First-Principle Study of the Structural, Electronic and Magnetic Properties of Bulks Cu_2O and CuO

Dipak Kumar Acharya*[1], Anil Kumar Gurung[2], Tarani Prasad Yadav [2], Gyan Prasad Paudel[3]

[1, 2, 3]*Central Department of Physical and Mathematical Sciences, Mid-West University, Surkhet, Nepal*

**Correspondance: dipakkumaracharya912@gmail.com; Ph. 9848037147*

Keywords
First-principle
DFT
Cu_2O
CuO
Structural

Received: 24 November 2024
Revised: 12 December 2024
Accepted: 21 December 2024

ISSN: 3059 - 9687

Abstract

First-principle calculation was applied to explore structural, electronic and magnetic properties of both the bulks Cu_2O and CuO. Density Functional Theory (DFT) based calculators of exchange-correlation functions LSDA+U, SGGA+U and SMGGA were used for the comparatively study of both oxides. These calculations showed the diamagnetic and the antiferromagnetic behaviors of both the p-type semiconductors Cu_2O and CuO respectively. The calculators measured the band gaps of Cu_2O approximately 0.70, 0.56 and 0.79 eV while the band gaps of CuO approximately 2.42, 2.22, and 2.20 eV respectively. The corresponding experimental values are 2-2.2 eV and 1.2-1.9 eV. These calculators are more accurate for the measurement of the band gap of CuO than the band gap of Cu_2O. Both oxides are used in various applications as photo catalysis, magnetic storage media, sensors, electronics etc.

Introduction

Cu_2O and CuO transition-metal oxides (Wang *et al.*, 2016) are prototypical materials (Heinemann *et al.,*2013) which show quite peculiar characteristics. Both copper oxides are nontoxic, abundant and inexpensive p-type semiconductors (Barreca, *et al*., 2007). The cubic crystal Cu_2O (space group Pm3n, No. - 225) consists of $4Cu^{+1}$ and $2O^{-2}$ ions and has lattice parameters (a) = 4.27ang., band gap (E_f) = 2.02 - 2.17eV and net magnetic moment (m_B) = 0 experimentally. The monoclinic crystal CuO (space group C2/c, No. - 15) consists of $4Cu^{+2}$ and $4O^{-2}$ ions and has lattice parameters (a) = 4.684ang., b = 3.423 ang., c = 5.12981ang., ß = 99.5481, band gap (E_f) = 1.2 - 1.9 eV and net magnetic moment (m_B) = 0.68μ_B experimentally (Ghijsen *et al.*, 2014; Ekuma *et al*., 2014). Cu_2O and CuO are promising materials for industrial, engineering and medical fields and used in various applications as photocatalysis, photovoltaic, photothermal, thermoelectric, magnetic storage media etc. Their nanosized have been widely used as fungicide, anti-fouling paints and also great impact in various research fields including with sensors, superconductors, electrochemistry, optics and electronics (Zhang *et al.*, 2014; Cao *et al*.,2018; Isseroff & Carter, 2013; Nolan and Elliott, 2006). The both oxides have been widely studied through theoretical, experimental and computational methods. Hanxing Cao et. al. studied monoclinic and cubical structures of the bulk CuO in LDA and GGA and found m-CuO, showing metallic behavior, is more stable than c-CuO structure (Cao *et al*.,2018; Isseroff & Carter, 2013, Nolan and Elliott, 2006; Tran & Nguyen, 2014). It shows LDA and GGA within DFT fail to explain the bulk

CuO as p-type semiconductor. Y. Wang *et al*, found band gap 0.99 vs 2.17 eV of Cu_2O and 2.74 vs 1.57 eV of CuO in LDA+U with Heyd-Scuseria-Ernzerhof (HSE) hybrid functional (Heinemann *et al*.,2013; Zoolfakar *et al*., 2014; Grant, 2008; Abdu & Musa, 2009). Markus Heinemann *et al*., estimated magnetic moments $0.66\mu_B$ and $0.54\mu_B$ of CuO in LDA+U and HSE06 respectively (Ghijsen *et al*., 1988; Bello *et al*., 2014; Bednorz & Muller, 1986; Chang *et al*., 2012). We have to be interested for, computationally, studying the structural, electronic and magnetic properties of the optimized Cu_2O and CuO through LSDA+U, SGGA+U and SMGGA within density functional theory (DFT).

In this article, we concentrate towards the binding energy per atom, band gap, magnetic moment for the identification of structural stability, electronic and magnetic properties of Cu_2O and CuO. The rest sections of this article are organized as follows. After this introduction in section 1, method and computational details are given in section 2 and then results and discussion in section 3 before conclusion in section 4. At last, acknowledgement and references are also included.

Methods and Computational Details

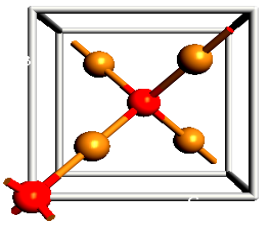
A powerful set of tools as Atomistix ToolKit (ATK) based on density functional theory (DFT) including with the non-equllibrium Green's Function (NEGF) has been used for the optimization, simulation and calculation of the structural, electronic and magnetic properties of the bulks Cu_2O and CuO. The exchange-correlation functionals Local Spin Density Approximation (LSDA) and Spin Generalized Gradient Approximation (SGGA) with additional Hubbard function (U) and Meta- Generalized Gradient Approximation (MGGA) with suitable parameterizations Perdew-Zungger (PZ), revised-Perdew-Burke-Ernzerhof (rPBE) and TB09LDA are applied to find band gap of both copper oxides (Khon & Sham, 1965; Perdew *et al*., 1996; Soler *et al*., 2002). During their optimizations and simulations, we selected linear combination of atomic orbitals (LCAO's) of the eigenfunctions, the basic set double-zeta-polarized for pseudopotentials, brillouin zone routes G, X, M, G, R, X, R, M for cubic bulk Cu_2O and G, Y, C, Z, E, A, G, B, G, Z, G for monoclinic bulk CuO, electron temperature 300K, grid mesh cut off 75 Hartree, charge 0, spin polarized, k- point sampling ($7\times7\times7$). The corresponding optimization geometry was set at force tolerance $0.05eV/A^0$, stress tolerance 0.05GPa, maximum number of steps 200 and maximum step size $0.2\ A^0$ [20]. Our computed values of different parameters of both the bulks of Cu_2O and CuO through required calculators have been reported in Table 1.

Results and Discussion

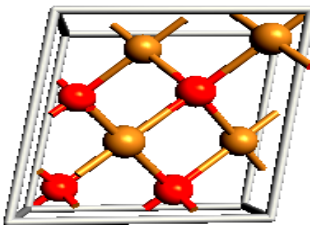
Our computational results for structural, electronic and magnetic properties of the bulks of Cu_2O and CuO are described in different steps 3.1, 3.2 and 3.3 as following:

Structural property

We investigated the optimized structures of bulks Cu_2O and CuO through ATK-DFT calculator as shown in Figures 1(a) and 1(b) respectively. The yellow and red colors spheres represent copper and oxygen atoms respectively. The computational values of lattice parameters a, b, c, α, β and γ and the minimum binding energies (Parra & Farrell, 2009; Paudel *et al.,* 2018; Morup *et al.,* 2010; Han *et al.,* 2019; Chalsani *et al.,* 2007; Yadav *et al.,* 2021; Yadav *et al.,* 2020a) with their experimental values of both copper oxides are reported in Table 1.



Cu_2O Bulk
Fig. 1(a)



CuO Bulk
Fig. 1(b)

Figure 1 The bulk configurations of Cuprous Oxide (Cu_2O) and Cupric Oxide (CuO)

$$E_b = \frac{[E_{total}-(N\times E_{Cu})-(M\times E_O)]}{N+M} \quad \text{.....(i)}$$

The binding energy has been calculated by using an equation (i), where E_b, E_{total}, E_{Cu} and E_O are binding energy, total energy, isolated energy of copper and isolated energy of oxygen, respectively. N and M are numbers of copper and oxygen atoms respectively. MGGA calculated minimum binding energy -2.9525 eV of bulk Cu_2O and LSDA+U calculated minimum binding energy -3.10581 eV of bulk CuO in comparison to other two calculators and their corresponding values of interatomic distance of Cu-O are 1.89 Å and 1.98 Å and cell volumes 83.58 $Å^3$ vs 76.49 $Å^3$ (exp.) and 74.76 $Å^3$ vs 81.17 $Å^3$ (exp.) listed in Table 1.

Table 1. Crystallographic properties of Cu_2O and CuO (ref. Wang *et al.,* 2016; Heinemann *et al.,* 2013; Barreca *et al.,* 2007; Ghijsen *et al.,* 1988; Ekuma *et al.,* 2014; Zhang *et al.,* 2014)

Parameters	Cu_2O (C2/c, 225)				CuO (Pn3m, 15)			
	Cubic				Monoclinic			
	Theoretical values			Experimental values	Theoretical values			Experimental values
Lattice	LSDA+U	SGGA+U	SMGGA	EXP.	LSDA+U	SGGA+U	SMGGA	EXP.
a (Å)	4.27	4.56	4.37	4.25	4.81	4.65	4.78	4.67
b (Å)	4.27	4.56	4.37	4.25	3.19	3.41	3.25	3.42
c (Å)	4.27	4.56	4.37	4.25	5.03	5.11	5.19	5.13
α (°)	90	90	90	90	90	90	90	90
β (°)	90	90	90	90	104.81	99.54	99.21	99.59
γ (°)	90	90	90	90	90	90	90	90
	Shortest distance (Å)							
Interatomic distance Cu-O	1.85	1.97	1.89	1.84	1.98	1.93	1.95	1.95
Interatomic distance O-O	3.70	3.95	3.79	3.68	2.89	2.89	2.89	2.62
Interatomic distance Cu-Cu	3.02	3.22	3.09	3.01	2.98	3.07	3.06	2.90
Cell volume ($Å^3$)	77.83	94.71	83.58	76.49	74.76	79.88	79.52	81.17
Number of atoms in Cell	6	6	6	6	8	8	8	8
Binding energy/atom	-2.5653	-2.9487	-2.9525	-	-3.10581	-2.6537	-2.1904	-
Band gap (eV)	0.70	0.56	0.79	2.0-2.2	2.42	2.22	2.20	1.2-1.9

Electronic Property

The band structures and DOS profiles shown in Figures 2 and 3 described the electronic properties of Cu_2O and CuO. The band gap in conduction band is narrower than in valance band of Cu_2O appeared as semiconductor of band gap underestimated 0.56-0.79 eV vs 2-2.22 eV (Exp.) shown in Figure 2. The bulk CuO also having band gap overestimated 2.2-2.42 eV vs 1.2-1.9 eV (Exp.) appeared as semiconductor shown in Fig. 3 and reported in Table 1.

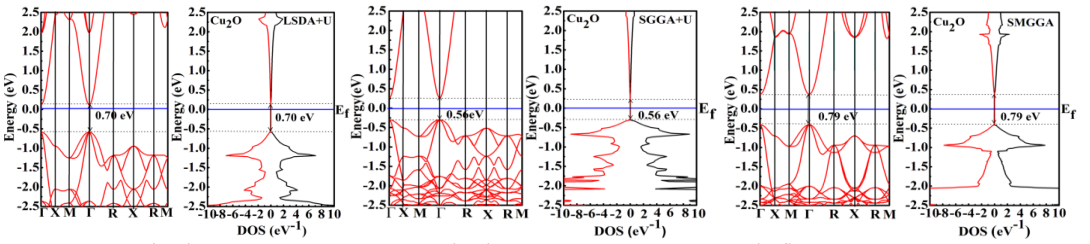


Fig. 2(a, b) Fig. 2(c, d) Fig. 2(e, f)

Fig. 2. The electronic band structure with DOS of Cuprous Oxide (Cu_2O)

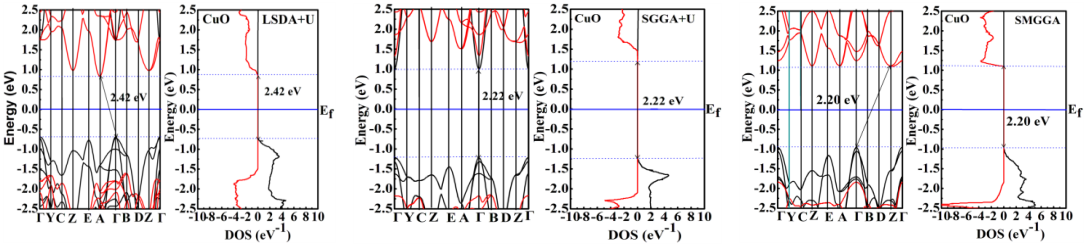


Fig. 3(a, b) Fig. 3(c, d) Fig. 3(e, f)

Fig. 3. The band structure with DOS of Cupric Oxide (CuO).

The TB09 meta-GGA (MGGA), a higher-level approximation, provided more accuracy values of band gaps 0.79 eV and 2.20 eV of Cu_2O and CuO at Fermi Level than LSDA+U and SGGA+U.

Magnetic Property

The magnetic moments of the bulks Cu_2O and CuO are produced due to the hybridization $Cu(4d^{10}3s^1)$ and $O(2P^4)$, and $Cu(4d^93s^2)$ and $O(2p^4)$, respectively. The PDOS profiles of both oxides shown in Figure 4(a) and Figure 4(b) marked their diamagnetic and antiferromagnetic behaviors. The up and down spins in Cu_2O are equal and opposite which cancel net magnetic oment of its compound while in CuO, up-spin maximum and down-spin minimum in conduction band, but reverse in valance band near the Fermi level which may cause of net magnetic moment.

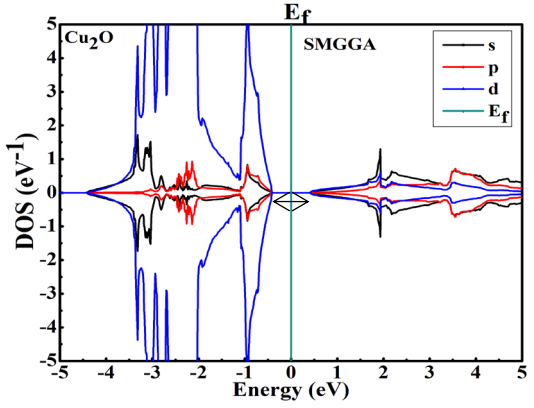


Fig. 4(a)

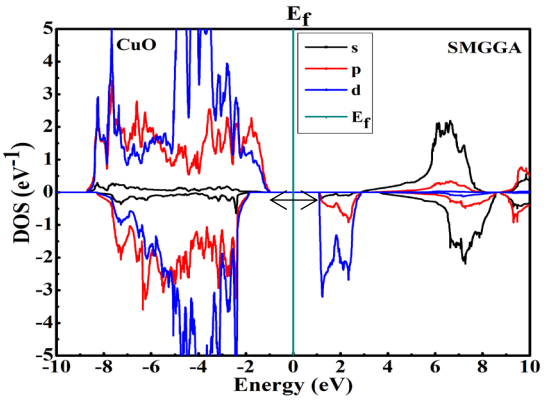


Fig. 4(b)

Fig. 4. The PDOS profiles of Cuprous Oxide (Cu_2O) and Cupric Oxide (CuO).

Heinemann et. al. (2013) found magnetic moment 0.66μ_B of CuO by applaying LDA+U which is approximately to the experimental value 0.68μ_B (Ghijsen *et al.,* 1988). This computational PDOS profile also supports theoretical and experimental values. The following equations (ii) of magnetic moment and (iii) of spin polarization may be also usefulness for distinguishing magnetic behaviors of the bulks Cu_2O and CuO (Morup et al., 2010; Han et al., 2019; Chalseni et al., 2007; Yadav et al., 2021; Yadav et al., 2020a, 2020b).

$$\mu_{total} = \frac{m_B}{atom} = [n\uparrow(E_f) - n\downarrow(E_f)]\mu_B/atom \quad \text{.....(ii)}$$

and $$P = \frac{[n\uparrow(E_f) - n\downarrow(E_f)]}{[n\uparrow(E_f) + n\downarrow(E_f)]} \quad \text{.....(iii)}$$

where, m_B, μ_{total}, μ_B, $n\uparrow(E_f)$, $n\downarrow(E_f)$ and P are magnetic moment, magnetic moment per atom, spin dipole moment, up-spin and down-spin at Fermi level, and spin polarization respectively.

Conclusion

ATK-DFT calculators LSDA+U, SGGA+U and SMGGA based First-Principle have been applied for the comparatively study of Cu_2O and CuO. Our reports identified diamagnetic and p-semiconducting behaviors of Cu_2O whereas antiferromagnetic and p-semiconducting natures of CuO. The calculators computed band gaps 0.70, 0.56 and 0.79 eV vs 2-2.2 eV (Exp.) in Cu_2O while 2.42, 2.22 and 2.20 eV vs 1.2-1.9 eV (Exp.) in CuO. The binding energies -2.9525 eV of Cu_2O and -2.1904 eV of CuO were estimated by SMGGA. The applications of both oxides may be photocell, storage media, gas sensors, electronics etc.

References

Abdu, Y., & Musa, A. O. (2009). Copper (I) oxide (Cu2O) based solar cells - A review. *Bajopas, 2*(2), 46-52.

Barreca, D., Gasparotto, A., & Tondello, E. (2007). CVD Cu2O and CuO nanosystems characterized by XPS. *Surface Science Spectra, 14*, 1-6.

Bednorz, J. G., & Müller, K. A. (1986). Possible high Tc superconductivity in the Ba-La-Cu-O system. *Z. Phys. B- Condensed Matter, 64*, 189-193. https://doi.org/10.1007/BF01303701

Bello, A., Dodoo-Arhin, D., Makgopa, K., Fabiane, M., & Manyala, N. (2014). Surfactant assisted synthesis of copper oxide (CuO) leaf-like nanostructures for electrochemical applications. *American Journal of Materials Science, 4*(2), 64-73.

Cao, H., Zhou, Z., Yu, J., & Zhou, X. (2018). DFT study on structural, electronic, and optical properties of cubic and monoclinic CuO. *Journal of Computational and Theoretical Electronics, 17*, 21-28.

Chalsani, P., Upadhyay, S. K., Ozatay, O., & Buhrman, R. A. (2007). Andreev reflection measurements of spin polarization. *Physical Review B, 75*, 094417.

Chang, Y. N., Zhang, M., Xia, L., Zhang, J., & Xing, G. (2012). The toxic effects and mechanisms of CuO and ZnO nanoparticles. *Materials, 5*, 2850-2871. https://doi.org/10.3390/ma5122850

Ekuma, C. E., Anisimov, V. I., Moreno, J., & Jarrell, M. (2014). Electronic structure and spectra of CuO. *European Physical Journal B, 87*, 23.

Ghijsen, J., Tjeng, L. H., van Elp, J., Eskes, H., Westerink, J., Sawatzky, G. A., & Czyzyk, M. T. (1988). Electronic structure of Cu2O and CuO. *Physical Review B, 38*(16), 11301-11310.

Grant, P. M. (2008). Electronic properties of rocksalt copper monoxide: A proxy

structure for high temperature superconductivity. *Journal of Physics: Conference Series, 129*, 012042.

Han, X., Mi, W., & Wang, X. (2019). Spin polarization and magnetic properties at the C60/Fe4N(001) spinterface. *Journal of Materials Chemistry C, 7*, 8325-8332.

Heinemann, M., Eifert, B., & Heiliger, C. (2013). Band structure and phase stability of the copper oxides Cu2O, CuO, and Cu4O3. *Physical Review B, 87*(11), 115111.

Isseroff, L. Y., & Carter, E. A. (2013). Electronic structure of pure and doped cuprous oxide with copper vacancies: Suppression of trap states. *Chemistry of Materials, 25*, 253-265.

Kohn, W., & Sham, L. J. (1965). Self-consistent equations including exchange and correlation effects. *Physical Review, 140*(A), A1133.

Mørup, S., Hansen, M. F., & Frandsen, C. (2010). Magnetic interactions between nanoparticles. *Beilstein Journal of Nanotechnology, 1*, 182-190.

Nolan, M., & Elliott, S. D. (2006). The p-type conduction mechanism in Cu2O: A first principles study. *Physical Chemistry Chemical Physics, 8*, 5350-5358.

Parra, R. D., & Farrell, H. H. (2009). Binding energy of metal oxide nanoparticles. *Journal of Physical Chemistry C, 113*, 4786-4791.

Paude, S., Yadav, T. P., Srivastava, A., & Kaphle, G. C. (2018). Magnetic moment of zigzag CuO nanotubes at different temperature and size: Ab-initio study. *Journal of Materials Science and Nanotechnology, 6*(1), 102.

Perdew, J. P., Burke, K., & Ernzerhof, M. (1996). Generalized gradient approximation made simple. *Physical Review Letters, 77*, 3865-3868.

Soler, J. M., Artacho, E., Gale, J. D., et al. (2002). The SIESTA method for ab initio order-N materials simulation. *Journal of Physics: Condensed Matter, 14*, 2745-2779.

Synopsys. (2019). *QuantumATK Atomic-Scale Modeling for Semiconductor & Materials*. Retrieved from https://www.synopsys.com/silicon/quantumatk.html

Tran, T. H., & Nguyen, V. T. (2014). Copper oxide nanomaterials prepared by solution methods, some properties, and potential applications: A brief review. *International Scholarly Research Notices, 2014*, 856592.

Wang, Y., Lany, S., Ghanbaja, J., Fagot-Revurat, Y., Chen, Y. P., Soldera, F., Horwat, D., Mücklich, F., & Pierson, J. F. (2016). Electronic structures of Cu2O, Cu4O3, and CuO: A joint experimental and theoretical study. *Physical Review B, 94*(24), 245418.

Yadav, T. P., Srivastawa, A., & Kaphle, G. C. (2020a). DFT analysis of ferromagnetism in zigzag and armchair CuO nanosheets. *Journal of Physics and Solid State, 62*, 1361-1369.

Yadav, T. P., Srivastawa, A., & Kaphle, G. C. (2020b). Computational study of the structural, electronic, and magnetic properties of nanoclusters of Cu2O and CuO: Ab-initio approach. *Journal of Nano and Particle Science, 6*(1), 68-72.

Yadav, T. P., Srivastawa, A., & Kaphle, G. C. (2021). Magnetism in zigzag and armchair CuO nanoribbons: Ab-initio analysis. *Journal of Physics and Solid State, 63*(2), 270-285.

Zhang, Q., Zhang, K., Xu, D., Yang, G., Huang, H., Nie, F., Liu, C., & Yang, S. (2014). CuO nanostructures: Synthesis, characterization, growth mechanisms, fundamental properties and applications. *Progress in Materials Science, 60*, 208-337.

Zoolfakar, A. S., Rani, R. A., Morfa, A. J., O'Mullane, A. P., & Zadeh, K. K. (2014). Nanostructured copper oxide semiconductors: A perspective on materials, synthesis methods and applications. *Journal of Materials Chemistry C, 2*, 5247-5262.