ecalj CMD course menu

Monday 15:00~17:00,17:20~19:20

- LECTURE1: PMT method
  How to solve one-body problem? →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 9:00~10:30 (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

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

Muffin-tin

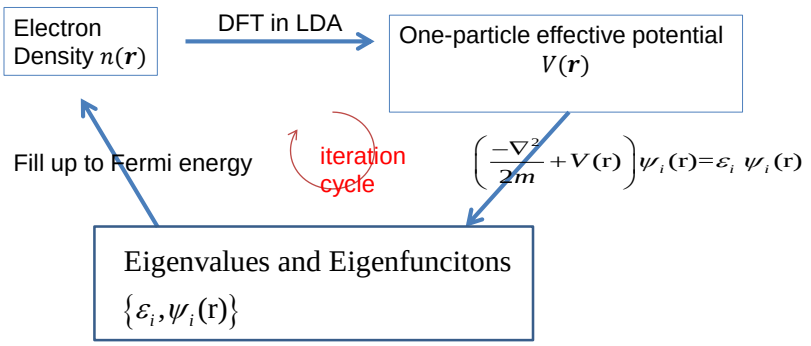
Takao Kotani (tottori-u)

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

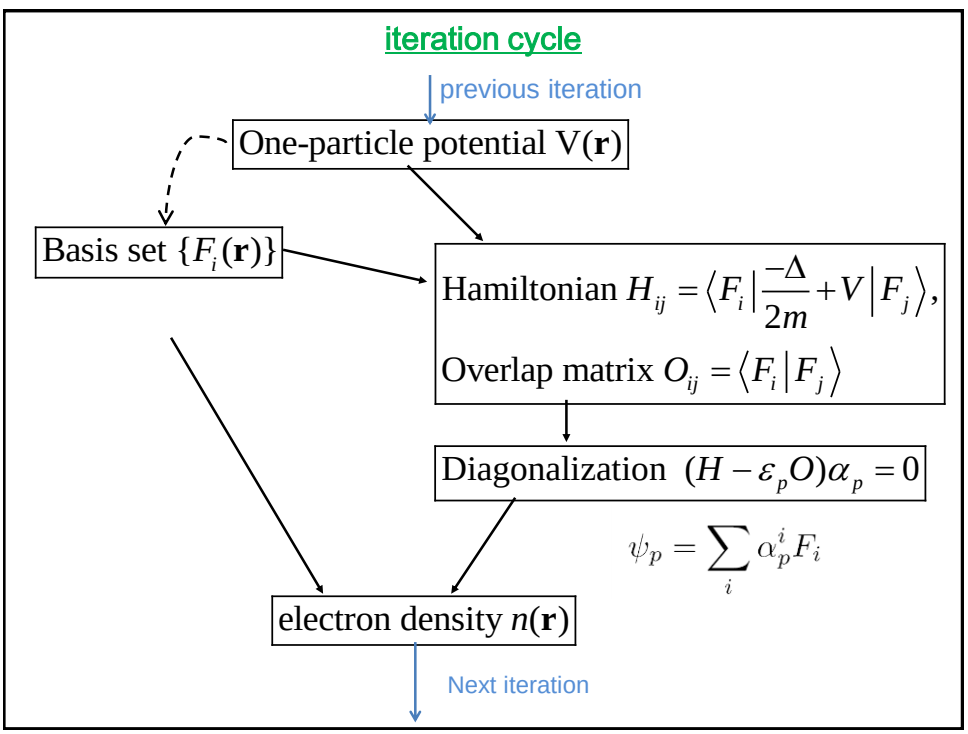
- **Basis set (finite number of basis)**
  - → We assume eigenfunctions are given as:

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

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

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

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



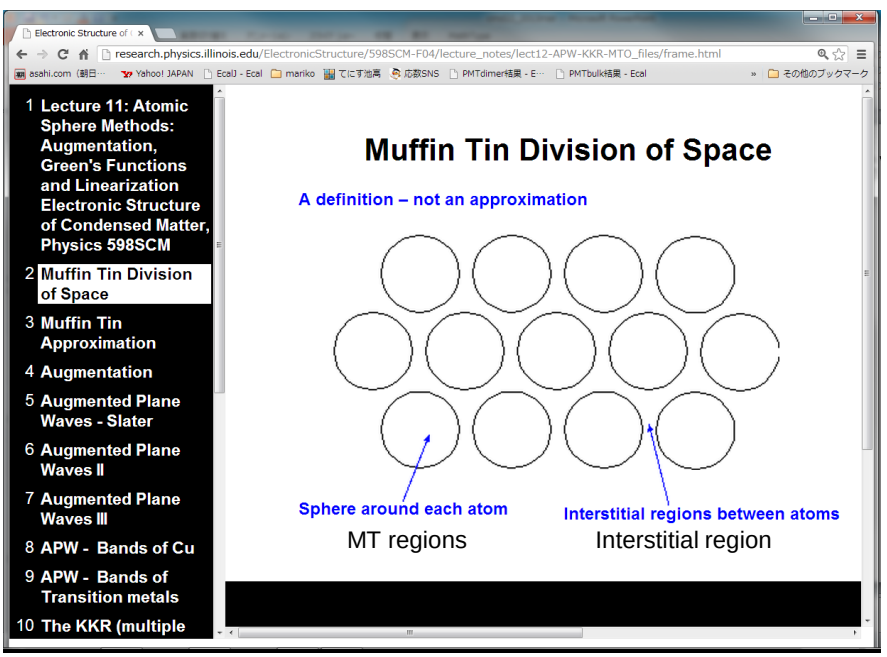
How to choose the good basis?

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

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

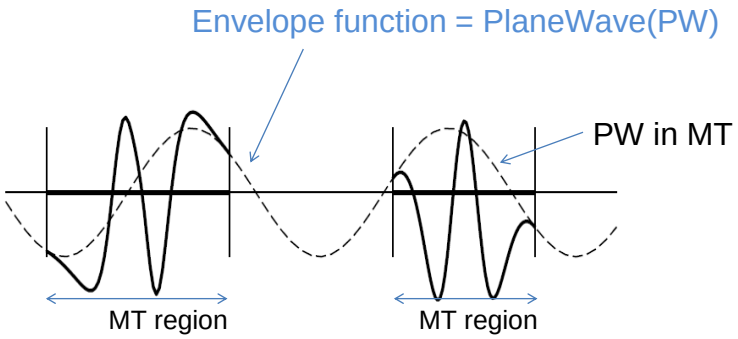
My conclusion:
To overcome shortcomings in APW basis and MTO basis, we should use both of **APW and MTO together. →this means the PMT method**

But wait…
What is the APW and MTO?→ next page.



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

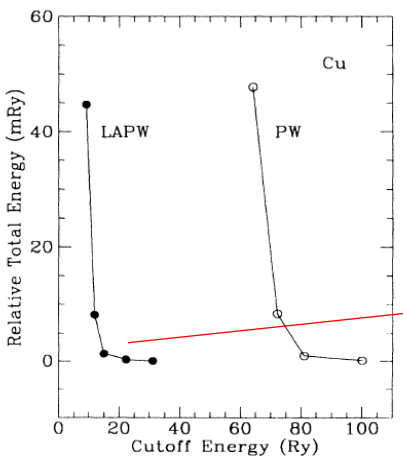


FIG. 1. Relative total energy of fcc Cu plotted against plane-wave cutoff energy.

D.Singh et al PRB49,17424

fcc Cu

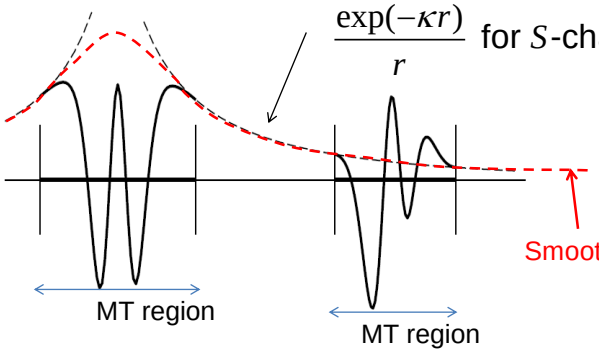
plane wave is not so efficient for *3d*

15Ry or more for ~1mRy convergence

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

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).
Detailed Formulation
J. Phys. Soc. Jpn. 84, 034702 (2015)

Basis function

MT center at **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**

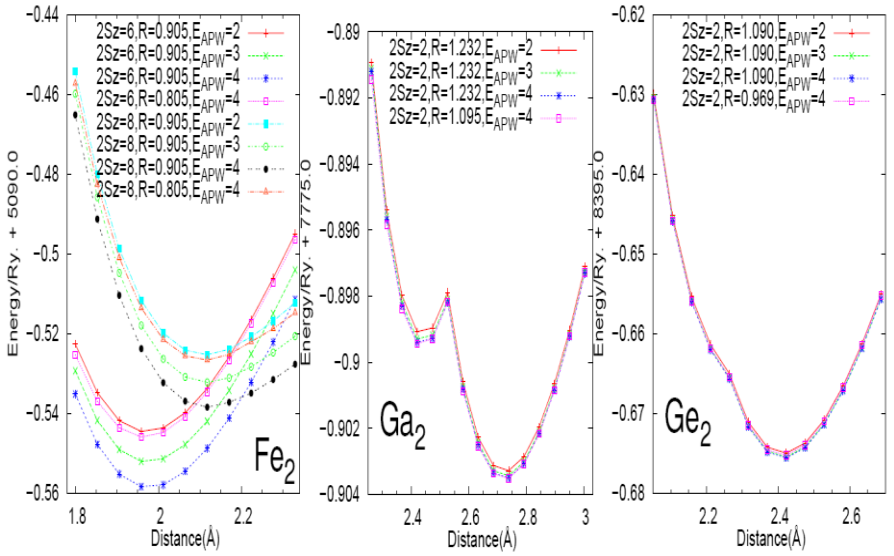
$$F_j(\mathbf{r}) = F_{0j}(\mathbf{r}) + F_{1j}(\mathbf{r}-\mathbf{R}) - F_{2j}(\mathbf{r}-\mathbf{R})$$

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.

Mean field theory gives independent-particle picture

- Hartree-Fock theory
- Density functional theory

Eigenvalues and Eigenfuncitons $\{\varepsilon_i, \psi_i(\mathrm{r})\}$

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

The minimization determines

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

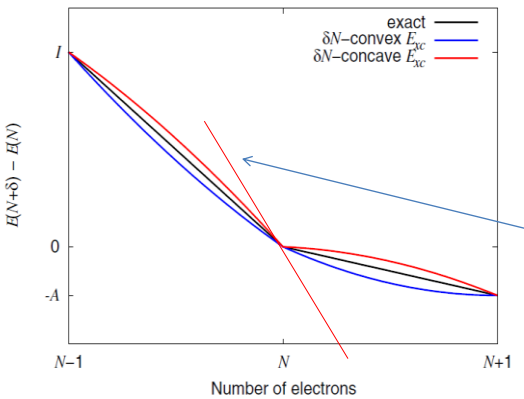
$n_i = 0$ for $\varepsilon_i > \varepsilon_{\mathrm{FERMI}}$ (unoccupied states)

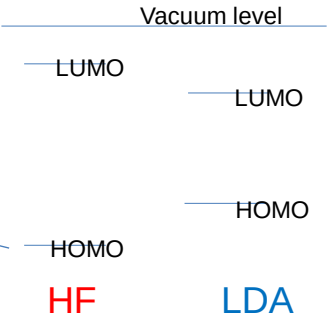
Janak(Koopman's) theorem

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

Ionization energy of an atom A.J.Cohen, P. Mori-Sanchez, W.Yang, Science321,792(2008)

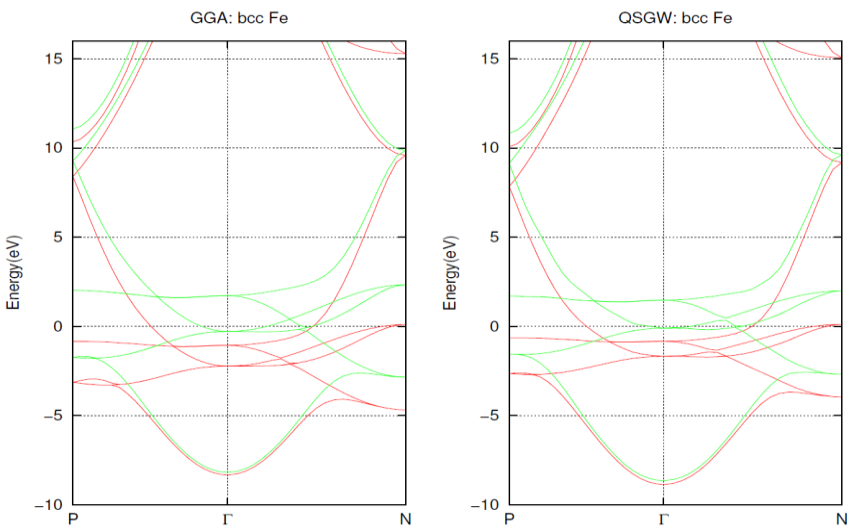
PRL **100,** 146401 (2008) PHYSICAL RE





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

How about solid (infinite system)→ $\varepsilon_i = \frac{\partial E}{\partial n_i} = \frac{\Delta E}{\Delta n_i}$ is satisfied.



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。

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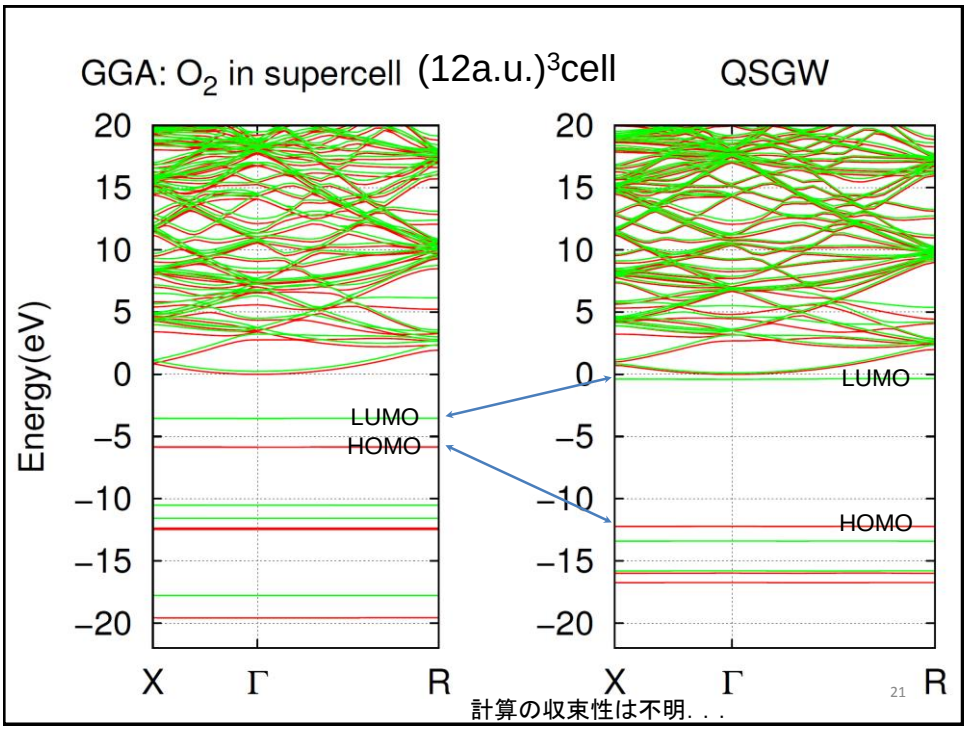


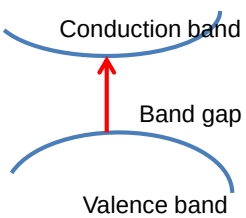
計算の収束性は不明. . .

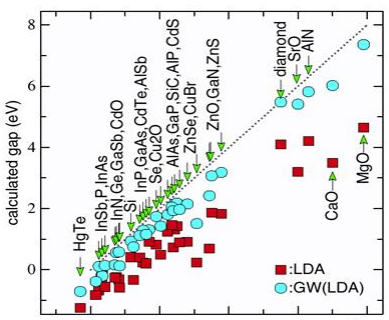
If $\varepsilon_i = \dfrac{\partial E}{\partial n_i} = \dfrac{\Delta E}{\Delta n_i}$ (linear line),

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

How accurate they are?

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





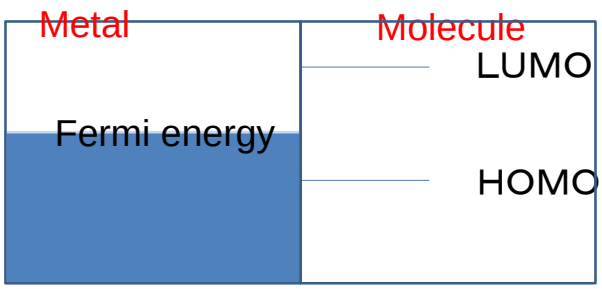
LDA gives too small
HF(not shown) gives too large

GW method and QSGW method

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.

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(preparation) What is Green's function?

Example: Laplace eq. $\Delta\phi = \rho(\mathbf{r})$

$$\Delta \frac{1}{4\pi|\mathbf{r}-\mathbf{r}'|} = \delta(\mathbf{r}-\mathbf{r}')$$

$$G_0 = \frac{1}{4\pi|\mathbf{r}-\mathbf{r}'|} \quad \rightarrow \quad \phi(\mathbf{r}) = \int G_0(\mathbf{r}-\mathbf{r}')\rho(\mathbf{r}')d\mathbf{r}'$$

$$H_0 = -\frac{\nabla^2}{2m} + V_{\text{eff}}(\mathbf{r},\mathbf{r}') \qquad \left(i\frac{\partial}{\partial t} - H_0\right)\varphi(\mathbf{r},t) = F(\mathbf{r},t)$$

$$\left(i\frac{\partial}{\partial t} - H_0\right)G_0 = \delta(t-t')\delta(\mathbf{r}-\mathbf{r}')$$

$$\Rightarrow G_0 = \frac{1}{i\frac{\partial}{\partial t} - H_0} = \frac{1}{\omega - H_0}$$

(note boundary condition)

Note: $G_0 = G_0\text{electron} + G_0\text{hole}$

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Many-body perturbation theory(picture)

The many-body Hamiltonian is decomposed to

$H = H_0 +$ Vee + residual term

. H_0 is despribed by G_0.

Many electrons are interacting each other. Add electrons and holes, and observe this afterwards.

Time axis

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polarization

External field

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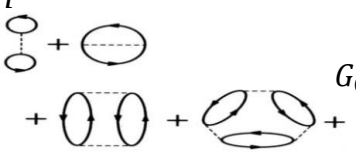
GW is based on the "RPA total energy"

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

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

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

$E_{\mathrm{H}} + E_{\mathrm{X}} + E_{\mathrm{C}} =$ 

$G_0 = \frac{1}{\omega - H_0}$ で展開

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

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

This is one-shot GW

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

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

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How to determine better H_0 ?

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

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

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

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

An average procedure
(not shown here)

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

I. Localized electrons ← LDA+U type effect

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

It can break time-reversal symmetry → No orbital moment.

II. Extended electrons ← GW type effect for semiconductor.

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

(required to distinguish "bonding orbital"

and "anti-bonding" orbitals.) →next page

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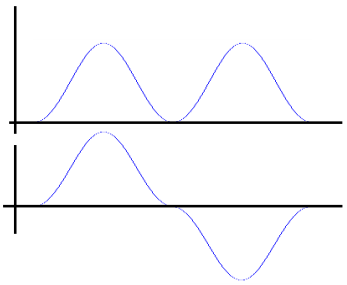
Schematic explanation on off-site exchange

If



Bonding HOMO

Anti-Bonding, LUMO,

square of them are the same.

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

→Local potential can not distinguish LUMO and HOMO.

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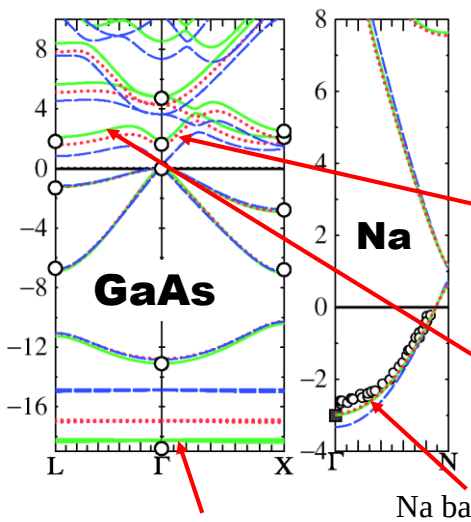
sp bonded systems



LDA: broken blue
QSGW: green
$G^{LDA}W^{LDA}$: Dotted red
O: Experiment

m^* (QSGW) = 0.073
m^* (LDA) = 0.022
m^* (expt) = 0.067

Gap too large by ~0.3 eV
Band dispersions ~0.1 eV

Na bandwidth reduced by 15%

Ga *d* level well described

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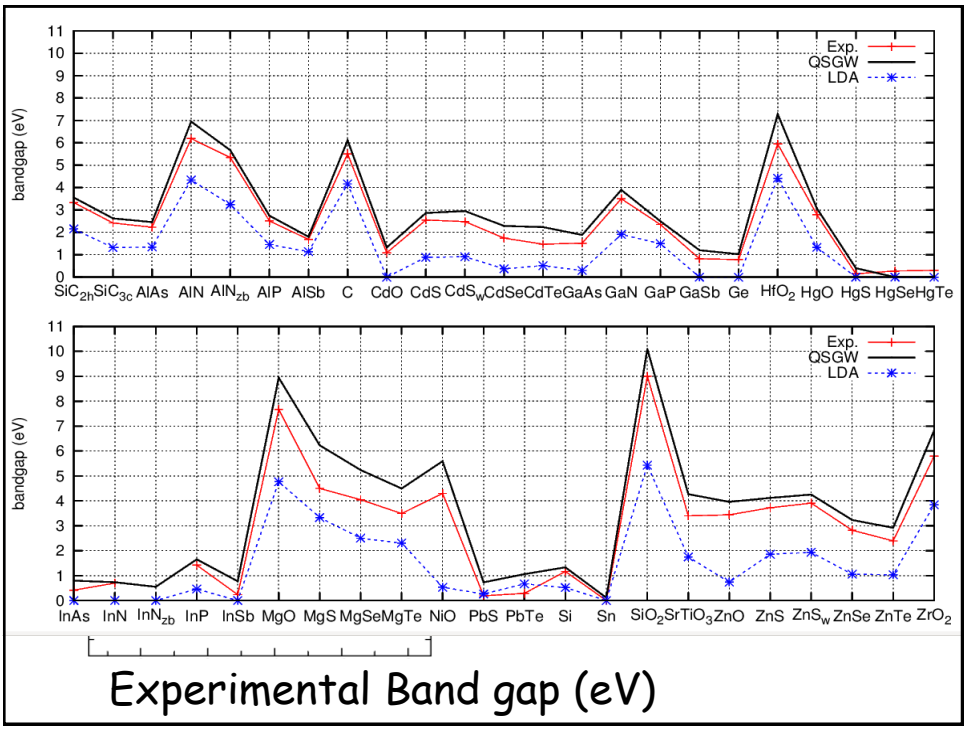

Physics in QSGW

LDA（GGA）→ homogeneous gas OK! （Physics）

Hartree-Fock → H-atom OK! （chemistry）

"True results" may be between its middle;

➔Hybrid methd（B3LYP, HSE…） $\frac{1}{4} \times \mathrm{HF} + \frac{3}{4} \times \mathrm{LDA}$

•Problem：the mixing ratio may be dependent on materials.

–QSGW： **Instead of bare Coulmb v,**

– **we use "Dynamically Screened Coulom interaction W".**

– **W is determined self-consistently simultaneously.**

Independent-particle theory where we take into account the charge fluctuation at the RPA self-consistently.

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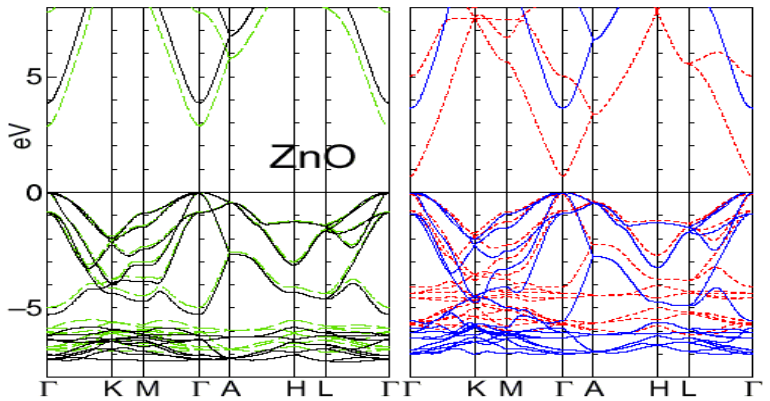


Black:QSGW 3.87eV

Red:LDA 0.71eV

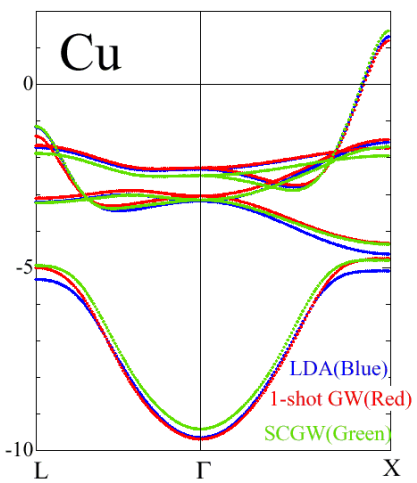
Green:$G^{LDA}W^{LDA}$ (Z=1,Offdiagonal included) 3.00eV

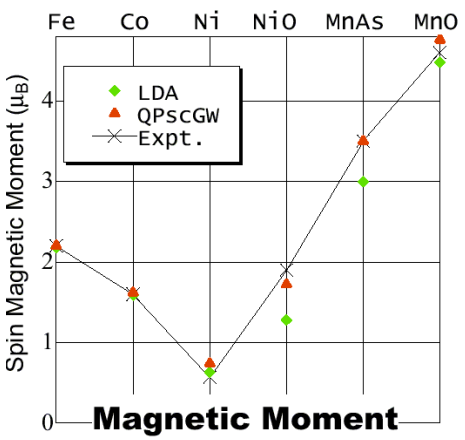
Blue:e-only self-consistency 3.64eV

Experiment(+correction) 3.60eV

Kotani et al PRB76,165106(2007)

d systems





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

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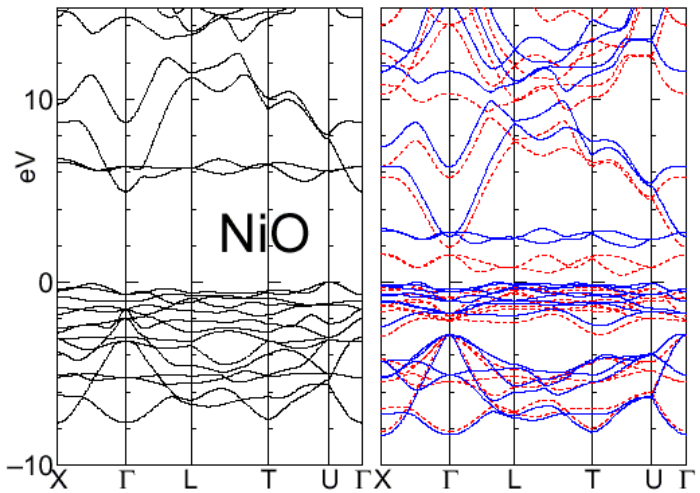

Black:QSGW Red:LDA Blue: e-only

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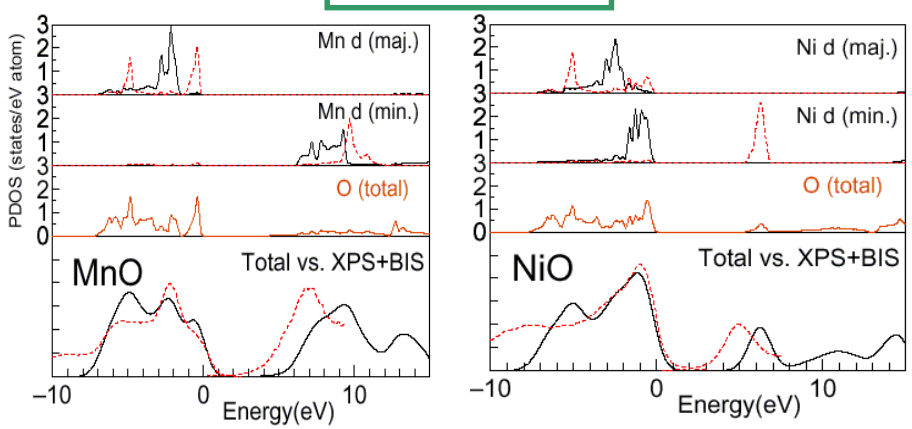
Black:t2g Red:eg



Red(bottom): expt

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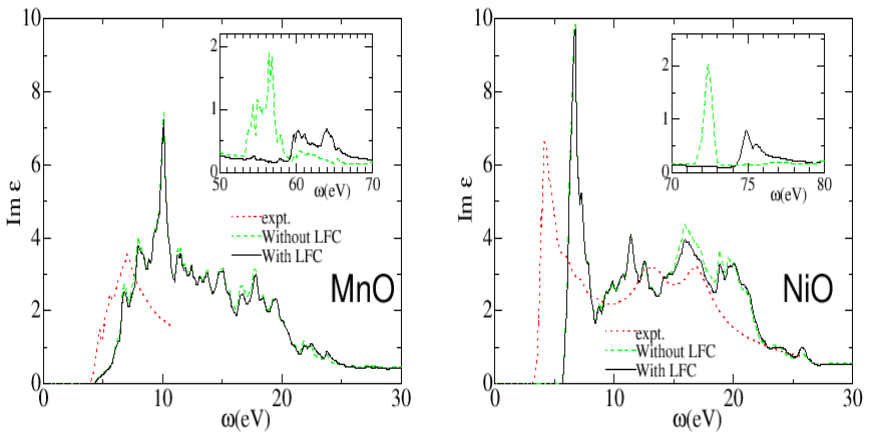

Black:Im eps with LFC Red:expt

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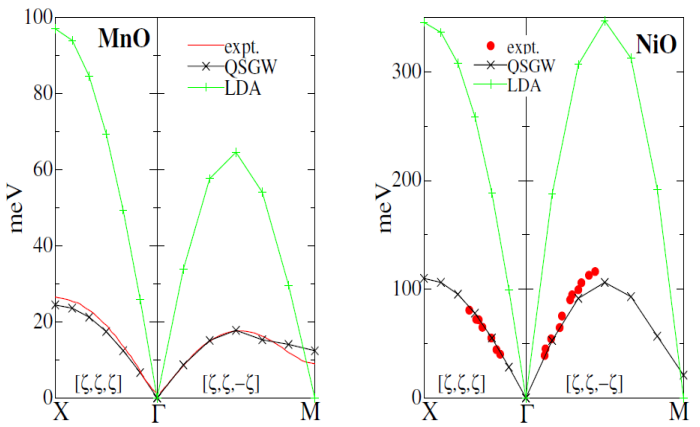
Spin wave dispersion based on QSGW

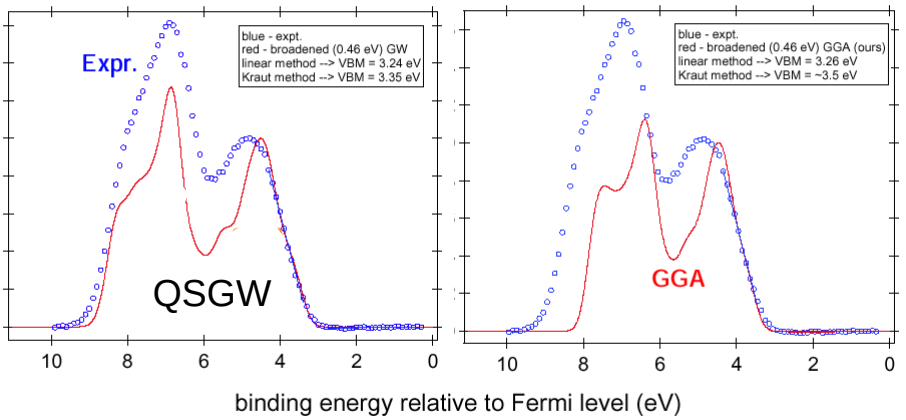


J.Phys.C20 (2008) 295214,
PRB83, 060404(R) (2011) for CaFe2As2 for spectrum of χ^{+-}.

40

SrTiO3 Valence DOS

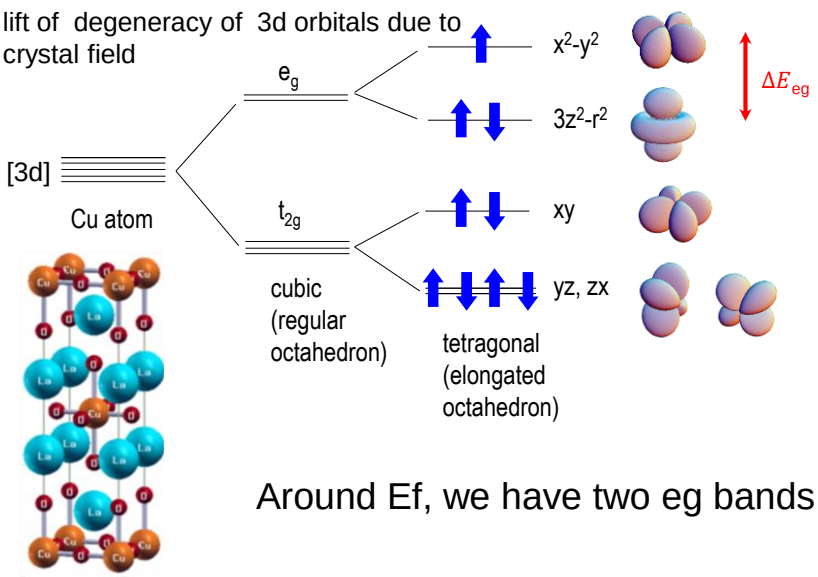
fit of properly broadened theoretical DOS with experiment
n-STO(001) VB excited with monochromatic AlKα x-rays (resolution = 0.46 eV)



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}

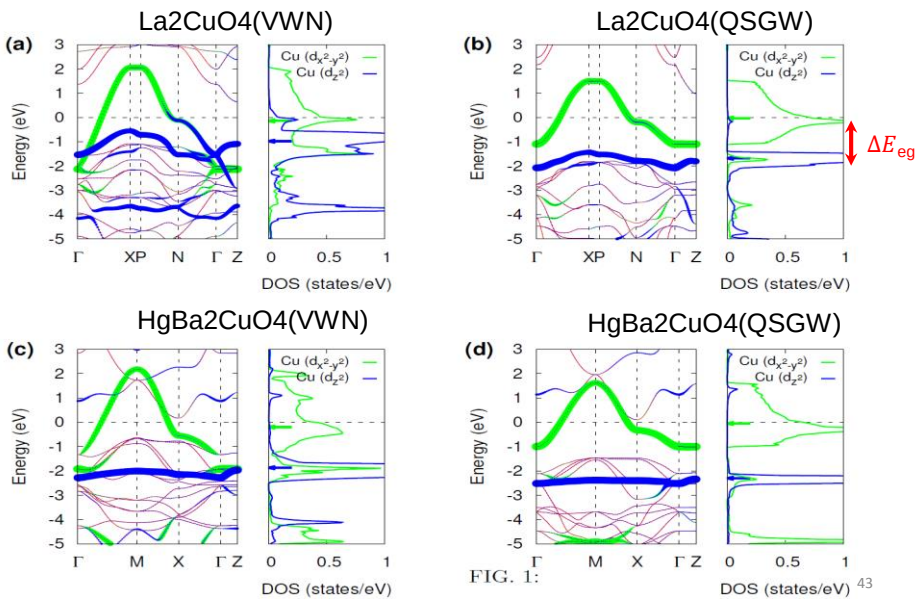
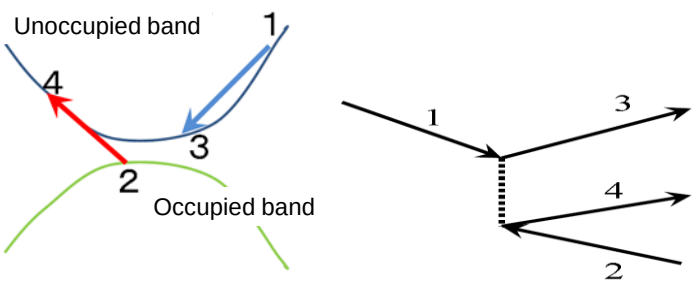


FIG. 1:

43

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＞

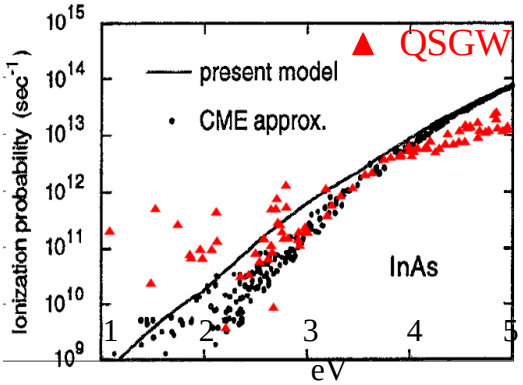
（Energy conservation and Momentum conservation）

44

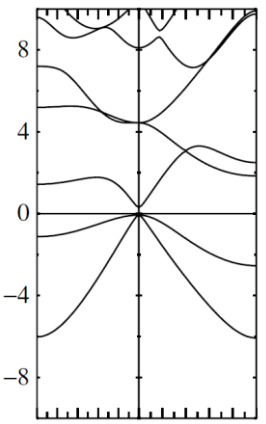
InAs impact ionization rate

(=auger process

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



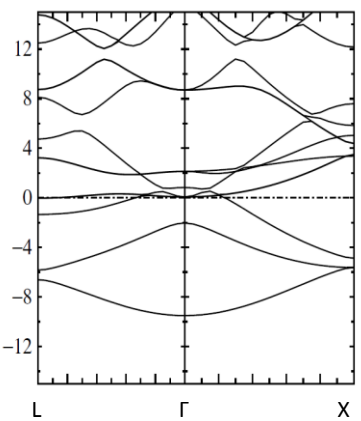
direct gap 0.38eV



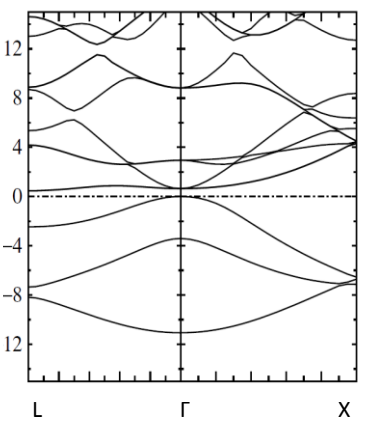
Present model: Sano and Yoshii JAP77 2020 (1995)

YH3(fcc structure 6x6x6)

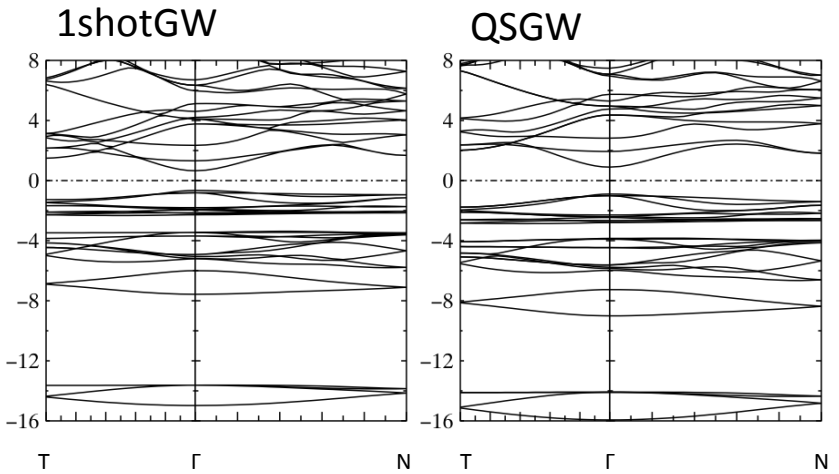
GGA



QSGW



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



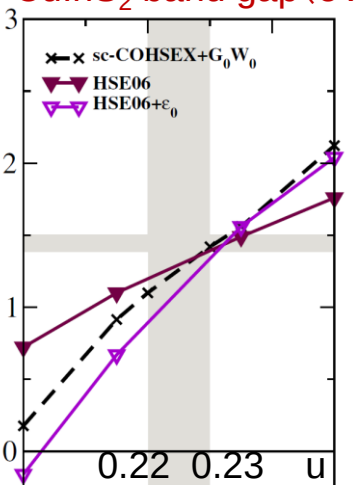
Band gap GGA:0.4eV, GW(1shot noZ) 1.37 eV,
QSGW(1.79eV) Exper. 1.63, 1.67, 1.73eV

Band gap for $CuAB_2$ (eV)

A / B	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)

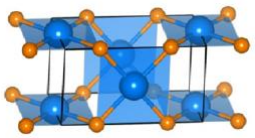


J.Vidal, PRL 104, 056401 (2010)

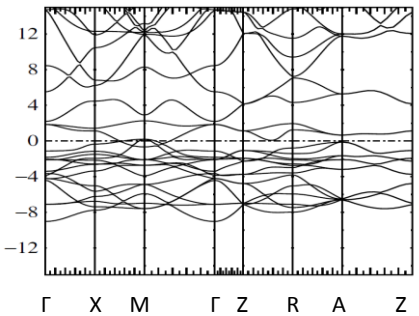
3x3x3 calculation(need check)

48

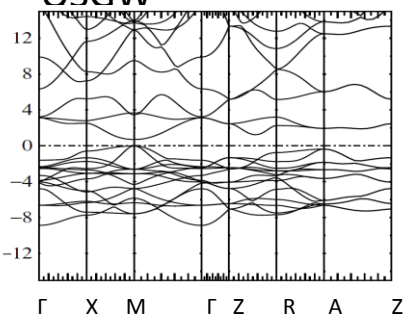
PdO(tetragonal , four atoms per cell 3x3x2 calculation , 1hour per iteration)



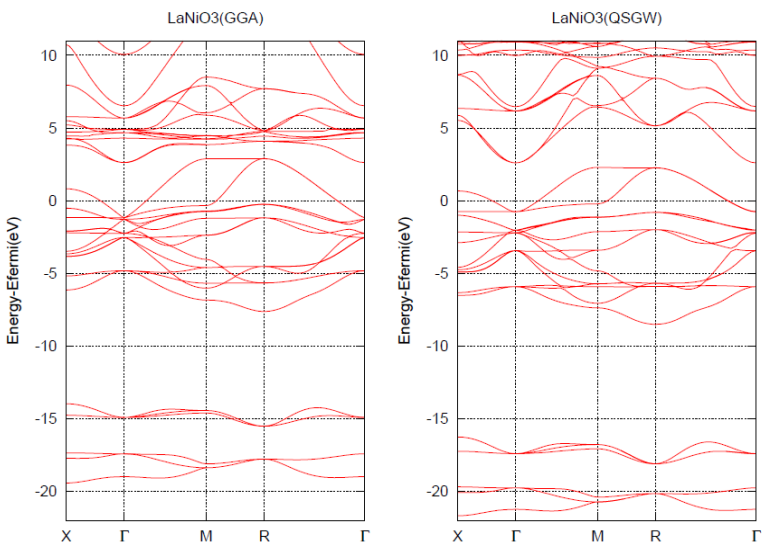
GGA



OSGW



Band gap about 0.7 eV



LaNiO3

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

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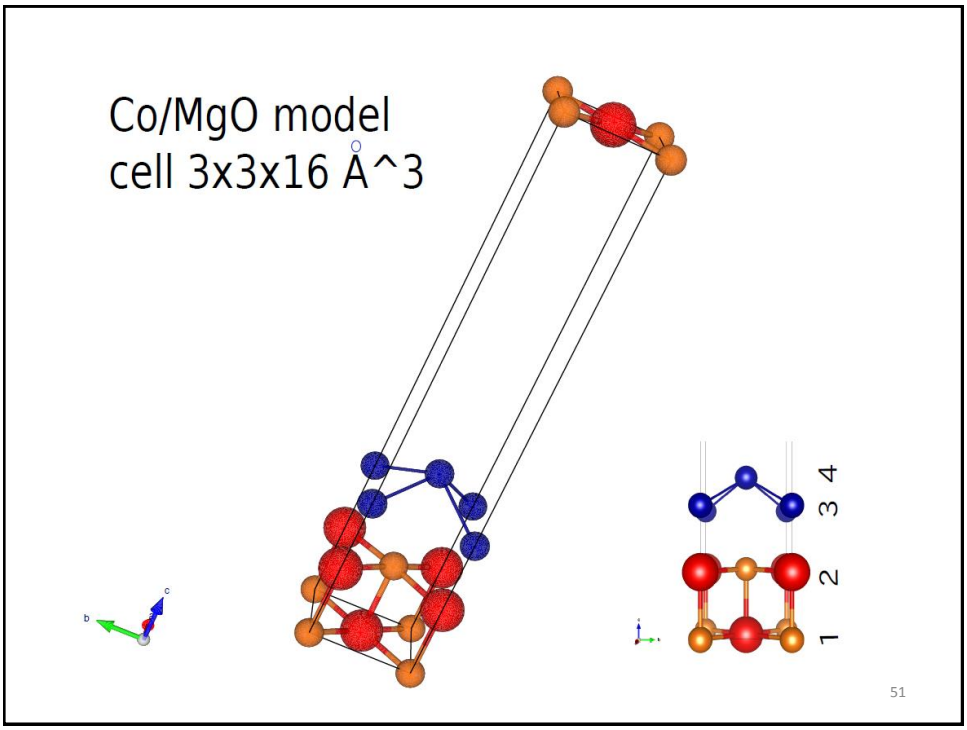
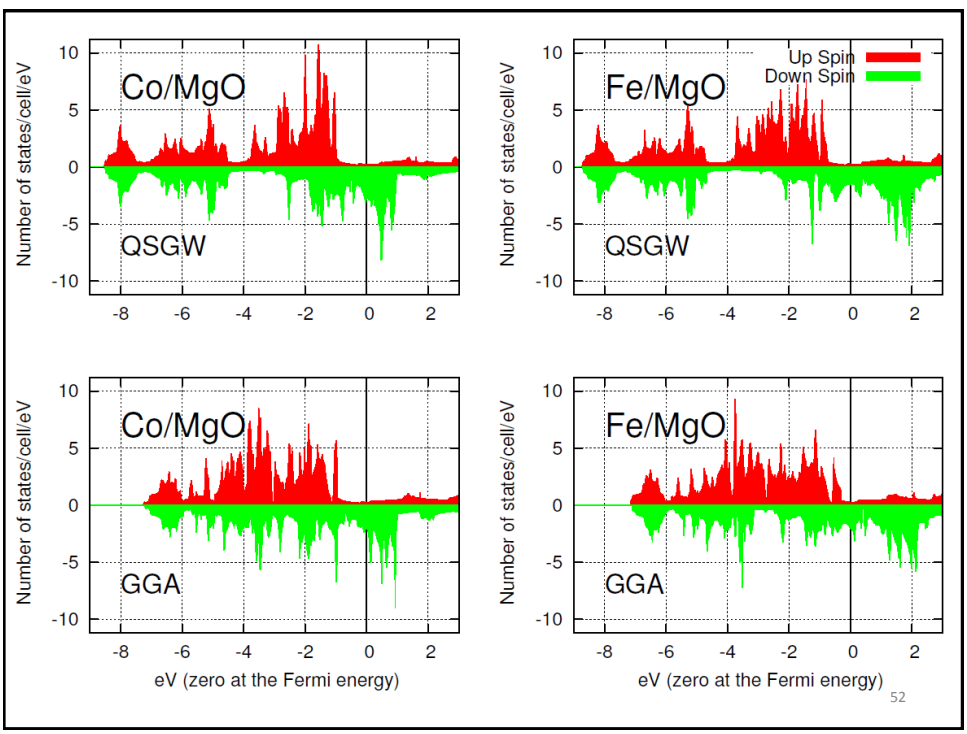

Co/MgO model
cell 3x3x16 Å^3
1
2
3
4
51


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)
52

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)