Electronic excitations in materials for solar cells beyond standard density functional theory

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Outline

1. CIGS and CZTS absorbers
2. Electronic excitations: beyond standard DFT?
3. Results and open problems
   - Band structures
   - Optical spectra
4. Conclusions and perspectives
Projects realised so far do not yet represent the full range of products available on the market: these include integratable crystalline modules, thin-layer modules, transparent and shading modules, solar roof tiles, photovoltaic roof foils or complete solar roofs.

**Playing with light and glass:** building-integrated photovoltaics opens new creative opportunities for architects.
CIGS and CZTS absorbers

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

Würth Elektronik GmbH & Co.
Efficiency = 13 %
CIGS and CZTS absorbers

CIGS vs. CZTS absorbers

$\text{Cu(In,Ga)(S,Se)}_2$:  
- high optical absorption $\Rightarrow$ thin-layer films  
- optimal bandgap (record efficiency 20.1%)  
- self-doping with native defects $\Rightarrow$ p-n junctions  
- extraordinary stability under operating conditions: tolerance to stress, defects, off-stoichiometries

$\text{Cu}_2\text{ZnSnS}_4$:  
- very similar properties, and only abundant, non-toxic elements  
- Ideal gaps: 1.35-1.5 eV  
- But record efficiency 9.6% (IBM 2010)
Problems of standard DFT

Modeling electronic excitations in complex systems

Objectives

- Predict accurate values for fundamental opto-electronical properties: gap, absorption spectra, excitons → excited states
- Simulate real materials: nanostructured systems, defects, doping, interfaces → large unit cells

Find a compromise between accuracy and computational effort
Problems of standard DFT
Modeling electronic excitations in complex systems

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Density functional theory

In literature most used computational approach for band structures:

Kohn-Sham (KS) equations

\[
-\frac{\nabla^2}{2} + v_{\text{ext}}(r) + v_{\text{Hartree}}(r) + v_{\text{xc}}(r) \varphi_i(r) = \varepsilon_i \varphi_i(r)
\]

- Structural parameters and formation energies are usually good using standard LDA or GGA
- Kohn-Sham energies are not meant to reproduce quasiparticle band structures: one often obtains good band dispersions but band gaps are systematically underestimated
- Independent-particle transitions inadequate for optical absorption

Hohenberg&Kohn, PR 136, B864 (1964); Kohn&Sham, 140, A1133 (1965)
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Problems of standard DFT

An example: DFT-LDA for Cu(In,Ga)Se$_2$

CuGaSe$_2$  CuInSe$_2$

Se 4s  Se 4s
Cu d - Se p  Cu d - Se p
In-Se bond  In-Se bond
Ga-Se bond

Silvana Botti  Electronic excitations & photovoltaics
Problems of standard DFT

An example: DFT-LDA for Cu(In,Ga)Se$_2$

CuGaSe$_2$  CuInSe$_2$

- The diagrams show the electronic band structures of CuGaSe$_2$ and CuInSe$_2$.
- Cu d - Se p  In-Se bond
- Ga-Se bond  Se 4s
- In 4d  Cu d - Se p
- Se 4s

Electronic excitations & photovoltaics

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Green’s function and Hedin’s equations

Propagation of an extra particle (electron or hole):

\[ G(r_1, r_2, t_1 - t_2) = -i \langle N | T[\hat{\psi}(r_1, t_1)\hat{\psi}^\dagger(r_2, t_2)] | N \rangle \]

Hedin’s equations should be solved self-consistently
Problems of standard DFT

Beyond Standard GW

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)

Our choice is to get a better starting point for $G_0W_0$ using scCOHSEX
Also working on improved hybrids! See PRB 83, 035119 (2011)

Problems of standard DFT

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Results and open problems

- Band structures
- Optical spectra


Band structures of CuGaSe$_2$

- Good for all CIGS family
- No need to have $d$ electrons of Ga in the valence, in contrast with In
- Agreement with experimental gap within less than 0.1 eV using the exp. $u$ (careful!)
Band structures of kesterite \( \text{Cu}_2\text{ZnSnS}_4 \)

- Good for \( \text{CZT(S,Se)}, \) kesterites and stannites
- If exp. internal coordinates are unknown, use hybrid functionals and not LDA or GGA to obtain \( u \) (careful!)
## Results and open problems

### Band structures

#### Anion displacement for CZTS

<table>
<thead>
<tr>
<th>Compound</th>
<th>Basis</th>
<th>( u )</th>
<th>( u_x )</th>
<th>( u_y )</th>
<th>( u_z )</th>
<th>( E_{\text{scGW}}^{\text{exp}} ) gap</th>
<th>( E_{\text{exp}}^{\text{exp}} ) gap</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Cu}_2\text{ZnSnS}_4 )</td>
<td>exp.</td>
<td>0.244</td>
<td>0.243</td>
<td>0.128</td>
<td>1.64 eV</td>
<td>≃ 1.5-1.6 eV</td>
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<tr>
<td></td>
<td>LDA</td>
<td>0.240</td>
<td>0.231</td>
<td>0.130</td>
<td>1.13 eV</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>HSE06</td>
<td>0.245</td>
<td>0.241</td>
<td>0.128</td>
<td>1.57 eV</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{Cu}_2\text{ZnSnSe}_4 )</td>
<td>exp.</td>
<td>0.240</td>
<td>0.135</td>
<td>0.92 eV</td>
<td>0.92 eV</td>
<td>≃ 1.35 eV</td>
<td></td>
</tr>
<tr>
<td></td>
<td>LDA</td>
<td>0.245</td>
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</table>

*Note: LDA and HSE06 are different density functional theory methods.*

![Diagram of kesterite and stannite structures](image_url)
Anion displacement: \( u = \frac{1}{4} + \left( \frac{R_{\text{Cu-(S,Se)}}^2 - R_{\text{In-(S,Se)}}^2}{a^2} \right) \neq \frac{1}{4}. \)

The exp. dispersion of \( u \) is large

Hybrid functionals and GGA+U give structural parameters closer to experiments

Note that for Ga compounds GGA gives \( u \) close to experiments

Stability of the gap in In compound

- Strong dependence of the gap on $u$
- modified-HSE06 (the mixing parameter of the screened Fock exchange is proportional to the screening) gives the sc-GW slope

J. Vidal, S. Botti, P. Olsson, J.-F. Guillemoles, and L. Reining,

Dependence of kesterite CZTS gap on $u$

Strictly analogous to the case of CIGS!

\[
\begin{align*}
\text{Energy gap (eV)} & \quad \text{scCOHSEX+G} & \quad 0 \quad W & \quad 0 \\
& \quad \text{HSE06} & \quad \text{LDA} & \\
\end{align*}
\]

$u_z = 0.13$ (exp 0.128)
Why is the experimental gap so stable?

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

\[ \Delta u \rightarrow \Delta E_g \rightarrow \Delta H_f(V_{Cu}) \rightarrow \Delta [V_{Cu}] \rightarrow \Delta E_g \]
Why is the experimental gap so stable?

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\[
\Delta u \rightarrow \Delta E_g \rightarrow \Delta H_f(V_{Cu}) \rightarrow \Delta[V_{Cu}]
\]

\[
E_g = 1.6663 + 0.231 \times \ln \left( \frac{[V_{Cu}]}{N_{Cu}} \right)
\]

\[
E_g = -5.975 + 32.1 \times u
\]

\[
\Delta E_v^{scGW} = 2.1335 - 11.06 \times u
\]

\[
\Delta VBM \quad [\text{eV}]
\]
Why is the experimental gap so stable?

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

\[ \Delta u \rightarrow \Delta E_g \rightarrow \Delta H_f(V_{Cu}) \rightarrow \Delta [V_{Cu}] \]

- Experimental variation of \( u \) is 0.02 \( \Rightarrow \Delta E_g \approx 0.65 \text{ eV} \)
- Considering variations of \( u \) and \([V_{Cu}] \) \( \Rightarrow \Delta E_g \approx -0.04 \text{ eV} \)
Results and open problems

Band structures

What about hybrids and GGA+U bands?

Focus on the region around the gap: \( p-d \) hybridization

http://cms.mpi.univie.ac.at/vasp/
**Optical absorption of CuGaS$_2$**

- **Comparison RPA and model kernels**

![Graph showing comparison between TDLDA, GW-RPA, TDDFT dynamic LRC, and BSE with experimental data for CuGaS$_2$.](image)
Optical absorption of CuGaS$_2$

- Excitonic binding energy of about 0.05 eV
- Experimental optical gap at 2.5 eV
Interpretation of experiments is often not straightforward – many coupled effects!

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

A better starting point than LDA is absolutely necessary for d-electrons

- Self-consistent COHSEX+$G_0W_0$ gives a very good description of quasi-particle states
- Hybrid functionals are reasonably good, but still expensive
- GGA+U is not so good when there is hybridization of $p–d$ states, sometimes it can be the only possible compromise

In progress now:
- Absorption spectra for all compounds
- Defects using GGA+U and “improved” hybrid functionals
Thanks!

Thanks to all collaborators! Thank you!

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- Fabien Bruneval

http://www.etsf.eu
http://www.abinit.org
www.yambo-code.org