ZnO Monolayer, a theoretical study using density functional theory

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Abstract

ZnO 2D monolayer had been simulated using density functional theory (DFT). Several properties had been evaluated for the monolayer such as the monolayer geometry, the band structure and band gap and the density of states. The results are important for understanding the physical properties of the monolayer and for the development of new materials. For instance, the ZnO is widely used as a gas sensor. It can be used as a thin film, nanotube, or a one layer that will be added on another material thin film. The ZnO monolayer that had been studied in this article will give a good results for both of the nanotube and the layer on another material. Where the monolayer is good approximation for a large nanotube. Moreover, understanding the monolayer geometry and electronic structure will indicate its ability to be added on another material based on the material stable geometry and electronic structure.

1 Introduction

ZnO is a semiconductor with a wide band gap (about 3.37 eV) at room temperature, and with an exciton-binding energy about $60meV$ [1]. These properties make ZnO a promising material for gas sensors. ZnO hexagonal monolayer is a good stable structure to be studied to use its results for enhancing the gas sensing. For instance, it can be used on another materials, or to use the nanotube ZnO as a gas sensor such as building a field effect transistor [2].

Several studies had been done on the ZnO monolayer to obtain its properties. The studies used density functional theory method for simulate the structures sued in that studies. The work on [3] studied the chemical functionalization of ZnO monolayer. It had been done by studying the effects on the monolayer geometry, band gap, and phonon dispersion by adsorbing different gases on the surface of the monolayer such as Hydrogen, Fluorine, and mix of Hydrogen with Fluorine. The result showed that the chemical adsorption will functionalize the ZnO monolayer except for the fully hydrogenated ZnO monolayer which is not stable energetically and mechanically. Another work was in [4] which studied the effect of adsorbing NO_2 molecule on the ZnO and V_o-ZnO monolayer. The results showed that NO_2 makes the system change from nonmagnetic to magnet. Moreover, it has a strong effect on the band gap and density of state.

Density functional theory model (DFT) had been established by Walter Kohn who won a Nobel Prize in Chemistry in 1998. Then the theorems extended by Hohenberg, Kohn and Sham in the 20th century [5, 6]. This model is a powerful tool to approximate the charge density of the system which can be used to find its electronic structure.

In this work, DFT model had been implemented using Quantum Espresso software [7] for simulating the ZnO monolayer. The monolayer geometry, the band structure and the density of states had been evaluated.

2 Theory

DFT model is based on minimizing a convex energy functional to find the optimal charge density of the system and then the wavefunction. The energy functional defined as Kohn-Sham equation as [eq: 1].

$$E[\rho] = T[\rho] + V_{\text{ext}}[\rho] + V_H[\rho] + V_{xc}[\rho] \tag{1}$$

Where ρ is the electron density, T is the kinetic energy, V_{ext} is the electron ions interaction potential, V_H is the

Hartree potential which is the electron-electron interaction potential and V_{xc} is the exchange-correlation potential [8]. One of the approximations for the exchange-correlation potential is the Generalized Gradient approximation (GGA) which based on a the free electron gas with an approximation term depends on the gradient of the electrons density [9].

The algorithm for solving the problem is based on using the self-consistent field (SCF) method on the Kohn-Sham hamelonian. Kohn-Sham hamelonian came form the functional derivative of the energy functional in [eq: 1]. Then the (SCF) algorithm is an iterative method that start with an initial guess for the wavefunction such as the plane wave which is used in quantum espresso software, then by solving the Kohn-Sham Hamiltonian once can find the charge density and use it again to find a new wavefunction from the Kohn-Sham equation. The iterative process will be continue until a convergence in the energy from the eigenvalues reached [8].

3 Computational Method parameters

Quantum espresso software had been used in several steps. Firstly, for finding the stable structure for the ZnO monolayer. The structure conventional cell included 18 atoms. The exchange correlation functional was Generalized Gradient Approximation Becke-Lee-Yang-Pa (GGA-BLYP). The kinetic energy cutoff for charge density and potential was 800 Ry. The kinetic energy cutoff for the wavefunction was 80 Ry. The k-points mesh grid was $1 \times 1 \times 1$.

After that, the (SCF) simulation for the ZnO monolayer using the same system's atoms and exchange correlation functional. The kinetic energy cutoff for charge density and potential was 700 Ry. The kinetic energy cutoff for the wavefunction was 80 Ry. The k-points mesh grid was $5 \times 5 \times 1$.

4 Results

In this section, the results for the ZnO monolayer geometry, band structure and density of state had been evaluated.

4.1 Geometry

The relax calculation shows the structure of the monolayer as figure 1

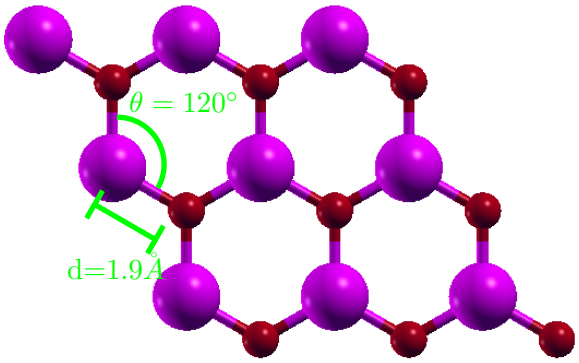

Figure 1: The stable structure of the ZnO monolayer (Zn in purple, O in red)

This result is very close to the calculation in [3] and the experimental result in [10].

4.2 Band Structure

The calculation of the band structure is very crucial for understanding the electronic properties for the monolayer basically the band gap that related directly to the conductivity. The band structure had been calculated for selected 2D path in the reciprocal lattice as [fig: 3].

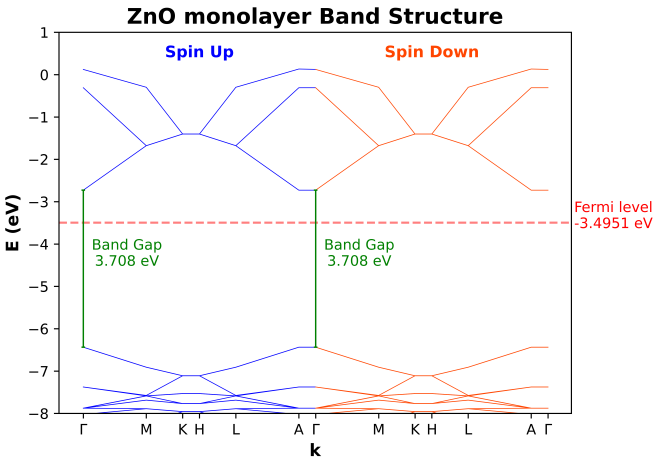

Figure 3: The band structure of the ZnO monolayer

This result shows a small variation from the band gap

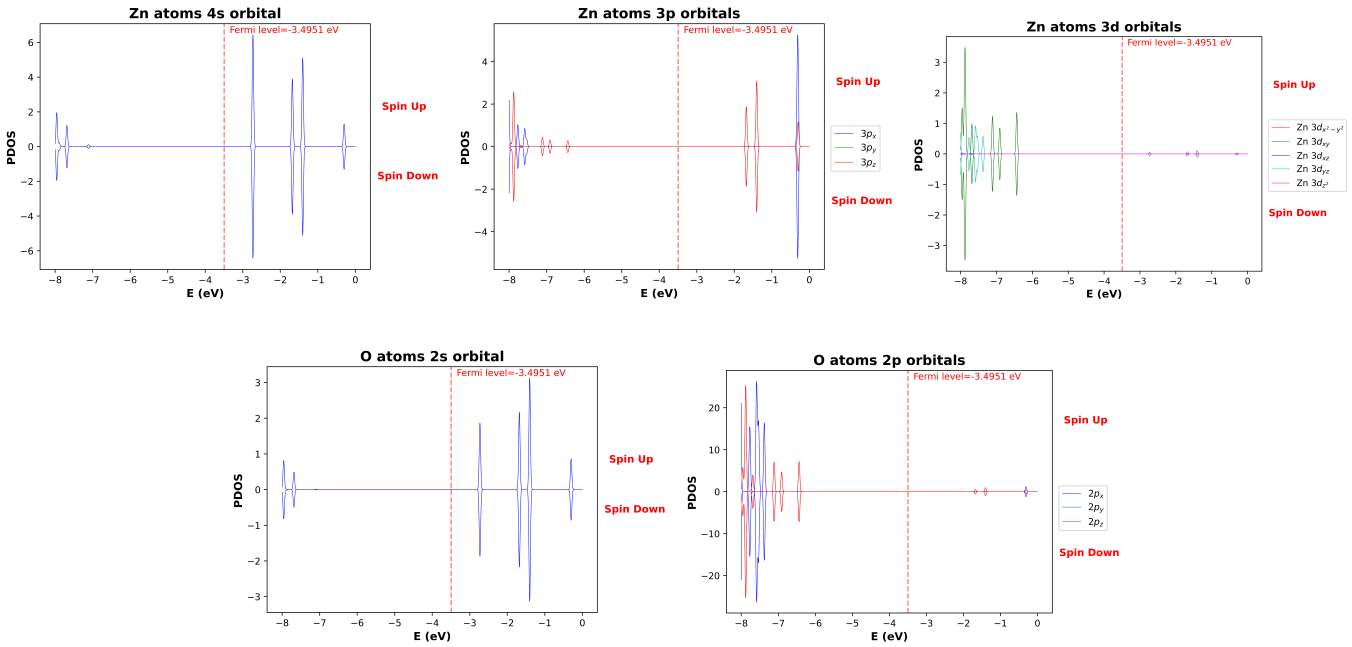

Figure 2: ZnO monolayer projected and total density of states

for the ZnO bulk structure which is about 3.44 eV. Moreover, there is no difference between the spin up and spin down band structure. So, the pure ZnO monolayer does not involve magnetic property

Moreover, the density of states had been evaluated for the ZnO monolayer as figure 4

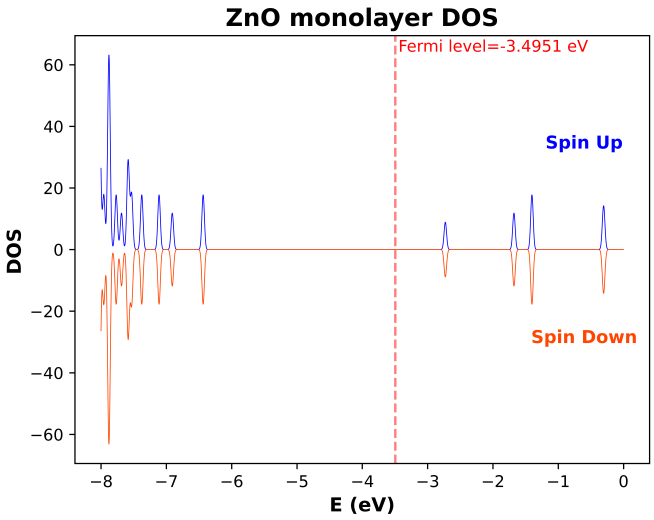

Figure 4: The density of states of the ZnO monolayer

4.3 Projected Density of State

The projected density of state is a useful tool to understand the electronic properties of the material. The result shows the orbitals where the bonds are formed between the atoms in the structure. This result shows the projected density of state for the ZnO monolayer as figure 2

The result shows that the Zn−O bonds created between Zn−4 s and Zn−3 p with O−2 s.

5 Conclusion

In conclusion, the ZnO graphene like monolayer is an important structure to be studied. The results can be helpful to be used in metal oxide surface with ZnO layer at the top. Moreover, it is good approximation for the ZnO nanotube structure. The structure appear to be stable in the geometry of graphene like monolayer. The monolayer shows that the band gap is slightly smaller than the ZnO bulk structure. Which indicates that the conductivity can be better when dealing with one ZnO layer.

References

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