# Using Quantum Espresso to study optical properties of ZnO

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## Abstract

Zinc oxide (ZnO) powder has been a mainstay in white paint pigments and industrial processing chemicals for nearly a century and a half. However, the mid-20th century saw a resurgence of interest in ZnO, driven by the recognition of its unique and promising properties, including the production of the first brass metal, the development of purified ZnO for medical purposes, and even attempts by early alchemists to transmute base metals into gold. This renewed interest was fueled by both the scientific community and industry leaders. These properties hold significant potential for diverse applications beyond their traditional uses. ZnO has emerged as a front-runner for the next generation of electronic devices. The study of ZnO experienced significant peaks in 1990 and 2010. In 2010, over 5,000 publications contained ZnO in the title, abstract, or keywords. This occurred because ZnO possesses a wide range of properties, depending on doping, including conductivity ranging from metallic to insulating, high transparency, piezoelectricity, wide band gap semiconductor properties, room temperature ferromagnetism, and significant magneto-optical and chemical sensing effects. Due to these properties, there has been a significant increase in the number of relevant publications.

## Computational Methods

We use Quantum Espresso (QE) to calculate the 4-atom structure of ZnO with Norm-Conserving pseudopotentials, employing the Generalized Gradient Approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional. We investigate its optical properties through simulations using Density Functional Theory (DFT), specifically employing Quantum Espresso.

**Step-by-Step Procedure**

1) **Perform convergence calculations**
2) **Relax the atomic structure**
3) **Perform Self-Consistent Field (SCF) calculations**
4) **Perform Non-Self-Consistent Field (NSCF) calculations**
5) **Perform Density of States (DOS) calculations**
6) **Perform band structure calculations**
7) **Perform optical properties calculations**

## ZnO Structural Properties Details

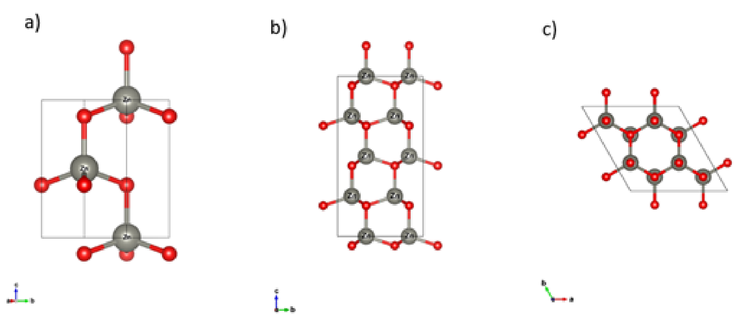


Fig. 1. Representation of the wurtzite crystalline structure of ZnO. Zinc (Zn) atoms are at the corners of the hexagonal unit cell, while oxygen (O) atoms are at the centers of the hexagonal faces and within the unit cell. (b) shows a view along the a-axis, and (c) shows a view along the c-axis. Gray and red spheres represent Zn and O atoms, respectively.

**Table 1 Material Properties of wurtzite Zinc Oxide**

| Material properties | Material parameters |
|---|---|
| Material type | II-VI compound semiconductor |
| Crystal Structure and type | Hexagonal, P 63 mc space group |
| Zn-O distance along the a-axis | 1.90 Å |
| Zn-O distance along the c-axis | 1.98 Å |
| Lattice parameter | a= 3.249 Å and c= 5.206 Å |
| Unit cell volume | 47.63 $Å^3$ |
| Density | 5.606 g $cm^{-3}$ |
| Bandgap | 3.37 eV at 300K, direct |
| Exciton binding energy/diameter | 60 meV at 300K/2nm |
| Other associated properties | Piezoelectric, pyroelectric |

## DFT

**Band Structure**

- **Definition**:
  - Describes the distribution of electronic energy levels in a solid material.
- **Importance**:
  - Provides information about the allowed energy states for electrons in a crystalline system.
  - Crucial for understanding the electronic properties and behavior of materials.
- **Obtained By**:
  - Solving the Kohn-Sham equation.

$$\left(-\frac{\hbar^2}{2m_e}\nabla^2 + V_{eff}(\boldsymbol{r})\right)\psi_i(r) = \epsilon_i\psi_i(r) \quad (1)$$

where $\nabla^2$ is the Laplacian operator, $V_{eff}(\boldsymbol{r})$ is the effective potential, $\psi_i(r)$ are the Kohn-Sham orbitals, and $\epsilon_i$ are the corresponding eigenvalues.

**Density of States (DOS)**

- **Definition**:
  - Describes the distribution of electronic states with respect to their energy levels in a material.
- **Importance**:
  - Provides insights into the electronic structure and properties of materials.
  - Crucial for understanding their behavior.
- **Calculation**:
  - Based on the electronic wave functions obtained from solving the Kohn-Sham equation.
- **Representation**:
  - Plotted as the number of electronic states per unit energy interval as a function of energy.

## Band Structure

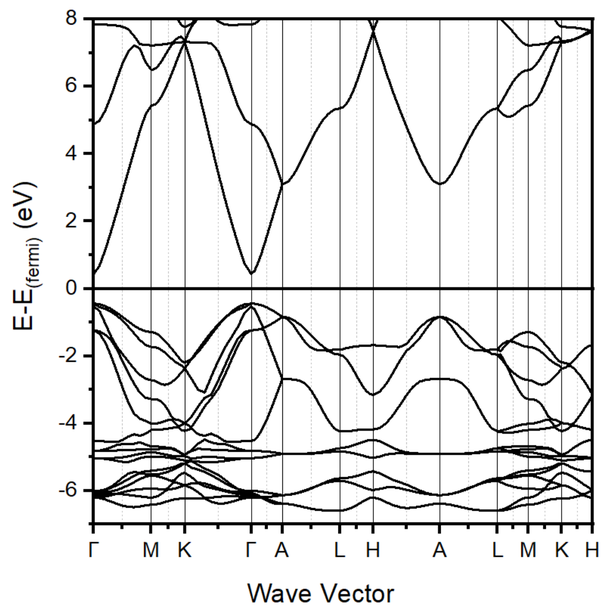


Fig. 3 Band structure calculated using DFT in Quantum espresso, the band structure around the Γ – M – K – Γ – A – L – H – A – L – M – K – H symmetry points, and the fermi energy located in the middle of the band gap, as expected for a semiconductor

- **Direct Band Gap**:
  - The valence band maximum and the conduction band minimum are located at the Γ point, resulting in a direct band gap.
- **Band Gap Energy**:
  - Using PBE-GGA, the band gap energy is 0.814 eV.
- **Band Structure of w-ZnO**:
  - **Valence Bands at Γ.**
  - **First Valence Band**: Located between 0 and -1 eV.
  - **Second Valence Band**: Located in the region -4 eV to -5 eV.

## Density of States (DOS)

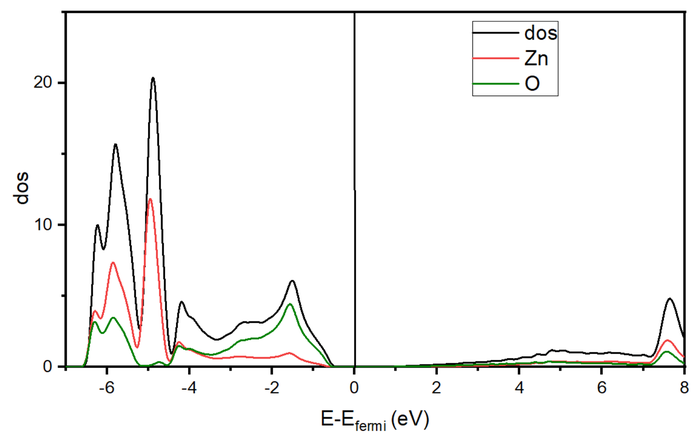


Fig. 2. The total density of states, with contributions from zinc in red and oxygen in green.

- Total and partial densities of states are shown for the energy range -7 eV to +8 eV

## Optical properties

The optical properties plays an active role in comprehending how light interacts with materials and provides insight into the material's potential use in optoelectronic devices.

**Interaction with Photons**:

- Described as time-dependent perturbations of the ground-state electronic states.

**Photon-Electron Interaction**

**Mechanism**:

- Interaction occurs between photons and electrons in the material.
- Transitions between occupied and unoccupied states are driven by the electric field of the photon.

**Spectra Description**:

- Resulting spectra from these transitions can be described as a joint density of states between the valence and conduction bands.

**Optical Response**

The material's response to the electromagnetic field across all energy levels is described by the complex dielectric function ϵ(ω)

$$\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega) \quad (2)$$

where $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ are the real and imaginary parts of the dielectric function, respectively. The real part of the dielectric function, $\epsilon_1(\omega)$, represents the dispersion of the incident photons by the material, while the imaginary part of the dielectric function, $i\epsilon_2(\omega)$, corresponds to the energy absorbed by the material.

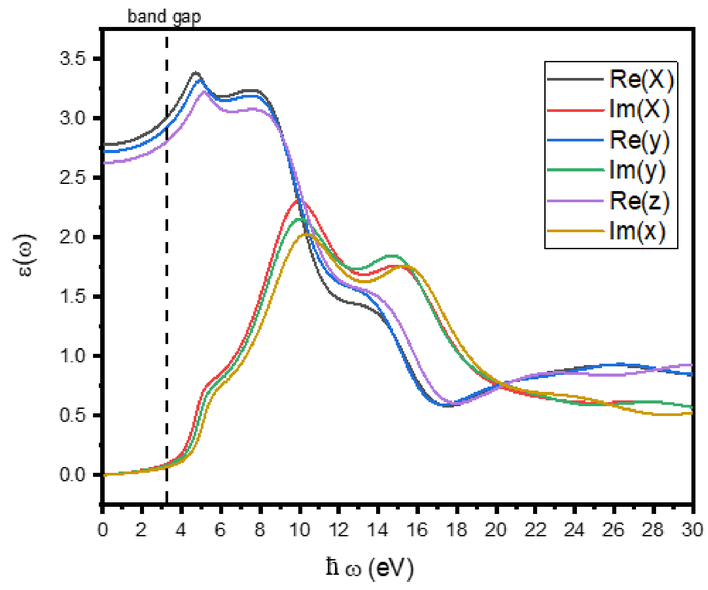


Fig. 4. Real and imaginary parts of the dielectric function calculated in the x, y, and z directions.

## Conclusions and Future work

- ✓ DFT Analysis: Calculated and analyzed ZnO using Density Functional Theory (DFT).
- ✓ Property Study: Focused on WZ ZnO phases with GGA-PBE for optical properties.
- ✓ Structural Relaxation: Relaxed the structure to find the ground state and examined atomic positions and lattice parameters.
- ✓ Further Calculations: Calculated band structure, density of states (DOS), and optical properties.
- ✓ Results: Provided a detailed understanding of ZnO's electronic and optical characteristics.
- ✓ Future Directions: Expand the cell and perform calculations for 72 atoms generated by the Special Quasirandom Structure (SQS) method doped with Ag at different concentrations. Perform all calculations also for hybrid functionals.

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