Investigation of the Electronic and Optical Properties of the Strained CdTe/ZnTe (001) Superlattices

Amna Abdulla Ahmed Al-Zarouni

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INVESTIGATION OF THE ELECTRONIC AND OPTICAL PROPERTIES OF THE STRAINED CdTe/ZnTe (001) SUPERLATTICES

A Thesis Submitted to The Dean of Graduate Studies of The United Arab Emirates University

BY

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In Partial Fulfillment of The Degree of M.Sc in Materials Science and Engineering

May 2002
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<td>BCC</td>
<td>Body Centered Cubic</td>
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<td>BZ</td>
<td>Brillouin Zone</td>
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<td>CB</td>
<td>Conduction Band</td>
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<td>CBO</td>
<td>Conduction Band Offset</td>
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<td>FCC</td>
<td>Face Centered Cubic</td>
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<td>HH</td>
<td>Heavy Hole</td>
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<td>HWE</td>
<td>Hot Wall Epitaxy</td>
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<td>LDF</td>
<td>Local Density Function</td>
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<td>LDOS</td>
<td>Local Density of State</td>
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<td>Light Hole</td>
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<td>MBE</td>
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<td>MOCVD</td>
<td>Metal Organic Chemical Vapor Deposition</td>
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<td>MQW</td>
<td>Multiple Quantum Well</td>
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<td>MSA</td>
<td>Model Solid Approach</td>
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<td>Macroscopic Theory of Elasticity</td>
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<td>Total Density of State</td>
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<td>Transmission Electron Microscopy</td>
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<td>Valence Band</td>
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<td>Valence Band Offset</td>
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Abstract

Semiconductors are distinguished among all materials by having a non-vanishing energy band gaps. They are often used in industry in the form of alloys or heterostructures in order to tailor energy gaps suitable for the desired applications. In general, semiconductor materials have broad applications in industry, ranging from micro-electronic devices, to light emitters and detectors, to laser and solar cells. In the last two decades, particular attention has been given to the II-VI semiconductor heterostructures because of their suitability as photoelectronic devices covering from the infra-red to the ultra-violet spectral ranges. The scope of this thesis belongs to the field of band gap engineering and deals with an investigation of the main parameters directly affecting the electronic band structures and optical properties of the strained CdTe/ZnTe(001) superlattices (SLs). As many other common-anion heterostructures, the valence-band offset (VBO) is also finitely small for these SLs. This fact makes both the biaxial strain and the spin-orbit coupling important parameters in controlling the SL character because they affect the level splitting of the valence-band top states. For this reason, we have used in our computation the sp³s* tight-binding method with inclusion of strain and spin-orbit effects. We have calculated the band structures, densities of states, and oscillator strengths versus SL layer thicknesses, biaxial strain state, and VBO. Our results show that the electron is always localized within CdTe slabs whereas the hole behavior controls the SL character. Our results are further compared to photoluminescence experiments and shown to be consistent with the strain morphology and structural and optical properties of the experimental samples.
Preface

The band offsets at semiconductor heterojunctions play an essential role in the electrical and optical properties of the heterostructures. Understanding the mechanisms and factors controlling the band offsets is a formidable task in tailoring properties suitable for technological applications. Toward this goal, in chapter 1, we first give definitions of various types of heterojunctions and show their applications in superlattices and multiple-quantum wells. In the same chapter, we have introduced the model-solid approach (MSA) as being the simplest technique to be used in: (i) predicting the atomic structures especially in the case of strained superlattices by making use of the macroscopic theory of elasticity; (ii) estimating the band offsets; and (iii) roughly predicting the character of the heterojunction. We have used the MSA to estimate both the valence-band offset (VBO) and the conduction-band offset (CBO) at the strained CdTe/ZnTe (001) heterojunctions. In this approach, both strain and spin-orbit effects have been convoluted in evaluating the VBO and CBO for three strain states corresponding to a pseudomorphic growth with a substrate: (i) CdTe; (ii) ZnTe; (iii) free-standing growth. As a matter of fact, the MSA does give a reliable preliminary prediction of the character (or the type) of the superlattice.

In chapter 2, we discuss the tight-binding (TB) technique and its historical development. The TB method first started by the Slater-Koster scheme (1954) with a basis set of sp\(^3\) orbitals which is of interest in the electronic structures of semiconductors. The first subsequent development was due to Vogl and coworkers (1983), who incorporated the excited s* orbital into the basis set. This sp\(^3\)s* model gave better description of band dispersions and, indeed, yielded energy gap, carrier effective masses, and deformation potentials in good agreement with experimental data. Furthermore, specifically in the case of most of the II-VI compound semiconductors, the spin-orbit interaction is crucially important. The original idea of spin-orbit inclusion, due to James Chadi (1977), has been explored and incorporated into the sp\(^3\)s* tight-
binding Hamiltonian by Sankey and coworkers (1982). Last but not least, the strain has also been successfully incorporated into the latter TB Hamiltonian scheme in various ways and we have preferred to discuss its details in chapter 3, where it was used to produce the main results of this thesis.

In chapter 3, we first describe the computationally challenging problem of how to incorporate the biaxial strain into sp^1s\(^*\) tight-binding Hamiltonian. In this thesis, the strain has been considered as a perturbation and posteriorly added to the tight-binding Hamiltonian of the superlattice. In fact, this idea was originally suggested by Bertho and coworkers (1994). We mention here that the biaxial strain plays an important role in the splitting of the the valence-band top states. This strain-induced splitting becomes even more pronounced in the case of a heterojunction of vanishing VBO such as the case of the common-anion II-VI superlattices. Similar splitting effect is also played by spin-orbit interaction. Therefore to study the CdTe/ZnTe (001) superlattices (SLs) using TB method, it becomes necessary to include both spin-orbit interaction and strain effects. We have calculated the band structures, densities of states, and oscillator strengths for these SLs, and studied the effects of biaxial strain state, SL layer thicknesses, and VBO. Concerning the biaxial strain state we have considered three differently strained SLs with respective substrates: (i) CdTe, (ii) ZnTe, and (iii) free-standing SL.

In the latter SL, the strain is homogeneously distributed between the two SL constituents and it does represent the limiting case where the SL is relaxed after the occurrence of misfit dislocation. Moreover, a particular attention, in our investigation, has been paid to the free-standing SL because of its important application in interpreting the photoluminescence (PL) experiments. Regarding the effect of the SL layer thicknesses, we have studied the variation of \(E_g\) of (CdTe\(_n\))(ZnTe\(_n\)) (001) SLs versus \(n\) under various strain states. We have shown that \(n\) controls only the degree of confinement. The last parameter is the VBO. We have shown that its variation drastically affects the SL character. Particularly, for the free-standing SL, we have shown the existence of a critical VBO of about 40 meV, corresponding to the type-I to type-II
transition. Finally, taking VBO as a free parameter, we have modelled some available PL data and shown that our theoretical results are consistent with the experimental predictions regarding the strain morphology, structural and optical qualities of the experimental samples. Thus our investigation may be useful in predicting the occurrence of misfit-dislocations in the experimentally grown SLs.
CHAPTER I

Model-Solid Approach For Band Offsets
1.1 Introduction:

Semiconductor heterojunctions and superlattices have, recently shown tremendous potential for electronic device applications because of their flexibility in tailoring the electronic band structures. This can be obtained by the variation of the thickness of the layers and the state of strain. The main method used for designing the strained-heterojunction band offset is to accommodate the superlattice in-plane constant to the substrate material's lattice constant. Since the band offsets are important parameters for governing the transport properties at semiconductor heterojunctions, their theoretical predictions is crucially important in designing and optimizing new devices [1]. The improvement of novel growth techniques have made it possible to produce high-quality epitaxial interfaces, not only between lattice-matched semiconductors, but even between highly lattice-mismatched materials (of up to 7% mismatch).

It is important to study the discontinuities in valence and conduction bands at semiconductor interfaces in order to analyze the properties of any heterojunction. Numerous approaches have been followed to determine the band offsets at the semiconductor interface. Reliable calculations of specially the VBO are based on the local-density functional (LDF) theory using the ab initio pseudopotentials [2]. These state-of-the art techniques are extremely successful in the description of the ground state. Thus, they are widely used for particularly the lattice matched interfaces, but due to the computational complexity, such as in the case of strained-layer interfaces, these methods have been limited by the system sizes.

An alternative, which has been developed to deal with both lattice-matched and strained layers interface without the need for heavy calculations, is the so-called “Model-Solid Approach” (MSA) which mainly relies on the macroscopic theory of elasticity, and is described in some details herebelow in this chapter.
1.2 Band Offset Problem:

The valence-band offset (VBO) and conduction-band offset (CBO) are respectively defined as the difference between the valence band edges and conduction-band edges of the two constituents as shown in figure 1.1.

Figure 1.1: Spatial variation, along the growth direction, of the energy-band edges for a) homojunction b) heterojunction [3]

Figure 1.1(a) illustrates the case of homojunction which is an interface between one semiconductor but differently doped from one side to the other (like a PN-junction). The energy gaps on both sides are almost the same and the bands are smoothly matched through the depletion zone with an effect of band bending. Here $VBO=CBO=\Delta V$, where $\Delta V$ is just the electrostatic potential lineup due to the charge carrier distribution at the interface as a consequence of Fermi level alignment, across the junction.

Figure 1.1(b) illustrates the case of a heterojunction, which consists of an interface between two different semiconductors, of course with two different energy band gaps. In this
case the valence and conduction bands are matched from one side to the other through a complex mechanism which is composed of (1) interface specific effects which include the interface atomic relaxation, (2) charge carrier distribution. These make the band bending not smooth but rather rough. The \( VBO = E_v(B) - E_v(A) \) between the two VB edges and \( CBO = E_c(B) - E_c(A) \) between the two CB edges.

Many theoretical approaches have been proposed to calculate the band offsets, most of them avoid the calculation of the local density of states and use directly the integrated density of states of the two materials. In terms of the integrated density of states the band offset is determined by a rigid shift of the two bulk band structures, and the problem of band line up is thus to determine such shift (for instance using the density-functional theory). Many model theories assume that the VBO is determined only by the bulk properties and, hence, neglecting the interface specific effects as well as assuming the vacuum level to be an energy reference for each material.

So if we consider \( Evac \) as a reference energy level then the position of valence-band maximum relative to the vacuum level \( Evac \) is:

\[
E' = E_v - Evac
\]

If we have the heterojunction \( A/B \), we must line up both the reference levels of the two semiconductors:

\[
\Delta Evac = Evac(B) - Evac(A) = 0
\]

So the valence-band offsets \( VBO = E'_v(B) - E'_v(A) \)

In this case, the semiconductors are not interacting and the interface details are not important. The effects of interaction of two surfaces, when put into contact, and the role of interface details are taken into account by some model theories. They start from the picture of an absolute energy scale with a rigid alignment of the band structures, and then by modeling the rearrangement of the charge densities at the interface, they determine the additional potential shift, which is the
potential line up $\Delta V$, due to the charge distribution at the interface, which yields the final energy band discontinuities.

The energy-band discontinuity can be written as a sum of two different contributions: one is solely dependent on the bulk properties of the two materials forming the heterojunction; whereas the other depends on the actual structure of the interface and therefore is controlled by the interface-specific effects. This last contribution does require a super-cell calculation, such as the one used in the first-principle (ab-initio) technique.

The VBO can be written as follows:

$$VBO = \Delta E_v + \Delta V$$

Where $\Delta E_v = E_v(B) - E_v(A)$ is the difference between the VB edges of both materials in their strained configurations and $\Delta V$ is the electrostatic potential line up.

Figure 1.2 shows a profile of the band edges before and after the contact. It shows the VBO with both $\Delta E_v$ and $\Delta V$. In the general case, $V_A \neq V_B$ which means that Fermi levels are different between materials A and B, and this results in a creation of depletion zone with $\Delta V \neq 0$.

![Figure 1.2: VBO versus electrostatic potential line up, $\Delta V$, $\Delta E_v$ [3]](image-url)
As mentioned above, some model theories take the interface details into account. One among these theories is the self-consistent pseudopotential calculations which give an accurate description of the electronic charge distribution at the interface and has proven its superiority to predict the ground state properties. The scope of this thesis, however, will focus on model-solid approach (MSA) and on the tight binding (TB) method. The former will be described in the following sections of this chapter, whereas the later will be the subject of the next chapter.

1.3 Semiconductor Heterostructures:

Semiconductor heterostructures are layers of two (or more) semiconductor materials, of different band gap energies, grown with one common crystal structure.

They are classified as follows:

1.3.1 Heterojunction, quantum wells, and superlattices:

The semiconductors heterostructure includes many systems such as simple heterostructure (like thin films), double heterojunction (like: quantum wells) and repeated heterojunction (such as: multiple quantum wells and superlattices) [3,4]. Semiconductor heterostructures are largely used in optical and microelectronic devices based on band gap engineering. The combination of controlled variations in composition, strain, and the thicknesses of deposited layers provide the possibility of tuning the electronic and optical properties, which give to the heterostructures a great flexibility and make them suitable for device design.

In heterojunction systems, the valence and conduction band edges are discontinuous because of the difference in the two forbidden gaps and the levels of the band edges. For different systems of heterostructures, we have different interfaces at the junction in terms of the interface morphology and, therefore, the bandoffsets.
In the case of double heterojunction, the band discontinuities may give rise to a square-shape potential barrier for the charge carriers. This is the so-called “Single Quantum Well” (SQW), where one has thick barriers, and the carrier’s wave functions are very localized within the well and with tails in the adjacent barrier layers.

Multilayers structure such as multiple quantum wells (MQW) and superlattices (SLs) are formed by repeated heterojunction have different characteristics according to the length scale on which they are realized (Figure 1.3). If the wave functions overlap from well to well, the quantum structure is called a superlattice. On the other hand, if the wave functions are not interacting (not overlapping), the heterostructure is named MQW.

![Figure 1.3: Spatial variation, along the growth direction, of the energy-band edges for a) MQW b) SL [3]](image)

The most important parameters, which determine the atomic structure of heterojunction, are the lattice constants of the two different semiconductors and based on these one can classify the semiconductor junction as either a lattice-matched or a lattice-mismatched heterojunction. In the lattice matched case, the substrate and the overlayer materials have the same crystal structure, and the materials grow with no lattice distortions with change happening only in the atomic species filling the nodes of crystal lattice. In the other case (lattice mismatched) with a given substrate, the grown overlayer modifies its structure to adjust itself to the substrate, resulting in a strained configuration.
For pseudomorphic growth, the in-plane lattice constant is accommodated to the one of the substrate. The inter-plane constant, however, is either expanded in the case where the overlayer’s lattice constant being greater than that of the substrate (as shown in figure 1.4), or compressed in the case where the overlayer’s constant being less than that of the substrate. From theoretical point of view, the structure can be either roughly predicted using the model-solid theory approach or rigorously calculated using ab-initio methods, where the results include the interface relaxation and does have a precision within the experimental errors.\[3\]

**Figure 1.4:** Interface formation between lattice-matched semiconductors [3].

### 1.3.2 Types of Heterojunctions:

It is useful to classify the semiconductors according to their band structure characteristics [3,5]. The relative positions of the energy bands at the interface between two semiconductors can vary in nature and can be classified into four categories as illustrated in figure 1.5:
Figure 1.5: Energy-band discontinuities at different types of heterojunction interfaces [3].

i) Type-I: semiconductor A has its band edges between those of semiconductor B

ii) Type-II staggered: semiconductor A has both band edges either higher or lower, in energy, than semiconductor B.

iii) Type-II misaligned: semiconductor A has an energy gap either fully higher or fully lower than that of semiconductor B.

iv) Type-III: semiconductor A has a vanishing energy gap (being a semimetal) and coincides with the energy gap of semiconductor B. (In this situation, we recall the case of HgTe/CdTe heterojunction, which is of importance in infra-red detection).

The alignment of the energy bands may depend on both intrinsic and extrinsic factors, like the bulk lattice constants (which means strain), band gaps, chemical impurities, structural defects.

It is essential to know which factors are important and by how much, for instance, the band offsets can they be predicted using only the different bulk properties of the two materials? Or are they also be controlled by the interface specific effects?
As answers to these questions, by now, it has been well established that for the case of lattice-matched heterojunction, the band offsets are very much dependent on the bulk properties of the two constituents. Particularly the valence band offset (VBO) has been proven to fulfill the following properties (displayed in figure 1.6):

\begin{align*}
\text{(c)} \quad VBO(001) & \approx VBO(110) \approx VBO_{A/B} (\text{non abrupt}) \\
& \approx VBO(111)
\end{align*}

\begin{figure}[h]
\centering
(a) \begin{tikzpicture}
  \node (A) at (0,0) {A};
  \node (B) at (1,0) {B};
  \draw (A) -- (B);
\end{tikzpicture} \hspace{2cm}
(a) \begin{tikzpicture}
  \node (B) at (0,0) {B};
  \node (A) at (1,0) {A};
  \draw (B) -- (A);
\end{tikzpicture}
\end{figure}

\begin{figure}[h]
\centering
(b) \begin{tikzpicture}
  \node (A) at (0,0) {A};
  \node (B) at (1,0) {B};
  \draw (A) -- (B);
\end{tikzpicture} \hspace{2cm}
(b) \begin{tikzpicture}
  \node (A) at (0,0) {A};
  \node (B) at (1,0) {B};
  \node (C) at (2,0) {C};
  \draw (A) -- (B) -- (C);
\end{tikzpicture} \hspace{2cm}
(b) \begin{tikzpicture}
  \node (A) at (0,0) {A};
  \node (B) at (1,0) {B};
  \node (C) at (2,0) {C};
  \draw (A) -- (B) -- (C);
\end{tikzpicture}
\end{figure}

\textbf{Figure 1.6:} Schematization of three main questions concerning the band offset problem [3]: (a) Commutativity, (b) Transitivity, and (c) role of the interface orientation and abruptness.

\textbf{a) Commutativity rule :} \( VBO_{A/B} = - VBO_{B/A} \)

If material B is grown on material A, the VBO remains invariant as in the case of when material A is grown on material B. The minus sign is just due to the convention that:

\( VBO = E_v(\text{overlayer}) - E_v(\text{substrate}) \).
b) Transitivity rule: \( VBO_{AB} = VBO_{AC} + VBO_{CB} \)

The VBO between the valence band edges of A and B is found to be equal to the sum of \( VBO_{AC} \) and \( VBO_{CB} \). This is a very important rule which precists its validity mainly in the case of lattice-matched heterostructures.

c) Independence of VBO on the interface orientation and abruptness

It has been proven [3] that in the case of lattice-matched heterostructures the VBO is independent on the interface specific effects such as growth orientation and interface abruptness (i.e. interatomic diffusion at the interface).

1.4 Model-Solid Approach:

The model-solid theory is an extension of the macroscopic theory of elasticity and assumes the validity of two main aspects:

1) The generation of an accurate band structure.

2) The alignment of the band structures is referred to an "absolute energy scale".

- The first aspect is accomplished by performing density-functional calculations on individual bulk semiconductors, described by ab initio pseudopotentials.

- For the second property, the absolute energy scale can be established when the energies in the bulk semiconductors can be referred to the "vacuum level". This allows us to derive band lineups by simply substracting values from absolute energy scale. For many semiconductors the model-solid approach gives us the information about the position of the average valence band on the absolute energy scale \( E_{v,av} \) (at \( \Gamma \) - point). It also gives us the variation of this energy when strain is present in the system [36].
1.5 Atomic structure of the interface in presence of strain:

From a computational point of view, several assumptions are considered, for instance:

All interfaces are assumed to be ideal (i.e. the growth is assumed to be pseudomorphic)

Other assumptions are included in the strategy below:

Of course, it is obvious that the imprefections can influence the values of the band line ups in many ways.

The steps to obtain values for band lineups are as follows:[36]

1) An appropriate strain must be included in each of the materials to construct a pseudomorphic interface (this strains can be determined by minimizing the macroscopic elastic energy)

2) A perfect pseudomorphic (dislocation-free) interface is considered.

3) Practical growth for the over-layers should not exceed a certain critical thickness after which the appearance of misfit dislocations occurs.

4) For a system in which \( h_1 \) & \( h_2 \) are the respective thicknesses of unstrained layers of semiconductors (1) & (2), one may write the following relations [36]

\[
a_{\parallel} = \frac{a_1 G_1 h_1 + a_2 G_2 h_2}{G_1 h_1 + G_2 h_2} \quad (1.1)
\]

\[
\varepsilon_{\parallel} = \frac{a_{\parallel}}{a_i} - 1 \quad (1.2)
\]

\[
a_{\perp} = a_i \left[ 1 - D_i \left( \frac{a_{\parallel}}{a_i} - 1 \right) \right] \quad (1.3)
\]

\[
\varepsilon_{\perp} = \frac{a_{\perp}}{a_i} - 1 \quad (1.4)
\]

where \( a_{\parallel} \): is the parallel lattice constant of the whole SL.

\( a_{\perp} \): is the perpendicular lattice constant of material (i).

\( G_i \): is the shear modulus of material (i).

The constant \( D_i \) depends on the elastic constants \( c_{11} \) and \( c_{12} \) of the respective materials and on the interface orientation, for instance in the case of a growth in the direction (001), one has:
The e value of Do01 are tabulated for various materials in reference [36]. These in addition to other parameters are summarized in table 1.1

<table>
<thead>
<tr>
<th>Parameters</th>
<th>α (Å°)</th>
<th>D_o01</th>
<th>G_o01</th>
<th>Δ_o(eV)</th>
<th>E_v,av(eV)</th>
<th>E_c (eV)</th>
<th>α_c (eV)</th>
<th>b (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdTe</td>
<td>6.48</td>
<td>1.402</td>
<td>0.807</td>
<td>0.93</td>
<td>-7.07</td>
<td>-5.17</td>
<td>-3.96</td>
<td>-1.20</td>
</tr>
<tr>
<td>ZnTe</td>
<td>6.08</td>
<td>1.142</td>
<td>1.311</td>
<td>0.91</td>
<td>-7.17</td>
<td>-4.48</td>
<td>-5.83</td>
<td>-1.26</td>
</tr>
</tbody>
</table>

**Example (1.1): (Interface structure)**

Here, we will illustrate the procedure for calculating the structure of the ZnTe/CdTe (001) interface as useful example in this thesis.

We consider that CdTe is the substrate and that ZnTe is the over-layer. So the in-plane lattice constant is \( a_{||} = a_{CdTe} \), and one obtains:

\[
a_{||} = a_{CdTe} = 6.48 \, \text{Å}
\]

For the overlayer (ZnTe) one gets:

\[
\varepsilon_{2||} = \frac{a_{||}}{a_2} - 1 = \frac{6.48}{6.08} - 1 = 0.06579
\]

\[
a_{2\perp} = a_2 \left( 1 - D_2 \varepsilon_{2||} \right) = 6.08 \left( 1 - 1.142 \times 0.06579 \right) = 5.623 \, \text{Å}
\]

\[
\varepsilon_{2\perp} = \frac{a_{2\perp}}{a_2} - 1 = \frac{5.623}{6.08} - 1 = -0.0751
\]

The relative change in the volume of unit cell of material (2) is
\[ \frac{\Delta \Omega_2}{\Omega_2} = Tr(\bar{\epsilon}) = \epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz} \]
\[ = 2\epsilon_{22} + \epsilon_{21} \]
\[ = 2(0.06579) - 0.0751 \]
\[ = 0.05648 \]

This means that there is a volumic expansion in the overlayer. This obtained values of \( \frac{\Delta \Omega}{\Omega} \) will be useful in determination of the shift of the conduction band edges under the effect of strain and this will be the subject of the next section.

1.6 Strain Splitting and deformation potential:

In this section we will discuss the semiconductors that have zinc-blende structure, whose band structure includes three degenerate top-valence bands at \( \Gamma \)-point (in neglect of spin degeneracy, these bands are splitted under the effect of strain and/or spin-orbit interactions).

The top valence bands are labeled by \( E_{v1} \), \( E_{v2} \) and \( E_{v3} \).

- \( E_{v1} \): stands for the light hole (LH) band.
- \( E_{v2} \): stands for the heavy hole (HH) band.
- \( E_{v3} \): stands for the split-off (SO) band.

In the case of strain along the growth direction (001), the energy shifts are calculated using the model-solid approach as explained in reference [36] as follows:

\[ \Delta E_{v,2} = \frac{1}{3} \Delta \epsilon - \frac{1}{2} \delta E_{001} \] \hspace{1cm} (1.5)

\[ \Delta E_{v,1} = -\frac{1}{6} \Delta \epsilon + \frac{1}{4} \delta E_{001} + \frac{1}{2} [\Delta \epsilon^2 + \Delta \epsilon \delta E_{001}] + \frac{1}{4} (\delta E_{001})^2 \] \hspace{1cm} (1.6)

\[ \Delta E_{v,3} = -\frac{1}{6} \Delta \epsilon + \frac{1}{4} \delta E_{001} - \frac{1}{2} [\Delta \epsilon^2 + \Delta \epsilon \delta E_{001}] + \frac{1}{4} (\delta E_{001})^2 \] \hspace{1cm} (1.7)

where \( \delta E_{001} = 2b(\epsilon_{zz} - \epsilon_{xx}) \) is the strain energy; \( b \) is the shear deformation potential, and \( \Delta \) is the spin-orbit coupling energy.

Here we have two cases:
(a)- If the strain = 0

(only spin orbit effect like the situation in the substrate material)

\[ \delta E_{001} = 0 \], so substituting in equations 1.5, 1.6 and 1.7, one obtains:

\[ \Delta E_{v,2} = \frac{1}{3} \Delta_0 \]

\[ \Delta E_{v,1} = -\frac{1}{6} \Delta_0 + \frac{1}{2} \Delta_0 = \frac{1}{3} \Delta_0 \]

\[ \Delta E_{v,3} = -\frac{1}{6} \Delta_0 - \frac{1}{2} \Delta_0 = -\frac{2}{3} \Delta_0 \]

(b)- If the spin orbit is absent (\( \Delta_\sigma = 0 \))

(only strain effect is present) one obtains:

\[ \Delta E_{v,2} = -\frac{1}{2} \delta E_{001} \]

\[ \Delta E_{v,1} = \frac{1}{4} \delta E_{001} + \frac{3}{4} \delta E_{001} = \delta E_{001} \]

\[ \Delta E_{v,3} = \frac{1}{4} \delta E_{001} - \frac{3}{4} \delta E_{001} = -\frac{1}{2} \delta E_{001} \]

In real life, if strain = 0 then the edge of the valence band consists of both LH & HH

If strain \( \neq 0 \) either HH or LH should consist the valence band edge depending on whether the strain is tensile or compressive respectively. Therefore, it seems that the split off state is for sure always the lowest level.

In the following examples, we will calculate VBO & CBO for the strained CdTe/ZnTe(001) heterojunction strained to various substrates, using the model-solid approach (MSA). Namely, example (1.2) considers CdTe as a substrate; whereas example (1.3) considers ZnTe as a substrate.
**Example (1.2): CdTe as a substrate.**

Consider the strained CdTe/ ZnTe (001) superlattice, where CdTe is a substrate (or a buffer). For the unstrained fcc bulk materials we have the following data:

<table>
<thead>
<tr>
<th>Material</th>
<th>a (Å)</th>
<th>$E_g$(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdTe</td>
<td>6.48</td>
<td>1.59</td>
</tr>
<tr>
<td>ZnTe</td>
<td>6.08</td>
<td>2.39</td>
</tr>
</tbody>
</table>

The CdTe substrate is in cubic structure (unstrained)

The ZnTe overlayer is under compressive distortion (strained)

The structural data corresponding to this case can be found in the Example (1.1). So, here below, we just calculate the energy levels as well as VBO and CBO values.

**i) CBO Calculation:**

In this calculation, the spin-orbit coupling is irrelevant but only strain has an effect on the shift of the CB edges. It is worth noting that we use the same data calculated by Van de Walle in reference [36] and are summarized in table 1.1. For the substrate which is unstrained the $E_c$ remains invariant at its bulk value given by (Table 1.1) as

$E_c$(CdTe) = -5.17 eV

Using the CB deformation potential $\alpha_c$ of ZnTe, one can calculate the value of $E_c$ of ZnTe under the compressive strain of the SL and get:
\[ \text{Ec(ZnTe)} = E_c' + \Delta E_c \]
\[ = E_c' + a_c \frac{\Delta \Omega_c}{\Omega_c} \]
\[ = -4.48 - 5.83 (0.05648) = -4.81 \text{ eV} \]

From these values, one can deduce the value of CBO:
\[ \text{CBO} = E_c(ZnTe) - E_c(CdTe) \]
\[ = -4.8093 + 5.17 \]
\[ = +0.361 \text{ eV} \]

which shows that the CB edge of ZnTe is higher in energy than that of CdTe.

\[ \text{Vacuum} = 0 \]
\[ \rightarrow \text{Growth direction} \]
\[ E_c(A) = -5.17 \text{ eV} \]
\[ -4.81 \text{ eV} = E_c(B) \]

ii) VBO Calculation:

For the substrate (CdTe) only spin-orbit would have some effect because it is unstrained. So using the MSA one can calculate the energy split of the VB top states of CdTe as follows:

\[ \Delta E_{v,1} = \Delta E_{v,2} = \frac{1}{3} \Delta \alpha = \frac{1}{3} (0.93) = 0.31 \text{ eV} \]

\[ \Delta E_{v,3} = -\frac{2}{3} \Delta \alpha = -\frac{2}{3} (0.93) = -0.62 \text{ eV} \]

From these one calculates the levels:

\[ E_{v,1} = E_{v,2} = E_{v,av} + \Delta E_{v,1,2} = -7.07 + 0.31 \]
\[ = -6.76 \text{ eV} \] (The edge of VB for the substrate)

\[ E_{v,3} = E_{v,av} + \Delta E_{v,3} = -7.07 - 0.62 = -7.69 \text{ eV} \]

Therefore the LH and HH consist the VB edge of the substrate with an energy equals to:

\[ E_v(\text{substrate}) = -6.76 \text{ eV} \]
For the overlayer (ZnTe), both the spin orbit interaction and the strain effects are important and in the MSA both are convoluted and the calculation of the energy parameters are as follows:

First the strain energy of the overlayer (ZnTe) is:

\[ \delta E_{001} = 2 \, b (e_{zz} - e_{xx}) \]

\[ = 2 (-1.26) (e_{zz} - e_{xx}) \]

\[ = 2 (-1.26) (-0.0751 - 0.06579) \]

\[ = +0.355 \, \text{eV} \]

Then we calculate the VB level-split energies:

\[ \Delta E_{v,2} = \frac{1}{3} \Delta_3 - \frac{1}{2} \delta E_{001} \]

\[ = \frac{1}{3} (0.91) - \frac{1}{2} (0.355) = +0.126 \, \text{eV} \]

\[ \Delta E_{v,1} = -\frac{1}{6} \Delta_3 + \frac{1}{4} \delta E_{001} + \frac{1}{2} [\Delta_3 + \Delta_3 \delta E_{001} + \frac{9}{4} (\delta E_{001})^2]^{1/2} \]

So we start calculating the quantity:

\[ [\Delta_3^2 + \Delta_3 \delta E_{001} + \frac{9}{4} (\delta E_{001})^2]^{1/2} = [(0.91)^2 + 0.91 (0.355) + \frac{9}{4} (0.355)^2]^{1/2} = 1.198 \]

Then we calculate:

\[ \Delta E_{v,1} = -\frac{1}{6} (0.91) + \frac{1}{4} (0.355) + \frac{1}{2} (1.198) \]

\[ = +0.536 \, \text{eV} \ (\text{the highest value}) \]

and the last shift:

\[ \Delta E_{v,3} = -\frac{1}{6} \Delta_3 + \frac{1}{4} \delta E_{001} - \frac{1}{2} [\Delta_3^2 + \Delta_3 \delta E_{001} + \frac{9}{4} (\delta E_{001})^2]^{1/2} \]

\[ \Delta E_{v,3} = -\frac{1}{6} (0.91) + \frac{1}{4} (0.355) - \frac{1}{2} (1.198) \]

\[ = -0.662 \, \text{eV} \]
Now, one can obtain the values of the energy levels of VB top states as:

\[ E_{v,1} = E_{v,v} + \Delta E_{v,1} = -7.17 + 0.536 = -6.634 \text{ eV} \]

\[ E_{v,2} = E_{v,v} + \Delta E_{v,2} = -7.17 + 0.126 = -7.044 \text{ eV} \]

\[ E_{v,3} = E_{v,v} + \Delta E_{v,3} = -7.17 - 0.662 = -7.832 \text{ eV} \]

It is clear that LH \((E_{v,1})\) consists the VB edge of the overlayer\((ZnTe)\). So, one can obtain:

\[
\text{VBO} = E_v(ZnTe) - E_v(CdTe)
\]

\[ = -6.634 + 6.76 \]

\[ = 0.126 \text{ eV} \]

Finally, one make the conclusion that in using the MSA, if the CdTe is taken as a substrate, the heterojunction is expected to be of type II as illustrated below:

\[
\begin{align*}
\text{CBO} &= 0.36 \text{ eV} \\
\text{Type II} & \quad \text{VBO} = 0.126 \text{ eV} \\
\text{CdTe} & \quad \text{ZnTe (strained)}
\end{align*}
\]

\textbf{Figure 1.8:} Profile of bandedges of CdTe/ZnTe SL when CdTe is a substrate.

\textbf{Example (1.3) ZnTe as a substrate:}

The schematic view of the ZnTe/CdTe(001) superlattice as strained to ZnTe substrate (or buffer) is shown in figure 1.9 below.

\textbf{Figure 1.9}
Pseudo-morphic growth of CdTe on ZnTe substrate
In this case, the ZnTe consists the substrate and is unstrained (has a cubic fcc structure). Whereas the CdTe is under tensile strain (has a tetragonal strained structure).

First, we recall that the lattice mismatch is:

\[ \frac{\left| a_1 - a_2 \right|}{\frac{a_1 + a_2}{2}} = \frac{0.4}{6.23} = 6.4\% \]

and here below, we show the calculation of the structural parameters following the MSA.

The in-plane lattice constant of the SL is:

\[ a = a_{\text{ZnTe}} = 6.08 \text{ Å} \]

and the overlayer (CdTe) would have the following data:

\[ \varepsilon_{2||} = \frac{a_{2||}}{a_2} - 1 = \frac{6.08}{6.48} - 1 = -0.06173 \]

\[ a_{2\perp} = a_2 \left[ 1 - D_2 \varepsilon_{2||} \right] \]

\[ = 6.48 \left[ 1 - 1.142 \times (-0.06173) \right] \]

\[ = +7.0408 \text{ Å} \]

\[ \varepsilon_{2\perp} = \frac{a_{2\perp}}{a_2} - 1 = \frac{7.0408}{6.48} - 1 = +0.08654 \]

So the relative change in volume of unit cell of CdTe is:

\[ \frac{\Delta \Omega_2}{\Omega_2} = Tr(\varepsilon) = \varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz} \]

\[ = 2 \varepsilon_{2||} + \varepsilon_{2\perp} \]

\[ = 2 (-0.06173) + 0.086543 \]

\[ = -0.037 \]

Of course, \( \varepsilon (\text{ZnTe}) = 0 \) and \( \varepsilon (\text{CdTe}) = \frac{\Delta \Omega_2}{\Omega_2} = -0.037 \)

i) CBO Calculation:

Here, we recall once more that only the strain effect is relevant for the overlayer (CdTe). One gets:

\[ E_c(\text{ZnTe}) = E_c^* = -4.48 \text{ eV} \]
Ec(CdTe) = E_c + \alpha c \Delta \Omega / \Omega

= -5.17 - (3.96) (-0.036917)

= -5.0238 eV

Therefore, one obtains the CBO value:

CBO = E_c(CdTe) - E_c(ZnTe)

= -5.0238 + 4.48

= -0.5438 eV

The CB edge of CdTe is lower in energy than that of ZnTe

\textit{ii) VBO Calculation:}

The VB states of the unstrained substrate (ZnTe) exhibit only spin-orbit interaction effect:

$\Delta E_{v,2} = \frac{1}{3} \Delta \alpha = \frac{1}{3} (0.91) = 0.303 \text{ eV}$

$\Delta E_{v,1} = \frac{1}{3} \Delta \alpha = \frac{1}{3} (0.91) = 0.303 \text{ eV}$

$\Delta E_{v,3} = -\frac{2}{3} \Delta \alpha = -\frac{2}{3} (0.91) = -0.606 \text{ eV}$

So the VB top states of the substrate (ZnTe) are:

$E_{v,1} = E_{v,2} = E_{v,av} + \Delta E_{v,1,2} = -7.17 + 0.303$

$= -6.867 \text{ eV} \quad \text{(The edge of VB for the substrate)}$

$E_{v,3} = E_{v,av} + \Delta E_{v,3} = -7.17 - 0.606 = -7.77 \text{ eV}$

It is clear that the HH and LH consist the VB edge of the substrate with energy $E_v(\text{substrate}) = -6.867 \text{ eV}$. 
Now, regarding the VB edge states of the over-layer (CdTe), both the spin-orbit interaction and the strain effects should be considered as follows:

The strain energy of the overlayer is:

\[ \delta E_{001} = 2 b (\epsilon_{z'} - \epsilon_{xx}) \]
\[ = 2 (-1.2) (\epsilon_2 - \epsilon_{z'}) \]
\[ = 2 (-1.2) (0.086543 + 0.06173) \]
\[ = -0.3558 \text{ eV} \]

From these values, one obtains the position of the VB top states for the CdTe overlayer as:

\[ E_{v,1} = E_{v,v} + \Delta E_{v,1} = -7.07 + 0.2085 = -6.8615 \text{ eV} \]
\[ E_{v,2} = E_{v,v} + \Delta E_{v,2} = -7.07 + 0.4875 = -6.583 \text{ eV (top VB state)} \]
\[ E_{v,3} = E_{v,v} + \Delta E_{v,3} = -7.07 - 0.6964 = -7.7664 \text{ eV} \]

Hence, it is clear that the HH consists of the VB edge of the overlayer (CdTe). Thus, the VBO value is:

\[ \text{VBO} = E_v(\text{CdTe}) - E_v(\text{ZnTe}) \]
\[ = -6.583 + 6.867 \]
\[ = 0.284 \text{ eV} \]

As a final conclusion, if the ZnTe is the substrate, the heterojunction is expected to be of type I as shown in the figure below:

![Figure 1.10](image)

**Figure 1.10:** Profile of band edges of CdTe/ZnTe SL when ZnTe is a substrate.

In this heterojunction, the SL's valence band edge is expected to be characterized by the HH band of CdTe.
Finally, we summarize our results of band offsets calculations using the MSA versus the strain configuration controlled by the variation of the substrate composition. We considered three cases of superlattices strained to the following substrates: (i) CdTe, (ii) and Cd$_{0.5}$Zn$_{0.5}$Te and (iii) ZnTe. The results are in Table 1.2 below:

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Band offset</th>
<th>CdTe</th>
<th>Cd$<em>{0.5}$Zn$</em>{0.5}$Te</th>
<th>ZnTe</th>
</tr>
</thead>
<tbody>
<tr>
<td>VBO</td>
<td>0.126</td>
<td>-0.091</td>
<td>-0.284</td>
<td></td>
</tr>
<tr>
<td>CBO</td>
<td>0.361</td>
<td>0.452</td>
<td>0.544</td>
<td></td>
</tr>
</tbody>
</table>

Table-1.2 Band offsets versus the strain configuration
CHAPTER II

The Tight-binding Method For the Electronic Structure Calculation
2.1 Introduction

The tight binding method has been used since its inception in 1954 by Slater and Koster [17] and has been successfully applied to various electronic systems ranging from disordered oxides, to semiconductor alloys, to microscopic systems such as quantum dots, wires, and superlattices. Its biggest advantage is that it uses a small basis set so that it paves the way for the investigation of large systems while it incorporates the point group symmetry into account. In the case of semiconductors, the basis set $sp^3$ has been extended by adding the excited $s^*$ orbital by Vogl et al. (1983) [28]. This new $sp^3s^*$ basis set was necessary in order to get band dispersions in good agreement with those obtained via the state-of-art methods such as ab-initio pseudopotential technique. In fact, the $sp^3s^*$ models yield not only good band dispersions but also the energy gaps, carrier effective masses, and deformation potentials in good agreement with experimental data.

Furthermore, the spin-orbit interaction was incorporated in the $sp^3s^*$ scheme [30]. This was necessary especially in the case of heterojunctions of small valence-band offsets, such as the case of common-anion heterojunction, because the spin-orbit effect control the level splitting of the top VB states. The spin-orbit coupling has also its importance in semiconductor of small or vanishing bandgap for the same reason previously mentioned. The original work of spin-orbit incorporation to the $sp^3s^*$ basis set was done by Sankey et al [30] who just implemented the idea of James Chadi [31].

In the present chapter, we give an overview on this development. Section 2.2 gives a description of the SL atomic structures used in our calculations as well as the Brillouin zones of the FCC and tetragonal structures showing the high-symmetry points and lines. Section 2.3 describes the original $sp^3$ tight-binding method in the Slater-Koster scheme. Section 2.4 illustrates a brief summary of the $sp^3s^*$ tight-binding method. The last section gives a brief description of the $sp^3s^*$ TB method with inclusion of spin-orbit interaction. At last, we would
like to mention that the incorporation of strain to the sp^3s*-TB scheme is included in chapter 3 where all the computational results of this insertion are discussed.

2.2 Superlattice Atomic Structure:

a) Cubic Zinc Sulfide Structure:

The diamond structure may be viewed as two FCC structures displaced from each other by one quarter of a body diagonal. The cubic zinc sulfide (zinc blende) structure results when Zn atoms are placed on one FCC lattice and S atoms on the other FCC lattice as shown in figure 2.1(a). The conventional cell is a cube. The coordinates of the Zn atoms are: (0,0,0), (0, \( \frac{a}{2}, \frac{a}{2} \)); (\( \frac{a}{2}, 0, \frac{a}{2} \)); (\( \frac{a}{2}, \frac{a}{2}, 0 \)), where \( a \) is the lattice constant, the coordinates of the S atoms are: (\( \frac{a}{4}, \frac{a}{4}, \frac{a}{4} \)); (\( \frac{3a}{4}, \frac{3a}{4}, \frac{3a}{4} \)); (\( \frac{3a}{4}, \frac{3a}{4}, \frac{a}{4} \)). The lattice is FCC with a basis of two atoms ZnS. There are four molecules of ZnS per conventional cell. About each atoms there are four equally distant atoms of the opposite kind arranged at the corners of a regular tetrahedron.

The corresponding Brillouin Zone (BZ) to the FCC structure is shown in figure 2.1(b). This latter figure also shows the high symmerty points and lines. The zone center is at \( \Gamma \) and the coordinates of \( X \) is \( (2\pi/a)(1,0,0) \), \( L \) is \( (2\pi/a)(1/2,1/2,1/2) \), and \( K \) is \( (2\pi/a)(3/2,3/2,0) \). The irreducible wedge consists 1/48-th of the BZ volume. The most relevant high-symmetry lines along which usually the bands are calculated are: \( \Lambda = L \Gamma \) line, \( \Delta = \Gamma X \) line, and \( \Sigma = K \Gamma \) line.

![Figure 2.1: (a) Crystal structure of cubic zinc blende, (b) Brillouin zone of the FCC lattice [6]](image-url)
**b) Superlattice Structure:**

Periodically repeated supercells suitably chosen are used to study differently oriented interfaces [3]. For instance, the (001) oriented heterojunction is described by a tetragonal supercell (see figure 2.2a), the longest side corresponding to the growth direction <001> (Z-axis) of the heterojunction. We emphasize that the x and y axes of the tetragonal cell of figure 2.2a consist of the orientations <110> and <110> in figure 2.1a (i.e. the (001) supercell in-plane lattice constant $A = a_{ij} / \sqrt{2}$ where $a_{ij}$ is the in-plane lattice constant of the substrate, and the first layer of atoms have coordinates of (0,0,0); ($a_{ij} / \sqrt{2}$, $a_{ij} / \sqrt{2}$,0); ($a_{ij}$,0,0); ($a_{ij} / \sqrt{2}$,-$a_{ij} / \sqrt{2}$,0) as coordinated in figure 2.1a. The inter-plane lattice constants are calculated using either the macroscopic theory of elasticity or the Ab-initio techniques.) Figure 2.2a contains 12 atoms, i.e. three double layers of each of the two materials. Many atoms shown are just mirrors to each others because of the periodic boundary conditions.

The corresponding Brillouin zone to the tetragonal (superlattice) structure is shown in figure 2.2b. This latter figure also shows the high-symmetry points and lines. The irreducible wedge consists 1/16 of the BZ volume. The coordinates of some of the high-symmetry points are:

$X=(\pi/A,0,0)$; $M=(\pi/A, \pi/A,0)$; $R=(\pi/A, 0, \pi/C)$; $Z=(0, 0, \pi/C)$ where $C$ is the length of the supercell in the $Z$-direction. It is very common to draw the band structures along the symmetry lines $\Delta=\Gamma X$ line, $Y=XM$, $\Sigma = M \Gamma$ line and $\Lambda = L \Gamma$ line. For direct-gap semiconductors, it might be enough to plot the bands along only two symmetry lines such as $\Gamma X$ and $\Gamma Z$.

**Figure 2.2(a)** Supercell used for (001) oriented heterojunction and corresponding basis vectors. The case of $(GaAs)_3(AlAs)_3$ is illustrated. **(b)** The tetragonal Brillouin zone showing the irreducible wedge. [3]
2.3 Linear Combination of Atomic Orbitals (LCAO)

This is one of the standard methods for solving a single-particle Schrödinger equation for the periodic potential problems in solids. This method was proposed by Bloch, and has many attractive features. It gives solutions showing all the correct symmetry properties of the energy bands and takes into account the point-group symmetry of the material. Moreover, the tight binding (TB) method describes the states of the whole Brillouin Zone which is necessary when states both near and far from the zone center must be considered at the same time, such as the case of an indirect band gap materials.

Description of TB Method:

We consider that we have two neutral separated atoms, each with one electron in the ground state. The wave functions $\phi_A, \phi_B$ on the separated atoms are shown in figure (2.3.a) [6]

![Figure 2.3](image)

*Figure 2.3:* (a) Schematic drawing of wavefunctions of electrons on two hydrogen atoms at large separation. (b) Ground state wavefunction at closer separation. (c) Excited state wavefunction. [6]

As the atoms are brought closer together and their wave functions overlap, the Coulomb interaction between atomic cores and the electrons splits the energy levels and spread them into a band of energies as an effect of interatomic bonding. Bands may coincide in energy at certain values of wave number ($k$) in the Brillouin zone. As the atoms are brought together, the description of the hybrid states should be obtainable by correcting the free-atom states. In
particular, we write a wave function for the system as a linear combination of atomic orbitals centered on the individual atoms. In order to obtain an exact expansion of wave function, it would be necessary to include the expansion of those states which correspond to dissociated electrons [6-8]. Suppose that the ground state wave function of an electron moving in a Coulomb potential \( U(r) \) of an isolated atom is \( \Phi(r) \). We obtain an approximate wave function for one electron in the whole crystal by taking the linear combination [6,9-12]

\[
\psi_k(\vec{r}) = \langle \vec{r} | \Phi \rangle = N^{-1/2} \sum_j e^{i \vec{k} \cdot \vec{r}_j} \Phi(\vec{r} - \vec{r}_j)
\]  

(2.1)

Now we consider a translation \( \vec{T} \) connecting two lattice points:

\[
\psi_k(\vec{r} + \vec{T}) = N^{-1/2} \sum_j e^{i \vec{k} \cdot \vec{T}} \Phi(\vec{r} + \vec{T} - \vec{r}_j)
\]

\[
= e^{i \vec{k} \cdot \vec{T}} N^{-1/2} \sum_j e^{i \vec{k} \cdot \vec{r}_j} \Phi(\vec{r} + \vec{T} - \vec{r}_j)
\]

\[
= e^{i \vec{k} \cdot \vec{T}} \psi_k(\vec{r} + \vec{T})
\]  

(2.2)

Therefore \( \psi_k(\vec{r}) \) obeys Bloch’s theorem. To find the first order energy, we calculate the diagonal elements of the Hamiltonian of the crystal.

\[
\langle \vec{k} | H | \vec{k} \rangle = N^{-1} \sum_m \sum_j e^{i \vec{k} \cdot \vec{p}_m} \Phi_m | H | \Phi_j >
\]

where \( \Phi_m = \Phi_m(\vec{r} - \vec{r}_j) \), let \( \vec{p} = \vec{r}_m - \vec{r}_j \) so one may write:

\[
\langle \vec{k} | H | \vec{k} \rangle = - \alpha - \lambda \sum_m e^{-i \vec{k} \cdot \vec{p}_m} = \varepsilon_i
\]

Where: \( \alpha = E_0 \) the on-site energy and \( \lambda \) is the overlap energy of interaction between two nearest neighbours. For instance, in a simple cubic (SC) structure the nearest-neighboring atoms are at the positions

\[ \vec{p}_m = (\pm a, 0, 0); (0, \pm a, 0); (0, 0, \pm a) \]

This yields a band dispersion:

\[
\varepsilon_i = - \alpha - 2\lambda (\cos k_x a + \cos k_y a + \cos k_z a)
\]  

(2.3)

The profile of band dispersion for a single particle is shown in figure 2.4
For a body-centered cubic (BCC) structure with 8 nearest neighbors, one obtains a band dispersion given by:

$$\varepsilon_r = -\alpha - 8\lambda (\cos \frac{1}{2} k_x a + \cos \frac{1}{2} k_y a + \cos \frac{1}{2} k_z a)$$

(2.4)

For a face-centered cubic (FCC) structure with 12 nearest neighbors [6], one also gets:

$$\varepsilon_r = -\alpha - 4\lambda (\cos \frac{1}{2} k_x a \cos \frac{1}{2} k_y a + \cos \frac{1}{2} k_x a \cos \frac{1}{2} k_z a + \cos \frac{1}{2} k_y a \cos \frac{1}{2} k_z a)$$

(2.5)

Figure 2.5 shows the constant-energy surface of an FCC structure where $\varepsilon_r = -\alpha - 2|\lambda|$ for just a demonstration of band filling with a dispersion law of the form given previously by TB picture.

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**Figure 2.4:** Tight-binding $s$ bands in a simple-cubic structure with inclusion of nearest-neighbor overlaps. The onset represents the Brillouin zone of SC structure. $\alpha = E_o = 0$ is taken as an energy reference [12]

**Figure 2.5:** A constant energy surface of an FCC crystal structure, in the nearest-neighbor tight-binding approximation.[6]
2.4 Tight Binding model based on sp$^3$s* basis set:

As a matter of fact, the sp$^3$ basis set is sufficient to give a full description of the sp$^3$-hybridization which occurs in the bonding of semiconductor materials. However, in order to improve the band dispersions which involve a fit to experimental data of the energy gap ($E_g$), carrier effective masses ($m_e,m_h$) and deformation potentials; a new excited $s^*$ state has been added to the atomic basis set. Vogl and coworkers[28] were among the first to introduce such a scheme which indeed improved the calculated band structures and optical properties of several semiconductor materials especially those of indirect bandgap.

As regards this new sp$^3$s* description, the TB Hamiltonian is constructed in a basis of quasi-atomic functions:[28]

$$|n,b,k> = N^{-1/2} \sum_j \exp (i \tilde{k} \cdot \tilde{R}_j + i \tilde{k} \cdot \tilde{r}_b) |n,b,R_j>$$  \hspace{1cm} (2.6)

The quantum numbers $n$ runs over the s, px, py, pz and s*, the N wave vectors $k$ lie within the first Brillouin zone, $b$ is either anion(a) or cation(c) atom at position $\tilde{r}_b$.

The Schrödinger equation, whose solutions are the Bloch functions $|\tilde{k} \lambda>$, is given by:

$$(H - \varepsilon(\tilde{k} \lambda)) |\tilde{k} \lambda> = 0$$  \hspace{1cm} (2.7)

where $\lambda$ is a band index, and equation (2.7) can be expressed in this basis:

$$\sum_{m,b'} \langle <n,b,k \mid H \mid m,b',\tilde{k} > - \varepsilon(\tilde{k} \lambda) \delta_{n,m} \delta_{b,b'} \rangle \langle n,b,\tilde{k} \mid \tilde{k} \lambda > = 0$$  \hspace{1cm} (2.8)

The solutions are the Bloch functions given by:

$$|\tilde{k} \lambda > = \sum_{n,b} |n,b,\tilde{k} > \langle n,b,\tilde{k} \mid \tilde{k} \lambda >$$  \hspace{1cm} (2.9)

The sp$^3$s* tight binding Hamiltonian for the bulk fcc zinc-blende structure requires the inclusion of only 2 atoms and is given by

$$H = \begin{pmatrix} E_e & U_{ee} \\ U_{ee} & E_e \end{pmatrix}$$  \hspace{1cm} (2.10)

Where each element is a 5 x 5 matrix.
The matrices $E_c$ and $E_a$ are diagonal and represent the on-site energies of cations and anions, whereas $U_{ca}$ and $U_{ac}$ involve the transfer matrix elements connecting orbitals on neighboring sites.

The elements of these matrices are [29]

$$
E_b = \begin{pmatrix}
E(s, b) & 0 & 0 & 0 & 0 \\
0 & E(p, b) & 0 & 0 & 0 \\
0 & 0 & E(p, b) & 0 & 0 \\
0 & 0 & 0 & E(p, b) & 0 \\
0 & 0 & 0 & 0 & E(s^*, b)
\end{pmatrix}
$$

Where $b = c$ or $a$

$$
U_{ac} = \begin{pmatrix}
V(s, s)g_0 & V(sa, pc)g_1 & V(sa, pc)g_2 & V(sa, pc)g_3 & 0 \\
-V(sc, pa)g_1 & V(x, x)g_0 & V(x, y)g_1 & V(x, y)g_2 & -V(pa, s^* c)g_1 \\
-V(sc, pa)g_2 & V(x, y)g_3 & V(x, x)g_0 & V(x, y)g_1 & -V(pa, s^* c)g_2 \\
-V(sc, pa)g_3 & V(x, y)g_2 & V(x, y)g_3 & V(x, x)g_0 & -V(pa, s^* c)g_3 \\
0 & V(s^* a, pc)g_1 & V(s^* a, pc)g_2 & V(s^* a, pc)g_3 & 0
\end{pmatrix}
$$

Where:

$$
g_0 = \cos(\lambda_1)\cos(\lambda_2)\cos(\lambda_3) - i \sin(\lambda_1) \sin(\lambda_2) \sin(\lambda_3)
$$

$$
g_1 = -\cos(\lambda_1)\sin(\lambda_2)\sin(\lambda_3) + i \sin(\lambda_1) \cos(\lambda_2) \cos(\lambda_3)
$$

$$
g_2 = -\sin(\lambda_1)\cos(\lambda_2)\sin(\lambda_3) + i \cos(\lambda_1) \sin(\lambda_2) \cos(\lambda_3)
$$

$$
g_3 = -\sin(\lambda_1)\sin(\lambda_2)\cos(\lambda_3) + i \cos(\lambda_1) \cos(\lambda_2) \sin(\lambda_3)
$$

with $\lambda_1 = k_x a_L / 4$, $\lambda_2 = k_y a_L / 4$, $\lambda_3 = k_z a_L / 4$ and $a_L$ is the lattice constant.

Final remark about the sp$^3$s* scheme is that for any given material, it requires the knowledge of 13 parameters in order to yield reliable band structure in neglect of spin-orbit interaction. The inclusion of this latter will be the subject of the next section.

For the sake of illustration, we show the band structure of bulk GaAs due to the work by Vogl and coworkers[28] in figure 2.6 using the TB parameters of table 2.1 [28].
Table 2.1 Tight-binding parameters of sp$^3$s* model for GaAs due to Vogl et al [28]

<table>
<thead>
<tr>
<th>TB Parameter</th>
<th>GaAs</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{v,s}$</td>
<td>-8.3431</td>
</tr>
<tr>
<td>$E_{p,s}$</td>
<td>1.0414</td>
</tr>
<tr>
<td>$E_{v,c}$</td>
<td>-2.6569</td>
</tr>
<tr>
<td>$E_{p,c}$</td>
<td>3.6686</td>
</tr>
<tr>
<td>$4V_{s,p}$</td>
<td>-0.4513</td>
</tr>
<tr>
<td>$4V_{c,c}$</td>
<td>1.9546</td>
</tr>
<tr>
<td>$4V_{c,y}$</td>
<td>5.0779</td>
</tr>
<tr>
<td>$4V_{c,p}$</td>
<td>4.4800</td>
</tr>
<tr>
<td>$4V_{p,s}$</td>
<td>5.7839</td>
</tr>
<tr>
<td>$E_{c,v,p}$</td>
<td>8.5914</td>
</tr>
<tr>
<td>$E_{c,c}$</td>
<td>6.7386</td>
</tr>
<tr>
<td>$4V_{p,p}$</td>
<td>4.8472</td>
</tr>
<tr>
<td>$4V_{p,v}$</td>
<td>4.8077</td>
</tr>
</tbody>
</table>

Figure 2.6: Band structure $E(k)$ of GaAs in the pure fcc bulk structure [28]
2.5 Tight binding model based on the sp³s* basis set with inclusion of spin-orbit interaction:

In the sp³s* scheme with inclusion of spin-orbit interaction, to define the tight-binding Hamiltonian matrix elements, we begin by constructing, for each orbital i of atom b, a Bloch sum of wave vector $\vec{k}$ as follows:

$$|b,i,\sigma, \vec{k} > = N^{-1/2} \sum_{\vec{R}} \exp \{ i \vec{k} \cdot (\vec{R} + \vec{\tau}_b) \} \times |b,i,\sigma, \vec{R} + \vec{\tau}_b >$$

Where $\sigma$ is the spin polarization state, which can be either up (↑) or down (↓).

And $\vec{\tau}_b$ is the position vector of b-th atom in the unit cell (for instance: $\vec{\tau}_b = (0,0,0)$ for anion and $\vec{\tau}_b = a_t/4(1,1,1)$ for cation).

The empirical tight binding Hamiltonian may be written as:

$$H_0 = \sum_{\vec{R},\sigma,i} \left( |a,i,\sigma, \vec{R} > E_{i,a} < a,i,\sigma, \vec{R} | + |c,i,\sigma, \vec{R} + \vec{d} > E_{c,i} < c,i,\sigma, \vec{R} + \vec{d} | \right)$$

$$+ \sum_{\vec{R},\vec{R}',\sigma,i,j} \left( |a,i,\sigma, \vec{R} > V_{ij} (\vec{R}, \vec{R}' + \vec{d}) < c,j,\sigma, \vec{R}' + \vec{d} | + h.c \right)$$

(2.11)

where h.c is the Hermitian conjugate part of the last sum.

$\vec{R}$ : is the fcc lattice positions of anions.

i and j are the basis orbitals like s, pₓ, pᵧ, pᶻ and s*.

$\vec{d} = \vec{\tau}_c - \vec{\tau}_a$: the position of the cation relative to the anion in the $\vec{R}$ - th cell.

$\vec{d} = a_t/4(1,1,1)$

The off-diagonal matrix elements $V_{ij}$ vanishes unless $\vec{R}$ and $\vec{R}' + \vec{d}$ refer to nearest neighbor atoms.

Each atom has five orbitals; namely the sp³ participates to obtain correct covalent bonding, and the excited state s* for simulating the lowest energy excited states in the conduction bands.

In contrast with the last section, here we use 15 parameters to reproduce the band structure of any material. For illustration, we show the band structure of CdTe due the work by Otto Sankey et al [30] in figure 2.7 using the TB parameters summarized in Table 2.2.
Table 2.2: Tight-binding parameters of CdTe including spin-orbit interactions due to the work by Sankey and coworkers [30]

<table>
<thead>
<tr>
<th>TB Parameter</th>
<th>CdTe</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{x^*}$</td>
<td>-8.891</td>
</tr>
<tr>
<td>$E_{p,3}$</td>
<td>0.915</td>
</tr>
<tr>
<td>$E_{p,c}$</td>
<td>-0.098</td>
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<tr>
<td>$E_{p,c}$</td>
<td>4.315</td>
</tr>
<tr>
<td>$4V_{x,p}$</td>
<td>-4.779</td>
</tr>
<tr>
<td>$4V_{x,c}$</td>
<td>4.355</td>
</tr>
<tr>
<td>$4V_{p,c}$</td>
<td>1.739</td>
</tr>
<tr>
<td>$4V_{p,p}$</td>
<td>-4.767</td>
</tr>
<tr>
<td>$E_{x^*,x}$</td>
<td>7.0</td>
</tr>
<tr>
<td>$E_{p^*,c}$</td>
<td>7.5</td>
</tr>
<tr>
<td>$4V_{p^*,p}$</td>
<td>1.949</td>
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<td>$4V_{p^*,c}$</td>
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<tr>
<td>$\lambda_{a}$</td>
<td>0.367</td>
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<tr>
<td>$\lambda_{c}$</td>
<td>0.013</td>
</tr>
</tbody>
</table>

Figure 2.7: Band structure $E(\vec{k})$ of CdTe using the $sp^3s^*$ TB model including spin-orbit interactions [30]

In this scheme, the k-space Hamiltonian $H_0(\vec{k})$, in the 20-state basis set, can be written in the block forms as follows:

$$H_0(\vec{k}) = \begin{pmatrix} H_{aa} & H_{ac} \\ H_{ca} & H_{cc} \end{pmatrix} \quad (2.12)$$
The block matrices $H_{aa}$ and $H_{cc}$ are diagonal with elements given in table 2.3

Table 2.3 The diagonal elements in the k-space Hamiltonian in $sp^3s^*$ scheme with inclusion of spin-orbit interaction

<table>
<thead>
<tr>
<th>$b, s^*, \uparrow$</th>
<th>$b, s^*, \downarrow$</th>
<th>$b, s^\uparrow$</th>
<th>$b, s^\downarrow$</th>
<th>$b, 3/2, 3/2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{s^*, h}$</td>
<td>$E_{s^*, h}$</td>
<td>$E_{s^h}$</td>
<td>$E_{s^h}$</td>
<td>$E_{p, b} + \lambda_b$</td>
</tr>
<tr>
<td>$b, 3/2, 1/2$</td>
<td>$b, 3/2, -1/2$</td>
<td>$b, 3/2, -3/2$</td>
<td>$b, 1/2, 1/2$</td>
<td>$b, 1/2, -1/2$</td>
</tr>
<tr>
<td>$E_{p, b} + \lambda_b$</td>
<td>$E_{p, b} + \lambda_b$</td>
<td>$E_{p, b} + 2\lambda_b$</td>
<td>$E_{p, b} - 2\lambda_b$</td>
<td></td>
</tr>
</tbody>
</table>

The off-diagonal block matrix $H_{ac}$ is given in table 2.4

Table 2.4 The off-diagonal elements in the k-space Hamiltonian in $sp^3s^*$ scheme with inclusion of spin-orbit interaction

<table>
<thead>
<tr>
<th>$a, s^*, \uparrow$</th>
<th>$c, s^*, \uparrow$</th>
<th>$c, s^*, \downarrow$</th>
<th>$c, s^\uparrow$</th>
<th>$c, s^\downarrow$</th>
<th>$c, 3/2, 3/2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$U_{c, s^h}$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$-U_{c, s^h}/\sqrt{2}$</td>
</tr>
<tr>
<td>$-U_{c, s^h}/\sqrt{2}$</td>
<td>$0$</td>
<td>$-U_{c, s^h}/\sqrt{2}$</td>
<td>$0$</td>
<td>$0$</td>
<td></td>
</tr>
<tr>
<td>$a, 3/2, 3/2$</td>
<td>$-iU_{c, s^h} g/\sqrt{2}$</td>
<td>$0$</td>
<td>$-iU_{c, s^h} g/\sqrt{2}$</td>
<td>$0$</td>
<td>$U_{c, s^h}$</td>
</tr>
<tr>
<td>$a, 3/2, 1/2$</td>
<td>$-\sqrt{2} U_{p, s^h} g/\sqrt{3}$</td>
<td>$-iU_{c, s^h} g/\sqrt{6}$</td>
<td>$\sqrt{2} U_{p, s^h} g/\sqrt{3}$</td>
<td>$-iU_{c, s^h} g/\sqrt{6}$</td>
<td>$-U_{c, s^h} g/\sqrt{3}$</td>
</tr>
<tr>
<td>$a, 3/2, -1/2$</td>
<td>$-iU_{c, s^h} g/\sqrt{6}$</td>
<td>$\sqrt{2} U_{p, s^h} g/\sqrt{3}$</td>
<td>$-iU_{c, s^h} g/\sqrt{6}$</td>
<td>$-\sqrt{2} U_{p, s^h} g/\sqrt{3}$</td>
<td>$-iU_{c, s^h} g/\sqrt{3}$</td>
</tr>
<tr>
<td>$a, 3/2, -3/2$</td>
<td>$0$</td>
<td>$-iU_{c, s^h} g/\sqrt{2}$</td>
<td>$0$</td>
<td>$0$</td>
<td></td>
</tr>
<tr>
<td>$a, 1/2, 1/2$</td>
<td>$U_{p, s^h} g/\sqrt{3}$</td>
<td>$-iU_{c, s^h} g/\sqrt{3}$</td>
<td>$U_{p, s^h} g/\sqrt{3}$</td>
<td>$-iU_{c, s^h} g/\sqrt{3}$</td>
<td>$U_{c, s^h} g/\sqrt{6}$</td>
</tr>
<tr>
<td>$a, 1/2, -1/2$</td>
<td>$iU_{p, s^h} g/\sqrt{3}$</td>
<td>$-U_{c, s^h} g/\sqrt{3}$</td>
<td>$iU_{p, s^h} g/\sqrt{3}$</td>
<td>$-U_{c, s^h} g/\sqrt{3}$</td>
<td></td>
</tr>
</tbody>
</table>

$g_1$, $g_2$, $g_3$, and $g_4$ are mentioned in section 2.4 and:

$g_1 = g_2 - ig_3$

$g_4 = g_3 + ig_3$
The parameters $U_{ij}$ are related to the nearest neighbor matrix elements $V_{ij}$ as follows:

\[
U_{s,s} = 4V_{s,s} = 4 < a_{s}, \sigma, 0 | H \| c_{s}, \sigma, d > ,
\]

\[
U_{x,y} = 4V_{x,y} = 4 < a_{p_{x}}, \sigma, 0 | H \| c_{y}, \sigma, d > ,
\]

\[
U_{x,x} = 4V_{x,x} = 4 < a_{p_{x}}, \sigma, 0 | H \| c_{x}, \sigma, d > ,
\]

\[
U_{s,p} = 4V_{s,p} = 4 < a_{s}, \sigma, 0 | H \| c_{p}, \sigma, d > ,
\]

\[
U_{p,s} = -4V_{p,s} = -4 < a_{p_{y}}, \sigma, 0 | H \| c_{s}, \sigma, d > ,
\]

\[
U_{s*,p} = 4V_{s*,p} = 4 < a_{s}, \sigma, 0 | H \| c_{p}, \sigma, d > ,
\]

\[
U_{p,s*} = -4V_{p,s*} = -4 < a_{p_{y}}, \sigma, 0 | H \| c_{s*}, \sigma, d > ,
\]

Where $j = x, y, \text{ or } z$. and $U_{x,y} = U_{y,x} = U_{z,x}$ and $U_{x,x} = U_{y,y} = U_{z,z}$

Finally we note that in the calculation for the case of strained superlattices, the application of the corresponding TB models to various materials requires one further addition to simulate the strain. In the next chapter, we will show how the strain is inserted in the TB Hamiltonian of sp$^3$s* basis set with inclusion of spin-orbit interaction.
CHAPTER III

The Electronic and Optical Properties of the Strained CdTe/ZnTe (001) Superlattices
3.1 Introduction

Recently, there has been a prominent growing interest in the II-VI semiconductor heterostructures because of their unique optical and electrical properties [13]. These compound semiconductors have a very wide variety of bandgap values (mostly direct) ranging from zero of the semimetal HgTe to 3.8 eV of ZnS. Moreover, the progress in the novel growth techniques, such as the development of the flow-rate modulated beam epitaxy, has made it possible to grow high-quality semiconductor heterostructures even from heavily lattice mismatched materials, up to 7% if the strained slabs are kept sufficiently thin. Besides the standard effects of bulk band discontinuity and slab thicknesses, the strain has indeed added a new degree of freedom to the growth technology to be explored in the band gap engineering.

On the experimental side, strained-layer CdTe ZnTe superlattices have been grown for the first time by G. Monfroy et al [14] using the molecular-beam epitaxy (MBE) technique. This group characterized their samples by electron and x-ray diffractions and, despite the large mismatch between CdTe and ZnTe (Δa/a = 6.4%, is referred to as Δ hereafter), they claimed the success in growing superlattices (SLs) of high quality. Subsequently, other growth techniques, such as the metal-organic-chemical-vapor deposition (MOCVD) [15] have also been reliably used for successful growth of the same kind of SLs. However, whatever advances were achieved in the growth conditions, misfit dislocations inevitably still occurred in the experimental SLs as these latter are beyond the control of the growth techniques, and the limitations are mainly dependent on the elastic properties of the SL constituent materials. As a matter of fact, for any arbitrarily small lattice mismatch (Δ ≥ 0.3%) between the buffer and the overlayer, there always exists a critical layer thickness $d_\text{c}$ beyond which the misfit dislocations appear in the samples. For this aim, Miles et al [16] have used photoluminescence and in-situ reflection high-energy electron diffraction (RHEED) measurement to draw a map of $d_\text{c}$ versus Δ for the strained $\text{Cd}_{x}\text{Zn}_{1-x}\text{Te/Cd}_{z}\text{Zn}_{1-z}\text{Te}$ common-anion SLs [16]. Many of these experiments have demonstrated that the substrates does not play a crucial role in controlling the character of the grown SLs, because due
to the misfit dislocations, the lattice constant jumps to that of a free-standing superlattice structure. In fact, one of the aims of the present work is to investigate the structural quality of the experimental SLs. This by itself is of essential importance as these particular SLs have potential for applications to optoelectronics such as intense-visible light emitters.

On the theoretical side, several computational techniques have been used but were limited either by the system size and the applicability only to the ground state properties, such as the first principle methods, or the complete neglect of the band mixing effects, such as the effective-mass approach (based on the Kronig-Penney model) or the Hückel method. To overcome such difficulties, we have used the $sp^3s^*$ tight-binding (TB) method with inclusion of spin-orbit interaction, which are crucially important in the case of II-VI materials. The TB method has proven its reliability to successfully simulate the experimental data while it incorporates the microscopic description of the material, where the point group symmetry of the system is included. Within the Slater-Koster scheme [17], the TB method uses a small basis set of atomic orbitals and this gives the method the ability to deal with large systems, meanwhile it takes account of the band-mixing effects which are essential in the band structures of systems like quantum dots, wires, SLs, and quantum wells. Consistent with this, one of the striking features of II-VI common-anion SLs is a vanishing or very small valence-band offset (VBO). This makes the mixing of valence bands very essential and the interplay between the biaxial strain and the vanishing VBO is of interest in its own right. Furthermore, it is worth mentioning that, in zinc-blend bulk semiconductors, the valence band (VB) maximum is located at $\Gamma$-point and is four-fold degenerate (including spin). Under the effect of biaxial strain as in the case of SLs, this degeneracy is further lifted by splitting the heavy-hole ($M_J = \pm 3/2$) and the light-hole ($M_J = \pm 1/2$) bands. Thus zero VBO in an unstrained case transforms to a finite VBO in the strained case due to the strain-induced level splitting. Confinement and band-mixing effects may thus compete with strain effects. Hence, the CdTe/ZnTe SLs should be a good candidate to
follow the evolution of the electronic structure as a function of the SL layer thicknesses, VBO, and strain configuration.

For all the reasons mentioned above, we have employed the $sp^3s^*$ tight-binding method, with inclusion of spin-orbit coupling and strain effects, to investigate the electronic and optical properties of the strained $CdTe/ZnTe$ (001) SLs. It is worth mentioning here that in the literature, several attempts have been made to incorporate the strain effects within the TB Hamiltonian [18-26]. More specifically in the case of mismatched superlattices, the biaxial strain results mainly in two structural distortions: (i) bond-length distortion, and (ii) angular distortion. The former distortion is usually described by scaling the off-diagonal energy elements (i.e. the overlap integrals) according to the famous Harrison $1/r^2$ rule, or other functional rule such as that of Priester et al. [27]. However, in the TB framework, this particular distortion cannot lift the degeneracy of the HH and LH states at the Brillouin-zone center (Γ-point), but it rather shifts the band edges. On the other hand, the second distortion affects the bond-directional cosines $(l,m,n)$ which make the $p_x,p_y,$ and $p_z$ orbitals asymmetrically contribute to the TB Hamiltonian. As a consequence, in the presence of biaxial strain, the LH-HH degeneracy at the Γ-point is lifted [26] when the Hamiltonian is expressed in the Slater-Koster scheme [17] with the $sp^3$ basis set and in the neglect of spin-orbit interaction. A subsequent development to this model is the addition of an excited $s^*$ state to this latter basis set by Vogl et al. [28]. The need for the $sp^3s^*$ models was essential especially for semiconductor materials, as they do not yield only band dispersions in good agreement with those obtained by the state-of-art methods, but rather they accurately reproduce the experimental bandgaps, carrier effective masses, and deformation potentials [19,28-29]. Even prior to this work, Kobayashi et al. [30] had proposed a TB scheme which not only adds the $s^*$ orbital to the $sp^3$-basis set, but rather incorporates the idea [31] of the inclusion of the spin-orbit interactions, which are crucially important in the case of II-VI compound semiconductors, particularly in the case of heterojunction of a vanishing VBO. The overlap integrals, in this new 10-orbitals/site basis set, are carried up only to nearest neighbors. We recall
that the point-group symmetry of the unstrained zinc-blende structure is $T_d$ and, in the presence of the spin-orbit interaction, the upper valence bands are formed by a four-fold degenerate $\Gamma_8$ states: $|E_{\nu_2}\rangle = |\frac{3}{2}, \pm \frac{3}{2}; \nu\rangle$, and $|E_{\nu_1}\rangle = |\frac{3}{2}, \pm \frac{1}{2}; \nu\rangle$ (usually labelled heavy holes (HH) and light holes (LH) respectively), and a two-fold degenerate $\Gamma_7$ split-off (SO) states: $|E_{\nu_3}\rangle = |\frac{1}{2}, \pm \frac{1}{2}; \nu\rangle$. However, in this latter model in presence of biaxial strain, the LH-HH degeneracy at $\Gamma$-point cannot numerically be lifted because the directional cosines $(l,m,n)$ alter the Hamiltonian only through the phase shifts $\exp(i\vec{k}\cdot \vec{r})$, and this latter factor has a vanishing effect on the Hamiltonian at $\Gamma$-point ($\vec{k} = \vec{0}$). An attempt to sort out such problem, Priester et al. [19] used a self-consistent TB technique where the diagonal elements are variationally shifted along the growth direction as a consequence of charge redistribution due to the strain effect. Other authors, such as Arriaga et al. [22,23], used a version of the surface Green-function matching method adapted to strained SLs. These latter authors obtained that the splitting between LH and HH states is linearly proportional to the strain. More recently, however, Bertho et al. [21] proposed a new scheme to incorporate the strain effects in the $s\gamma's*$ TB Hamiltonian with the inclusion of the spin-orbit interactions. They treated the strain as a perturbation posteriorly added to the TB Hamiltonian (see next section for more details). As an effect of the reduced symmetry, in this latter scheme, the perturbation takes care of the interaction between all the states which belong to the same irreducible representations of the tetragonal point group $D_{2d}$.

The main result of this work [21] is that the biaxial strain may cause the upper-conduction and valence interband mixing which, in turn, induces a non-linear splitting of LH and HH states at $\Gamma$-point. The hydrostatic band mixing contributes to the non-linear behavior of the band edges in high-pressure experiments and is one of the reasons for the sublinear pressure dependence observed for the fundamental bandgap $E_g(P)$ in III-V and II-VI materials [21]. The mixing effect demonstrates the complex hybridization mechanism of barrier-related and well-related states for building resonant-state wavefunctions in superlattices. This idea of strain-induced band mixing...
has been corroborated by several experimental works. For instance, the evolution of the high-energy part of the reflectivity spectra versus the uniaxial stress in the $Ga_{1-x}In_{x}As:GaAs$ SLs has been well interpreted using this new TB scheme [32]. The same model also yields a HH-LH splitting variation with pressure $P$ in excellent agreement with the optical transitions of the photoluminescence (PL) experiments [18-21,33]. Finally, we mention that this method of incorporating the strain in the TB Hamiltonian may exhibit electronic properties impossible to describe using the standard envelope-function approach and the usual deformation potential theory.

In this present work, we have adapted the same formalism of Bertho et al. [21] of incorporating the strain within the $sp^{3}s^{*}$ TB scheme with inclusion of spin-orbit coupling. We calculated the band structures and oscillator strengths of the $CdTe/ZnTe$ (001) SLs versus the biaxial strain, layer thicknesses, and VBO. This chapter is organized as follows: In section 3.2, within this scheme, we give a brief description about the calculations of the electronic band structure, density of states, and oscillator strength. This latter quantity is proportional to the dipole matrix elements and does measure the efficiency of the optical transitions. Section 3.3 illustrates a detailed discussion of our obtained results. Special emphasis is given to the effect of VBO on the electronic properties of SLs and, as applications, our results are compared to the photoluminescence data. The last section summarizes our conclusions.

3.2 Computational Details

3.2.1 Bandstructure and density of states:

Within the tight-binding framework, and in the presence of spin-orbit coupling and the absence of strain, the electronic wavefunction is expressed in terms of a basis of symmetrically orthogonalized atomic orbitals $| b, \mu, \vec{R}, >$, known as the Lowdin orbitals [34]. Here $\vec{R}$ denotes a Bravais lattice point referred to the primitive cell, $b$ is a basis atom in this primitive cell, and $\mu$
denotes an orbital (such as \( |s, \frac{1}{2} \rangle, |s, -\frac{1}{2} \rangle, \ldots \)) which include the spin-orbit coupling. The Hamiltonian is usually expressed [30] in terms of a basis \( |b, \mu, \vec{k} \rangle \) which is obtained via a discrete Fourier transformation of the localized orbitals \( |b, \mu, \vec{R} \rangle \) given by:

\[
|b, \mu, \vec{k} \rangle = \frac{1}{\sqrt{N_N}} \sum_j e^{iQj} |b, \mu, \vec{R} \rangle
\]  

(3.1)

where \( N_N \) is the number of \( \vec{k} \)-vectors taken either from within the irreducible wedge of the Brillouin zone (BZ) if the density of states is calculated, or along the high-symmetry lines if the band structure is evaluated.

The Schrödinger equation whose solutions are the Bloch functions \( |n \vec{k} \rangle \) is given by:

\[
(H_{sor} - E_{nk}) |n \vec{k} \rangle = 0
\]  

(3.2)

where \( H_{sor} \) is the Hamiltonian of the system with inclusion of spin-orbit coupling.

Equation (3.2) can be expressed in terms of the Lowdin basis as:

\[
\sum_{j,v} \left[ \langle i, \mu, \vec{k} | H_{sor}, j, v, \vec{k} \rangle \cdot E_{nk} \delta_{i,j} \delta_{v,v} \right] |j,v, \vec{k} \rangle = 0
\]  

(3.3)

where \( E_{nk} \) is the eigen-energy corresponding to the eigen-function \( |n \vec{k} \rangle \), \( n \) is a band index, \( i \) and \( j \) denote basis atoms, and \( \mu \) and \( v \) denote orbitals of these respective atoms. The Hamiltonian of either the bulk fcc or the superlattice structure uses the empirical TB parameters given in table 3.1. In this table, the CdTe parameters are due to reference [30], whereas the ZnTe parameters are due to reference [35]. These two respective sets of parameters yield the energy bandgap values of 1.59 eV and 2.39 eV, which are in excellent agreement with experimental values [36]. Moreover, the band dispersions possess carrier effective masses and deformation potentials compatible with experimental values.
Table 3.1 The empirical $sp^3s^*$ tight-binding parameters, with inclusion of spin-orbit coupling, for CdTe and ZnTe, in units of eV. The same notation as in reference [30] is used. The lattice constants ($a_i$) are in Å units.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$a_i$</th>
<th>$E_s^a$</th>
<th>$E_p^a$</th>
<th>$E_s^c$</th>
<th>$E_p^c$</th>
<th>$4V_{xx}$</th>
<th>$4V_{xy}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdTe</td>
<td>6.48</td>
<td>-8.891</td>
<td>0.915</td>
<td>-0.589</td>
<td>4.315</td>
<td>-4.779</td>
<td>2.355</td>
</tr>
<tr>
<td>ZnTe</td>
<td>6.08</td>
<td>-9.190</td>
<td>0.627</td>
<td>-1.420</td>
<td>3.779</td>
<td>-6.642</td>
<td>1.940</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compound</th>
<th>$4V_{sp}^{ac}$</th>
<th>$4V_{pp}^{ac}$</th>
<th>$E_s^{ac}$</th>
<th>$E_p^{ac}$</th>
<th>$4V_{sp}^{ac}$</th>
<th>$4V_{pp}^{ac}$</th>
<th>$\lambda_s$</th>
<th>$\lambda_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdTe</td>
<td>1.739</td>
<td>-4.767</td>
<td>7.0</td>
<td>7.5</td>
<td>1.949</td>
<td>-2.649</td>
<td>0.367</td>
<td>0.013</td>
</tr>
<tr>
<td>ZnTe</td>
<td>5.925</td>
<td>-4.673</td>
<td>6.227</td>
<td>6.779</td>
<td>6.779</td>
<td>-3.827</td>
<td>0.362</td>
<td>0.027</td>
</tr>
</tbody>
</table>

In the case of presence of strain, such as in the superlattice structure, the strain is treated as a perturbation posteriorly added to the Hamiltonian [21]. In order to make this present work self-contained, we briefly summarize the process of making this correction in the Appendix.

One further remark about the heterostructure calculation is that the VBO is considered constant, and added to the diagonal elements of the overlayer (i.e. to one of the two materials in the case of SL structure; for instance is added to the ZnTe slabs in our present work).

The obtained energy spectrum $E_{nk}$ and corresponding wavefunctions $|n, \tilde{k}>$, from equation (3.3), are used to calculate the following quantities: (i) The total density of states (TDOS) given by:

$$N(E) = \frac{1}{N_w} \sum_{n,k}^{N_k} \delta (E - E_{nk})$$  \hspace{1cm} (3.4)

(ii) The local density of states (LDOS), due to the orbital $\mu$ on the atom $b$, which is given by:

$$N_{b,\mu}(E) = \frac{1}{N_w} \sum_{n,k}^{N_k} |<b,\mu, \tilde{R}, |n, \tilde{k}>|^2 \delta (E - E_{nk})$$  \hspace{1cm} (3.5)

(iii) The partial density of states (PDOS), due to the atomic species of type $\alpha$ (such as Cd, Zn, or Te atoms), which is given by:

$$N_\alpha (E) = \sum_{b,\mu} N_{b,\mu}(E)$$  \hspace{1cm} (3.6)

where the sum runs over all the orbitals of all the sites of type $\alpha$. 
We emphasize that the \( \vec{k} \)-space integration carried out in evaluating equations (3.4) and (3.5) is performed using the Monkhorst-Pack technique [37], and the \( \delta \)-function is numerically approximated by a Gaussian:

\[
\delta(x) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp \left[ -\frac{x^2}{2\sigma^2} \right] \tag{3.7}
\]
of width \( \sigma = 0.05 \) eV. All of the TDOSs are normalized to ten states (i.e. one zinc-blend molecule).

### 3.2.2. Oscillator strength

Usually, the empirical tight-binding model is not the best approach for computing the optical-transition probabilities due to the lack of the precise spatial form of the atomic wave-functions. Despite of this, some attempts have been done to compute some optical matrix elements [38].

The common optical matrix elements are: the dipole matrix element \( \vec{P}_{mn} \) and the oscillator strength \( f_{mn} \), which are both defined below:

\[
\vec{P}_{mn}(\vec{k}) = \frac{m}{\hbar} (E_{nk} - E_{mk}) \langle m\vec{k} | \vec{r} | n\vec{k} \rangle \tag{3.8}
\]

\[
f_{mn}(\vec{k}) = \frac{2}{m} \frac{|\vec{P}_{mn}|^2}{E_{nk} - E_{mk}} \tag{3.9}
\]

Here \( m \) is the free-electron mass and \( m \) and \( n \) are band indices for states of unequal energies. The momentum matrix element is the most natural representation for crystals and, with the help of group theory, readily provides the selection rules for the optical transitions. So, the dipole matrix element is particularly informative for quantum wells since it can be of order of the well width for inter-subband transitions. The oscillator strength is more familiar in atomic physics and easily related to the absorption strength. Moreover, the momentum operator \( \vec{P} \) is usually taken parallel to the growth direction (c-axis in our case of (001) SLs) in order to assess the localization effects. The results of our calculations will be presented in the next section.
3.3. Results and discussions

3.3.1. FCC bulk bandstructure

In figures 3.1 and 3.2, we display the electronic band structures of bulk CdTe and bulk ZnTe respectively. These results were obtained using the twenty-band (sp^3s* with inclusion of spin degeneracy) model whose parameters are given in table 3.1. The top of valence band is chosen as an energy reference. The energy gaps, obtained are direct and of values $E_g = 1.59$ and 2.39 eV for CdTe and ZnTe respectively, which are the same as the experimental values [24].

The irreducible representations corresponding to the point-group symmetry of the eigenfunctions are also shown in figures 3.1a and 3.2a for the high-symmetry points $\Gamma$ and $X$ of the Brillouin zone. In both of these latter panels, the lowest group of bands is dominated by contribution from the s-orbitals of anion (Te) atoms. The second group, which forms the valence band (VB), consists of the cationic s-states and all the p-states. For the CdTe (Figure 3.1), the VB and CB have bandwidths of values 5.3 eV and 7.2 eV respectively. Whereas, the respective bandwidths of the VB and CB of ZnTe (Figure 3.2) are 5.8 eV and 7.2 eV. Here, it is worth mentioning the following two quantitative trends: (i) In general, as the lattice constant decreases, the valence band width increases (compare figures 3.1b and 3.2b). This can be ascribed to a reduction of hybridization with increasing separation of the atomic constituents. Moreover, predominantly ionic materials have wider VB than do predominantly covalent materials. (ii) The other trend is that the optical gap in common-anion (or cation) semiconductors decreases with the heavier cation (or anion). The third group of bands, which form the conduction band (CB) are mainly due to contributions from the p and s* orbitals.

In figure 3.3, we display the total and partial densities of states for the CdTe, which more likely would play the role of well in the SLs. Similar trends are observed for ZnTe. As it can be seen in panel 3.3a and 3.3b, Cd and Te atoms experience the same point-group symmetry ($T_d$) and, as a consequence, they have very similar splittings and LDOS profiles. One also may notice
Figure 3.1: The electronic band structure of fcc bulk CdTe calculated using the $sp^3s^*$ tight-binding model, with the inclusion of spin-orbit coupling. (a) the energy bands; (b) the density of states. The top of VB is taken as an energy reference and the DOS is normalized to ten electrons.
Figure 3.2: Same as figure 3.1, but for fcc bulk ZnTe.
Figure 3.3: Partial density-of-states contributions from orbitals on (a) Cd atoms and (b) Te atoms to (c) the TDOS of pure CdTe. TDOS is normalized to ten electrons.
that the first group of bands consists mainly of Te atoms contributions. Furthermore, Te atoms contribute to the VB with a weight bigger than that of Cd atoms. These latter atoms contribute more to the CB structure. This, indeed, reflects the fact that CdTe is a polar material with a partial ionic character.

In figure 3.4, we decompose the TDOS into PDOSs due to: (a) all the s* orbitals, (b) all the s orbitals, and (c) all the p orbitals. It is clear that the s* orbitals contribute only to the CB and predominantly to the higher conduction bands. By taking the superposition of figure 3.3 and figure 3.4, it should be clearly seen that the first group is mainly due to the anionic s orbitals. Furthermore, figure 3.4 shows that the VB and CB are due to an admixture of all s and p orbitals in the hybridization process and, therefore, again reflecting the covalent character of CdTe.

3.3.2. Strained bulk bandstructure

The purpose here is to put under the scope the strain effects as a component separated from the global band offset problem. Of course, the biaxial strain significantly affect the level splittings at the top of the VB. In this sub-section, we aim to discuss the strain effects on the VBO in each of the bulk materials under the same strained configuration corresponding to the structure of the SL, eventually to be studied.

As has been mentioned in the last section, the strain has been treated as a perturbation added posteriorly to the TB Hamiltonian. Besides this, the off-diagonal TB parameters have been scaled according to Priester's rule [27] in order to take account of the bond-length distortion due to the strain. The results for CdTe and ZnTe are shown in figures 3.5a and 3.5b respectively. The calculations have used a tetragonal unit cell of 4 atoms whose in-plane lattice constant has been varied from 6.08 Å (of cubic ZnTe) to 6.48 Å (of cubic CdTe). The inter-plane lattice constant has been calculated using the macroscopic theory of elasticity [36]. Since both materials possess direct bandgaps, we have assessed the level splittings only at Γ-point. The energy
Figure 3.4: Orbital density-of-states contributions from (a) $s^*$ orbitals, (b) $s$ orbitals, and (c) all the $p$ orbitals to the TDOS of pure bulk CdTe.
Figure 3.5: Energy variation of the lowest CB state and the top VB states (HH, LH and SO) under the effect of the biaxial strain. (a) CdTe under compressive strain; (b) ZnTe under tensile strain.
reference has been taken to be the VB edge of either materials in their unstrained fcc-bulk structures.

Now, in the strained SLs, the biaxial strain is tensile for ZnTe and compressive for CdTe. Figure 3.5 shows the variation of the energies of the top VB states (namely: the spin-off (SO) state represented by $\bigcirc$, the heavy-hole (HH) state represented by $\bigcirc$, and the light-hole (LH) state represented by $\nabla$) and the lowest CB state, denoted by $\square$, versus the strain (i.e., the in-plane lattice constant $a$). The $E_g$ of CdTe seems to be insensitive under the compressive strain, contrarily to the $E_g$ of ZnTe which decreases under the tensile strain. This is consistent with the contrast between the bandgaps which we have drawn in figures 3.1 and 3.2. It seems a real fact that if the cation (or anion) atom is substituted by a larger atom the $E_g$ is reduced. In the case of CdTe (Figure 3.5a), the HH lies above LH when a compressive strain is applied. On the other hand, the LH lies above the HH when a tensile strain is applied on ZnTe (Figure 3.5b). The maximum splitting energy between HH and LH is 0.32 eV and 0.19 eV for CdTe and ZnTe, respectively. The non-linearity of the splitting is clearly seen in the behavior of the SO state and does have experimental evidence for it [39].

Another significant effect of the biaxial strain is that it alters the orbital character of the electronic states and, therefore, affecting the optical properties. The CB edge persists always to be s-like and the HH state maintains equal strengths in $p_x$-like and $p_y$-like characters. On the contrary, the LH and SO states, with a varying admixture of $p$ orbitals, undergo a substantial change in the relative proportion of strengths as strain increases. For instance, the LH in the strained CdTe, becomes almost $p_z$-like while SO state becomes more $p_{x,y}$-like with very small fraction of $p_z$-like character. Thus, the strain has very significant effects on the spectral properties of the VB edge states, as it changes substantially the orbital character.

3.3.3. Superlattice bandstructure

In the SL calculations, two assumptions are made: (i) the heterostructure to be pseudomorphic (defect-free), and (ii) the macroscopic theory of elasticity in predicting the SL
atomic structure to be valid. Therefore, despite of the large lattice mismatch (≈6.4 %), the thickness of each slab is assumed to be below the critical thickness \(d_c\) corresponding to the appearance of the misfit dislocations. In real life, these latter inevitably occur in the experimental samples and will be the subject of the next subsection.

To map the strain effect, we have chosen to work on three differently strained superlattices. Two among which are the ones extremely strained to either \(CdTe\) substrate (panel 3.6a) or \(ZnTe\) substrate (panel 3.6c). The third one is the free-standing SL and is chosen with its strain state lying between (a) and (c) and, meanwhile, is of crucial importance for physical applications. Of course, within the TB framework, to calculate the SL bandstructure, one must take into account the band offsets. As mentioned in the last section, the VBO is considered as a constant and added to the diagonal elements of the Hamiltonian matrix. Namely, we have added \(VBO = E_{\nu}(ZnTe) - E_{\nu}(CdTe)\) to the on-site elements of the \(ZnTe\) slabs. Here, \(E_{\nu}\) is the VB edge of the material, shown in brackets, under the strained configuration corresponding to the SL structure. In figure 3.6, two extreme VBO values are considered for each strain state and are displayed on each panel. As it is well known fact that the II-VI common-anion SLs possess vanishing or very small VBO, we took \(VBO = 0\) as one of our choices. The second VBO value, which is a kind of an overestimate, is due to the model-solid approach of Van de Walle [36]. To the best of our knowledge, all the VBOs, found in the literature, lie in between these two extremes. In addition to the strain state and the VBO, the third parameter controlling the SL bandstructure is the slab thicknesses. In figure 3.6, we have chosen to investigate the \((CdTe)_n(ZnTe)_n(001)\) strained SLs, where both slabs have the same number of monolayers. Since both materials possess direct bandgaps, we have just used \(\Gamma\)-point to calculate the energy gap \(E_g\) versus layer thickness \((n=N)\). We found that the electron is always confined within the \(CdTe\) slab. Hence, the SL character is fully determined by the hole behavior. In figure 3.6, for each specific strain state and specific VBO value, and particular slab thickness \((n)\), the SL is characterized by one of three symbols: (i) The symbol \(\Box\) denotes the SL of type-I, where the hole
Figure 3.6: The variation of the energy gap of the \((\text{CdTe})_N(\text{ZnTe})_M(001)\) SL versus \(N\). Each panel represents one biaxial strain state. Two extreme values of VBOs are considered for each panel. The character of the SL is indicated by the shown symbols (see the text for details).
(HH) is confined in the CdTe slab; (ii) The symbol \( x \) denotes the SL of type-II, where the hole (LH) is localized within the ZnTe slab; (iii) the symbol of \( \Box \) stands for a SL not well characterized as the hole is extended over the whole SL slabs.

As shown in the three panels of figure 3.6, the variation of strain causes the increase in the \( E_g \) when the substrate lattice constant is reduced from that of CdTe to the one of ZnTe. Furthermore, the strain does have effect on the character of the SL as it enhances the admixture of the \( p_x, p_y \), and \( p_z \) orbitals as described in the previous sub-section.

In figure 3.6a, the VBO has a positive sign and, therefore, makes the VB edge of ZnTe higher than that of CdTe. This yields a SL of type-II, which seems to be more sensitive to the variation of VBO especially for large \( n \) as the confinements of the electron and the hole are completely independent. On the other hand, in figure 3.6b and 3.6c, the VBO is negative and yields a SL of type-I. The SL \( E_g \) seems not to be too sensitive to the variation of VBO because both the electron and the hole are localized in the CdTe slab and there exists a compromise in their confinement characters. Now, we discuss the \( E_g \) versus \( n \). Of course, it is evident that the variation of \( E_g \) tends toward the \( E_g (CdTe) = 1.59 \text{ eV} \) when \( n \) is very large as an effect of confinement and this explains the reduction of \( E_g \) as \( n \) increases. For small values of \( n \), however, \( E_g \) seems to increase and has a maximum value when \( n=2 \) then starts its decrease. This may be interpreted as a strong band mixing to occur within the valence bands.

In figure 3.7, we display the behaviors of the wave-functions, calculated at \( \Gamma \)-point, corresponding to the electron and upper hole states of the CB and VB respectively. The abscissa axis represents the c-direction of the SL, and the ordinate axis gives the variation of the planar-averaged squared amplitude of the wave-function. Figure 3.7 shows the results of a free-standing (CdTe)_n(ZnTe)_n (001) SL, with \( n=10 \), for two cases of VBO: (a) VBO = 0 eV, and (b) VBO = - 0.134 eV. Actually, these two cases correspond to two data points in figure 3.6b. It can clearly be seen that the electron (Ec1) is always localized in the CdTe slab. For VBO = 0, the hole (Ev1) is delocalized along the whole SL. Whereas for VBO = - 0.134, the top hole (HH)
Figure 3.7: The calculated wavefunction amplitudes for the free-standing \((\text{CdTe})_{10}(\text{ZnTe})_{10}(001)\) SL using: (a)\(\text{VBO}=0\) and (b)\(\text{VBO}=-0.134\) eV. \(\text{Ec1}\) corresponds to the lowest CB electron state, whereas \(E_{v1}, E_{v2}\) and \(E_{v3}\) correspond to the three highest VB hole states.
gets confined within the \textit{CdTe} region and, therefore, yields a SL of type-I. The final remark about figure 3.7 is that the third hole state (Ev3) is found to have tendency to localize at the interface when VBO is vanishing. The same observation was also reported by Quiroga et al.\cite{24} and just reflects the strong mixing effects occurring within the valence bands.

Figure 3.8 displays the band structures of the two SLs previously discussed in figure 3.7, which are the free-standing SLs with n=10 and: (a) VBO = 0 eV, and (b) VBO = -0.134 eV. In both, the SL valence bandedge is considered as an energy reference and the lowest CBs as well as upper VBs are shown, when $\vec{k}$-vector is varied along $Z\Gamma$-line and along one portion of $\Gamma X$-line of the Brillouin zone. The $Z\Gamma$ line is, effectively, sufficient to give prediction about the confinement state of charge carriers. It is obvious that the electron in both panels (a) and (b) is localized with respect to the c-axis, as its conduction band is flat along the $Z\Gamma$ line. The HH state (H1) gets also localized within \textit{CdTe} when VBO = -0.134 eV and this is also shown by the nesting H1 band in panel (b) along the $Z\Gamma$ line.

Figure 3.9 presents the results of oscillator strength versus the slab thickness (n) for the strained (CdTe)$_n$(ZnTe)$_n$ (001) SLs, with n=10. The solid line corresponds to the free-standing SL with VBO = -0.134 eV, which is model of type-I; whereas the dotted curve corresponds to the SL of \textit{CdTe} substrate with VBO = +0.126, which is model of type-II. For the latter SL, the oscillator strength (OS) reaches its maximum for n=2 then vanishes for n $\geq$ 3. This may be explained as an effect of band mixing because, for n $\leq$ 2, the electron (or hole) is localized in \textit{CdTe} (or ZnTe) and the separation between them is smaller than the exciton radius. For the former SL, the OS increases up to n=4, then becomes negligibly small for n $\geq$ 5. Despite of the fact that both carriers being localized within the same region (\textit{CdTe} slab), as far as the the well becomes wider than the exciton radius, the electron-hole pair becomes decoupled. The critical distance corresponding to n=5 might suggest a theoretical estimate of the exciton radius in \textit{CdTe} material to be R $\approx$ 17 Å.
Figure 3.8: Electronic band structures for the case of the free-standing (CdTe)$_{10}$(ZnTe)$_{10}$(001) superlattices calculated with: (a) VBO=0 and (b) VBO=-0.134 eV. In both panels, the VB edge is taken as an energy reference.
Figure 3.9: The calculated oscillator strength for the \((\text{CdTe})_x(\text{ZnTe})_{1-x}(001)\) SL versus \(N\).
Figure 3.10 presents the variation in energy of the two upper VB states, calculated at Γ-point, versus VBO. These results are shown for the free-standing (CdTe)\textsubscript{10} (ZnTe)\textsubscript{10} (001) SL, which are of interest in modelling the PL experimental data (next subsection). We emphasize the following observations: (i) For a free-standing SL made up of two semiconductor materials having the same number of monolayers N, the in-plane lattice constant should be independent of N (a\textsubscript{\parallel} = 6.238 Å). The variation of N only changes the confinement energy. (ii) For the considered range of VBOs, the electron is always localized within the \textit{CdTe} slab. (iii) H and L denote the nature of the SL states at the zone center according to whether, mainly or wholly, they originate from the bulk heavy- or from light-hole states. The valence states are strongly dependent on VBO. When VBO=0, \textit{CdTe} is the well material for the HH state and the superlattice is of type-I. For negative VBO values, the localization of HH state (H1) in \textit{CdTe} layers increases and the band gap is reduced. The LH state L1 remains extended and lower than H1 in energy. The case of positive values of VBO presents more interesting features and gives evidence of a SL type-I to type-II transition. The increase of VBO lowers the barrier height for the HH which becomes extended in all the SL and increases the localization of the LH state, which becomes the SL hole ground state. So, VBO = 40 meV appears as the value for which the transition occurs. For VBO > 40 meV, the LH state L1 lies above the HH state H1 and the superlattice is of type-II. The exciton transition becomes \textit{indirect} in real space with weak oscillator strength.

3.3.4. Modelling of photoluminescence experiments

The first photoluminescence (PL) measurements, for the CdTe/ZnTe SLs, have been reported by Miles et al.\cite{40}. The grown SLs displayed intense visible photoluminescence spectra, which made the systems promising devices of light sources and photo-detectors. As mentioned in the introduction, the same research group of reference \cite{14} was the first to report a successful growth of such high quality SLs. In their samples, \textit{CdTe} layers varied in thickness between 20 to 49 Å, while \textit{ZnTe} barriers were between 20 to 51 Å wide. The SLs were grown
Figure 3.10: Variation of the two highest-energy VB states versus VBO, for the free-standing \((\text{CdTe})_{10}(\text{ZnTe})_{10}(001)\) SL.
on either (001) CdTe, ZnTe, or Cd\textsubscript{x}Zn\textsubscript{1-x}Te buffer layers. The experimental results of PL measurements (at 5\textdegree K) done on various samples are summarized in Table 3.2. On the other hand, in our computation, we have assumed a pseudomorphic SL structure and used the macroscopic theory of elasticity (MTE) [36] to fit the experimental structural data. Furthermore, the validity of MTE is assumed even in the ultimate limit of one nominal strained monolayer. In our theoretical work, the VBO is taken as a free parameter to be adjusted to yield the best fit to the PL data. The results of our TB method, which includes spin-orbit coupling, are summarized also in Table 3.2 for the sake of comparison. We emphasize that these theoretical results correspond to the free-standing SL case; and that the $E_g$ values are much lower than experimental data if one took the same experimental buffer. Furthermore, the SL’s $E_g$ decreases with the increasing VBO.

Our theoretical results predicts that the top VB state is either extended or a LH localized in the ZnTe slabs; and hence favors more the character of SLs of type-II. Therefore, it seems that the distribution of strain between CdTe and ZnTe layers is found to be difficult to determine or to map through the choice of substrate as the large lattice mismatch causes a rapid relaxation and the lattice constant of the SL jumps into the one of a free-standing SL as soon as the primary misfit dislocation appears. Obviously, the strain distribution (morphology) plays a crucial role in determining the SL bandgap and character.

Table 3.2 The theoretical VBO, shown here, is for the case of the free-standing (CdTe)\textsubscript{m}(ZnTe)\textsubscript{n}(001) superlattice and corresponds to the best fit of the experimental $E_g$. Theoretically, the number of monolayers $m$ and $n$ are determined using the macroscopic theory of elasticity [36].

<table>
<thead>
<tr>
<th>Sample</th>
<th>Superlattice\textsuperscript{a} (CdTe/ZnTe)\textsuperscript{b} ($\AA$)</th>
<th>Buffer layer\textsuperscript{a}</th>
<th>$E_g$(eV)\textsuperscript{a, b}</th>
<th>VBO(meV)\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25/35</td>
<td>CdTe</td>
<td>1.87</td>
<td>6</td>
</tr>
<tr>
<td>2</td>
<td>28/21</td>
<td>CdTe</td>
<td>1.81</td>
<td>6</td>
</tr>
<tr>
<td>3</td>
<td>51/50</td>
<td>CdTe</td>
<td>1.69</td>
<td>86</td>
</tr>
<tr>
<td>4</td>
<td>27/30</td>
<td>ZnTe</td>
<td>1.81</td>
<td>46</td>
</tr>
<tr>
<td>5</td>
<td>21/30</td>
<td>Cd, Zn, Te</td>
<td>1.83</td>
<td>116</td>
</tr>
<tr>
<td>6</td>
<td>26/33</td>
<td>Cd, Zn, Te</td>
<td>1.82</td>
<td>41</td>
</tr>
<tr>
<td>7</td>
<td>34/36</td>
<td>Cd, Zn, Te</td>
<td>1.74</td>
<td>86</td>
</tr>
<tr>
<td>8</td>
<td>22/18</td>
<td>Cd, Zn, Te</td>
<td>1.78</td>
<td>176</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Experimental data due to reference [40]

\textsuperscript{b} Present work
More recent PL experimental data are due to Kuwabara et al. [41]. The \textit{CdTe/ZnTe} strained-layer SLs are grown on \textit{ZnTe} buffer layer, using hot-wall epitaxy (HWE). The cross-sectional transmission electron microscopy (TEM) image shows that the critical thickness of the \textit{CdTe} well layer is about $d_c \approx 12^\circ \text{A}$. The experimental results of the picosecond time-resolved PL spectra are shown in table 3.3. Our theoretical TB results are also shown for SLs strained to \textit{ZnTe} substrate for comparison. The VBO is varied to yield the best fit to the experimental data. In table 3.3, the theoretical results show that the SLs 1 and 2 are of type-I because their corresponding VBO is less than the critical value of 40 meV. The other SLs are of type-II. This, indeed, is consistent with TEM predictions [41] as the thickness of the \textit{CdTe} well is less than the critical value $d_c$ in the case of SLs 1 and 2. Hence, our TB results suggest that the strain is not anymore confined in the \textit{CdTe} slabs in case of samples 3 and 4. We emphasize, here, that this is not a problem related to the growth technique but rather it is an intrinsic effect related to the elastic properties of the SL constituents.

Table 3.3 Same as table 3.2 but experimental data correspond to reference [41] where the buffer is \textit{ZnTe} and the theoretical VBOs correspond to SLs of \textit{ZnTe} substrate as well.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Superlattice $^a$ (\textit{CdTe/ZnTe})($\text{A}'$)</th>
<th>$E_g$ (eV) $^{a,b}$</th>
<th>VBO (meV) $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9/40</td>
<td>2.24</td>
<td>-84</td>
</tr>
<tr>
<td>2</td>
<td>12/40</td>
<td>2.15</td>
<td>-49</td>
</tr>
<tr>
<td>3</td>
<td>24/40</td>
<td>1.82</td>
<td>136</td>
</tr>
<tr>
<td>4</td>
<td>40/40</td>
<td>1.74</td>
<td>121</td>
</tr>
</tbody>
</table>

(a) Experimental data due to reference [41]
(b) Present work

3.4. Conclusions

We have used the $sp^3s^*$ tight-binding method, with inclusion of spin-orbit coupling, to investigate the electronic and optical properties of the strained \textit{CdTe/ZnTe} (001) superlattices. Within the TB scheme, we have calculated the SL band structure, various densities of states, and oscillator strengths versus the strain state, layer thicknesses, and band offsets.
Since the II-VI semiconductor heterostructures are expected to have either vanishing or small valence band offsets, the biaxial strain plays an essential role in determining the SL character as it controls the splittings of the top VB states. We have deconvoluted the band offset problem into separable components. The first one, we could separate, is the biaxial strain effect. From computational point of view, within the TB framework, the strain has been treated as a perturbation posteriorly added to the Hamiltonian. The results have shown that the top VB state is a HH-like for CdTe under compressive strain, and is a LH-like for ZnTe under tensile strain.

In the calculation on the strained SLs, the electron is found to be always confined within the CdTe slabs, whereas the hole is sensitive to the VBO, and its behavior controls the SL character. Since the SL constituents are of relatively large lattice mismatch (≈ 6.4 %), misfit dislocations inevitably can occur in the grown experimental samples. For this reason, we have given special attention to the study of the free-standing superlattices, which might be the limit case of the relaxed SL structure. For the free-standing (CdTe)$_n$(ZnTe)$_m$(001) SL, the electronic band-structures and oscillator strengths are studied versus layer thickness (n) and VBO. Two extreme values of VBO, which correspond to a vanishing value and the one obtained using the model solid approach, are taken. It is found that the effect of n is only to control the degree (energy) of confinement in the CdTe well. However, the variation of VBO predicted the SL character to exhibit a type-I to type-II transition for a critical VBO value of about 40 meV. For VBO < 40 meV, the heavy-hole is localized within the CdTe slabs and the SL is of type-I. On the other hand, if VBO > 40 meV, the LH localized within the ZnTe slab becomes the top SL valence band state and therefore the SL is of type-II. We have shown the use of the oscillator strength in measuring the radiative efficiency of the SLs and understanding their characters.

The results of our work have been shown to be useful in interpreting the photoluminescence data. Mainly, they were used in determining the strain distribution and the SL character. Some valuable information regarding the structural and optical qualities of the SLs have also been drawn.
Appendix

In the framework of the $sp^3s^*$ tight-binding, with the inclusion of spin-orbit interaction, the biaxial strain is incorporated into the Hamiltonian in a perturbative fashion as follows:

$$H = H_0 + H_s(\varepsilon)$$

where $H_0$ is the $sp^3s^*$ TB Hamiltonian which includes the spin-orbit coupling effects, $H_s(\varepsilon)$ is the strain part which shall be posteriorly added as a perturbation to the system. In this latter part, the interaction is switched on between eigenstates which belong to the same irreducible representations at the Brillouin zone center ($\Gamma$-point). As far as the lowest CB states and the top VB states are concerned in the case of strained bulk material, the strain involve the mixing between mainly six states (namely in figures 3.1a and 3.2a: $|E_{v3}^s>$ and $|E_{v1}^s>$ with $|E_{v2}^s>$ corresponding to the SO and LH/HH states of the respective irreducible representations $\Gamma_\gamma$, and $\Gamma_\delta$, whereas $|E_{v3}^s>$ and $|E_{v1}^s>$ with $|E_{v2}^s>$ correspond to the upper-CB states of the respective irreducible representations $\Gamma_\gamma$ and $\Gamma_\delta$), which were obtained by diagonalizing $H_0$, in the absence of strain.

For a biaxial strain, $H_s$ can be linked with the deformation potential and written as follows:

$$
\begin{align*}
\begin{bmatrix}
|E_{v2}^s> & |E_{v1}^s> & |E_{v3}^s> & |E_{v4}^s> & |E_{v5}^s> & |E_{v6}^s> \\
< E_{v2}^s | & a_{v2}^s Tr(\varepsilon) - \varepsilon_{v2} & a_{v1}^s Tr(\varepsilon) - \varepsilon_{v1} & 0 & 0 & 0 \\
< E_{v1}^s | & a_{v1}^s Tr(\varepsilon) - \varepsilon_{v1} & E_{c2}^s - a_{v1}^s Tr(\varepsilon) + \varepsilon_{v1} & 0 & 0 & 0 \\
< E_{v3}^s | & 0 & 0 & a_{v3}^s Tr(\varepsilon) + b_{v3}^s & i\sqrt{2}b_{v3}^s & a_{v3}^s Tr(\varepsilon) + b_{v3}^s - i\sqrt{2}b_{v3}^s \\
< E_{v4}^s | & 0 & 0 & \varepsilon_{v4} & -a_{v4}^s Tr(\varepsilon) + b_{v4}^s & i\sqrt{2}b_{v4}^s \\
< E_{v5}^s | & 0 & 0 & -i\sqrt{2}b_{v5}^s & E_{c1}^s - a_{v5}^s Tr(\varepsilon) - \varepsilon_{v5} & -i\sqrt{2}b_{v5}^s \\
< E_{v6}^s | & 0 & 0 & i\sqrt{2}b_{v6}^s & a_{v6}^s Tr(\varepsilon) & E_{c1}^s - a_{v6}^s Tr(\varepsilon)
\end{bmatrix}
\end{align*}
$$

where $\varepsilon$ is the strain tensor and $\varepsilon_{v}\equiv (\varepsilon_{||} - \varepsilon_{\perp})/3$; $a$, ($a'$), is the intraband hydrostatic deformation potential for the heavy-hole and light-hole states (the split-off states); $a_{v\alpha}$ is the interband hydrostatic deformation potential coupling the heavy-hole states $E_{v\alpha}$ (light-hole states $E_{\alpha}$) to the conduction states $E_{c\alpha}$ ($E_{c\alpha}$), $a'_{v\alpha}$ is the interband hydrostatic deformation potential coupling the
split-off states $E_{v}\rightarrow$ to the conduction states $E_{c}$, $b$ (respectively, $b_r$) describes the linear splitting of the valence $|E_{v1}^>\rangle$ and $|E_{v2}^>\rangle$ states or the conduction $|E_{c1}^>\rangle$ and $|E_{c2}^>\rangle$ states respectively), within the tight-binding model: $b=b_r=-b_r$; $b'$ is related to the mixing of $|E_{c1}^>\rangle$ with $|E_{v1}^>\rangle$ in the VB and of $|E_{c1}^>\rangle$ with $|E_{c2}^>\rangle$ in the CB. $b_r$ describes the upper-conduction-valence mixing of $|E_{c1}^>\rangle$ with $|E_{c2}^>\rangle$ states and $b'_r$ is related to the upper-conduction-valence mixing of $|E_{c1}^>\rangle$. We also recall that the eigen-energies of the pure bulk lattice are given by:

$$E_{v1}^> = E_{c2}^> = 0,$$

$$E_{v3}^> = -\Delta_r = \frac{E_p^a - 2\lambda - E_p^c - 2\lambda_r}{2} - \frac{1}{2}\sqrt{(E_p^a - 2\lambda - E_p^c + 2\lambda_r)^2 + 4V_{a}^r};$$

$$E_{c1}^> = E_{c1}^> = E_c^> + \Delta_r' = \frac{E_p^a + \lambda + E_p^c + \lambda_r}{2} + \frac{1}{2}\sqrt{(E_p^a + \lambda - E_p^c - \lambda_r)^2 + 4V_{r}^c};$$

$$E_{c1}^> = E_{c1}^> = \frac{E_p^a - 2\lambda + E_p^c - 2\lambda_r}{2} + \frac{1}{2}\sqrt{(E_p^a - 2\lambda + E_p^c + 2\lambda_r)^2 + 4V_{a}^c};$$

where $E_p^a, E_p^c, \lambda, \lambda_r$, and $V_{a}$ are the tight-binding parameters shown in table 3.1. The intraband and interband deformation potentials for both CdTe and ZnTe are summarized in table 3.4 and they are due to the work by reference [21].

**Table-3.4** Intraband and interband hydrostatic and uniaxial deformation potentials (in eV) for both CdTe and ZnTe, due to reference [21].

<table>
<thead>
<tr>
<th>Compound</th>
<th>$a_v$</th>
<th>$a'_v$</th>
<th>$a_{cv}$</th>
<th>$a'_{cv}$</th>
<th>$b$</th>
<th>$b'$</th>
<th>$b_{cv}$</th>
<th>$b'_{cv}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdTe</td>
<td>1.10</td>
<td>0.93</td>
<td>2.16</td>
<td>2.22</td>
<td>-1.20</td>
<td>-1.13</td>
<td>-2.47</td>
<td>-2.51</td>
</tr>
<tr>
<td>ZnTe</td>
<td>1.30</td>
<td>1.13</td>
<td>3.37</td>
<td>3.43</td>
<td>-1.20</td>
<td>-1.12</td>
<td>-3.11</td>
<td>-3.14</td>
</tr>
</tbody>
</table>
References


[26] Lin-Chung P J and Yang M J, “Tight-binding calculations of energy gaps in \((001)-(\text{InAs})_n(\text{InSb})_m\)”, 2000 *J. Appl. Phys.* 87 4319-4323


In summary, the behavior of the transport in the first domain is strongly influenced by the geometry and properties of the domain. This is particularly true in domains with complex geometries or heterogeneities, where the effective transport properties can be significantly different from those calculated in the second domain.

The results of the simulations show that the transport properties in the first domain can be accurately predicted using appropriate models, taking into account the specific characteristics of the material and the geometry of the domain. This is important for the design and engineering of systems where transport processes play a crucial role.

In conclusion, the study of transport properties in complex domains is essential for the development of accurate models and effective strategies for the design and optimization of systems. It highlights the importance of considering the specific characteristics of the materials and geometries involved in the transport processes.
الإشراف على الرسالة

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أستاذ مشارك في الفيزياء الحسابية
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جامعة الإمارات العربية المتحدة
دراسة الخصائص الإلكترونية والضوئية للنظام المتعدد الطبقات CdTe / ZnTe (001)

أطروحة مقدمة إلى
عمادة الدراسات العليا
جامعة الإمارات العربية المتحدة

أمينة عبد الله أحمد الزرعوني

لمتطلبات الحصول على درجة الماجستير
في
علوم وهندسة المواد

2002