

ecalj course menu

Monday 15:40~17:40, 17:50~19:20

- **LECTURE1: PMT method**
How to solve one-body problem? \rightarrow PMT = LAPW + LMTO
- **LECTURE2: Quasiparticle self-consistent GW method**
theory and results until now.
Some kinds of numerical techniques.
- **Get Started!**
Install ecalj, and go through “ecalj tutorial”.
Observe how it works.

Tuesday: 9:00~17:20, Wednesday 9:00~11:00 (or to 12:10).

- ctrl file and output.
- Numerical technique and GWinput.
- Read output (console output, data).
- Check points (How to get reliable results?)

The **PMT** method: a new linearized method

$$\text{PMT} = \text{A}\underline{\text{P}}\text{W} + \underline{\text{MT}}\text{O}$$

Muffin-tin

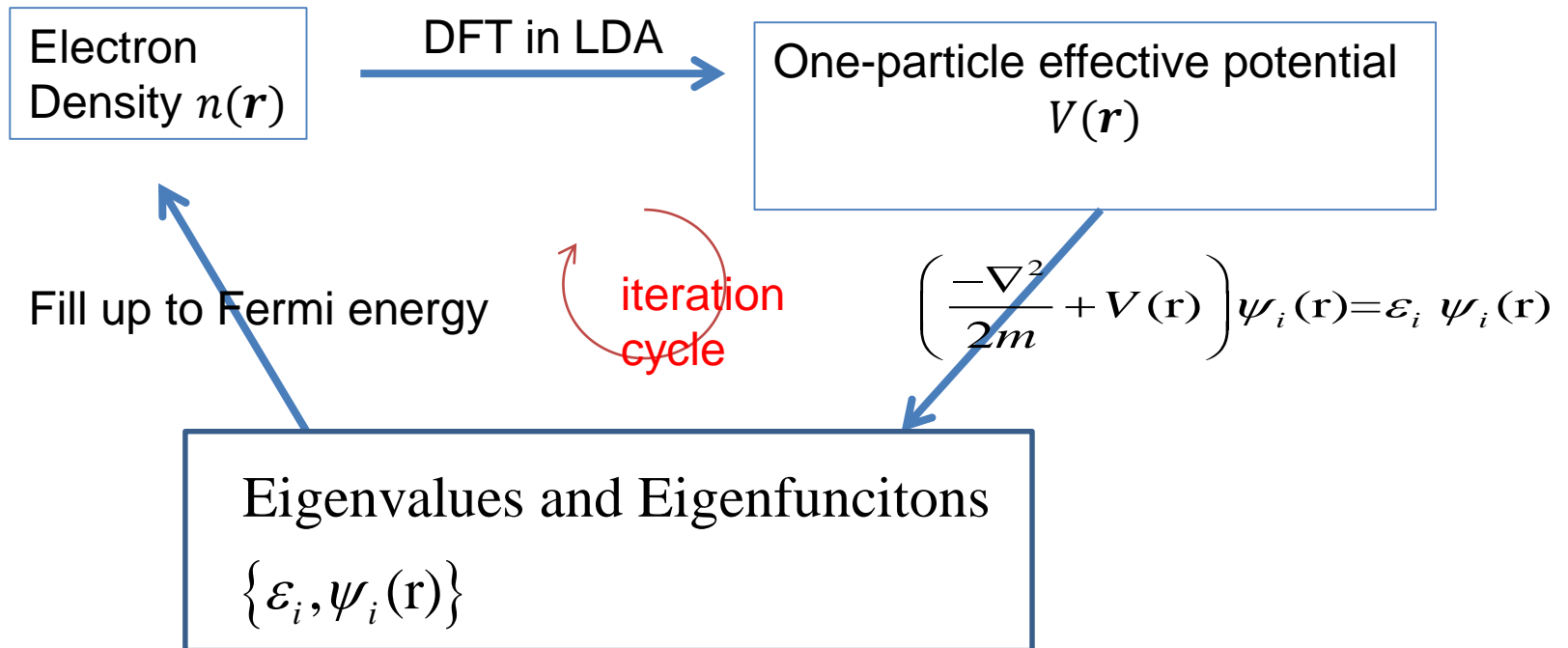
Takao Kotani (tottori-u)

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:

$$\psi_p(\mathbf{r}) = \sum_j \alpha_p^j F_j(\mathbf{r}) \quad \left\{ F_j \right\} : j = 1, 2, \dots, N$$



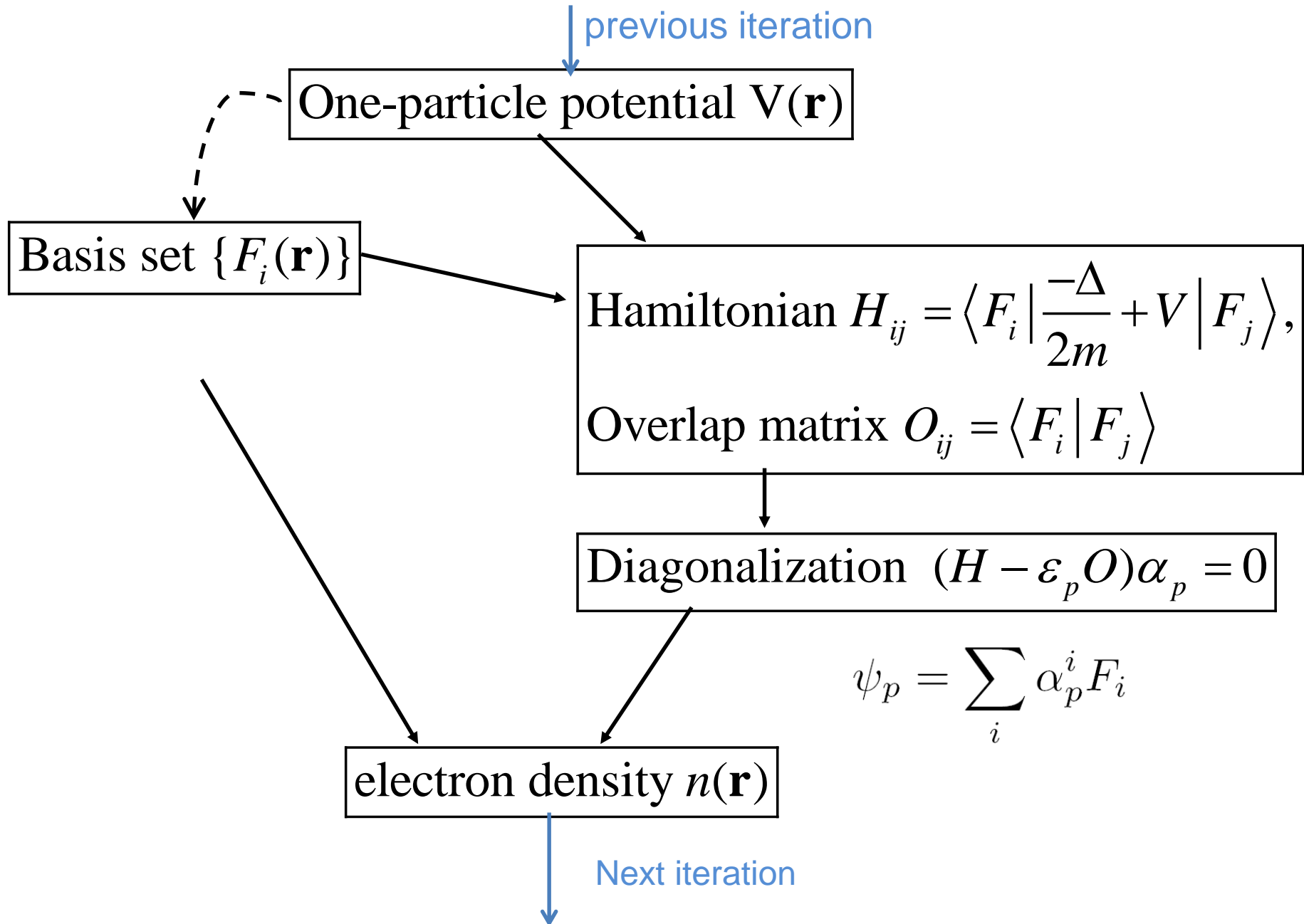
$$\text{Hamiltonian } H_{ij} = \left\langle F_i \left| \frac{-\Delta}{2m} + V \right| F_j \right\rangle,$$

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

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

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

iteration cycle



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.

Electronic Structure of ...

research.physics.illinois.edu/ElectronicStructure/598SCM-F04/lecture_notes/lect12-APW-KKR-MTO_files/frame.html

asahi.com (朝日... Yahoo! JAPAN EcalJ - Ecal mariko てにす池高 応数SNS PMTdimer結果 - E... PMTbulk結果 - Ecal » その他のブックマーク

Muffin Tin Division of Space

A definition – not an approximation

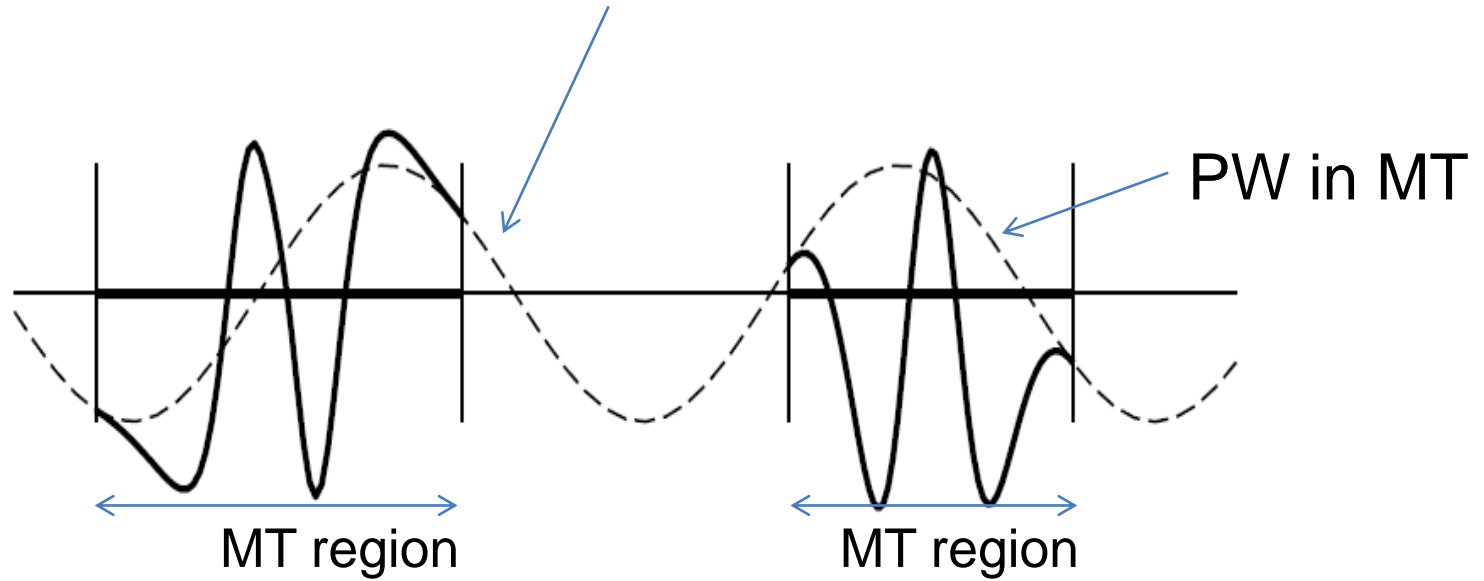
Sphere around each atom
MT regions

Interstitial regions between atoms
Interstitial region

- 1 Lecture 11: Atomic Sphere Methods: Augmentation, Green's Functions and Linearization Electronic Structure of Condensed Matter, Physics 598SCM
- 2 **Muffin Tin Division of Space**
- 3 Muffin Tin Approximation
- 4 Augmentation
- 5 Augmented Plane Waves - Slater
- 6 Augmented Plane Waves II
- 7 Augmented Plane Waves III
- 8 APW - Bands of Cu
- 9 APW - Bands of Transition metals
- 10 The KKR (multiple

APW

Envelope function = PlaneWave(PW)

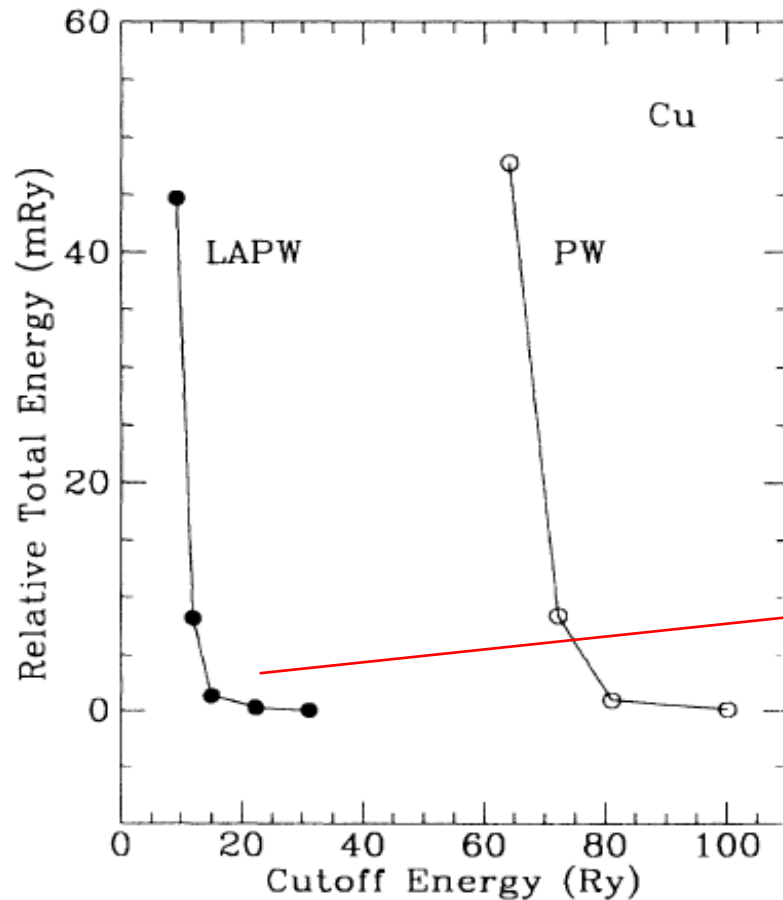


3-components

PW + Atomic-like part — Counter part:
0th 1st PW within MT 2nd

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

Linearized APW



fcc Cu

plane wave is not
so efficient for 3d

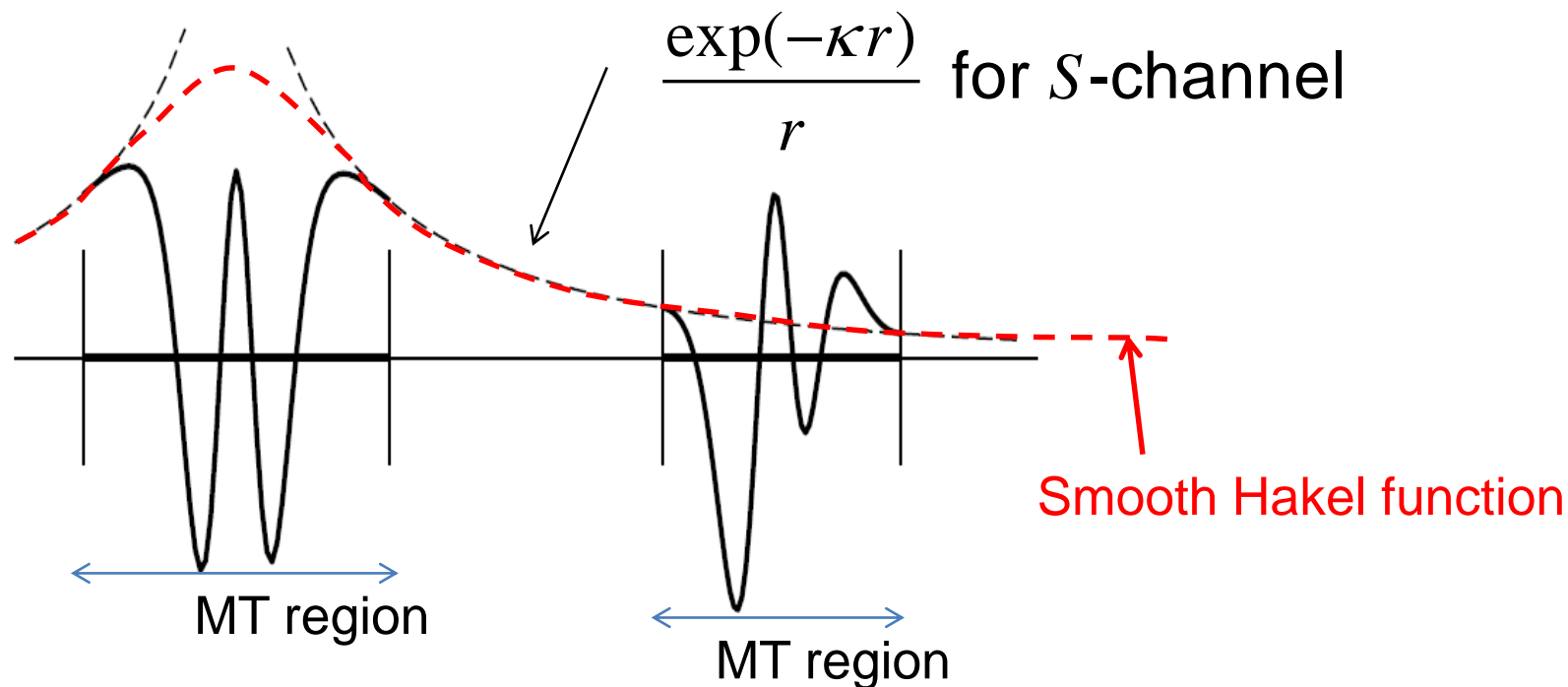
15Ry or more for
~1mRy convergence

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

D.Singh et al PRB49,17424

MTO

Atom-centered Hankel function, e.g,



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

$$\text{PMT} = \text{A}\underline{\text{P}}\text{W} + \underline{\text{M}}\text{T}\text{O}$$

T.K and M.van Schilfgaarde

arXiv:0808.1604

Phys. Rev. B 81, 125117 (2010)

T.K and H. Kino

Supercell calculations from H₂ through Kr₂.

Almost automatic setting of MTOs with APWs
(Energy cutoff 3~4Ry) .

Journal of the Physical Society of Japan,
vol. 82, no. 12, p. 124714, (2013).

Basis function

MT center at \mathbf{R} . Radius 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: $l \leq l_{\max} \sim 4$, **Radial-part expansion**

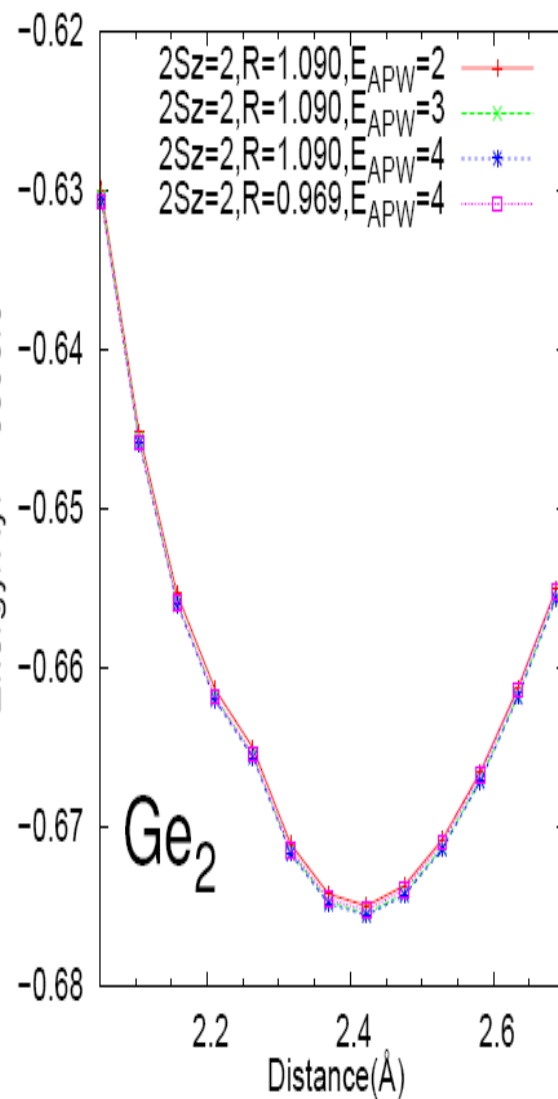
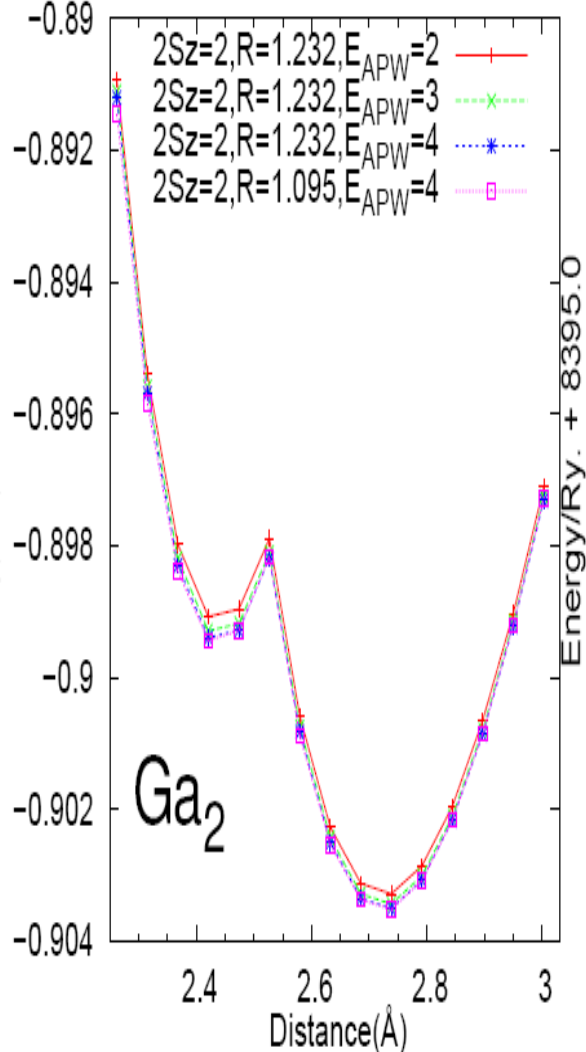
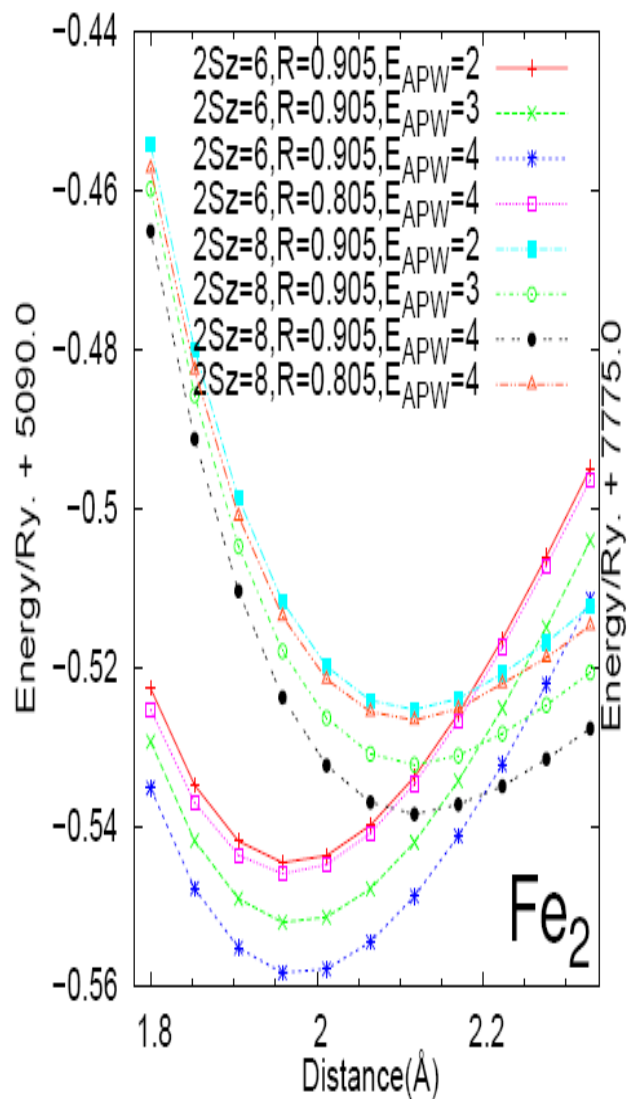
$$F_j(\mathbf{r}) = F_{0j}(\mathbf{r}) + F_{1j}(\mathbf{r} - \mathbf{R}) - F_{2j}(\mathbf{r} - \mathbf{R})$$

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

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

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

This is also used together.



$$N_{\text{basis}} = 1081 + 36 \times 2, \quad 1973 + 36 \times 2, \quad 3025 + 36 \times 2$$

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.

Mean field theory gives independent-particle picture

- Hartree-Fock theory
- Density functional theory

Eigenvalues and Eigenfunctions $\{\varepsilon_i, \psi_i(\mathbf{r})\}$

are determined by minimization of $E[\{\psi_i(\mathbf{r})\}, n_i]$

The minimization determines

$n_i = 1$ for $\varepsilon_i < \varepsilon_{\text{FERMI}}$ (occupied states)

$n_i = 0$ for $\varepsilon_i > \varepsilon_{\text{FERMI}}$ (unoccupied states)

Janak(Koopman's) theorem

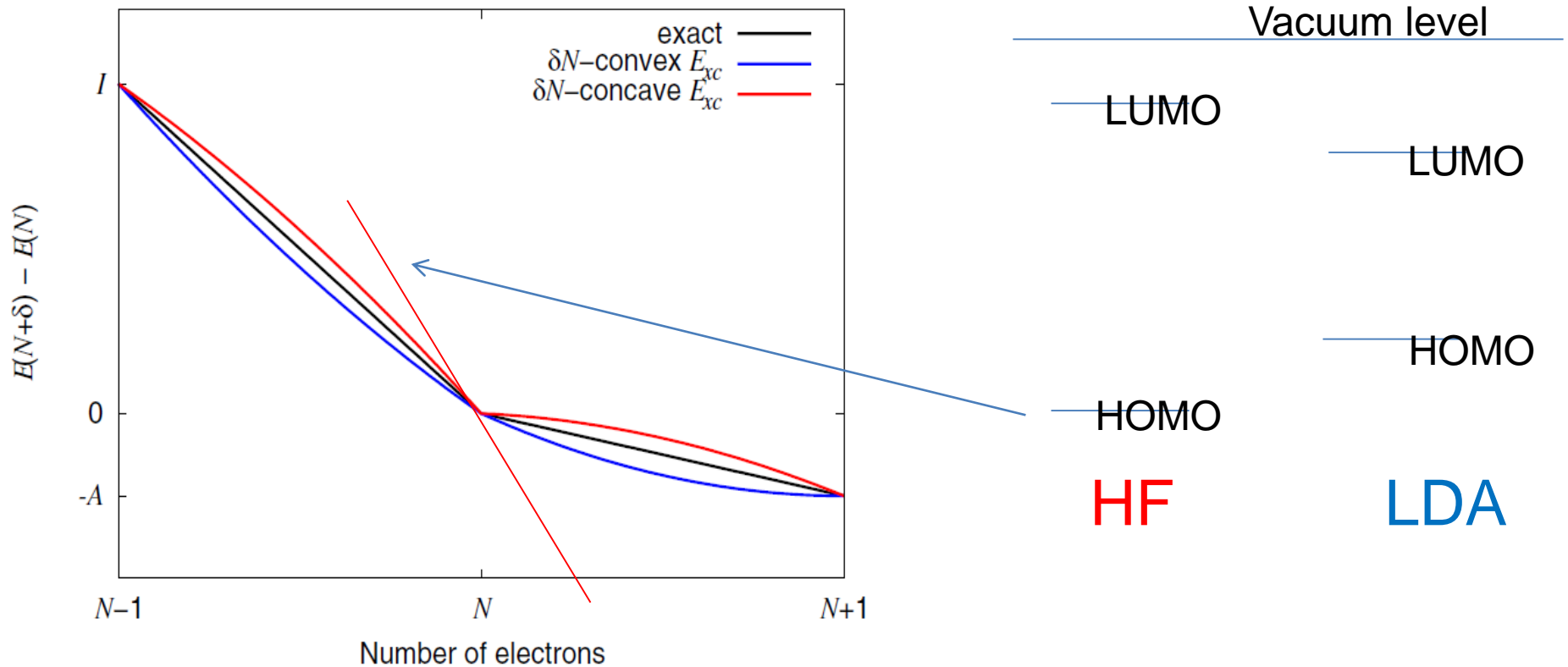
$$\frac{\partial E}{\partial n_i} = \varepsilon_i$$

Ionization energy of an atom

A.J.Cohen, P. Mori-Sanchez, W.Yang, Science 321, 792 (2008)

PHYSICAL REVIEW

PRL **100**, 146401 (2008)



$$\varepsilon_i = \frac{\partial E}{\partial n_i} \approx \frac{\Delta E}{\Delta n_i} \quad (\text{but a little different})$$

How about solid (infinite system)? →

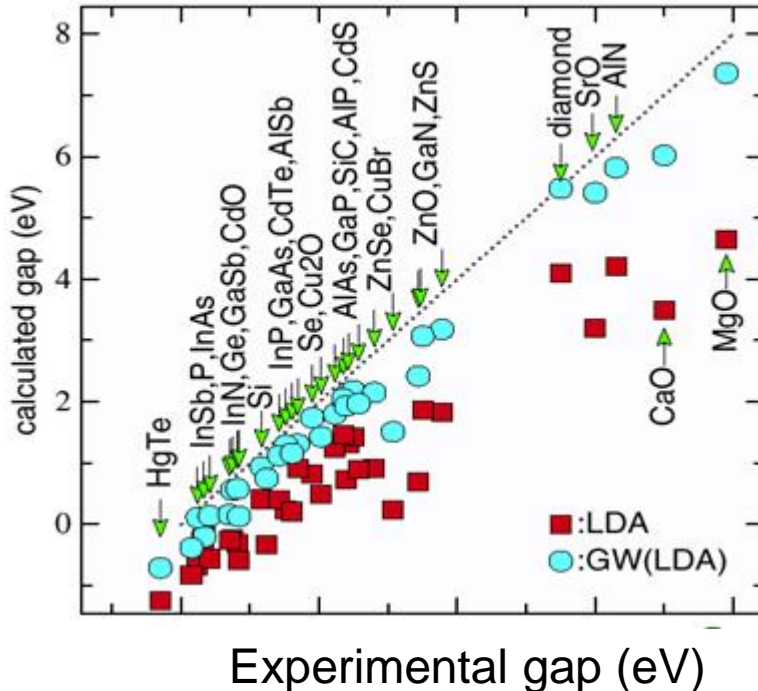
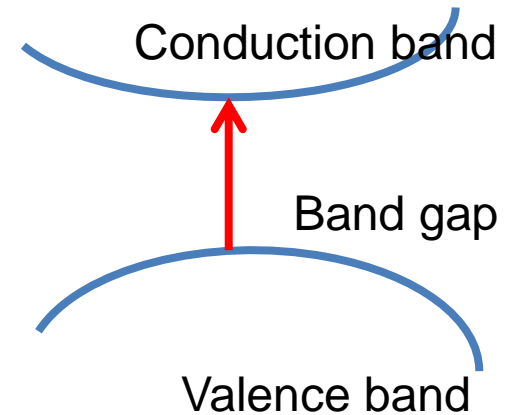
$$\varepsilon_i = \frac{\partial E}{\partial n_i} = \frac{\Delta E}{\Delta n_i} \quad \text{is satisfied.}$$

If $\varepsilon_i = \frac{\partial E}{\partial n_i} = \frac{\Delta E}{\Delta n_i}$ (linear line),

we have better excitation energies $\varepsilon_i - \varepsilon_j$

How accurate they are?

band gap ($\varepsilon_{\text{CBM}} - \varepsilon_{\text{VBM}}$)



LDA gives too small
HF(not shown) gives too large

GW method and QSGW method

GW is based on the “RPA total energy”

We start from $H_{\text{LDA}} \rightarrow \{\varepsilon_i, \psi_i(\mathbf{r})\}$

$$E = E_{0\text{k}} + E_{0\text{ext}} + E_{\text{H}} + E_{\text{X}} + E_{\text{C}}$$

$$= \sum_i^{\text{OCC.}} \left\langle \varphi_i \left| \frac{-\Delta}{2m} \right| \varphi_i \right\rangle + \sum_i^{\text{OCC.}} \left\langle \varphi_i \left| V_{\text{ext}}(\mathbf{r}) \right| \varphi_i \right\rangle + E_{\text{H}} + E_{\text{X}} + E_{\text{C}}$$

$$E_{\text{H}} + E_{\text{X}} + E_{\text{C}} = \text{diagrams} + G_0 = \frac{1}{\omega - H_0} \text{で展開}$$

The diagrams represent the many-body perturbation theory expansion for the exchange and correlation energy. They include a single electron loop, a two-electron loop, and a three-electron loop, each with arrows indicating the direction of electron flow.

$$E_i \equiv \frac{\partial E}{\partial n_i} = \left\langle \varphi_i(\mathbf{r}) \left| \frac{-\Delta}{2m} + V_{\text{ext}} + V_{\text{H}} + \Sigma(\varepsilon_i) \right| \varphi_i(\mathbf{r}) \right\rangle$$

$$= \varepsilon_i + \left\langle \varphi_i(\mathbf{r}) \left| \left(\Sigma(\varepsilon_i) - V_{\text{XC}}^{\text{LDA}} \right) \right| \varphi_i(\mathbf{r}) \right\rangle$$

This is one-shot GW

Historically, $E_i = \varepsilon_i + \left\langle \varphi_i(\mathbf{r}) \left| \left(\Sigma(E_i) - V_{\text{XC}}^{\text{LDA}} \right) \right| \varphi_i(\mathbf{r}) \right\rangle$,

(but $E_i = \varepsilon_i + \left\langle \varphi_i(\mathbf{r}) \left| \left(\Sigma(\varepsilon_i) - V_{\text{XC}}^{\text{LDA}} \right) \right| \varphi_i(\mathbf{r}) \right\rangle$ is better)²²

How to determine better H_0 ?

$$E_i = \frac{\partial E}{\partial n_i} = \left\langle \varphi_i(\mathbf{r}) \left| \frac{-\Delta}{2m} + V_{\text{ext}} + V_H + \Sigma(\varepsilon_i) \right| \varphi_i(\mathbf{r}) \right\rangle$$

$$\frac{\delta E_i}{\delta \varphi_i} = 0 \quad \rightarrow \quad \left(\frac{-\Delta}{2m} + V_{\text{ext}} + V_H + \Sigma(\varepsilon_i) \right) \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r})$$

$\Sigma(\mathbf{r}, \mathbf{r}', \omega) \rightarrow \omega$ -independent $V_{\text{xc}}(\mathbf{r}, \mathbf{r}')$

$$H_0 = \frac{-\Delta}{2m} + V_{\text{ext}} + V_H + V_{\text{xc}}(\mathbf{r}, \mathbf{r}') \rightarrow \Sigma(\mathbf{r}, \mathbf{r}', \omega)$$

An average procedure
(not shown here)

Non-local potential term (as Fock exchange term) is important.

I. Localized electrons \leftarrow LDA+U type effect

(Onsite non-locality. self-interaction included).

It can break time-reversal symmetry \rightarrow No orbital moment.

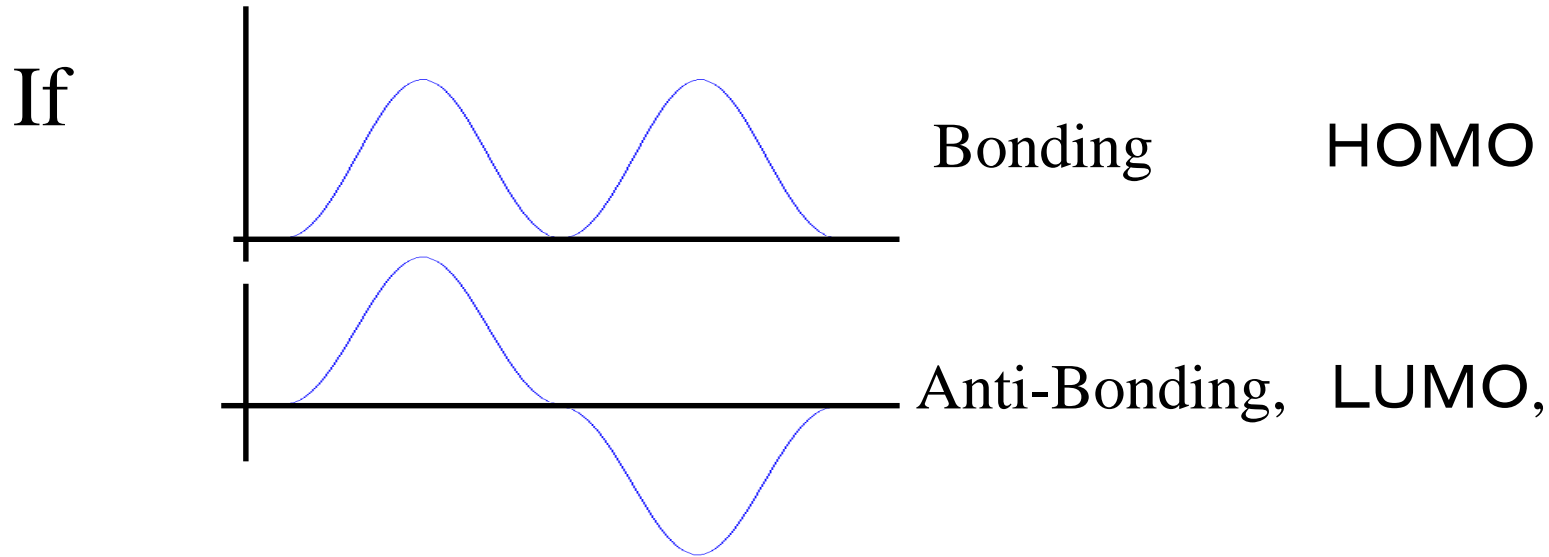
II. Extended electrons \leftarrow GW type effect for semiconductor.

Important to describe band gap. Off-site non-locality.

(required to distinguish “bonding orbital”

and “anti-bonding” orbitals.) \rightarrow next page

Schematic explanation on off-site exchange



square of them are the same.

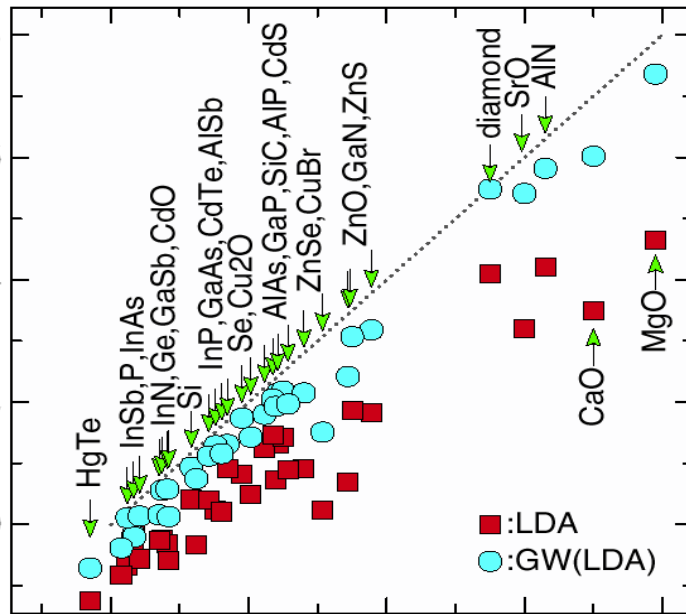
$$\left\langle \psi_{\text{bonding}} \left| V(r) \right| \psi_{\text{bonding}} \right\rangle = \left\langle \psi_{\text{anti-bonding}} \left| V(r) \right| \psi_{\text{anti-bonding}} \right\rangle.$$

→ Local potential can not distinguish
LUMO and HOMO.

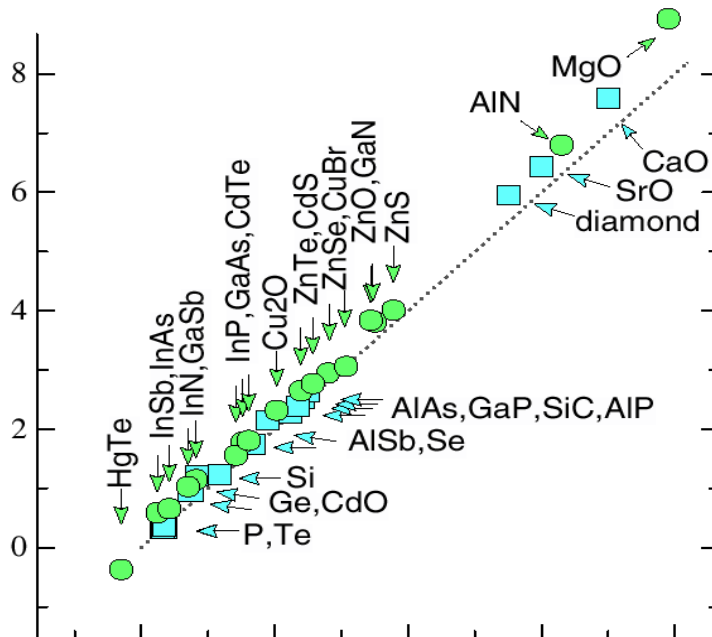
Calculated(eV)

BAND GAP

← LDA, one-shot GW

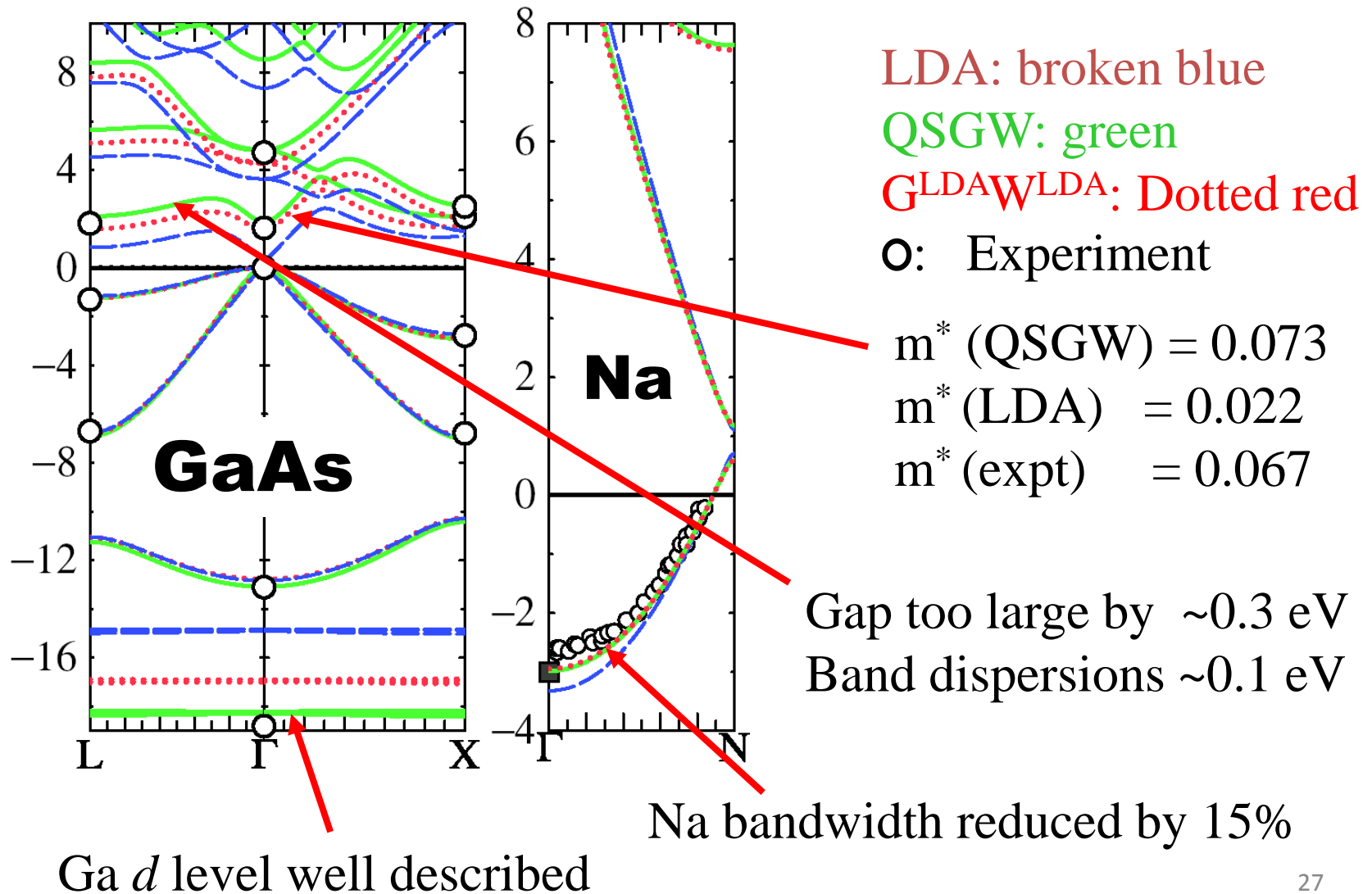


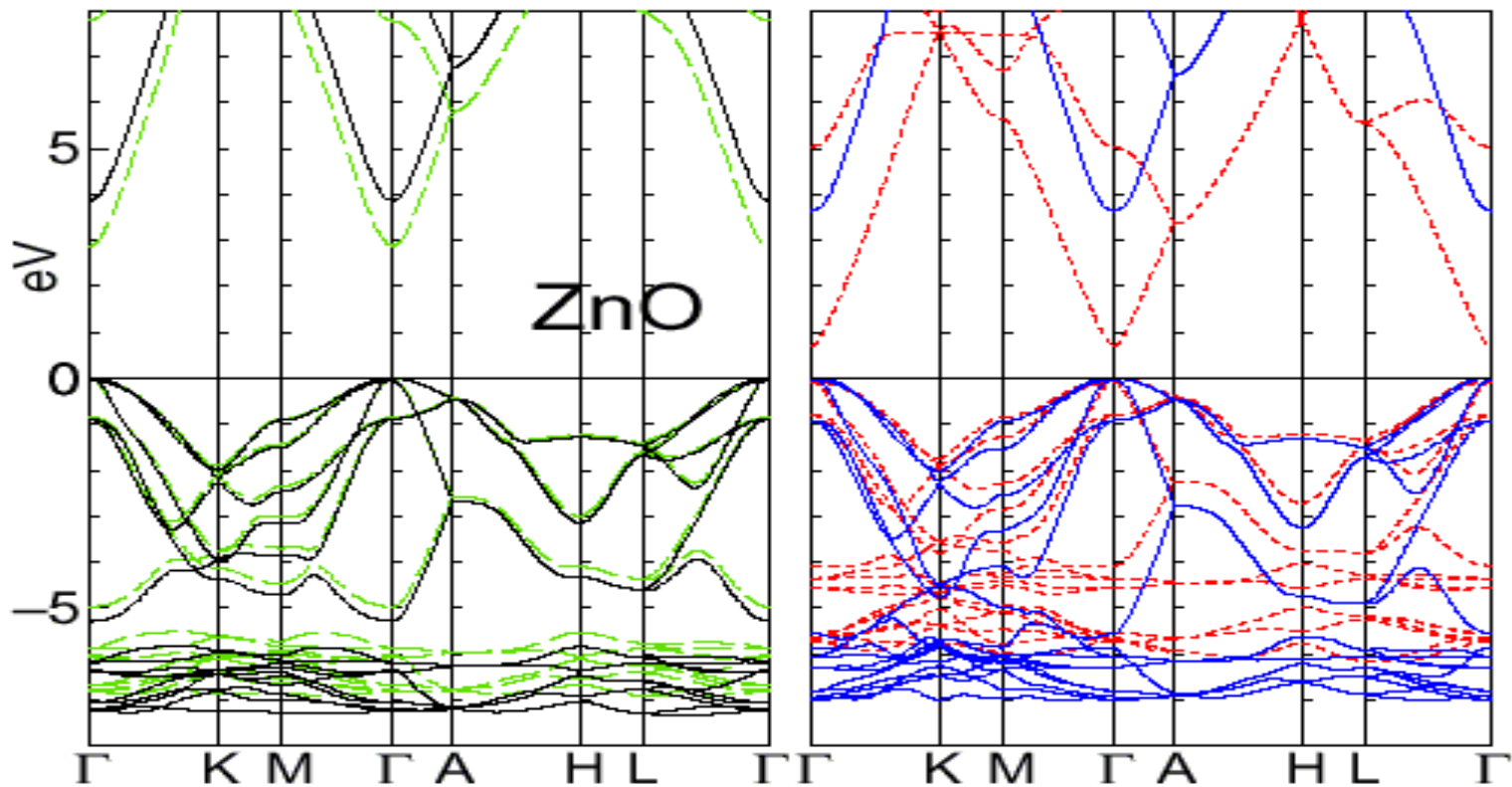
← QSGW
(we see systematic over estimation).



Experimental Band gap (eV)

sp bonded systems





Black:QSGW

3.87eV

Red:LDA

0.71eV

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

3.00eV

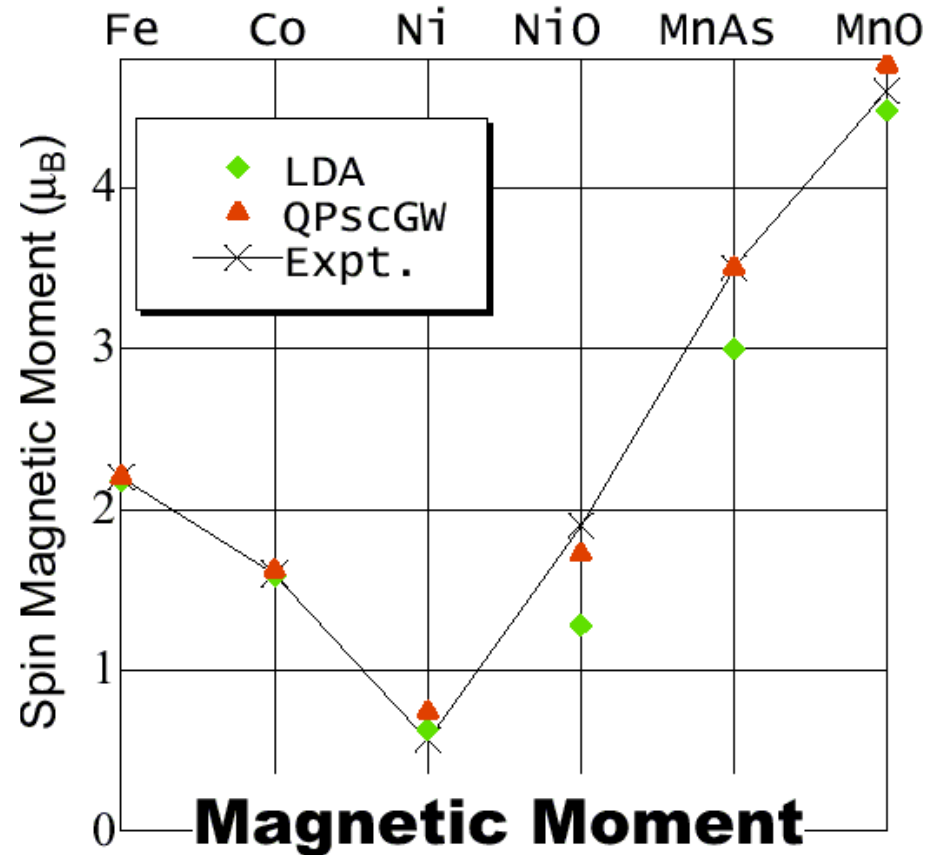
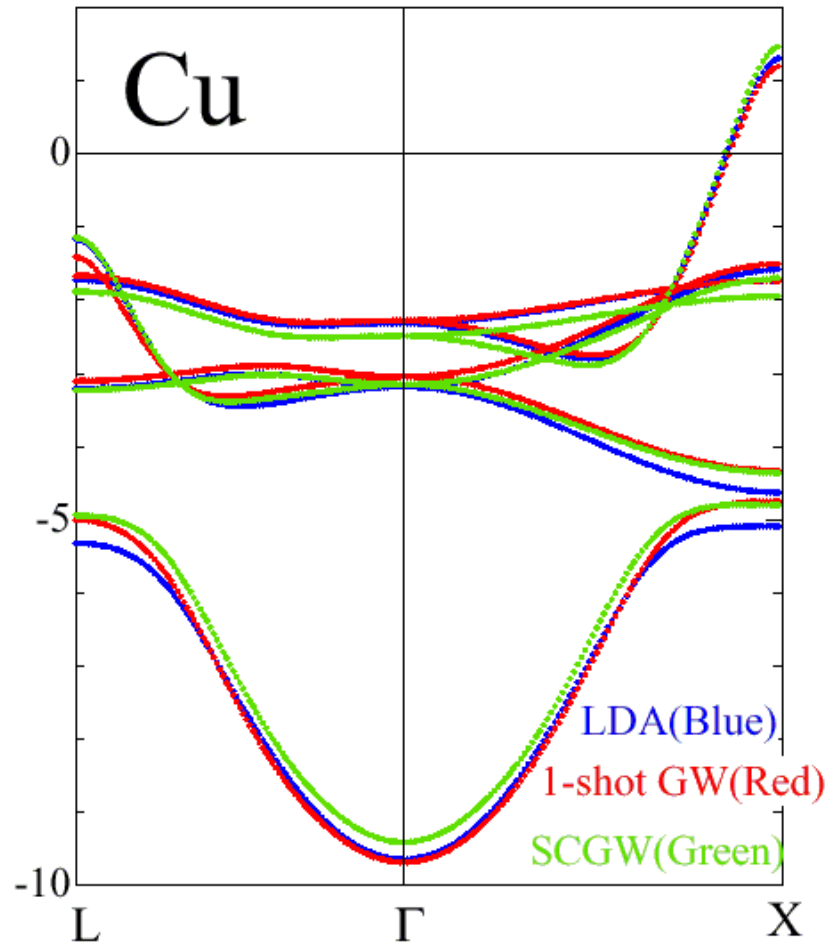
Blue:e-only self-consistency

3.64eV

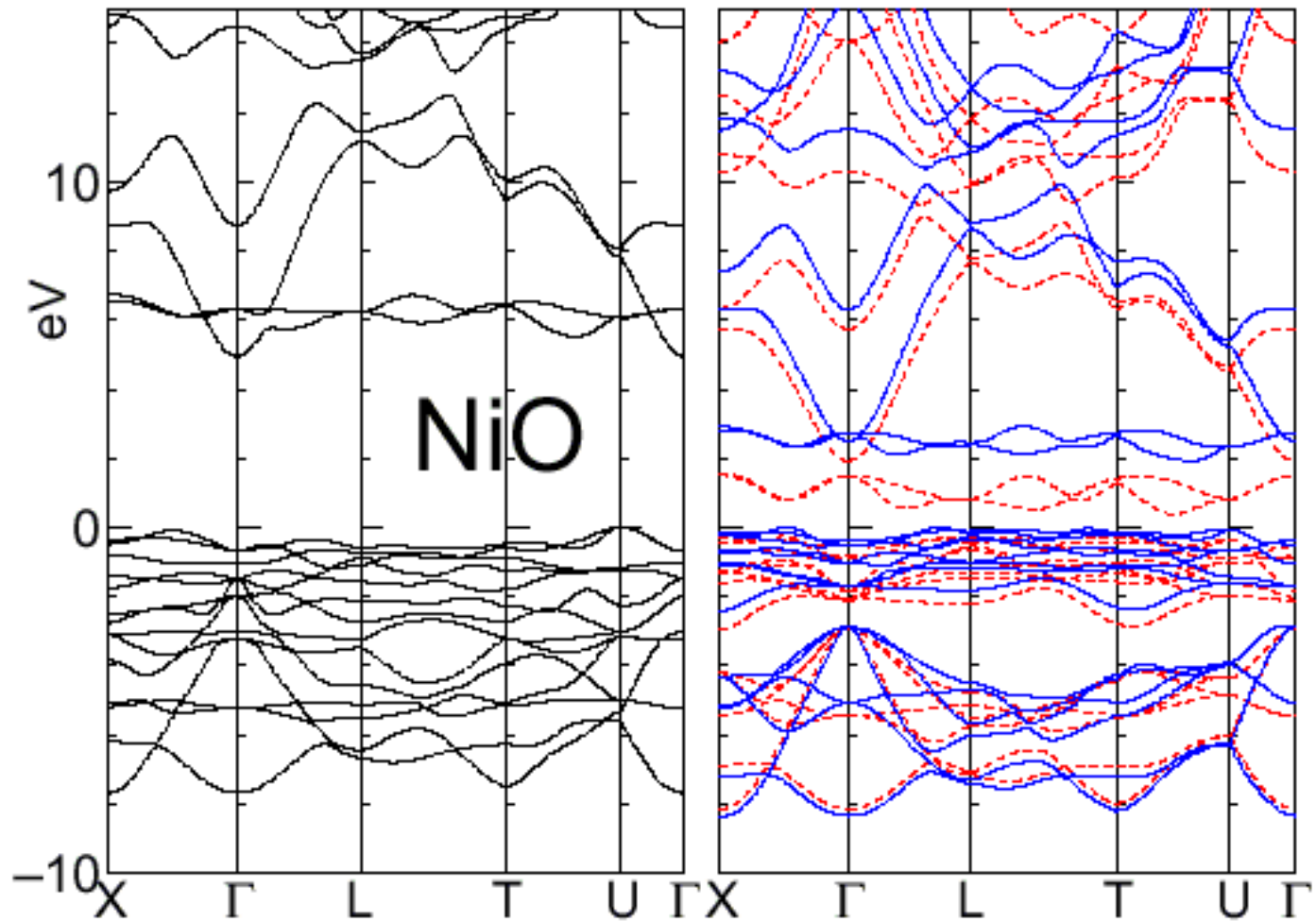
Experiment(+correction) 3.60eV

Kotani et al PRB76,165106(2007)

d systems

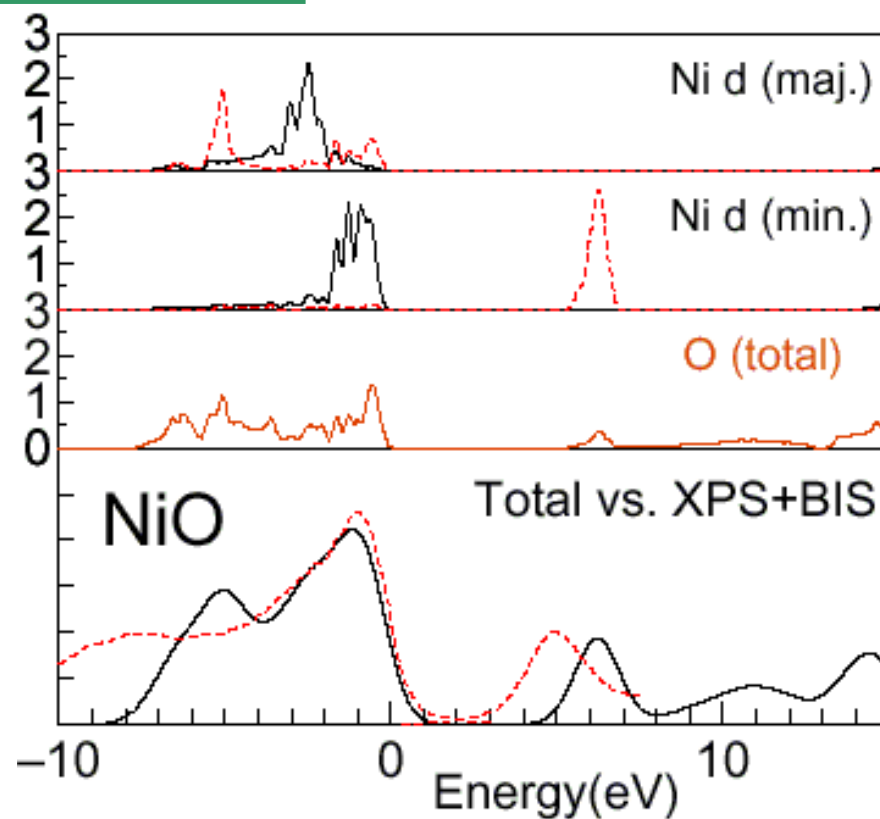
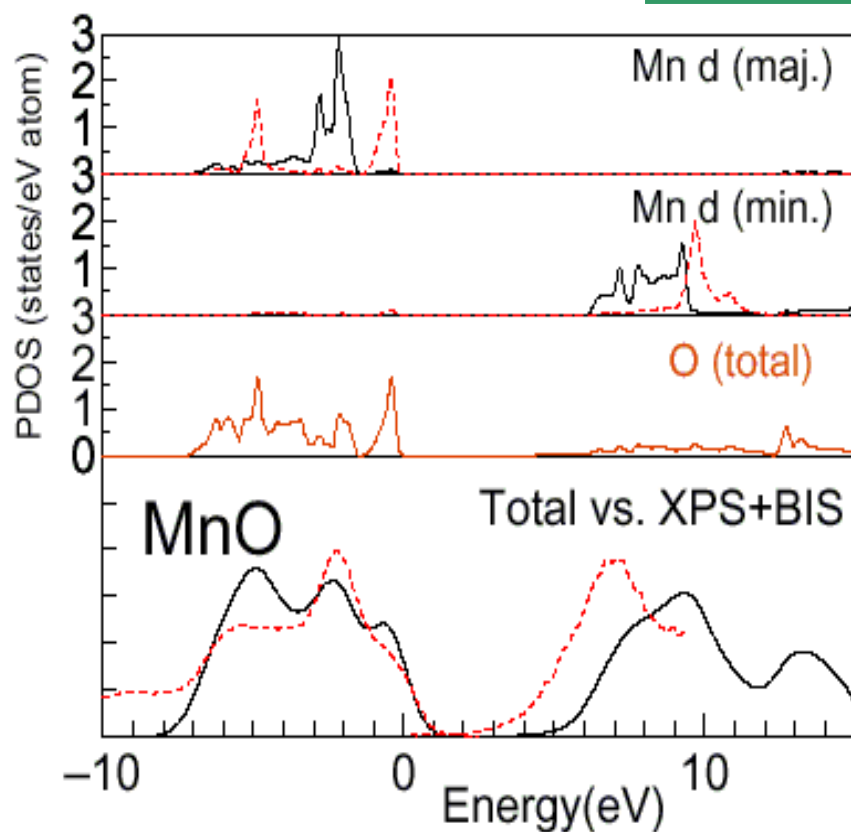


“No Pushing down 3d-band” in GW.

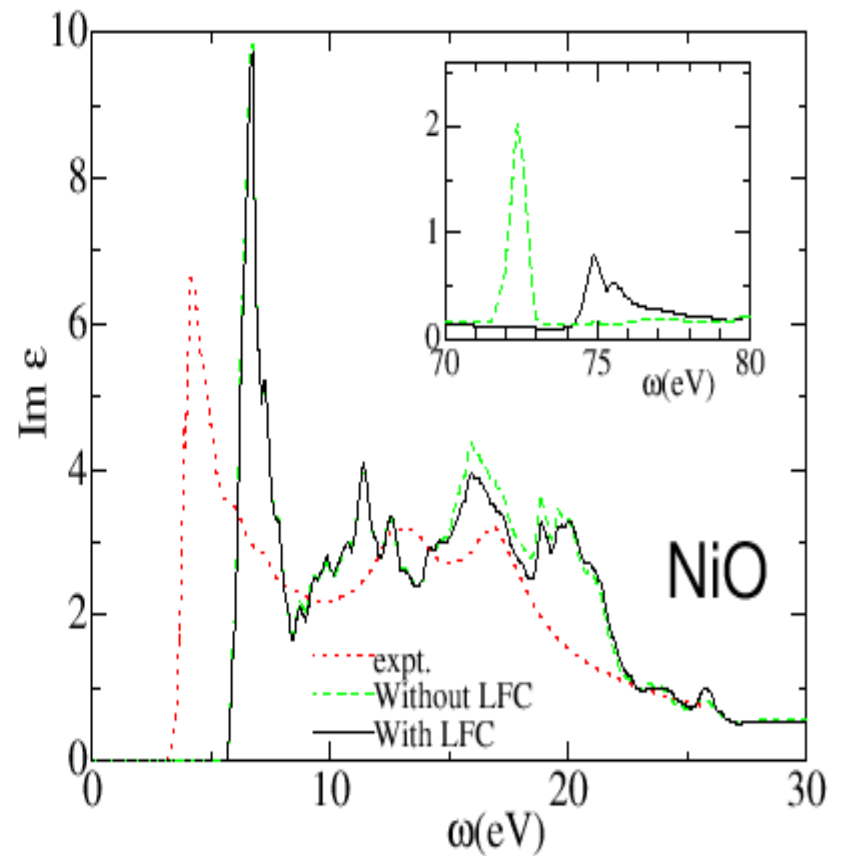
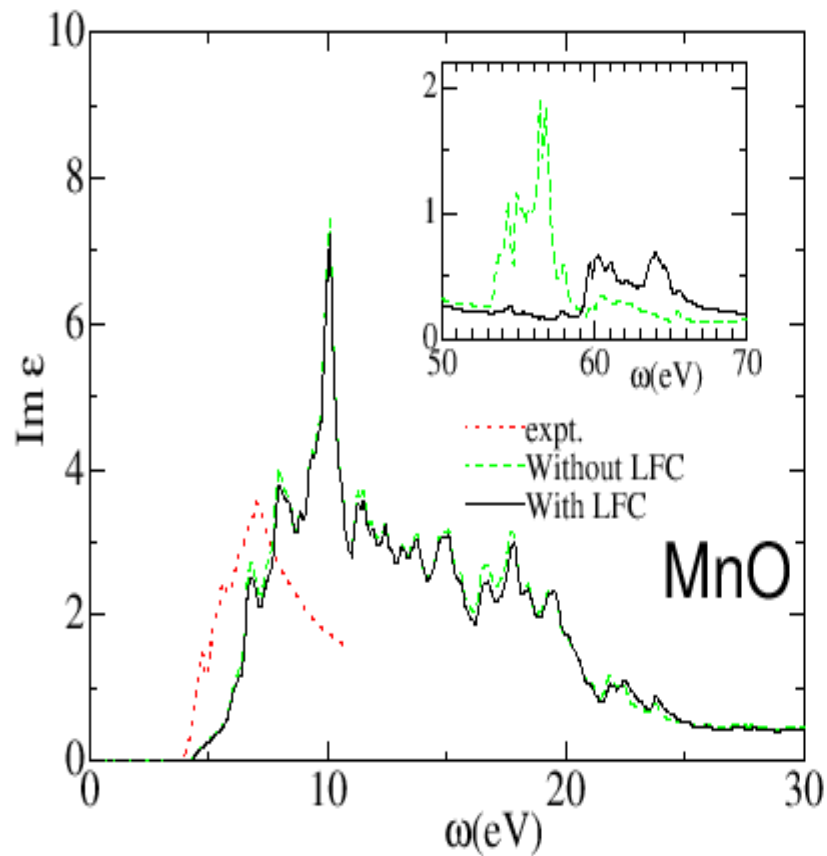


Black:QSGW Red:LDA Blue: e-only

Black:t2g Red:eg

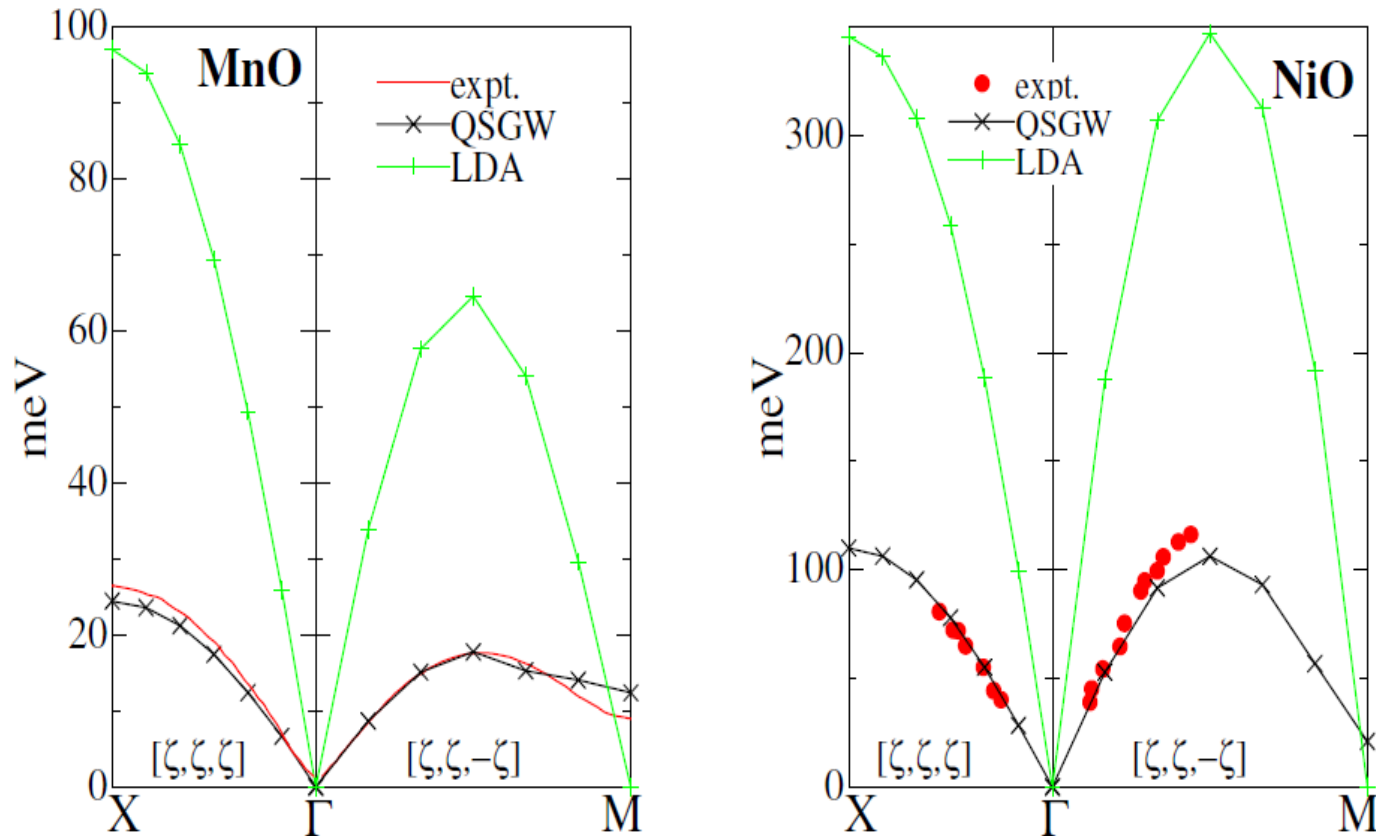


Red(bottom): expt



Black: $\text{Im } \epsilon$ with LFC Red: expt

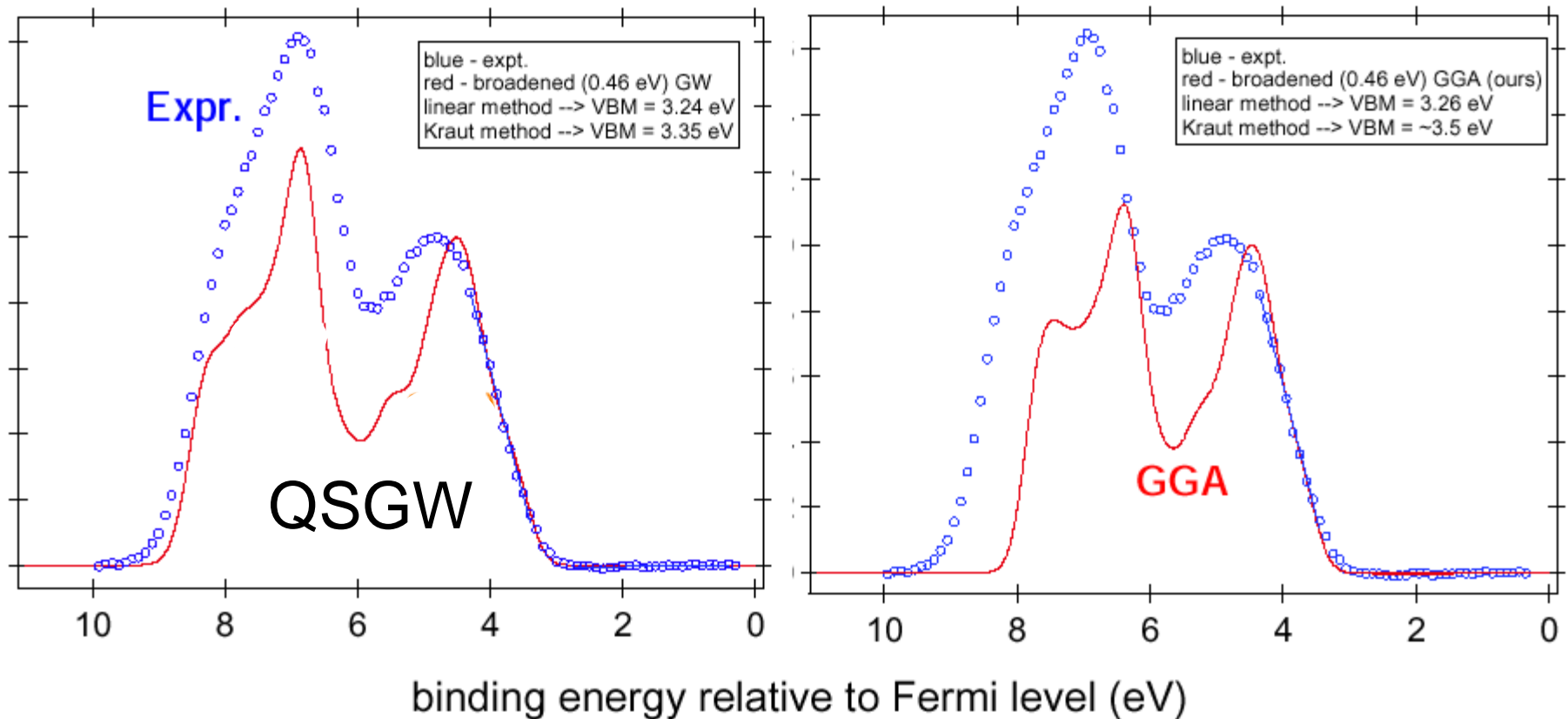
Spin wave dispersion based on QSGW



J.Phys.C20 (2008) 295214,
PRB83, 060404(R) (2011) for CaFe_2As_2 for spectrum of χ^{+-} .

SrTiO₃ Valence DOS

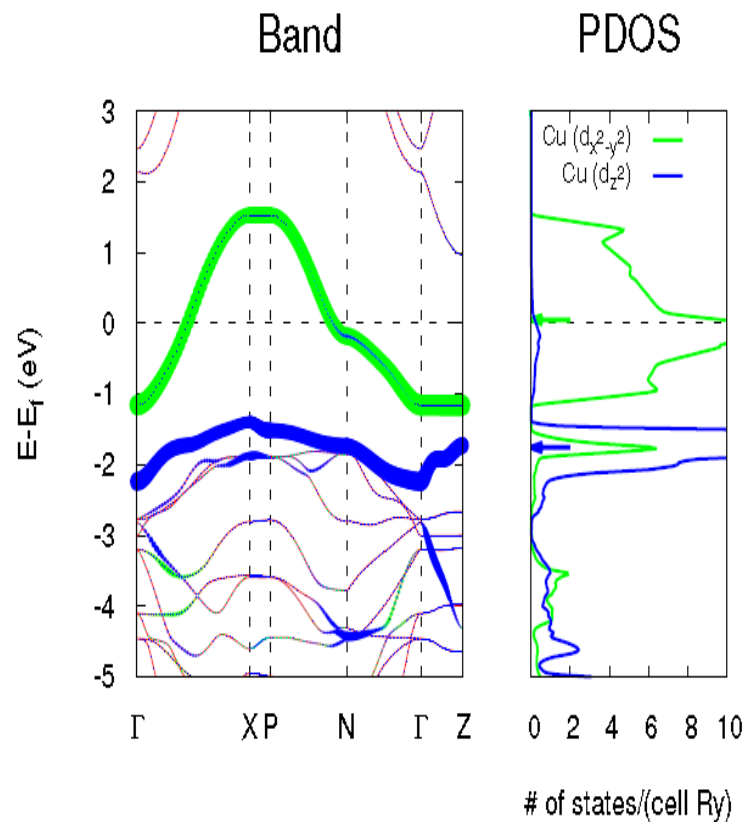
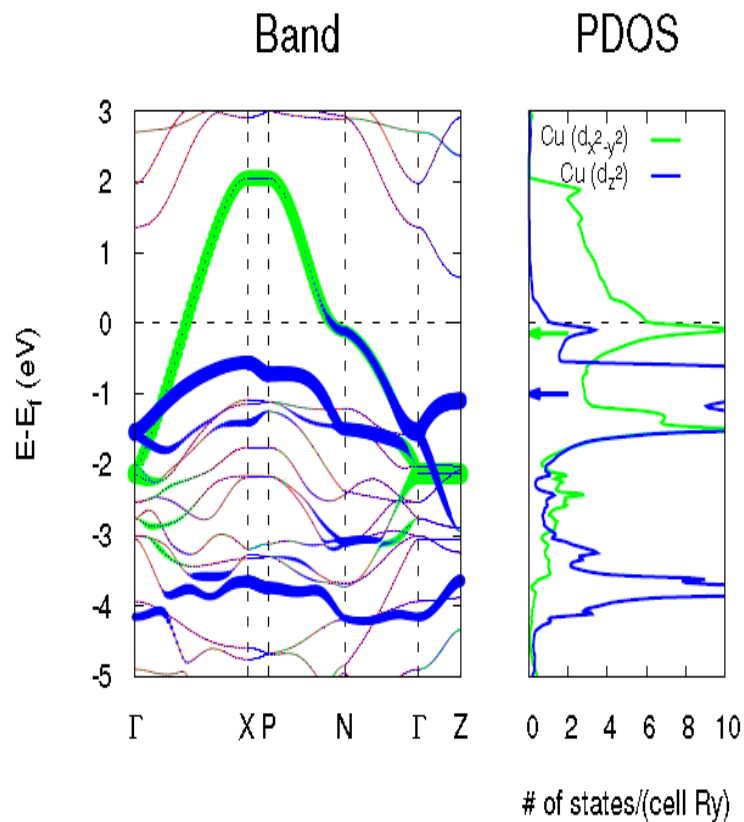
fit of properly broadened theoretical DOS with experiment
n-STO(001) VB excited with monochromatic AlK α x-rays (resolution = 0.46 eV)



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

La₂CuO₄ (LDA)

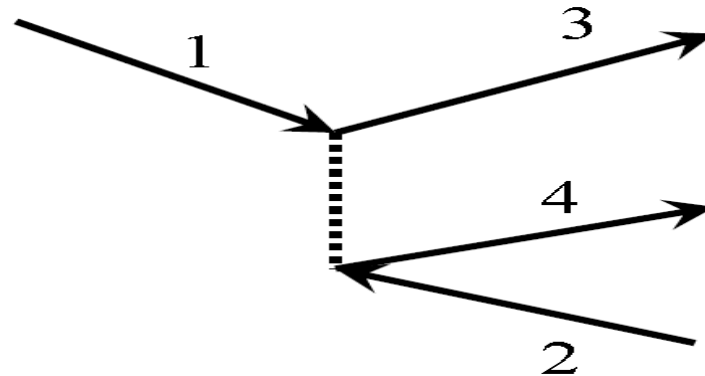
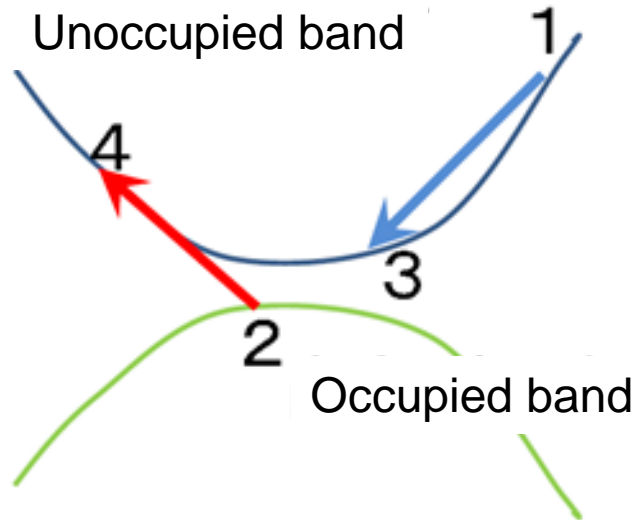
La₂CuO₄ (QSGW)



Large d(x²-y²) - d(z²) separation.

SW.Jang,MJ.Han,H.Kino,K.Kuroki,TK in preparation

Impact ionization rate(auger process)



Fermi's Golden rule \rightarrow transition rate. Sum up for all final states. Matrix element of transition is $\langle 1,3 | \text{electron-electron interaction} | 4,2 \rangle$

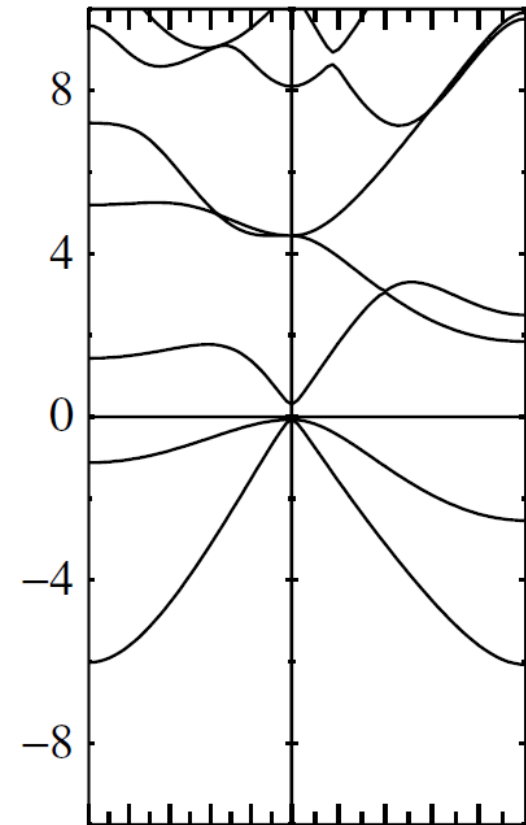
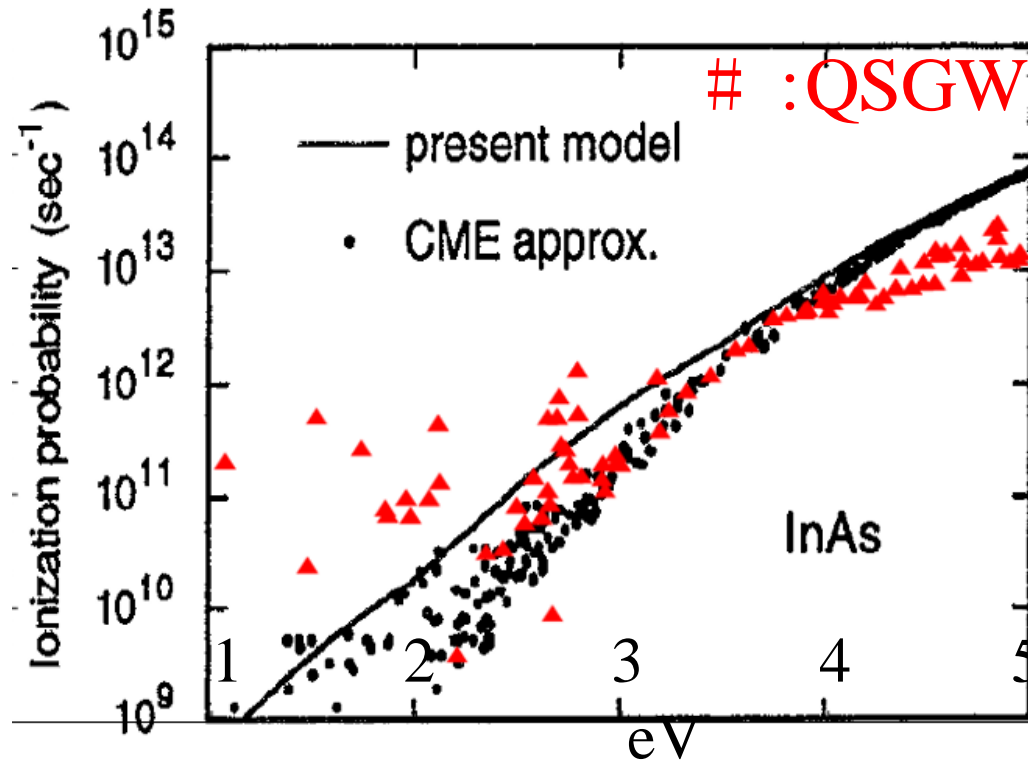
(Energy conservation and Momentum conservation)

InAs impact ionization rate

(=auger process

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

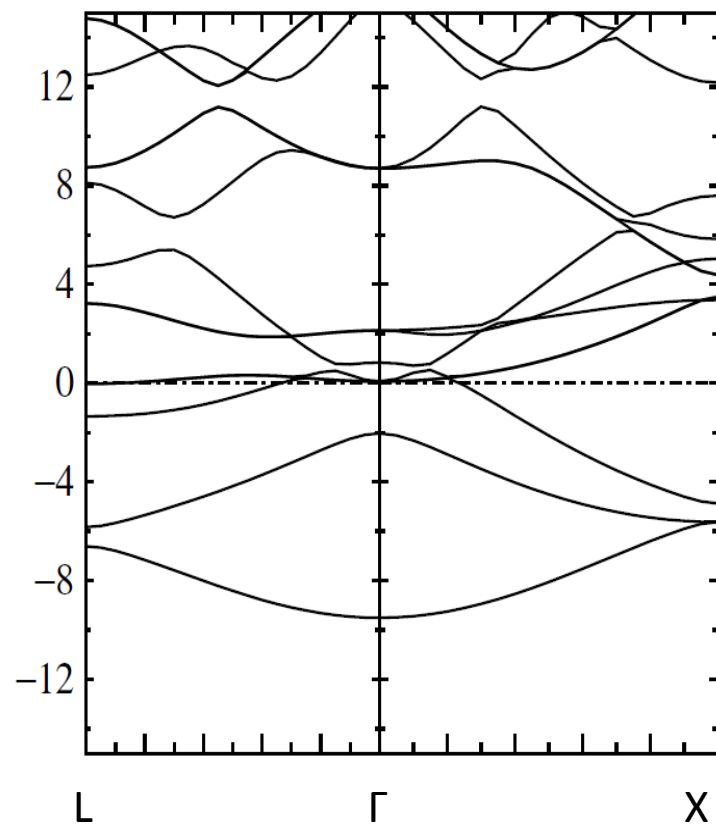
direct gap 0.38eV



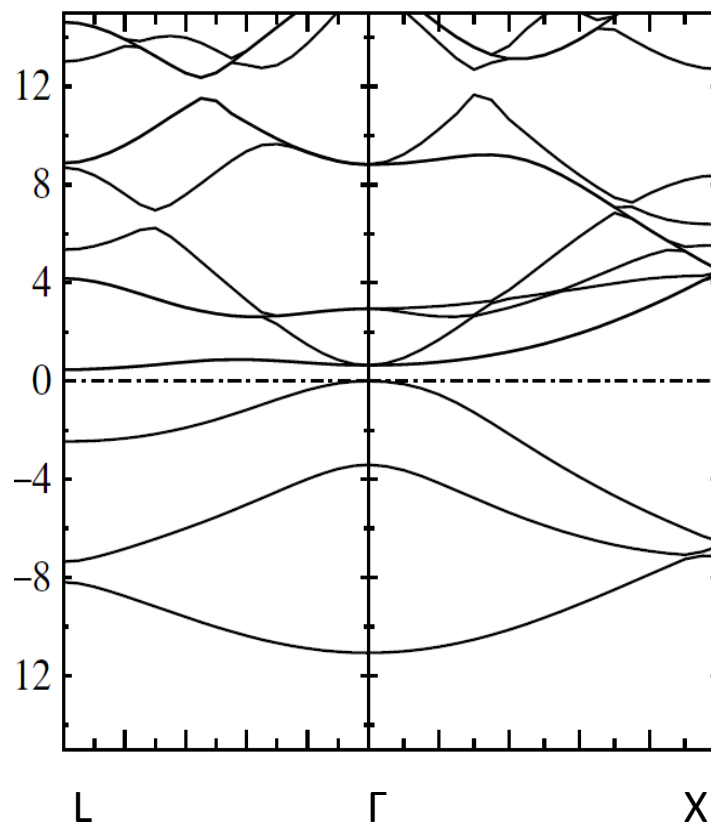
Present model: Sano and Yoshii JAP77 2020 (1995)

YH₃(fcc structure 6x6x6)

GGA

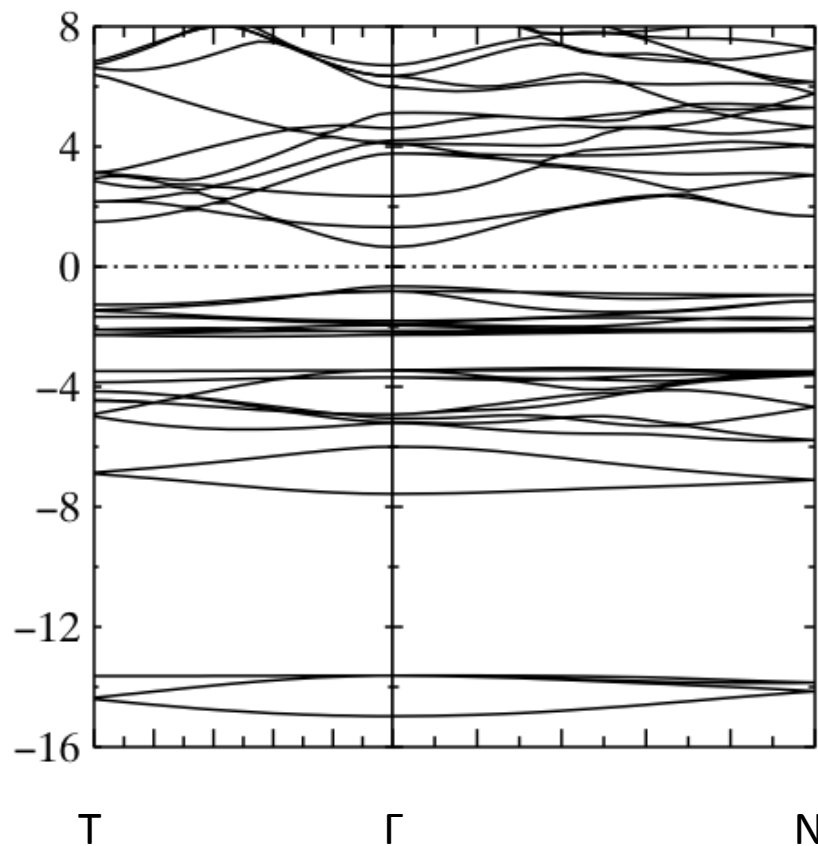


QSGW

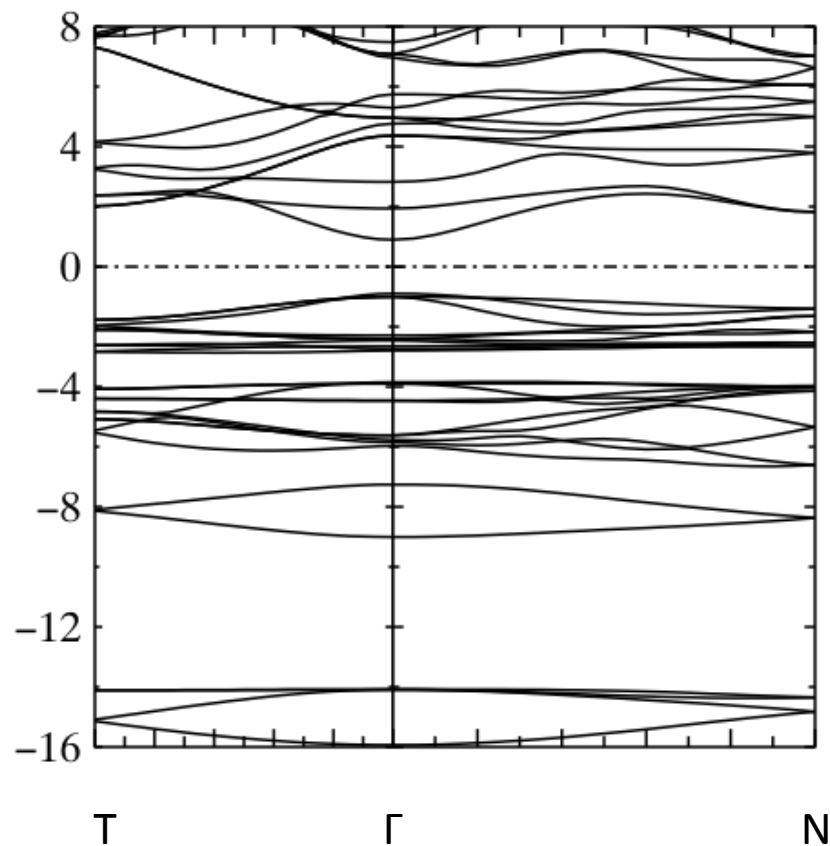


CuGaSe₂ (eight atoms in cell, 2x2x2. ~3hours per iteration by single core)

1shotGW



QSGW



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

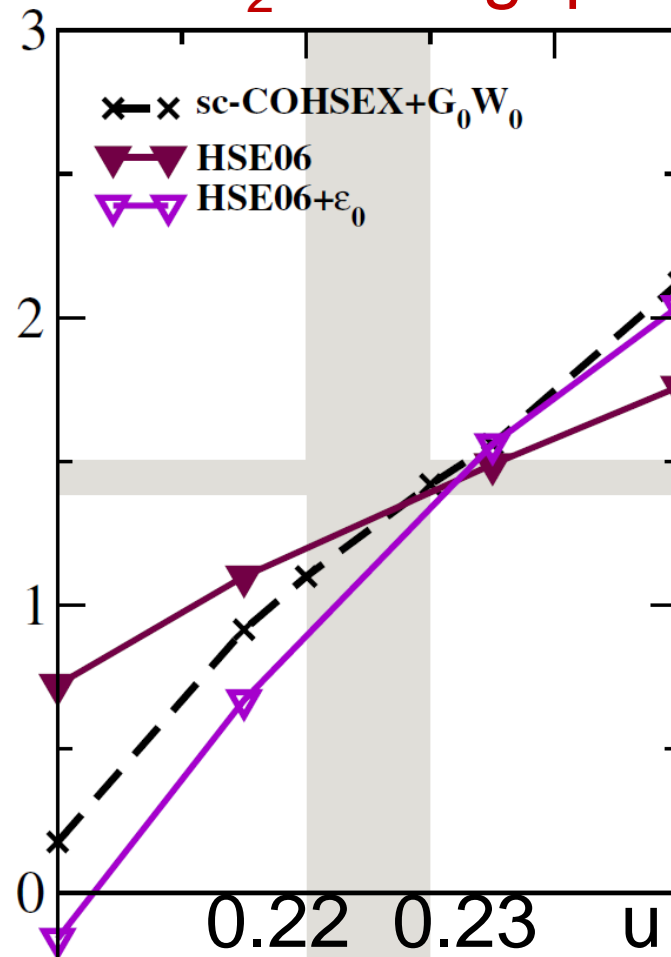
Band gap for CuAB₂ (eV)

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 (...)

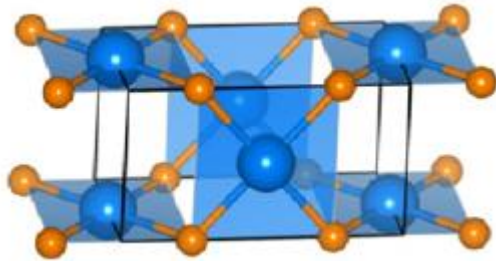
3x3x3 calculation(need check)

CuInS₂ band gap (eV)

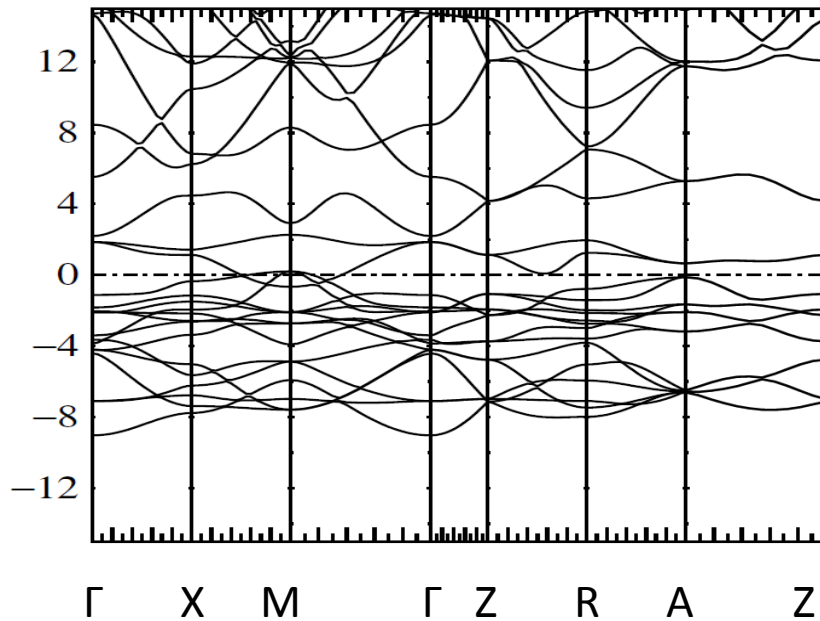


J.Vidal, PRL 104, 056401 (2010)

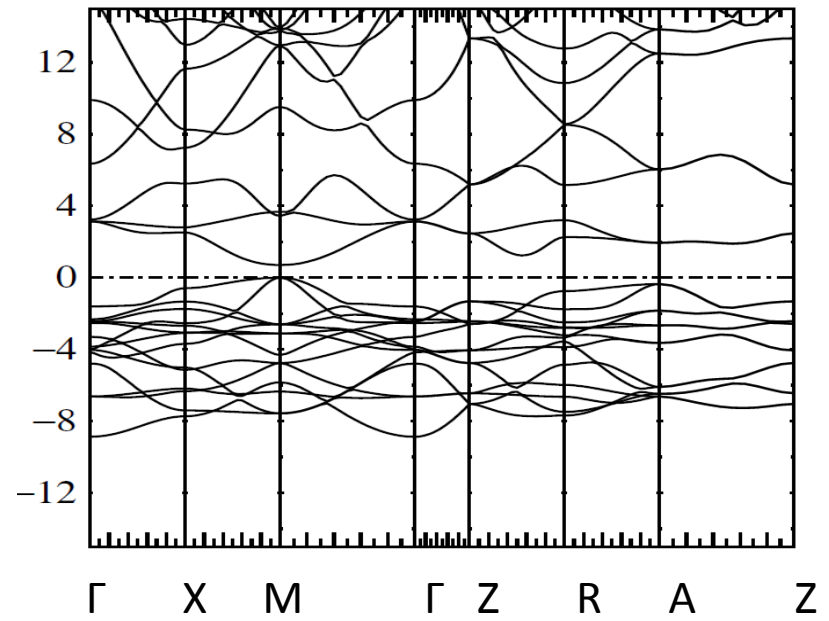
PdO (tetragonal, four atoms per cell 3x3x2 calculation, 1 hour per iteration)



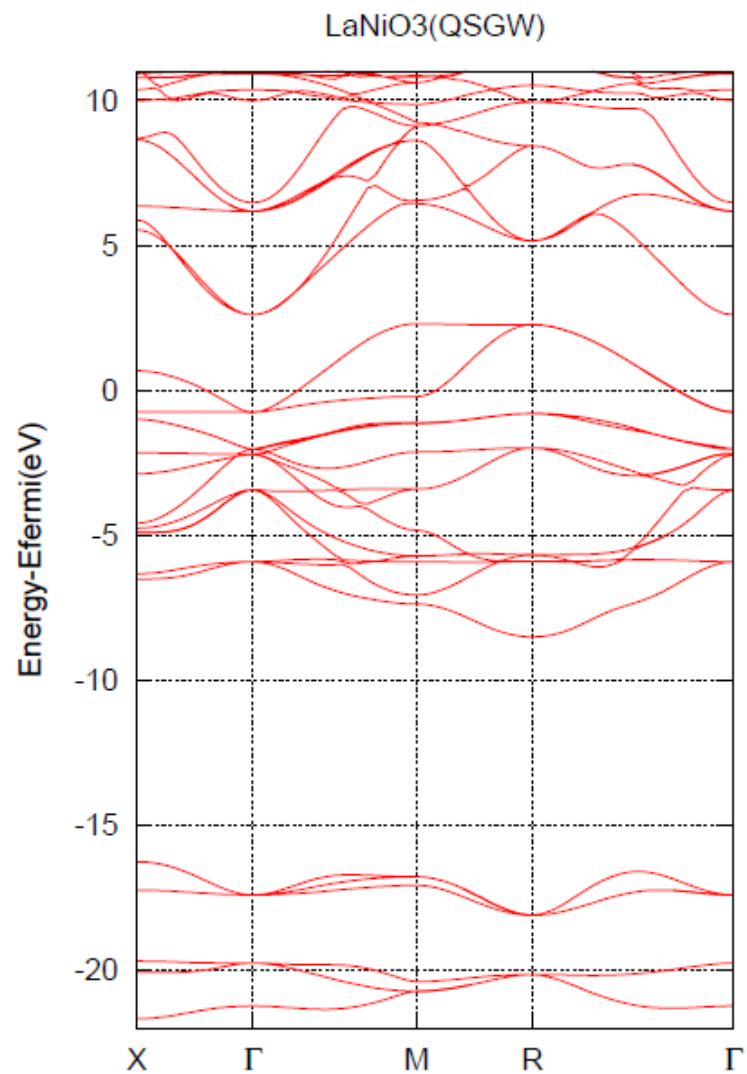
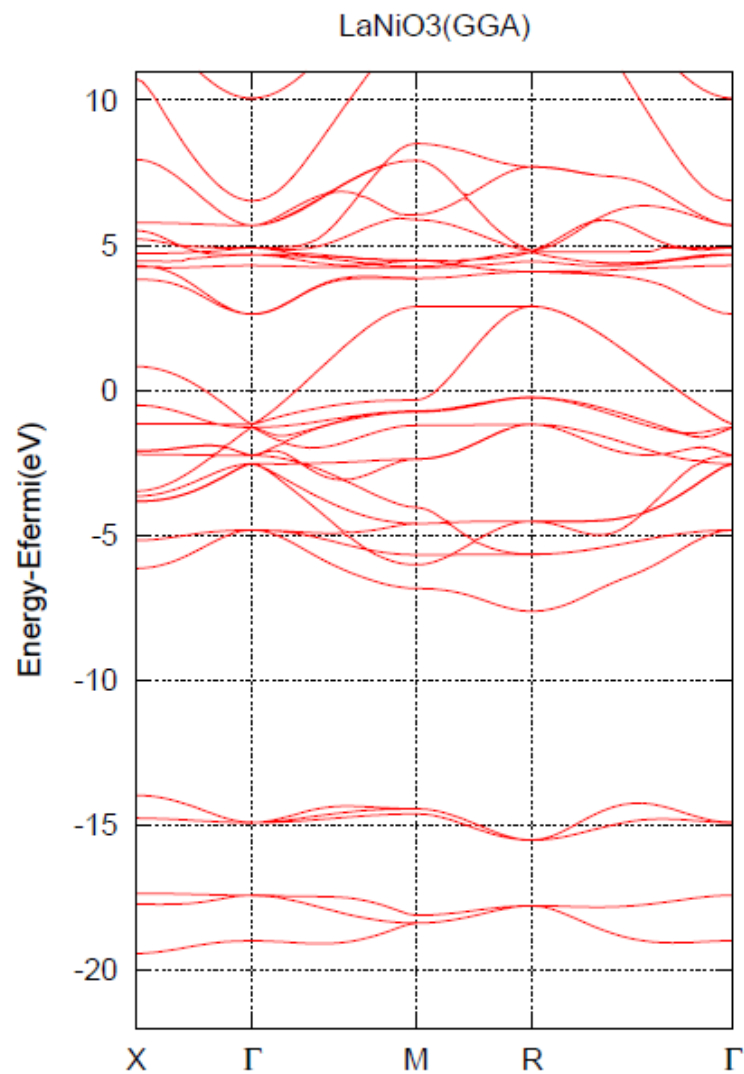
GGA



OSGW



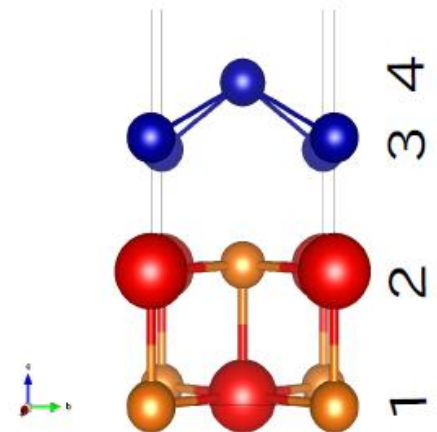
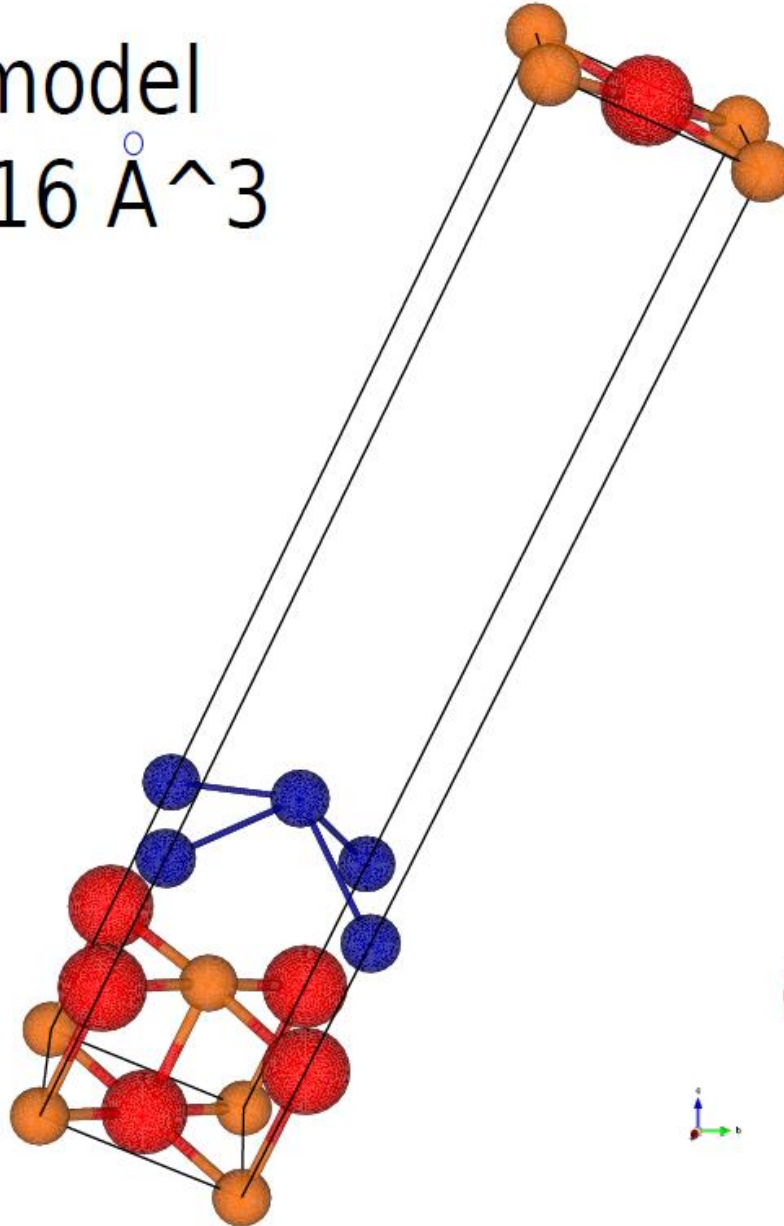
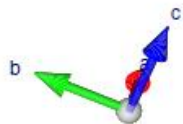
Band gap about 0.7 eV

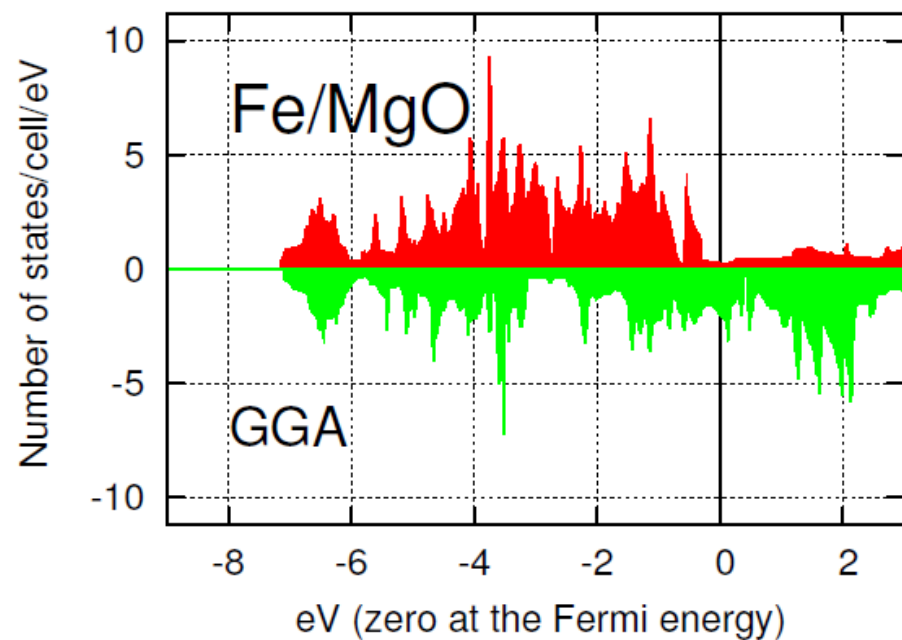
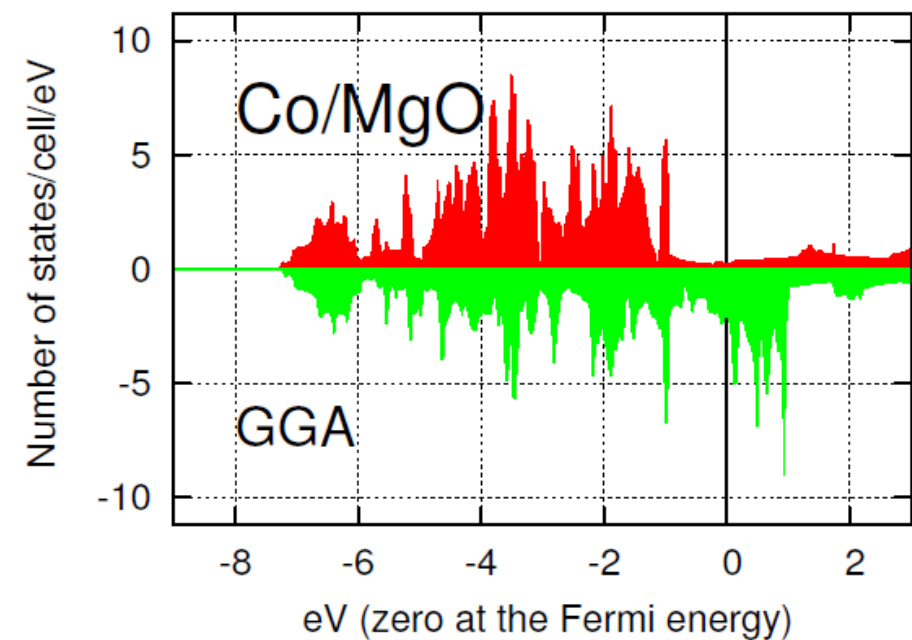
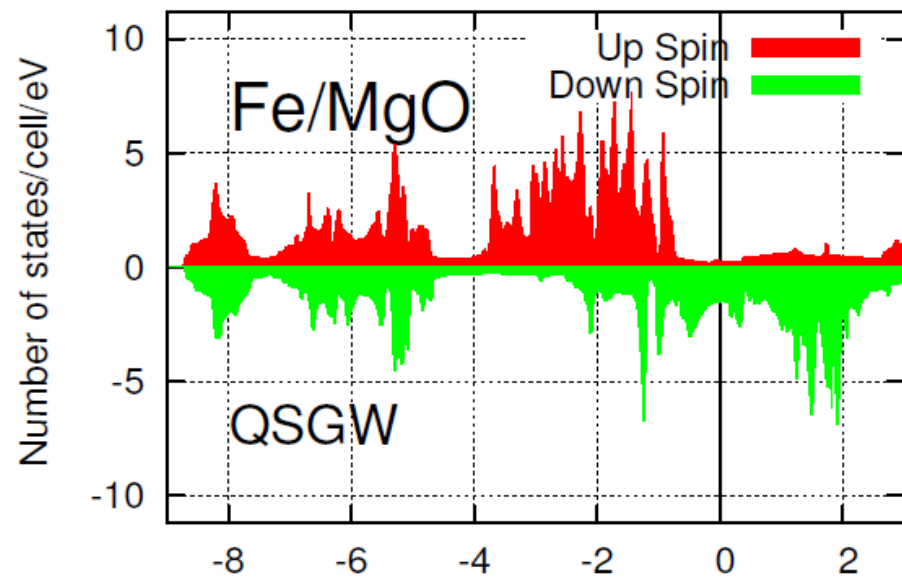
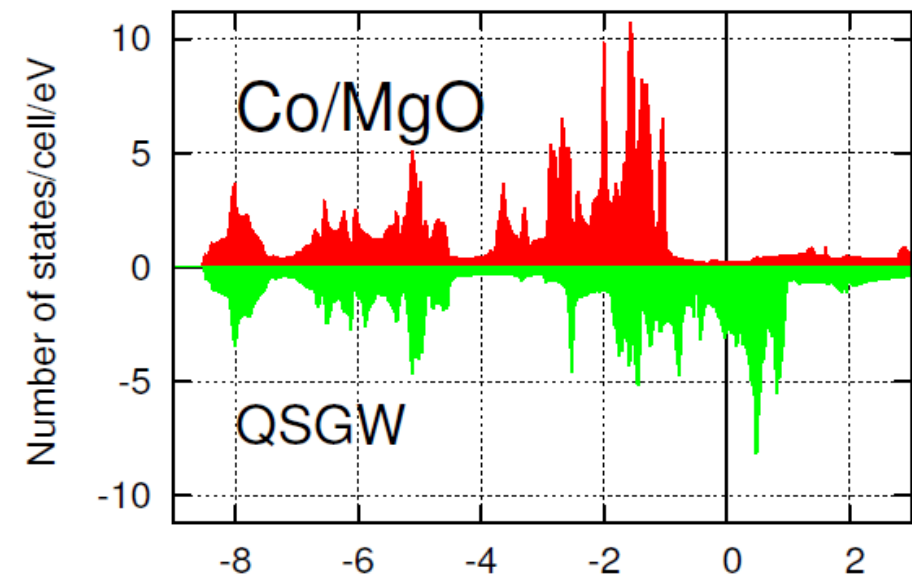


LaNiO₃

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

Co/MgO model
cell $3 \times 3 \times 16 \text{ \AA}^3$





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)