ecalj CMD2019 course menu

Sep.4th Wed 4 hours, Thus 6 hours , Fri 2 hours.

- Introduction
  What we can do in ecalj?

- ecalj package
  Install
  Minimum usage
  Band structure calculation. GW calculation.

- Theory
  Band theory. LMTO+LAPW method, GW method

- Usage, Read output and Practice

Give a glance to https://github.com/tkotani/ecalj/

(This documents contains some theory --- I will change this documents more…)

The PMT method: a new linearized method

PMT =A**P**W + **MT**O

Muffin-tin

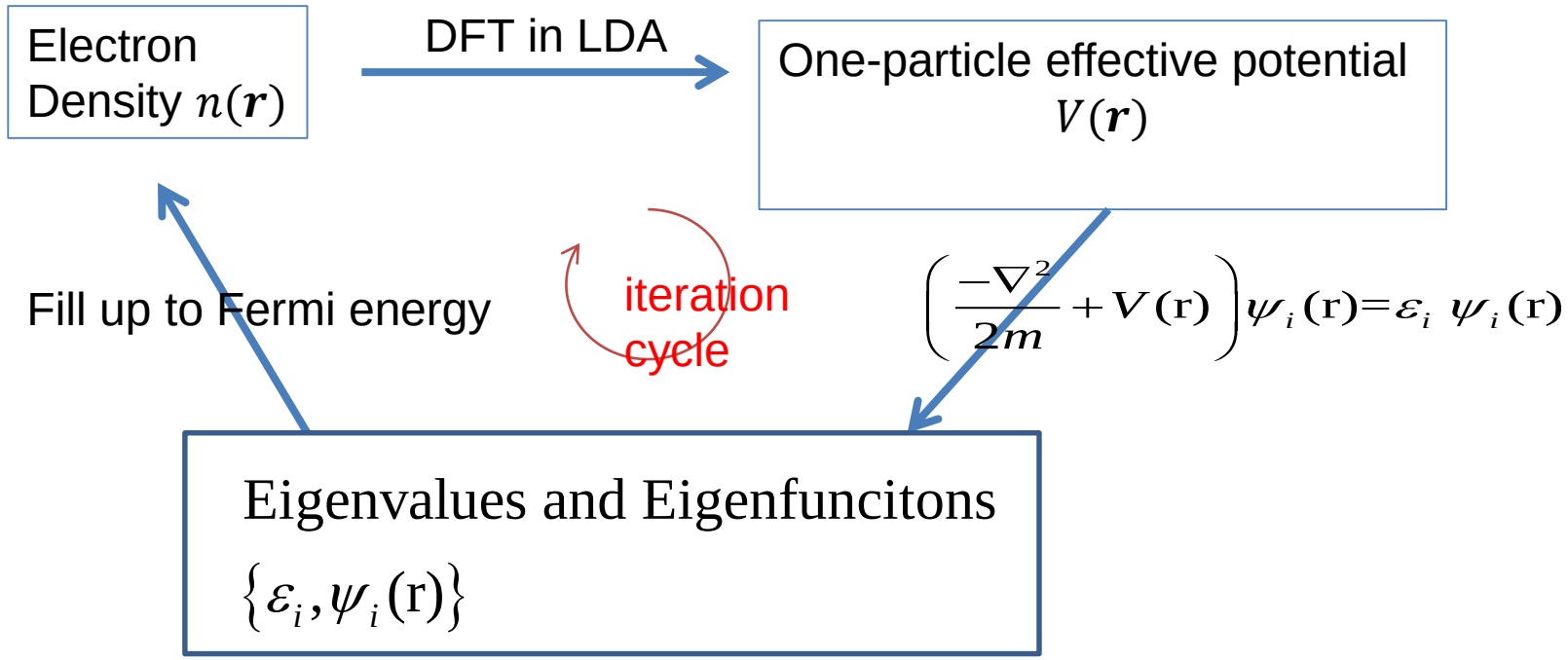
Takao Kotani (tottori-u)

Key point:

1. Iteration cycle.
2. eigenfunctions are expanded with
   APWs(augmented plane wave)
   and MTOs(muffin-tin orbital)

Independent particle picture and total energy

These can be obtained by the density functional theory (DFT) in LDA.



This iteration cycle until converged = total energy minimization

How to represent density and so on in computer?
How to solve it numerically?

Lists of the Full-potential methods

- **KKR**
- **Pseudopotential method**
- **PAW**
- **LMTO**
- **LAPW**

} Linearized xxx methods

(why do we call them ” linearized” method?
→from the view of “exact ” APW method)

Finite basis set

- **Basis set (finite number of basis)**
  - → We assume eigenfunctions are given as:

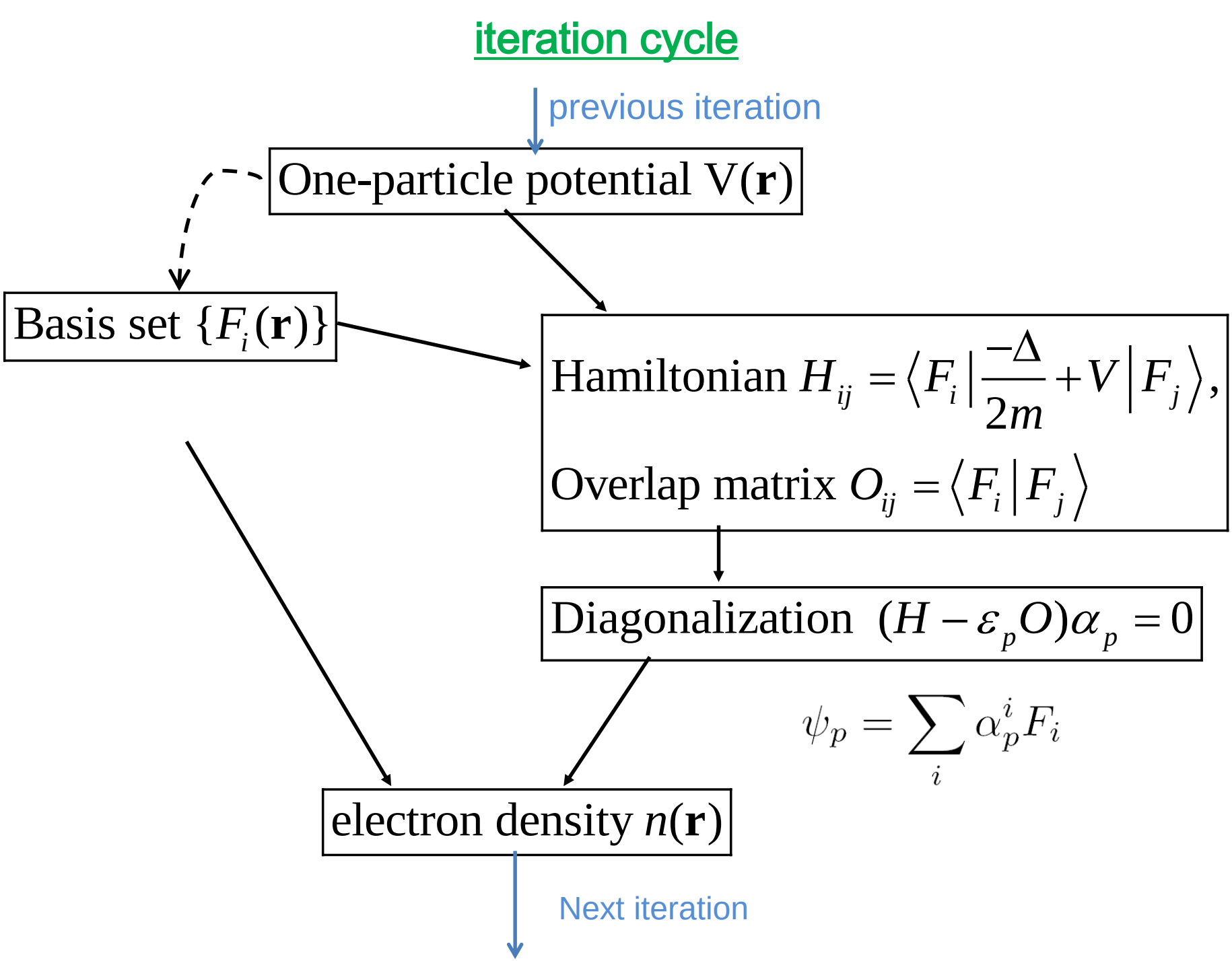
$$\psi_p(\mathbf{r}) = \sum_j \alpha_p^j F_j(\mathbf{r}) \qquad \{F_j\} : j = 1, 2, \ldots N$$

$$\text{Hamiltonian } H_{ij} = \left\langle F_i \left| \frac{-\Delta}{2m} + V \right| F_j \right\rangle,$$

$$\text{Overlap matrix } O_{ij} = \left\langle F_i \middle| F_j \right\rangle$$

$$\left(H_{ij} - \varepsilon\, O_{ij} \right) \alpha^j = 0$$

Finite dimension problem(as the same as LCAO/Gaussian)


iteration cycle
previous iteration
One-particle potential V(r)
Basis set $\{F_i(\mathbf{r})\}$
Hamiltonian $H_{ij} = \left\langle F_i \left| \frac{-\Delta}{2m} + V \right| F_j \right\rangle$,
Overlap matrix $O_{ij} = \left\langle F_i \middle| F_j \right\rangle$
Diagonalization $(H - \varepsilon_p O)\alpha_p = 0$
$\psi_p = \sum_i \alpha_p^i F_i$
electron density $n(\mathbf{r})$
Next iteration

How to choose the good basis?

- APW (augmented plane wave)
- MTO (muffin-tin orbital)

are the names of the basis functions.
Both of them are made by “augmentation”.

My conclusion:

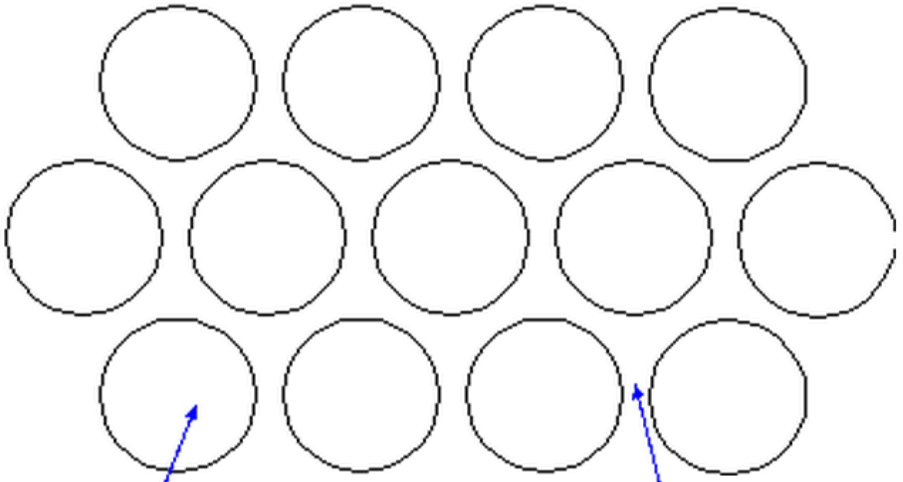
To overcome shortcomings in APW basis and MTO basis, we should use both of **APW and MTO together. →this means the PMT method**

But wait…

What is the APW and MTO?→ next page.

Muffin Tin Division of Space

A definition – not an approximation



Sphere around each atom

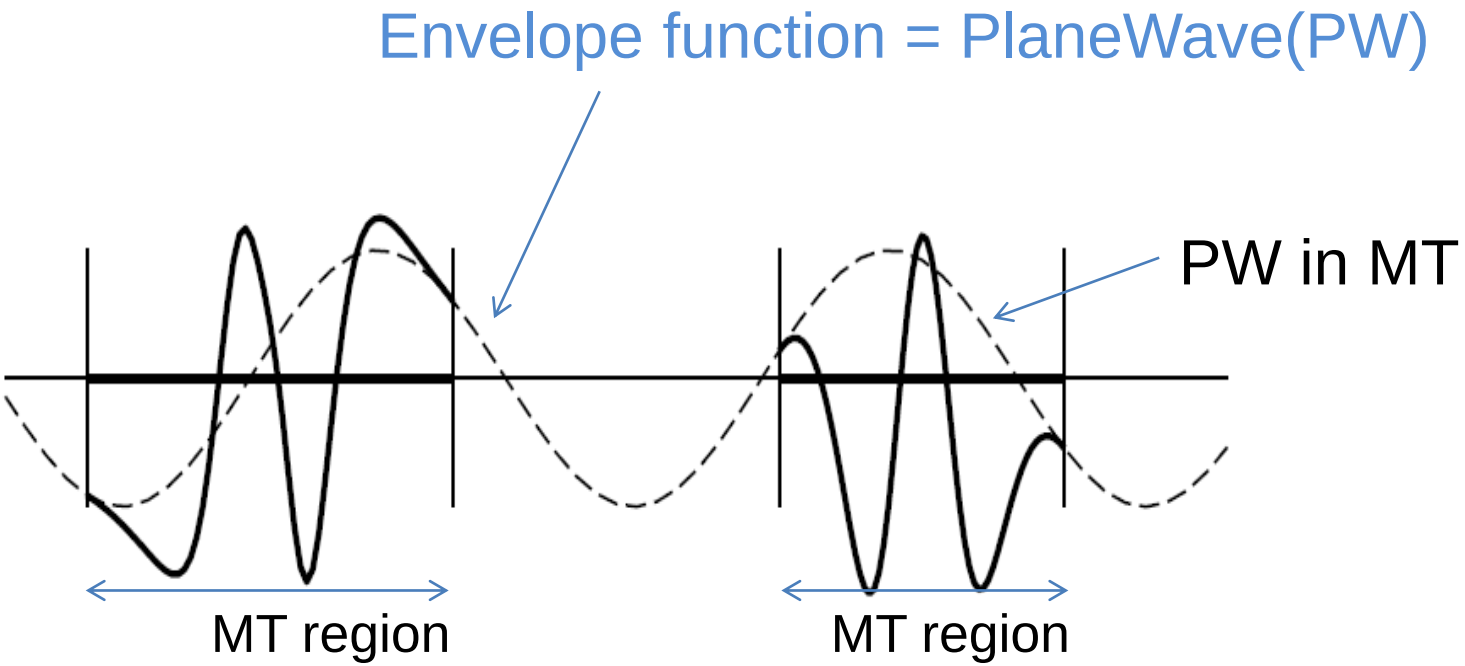
MT regions

Interstitial regions between atoms

Interstitial region

http://research.physics.illinois.edu/ElectronicStructure/598SCM-F04/lecture_notes/

APW



3-components

PW ＋ Atomic-like part － Counter part:
PW within MT

0th 1st 2nd

- Good for Na(3s), high energy bands.
- Not so good for Cu(3d), O(2p)
- Systematic

Linearized APW

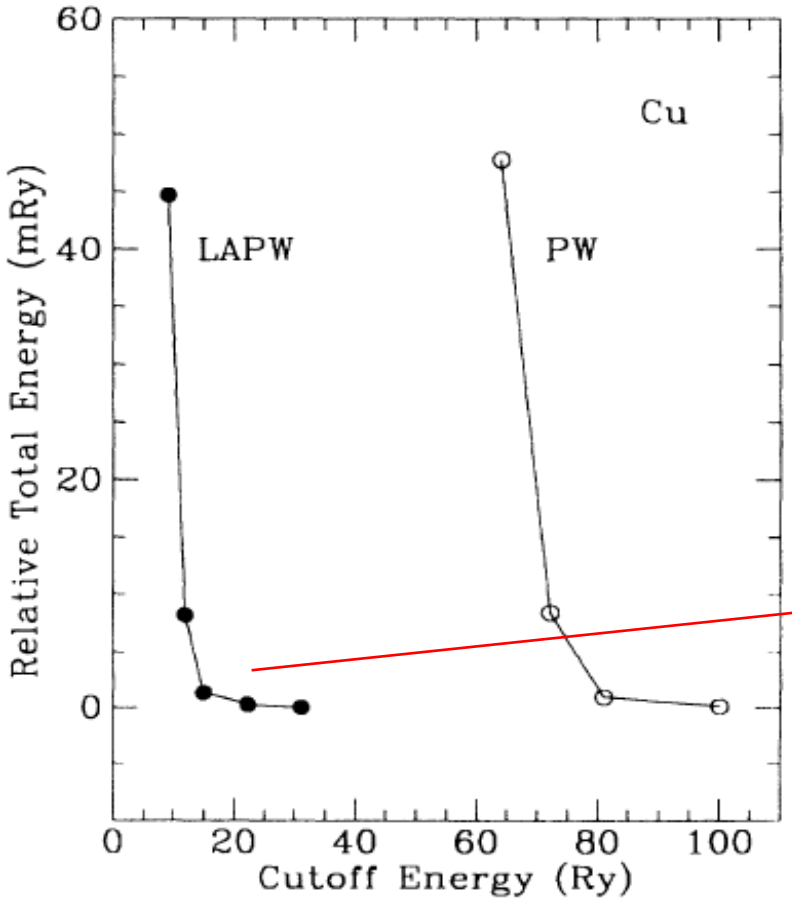


FIG. 1. Relative total energy of fcc Cu plotted against plane-wave cutoff energy.

fcc Cu

plane wave is not so efficient for *3d*

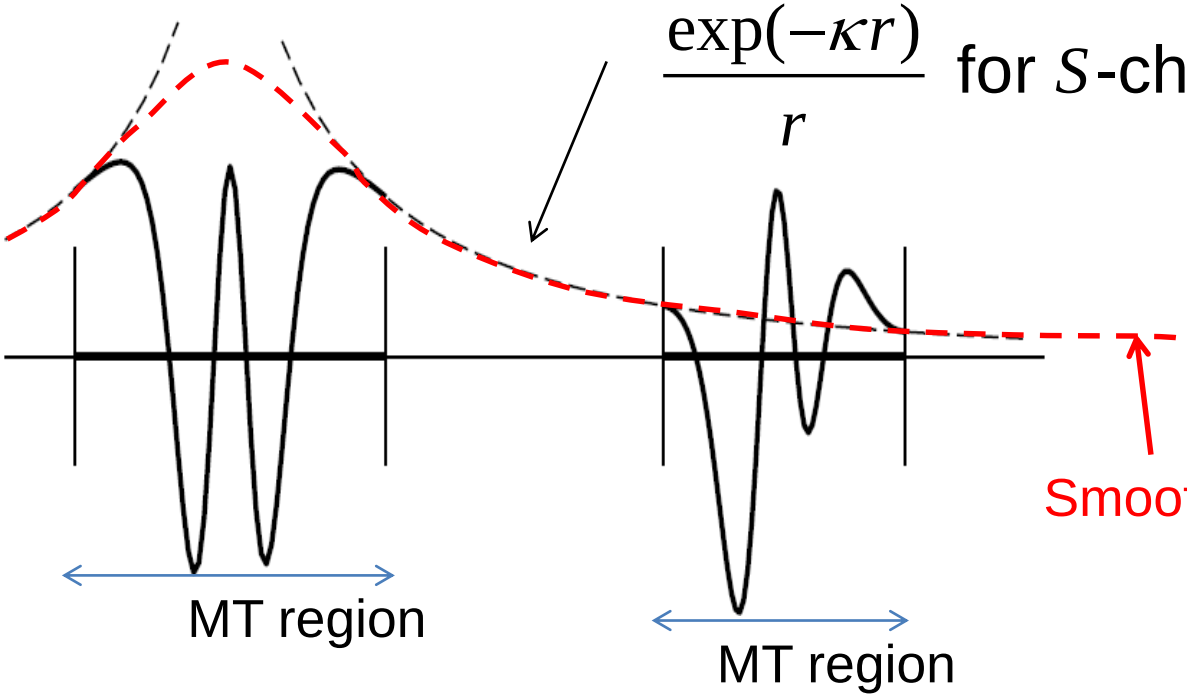
15Ry or more for ~1mRy convergence

D.Singh et al PRB49,17424

MTO

Atom-centered Hankel function, e.g,

$\frac{\exp(-\kappa r)}{r}$ for S-channel



3-components

Hankel (0^{th}) + Atomic-like part (1^{st}) − counter part of Hankel (2^{nd})

- Good for localized orbitals such as Cu(3d), O(2p)
- Not so good for extended states, surface.
- Not systematic

PMT =APW + MTO

T.K and M.van Schilfgaarde
Phys. Rev. B 81, 125117 (2010)

T.K, H. Kino, and H.Akai
Supercell calculations from H_2 through Kr_2.
Almost automatic setting of MTOs with APWs
(Energy cutoff 3~4Ry) .
J. Phys. Soc. Jpn. 82, 124714, (2013)
J. Phys. Soc. Jpn. 84, 034702 (2015)

Basis function

MT center at $\mathbf{R}$. Radis R.

a basis $F_j(\mathbf{r})$ consists of

$F_{0j}(\mathbf{r})$,
Envelope function
PW or smHankel

$F_{1j}(\mathbf{r})$,
Atomic-like parts
for $|\mathbf{r}| < R$

$F_{2j}(\mathbf{r})$
Counter part
for $|\mathbf{r}| < R$

Augmentation parts

Cutoff: $l \le l_{\max} \sim 4$, **Radial-part expansion**

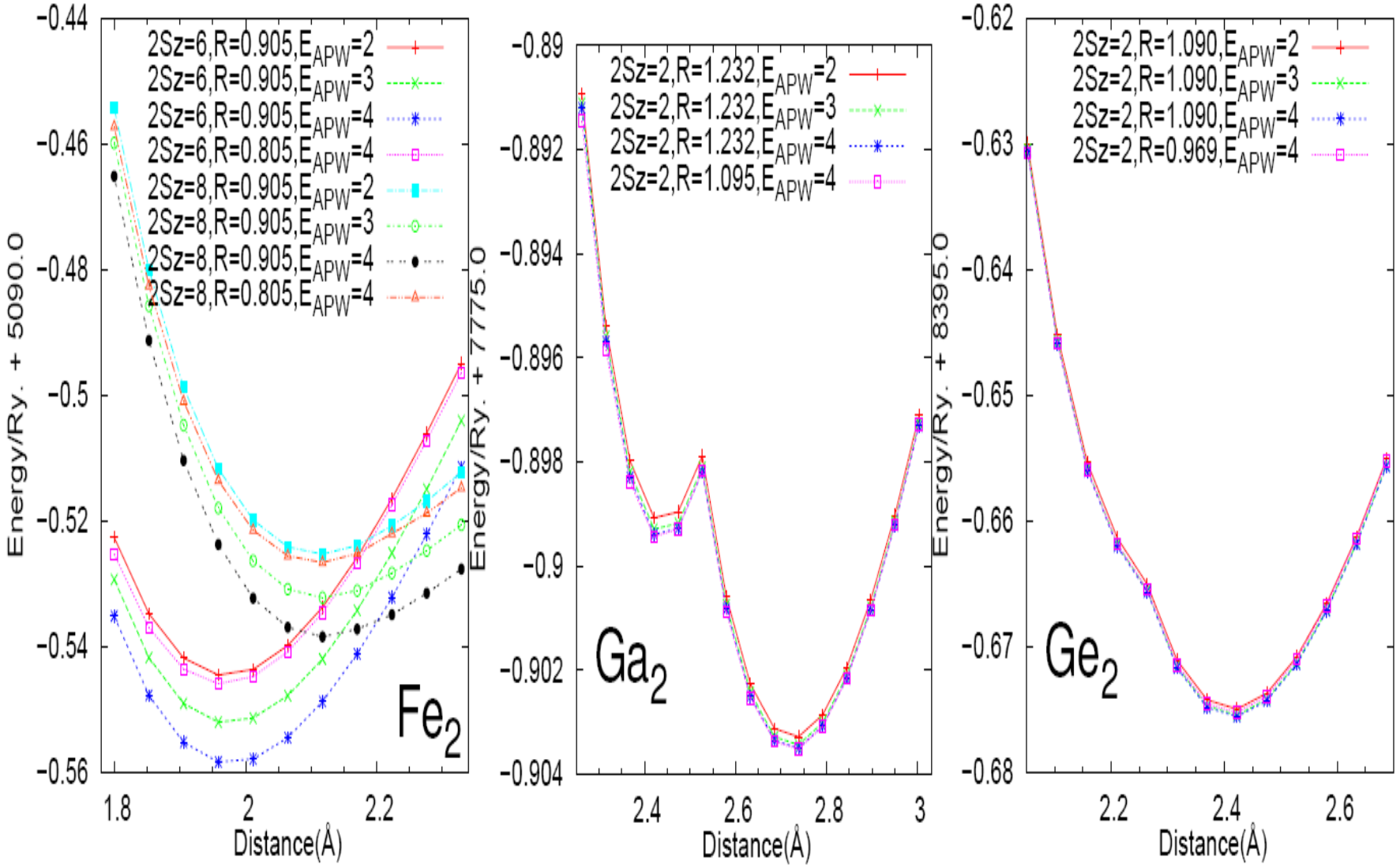
$$F_j(\mathbf{r}) = F_{0j}(\mathbf{r}) + F_{1j}(\mathbf{r}-\mathbf{R}) - F_{2j}(\mathbf{r}-\mathbf{R})$$

Electron density $n(\boldsymbol{r})$ and potential $V(\boldsymbol{r})$ are expanded in a similar manner.

Local orbitals(lo): basis functions which are Non-zero only wihtin MTs.

e.g, see http://www.wien2k.at/lapw/index.html

This is also used together.



N_{basis}=1081+36×2, 1973+36×2, 3025+36×2

Comparison with Gaussian

		r_e (Å)	D_e(Kcal/mol)	ω_e (cm^{-1})
$H_2, 2S_z=0$	PMT	0.749	104.678	4317.959
	PMT(NR)	0.750	104.764	4311.202
	GTO	0.752	104.552	4311.816
$O_2, 2S_z=2$	PMT	1.218	143.741	1564.787
	PMT(NR)	1.218	144.984	1568.867
	GTO	1.220	~~139.815~~	1554.249
	VASP		143.3	
$Cr_2, 2S_z=0$	PMT	1.591	32.833	813.296
	PMT(NR)	1.589	30.191	818.483
	GTO	1.595	26.192	808.148
$Fe_2, 2S_z=6$	PMT	1.977	57.596	397.673
	PMT(NR)	1.991	58.770	386.597
	GTO	2.012	56.902	397.228
$Cu_2, 2S_z=0$	PMT	2.218	51.169	269.326
	PMT(NR)	2.251	48.503	254.321
	GTO	2.251	48.645	255.768

NR : non relativistic GTO : 6-311+G(d,p)

Quasiparticle self-consistent GW

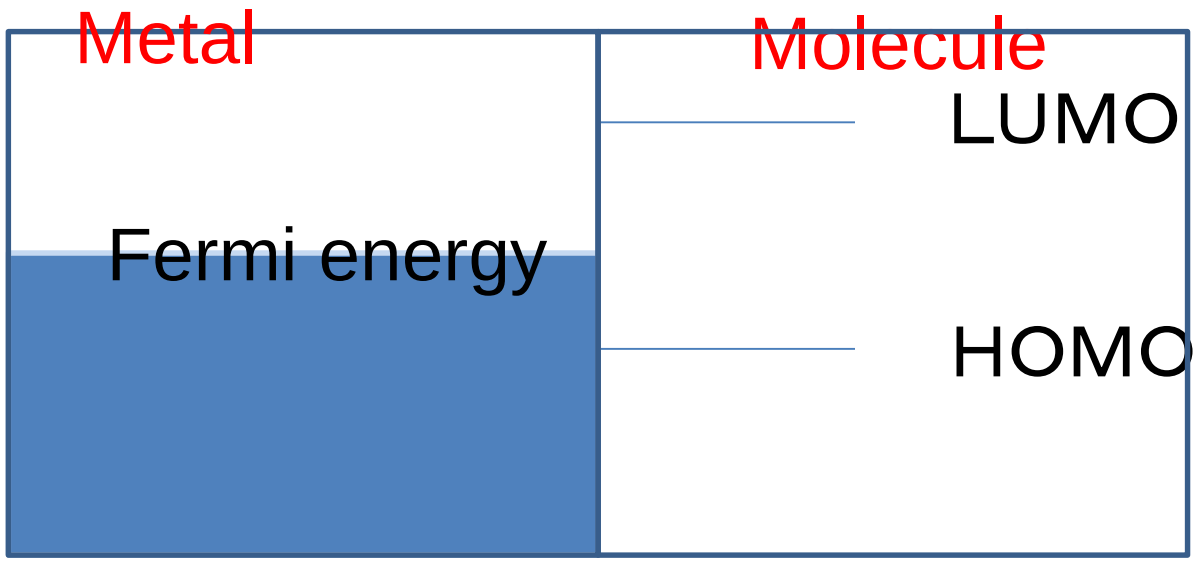
Takao kotani*(tottori university)*

- Mean field theory.
  What the eigenvalue means?
- GW, and QSGW method
  Minimum and previous results.

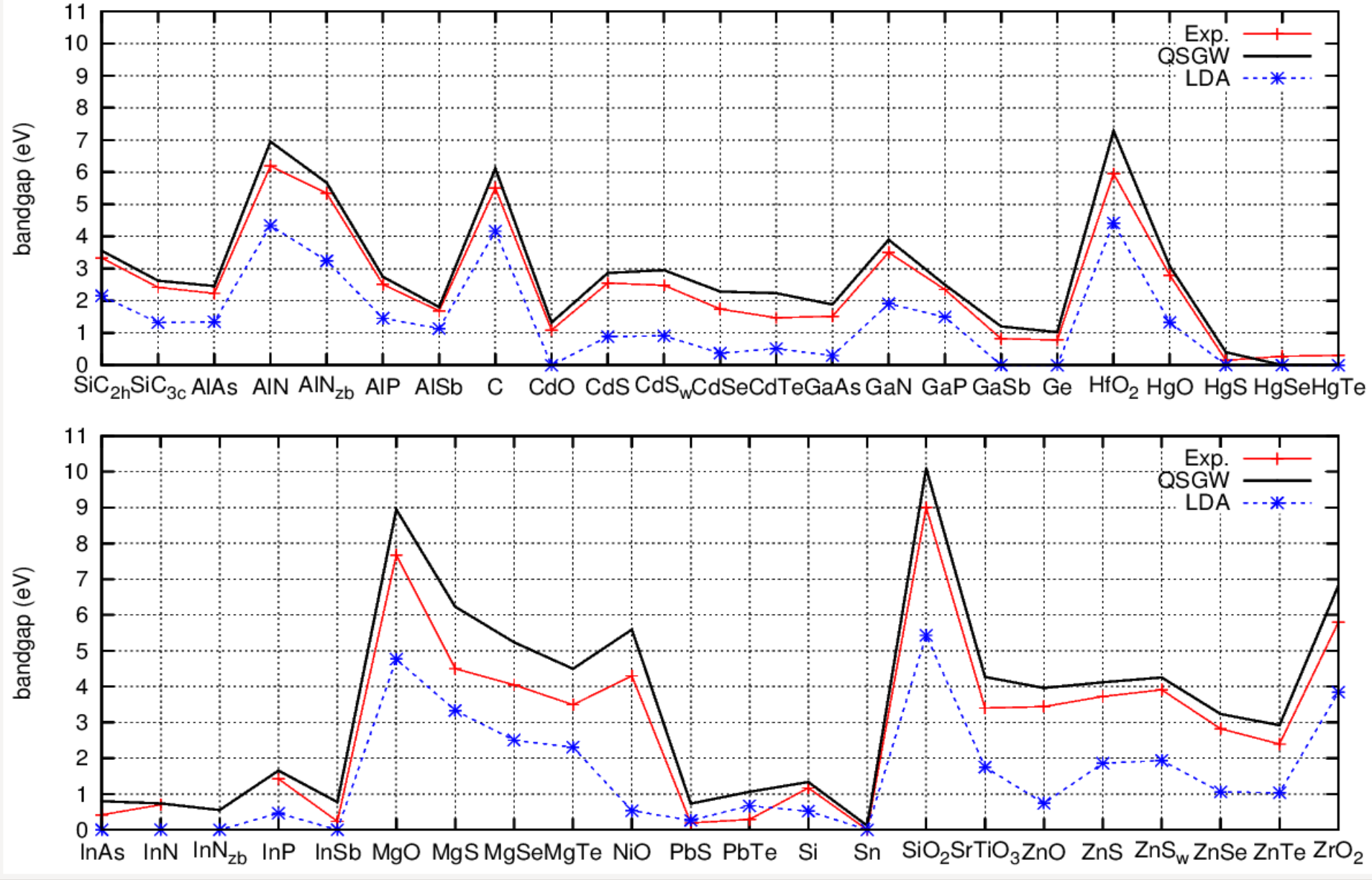
Why QSGW？

We need good independent particle picture in order to calculate linear responses (magnetic optical, transport…). H0 (eigenvalue and eigenfunctions) are required.

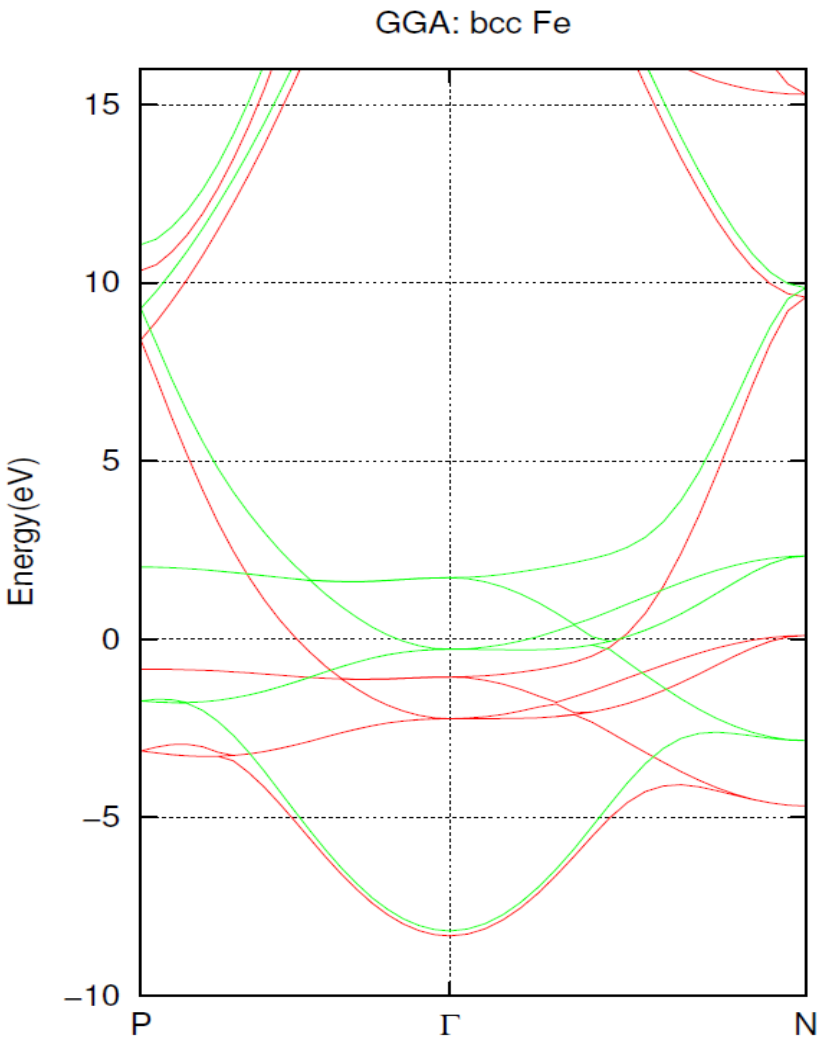
- **Band gap, Effective mass**
- **Relative position of levels.**
  LUMO－HOMO, Fermi energy…

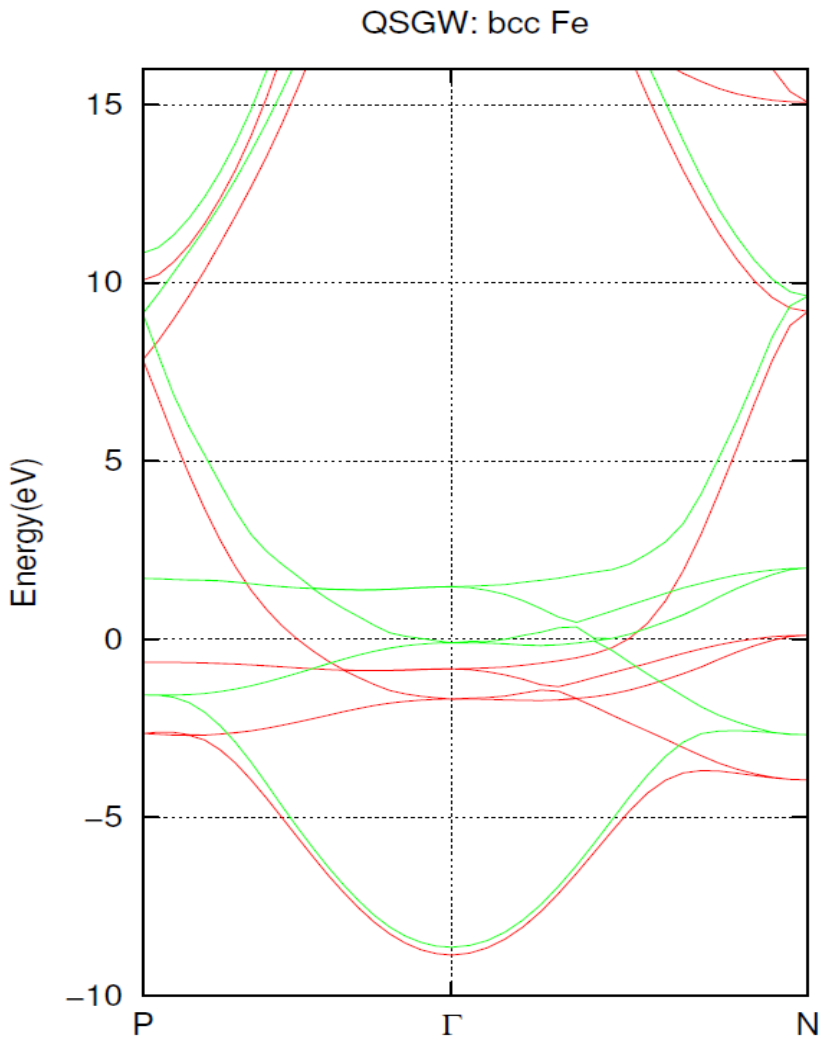


Molecule on top of metal.



Experimental Band gap (eV)

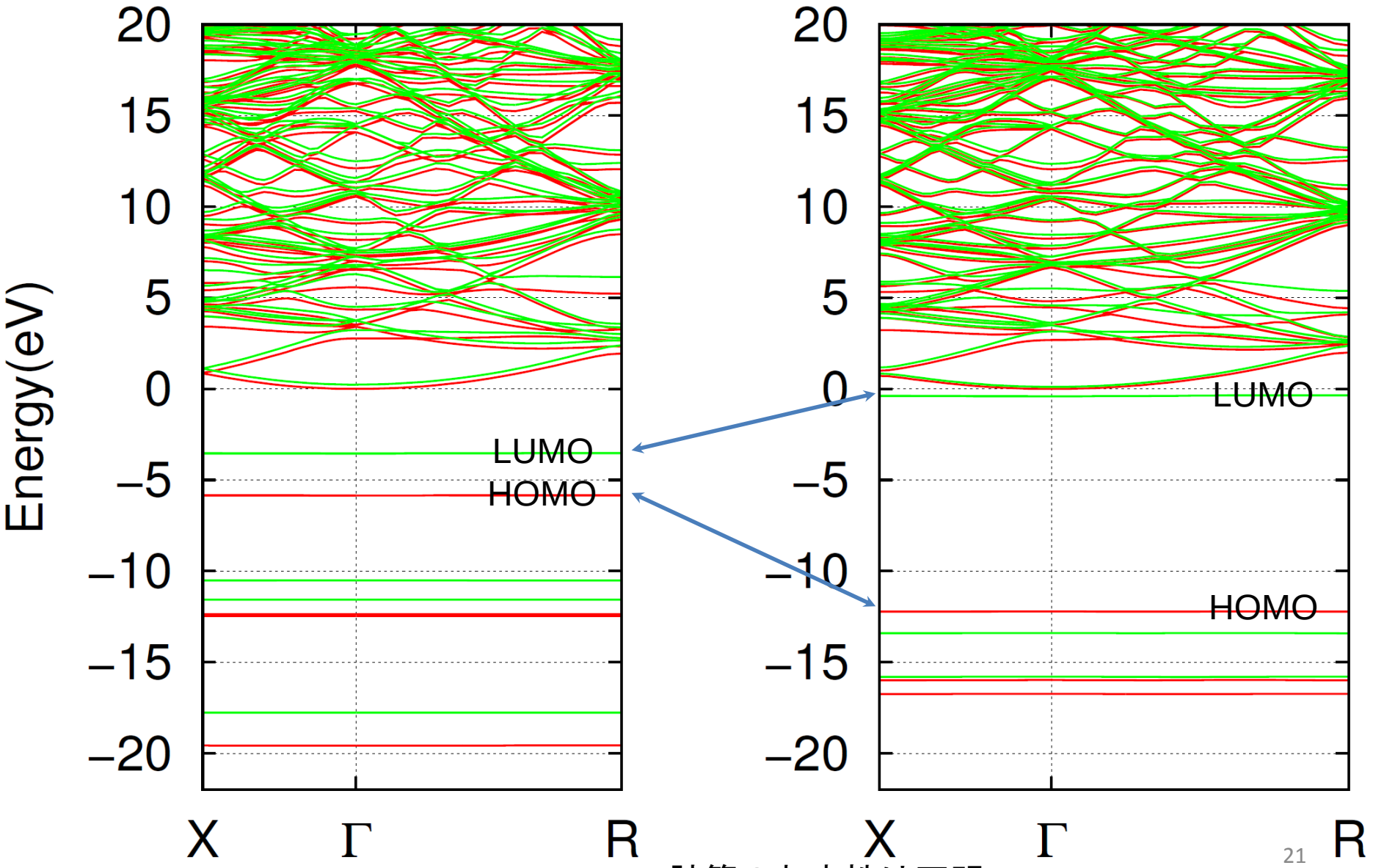




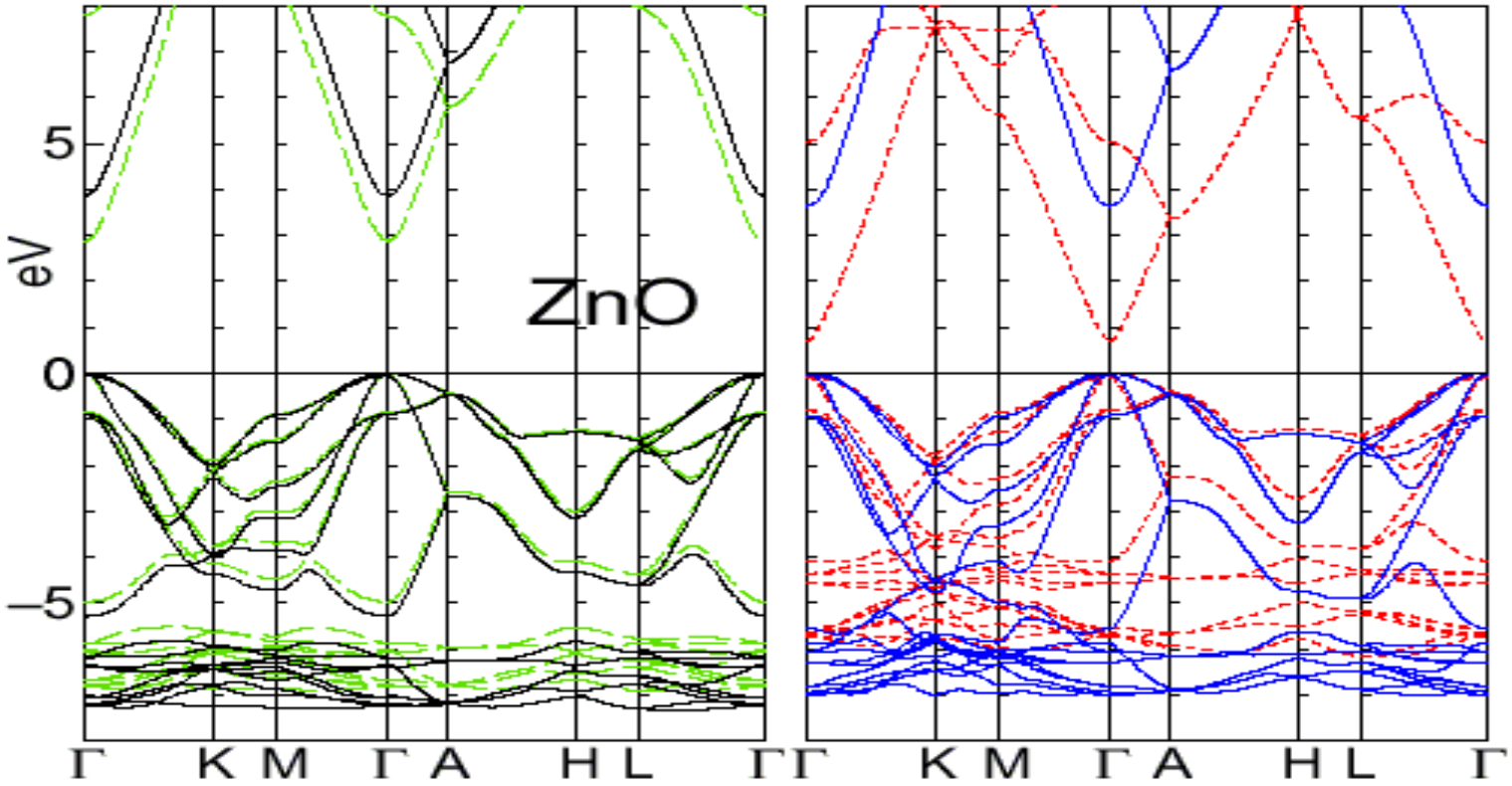
金属的なもの→QSGWでOK.
ハイブリッド法では場合によりうまくいかない。

GGA: O_2 in supercell $(12a.u.)^3$cell

QSGW



計算の収束性は不明. . .



Black:QSGW 3.87eV

Red:LDA 0.71eV

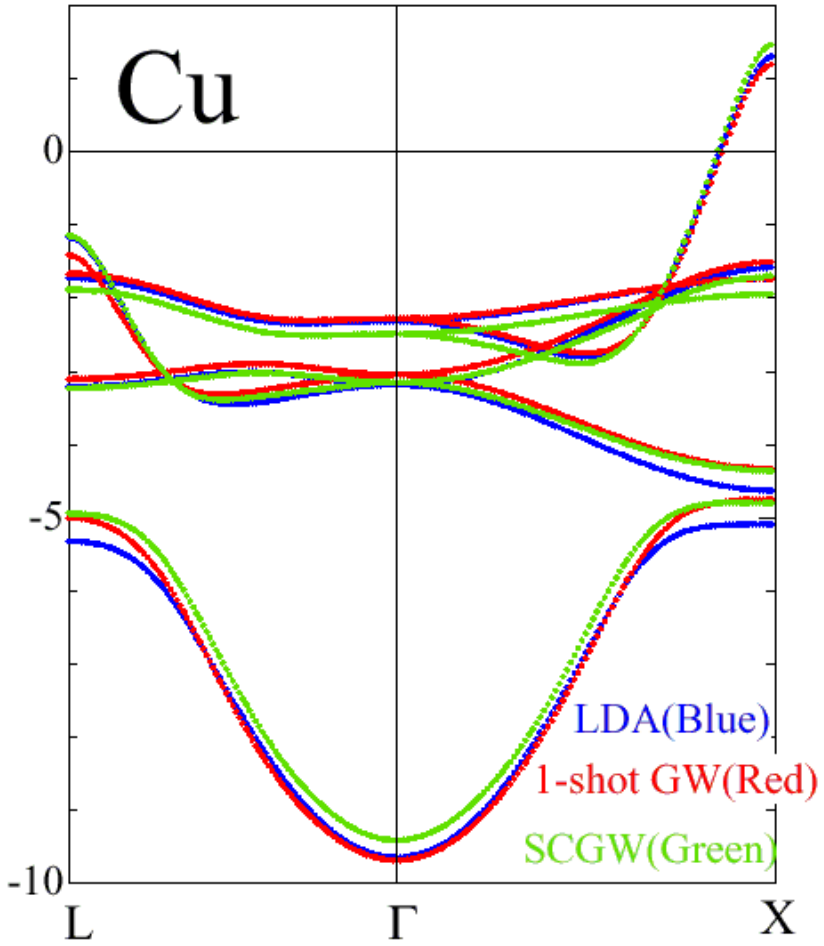
Green:$G^{LDA}W^{LDA}$ (Z=1,Offdiagonal included) 3.00eV

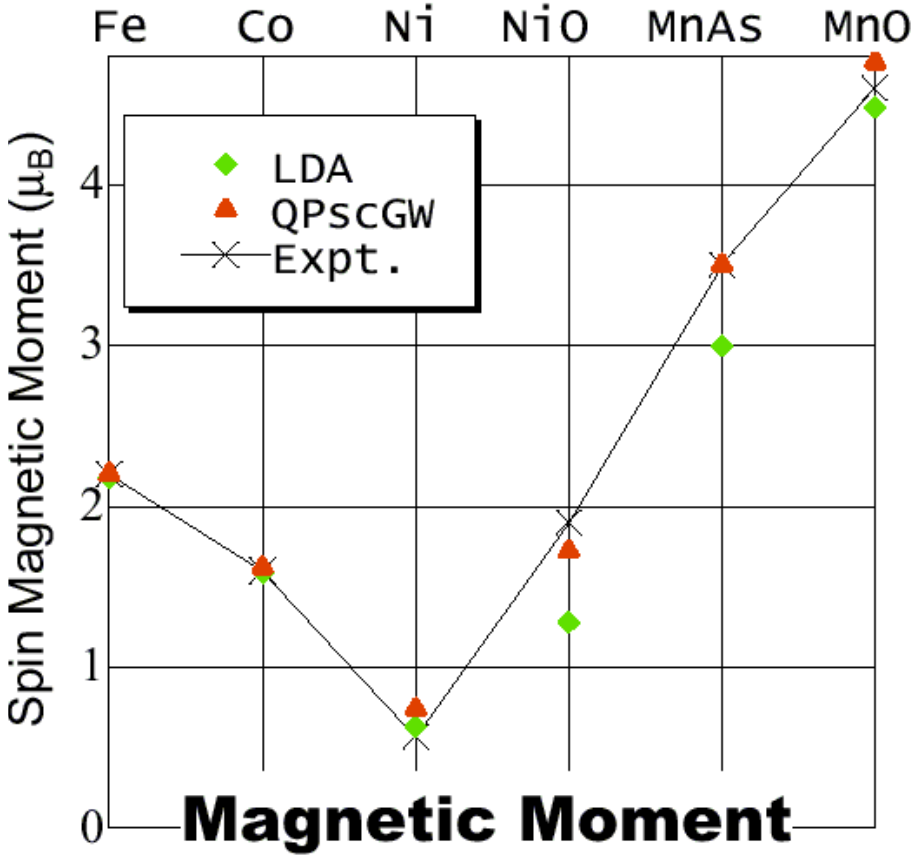
Blue : e-only self-consistency 3.64eV

Experiment(+correction) 3.60eV

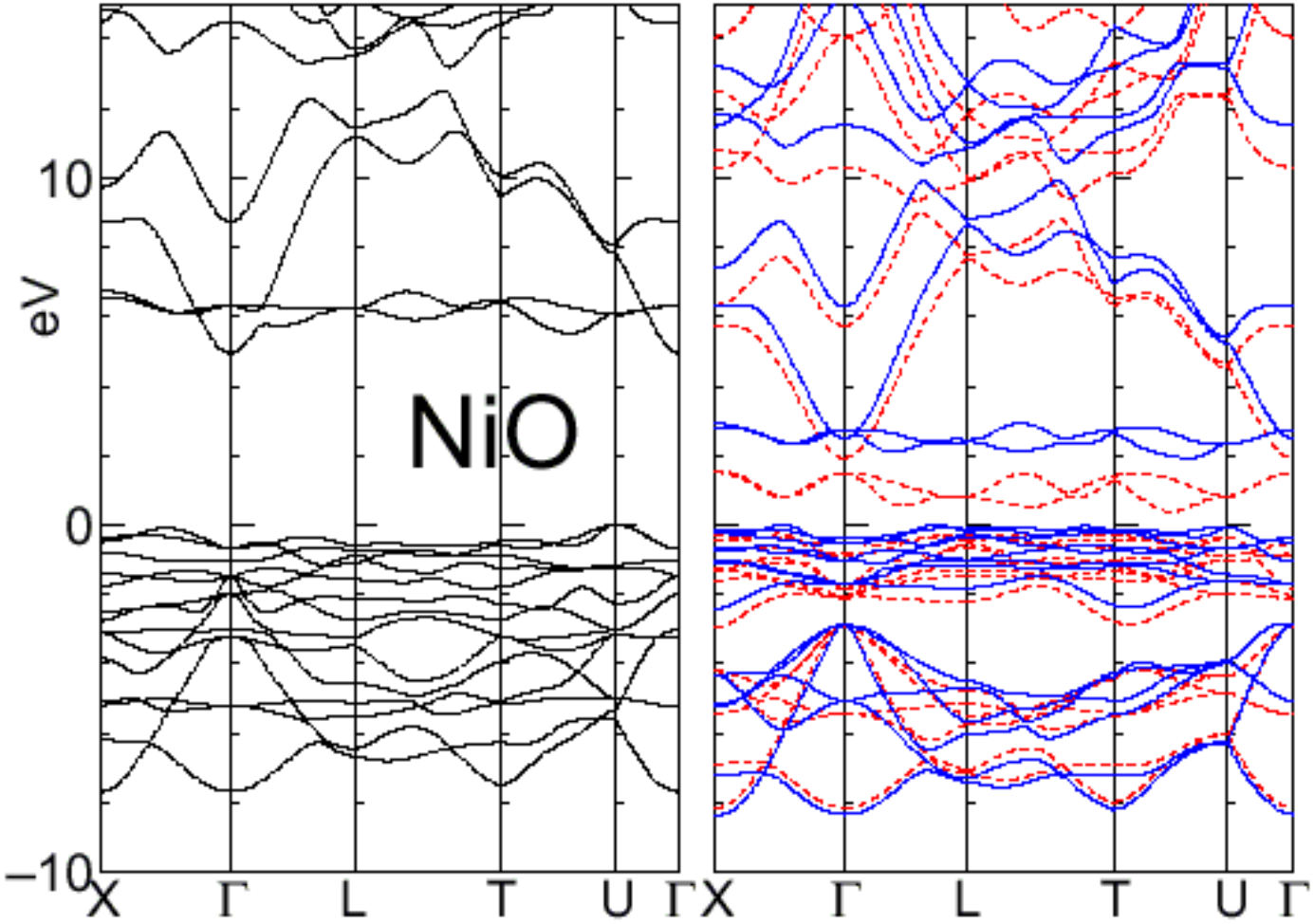
Kotani et al PRB76,165106(2007)

d systems



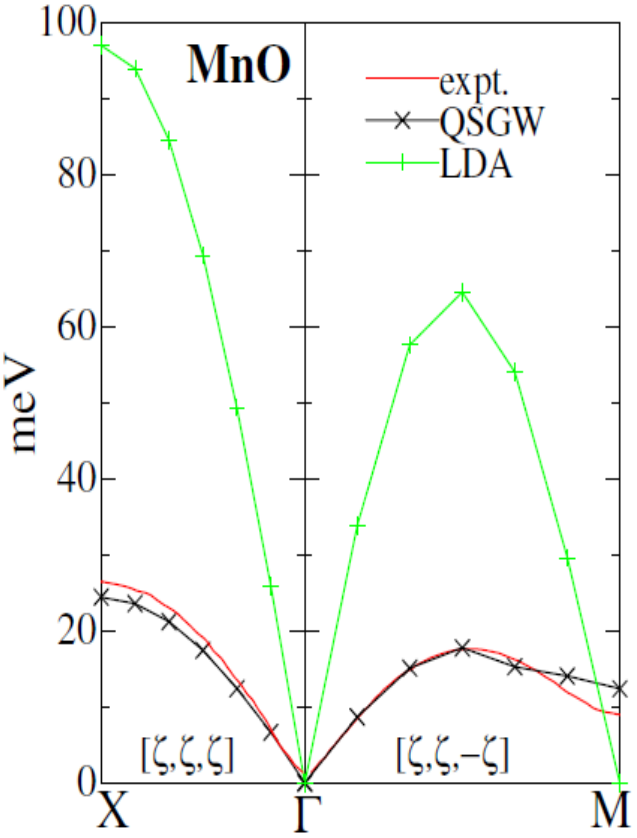


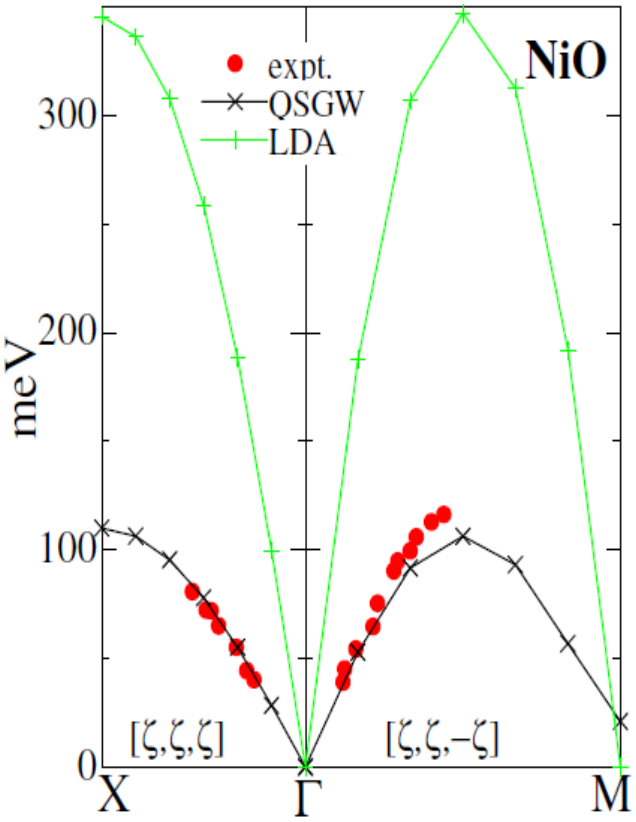
"No Pushing down 3d-band" in GW.



Black:QSGW Red:LDA Blue: e-only

Spin wave dispersion based on QSGW

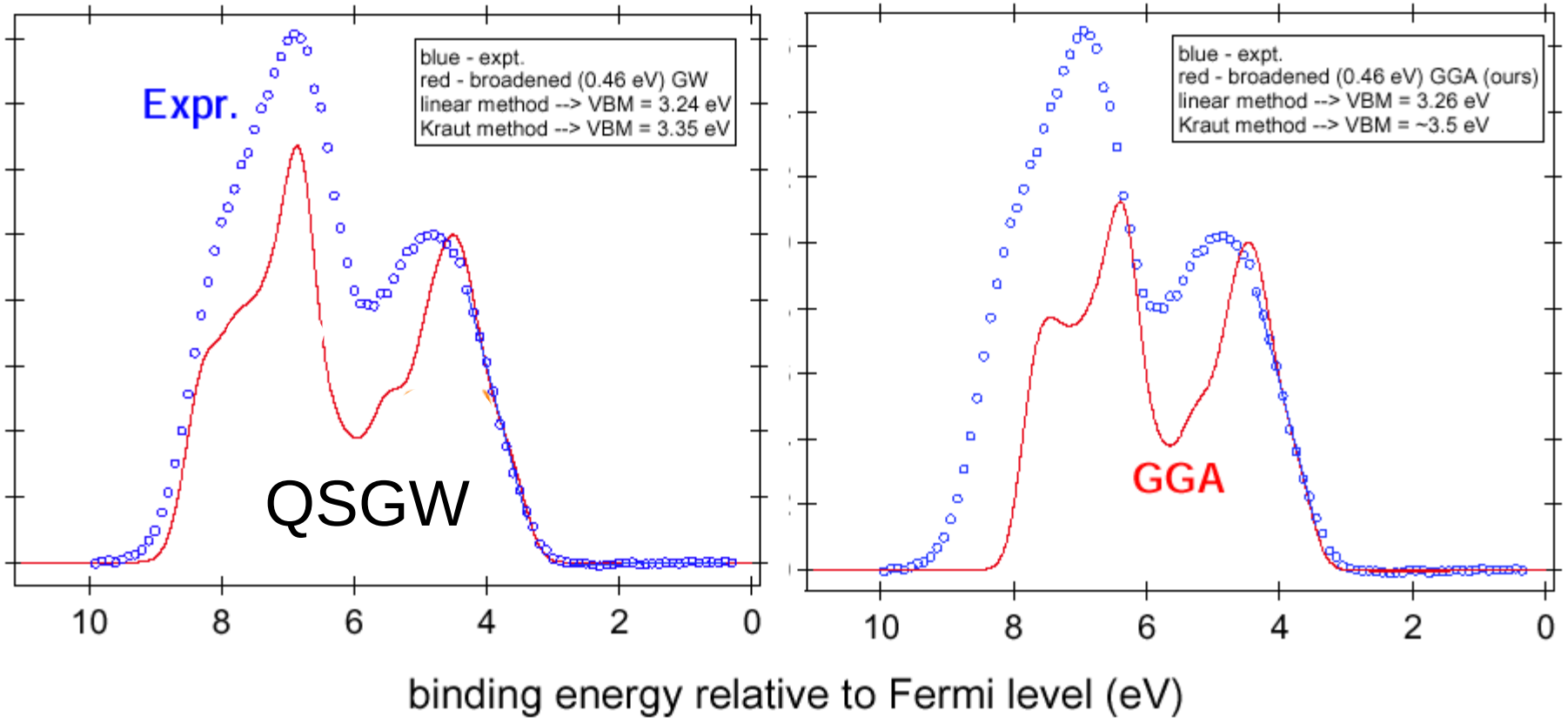




J.Phys.C20 (2008) 295214,
PRB83, 060404(R) (2011) for CaFe2As2 for spectrum of χ^{+-}.

SrTiO3 Valence DOS

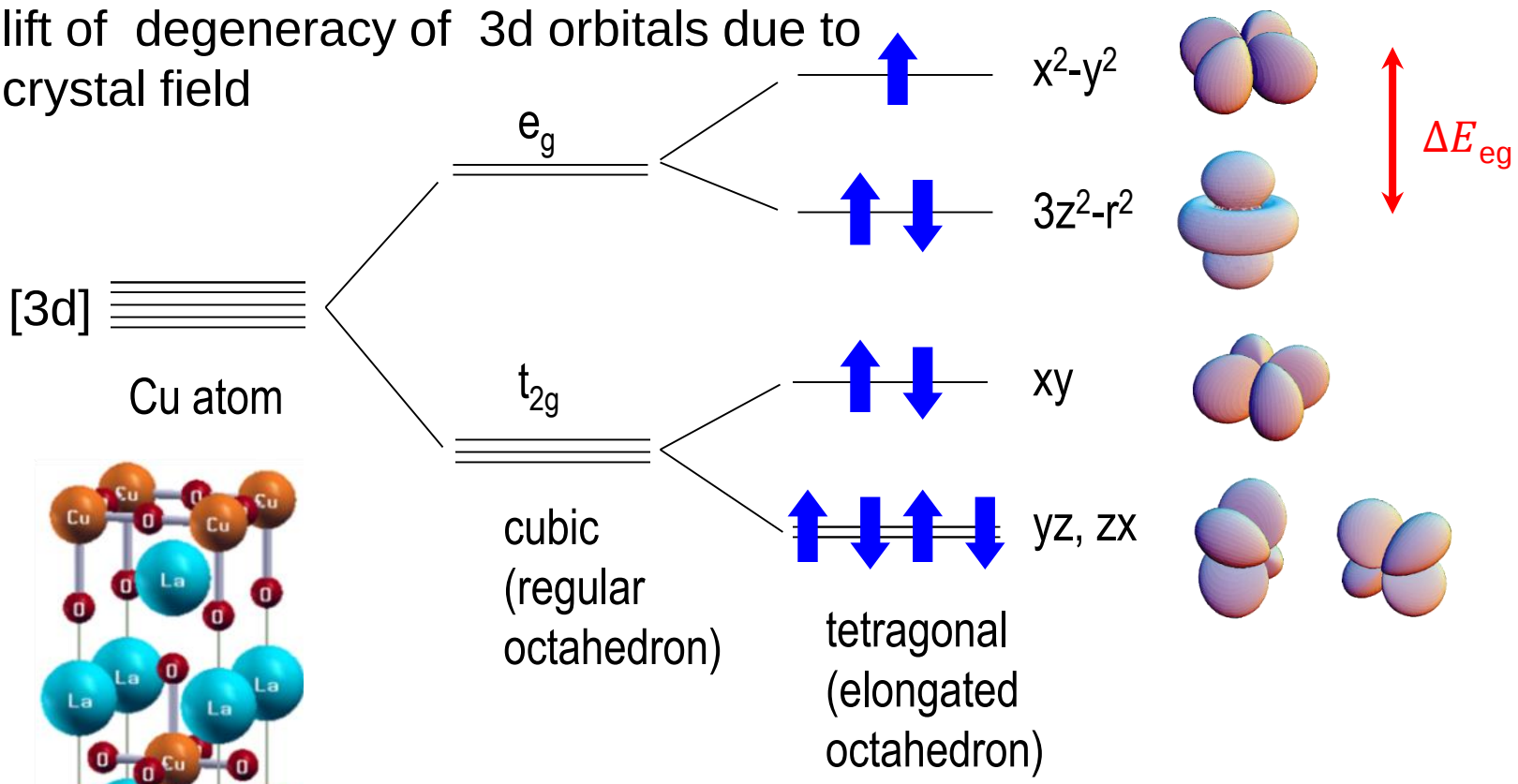
fit of properly broadened theoretical DOS with experiment
n-STO(001) VB excited with monochromatic AlKα x-rays (resolution = 0.46 eV)



S. A. Chambers et al, Surface Sci 554,81-89 (2004)

Electron configuration

lift of degeneracy of 3d orbitals due to crystal field



Around Ef, we have two eg bands.

Band structure: Band width and ΔE_{eg}

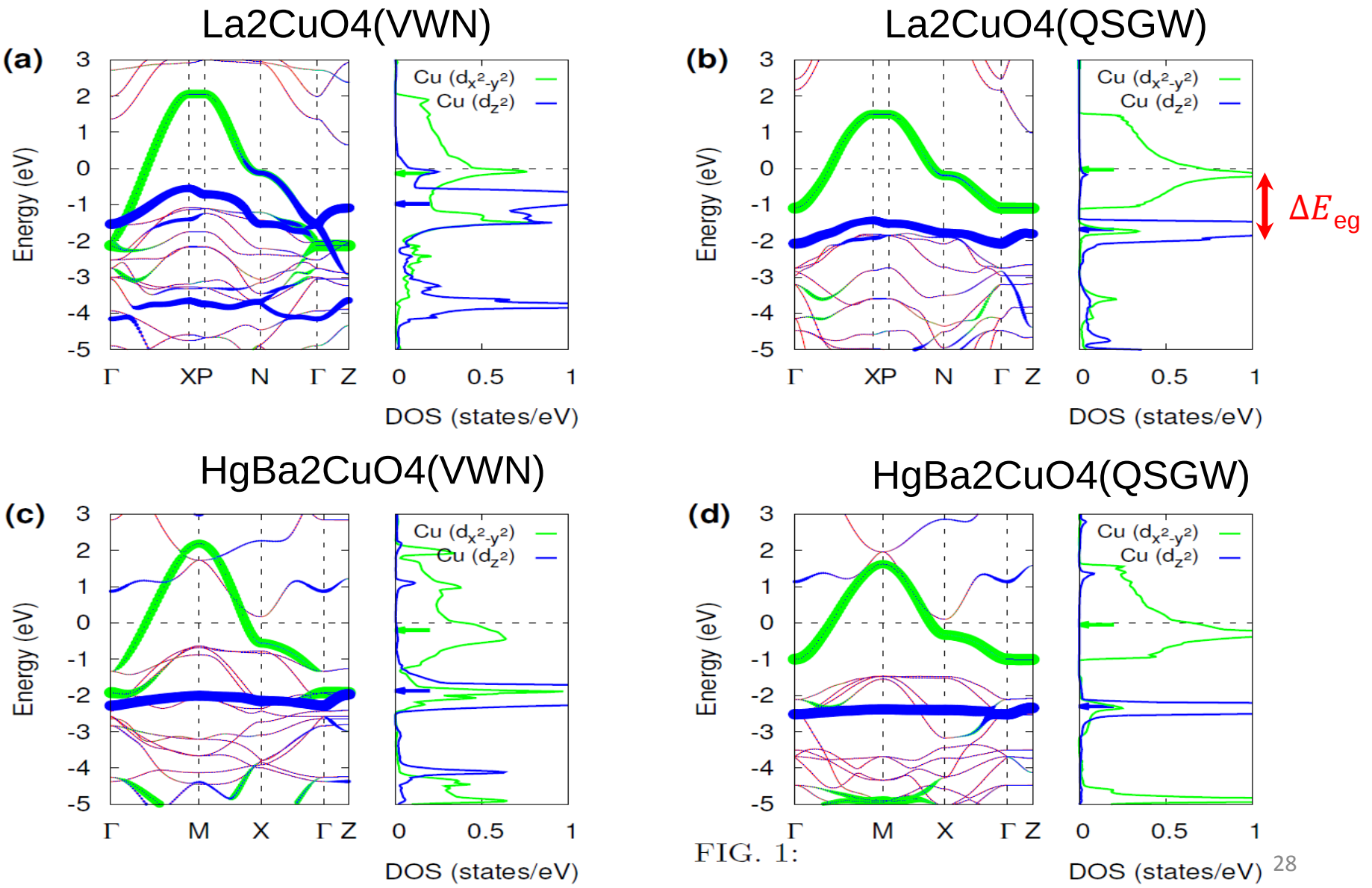
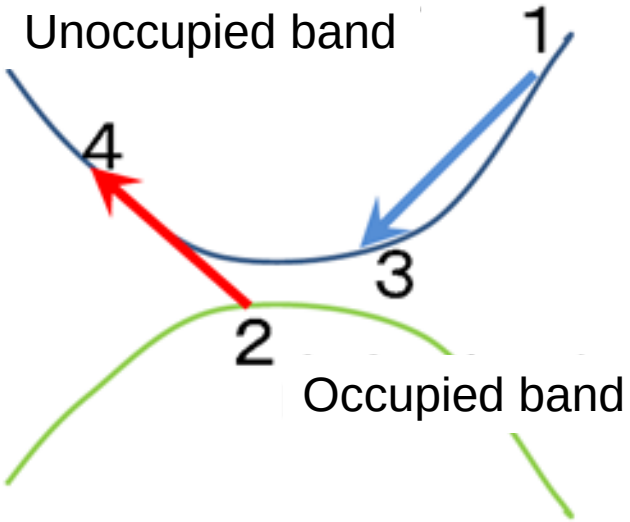
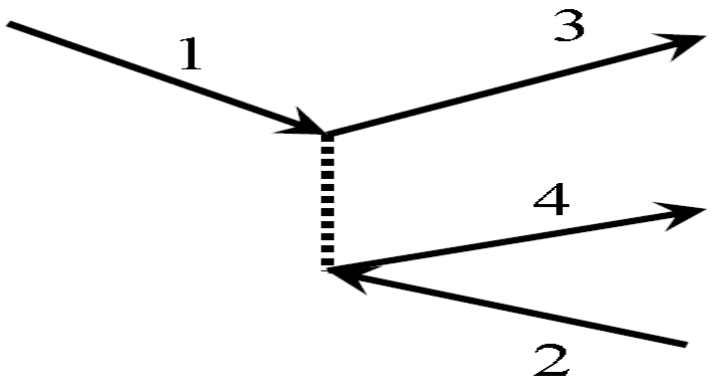


FIG. 1:

Impact ionization rate(auger process)





Fermi's Golden rult → transition rate. Sum up for all final states. Matrix element of transition is

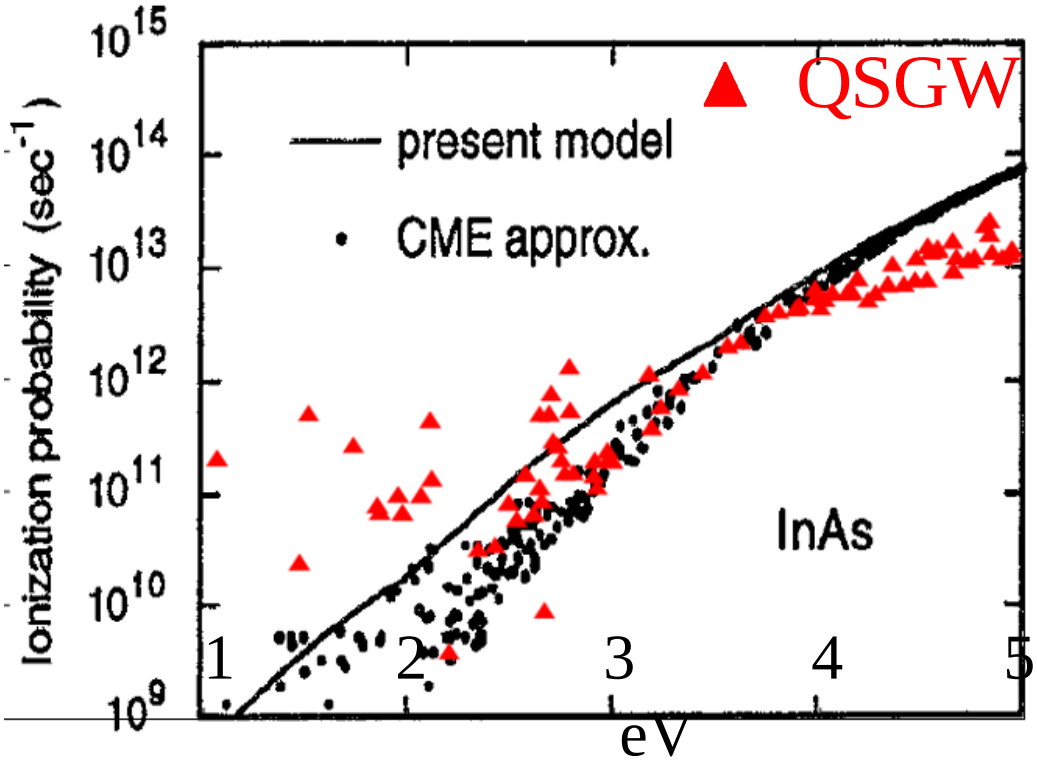
＜1,3｜electron-electron interaction｜4,2＞

（Energy conservation and Momentum conservation）

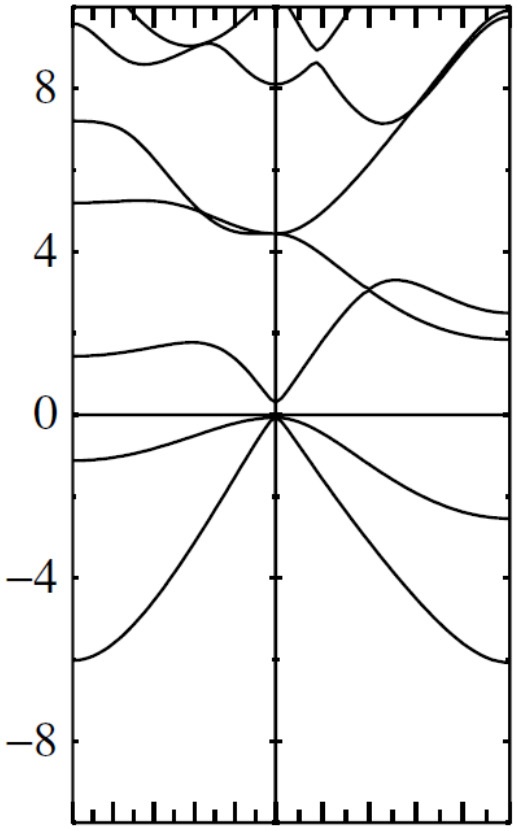
InAs impact ionization rate

(=auger process

= high energy electron lose energy with e-h pair)



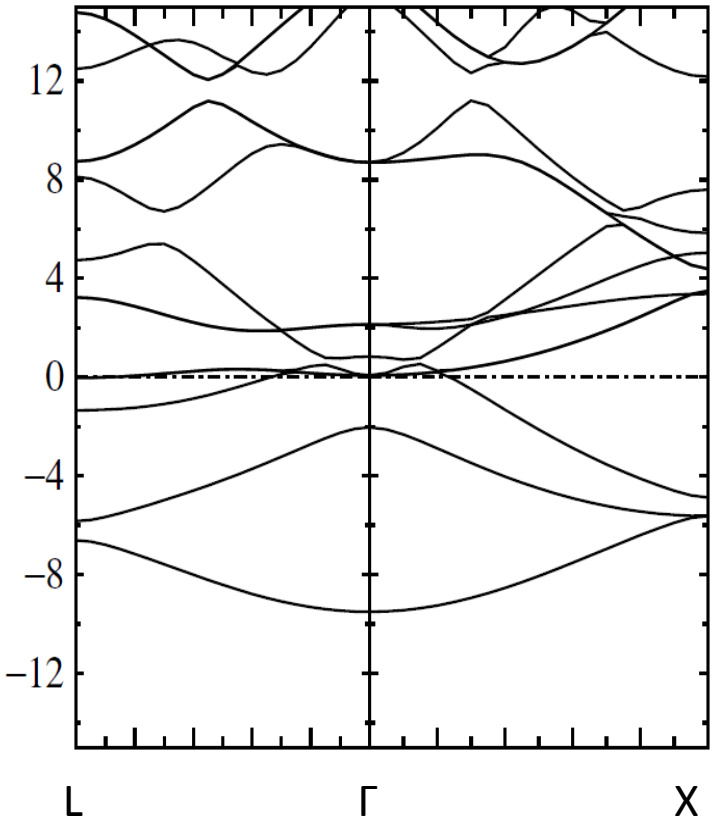
direct gap 0.38eV



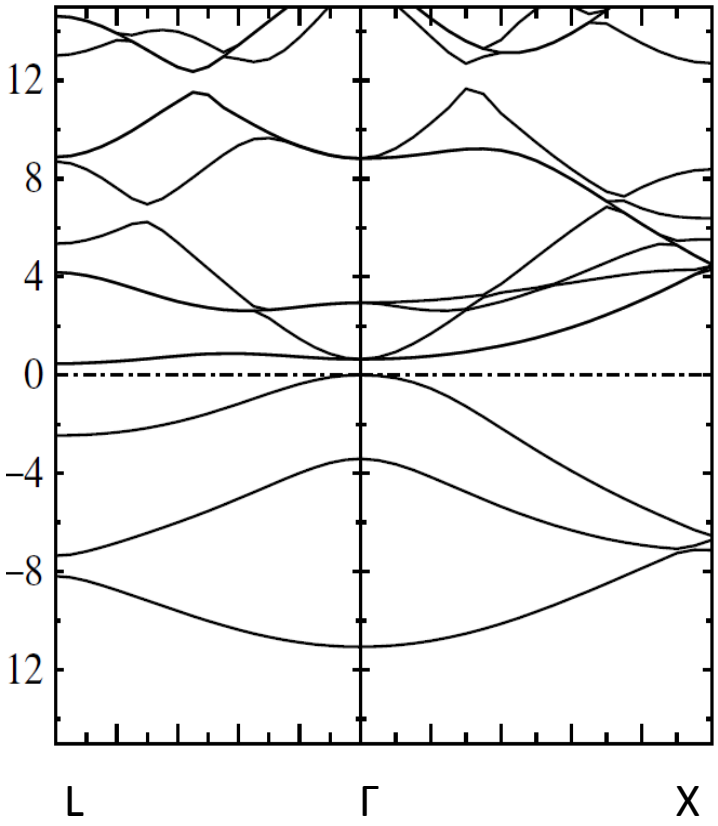
Present model: Sano and Yoshii JAP77 2020 (1995)

YH3(fcc structure 6x6x6)

GGA

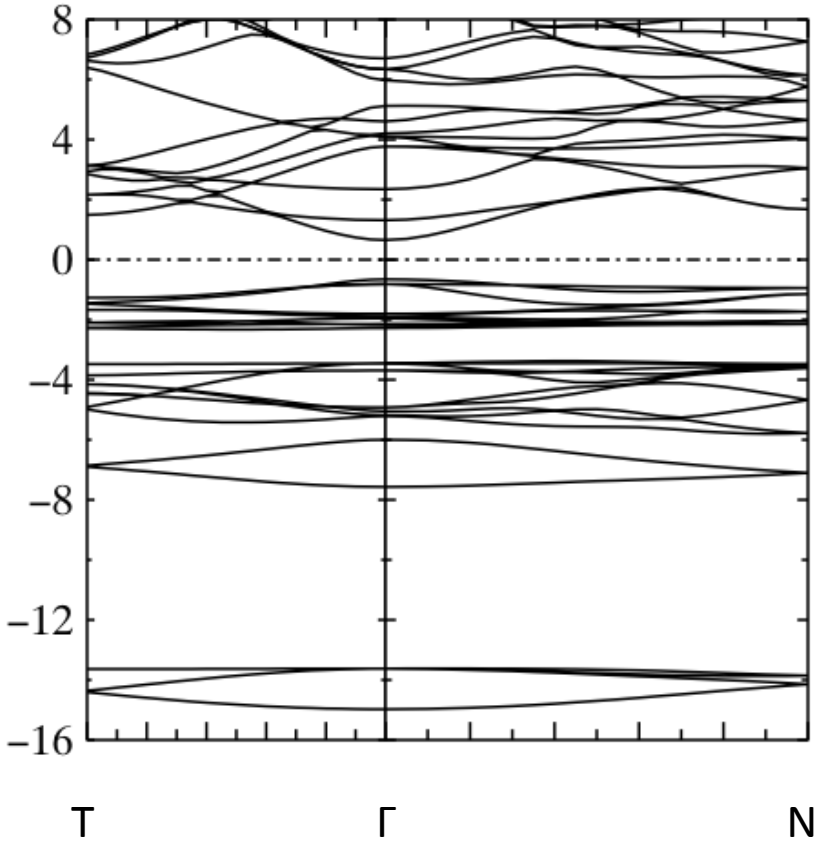


QSGW

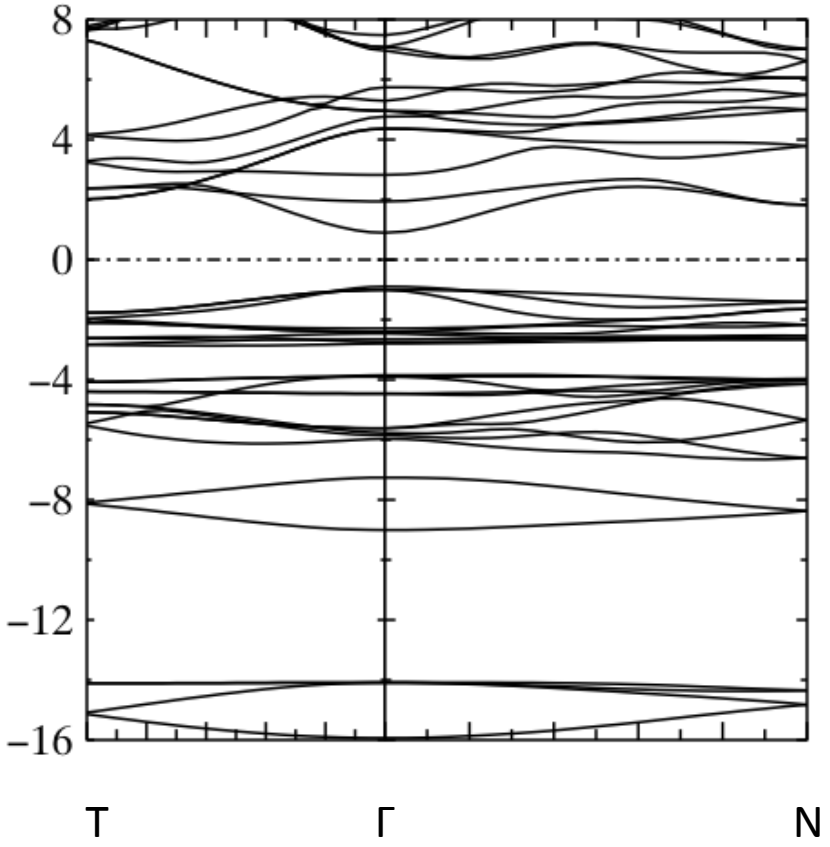


CuGaSe2 (eight atoms in cell, 2x2x2. ~3hours per iteration by single core)

1shotGW



QSGW



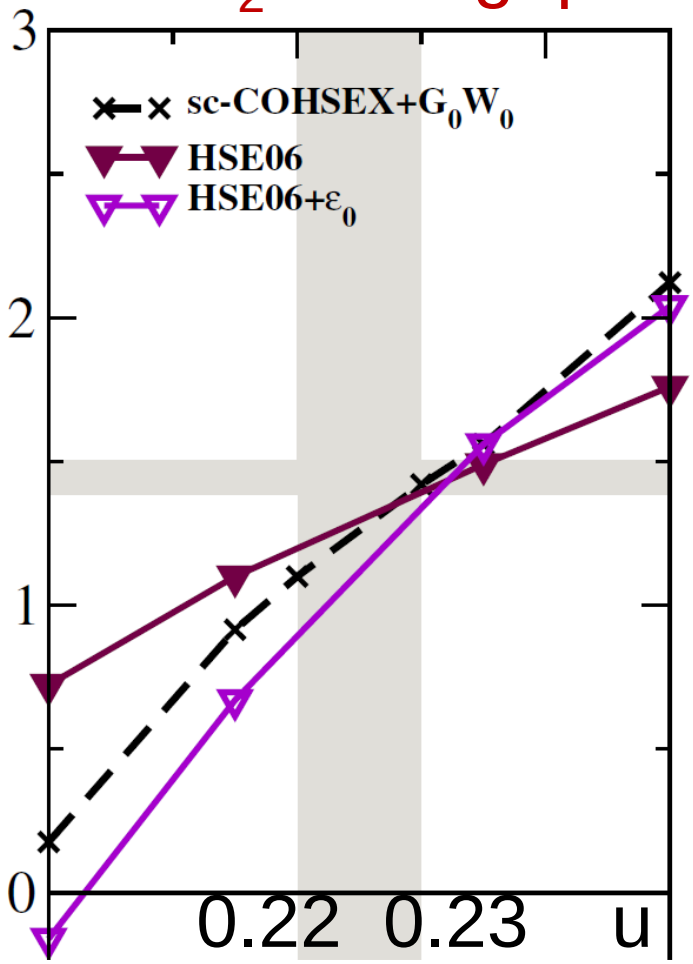
Band gap GGA:0.4eV, GW(1shot noZ) 1.37 eV,
QSGW(1.79eV) Exper. 1.63, 1.67, 1.73eV

Band gap for $CuAB_2$ (eV)

B \ A	S	Se
Al	3.62 (3.49)	2.91 (2.67)
Ga	2.83 (2.43)	1.69 (1.68)
In	1.22(u=0.22) 1.48(u=0.23) (1.53)	---- (1.04)

Experiments in (…)

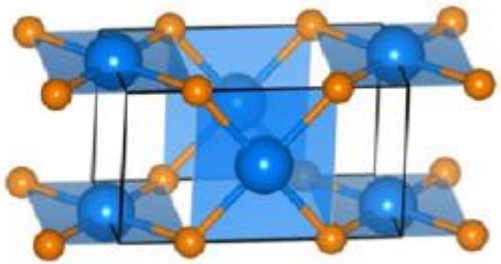
$CuInS_2$ band gap (eV)



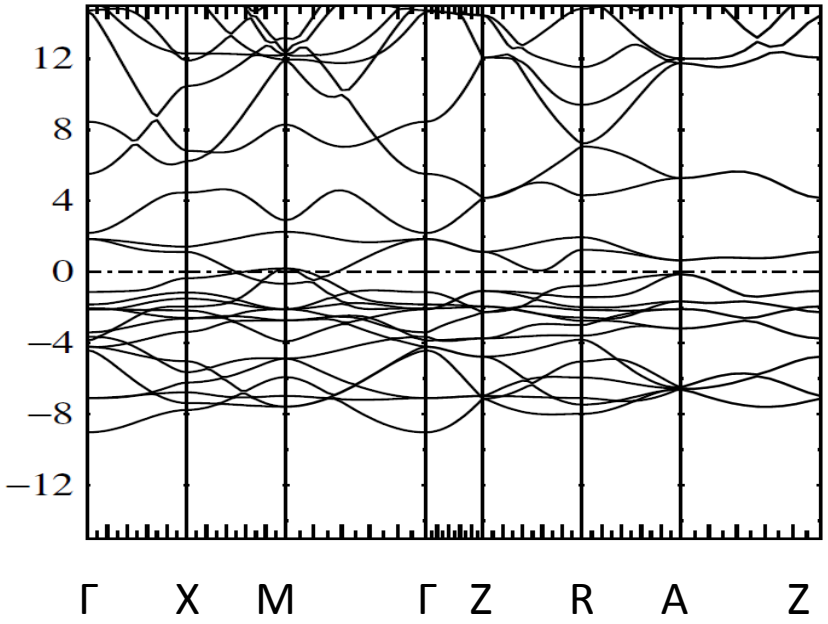
J.Vidal, PRL 104, 056401 (2010)

3x3x3 calculation(need check)

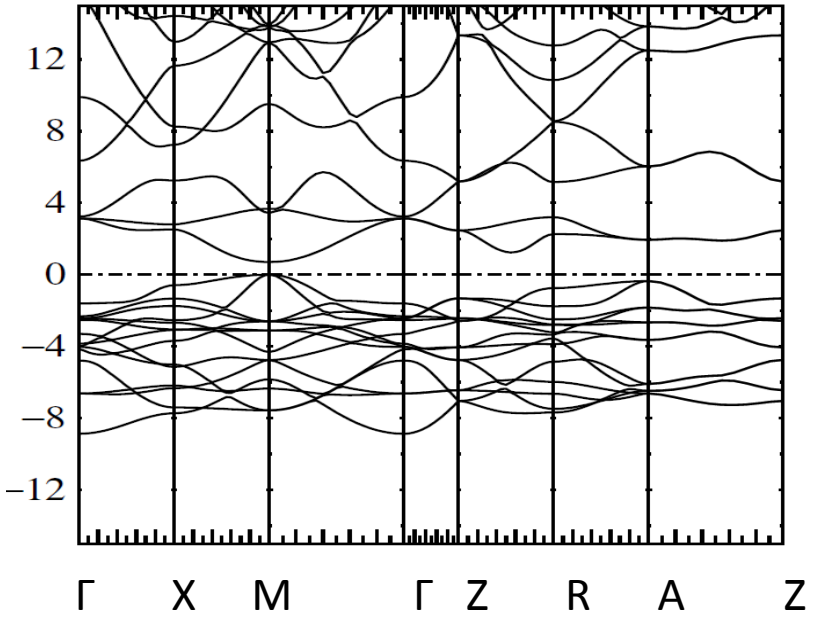
PdO(tetragonal , four atoms per cell 3x3x2 calculation , 1hour per iteration)



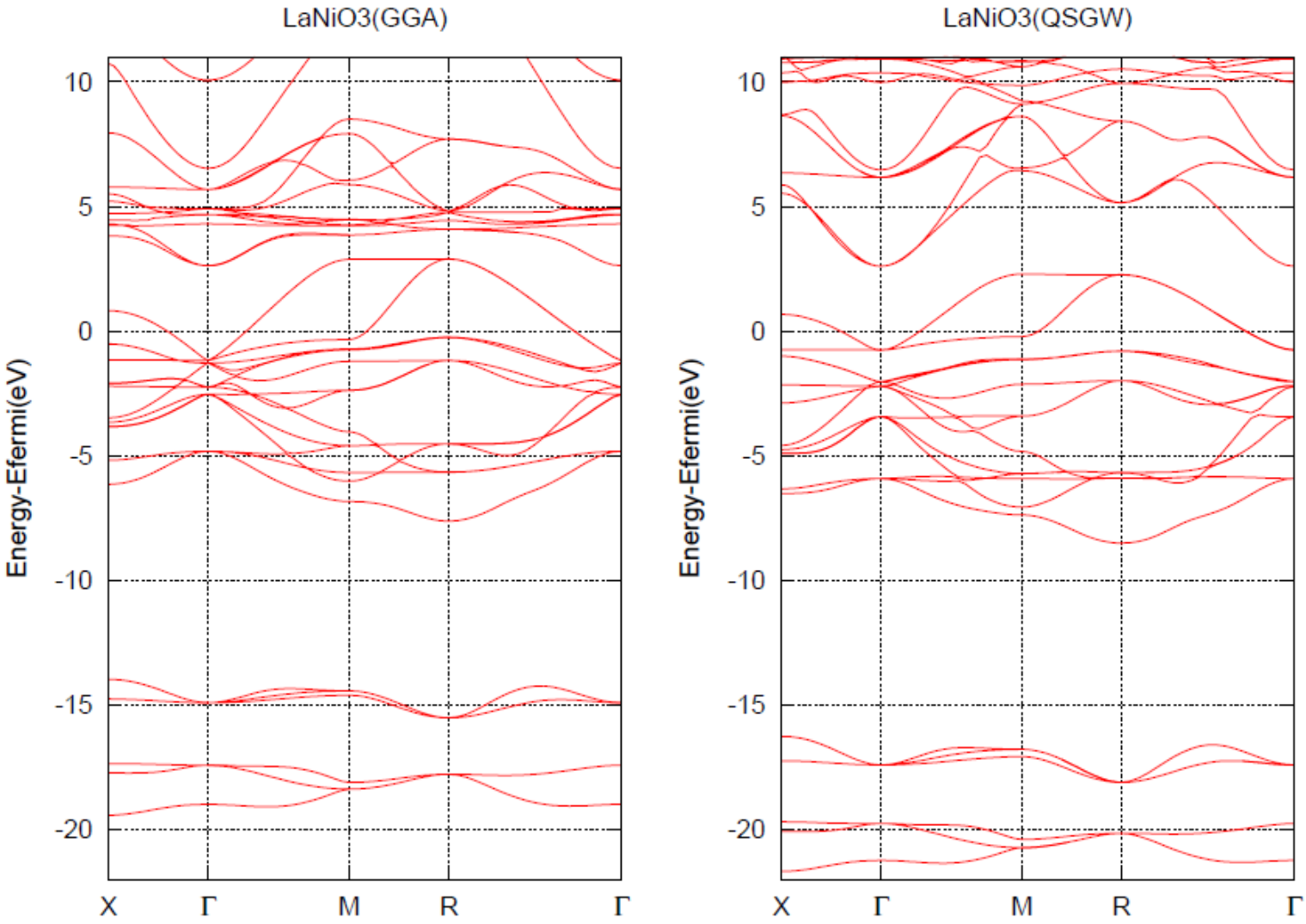
GGA



OSGW



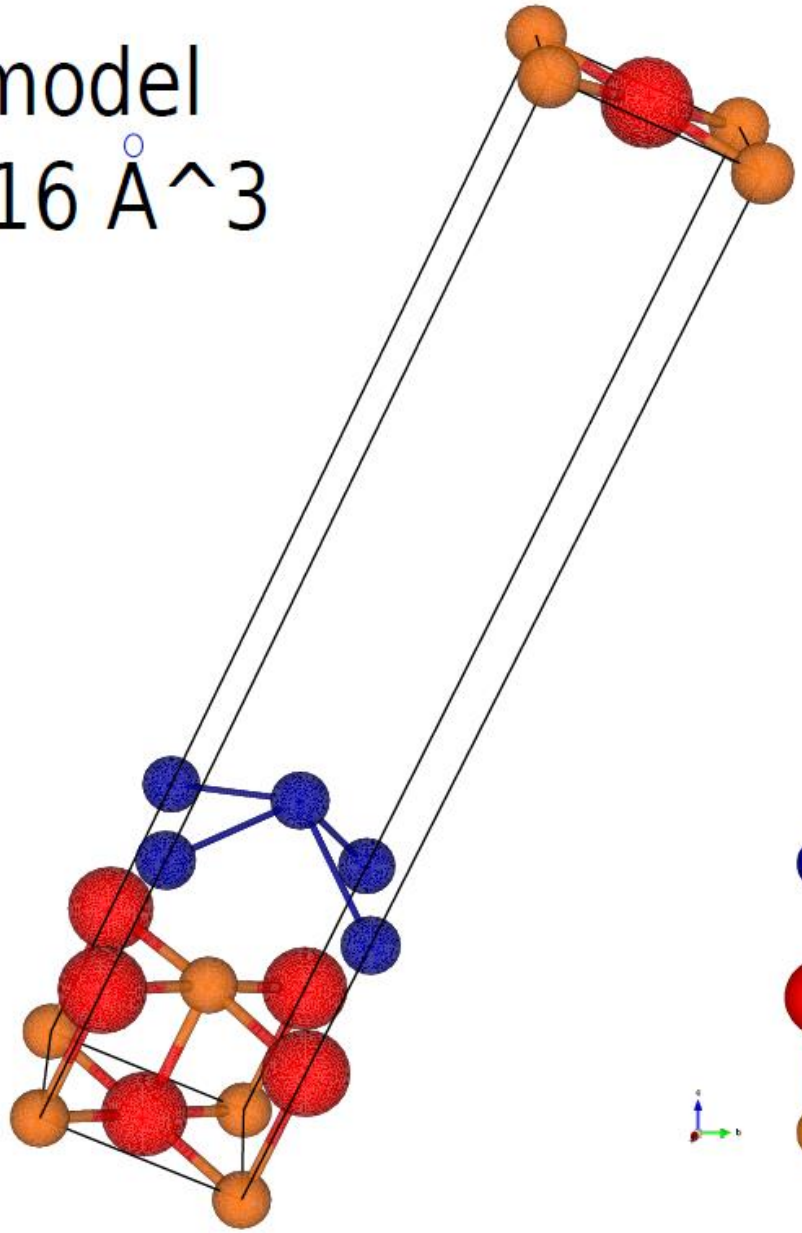
Band gap about 0.7 eV

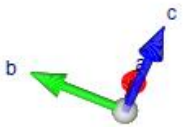


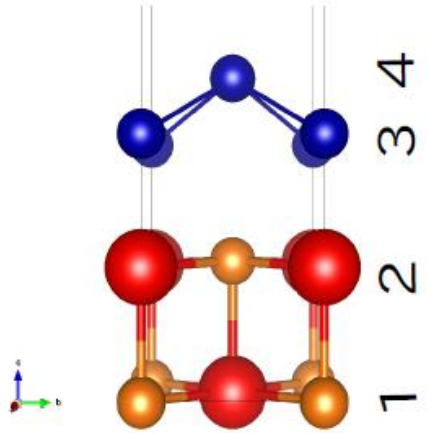
LaNiO3

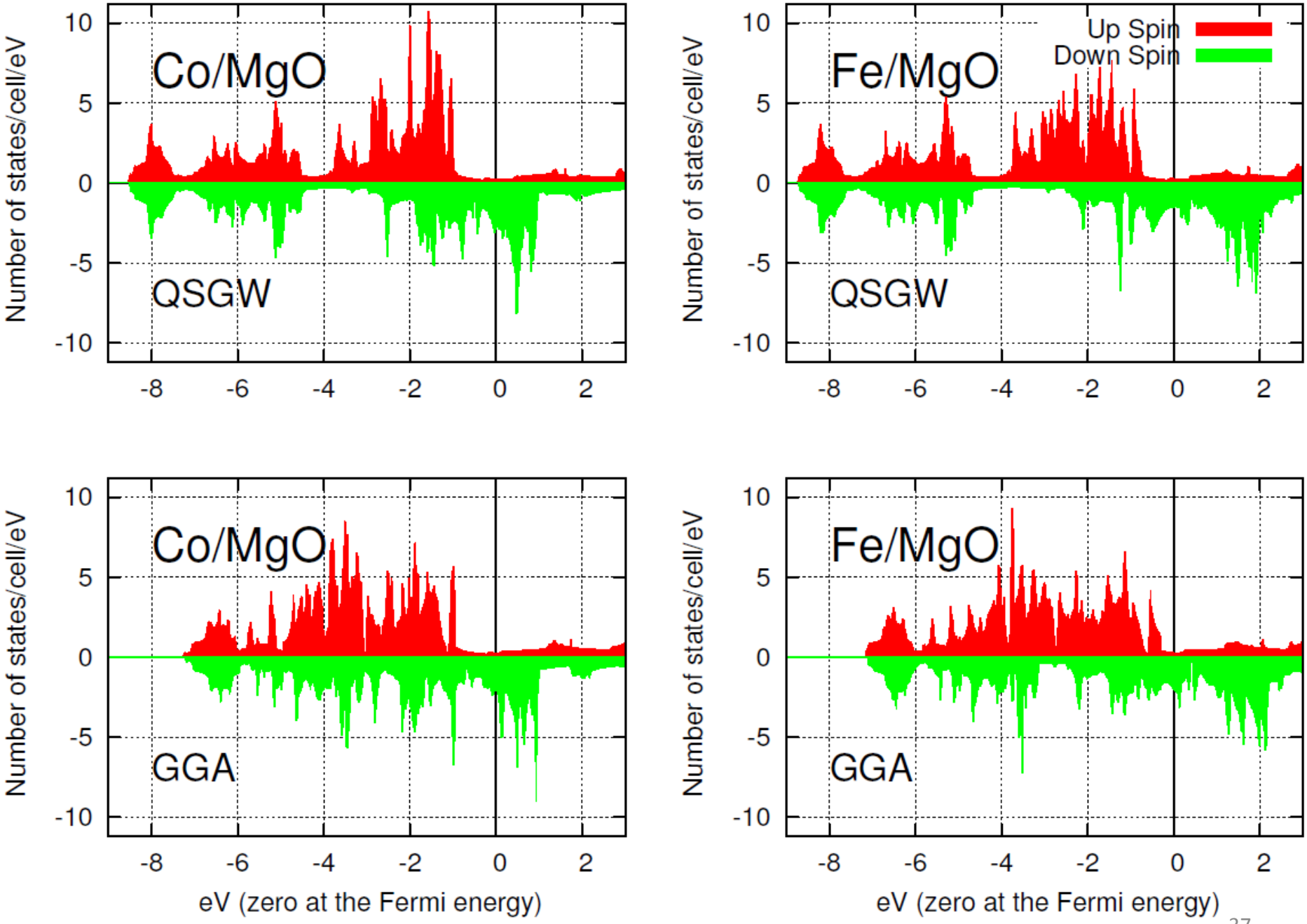
M.J.Han, H.Kino, T.K (arXiv:1402.4915)

Co/MgO model
cell 3x3x16 Å^3








Co/MgO
QSGW
Fe/MgO
QSGW
Up Spin
Down Spin
Co/MgO
GGA
Fe/MgO
GGA
Number of states/cell/eV
eV (zero at the Fermi energy)
10
5
0
-5
-10
-8
-6
-4
-2
0
2

summary

- Mean field theory and excitation energy
  LDA, Hartree-Fock and QSGW
  Janak theorem, finite vs.infinite system

- RPA total energy
  QSGW method

- Some Results
  Band gap, GaAs and Na, Cu
  NiO, Spin Wave, ZnO, LaMnO3,
  InAs (impact ionization), YH3, CuGaSe2,PdO

  - How QSGW works for atoms and molecules?
    See F.Bruneval J.Chem.Phys 136,194107(2012)