Supplementary Material: Conventional optics from unconventional electronics in ZnO Quantum Dots

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Notes on the wurtzite structure

For the "ideal" case where $c/a = 1.6333$ and the internal parameter $u = 0.375$, the wurtzite structure differs from the zinc-blende structure only in the stacking sequence of the A-B atoms in the [111] direction of the compound AB (staggered vs. eclipsed arrangement, see e.g.1). But for most wurtzite crystals, as happens also for ZnO, the $c/a$ ratio and $u$ deviate from the ideal values, which result in two different nearest-neighbor distances: one with a length $R^{(1)} = uc$ and the other three of length $R^{(2)} = \left[ \frac{c^2}{3} + \left( \frac{1}{2} - u \right)^2 c^2 \right]^{\frac{1}{2}}$. For the ideal wurtzite structure $R^{(1)} = R^{(2)}$. Furthermore the crystal field splitting $\Delta_c$ which appears in wurtzite structures is proportional to the deviation of the structural parameters $c/a$ and $u$ from their ideal values.

Computational Details

The present work reports a new band structure calculation of wurtzite ZnO based on local (EPM).

With the polar $c$-axis chosen along the z-direction, the lattice vectors are given in Table 1 and the
atomic positions of the four atoms in the primitive cell are given in Table 2, where \(a\), \(c\) and \(u\) are given in Table 2 of the paper.

Fitting the pseudopotential (Eq. 2 of the paper) in reciprocal space to obtain the energy gaps at high-symmetry points as well as the electron and hole effective masses at \(\Gamma\) point with experimental target values, we obtain the empirical pseudopotential parameters which are shown in Table 3 of the paper. In Figure 1 we are depict the volume normalized local parts of the Zn and O pseudopotentials as computed in the present work. Using the above pseudopotentials the full band structure of bulk wurtzite ZnO with SO interaction is depicted in Figure 2.

**Table 1: Primitive lattice vectors in the Wurtzite structure**

<table>
<thead>
<tr>
<th></th>
<th>(\hat{x})</th>
<th>(\hat{y})</th>
<th>(\hat{z})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a_1)</td>
<td>(\frac{1}{2}a)</td>
<td>(-\frac{\sqrt{3}}{2}a)</td>
<td>0</td>
</tr>
<tr>
<td>(a_2)</td>
<td>(\frac{1}{2}a)</td>
<td>(\frac{\sqrt{3}}{2}a)</td>
<td>0</td>
</tr>
<tr>
<td>(a_3)</td>
<td>0</td>
<td>0</td>
<td>(c)</td>
</tr>
</tbody>
</table>

The energy cutoff we used was higher than in most previous studies with 8.5 Ryd. We did not “rescale” the kinetic energy.

**Table 2: Atomic Positions in the Wurtzite structure**

<table>
<thead>
<tr>
<th>Atom</th>
<th>(a_1)</th>
<th>(a_2)</th>
<th>(a_3)</th>
<th>(\hat{x})</th>
<th>(\hat{y})</th>
<th>(\hat{z})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(_1)</td>
<td>1/3</td>
<td>2/3</td>
<td>0</td>
<td>(\frac{1}{2}a)</td>
<td>(-\frac{1}{2\sqrt{3}}a)</td>
<td>0</td>
</tr>
<tr>
<td>Zn(_2)</td>
<td>2/3</td>
<td>1/3</td>
<td>1/2</td>
<td>(\frac{1}{2}a)</td>
<td>(-\frac{1}{2\sqrt{3}}a)</td>
<td>(\frac{1}{2}c)</td>
</tr>
<tr>
<td>O(_1)</td>
<td>1/3</td>
<td>2/3</td>
<td>(u)</td>
<td>(\frac{1}{2}a)</td>
<td>(-\frac{1}{2\sqrt{3}}a)</td>
<td>(uc)</td>
</tr>
<tr>
<td>O(_2)</td>
<td>2/3</td>
<td>1/3</td>
<td>(1/2+u)</td>
<td>(\frac{1}{2}a)</td>
<td>(-\frac{1}{2\sqrt{3}}a)</td>
<td>((\frac{1}{2}+u)c)</td>
</tr>
</tbody>
</table>

**ZnO quantum wells**

In order to test the suitability of the artificial high-band gap material used in the quantum dot calculations, we construct ZnO quantum wells of varying width, surrounded by the high band gap material. The passivation of dangling bonds we are intending with the high band gap artificial material can lead to surface/interface states which may pollute the gap. Our intent is to demonstrate that the surface/interface states are remote from the gap region. In Fig. Figure 3 we plot
Figure 1: (Color online) Normalized atom pseudopotentials for Zn and O.
Figure 2: (Color online) Band structure of wurtzite ZnO including SO interaction.
the conduction and valence band states for QWs of varying width. We can see the appearance of states independent on the QW width, akin surface of interface states. These states are remote from the gap (2 eV above the CBM and 0.4 eV below the VBM) and will not affect our quantum dot calculations.

The confinement effects are expectedly larger on the conduction band than on the valence band for any given width of the QW. The band gap is consequently mainly dominated by the shift in the conduction band edge. This is a consequence of the lighter electron effective mass compared to the hole effective mass. Subtracting the lowest conduction band energy curve from the highest valence band energy curve, we obtain the single particle band gap energy (Figure 4) as a function of the QW width. As is clearly seen, the band gap energy increases as the QW width decreases and takes almost its bulk value for widths greater than 5 nm.

**ZnO quantum dots**

Working in the same way as in quantum wells but now with the geometry of quantum dots we obtain the conduction and valence band energies for different QD diameters. Then subtracting the lower conduction band energy curve from the highest valence band energy curve, we obtain the single particle band gap energy at Σ symmetry point (Figure 3c of the paper: gray line) as a function of the QD diameter.

Finally for the screened Coulomb interaction \( v(r_{e}, r_{h}) \) we used the phenomenological isotropic and uniform model proposed by Resta. The values of the corresponding parameters in atomic units are:

\[
\varepsilon_{\infty} = 3.70 , \quad \varepsilon_{0} = 8.55 , \quad k_{F} = 1.434 , \quad q_{TF} = \sqrt{\frac{4k_{F}}{\pi}} = 1.351 , \quad \rho_{\infty} = 2.332 .
\]

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**References**

Figure 3: (Top) Conduction band energies versus quantum well width (in nm). (Bottom) Valence band energies versus quantum well width (in nm). The inset shows the crossing of bands in more detail.
Figure 4: Band gap energy at Γ point versus quantum well width (in nm). The dashed line defines the bulk limit.