Photoelectronic properties of chalcopyrites for photovoltaic conversion: self-consistent GW calculations

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Outline

1. Photovoltaic materials
2. Beyond Standard DFT
3. Beyond Standard GW
Photovoltaic materials

Present state of photovoltaic efficiency

Best Research-Cell Efficiencies

from National Renewable Energy Laboratory (USA)
CIS solar cell

Devices have to fulfill **2 functions**:

- Photogeneration of electron-hole pairs
- Separation of charge carriers to generate a current

**Structure:**

- Molybdenum back contact
- **CIS** layer (p-type layer)
- CdS layer (n-type layer)
- ZnO:Al transparent contact

Efficiency = 13 %
CuIn(S,Se)$_2$ are among the best photovoltaic absorber materials:

- **High optical absorption** $\Rightarrow$ thin layer films
- **Optimal** photovoltaic gap (record efficiency 19.9 %)
- **Self-doping** with native defects $\Rightarrow$ p-n junctions
- Electrical **tolerance** to large off-stoichiometries: not yet understood
- **Benign** character of defects: not yet understood
DFT in its standard form is a **ground state theory**

- **Structural parameters**: lattice parameters, internal distortions are OK, even in LDA or GGA
- **Formation energies** for defects calculated from total energies are reliable
- Kohn-Sham energies are not meant to reproduce *quasiparticle band structures*: often one obtains good *band dispersions* but *band gaps* are systematically **underestimated**
- Kohn-Sham DOS is not meant to reproduce *photoemission*
State of the art for CuIn(S,Se)$_2$

- First ab initio calculation for chalcopyrite
  \textit{Jaffe et al., PRB 28, 10 (1983)}

- Formation energies of intrinsic defects and defect levels in the gap
  \textit{Zhang et al., PRB 57, 9642 (1998)}

- Correction of the bandgap DFT+U $\Delta E_v = -0.37$ eV
  \textit{Lany et al., PRB 72 035215 (2005)}

- Metastability caused by the vacancy complex $V_{Se}$-$V_{Cu}$
  \textit{Lany et al., JAP, 100, 113725 (2006)}
Modeling photovoltaic materials

Objectives

- Predict accurate values for fundamental opto-electronical properties of materials
- Deal with complex materials (large unit cells, defects)
van Schilfgaarde, Kotani, and Faleev, PRL 96 (2006)
### Photovoltaic materials

#### LDA Kohn-Sham energy gaps for CIS

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![Graph showing energy bands](image-url)
Beyond standard DFT

For photovoltaic applications we are interested in evaluating
- quasiparticle band gap
- optical band gap
- defect energy levels
- optical absorption spectra

All these quantities require going beyond standard DFT
In the many-body framework, we know how to solve these problems:

- **GW** for quasi-particle properties
- **Bethe-Salpeter equation** for the inclusion of electron-hole interaction

The first step can be substantially more complicated than the second, so in the following we will focus on **GW**
Hedin’s equations

\[ \Sigma = GW \]

\[ G = G^0 + G^0 \Sigma G \]

\[ W = v + vPW \]

\[ P = GG \Gamma \]

Self-energy and screened interaction

Self-energy: nonlocal, non-Hermitian, frequency dependent operator. It allows to obtain the Green’s function $G$ once that $G_0$ is known.

For the Hartree-Fock case:

$$\Sigma_x(r_1, r_2) = iG(r_1, r_2, t, t^+)\nu(r_1, r_2)$$

For the GW case:

$$\Sigma(r_1, r_2, t_1 - t_2) = iG(r_1, r_2, t_1 - t_2)W(r_1, r_2, t_2 - t_1)$$

$W = \epsilon^{-1}\nu$: screened potential (much weaker than $\nu$!)

Ingredients:

- KS Green’s function $G_0$, and RPA dielectric matrix $\epsilon_{G,G'}^{-1}(q, \omega)$

L. Hedin, Phys. Rev. 139 (1965)
Kohn-Sham equation:

\[ H_0(r) \varphi_{KS}(r) + v_{xc}(r) \varphi_{KS}(r) = \varepsilon_{KS} \varphi_{KS}(r) \]

Quasiparticle equation:

\[ H_0(r) \phi_{QP}(r) + \int dr' \Sigma(r, r', \omega = E_{QP}) \phi_{QP}(r') = E_{QP} \phi_{QP}(r) \]

Quasiparticle energies 1st order perturbative correction with \( \Sigma = iGW \):

\[ E_{QP} - \varepsilon_{KS} = \langle \varphi_{KS} | \Sigma - v_{xc} | \varphi_{KS} \rangle \]

Basic assumption: \( \phi_{QP} \approx \varphi_{KS} \)

Hybersten and Louie, PRB 34 (1986); Godby, Schlüter and Sham, PRB 37 (1988)
van Schilfgaarde, Kotani, and Faleev, PRL 96 (2006)
### Quasiparticle energies within $G_0W_0$ for CIS

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Beyond Standard GW

Looking for another starting point:

- DFT with another approximation for $\nu_{xc}$: GGA, EXX,... (e.g. Rinke et al. 2005)
- Semi-empirical hybrid functionals (e.g. Fuchs et al. 2007)

Self-consistent approaches:

- scCOHSEX scheme (Hedin 1965, Bruneval et al. 2005)
- GWscQP scheme (Faleev et al. 2004)
Looking for another starting point:

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Beyond Standard GW

Self-consistent COHSEX

Coulomb hole:

\[ \Sigma_{\text{COH}}(r_1, r_2) = \frac{1}{2} \delta(r_1 - r_2)[W(r_1, r_2, \omega = 0) - v(r_1, r_2)] \]

Screened Exchange:

\[ \Sigma_{\text{SEX}}(r_1, r_2) = - \sum_i \theta(\mu - E_i) \phi_i(r_1) \phi_i^*(r_2) W(r_1, r_2, \omega = 0) \]

- The COHSEX self-energy is static and Hermitian
- Self-consistency can be done either on energies alone or on both energies and wavefunctions
- Representation of WFs on a restricted LDA basis set
Beyond Standard GW

Self-consistent GW à la Faleev

Make self-energy Hermitian and static

\[ \langle k_i | \tilde{\Sigma} | k_j \rangle = \frac{1}{4} \left( \langle k_i | \Sigma(\varepsilon_{k_j}) | k_j \rangle + \langle k_j | \Sigma(\varepsilon_{k_i}) | k_i \rangle^* \right. \\
+ \langle k_i | \Sigma(\varepsilon_{k_i}) | k_j \rangle + \langle k_j | \Sigma(\varepsilon_{k_i}) | k_i \rangle^* \right) \]

- \( | k_i \rangle \) and \( \varepsilon_{k_i} \) are self-consistent eigensolutions of the iterative procedure
- Representation of WFs on a restricted LDA basis set
- Requires sums over empty states

Faleev, van Schilfgaarde, and Kotani, PRL 93 2004
Advantages of COHSEX:

- Old approximation physically motivated: accounts for Coulomb-hole and screened-exchange
- Computationally “inexpensive”: static; only sums over occupied states
- sc-COHSEX wave-functions very similar to sc-GW

Disadvantages of COHSEX:

- Dynamical correlations are missing
- Quasiparticle gaps are better (10-20% higher than experiment), but still not OK

One-shot GW on top of sc-COHSEX corrects the energy gap!
Beyond Standard GW

Energy gap within sc GW

van Schilfgaarde, Kotani, and Faleev, PRL 96 (2006)
# Quasiparticle energies within sc-GW for CIS

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sc-GW is here sc-COHSEX+$G_0W_0$
Self-consistency in the energies suffices to correct the gap.

Self-consistency in the wave-functions is necessary to correct deeper states.

Spin-orbit coupling is important for Se compound:
- Can be added perturbatively within DFT
- Experiment: 0.2 eV  Calculation: 0.16 eV
Beyond Standard GW

Example: Insulating phase of Vanadium Oxide

LDA valence WF

metal

sc-GW: variation of WF

$E_g = 0.65 \text{ eV}$

The variation of the wave-functions is essential to open up the gap (metal both in LDA and $G_0W_0$!)

Gatti et al., PRL 99 (2007)
Beyond Standard GW

Quasi-particle corrections for CuInS$_2$

- Corrections depend on the character of the band
  → Models for quasi-particle corrections for defects
Corrections are independent of the k-point (within 0.1 eV)

→ Effective masses remain unchanged
Beyond Standard GW

Quasi-particle corrections for CuInSe$_2$

- blue: $G_0W_0$
- black: sc-COHSEX
- red: sc-COHSEX + $G_0W_0$
Beyond Standard GW

Quasi-particle corrections for CuInS$_2$

- blue: $G_0W_0$
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KS Energies [eV]

DOS [a.u.]
Defects

a) Perfect crystal  b) V\textsubscript{Cu}  c) V\textsubscript{Se}  d) 2V\textsubscript{Cu}ln\textsubscript{Cu}

- Gap in the valence disappears in the presence of defects
Methods that go beyond ground-state DFT are by now well established

- GW and BSE

Self-consistency is absolutely necessary for d-electrons

- Self-consistent GW gives a very good description of quasi-particle states
- Self-consistent COHSEX good starting point for one-shot GW
  - In all cases we studied this proved to be at the level of scGW
  - Much more friendly from the computational point of view

In progress

- Defects
- Absorption spectra from the Bethe-Salpeter equation
Beyond Standard GW

Thanks!!!

http://www.etsf.eu
http://etsf.polytechnique.fr

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