Electronic excitations in materials for photovoltaics
Self-consistent GW and Bethe-Salpeter equation

Silvana Botti

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2 LPMCN, CNRS-Université Lyon 1, France
3 European Theoretical Spectroscopy Facility

September 7, 2012 – Journée CFCAM
1. Cu-based absorbers for thin-film solar cells
2. Why do we need to go beyond standard DFT?
3. Examples of calculations
   - Stability of the CIGS band gap
   - Optical spectra of CIGS from Bethe-Salpeter
   - Engineering direct gap silicon
4. Conclusions and perspectives
Outline

1. Cu-based absorbers for thin-film solar cells
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devices have to fulfill 2 functions:

- Photogeneration of electron-hole pairs
- Separation of charges to generate a current

Würth Elektronik GmbH & Co.

**Efficiency = 13 %**

- Molybdenum back contact
- CIGS layer (p-type layer)
- CdS layer (n-type layer)
- ZnO:Al TCO contact
Chalcogenide thin-film solar cell

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**Cu(In,Ga)(S,Se)$_2$ (CIGS)**

- Optimal bandgap for high efficiency
- High optical absorption
- Self-doping with native defects
- Extraordinary stability under operating conditions

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\( \text{Cu}_2\text{ZnSn(S,Se)}_4 \) (CZTS)

- very similar electronic and optical properties
- only abundant and non-toxic elements

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Objectives

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

Cu-based absorbers are not simple sp compounds!
Find a compromise between accuracy and computational effort
Modeling electronic excitations in complex systems

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Theoretical approaches

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State-of-the-art of theory

<table>
<thead>
<tr>
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<th>Computational cost</th>
<th>Accuracy</th>
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<td>DFT + model U: corrects localization of ( d ) states, usually better gaps, reliability depends too much on the system</td>
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Band structures of kesterite Cu$_2$ZnSnS$_4$

SB, D. Kammerlander and M.A.L. Marques, APL 98, 241915 (2011)
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

However, these many-body approaches are computationally expensive!
Theoretical approaches

Green’s function and Hedin’s equations

Hedin’s equations should be solved self-consistently

\[ \Sigma = GW \]
\[ G = G_0 + G_0 \Sigma G \]
\[ P = GG \]
\[ W = v + vPW \]

Hedin’s equations should be solved self-consistently:

\[ \text{scCOHSEX} + G_0 W_0, \text{QPscGW} \]

http://www.abinit.org
http://cms.mpi.univie.ac.at/vasp/
http://www.yambo-code.org/

V. Faleev et al., PRL 93, 126406 (2004); Bruneval et al. PRB 74, 045102 (2006)
Self-energy: nonlocal, non-Hermitian, frequency dependent operator
It allows to obtain the Green’s function $G$ once that $G_0$ is known

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

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

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

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

L. Hedin, Phys. Rev. 139 (1965)
Perturbative GW: “best G, best W”

Kohn-Sham equation:

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

Quasiparticle equation:

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

Quasiparticle energies 1st order perturbative correction with \[ \Sigma = iGW \]:

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

Basic assumption: \[ \psi_{QP} \simeq \varphi_{KS} \]

Hybersten&Louie, PRB 34 (1986); Godby, Schlüter&Sham, PRB 37 (1988)
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Kohn-Sham equation:

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

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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, Rödl et al. 2009)

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! (Marques et al. 2011)

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COHSEX: approximation to GW self-energy

Statically screened exchange:

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

Induced classical potential due to an extra point charge:

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

Technical problem: convergence with bands

- GW codes usually 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 gaps.
- Using a value of 9.5 Ha, we could do our calculations using only 200 bands for CuInO$_2$.

F. Bruneval and X. Gonze, PRB 78, 085125 (2008)
A. Berger, L. Reining and F. Sottile, PRB 82, 041103(R) (2010)
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Anion displacement of CuInS$_2$

Body-centered tetragonal cell

The anion displacement $u$ defines the position of the anion (S,Se) in the conventional cell:

$$u = \frac{1}{4} + \frac{1}{a^2} \left( R_{\text{Cu-(S,Se)}}^2 - R_{\text{In,Ga-(S,Se)}}^2 \right)$$

$$u \neq \frac{1}{4}$$
Anion displacement of CuInS$_2$

Experiments:
large dispersion of values of $u$

Theory:
even larger dispersion!

Hybrids and GGA+U in experimental range

Dependence of the gap on $u$

The self-consistent screening is the essential ingredient to describe the variation of the gap.

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:

\[ E_{xc} = aE_{Fock}[\varphi_i] + (1 - a)E_{DFT}[n] \]

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

\[ v_{xc}(r, r') = a v_{Fock}(r, r') + (1 - a) v_{DFT}(r) \]
What is the mixing parameter?

Let us look at the quasi-particle equation:

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

**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**

$$\Sigma = - \sum_{i}^{\text{OCC}} \phi_{i}^{\text{QP}}(r) \phi_{i}^{\text{QP}}(r') a \nu(r - r') + \delta(r - r')(1 - a) \nu_{\text{DFT}}(r)$$

$$\implies a \sim \frac{1}{\epsilon_{\infty}}$$
Examples of calculations

Stability of the CIGS band gap

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

Optimal mixing obtained with a PBE0 form.
Examples of calculations

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

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

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

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

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

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<th>PBE</th>
<th>HF+c</th>
<th>PBE0</th>
<th>PBE0(\epsilon_{\infty})</th>
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Other properties (structural, band dispersions, etc.)?

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Electronic excitations & photovoltaics
Density-based mixing for hybrids

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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- 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
Examples of calculations

Stability of the CIGS band gap

Measurements of band gap in Cu-poor CuInSe$_2$

**Experiments:**
the band gap decreases slightly for Cu/In < 1

**Theory:**
the band gap increases when [$V_{Cu}$] increases

What are we missing? Structural variations!

The feedback loop model can explain the stability of the band gap:

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

J. Vidal, SB, P. Olsson, J-F. Guillemoles, L. Reining, PRL 104, 056401 (2010);
What are we missing? Structural variations!

$$\Delta E_g(u, [V_{Cu}]) = \left\{ \frac{\partial E_g}{\partial [V_{Cu}]} + \frac{\partial E_g}{\partial u} \frac{\partial u}{\partial [V_{Cu}]} \right\} \Delta [V_{Cu}]$$

We extract the partial derivatives from *ab initio* calculations for the primitive cell and 15–, 32–, 63–atom supercells:

For $0.95 < \text{Cu/In} < 1$ (experimental range):

- Considering only the variation of $[V_{Cu}] \Rightarrow \Delta E_g \approx 0.13 \text{ eV}$
- Considering variations of $u$ and $[V_{Cu}] \Rightarrow \Delta E_g \approx -0.03 \text{ eV}$

J. Vidal, SB, P. Olsson, J-F. Guillemoles, L. Reining, PRL 104, 056401 (2010);
Examples of calculations

**Bethe-Salpeter equation: electron-hole interaction**

Absorption can be obtained from the 4-point reducible polarizability $L$:

$$
\epsilon_M = 1 - \lim_{q \to 0} \nu(q) \lambda \int dr dr' e^{-i\mathbf{q} \cdot (\mathbf{r} - \mathbf{r'})} L(\mathbf{r}, \mathbf{r'}, \mathbf{r'}, \mathbf{r'}; \omega)
$$

that satisfies the **Bethe-Salpeter equation (BSE)**

\[
L = L_0 + L_0 \left( 4 \bar{\nu} - 4 \bar{W} \right) L
\]

with \(4 \bar{\nu}(1, 2, 3, 4) = \delta(1, 2)\delta(3, 4)\bar{\nu}(1, 3)\) and \(4 \bar{W}(1, 2, 3, 4) = \delta(1, 3)\delta(2, 4)W(1, 2)\)

The **ingredients** are:

- Kohn-Sham or quasiparticle states
- (sc)GW corrected energies
- RPA screening matrix \(\varepsilon_{GG'}^{-1}(\mathbf{q})\)

Salpeter and Bethe, Phys. Rev. **84**, 1232 (1951)
Examples of calculations
Optical spectra of CIGS from Bethe-Salpeter

Bethe-Salpeter equation: electron-hole interaction

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$$

that satisfies the Bethe-Salpeter equation (BSE)

![](rapidly_varying_eq.png)

with $^4\bar{\nu}(1, 2, 3, 4) = \delta(1, 2)\delta(3, 4)\bar{\nu}(1, 3)$ and $^4W(1, 2, 3, 4) = \delta(1, 3)\delta(2, 4)W(1, 2)$

The ingredients are:

- Kohn-Sham or quasiparticle states
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- RPA screening matrix $\varepsilon_{GG'}^{-1}(\mathbf{q})$

Salpeter and Bethe, Phys. Rev. 84, 1232 (1951)
Optical absorption of CuGaSe$_2$

Need for **speed-up** in solving Bethe-Salpeter equation: we use a **double-grid method** using **Wannier interpolation**

New low-energy sp$^3$ phases of silicon

Structural search using minima hopping method (MHM)

- R8 and BC8 phases observed and calculated
- Si-VIII, Si-IX, Si-XIII observed but not yet fully characterized
- BCT, ST12, Ibam predicted in literature

Minima hopping method

The system is moved from one configuration to the next by consecutive molecular dynamics escape steps and geometry relaxations.

- Initial velocities for dynamics are aligned along soft-mode directions to favor the escape to low-enthalpy configurations.
- Revisiting already known structures is avoided by a feedback mechanism.

New low-energy sp$^3$ phases of silicon

- P2/m
- Cmcm
- C222$_1$
- P2$_1$/c
- Imma
- P-1
Examples of calculations  Engineering direct gap silicon

Optical absorption of the new phases

- strong absorption in the visible
- indirect band gaps of more than 1 eV
- absorbed irradiance close to CIGS

Conclusions and perspectives

Outline

1. Cu-based absorbers for thin-film solar cells
2. Why do we need to go beyond standard DFT?
3. Examples of calculations
4. Conclusions and perspectives
Interpretation of experiments is not straightforward – coupled effects!

Methods beyond ground-state DFT are well established and absolutely necessary for systems with d-electrons.

Improvement of efficiency of scGW + BSE calculations.

New frontiers: structural search to design better materials and study phase diagrams with minima hopping method.
Thanks!

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