

# Quantum Confinement Effects on Optical Properties of ZnO Quantum Dots

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## ABSTRACT

The quantum confinement (QC) effects in ZnO quantum dots embedded in MgO matrix are theoretically investigated using tight-binding method. The effects on bound states and optical gap are studied versus the QD size and valence-band offset (VBO). Excellent agreement was obtained between theoretical results and available photoluminescence (PL) data versus dot size, especially when  $VBO \approx 1.0$  eV, which correspond to maximal compromised confinement characters of both holes and electrons. The strong QC of excitons would further enhance the oscillator strength and recombination rate.

**Keywords:** ZnO quantum dots and nanocrystals, radiative recombination, oscillator strength, photoluminescence

## 1 INTRODUCTION

The multifunctional properties of ZnO have induced many breakthroughs in various fields and paved the way for this material to extend its applications beyond those of GaN. (i) In photonics, the simultaneously large band-gap (3.37 eV) and exciton binding energy (60 meV) made ZnO a suitable candidate for ultraviolet LEDs and lasers to operate at room temperature [1] besides achieving efficient dye-sensitized solar cells [2]; (ii) In electronics, the recent achievement of p-doping [3,4] has paved the way for promising applications such as compact solid-state lasers that could operate in green region. The success in p-doping has put ZnO in the category of the best transparent conducting materials; (iii) In biomedical field, two unique properties coexisting in ZnO nano-particles (NPs), which are the non-toxicity and high-radiative efficiency, made ZnO NPs very useful in both medical imaging and cancer therapy [5]; (iv) In gas-sensing, ZnO is among best oxides besides SnO<sub>2</sub>, which has the ability to detect hazardous gases such as H<sub>2</sub>S [6].

In the present investigation, we employ a realistic 3D tight-binding (TB) method to probe the electronic and optical properties of spherical ZnO QDs embedded in MgO matrix. From a theoretical point of view, the latter insulator

should be equivalent to the passivation of the dangling bonds at the surface of ZnO NPs by hydrogen or OH group as is the case in solvents.

In another related work, we have studied the radiative properties of Si NPs and found that the oscillator strength (OS) and recombination rate (RR) increase with decreasing the NP size [7]. However, the behaviors of OS and RR for ZnO QDs seem to be completely different from those in Si NPs. The exciton's life-time is reported to decrease versus QD size [8,9] to reach a minimum then increase thereafter. Both the large QC and exciton binding energy are the reasons behind this compromised behavior [8,9]. In the present work we shall investigate the effect of QC on the electronic structure and the optical gap.

The present paper is organized as follows: Next section gives a brief description about the model and method of computation. Section 3 shows the results and the last section summarizes our main findings.

## 2 TIGHT-BINDING METHOD

The empirical TB method with minimal  $sp^3$  basis set is used to probe the electronic band structure, density of states and wavefunctions in order to investigate the number and confinement energies of the bound states in ZnO QDs. The suitability of the TB method for such task stems from the fact that it uses few basis set of atomic orbitals, while it takes account of the crystal symmetry and band-mixing effects. Thus, it has the advantage to easily deal with very large systems containing thousands of atoms.

Both composites ZnO and MgO have wurtzite crystal structures with Zn atom being larger than Mg atom. In the computational Supercell, we have considered a spherical ZnO QD, centered at one Zn atom and of radius R, barriered in MgO matrix. ZnO is assumed to have the same lattice constants as the host crystal MgO; so the QD is under compressive strain. We have assumed the validity of the macroscopic theory of elasticity. Besides, this model has no dangling bonds (no defects) so one should focus to investigate purely the QC effects.

In the present work, we used TB models developed by Kobayashi and coworkers [10] and Lin et al. [11] for

wurtzite structures of ZnO and MgO, respectively. The problem of energy reference between the two sets of TB parameters is sorted out by taking into account the valence band offset (VBO). For instance, the valence-band (VB) edge of ZnO stands higher in energy than the one of MgO when an ideal interface is formed between these two materials (i.e.,  $VBO = E_V(\text{ZnO}) - E_V(\text{MgO}) > 0$ ). Using the state-of-the-art *ab-initio* method, the VBO is reported to be about 1.0 eV for ZnO/MgO hetero-junction [12]. It is worth to mention that the latter interface violates the famous common-anion rule, whose domain of validity comprises lattice-matched zinc-blende semiconductor hetero-junctions. The band-gap energies of bulk ZnO and MgO obtained using the above TB parameters are 3.30 eV and 5.94 eV, respectively. We emphasize that by taking  $VBO = 1.0$  eV, MgO would play the role of an insulating material to keep both charge carriers confined within the ZnO QD. Hence, the conduction-band offset (CBO) and VBO should consist the well depths for electrons and holes, respectively.

In most of our calculations, we have considered a super-cell of size  $8 \times 8 \times 4$  primitive cells (containing 1024 atoms) to calculate band-gap energies, wavefunctions, and both local and total densities of states. These quantities are studied versus QD size and VBO.

### 3 RESULTS AND DISCUSSIONS

#### 3.1 Modeling of PL data

Figure 1 shows a comparison between our theoretical results and the experimental data reported by two groups; Meulenkamp [13] and Wood et al.[14]. The former has prepared ZnO NPs in size ranging from 2 to 7 nm by adding LiOH to an ethanolic zinc acetate solution. The latter group prepared ZnO colloids with size ranging from 1 to 6 nm using tetraalkylammonium hydroxides. The characterization of ZnO colloids was carried out using high-resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD), and ultracentrifugation (UC) [14]. The UV-vis absorption and fluorescence spectra of the particles yielded exciton energies shown by blue empty up-triangles. Whereas, the results of exciton energies obtained in reference [13] are shown in red empty squares.

Our theoretical results of band-gap energies of QDs with size ranging from 0.1 to 2 nm are shown in empty and solid green circles corresponding to  $VBO = 0$  and  $VBO = 1$  eV, respectively. It is obvious that the QC effects start to get into play when the QD radius gets larger than 0.3 nm. The least square fitting of the theoretical results of  $VBO = 1$  eV is shown by the solid green curve. The formula used for best fit is:

$$E_g^{QD} = A + \frac{B}{d^C}$$

The fitting yields:  $A = 3.109$ ,  $B = 0.926$  and  $C = 1.07$ . The curve represents excellent fit to both results of  $VBO = 1$  eV and experimental data of references [13,14].

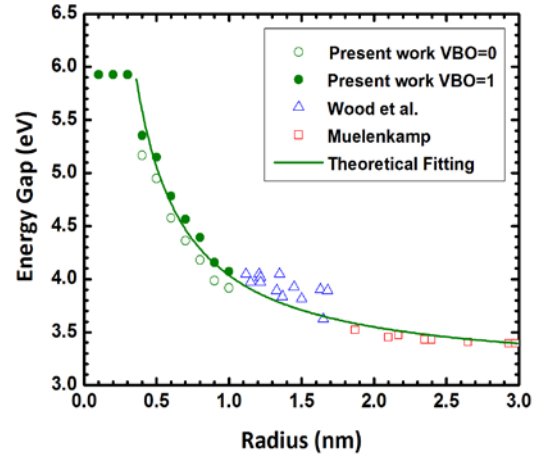


Figure 1: Comparison of theoretical band-gap energies and experimental PL data.

#### 3.2 Band structures

Figure 2 shows the band structures along  $\Gamma Z$  high-symmetry line of the Brillouin zone, corresponding to a QD of size 1.2 nm using  $VBO = 0$  ( $CBO = 2.64$  eV) and  $VBO = 1$  eV ( $CBO = 1.64$  eV), corresponding to panels 2a and 2b respectively. Figure 2a shows 4 CBs to be nesting (flat) inside the electron well (e-Well), yielding an energy gap of value  $E_g = 4.577$  eV due mainly to electron confinement  $E_{Conf}^e = 1.277$  eV. Moreover, two hole states  $V1-V2$ , corresponding to the heavy-hole and light-hole states, seem to have weak dispersion as they have tendency to localize around the interface between the QD and the host MgO matrix. This behavior might be caused by the strain field.

On the other hand, in Figure 2b, only one CB is clearly localized deeply in the e-Well (see C1). Ten VBs ( $V1-V10$ ) are also clearly shown to be dispersion-less as to correspond to bound states in the hole well (h-Well). The confinement energies of ground hole and electron states are:  $E_{Conf}^h = 0.458$  eV and  $E_{Conf}^e = 0.98$  eV, respectively. The combined quantum confinements produce an energy gap of  $E_g = 4.782$  eV.

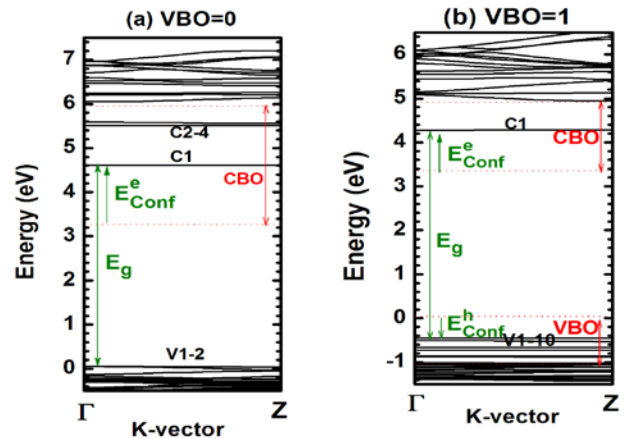


Figure 2: Bandstructures of ZnO QD of size 1.2 nm with  $VBO = 0$  and 1 eV.

### 3.3 Bound states' eigenfunctions

The QD size is kept fixed at radius  $R = 6 \text{ \AA}$  and the eigen-functions corresponding to the eigen-energies around the band-gap are calculated at  $\Gamma$ -point. Figure 3 shows the radial probability density versus the radial distance from the center of the ZnO QD for two values of VBO (0 and 1 eV), same values as in previous Figure. Figure 3a of VBO = 0 shows that the e-Well contains 4 bound states (C1-C4) with localization length of  $\xi_b \approx 3.67 \text{ \AA}$ . On the other hand, with VBO = 1 eV, the h-Well contains 10 bound states and e-Well has 4 electronic bound states (see Table 1). This Figure 3b also shows that the 10 bound hole states to be localized in the QD within a localization length of about same order as the electronic states. Thus, these results are consistent with those discussed in Figure 2.

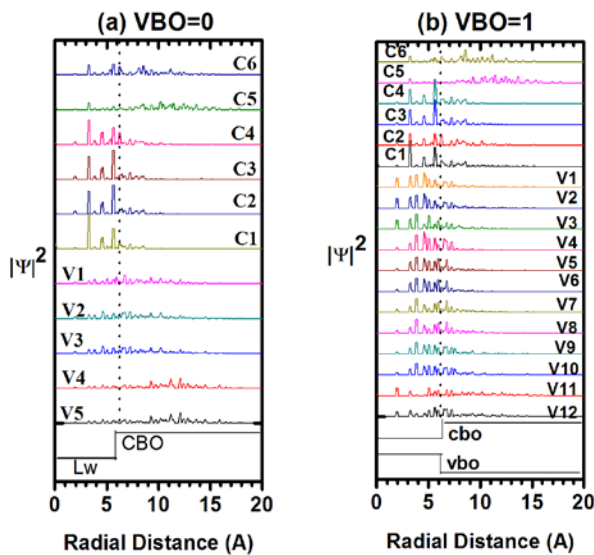


Figure 3: Top VB and bottom CB radial eigen-functions for ZnO QD of radius 0.6 nm.

Radius (Å)	1	2	3	4	5
Nh states	3	3	3	3	6
Ne states	1	1	1	1	1
Eg (eV)	5.928	5.928	5.928	5.352	5.149

Radius (Å)	6	7	8	9	10
Nh states	10	19	23	35	>40
Ne states	4	4	4	7	7
Eg (eV)	4.782	4.564	4.392	4.159	4.072

Table 1: Number of hole and electron bound states in ZnO QD versus Radius.

### 3.4 Density of states

Figure 4 shows the results of densities of states of a super-cell of size  $6 \times 6 \times 4$  primitive cells, containing ZnO QD of radius  $6 \text{ \AA}$  concentric at the central Zn atom in the SCell.

The total density of states of the whole system (TDOS) is normalized to contain 8 electrons and the VB-edge of ZnO bulk is taken as an energy reference. Figure 4a shows TDOS in red curve and its two partial densities of states (PDOSs) due to contributions from ZnO atoms located inside the QD (green curve) and MgO atoms located outside the QD (blue curve). As a function of energy, TDOS is basically composed of three groups: (i) The lowest group composed mainly by the oxygen s-orbitals and is so deep in energy (around -20 eV) that should be considered among core states; (ii) The valence band in the energy range [-5.5,0] eV which is composed from the bonding states due to the  $sp^3$  hybridization between Zn-O and Mg-O; and (iii) The conduction band which is very extended on an energy range of about [6,24] eV with few gap states at about 4.58, 5.43 and 5.57 eV. The system (or supercell of  $6 \times 6 \times 4$  primitive cells) contains 576 atoms whereas the QD contains 77 atoms (39 Zn + 38 O atoms) so that the ratio of ZnO PDOS to TDOS is  $77:576 \approx 13.4\%$ . The PDOS of QD, in turn, is decomposed into atomic species' contributions as shown in Figures 4b and 4c.

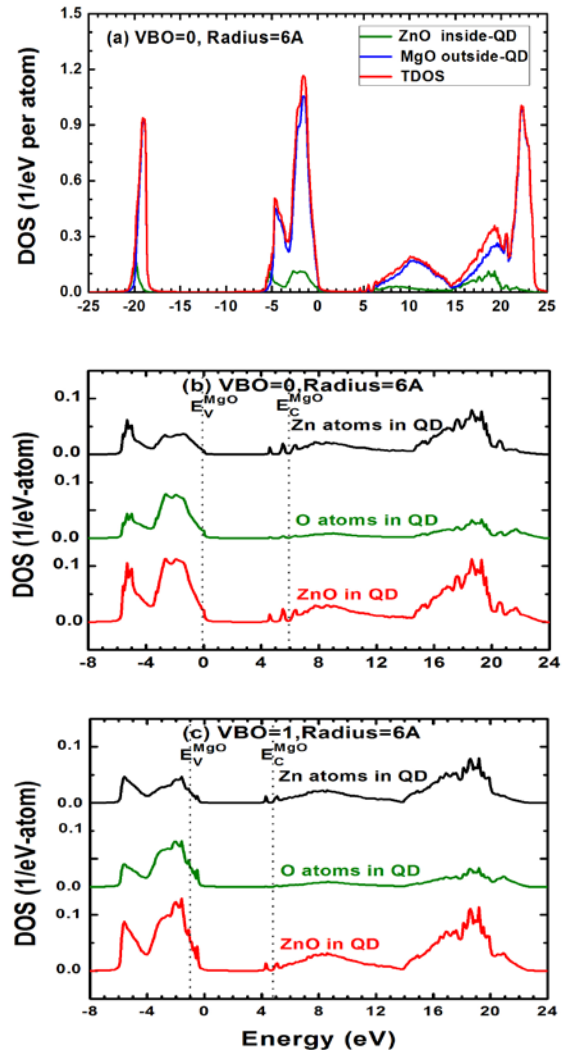


Figure 4: DOS and PDOS versus VBO

Figure 4b and 4c show the contributions of Zn atoms (in black curve) and O atoms (in green curve) to the PDOS (in red curve) of ZnO QD of radius 6 Å corresponding to VBO = 0 and 1 eV, respectively. The dotted vertical lines correspond to the VB and CB edges of MgO. Figure 4b corresponds to the QD with e-Well of depth CBO = 2.64 eV and clearly shows the existence of 4 electronic bound states. Figure 4c corresponds to the QD with h-Well of depth 1 eV and e-Well of depth 1.64 eV. As a matter of fact, the h-Well contains 10 hole bound states and the e-Well contains one deep and three shallow electronic bound states. One last remark about Figure 4 is the fact that the VB is populated with states originating from O atoms whereas the CB has contributions from states originating from Zn atoms. This reveals the fact that Zn-O bond to be covalent with partial ionic character and that the O atom is more electronegative than the Zn atom. Thus, the electronic bound states in e-Well do originate at Zn atoms in QD.

#### 4 CONCLUSIONS

Theoretical investigation of QC effects on the electronic and optical properties of ZnO spherical QDs embedded in MgO matrix have been presented. The electronic band structures have been studied versus QD size (well width), well depths (VBO and CBO) and barrier thickness. The results shall be summarized as follows:

- (i) The barrier thickness has a negligible effect on the number of bound states. The ground bound states have localization length of 3.67 Å. So, in order to decouple ZnO QDs, a separation of  $L_b = 7\text{Å}$  must be provided.
- (ii) The theoretical results of  $E_g$  versus ZnO QD size (i.e., well width) yield excellent fit to the experimental PL data when VBO = 1 eV is used. This latter value yields the maximum compromised confinement between ground hole and electron states. The confinement is shown to be power law revealing strong QC character.
- (iii) The model we used in the calculation contains no defects. The excellent fitting to the available PL data suggest that ZnO QDs exhibit strong QC characters. This latter should be responsible for the behavior of oscillator strength reported by Fonoberov and Balandin [8] and Gil and coworkers [9].
- (iv) Our theoretical results are very encouraging and the strong radiative characters found in ZnO QDs should make them potential candidates for utilization in biomedical field. Hence, the ZnO NPs should consist a promising investment.

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