe interface. The effects of strain due to hydrostatic and biaxial strain and the internal electric fields, due to the spontaneous and piezoelectric polarization are taken into consideration. The dielectric mismatch, through the effective potential, is introduced between the dielectric constants of the dot and the barrier materials. The interband emission energy as a function of dot radius is computed for various Zn alloy content. The optical gain spectra of heavy hole exciton for various Zn concentration are studied. Calculations are obtained for different confinement potentials with the inclusion strain effect. These results show that (i) the potential taking into account the effects of PB potential due to the dielectric mismatch enhances the exciton binding energy and (ii) the geometry of quantum dot, the strain effects and the Zinc alloy content have great influences on the electrical and optical properties of the dot.
3.2 Introduction

CdTe/ZnTe heterostructure, among II-VI materials, attracts much attention nowadays due to its potential application in short wavelength electronic devices such as light emitting diodes, laser diodes, photovoltaic cells and high efficiency multi-junction solar cells. Quantum dot fabricated using CdTe/ZnTe material shows unique property of higher exciton binding energy which can be applied for making some opto-electronic devices operating in green and blue region in electromagnetic spectrum. Due to the latest and sophisticated manufactured techniques such as Molecular Beam Epitaxy, Metal Organic Chemical Vapour Deposition and Electron lithography, it is possible to produce high quality of CdTe/ZnTe crystals with any variation of Zn or Cd alloy content [1-3].

ZnTe can crystallize in either the wurtzite or zinc-blend phase. ZnTe is strained in the opposite sense to the CdTe in CdTe/ZnTe heterostructures. However, zinc blend based systems have more advantages over wurtzite systems [4]. The potential barrier height of any semiconductor heterostructure is determined by the band offsets and band lineups at the interface. A vast variation of band offset ratio in CdTe/ZnTe heterostucture exists due to the strong built-in elastic strain, electrostatic fields and the mismatch of crystal parameters. The band offsets of some II-VI materials have been investigated by means of low temperature cathodoluminescence and electrical current deep level transient spectroscopy methods [5]. The electronic structure and the phase stability of some II-VI materials have been examined recently by Yang et al., [6] who analyzed the band gap, valance band maximum, the deformation potentials and the band offset. The enhancement of exciton stability due to quantum confinement and exciton phonon interaction on some wide band gap nanostructures have been discussed earlier [7-9].
The study of geometrical confinement, induced strain and the internal field on the electronic and optical properties of any quantum dot heterostructures are interesting issues. They are very important in understanding of band gap tuning in opto-electronic features in semiconductors [10]. The overlap of electron and hole wave functions is considerably affected by the internal electric fields. Kowalik et al., [11] have observed the stronger influence of the electric field on the excitonic states of lower binding energy in CdTe/ZnTe self assembled quantum dot. The effective masses of electron and hole, the band offsets and the band lineups decide the strength of wave functions inside the dot and the importance of interface of the quantum dot and the barrier material [12]. The strain fields around quantum dot, in the matrix method, based on the elastic theory have been discussed very recently [13]. The same investigators [14] observed the effects of wetting layer of CdTe/ZnTe quantum dots on the temperature-dependent photoluminescence measurement of the interband transition energies from the ground electronic subband to the ground heavy-hole subband and further they have shown that interband transition energies decrease with increasing temperature. The effects of temperature on the strain distribution, the electronic and the optical properties of quantum dots have been dealt very recently by Hong and Park [15] who demonstrated the optical gain spectra having the different polarization distributions due to the structure elements in the optical matrix.

In the present chapter, the ground state heavy hole exciton binding energies are investigated in a strained Zn$_x$Cd$_{1-x}$Te/ZnTe quantum dot nanostructure for various Zn alloy content. The effects of strain and the internal electric fields are involved in the calculations. The band lineups are computed using model solid theory. The optical gain of heavy hole
exciton and the interband emission energy as a function of dot radius for various Zn alloy content are studied. Calculations are obtained for different confinement potentials considering the internal electric fields. In Section 3.3, the theoretical model used in the calculations of strain effect, model solid theory, the obtained eigen functions and eigen energies of electron states and the optical gain are discussed. The results and discussion are presented in Section 3.4. A brief summary and results are presented in the last section.

3.3 Model and calculations

3.3.1 Effects of strain and polarization

The band profile in the strained material includes the strain effects and the spin-orbit coupling effects. The effects of strain bring out the knowledge of band edges of conduction and valence bands. The hydrostatic effect causes the conduction band edge shifting downwards whereas the splitting induced by shear strain increases in the valence band. The strain effect modifies the lattice constants, dielectric constants, effective mass of the materials.

The biaxial lattice matched induced strains in the dot and the barrier are given by

\[ \epsilon_{xx} = \epsilon_{yy} = \epsilon_{\parallel} = \frac{a_{\parallel} - a_{\text{bulk}}}{a_{\text{bulk}}} \]  \hspace{1cm} (3.1)

\[ \epsilon_{xx} = \epsilon_{\perp} = -\frac{2C_{12}}{C_{11}} \epsilon \]  \hspace{1cm} (3.2)

where \( a_{\text{bulk}} \) is the bulk lattice constant of the dot material without strain and \( a_{\parallel} \) is the strained lattice constant in the dot. \( C_{ij} \) are the elastic
constants of the materials. The biaxial strain is the combination of hydrostatic and uniaxial strain components. The former changes the volume of the cell of crystal leading to the changes of periodicity of the lattice, eventually the band offset and the edges of conduction and valence bands change whereas the latter will affect the symmetry of the cubic crystal leading to the non-degenerate level at $\Gamma_8$ band.

To determine the strain in the quantum dot, the deformation potentials for the low dimensional semiconductor systems are followed. The expression for effective deformation potential is given by [16]

$$a_c = \frac{\chi E_g}{3} - (\chi - 1) \frac{\hbar^2 q_0^2}{4m_e^*} + (\chi - 2) \frac{\pi^2 \hbar^2}{2m_e^* L^2}$$

(3.3)

where $E_g$ is the band gap of the quantum dot, $q_0$ is the wave vector, $L$ is the height of the cylindrical quantum dot and the phenomenological parameter, $\chi$, is given by

$$\chi = \frac{(C_{11} + 2C_{12})}{E_g} \frac{dE_g}{dP}$$

(3.4)

where $dE_g/dP$ is the pressure dependent band gap and the related pressure coefficients are given in Table 3.1. Similarly, the same calculations pertaining to the effective deformation potentials for valence band are carried out by including the heavy hole mass.

The change in the effective conduction band and valence band edge positions are given by

$$\Delta E_c = a_c \frac{\Delta V}{V}$$

(3.5)
\[ \Delta E_v = a_v \frac{\Delta V}{V} \]  

(3.6)

where \( V \) is the volume of unstrained primitive cell, \( a_c \) and \( a_v \) are the deformation potentials of conduction and valence band respectively. The valence band is usually split due to the spin orbit effects even in the absence of strain effect, hence,

\[ E_v = \Delta E_v + \frac{\Delta_0}{3} \]  

(3.7)

Thus,

\[ \Delta (E_c - E_v) = \Delta E_g = (a_c - a_v) \frac{\Delta V}{V} \]  

(3.8)

where, the fractional volume change is given by,

\[ \frac{\Delta V}{V} = \varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz} \]  

(3.9)

For cubic lattice and \( \langle 100 \rangle \) orientation, it is obtained as

\[ \frac{\Delta V}{V} = 2\varepsilon + \varepsilon_{zz} = \varepsilon_{zz} \frac{2(C_{11} - C_{12})}{C_{11}} \]  

(3.10)

Using Eq.(3.5) and Eq.(3.6), the conduction and valence band edges due to strain are obtained as

\[ \Delta E_c = 2a_c \varepsilon_{zz} \frac{(C_{11} - C_{12})}{C_{11}} \]  

(3.11)

and

\[ \Delta E_{vh} = 2a_v \varepsilon \frac{(C_{11} - C_{12})}{C_{11}} + b\varepsilon \frac{(C_{11} + 2C_{12})}{C_{11}} \]  

(3.12)
The built-in electric fields due to the spontaneous and piezoelectric polarizations are different in the dot and barrier materials. The polarization in a self formed wurtzite quantum dot will have both spontaneous and piezoelectric components. The piezoelectric tensor will have three independent nonvanishing components \( e_{31}, e_{33}, e_{15} \) but the \( z \) component of the spontaneous polarization is nonzero \([16]\). Thus, the total polarization, \( \vec{P}_{\text{tot}} \) is the sum of spontaneous polarization \( \vec{P}_{\text{SP}} \) and the piezoelectric polarization \( \vec{P}_{\text{PE}} \) without the external electric field. The built-in electric field is caused by the polarization in the quantum dot. Thus, it is obtained as from \([17]\)

\[
F_{\text{ZnCdTe}} z_{\text{ZnCdTe}} + F_{\text{ZnTe}} z_{\text{ZnTe}} = 0. \tag{3.13}
\]

Using the boundary condition of the continuity of the electric displacement vector at the hetero interfaces of the quantum dot, it is obtained as,

\[
\varepsilon_e(\text{ZnTe})\varepsilon_0 F_{\text{ZnTe}} - \varepsilon_e(\text{ZnCdTe})\varepsilon_0 F_{\text{ZnCdTe}} = P_{\text{SP}(\text{ZnCdTe})} + P_{\text{PE}(\text{ZnCdTe})} - P_{\text{SP}(\text{ZnTe})} \tag{3.14}
\]

where \( \varepsilon_0 \) is the dielectric constant of the respective material. Using, Eq.(3.13) and Eq.(3.14), the built-in electric field can be obtained as

\[
F_{\text{ZnTe}} = \frac{(P_{\text{SP}(\text{ZnCdTe})} + P_{\text{PE}(\text{ZnCdTe})} - P_{\text{SP}(\text{ZnTe})})z_{\text{ZnCdTe}}}{\varepsilon_0(\varepsilon_e(\text{ZnTe})z_{\text{ZnTe}}^2 + \varepsilon_e(\text{ZnCdTe})z_{\text{ZnCdTe}}^2)} \tag{3.15}
\]

and

\[
F_{\text{ZnCdTe}} = -\frac{(P_{\text{SP}(\text{ZnCdTe})} + P_{\text{PE}(\text{ZnCdTe})} - P_{\text{SP}(\text{ZnTe})})z_{\text{ZnTe}}}{\varepsilon_0(\varepsilon_e(\text{ZnTe})z_{\text{ZnTe}}^2 + \varepsilon_e(\text{ZnCdTe})z_{\text{ZnCdTe}}^2)} \tag{3.16}
\]
The direction of built-in electric field, $F$, depends on the orientation of the piezoelectricity and spontaneous polarization. In this case, the direction of the piezoelectricity and spontaneous polarization is along the $z$ direction. The above values can be generally calculated by the polarity of the crystal and the strains of the quantum nanostructure. The heterostructure will have spontaneous polarization and the piezo-electric polarization due to strain caused by the lattice mismatch between CdTe and ZnTe material.

The piezo electric polarization along the $c$-axis is given by

$$P_{PZ} = e_{31}(\varepsilon_{xx} + \varepsilon_{yy}) + e_{33}\varepsilon_{zz} \quad (3.17)$$

with $\varepsilon_{xx} = \varepsilon_{yy} = \frac{a(ZnTe) - a(ZnCdTe)}{a(ZnTe)}$ and $\varepsilon_{zz} = -2\frac{C_{13}}{C_{33}}\varepsilon_{xx}$. The piezo-electric polarization is given by

$$P_{PZ} = 2\varepsilon_{xx}\left(e_{31} - e_{33}\frac{C_{13}}{C_{33}}\right). \quad (3.18)$$

Thus the total polarization is given by

$$\bar{P} = \bar{P}_{PZ} + \bar{P}_{SP}. \quad (3.19)$$

The band alignments of conduction and valence states of $\text{Zn}_{x}\text{Cd}_{1-x}\text{Te}/\text{ZnTe}$ are calculated using the model solid approach in the following section.

3.3.2 Model solid theory

The model solid theory which is suitable for calculating the band lineups of the materials in the same block predicts the alignment of any
band structure on the absolute energy level. Particularly, it relates the average electrostatic potential within the semiconductor nanostructures. Eventually, the band lineups can be calculated by subtracting corresponding individual values. The standard deformation potential theory is applied to calculate the strain induced confinement potentials in the dot and the surrounding barrier. The splitting of the valence band will take place when the shear strains are introduced, expecting the shifts in average valence band potential. In addition, the bands in the band structure shift when a semiconductor is compressed. On the other hand, a relative shift is expected in the conducting band correspondingly. For Zn$_x$Cd$_{1-x}$Te/ZnTe strained layer interfaces, the strain components are calculated as shown below.

The shift in average valence band electrostatic potential is given by

$$\Delta E_{v,av} = a_v \frac{\Delta \Omega}{\Omega}. \quad (3.20)$$

where $a_v$ is the hydrostatic deformation potential of the valence band in the host material. In general, the valence band, in the absence of shear strain, is split due to spin-orbit effects. Hence, the position of the topmost valence band is given by

$$E_v = E_{v,av} + \frac{\Delta \Omega}{3}. \quad (3.21)$$

where $E_{v,av} = (E_{hh} + E_{lh} + E_{SO})/3$ and the fractional volume change, leading to the hydrostatic strain, is given by

$$\frac{\Delta \Omega}{\Omega} = \text{Tr}(\epsilon) = \epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz} \quad (3.22)$$
where $\varepsilon_{||}$ is the strain tensor as given by

$$\varepsilon_{||} = \varepsilon_{xx} = \varepsilon_{yy} = \frac{a_{ZnTe} - a_{ZnCdTe}}{a_{ZnTe}}$$

(3.23)

and

$$\varepsilon_{\perp} = \varepsilon_{zz} = -2 \frac{C_{12}}{C_{11}} \varepsilon_{||}$$

(3.24)

where $C_{11}$ and $C_{12}$ are the elastic constants of the dot materials as given in Table 3.1. Similarly, the shift in conduction band is given by

$$\Delta E_c = a_c \frac{\Delta \Omega}{\Omega}.$$  

(3.25)

Using Eq.(3.21), the position of conduction band is obtained as

$$E_c = E_v + E_g.$$  

(3.26)

Since the materials, CdTe and ZnTe are in the same block one can expect the most reliable results rather from the materials belonging to different blocks [18]. Using above equations, the band lineups at the interface of $Zn_xCd_{1-x}Te/ZnTe$ for different Zn alloy content are calculated by properly combining the contribution of strain and the effect of spin-orbit splitting as shown in Fig.3.1. The valence band offset related to heavy holes in the CdTe/ZnTe heterostructure interface is given by

$$\Delta E_{v,hh} = \Delta E_{v,hh}^{B}(ZnTe) - \Delta E_{v,hh}^{D}(Cd_{1-x}Zn_xTe) + \delta E_{v,hh}$$

(3.27)
where $\Delta E_{v,hh}^B (ZnTe)$ is the unstrained outer barrier material of the dot, for other values in the dot are linearly interpolated the other data taken from Table 3.1. $\Delta E_{v,hh}^B (Cd_{1-x}Zn_xTe)$ is the strained inner material in the dot and $\delta E_{v,hh}$, the shift in the heavy hole valence band energy due to strain, is expressed as

$$\delta E_{v,hh} = a_v(2\varepsilon + \varepsilon_{zz}) - b(\varepsilon_{zz} - \varepsilon) \quad (3.28)$$

where $a_v$ hydrostatic deformation potential in the valence band, $b$ is the shear deformation potential. Varying the alloy composition (Zn in CdTe) leads the variation in the lattice constants. This property tailors the electronic properties of the heterostructures. Similarly, the valence band offset for light hole is calculated as

$$\Delta E_{v,hl} = \Delta E_{v,hl}^B (ZnTe) - \Delta E_{v,hl}^D (Cd_{1-x}Zn_xTe) + \delta E_{v,hl} \quad (3.29)$$

where $\delta E_{v,hl}$, the shift in the light hole valence band energy due to strain, is expressed as

$$\delta E_{v,hl} = a_v(2\varepsilon + \varepsilon_{zz}) - \frac{1}{2}\Delta_0 + \frac{1}{4}b(\varepsilon_{zz} - \varepsilon)$$

$$+ \frac{1}{2}\sqrt{\Delta_0^2 + \Delta_0 b(\varepsilon_{zz} - \varepsilon) + \frac{9}{4}(b(\varepsilon_{zz} - \varepsilon))^2} \quad (3.30)$$

where $\Delta_0$ is the spin orbit splitting. The conduction band offset is given by

$$\Delta E_c = \Delta E_c^B (ZnTe) - \Delta E_c^D (Cd_{1-x}Zn_xTe) + \Delta E_g + \delta E_c \quad (3.31)$$

where $\Delta E_g$ is band gap energy is given by [19]
\[ \Delta E_g = 1.51 + 0.45x + 0.31x^2 \] (3.32)

The above expression of band gap has been obtained by varying Zn concentration in Zn\(_x\)Cd\(_{1-x}\)Te / ZnTe quantum dot. The quadratic term in Eq.(3.32) is correlated with the bowing of optical band gap. And

\[ \delta E_c = a_c (2\varepsilon + \varepsilon_{zz}) \] (3.33)

The effects of band offsets and the lattice mismatch directly affect the electron and hole potentials. The \( V_c \) and \( V_h \) are calculated using the following expression.

\[ V_c = E_{cZnTe} - E_{cZn_xCd_{1-x}Te} \] (3.34)

\[ V_h = E_{hhZnTe} - E_{hhZn_xCd_{1-x}Te} \] (3.35)

where \( E_{cZnTe} \) and \( E_{hhZnTe} \) are the strain shifts of the energies of conduction and heavy hole bands in the barrier dot, \( E_{cZn_xCd_{1-x}Te} \) and \( E_{hhZn_xCd_{1-x}Te} \) are the strain shifts of the energies of conduction and heavy hole bands in the inner dot.

### 3.3.3 Strain induced exciton binding energy

An exciton located at the centre of a Zn\(_x\)Cd\(_{1-x}\)Te cylindrical dot confined by a potential barrier (ZnTe) is considered. Since these materials are chemically related, the envelop wave function based on the single band effective mass approximation is used. The confining potential is assumed to be zero inside and \( V \) outside. The Hamiltonian of an exciton with the effect of electron-LO phonon interaction in a Zn\(_x\)Cd\(_{1-x}\)Te/ZnTe strained semiconductor heterostructure, within the single band effective mass approximation, is given by
$$\hat{H} = -\frac{\hbar^2}{2\mu_+(x)} \frac{1}{\rho_j} \frac{\partial}{\partial \rho_j} \rho_j \frac{\partial}{\partial \rho_j} - \frac{\hbar^2}{2m_e^*(x)} \frac{\partial^2}{\partial z_e^2} - \frac{\hbar^2}{2m_h(x)} \frac{\partial^2}{\partial z_h^2} - \frac{e^2}{\varepsilon(r)} + V_e(z_e) + V_h(z_h) + V_{PB}(r) + V_{KT}(r) + E_{self}$$

(3.36)

where $e$ is the absolute value of the electronic charge, $j=e, h$, $m_{e,h}^*(x)$ is the Zn-dependent effective mass of electron and hole of Zn$_x$Cd$_{1-x}$Te, $z_e$ and $z_h$ are the electron and hole co-ordinates along the growth direction of the structure, $V_{e,h}(x)$ is the Zn-dependent strain induced confined potential for electrons and holes, $V_{PB}(r)$ is the effective potential between an electron and a hole, $V_{KT}(r)$ is the effective potential due to the effect of dielectric confinement in the image charge method [20], $\varepsilon(r)$ is the size dependent dielectric function and $r = \sqrt{\rho^2 + (z_e - z_h)^2}$ with $\rho$ is the electron (hole) coordinate in the plane perpendicular to the cylinder axis. The $\mu_+$ is the reduced mass of the exciton given by [21], $m_0$ is the free electron mass and $m_e^*$ is the electron effective mass. The parameter $m_+$ is hole effective mass given by

$$\frac{1}{m_+} = \frac{1}{m_0} (\gamma_1 - 2\gamma_2)$$

(3.37)

The size dependent dielectric function [22] and the oscillator strength for the quantum dot interband transition are given by [23]

$$\varepsilon(\omega) = \varepsilon + \frac{2}{V_{QD}} \left[ f_e(E_e - f_{v'}(E_{v'})) - \frac{e^2 f / m_0 \varepsilon_0}{\omega^2 - \omega_0^2 + i2\omega\gamma} \right]$$

(3.38)

and
respectively. In the above expressions, \( f_e \) and \( f_h \) are the carrier distribution functions. Taking into account the spin degeneracy the dipole density \( (N) \) is replaced by \( 2/V_{QD} \) given by \( (4\pi/3)R^3 \) where \( R \) is the radius of the quantum dot. All the other values have been followed as in Ref. [22] and Ref.[24].

The effect of exciton and the LO phonon interaction are derived by the effective potential \( (V_{PB}) \) between the electron and hole along with the self energy term \( (E_{self}) \) as given below. The quantum dot confinement effective potential of the electron and hole is given by [25]

\[
V_{PB}(r) = -\frac{e^2}{\varepsilon^* r} \left[ \frac{C^4}{B^4} - \frac{m_e^* h_e}{\Delta m} \exp\left( -\frac{rA_e}{R_e} \right) + \frac{m_h^* h_h}{\Delta m} \exp\left( -\frac{rA_h}{R_h} \right) \right] - \left( h_\mu + \frac{C^3 r}{2B^2 a_{ex}} \right) \exp\left( -\frac{rB}{R_\mu} \right)
\]

(3.40)

where \( \varepsilon^* = (1/\varepsilon_\infty - 1/\varepsilon_s)^{-1} \), \( \varepsilon_\infty \) and \( \varepsilon_s \) are the optical and static dielectric constants of the CdTe material and \( \Delta m \) is the difference in effective mass of electron and hole. \( r = \sqrt{\rho^2 + (z_e - z_h)^2} \) with \( \rho \) is in-plane radius. When a dot material is embedded on a barrier material, the field effect caused by the charge distribution will enhance the Coulomb interaction.

The self energy term is given by [26]

\[
E_{self} = -(\alpha_e g_e + \alpha_h g_h - \alpha_\mu g_\mu) \hbar \omega_{LO}
\]

(3.41)
where $\hbar \omega_{LO}$ is the LO phonon energy. The calculations of other material parameters in Eq.(3.38) and Eq.(3.19) are followed from Ref.[21].

The effective potential due to the effect of dielectric confinement on the interaction between the electron and the hole is calculated below. The effect of electron–hole confinement in the image charge method is given by the effective potential as [20]

$$V_{KT}(r) = -\sum_{n=-\infty}^{\infty} \frac{\xi^{|p|}}{\varepsilon_s \sqrt{\rho^2 + (z_e - (-1)^n z_h + nL)^2}}$$ (3.42)

where $\xi = (\varepsilon^w_s - \varepsilon^b_s)/(\varepsilon^w_s + \varepsilon^b_s)$ and $\varepsilon^w_s$ and $\varepsilon^b_s$ are the static dielectric constants of the dot and the barrier material respectively. \(\rho\) is the electron (hole) coordinate in the plane perpendicular to the cylinder axis. And \(L\) is the width of the cylindrical quantum dot.

The lowest binding energies of the electron and the heavy hole are found by getting the solution of a suitable trial wave function. Since an exciton in a $\text{Zn}_x\text{Cd}_{1-x}\text{Te}/\text{ZnTe}$ quantum dot is solved with the single band effective mass approximation, it is necessary to use a variational scheme to calculate the eigen function and eigen value of the Hamiltonian and to compute the exciton binding energy using a trial wave function with double variational parameters. Taking into account the connection between the electron-hole relative motion, the trial wave function is considered as,

$$\Psi(\vec{r}_e, \vec{r}_h) = N \phi_e(\rho_e)\theta_e(z_e)\phi_h(\rho_h)\theta_h(z_h)e^{-\alpha^2\rho^2}e^{-\beta z^2}$$ (3.43)
where $N$ is the normalization constant, $\phi_e$ and $\phi_h$ are the ground state solutions of Schrödinger equation for the electrons and holes in the absence of the Coulomb interaction. With,

$$\phi_i(\rho) = J_0(\theta_0 \rho / R) \text{, } \theta_i(z) = \cos(z \pi / L) \quad (i = e, h) \tag{3.44}$$

where $J_0$ is the Bessel function of zero order, $\theta_0 = 2.404825577$ is its first zero. The Eq.(3.43) describes the relation between the electron-hole relative motion. $\alpha$ and $\beta$ are variational parameters responsible for the in-plane correlation and the correlation of the relative motion in the $z$-direction respectively. $z$ is the electron (hole) the co-ordinate along the growth direction of the material and $\rho$ is the electron (hole) coordinate in the plane perpendicular to the cylinder axis. The normalization constants are found except the variational parameters by matching the wave functions and the effective mass and their derivatives at boundaries of the quantum dot and along with the normalization. And hence, the chosen wave function completely brings out the correlation of the electron-hole relative motion.

Thus, the minimized exciton energy in the ground state is obtained by computing the expectation value of the energy of the Hamiltonian, Eq.(3.36), as

$$\langle E \rangle = \min_{\alpha, \beta} \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \tag{3.45}$$

The exciton binding energy and the interband emission energy are calculated using the following equations,

$$E_{\text{exc}} = E_{e,h} - \langle H_{\text{min}} \rangle \tag{3.46}$$

and

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\[ E_{ph} = E_e + E_h + E^\Gamma_g(x) - E_{exc} \]  

(3.47)

where \( E_e \) and \( E_h \) are the confinement energies of the electron and hole respectively. \( E^\Gamma_g(x) \) is the Zn-dependent band gap energy of CdTe material as given by the Eq.(3.32).

### 3.3.4 Optical gain

The optical gain is calculated as [27]

\[
g(\hbar \omega) = \frac{e^2}{m_0 \omega} \sum_{n,m} \frac{1}{\hbar \omega} \left| \vec{e} \cdot M_{nm} \right|^2 \times \frac{\hbar / \Gamma_{in}}{+(E_{hm} - \hbar \omega)^2 + (\hbar / \Gamma_{in})^2} (f^n_c - f^m_v) \]

(3.48)

where \( e \) is the electronic charge, \( m_0 \) is the free-electron mass, \( \Omega \) is the angular frequency, \( \mu_0 \) is the vacuum permeability, \( \epsilon_0 \) is the dielectric constant, \( M \) is the optical momentum matrix elements, \( f^n_c \) and \( f^m_v \) are Fermi-Dirac distributions of electrons and holes for the conduction and the valence subbands, respectively, \( E^{en}_{hm} \) is the interband transition energy between the electron and the hole, and \( \Gamma_{in} \) is the interband relaxation time [28]. And the homogeneous line width of the exciton taken in this calculation is \( \hbar \Gamma = 3 \) meV [29]. The indices \( n \) and \( m \) denote the electron and the hole states in the conduction and the valence subbands, respectively. For this purpose, the single band effective mass approximation is used and the electron wave function is expanded in an appropriate set of orthonormal functions. Then, by using the density matrix approach, within a two-level system approach, the explicit expressions for the nonlinear optical properties are computed in a saturation limit.
3.4 Results and discussion

The ground state exciton binding energies of exciton located at the centre of a strained \( \text{Zn}_x\text{Cd}_{1-x}\text{Te}/\text{ZnTe} \) quantum dot, induced by the spontaneous and piezoelectric polarizations are calculated with various Zn content with the inclusion of dielectric confinement due to the image charge potential. The effect of \( z \)-confinement is calculated through a finite quantum dot model with the confinement potential determined by the band offsets and strain effects. Calculations are performed for different confinement potentials of barrier height. The atomic units have been followed in the determination of electronic charges and wave functions in which the electronic charge and the Planck’s constant have been assumed as unity. All the other values of \( \text{Zn}_x\text{Cd}_{1-x}\text{Te} \) parameters which are interpolated from the data mentioned in the Table 3.1. The effective mass of heavy hole in the \( z \)-direction is calculated as \( m_+ = 1/(\gamma_1 - 2\gamma_2) \). All the relevant parameters have been obtained by linear interpolation of CdTe and ZnTe parameters as followed by the equation

\[
T(\text{Zn}_x\text{Cd}_{1-x}\text{Te}) = (1-x)TCdTe + xTZnTe,
\]

where \( T \) refers various physical parameters used in the calculations as shown in Table 3.1. The two structures of the materials taken in our calculations can be either zinc-blend or wurtzite. The band structures of the two different crystal structures are essentially the same, except for small shifts of energy levels [30].
Table 3.1 Material parameters* used in the calculations
(all the other parameters are linearly interpolated)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>CdTe</th>
<th>ZnTe</th>
<th>Zn$<em>x$Cd$</em>{1-x}$Te</th>
</tr>
</thead>
<tbody>
<tr>
<td>$m^*_e$</td>
<td>0.11</td>
<td>0.2</td>
<td>0.11+0.091x</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>10.4</td>
<td>9.4</td>
<td>10.4-1.0x</td>
</tr>
<tr>
<td>$a$ (nm)</td>
<td>0.6481</td>
<td>0.61037</td>
<td>0.457-0.031x</td>
</tr>
<tr>
<td>$C_{11}$ (GPa)</td>
<td>53.8</td>
<td>72.2</td>
<td>53.8+18.397x</td>
</tr>
<tr>
<td>$C_{12}$ (GPa)</td>
<td>37.4</td>
<td>40.9</td>
<td>37.4 + 3.471x</td>
</tr>
<tr>
<td>$e_{14}$ (C/m$^2$)</td>
<td>0.91</td>
<td>0.028</td>
<td>0.91 – 0.88x</td>
</tr>
<tr>
<td>$E^r_g$ (eV)</td>
<td>1.51</td>
<td>2.27</td>
<td>1.51 + 0.45x +0.31x$^2$</td>
</tr>
<tr>
<td>$\Delta$ (eV)</td>
<td>0.93</td>
<td>0.91</td>
<td>0.93-0.91x</td>
</tr>
<tr>
<td>$\gamma_1$</td>
<td>4.14</td>
<td>3.96</td>
<td>4.14-0.18x</td>
</tr>
<tr>
<td>$\gamma_2$</td>
<td>1.019</td>
<td>0.86</td>
<td>1.019-0.159x</td>
</tr>
<tr>
<td>$a_c$ (eV)</td>
<td>-3.96</td>
<td>-5.83</td>
<td>-3.96-1.87x</td>
</tr>
<tr>
<td>$a_v$ (eV)</td>
<td>0.55</td>
<td>0.79</td>
<td>0.55+0.24x</td>
</tr>
<tr>
<td>$b$ (eV)</td>
<td>-1.0</td>
<td>-1.4</td>
<td>-1.0-0.4x</td>
</tr>
<tr>
<td>$E_g/dP$ (meV/Gpa)</td>
<td>83</td>
<td>103</td>
<td>83+20x</td>
</tr>
</tbody>
</table>

*Ref. [19,42]
Fig. 3.1 shows the band lineups in a CdTe/ZnTe interface, the discontinuity in the average valence bands and the band offsets are calculated from the Model solid theory. These calculations include the effects of strain shifts and spin orbit splitting. From Table 3.1 and using Eq. (3.20) and Eq. (3.21),

\[ E_{v,av}^{CdTe} = -7.08 \text{ eV} \]  
\( (3.49) \)

and

\[ E_{v,av}^{ZnTe} = -7.17 + 0.55 \times 0.21 = -7.055 \text{ eV} \]  
\( (3.50) \)

Thus, the discontinuity in the average valence bands is given by

\[ \Delta E_{v,av} = E_{v,av}^{CdTe} - E_{v,av}^{ZnTe} = -0.016 \text{ eV} \]  
\( (3.51) \)

which leads lower in CdTe. On the other side, for the conduction band, it is found that

\[ E_{c,ac}^{CdTe} = -5.17 \text{ eV} \]  
\( (3.52) \)

and

\[ E_{c,ac}^{ZnTe} = -4.48 + (\text{3.96}) \times 0.21 = -5.32 \text{ eV} \]  
\( (3.53) \)

This results in the discontinuity in the average conduction bands as given by

\[ \Delta E_{c,ac} = E_{c,ac}^{CdTe} - E_{c,ac}^{ZnTe} = -0.142 \text{ eV} \]  
\( (3.54) \)
These band lineups are shown in Fig 3.1. Thus, the strain effects (increasing Zn alloy content in CdTe) causes a relative shift of valence band edges, moving the ZnTe average valence band edge top up and that of CdTe down. In the earlier literature, some data are available to be compared, using Kronig-Penney calculations, Mathieu et al., [31] have investigated $\Delta E_v = 0.060 \pm 0.020 \ eV$ and $\Delta E_v = -0.055 \pm 0.040 \ eV$, with different sets of deformation potentials to fit one set of experimental results by comparison with the experiment and theory. Then, Gil et al., [32] proposed $\Delta E_v = 0.075 \ eV$ by comparison of photoluminescence at high pressure with Bastard envelope function calculations.
Fig. 3.1 Band lineups in a CdTe/ZnTe interface, the band offsets are calculated from the Model solid theory
In Fig.3.2 the piezoelectric field with the in-plane strain as a function of Zn alloy content is shown for Zn$_x$Cd$_{1-x}$Te/ZnTe quantum dot. The splitting of the valence bands is due to the shear strain in ZnTe material. Since the effect on piezoelectric potential is important in II-VI materials, it is required to study their electronic structure and optical properties. Since the band offsets and the effective masses of electron and hole determine the stability of the wave functions, the contribution of piezoelectric potential is important especially at the interface of dot and the barrier material and they change material properties significantly. The non-linear piezoelectric behaviour is observed when the in-plain strain is increased but the observed fields are very small in the range of mV/Å. This non-linearity of elastic constants have been investigated earlier [33, 34]. The piezoelectronic polarization contributes the ionic and electronic involvement. The non-linearity effect arises due to the above contribution behaving opposite manner [35]. Moreover, it is observed that as Zn alloy content increases the in-plain strain contribution also increases. The strain affects the relative alignment of valence and conduction bands and the hydrostatic component of the strain shifts the valence and conduction bands relative to one another.
Fig. 3.2 Piezoelectric field with the in-plane strain as a function of Zn alloy content in Zn$_x$Cd$_{1-x}$Te/ZnTe
Fig. 3.3 displays the variation of exciton binding energies of heavy holes as a function of dot radius for a Zn$_x$Cd$_{1-x}$Te/ZnTe quantum dot for various Zn content with the inclusion of effective potential and the insert figure shows the variation of heavy hole exciton binding energies as a function of dot radius in a Zn$_{0.8}$Cd$_{0.2}$Te/ZnTe quantum dot with and without the inclusion of PB potential, using Eq.(3.40), and the dielectric mismatch which have been found more effective in the strong confinement region. It also results that the Coulomb interaction is distorted as the dot radius becomes small. In all the cases, it is observed that the binding energy increases first with decreasing dot radius and it reaches the maximum value for a critical dot size and then rapidly decreases when the dot radius is still reduced for all the cases of Zn incorporation in CdTe material. It is because an increase in the dot radius results in a spreading of wave function which causes the lowering binding energy and the contribution of confinement is dominant for smaller dot radii making the exciton unbound and ultimately tunnels through the barrier. Eventually, the electron and hole wave functions penetrate into the barrier for narrow dots. Moreover, the contribution of confinement is dominant for smaller dot radii making the exciton unbound with the spread of the wave functions through the barrier [36]. The calculated exciton binding energy for the heavy holes as the heavy excitons are more common in experimental results. The enhancement of exciton binding energy with the increase of geometrical confinement strength is similar to the earlier investigations [37]. Thus, the Coulomb interaction is enhanced in the strong confinement region. Exciton binding energy is found to be prominently reduced in the weak confinement region due to a large separation of electron and hole resulting little overlap of wave functions.
As shown in the insert Fig.3.3, it is observed that the enhancement of binding energy, due to phonon-carrier interaction, is larger for all the dot radii but it is noticed that the binding energy is more influence for smaller dot radii than the larger dot radii due to the geometrical confinement. It shows the effects of PB potential including dielectric mismatch. It is found that the exciton binding energy obtained using static screened Coulomb potential is lower than the exciton binding energy with the inclusion of effective potential. It is also observed that the dielectric mismatch effect enhances the exciton binding energy. It implies that the effect of dielectric mismatch on the exciton binding energy is very important and it should be considered in low dimensional semiconductor heterostructures. Hence, it is concluded that dielectric confinement due to image charge potential enhances the exciton binding energy [38].
Fig.3.3 Variation of exciton binding energies of heavy holes as a function of dot radius for a Cd$_{1-x}$Zn$_x$Te/ZnTe quantum dot for various Zn content and the insert figure shows the variation of heavy hole exciton binding energies as a function of dot radius in a Zn$_{0.8}$Cd$_{0.2}$Te/ZnTe quantum dot with and without the inclusion of PB potential (Eq.(3.40)) and the dielectric mismatch.
The variation of interband emission energy as a function of dot radius for various concentration of Zn alloy content in Zn$_x$Cd$_{1-x}$Te/ZnTe quantum dot is shown in Fig.3.4 and the insert figure shows the variation of interband emission energy as a function of Zn alloy content for three different dot sizes. It is noted that the interband emission energy increases monotonically as the dot radius is decreased in all the cases. This is due to the confinement of electron-hole with respect to $z$-plane when the dot radius is increased. Moreover, it is clearly shown that the effect of exciton has influence on the interband emission energy. This representation clearly brings out the quantum size effect. A quadratic fit of the effective band gap as a function of Zn alloy content is obtained as $E_g(x) = 1.548 + 0.279x + 1.159x^2$, for 50 Å quantum dot. The energy is expressed in eV. The above expression is in good agreement with the previous investigator for $x = 0.2$ [39]. Moreover, it is observed that the magnitude of the interband emission energy increases with the Zn alloy content into CdTe material and it is more for all the dot sizes due to the increase in the barrier height and the exciton binding energy. The insert figure brings out the quantum size effect. It is also noticed that interband emission energy increases not only with the increase in Zn alloy content but also with the decrease in dot radius. It is due to the geometrical confinement.
Fig. 3.4 Variation of interband emission energy as a function of dot radius for different concentration of Zn alloy content in Zn$_x$Cd$_{1-x}$Te/ZnTe quantum dot is shown in Fig 3.4 and the insert figure shows the variation of interband emission energy as a function of Zn alloy content for three different dot sizes.
In Fig. 3.5, the variation of optical gain as a function of photon energy for various Zn alloy content in a 50 Å dot radius and L = 10 Å of the strained Zn_xCd_{1-x}Te/ZnTe quantum dot is presented. The strain distribution and the variation of Zn content in CdTe will directly affect the electrical and optical properties of the material. It is found that the optical gain spectra in the Zn_xCd_{1-x}Te/ZnTe quantum dot behave similar shape when the Zn-alloy content is varied. The larger gain depends on the optical transition in the optical matrix element. A quantum dot and its matrix affect the strain distribution around the quantum dot and subsequently alter the optical properties of the heterostructures. As the Zn alloy content increases there occurs the blue shift of the spectrum. The shift of the peak for structures with the addition of Zn alloy content is due to the change of lattice parameters. The peak of optical gain decreases with the increases in Zn alloy content. It is because the optical matrix elements decrease with increasing Zn alloy content [40]. All the calculations include the strain effects due to the hydrostatic and biaxial strains. Higher excitonic binding energies are extremely advantageous for potential applications in optoelectronics devices operating in the green region of the spectrum [41].
Fig. 3.5 Variation of optical gain as a function of photon energy for various Zn alloy content in a strained $\text{Zn}_x\text{Cd}_{1-x}\text{Te}/\text{ZnTe}$ quantum dot.
3.5 Conclusion

In conclusion, the ground state heavy hole exciton binding energies have been investigated in a strained Zn$_x$Cd$_{1-x}$Te/ZnTe polar quantum dot nanostructure with the influence of strain in this chapter. The internal electric fields related to spontaneous and piezoelectric polarizations have been included to study the optical properties of heavy hole exciton for various Zn composition. The interband emission energy as a function of dot radius has been discussed for various Zn alloy content. Calculations have been obtained for different confinement potentials of barrier height considering the internal fields. The magnitude of the optical gain increases for transitions between higher levels with the inclusion of phonon effect and the blue shift has been observed when the Zn content is increased. The results of free heavy exciton energies have been presented for various dot sizes, Zn alloy content and the confining potential. It is hoped that the obtained results will pave the way for selecting the best material for opto-electronic devices leading to photovoltaic applications among II-VI semiconductors.
References