

Chapter I

Diluted magnetic semiconductor quantum dots

I.1 II-VI semiconductor quantum dots

I.1.1 Band structure of CdTe/ZnTe

ZnTe and CdTe are two II-VI semiconductor, meaning they are composed of an anion from the column VI of periodic table (Te), and a cation from the column II (Cd and Zn). They both crystallize as zinc blend when grown in Molecular Beam Epitaxy. As shown in Fig. I.1, in this structure, each species is organized in a face centred lattice, one them being shift from the other by a quarter of the [111] diagonal. Each ion is then in a tetragonal environment, meaning the zinc-blende structure is of the T_d space-group.

The external orbital of the cation are s for the cation ($4d^{10}5s^2$ for Cd, $3d^{10}4s^2$ for Zn) and p for the anion ($4d^{10}5s^25p^4$ for Te). Considering a N unit crystal, it then contain $8N$ valence electron, coming from the s and p levels of the ions. The s and p orbital of these atoms hybridize to form 8 levels, 4 bonding and 4 anti-bonding.

The lowest band of the bonding levels, coming from s orbitals, will be filled by $2N$ valence electron. $6N$ will be taken to fill the three higher energy bonding band, formed by the hybridization of p orbitals. Those bonding states form the valence band. At higher energy, the anti-bonding states form the conduction band. Since all the electron available are used to fill the valence band, the conduction band is empty in the ground state. The lower energy band of the conduction band are formed by the anti-symmetric combination of the s orbitals. At higher energy, the anti-symmetric hybridization of p orbitals form three other bands.

Introducing the spin-orbit interaction, the conduction band, formed by the hybridazation of s orbitals, is of Γ_6 (spherical) symmetry at the center of the

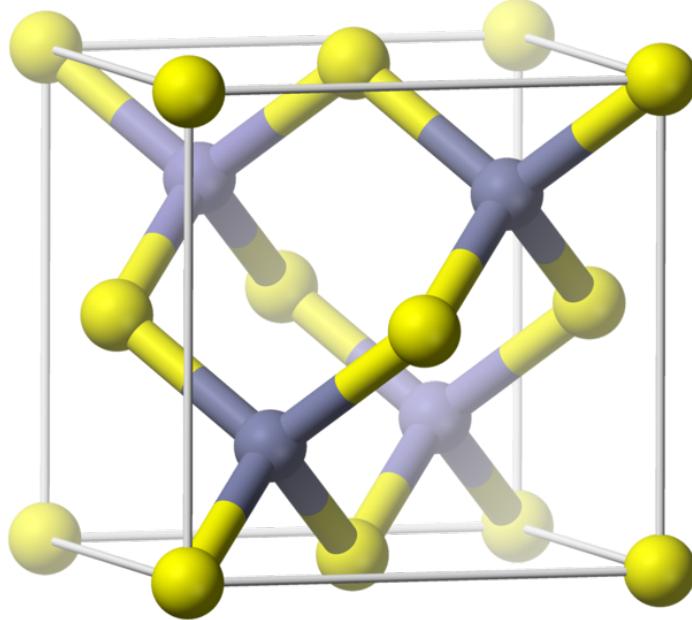


Figure I.1: Zinc-blende crystal structure and first Brillouin zone.

Brillouin zone, two-fold degenerated, with an orbital momentum (spin) $\sigma = 1/2$. In a similar fashion, the valence band will be split into two bands: a first one of Γ_8 symmetry, with a spin $J = 3/2$, four-fold degenerated ; and the second one, at lower energy, of Γ_7 symmetry, with a spin $1/2$, two-fold degenerated. The splitting $\Gamma_7 - \Gamma_8$ is of $\Delta_{SO} \simeq 0.9$ eV in II-VI semiconductor.

The whole CdTe band structure is presented on Fig. I.2. One can note that CdTe is a direct gap semiconductor: the highest energy point of the valence band corresponds to the lowest energy point of the conduction band, in Γ . As we move away from this point, the valence band splits into two branches: one with small curvature, meaning a high effective mass for the carriers on it, is called the heavy-hole (hh) band, while the one presenting the highest curvature and smallest effective mass is called the light-hole (lh) band.

One way to understand this evolution is to apply the $\mathbf{k}\cdot\mathbf{p}$ approximation, as proposed by Kane in 1957 [1]. This model gives an estimation of the electronic band structure starting from the exact solution and energy of the Schrödinger equation at the center of the Brillouin. The hamiltonian to resolve is then :

$$\left(\frac{p^2}{2m_0} + U(\mathbf{r}) \right) \psi_{n,\mathbf{k}} = E_{n,\mathbf{k}} \psi_{n,\mathbf{k}} \quad (\text{I.1})$$



Figure I.2: CdTe/ZnTe band structures

with $U(\mathbf{r})$ the potential of the crystal and $\psi_{n,\mathbf{k}}$ the Bloch wave, separated between a periodic part $u_{n,\mathbf{k}}(\mathbf{r})$ and plane-wave part $e^{i\mathbf{k}\cdot\mathbf{r}}$ as follow :

$$\psi_{n,\mathbf{k}} = u_{n,\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}} \quad (\text{I.2})$$

Neglecting the Γ_7 band at lower energy, we solve this hamiltonian for carrier on the Γ_6 and Γ_8 bands [2]. The z -axis is defined along the growth direction of the semiconductor and chosen as the quantization axis. We then find the energy:

$$\begin{aligned} E_c(k_z) &= E_c + \frac{\hbar^2 k_z^2}{2m_c} \\ E_{v,\pm\frac{1}{2}}(k_z) &= E_v - \frac{\hbar^2 k_z^2}{2m_{lh}} \\ E_{v,\pm\frac{3}{2}}(k_z) &= E_v + \frac{\hbar^2 k_z^2}{2m_0} \end{aligned} \quad (\text{I.3})$$

with E_c (E_v) the energy of the conduction band (respectively, the valence band), m_c the effective mass of the carrier on the conduction and m_{lh} the effective mass of the light hole. One can see that the splitting of the valence band separate the carrier with a spin $J_z = \pm\frac{3}{2}$ (hh) from the one with a spin $J_z = \pm\frac{1}{2}$ (lh). However, the neglecting of the bands other than Γ_6 and Γ_8 lead to a positive curvature for the hh. To correct this problem, we would have to take into account higher energy conduction band, which will repel the hh band and give it its negative curvature.

Another solution to have the matrix describing the Γ_8 band is to use symmetry consideration. Luttinger showed in 1956 [3] that the only Hamiltonian fulfilling the cubic symmetry is:

$$\mathcal{H}_L = -\frac{\hbar^2}{2m_0} \left(\gamma_1 k^2 I_4 - 2\gamma_2 \sum_i k_i^2 \left(J_i^2 - \frac{1}{3} J^2 \right) - 2\gamma_3 (k_x k_y (J_x J_y + J_y J_x) + c.p.) \right) \quad (\text{I.4})$$

with γ_1 , γ_2 and γ_3 the Luttinger parameters, I_4 the 4×4 identity matrix, \mathbf{k} a vector of the Brillouin zone, \mathbf{J} the orbital momentum operator with J_x , J_y and J_z being 4×4 matric satisfying $[J_x, J_y] = iJ_z$ and circular permutation, and *c.p* standing for "circular permutation". This hamiltonian can be simplified using the parameters:

$$\begin{aligned} A &= \gamma_1 + \frac{5}{2}\gamma_2 \\ B &= 2\gamma_2 \\ C &= 2(\gamma_3 - \gamma_2) \end{aligned} \quad (\text{I.5})$$

Using these, the Luttinger hamiltonian can be rewritten:

$$\mathcal{H}_L = -\frac{\hbar^2}{2m_0}(Ak^2I_4 - B(\mathbf{k}\cdot\mathbf{J})^2 + C(k_xk_y(J_xJ_y + J_yJ_x) + c.p.)) \quad (\text{I.6})$$

The *B*-term lift the degeneracy of the Γ_8 band into two sub-bands as shown above, and is invariant under arbitrary rotations. The *C*-term describes the warping of the valence band.

In the spherical approximation, the Luttinger hamiltonian has two eigenvalues:

$$\begin{aligned} E_{hh} &= -\frac{\hbar^2k^2}{2m_0(A-2.25B)^{-1}} = -\frac{\hbar^2k^2}{2m_0(\gamma_1-2\gamma_2)^{-1}} = -\frac{\hbar^2k^2}{2m_{hh}} \\ E_{lh} &= -\frac{\hbar^2k^2}{2m_0(A-0.25B)^{-1}} = -\frac{\hbar^2k^2}{2m_0(\gamma_1+2\gamma_2)^{-1}} = -\frac{\hbar^2k^2}{2m_{lh}} \end{aligned} \quad (\text{I.7})$$

We find back the value of the effective mass for the lh, along with a value for the hh. The hh band also presents here a negative curvature, as expected.

The parameters and carriers effective masses are given in the Tab. ??.

I.1.2 Lattice mismatch and the Bir-Pikus Hamiltonian

ZnTe crystal has a lattice parameter of 6.10Å, while CdTe one is of 6.48Å. This lattice mismatch will induce strain in a CdTe layer grown on a ZnTe substrate.

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	CdTe	ZnTe
E_g	1606 meV	2391 meV
ϵ_r	10.6	9.7
a_0	6.48 Å	6.10 Å
Δ_{SO}	0.90 eV	0.91 eV
γ_1	4.8	4.07
γ_2	1.5	0.78
γ_3	1.9	1.59
$m_{hh,z}$	0.556	0.398
$m_{hh,\perp}$	0.159	0.206
$m_{lh,z}$	0.128	0.178
$m_{lh,\perp}$	0.303	0.303
m_e	0.096	0.116

Table I.1: Physical parameters for CdTe and ZnTe.

I.1.3 Electron-hole interaction in confined structure

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Figure I.3: Dots STM images

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I.1.4 Valence band mixing

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I.2 Exchange interaction between carrier and magnetic atom

I.2.1 Exchange interaction in Diluted Magnetic Semiconductors

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I.2.2 Mn case

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I.2.3 Cr case

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I.2.4 Effect of the confinement

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I.3 Fine and hyperfine structure of a magnetic atom in II-VI semiconductor

I.3.1 Mn atom in II-VI semiconductor

Mn in a lattice -> modification of orbital -> spin-orbit interaction. Magnetic anisotropy + anisotropy of strain. (Mn has nuclear spin 5/2 -> hyperfine interaction?)

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Figure I.4: Mn in Zinc-Blend lattice

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Figure I.5: Mn fine and hyperfine structure

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I.3.2 Cr atom in II-VI semiconductor



Figure I.6: Cr in Zinc-Blend lattice

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Figure I.7: Atomic configuration in Jahn-Teller effect + three minima



Figure I.8: Degeneracy breaking under Jahn-Teller effect

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Figure I.9: Strain effect on ground state + degeneracy breaking by this symmetry reduction



Figure I.10: Overall energy structure (with +/- 2 which doesn't luminesce)

I.4 A simple example: the X-Mn system

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Figure I.11: QD spectra 0 Mn, 1 Mn, 2 Mn

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Figure I.12: Mn energy level in a QD

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