

Study of Ground State Properties of Wurtzite Zinc Oxide

Ashok Kumar Singh¹ & K. B. Singh²

¹*Department of Physics, HNK Inter College, Ara (Bhojpur), Bihar, India.
E-mail-ashokkumarsingh781@gmail.com*

²*Department of Physics, Samastipur College Samastipur, Bihar, India.
Email: kbsaku@gmail.com*

Abstract: *In this present paper the frequency dependence of the dielectric function is computed within the random phase approximation. We have applied the all electron Gw calculation for wurtzite zinc oxide. The Gw calculation overestimates the screening effect for localized states such as the Zn 3d states, because for the random phase approximation and local density approximation band structure.*

Keywords: Eigen Functions, Brillouin Zone, Gw Calculation, Green Function.

1. Introduction

The main objectives of this model is to have a comprehensive set of results obtained by a state of the art method that could be the basis for their studies in these materials. The semi-ab-initio approach with a minimal basis set gave results far more superior than the semi empirical tight binding method with only a modest increase in computational effort. The transferability of the basis set and the potential makes it ideal for studying more complex configuration of the semi conductor systems and compounds or for more demanding calculations such as non linear optical properties. Almost all of the tin wurtzite crystals are materials of increasing importance in modern technology. BeO is a pyroelectric material composed of very high elements BN and SiC are known for their superior mechanical properties that are especially valuable in high temperature applications. Although the stable phase of BN is the hexagonal phase and SiC has a number of polytypes with ZB being the most common one, the wurtzite phase is important in connection with stability in the epitaxial growth of thin films and in the structural phase transitions under pressure.

The Kohn-Sham form of the exchange correlation potential with Wigner interpolation formula for additional exchange effects were used. We have applied a full basis set consisting of linear combinations of atomic orbitals expressed as sum of Gaussian type orbitals. In the calculation the 3d orbitals of Al, Ga and Se and the 4d orbitals of Cd and In were treated as valence orbitals. Extra orbitals corresponding to excited states for each atom were included to ensure sufficient convergence in the basis set expansion. For the optical calculation, the real part of the frequency dependent inter band optical conductivity was evaluated first with all the optical transition matrix elements between the unoccupied valence bands and the occupied conduction bands. The local density approximation Eigen values should not necessarily identified with the quasiparticle energies, although eigen value differences are often used to describe the excited state. Time dependent density functions theory can in practice describe the excited state, but a good approximation for the time dependent exchange-correlation kernel is not known. The Gw approximation of Hedin¹ provides a practical method to calculate the quasiparticle energy Hybertsen and Louie² presented the first Gw calculation for real material. They employed eigen-functions given by the Local density approximation as input, using additionally a pseudopotential approximation. Several methods have been developed within various band structure-calculation schemes³.

The mixed basis is by construction essentially a complete basis for the expansion G_w , therefore, for given-eigen⁴ functions as input our method can produce reasonably well converged quasiparticle energies rather more efficiently than a method that expands w in-plane waves alone.

We have applied this approach to Wurtzite- type Zincoxide, whose valence bands consists extended 0 2p and Zn 4s orbitals and rather lcoalizedZn 3d and 0 2s orbitais. Zno is important for optical device technology since the material is optically transparent and can be doped with electrons and holes. Compared with most the II-IV and III-V Compounds such as ZnS, GaN, the position of the cation d levels is rather high and relatively close to the anion p-derived valence band maximum.

2. Mathematical Analysis

In the Green's function approach, the quasiparticle energy and wave function of many-electron system are given as solution of the equation,

$$[E_{kn} - T - V_H(r)] F_{km}(r) - \int \sum(r, r', E_{kn}) f_{kn}(r') d^3 r' = 0 \quad (1)$$

Where T is the kinetic energy operator, V_H is the Hartree potential plus the electrostatic potential from nuclei and Σ is the self energy. In the G_w approximation, the self energy written as

$$\Sigma(r, r', \omega) = i \int_{-\infty}^{\infty} d\omega' / 2\pi e^{i\omega' \delta} G(r, r', \omega + \omega'). W(r, r', \omega') \quad (2)$$

A perturbative approach to find E_{kn} is

$$[E_{kn} - T - V_H(r) - V_{xc}^{LDA}(r)] \Psi_{kn}(r) = 0 \quad (3)$$

The first order energy in the Hartree-Fock approximation

$$E_{kn}^{HFA} = E_{kn} + \langle \Psi_{kn} | \Sigma_x | \Psi_{kn} \rangle - \langle \Psi_{kn} | V_{xc}^{LDA} | \Psi_{kn} \rangle \quad (4)$$

The interstitial plane wave is given by

$$\rho_g^k(r) = \begin{cases} 0 & \text{in the muffin-tin sphere region} \\ e^{i(k+G) \cdot r} & \text{in the interstitial region} \end{cases}$$

The interactions V and W are expressed by the product of two K_s eigen functions in our perturbative treatment. The G_w Calculation is performed with 32k points in the Brillouin zone. The energy cut off of the interstitial plane wave is 10Ry for the Coulomb matrix. All the core and valence electrons are included into calculation of the exchange part of the self-energy. We have also examined the Convergence of the quasiparticle energies in k Points, plane waves, unoccupied states and product functions. The electronic band structure of α -GaN, obtained with the optimum basis set of calculation II. The zero of the energy is set at the top of the valence band. In our nonrelativistic calculations, the effect of spin-orbit interaction is not considered. Table 1 lists the energy levels at high symmetry points in the Brillouin zone for both sets of lattice constants. It also shows, for the same points, the LDA and G_w results of Rubio et al. Our results in columns two and seven (calculation A) are the ones to compare with the G_w findings of Rubio et al., as they are obtained with the same low temperature lattice constants specified in Table 1. The LDA results of Rubio et al. were obtained at slightly different lattice constants representing their theoretical LDA values ($a = 3.126\text{\AA}$, $c = 5.119\text{\AA}$, $u = 0.377$). Our results in columns three and eight were obtained for room-temperature values of the lattice parameters. The effective mass is a measure of the quality of the calculated bands. Specially, the agreement between calculated and measured effective masses indicates an accurate determination of the shape of the bands. Our calculated effective mass for the n-type carriers of α -GaN near the Γ point is $0.22 \pm 0.03 m_0$. This result is in a good agreement with the experimental data of $0.2 \pm 0.02 m_0$.

3. Ground State properties of WurtziteCrystal

We have calculated the electronic properties of wurtziteGaN (α -GaN) using the recently introduced procedure. Succinctly stated, the implementation of the calculation procedure first consisted of carrying out completely self-consistent calculations for GaN using a minimal LCAO basis set. Namely, the initial charge density for α GaN was calculated using the atomic orbitals of Ga ($1s2s3s4s$, $2p3p4p$, $3d$) and ($1s2s, 2p$).

We then repeated the self-consistent calculation using the above basis set as augmented by the orbitals describing the first excited state (i.e., the lowest in energy) of Ga. Hence, $Ga(4d^0)$

orbitals were added to the basis set. The superscript index of zero indicates that these states are unoccupied in the free atoms (ions). We then plotted the energy bands obtained from these two distinct self-consistent calculations. The solid and dashed lines represent the calculated results from the first and second calculations, respectively. The occupied bands from the two calculations differ slightly. In particular, the difference is not a rigid shift of one set of bands with respect to the other. Hence, as noted above, the larger basis set, for the second self-consistent calculation is preferred to that for the first. This preference is based on physical considerations, i.e., actual, physical inter actions are responsible for the difference between the two sets of bands. Completeness requirements, partly to describe the redistribution of the electronic cloud in the solid environment, dictate this preference. The next natural step was to repeat our procedure, for a third tie, with a new basis set that includes a $N(3s^0)$ orbital. The calculated bands for occupied states are fully converged. In particular, the changes in occupied energies, from calculation II to III, are in the range of computational errors and possible limitations of LDA. In contrast to the unchanged nature of the occupied states, the lowest unoccupied states at the Γ and A symmetry points are shifted downward by approximately 0.8 eV.

TABLE 1. The calculated electronic energy levels (in eV) for wurtzite GaN using two sets of lattice constants. Calculation A (LDA A): $a = 3.160\text{\AA}$, $c = 5.125\text{\AA}$, and $u = 0.377$. Calculation B (LDA B): $a = 3.1878\text{\AA}$, $c = 5.1850\text{\AA}$, and $u = 0.375$. The lattice constants in GW calculation of Rubio et al. are those for calculation A. The minimum band gaps are the energies at Γ_{1c} . See our theoretical DOS for the calculated, low temperature, "practical" band gap of 3.4 eV.

GaN	LDA A	LDA B	Rubio LDA	Rubio GW		LDA A	LDA B	Rubio LDA	Rubio GW
Γ_{3v}	-7.1	-7.0	-7.4	-8.0	M_{1v}	-6.5	-6.3	-6.8	-7.4
Γ_{5v}	-1.1	-1.0	-1.1	-1.2	M_{3v}	-5.3	-5.1	-5.6	-6.1
Γ_{5v}	-1.1	-1.0	-1.1	-1.2	M_{1v}	-4.3	-4.2	-4.4	-4.9
Γ_{1v}	0.0	0.0	0.0	0.0	M_{2v}	-2.8	-2.7	-2.8	-3.1
Γ_{6v}	0.0	0.0	0.0	0.0	M_{3v}	-2.3	-2.2	-2.4	-2.6
Γ_{6v}	0.0	0.0	0.0	0.0	M_{4v}	-1.1	-1.0	-1.0	-1.1
Γ_{1c}	3.2	3.0	2.3	3.5	M_{1c}	5.3	5.3	5.1	6.5
Γ_{3c}	5.1	4.9	4.6	5.9	M_{3c}	5.9	5.8	5.7	7.4
Γ_{6v}	10.2	10.1	10.1	11.9	M_{3c}	7.0	6.7	6.2	8.1
Γ_{1c}	10.3	10.1	9.5	12.1	M_{1c}	9.3	9.1	9.1	11.5
$A_{1,3v}$	-3.8	-3.8	-4.1	-4.6	$L_{1,3v}$	-6.7	-6.5	-7.0	-7.6
$A_{5,6v}$	-0.6	-0.5	-0.5	-0.6	$L_{2,4v}$	-2.0	-1.9	-2.0	-2.2
$A_{5,6v}$	-0.6	-0.5	-0.5	-0.6	$L_{1,3v}$	-1.9	-1.9	-2.0	-2.2
$A_{1,3c}$	5.4	5.2	4.6	6.1	$L_{1,3c}$	4.7	4.6	4.4	6.0
$A_{5,6c}$	9.2	9.0	8.7	10.8	$L_{1,3c}$	8.3	8.1	8.0	9.9
K_{1v}	-5.4	-5.2	-5.6	-6.1	H_{3v}	-6.2	-6.1	-6.4	-7.1
K_{3v}	-5.3	-5.2	-5.5	-6.1	$H_{1,2v}$	-4.3	-4.1	-4.6	-4.9
K_{3v}	-3.1	-3.0	-3.2	-3.5	H_{3v}	-1.5	-1.5	-1.5	-1.6
K_{2v}	-2.8	-2.6	-3.0	-3.2	H_{3c}	6.8	6.7	6.6	8.3
K_{2c}	5.3	5.3	4.9	6.6	$H_{1,2c}$	7.5	7.4	7.4	9.4
K_{3c}	8.6	8.4	8.3	10.6					

In light of the iteration procedure described above, and that only includes the wave functions of occupied states in the reconstruction of the charge density, potential, and Hamiltonian, the preferred basis set is that in calculation. The drastic changes in the unoccupied states, in going from calculation, are believed to be simple consequences of the variational theorem noted

above. Namely, this lowering may not be due to a physical interaction, but rather to a mathematical artifact stemming from the variational theorem. While no other graphs are shown here, we continued to add orbitals of higher and higher excited states to the basis set for calculation four and four. As expected, these calculations did not lead to changes in the occupied states. They led, expectedly, to drastic in higher and higher, unoccupied bands.

4. Conclusion

The band gap, until now, has been generally calculated as the difference between the energies for the minimum of the conduction band and the maximum of the valence band. We refer to this band gap, calculated in this fashion, as the theoretical, "minimum" band gap. Our calculation A, with low-temperature lattice parameters, found a minimum gap of 3.2 eV, while the LDA and GW works of Rubio et al., respectively, reported 2.3 and 3.5 eV. These minimum band gaps are the energies at Γ_{1c} in Table 1. These gaps, as per Table 1, are direct gaps found at the Γ point. Our total DOS curve particularly in inset, shows that the calculated, "practical," and measurable band gap for low-temperature GaN is 3.4eV - in excellent agreement with experiment. Indeed, the specially parabolic feature of the bands around Γ_{1c} leads to the very small tail structure that is likely to be difficult to measure. The reported experimental optical-absorption spectrum actually shows the need to define a "practical" band gap, distinct from the minimum band gap. The GW minimum gap of 3.5 eV is therefore expected to lead to a measurable band of approximately 3.7 eV or higher, assuming that the GW bands preserved the parabolic structure Γ_{1c} . Our calculation B, with room-temperature lattice constants specified in Table 1, found a minimum band gap of 0.3 eV and a practical band gap of 3.2 eV, in excellent agreement with room temperature experiment.

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