Theoretical Investigations of Excitonic Absorption in Quasi Two-dimensional CdSe Nanoplatelets

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Abstract—**Optical absorption is an important characteristic of CdSe nanoplatelets (NPLs) used for optoelectronic applications. Here, we theoretically investigate the absorption spectra of CdSe NPLs considering Sommerfeld enhancement and excitonic effects and study its relation with the electronic structure and optical transition matrix elements.**

Index Terms—**Excitonic optical absorption, Electronic structure, CdSe NPLs, Optical transition matrix element, $k \cdot p$ method**

I. INTRODUCTION

Quasi two-dimensional CdSe nanoplatelets (NPLs) are a recently developed class of colloidal nanoparticles [1] that have gained growing research interest in the recent years, owing to their useful optoelectronic characteristics [1]–[3]. Their lateral dimensions are of the order of tens of nanometer and vertical thicknesses about several monolayers (ML). Due to the strong anisotropic quantum confinement which they are subjected to, NPLs exhibit spectrally narrow absorption and photoluminescence peaks even at room temperature [4]. They offer superior opto-electronic properties over quantum dots (QDs), such as narrow emission linewidth, reduced auger recombination, reduced inhomogeneous broadening and giant absorption cross-section [5], [6]. Recent research has shown that the continuum intrinsic absorbance of NPLs is considerably larger when compared to QDs [4]. This makes them more efficient absorbers with increased light−matter interaction, which can be leveraged for applications in light-conversion layers, solar cells, etc. In this work, we lay down a theoretical framework to calculate and study the excitonic absorption in quasi two-dimensional CdSe NPLs.

II. THEORETICAL FRAMEWORK

We have used the Kane's 8-band $k \cdot p$ method to calculate the electronic bandstructure of the CdSe NPLs considering they are grown in the zincblende phase. The 8-band Hamiltonian containing both kinetic and strain terms are given by Eq. 1. The main diagonal terms C, H, L, V account for the conduction band, heavy-hole, light-hole and split-off hole bands respectively. The off-diagonal terms account for the coupling effects. Here, $H_{ij} = H_{ij}^*$, represented by cc (complex conjugate). Detailed expressions for the Hamiltonian elements are enlisted in a previous work [7], which uses the Luttinger parameters. They are $\gamma_1 = 3.265, \gamma_2 = 1.162, \gamma_3 = 1.443$ for

CdSe [6]. Using Eq. 1, we can obtain the energy dispersion in the vicinity of the Γ-point by diagonalizing the 8-band $k \cdot p$ Hamiltonian matrix. Material parameters for CdSe used in our simulation, such as spin-orbit splitting energy, deformation potentials, Kane matrix element and others are from ref. [8].

$$H = \begin{bmatrix} C & cc & cc & cc & cc & cc & cc & cc \\ 0 & C & cc & cc & cc & cc & cc & cc \\ \frac{P_-}{\sqrt{2}} & 0 & H & cc & cc & cc & cc & cc \\ -\sqrt{\frac{2}{3}}P_z & \frac{P_-}{\sqrt{6}} & S^* & L & cc & cc & cc & cc \\ \frac{-P_+}{\sqrt{6}} & -\sqrt{\frac{2}{3}}P_z & -R^* & 0 & L & cc & cc & cc \\ 0 & \frac{-P_+}{\sqrt{2}} & 0 & -R^* & -S^* & H & cc & cc \\ \frac{-P_z}{\sqrt{3}} & \frac{-P_-}{\sqrt{3}} & \frac{S^*}{\sqrt{2}} & -D & -\sqrt{\frac{3}{2}}S & \sqrt{2}R & V & cc \\ \frac{-P_+}{\sqrt{3}} & \frac{P_z}{\sqrt{3}} & -\sqrt{2}R^* & -\sqrt{\frac{3}{2}}S^* & D & \frac{S}{\sqrt{2}} & 0 & V \end{bmatrix} \tag{1}$$

We also calculate the squared optical transition matrix elements (TME) given by Eq. 2, which is a measure for the momentum of the transitions between the electron and hole subbands.

$$Q_i^{n_c n_v} = \frac{2}{m_0} |\langle \Psi_{n_c} | \hat{\varepsilon} \cdot p_i | \Psi_{n_v} \rangle|^2, i = x, y, z \tag{2}$$

Here $\hat{\varepsilon}$ is the unit vector in the direction of the electric field, p_i is the momentum operator, and Ψ_{n_c} and Ψ_{n_v} are the real electron and hole wavefunctions, respectively. The real wavefunction is the product of the Bloch wavefunctions and envelope wavefunctions.

To study the absorption spectra of NPLs, we have used the density-matrix equation dependent on the transition strengths based on the TME. Considering the excitonic effects, it can be expressed as the sum of contributions from band-to-band continuum-states with Sommerfeld enhancement (α^{bb}) and that from the excitonic bound states (α^{ex}); given by Eq. 3 and 4, respectively.

$$\alpha^{bb}(E) = \frac{\pi e^2 \hbar}{2 E n m_0 \varepsilon_0 c} \sum_{n_c, n_v} \iint \frac{Q_T^{n_c n_v}}{4\pi^2 L_z} C_S \frac{\tau}{n_c n_v \hbar} \times$$
$$\text{sech}\left[(E_{eh} - E) / (n_c n_v \hbar / \tau) \right] dk_x dk_y \tag{3}$$

$$\alpha^{ex}(E) = \frac{\pi e^2 \hbar}{2Enm_0\varepsilon_0 cL_z} \sum_{n_c,n_v} Q_T^{n_c n_v}(0)|I_{nm}|^2 |\varphi(0)|^2 \frac{\tau_{ex}}{n_c n_v \hbar} \times$$
$$\text{sech}\left[\left(E_{eh} - E_{nb} - E\right)/\left(n_c n_v \hbar/\tau\right)\right] \quad (4)$$

where $Q_T^{n_c n_v} = 2|Q_i^{n_c n_v}|^2/m_0$ is derived from the TME (Eq. 2). C_S is the Sommerfeld enhancement factor. τ is the intraband relaxation time. τ_{ex} is the intraband relaxation time for exciton. I_{nm} is the free electron and free hole wavefunction overlap integration. E_{nb} is the absolute value of exciton binding energy, given by $E_{nb} = E_b^{3D}/(n-0.5)^2$, where E_b^{3D} is the exciton binding energy for bulk material. And $|\varphi(0)|^2 = 1/\pi a_B^{3D}(n-0.5)^2$, where a_B^{3D} is the exciton Bohr radius for bulk material.

III. Results and Discussion

Here we will study the electronic structure and absorption characteristics of CdSe NPL of 4 ML thickness (1.2 nm). Fig. 1 (a) shows the energy dispersion curves for the first 3 electron and the first 5 holes subband states for **k** along [100] and [110]. For these subbands, Fig. 1 (b) shows the squared wavefunction levels at **k** = 0. Each of the subbands are identified as E1, E2 or HH1, LH1, SO1 and so on for both, the energy dispersion curves and the squared wavefunctions. The E1 has appreciable overlap with HH1, LH1 and SO1.
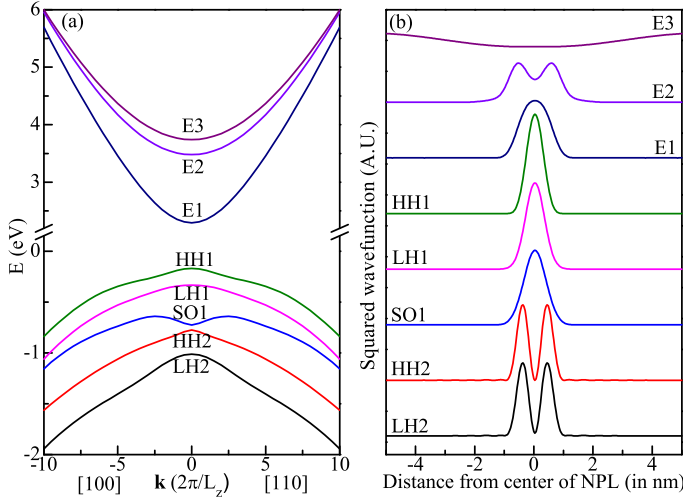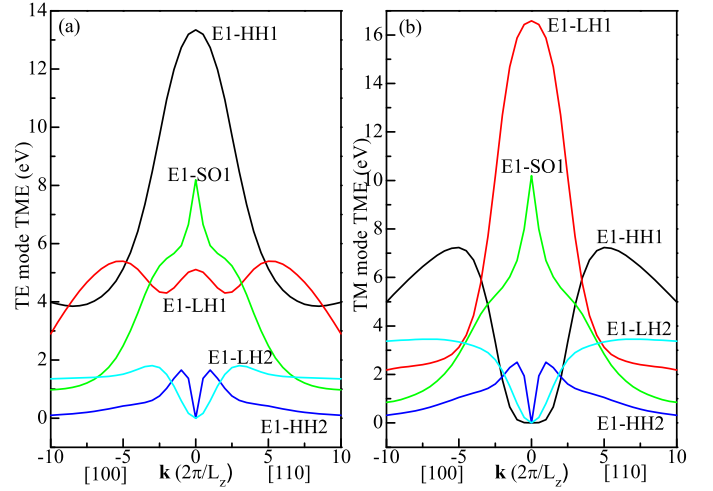
Figure 2. Optical transition matrix element (TME) values for transition from E1 to HH1, LH1, SO1, HH2 and LH2 in the (a) TE mode and (b) TM mode.
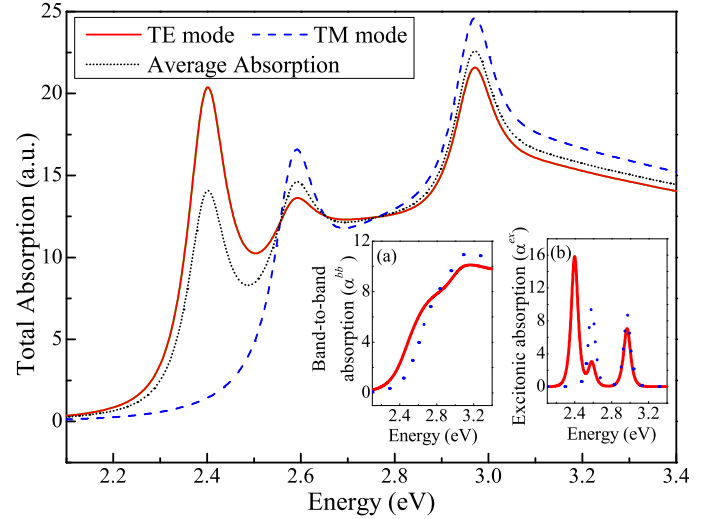
Figure 3. Total excitonic absorption, and (inset: a) Band-to-band absorption, (inset:b) Excitonic bound state absorption for TE mode (red solid line) and TM mode (blue dashed line). Black dotted line gives the average absorption.

Figure 1. (a) Energy dispersion curves and (b) Squared wavefunctions at **k** = 0 (Γ-point) for 4 ML CdSe NPL. **k** is the wavevector. E stands for electron, HH for heavy hole, LH for light hole and SO for split-off hole. E1--HH1 is 2.46 eV.

Fig. 2 shows the TME values for the transverse electric (TE) and transverse magnetic (TM) mode [i.e. $Q_{x,y}^{n_c n_v}$ and $Q_z^{n_c n_v}$ respectively (Eq. 2)] for transitions from E1 to HH1, LH1, SO1, HH2 and LH2 states. The dominant transition in the TE mode is E1—HH1 (2.46 eV), while in the TM mode it is E1--LH1 (2.63 eV). E1–SO1 (3 eV) is the second most dominant in both cases. The effect of this can be seen in Fig. 3, which shows the absorption spectrum of the 4 ML CdSe NPL. The strongest peak for TE mode is at 2.46 eV (for E1--HH1),

followed by 3 eV (E1--SO1) and 2.63 eV (E1—LH1) – in accordance to the TME strengths. Similarly, for TM mode, the peaks are at 2.63 eV (E1—LH1) and 3 eV (E1–SO1), as per the TME.

In Fig. 3, the dotted black line gives the average absorption, while the solid red line gives the TE mode gain, and the dashed blue line gives the TM mode gain. Insets (a) and (b) in Fig. 3 show the band-to-band continuum-states absorption (α_{bb}) and the excitonic bound states absorption (α_{ex}), which contribute the total absorption as discussed for Eq. 3 and 4. The excitonic bound states absorption has a greater magnitude and a sharper linewidth compared to the band-to-band continuum-states absorption.

IV. Summary and Conclusion

We have used an 8-band $\mathbf{k \cdot p}$ method and density-matrix equation based excitonic effects to theoretically calculate the electronic structure and optical absorption of CdSe NPLs. Energy dispersion curves and the squared wavefunctions for the NPL is calculated. The transition matrix element (TME) values in TE and TM optical mode determines the total absorption spectra.

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