CMD23 ecalj course

Takao kotani, tottori-u

- PMT method
  PMT=LMTO+LAPW
- QSGW method
  a self-consistent GW

- ecalj package.
  read input and output.

  crystal structure
  → Band, DOS, PDOS plot

ecalj course menu

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

- 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 9:00~11:00 (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

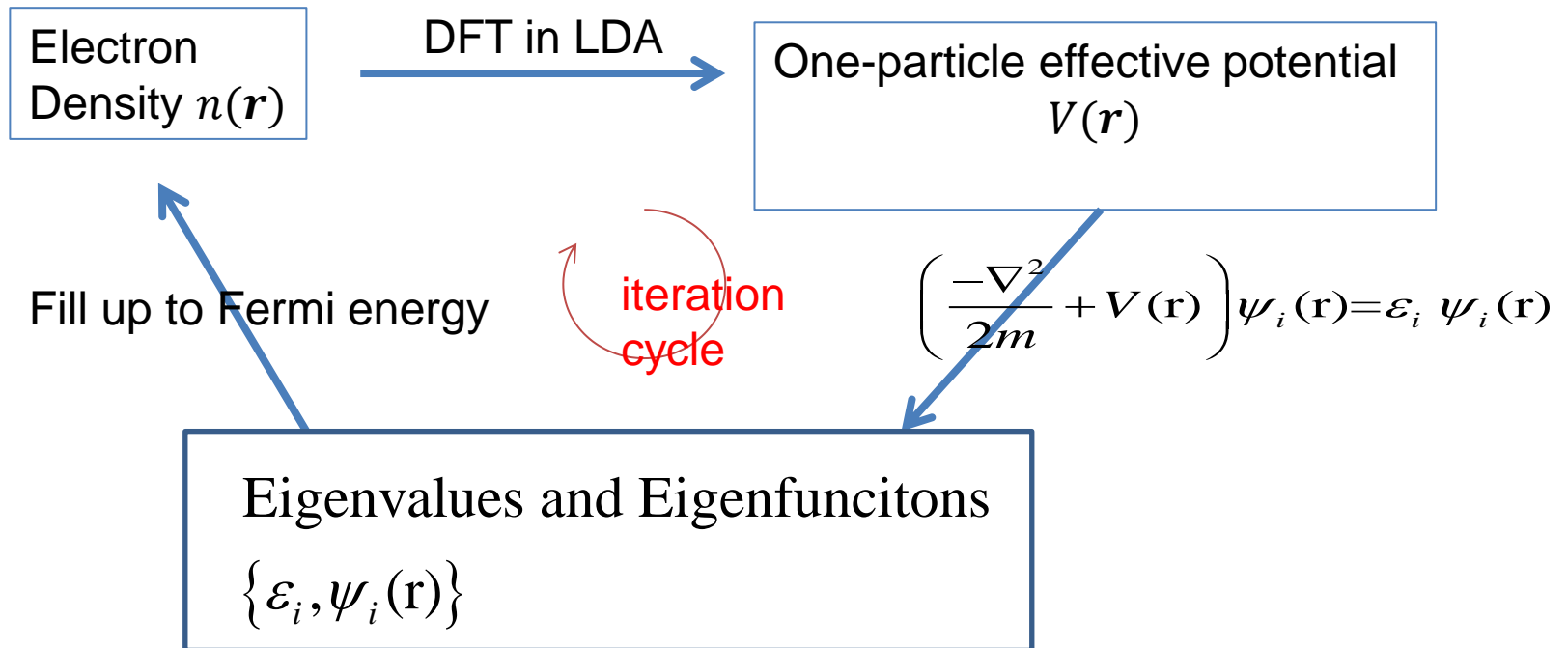$$\boxed{\textbf{PMT} = A\underline{P}W + \underline{\textbf{MT}}O}$$

Muffin-tin

Takao Kotani (tottori-u)

Key point:

1. Iteration cycle.

2. eigenfunctions are represented by APW(augmented plane wave) and MTO(muffin-tin orbital)

Independent particle picture and total energy

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

Electron Density $n(\boldsymbol{r})$

DFT in LDA →

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

Fill up to Fermi energy

iteration cycle

$$\left(\frac{-\nabla^2}{2m} + V(\mathbf{r})\right)\psi_i(\mathbf{r}) = \varepsilon_i\,\psi_i(\mathbf{r})$$

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

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:

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

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

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

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
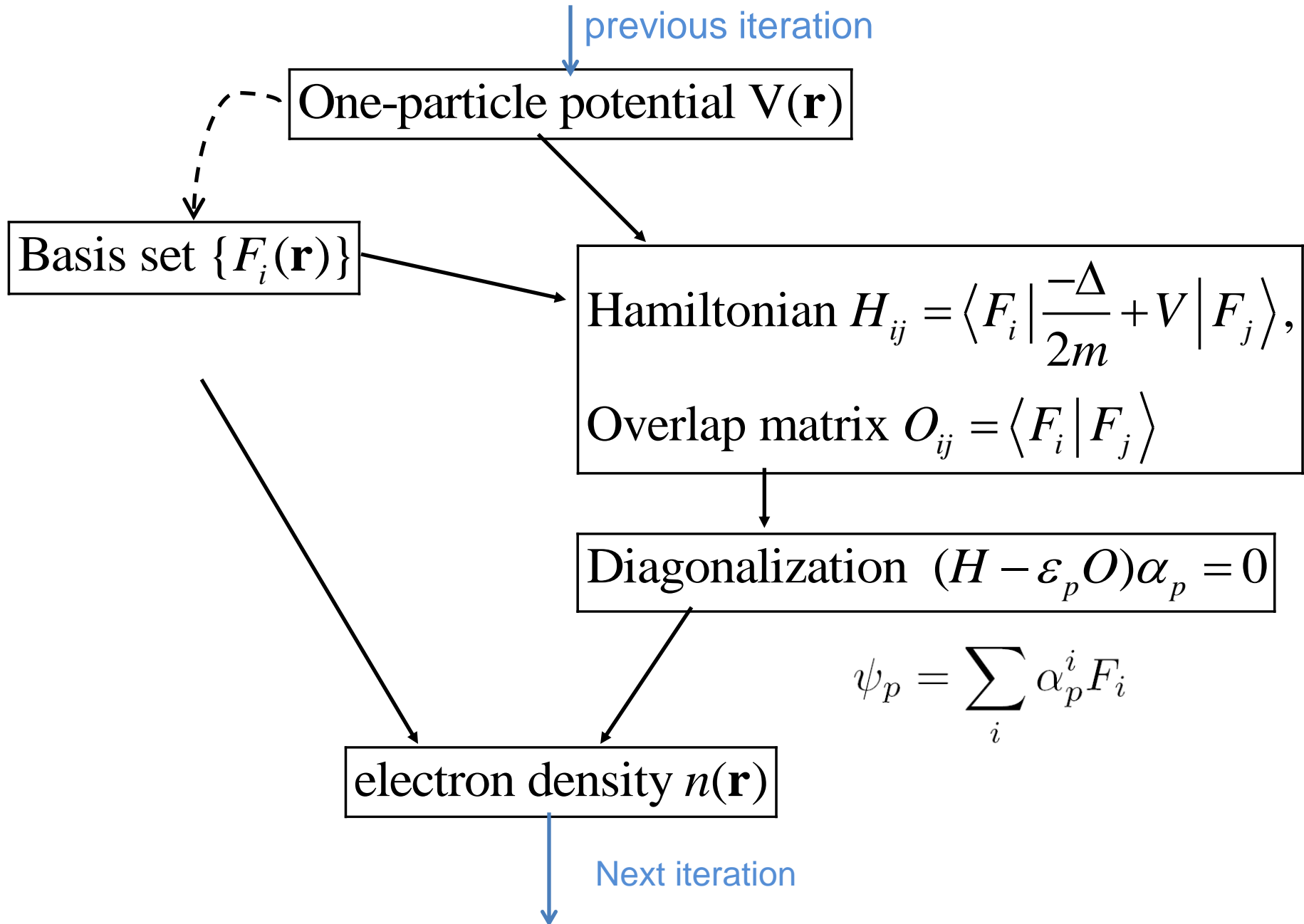
How to choose the good basis?

- 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**

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

APW

Envelope function = PlaneWave(PW)

PW in MT

MT region   MT region
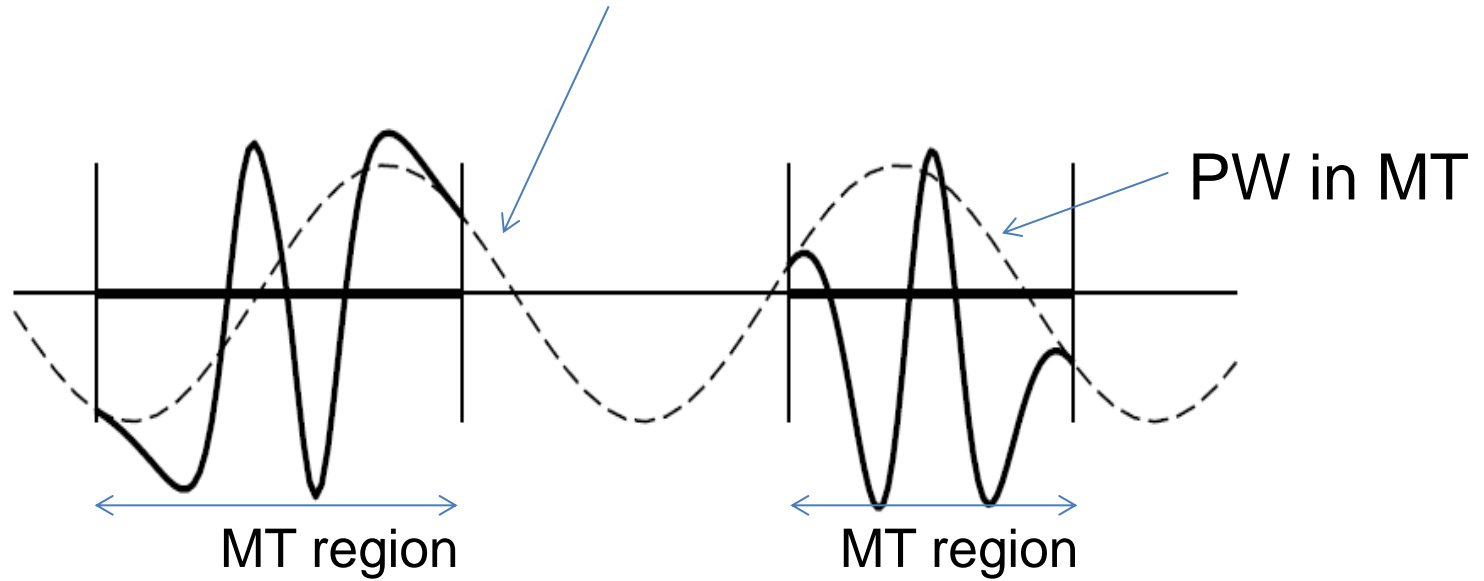
3-components
PW + Atomic-like part − Counter part:
PW within MT

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.
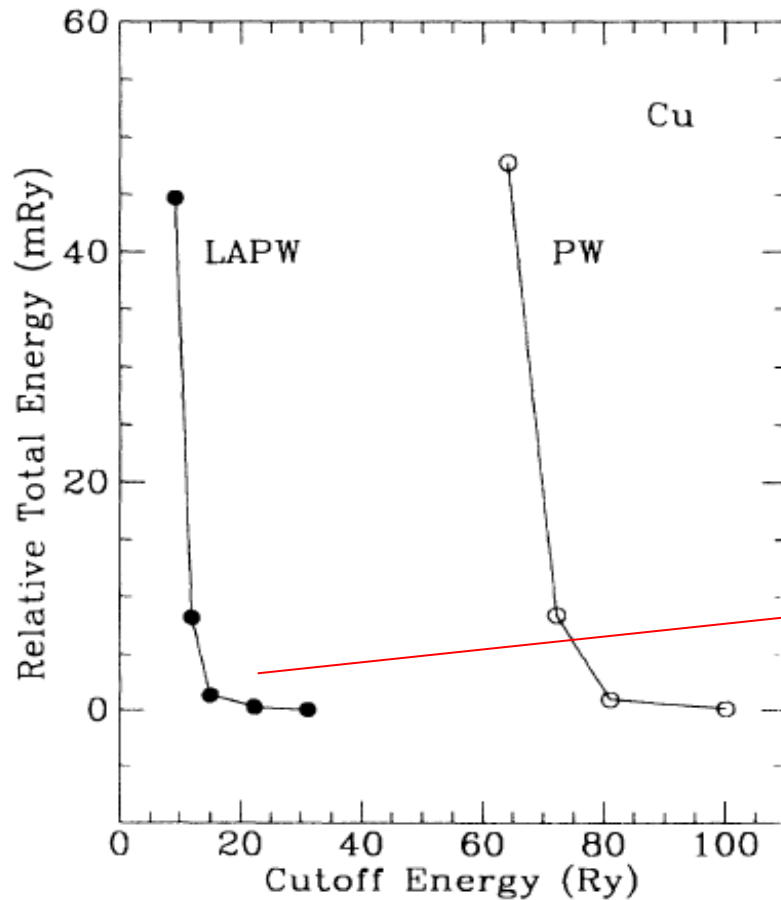
fcc Cu

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,

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

MT region

MT region

Smooth Hakel function
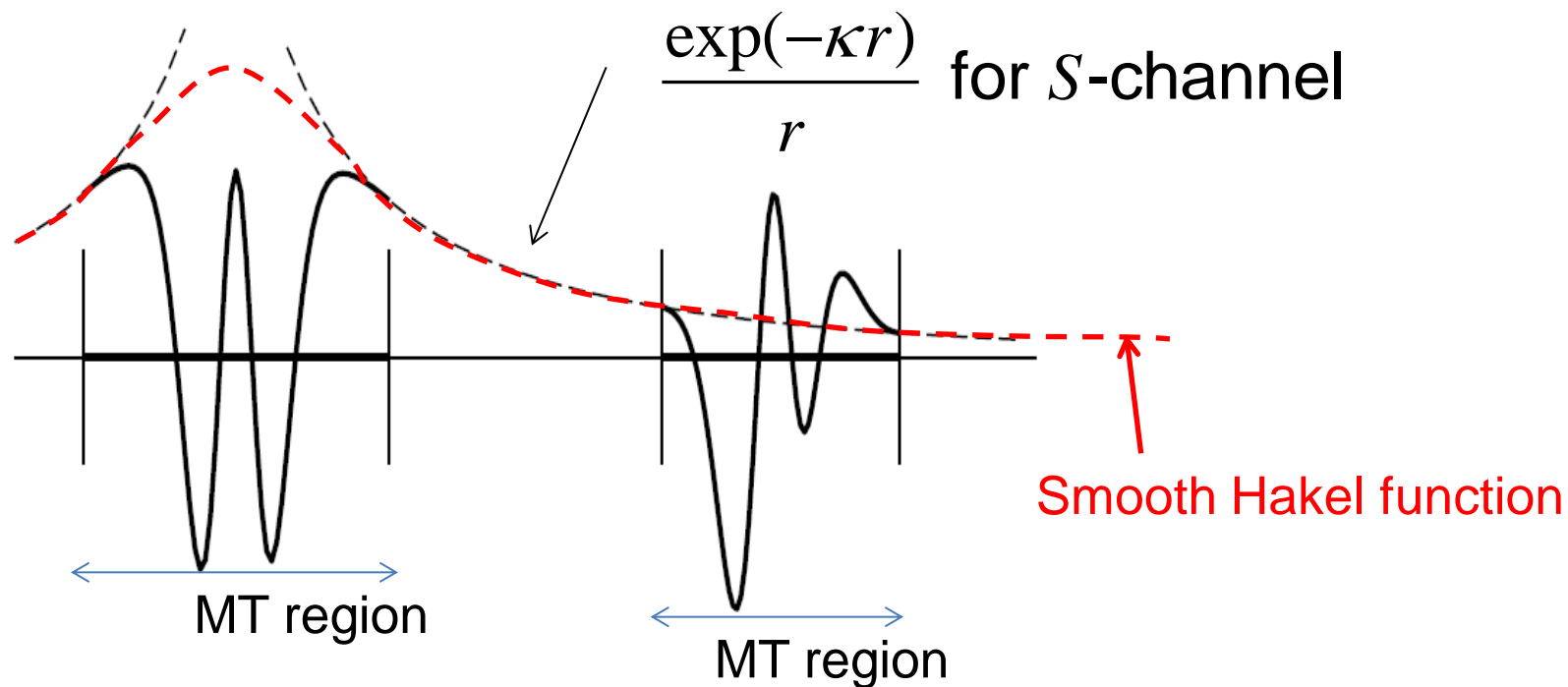
3-components
Hankel $+$ Atomic-like part $-$ counter part of Hankel
0th 1st 2nd

- 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
 arXiv:0808.1604
 Phys. Rev. B 81, 125117 (2010)

Recent work (now revising)… *T.K and Hiori Kino*
PMT works well even for diatomic molecules(H_2 through Kr_2)
 Simple setting of MTOs with APWs (Energy cutoff 3~4Ry) .

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   Atomic-like parts   Counter part
PW or smHankel   for $|\mathbf{r}| < R$ 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 $n(\mathbf{r})$ 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.
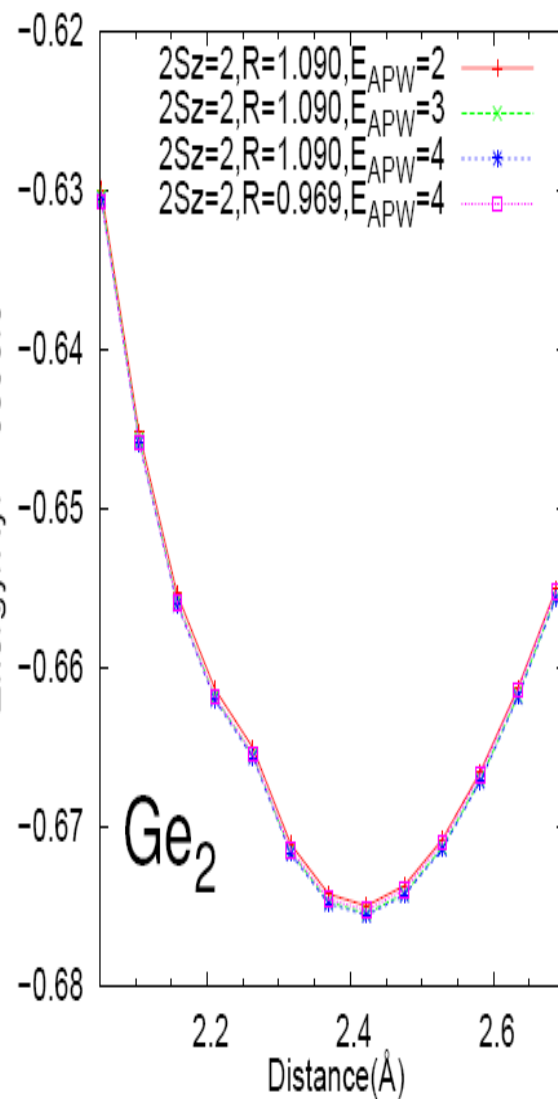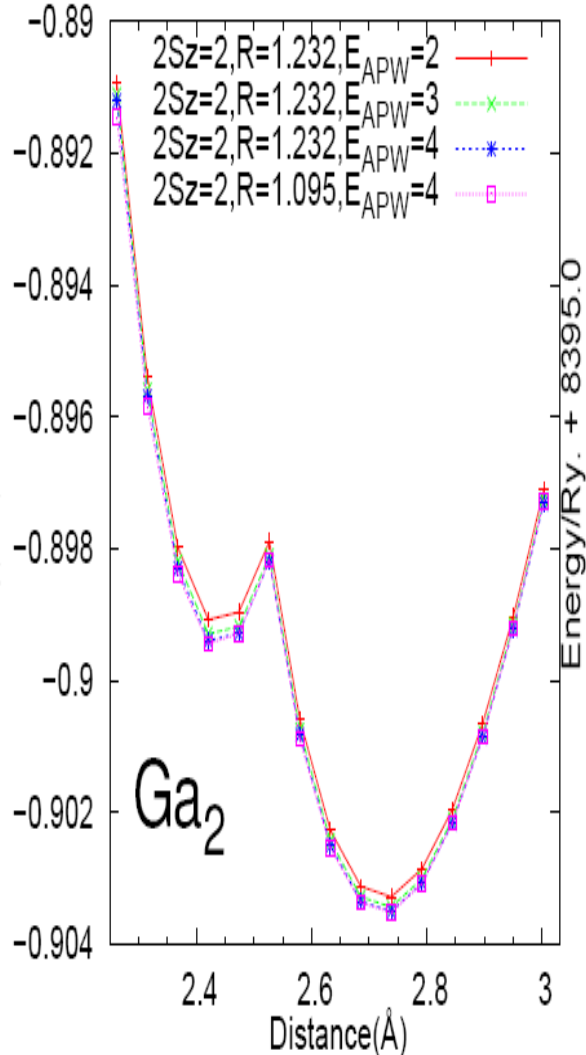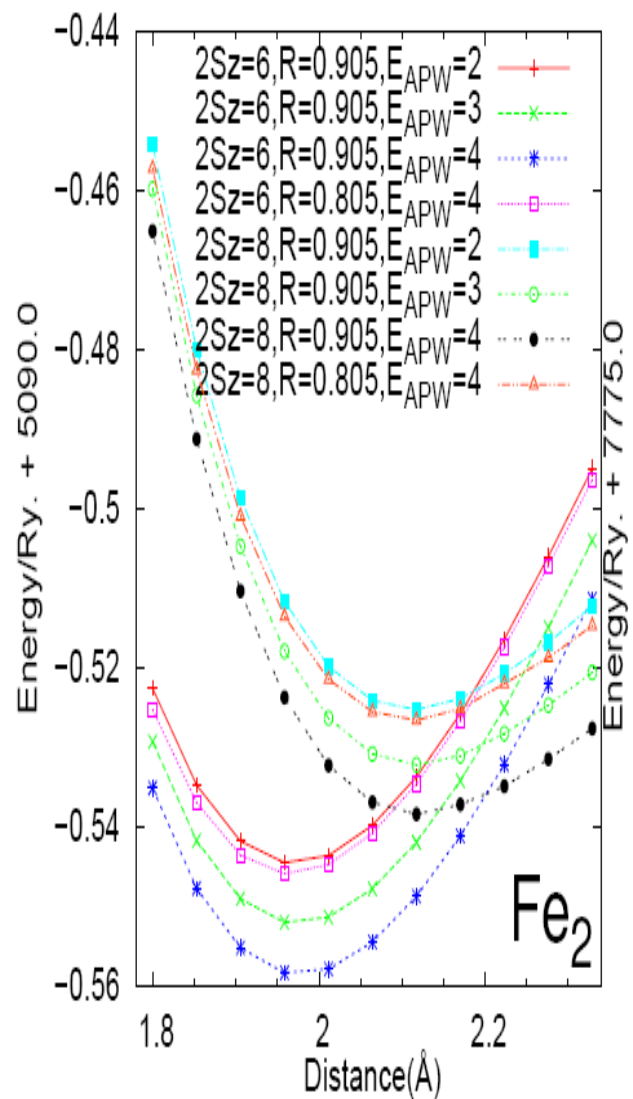
N_{basis}=1081+36 × 2,   1973+36 × 2,   3025+36 × 2

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 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

PHYSICAL RE

Vacuum level

LUMO

LUMO

HOMO

HOMO

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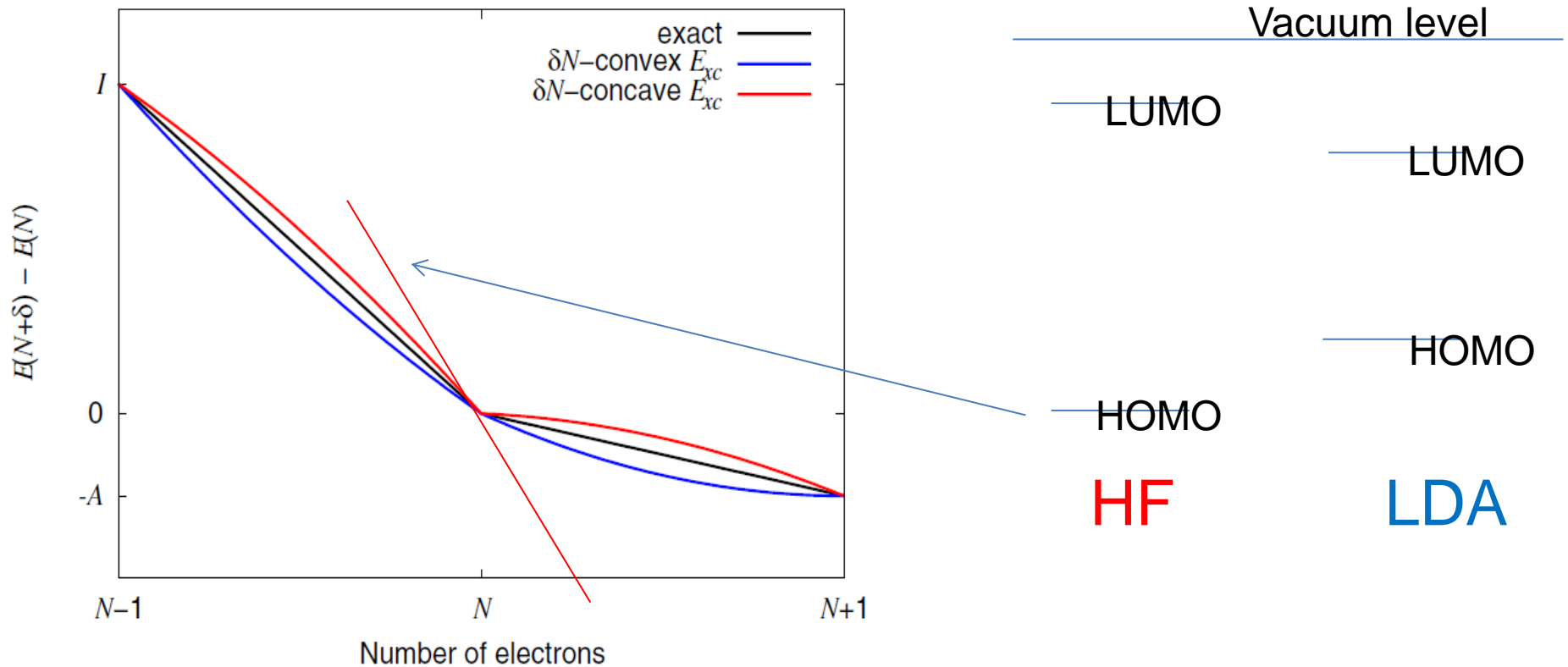
$$\varepsilon_i = \frac{\partial E}{\partial n_i} \approx \frac{\Delta E}{\Delta n_i} \quad \text{(but a little different)}$$

How about solid (infinite system)? → $\varepsilon_i = \dfrac{\partial E}{\partial n_i} = \dfrac{\Delta E}{\Delta n_i}$ 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 $(\varepsilon_{\text{CBM}} - \varepsilon_{\text{VBM}})$

Conduction band

Band gap

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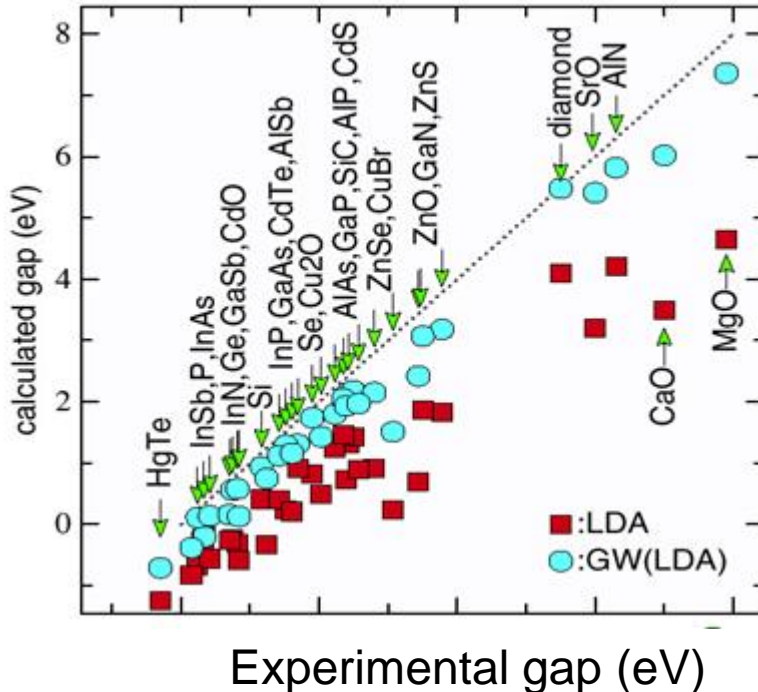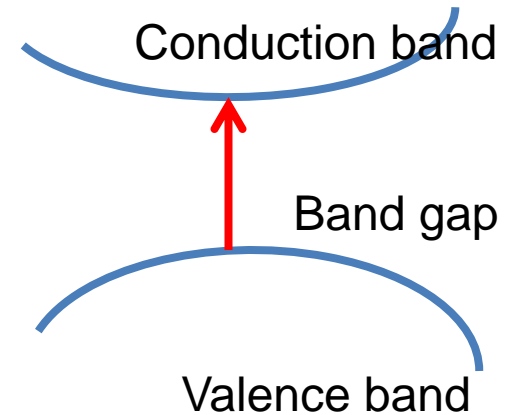
LDA gives too small
HF(not shown) gives too large

GW method and QSGW method

GW is based on the "RPA total energy"

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

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

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

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

$G_0 = \frac{1}{\omega - H_0}$ で展開

$\cdots$

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

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

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) 23

How to determine better H_0 ?

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

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

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

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

An average procedure
(not shown here)

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
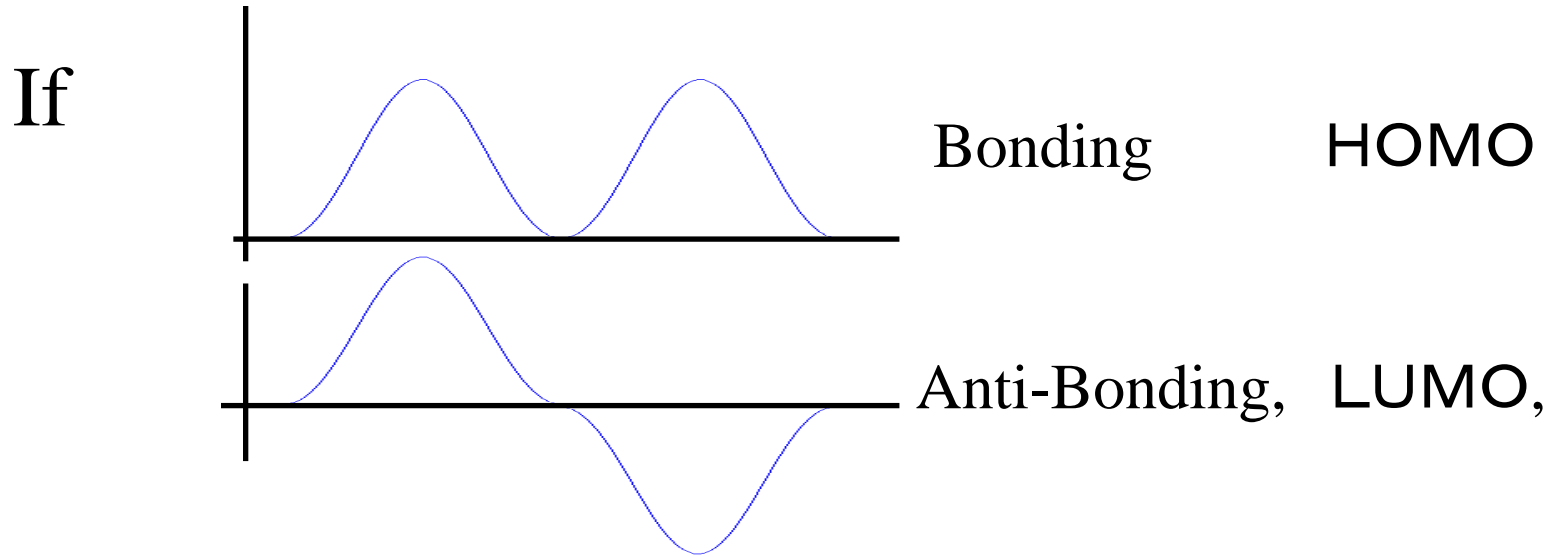
Anti-Bonding,   LUMO,

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.

BAND GAP

LDA, one-shot GW
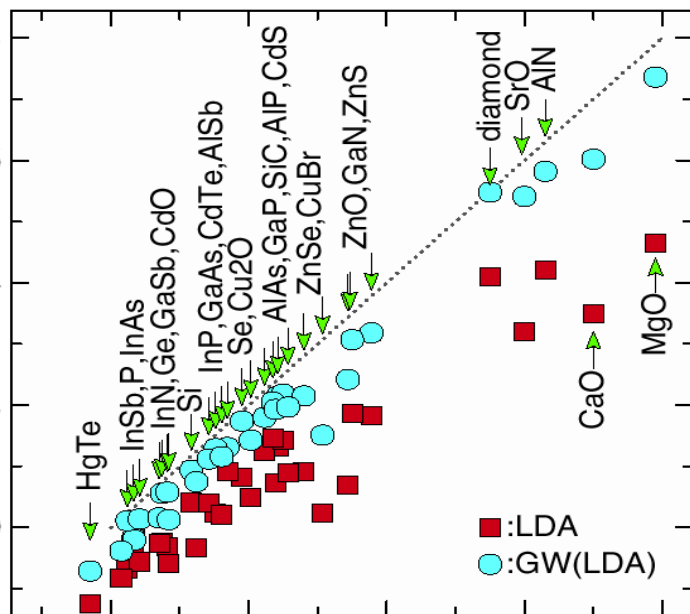
QSGW
(we see systematic
over estimation).

Calculated(eV)
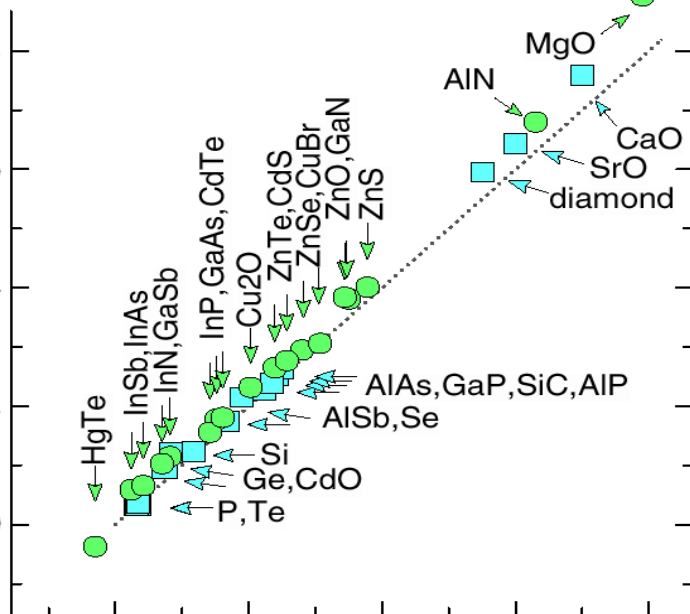
Experimental Band gap (eV)

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
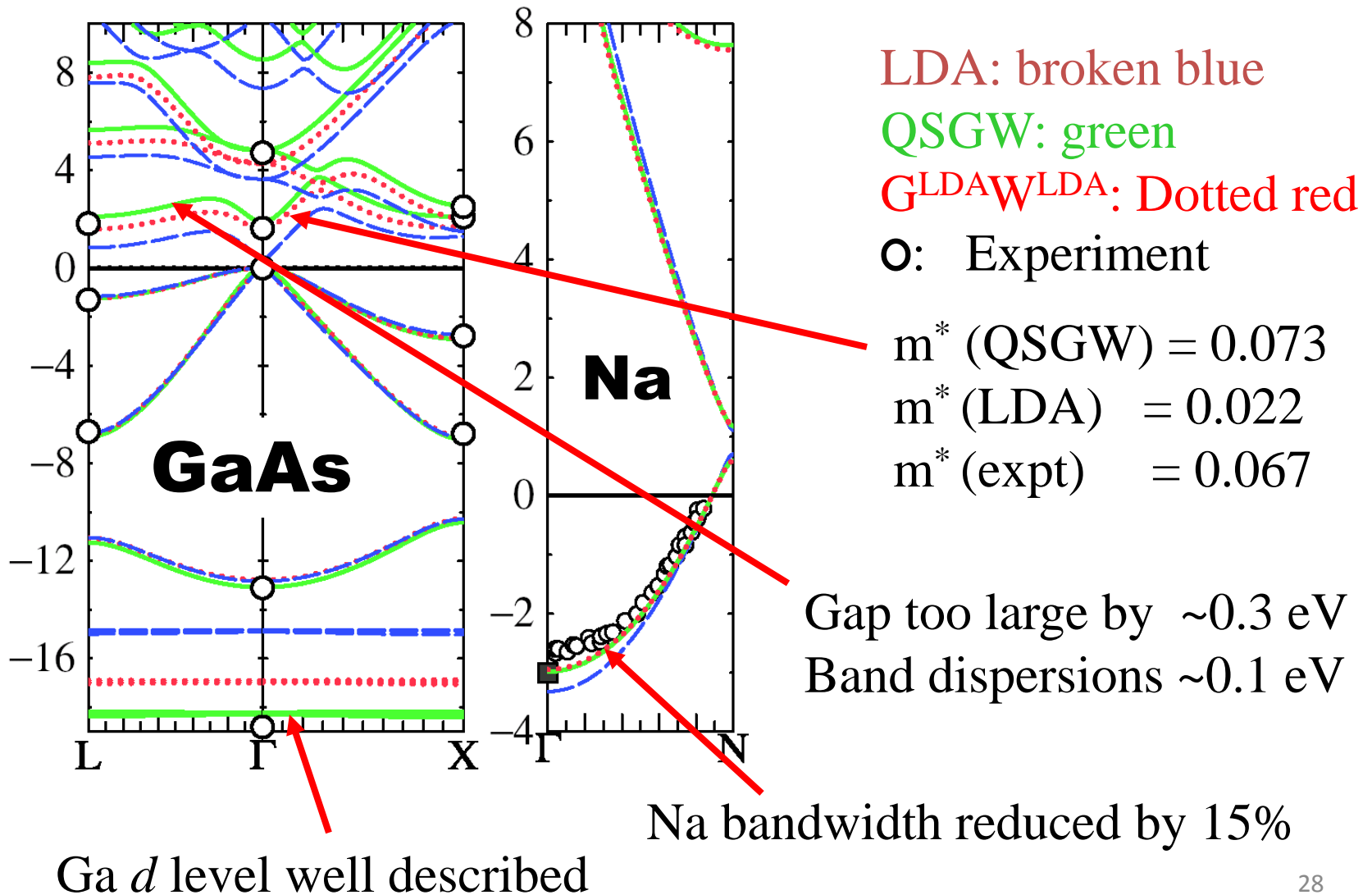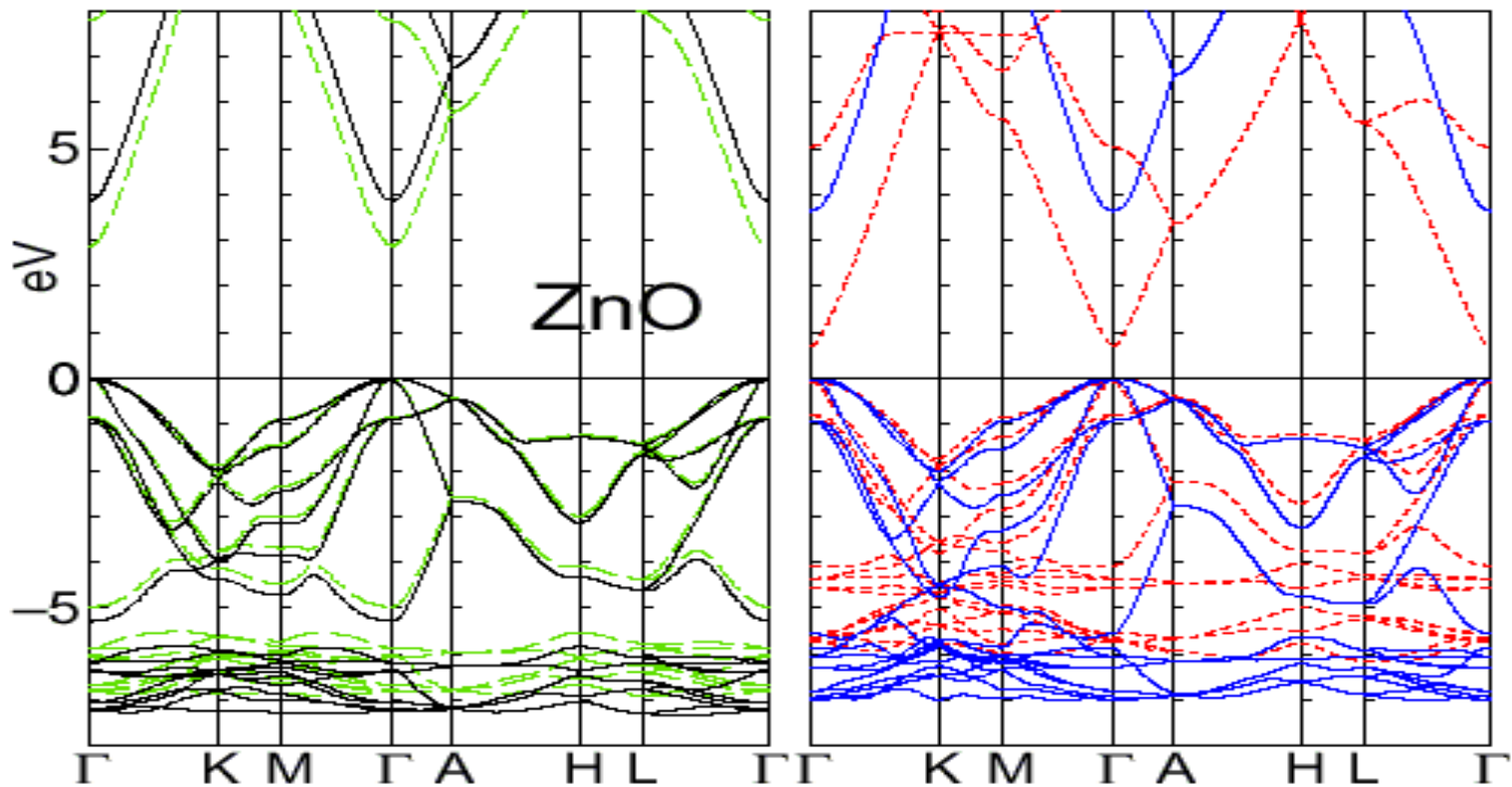
Black:QSGW   3.87eV

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)

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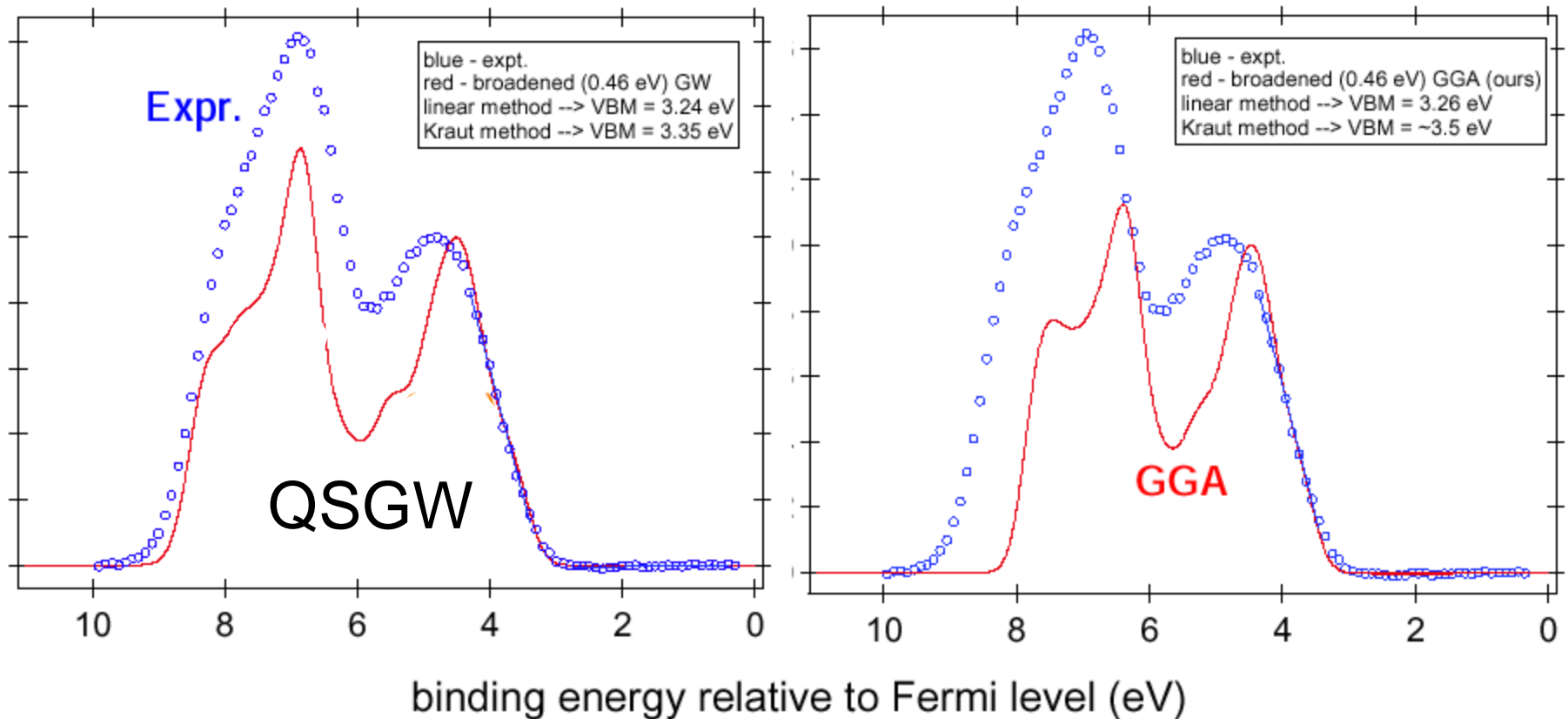
S. A. Chambers et al, Surface Sci 554,81-89 (2004)

d systems
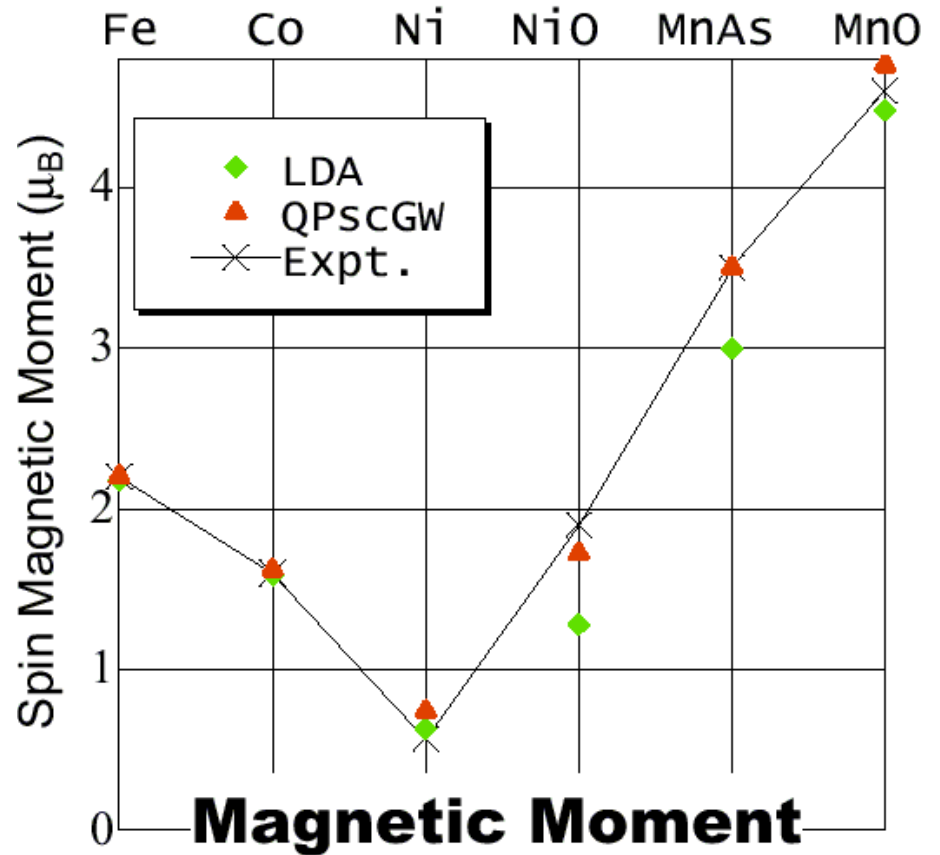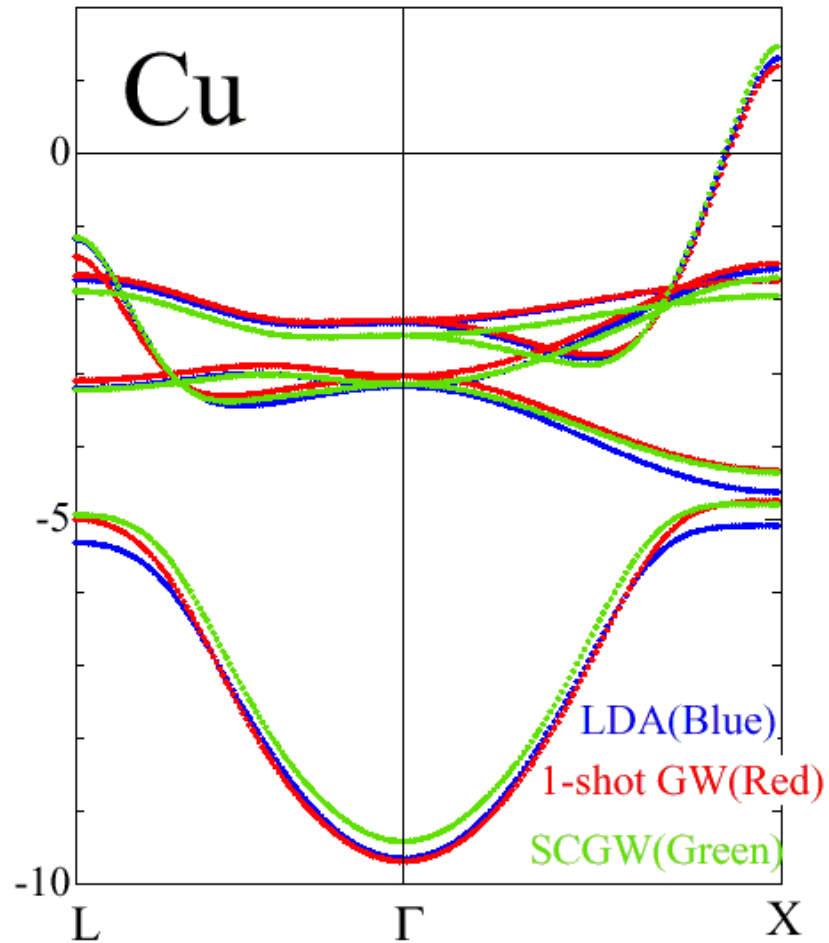
"No Pushing down 3d-band" in GW.
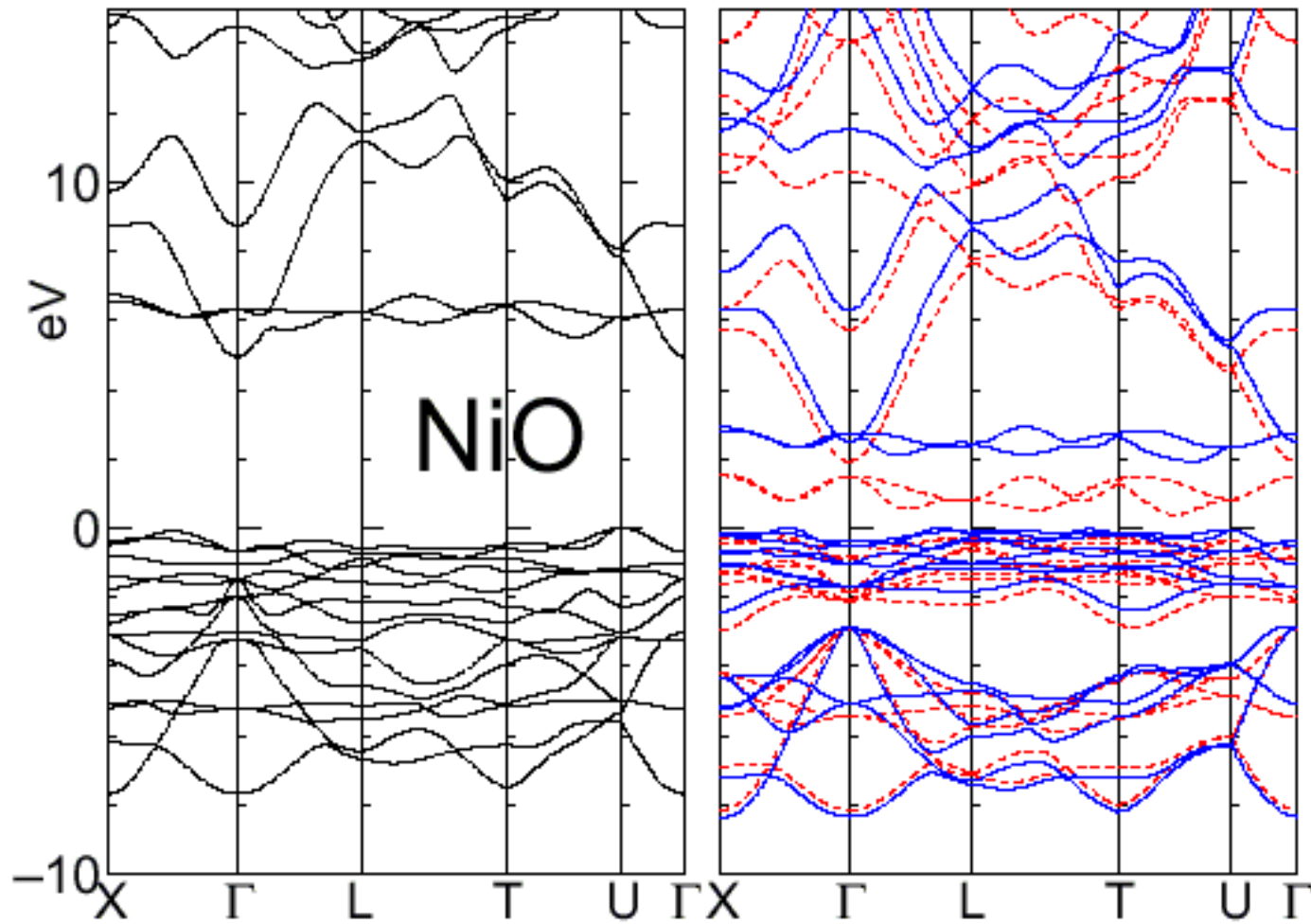
Black:QSGW Red:LDA Blue: e-only

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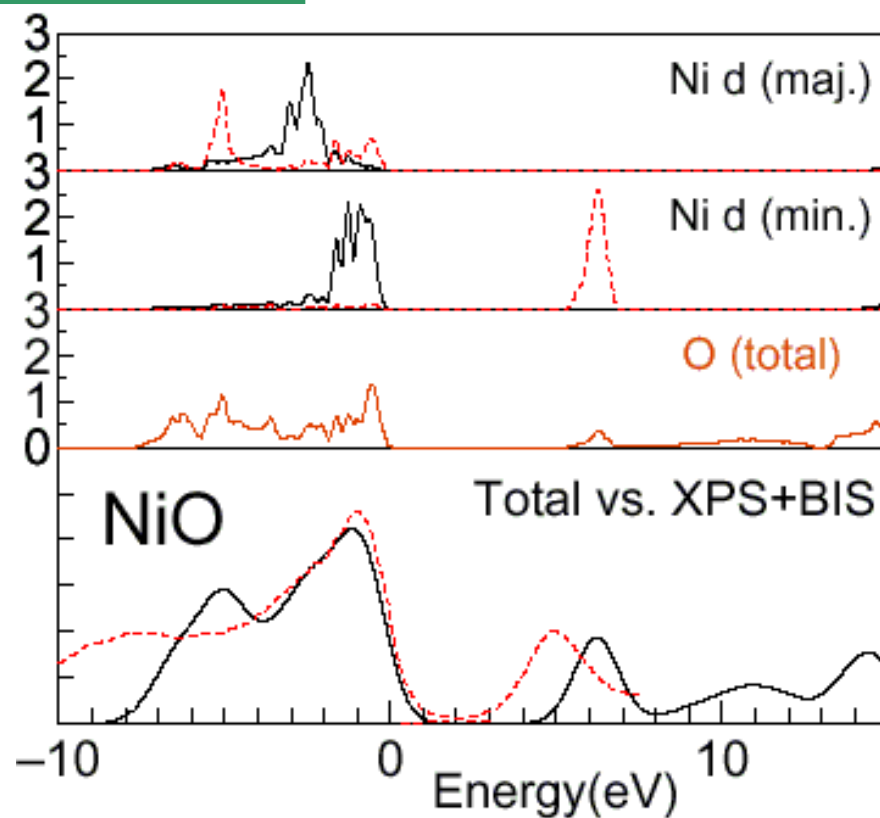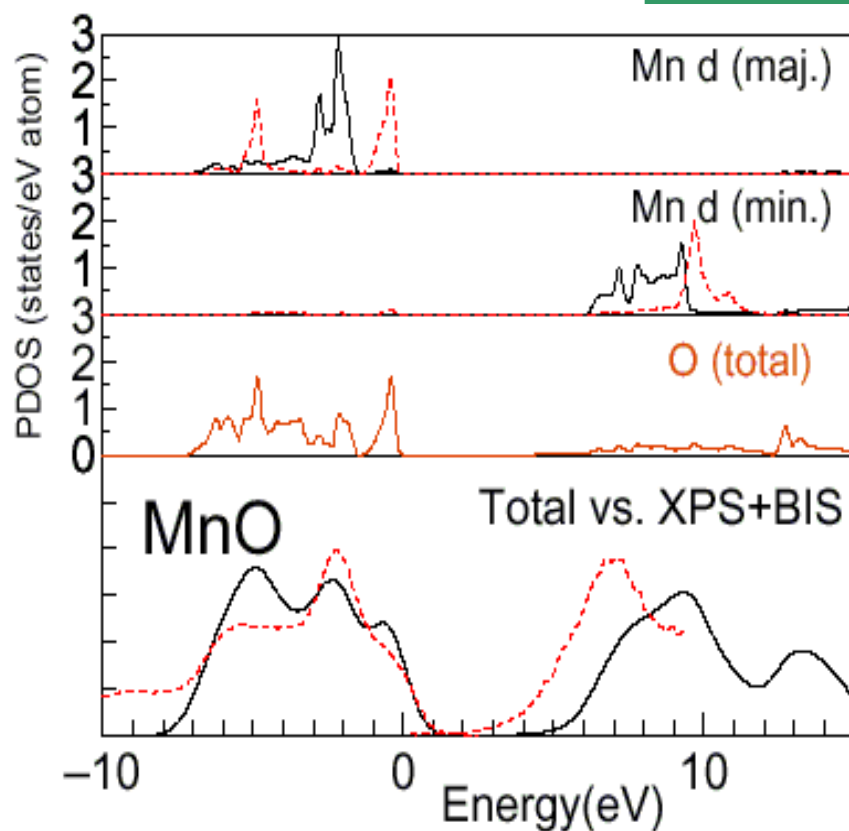
Red(bottom): expt
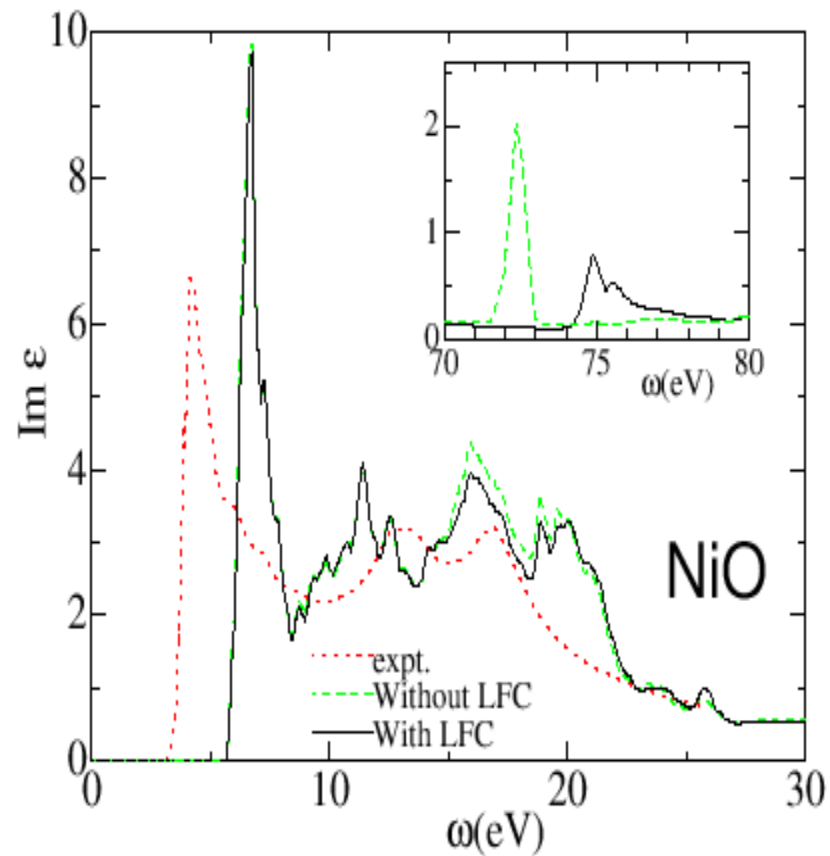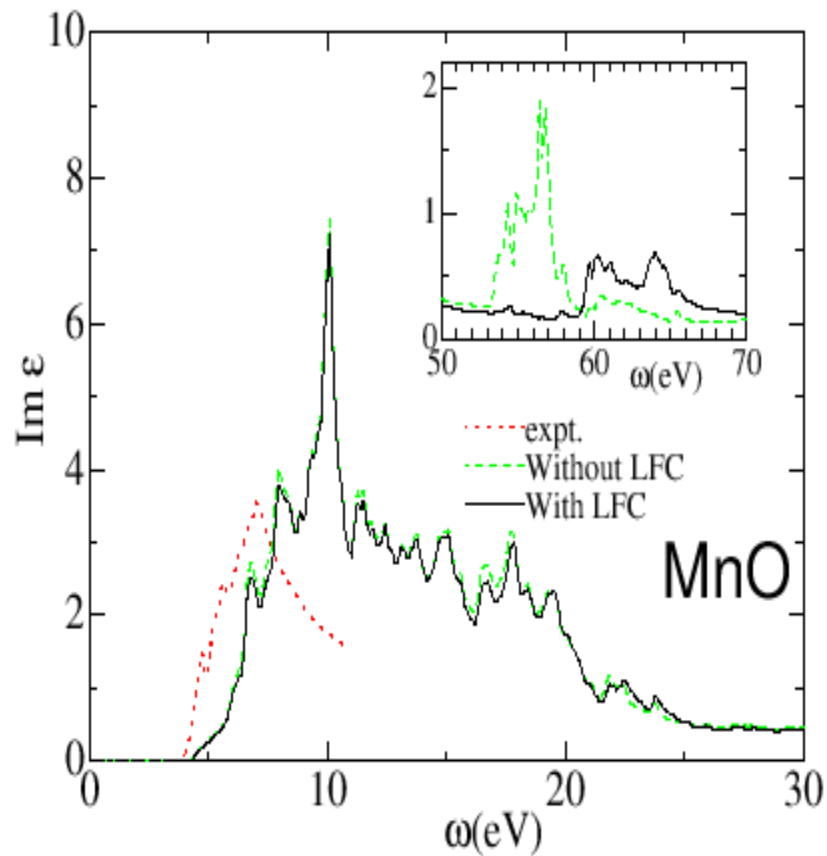
Black:Im eps with LFC   Red:expt

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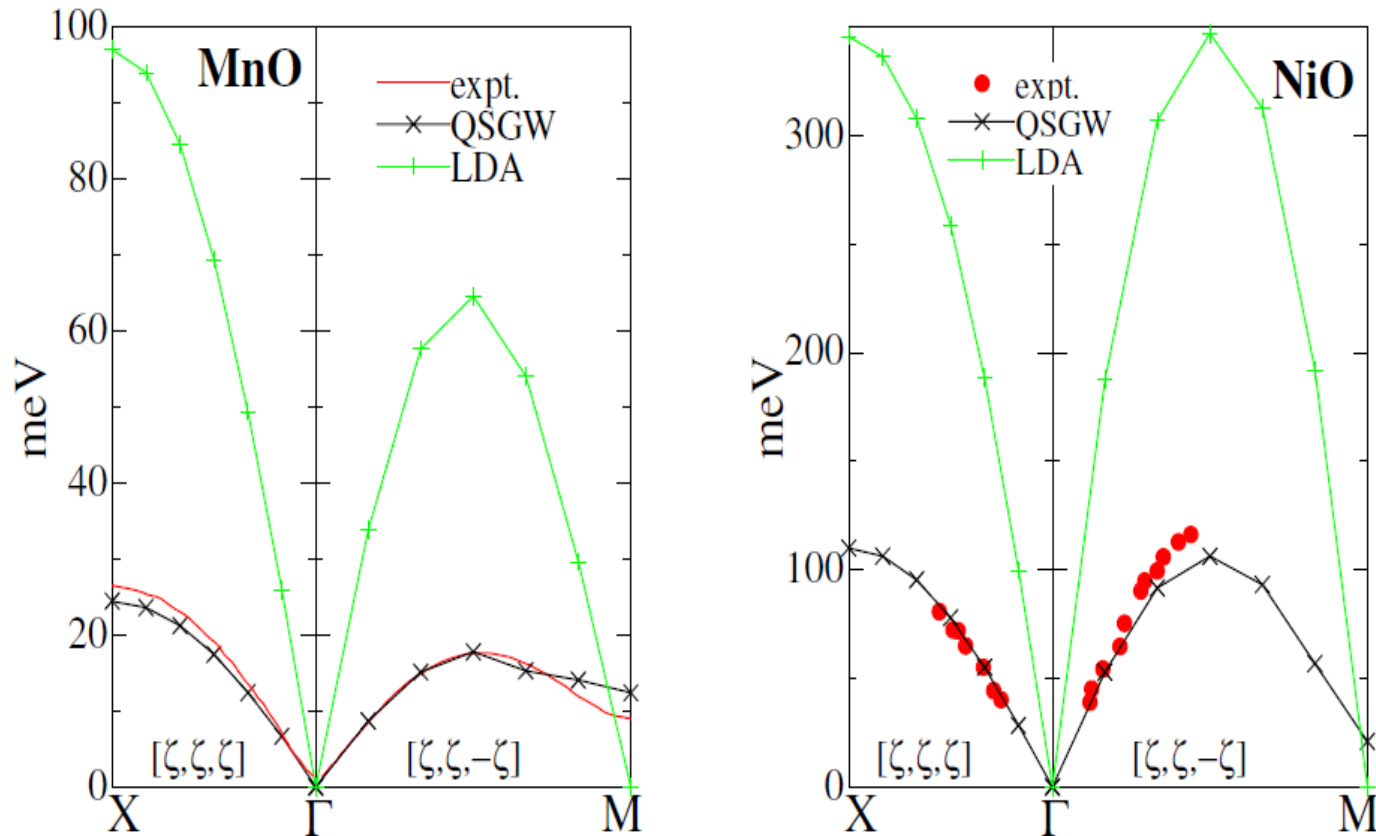
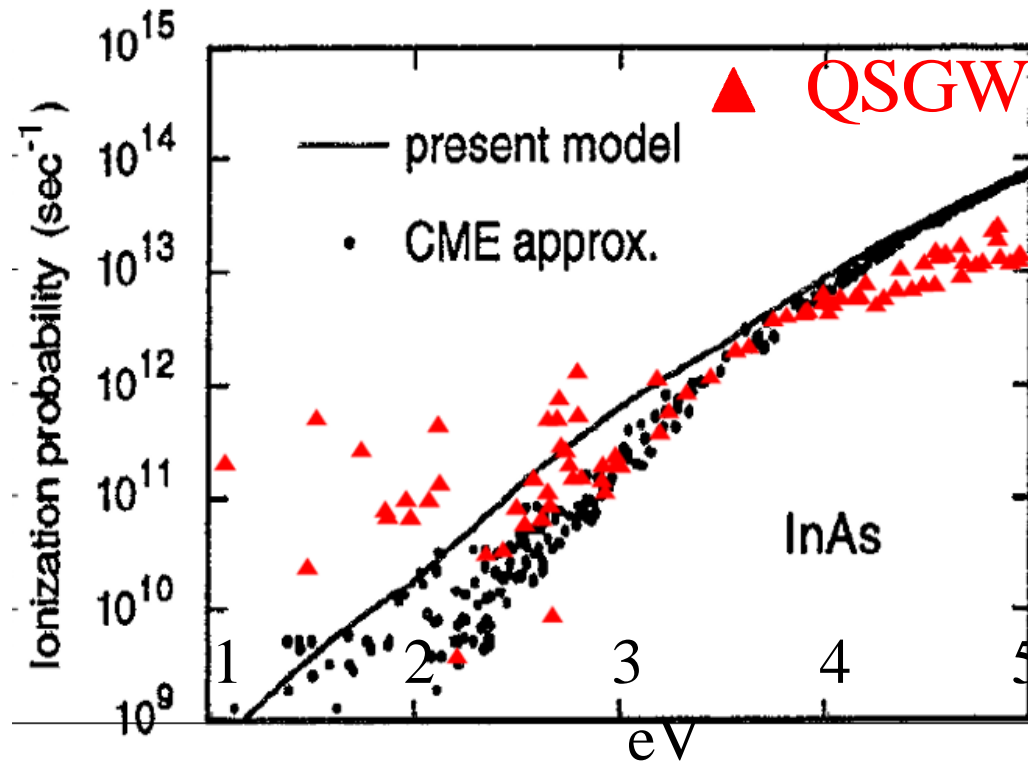J.Phys.C20 (2008) 295214,
PRB83, 060404(R) (2011) for CaFe2As2 for spectrum of χ^{+-}.

La$_x$Ba1$_{1-x}$MnO3

LDA

QSGW

0.8eV

1eV

t2g

eg

E$_{fermi}$
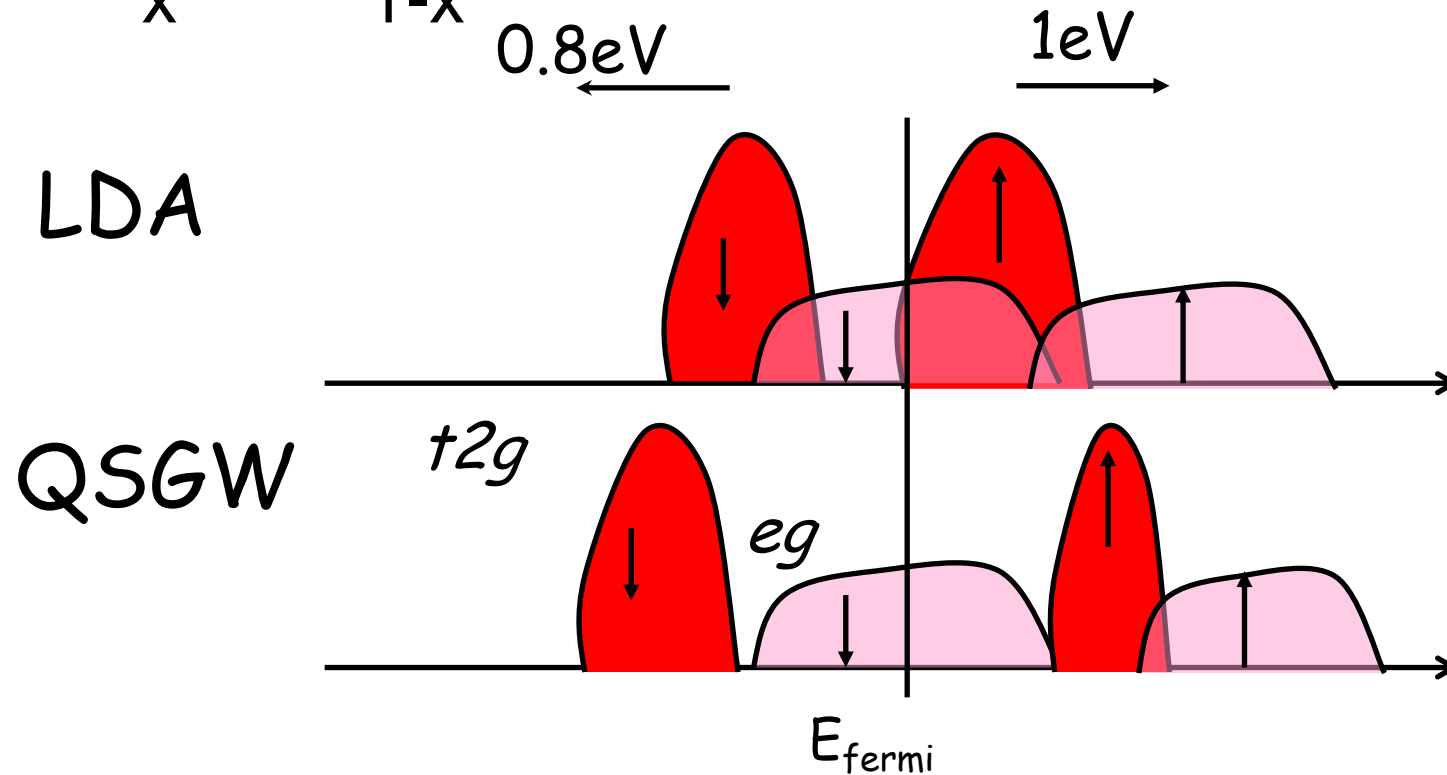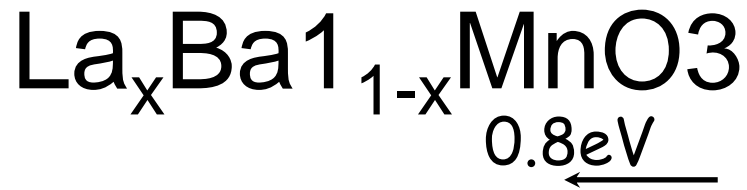
It is Half metal in QSGW

TK and H,Kino *J. Phys.C* **21** 266002(2009)

InAs impact ionization rate
(=auger process
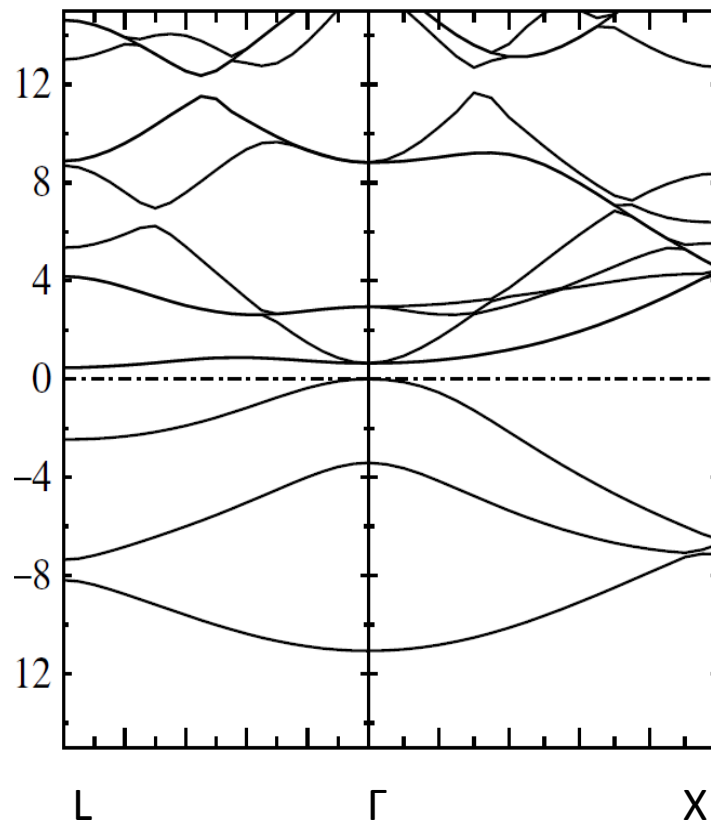= high energy electron lose energy with e-h pair)

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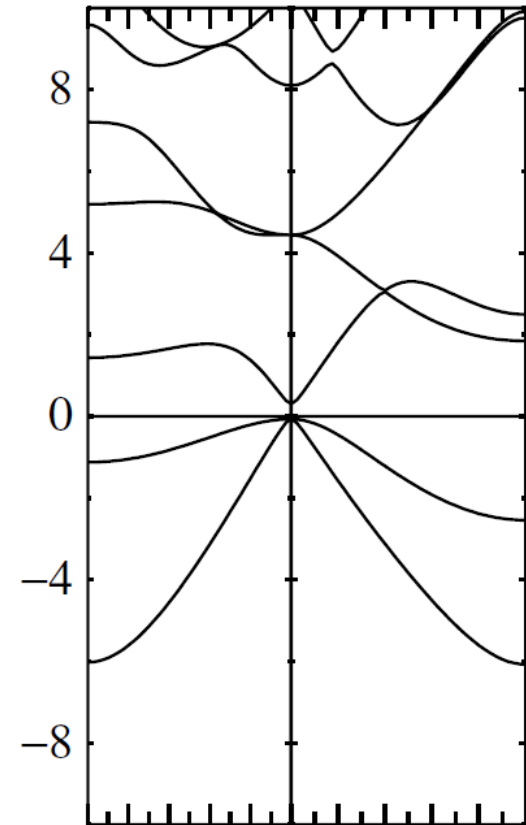
Present model: Sano and Yoshii JAP77 2020 (1995)

YH3(fcc structure 6x6x6)
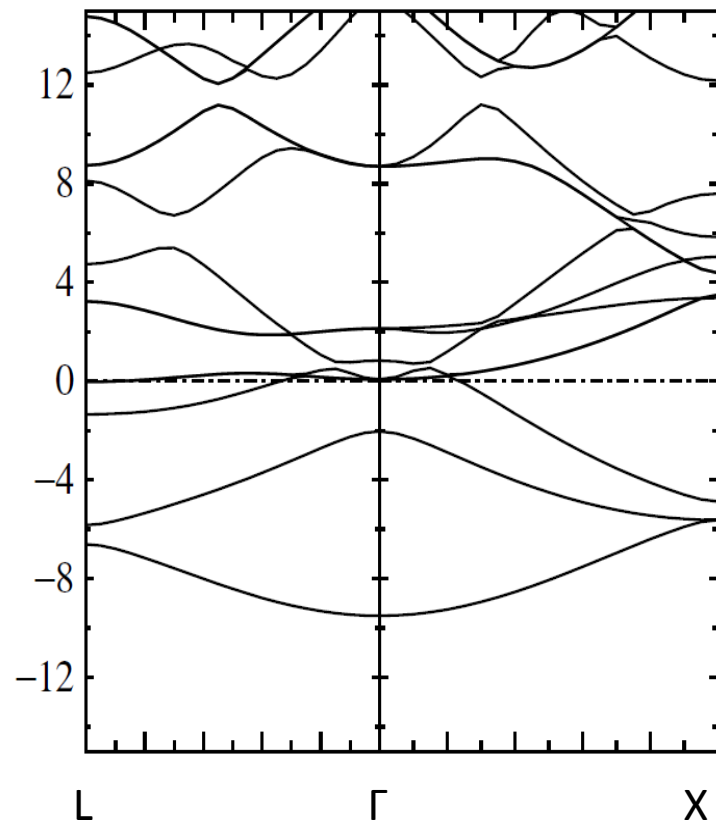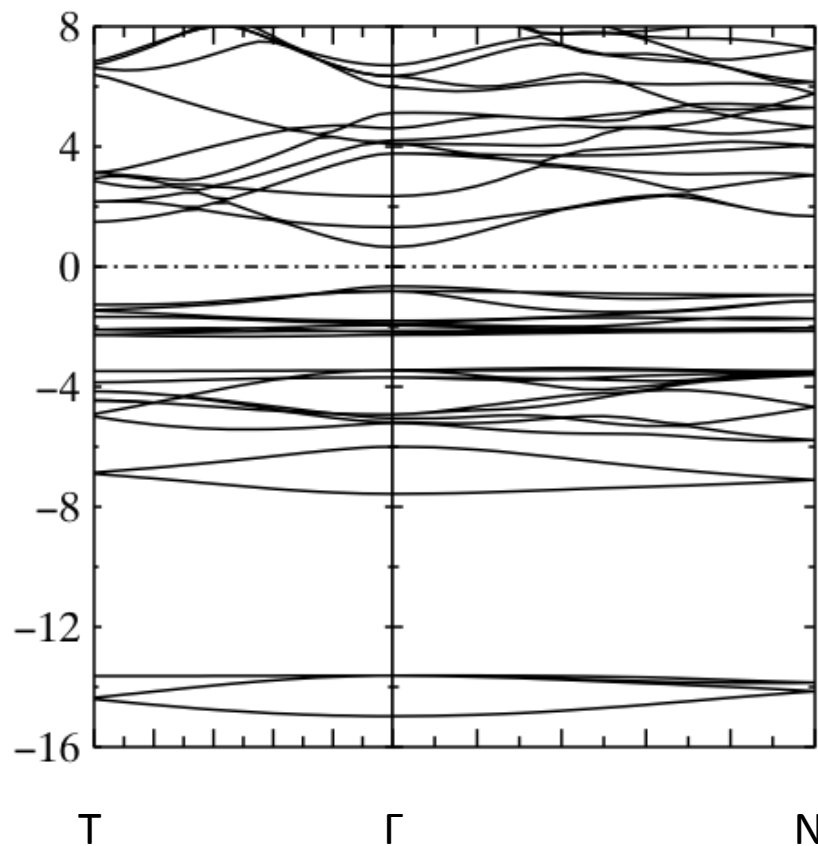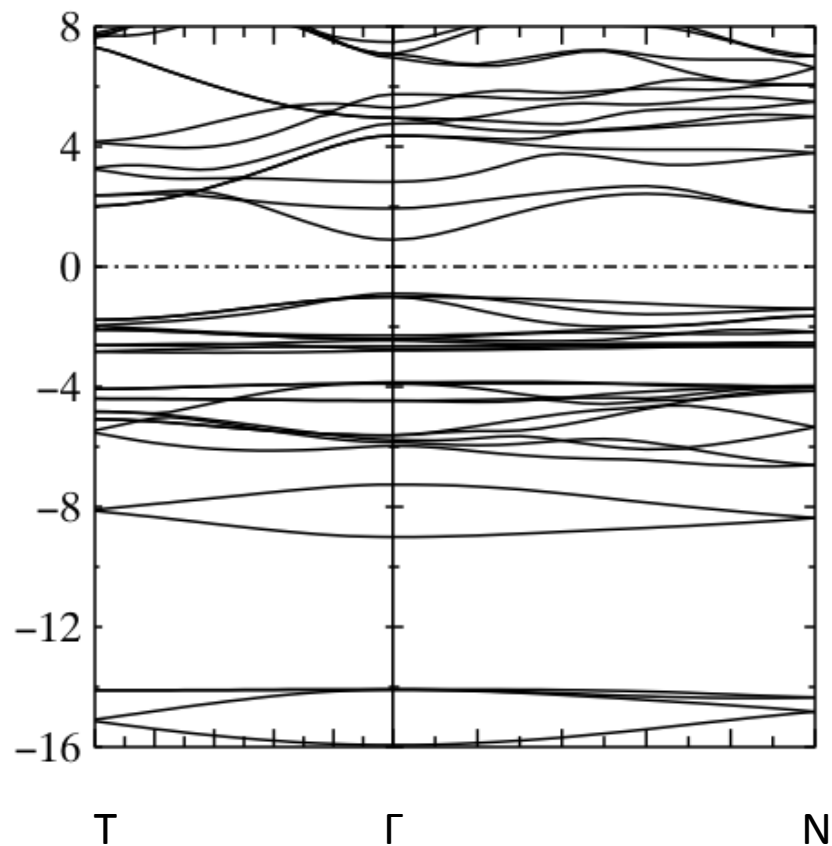
CuGaSe2 (eight atoms in cell, 2x2x2. ~3hours per iteration by single core)
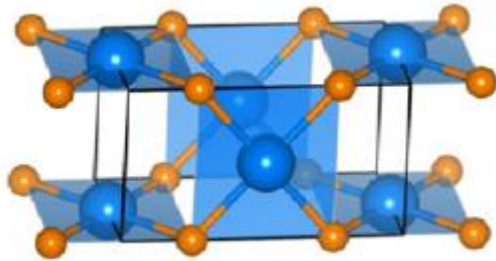
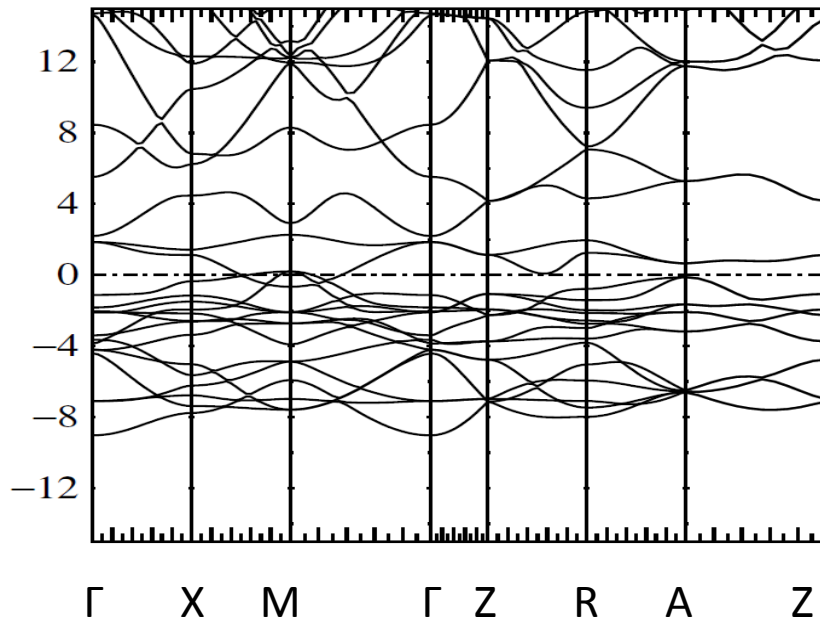## 1shotGW

QSGW

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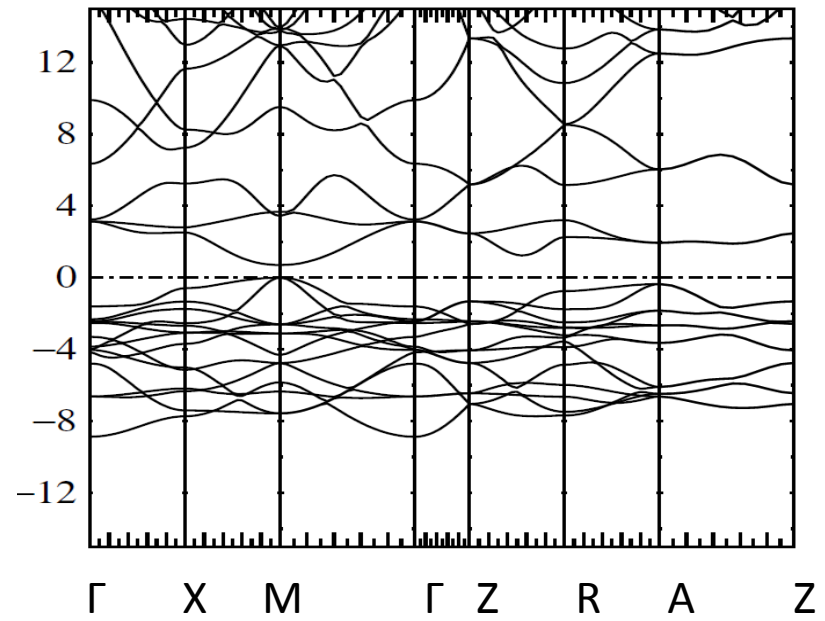QSGW(1.79eV)   Exper. 1.63, 1.67, 1.73eV

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

GGA

QSGW

Band gap about 0.7 eV

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)