Electronic properties of materials for thin-film solar cells

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CEA Saclay
Fabien Bruneval

Electronic excitations in solar cells
Outline

1. Thin-film photovoltaic materials
2. What can we calculate within standard DFT?
3. How to go beyond standard DFT? GW vs. Hybrids
4. How to compare with experiments for “real” materials?
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Thin-film photovoltaic materials

Present state of photovoltaic efficiency

Best Research-Cell Efficiencies

- Multijunction Concentrators
  - Three-junction (2-terminal, monolithic)
  - Two-junction (2-terminal, monolithic)
- Single-Junction GaAs
  - Single crystal
  - Concentrator
  - Thin film
- Crystalline Si Cells
  - Single crystal
  - Multicrystalline
  - Thick Si film
- Thin-Film Technologies
  - Cu(In,Ga)Se_2
  - CdTe
  - Amorphous Si:H (stabilized)
  - Nano-, micro-, poly-Si
  - Multijunction polycrystalline
- Emerging PV
  - Dye-sensitized cells
  - Organic cells (various technologies)

from National Renewable Energy Laboratory (USA)
CIGS 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
- CIGS layer (p-type layer)
- CdS layer (n-type layer)
- ZnO:Al TCO contact

Efficiency = 13%
Objectives

- Predict accurate values for fundamental opto-electronical properties (gap, absorption spectra, excitons, ...)
- Simulate real materials (large unit cells, defects, doping, interfaces, ...)

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What can we calculate within standard DFT?

Density functional theory

DFT in its standard form is a **ground state theory**:

- **Structural parameters**: lattice parameters, internal distortions are usually good in LDA or GGA
- Formation energies for defects calculated from total energies are often reliable

... but ...

- Kohn-Sham energies are not meant to reproduce quasiparticle band structures: one often obtains good band dispersions but band gaps are systematically underestimated
- Kohn-Sham DOS is not meant to reproduce photoemission
- How to calculate the optical absorption?
What can we calculate within standard DFT?

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- Kohn-Sham DOS is not meant to reproduce **photoemission**
- How to calculate the **optical absorption**?
What can we calculate within standard DFT?

Excitation energies: photoemission

Photoemission process:

\[ h\nu - (E_{\text{kin}} + \phi) = E_{N-1,\nu} - E_{N,0} = -\varepsilon_{\nu} \]
What can we calculate within standard DFT?

Excitation energies: photoemission

Inverse photoemission process:

\[ h\nu - (E_{\text{kin}} + \phi) = E_{N,0} - E_{N+1,c} = -\varepsilon_c \]
What can we calculate within standard DFT?

Excitation energies: energy gap

Photoemission gap:

\[ E_{\text{gap}} = I - A = \min_{k,l} \left( E_{N-1,k} + E_{N+1,l} - 2E_{N,0} \right) \]
What can we calculate within standard DFT?

**Excitation energies: energy gap**

**Optical gap:**

\[ E_{\text{gap}} = I - A - E_{\text{exc}}^{\text{binding}} \]
What can we calculate within standard DFT?

### LDA Kohn-Sham energy gaps for CIS

<table>
<thead>
<tr>
<th>Material</th>
<th>DFT-LDA</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CuInS$_2$</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_g$</td>
<td>-0.11</td>
<td>1.54</td>
</tr>
<tr>
<td>In-S</td>
<td>6.5</td>
<td>6.9</td>
</tr>
<tr>
<td>S s band</td>
<td>12.4</td>
<td>12.0</td>
</tr>
<tr>
<td>In 4 d band</td>
<td>14.6</td>
<td>18.2</td>
</tr>
<tr>
<td><strong>CuInSe$_2$</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_g$</td>
<td>-0.29</td>
<td>1.05</td>
</tr>
<tr>
<td>In-Se</td>
<td>5.8</td>
<td>6.5</td>
</tr>
<tr>
<td>Se s band</td>
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</tr>
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Outline

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3. How to go beyond standard DFT? GW vs. Hybrids

4. How to compare with experiments for “real” materials?
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
Hedin’s equations

\[ \Sigma = G \Gamma \]
\[ G = G^0 + G^0 \Sigma G \]
\[ W = v + vP \]
\[ P = GG \Gamma \]

Hedin’s equations

\[ \Sigma = G W \Gamma \]

\[ G = G_0 + G_0 \Sigma G \]

\[ W = v + v P W \]

\[ P = G G \]

\[ \Gamma = 1 + (\delta \Sigma / \delta G) G G \]

\[ P = G G \Gamma \]

How to go beyond standard DFT? GW vs. Hybrids

Standard one-shot GW

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: \( \phi_{QP} \simeq \varphi_{KS} \)

Hybersten and Louie, PRB 34 (1986); Godby, Schlüter and Sham, PRB 37 (1988)
Standard one-shot GW

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**Quasiparticle energies within \( G_0W_0 \) for CIS**

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<tr>
<th></th>
<th>CuInS(_2)</th>
<th>CuInSe(_2)</th>
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<tbody>
<tr>
<td></td>
<td>DFT-LDA</td>
<td>( G_0W_0 )</td>
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<td>( E_g )</td>
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Looking for another starting point:

- DFT with another approximation for $v_{xc}$: GGA, EXX,... (e.g. Rinke et al. 2005)
- LDA/GGA + $U$ (e.g. Kioupakis et al. 2008, Jiang et al. 2009)
- Hybrid functionals (e.g. Fuchs et al. 2007)

Self-consistent approaches:

- GWscQP scheme (Faleev et al. 2004)
- scCOHSEX scheme (Hedin 1965, Bruneval et al. 2005)
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In both sc approaches the self-energy is made **hermitian** and **static**

**Advantages of sc-COHSEX**

- physically motivated: accounts for Coulomb-hole and screened-exchange
- computationally friendly: only occupied states
- sc-COHSEX wave-functions very similar to GWscQP ones
- still a “best G, best W” approach
- dynamical correlations added in the G$_0$W$_0$ step

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### Quasiparticle energies within sc-GW for CIS

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<th>CuInS₂</th>
<th>CuInSe₂</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>DFT-LDA</td>
<td>G₀W₀</td>
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sc-GW is here sc-COHSEX+G₀W₀
How to compare with experiments for “real” materials?

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Cu(In,Ga)(S,Se)$_2$ are among the best absorbers:

- high optical absorption $\Rightarrow$ thin-layer films
- optimal photovoltaic gap (record efficiency 19.9 %)
- self-doping with native defects $\Rightarrow$ p-n junctions
- extraordinary stability under operating conditions:
  - tolerance to large off-stoichiometries, stress, defects (not yet understood)
CIGS properties

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How to compare with experiments for “real” materials?

Stability of the gap

Is the gap stable under lattice distortion?

Experiments measure a stable gap (within 10%)

- Large dispersion of $u$
- Only hybrid-DFT calculations overlap with experiments

Anion displacement: $u = \frac{1}{4} + \left( R_{Cu-S,Se}^2 - R_{In-S,Se}^2 \right) / a^2 \neq \frac{1}{4}$.

Jaffe&Zunger, PRB 29, 1882 (1984); Merino, J. Appl. Phys. 80, 5610 (1996);
How to compare with experiments for “real” materials?

Stability of the gap

Strong variations in DFT-LDA (in agreement with literature)

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How to compare with experiments for “real” materials?

Stability of the gap

$E_g$ [eV] vs $u$

$G_0 W_0$ does not change the slope . . .

CuInS$_2$

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How to compare with experiments for “real” materials?

Stability of the gap

... unless the gap is already open!

CuInS$_2$

$E_g$ [eV]

DFT-LDA

$G_0W_0$

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How to compare with experiments for “real” materials?

Stability of the gap

CuInS$_2$

$E_g$ [eV] vs $u$

- **DFT-LDA**
- **G$_0$W$_0$**
- **scGW**

**sc-GW** enhances the gap variation

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How to compare with experiments for “real” materials?

Stability of the gap

HSE06 hybrid gives an intermediate slope

\[ E^{\text{HSE06}}_{xc} = E^{\text{GGA}}_{xc} + \frac{1}{4} E^{\text{HF, sr}}_{x} - \frac{1}{4} E^{\text{GGA, sr}}_{x} \]
How to compare with experiments for “real” materials?

Stability of the gap

- a modified-HSE06 (the mixing parameter of the screened Fock exchange is proportional to the screening) gives the sc-GW slope

\[
E^\text{GGA}_x + \frac{1}{\epsilon_\infty} E^\text{HF,sr}_x - \frac{1}{\epsilon_\infty} E^\text{GGA,sr}_x
\]
Is the gap stable **under lattice distortion**?

- sc-GW and hybrid calculations predict even **stronger** variations than LDA
- The gap is **not stable** under lattice distortion alone
Stability of the gap

Is the gap stable under lattice distortion?

- sc-GW and hybrid calculations predict even stronger variations than LDA
- The gap is not stable under lattice distortion alone
The formation energy of $V_{\text{Cu}}$ varies under lattice distortion:

$$\Delta E_f = \Delta E_{\text{f DFT}} - \Delta E_{\text{scGW VBM}}$$
How to compare with experiments for “real” materials?

**Formation energy of Cu vacancies**

The formation energy of $V_{Cu}$ varies under lattice distortion:

$$\Delta E_f = \Delta E_f^{\text{DFT}} - \Delta E_{\text{VBM}}^{\text{scGW}}$$

- It is essential to go beyond DFT-LDA
- **LDA+U** (blue lines) gives only constant shifts

A feedback loop can explain the stability of the band gap:

\[ \Delta u \rightarrow \{ \Delta VBM \rightarrow \Delta E_f \rightarrow \Delta [V_{Cu}] \} \rightarrow \Delta E_g \]
How to compare with experiments for “real” materials?

Why is the experimental gap so stable?

A **feedback loop** can explain the stability of the band gap:

\[
\Delta u \rightarrow \{ \Delta V_{\text{BM}} \rightarrow \Delta E_f \rightarrow \Delta [V_{\text{Cu}}] \}
\]

\[
\Delta E_g = \frac{\partial E_g}{\partial u} \Delta u + \frac{\partial E_g}{\partial [V_{\text{Cu}}]} \Delta [V_{\text{Cu}}]
\]

- Experimental variation of \( \Delta u = 0.02 \Rightarrow \Delta E_g \approx 0.65 \text{ eV} \)
- Considering variations of \( \Delta u \) and \([V_{\text{Cu}}]\) \( \Rightarrow \Delta E_g \approx -0.04 \text{ eV} \)
**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  
  - $\rightarrow$ stacked cells with increased efficiency  
  - $\rightarrow$ functional windows  
  - $\rightarrow$ transparent transistors
How to compare with experiments for “real” materials?

The long dispute about delafossite gaps

The most studied compound is CuAlO$_2$:

- Indirect gap
- Minimum direct gap at $L$: dipole allowed
- Experimental data far from sc-GW calculations!

Is sc-GW wrong in this case?
How to compare with experiments for “real” materials?

The long dispute about delafossite gaps

Experimental data are for optical gap: exciton binding energy $\approx 0.5$ eV
[Laskowski et al. PRB 79, 165209 (2009)]

Strong lattice polaron effects are expected $\approx 1$ eV
[Bechstedt et al. PRB 72, 245114 (2005)]
How to compare with experiments for “real” materials?

The long dispute about delafossite gaps

All results for CuInO$_2$ are consistent with results for CuAlO$_2$

- Only 2 optical experiments
- Minimum direct gap at $\Gamma$: dipole forbidden

[Nie et al. PRL 066405 (2002)]
How to compare with experiments for “real” materials?

Bands of CuAlO$_2$ from LDA+$U$

- LDA+$U$ direct gap close to experiment
- CB are rigidly shifted
How to compare with experiments for “real” materials?

Bands of CuAlO$_2$ from sc-GW calculations

- GW corrections strongly $k$-dependent
- CBM moves from $\Gamma$ to $L$
- gap becomes quasi-direct
- direct gap 1.5 eV larger than experiment
How to compare with experiments for “real” materials?

Comparison with hybrid functional calculations

Strong differences both in dispersion and energy gaps
Are hybrids a good compromise?
Preliminary results for CuInO$_2$:

Strong excitonic effects also for the In compound!
How to compare with experiments for “real” materials?

Conclusions and perspectives

Methods that go beyond ground-state DFT are by now well established

- (sc)GW and BSE

Interpretation of experiments is however not straightforward!
A better starting point is absolutely necessary for d-electrons

- Self-consistent COHSEX+$G_0W_0$ gives a very good description of quasi-particle states
  - In all cases we studied this proved to be at the level of scGW
  - Much more friendly from the computational point of view

- Hybrid functionals give better structural parameters and are a good compromise for band structures

In progress now:

- Defects using VASP (hybrid functionals)
  - supercells up to 300 atoms
- Absorption spectra from the Bethe-Salpeter equation


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