GW+BSE

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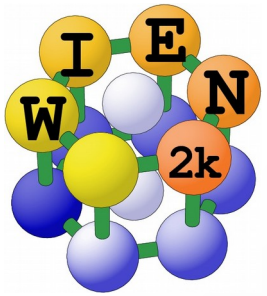
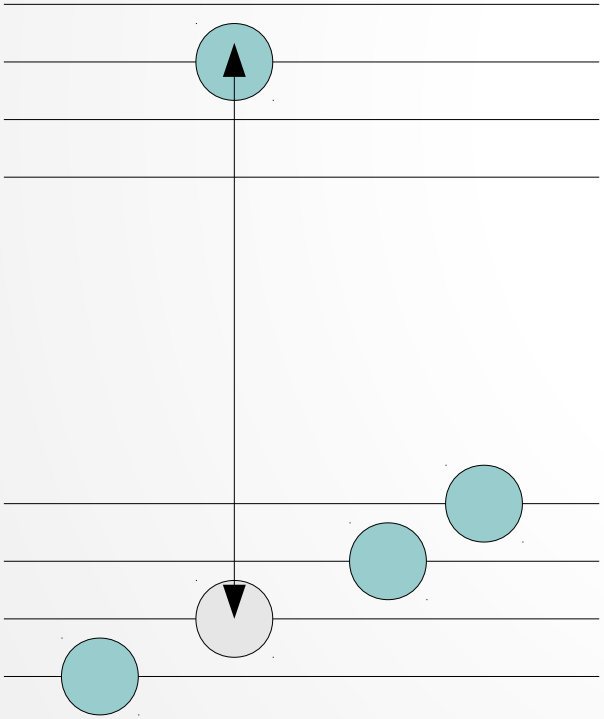


outline

- Thanks to Hong Jiang from College of Chemistry, Peking University, contributing GW package, and portion of the slides
- BSE package contributed by Robert Laskowski

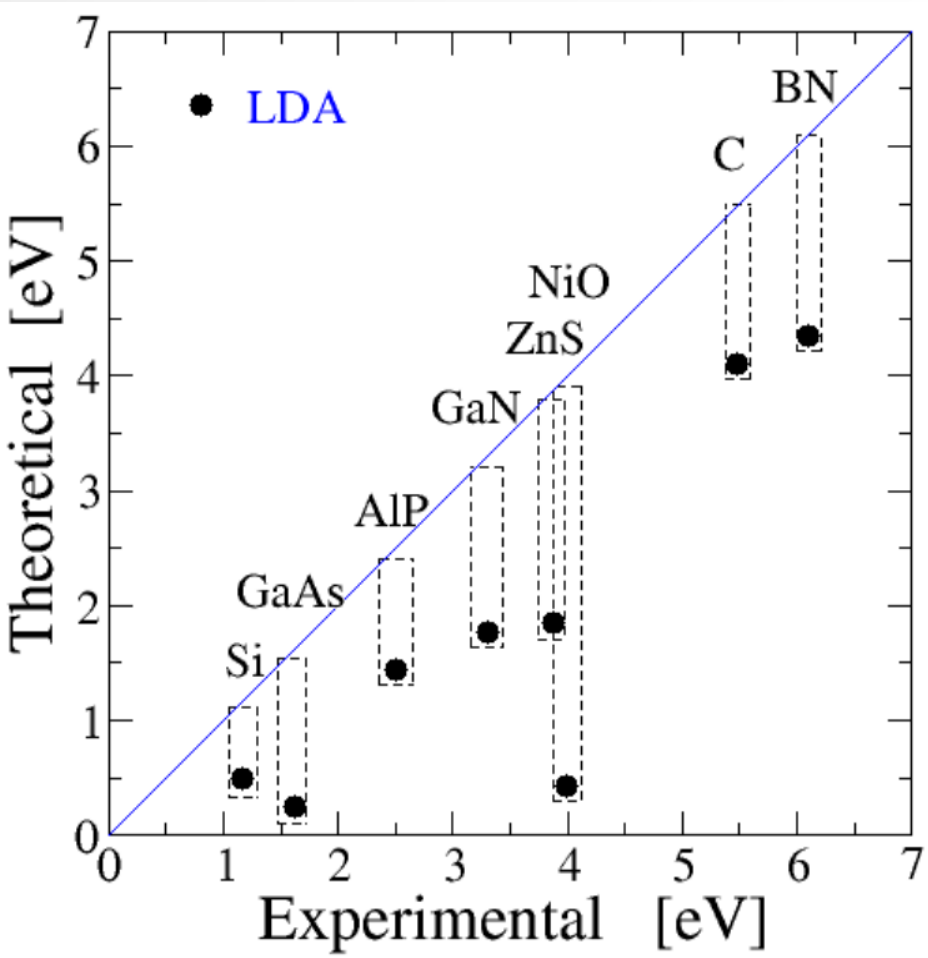
Simple picture, independent particles

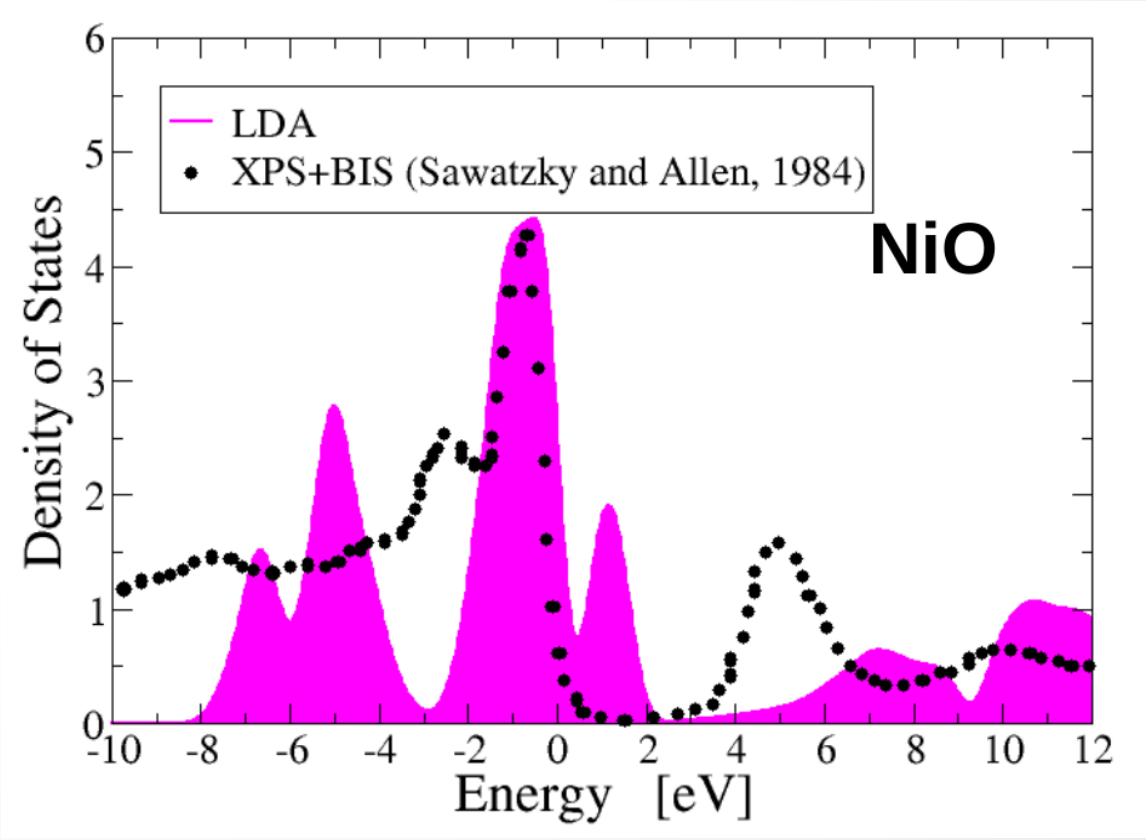
$$\Im(\epsilon_{ij}) = \frac{16\pi^2}{\Omega\omega^2} \sum_{vck} \langle vk | p_i | ck \rangle \langle ck | p_j | vk \rangle \delta(\varepsilon_{kc} - \varepsilon_{vk} - \omega)$$



- Energy levels calculated within DFT are not true addition and removal energies
- absorption or emission is more complex process than just electrons jumping between energy levels

Energy levels calculated within DFT





Beyond standard DFT

- Effective functionals (mBJ, F. Tran)

F. Tran, P. Blaha PRL 102, 226401 (2009)

$$v_{x,\sigma}^{\mathrm{MBJ}}(\mathbf{r}) = c\,v_{x,\sigma}^{\mathrm{BR}}(\mathbf{r}) + (3c-2)\frac{1}{\pi}\sqrt{\frac{5}{12}}\sqrt{\frac{2t_\sigma(\mathbf{r})}{\rho_\sigma(\mathbf{r})}},$$

$$v_{x,\sigma}^{\mathrm{BR}}(\mathbf{r}) = -\frac{1}{b_\sigma(\mathbf{r})}\left(1 - e^{-x_\sigma(\mathbf{r})} - \frac{1}{2}x_\sigma(\mathbf{r})e^{-x_\sigma(\mathbf{r})}\right)$$

- scissor shift

$$\varepsilon_{ck}^{QP} = \varepsilon_{ck}^{LDA} - \Delta_{scissor}$$

$$\varepsilon_{vk}^{QP} = \varepsilon_{vk}^{LDA}$$

$$\langle vk|p|ck\rangle^{QP} = \frac{E_{ck}-E_{vk}}{\varepsilon_{ck}-\varepsilon_{vk}}\langle vk|p|ck\rangle$$

$$\Im\,\varepsilon(\omega) = \Im\,\varepsilon(\omega-\Delta)$$

non-locality of the self energy operator or scissor shift

Beyond standard DFT

- Hybrid DFT (thanks to F. Tran in wien2k)

  H-F Exchange energy included into KS theory

$$E_{x,\mathrm{vv}}^{\mathrm{HF}} = -\frac{1}{2}\sum_{\sigma}\sum_{n,\mathbf{k},n',\mathbf{k}'} w_{n\mathbf{k}}^{\sigma} w_{n'\mathbf{k}'}^{\sigma} \int_{\Omega}\int_{\mathrm{crystal}} \psi_{n\mathbf{k}}^{\sigma *}(\mathbf{r})\psi_{n'\mathbf{k}'}^{\sigma}(\mathbf{r})$$
$$\times\, v(|\mathbf{r}-\mathbf{r}'|)\psi_{n'\mathbf{k}'}^{\sigma *}(\mathbf{r}')\psi_{n\mathbf{k}}^{\sigma}(\mathbf{r}')d^3r'd^3r,$$

F. Tran, P. Blaha PHYSICAL REVIEW B 83, 235118 (2011)

- GW method (available for wien2k)

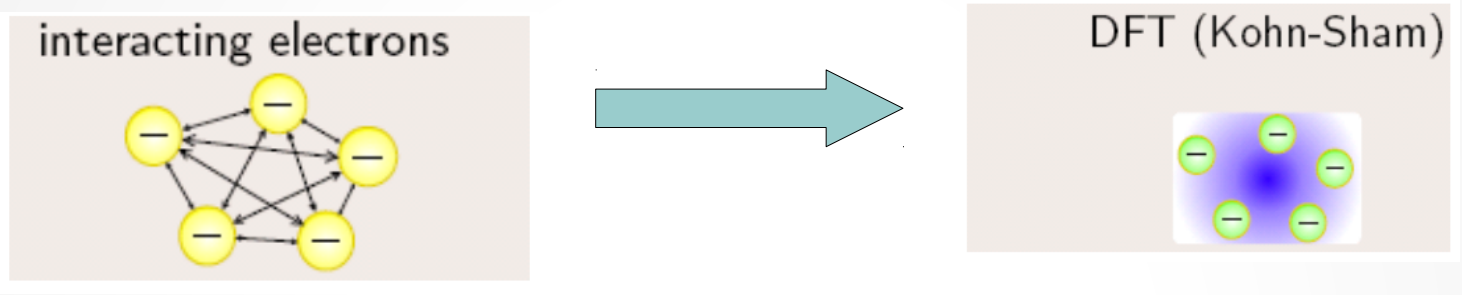
Self-energy $$\Sigma(r,r',\omega)=\frac{i}{2\pi}\int d\omega' G(r,r,\omega-\omega')W(r,r',\omega)$$

$$\varepsilon_{nk}^{QP}=\varepsilon_{nk}^{LDA}-\langle nk|\Sigma(\varepsilon_{nk}^{QP})-V_{xc}^{LDA}|nk\rangle$$

M. S. Hybertsen and S. G. Louie, Phys. Rev. Lett. 55, 1418 (1985)
M. S. Hybertsen and S. G. Louie, Phys. Rev. B 34, 5390 (1986)
R. Gómez-Abal, et al, PRL 101, 036402 (2008).

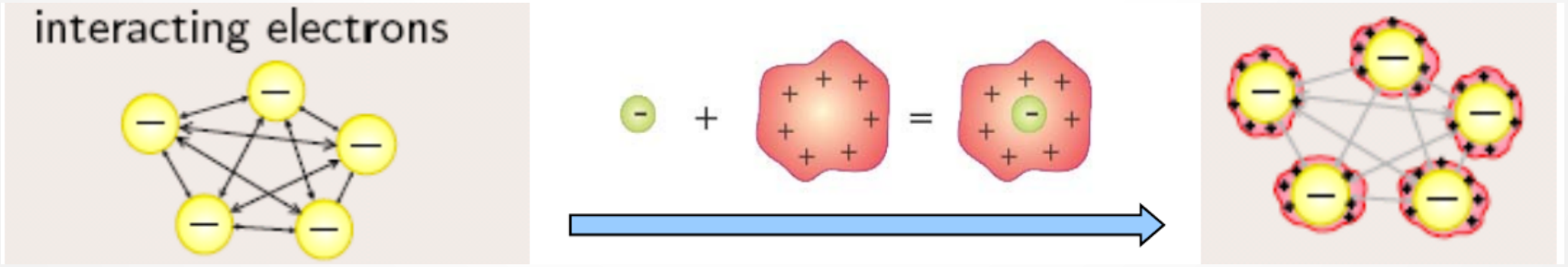
Quasi-particles

- Can mean field approach do the good job ?



$$\left[-\frac{\nabla^2}{2} + V_{\rm ext}(\mathbf{r}) + V_{\rm H}(\mathbf{r}) + V_{\rm xc}(\mathbf{r})\right]\psi_{n\mathbf{k}}(\mathbf{r}) = \epsilon_{n\mathbf{k}}\psi_{n\mathbf{k}}(\mathbf{r})$$

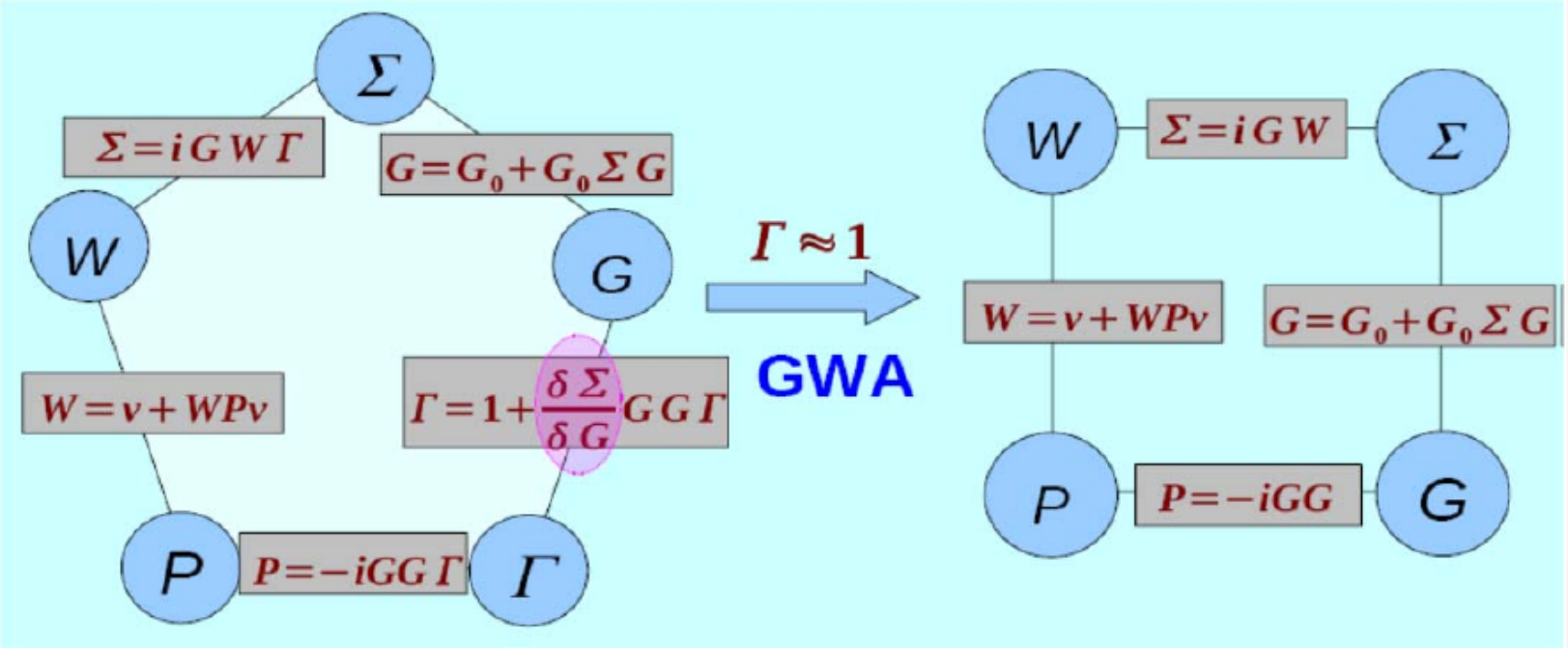
- Quasi-particle approach



$$\left[-\frac{\nabla^2}{2} + V_{\rm ext}(\mathbf{r}) + V_{\rm H}(\mathbf{r})\right]\Psi_{n\mathbf{k}}(\mathbf{r}) + \int d^3\mathbf{r}'\Sigma_{\rm xc}(\mathbf{r},\mathbf{r}';E_{n\mathbf{k}})\Psi_{n\mathbf{k}}(\mathbf{r}') = E_{n\mathbf{k}}\Psi_{n\mathbf{k}}(\mathbf{r})$$

GW approximation

$$\left[-\frac{\nabla^2}{2} + V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r})\right]\Psi_{n\mathbf{k}}(\mathbf{r}) + \int d^3\mathbf{r}'\Sigma_{\text{xc}}(\mathbf{r},\mathbf{r}';E_{n\mathbf{k}})\Psi_{n\mathbf{k}}(\mathbf{r}') = E_{n\mathbf{k}}\Psi_{n\mathbf{k}}(\mathbf{r})$$



Hedin's self-consistent equations

L. Hedin, Phys. Rev. 139, A769 (1965)

F. Aryasetiawan, O.Gunnarsson, Rep. Prog. Phys. (1998)

G_0W_0 Approximation

$$\varepsilon_{n\mathbf{k}}^{(\mathrm{QP})} = \varepsilon_{n\mathbf{k}} + Z_{n\mathbf{k}}\langle\psi_{n\mathbf{k}}|\Sigma_{\mathrm{xc}}(\varepsilon_{n\mathbf{k}}) - V_{\mathrm{xc}}|\psi_{n\mathbf{k}}\rangle$$

$$Z_{n\mathbf{k}} = \left[1 - \left(\frac{\partial}{\partial\epsilon}\langle\psi_{n\mathbf{k}}|\Sigma_{\mathrm{xc}}(\epsilon)|\psi_{n\mathbf{k}}\rangle\right)_{\epsilon=\varepsilon_{n\mathbf{k}}}\right]^{-1}$$

$$\langle\psi_{n\mathbf{k}}|\Sigma_{\mathrm{xc}}(\omega)|\psi_{n\mathbf{k}}\rangle = N_c^{-1}\sum_{\mathbf{q}}\sum_{m}\sum_{i,j}\frac{i}{2\pi}\int_{-\infty}^{\infty}d\omega' e^{i\omega'\eta} \times \frac{\left[M_{nm}^{i}(\mathbf{k},\mathbf{q})\right]^{*} W_{ij}(\mathbf{q},\omega') M_{nm}^{j}(\mathbf{k},\mathbf{q})}{\omega + \omega' - \varepsilon_{m\mathbf{k}-\mathbf{q}}}$$

$$M_{nm}^{i}(\mathbf{k},\mathbf{q}) \equiv \int \left[\chi_i^{\mathbf{q}}(\mathbf{r})\ \psi_{m\mathbf{k}-\mathbf{q}}(\mathbf{r})\right]^{*}\psi_{n\mathbf{k}}(\mathbf{r})d\mathbf{r}$$

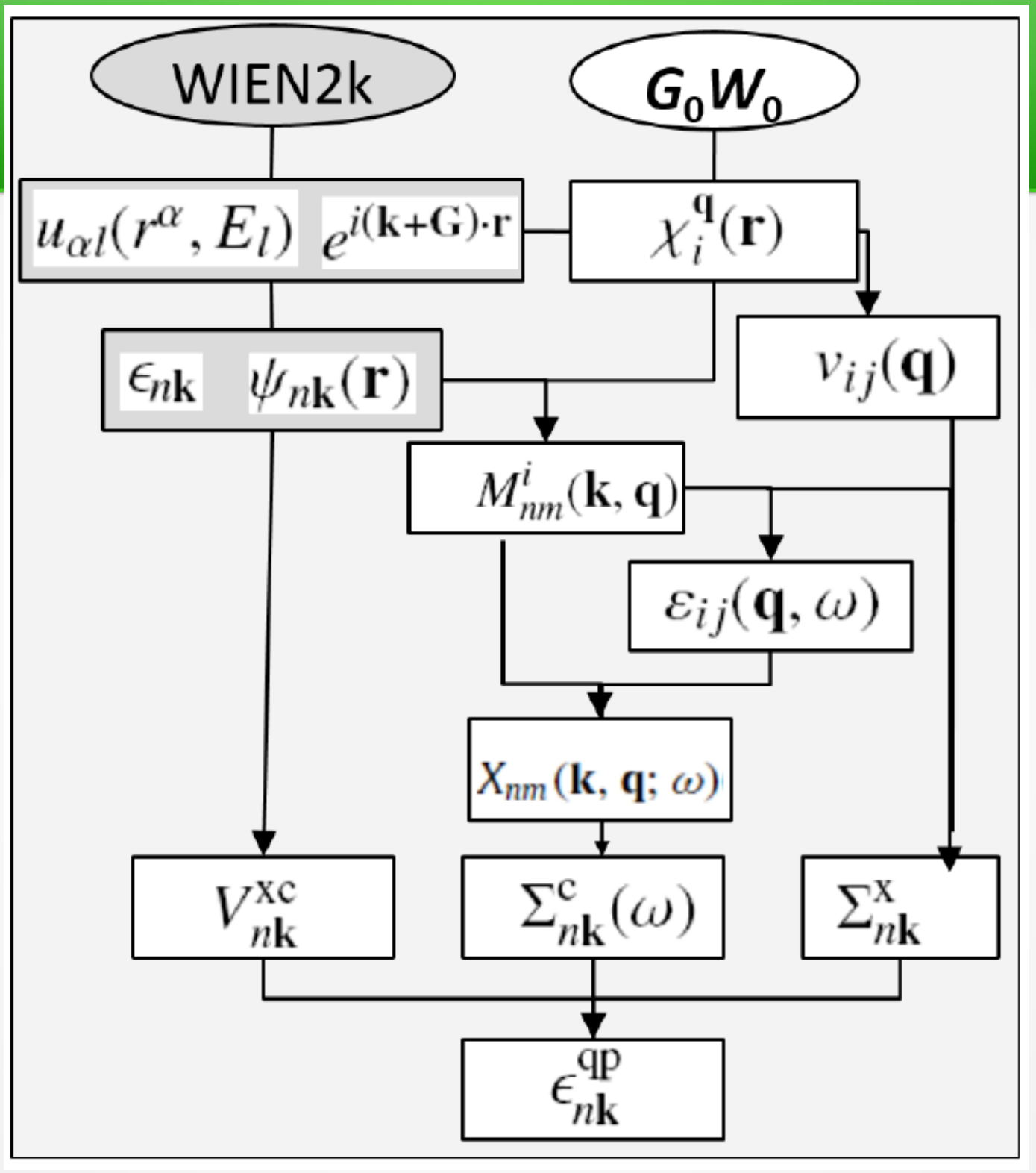
$$W(\mathbf{r},\mathbf{r}';\omega) = \int \varepsilon^{-1}(\mathbf{r},\mathbf{r}'';\omega)v(\mathbf{r}''-\mathbf{r}')d\mathbf{r}''$$

Hybertsen and Louie(1985); Godby, Schlüter and Sham (1986)

FHI-gap: a LAPW GW code[1]

- Based on the FP-LAPW basis set
- Mixed basis set to expand the GW -related quantities
- Interfaced with WIEN2k
- G0 W0 , GW0 @LDA/GGA(+U)
- http://www.chem.pku.edu.cn/jianghgroup/codes/fhi-gap.html

[1]H. Jiang et al., Comput. Phys. Comput. 184, 348 (2013)


WIEN2k
G_0W_0
$u_{\alpha l}(r^{\alpha}, E_l)$ $e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$
$\chi_i^{\mathbf{q}}(\mathbf{r})$
$\epsilon_{n\mathbf{k}}$ $\psi_{n\mathbf{k}}(\mathbf{r})$
$v_{ij}(\mathbf{q})$
$M^i_{nm}(\mathbf{k}, \mathbf{q})$
$\varepsilon_{ij}(\mathbf{q}, \omega)$
$X_{nm}(\mathbf{k}, \mathbf{q}; \omega)$
$V^{\mathrm{xc}}_{n\mathbf{k}}$
$\Sigma^{\mathrm{c}}_{n\mathbf{k}}(\omega)$
$\Sigma^{\mathrm{x}}_{n\mathbf{k}}$
$\epsilon^{\mathrm{qp}}_{n\mathbf{k}}$

FHI-gap: workflow

Run a WIEN2k SCF calculation

prepare the input files for FHI-gap in *gwdir*:

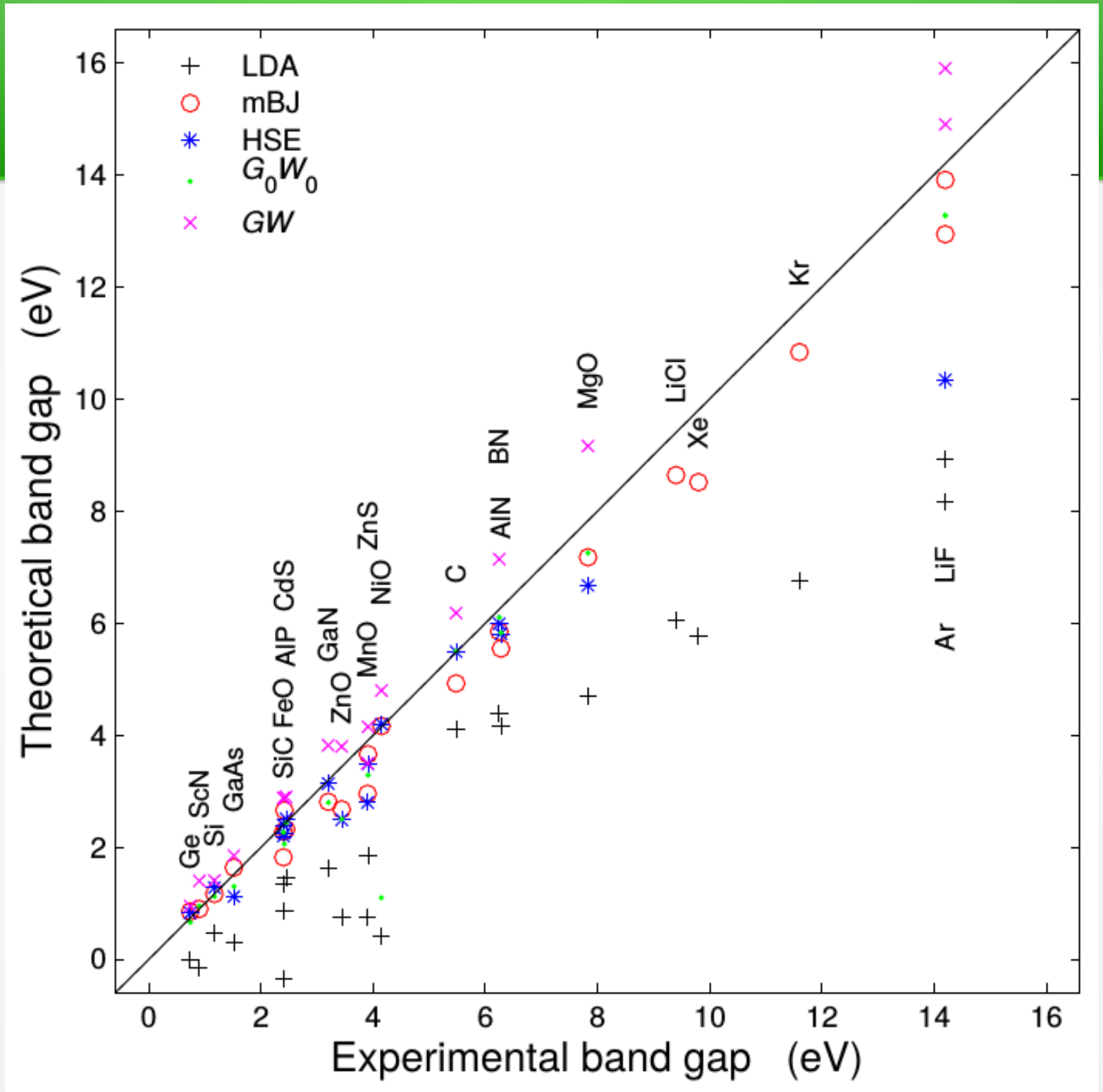
- **gap_init** -d <gwdir> -nkp <nkp> -s 0/1/2 -orb -emax <emax>
- modify gwdir.ingw

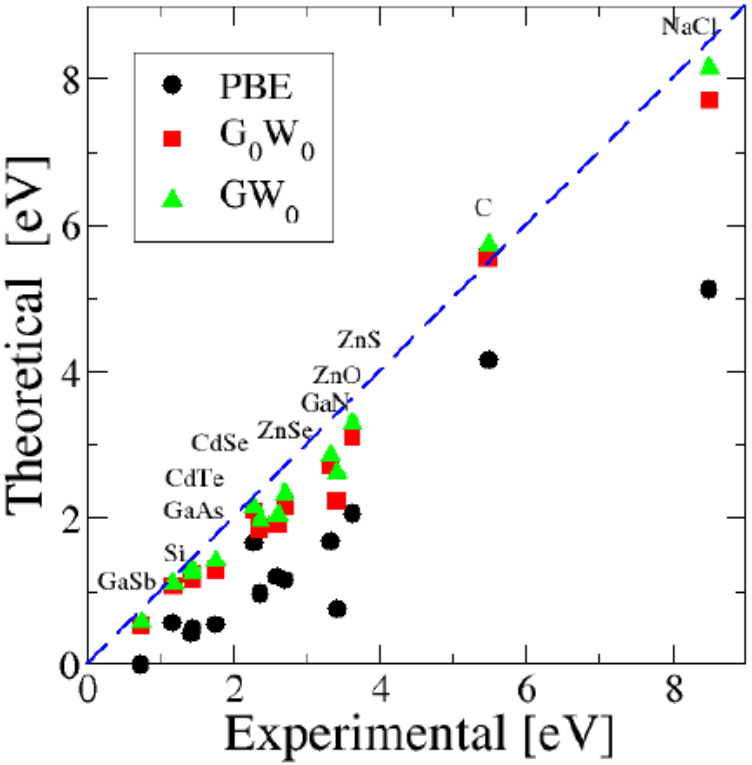
Execute **gap.x** or **gap-mpi.x** in *gwdir*

Analyse the results from:

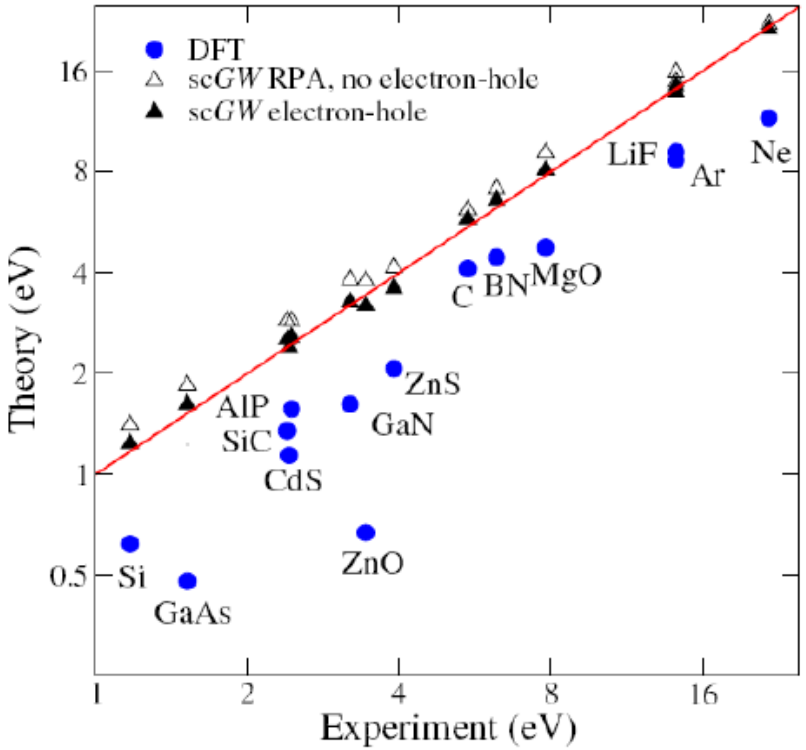
- Look at *gwdir.outgw*
- the plot of the DOS/band structure generated by **gap_analy**

http://www.chem.pku.edu.cn/jianghgroup/codes/fhi-


LDA
mBJ
HSE
G_0W_0
GW
Theoretical band gap (eV)
Experimental band gap (eV)
0
2
4
6
8
10
12
14
16
Ge
ScN
Si
GaAs
SiC
FeO
AlP
CdS
ZnO
GaN
MnO
NiO
ZnS
C
AlN
BN
MgO
LiCl
Xe
Kr
Ar
LiF

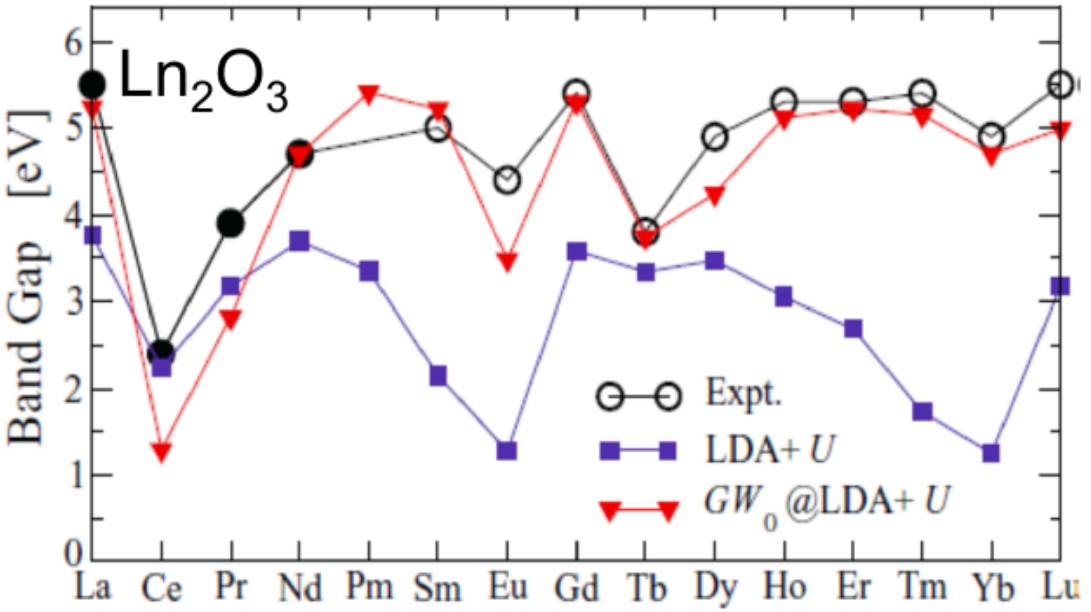


(H. Jiang, unpublished)



M. Shishkin et al,

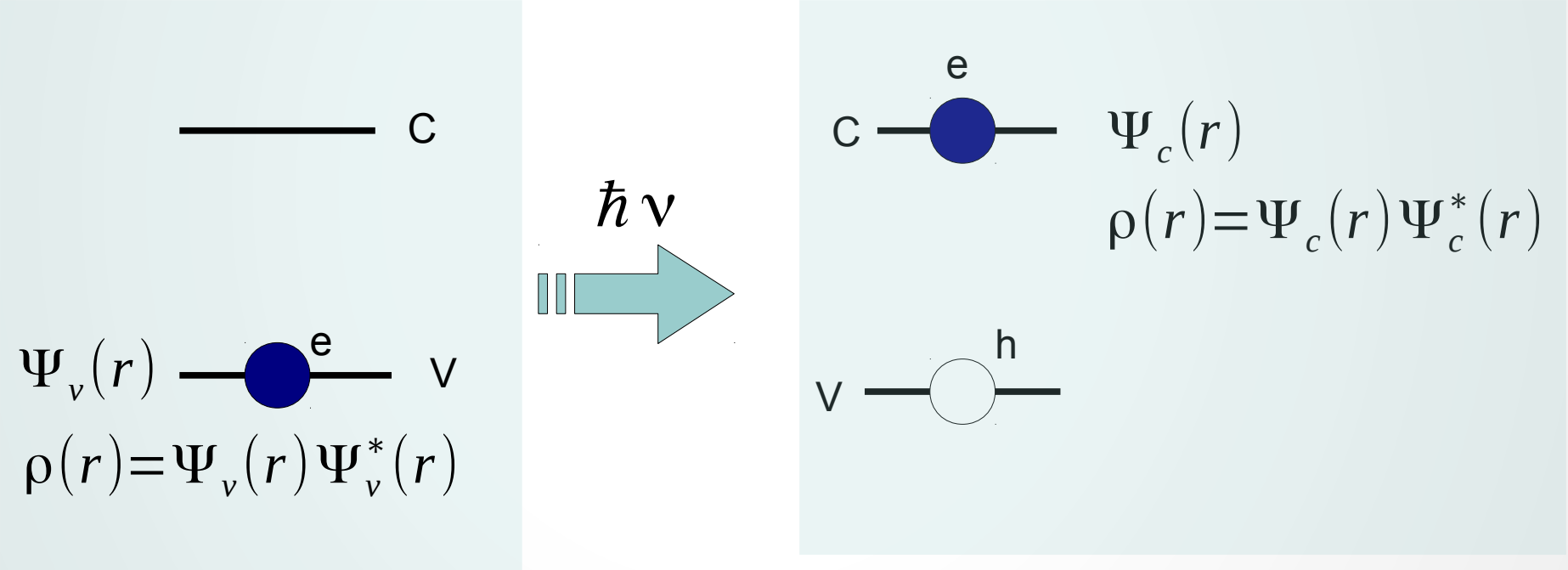
Phys. Rev. Lett. **99**, 246403 (2007).



H. Jiang *et al*. *Phys. Rev. Lett*. 102, 126403 (2009).
H. Jiang *et al*, *Phys. Rev. B* 86, 125115 (2012).

Independent particles

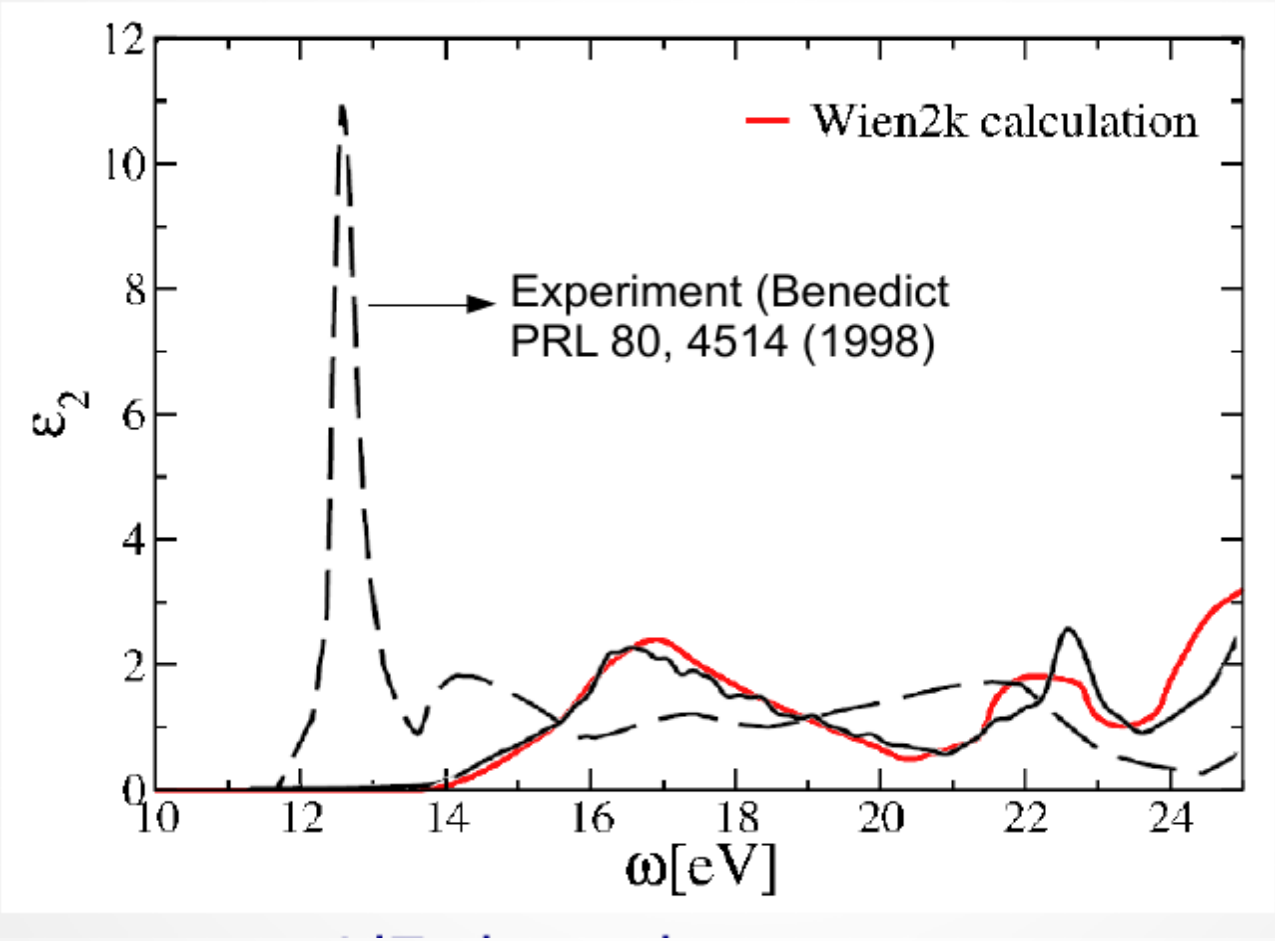
- absorption or emission is more complex process than electrons jumping between energy levels



$$\rho_c(r) \neq \rho_v(r)$$

$$H_{initial} \neq H_{final}$$

When independent particles picture fails



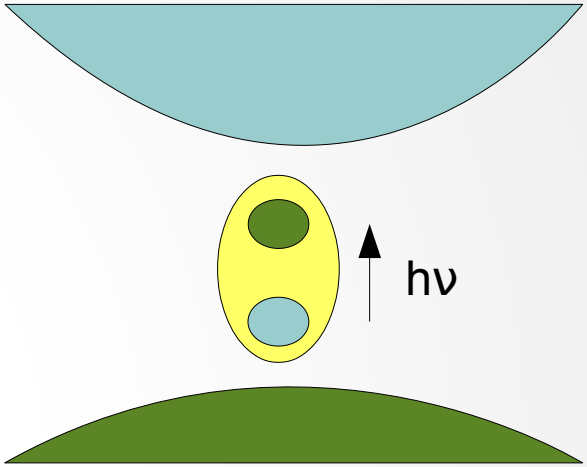
LiF absorption spectra

Bethe-Salpeter Equation

- excitation is a two-particle process (electron-hole pair is created)

$$L(12;1'2') = L_0(12;1'2') + \int d(3456) \times L_0(14;1'3') K(35;46) L(62;52')$$

equation of motion of two particle Green's function



- BSE is simplified into a two particles eigenvalue equation (in a basis of valence (*vk*) and conduction (*ck*) states)

$$(E_c - E_v) A^{\lambda}_{vc} + \sum_{v'c'} K_{vc,v'c'}(E_\lambda) A^{S}_{v'c'} = E_\lambda A^{S}_{vc}$$

band energies

$K = V^x + W^d$
interaction kernel

excitation energies

e-h coupling coef.

G. Strinati, Phys. Rev. Lett. 49, 1519 (1982).
M. Rohlfing and S. G. Louie, Phys. Rev. B 62, 4927(2000)
P Puschnig and C. Ambrosch-Draxl PRB 66, 165105 (2002)

BSE, kernel and dielectric function

Exchange:

$$\langle vc|V^x(E_\lambda)|v'c'\rangle = \int dr\,dr'\,\psi_c^*(r)\psi_{c'}(r')\upsilon(r,r')\psi_v(r')\psi_{v'}^*(r)$$

Direct term:

$$\langle vc|W^d(E_\lambda)|v'c'\rangle = \int dr\,dr'\,\psi_c^*(r)\psi_{c'}(r)\psi_v(r')\psi_{v'}^*(r')\frac{i}{2\pi}\int d\omega\, e^{i\omega 0^+} W(r,r',\omega)$$
$$\times\left[\frac{1}{E_\lambda-\omega-(E_{c'}-E_{v'})+iO^+}+\frac{1}{E_\lambda+\omega-(E_c-E_v)+iO^+}\right]$$

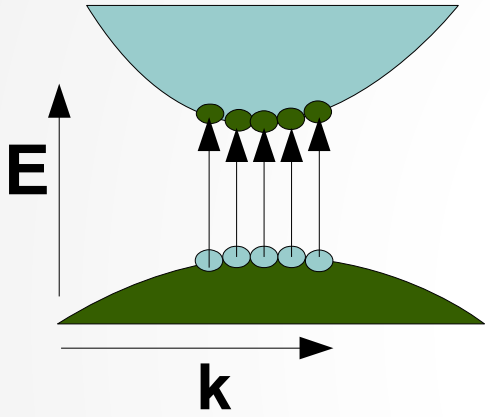
screened e-h interaction

Usual approximation valid for: $(E_c-E_v)\approx E_\lambda$

$$\langle vc|W^d(E_\lambda)|v'c'\rangle = \int dr\,dr'\,\psi_c^*(r)\psi_{c'}(r)\psi_v(r')\psi_{v'}^*(r')W(r,r',\omega=0)$$

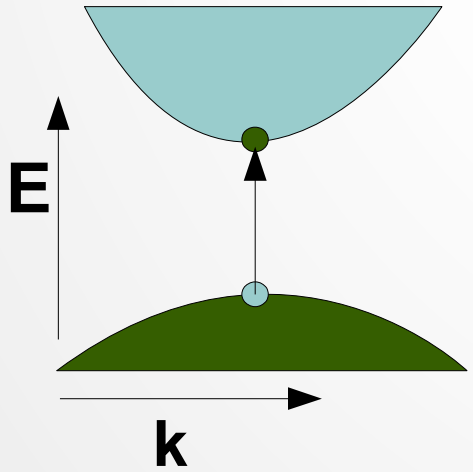
BSE, kernel and dielectric function

macroscopic dielectric function from BSE



$$\Im\,\epsilon_M(\omega) = \sum_{\lambda} \left| \sum_{vck} A^{\lambda}_{vck} \frac{\langle vk|p|ck\rangle}{(\varepsilon_{ck} - \varepsilon_{vk})} \right|^2 \delta(E_\lambda - \hbar\omega)$$

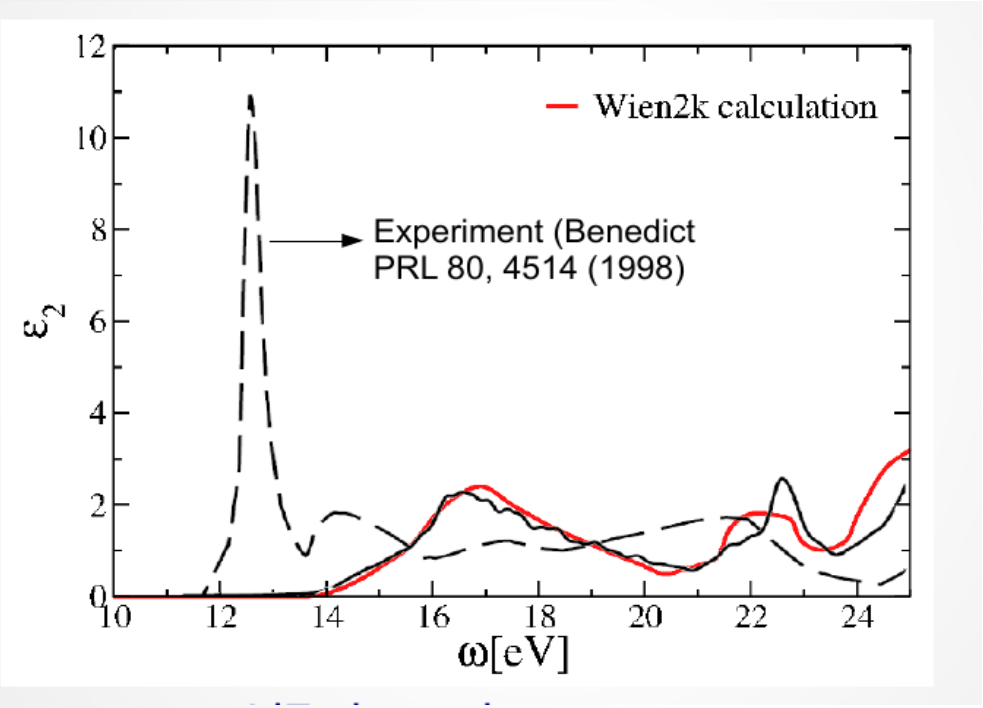
oscillator strength are proportional to coherent sum of the momentum matrix elements

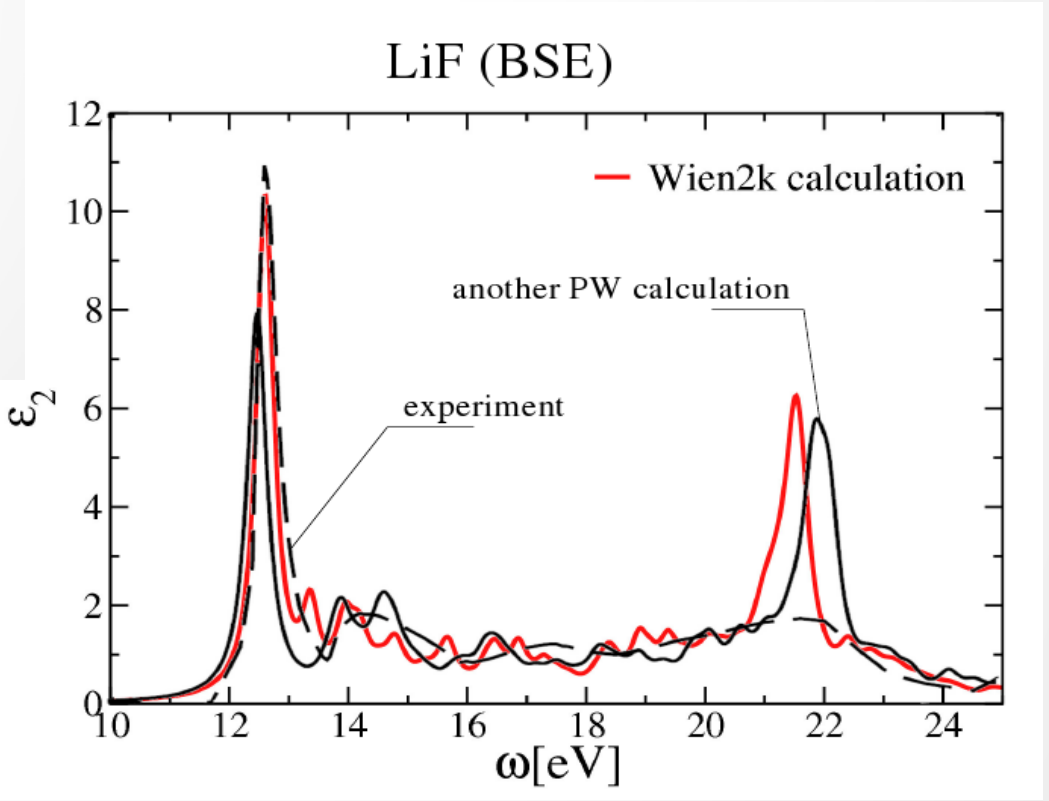


macroscopic dielectric function from DFT

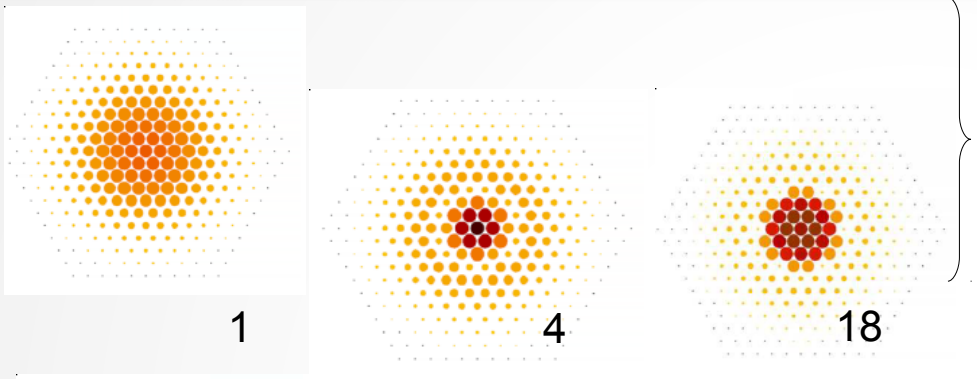
$$\Im\,\epsilon_M(\omega) = \sum_{\lambda = vck} \left| \frac{\langle vk|p|ck\rangle}{(\varepsilon_{ck} - \varepsilon_{vk})} \right|^2 \delta(E_\lambda - \hbar\omega)$$

LiF absorption spectra

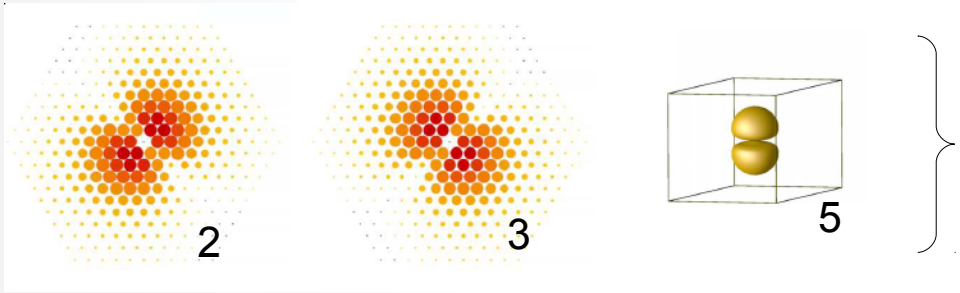




Exciton envelope function in AlN



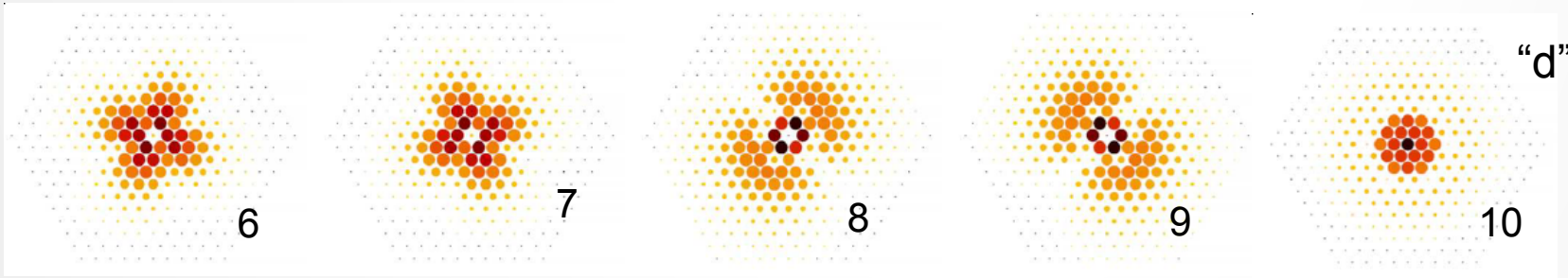
"s"- dipole active



"p"- dipole inactive

$$E_n = E_g - E_B \frac{1}{n^2}$$

$$oscil.\,strength \sim \frac{1}{n^3}$$



"d" - dipole inactive

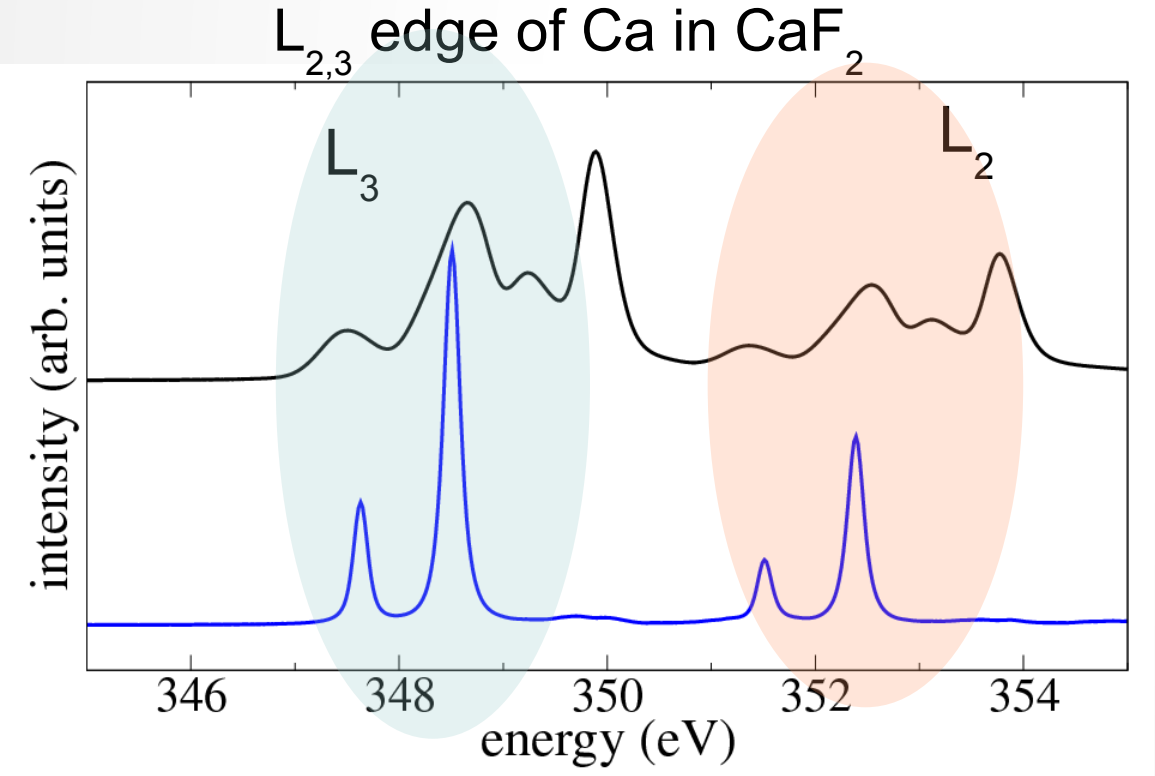
$\left|A^{\lambda}_{vck}\right|$ in BZ plotted for "s", "p" and "d" excitons

X-ray absorption

- in IPA X-ray absorption is proportional to the projected DOS of the conduction band

$$\Im \epsilon_M(\omega) = \sum_{\lambda} \left| \frac{\langle vk|p|ck\rangle}{(\varepsilon_{ck} - \varepsilon_{vk})} \right|^2 \delta(E^{\lambda} - \hbar\omega)$$

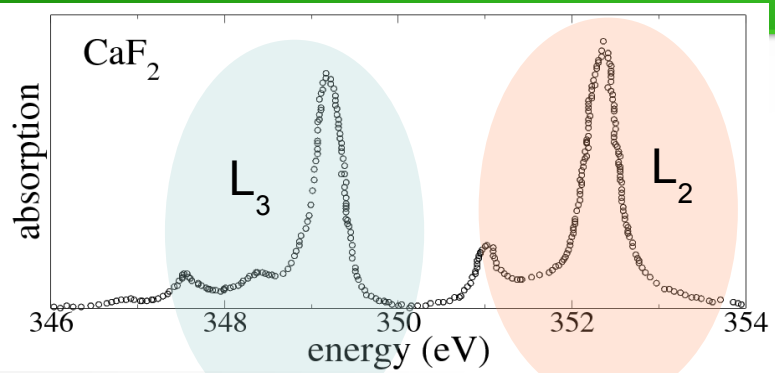
- branching ratio (L_2/L_3) is 1:2 (proportional to occupation of $2p_{1/2}$, $2p_{3/2}$)

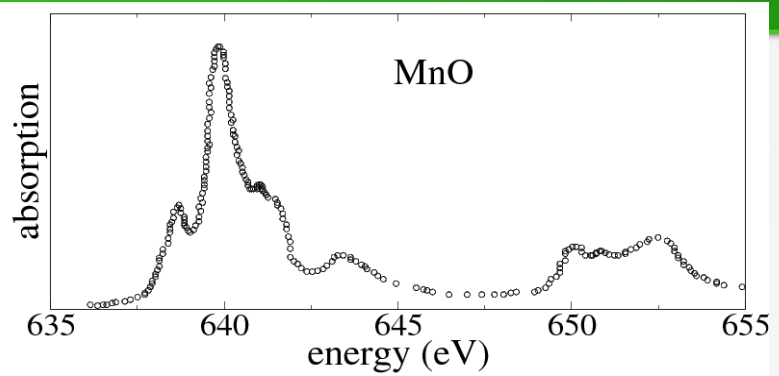


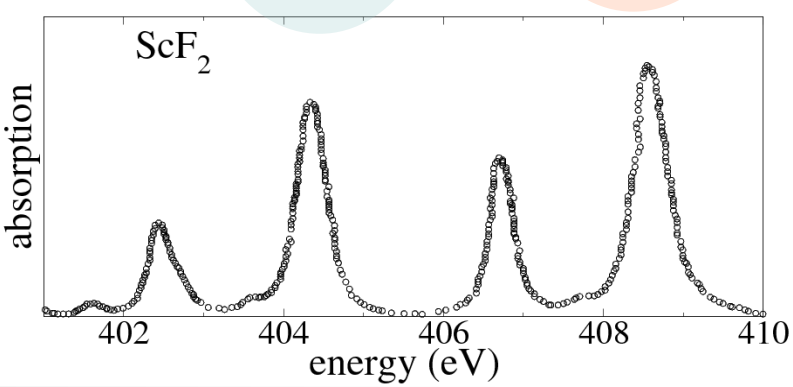
plain DFT

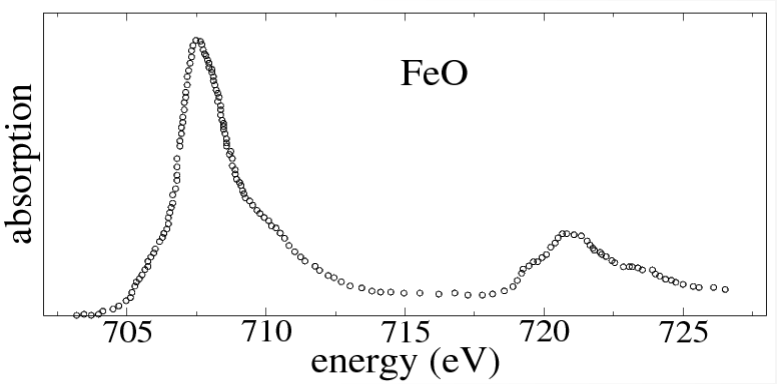
"core hole" DFT
(supercell with core hole on excited atom, wrong branching ratio)

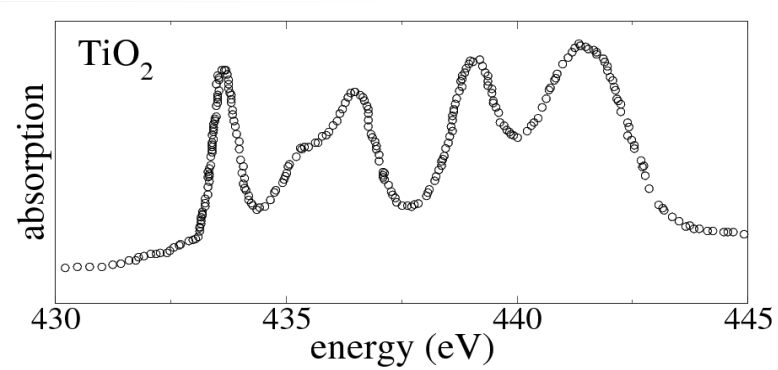
Measured L edges of 3d metals

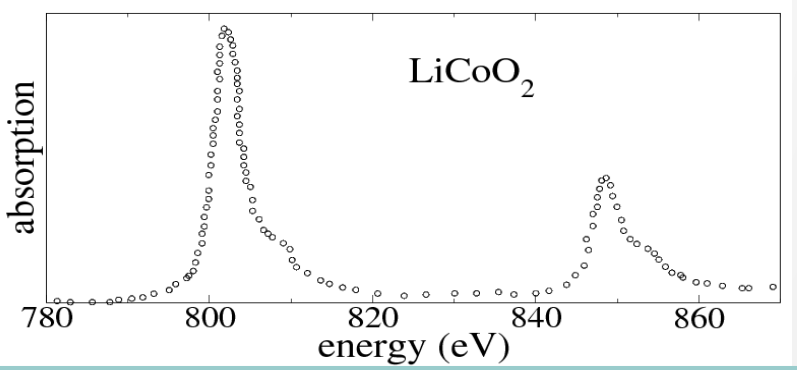






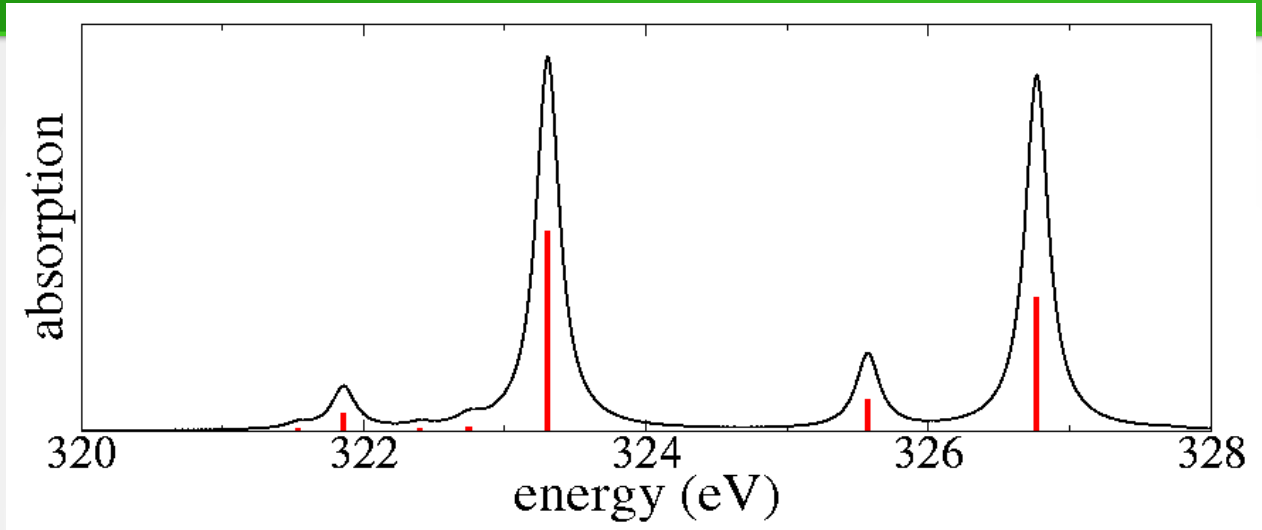




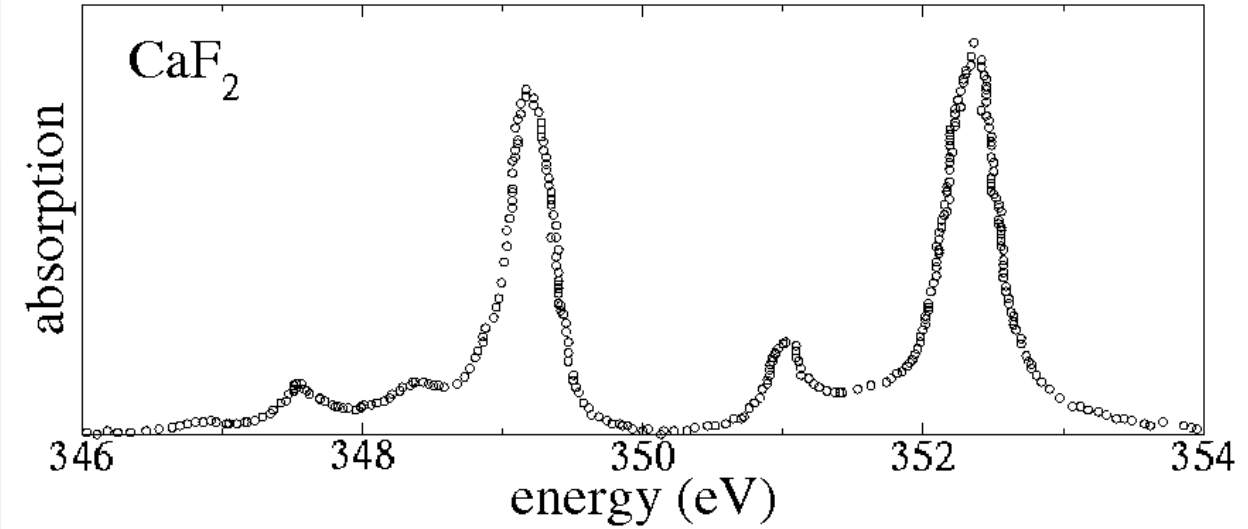


BSE gives correct L_2/L_3 branching rations

$L_{2,3}$ edge for Ca in CaF_2



transitions from $2p_{1/2}$ and $2p_{3/2}$ are included at the same time into the BSE Hamiltonian



experiment

- **Only coherent mixing of transitions from $2p_{1/2}$ and $2p_{3/2}$ results in proper branching ratio**

BSE in wien2k

Run a WIEN2k SCF calculation

prepare the input files for BSEwien2k :

- **init_bse** -??? (it creates new *bsedir*)
- Inside *bsedir* optionally, modify input files (master is called *input)*

Inside *bsedir* execute **bse.job** or optionally modify it before executing

Analyze results:

- Look at exciton_singlet/triplet*, epsilon_singlet/tripled*
- There are some programs usefult for detailed analysis of excitonic envelope function

init_bse

- init_bse -h (get help)

```
rolask@rlws:~/data/LiF/LiF_BSE> ~/SRC/BSE/BSE_SCRIPTS/init_bse -h

This prepares the input for BSE
You need to run this in a converged SCF calculation directory

Choose your options:
-h                      for this message
-p [path/to/BSE]        specify path to BSE [def: ${BSEROOT}]
-s                      will do spin-orbit
-f                      start from hybrid calc [experimental]
-n [cpu]                number of cores [def: 16]
-d [name]               specify the name of the new directory [def: *_BSE]
-b [VB,CB]              number of valence and conduction bands [def: 4,10]
-k [DMx:DMy:DMx,WDx:WDy:WDz,iWDx:iWDy:iWDz]     k-meshes for DM, WDVX and (optional) interpolation
-q                      shift q-mesh from Gamma
-g [DM,WD,VX,DM_max]    G-max for WD, VX and DM
-i [G-max]              do interpolated run (with specified G-max for interpolation)
-e [emin,emax]          in1 energy ranges [Ry] (def: from SCF)
-r [emin,emax,de,broad] energy ranges, step and broadening in BSE [eV] [def: 0.0,26.0,0.001]
-c [shift (eV)]         apply scissor shift (in eV) [def: 0]
-l [PW,sphere]          l value for expansion of PW and inside the spheres [def: 3,3]
-v [1-4]                screening level (1 - full, 2 - diagonal 1/eps_{gg}(q)
                       3 - diagonal eps_{gg}(q), 4 - long range (optional constant after colon))
```

- Prepares input files based on provided parameters
  - Copy vsp, vns, defines k-meshes, in1 for lapw1, ...

Bse.job

```
rolask@rlws:~/data/LiF/LiF_BSE> cat bse.job
#!/bin/bash -ex

echo $BSEROOT

$BSEROOT/execBSEkgen
$BSEROOT/execlapw1optic -DM
mpirun -machinefile .bse_machines -envall -np 12 $BSEROOT/DM > outputDM
$BSEROOT/execlapw1optic -WDVX
mpirun -machinefile .bse_machines -envall -np 12 $BSEROOT/WD    > outputWD
mpirun -machinefile .bse_machines -envall -np 12 $BSEROOT/VX   > outputVX
mpirun -machinefile .bse_machines -envall -np 12 $BSEROOT/BSE_diag   > outputBSE_diag
```

execBSEkgen	creates k-meshes for DM, WD,VX
execlapw1optic	executes lapw1, optic, generates eigenvectores, and momentum matric elements
DM	computes dielectric matrix
WD	computes direct part of the BSE Hamiltonian
VX	computes exchange part of the BSE Hamiltonian
BSE_diag	solves BSE equation

Input file (input)

```
scissors      0.0          # scissors shift [eV]
scalebands    1.0 1.0      # scaling factor for (valence, conduction) bands
eminmaxDM    -5.0  10.0    # energy cutoff for DM
gmax_WD        4.0       # maximum magnitude of G vector for exp(iGr)
gmax_VX        4.0       # maximum magnitude of G vector for exp(iGr)
gmax_DM        4.0
gmax_DM_max    4.0       # maximum magnitude of G vector for exp(iGr)
lmax_besel    3            # max of l in expansion of exp(-i(q+G)r)
lmax_wave     3            # max of l in expansion of wave function (sphere)
offesDM      1             # calculate off-diag elements of eps_GGp(q)
broadDM      0.0001
omegaDM      0.0
formatVXWD   1             # VX, WD files 0-ascii, 1-binary
nbandsVXWD   4 4           # number of (valence,conduction) bands in VX, WD
nbandsINT    4 4           # number of (valence,conduction) bands used in BSE
nbandsBSE    4 4           # number of (valence,conduction) bands used in BSE
noccbands    5            # number of occupied bands
noccbandsDM  5            # number of occupied bands
scrlevel     1             # screening level in WD:
                          #   1 - the full {g, g'} dependence is used
                          #   2 - a diagonal approximation is used (g = g') using
                          #       the inverse dielectric matrix eps^{-1}_{gg}(q)
                          #   3 - a diagonal approximation is used (g = g') using
                          #       the dielectric matrix eps_{gg}(q)
                          #   4 - a long range screening is used (constant tensor)

diroffBSE     1              # 0 : local field effects only (direct interaction = zero)
nexoutBSE      1000          # number of states writen into files
eminemaxBSE   0.0 26.0 0.001  # emin, emax, de in [eV]
broadBSE      0.1   0        # broadending of spectrum [eV], lineshape
polBSE        1              # polarization
spinBSE       1              # 1 -singlet, 2 - triplet
```

GW, BSE in wien2k

- GW calculations require large computational resources
- BSE is computationally very expensive