CMSI ecalj course feb.22.2016

> **目標： ecaljパッケージ（QSGW法）で何がどの程度できるのか？**
> **自分の目的に使えるかどうか？,可能性を知ってもらう.**
> **→共同研究**

セッション1（10:30~12：OO）

- **LECTURE1:** イントロ, PMT= LAPW+LMTO. ecaljでの一体問題解法
- **PRACTICE1**：インストールとLDAでのバンドプロット.

セッション2（1:15~14：30)+
セッション3（14：45~16：15．．．）

- **LECTURE2:** Quasiparticle self-consistent GW method
  QSGW近似で何ができるか？LDAの欠点がどのように解消するか？
  何ができるか？

- **PRACTICE2**： DOS, PDOSのプロット, QSGWでのバンドプロット.
  スピン軌道相互作用

- **その他の話題**
  ワニエ関数法，有効相互作用算出,インパクトイオン化

ecalj package

- **Github にて管理，公開.**
  tkotani ecaljで検索．Gitによるバージョン管理
  ワークショップ資料，ecaljmanual.pdfを含む
  　　　（詳細な開発者向きドキュメントは分離して管理）．
  利便性を意識（M1の学生を想定）．

- **独自性の高いPMT＝LAPW+LMTO，QSGW法を元にしたコード体系**
  また，そのための技術を利用した手法．
  LDA,GGA,構造緩和，LDA+U，ワニエ関数法，
  　スピン軌道相互作用（コリニア），GW，QSGW，誘電関数，
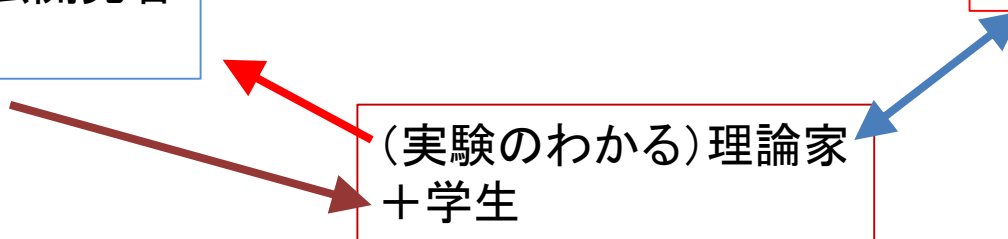 　スピン帯磁率，フォノン（進展中）
  　　　最適化が弱い点：並列化（k点並列のみ）．構造緩和．

研究活動の戦略　　1. 全エネルギーに関わるもの
　　　　　　　　　　　2. 原子位置はあまり動かないもの

プログラム・方法開発者
（小谷ら）

実験・研究現場

（実験のわかる）理論家
＋学生

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

$$\boxed{\textbf{PMT} = A\underline{P}W + \underline{\textbf{MT}}O}$$
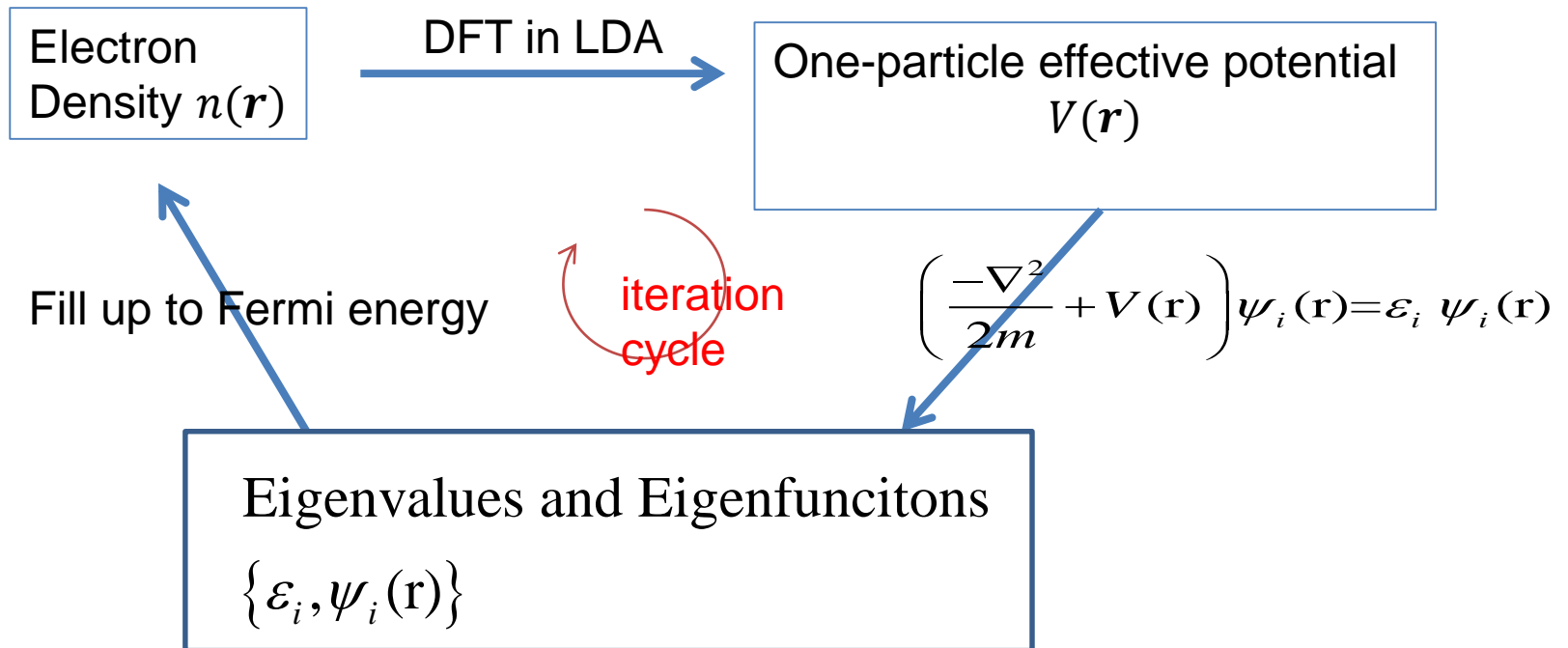
Muffin-tin

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:

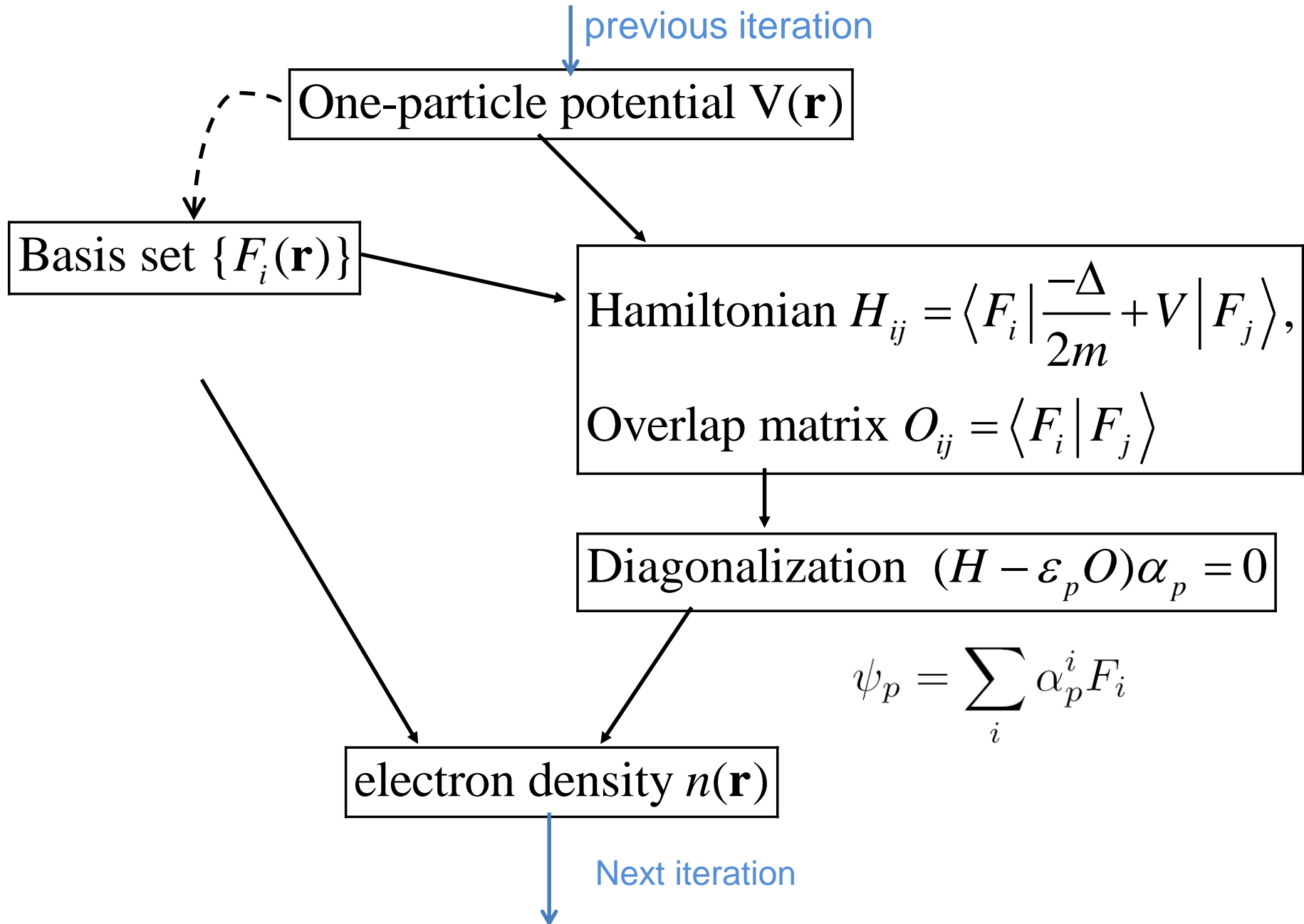$$\psi_p(\mathbf{r}) = \sum_j \alpha_p^j F_j(\mathbf{r}) \quad \left\{ F_j \right\} : j = 1, 2, ... N$$

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

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

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

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

iteration cycle

previous iteration

One-particle potential $V(\mathbf{r})$

Basis set $\{F_i(\mathbf{r})\}$

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

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

What is the APW and MTO?→ next page.

APW

Envelope function = PlaneWave(PW)

PW in MT

MT region   MT region
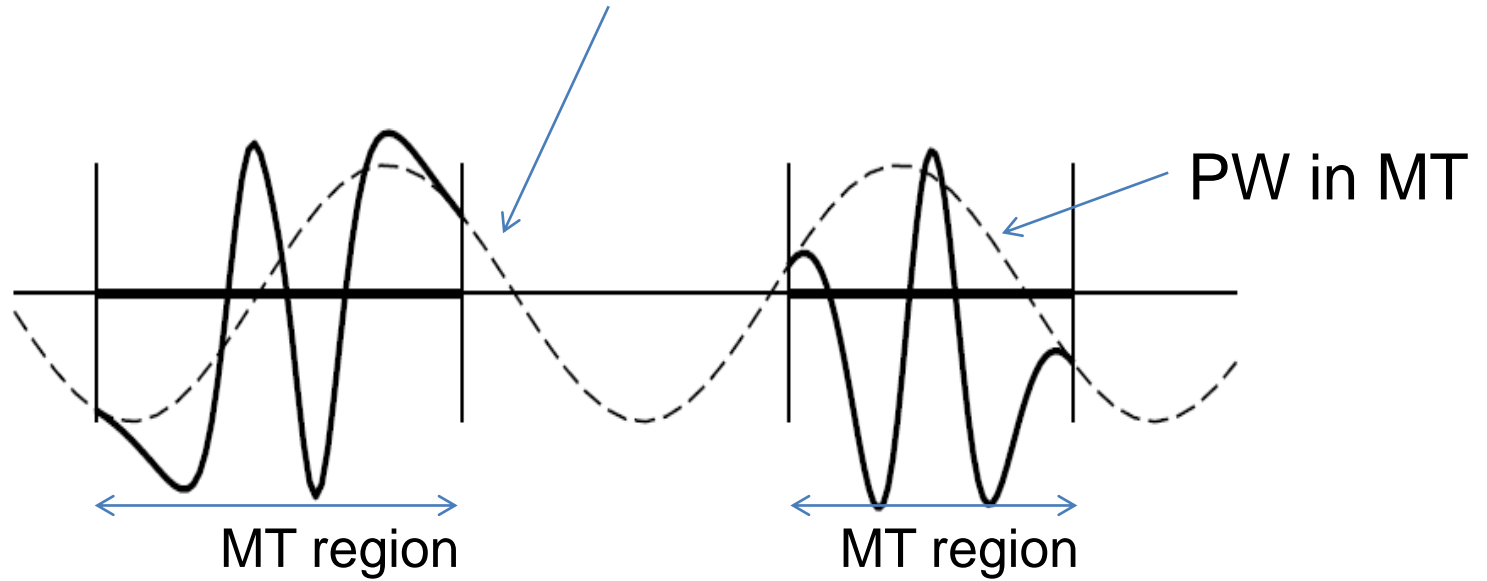
3-components

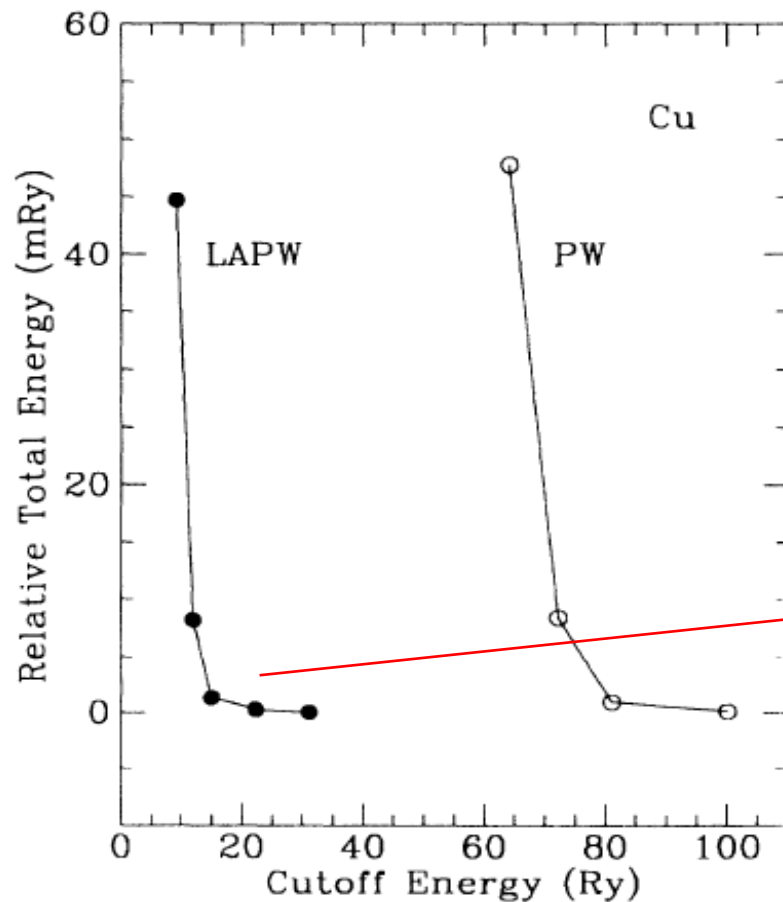PW ＋ Atomic-like part ー Counter part:
                                           PW within MT

0th   1st   2nd

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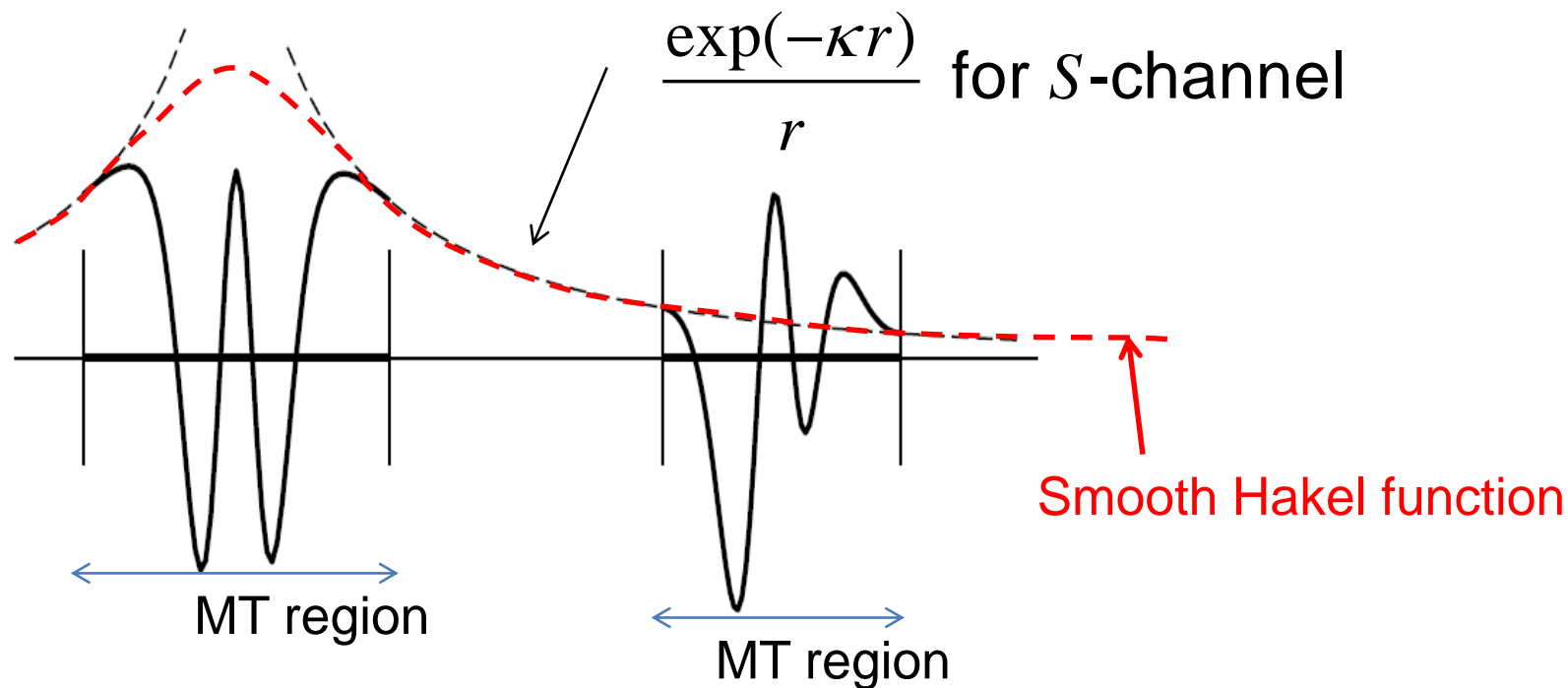- Not so good for Cu(3d), O(2p)
- Systematic

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,

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

Smooth Hakel function

MT region

MT region

3-components

Hankel $+$ Atomic-like part $-$ counter part of Hankel

0th   1st   2nd

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

PMT =A<u>P</u>W + <u>MT</u>O

T.K and M.van Schilfgaarde Phys. Rev. B 81, 125117 (2010)
T.K, H. Kino, and H.Akai
Supercell calculations from H2 through Kr2.
 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

$F_{0j}(\mathbf{r}),$ $F_{1j}(\mathbf{r}),$ $F_{2j}(\mathbf{r})$

Envelope function
PW or smHankel

Atomic-like parts
for $|\mathbf{r}| < R$

Counter part
for $|\mathbf{r}| < R$

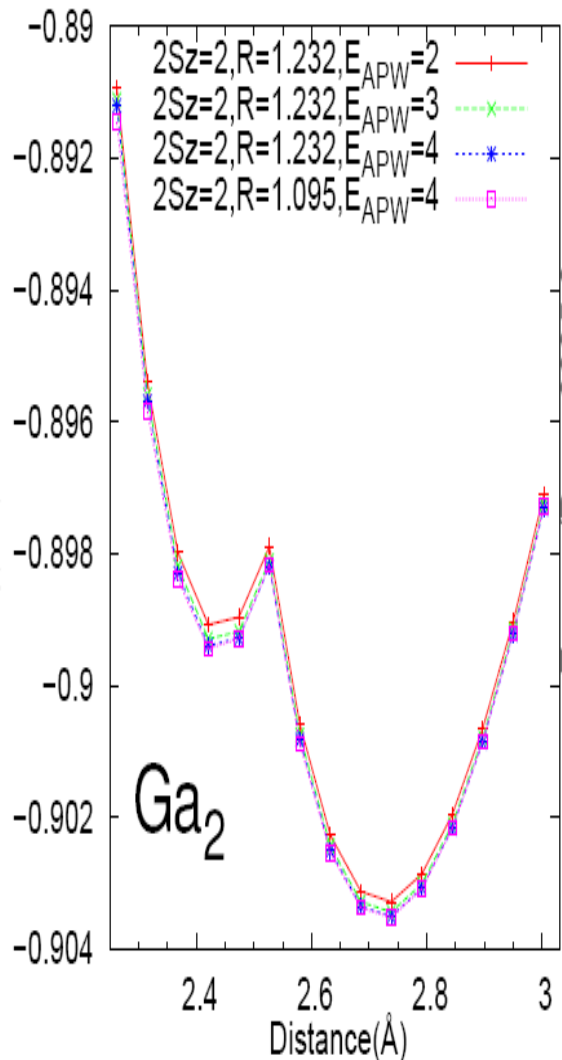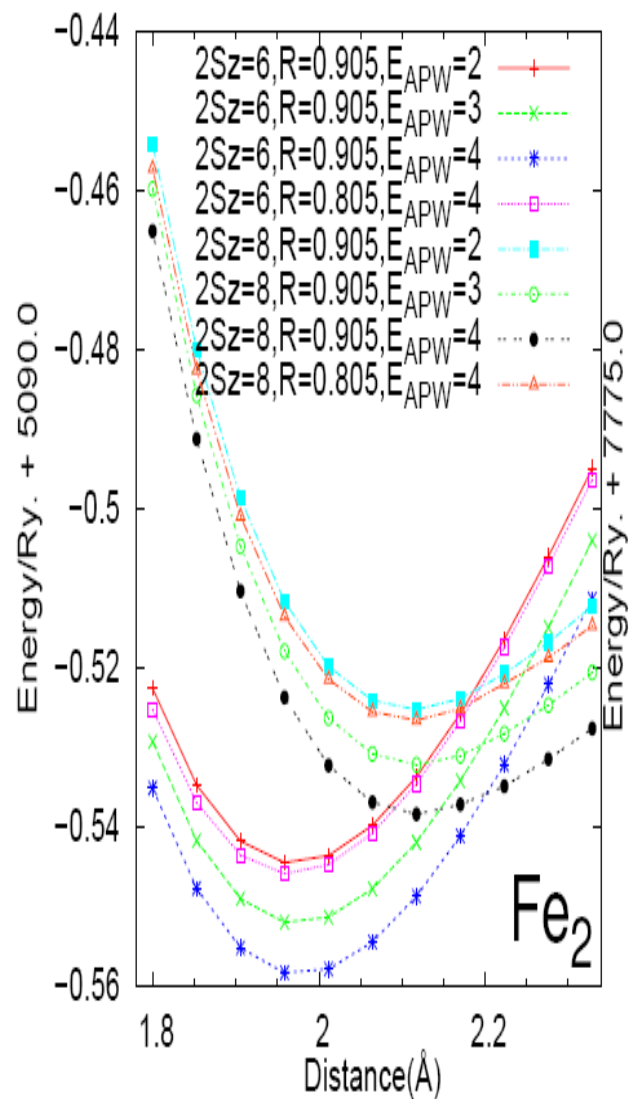**Augmentation parts**
Cutoff: $l \leq l_{\max} \sim 4,$ **Radial-part expansion**

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

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 wihtin MTs.

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

This is also used together.
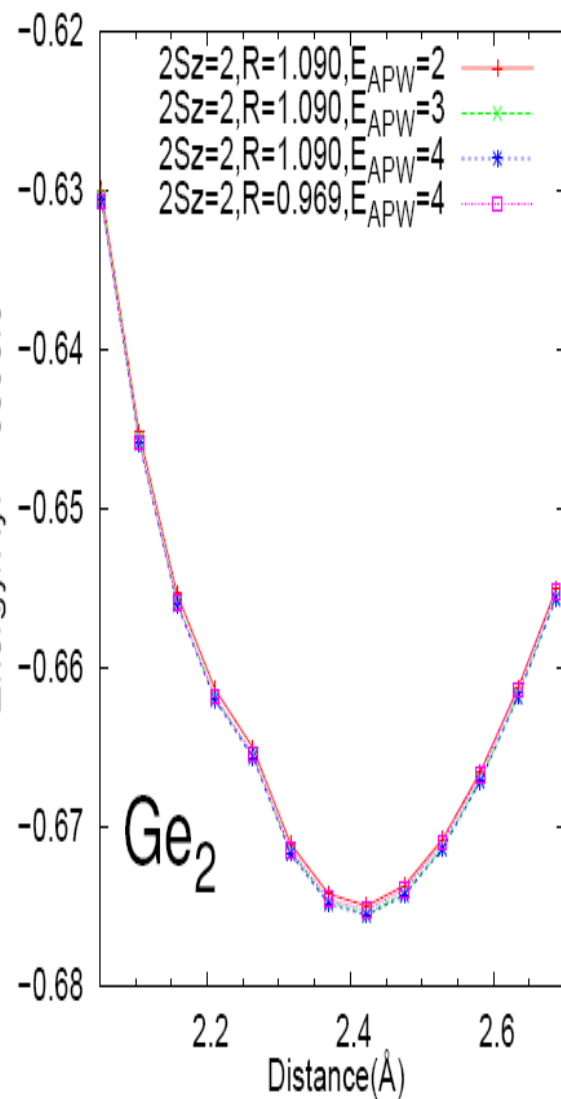
N_{basis}=1081+36×2,   1973+36×2,   3025+36×2

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 an independent-particle picture

- Hartree-Fock theory
- Density functional theory

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

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

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) .

NOTE: we can consider
A. configuration of excited states. → QUIZ (picturize this)
B. fractional occupancy (this is very theoretical)

We can describe "ground state" and "excited state" easily
by filling electron or removing electron from orbitals → **Independent particle picture**

But need to know its limitation.

True excited state energy is not so easy;
From a view, you can say "mean-field changes by filling electrons".

Confusing? But there is a key theorem for mean-field theories.

Janak(Koopman's) theorem

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

when we fill/remove electrons from orbital ψ_i

Left hand side is "True" excitation energy.
(caution: this is "derivative", not one-electron filled/removed.)

Ionization energy of an atom
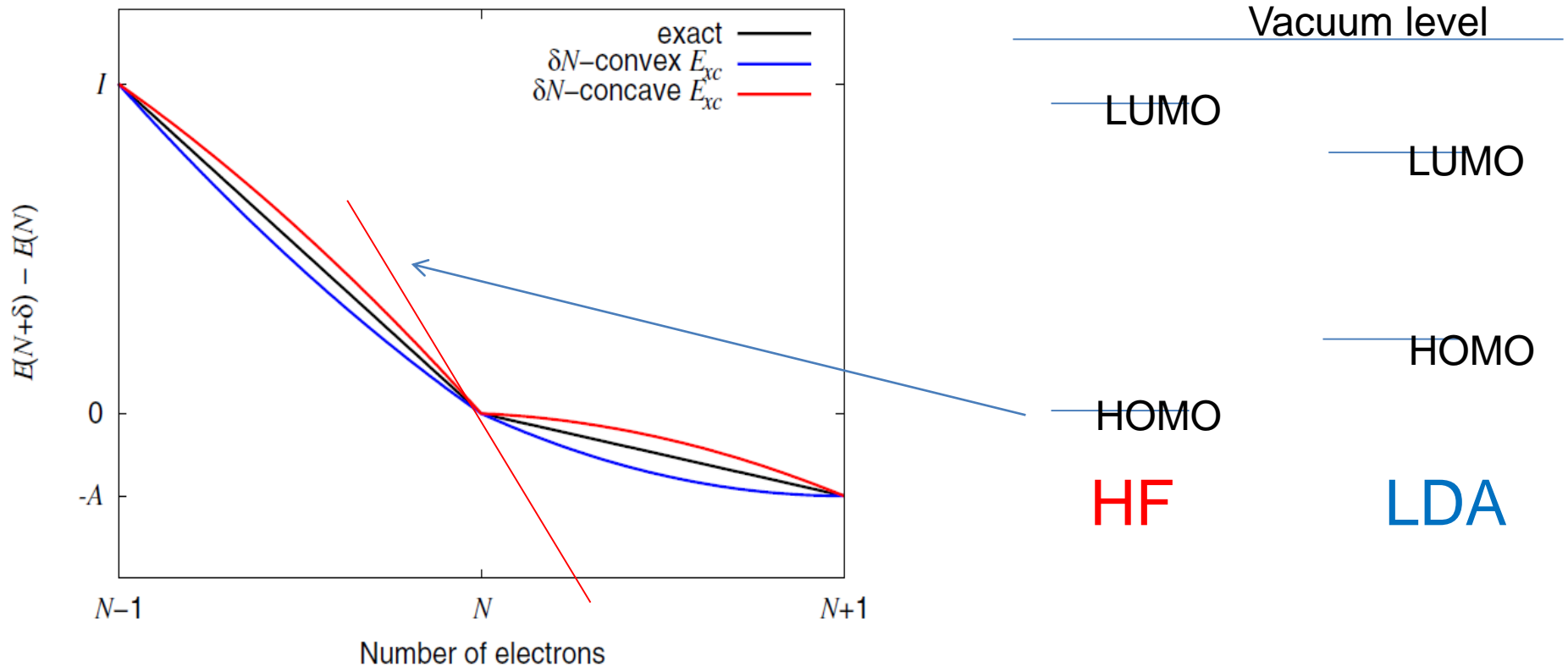
$$\varepsilon_i = \frac{\partial E}{\partial n_i} \approx \frac{\Delta E}{\Delta n_i}$$

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

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

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

How accurate they are?

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

Conduction band

Band gap

Valence band
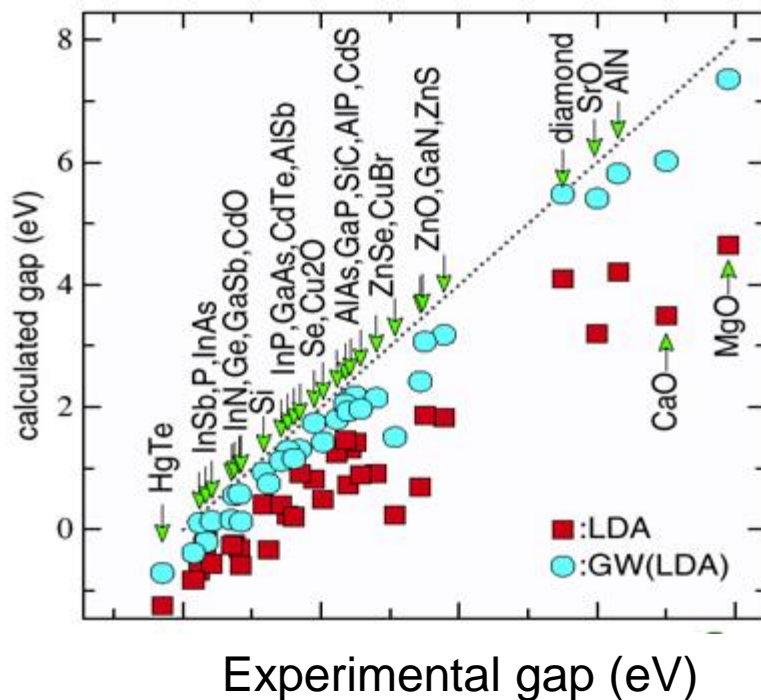
LDA gives too small
HF(not shown) gives too large
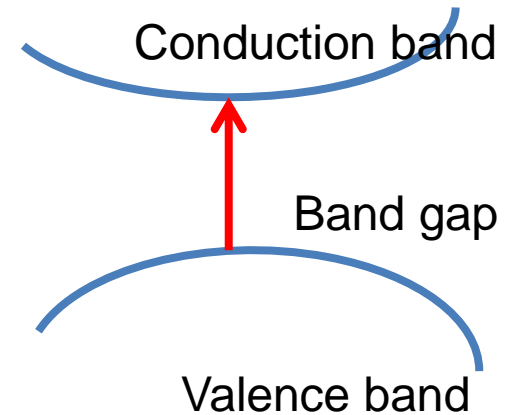
Key point : meanings of "eigenvalues and eigenfuncions" in the mean-field theory.

GW method and QSGW method

(preparation) What is Green's function?

*Example1: Poisson eq. $\Delta\phi = \rho(\mathbf{r})$ How to convert this to <u>integral equation</u>?

$$\Delta \frac{1}{4\pi|\mathbf{r}-\mathbf{r}'|} = \delta(\mathbf{r}-\mathbf{r}') \qquad G_0 = \frac{1}{4\pi|\mathbf{r}-\mathbf{r}'|} \text{ is Green function}$$

$$\phi(\mathbf{r}) = \int G_0(\mathbf{r}-\mathbf{r}')\rho(\mathbf{r}')d\mathbf{r}'$$

* Example2: $\left(i\frac{\partial}{\partial t} - E\right)\text{f(t)} = \rho(\text{t})$ $\rightarrow$ $\left(i\frac{\partial}{\partial t} - E\right)G_0(t-t') = \delta(t-t')$

$G_0 = \theta(t-t')e^{-iE(t-t')}$ or $G_0 = \theta(t'-t)e^{-iE(t'-t)}$

($\delta(t-t')$ means "impact force".)

* Fourier transformation: $\theta(t-t')e^{-iE(t-t')} \leftrightarrow \frac{1}{\omega-E+i\delta}$ or …quiz…

For given, $H_0 = -\frac{\nabla^2}{2m} + V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r},\mathbf{r}')$,

we like to calculate $\varphi(\mathbf{r},t)$ sasisfying $\left(i\frac{\partial}{\partial t} - H_0\right)\varphi(\mathbf{r},t) = F(\mathbf{r},t)$

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

$$\Rightarrow G_0 = \frac{1}{i\frac{\partial}{\partial t} - H_0} = \frac{1}{\omega - H_0} \qquad \text{(Note boundary condition)}$$

Boundary condition along time-axis

$$H_0 = H_0^{occ.} + H_0^{unocc.} = \sum_{occ.} \epsilon_i \; \varphi_i^*(\boldsymbol{r})\varphi_i(\boldsymbol{r'}) + \sum_{unocc.} \epsilon_i \; \varphi_i^*(\boldsymbol{r})\varphi_i(\boldsymbol{r'})$$

$$\rightarrow G_0 = \frac{1}{\omega - H_0} = \sum_{occ.} \frac{\varphi_i^*(\boldsymbol{r})\varphi_i(\boldsymbol{r'})}{\omega - \epsilon_i + i\delta} + \sum_{unocc.} \frac{\varphi_i^*(\boldsymbol{r})\varphi_i(\boldsymbol{r'})}{\omega - \epsilon_i - i\delta}$$

$$= - \sum_{occ.} \varphi_i(\boldsymbol{r'})\varphi_i^*(\boldsymbol{r}) \, \theta(t' - t) e^{-i\varepsilon_i(t' - t)}$$

$$+ \sum_{unocc.} \varphi_i(\boldsymbol{r})\varphi_i^*(\boldsymbol{r'}) \, \theta(t - t') e^{-i\varepsilon_i(t - t')}$$

(we measure ε_i from μ, or ε_i →all excitation is positive energy)

Quiz: check this G_0 satisfy differential eq at page.24

Why? → this is convenient due to Fermi statistics
(adding electron or "adding hole=removing electron").

Many body theory (rough explanation)

H_0 is interpreted in the second quantization.
"Fock space." An excited state can be written as

$$|1,1,0,0, \quad 1,0,1,1,0,1,1,1,1,1,1\rangle$$

Above Ef | Below Ef

Ef

In other words, it can be written as

$$a_4^\dagger a_3^\dagger a_{-2} a_{-5} |1,1,1,1,1,1,1,1,1,1,1\rangle$$
$$= a_4^\dagger \, a_3^\dagger a_{-2} a_{-5} |\mathbf{0}>$$

We need to treat a set $\Omega =${all possible excited+ground states}.
Quiz: Then what the operation H_0 mean? What is $1/(\omega - H_0)$?

$1/(\omega - H_0)$ in MBPT

時間軸

4

3

-2

-5

t t'
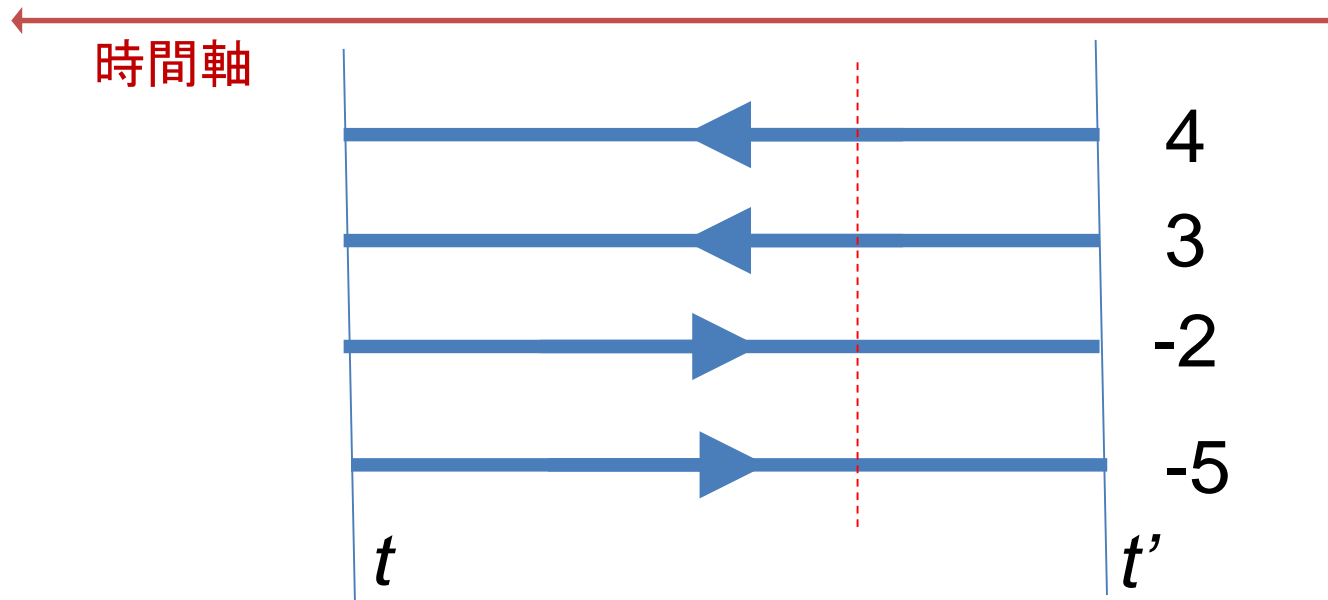
これは(4,3,-2,-5)が時間がたってもそのまま，（4,3, -2, -5)であることを意味する．エネルギーは和になっている．多体理論ではどうなるか？

$$\frac{1}{\omega - (H_0 + (H - H_0))}$$

NOTE: 畳み込み積分 $\int_0^t f(t-t')g(t-t')\,dt \leftrightarrow f(\omega)g(\omega)$

$$= \frac{1}{\omega - H_0} + \frac{1}{\omega - H_0}(H - H_0)\frac{1}{\omega - H_0} + \frac{1}{\omega - H_0}(H - H_0)\frac{1}{\omega - H_0}(H - H_0)\frac{1}{\omega - H_0}$$

$$+ \dots$$

これはT(exp(-iHt))などと書いたりもする．

$H = H_0$ + (electron-electron interaction) $- \Delta V(\mathbf{r})$

Illustration of Many-body perturbation theory(MBPT)

Example:

$V_{\mathrm{other}}(\mathbf{r})$

$V_{\mathrm{XC}}(\mathbf{r}, \mathbf{r}')$

Time-axis
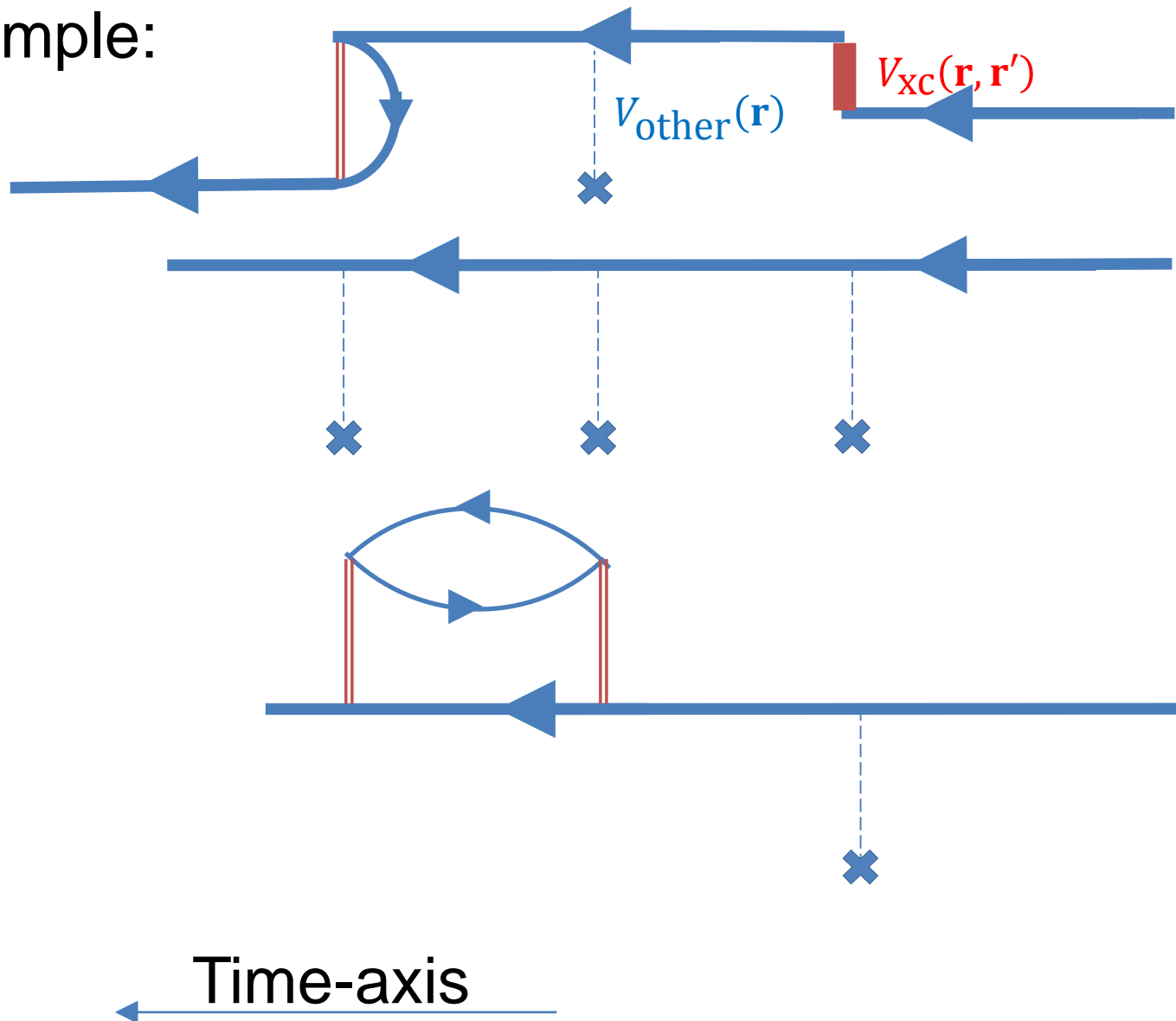
GW approximation

We concentrate on how G_0 is modified by $H_0 + (H - H_0)$

We assume H_0 is not so bad as starting point…

$$H_0 = -\frac{\nabla^2}{2m} + V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r}, \mathbf{r}')$$

1.交換効果

$(H - H_0)$ makes jump to another electron.
 Effect of Fock term. (and remove self-interaction)

2. 相関効果

When a test charge is moving in electron sea.
    The test charge is moving
 ➔ cause polarization of electrons
 ➔ affect force to the test charge.

Particle of H_0 ➔ Quasiparticle picture.

GW approximation： 1電子波動関数の時間発展

Start from any H_0

e.g. $= H^{\mathrm{LDA}}$

1.
$$H_0 = -\frac{\nabla^2}{2m} + V_{\mathrm{eff}}(\mathbf{r}, \mathbf{r}') \Leftrightarrow G_0 = \frac{1}{\omega - H_0}$$

$$n(\mathbf{r}) = G_0(\mathbf{r}, \mathbf{r}, 0-)$$

G_0
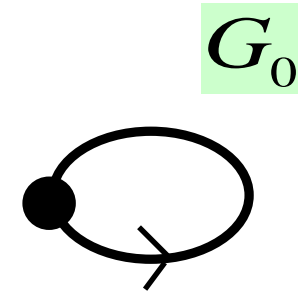
2. $\Pi = -iG_0 \times G_0$ Polarization function

Π is density response for one-particle potential.

3.
$$\Pi(\mathbf{r}, \mathbf{r}', t - t') = \frac{\delta n(\mathbf{r}, t)}{\delta V(\mathbf{r}', t')}$$

G_0

G_0
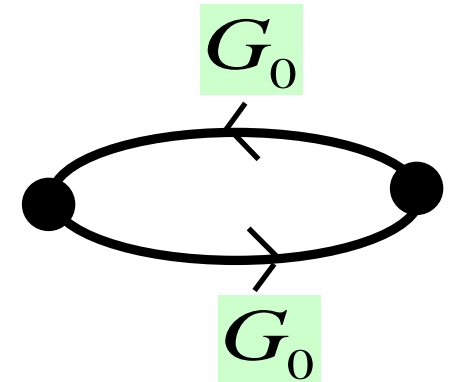
$$W = \varepsilon^{-1} v = (1 - \Pi v)^{-1} v \; W \text{ in the RPA}$$
(time-dependent Hartree approx.)

$$v(\mathbf{r}, \mathbf{r}') = \frac{e^2}{|\mathbf{r} - \mathbf{r}'|}$$

Self-energy（Many-body effect is downfolded into one-body propagetor）

4.
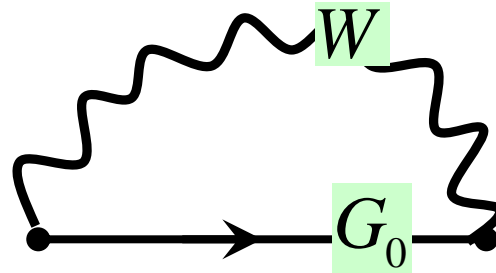
$\Sigma = i\, G_0 W$ Self-energy $\quad$ が「交換相関」を与える。

interpretation1：exchange hopping＋electron moving is other electrons

2: screened Coulomb interaction + Coulomb hole

$G_0 \rightarrow n \rightarrow V^H$ also

$$H\left(\mathbf{r},\mathbf{r}',\omega\right) = -\frac{\nabla^2}{2} + V^{\text{ext}}\left(\mathbf{r}\right) + V^{\text{H}}\left(\mathbf{r}\right) + \Sigma\left(\mathbf{r},\mathbf{r}',\omega\right)$$

$$\Rightarrow \quad G = \frac{1}{\omega - H}$$

$$NOTE : \text{In } \int d\mathbf{r}' dt'\, H\left(\mathbf{r},\mathbf{r}',t-t'\right)\varphi(\mathbf{r}',t'),$$

$$V^{\text{ext}}\left(\mathbf{r}\right) \text{is takes as } V^{\text{ext}}\left(\mathbf{r}\right)\delta(\mathbf{r}-\mathbf{r}')$$

$$\omega - \text{dependence of } \Sigma\left(\mathbf{r},\mathbf{r}',\omega\right) \text{ is very problematic}$$

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QSGW: How to determine better H_0?

$$H(\varepsilon_i)|\varphi_i(\mathbf{r})\rangle = \varepsilon_i|\varphi_i(\mathbf{r})\rangle$$

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

It is not so easy to treat energy-dependent potential!

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

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

An average procedure (not shown here)

This idea is supported by Quasiparticle picture (Landau-Silin's).

GW and the "RPA total energy"

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

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

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

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

$G_0 = \frac{1}{\omega - H_0}$ で展開

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

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

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) ³³

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

Schematic explanation on off-site exchange

If

Bonding   HOMO
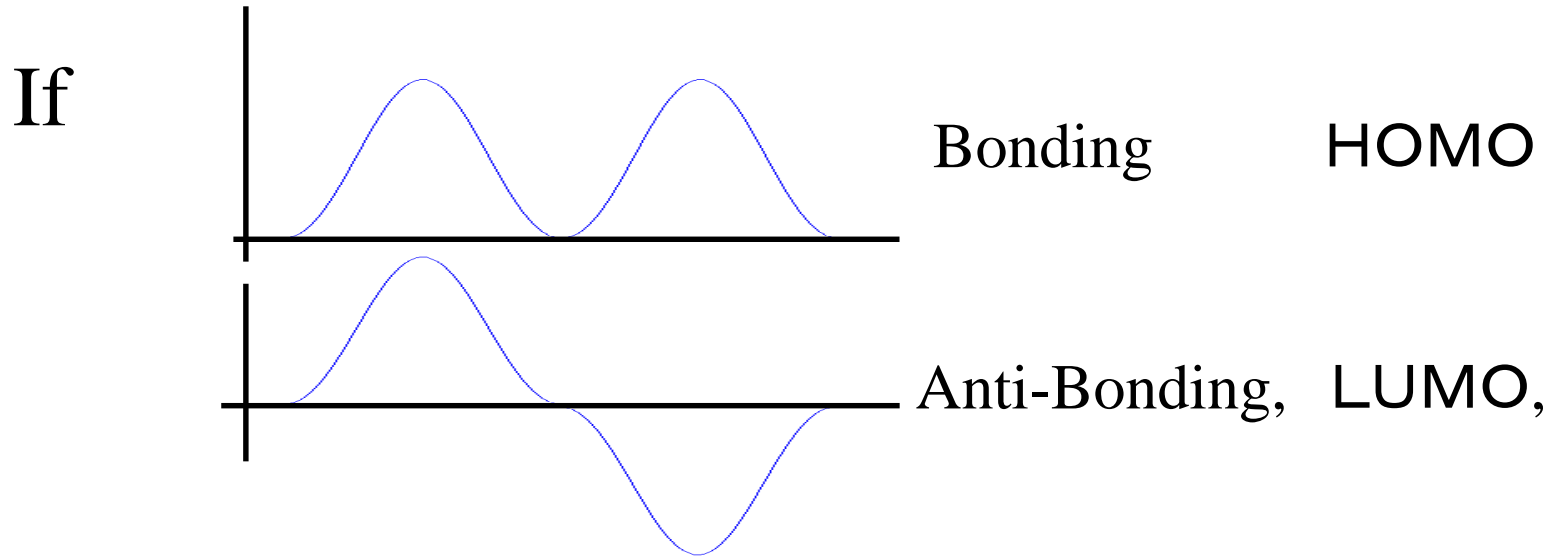
Anti-Bonding,   LUMO,

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.

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
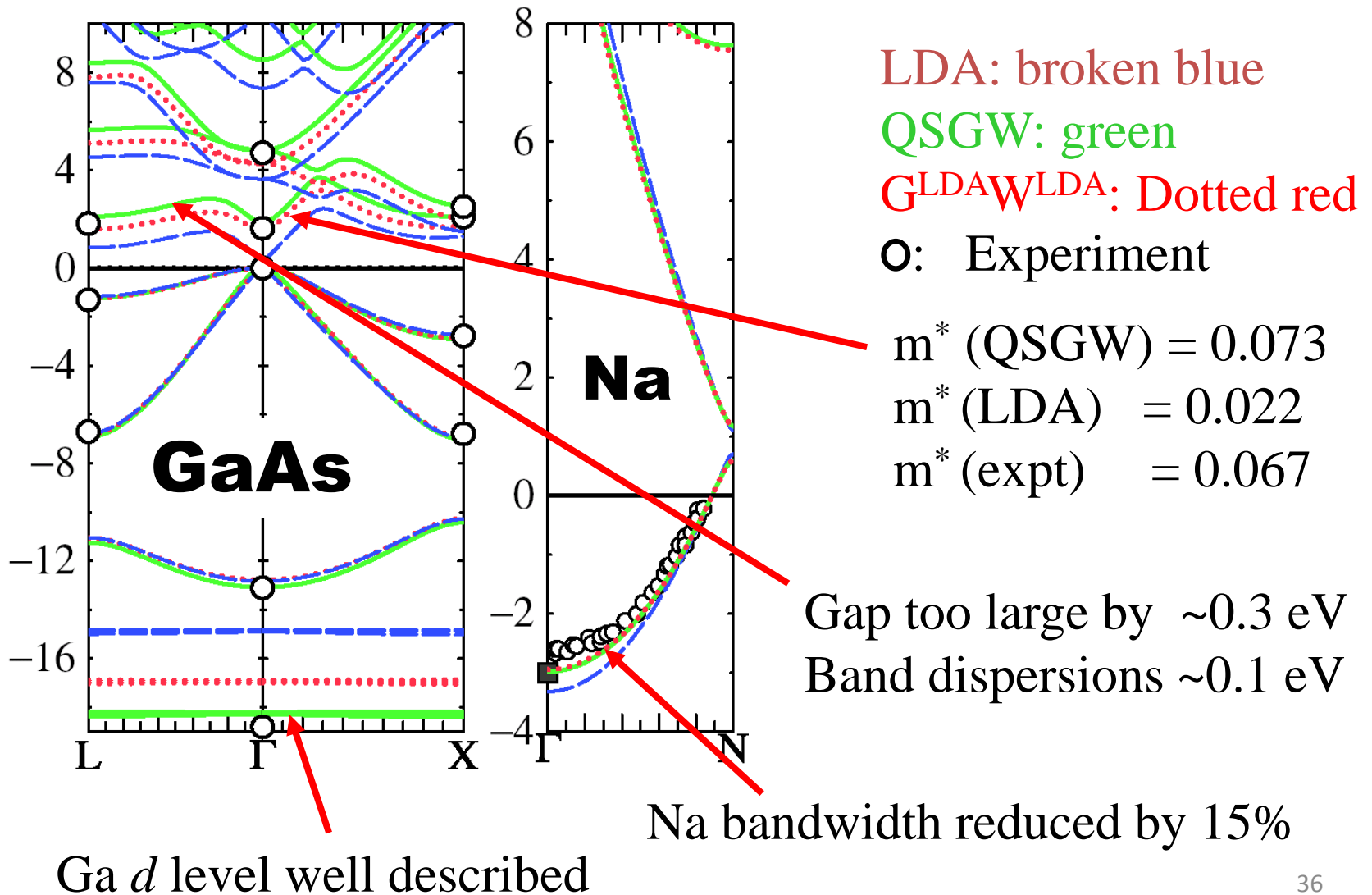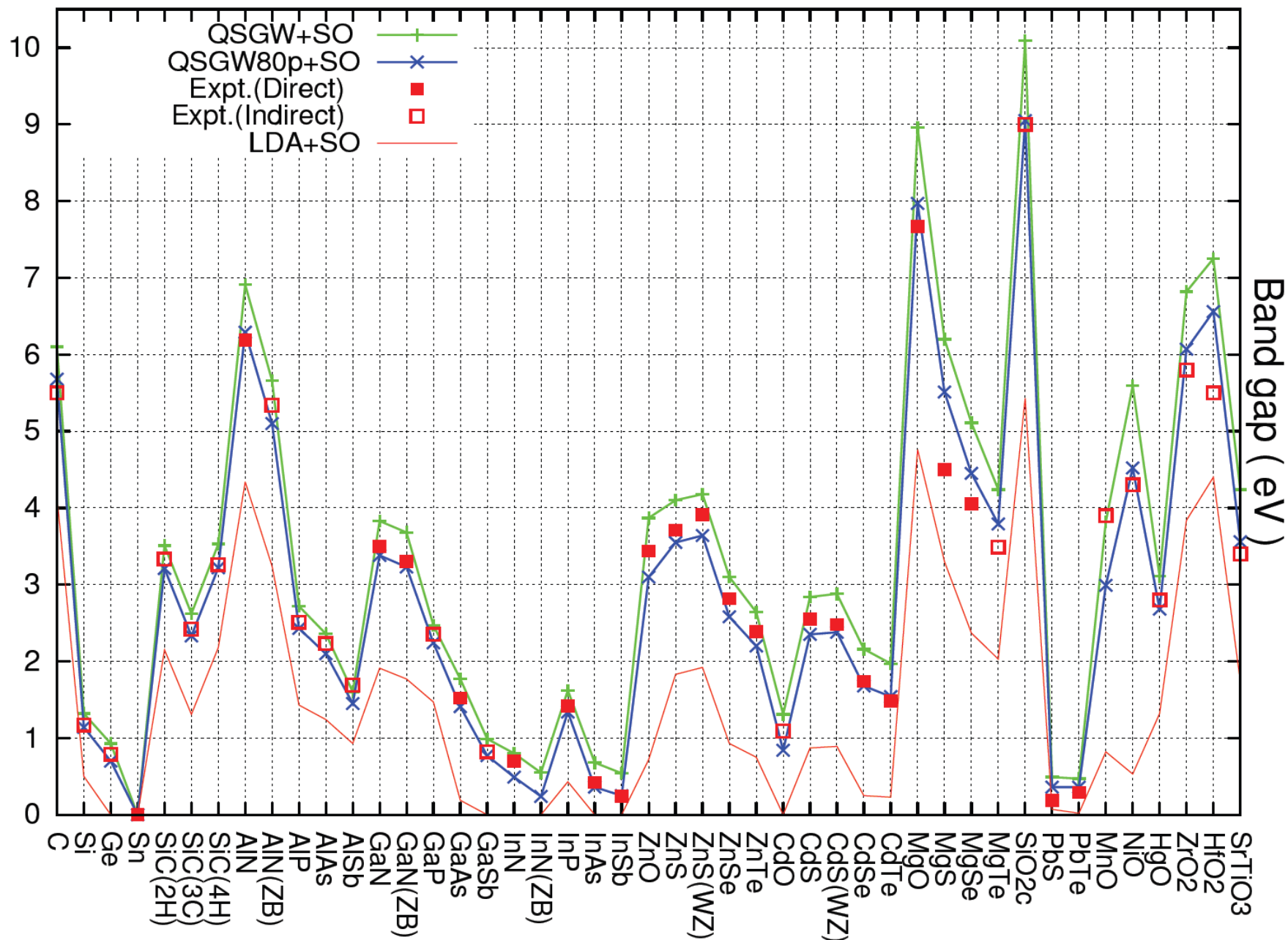
D.Deguchi, K.Sato,H.Kino, TK(JPSJ, arXiv:1512.06930)
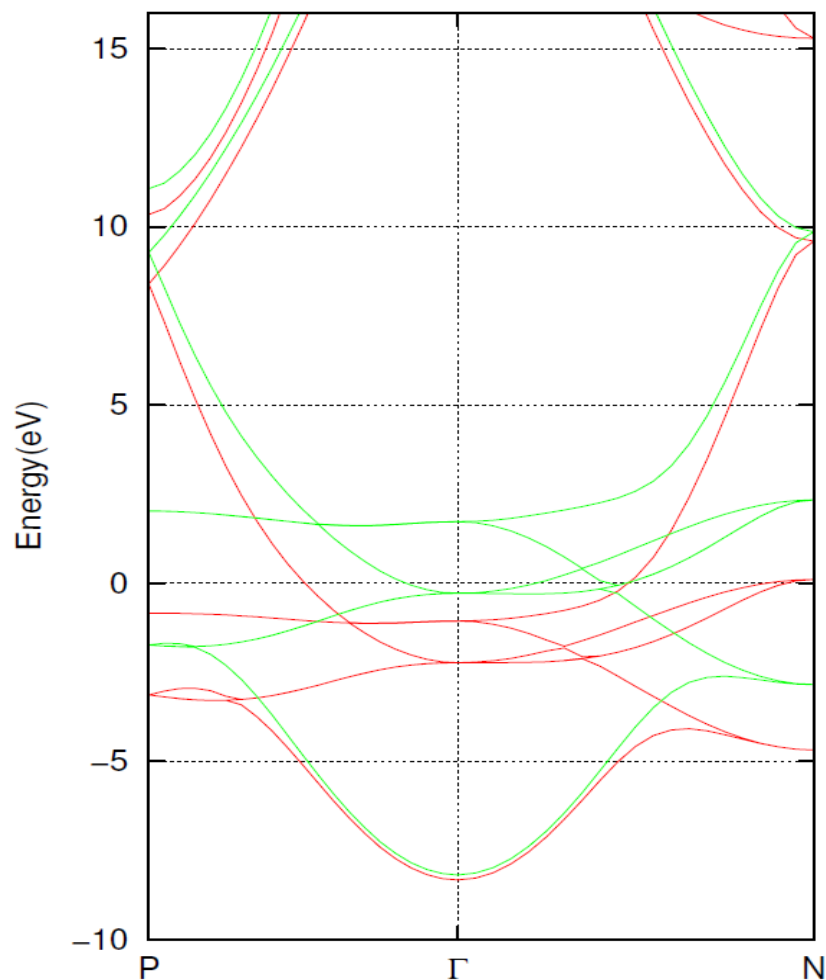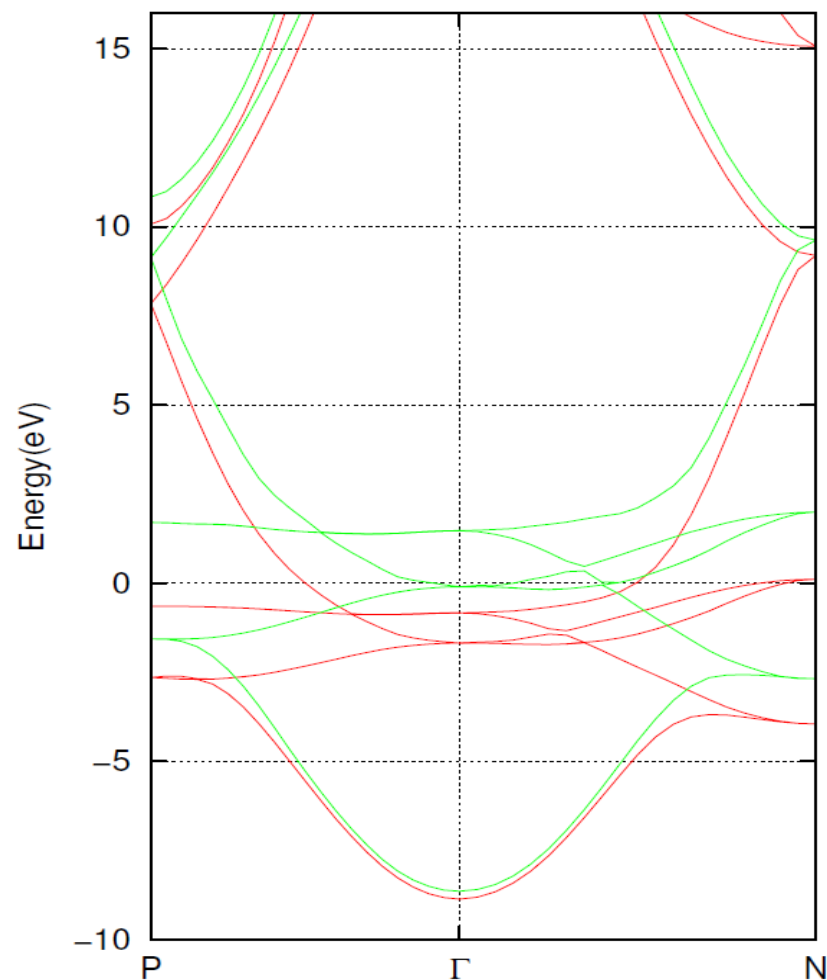
金属的なもの→QSGWでOK.
ハイブリッド法では場合によりうまくいかない。

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…）　$\dfrac{1}{4} \times$ HF $+$ $\dfrac{3}{4} \times$ 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.**

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

Why we need 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…

Metal	Molecule	Molecule on top of metal.
	LUMO	
Fermi energy		
	HOMO	
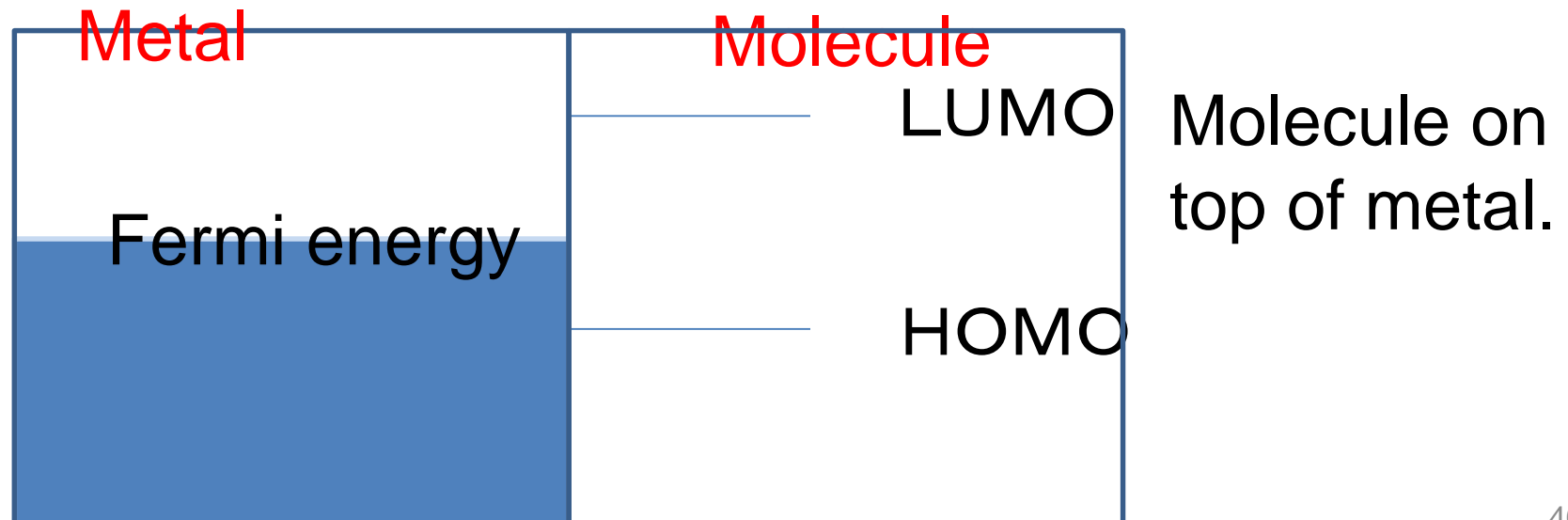
GGA: O$_2$ in supercell (12a.u.)^{3}cell QSGW

計算の収束性は不明. . .

ZnO
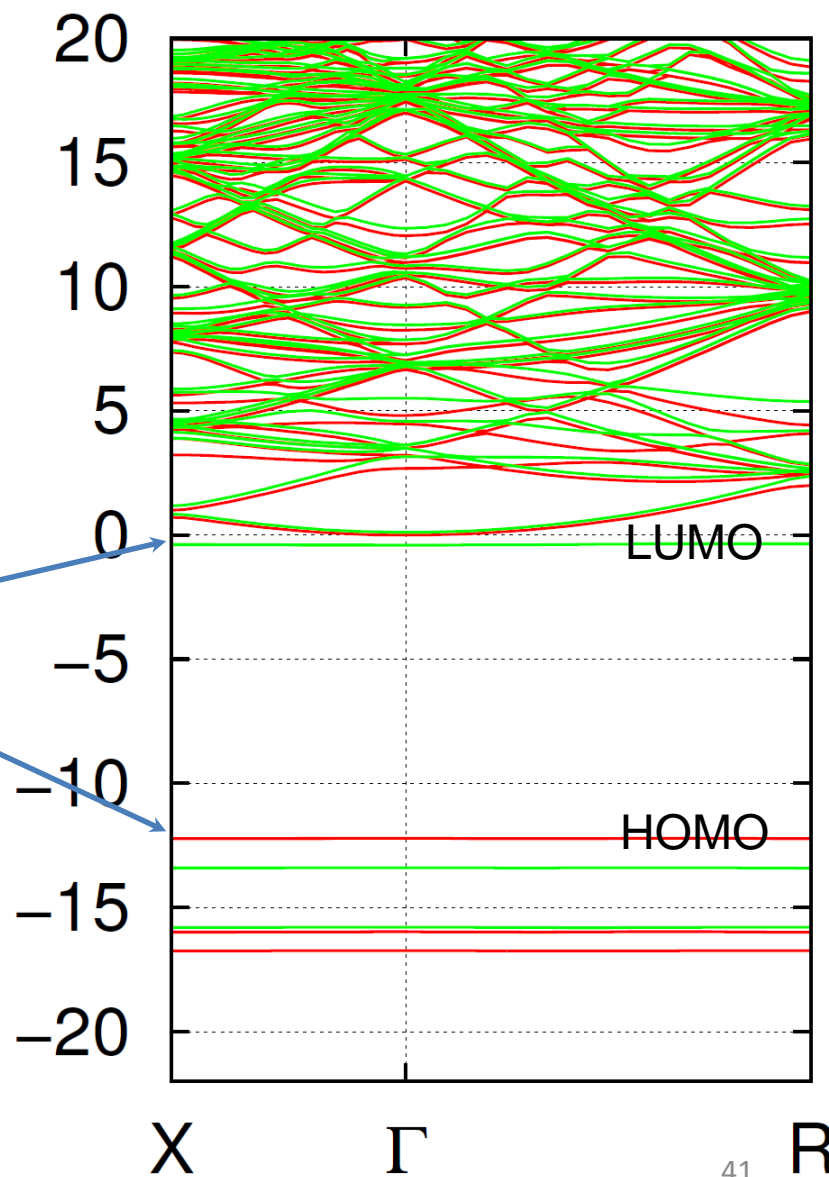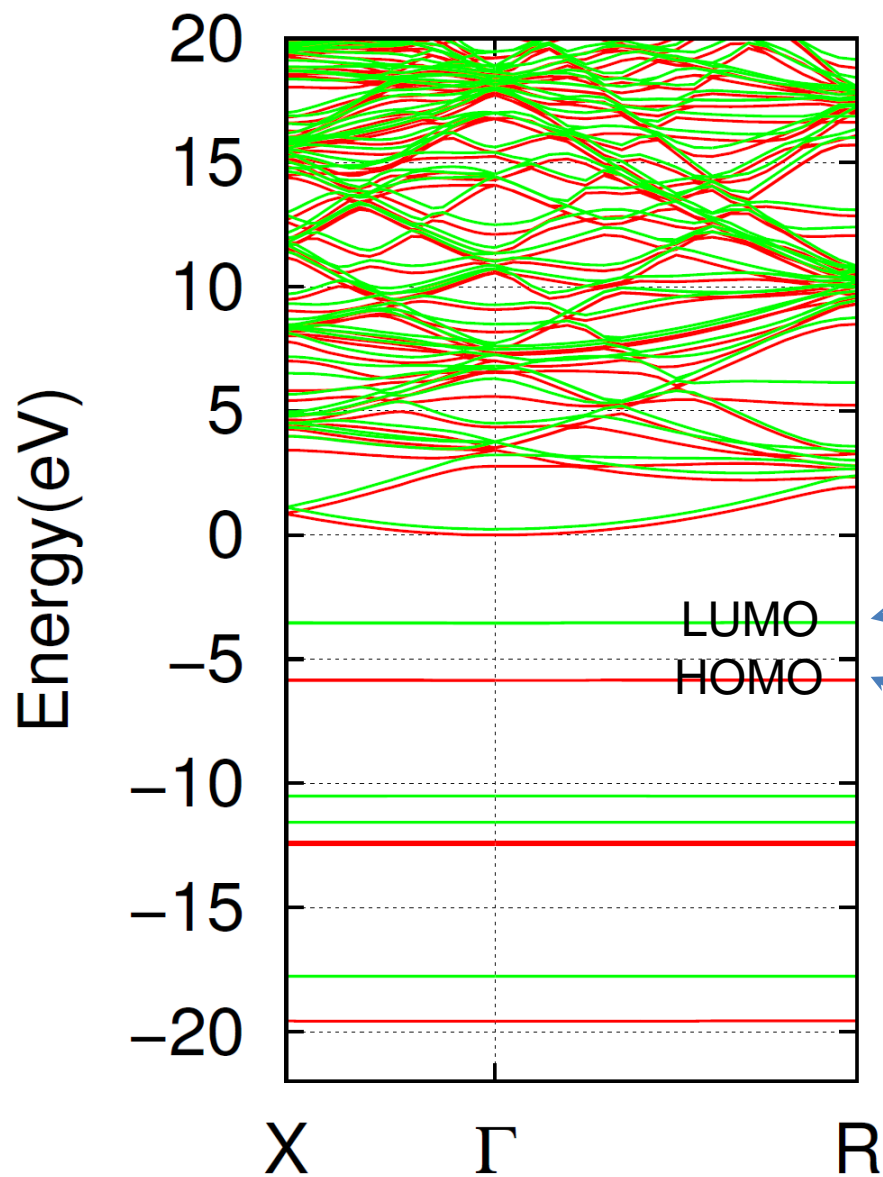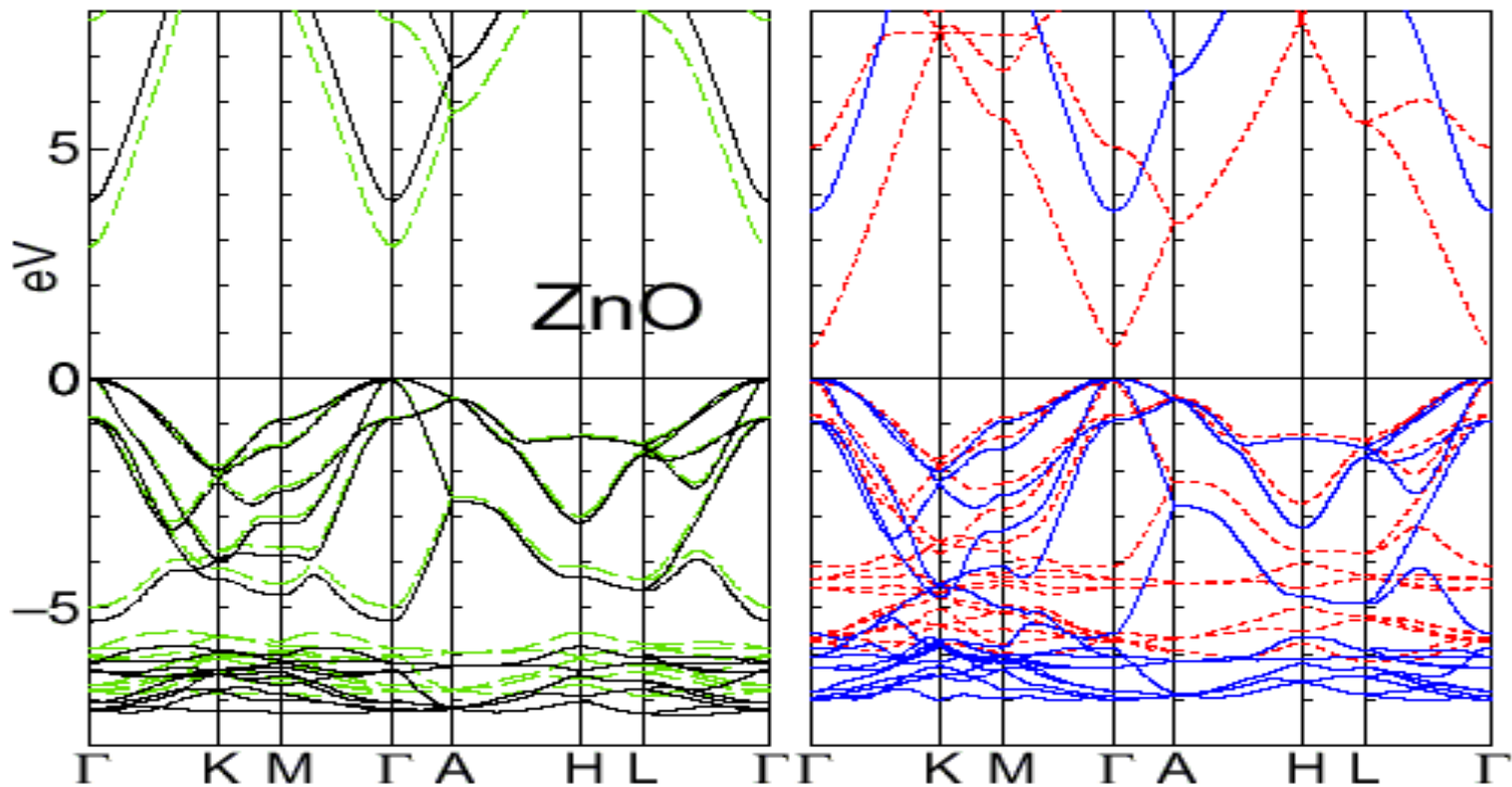
Black:QSGW   3.87eV
Red:LDA   0.71eV
Green:$G^{LDA}W^{LDA}$ (Z=1,Offdiagonal included) 3.00eV
Blue:e-only self-consistency   3.64eV
Experiment(+correction)   3.60eV

Kotani et al PRB76,165106(2007)

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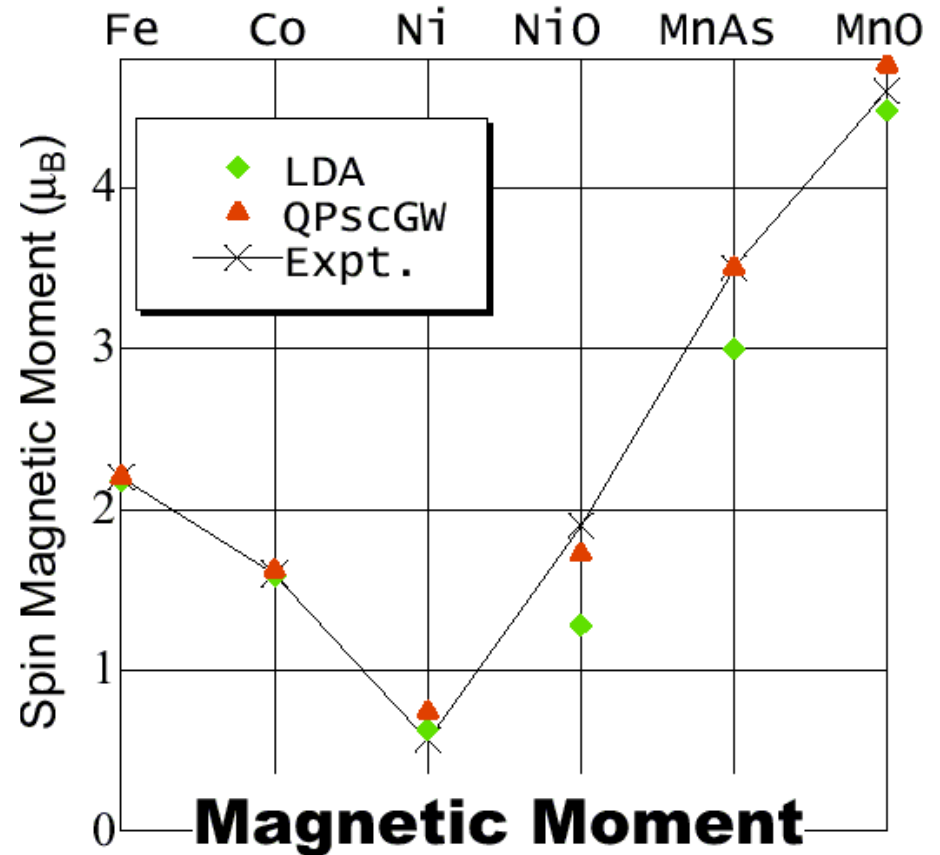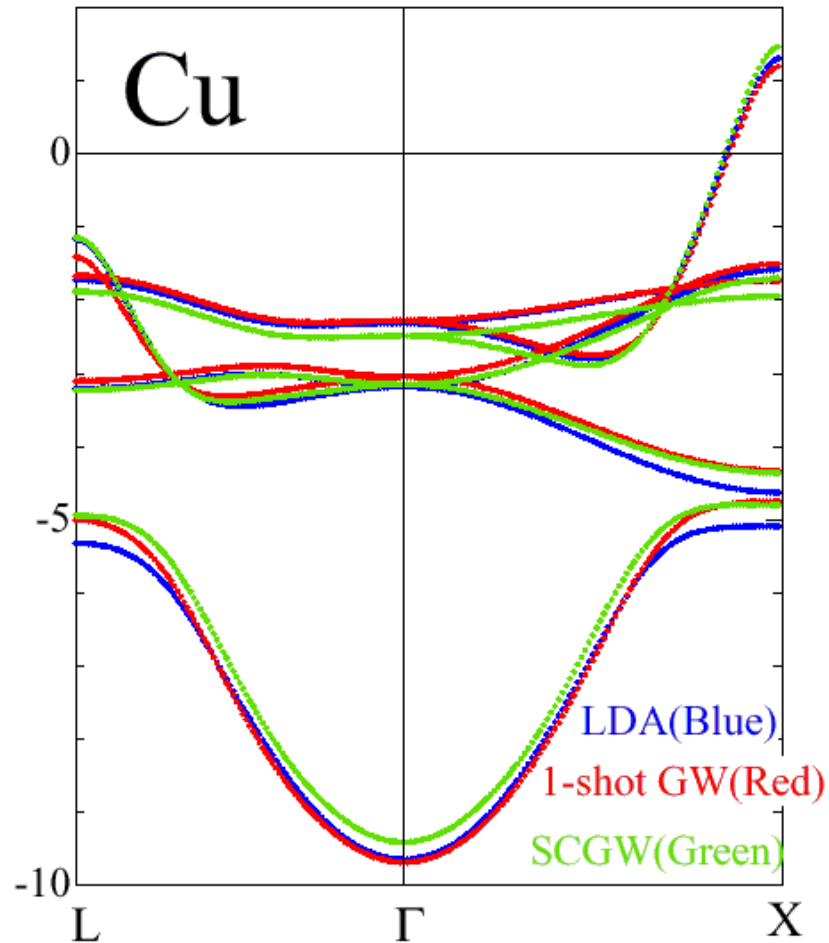
"No Pushing down 3d-band" in GW.

NiO
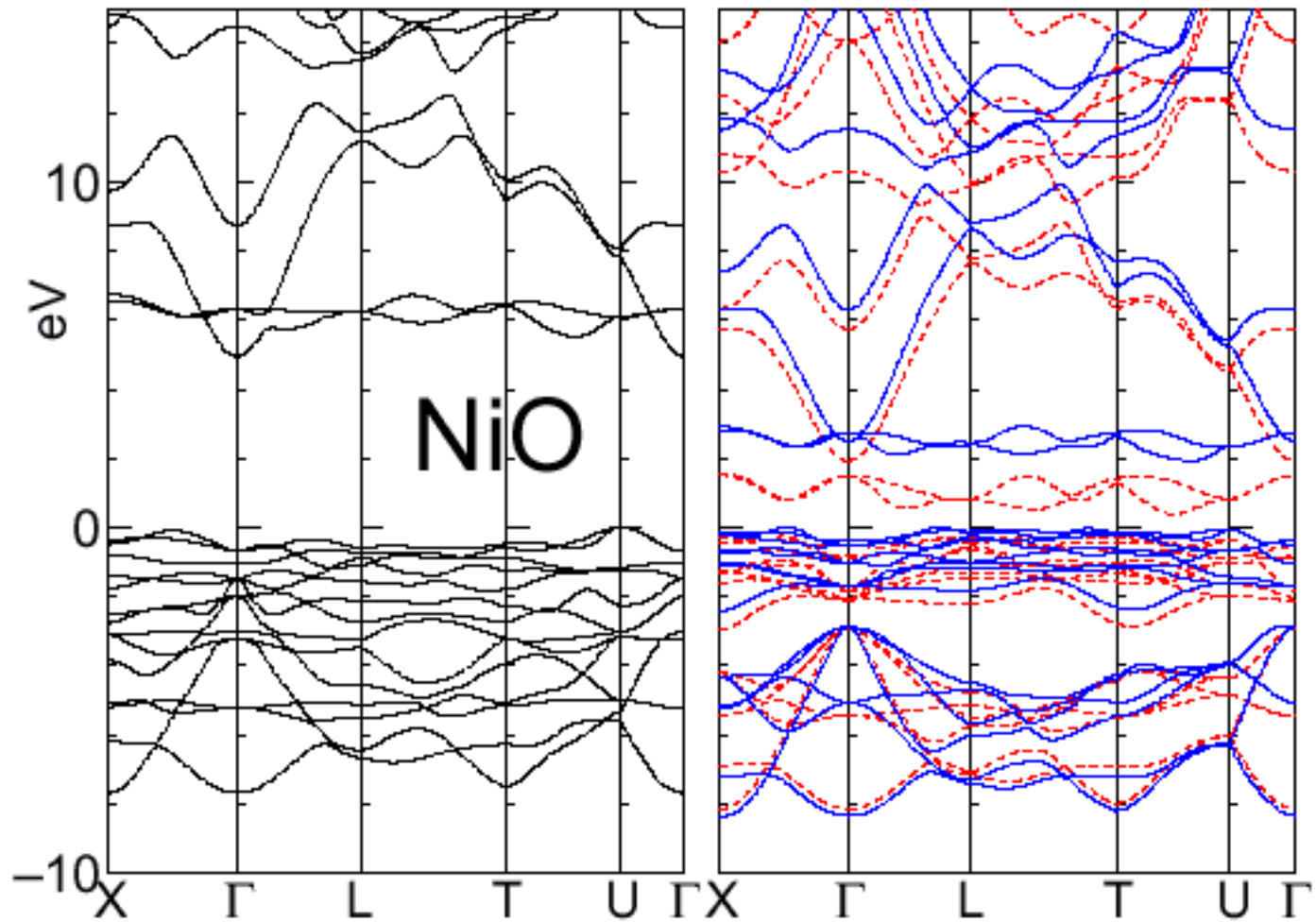
Black:QSGW Red:LDA Blue: e-only

Black:t2g Red:eg
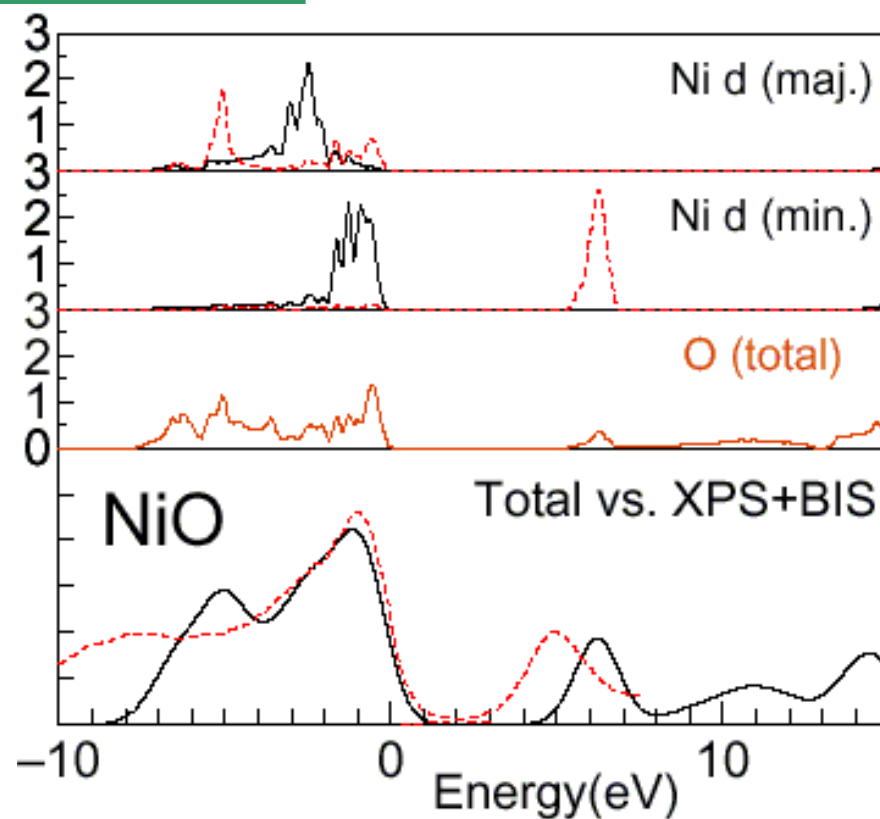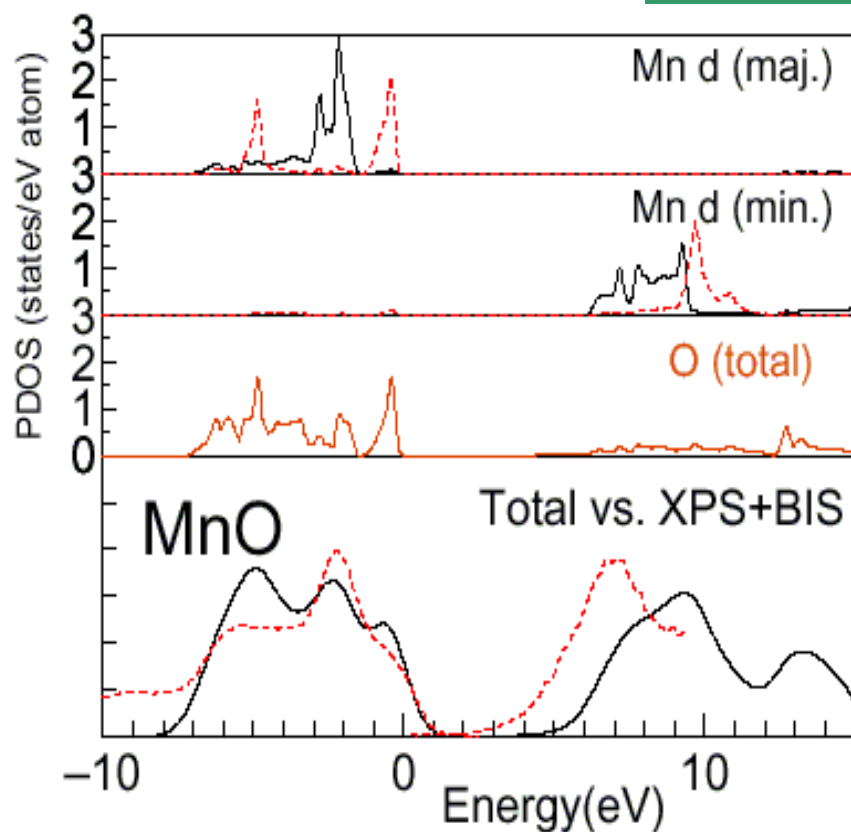
Red(bottom): expt
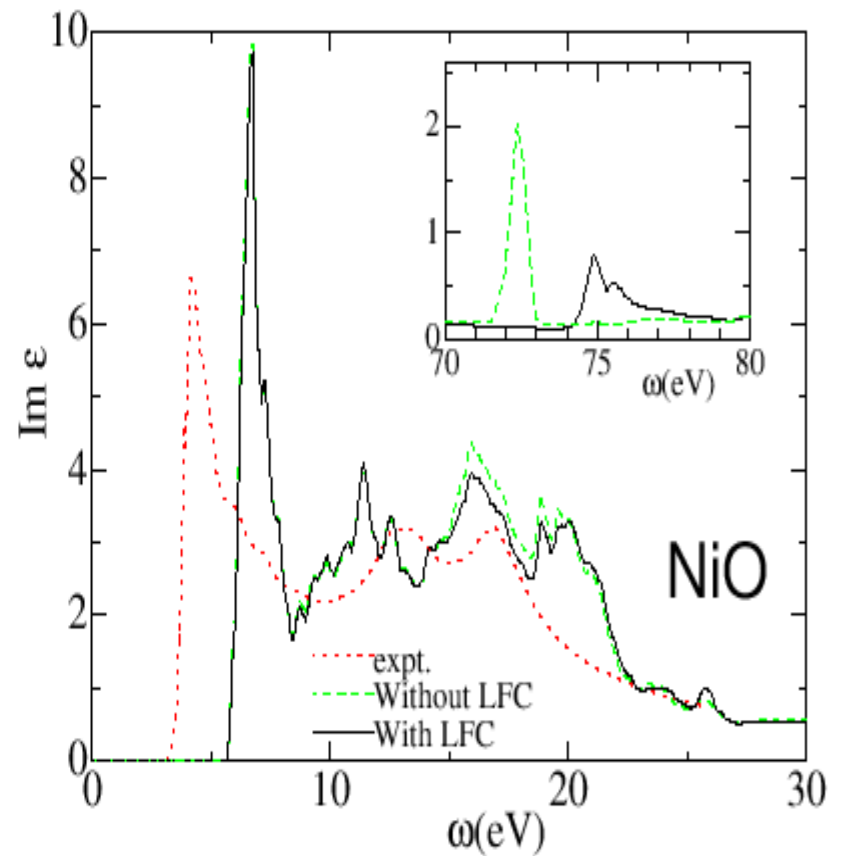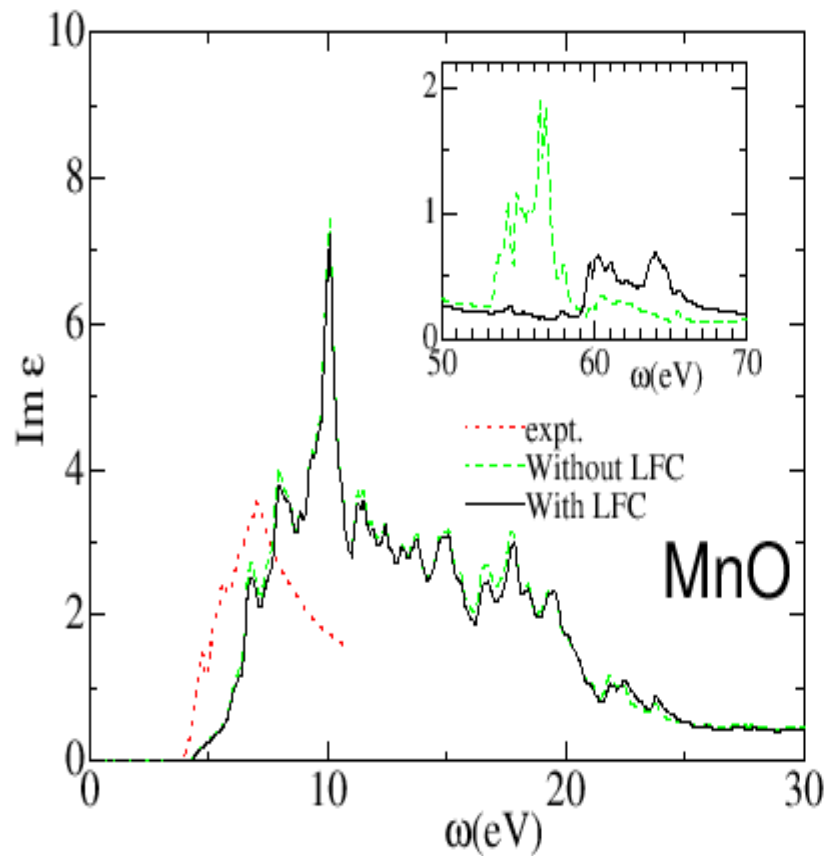
Black:Im eps with LFC   Red:expt

Spin wave dispersion based on QSGW
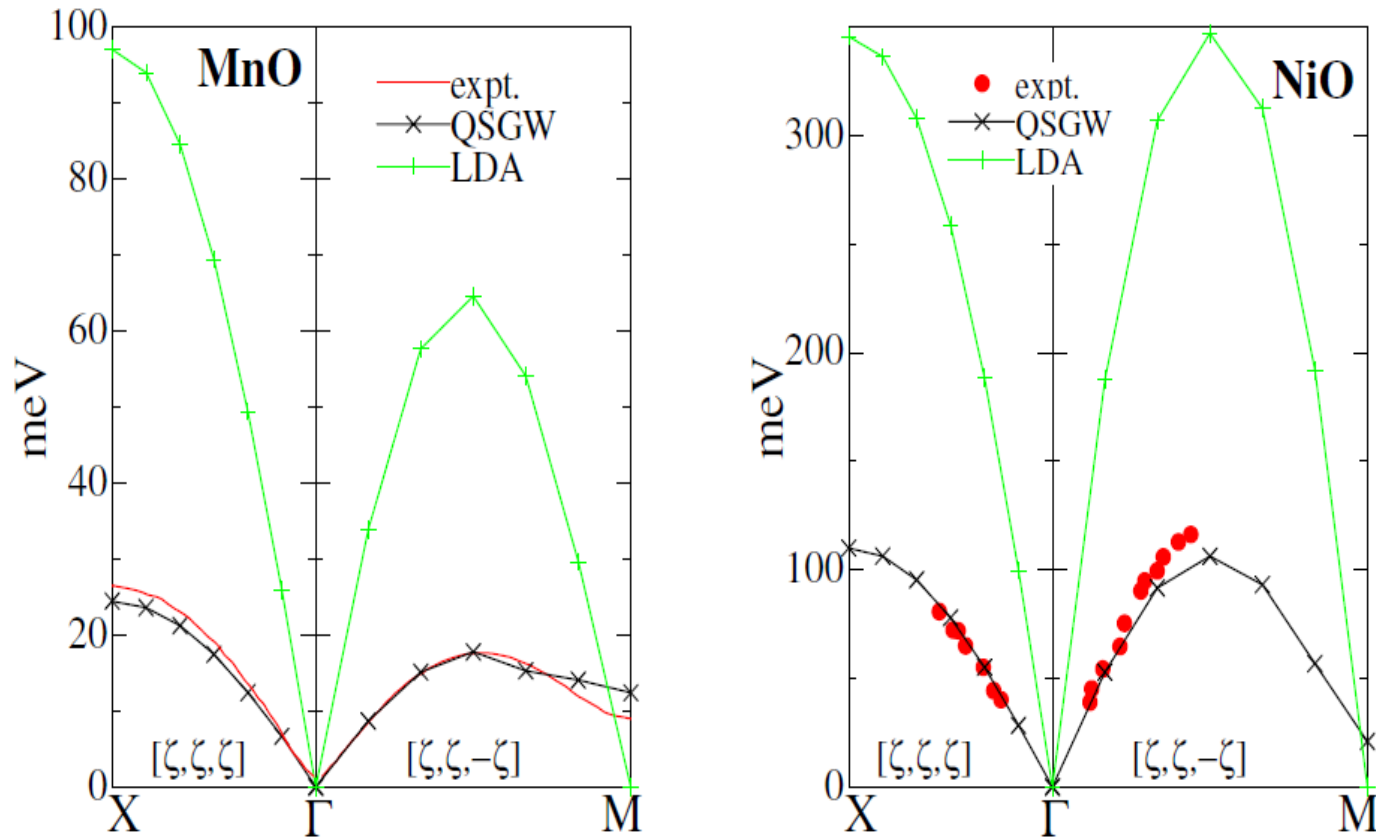
J.Phys.C20 (2008) 295214,
PRB83, 060404(R) (2011) for CaFe2As2 for spectrum of χ^{+-}.

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)

blue - expt.
red - broadened (0.46 eV) GW
linear method --> VBM = 3.24 eV
Kraut method --> VBM = 3.35 eV

Expr.

QSGW

blue - expt.
red - broadened (0.46 eV) GGA (ours)
linear method --> VBM = 3.26 eV
Kraut method --> VBM = ~3.5 eV

GGA

binding energy relative to Fermi level (eV)
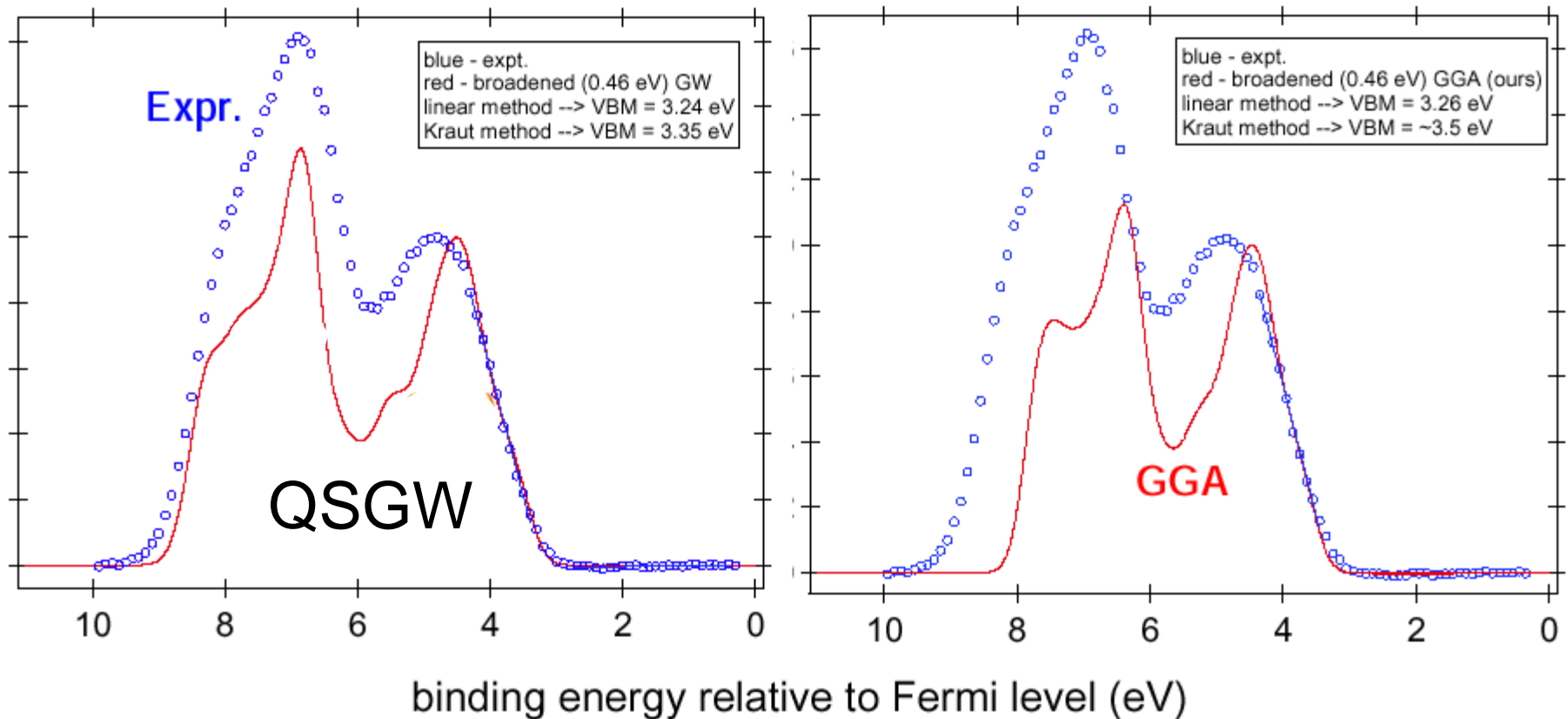
S. A. Chambers et al, Surface Sci 554,81-89 (2004)

Electron configuration

lift of degeneracy of 3d orbitals due to crystal field

[3d]

Cu atom

e_g

t_{2g}

cubic
(regular
octahedron)

x^2-y^2

$3z^2$-r^2

ΔE_{eg}

xy

yz, zx

tetragonal
(elongated
octahedron)
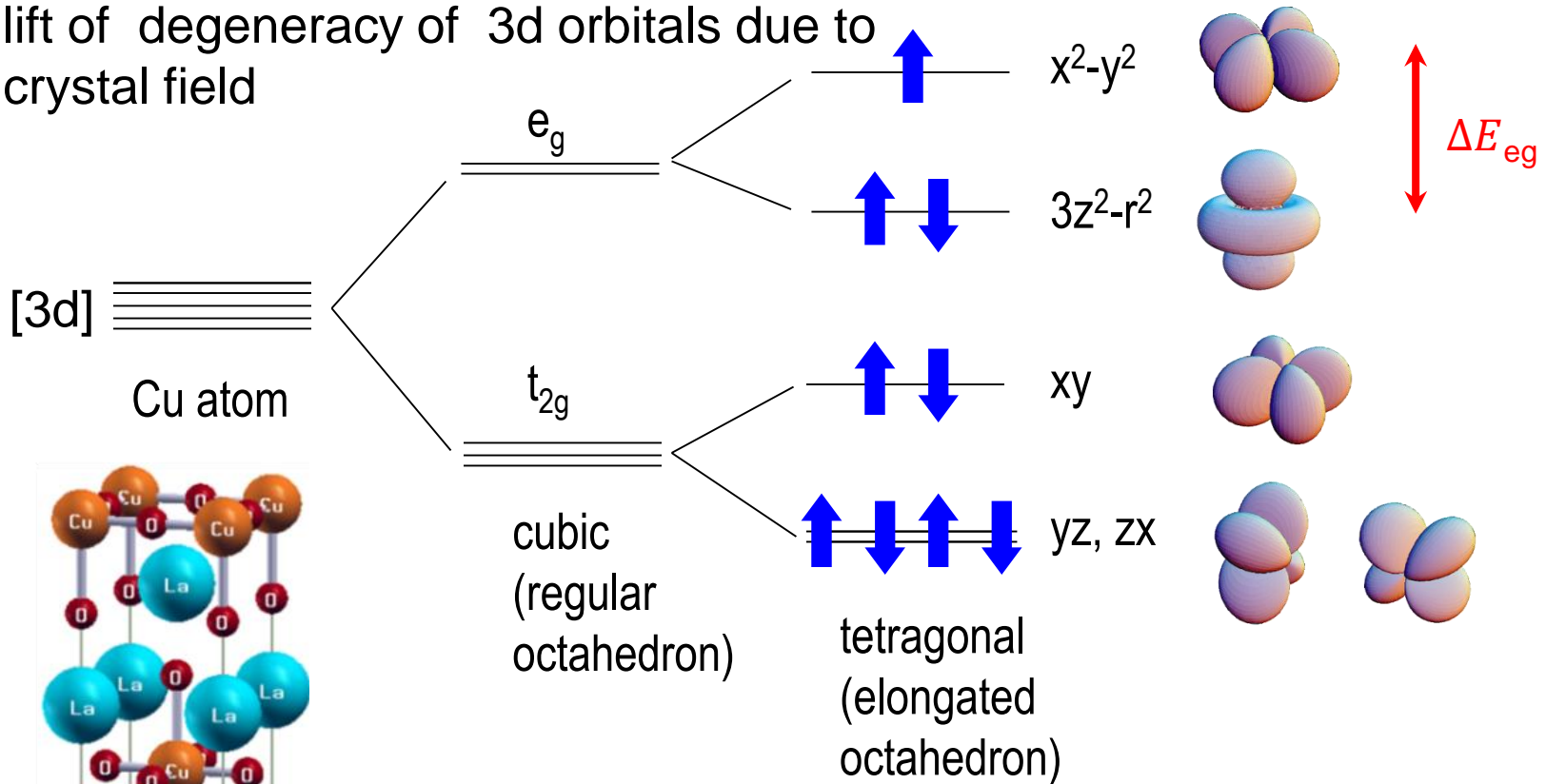
Around Ef, we have two eg bands.

Band structure: Two eg orbitals.
Band width and ΔE_{eg}

FIG. 1:
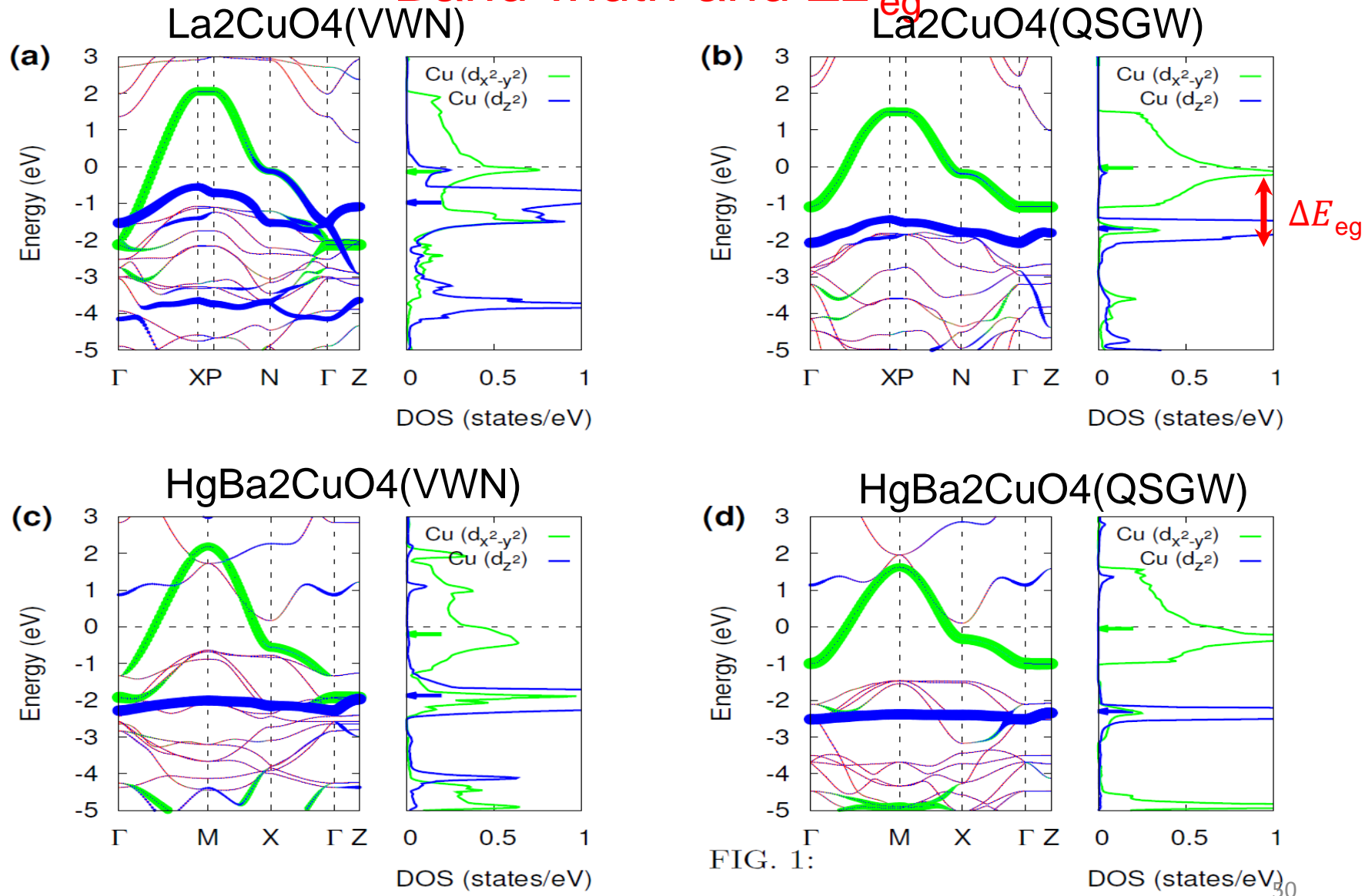
Wannier function method. Extract tight-binding parameters

La2CuO4(VWN)
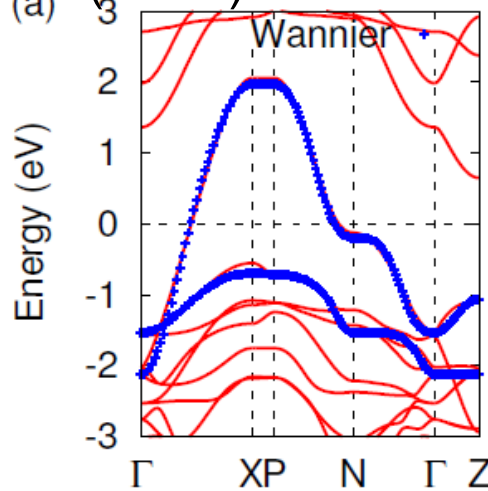
La2CuO4(QSGW)
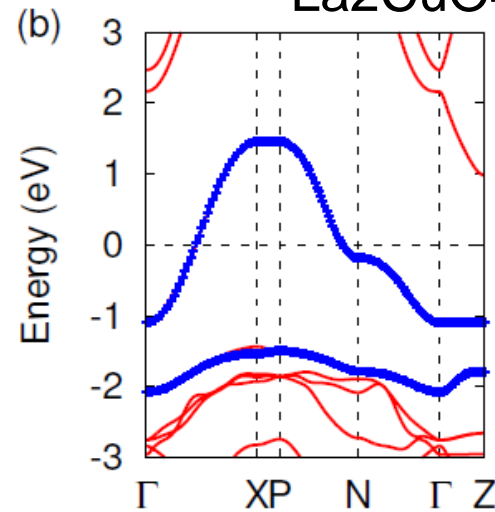
HgBa2CuO4(VWN)
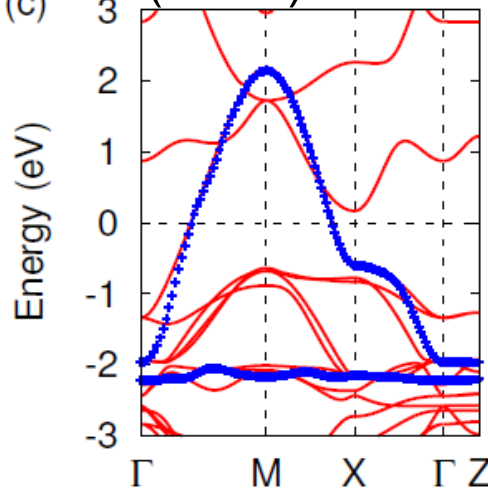
HgBa2CuO4(QSGW)
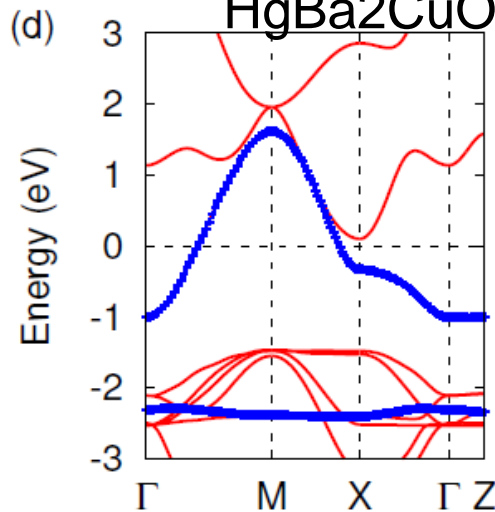
Miyake's Maxloc Wannier code is re-implemented(TK and H.Kino）.

La$_2$CuO$_4$: Effective interaction $U(\omega)$ for d_{z^2} and $d_{x^2-y^2}$

Our results (VWN)
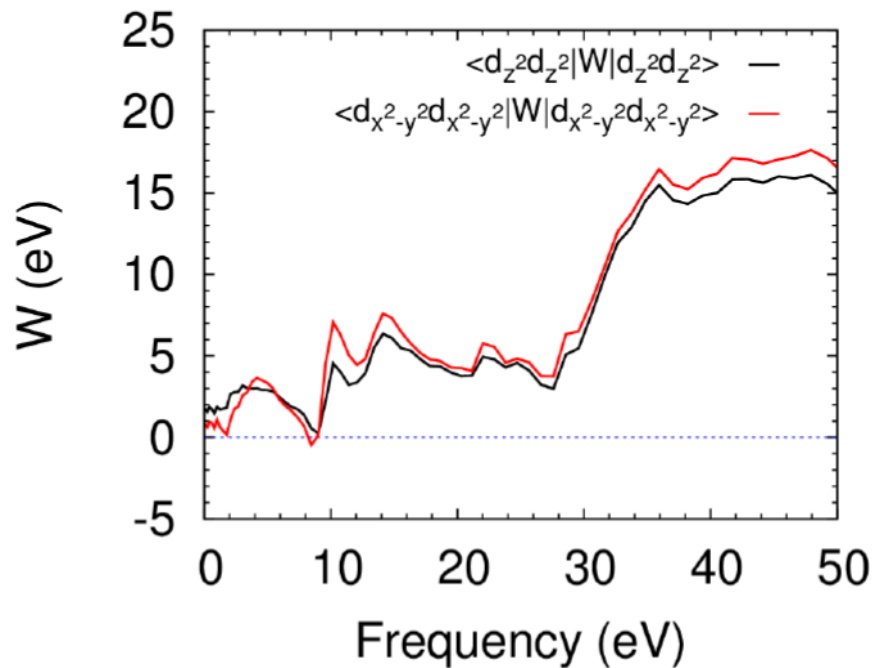
Our results (QSGW)

At $\omega = 0$ eV → $W(d_{z^2}) = 1.71$ eV
$W(d_{x^2-y^2}) = 0.77$ eV
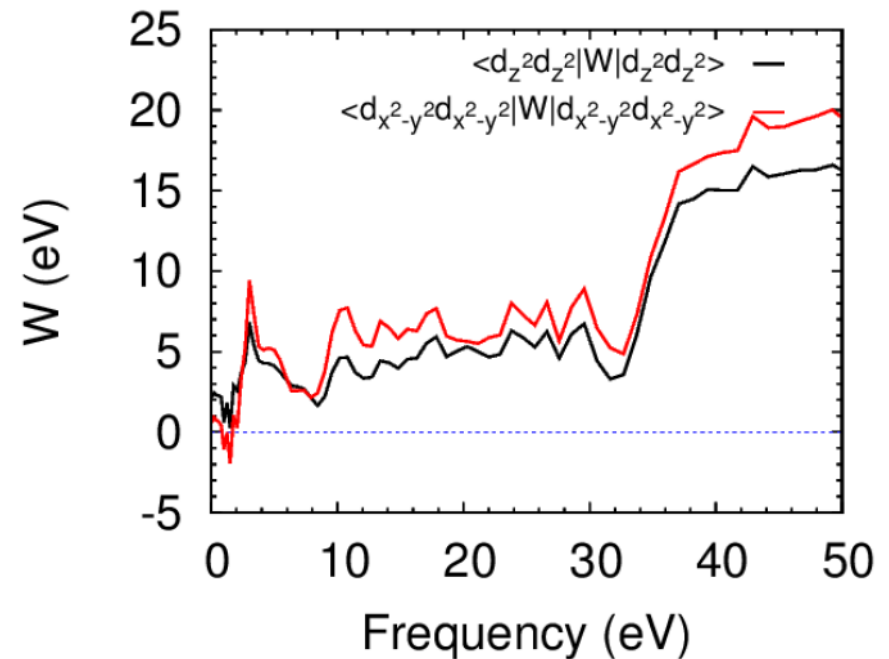
At $\omega = 0$ eV → $W(d_{z^2}) = 2.24$ eV
$W(d_{x^2-y^2}) = 0.69$ eV

* There is an anisotropy in W between $d_{x^2-y^2}$ and d_{z^2}

Impact ionization rate(auger process)
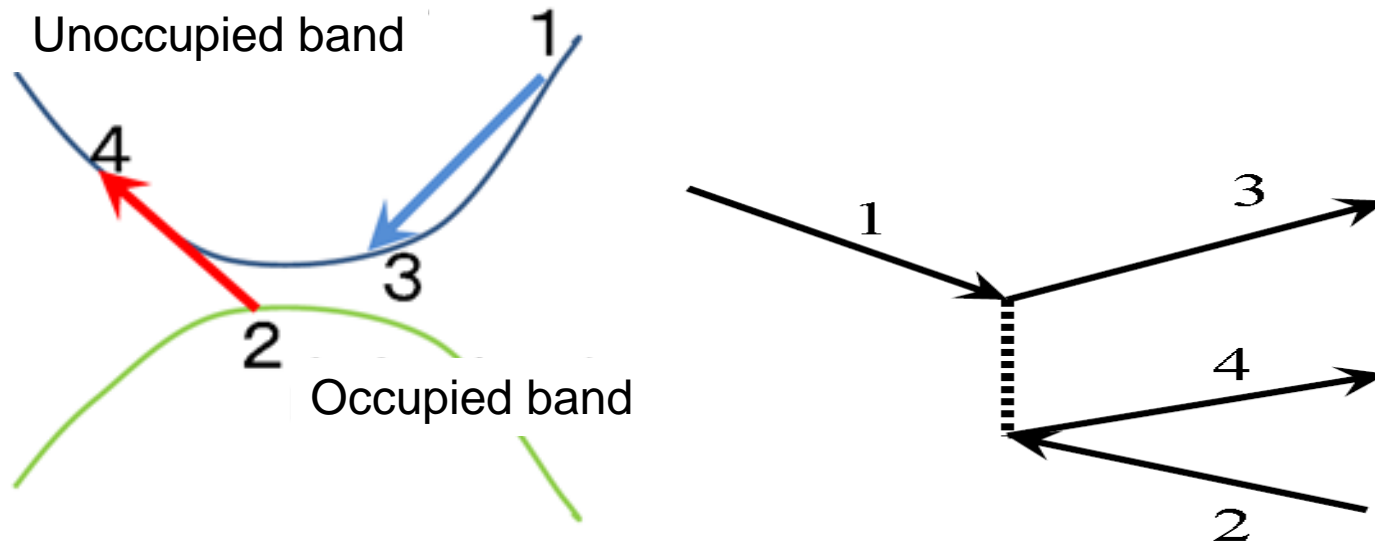
Fermi's Golden rult → transition rate. Sum up for all final states. Matrix element of transition is

＜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)
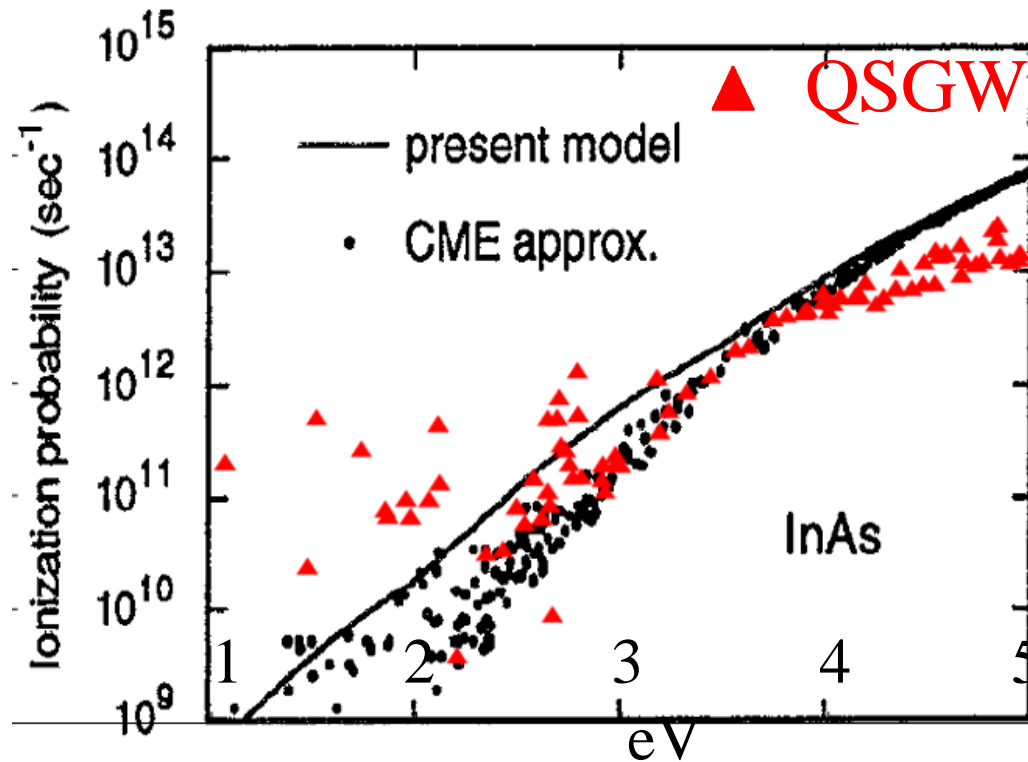
direct gap 0.38eV
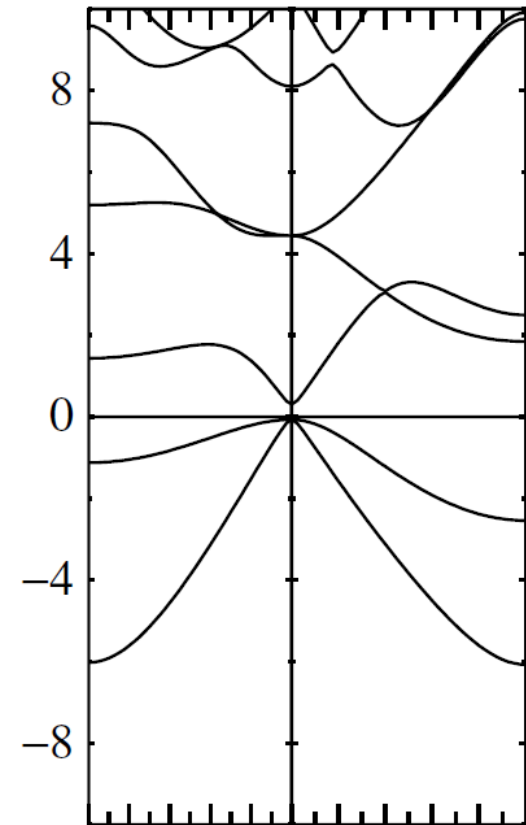
Present model: Sano and Yoshii JAP77 2020 (1995)

YH3(fcc structure 6x6x6)
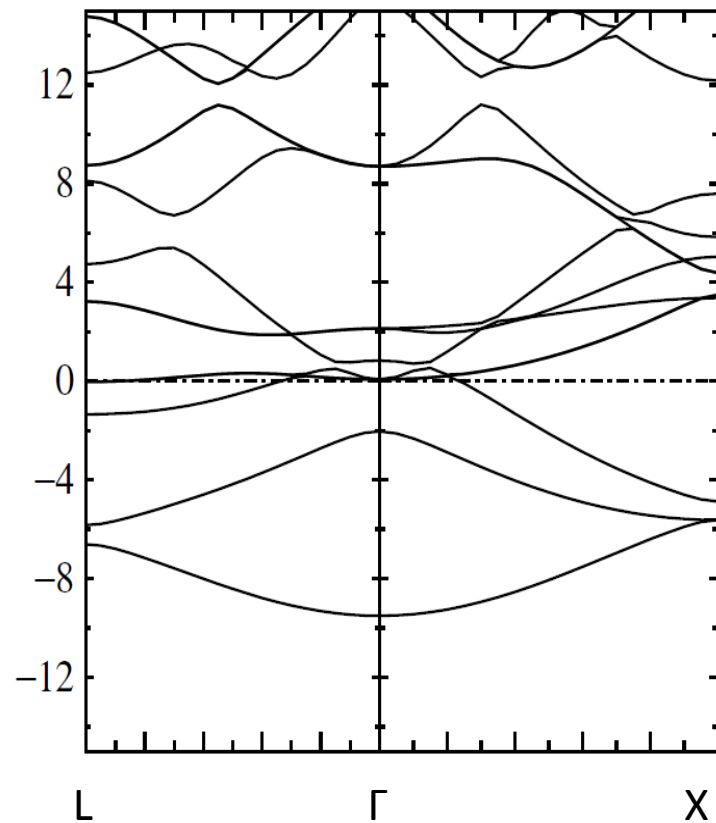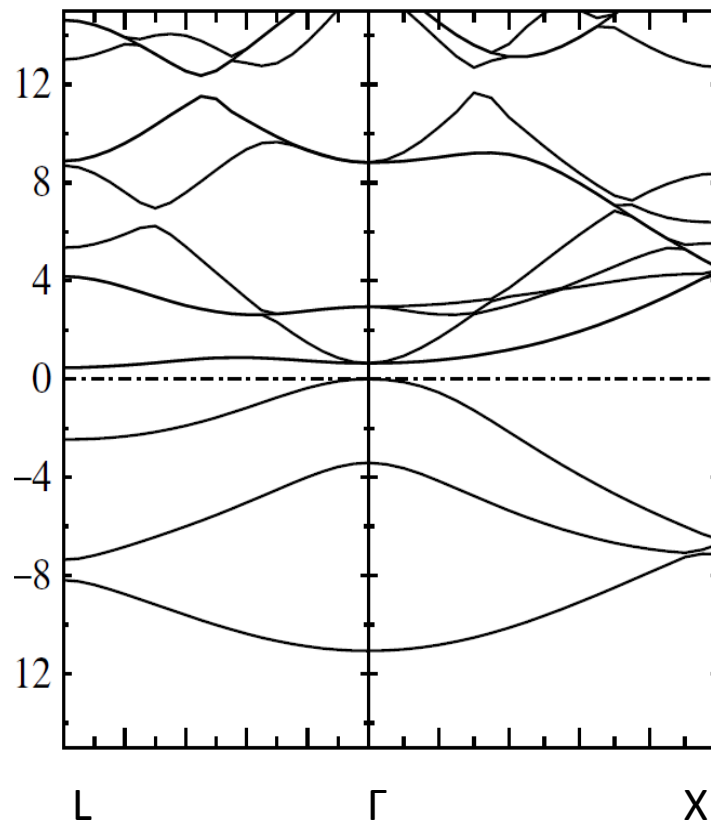
CuGaSe2 (eight atoms in cell, 2x2x2. ~3hours per iteration by single core)

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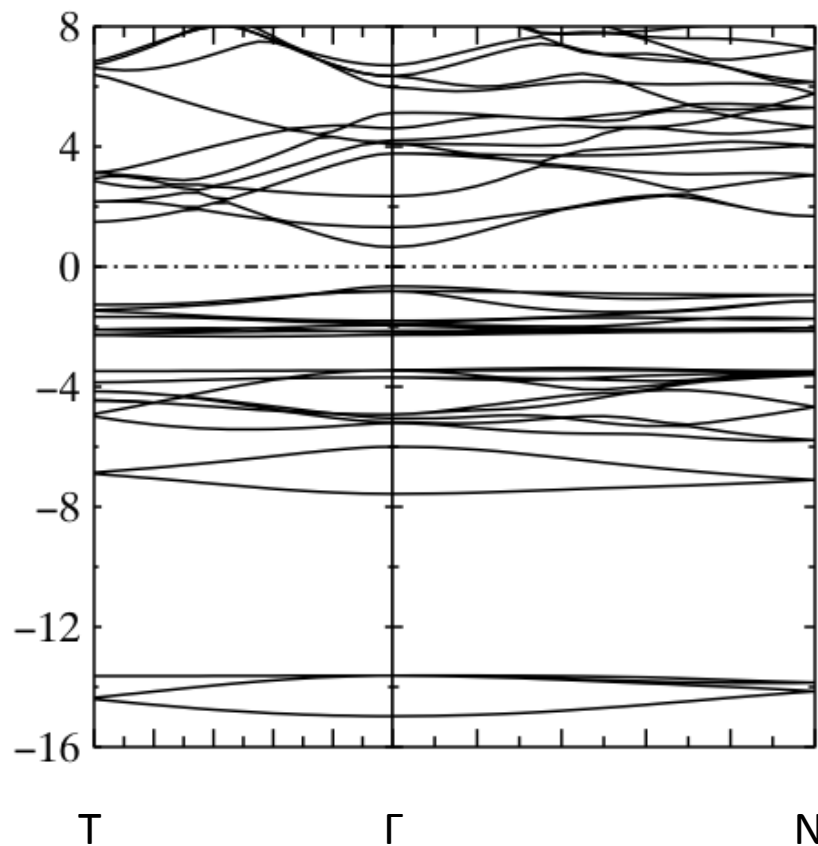
QSGW
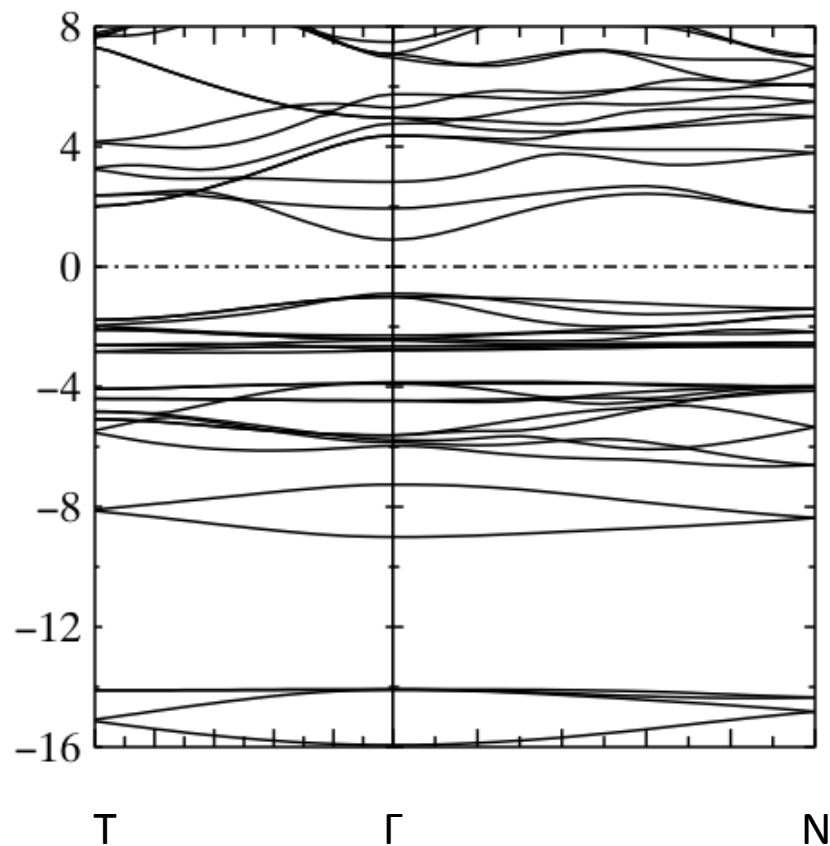
Band gap GGA:0.4eV,   GW(1shot noZ) 1.37 eV,
QSGW(1.79eV)   Exper. 1.63, 1.67, 1.73eV

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)
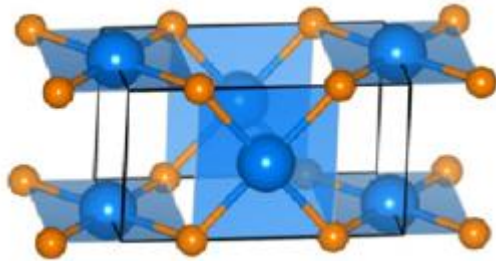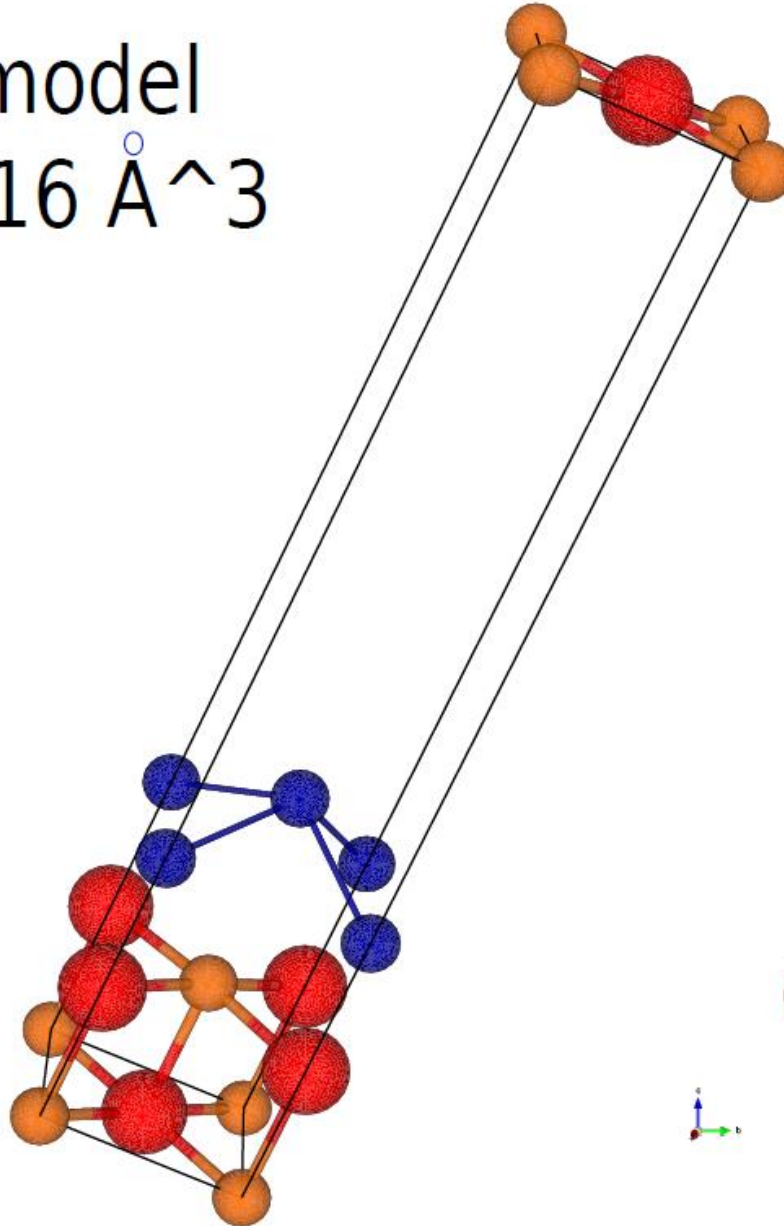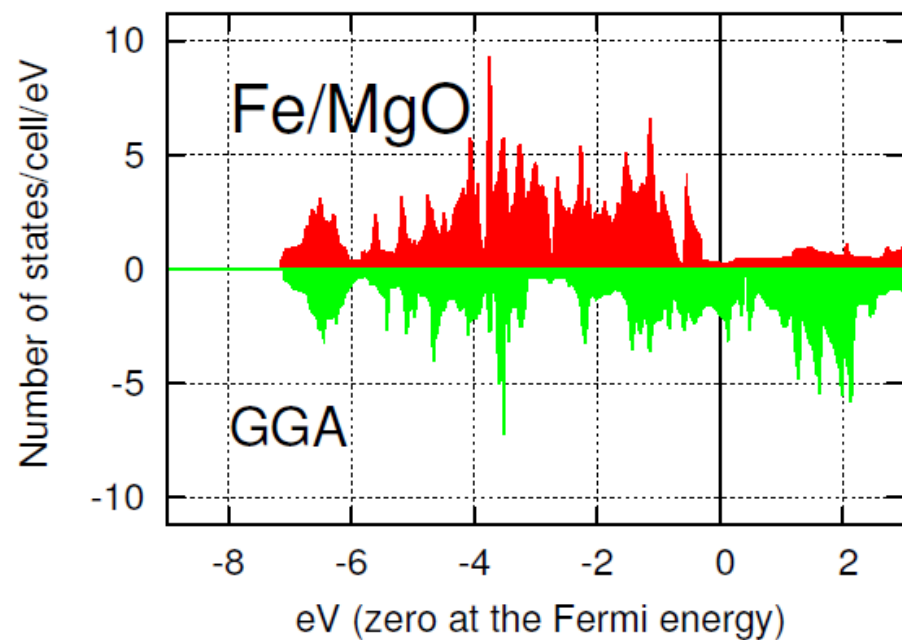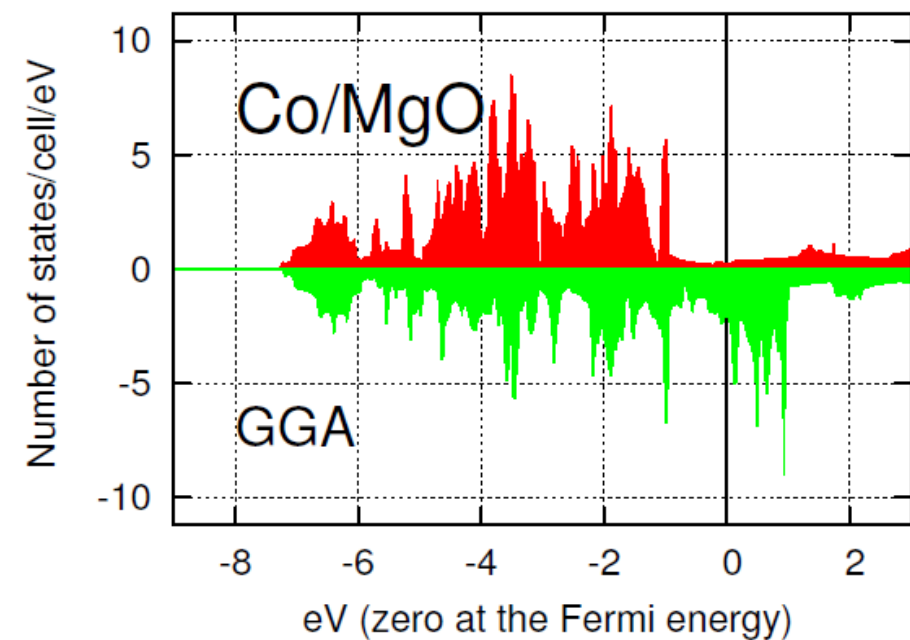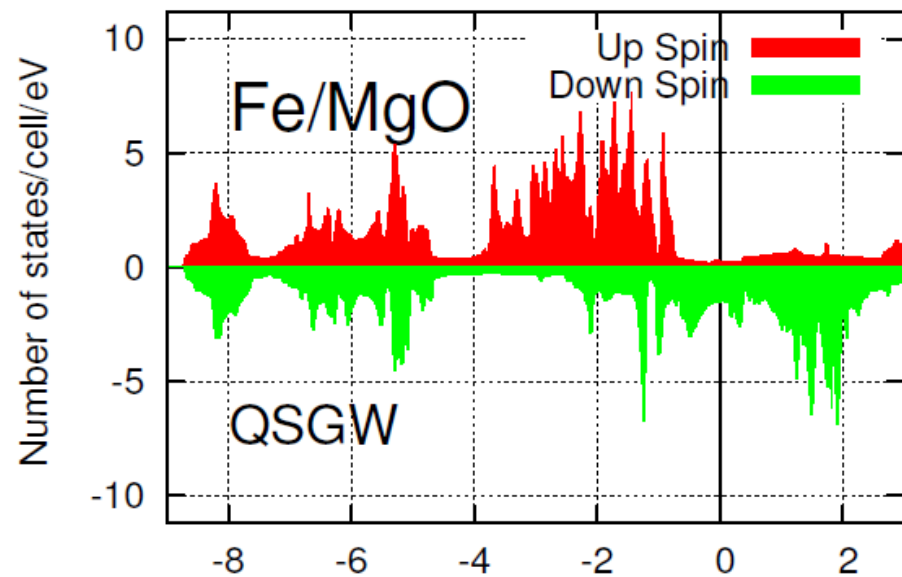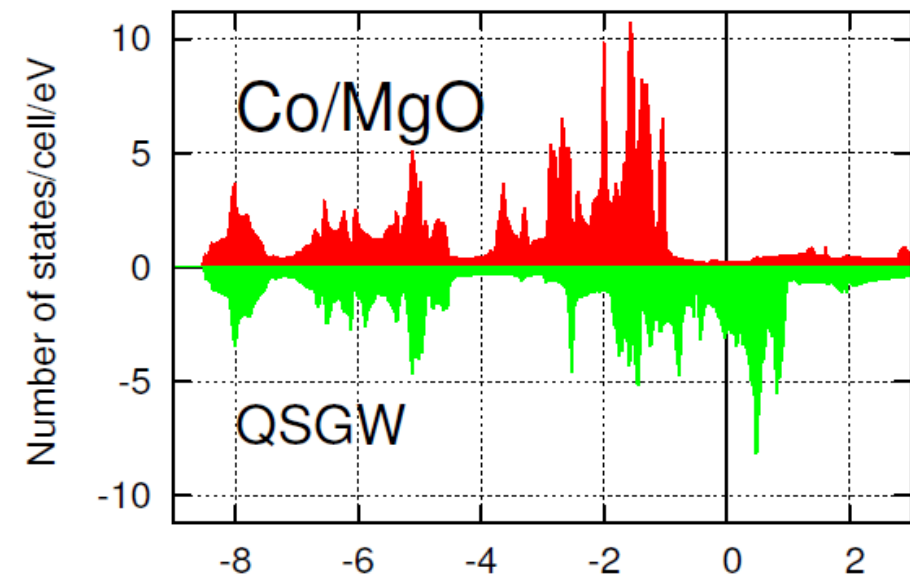

GGA
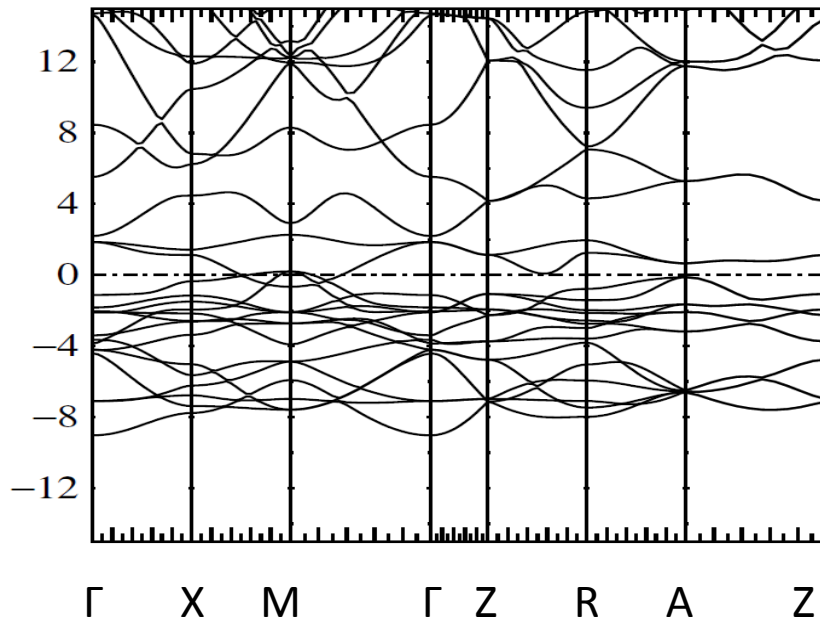
QSGW
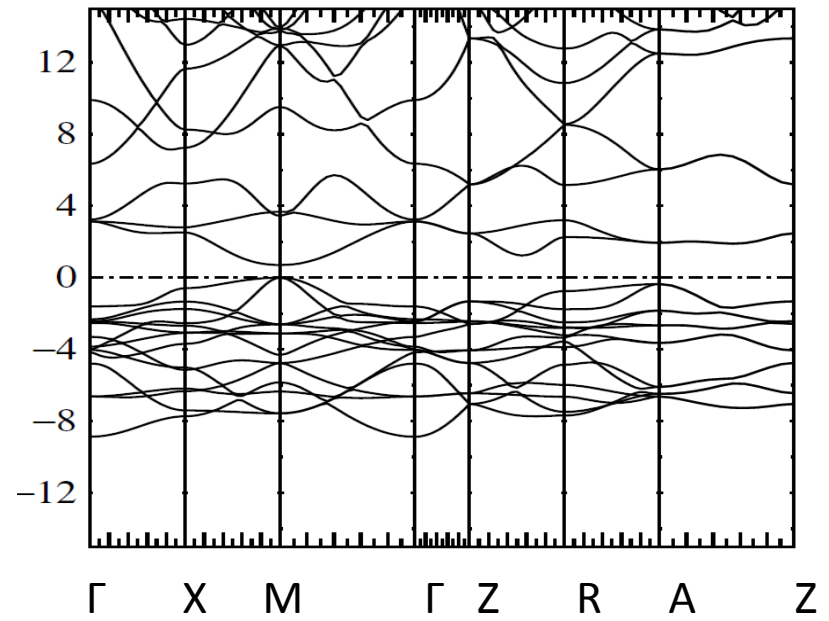
Band gap about 0.7 eV
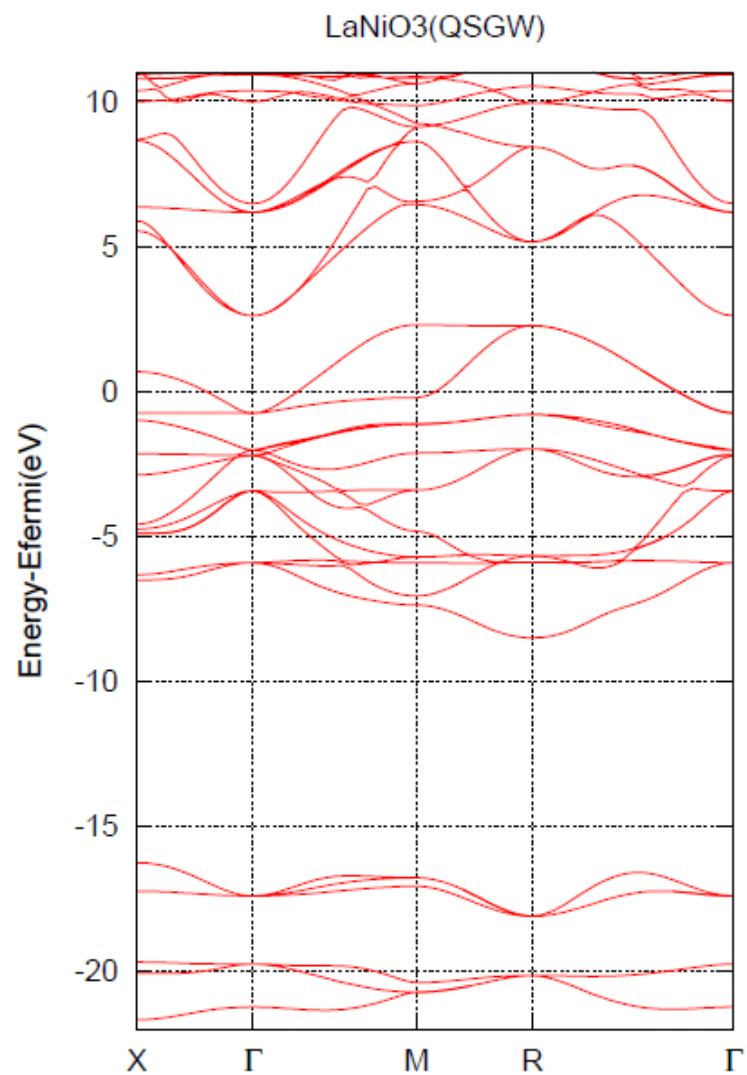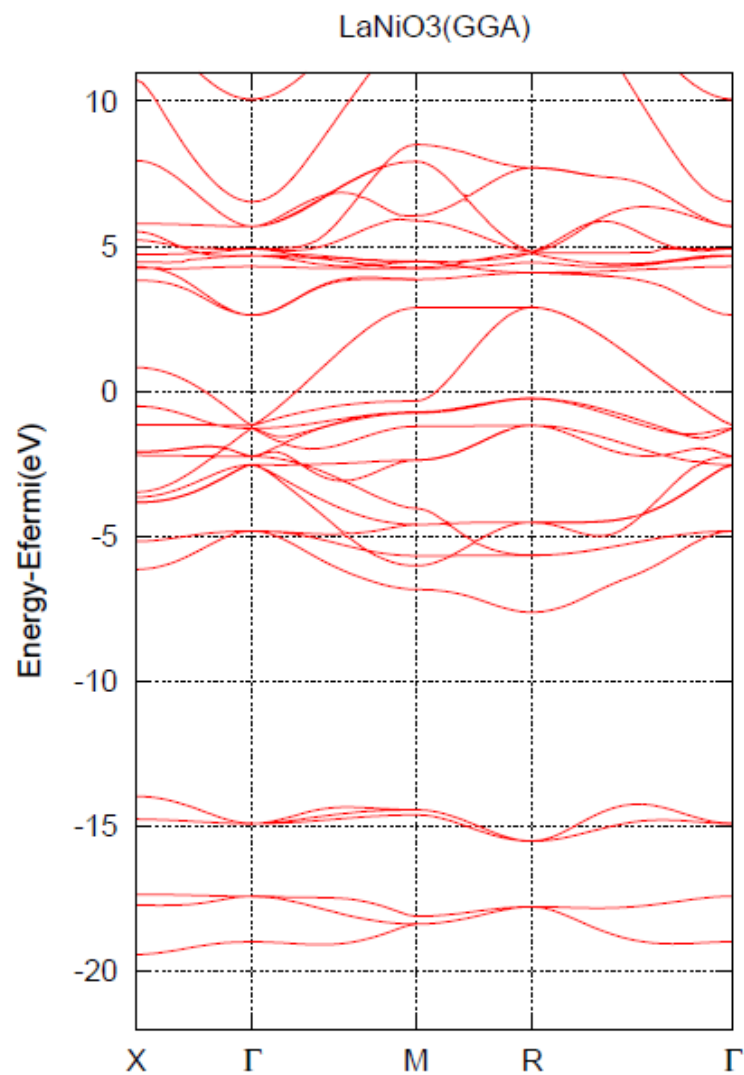
LaNiO3

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

Co/MgO model
cell 3x3x16 Å^3
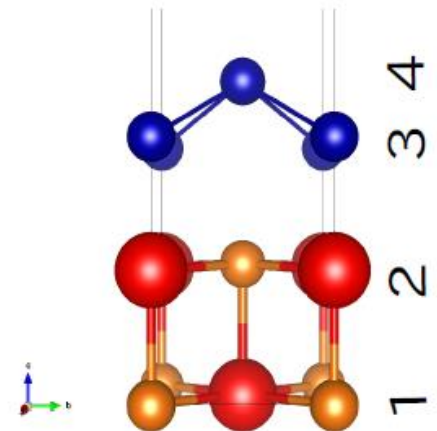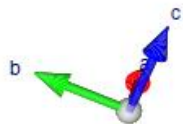
summary

- 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)