Self-Consistent *GW* Electronic Structure of Solids

Fabien Bruneval,
Nathalie Vast, and Lucia Reining

Laboratoire des Solides Irradiés, Ecole Polytechnique, Palaiseau, France
Dept. of Chemistry and Applied Biosciences, ETH-Zurich, Lugano, Switzerland

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Outline

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Density Functional Theory

Density Functional Theory (DFT) is the most used method for electronic calculations in solids.

$\longrightarrow$ Kohn-Sham equations introduce one-electron energies ϵ_i

$$\left[-\frac{\nabla^2}{2} + v_{\text{nuclei}}(\mathbf{r}) + \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + v_{xc}[\rho](\mathbf{r})\right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

Can we use the energies ϵ_i as a band structure ?

$\times$ No, for theoretical reasons

$\times$ No, for practical grounds

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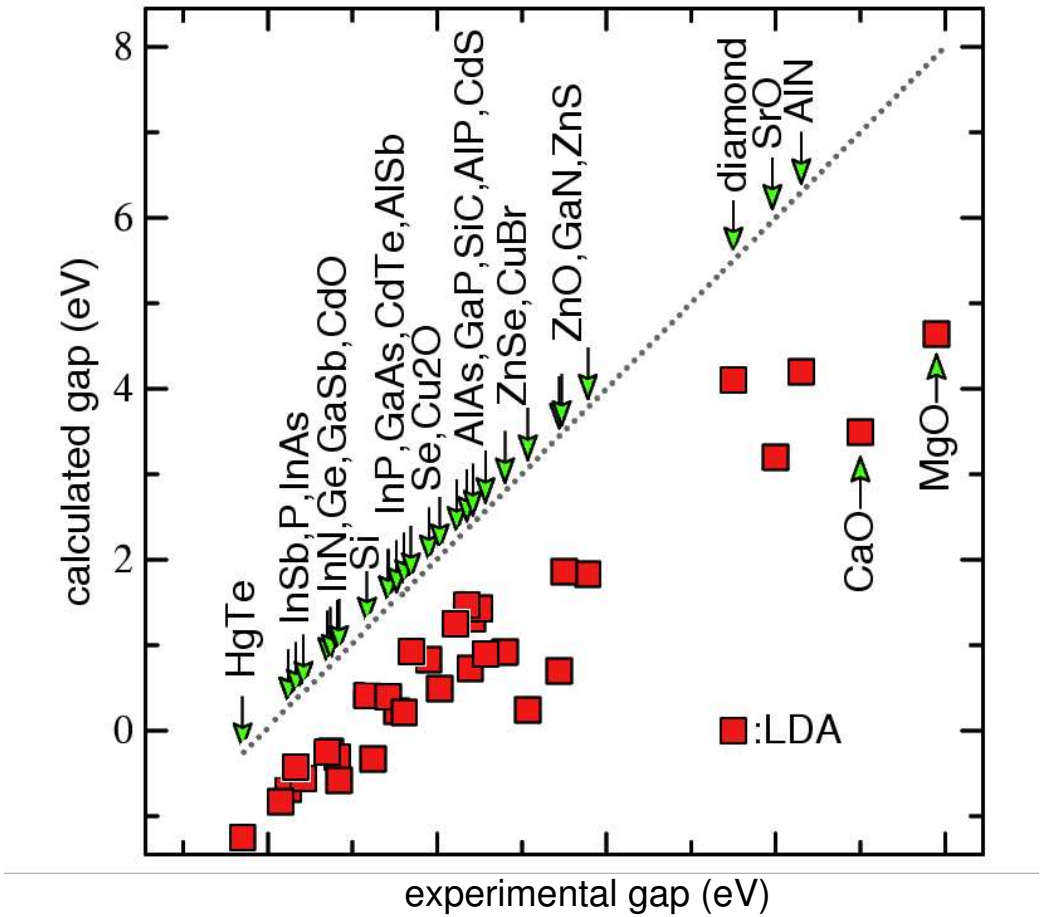
$\times$ No, for practical grounds

No! due to practical results

Band gaps of semiconductors



adapted from M. van Schilfgaarde *et al.*, PRL **96** 226402 (2006).

Electronic excitations through Green's functions

Alternative framework: **Green's function**

DFT Kohn-Sham

$$\rho(\mathbf{r})$$

$$\updownarrow$$

$$v_{xc}[\rho](\mathbf{r})$$

$$\downarrow$$

$$\epsilon_i^{\mathrm{KS}}$$

Green's functions

$$G(\mathbf{r}, \mathbf{r}', \omega)$$

$$\updownarrow$$

$$\Sigma_{xc}[G](\mathbf{r}, \mathbf{r}', \omega)$$

$$\downarrow$$

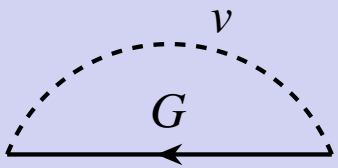
$$\epsilon_i^{\mathrm{QP}}$$

Approximations for the self-energy

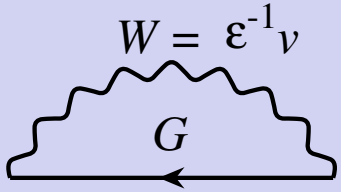
Systematic way to produce approximated Σ:

- Feynman diagrams
- Hedin's equations (1965).

Hartree-Fock Approximation

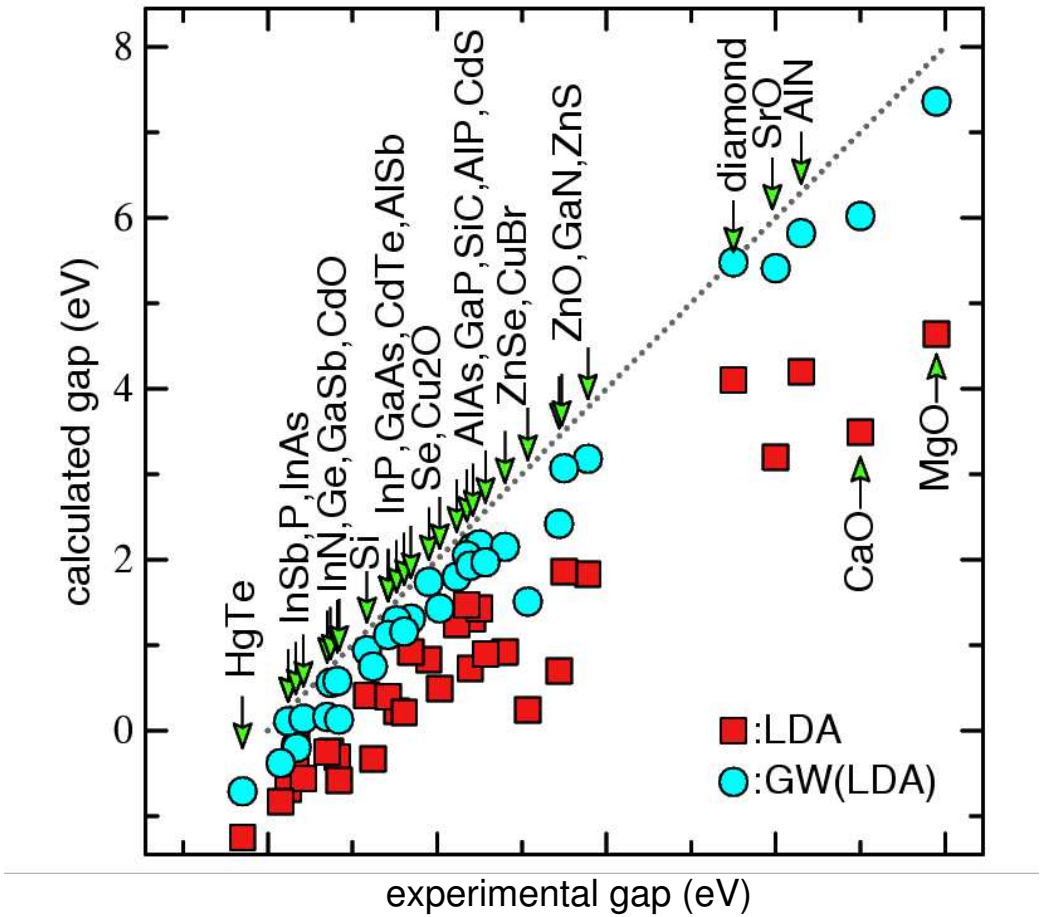
$\Sigma =$ 

GW Approximation

$\Sigma =$ 

Yes! *GW* band gaps

Band gaps of semiconductors



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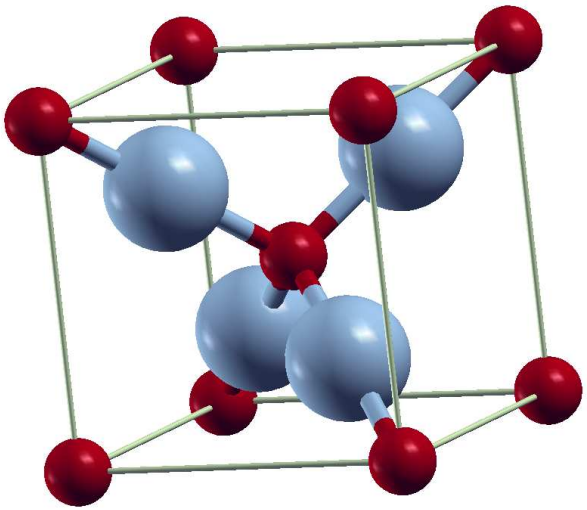
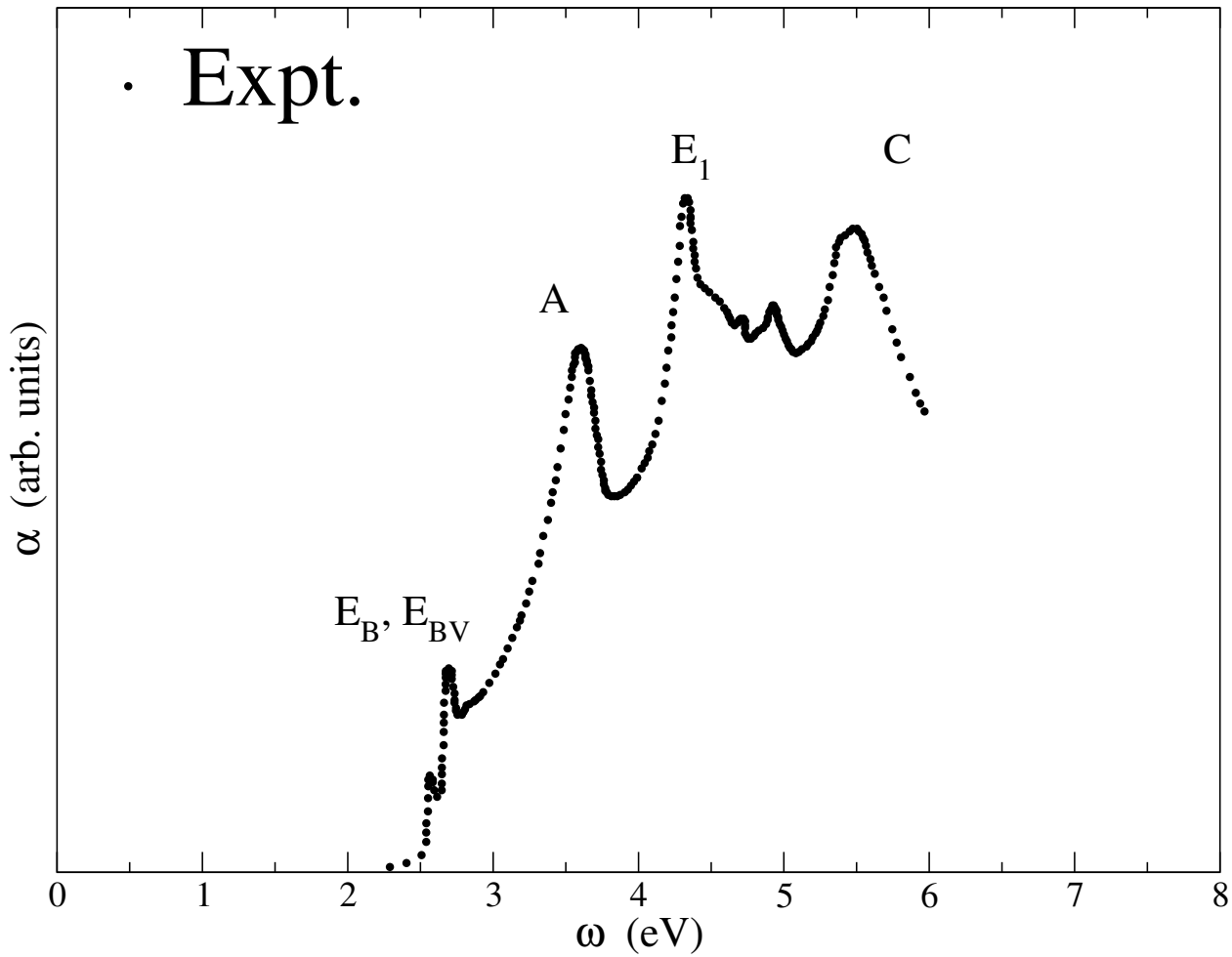
Cuprous oxide Cu_2O: a simple solid?



- Cu $3d^{10}$ shell
- semiconductor
- non-magnetic

Optical Absorption



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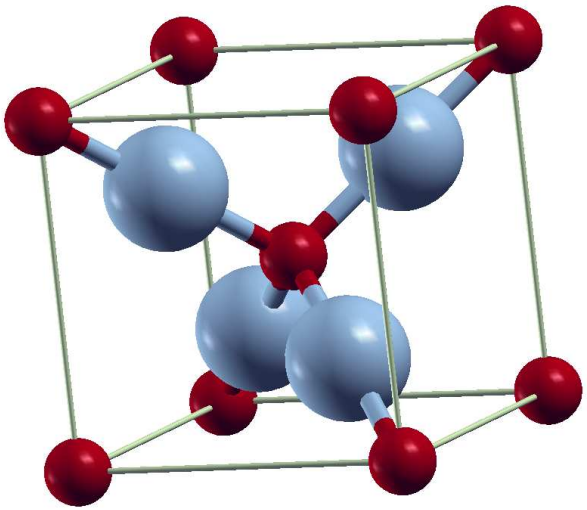

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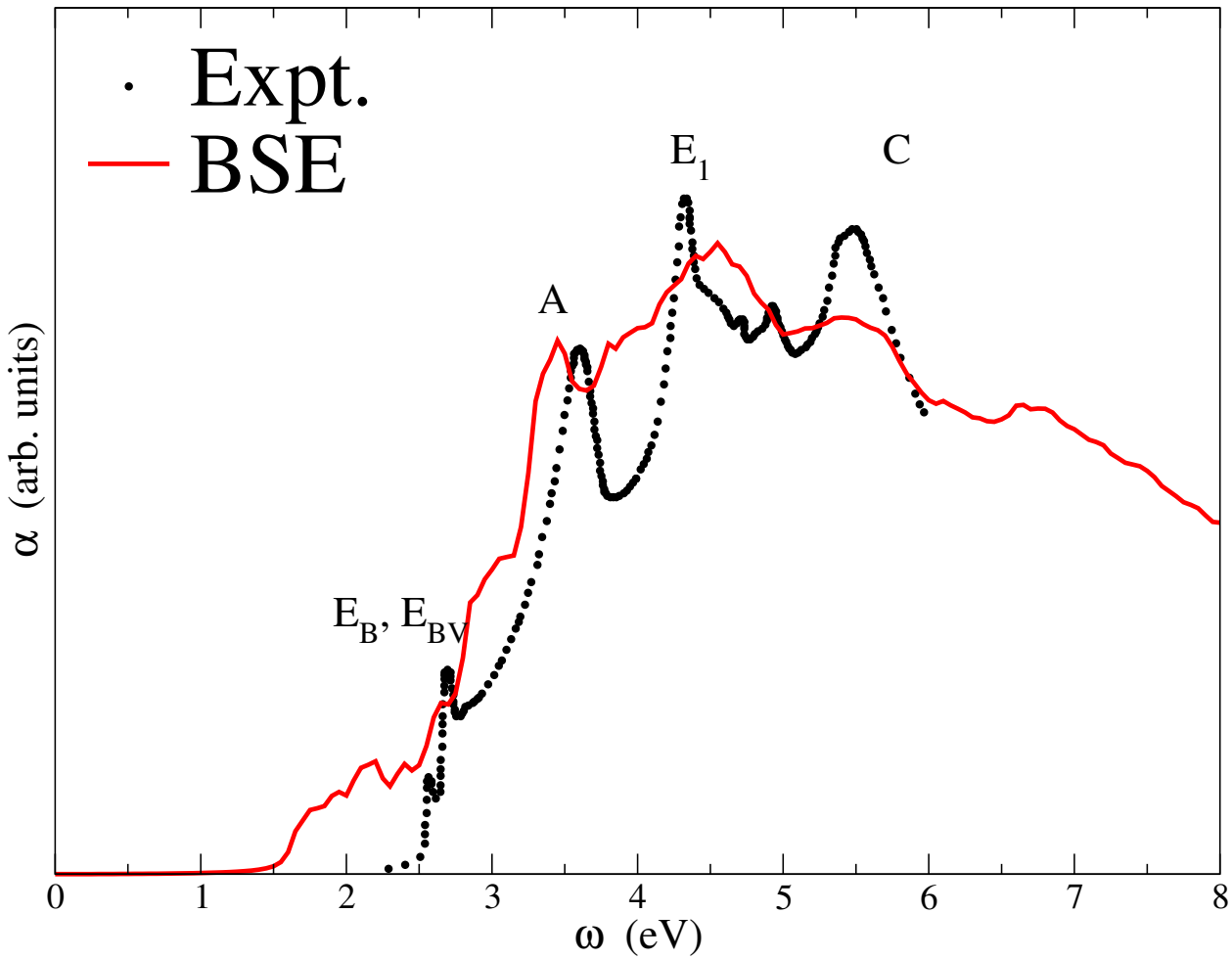

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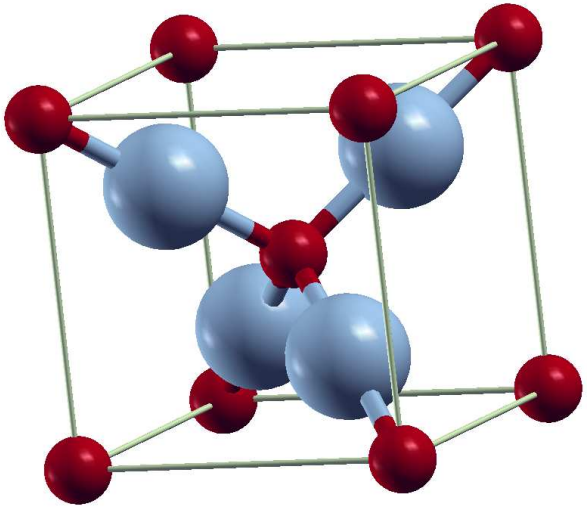
Cu_2O goes wrong!



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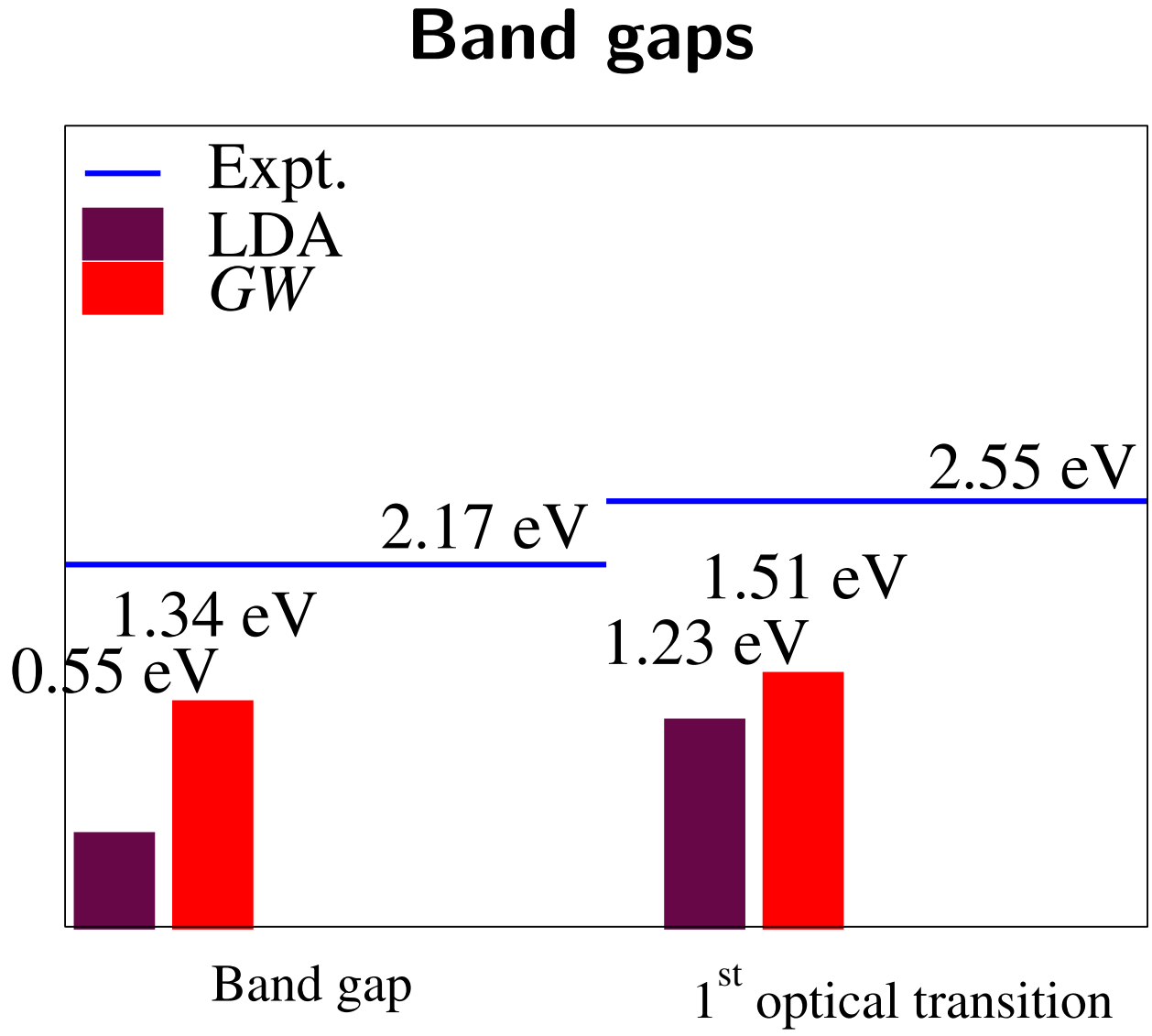
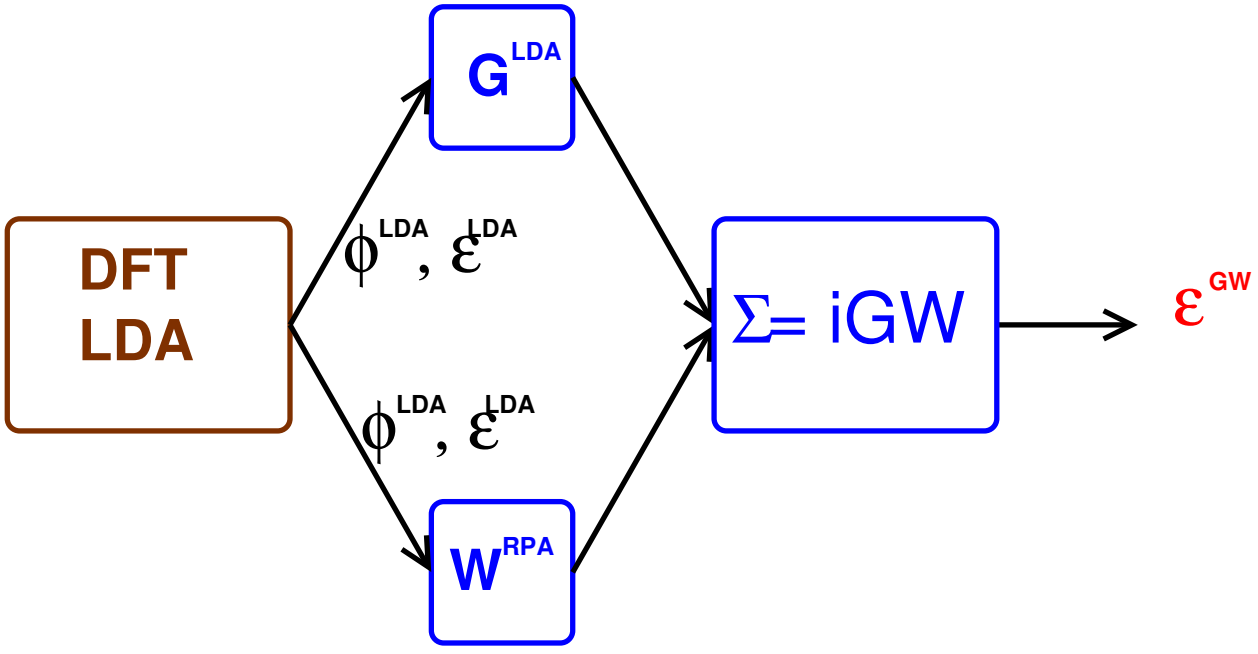


Ingredients of the *GW* calculation

Since the mid-80's,



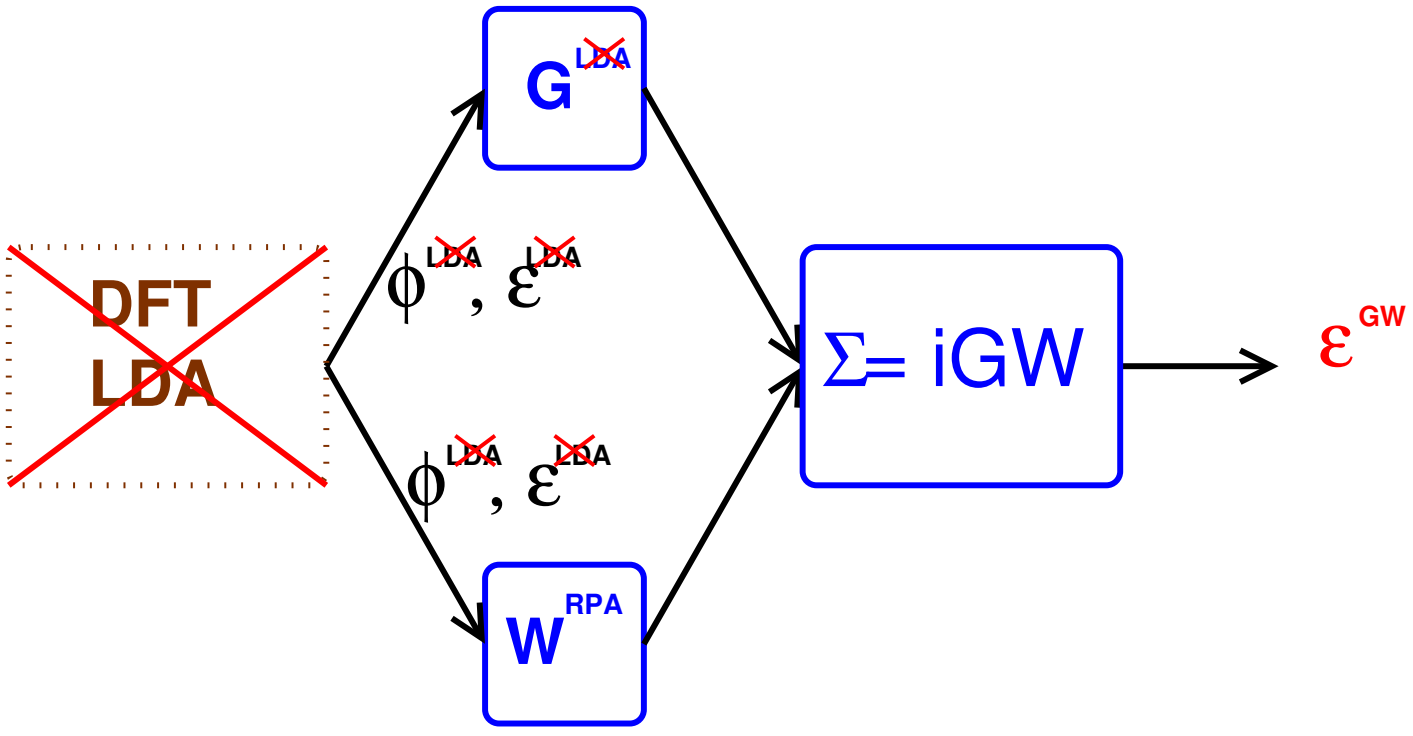
Hypothesis :

$\phi^{\text{LDA}} \approx \phi^{GW}$

$\epsilon^{\text{LDA}} \approx \epsilon^{GW}$

Getting rid of LDA

Looking for a better starting point



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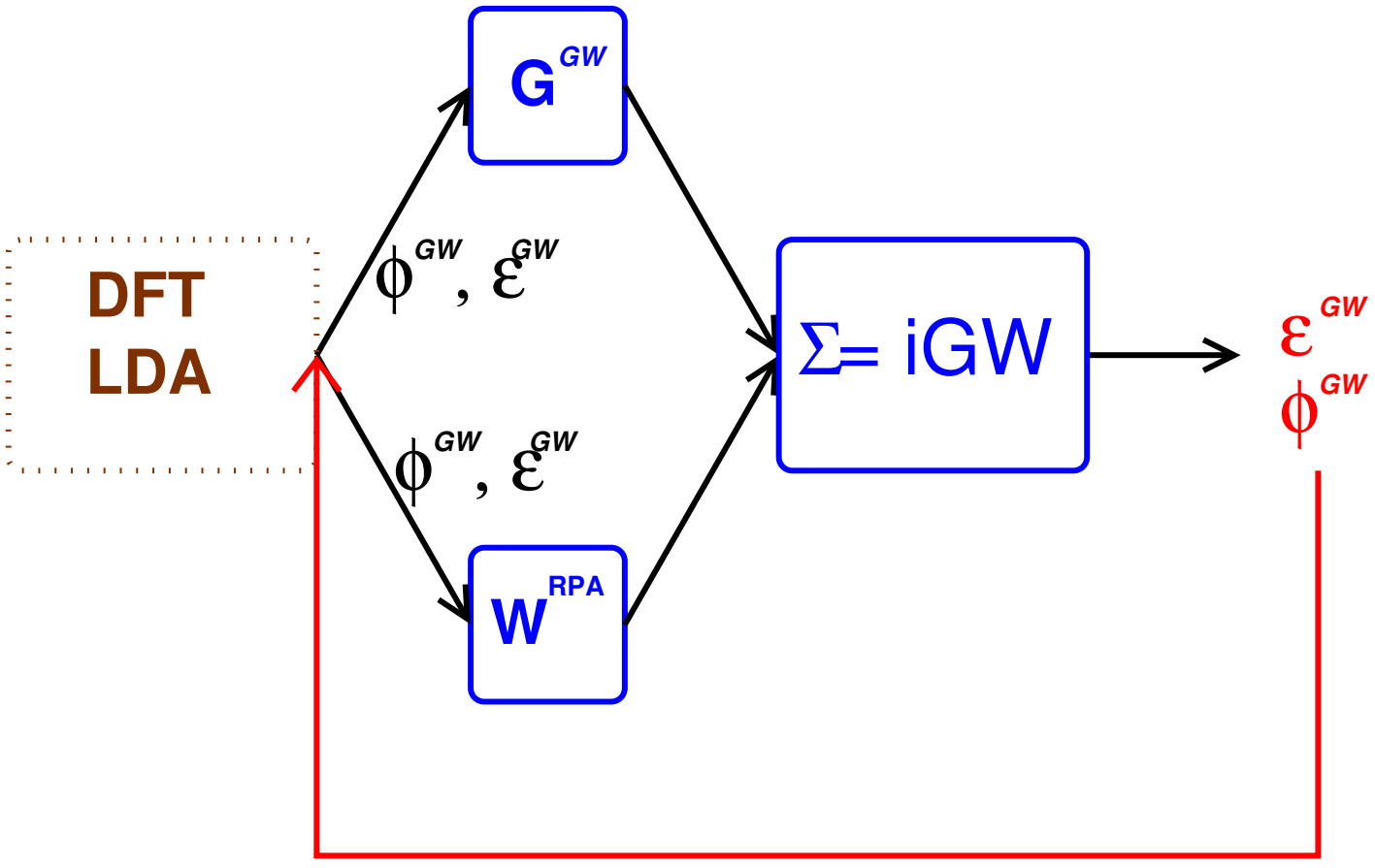
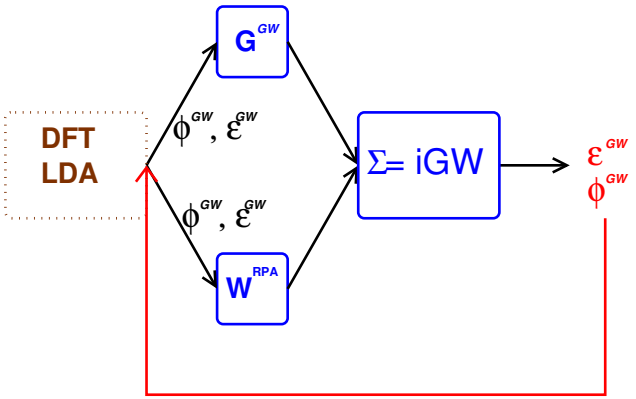


Outline

Quasiparticle self-consistent *GW*



based on Faleev, van Schilfgaarde and Kotani, PRL **93**, 126406 (2004).

In principle,

$$\langle \phi_i | \Sigma(\epsilon_j^{GW}) | \phi_j \rangle$$

Approximation:

$$\frac{1}{2} \Re \left[\langle \phi_i | \Sigma^{GW}(\epsilon_i^{GW}) | \phi_j \rangle + \langle \phi_i | \Sigma^{GW}(\epsilon_j^{GW}) | \phi_j \rangle \right]$$

$\longrightarrow$ **orthogonal** wavefunctions

LDA states as a basis set?

$$|\phi^{GW}_{\mathbf{k}i}\rangle = \sum_{j=1}^{N} c_{\mathbf{k}ij} |\phi^{\mathrm{LDA}}_{\mathbf{k}j}\rangle$$

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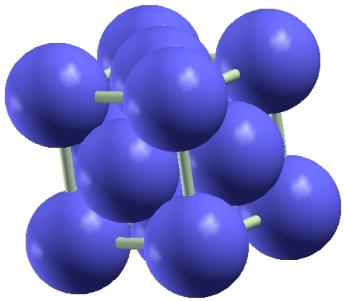
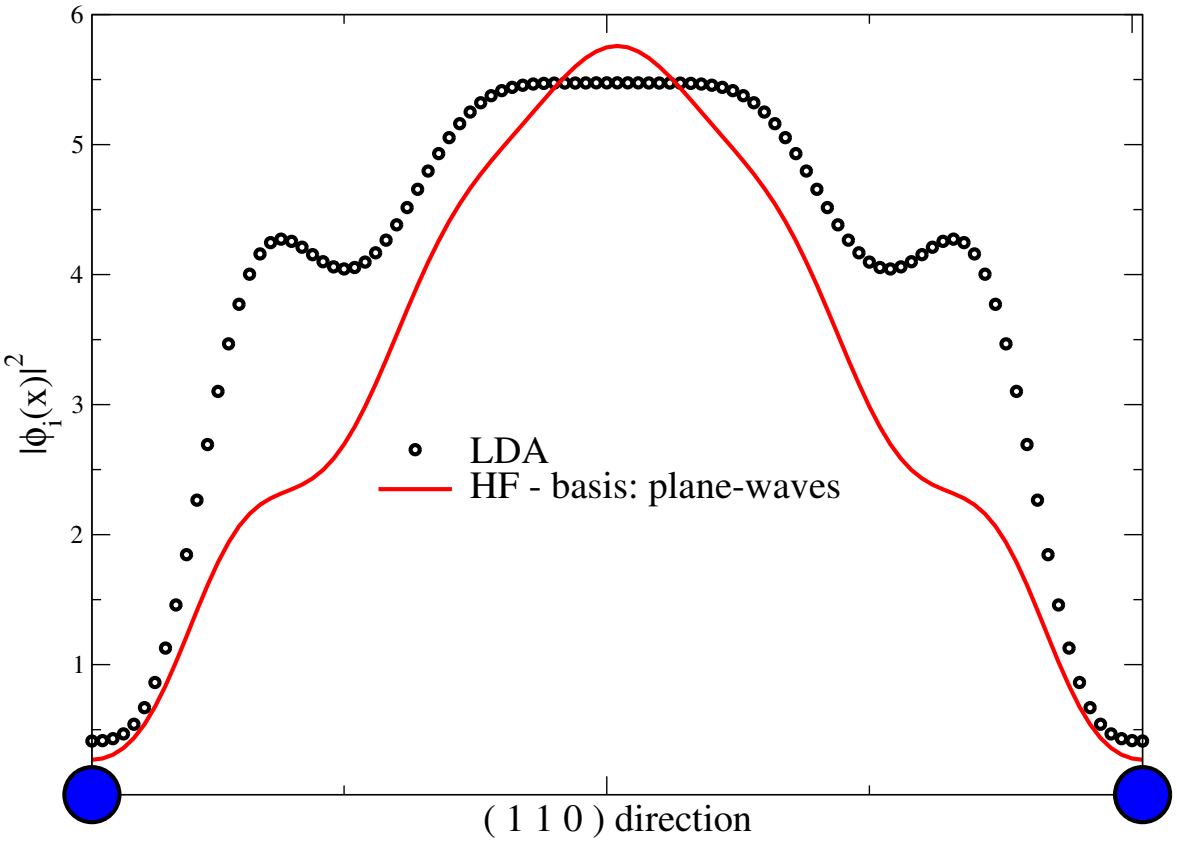
A conduction band within Hartree-Fock in Solid argon





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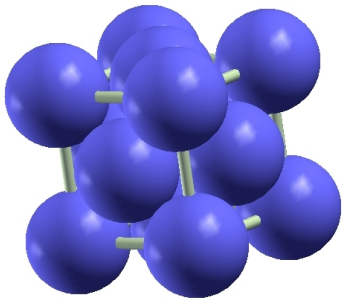

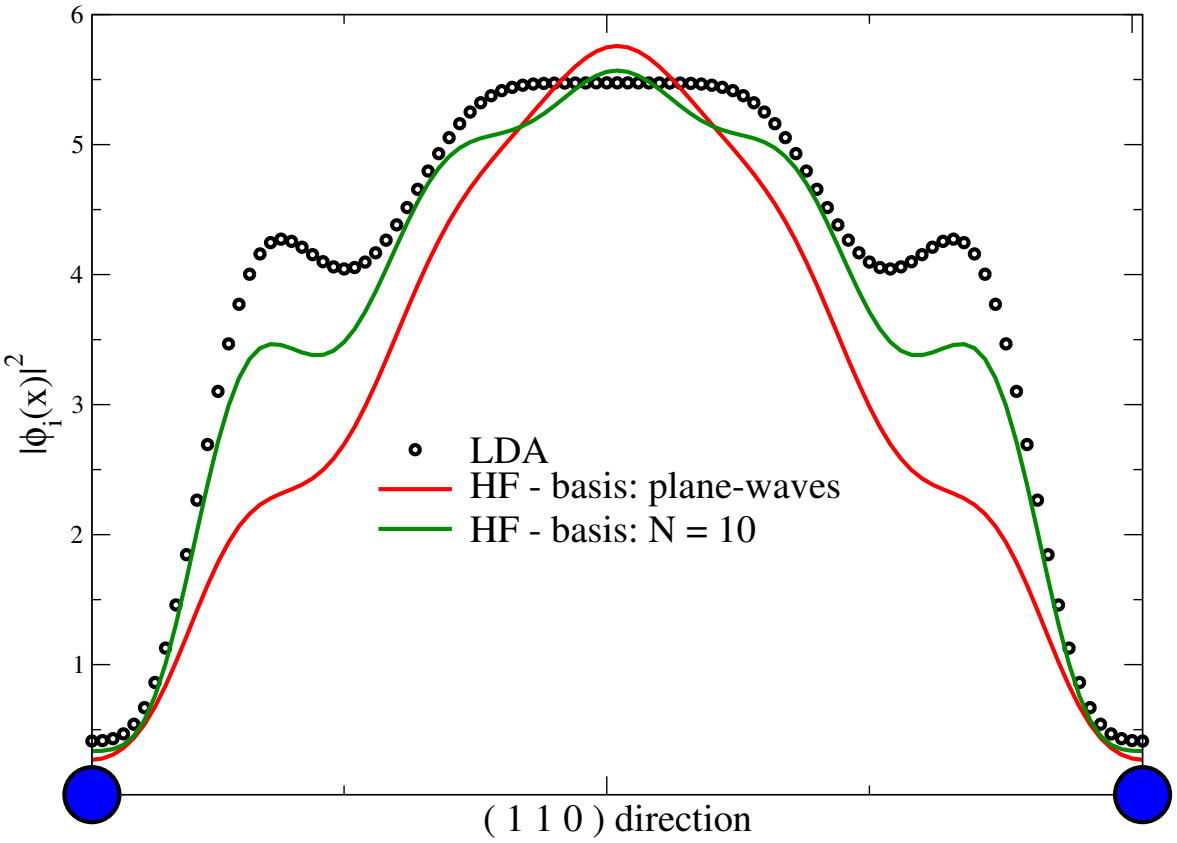

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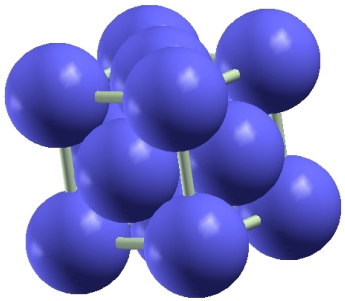
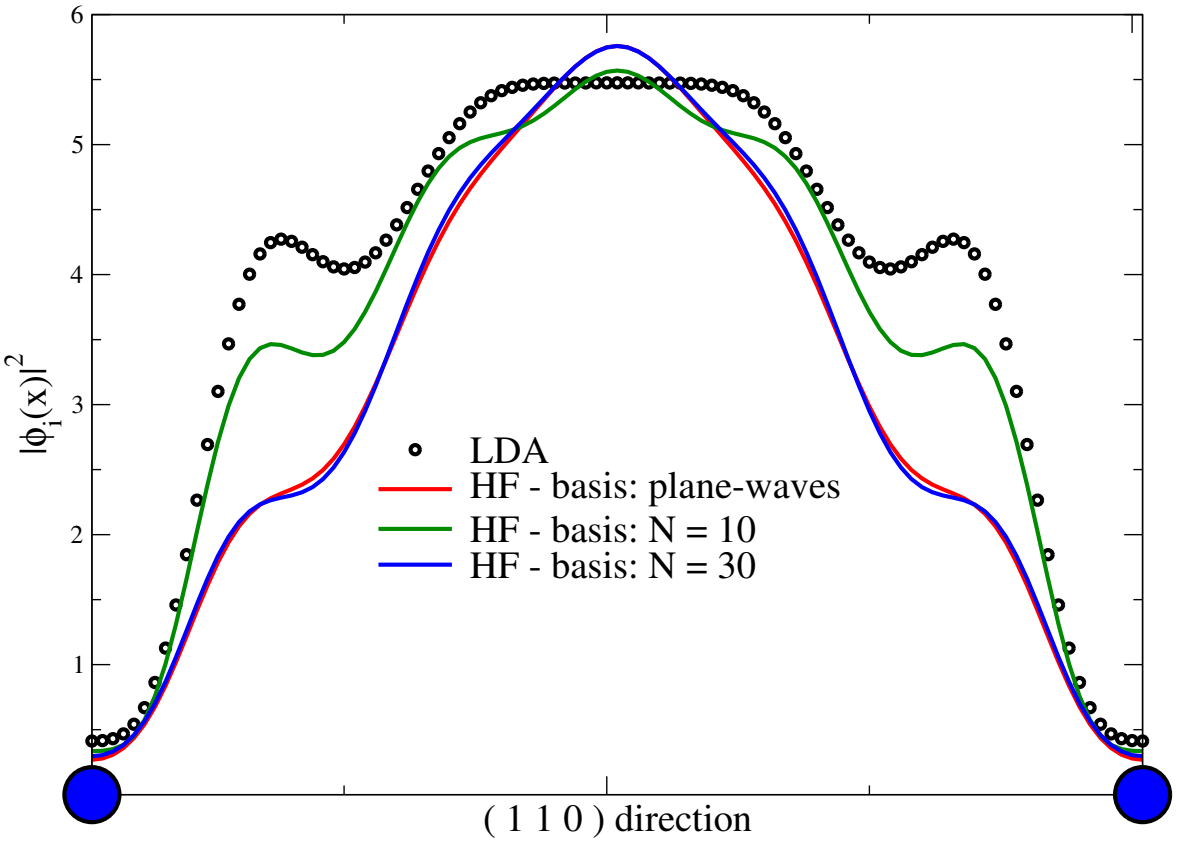
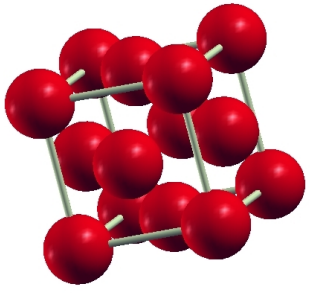
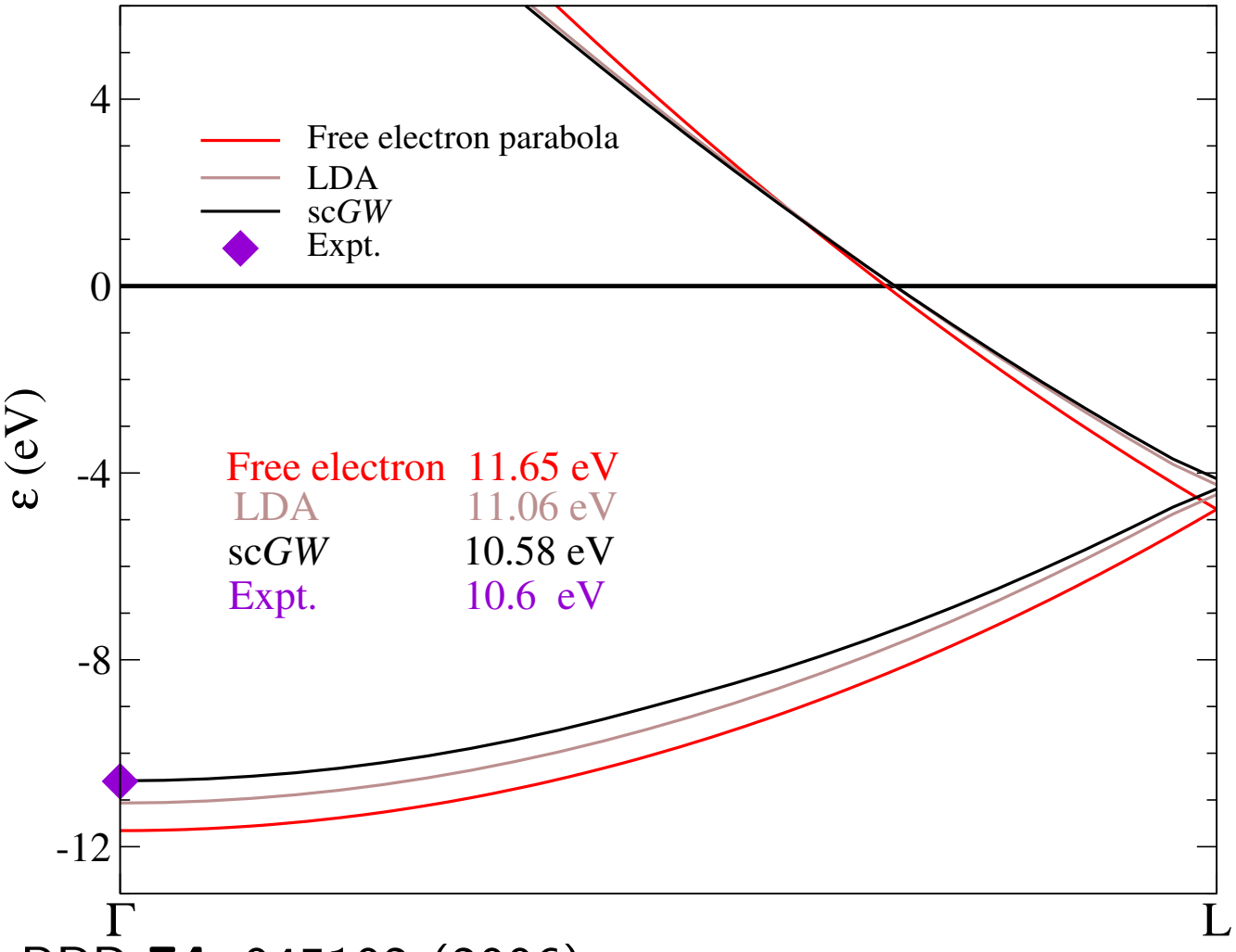




Band width of a simple metal

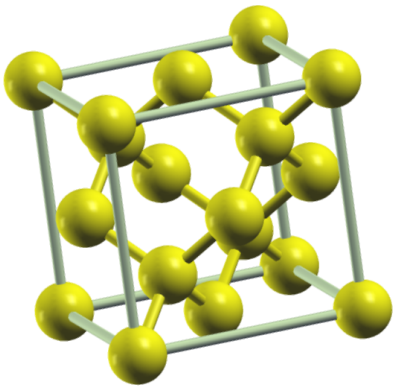
Aluminum



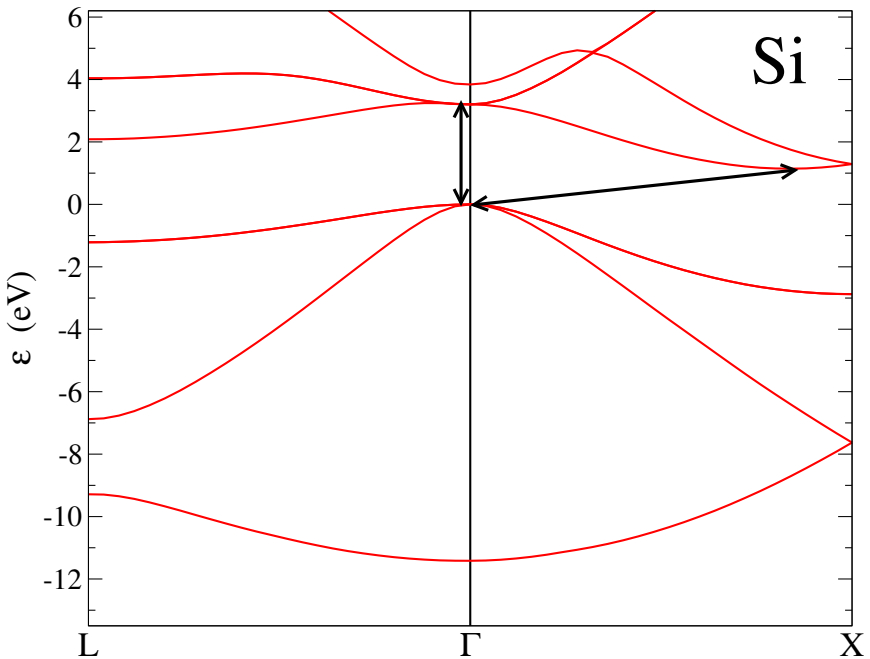


F. Bruneval *et al.* PRB **74**, 045102 (2006).

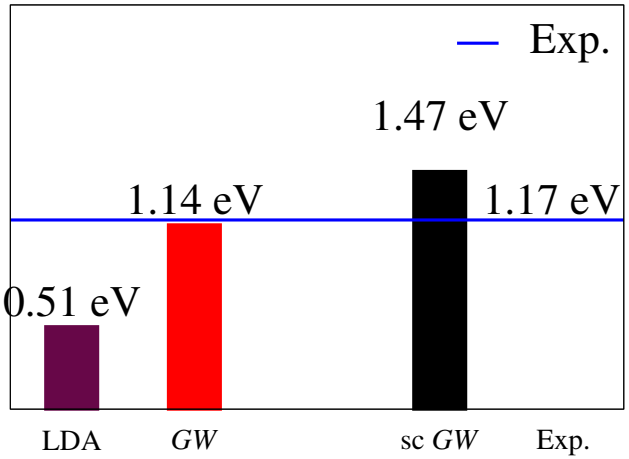
Band gap of a semiconductor



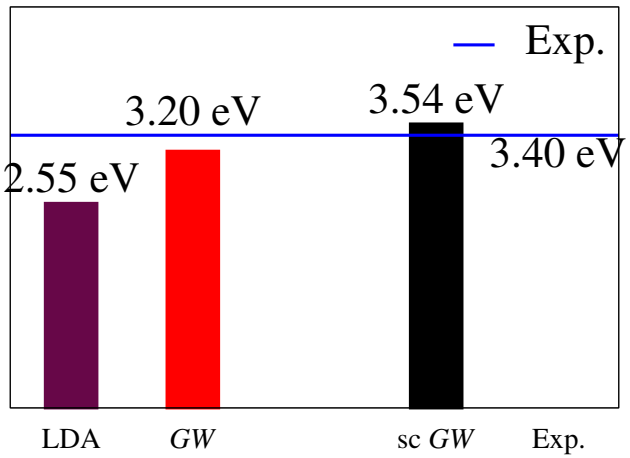
Silicon



Band gap

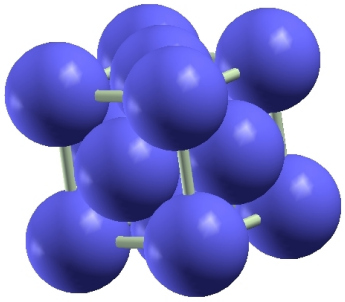


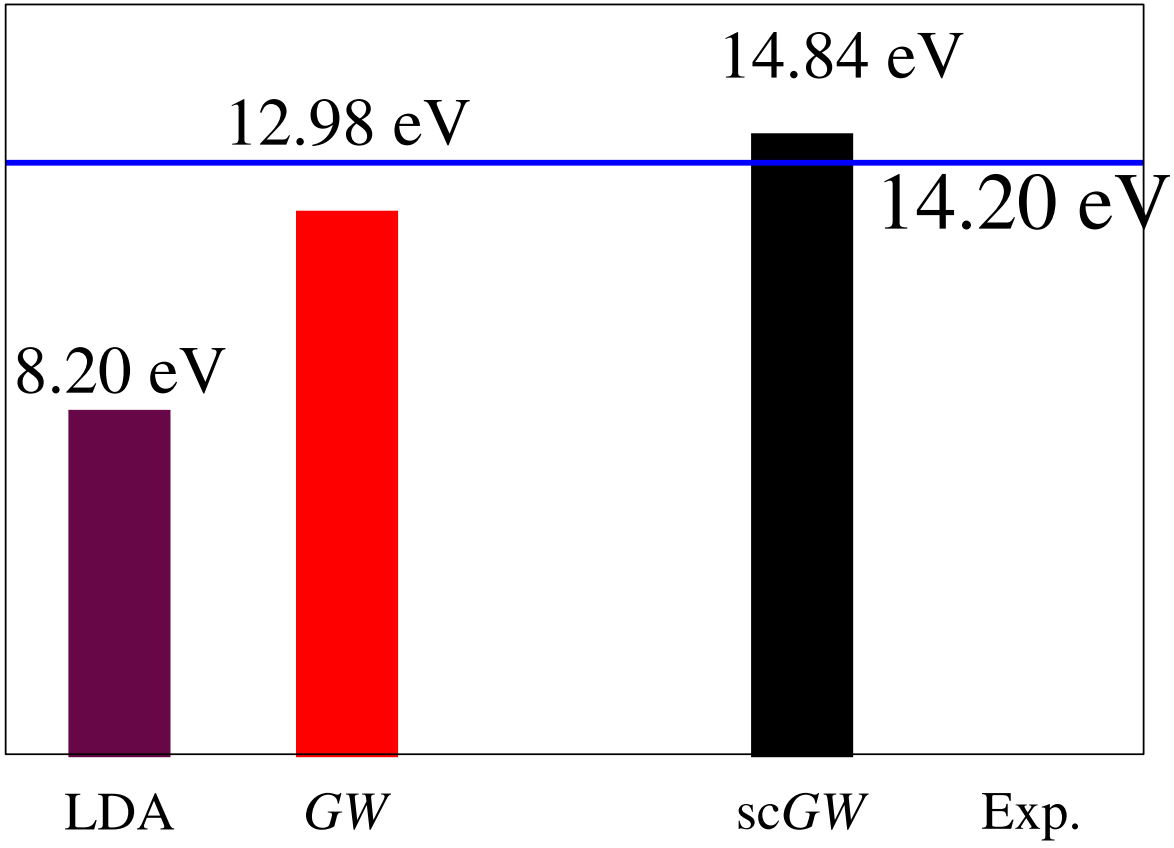
Band gap at Γ



Band gap of an insulator

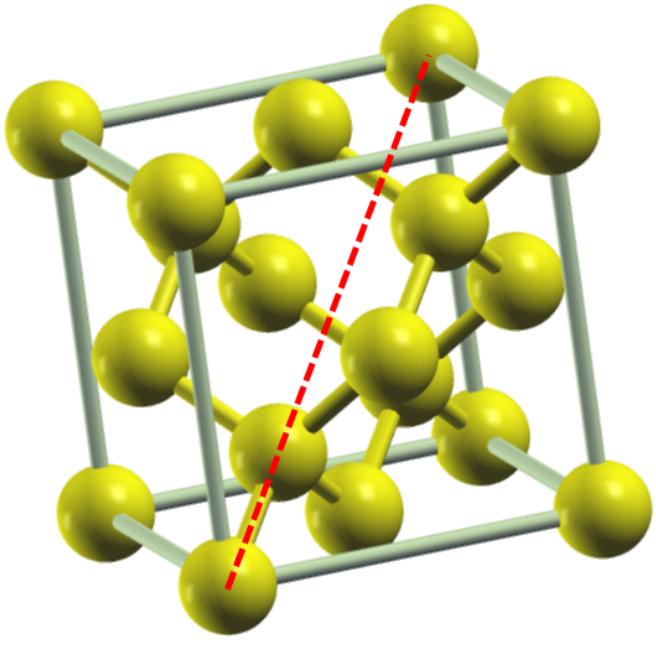
Solid argon



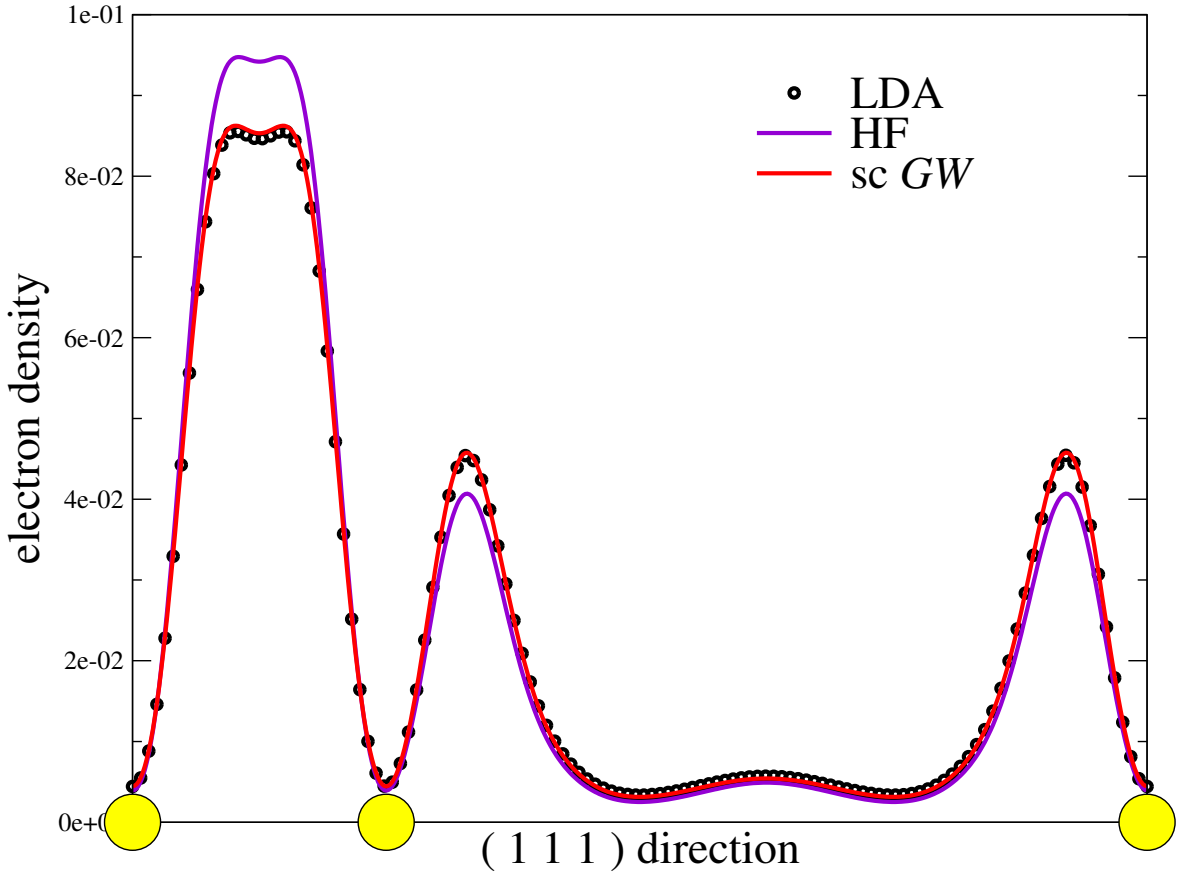


Density and wavefunctions

Bulk silicon



Electronic density

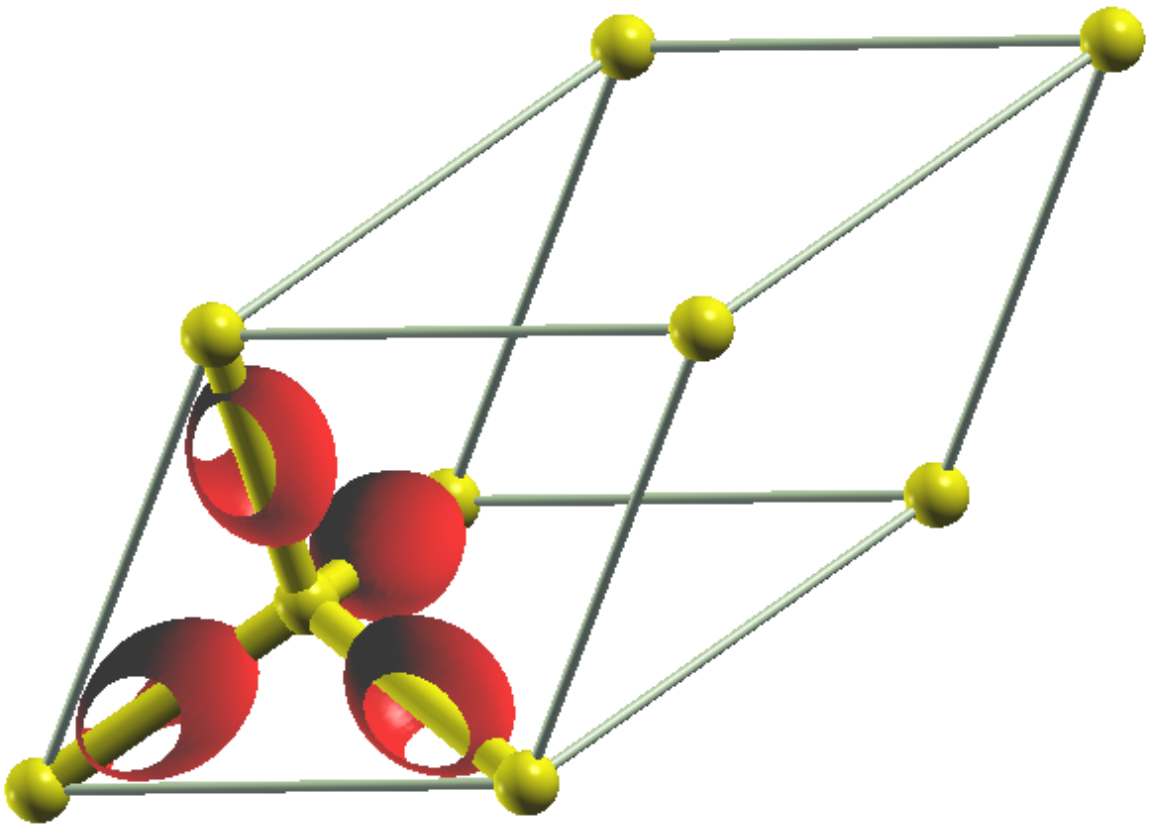


F. Bruneval *et al.* PRB **74**, 045102 (2006).

Density and wavefunctions

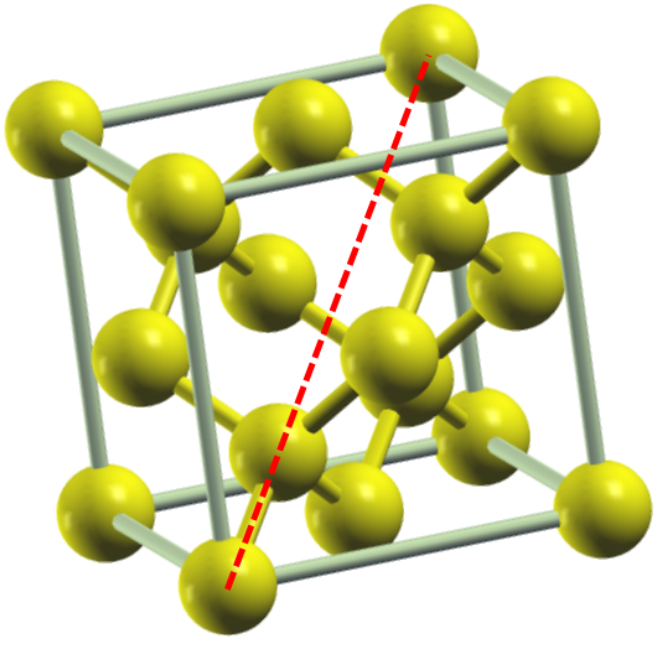
Difference between *GW* and LDA

Bulk silicon

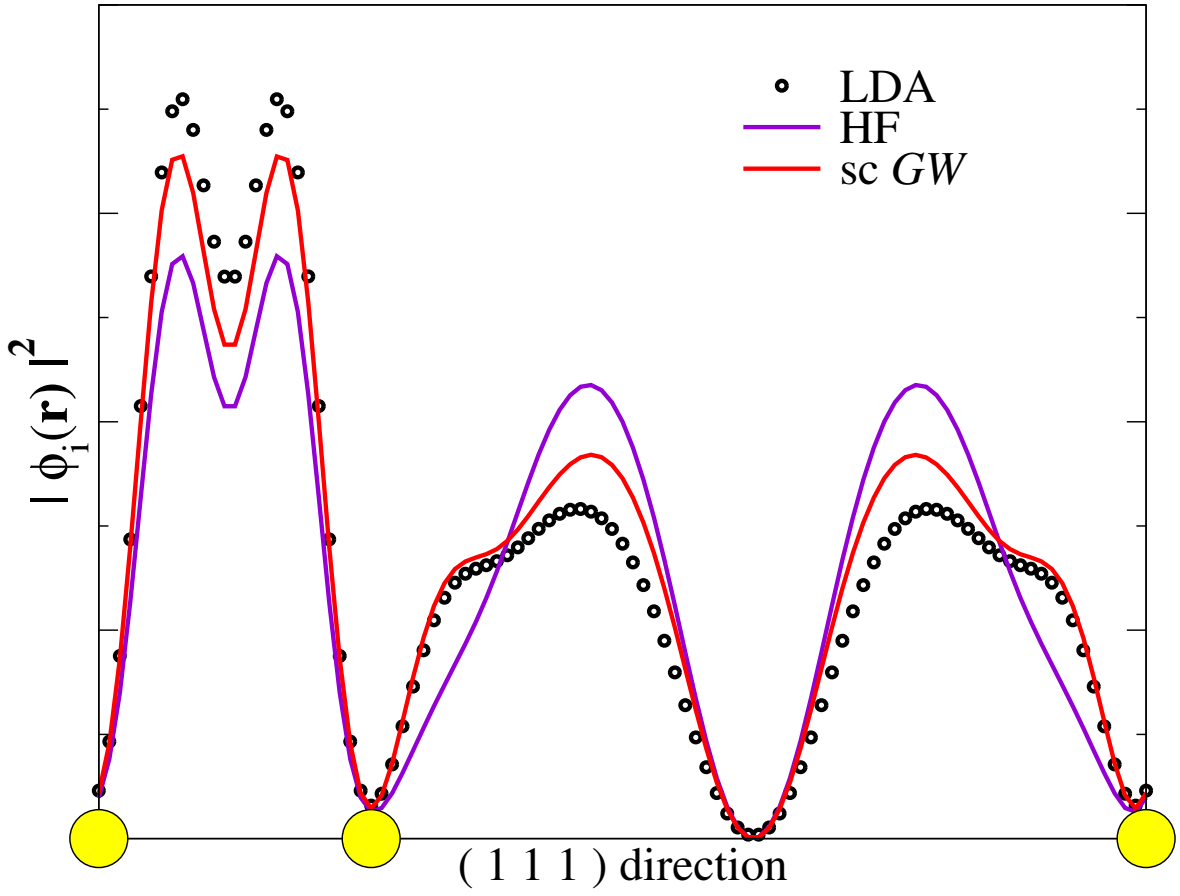


Density and wavefunctions

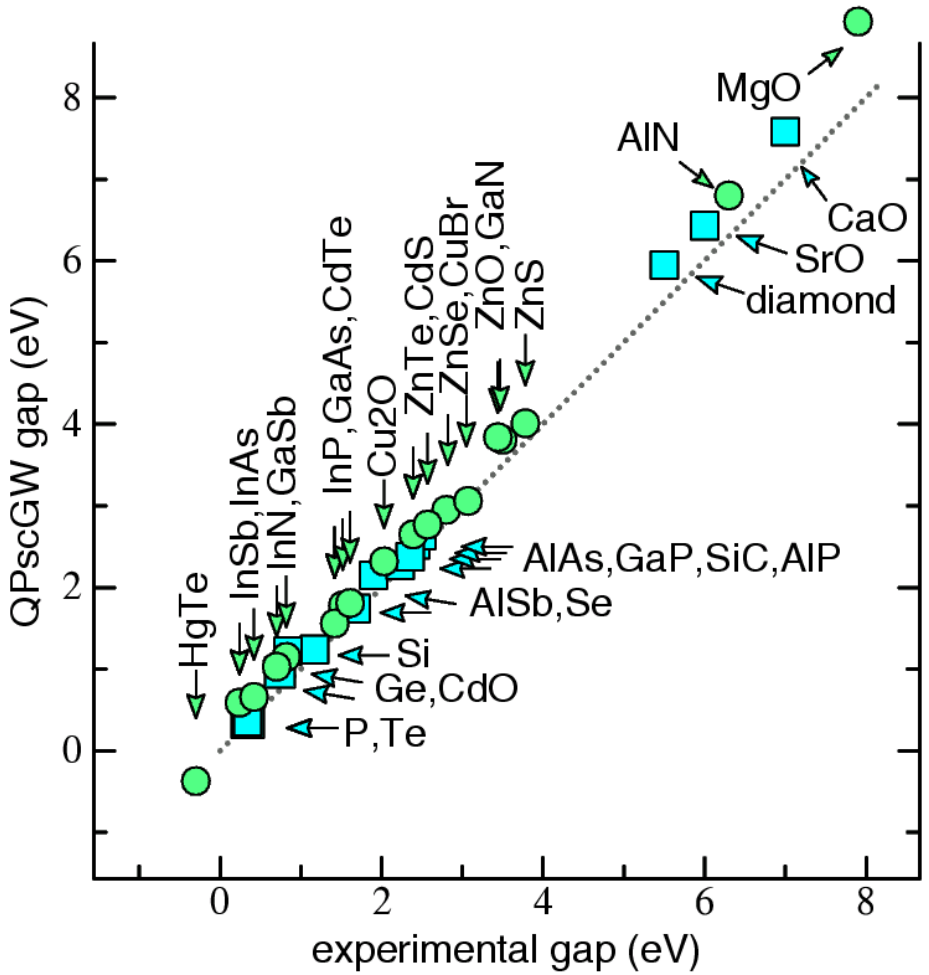
Bulk silicon



1st conduction state



Other materials

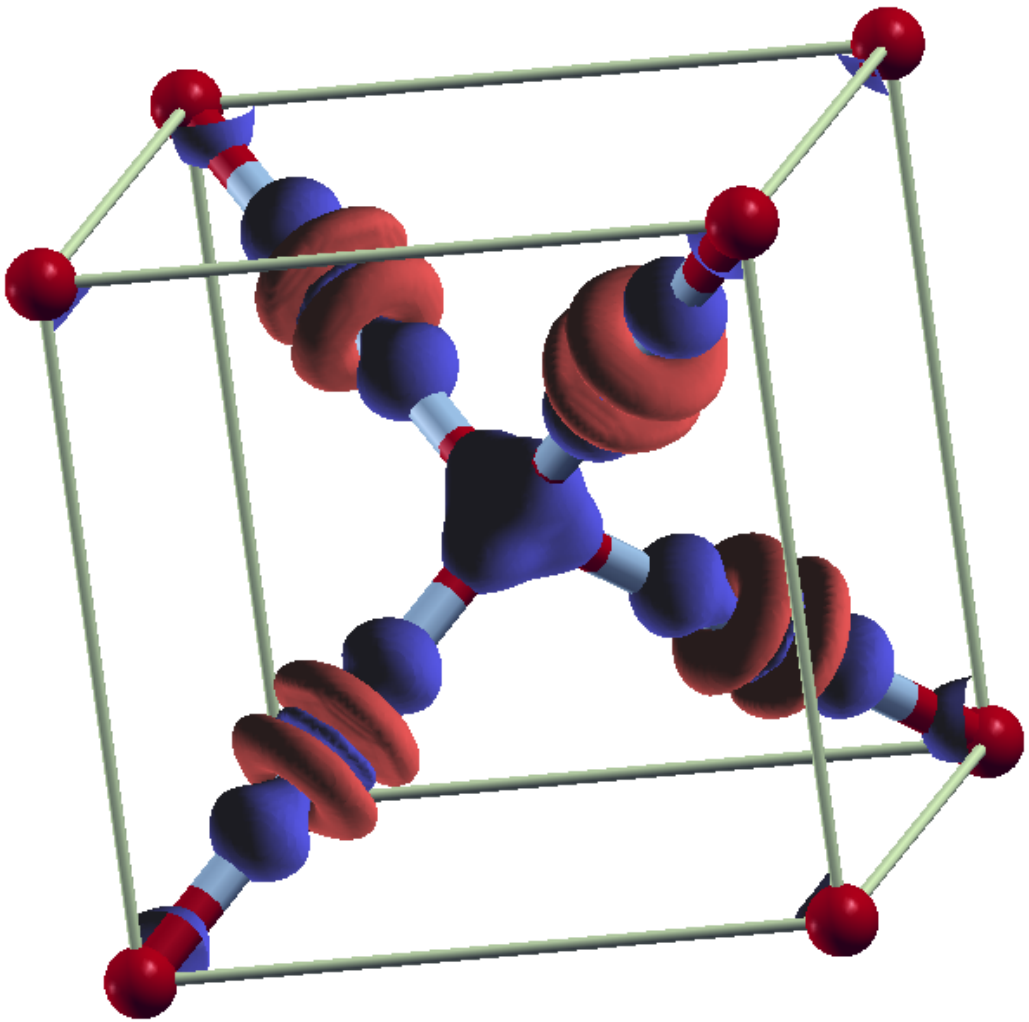


from M. van Schilfgaarde *et al.*, PRL **96** 226402 (2006).

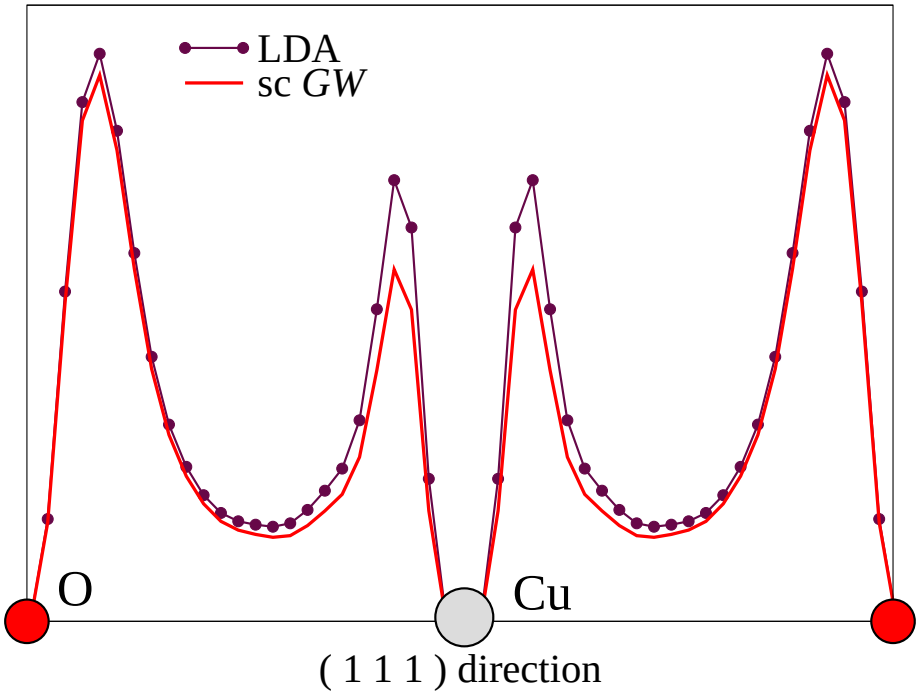
Outline

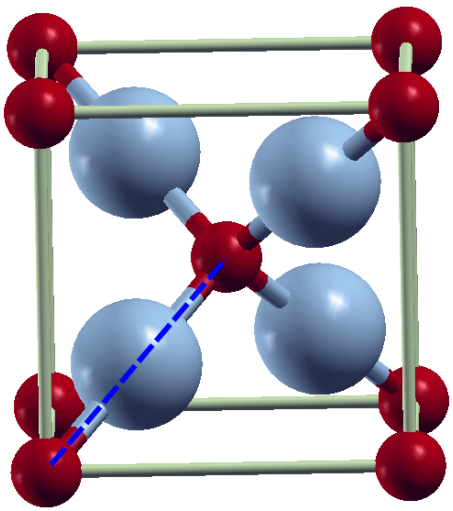
GW density Cu_2O

Difference of the density *GW* - LDA

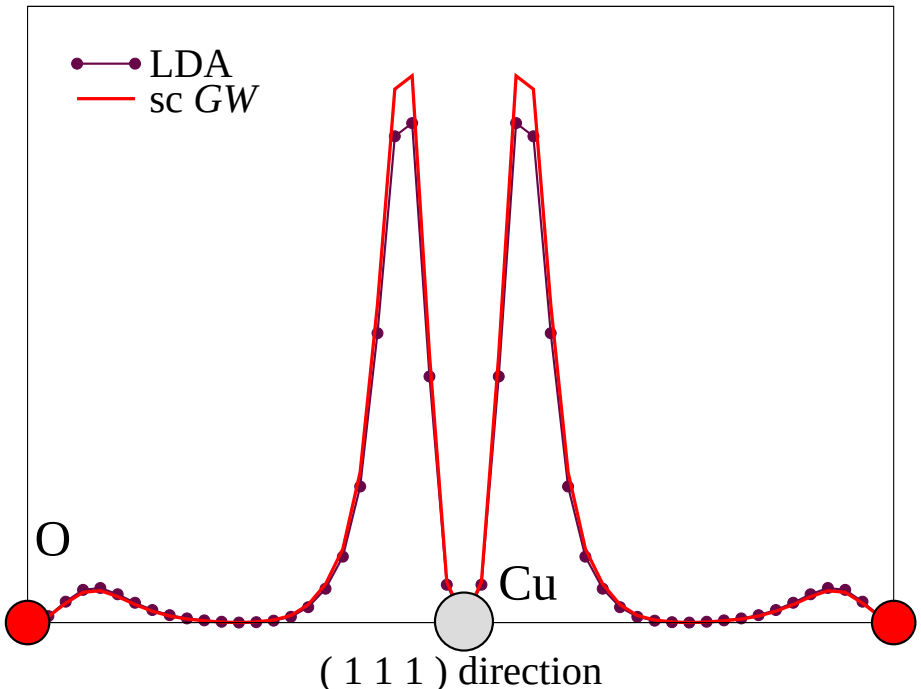


Valence wavefunctions

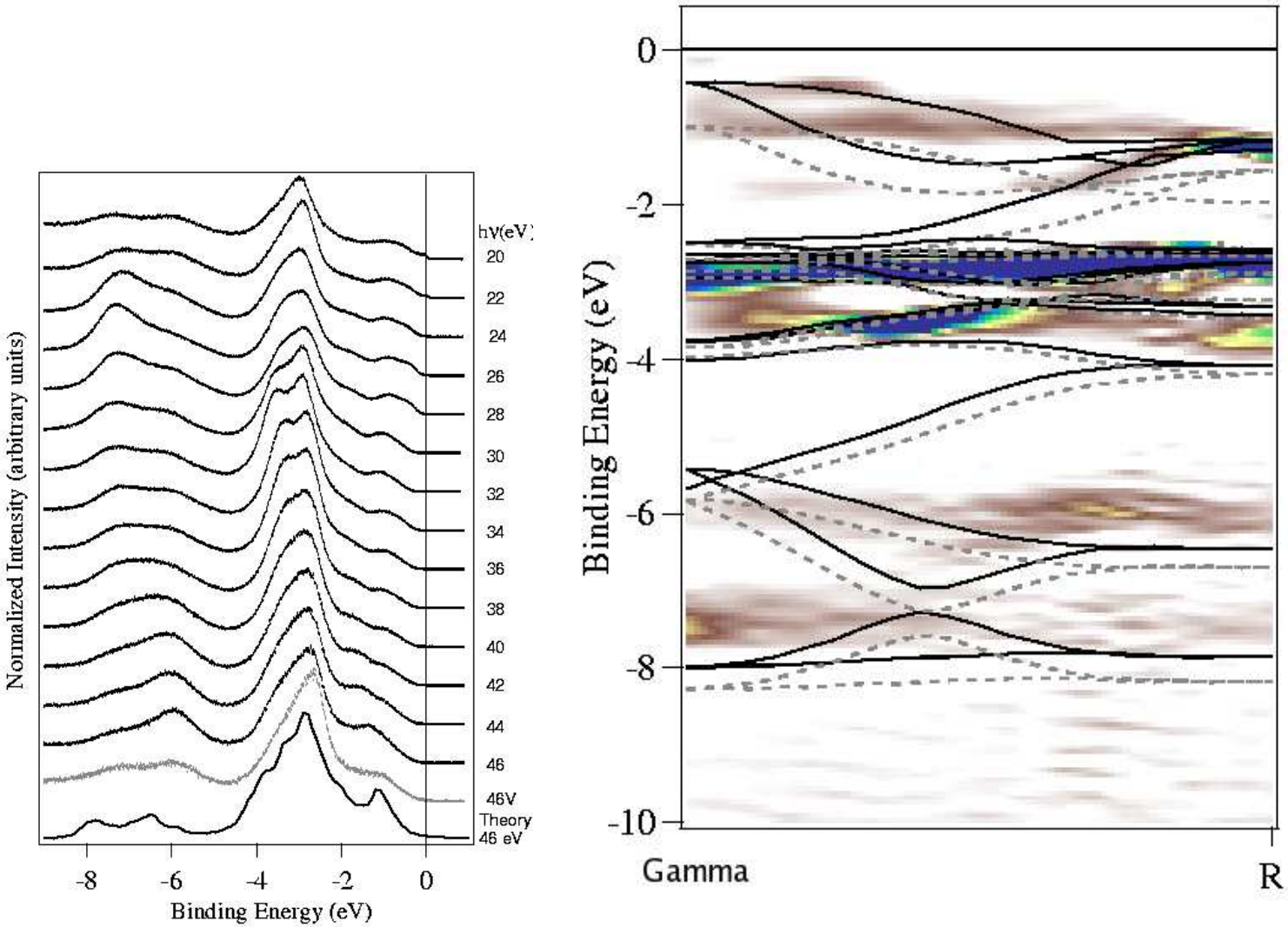




Γ'_{25} valence states

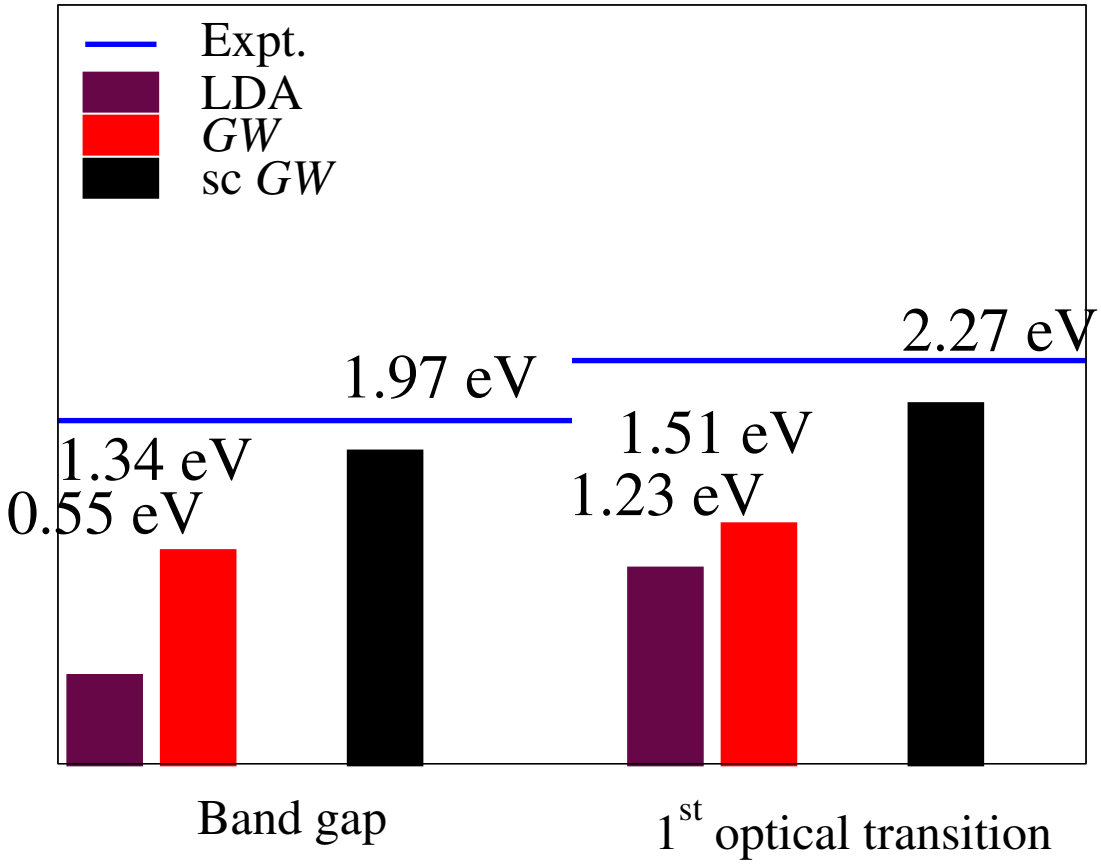


Valence band structure of Cu_2O



ARPES: APE Beamline, Elettra, Trieste (Italy).

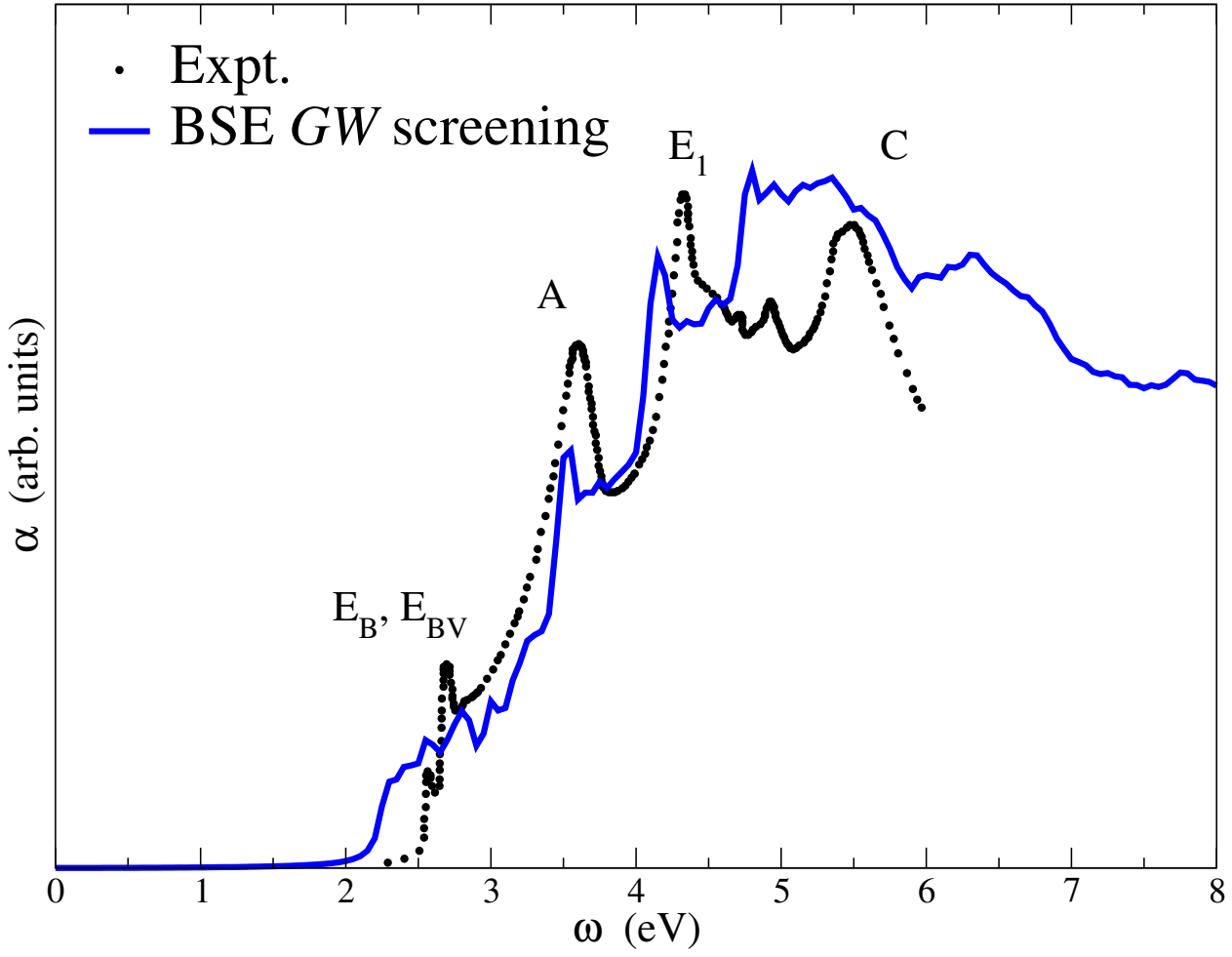
Band gaps of Cu_2O



- Self-consistent *GW* slightly underestimates

Optical absorption coefficient

Excitons through the Bethe-Salpeter equation with the **self-consistent** *GW* **eigenvalues** and *GW* **screening**



F. Bruneval *et al.*, PRL **97**, 267601 (2006).

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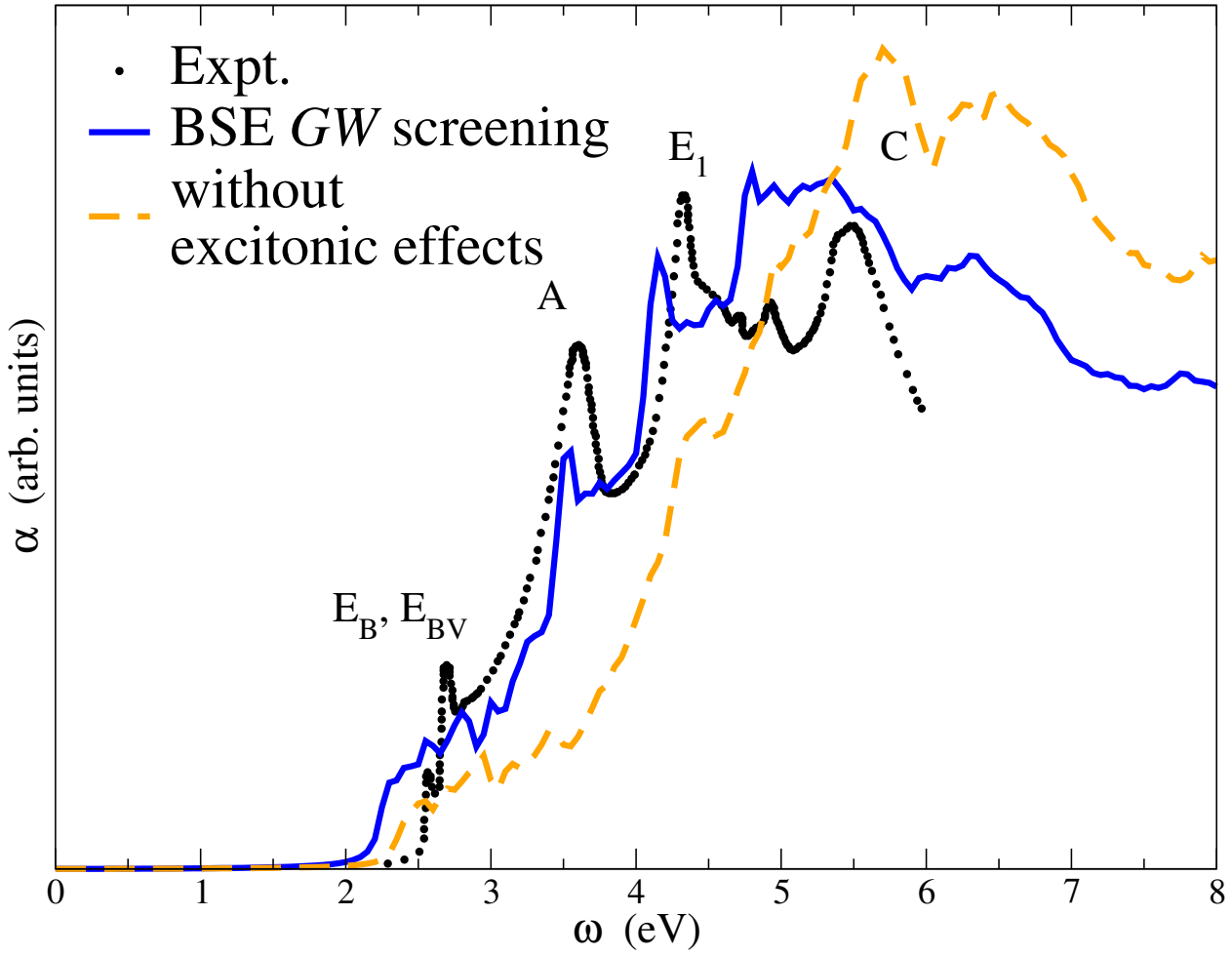

F. Bruneval *et al.*, PRL **97**, 267601 (2006).

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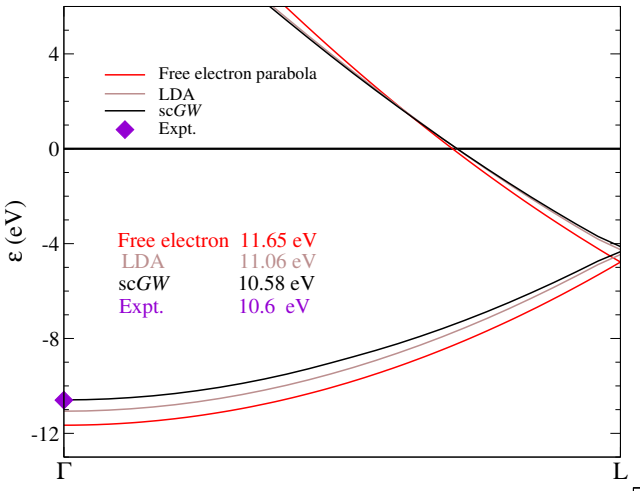
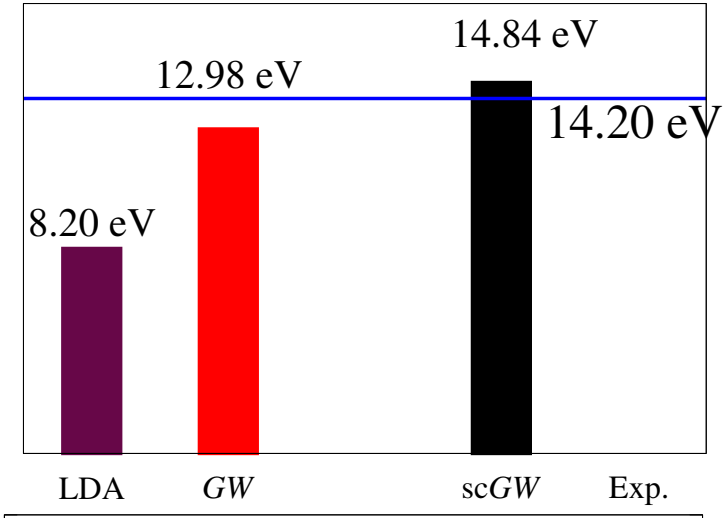
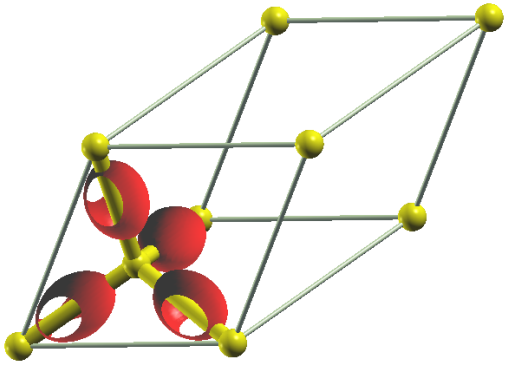
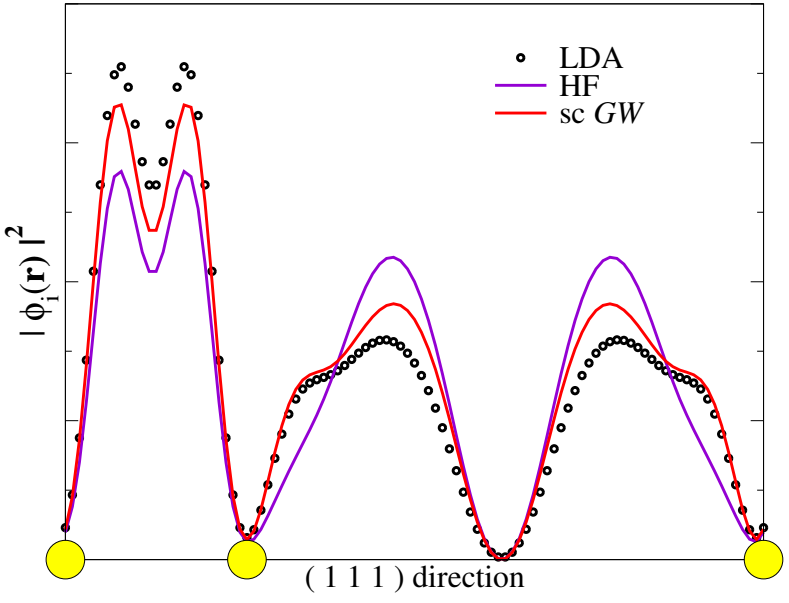
Summary

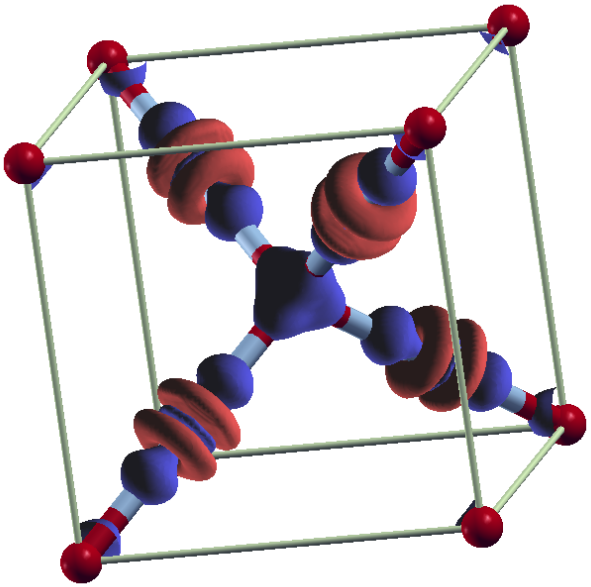

Free electron parabola
LDA
scGW
Expt.
ε (eV)
4
0
-4
-8
-12
Γ
L
Free electron 11.65 eV
LDA 11.06 eV
scGW 10.58 eV
Expt. 10.6 eV

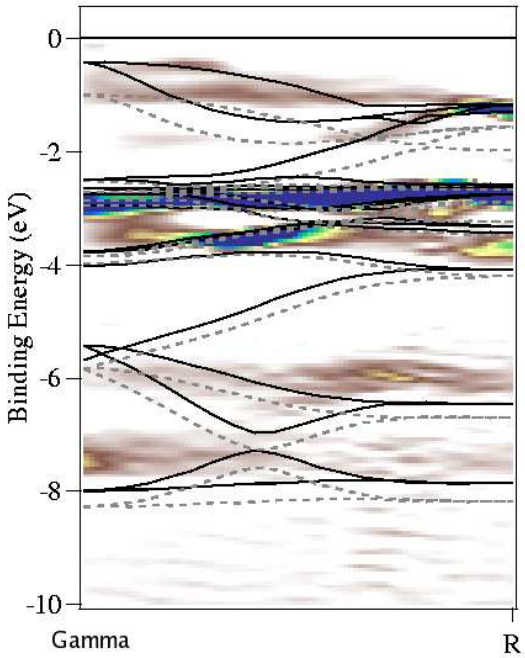

14.84 eV
12.98 eV
14.20 eV
8.20 eV
LDA
GW
scGW
Exp.

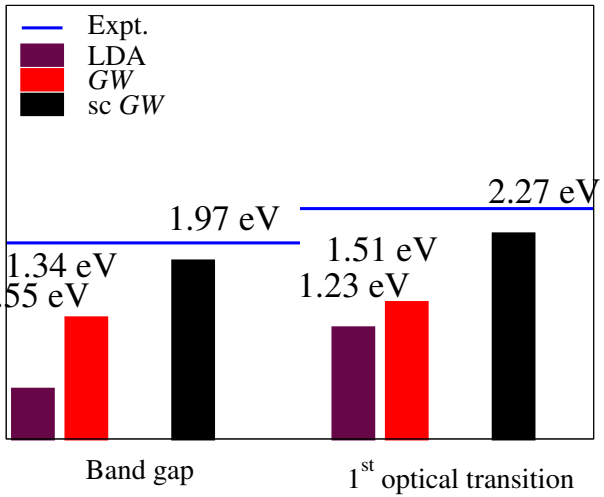


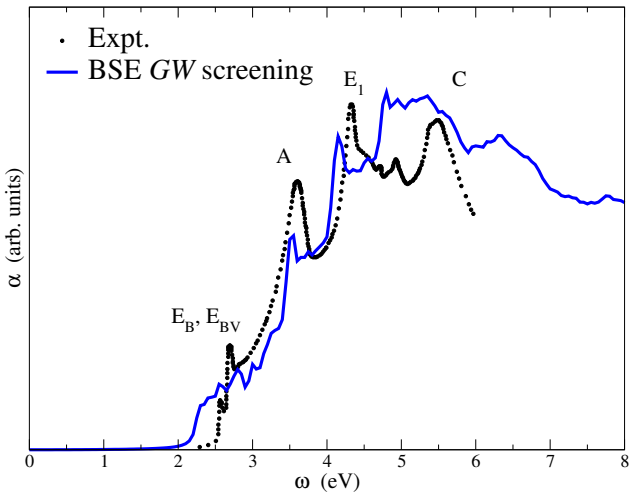

LDA
HF
sc GW
| φi(r) |2
(1 1 1) direction

Summary




0
-2
-4
-6
-8
-10
Binding Energy (eV)
Gamma
R


Expt.
LDA
GW
sc GW
1.97 eV
2.27 eV
1.34 eV
0.55 eV
1.51 eV
1.23 eV
Band gap
1st optical transition

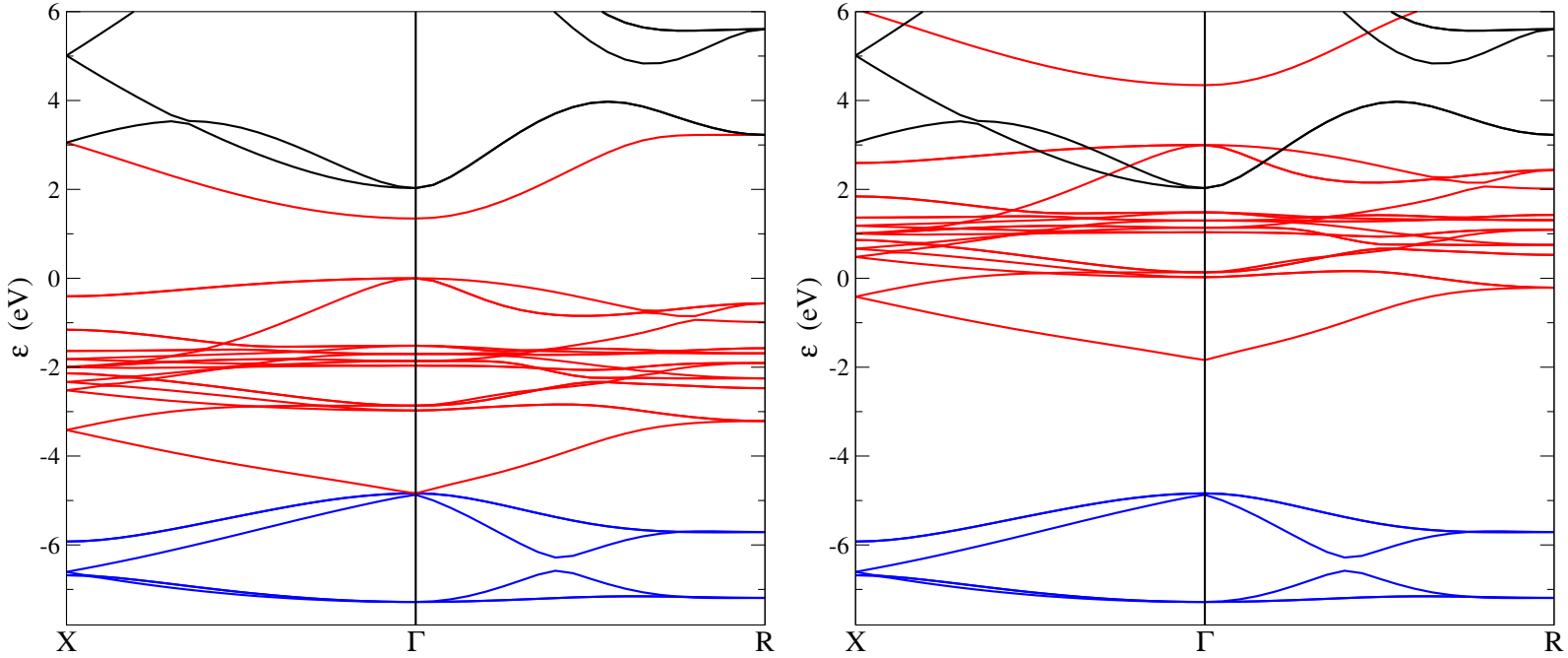

Expt.
BSE GW screening
E1
C
A
EB, EBV
α (arb. units)
0
1
2
3
4
5
6
7
8
ω (eV)

A new state-of-art?

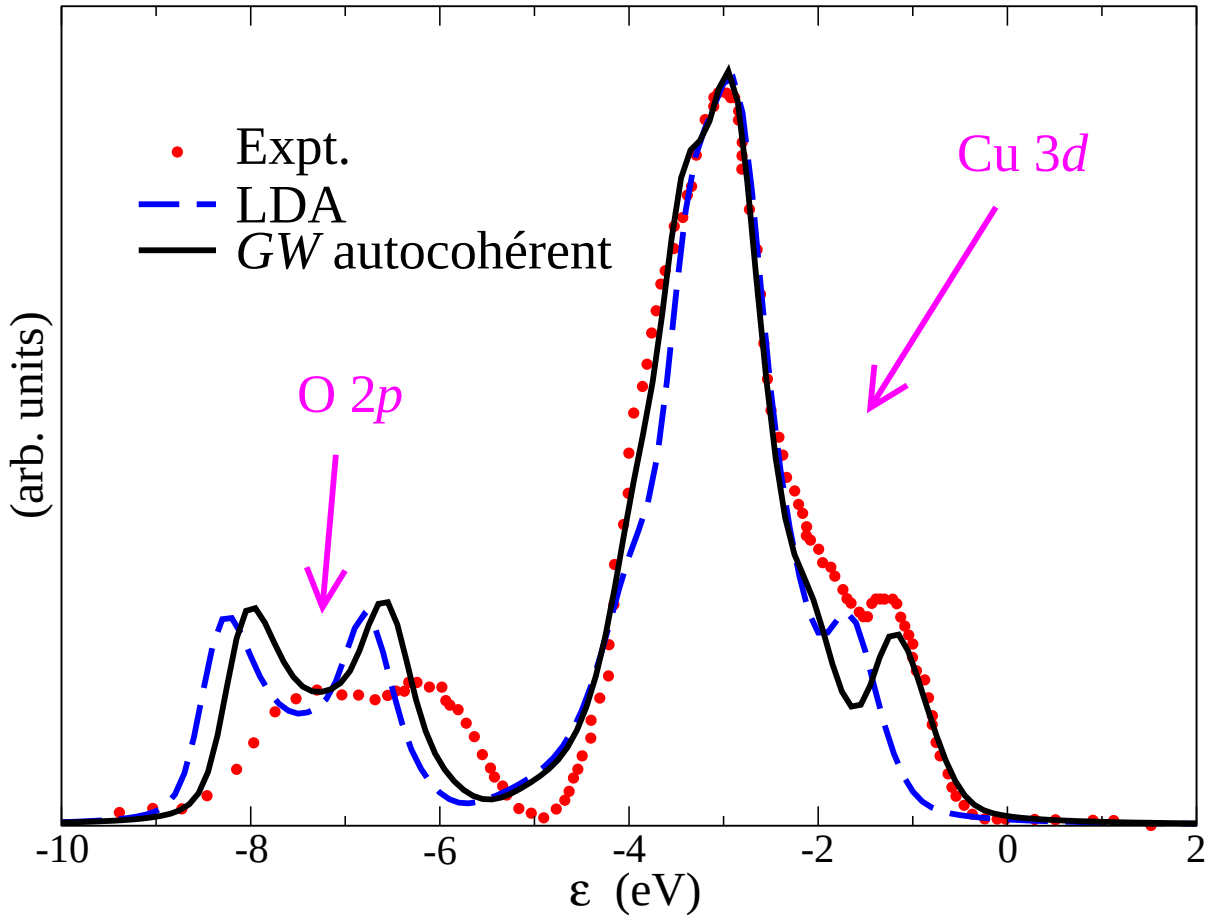
- Self-consistent *GW* is **cumbersome**.
- Apply the self-consistent method to **nasty cases**
  = Kohn-Sham DFT is qualitatively wrong.
  - semiconductors predicted metallic within LDA: InAs, InSb
  - junctions of semiconductors where the alignment of the bands matters.
  - finite systems where the LUMO is not correct in LDA: SiH_4
  - complex oxides where LDA is really off.
- sc*GW*: available in abinit.org
- BSE: 

Effect of semicore on *GW*

Semicore: Cu 3*s*,3*p*

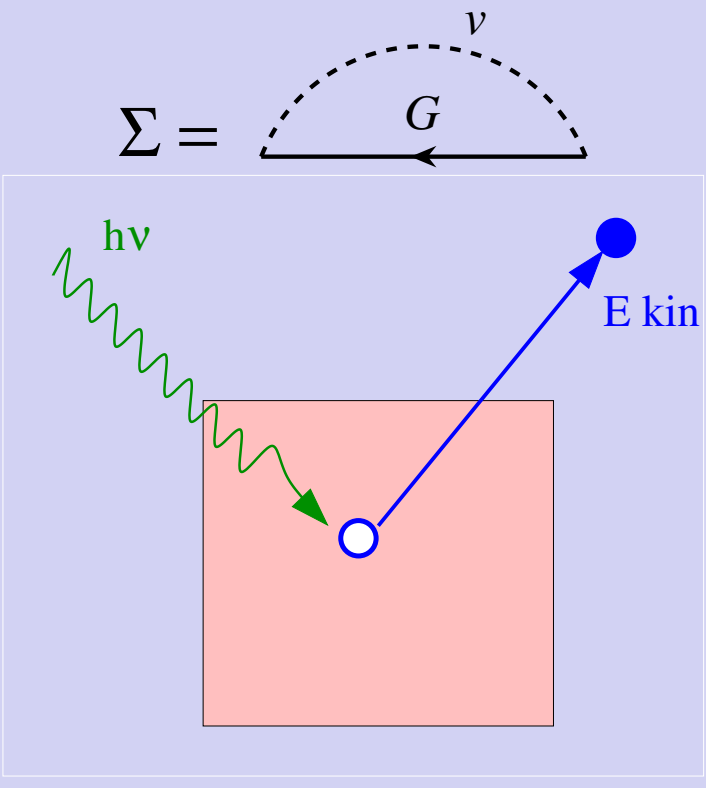


Valence states of Cu_2O

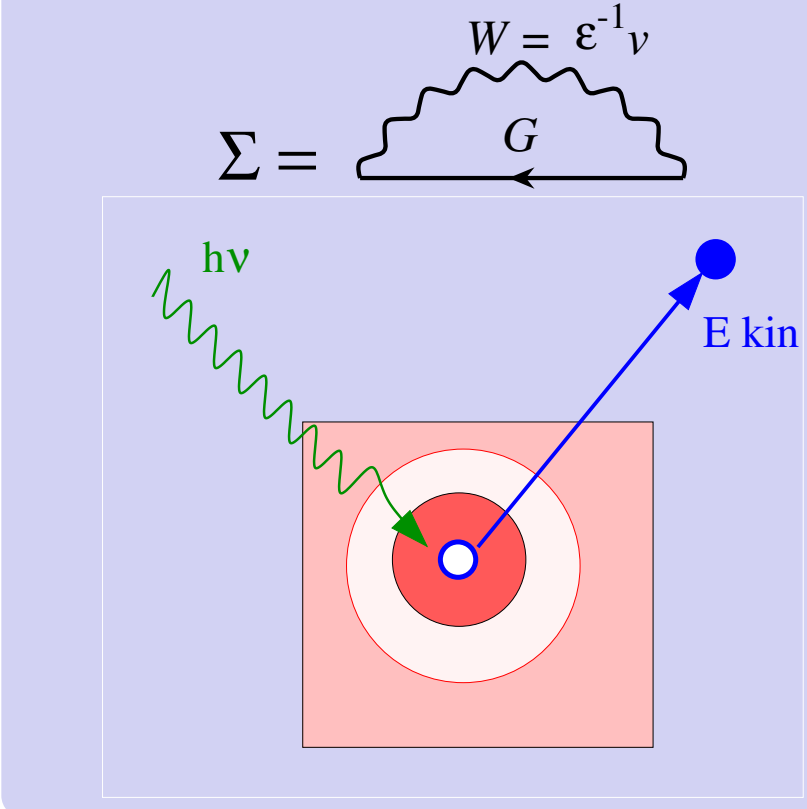


Theory & Photoemission

Hartree-Fock Approximation

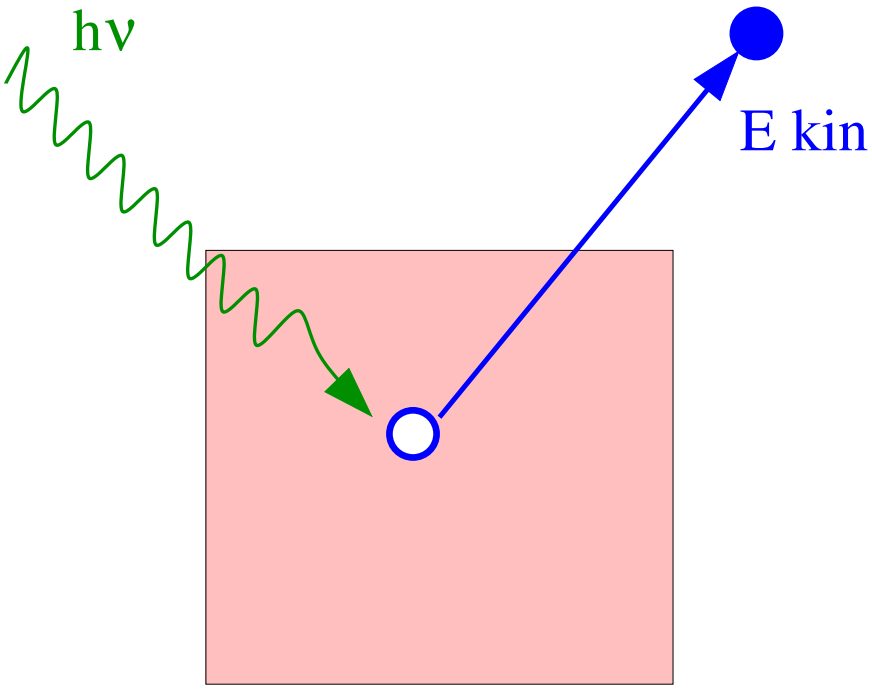


GW Approximation

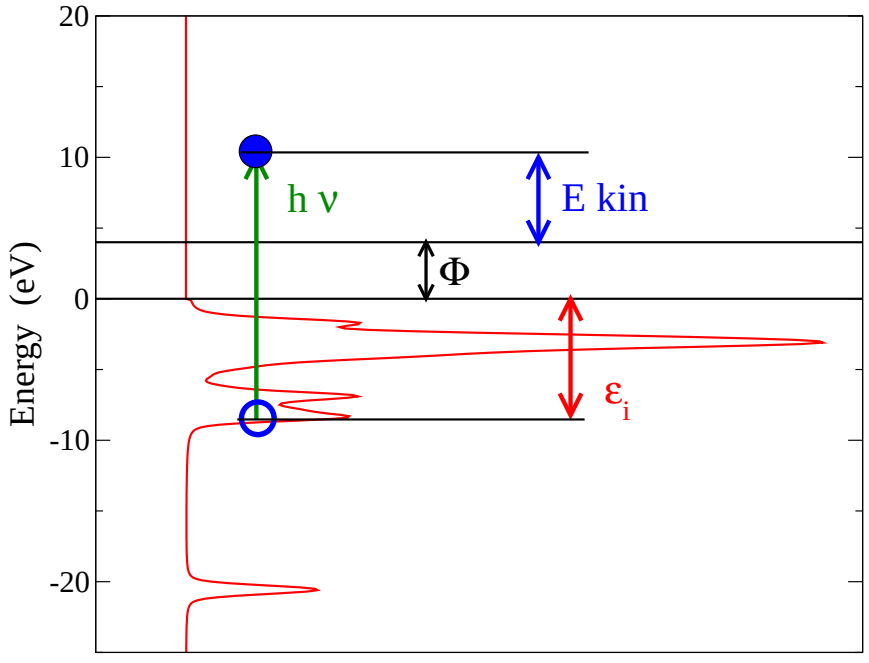


No! due to a theoretical argument

binding energy: $\epsilon_i = h\nu - E_{kin} - \Phi$



Density of States



→ **Excited state property**