Many-body effects of Cu-Phthalocyanine crystal for Solar Cell application

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Abstract. Performance of organic semiconductor material is very sensitive to the reactivity of electrical and optical properties. Structural properties of Cu-Phthalocyanine molecular crystal (β-CuPc) are studied via first-principles approach within density functional theory (DFT) framework. The calculated structural parameters are close to experimental result. Many-body perturbation theory (MBPT) based on convolution of non-interacting Green’s function ($G_0$) and a screened Coulomb interaction ($W_0$), $G_0W_0$ approximation were used for quasiparticle (QP) band structure and optical properties calculations. The bandgap value of 1.71 eV calculated with $G_0W_0$+RPA is in good agreement with experimental value. Optical properties calculations show that the results obtained within $G_0W_0$ plus random phase approximation (RPA) are close to available experimental results. Interestingly, optical gap of 1.71 eV and strong absorption of β-CuPc in the visible light and ultraviolet regions shows that the investigated material is suitable for optoelectronic and solar cells applications.

Keywords: Cu-Phthalocyanine, DFT, $G_0W_0$, Electronic, Optical spectra.

1. Introduction
Industrialization, a drastic rise in the population and globalization, has increased the demand of sustainable and clean energy sources manifold ever than before [1]. Moreover, conventional energy resources are rapidly depleting and concurrently creating problems such as global warming/environment pollution etc [2, 3]. In order to cope with these issues, clean and economical energy sources are in great demand as an alternative to oil and fossil fuels [4-6]. Hence, researchers have shown considerable interests in exploring alternative energy resources [7, 8]. As a matter of fact, the sun is the source that provides an abundance of renewable solar energy which viable in the dream of cheaper and green energy [9]. Apparently, the sunlight supplies approximately $10^4$ times larger energy than our present needs [10]. However, the biggest challenge is the conversion of solar energy into electrical energy in addressing the issue of world energy demands over a longer period of time through cheaper and environment-friendly technologies. In resolving the issue, photovoltaic (PV) technology is the most practical and attractive approach to exploit the sustainable energy source at all level as well as to overcome future energy crisis. The demands on PV technology are rapidly increasing with time [11]. The key to exploiting PV technology is majorly relying on the semiconductor materials (SMs) since solar energy are converted into electricity directly [12, 13] by manipulating the potential of SM materials. Day by day, this technology is attracting more and more attention of the researchers towards exploring, tailoring and investigating new and better SMs, because of showing great potential to realize the dream of green/sustainable energy. Although some SMs are already exploited in the technology, most of the modules are based on inorganic semiconductor materials (ISM)s. Recently, researchers
have diverted their interests in the organic SMs (OSMs) as well. It is due to the PV modules that are based on the conventional ISMs production costs more if compared to the OSMs. In fact, the optoelectronic device manufacturing based on the OSMs is easier and cheaper than ISMs [14-16]. Hence, the study of OSMs generally seeks opportunities to dominate in PV technology with enhanced performance over the current market of conventional crystalline silicon and ISMs.

Among the organic materials, phthalocyanines is chosen because of its stability, solubility, good efficiency, and its peculiar conducting properties. Therefore, in order to attain its respective properties, a comprehensive investigation on structure, electronic and optical properties are necessary. In this regard, the use of ab initio quantum mechanical computational techniques in performing virtual experiment may lead to a cheaper experiment and shorter developmental cycle. Computational ab initio methodologies based on Density Functional Theory (DFT) are intensely used by the theoretical researchers to solve the complex problems. It was found to be more reliable and provides better results concerning the electronic structure calculations in designing and modeling new materials and tuning their properties without prior experimental knowledge. This feature of DFT has brought a new insight into the investigation and education field.

In this work, calculations of structural parameters of β-CuPc are performed within the framework of DFT as implemented in Quantum Espresso package [17]. Electronic and optical properties are calculated using many-body perturbation theory (MBPT) via one-shot G0W0 as implemented in YAMBO package [18].

2. Methodology

The calculations presented in this work are performed within two open source simulation packages Quantum Espresso [17] and YAMBO [18] codes. Quantum Espresso (QE) is a software code under GNU general public license (GPL) for materials modelling and electronic structure calculations based on DFT pseudopotentials. Also, QE interface with YAMBO code for excited state calculation which use DFT results as its input. Yambo simulation package is a plane wave norm-conserving pseudopotential code designed for calculating quasiparticle (QP) energies and optical properties within time-dependent density functional theory (TDDFT) and many-body perturbation theory (MBPT). QP energies are calculated within one-shot G0W0 approximation for self-energy. The optical absorption spectra are computed by solving Bethe-salpeter equation (BSE). Yambo code is chosen in this study because of showing accuracy in band structure and optical properties calculations [19]. Accuracy in band gaps with this approach with experimental measurements is due to many-body perturbation theory (MBPT) by QP concept. Optical properties calculations using Yambo code for number of systems in several studies [10, 109, 135] show high accuracy approaching experimental values. Electronic structure and optical properties of β-CuPc molecular crystal calculations are performed based on Pseudopotential plane-wave method. Pseudopotential method is chosen in our study because is fast and efficient as previous shape approximation of the orbitals is not required. Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA) [20] exchange-correlation potential is used for lattice dynamics of β-CuPc. Norm-conserving pseudopotential was used in modeling interactions between ionic core potential and electrons of Cu and N atoms. The Brillouin zone integration is performed using Monkhorst-Pack grid of 11 × 10 × 11 k-points grids for structural and band structure calculations. 80 Ry cut-offs energy of the plane-wave basis set was used to expand the wave functions and 540 Ry for
charge density. Quasiparticle band structure and optical properties of β-CuPc molecular crystal were calculated by G_0W_0 approximation for the self-energy operator Σ. Specifically, frequency dependence of the dielectric matrix were treated by single one shot G_0W_0 approximation via Godby-Needs plasmon pole model [21, 22]. All many-body perturbation theory (MBPT) calculations were performed via Yambo package [18]. In the one-shot calculations, Converged results attained by kinetic energy cut-offs of 22 Ry for screening dielectric function with 1800 bands. In the G_0W_0 approximation, G_0 is built from Kohn-Sham orbitals, and QP energies are obtained as first order perturbation correction. QP energies were obtained by solving Dyson equation perturbatively as:

\[
E_n^{QP} = E_n + Z_{nk}(\Sigma(E_{nk}) - V_{nk}^{XC})
\]  

where E_{nk} is PBE-GGA KS energies, V_{nk}^{XC} is the exchange correlation potential, Σ is the expectation values of the self-energy, and Z_{nk} is the QP renormalization factor defined as[23]:

\[
\frac{1}{Z_{nk}} = 1 - \left[ \frac{d\Sigma(\omega)}{d\omega} \right]_{\omega=E_{nk}}
\]  

and the self-energy is spit into correlation part and screened-exchange [24]:

\[
\Sigma = \Sigma_X + \Sigma_c
\]

The optical properties of the studied material were computed by the complex dielectric function ε(ω).

\[
ε(ω) = ε_1(ω) + ε_2(ω)
\]

The complex dielectric function is an important function that describes the optical properties of a material. Using Eq. 5 the real part (ε_1(ω)) was calculated by employing the Kramers-Kronig relations while the imaginary part (ε_2(ω)) of the complex dielectric function is obtained by summing transitions from valence (occupied) to conduction (unoccupied) states (with fixed k) over the BZ as shown in Eq. 6 (34).

\[
ε_1(ω) = 1 + \frac{2}{\pi} P \int_0^{\infty} \frac{ω'ε_2(ω)}{(ω'^2 - ω^2)} dω'
\]

\[
ε_2(ω) = \frac{16πε^2}{ω^2} \sum_k \left| \langle O | \vec{v} | S \rangle \right|^2 \delta(ω - E_{ck}^{QP} + E_{vk}^{QP})
\]  

where P represents the Cauchy principal value, where \vec{λ} is the polarization vector of light. \langle O | \vec{v} | S \rangle is the optical transition matrix from valence to conduction states and \vec{v} is the single-particle velocity operator, E_{vk}^{QP} and E_{ck}^{QP} are the QP energies for the valence and conduction band states. The symbols ω and k denote the frequency of incident radiation and momentum operator respectively while the total energy is given by an integral part of Eq. 2. Consequently, with the knowledge of imaginary and real part of microscopic dielectric function other important optical spectra can be calculated (refractive index n(ω), absorption
index $\alpha(\omega)$, conductivity $\sigma(\omega)$ electron loss function $L(\omega)$, reflectivity $R(\omega)$ and extinction index $k(\omega)$)

### 3.0 Results and discussion

#### 3.1 Structural properties

Figure 1 displayed the optimized $\beta$-CuPc molecular crystal structure. The crystalline phase is built in a monoclinic symmetry with the space group of P21/a. During optimization, a powerful system can be a handful since the structure consumed plenty of time and memory in order to fully converge. The obtained lattice parameters of $\beta$-CuPc are $a = 19.849\text{"Å}$, $b = 4.720\text{"Å}$, $c = 14.800\text{"Å}$ with a $\beta$-angle of 122.280° and these values are in agreement with previous results [25, 26].

![Figure 1](image)

**Figure 1** Schematic view of $\beta$-CuPc molecular crystal. The pink, blue, grey, and white colors correspond to copper, nitrogen, carbon and grey atoms respectively.

#### 3.2 Electronic properties

Regardless of the structural properties, the $\pi$-interaction that perturbs the electronic and optical properties of $\beta$-CuPc is more important to be investigated. The electronic structure calculations of $\beta$-CuPc molecular crystal are carried using optimized structure my means of Perdew–Burke–Ernzerhof generalized gradient approximation (PBE-GGA) and GW within GOWO approximation. The band structures were calculated along high-symmetry directions of the irreducible Brillouin zone (BZ) ($Z \rightarrow \Gamma \rightarrow \Psi \rightarrow A \rightarrow B \rightarrow D \rightarrow E \rightarrow X$) and fermi energy level is set at 0 eV. For band structure calculation with PBE, the energy separation between the lowest conduction band and highest valence band was found to be 1.02 eV and this value is consistent with previous DFT result [27]. However, the value is smaller than experimental result of 1.7 eV [28, 29] and this effect is the limitation of DFT approach due to approximations used in the exchange-correlation potential. It is well known that the standard DFT functional such as GGA always underestimate band gap for the semiconductor compound. As can be seen in Figure 2, the valance band maxima (VBM) lie at the B point and the conduction band minima (CBM) occurred between B and A points of the first Brillouin-Zone for both (PBE-GGA) and GOWO approaches. This indicates that $\beta$-CuPc has indirect energy bandgap. Conversely, the direct and indirect band gaps differ by just 0.07 eV. Therefore, in practical applications, particularly in optoelectronic, $\beta$-CuPc can be considered as direct gap semiconductor material. However, to correct this inconsistency of the bare DFT calculation, we further performed G0W0 calculation. Interestingly, inclusion of GW protentional bring the fundamental band gap value to 1.63 eV and this value is in good
agreement with experimental value of 1.7 eV [28, 29]. The calculated electronic bandgaps along with experimental result are listed in Table 1. To explore further, we calculated the total density of states (TDOS) and partial density of states (PDOS) of β-CuPc. The density of states plays an important role in the formation of bands and the study of the band gap. Results of TDOS will assist to clearly understand the nature of the bands while PDOS provide information about the origin of the bands. The calculated TDOS and PDOS are displayed in Figure 2 (b). The occurrence of the valence band between -10 eV to -5 eV is due to the domination of the s- and p-s orbitals. The intermediate occurrence of the valence band closer to the Fermi level between -5 eV to 0 eV is due to the domination of the d- and p-orbitals. The lowest unoccupied conduction bands are due to the domination of the d-and p-orbitals. The s-orbital also contribute to the conduction band, but the contributions is very small.

Table 1. The energy gaps of β-phase molecular crystal of Cu-phthalocyanine

| Methods          | Energy gap of β-CuPc crystal, $E_g$ (eV) |
|------------------|-----------------------------------------|
| GGA-PBE          | 1.02                                    |
| G0W0             | 1.71                                    |
| Explement [28, 29]| 1.70                                    |

Figure 2 (a) Band structure (b) Density of states of β-CuPc molecular crystal

3.3 Optical Properties
The study of the optical properties of a material is crucial to get insight view about its characteristics for the applications in the optoelectronic system and devices. Optical properties of a material explain the behavior of the material when exposed to electromagnetic radiations. From the comprehensive literature review, it is found that the exploration of the optical features relating to Cu-Phthalocyanine is scarcely done. [30]. The optical properties of β-CuPc molecular crystal is computed using random phase approximation (RPA) based on G_0W_0 (G_0W_0+RPA). Although optical properties calculation using G_0W_0+RPA is computationally expensive, but it provides accurate description of absorption spectra. The optical parameters considered in this paper are imaginary \( \varepsilon_2(\omega) \) and real \( \varepsilon_1(\omega) \) parts of dielectric functions, optical conductivity, \( \sigma(\omega) \) and absorption coefficient, \( \alpha(\omega) \). The real part \( \varepsilon_1(\omega) \) of frequency dependent of the dielectric function provides the energy stored in material whereas imaginary part \( \varepsilon_2(\omega) \) of frequency dependent of the dielectric function is concerned with the absorption behavior and the electronic band structure of the material under investigation.

Figure 3 (a) shows a result of real part of frequency dependent of the dielectric function of β-CuPc. The real part of frequency dependent of the dielectric function of β-CuPc presents significant results, where at 0 eV it possesses a dielectric coefficient value of 3.44 which is called static dielectric constant \( \varepsilon_1(0) \). Our calculated static dielectric constant of 3.44 is in good agreement with experimental value of 3.51 [31]. Static dielectric constant \( \varepsilon_1(0) \) in low energy limit strongly depends on the band gap value of the material. With the help of screened plasma frequency (plasma energy), this value can be used to find the band gap value of the compound via Penn Model [32] as shown in Eq 7.

\[
\varepsilon(0) = \left( \frac{\hbar \omega_p}{E_g} \right)^2 + 1
\]  

Figure 3 (b) shows a graph of imaginary part of frequency dependent dielectric function. The first critical point sometimes called edge of optical absorption occurred at about 1.71 eV and this value is in good agreement with experimental results results [28, 29] results [28, 29] of 1.5 eV [29, 33]. This point splits the valence band maximum and conduction band minimum and is known as the fundamental absorption edge [34-36]. The transitions from different occupied states in the valence bands to different unoccupied states in conduction bands or higher empty orbitals generate several weak peaks. The highest peak appears at 2.91 eV indicating that β-CuPc is a promising candidate for optoelectric applications. The value of optical gap, reflectivity and static dielectric function together with experimental data are presented in Table 2. Remarkably, β-CuPc has strong absorption in the visible light region that depicts the appropriateness for solar cells application.
Figure 3 (a) Real part part of the dielectric function (b) Imaginary part of the dielectric function of β-CuPc

Table 2: β-CuPc $G_0W_0$+RPA results compared with experimental measurements

|                | Optical gap (eV) | Reflectivity | $\varepsilon(\infty)$ |
|----------------|------------------|--------------|------------------------|
| Our work       | $G_0W_0$+RPA     | 1.71         | 2.91                   | 3.44                   |
| Experiments    | 1.70 [28, 29]    | 2.87 [37]    | 3.5 [31]               |

Figure 4 (a) shows the frequency dependent absorption coefficient $\alpha(\omega)$. When light rays strike the surface of a material, part of it as energy is transferred to the surface while some are reflected back. This transfer of energy to the surface is called absorption of light. From Figure 4 (a), we can say that β-CuPc has good absorption coefficient value for visible light region and highest value of absorption coefficient appears at 5.3 eV. Since β-CuPc exhibit good absorption coefficient in UV/visible range, therefore, it can be used in optoelectronics devices and as solar cell material [38]. Within the energy range between 0.0 eV to 1.62 eV, the $\propto \omega$
is zero, and this indicates an absence of interaction between the medium and the incident photon.

Our theoretical study on $\beta$-CuPc molecular crystal for the first time with accurate method shows that it has an optical gap of 1.62 eV and thus can be used for optoelectronic applications particularly solar cells. This suggests that a device fabricated from this material can be operated on a wide range of the energy scale. Figure 4 (b) shows the optical conductivity $\sigma(\omega)$ for $\beta$-CuPc. Optical conductivity is a measurement of photoconductivity that gives information about electrical conductivity in any material under investigation and it is related to absorption spectrum. The frequency variation is described by energy between 0 to 20 eV. The material’s conductivity increases as the energy increases and from 2 eV to 7.5 eV the material under investigation it has the highest values of conductivity. Figure 5(a) represents the reflectivity of $\beta$-CuPc and it can be seen that $\beta$-CuPc has high reflectivity in the visible light range. The first edge of reflectivity was found to be 2.91 and this value aged well with experimental value of 2.89 [37]. This result indicates that the $\beta$-CuPc is transparent for photon energy less than 5 eV which is appropriate for applications in visible light region. Energy loss function $L(\omega)$ is an important factor that measures the energy dissipation of a fast-moving electron within the medium. The energy loss function $L(\omega)$ gives the energy loss of fast moving electrons in solids [39-41]. The graph of energy loss function is represented in Figure 5(b). This graph gives information about loss in energy of absorbed spectrum. Energy loss is indicated for UV region and maximum energy is lost at 9.3 eV. Energy loss could be
due to inelastic interactions, intra and inter intra band transitions, inner shell ionization, and phonon excitations. The effect of loss function on absorption represents in Figure 4 (a). In this graph, we can see that absorption coefficient show minimum value where energy loss function shows highest value. Now we can conclude that β-CuPc molecular crystal has good absorbance for UV range in addition to visible light.

4.0 Conclusion
In summary, we have presented optoelectronic properties of β-CuPc molecular crystal. First-principles calculations of the DFT as implemented in quantum Espresso was adopted. The calculated structural parameters are close to experimental results. The investigated electronic band structure reveals that β-CuPc molecular crystal is an indirect bandgap material. We found the band gap value in this work to be 1.02 eV and 1.71 eV using GGA+PBE and G$_0$W$_0$. The electronic bandgap value calculated with G$_0$W$_0$+RPA is in good agreement with experimental data. In addition to electronic properties, optical parameters is performed by evaluating dielectric function $\varepsilon(\omega)$ via RPA based on G$_0$W$_0$. Optical properties calculations show that the results obtained within G$_0$W$_0$+RPA are in good agreement with available experiments. Interestingly, optical gap of 1.71 eV and strong absorption of β-CuPc in the visible light and ultraviolet regions shows that the investigated material is suitable for optoelectronic and solar cells applications.
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