From band structures to thermoelectric properties
using state-of-the-art *ab initio* methods

Silvana Botti

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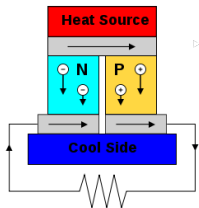[2]European Theoretical Spectroscopy Facility

December 6, 2012 – Lyon

Outline

Thermoelectric power generation

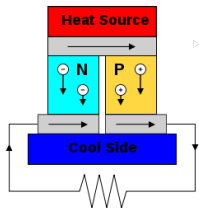Seebeck effect: converts temperature differences in electric voltages

$$\text{Seebeck coefficient } S = \frac{\Delta V}{\Delta T}$$

Thermoelectric power generation

Seebeck effect: converts temperature differences in electric voltages

Seebeck coefficient $S = \frac{\Delta V}{\Delta T}$

Thermoelectric power generation

Seebeck effect: converts temperature differences in electric voltages

Efficiency ($< 10 - 15\%$)

$$\eta_{\max} = \frac{T_{\text{hot}} - T_{\text{cold}}}{T_{\text{hot}}} \frac{\sqrt{1 + Z\bar{T}} - 1}{\sqrt{1 + Z\bar{T}} + \frac{T_{\text{cold}}}{T_{\text{hot}}}}$$

Figure of merit:

$$Z\bar{T} = \frac{(S_p - S_n)^2 \bar{T}}{[(\rho_p \kappa_p)^{1/2} + (\rho_n \kappa_n)^{1/2}]^2}$$

Seebeck coefficient $S = \frac{\Delta V}{\Delta T}$

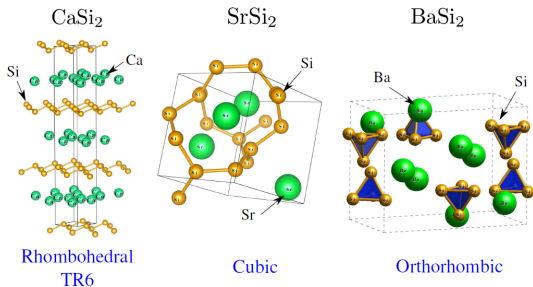Large $Z\bar{T}$ are needed for high efficiency
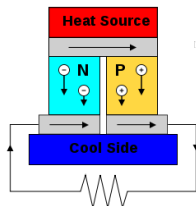
Electronic terms of the figure of merit

Objectives

- Predict accurate values for thermoelectric properties
- Deal with complexity (large cells, doping, nanostructuring, …)

$\Rightarrow$ Find efficient, cheap and environment-friendly new thermoelectrics!

$CaSi_2$ $SrSi_2$ $BaSi_2$

Rhombohedral   Cubic   Orthorhombic
TR6

Boltzmann theory of transport

Within linear response:

$$j_i = \sigma_{ij} E_j$$

The conductivity tensor is

$$\sigma_{ij} = \frac{1}{4\pi^3} \sum_n \int \tau_{n,\mathbf{k}} v_i(n, \mathbf{k}) v_j(n, \mathbf{k}) \left(-\frac{\partial f(n, \mathbf{k}, T)}{\partial E(\mathbf{k})} \right) d\mathbf{k}$$

in terms of the group velocity and the relaxation time

The group velocity is given by the dispersion of the bands

Constant relaxation time approximation: τ

- S is independent on τ
- σ is proportional to τ

Kohn-Sham band structure

Kohn-Sham (KS) equations

$$\left[-\frac{\nabla^2}{2} + v_{\text{KS}}\left(\boldsymbol{r}\right) \right] \varphi_i^{\text{KS}}\left(\boldsymbol{r}\right) = \varepsilon_i^{\text{KS}} \varphi_i^{\text{KS}}\left(\boldsymbol{r}\right)$$

$$\rho\left(\boldsymbol{r}\right) = \sum_i^{\text{occ.}} |\varphi_i^{\text{KS}}\left(\boldsymbol{r}\right)|^2$$

- It is common to interpret the solutions of the Kohn-Sham equations as one-electron states
- Often one obtains good band dispersions but band gaps are systematically underestimated
- Sometimes one gets bad band dispersions and band gaps!
- This happens, e.g., when there are localized d or f states

📄 W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

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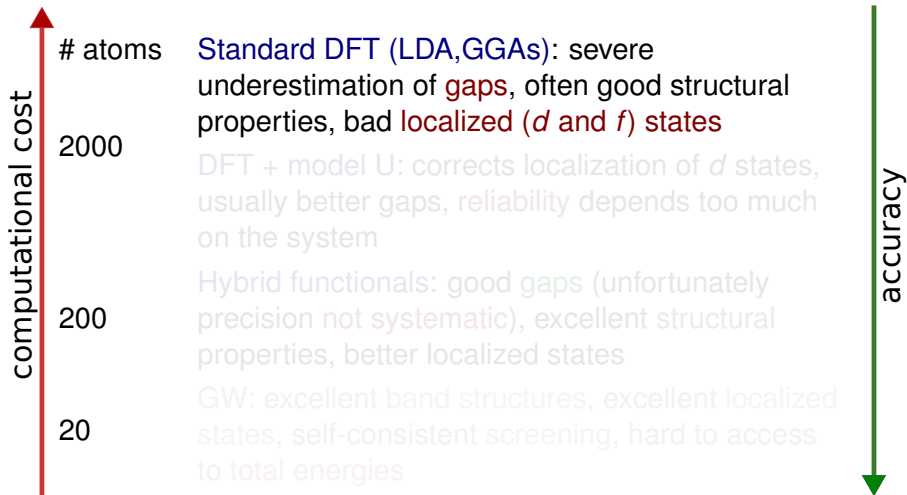
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State-of-the-art of theory

computational cost →

atoms

Standard DFT (LDA,GGAs): severe underestimation of gaps, often good structural properties, bad localized (*d* and *f*) states

2000

DFT + model U: corrects localization of *d* states, usually better gaps, reliability depends too much on the system

200

Hybrid functionals: good gaps (unfortunately precision not systematic), excellent structural properties, better localized states

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GW: excellent band structures, excellent localized states, self-consistent screening, hard to access to total energies

accuracy →

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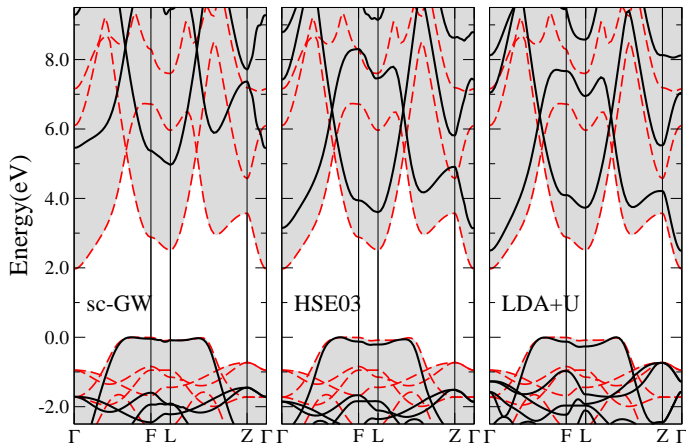
accuracy →

Comparative test: kesterite Cu_2ZnSnS_4
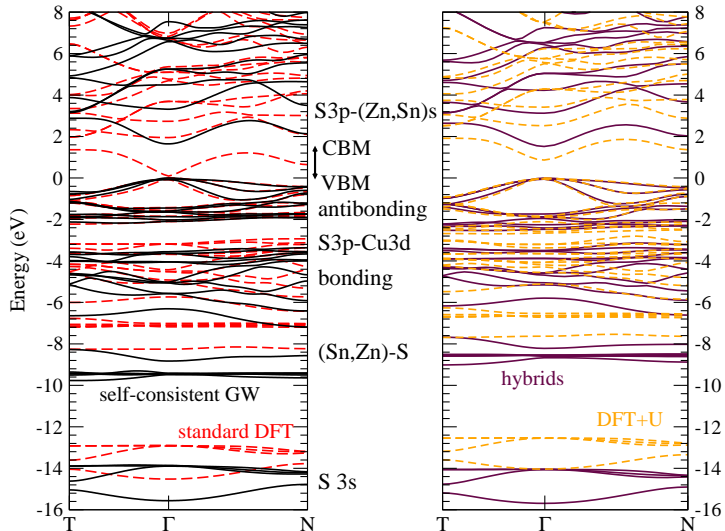
SB, D. Kammerlander and M.A.L. Marques, APL **98**, 241915 (2011)
C. Sevik and T. Çağin, PRB **82**, 045202 (2010)

Exploring new kesterites: Cu$_2$ZnGe(S,Se)$_4$

Cu$_2$ZnGeSe$_2$ kesterite
scGW gap (HSE geometry) = 1.44 eV
scGW gap (GGA geometry) = 0.91 eV
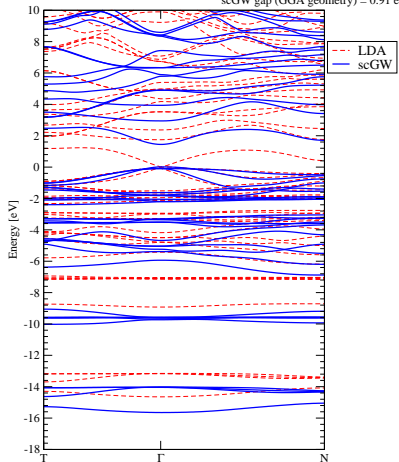
Cu$_2$ZnGeS$_2$ kesterite
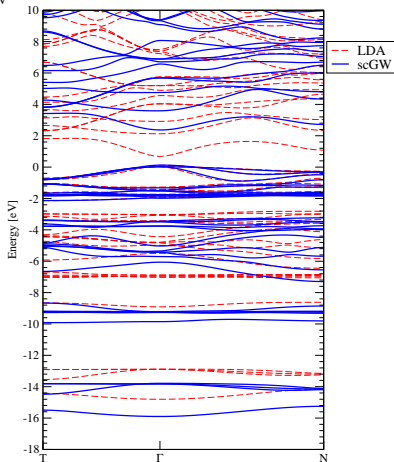
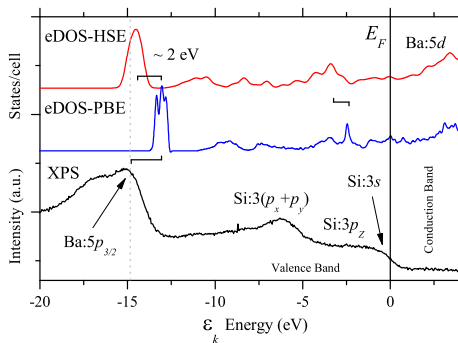# CuAlO$_2$ delafossite

Strong differences both in dispersion and energy gaps

J. Vidal, F. Trani, F. Bruneval, M.A.L. Marques, and S. Botti PRL **104**, 136401 (2010)

Quality of the density of states

- X-ray photoelectron spectroscopy (XPS) measured in $BaSi_2$
- Calculated electronic density of states using GGA-PBE and the hybrid functional HSE06

J. Flores-Livas, Ph.D. thesis, University of Lyon 1 (2012).

Seebeck coefficient

Electronic structure Fermi surface Thermopower

Substituted by

Ca

Sr

Ba
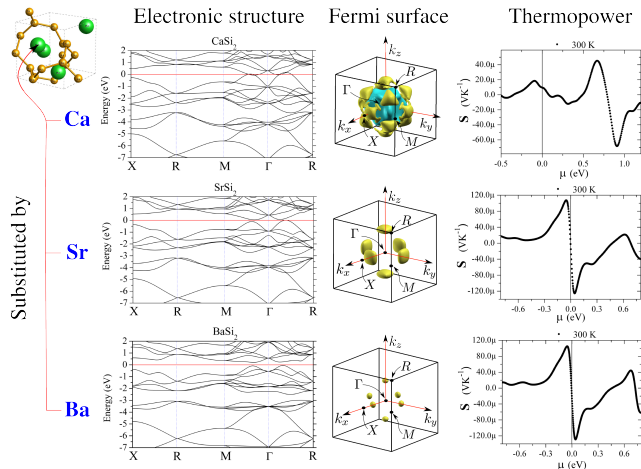
- GGA calculations
- orthorhombic $BaSi_2$ agrees with exp.
- S underestimated for $SrSi_2$ (metallic in GGA)

Conclusions and perspectives

In many cases the semi-classical theory of Boltzmann and the relaxation time approximation are reliable, provided that the band dispersions are good and the systems do not turn out metallic

Band-structure methods beyond ground-state DFT are well established and necessary for systems with d-states close to the Fermi energy

Hybrid functionals are often a reasonable compromise

Open problems:

- *ab initio* determination of the relaxation times
- *ab initio* determination of the thermal conductivity

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Thanks to all collaborators at LPMCN

- Miguel Marques, José Flores-Livas (theory)
- Stéphane Pailhés, Régis Debord, Valentina Giordano (experiments)

More information on our group home page:
`http://www.tddft.org/bmg/`

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