Ab-initio study of the optical spectra of the transparent conducting oxide CuInO$_2$

Internship Report
Université Claude Bernard – Lyon 1

Woyten Tielesch

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1 Introduction

Transparent Conducting Oxides such as Indium Tin Oxide (ITO) and Zinc Nickel Oxide (ZNO) are wide band gap semiconductors. They combine specific optical and electrical properties that rarely appear at the same time: transparency and conductivity. This make many applications, e.g. flat displays [1] and thin-film photovoltaic cells (Fig. 1) [2], possible.

While most TCOs (ZnO) can be n-doped to obtain electron conductivity, p-dopability has been for long harder to achieve. Finally p-type conductivity could be achieved in thin films of CuAlO$_2$ [3]. In CuInO$_2$ [4, 5] even bipolar conductivity (n- and p-type) could be observed in experiments.

Having a p-dopable transparent conductor may open the way to transparent p-n junctions [6] that would be the basis for future applications such as invisible electronics and stacked solar cells with improved efficiency [8–10].

1.1 CuInO$_2$

CuInO$_2$ belongs to the so-called delafossite family. Delafossites are solids of the form ABO$_2$ where A is a monovalent metal, B is a trivalent metal and O is oxygen. The spatial structure is depicted in Fig. 2. The different atom types are aligned in parallel planes that confine the electrons, yielding a strong anisotropy. The resulting effects are strongly bound excitons [11, 12], strong polaronic effects [13–16] and a low energy 2D plasmon [17]. Also a negative thermal expansion behavior could be observed [18].

Delafossites copper oxides have been studied extensively, in theory and experiment. CuAlO$_2$ was the first delafossite to be studied. Experiments showed a large difference between the direct and the indirect band gap [4]. Similar results were found for CuInO$_2$ and CuGaO$_2$ [3].

It was shown [11, 12] that the excitonic binding energy is as large as 0.5 eV and dominates the absorption at the direct edge of Cu-delafossites. This has always to be taken into account in quasiparticle calculations, as the optical gaps and quasiparticle gaps differ by the exciton binding energy.

From the theoretical point of view, early first-principle calculations for CuInO$_2$ had difficulties to reproduce the experimental measurements. This is due to a subtle hybridization of the copper $d$ states with the $p$ states of oxygen that lead to strong, hard to handle, exchange-correlation effects.

At the beginning, the only ab-initio method used to treat CuInO$_2$ was standard Density Functional Theory (DFT) [19], using the Local Density Approximation (LDA) [20] and General Gradient Approximations (GGAs) [7]. However, DFT has the well known problem of underestimating systematically the Kohn-Sham band gap by 50% to 100%.

Other methods beyond DFT as LDA+U or hybrid functionals were tested [11, 21, 22]. Although they are capable of improving the results for some materials, they have problems for other materials. [23, 24].
Furthermore they are not fully self-interaction free and often make use of empirical values.

Another approach, GW approximation, based on many-body perturbation theory, gives very accurate band gaps for a wide range of materials [25–27]. However, for many metal oxides band gaps are often underestimated, too. In this case, a recently proposed technique called self-consistent GW allows an enormous improvement [22, 26–30].

This work will not treat self-consistent GW corrections, but it will explain how these corrections can be applied together with DFT ground state calculations as a starting point to calculate optical absorption. Optical absorption spectra of CuInO$_2$ will be obtained and compared with the experiment.

2 Theoretical Framework

The solid CuInO$_2$ will be treated starting from first-principles, that means, the goal is to obtain all its properties by nothing but a theoretical framework. No outer (experimental) parameters are used except for the crystal structure.

The underlying theories will be Density Functional Theory (DFT) to investigate the ground state. This ground state will be post-processed by Linear Response Theory [31] in the Random Phase Approximation (RPA) [32] or according to the Bethe-Salpeter-Equation (BSE) [33]. The two of them are to a greater or lesser extent capable of calculating the optical properties in good agreement with the experiment.
2.1 Calculation Scheme

The following scheme is the basis for the following calculations

Starting from the crystal geometry, **ABINIT** will always be used to do a ground state calculation at the beginning. Subsequent **YAMBO** can obtain a spectrum using RPA (section 4.2) or BSE (section 5.1). To do a computation according to BSE, some data \( W \) have to be preprocessed. In addition, it is necessary to correct the Kohn-Sham eigenvalues with the GW approximation when one applies the BSE. All these steps will be explained in detail in the next sections.

3 **ABINIT**: Ground State using DFT and LDA

**ABINIT** [34] is a software that computes ground state properties and band structures using different methods. In our present case, **ABINIT** will be run using DFT within the Kohn-Sham Scheme (section 3.2) to obtain the ingredients to perform calculations of optical spectra.

3.1 General Problem of the many-body Schrödinger Equation

To do a ground state calculation, the first idea in mind is to solve the many-body Schrödinger equation

\[
\left[ \sum_{i=1}^{N} -\frac{\nabla_i^2}{2} + v_{\text{ext}}(\mathbf{r}_i) + \sum_{i \neq j}^{N} \frac{1}{2|\mathbf{r}_i - \mathbf{r}_j|} \right] \Psi_0(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \varepsilon_0 \Psi_0(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)
\]  

(1)

where \( \Psi_0(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \) is the many-electron wave function. Usually, the nuclei wave functions are not considered. This is called the Born-Oppenheimer approximation [35]: The nuclei of the ions are very heavy compared to the electrons, so their movements can be neglected. Consequently, their positions can be fixed to their experimentally or theoretically obtained values\(^1\).

The Schrödinger equation has, however, a fundamental problem, if one talks about first-principle calculations: For spin-unpolarized calculations the entire wave function is a function in \( 3N \) coordinates\(^2\) which exceeds today’s computational capacities. To have a result in one’s lifetime, one has to resort to other strategies.

3.2 Density Functional Theory and Kohn-Sham Scheme

**Density Functional Theory** (DFT) is a theory that allows to dramatically reduce the number of degrees of freedom and hence computational costs. The key quantity in DFT is the electronic density.

An invaluable tool is the Hohenberg-Kohn theorem which states that every physical ground state expectation value can be written as a functional of the electron density [19]. From this follows that the above

\(^1\) **ABINIT** is also capable of finding the nuclei’s positions. For CuInO\(_2\) theoretical lattice parameters obtained using the LDA are in close agreement (within 1\%) with the experiment [22].

\(^2\) \( N \) in solids is usually around \( 10^{25} \)!
problem can be reformulated in terms of an auxiliary system of non-interacting electrons, the Kohn-Sham Scheme:
\[
\left[ -\nabla^2 \over 2 + v_{\text{ext}}(\mathbf{r}) + v_{\text{H}}[n](\mathbf{r}) + v_{\text{xc}}[n](\mathbf{r}) \right] \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r}) \quad (2)
\]
where \( \varphi_i(\mathbf{r}) \) are the so-called Kohn-Sham wave functions (often \( \varphi_i^{\text{KS}}(\mathbf{r}) \)), \( v_{\text{ext}} \) is the external potential, generated by the ions, and \( v_{\text{H}}[n] \) the so-called Hartree potential, given by
\[
v_{\text{H}}[n](\mathbf{r}) = \int d\mathbf{r'} v(\mathbf{r}, \mathbf{r'}) n(\mathbf{r'}). \quad (3)
\]
The third potential term, \( v_{\text{xc}}[n] \), is called exchange-correlation potential and is the most important term in the Kohn-Sham equations. It is the term that contains the physics and must be chosen with care.

Two important features of the Kohn-Sham Scheme are:

**The potentials** \( v_{\text{H}}[n](\mathbf{r}) \) and \( v_{\text{xc}}[n](\mathbf{r}) \) **are functionals**: They do not only depend on \( \mathbf{r} \) but also on the electronic density \( n(\mathbf{r}) \) that is
\[
n(\mathbf{r}) = \sum_{i \in \text{occ.}} |\varphi_i(\mathbf{r})|^2. \quad (4)
\]
This points out the basic idea behind DFT: Quantities are functionals of the density. The many-body wave function that causes many problems is no longer needed.

Unlike the ordinary Schrödinger equation, (2) has the particularity of being a self-consistent equation. The eigenvalue condition has to be satisfied, as well as (4). The trick is that all the non-trivial correlation physics lie now in \( v_{\text{xc}}[n] \) and the real challenge becomes to find an expression for \( v_{\text{xc}}[n] \) that satisfies the following principle:

The ground state density \( n(\mathbf{r}) \) obtained by the Kohn-Sham-Equations (2) should be the same as the ground state density
\[
n(\mathbf{r}) = N \int dr_1 dr_2 \ldots dr_{N-1} |\Psi_0(r_1, r_2, \ldots, r_{N-1}, r)|^2 \quad (5)
\]
resulting from the Schrödinger equation (1).

The uniqueness of the \( v_{\text{xc}}[n] \) can be showed by the Hohenberg-Kohn theorems [19].

**Independence of the wave functions**: The wave functions are independent-particle wave functions. The word wave function loses herewith its usual sense. One should always keep in mind that we will always speak of non-physical Kohn-Sham wave functions and not of real quasiparticle wave functions.

### 3.3 Local Density Approximation

**Arunit** does its ground state calculation using different approximations. In the present case, the so-called **Local Density Approximation** (LDA) [32] will be used. The LDA gives an approximation for the exchange-correlation functional. It was supposed to work for homogeneous electron systems, but turned out to work quite well, also for systems whose electron density has small spatial variations. This is the reason why DFT has become a success because without a well working \( v_{\text{xc}}[n] \) DFT is worthless.

The exchange-correlation potential \( v_{\text{xc}}[n] \) has the following form in Local Density Approximation:
\[
E_{\text{xc}}^{\text{LDA}} = \int n(\mathbf{r}) \varepsilon_{\text{heg}}(n(\mathbf{r})) d\mathbf{r} \quad (6)
\]
where \( \varepsilon_{\text{xc}}(n) \) is the exchange-correlation functional for an homogeneous electron gas. This can be computed analytically in the high-density limit and, otherwise, using Quantum Monte Carlo methods [36–38].

As mentioned in section 1.1, LDA Kohn–Sham bands of CuInO\(_2\) are very different from GW bands (gap is strongly underestimated). However we can correct the LDA results using a GW correction that is explained in section 6.
3.4 Doing a Ground State Calculation

In order to find a good solution for (2), ABINIT does self-consistent iterations. That means, it starts with a particular density \( n_0(r) \) which is used to evaluate the two potential functionals in (2) and solves the eigenvalue equation. This returns the eigenenergies \( \varepsilon_i \) and the eigenvectors \( \varphi_i(r) \). With (4) a new density \( n_1(r) \) can be obtained which is used to update the potential functionals in (2). This procedure is repeated until the total energy does not change any more\(^3\).

ABINIT is executed with an input file and some pseudo potential files. These pseudo potential files are necessary due to the following simplification:

Only outer shell electrons are considered: Inner shell electrons are often localized around its ion and do not contribute to covalent bonds. So, instead of a physical potential for the nucleus and the inner electrons, a pseudo potential \( v_{\text{ext}}(r) \) is used that simulates the effects of a nucleus potential that is screened by its inner electrons. It can be read from a pre-calculated database.

In the case of CuInO\(_2\) the following outer electrons will appear in our calculations:

- **Cu:** \( 3d^9 + 3s^2 \)
- **In:** \( 5s^2 + 4d^{10} + 5p^1 \)
- **O:** \( 2s^2 + 2p^4 \)

3.4.1 The Input File

The ABINIT input file defines all the parameters ABINIT needs, for example the crystal structure and some options concerning the algorithm. Only the most important parameters will be presented in the following

**Definition of the crystal structure:** This is the most important parameter. The atoms, their positions and the size of the primitive cell have to be defined. The crystal structure was taken from [39], the experimental parameters for \( a, c \) and \( z \) from [18] and [21].

```plaintext
#Definition of the unit cell
acell 1.0 1.0 1.0 angstrom
rprim 1.6455 -0.950029868 5.796
      0.0000 1.900059736 5.796
      -1.6455 -0.950029868 5.796

#Definition of the atom types
ntypat 3
znucl 29 49 8

#Definition of the atoms
natom 4
typat 1 2 3 3
xred 0.0000 0.0000 0.0000
      0.5000 0.5000 0.5000
      0.1061 0.1061 0.1061
      -0.1061 -0.1061 -0.1061
```

\(^3\)That means the total energy change per iteration is less than a certain value, e.g. \(10^{-9}\) Ha that is smaller than the desired precision \(10^{-3}\) Ha.
**Setting an energy cutoff:** ABINIT decomposes the Kohn-Sham wave function into an infinite sum of plane waves:

\[ \varphi_{n,k}(\mathbf{r}) = \sum_G c^{(G)}_{n,k} e^{iG \cdot \mathbf{r}} \]

with the development coefficients \( c^{(G)}_{n,k} \).

In order that the sum can be evaluated numerically a parameter \( ecut \) has to be set that limits the summation to be executed only over \( \frac{(k+G)^2}{2} < ecut^4 \):

\[ ecut \quad 30.0 \]

**Sampling the Brillouin zone:** The density is obtained by a numerical integration over the first Brillouin zone:

\[ n(\mathbf{r}) = \sum_{n \in \text{occ.}} \int_{BZ} d\mathbf{k} |\varphi_{n,k}(\mathbf{r})|^2 \]

For this purpose, the Brillouin zone will be divided into equal parallelepipeds with the vectors \( ngkpt_1^{-1} \cdot b_1 \), \( ngkpt_2^{-1} \cdot b_2 \) and \( ngkpt_3^{-1} \cdot b_3 \) with \( b_1, b_2 \) and \( b_3 \) being the reciprocal lattice vectors of the crystal and \( ngkpt \) being the fineness of the division, defined by the lines:

\[ ngkpt \quad 6 \quad 6 \quad 6 \]

**3.4.2 Converging the Parameters**

The parameters \( Ecut \) and \( ngkpt \) have to be converged carefully. Too high values lead to high computing costs, too low values give imprecise results.

The variable \( ecut \) was converged first, afterwards \( ngkpt \). The convergence was considered to be achieved when the total energy did not change significantly any longer that means less than 1 mHa. Good values for \( ecut \) and \( ngkpt \) were 30 and \((6, 6, 6)\).

**3.5 Results**

Fig. 3 shows the band structure after having converged the parameters. The spectrum shows that the computed band gap is around 0.5 eV. The experimental value is, however, larger than 3 eV as it should be for a transparent material. The underestimation of the band gap is a systematical problem of Kohn-Sham LDA band structure, but can be widened manually. This will be done by applying a *scissor operator* that shifts all the unoccupied bands by 2.5 eV (section 6).

Apart from the direct band gap, the dispersion was compared with the dispersion obtained in [22] and we found a good agreement, even if two different pseudo potentials were used.

**4 YAMBO: Absorption Spectra using RPA**

YAMBO [40] is a software that calculates optical spectra using different approximations. Of special for us interest are the RPA (section 4.2) and the BSE (section 5.1). Contrary to the RPA, the BSE takes excitonic effects into account.

\[ energies \] are always given in Hartree (1 Ha = \( m_e \left( \frac{e^2}{4\pi \varepsilon_0 \hbar} \right)^2 = 27.21138386(68) eV \)) if no other unit is given.
Figure 3: Band structure obtained with ABINIT: The Fermi energy is at $E = 0$, the direct band gap is $E_{\text{gap}} = 0.46 \text{eV}$

4.1 The Macroscopic Dielectric Function

For transparent conducting oxides as CuInO$_2$, the absorption $\alpha(\omega)$, of course, is of special interest. $\alpha(\omega)$ is directly linked to the macroscopic dielectric function

$$\alpha(\omega) = \Im(\epsilon_M(\omega)).$$

(9)

The macroscopic dielectric function $\epsilon_M$ can be expressed in terms of the microscopic dielectric function: [41]

$$\epsilon_M(\omega) = \lim_{q \to 0} \frac{1}{\epsilon_0^2(q, \omega)}$$

(10)

where $\epsilon_{G,G^\prime}(q, \omega)$ is the Fourier transformation of $\epsilon^{-1}(r, r', \omega)$ considering the periodicity of the lattice. The $G$s are reciprocal lattice vectors. In real space for $\epsilon^{-1}$ holds

$$\epsilon^{-1}(r, r', \omega) = \delta(r - r') + \int \text{d}r'' v(r - r'')\chi(r'', r', \omega)$$

(11)

where $v$ is the bare Coulomb interaction. The challenge is to find the irreducible polarizability $\chi$ in an accurate and effective way.
4.2 Random Phase Approximation

A commonly used approximation is the Random Phase Approximation (RPA) that has the form of a Dyson equation. The irreducible polarizability in RPA becomes

$$\chi(r, r', \omega) = \chi_0(r, r', \omega) + \int dr_1 dr_2 \frac{1}{|r_1 - r_2|} \chi(r, r', \omega)$$

(12)

with $$\chi_0$$ being the independent-particle irreducible polarizability that is obtained by

$$\chi_0(r, r', \omega) = \sum_{i,j} 2(f_i - f_j) \frac{\phi_i^*(r) \phi_j^*(r') \phi_j(r') \phi_i^*(r')}{\omega - (\epsilon_j - \epsilon_i) + i\eta}$$

(13)

where $$f_i$$ is a Fermi occupation function that returns 1, if $$i$$ is an occupied state, 0 otherwise.

For the first calculation, the $$\frac{1}{|r_1 - r_2|}$$ (coulomb) term will be neglected ($$\epsilon_M(\omega) = \lim_{q \to 0} \epsilon_{0,0}(q, \omega)$$), that means, electron excitations are considered to be independent of each other. This is called RPA without local fields and is equivalent to applying Fermi’s golden rule. Local fields (depolarization effects) account for variations of the classical Hartree potential upon excitation. They measure the inhomogeneity of the sample.

Afterwards, local fields due to the coulomb term will be taken more and more into account by increasing the parameter NGsBlkXd (section 4.3.1). That defines the dimension of the $$\epsilon_{G,G'}$$ matrix.

4.3 Doing a RPA Calculation

In order to run Yambo the Kohn-Shame wave functions, obtained by Abinit must be loaded and initialized. Besides, another input file is needed that contains all the options that Yambo needs.

Many parameters can and have to be adjusted in Yambo. Otherwise, Yambo would probably take a very long time to finish. The parameters enable to do a computation in one’s lifetime by downsizing matrices and sums.

4.3.1 The Input File

Yambo’s input file is similar to that of Abinit. A distinctive feature is that a runlevel has to be given in the beginning that tells Yambo which method, RPA, BSE, etc. shall be used.

As in the previous section, only the most important parameters will be explained

**Setting up the number of bands:** The sum (13) runs over all the bands and is therefore infinite. A subset of bands has to be chosen, so that the sum becomes finite and numerically controllable.

| % BndsRnXd | 1 | 25 | # [Xd] Polarization function bands |
| %

**Including local field effects:** Yambo performs its calculations in reciprocal space. $$\chi_0$$ and $$\chi$$ become matrices that are connected with the real space in the following way:

$$\chi(0)(r_1, r_2, \omega) = \int_{BZ} dq \sum_{G,G'} e^{i(q+G') \cdot r_1} \chi_{(0)}(G,G')(q, \omega) e^{-i(q+G') \cdot r_2}$$

(14)

The coulomb potential $$v_{G,G'} = \delta_{G,G'} v_{G}$$ is defined in a similar way. To have control over the matrices, the variable NGsBlkXd can be used to give the dimension for $$\chi_0$$ and $$\chi$$. Higher values take more and more local field effects into account. A value of 1 neglects them completely.
Setting the damping: The theoretically obtained absorption peaks are $\delta$ peaks according to Fermi’s Golden Rule. The real spectrum will though be smeared out because of limited quasiparticle life times. To simulate this effect, YAMBO allows to set a Lorentz smearing manually which will, in the present case, be fixed to 0.1 eV all over the spectrum by the following lines:

```
% DmRngeXd
  0.10000 | 0.10000 | eV # [Xd] Damping range
%
```

Light polarization: In an anisotropic medium the light polarization is decisive. As CuInO$_2$ is an anisotropic medium, RPA calculations with different light polarizations were performed.

```
% LongDrXd
  1.000000 | 0.000000 | 0.000000 | # [Xd] [cc] Electric Field
%
```

4.3.2 Converging the Parameters
The parameters have been converged in the following order.

1. BndsRnXd $\rightarrow [1,25]$
2. NgsBlkXd $\rightarrow 30$
3. ngkpt $\rightarrow (12,12,12)$

After having converged the last value, it was appropriate to check, if the other parameters did not have to be reconverged.

As an example, the convergence for NgsBlkXd is depicted in Fig. 4. It can be seen that there exist slight differences between the graph with NgsBlkXd = 30 and the graph with NgsBlkXd = 40. However, this difference is not crucial and does not destroy the quantitative trend, so BgsBlkXd = 30 is considered to be already sufficiently converged.

4.4 Results
A spectrum that is converged in every parameter is shown in Fig. 5. Unfortunately, the spectrum is not yet fully converged in the number of k-points. But an augmentation of ngkpt would lead to much higher computing times without giving any additional qualitative character to the result. Besides, one has to take into account that the choice of the pseudo potential $v_{\text{ext}}$ and the exchange-correlation potential $v_{\text{xc}}[n]$ can already contribute to an error of $\pm 0.1$ eV.
Figure 4: Absorption spectrum for light polarized in \( xy \) plane using RPA: convergence of local fields

Anyway, the important features of the graph are visible: the highest absorption peak lies around 3.7 eV and the absorption edge is very low, at around 0.5 eV, due to the underestimation of the gap in Kohn-Sham LDA.

The calculation was also performed for light polarized in \( z \) direction (Fig. 6). We observe that the crystal is anisotropic as we expected from its structure.

5 \textbf{YAMBO: Absorption Spectra using BSE}

The RPA is, in our case, not sufficiently accurate, in comparison with experimental data. The next step will be to use an equation that has some analogies with the RPA, but takes, for example, excitonic effects into account.

5.1 Bethe-Salpeter Equation

In the framework of many-body perturbation theory, the Bethe-Salpeter Equation (BSE) has almost the same form as the RPA (12), but, unlike the RPA, it takes into account that the coulomb interaction will be screened due to repulsive electron-electron interactions. This screening lies in the screened interaction term \( W \) that weakens the Coulomb potential \( v \). In addition the BSE becomes a 4-point equation as it considers the propagation of electrons and holes [31]:

\[
^4L = ^4L^0 + ^4L^0(4v - 4W)^4L
\]  

(15)
Figure 5: Absorption spectrum for light polarized in $xy$ plane using RPA: convergence of last parameter ngkpt

where $^4L$ is the 4-point equivalent of the irreducible polarizability $\chi$, $^4L^0$ is the 4-point equivalent of the independent-particle polarizability $\chi_0$. The numbers ($i, j, \ldots$) in the following represent coordinates in an appropriate basis, for example ($r_i, \omega_i, r_j, \omega_j, \ldots$).

$\chi$ can be obtained by a 2-point contraction of $^4L$:

$$\chi(1, 2) = -^4L(1, 1, 2, 2)$$  

where $^4L$ has to be obtained by solving (15) using

$$(^4v - ^4W)(1, 2, 3, 4) = \delta(1, 2)\delta(3, 4)v(1, 3) - \delta(1, 3)\delta(2, 4)W(1, 2).$$  

The screened interaction $W$ is given by

$$W = \epsilon(1, 2, \omega = 0)^{-1}v$$

where $\epsilon$ is obtained by (11), a preliminary RPA calculation.

The 4-point character renders the description of excitons, hydrogen-like pairs of electrons and holes, possible.

### 5.2 Doing a BSE Calculation

As the YAMBO RPA method, the YAMBO BSE solver needs the Kohn-Sham wave functions and an input file with options. In addition the screened coulomb interaction $W$ is needed, that must be calculated in a
Figure 6: Absorption spectrum for light polarized in different directions using RPA: converged with \( \text{ngkpt} = (12, 12, 12) \) pre-step.

So the first step would be to create the \( W \) file.

5.2.1 The Input File (\( W \))

Setting up the number of bands: As in section 3.4.1.

\[
\begin{verbatim}
% BndsRnXs
1 60 # [Xs] Polarization function bands
%
\end{verbatim}
\]

Response block size: Gives the size of the \( W \) matrix. Calculations are performed in reciprocal (\( G \)) space. Smaller sizes decrease computing times.

\[
\begin{verbatim}
NGsBlkXs=30 RL # [Xs] Response block size
\end{verbatim}
\]
Light polarization: Usually the screened interaction is needed in all directions. To get a “mean” screened interaction, an arbitrary polarization, for example \((1, 2, 3)\), is used – the experience says that this approximation does not affect the results:

```
% LongDrXs
  1.000000 | 2.000000 | 3.000000 | # [Xs] [cc] Electric Field
%
```

5.2.2 The Input File (BSE)

Defining a scissor: The LDA results have been corrected using a scissor operator that simulates the corrections of the GW approximations by shifting all the energies greater than the Fermi energy. In the present case, this energy shift is 2.5 eV due to the GW corrections to the gap [22] (The scissor operator is a good approximation only if the WG corrections are weakly dependent on the wave vector):

```
% KfnQP_E
  2.50000 | 1.000000 | 1.000000 | # [EXTQP BSK BSS] E parameters (c/v)
%
```

Setting up the number of bands: As in sections 3.4.1 and 5.2.1.

```
% BSEBands
  8 | 29 |
  # [BSK] Bands range
%
```

Screened interaction block size: Gives the size of matrix \(W\) (i.e. of \(\epsilon\)) in \(\mathbf{G}\) space:

```
BSENGBlk= 30 RL # [BSK] Screened interaction block size
```

Exchange components: Gives the size of the Fourier expansion of the coulomb potential \(v\) (\(\mathbf{G}\) space):

```
BSENGexx= 30 RL # [BSK] Exchange components
```

Light polarization: As in section 5.2.1
5.2.3 Converging the Parameters

The parameters were converged in the following Order:

1. BSEBands → [8, 29]
2. BSENGBlk → 30
3. BSENGexx → 20
4. BndsRnXs → [1, 40]
5. NgsBlkXs → 30
6. ngkpt: not yet converged, but close

Figure 7: Absorption spectrum for light polarized in (1, 2, 3) direction using BSE: convergence of the bands sum governed by BSEBands

Our observations showed that a very time consuming operation is the sum over the bands which is governed by BSEBands. So this parameter has to be treated with special care.

The first calculation was performed with BSEBands = [16, 21], 3 occupied bands and 3 unoccupied bands\(^5\). Afterwards, the band range was augmented around the Fermi level until, at BSEBands = [08, 29], the result seemed to be converged. To assure that this was the case, BSEBands = [01, 29] and BSEBands = [08, 40] were tested as well. This is shown in Fig. 7.

\(^5\)CuInO\(_2\) has 18 outer shell electrons. So bands 16, 17 and 18 are occupied; 19, 20 and 21 are unoccupied.
5.3 Results

A spectrum that is converged in all parameters but \( \text{ngkpt} \) is shown in Fig. 8. At the moment there are not yet any BSE results for \( \text{ngkpt} = (10, 10, 10) \). The computing times for the BSE method with \( \text{ngkpt} = (8, 8, 8) \) were around several days when using around 10 processors on a cluster. Often, the random access memory was not sufficient, so that the number of processors per computer had to be reduced. Nevertheless, the last spectrum seems to be already very well converged. The essential features are visible: an absorption edge of around 3 eV and two peaks at around 5 eV and 6 eV.

Figure 8: Absorption spectrum for light polarized in (1, 2, 3) direction using BSE: convergence of last parameter \( \text{ngkpt} \); the arrow marks the experimental value.

These two peaks could not be seen in the RPA spectrum for light polarized in the \( xy \) plane (Fig. 4) where only one peak is identifiable. The two peaks are due to the fact that BSE takes excitonic effects into account. Excitonic effects redistribute oscillator strengths among the different structures of the spectrum. Further analysis of excitonic wave functions and transitions is necessary to interpret the spectrum. The peak shift is due to the \( GW \) energy corrections (section 6) that were not applied to the RPA method. In addition the peak shapes change, they become sharper in the BSE spectrum.

The BSE calculation was performed for light polarized in (1, 2, 3) direction while in the RPA method light was polarized in the \( xy \) plane and \( z \) direction. However, the comparison stays valid, because a RPA calculation in (1, 2, 3) direction should look like a mixture of Fig. 4 and Fig. 6 and should therefore contain the same features.
6 Abinit: quasiparticle Corrections using GW

As told before (section 1), Kohn-Sham LDA has problems to describe the bands of Cu-delafossites around the gap. The band gap energy is as usual much too small. However the LDA calculation was not useless because there are two possibilities to correct this issue.

The first possibility is to correct all the eigenenergies $\varepsilon_{n,k}$ per band index $n$ and quasi momentum $k$ separately by a GW calculation. These corrections can be obtained by ABINIT but will not be available in a format readable by YAMBO. To this purpose one has to write a converter that reads ABINIT’s GW output and writes a file in a format compatible with YAMBO. This will be a next project.

The second one would be to apply a scissor operator that does nothing else but shifting all energies $\varepsilon_i$ in (13) for $i>$ HOMO (Highest Occupied Molecular Orbit) by a constant – one speaks of opening the gap. This constant can be measured in experiment or obtained by a GW calculation. The latter was used – not to destroy the ab-initio character of the calculation. The GW calculation showed [22] that the energy corrections should not be constant, as they depend strongly on $n$ and $k$ with its mean energy shift being around 2.5 eV. To have a first impression of how an absorption spectrum looks like solving the BSE using GW corrections, a scissor with 2.5 eV was used in this work.

7 Conclusion

Experimental values for the direct optical gap of CuInO$_2$ lie between 3.9 eV and 4.45 eV [4, 42, 43] while the theoretical values are around 0.5 eV (RPA) and 3 eV (BSE). This is, in the latter case, a deviation of 1 eV from the experiment. Keeping in mind that only a scissor operator was used, the BSE results are already in much better agreement with the experiment.

Our results prove that excitonic effects in CuInO$_2$ are too strong to be neglected. In particular the BSE gives sharper and stronger peaks. So we have to go beyond the RPA and accept the higher computational costs of the BSE.

The GW corrections that take usually a lot of computing time have fortunately already been performed [22] and show a strong dependence on the band index $n$ and the wave vector $k$. These effects cannot be simulated by the scissor operator that gives a constant correction, so the real GW corrections should be applied. It is expected that this will improve even more the agreement between the theory and the experiment.
References

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[33] E. E. Salpeter and H. A. Bethe, Phys. Rev. 84, 1232 (1951)


