The electronic structure of delafossite transparent conductive oxides

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Outline

1. Delafossite transparent conductive oxides

2. What is the mixing of Hybrid functionals
Delafossite transparent conductive oxides


The delafossite crystal structure

Edge-sharing MO$_6$ octahedral layers $\rightarrow$

CuO$_2$ dumbbell layers $\rightarrow$

M is a group-III element (Al, Ga, In, B)
Delafossite transparent conductive oxides

**Delafossite TCO properties**

Cu(Al,In,Ga)O$_2$ thin-films are **transparent** and **conducting**:
- **p-type** or even **bipolar** conductivity
- combination of **n-** and **p-type** TCO materials allows
  - → stacked cells with increased efficiency
  - → functional windows
  - → transparent transistors

**very similar structure** of the Cu(Ga,In)(S,Se)$_2$ family of absorbers for thin-film photovoltaics.
Delafossite transparent conductive oxides

Literature - early results

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- Standard DFT yields excellent structural properties...
- ... but energy gaps are, at best half of experiment
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In many materials, perturbative \textit{GW} correct the LDA band gaps, and gives reasonable agreement with experimental data.

In most metal oxides, however, quasiparticle wavefunctions are badly reproduced by LDA wavefunctions, so the \textit{GW} correction is too small.

van Schilfgaarde, Kotani, and Faleev, PRL 96, 226402 (2006)
Real solution: self-consistent GW

A recipe to perform self-consistent GW has been given by Faleev, Kotani, and van Schilfgaarde. It is based on a procedure to make the self-energy static and Hermitian.

We use a similar approach, that turns out to yield very similar results, but is lighter from the computational point of view:

- start from an LDA band-structure and perform a self-consistent COHSEX (Coulomb Hole and Screened Exchange) calculation.
- add dynamical effects by performing a perturbative GW step on top of the self-consistent COHSEX.

This approach gives excellent results for many complex compounds, such as instance CuIn(S,Se)$_2$, Cu$_2$O, VO$_2$.

Technical problem: convergence with bands

- Production $GW$ codes require sums over virtual states. To speed-up convergence we use the trick of Bruneval and Gonze.
- Not just a technical point. Without any “tricks” the convergence is very slow, leading to an underestimation of the band gaps.
- Using a value of 9.5 Ha, the results are independent of the number of bands, so we could do our calculations using only 200 bands for CuMO$_2$.

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Upon going from LDA to $G_0W_0$ to sc$GW$, there is an upshift of the conduction band at $\Gamma$ with respect to $L$.

Within sc$GW$, the minimum of the conduction band is at $L$, the direct and indirect band gaps are almost identical.

Our results were confirmed by a recent, independent calculation reported by Christensen et al. Phys. Rev. B 81, 045203 (2010).

The sc$GW$ direct gap is more than 1 eV higher than experiment!
sc\textit{GW} corrections are strongly \( \mathbf{k} \)-dependent. No scissor operator possible.

Hybrids (HSE03) show a large difference with sc\textit{GW} in the conduction band, while the valence bands are very accurate.

LDA+U describes incorrectly both the gap and the band dispersion.
According to the experimental data, the polaron constant in CuAlO$_2$ is $\sim 1$.

In delafossites we have non negligible contribution of the lattice polarization to the electronic screening.

Lattice polarization effects can be included within $GW$, simply adding the ionic contribution to the dielectric matrix in the calculation of the screened potential $W$.

$$\varepsilon_{GG}(q, \omega) = \delta_{GG} + 4\pi P_{GG}(q, \omega) + 4\pi P_{lat}^{GG}(q, \omega)$$

Using the long wavelength contribution of the lattice polarizability $P_{00}^{lat}(q \to 0, \omega)$, and the Lyddane-Sachs-Teller relationship for the static case, a simple model for the lattice polarizability is derived from

- static dielectric constant $\varepsilon_0$
- low-frequency dielectric constant $\varepsilon_\infty$
- zone center optical frequencies $\omega_{LO}$ and $\omega_{TO}$

Experimental data are for optical gap: exciton binding energy $\sim 0.5$ eV

The agreement of LDA+U and HSE06 hybrid functional to the experiment is accidental

ScGW shows that the band gaps are much higher – no trace of an small indirect gap

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Results: CuAlO$_2$ band gaps

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The direct to indirect band gap difference increases on increasing the M atomic number.

Apart from the CuBO$_2$, scGW adds to the LDA direct band gap a constant amount of about 2.5 eV.
**scGW** solves to a large extent the problem of electron correlation for many transition metal oxides.

- Convergence with the number of empty bands has to be carefully checked.
- $GW$ corrections can be $k$-dependent: no scissor operator, please!

**scGW** calculations show that the band gaps of delafossite CuMO$_2$ are very wide.

- There is no trace of a low-energy indirect band gap. LDA+U and hybrid functionals must be used with care.
- Lattice polarization effects are very important, and their inclusion leads to a good agreement with experimental data.
Delafossites – conclusion

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What is the mixing of Hybrid functionals


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Hybrid functionals

The experimental values of some quantities lie often between they Hartree-Fock and DFT (LDA or GGA) values. So, we can try to mix, or to “hybridize” both theories.

1. Write an energy functional:

\[ E_{xc} = aE^{\text{Fock}}[\varphi_i] + (1 - a)E^{\text{DFT}}[n] \]

2. Minimize energy functional w.r.t. to the orbitals:

\[ \nu_{xc}(r, r') = a\nu^{\text{Fock}}(r, r') + (1 - a)\nu^{\text{DFT}}(r) \]

Note: for pure density functionals, minimizing w.r.t. the orbitals or w.r.t. the density gives the same, as:

\[ \frac{\delta F[n]}{\delta \varphi^*} = \int \frac{\delta F[n]}{\delta n} \frac{\delta n}{\delta \varphi^*} = \frac{\delta F[n]}{\delta n} \varphi \]
What is the mixing of Hybrid functionals?

What is the mixing parameter?

Let us look at the quasi-particle equation:

\[
\left[ -\frac{\nabla^2}{2} + v_{\text{ext}}(r) + v_H(r) \right] \phi_{i\text{QP}}(r) + \int d^3 r' \Sigma(r, r'; \varepsilon_{i\text{QP}}) \phi_{i\text{QP}}(r') = \varepsilon_{i\text{QP}} \phi_{i\text{QP}}(r')
\]

And now let us look at the different approximations:

- **COHSEX:**
  \[
  \Sigma = - \sum_{i}^{\text{occ}} \phi_{i\text{QP}}(r) \phi_{i\text{QP}}(r') W(r, r'; \omega = 0) + \delta(r - r') \Sigma_{\text{COH}}(r)
  \]

- **Hybrids**
  \[
  \Sigma = - \sum_{i}^{\text{occ}} \phi_{i\text{QP}}(r) \phi_{i\text{QP}}(r') a v(r - r') + \delta(r - r')(1 - a) v^{\text{DFT}}(r)
  \]

So, we infer that \( a \sim 1/\epsilon_\infty \)!
What is the mixing of Hybrid functionals

Does it work \( (a = 1/\epsilon_{\infty}) \)?

Optimal mixing obtained with a PBE0 form.
What is the mixing of Hybrid functionals

Does it work \( (a = 1/\epsilon_{\infty}) \)?

![Graph showing theoretical and experimental gaps for different functionals](image)

Errors: PBE (46%), Hartree-Fock (230%), PBE0 (27%), PBE0_{\epsilon_{\infty}} (16.53%)
Can we do better?

Screening is related to the gap. So, if we have an estimator of the gap of the material, we can also get an estimator of the dielectric constant.

There are several local estimators on the market:

- $G = \frac{1}{8} |\nabla n|^2 / n^2$ (Gutle et al. 1999)
- $|\nabla n| / n$ (Heyd et al. 2003; Krukau et al. 2008)
- $\tau_W = |\nabla n|^2 / 8n$ (Jaramillo et al. 2003)

These are however, local estimators and we need a global estimator. The solution is averaging. We follow the idea of the Tran and Blaha meta-GGA and define

$$\bar{g} = \frac{1}{V_{\text{cell}}} \int_{\text{cell}} d^3 r \sqrt{\frac{|\nabla n(r)|}{n(r)}}$$

F Tran and P Blaha, Phys. Rev. Lett. 102, 226401 (2009)
What is the mixing of Hybrid functionals

Is there a correlation?

Fit: $-1.00778 + 1.10507 \times \bar{g}$. Error in the gaps: 14.37%

Can one also do it with HSE?
### Results - Summary

What is the mixing of Hybrid functionals?

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<th>HF+c</th>
<th>PBE0</th>
<th>PBE0$\epsilon_{\infty}$</th>
<th>PBE0mix</th>
<th>HSE06</th>
<th>HSE0mix</th>
<th>TB09</th>
<th>G$_0$</th>
<th>W$_0$</th>
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$\Delta$ (%) – 47.32 250.23 29.42 16.53 14.37 16.92 10.36 9.85 11.25

Other properties (structural properties, band dispersions, etc.)?
Hybrids – Conclusions

The ab-initio determination of the mixing constant is:

- Cheap and easy to calculate.
- Physically motivated.
- Improves considerably electronic-gaps obtained with hybrid functionals.
- Both small-gap and large-gap (rare-gases) materials can be well-described.
- It is an energy functional – all properties can be in principle calculated.
- The solution to the size-consistency problem not yet implemented and tried.
- Need to obtain more properties to get a better working knowledge of the functional.
- Still has problems with d-electron systems.
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Thanks to all collaborators! Thank you!

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