

# Quasiparticle self-consistent GW and some recent developments.

*Takao Kotani, Tottori university*

1. Theory of Quasiparticle self-consistent GW (QSGW) method  
Independent-particle picture.

2. How QSGW works? Examples.

Band gaps and so on

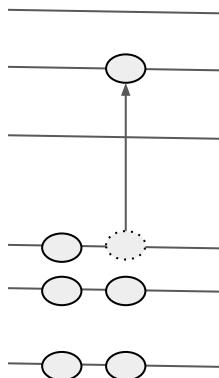
Some recent developments in our package [github/tkotani/ecalj](https://github/tkotani/ecalj).

3. Automatic QSGW with

Apply QSGW to ~1500 materials and machine learning of band gaps

4. GPU implementation with M.Obata and T.Oda (kanazawa-u),  
(Type 2 superlattice InAs/GaSb)

## Independent particle picture



We assume excitation can be described like this

- We assume no changes of orbitals when you move electrons.
- This is also for adding/removing an electron.

We need one-body Hamiltonian to describe the independent particle picture.

The independent particle picture is the very basis of material excitations.

One body Hamiltonian should determine the eigenvalues and eigenfunctions.  
Then we may take into account interaction between electrons.

How to get the best Hamiltonian for the independent particle picture?

# Hartree-Fock $H^0$ How it works?

$$H^0\psi_i(\mathbf{r}) = \left( \frac{-\hbar^2\nabla^2}{2m} - \sum_R \frac{e^2}{4\pi\epsilon_0} \frac{Z_R}{|\mathbf{r} - \mathbf{R}|} \right) \psi_i(\mathbf{r})$$

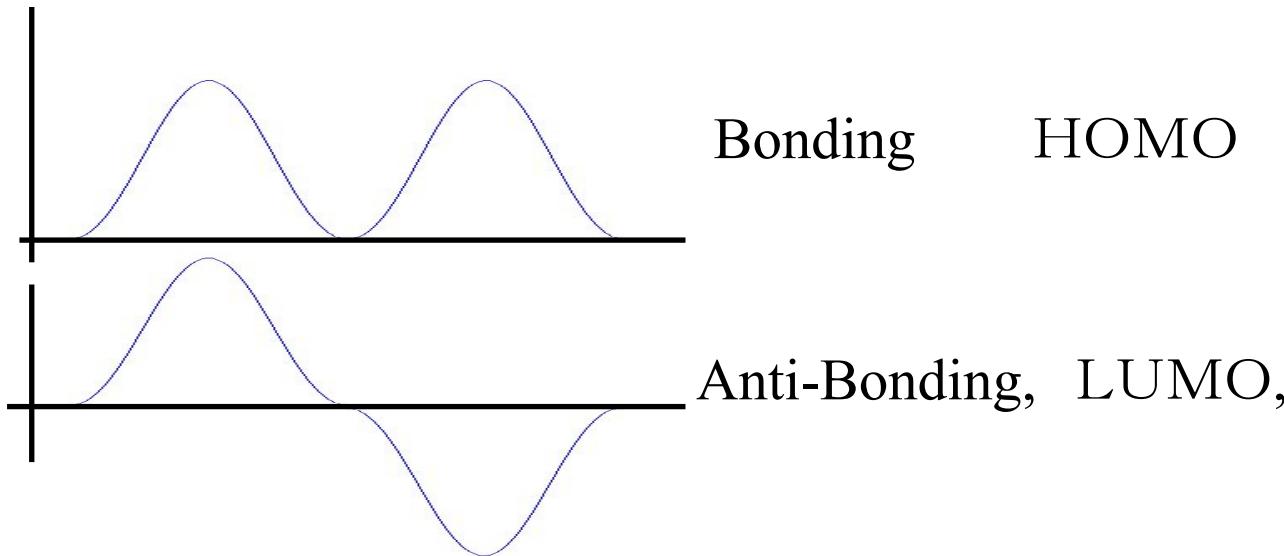
$$+ \frac{e^2}{4\pi\epsilon_0} \int d^3r' \frac{\sum_j^{\text{occupied}} \psi_j(\mathbf{r}') \psi_j^*(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \psi_i(\mathbf{r}) - \frac{e^2}{4\pi\epsilon_0} \int d^3r' \frac{\sum_j^{\text{occupied}} \psi_j(\mathbf{r}) \psi_j^*(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \psi_i(\mathbf{r}')$$

Hartree term (local potential)

Fock term (non-local)

- Hartree and Fock are  $\int d^3r' V_{ee}(\mathbf{r}') \delta(\mathbf{r} - \mathbf{r}') \psi(\mathbf{r}') + \int d^3r' V_x(\mathbf{r}, \mathbf{r}') \psi(\mathbf{r}')$
- If we replace  $\frac{1}{|\mathbf{r} - \mathbf{r}'|}$  with a constant, it is just a projector to the occupied states.  
Thus, the Fock term push down only occupied states.
- If we have one orbital only, the Hartree and the Fock completely cancels.  
Thus we can solve the Hydrogen atom exactly!
- Fock tem can localize the orbitals. Spins tends to be aligned.
- In DFT, we represent the Fock term with local potential.  
We use  $V_{xc}(\mathbf{r})$  instead of  $V_{xc}(\mathbf{r}, \mathbf{r}')$ .

**Local potential  $V(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')$  can not distinguish LUMO—HOMO gap !**



LUMO and HOMO gives almost the same electron density. Thus

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

That is, we can not control band gap by the control of  $V(\mathbf{r})$ .

We need the projection effect for occupied states in the Fock term.

- Note this is important for the band gap of Si (Off-site non-locality )
- Hund rule and effects of LDA+U (On-site non-locality )

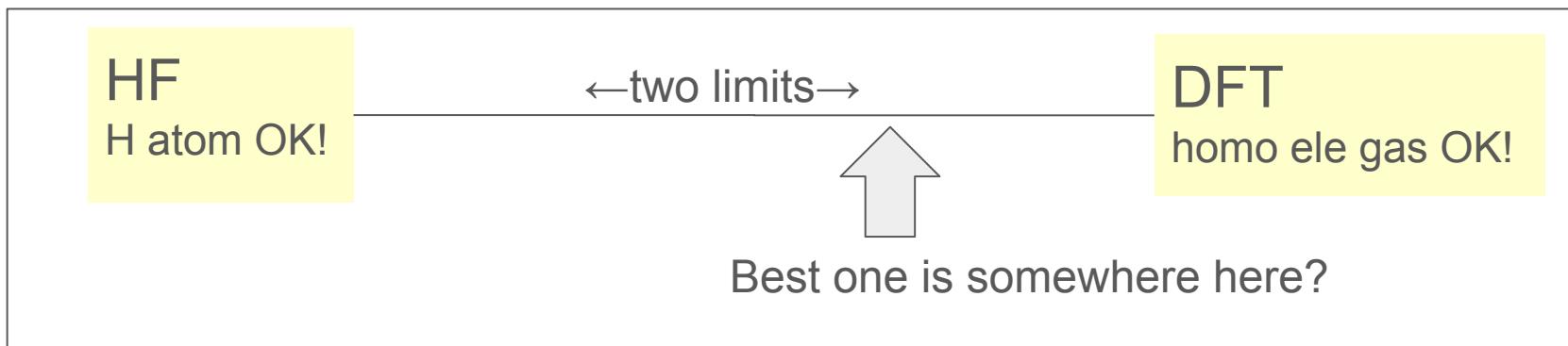
# Hartree Fock vs DFT for independent particle picture

	HF approximation	DFT
Homogeneous electron gas	DOS is zero at the Fermi energy	Free electron like band structure (dispersion). Usually good enough.
Si	Band gap $>10\text{eV}$	Band gap $\sim 0.5\text{eV}$
H atom	Good! Self-interaction cancellation.	Band gap is $\sim$ one-half of $13.6\text{eV}$ .

HF shows too large exchange effect!

What is the problem of HF ?

In materials , the effective interaction should be reduced by the polarization of electrons. Screening effects. We have to consider Screened exchange.



1. Some fixed mixing (25 percent HF)? → HSE06 Hybrid method
2. Apply screened HF for onsite 3d only → LDA+U

...

In principle, we have to consider the size of effective interaction  $W$ .  
H atom → HF limit.  
Homogeneous electron gas → DFT limit.

## Recipe of GW approximation

1. Prepare  $H_0 = \frac{-\nabla^2}{2m} + V(\mathbf{r}, \mathbf{r}')$
2. Get eigenvalues and eigenfunctions.
3. Calculate Fock exchange as  $\Sigma_x(\mathbf{r}, \mathbf{r}')$
4. Calculate polarization function  $\chi(\mathbf{r}, \mathbf{r}', \omega)$ .

Then we get the effective interaction  $W(\mathbf{r}, \mathbf{r}', \omega)$  in RPA.

5.  $\Sigma_c(\mathbf{r}, \mathbf{r}', t-t') = i G(\mathbf{r}, \mathbf{r}', t-t') (W(\mathbf{r}, \mathbf{r}', t-t') - v(\mathbf{r}, \mathbf{r}') \delta(t-t'))$
6.  $\Sigma = \Sigma_x + \Sigma_c$

Theoretical rearrangement of  $\Sigma$  gives an interpretation of GW as

GW approximation is interpreted as **Screened Exchange + Coulomb Hole**

- The Coulomb interaction  $v$  for exchange should be replaced with  $W$ .  
→ **Screened Exchange effect**
- When we put an electron, electron feels as if a heavy ball on carpet  
→ **Coulomb Hole effect**.  
( a test charge (e.g. muon) feels Coulomb Hole effects only.)

# 1.Theory of Quasiparticle self-consistent GW method

$$H = H_0 + (H - H_0)$$

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

$$\xrightarrow{\text{GW}} \frac{-\nabla^2}{2m} + V_{\text{core}}(\mathbf{r}) + V_H(\mathbf{r}) + \Sigma(\mathbf{r}, \mathbf{r}', \omega)$$

$$H = H_0 + (H - H_0)$$

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

$$\xrightarrow{\text{GW}} \frac{-\nabla^2}{2m} + V_{\text{core}}(\mathbf{r}) + V_H(\mathbf{r}) + \Sigma(\mathbf{r}, \mathbf{r}', \omega)$$

$$H = H_0 + (H - H_0)$$

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

$$\xrightarrow{\text{GW}} \frac{-\nabla^2}{2m} + V_{\text{core}}(\mathbf{r}) + V_H(\mathbf{r}) + \Sigma(\mathbf{r}, \mathbf{r}', \omega)$$

Until converged...

- If we treat  $(H-H_0)$  in the mean-field, this becomes HF approximation.

- We remove  $\omega$ -dependence by a simple average

$$\begin{aligned} & V_{\text{xc}}(\mathbf{r}, \mathbf{r}') \\ &= \sum_{i,j} \varphi_i(\mathbf{r}) \frac{\langle \varphi_i | \text{Re}[\Sigma(\mathbf{r}, \mathbf{r}', \varepsilon_i) + \Sigma(\mathbf{r}, \mathbf{r}', \varepsilon_j)] | \varphi_j \rangle}{2} \varphi_j^*(\mathbf{r}') \end{aligned}$$

## Advantage in QSGW

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

Hartree-Fock → H-atom OK! (chemistry)

**Truth is somewhere between LDA and HF.**

→ Hybrid methd(B3LYP, HSE...)  $\frac{1}{4} \times \text{HF} + \frac{3}{4} \times \text{LDA}$

**Problem : the mixing ratio can be dependent on materials.**

QSGW: "Instead of bare Coulmb v"

we use " Dynamically Screened Coulom interaction W ".

W(omega) is determined self-consistently.

## Band gap in QSGW

D.Deguchi, K.Sato,TK,H.Kino, JJAP.55.051201 (2016)

	LDA+SO	QSGW+SO	QSGW80+SO	Expt.
GaN	1.91	3.84	3.38	3.50
GaN(ZB)	1.77	3.69	3.23	3.30 <sup>26)</sup>
GaP	1.41	2.49	2.23	2.35
GaAs	0.19	1.89	1.41	1.52
GaSb	0.00	1.20	0.77	0.82
InN	0.00	0.80	0.49	0.7 <sup>27,28)</sup>
InN(ZB)	0.00	0.55	0.24	—
InP	0.43	1.65	1.34	1.42
InAs	0.00	0.80	0.36	0.42
InSb	0.00	0.77	0.25	0.24

QSGW80  
= 20% LDA  
mixing  
(ad hoc  
correction)

numerical accuracy ~0.1eV

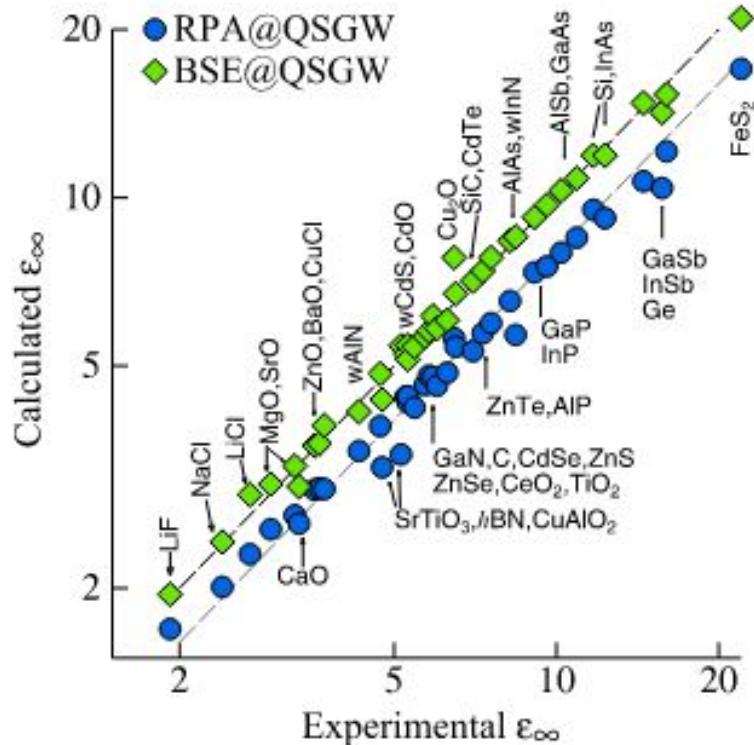
Effective mass	$m_e$	$m_{lh}$	$m_{hh}$	$m_{so}$	
InAs	0.024 (0.026)	0.028 (0.027)	0.344 (0.333)	0.100 (0.140)	Expt.

# QSGW80?

QSGW gives too large exchange effect.

This is because of too small screening effect.

QSGW80 is a quick fix (mimic W containing BSE, instead of W in RPA).



BSE:

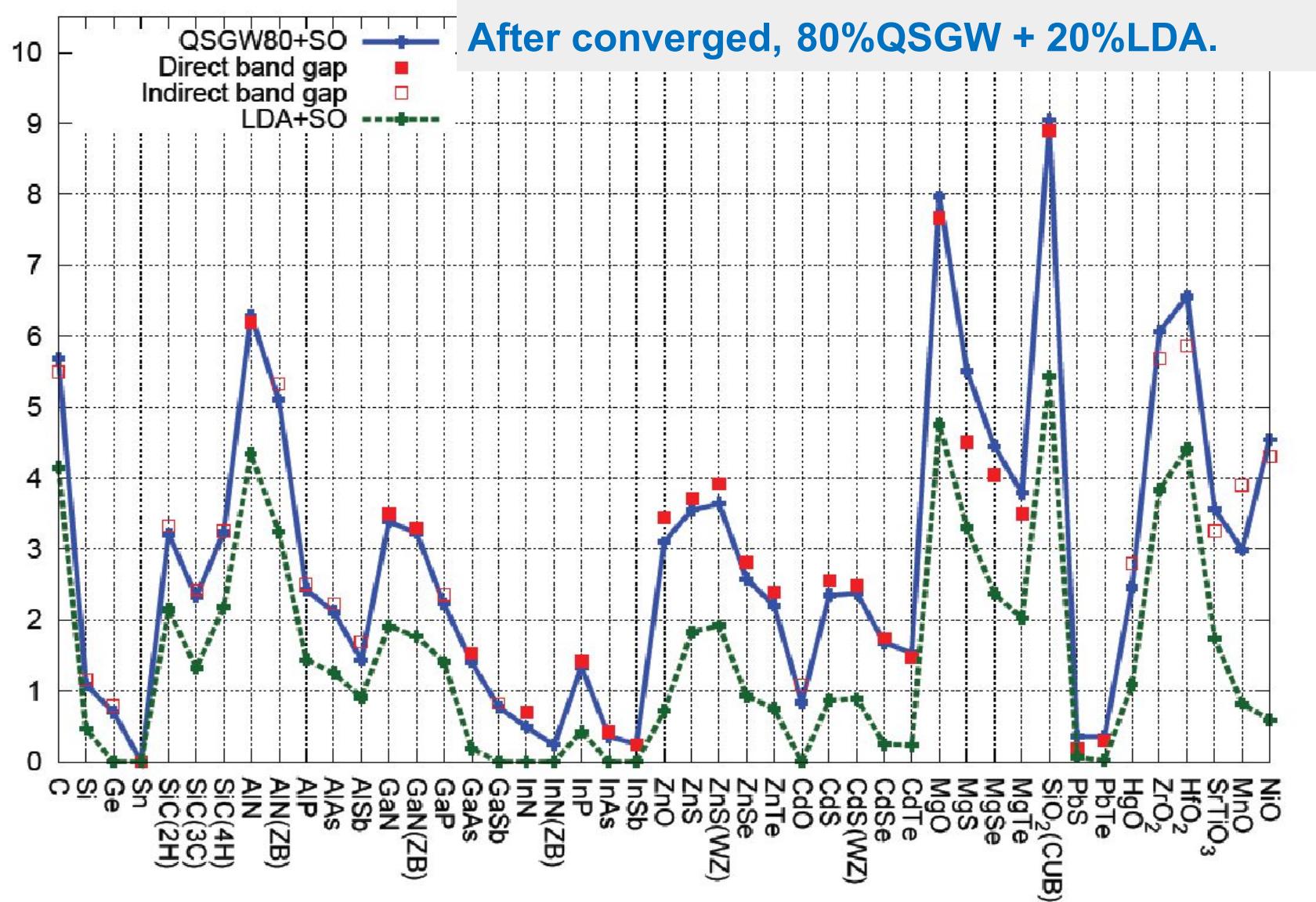
Intermediate states for the polarization function should have smaller energy because of the pair interaction.

QSGW80 looks not so bad.  
Anyway, we have room to improve theory along the line of QSGW

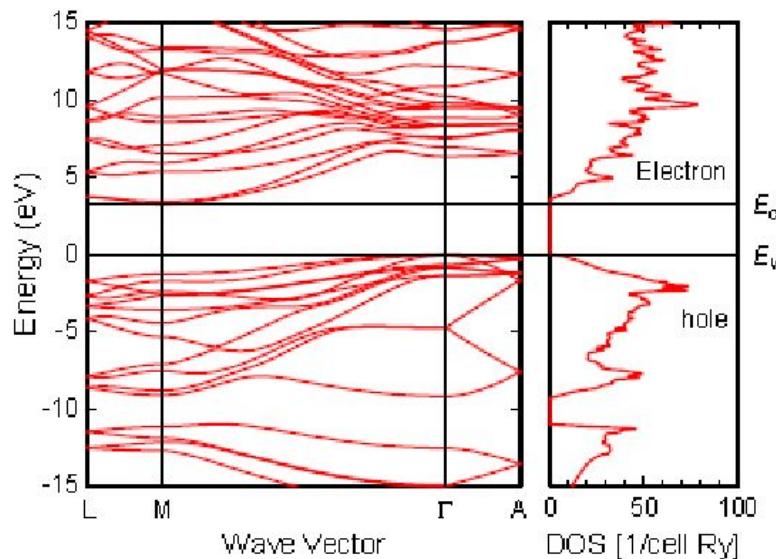
Cunningham et al. 10.1103/PhysRevB.108.165104 (2023)  
Questaal(Kings College London). branched from ecalj at 2009

## 2. How QSGW works? Basis example.

D.Deguchi, K.Sato,TK,H.Kino, JJAP.55.051201 (2016)



# Band Structure (4H-SiC)



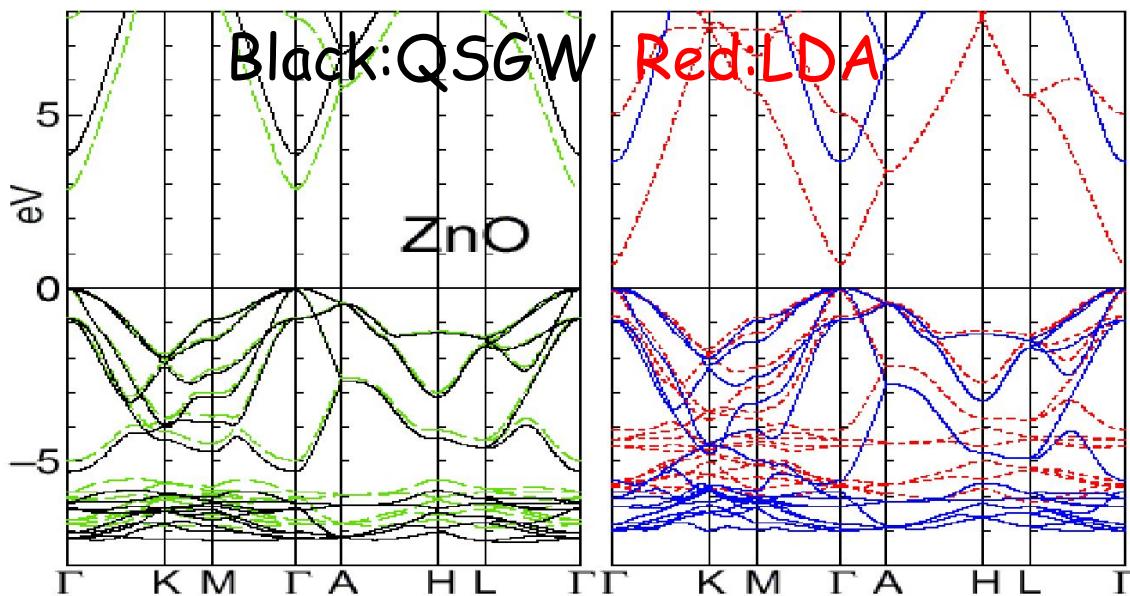
79.5% QSGW + 20.5% LDA  
to obtain  $E_g = 3.26$  eV

	Direct band gap energy at symmetry points (eV)		Effective mass at conduction band bottom ( $m_0^*$ )	
	$\Gamma$	M	$m_{M-\Gamma}^*$	$m_{M-K}^*$
Experiment	6.18 <sup>[a]</sup>	4.56 <sup>[a]</sup>	0.58 <sup>[b]</sup>	0.31 <sup>[b]</sup>
This work	6.36	4.50	0.53	0.28

<sup>[a]</sup> Demir et al., Appl. Phys. Lett. **84**, 3540 (2004)

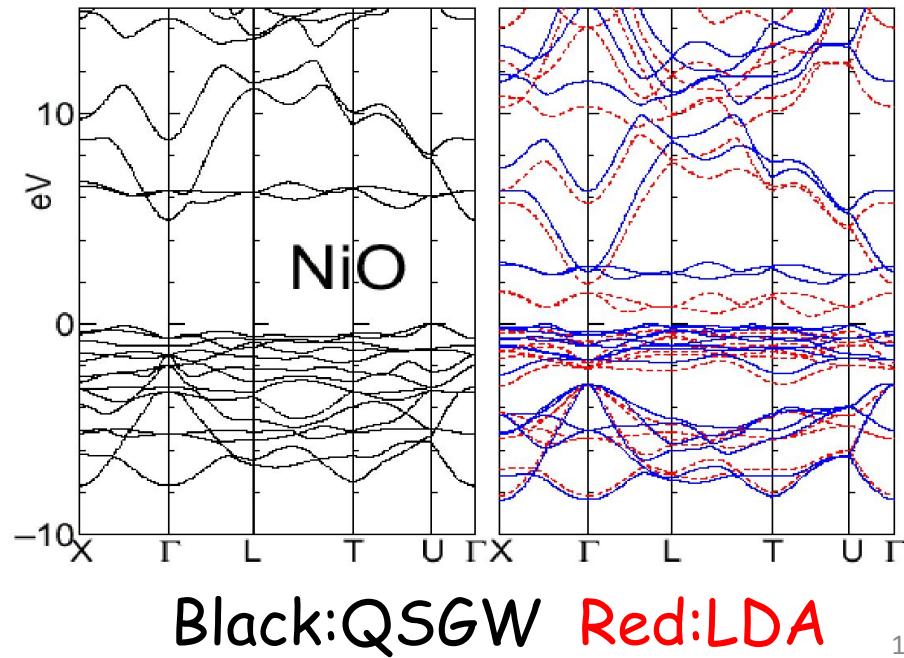
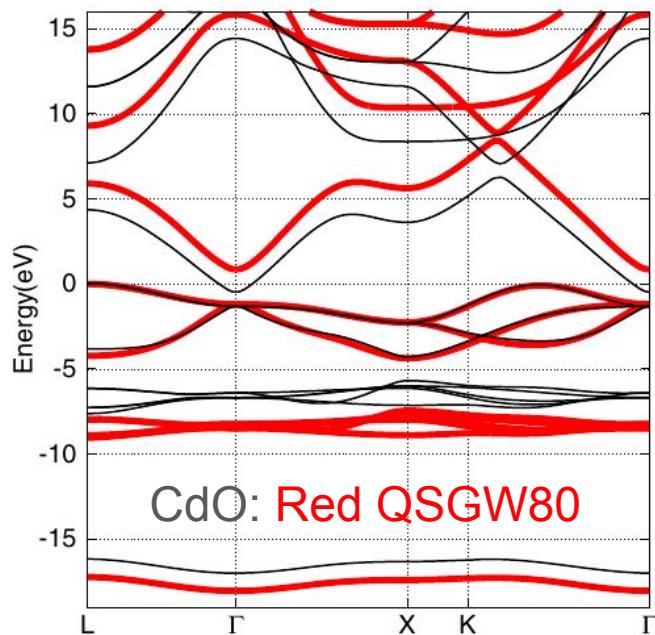
<sup>[b]</sup> Chen et al., Phys. Status Solidi A, **162**, 79 (2001)

## 2. How QSGW works? Examples.



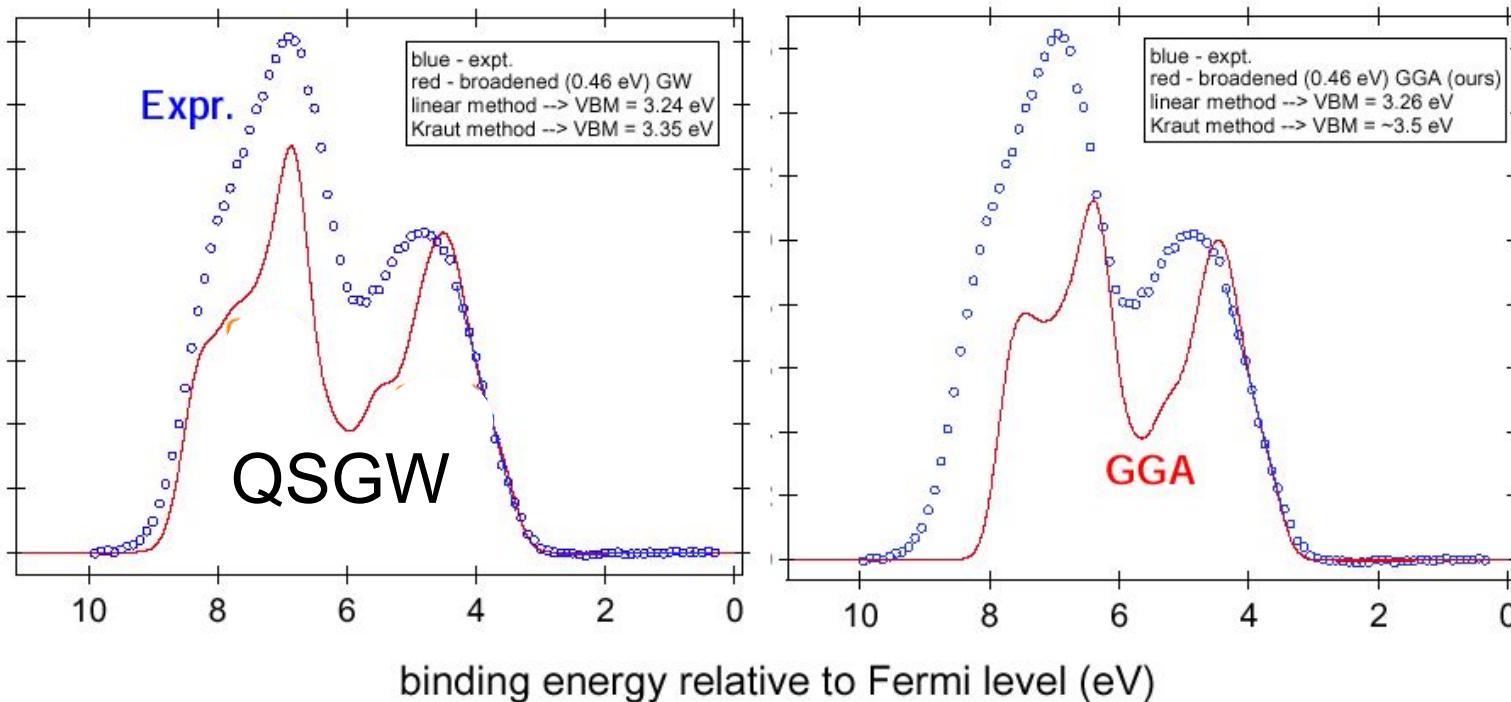
Kotani et al PRB76,165106(2007)

bandwidth, band positions.  
LDA+U effects  
and usual GW effects



## SrTiO<sub>3</sub> Valence DOS

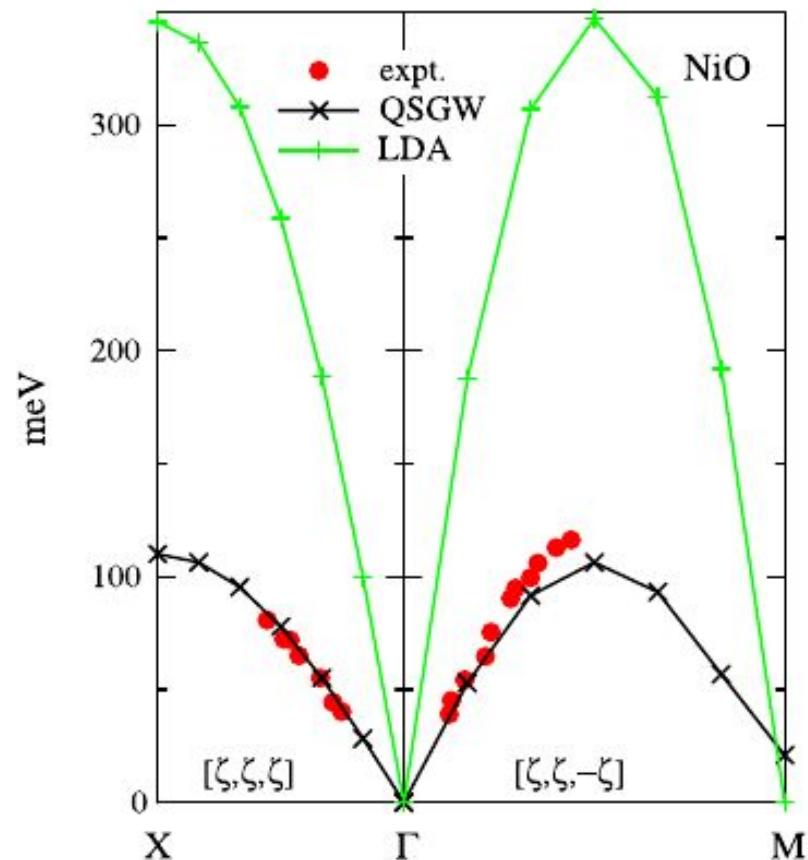
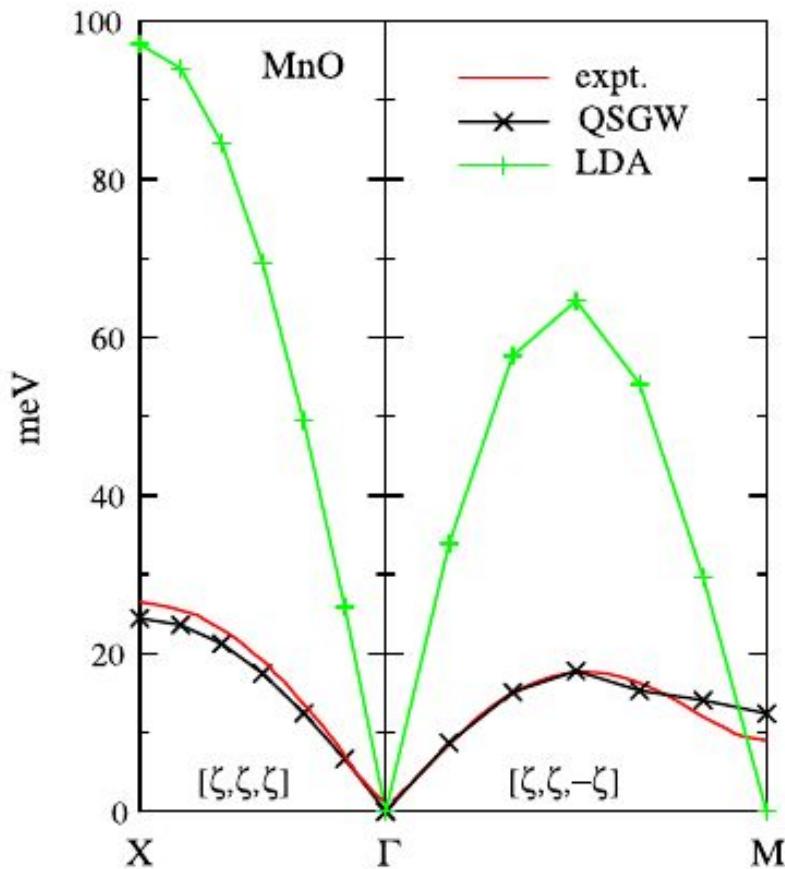
fit of properly broadened theoretical DOS with experiment  
n-STO(001) VB excited with monochromatic AlK $\alpha$  x-rays (resolution = 0.46 eV)



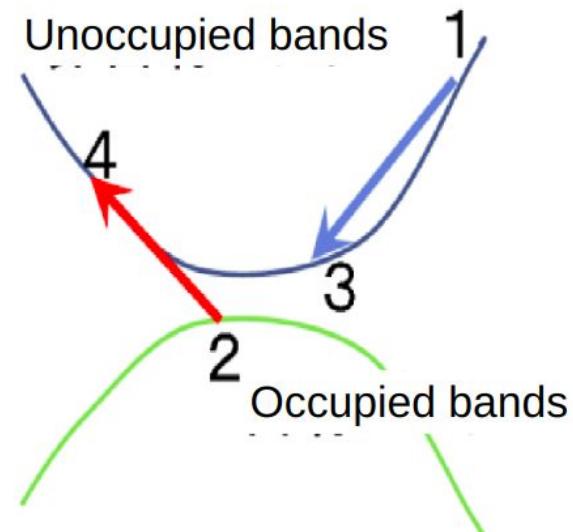
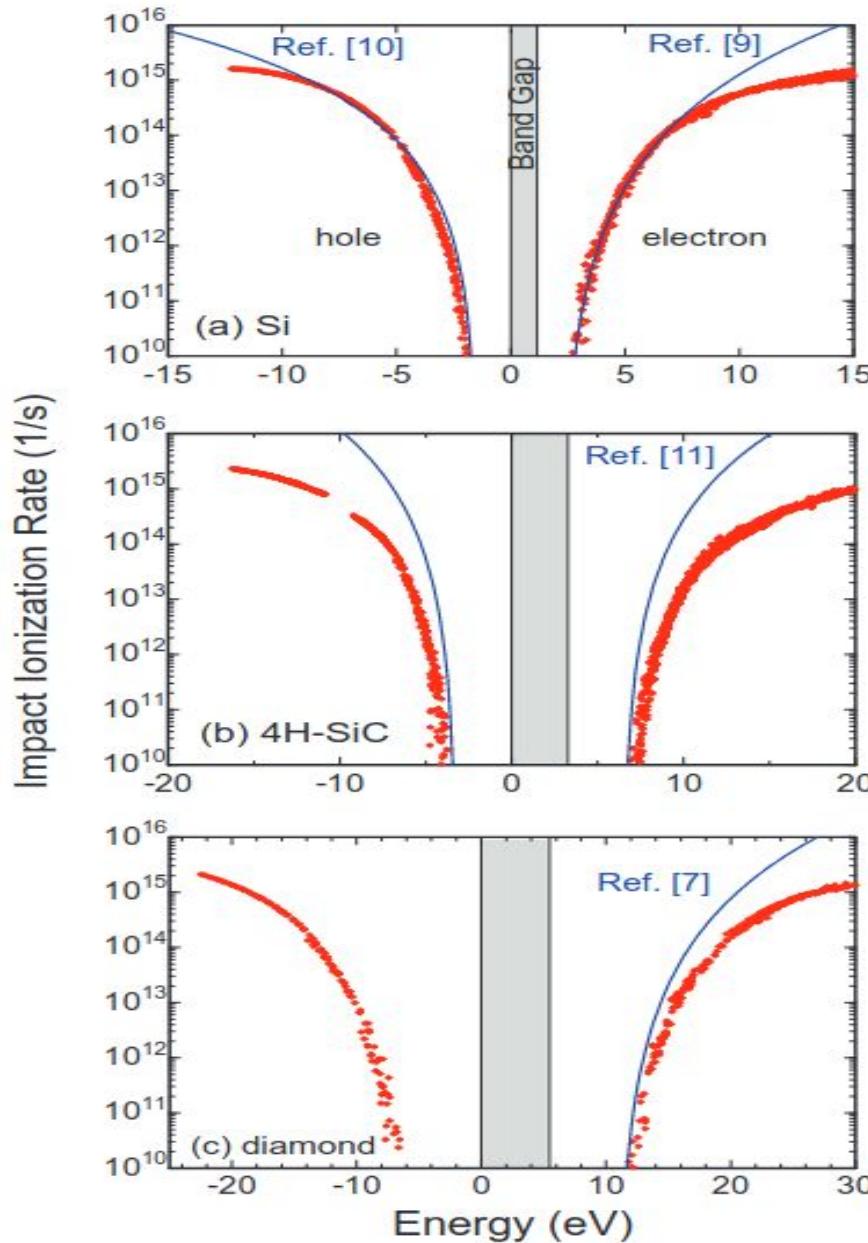
S. A. Chambers et al, Surface Sci 554, 81-89 (2004)

We have accurate description for O<sub>2</sub> band width.

## 2. How QSGW works? Examples.



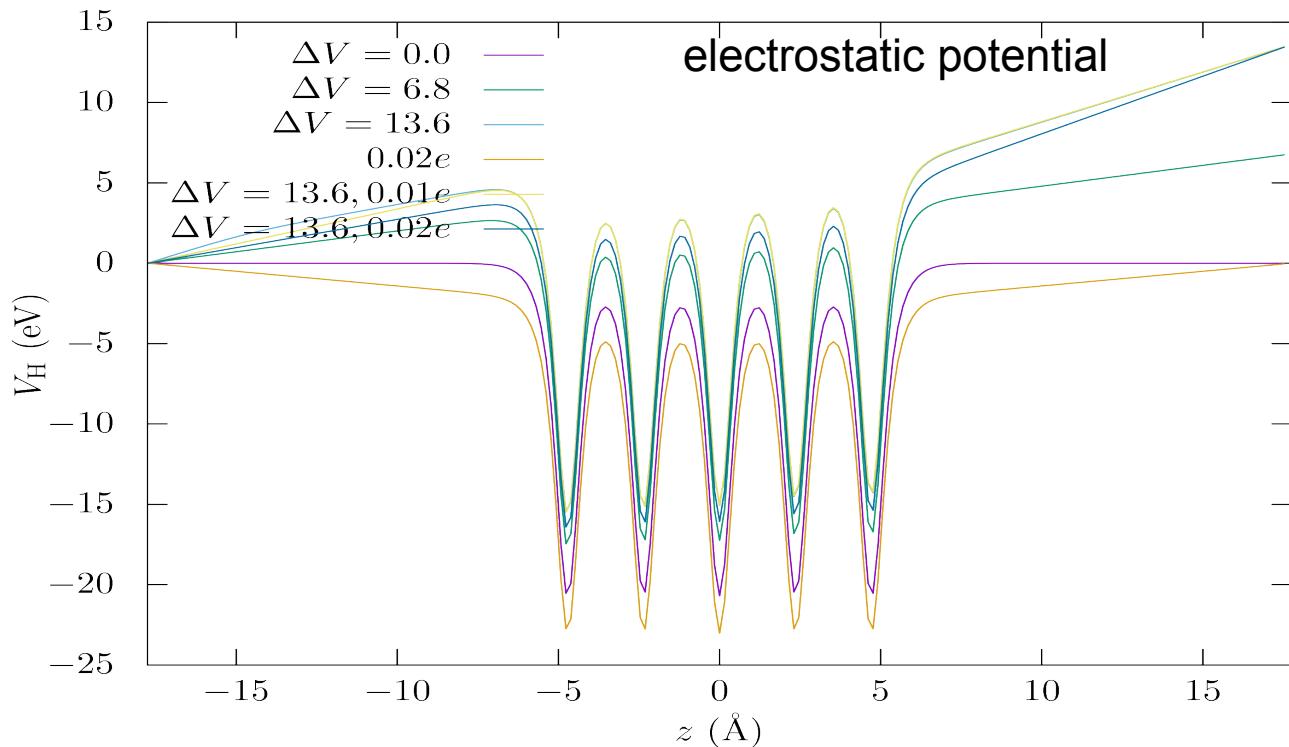
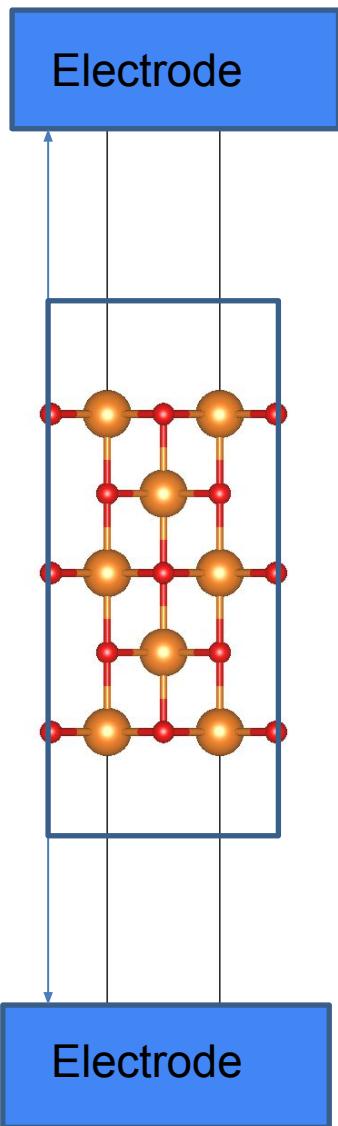
TK and M.van Schilfgaarde  
J. Phys.: Condens. Matter **20** (2008) 295214



**Impact ionization rate  
(Auger effect)**

We can calculate this  
from the imaginary part of  
self energy

# MgO 5ML



## Slab Model

Apply electric field to the Slab model.

Thus we can perform problems such as Field emission with ESM+QSGW.

## Spin susceptibility for Fe (a developments, apart from QSGW)

1000

(a)  $\text{Im}[\text{Tr}(R^{+-}(q, \omega))]$  $\omega$  [meV]

800

600

400

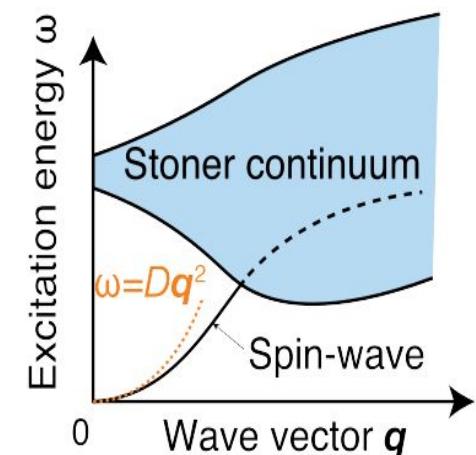
200

 $\Gamma$  $\frac{1}{3}$ [ $\xi$ 00] $\frac{2}{3}$  $\frac{4}{5}$ 

H



We see Spin waves, Multiple Stoner boundaries.



## Standard Heisenberg model

$$\hbar \dot{\mathbf{S}}_{\mathbf{R}}(t) = \mathbf{S}_{\mathbf{R}}(t) \times \sum_{\mathbf{R}'} (J_{\mathbf{R}\mathbf{R}'} \mathbf{S}_{\mathbf{R}'}(t) - g\delta_{\mathbf{R}\mathbf{R}'} \mu_B \mathbf{B}_{\mathbf{R}'}(t)).$$

- Lichtenstein formula gives  $J_{RR''}$

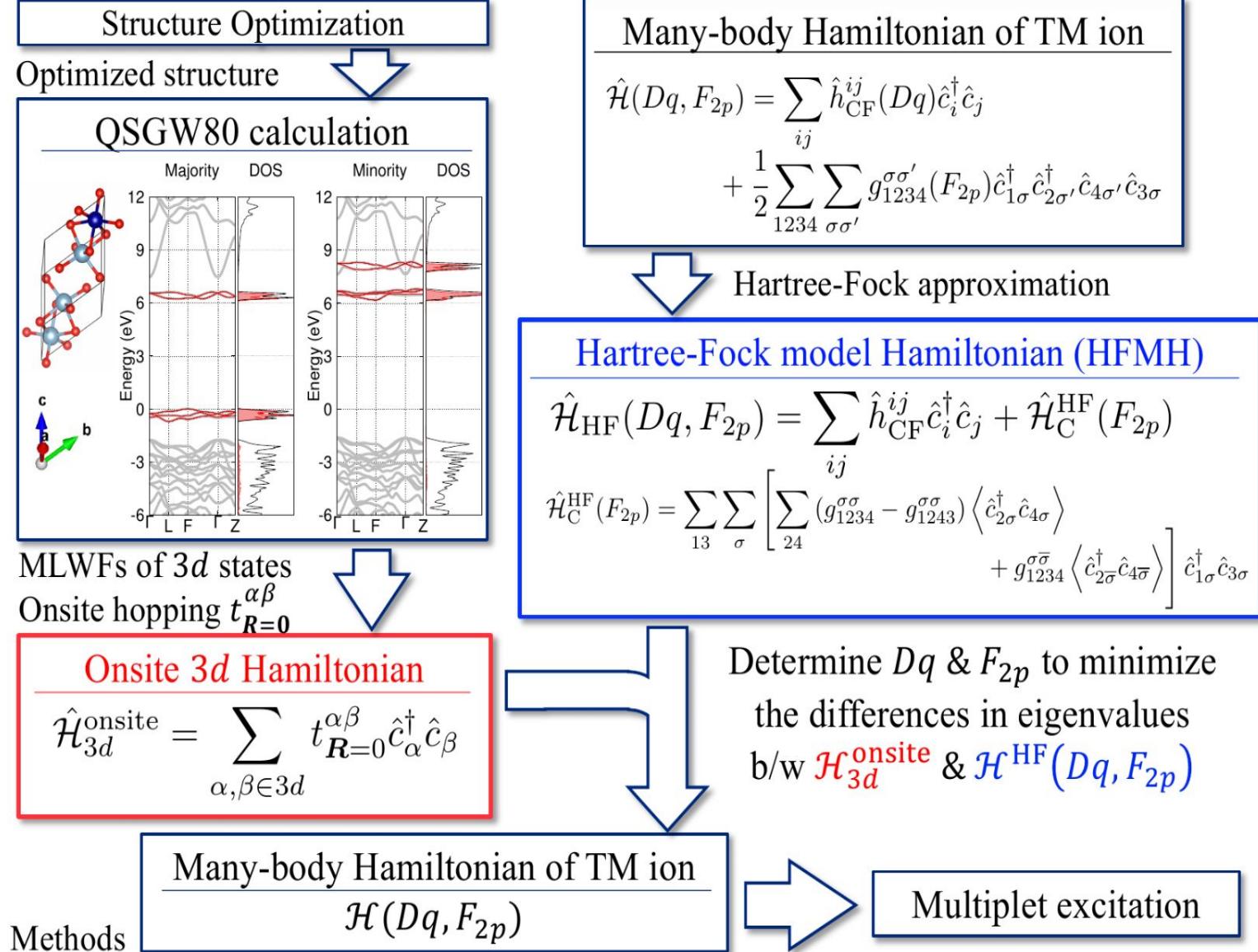
## Extended Heisenberg model (new idea)

$$\hbar \dot{\mathbf{S}}_{\mathbf{R}m}(t) = \mathbf{S}_{\mathbf{R}m}(t) \times \left( \sum_{\mathbf{R}'m'} \int_{-\infty}^{\infty} dt' (J_{\mathbf{R}m\mathbf{R}'m'}(t-t') \mathbf{S}_{\mathbf{R}'m'}(t') - g\mu_B \mathbf{B}_{\mathbf{R}'m'}(t') \delta(t-t')) \right)$$

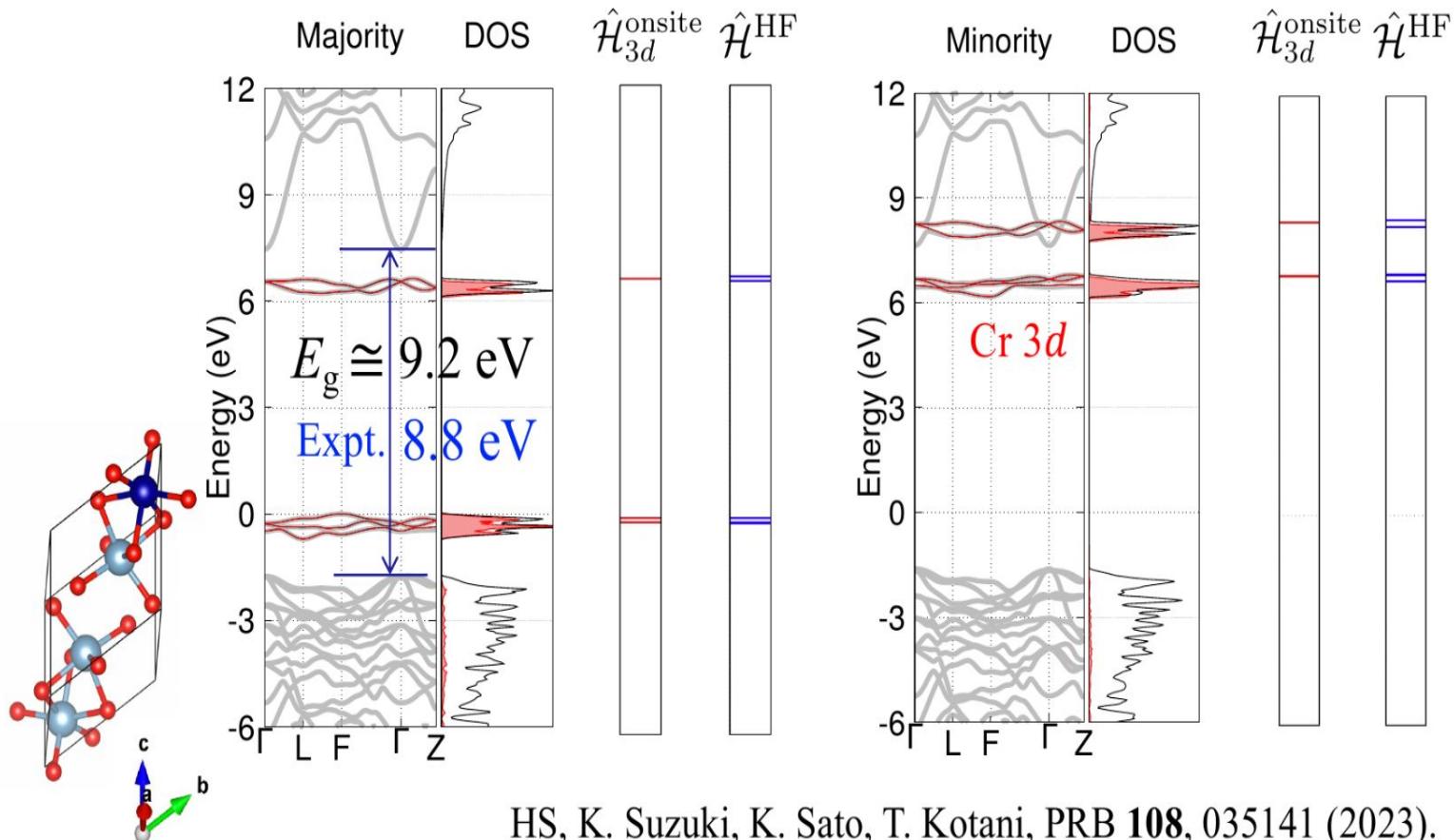
Spin fluctuation spectrum gives  $J_{RmR'm'}(t-t')$ .  
This specifies the non-Hermitian dynamics beyond LLG

# Ruby : Cr<sup>3+</sup> in Al<sub>2</sub>O<sub>3</sub>

Determine many-body model Hamiltonian.



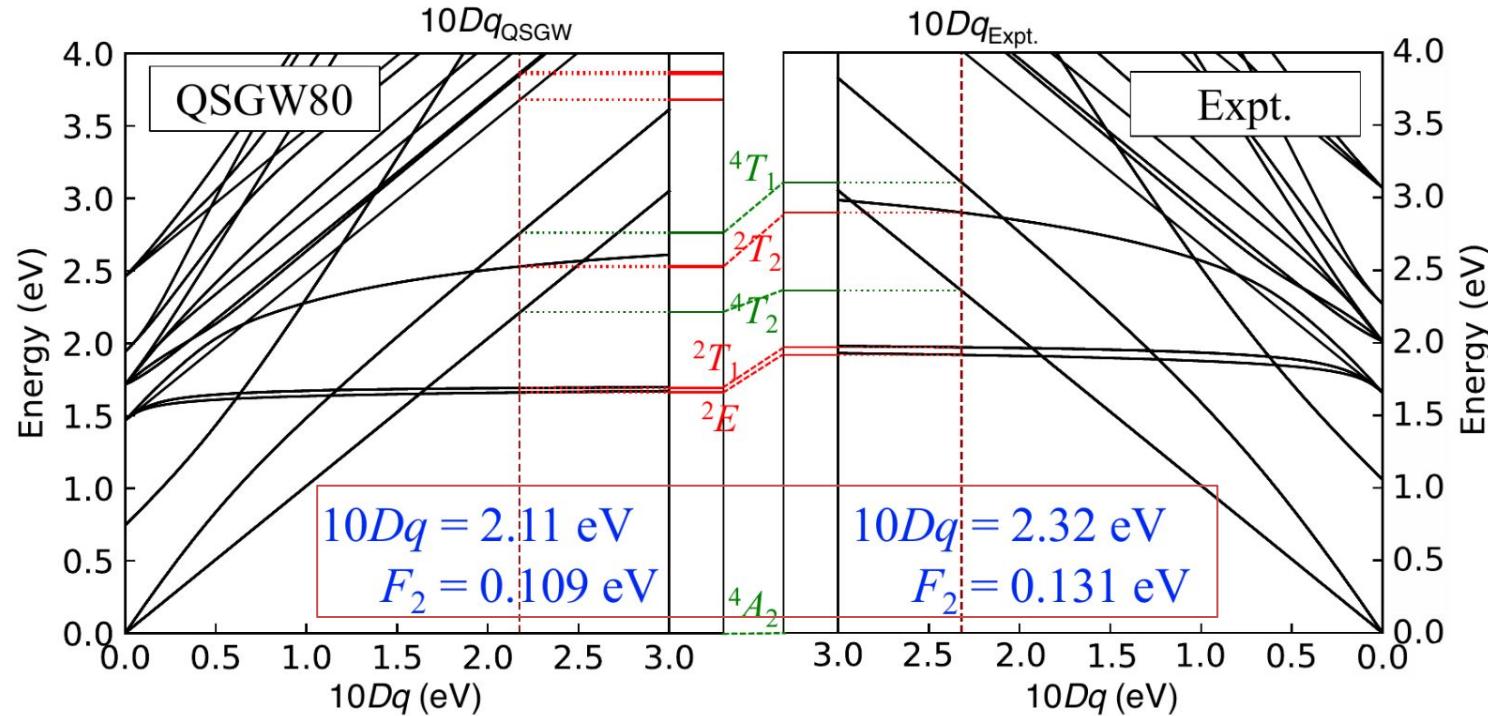
# Electronic structure of $\alpha\text{-Al}_2\text{O}_3:\text{Cr}^{3+}$ by QSGW80 7/18



HS, K. Suzuki, K. Sato, T. Kotani, PRB **108**, 035141 (2023).

- ✓ 3d orbitals of  $\text{Cr}^{3+}$  are well localized
- ✓ Good agreement between the eigenvalues of  $\hat{\mathcal{H}}_{3d}^{\text{onsite}}$  and  $\hat{\mathcal{H}}_{HF}$

# The Tanabe-Sugano diagram of $\alpha\text{-Al}_2\text{O}_3:\text{Cr}^{3+}$ 8/18



HS, K. Suzuki, K. Sato, T. Kotani, PRB **108**, 035141 (2023).

- ✓ Our method reproduced the excitation energies of  $\alpha\text{-Al}_2\text{O}_3:\text{Cr}^{3+}$  with  $\sim 10\%$  error

Results

## **Problems for applying QSGW to materials.**

### **1. Robustness**

—> Automatic setting.

- Automatic setting for basis set for eigenfunction: LMTO+LAPW+Lo method.  
(LAPW only up to ~3Ry)
- Mixed product basis to expand products of eigenfunctions.

Apply QSGW automatically to crystal structures in the Material Project.

### **2. Computational speed**

—> GPU implementation

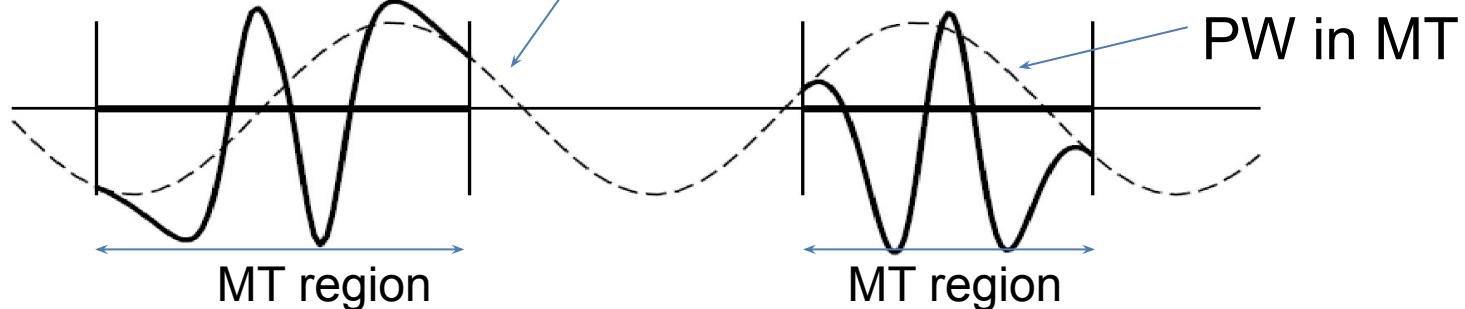
ecalj package is based on the

PMT method = a mixed basis method with APW+MTO.

TK,H.Kino,H.Akai, J. Phys. Soc. Jpn. 84, 034702 (2015)

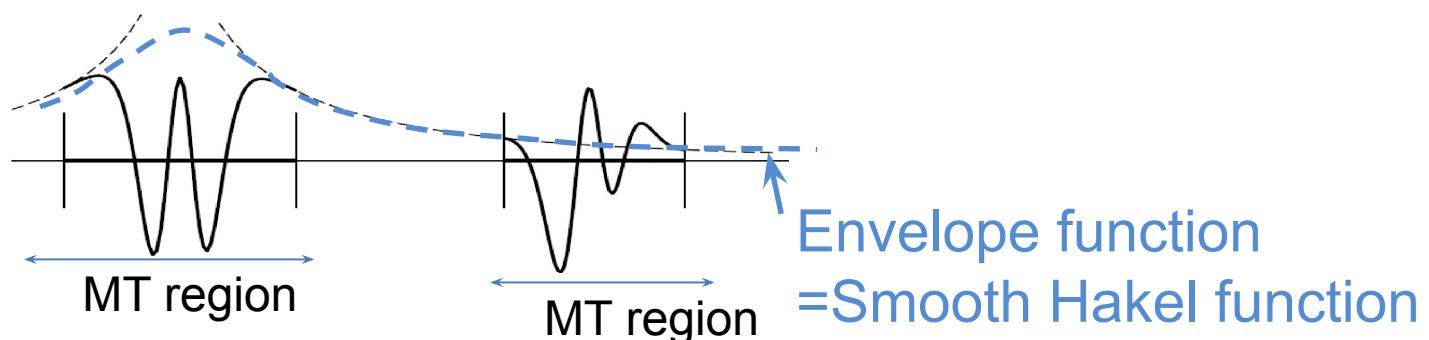
APW

Envelope function = PlaneWave(PW)



MTO

Very low-energy APWs only  $\sim 3\text{Ry}$ .

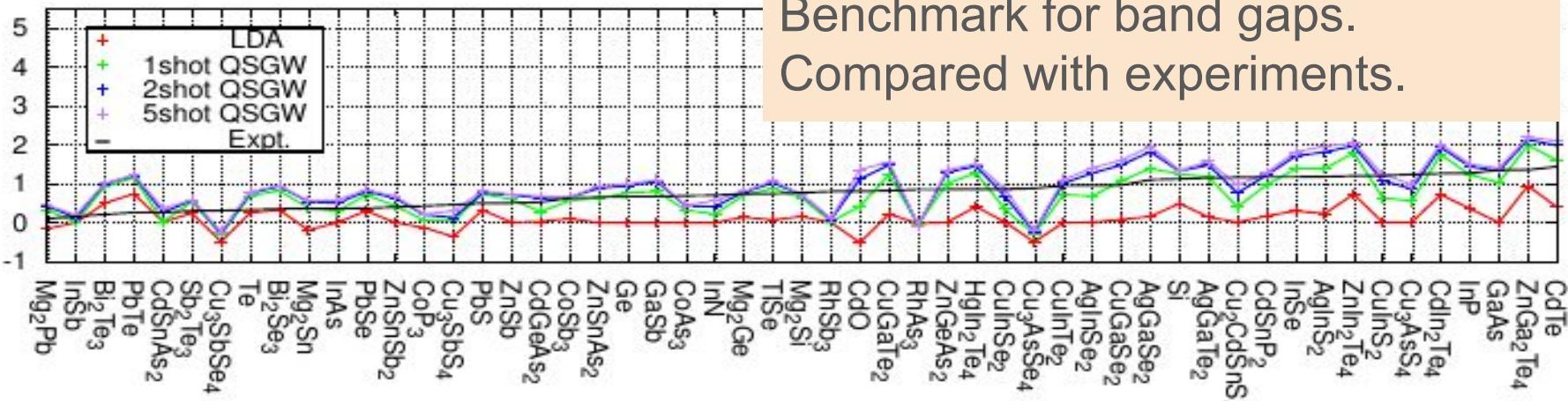


Very short-range MTOs only (damping factor  $\sim 1\text{a.u.}$ )

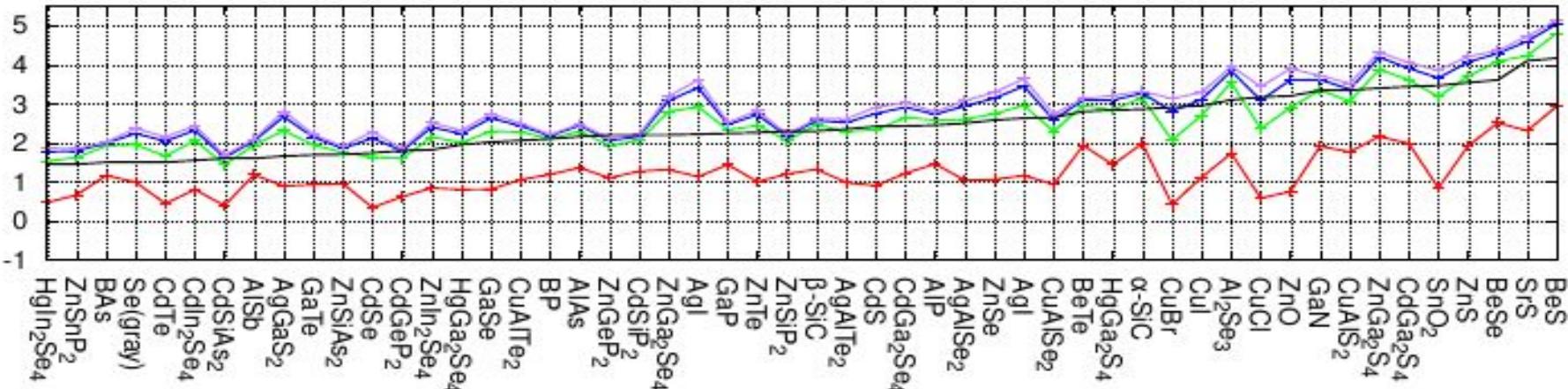
### 3. Automatic QSGW

Benchmark for band gaps.  
Compared with experiments.

( $\Delta E$ )



( $\Delta E$ )



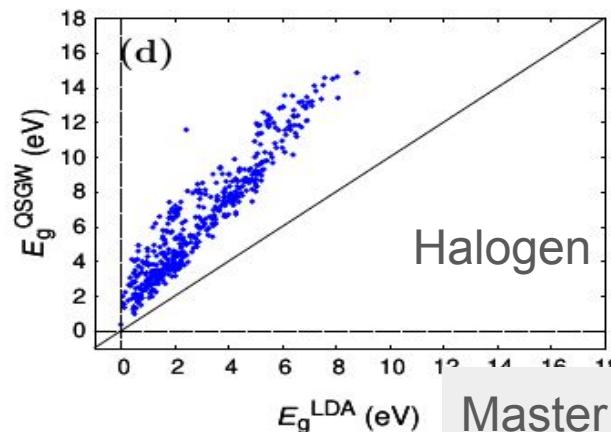
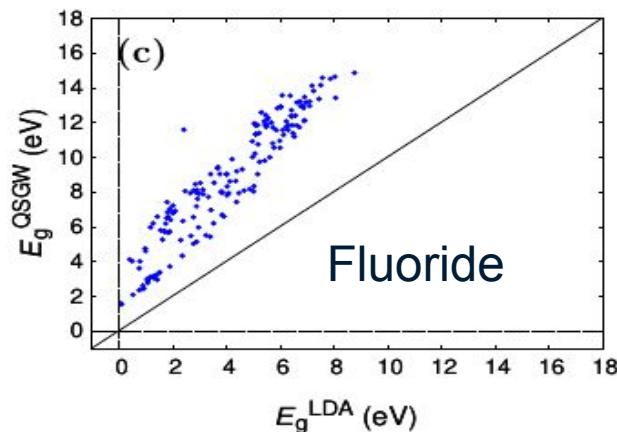
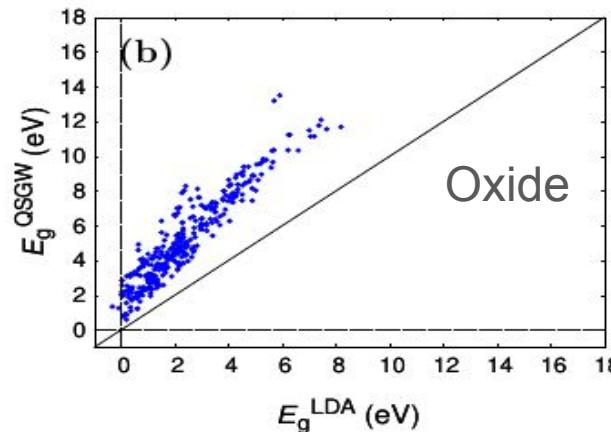
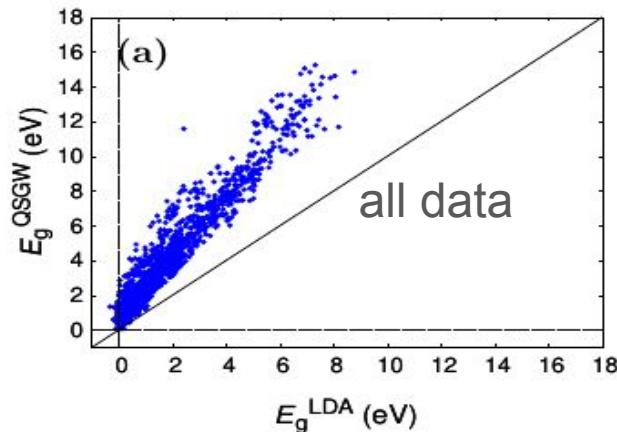
- Materials for experimental Band gap available (Black line).
- No SOC
- We see systematic over estimation in QSGW100.  
(QSGW80 results are not shown)
- Material project may give a little wrong crystal structures.

### 3. Automatic QSGW

Massive calculation for material design:

S.Takano (osaka-u, K.Sato group)

~1500 MaterialProject samples . No Spin Orbit Coupling.  
Without 4f/5f, Band gap in GGA, non-magnetic,  $\leq 8$  atoms/cel.

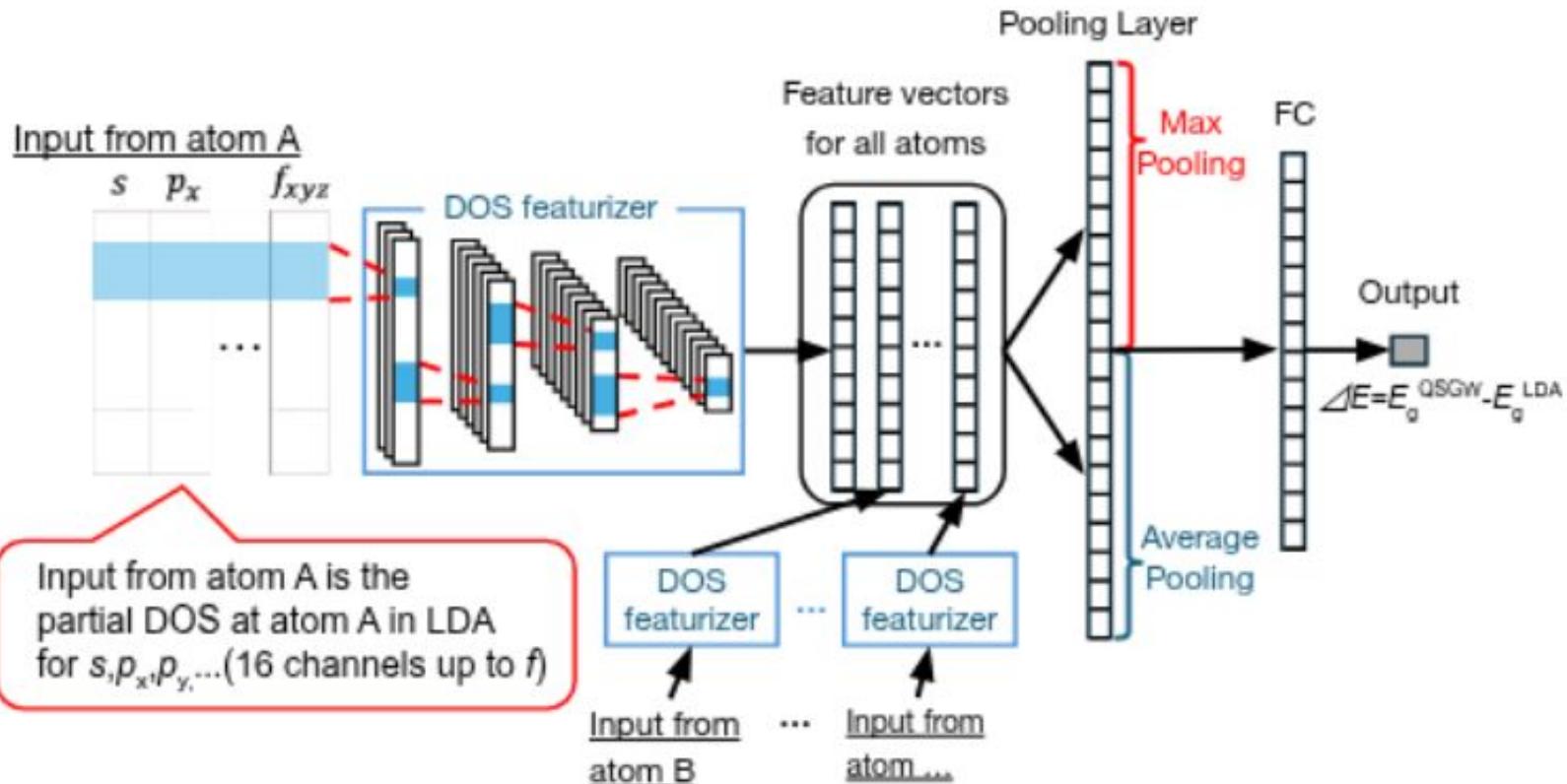


### 3. Automatic QSGW for machine learning

DOSnp

(Modify DOSNET: Fung, V., Hu, G., Ganesh, P. et al. *Nat Commun* 12, 88 (2021))

From PDOS in LDA, we predict QSGW band gap.



### 3. Automatic QSGW for machine learning

DOSnp test(materials not in training data set)

MPid	$N_a$	Composition	space group	LDA	QSGW	DOSnp	Literatures	
1105229	4	$\beta - \text{GaCuO}_2$	Pna2 <sub>1</sub>	$E_g(\text{eV})$ $m_e^*$	0.10 0.23	0.61 0.24	1.81	1.47 [37]
1243	10	$\alpha - \text{Ga}_2\text{O}_3$	R $\bar{3}$ c	$E_g(\text{eV})$ $m_e^*$	2.73 0.23	5.53 0.24	5.3 [38]	0.3-0.32 [39]
886	10	$\beta - \text{Ga}_2\text{O}_3$	C2/m	$E_g(\text{eV})$ $m_e^*$	2.16 0.23	5.22 0.25	5.07 0.28	4.9 [38] 0.28 [40]
1143	10	$\alpha - \text{Al}_2\text{O}_3$	R $\bar{3}$ c	$E_g(\text{eV})$ $m_e^*$	5.87 0.38	9.69 0.35	9.59 0.37	8.8 [38] 0.3 [41]
22323	10	$\alpha - \text{In}_2\text{O}_3$	R $\bar{3}$ c	$E_g(\text{eV})$ $m_e^*$	1.08 0.15	3.19 0.19	3.06 0.19	3.75 [42]
542734	10	$\alpha - \text{Rh}_2\text{O}_3$	R $\bar{3}$ c	$E_g(\text{eV})$	0.54	1.75	1.69	1.41 [43]
11794	16	$\beta - \text{AlAgO}_2$	Pna2 <sub>1</sub>	$E_g(\text{eV})$ $m_e^*$	0.71 0.30-0.43	3.64 0.32-0.42	3.16 0.33-0.41	2.95 [44] -
1096976	16	$\alpha - \text{GaAgO}_2$	R3m	$E_g(\text{eV})$ $m_e^*$	0.25 0.17	2.12 0.19-0.26	2.06 0.22	2.4 [44] 0.27-0.42 [45] <sup>U</sup>
1105293	16	$\beta - \text{GaAgO}_2$	Pna2 <sub>1</sub>	$E_g(\text{eV})$ $m_e^*$	0.21 0.16-0.27	2.53 0.22-0.28	2.10 0.24-0.30	2.1 [46] 0.14-0.33 [45] <sup>U</sup>

good agreement

(in preparation)

Machine Learning Band Gap Predictions: Linking Quasiparticle Self-Consistent GW  
and LDA-Derived Partial Density of States

Shota Takano,<sup>1,\*</sup> Takao Kotani,<sup>2,3</sup> Masao Obata,<sup>4</sup> Hitoshi Fujii,<sup>5</sup> Kazunori Sato,<sup>1,3,6</sup> Harutaka Saito,<sup>1</sup> and Tatsuki Oda<sup>4,3</sup>

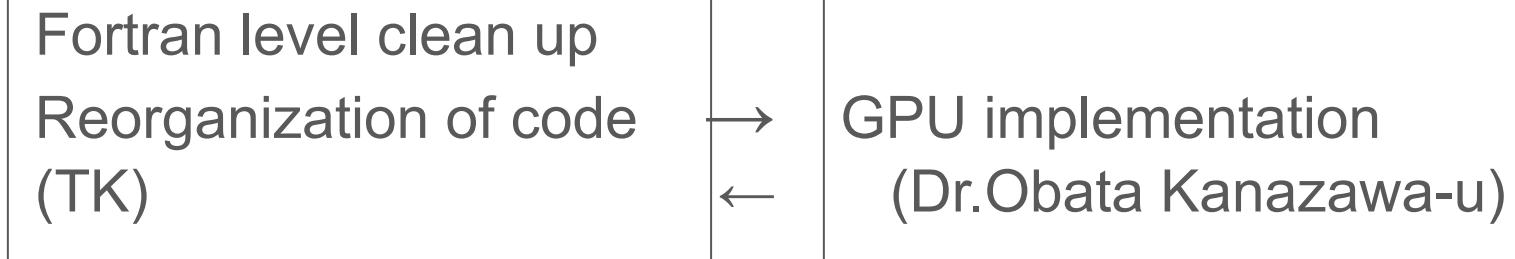
## QSGW fits to GPU:

### Another group:

H.Ness et al, PRB110,195301(2024). QSGW for  
138 atoms in a cell for InAs/AI interface.

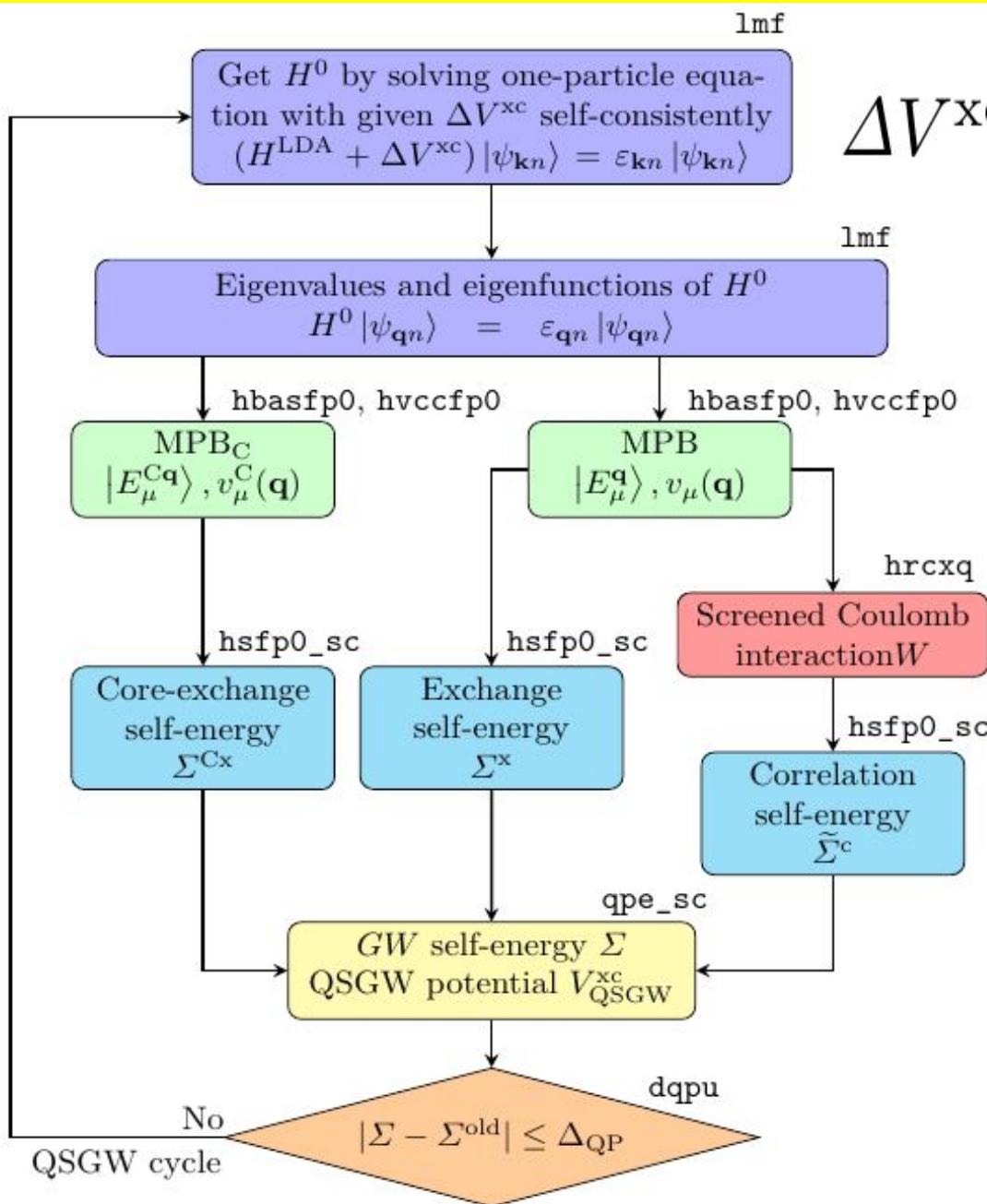
They use **1152 GPU** (NVIDIA A1).

- Their code and our code have the same origin.
- A little different basis set and so on.
- Pass data via modules in f90



ecalj: OpenSource(AGPLv3). It works on ohtaka and kugui (ISSP).

### 3. GPU implementation



$$\Delta V^{xc} = V_{QSGW}^{xc} - V_{LDA}^{xc}$$

Expensive parts are

1. Core exchange
2. Exchange
3. W
4. Correlation

### 3. GPU implementation

For example, W requires calculation of the Polarization

$$\text{Im}[\Pi_{\mu\nu}(\mathbf{q}, \omega_j)] = \frac{\pi}{i} \sum_{\mathbf{k}} \sum_n^{\text{BZ}} \sum_{n'}^{\text{occ unocc}} Z_{\mu n n'}^{\mathbf{k}, \mathbf{q} + \mathbf{k}} [Z_{\nu n n'}^{\mathbf{k}, \mathbf{q} + \mathbf{k}}]^* w_{n' n}^{\mathbf{q}, \mathbf{k}}(\omega_j),$$

$$Z_{\mu n' n}^{\mathbf{q} - \mathbf{k}, \mathbf{q}} = \langle E_{\mu}^{\mathbf{k}} \Psi_{\mathbf{q} - \mathbf{k} n'} | \Psi_{\mathbf{q} n} \rangle$$

For the T2SL InAs(10)/GaSb(10) (40 atoms per cell), we have

$\mathbf{q}$ : 9

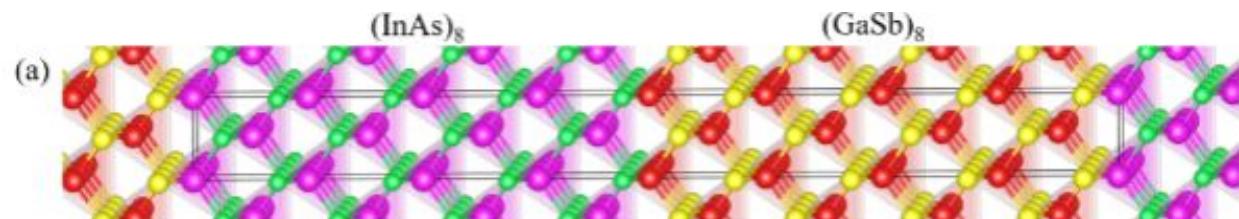
$\mathbf{k}$ : 16

noocc: 460

nunocc: 1348

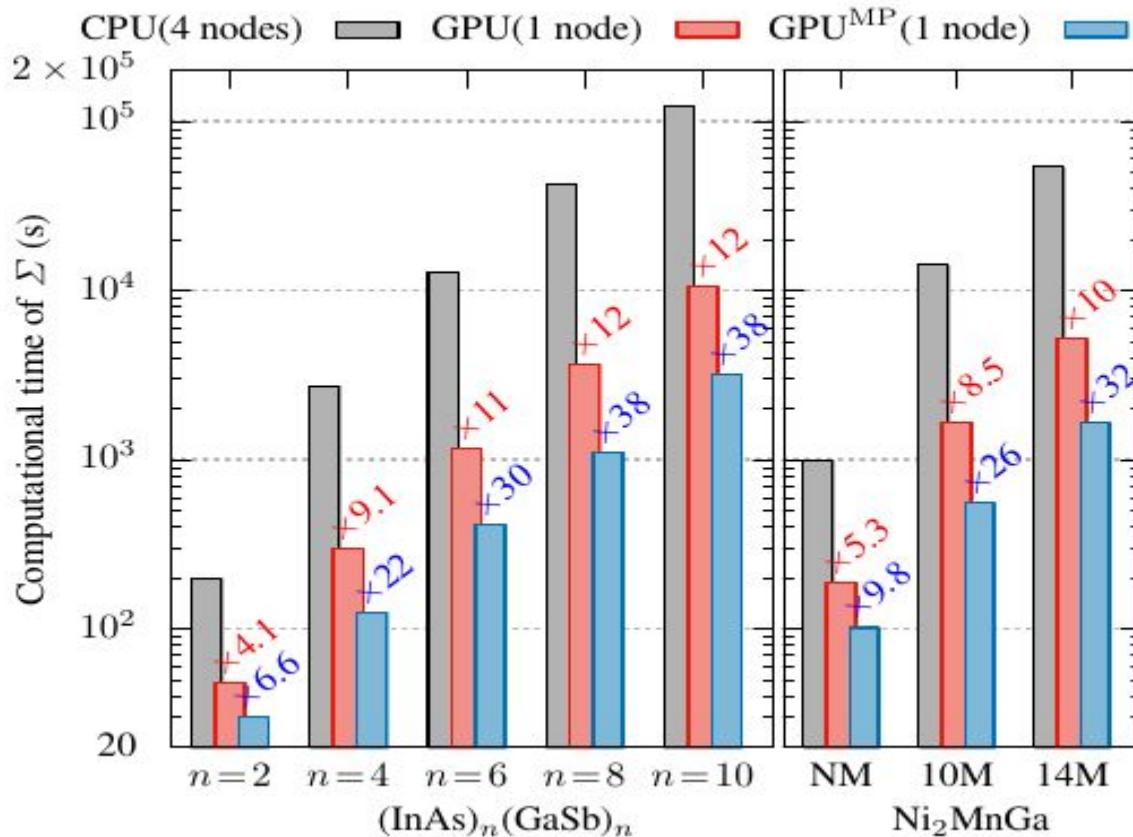
$\mu, \nu$  : 5231

$\omega_j$  : 100



Huge computational size.

### 3. GPU implementation



OpenACC, cuSOLVER

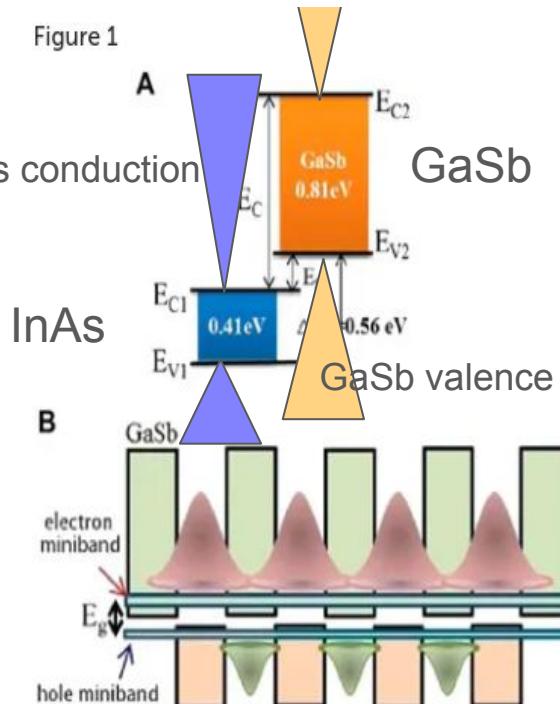
		speed
CPU	: 4 node (128 MPI process, 4x128= 512 cores)	x 1
GPU	: 4 GPU (NVIDIA A1), Kugui(ISSP)	x 12
GPU(MP)	: 4 GPU, Mixed precision with TF32	x 38

### 3. GPU implementation

#### TypeII superlattice InAs(10)/GaSb(10) in QSGW80

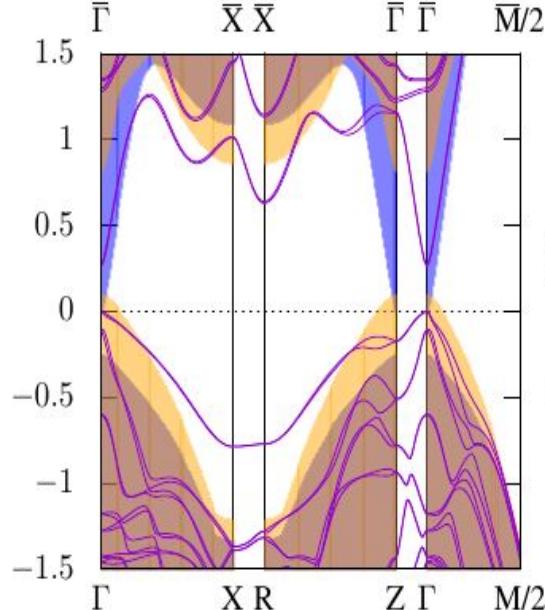
(SOC included)

Figure 1

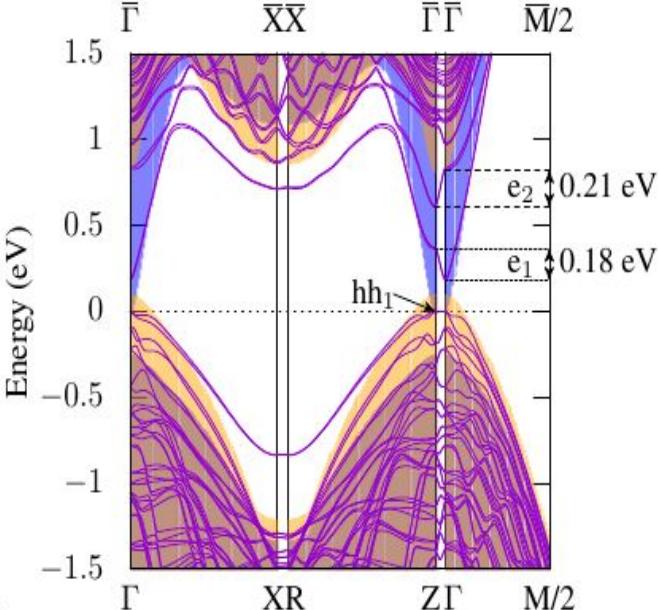


S.Fang, et al, Front.Phys, 14Apr(2022)  
<https://doi.org/10.3389/fphy.2022.822800>

InAs(3)/GaSb(3)



InAs(10)/GaSb(10)



Purple: InAs bulk

Orange: GaSb bulk

- Quantum well is described well(in preparation, M.Obata,T.Kotani, and T.Oda)
- 0.1 eV staggered band structure. Consistent with previous results.
- Easier than tight-binding theory

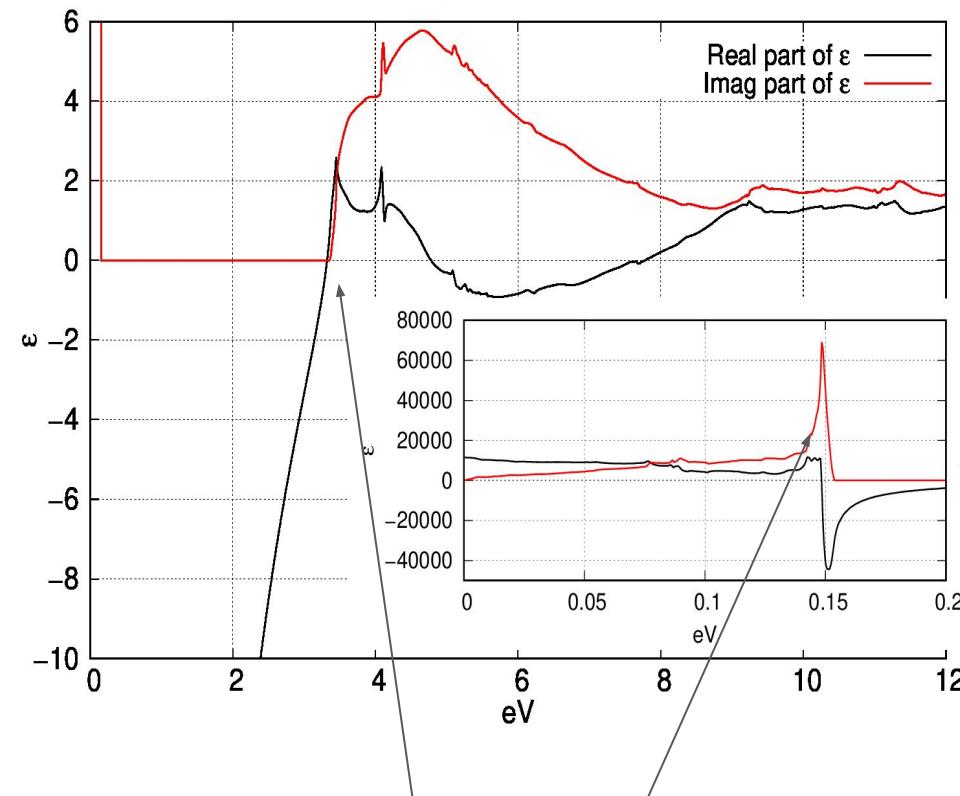
## Summary:

- QSGW works well for band structures, band gap and so on.
- Spin fluctuations, Lifetime, Cr<sup>3+</sup> impurity.
- We have applied QSGW to the dataset in the Material Project.  
Apply QSGW automatically to ~1500 materials.  
It can be used for PDOS-based Machine Learning.
- GPU implementation. GPU is very suitable for QSGW.  
InAs/GaSb(40 atoms) costs just ~3000 sec for self-energy  
in mixed precision calculation with 4GPU.

Than you!

## Dielectric function at small $q$ for metal

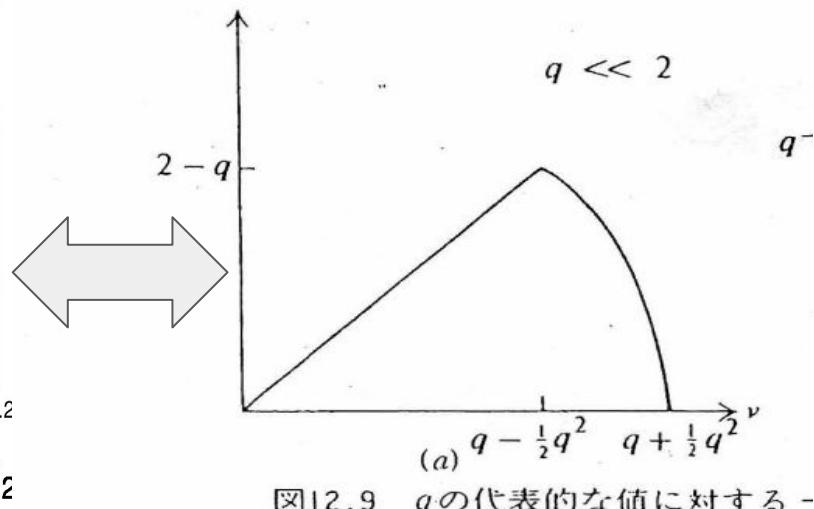
Calculated  $\epsilon$  for Ag at  $|q|=0.0154 \text{ \AA}^{-1}$  in QSGW80



PseudoPlasmon Pole when  $1/\epsilon$  is large.

Drude weight at finite  $q$

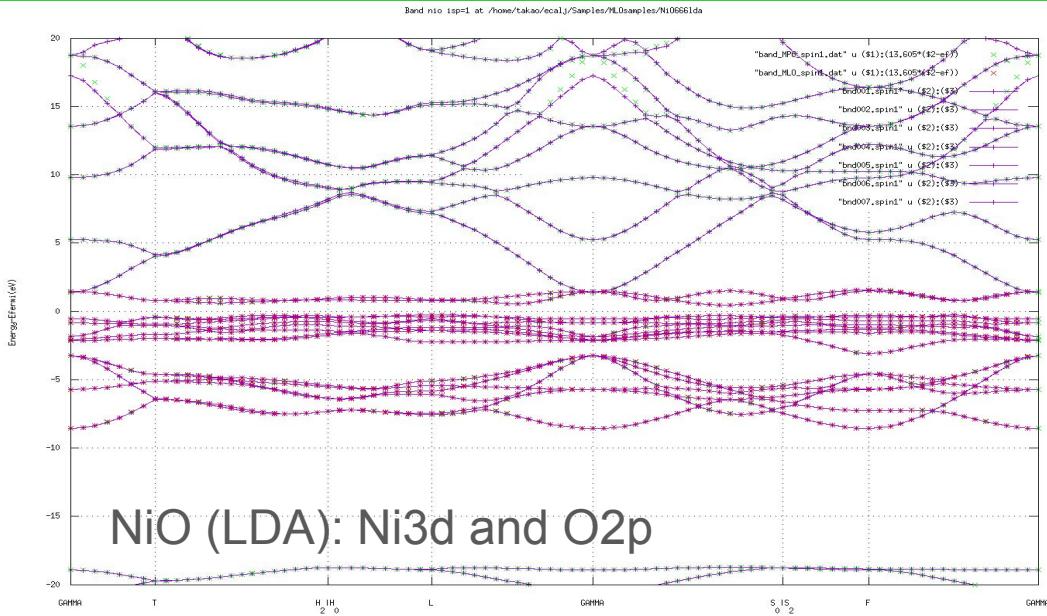
I80 第2部 基底状態(ゼロ温度)の定式化



Fetter & Walecka  
Drude term for small  $q$

## Developing....

Automatic band modeling based on the Muffin-tin orbitals ( $Y_{lm}$  preserved local orbitals. Overlap matrix needed. )



Red dots are models, while purple are full band structures.

1. Specify atomic orbitals
2. Need to set upper limit of inner window in cases.

(I am now trying to remove the second point).

