

Band structure of CdSe(Type II-VI) spherical semiconductor quantum dots

Introduction

Electron and hole energy levels are computed in the framework of k.p perturbation theory. The adiabatic electronic energy levels and wave functions have been calculated using non degenerate first-order perturbation theory, aka “effective-mass approximation”, while adiabatic hole energy levels and wave functions have been computed respecting the complex band structure at the highest valence band minimum of type II-VI zinc blende semiconductors, aka. “multiband effective mass approximation”. In both cases, an “envelope function approximation” is used such that the envelope functions obey Schrodinger’s equations for a infinite spherical well of the size of the dot radius, R, with hole/electron effective masses obtained using k.p theory.

Envelope function approximation

Following the work Luttinger and Kohn, the hamiltonian of a charge(electron or hole) confined in a spherical impurity of radius R with confinement potential V_{conf} , lattice potential V_{lat} and spin-orbit coupling V_{so} is given by

$$H = -\frac{\hbar^2}{2m} \nabla^2 + V_{lat} + V_{conf} + V_{so}$$

where

$$V_{conf} = \begin{cases} 0 & \text{for } r < R \\ \infty & \text{for } r \geq R \end{cases}$$

and

$$V_{so} = \frac{\hbar^2}{4m_e^2 c^2} (\nabla V_{lat} \times p) \cdot \sigma$$

where σ is the Pauli-spin vector with components σ_x , σ_y and σ_z , the Pauli-spin matrices. The solution to Schrodinger's equation for the Luttinger Kohn Hamiltonian was derived in reference and has the form

$$\Psi_i(r) = \sum_n u_{n0}^i(r) * F_n^i(r)$$

where $u_{n0}(r)$ are the valence/conduction band Bloch functions at the band minimum ($\mathbf{k}=0$) that captures essential symmetries, and the index i refers to any one such band, which will become clear later. For any \mathbf{k} within the first Brillouin zone for a particular ' i ', u_{nk} are solutions to Schrodinger's equation with the lattice potential and spin orbit interaction effects, satisfying

$$\left[-\frac{\hbar^2}{2m_e} \nabla^2 + V_{so} + V_{lat} \right] u_{nk}(r) = \varepsilon_{nk} u_{nk}(r)$$

F_n is defined as envelope functions that satisfy Schrodinger's equation including the confinement potential

$$\left[-\frac{\hbar^2}{2m^*} \nabla^2 + V_{conf} \right] F_n(r) = E \cdot F_n(r)$$

where m^* is the effective mass of the charge in the particular band corresponding to the index i , obtained using k.p perturbation theory.

k.p Perturbation Theory

Non-degenerate Conduction Band

The lowest conduction band electrons of CdSe, from band structure data, has Γ_1 symmetry and thus are doubly-degenerate. Ignoring the interaction of the lowest conduction band with other bands, which is a suitable approximation, the Bloch functions at the band minimum are just given by $|1/2, 1/2\rangle$ and $|1/2, -1/2\rangle$. In reference, Kane calculated the effective mass of the lowest conduction band by including the k.p interaction and spin orbit splitting using first order perturbation theory. The lowest conduction band electron effective mass is given by the expression

$$m_c = \frac{m_e}{1 + \frac{2P^2}{3m_0} \left(\frac{2}{E_g} + \frac{1}{E_g + \Delta} \right)}$$

where E_g is the band-gap of CdSe, P is the Kane matrix element, as defined in reference and Δ is the spin-orbit splitting, determined empirically, with values posted in Table 1.

Degenerate Valence Bands

The highest valence band-structure can be treated in the “multiband effective-mass” approximation. The highest valence band has six-fold degeneracy due to Γ_4 symmetry of the highest valence band minimum. The Bloch functions of the highest valence at the band minimum are $\left| \frac{3}{2}, \frac{3}{2} \right\rangle, \left| \frac{3}{2}, \frac{1}{2} \right\rangle, \left| \frac{3}{2}, -\frac{1}{2} \right\rangle, \left| \frac{3}{2}, -\frac{3}{2} \right\rangle, \left| \frac{1}{2}, \frac{1}{2} \right\rangle, \left| \frac{1}{2}, -\frac{1}{2} \right\rangle$.

Due to strong spin-orbit coupling, the six-fold degenerate valence band of CdSe is split into a four-fold degenerate band with $J=3/2$ and a two-fold degenerate spin-orbit split off band with $J=1/2$, where J is the total orbital angular momentum of the band-minimum Bloch function(s), and the coupling between these bands due to second order perturbation theory is removed in the strong-spin orbit coupling approximation. The $J=3/2$ states are split further by $J_z = 1/2, -1/2$ (light-hole) and $J_z = 3/2, -3/2$ (heavy-hole) bands due to the k.p interaction in first order perturbation theory. So, in the limit of strong spin-orbit coupling, a characteristic of Type II-VI semiconductors, the problem of diagonalizing the original 6X6 hamiltonian matrix for the highest conduction band energy levels is

simplified to diagonalizing three separate 2X2 blocks. Yu and Cardona in pages covers these technical issues in good detail.

The effective masses of holes in these sub bands can be calculated in this scheme to be

$$\frac{1}{m_{hh}} = \frac{\hbar^2}{m_e} \cdot (\gamma_1 - 2\gamma_2) \quad ; \quad \frac{1}{m_{lh}} = \frac{\hbar^2}{m_e} \cdot (\gamma_1 + 2\gamma_2)$$

$$\frac{1}{m_{so}} = \frac{1}{m_e} \left[1 - \frac{2}{3} \cdot \frac{p^2}{m_e(E_g + \Delta)} \right]$$

where γ_1 and γ_2 are Luttinger-Kohn parameters, determined from empirical band structure calculations, posted in table 1.

Electron and hole wave functions and energies

Electron and hole wave functions and energy levels in the lowest conduction band and highest valence band(s) can be calculated by solving the envelope function equation with the appropriate effective masses and boundary conditions on the boundary of the nanocrystal.

The wave functions of the lowest conduction band and highest valence bands (for heavy, light, and spin-split off band holes) of CdSe take the form

$$\Psi_{nlm}^e(r, \theta, \phi) = \sqrt{\frac{2}{\pi}} k_{n,l}^e Y_l^m(\theta, \phi) j_l(k_{n,l}^e r) \left[\frac{1}{\sqrt{2}} \left| \frac{1}{2}, -\frac{1}{2} \right\rangle + \frac{1}{\sqrt{2}} \left| \frac{1}{2}, \frac{1}{2} \right\rangle \right]$$

$$\Psi_{nlm}^{so}(r, \theta, \phi) = \sqrt{\frac{2}{\pi}} k_{n,l}^{so} Y_l^m(\theta, \phi) j_l(k_{n,l}^{so} r) \left[\frac{1}{\sqrt{2}} \left| \frac{1}{2}, -\frac{1}{2} \right\rangle + \frac{1}{\sqrt{2}} \left| \frac{1}{2}, \frac{1}{2} \right\rangle \right]$$

$$\Psi_{nlm}^{hh}(r, \theta, \phi) = \sqrt{\frac{2}{\pi}} k_{n,l}^{hh} Y_l^m(\theta, \phi) j_l(k_{n,l}^{hh} r) \left[\frac{1}{\sqrt{2}} \left| \frac{3}{2}, -\frac{3}{2} \right\rangle + \frac{1}{\sqrt{2}} \left| \frac{3}{2}, \frac{3}{2} \right\rangle \right]$$

$$\Psi_{nlm}^{lh}(r, \theta, \phi) = \sqrt{\frac{2}{\pi}} k_{n,l}^{lh} Y_l^m(\theta, \phi) j_l(k_{n,l}^{lh} r) \left[\frac{1}{\sqrt{2}} \left| \frac{3}{2}, -\frac{1}{2} \right\rangle + \frac{1}{\sqrt{2}} \left| \frac{3}{2}, \frac{1}{2} \right\rangle \right]$$

where

$$k_{n,l} = \frac{\alpha_{n,l}}{R}, \quad \alpha_{n,l} \text{ is the } n\text{th root of } l\text{-th order spherical Bessel function}$$

The energies of these levels are given by

$$E_{n,l}^e = E_g + \frac{\hbar^2 \alpha_{n,l}^2}{2m_e R^2} ; \quad E_{n,l}^{hh} = -\frac{\hbar^2 \alpha_{n,l}^2}{2m_{hh} R^2} ; \quad E_{n,l}^{lh} = -\frac{\hbar^2 \alpha_{n,l}^2}{2m_{lh} R^2} ; \quad E_{n,l}^{so} = -\Delta - \frac{\hbar^2 \alpha_{n,l}^2}{2m_{lh} R^2}$$