# BSE, wien2k

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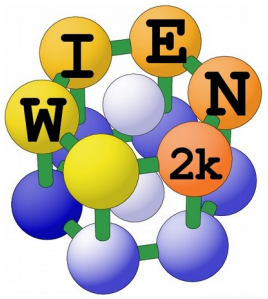
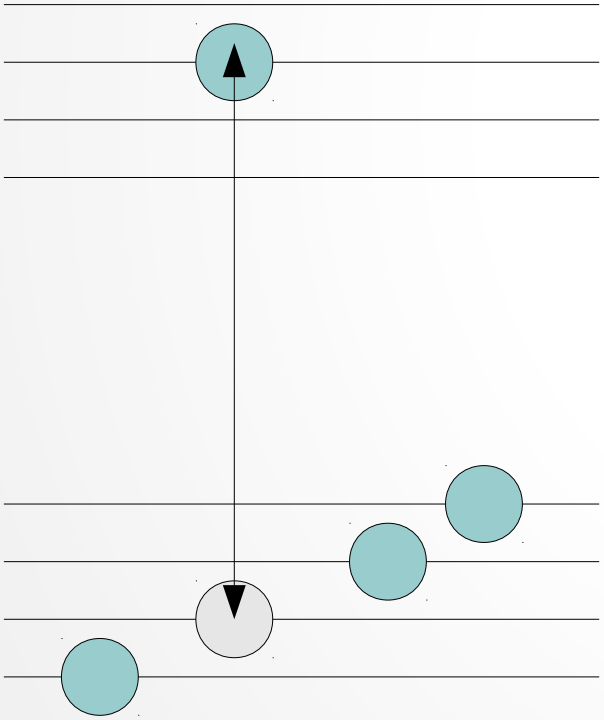


# Simple picture, independent particles

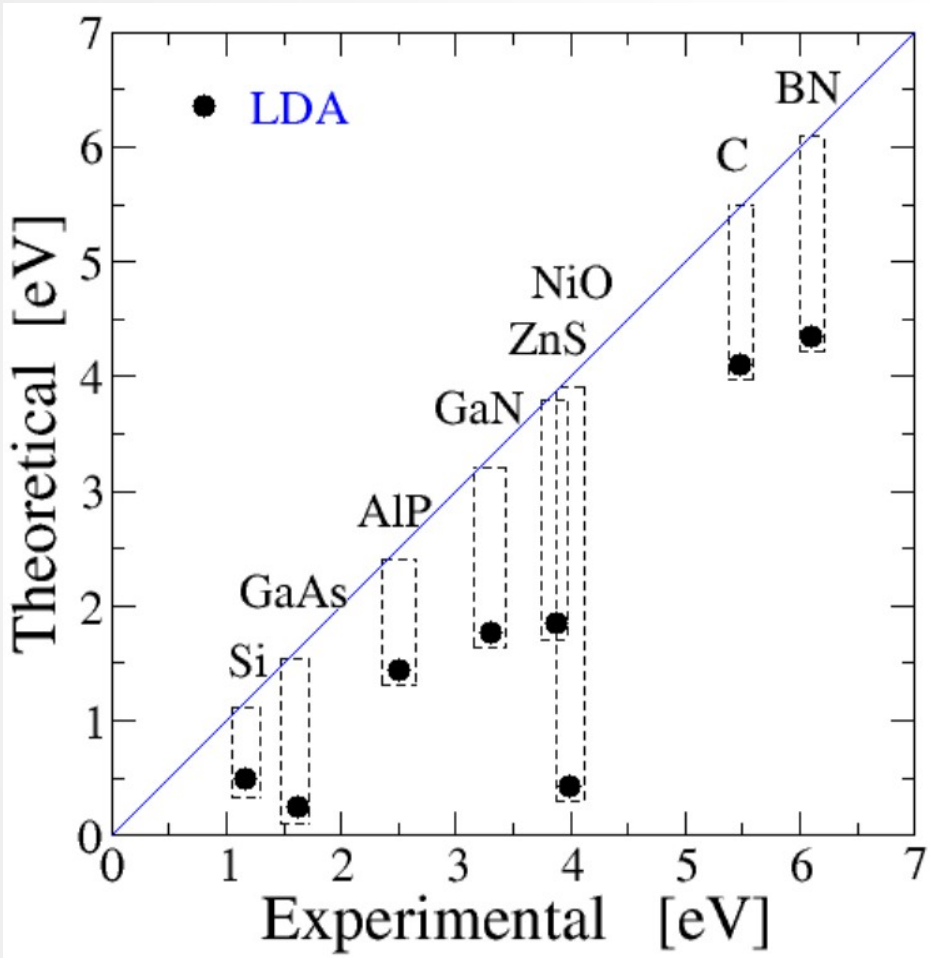
$$\Im(\epsilon_{ij}) = \frac{16\pi^2}{\Omega\omega^2} \sum_{vck} \langle vk | p_i | ck \rangle \langle ck | p_j | vk \rangle \delta(\varepsilon_{kc} - \varepsilon_{vk} - \omega)$$

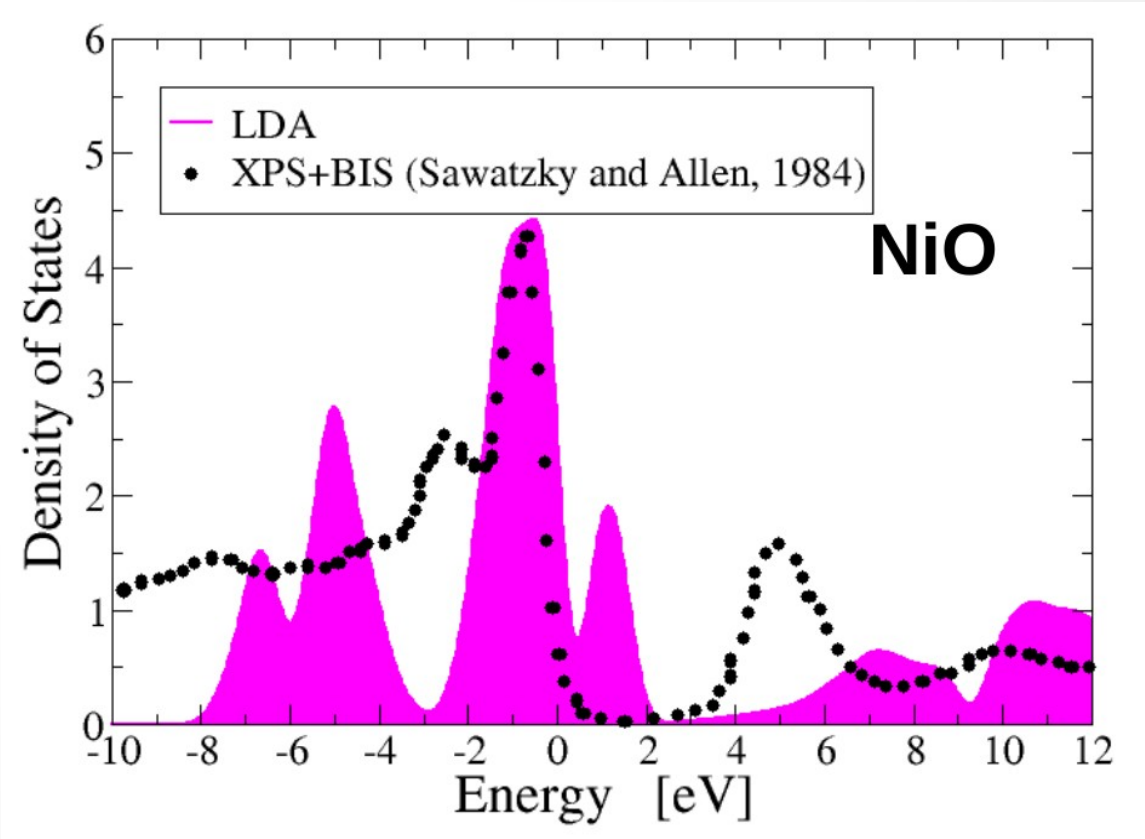


1) Energy levels calculated within DFT are not true addition and removal energies

2) 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).**

# $G_0W_0$ Approximation

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

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

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

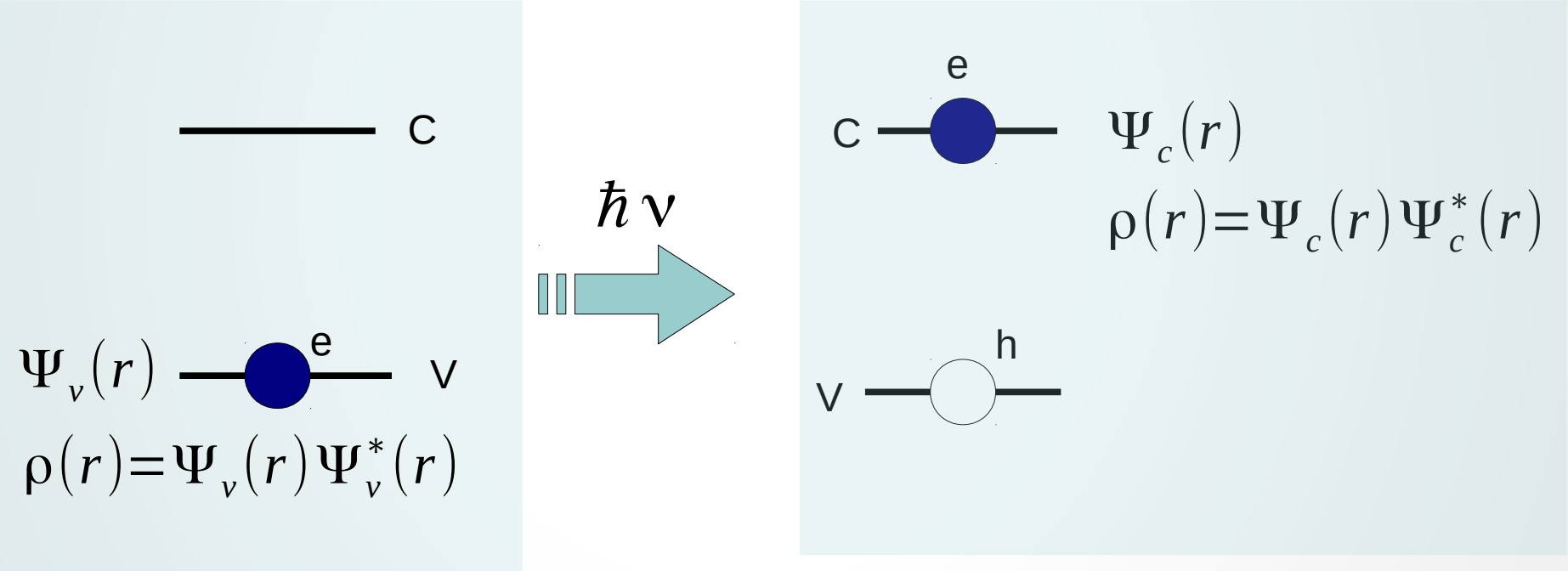
$$M_{nm}^{i}(\mathbf{k},\mathbf{q}) \equiv \int_{\Omega}\left[\chi_i^{\mathbf{q}}(\mathbf{r})\,\psi_{m\mathbf{k}-\mathbf{q}}(\mathbf{r})\right]^{*}\psi_{n\mathbf{k}}(\mathbf{r})d\mathbf{r}$$

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

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

# Independent particles

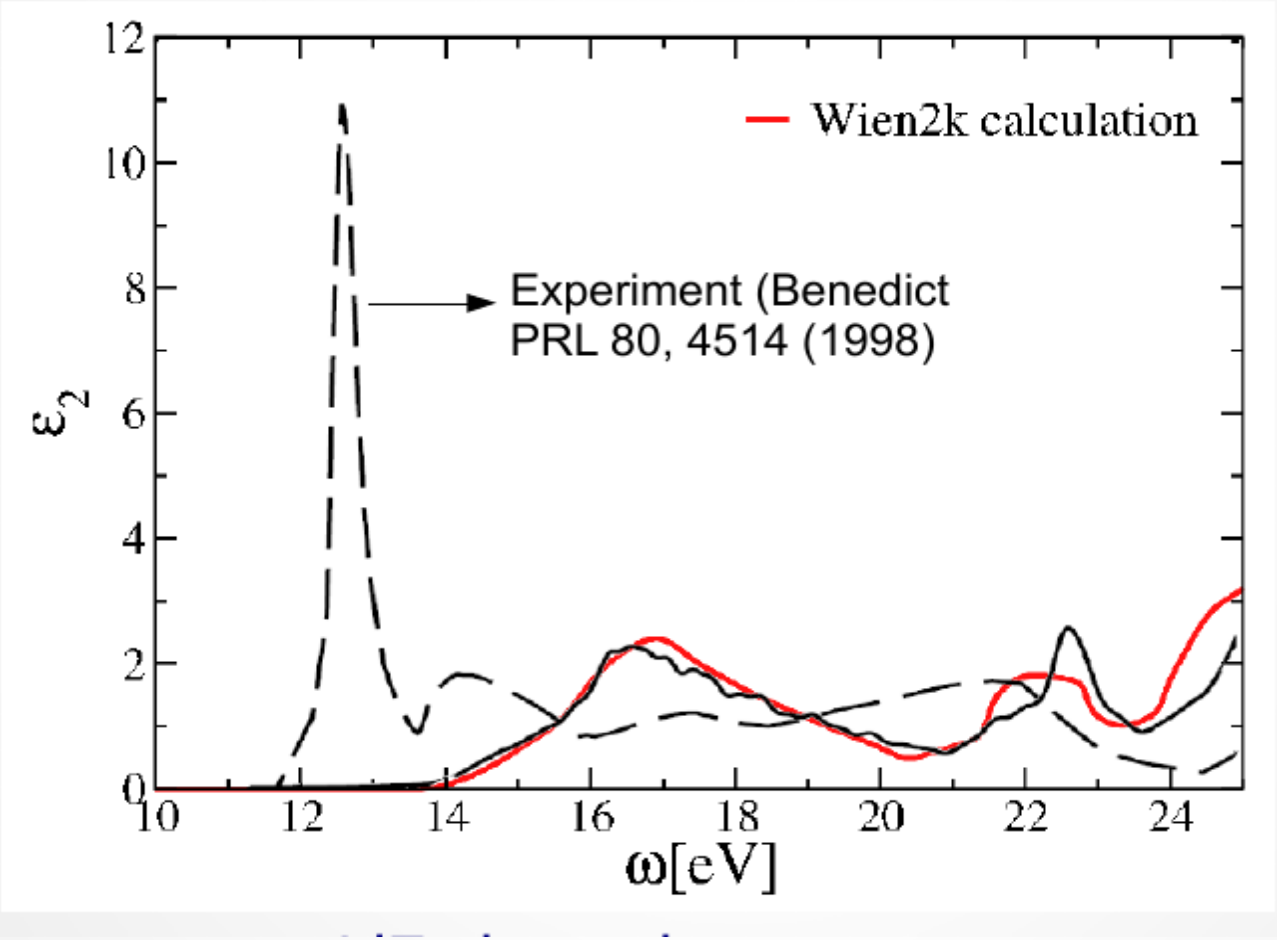
- absorption or emission  is more complex process than electrons jumping between energy levels




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

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

# When independent particles picture fails



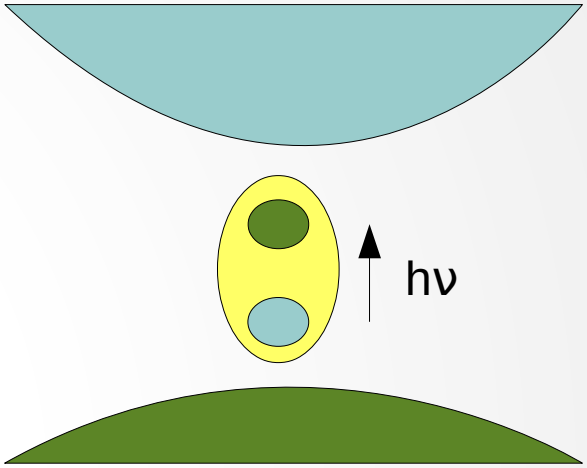

LiF absorption spectra

# 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:

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

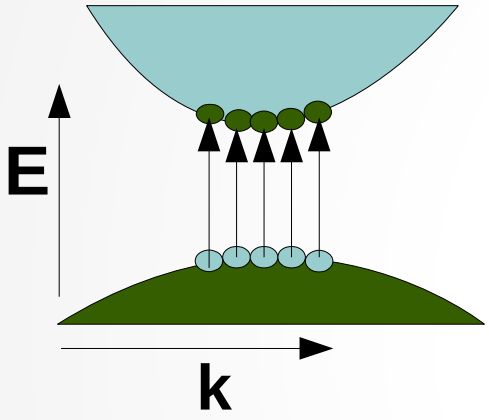
screened e-h interaction

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

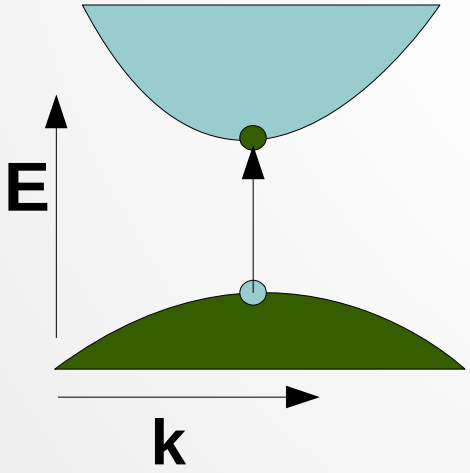
## macroscopic dielectric function from BSE




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

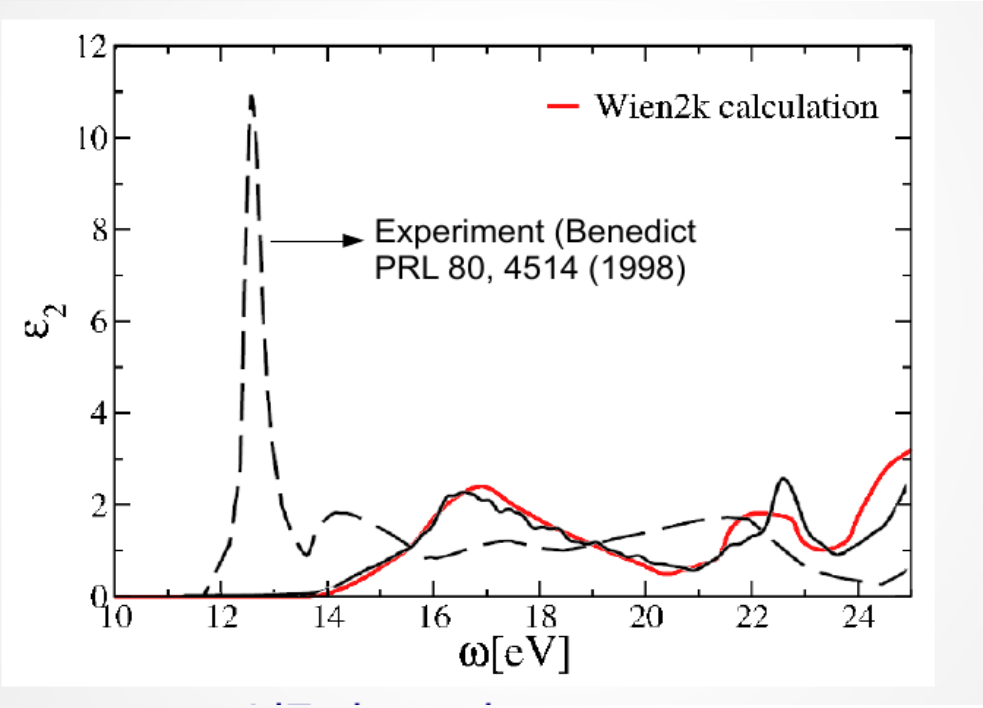
oscillator strength are proportional to coherent sum of the momentum matrix elements

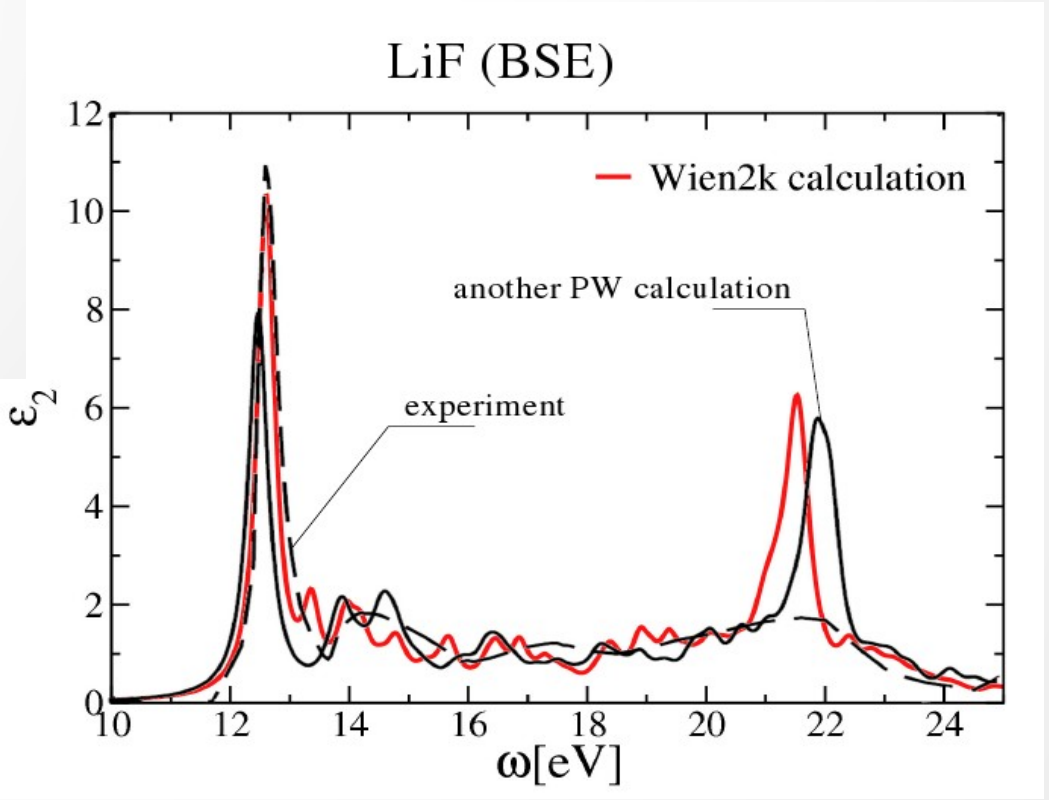
## macroscopic dielectric function from DFT



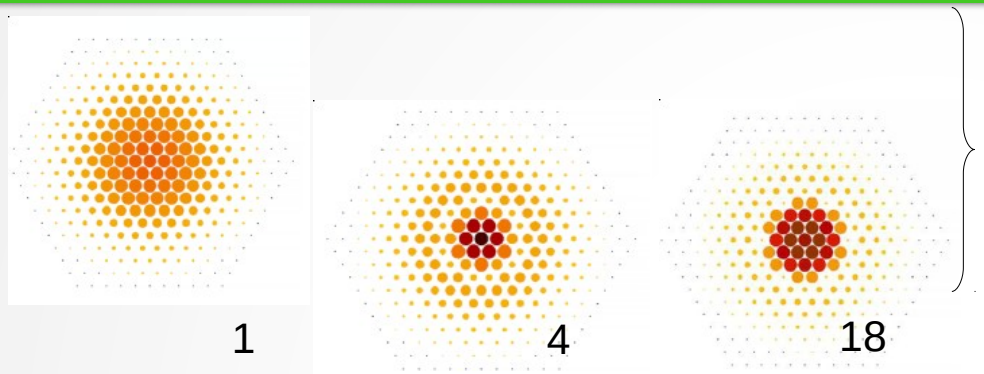

$$\Im\,\epsilon_M(\omega) = \sum_{\lambda = vck} \left| \frac{\langle vk|p|ck\rangle}{(\varepsilon_{ck} - \varepsilon_{vk})} \right|^2 \delta(E_\lambda - \hbar\omega)$$

# LiF absorption spectra

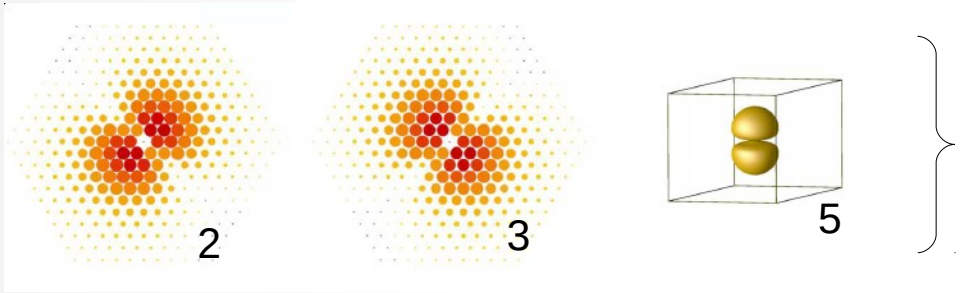


# Exciton envelope function in AlN



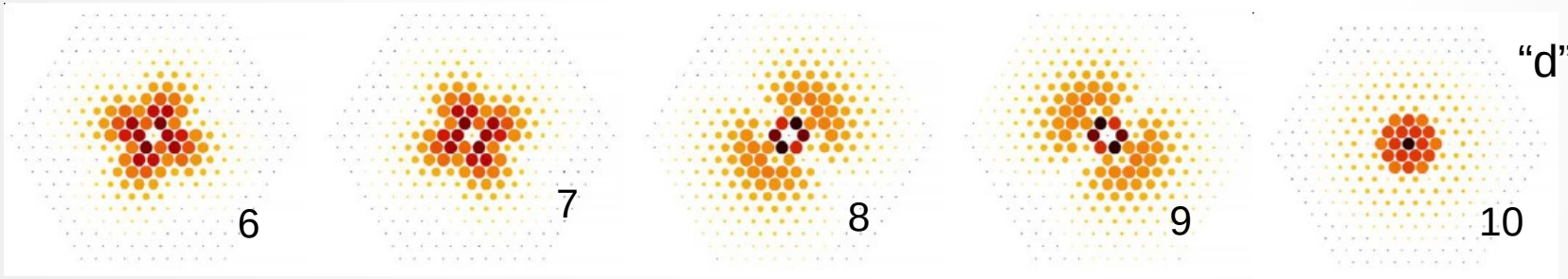

"s"- dipole active




"p"- dipole inactive

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

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




"d" - dipole inactive

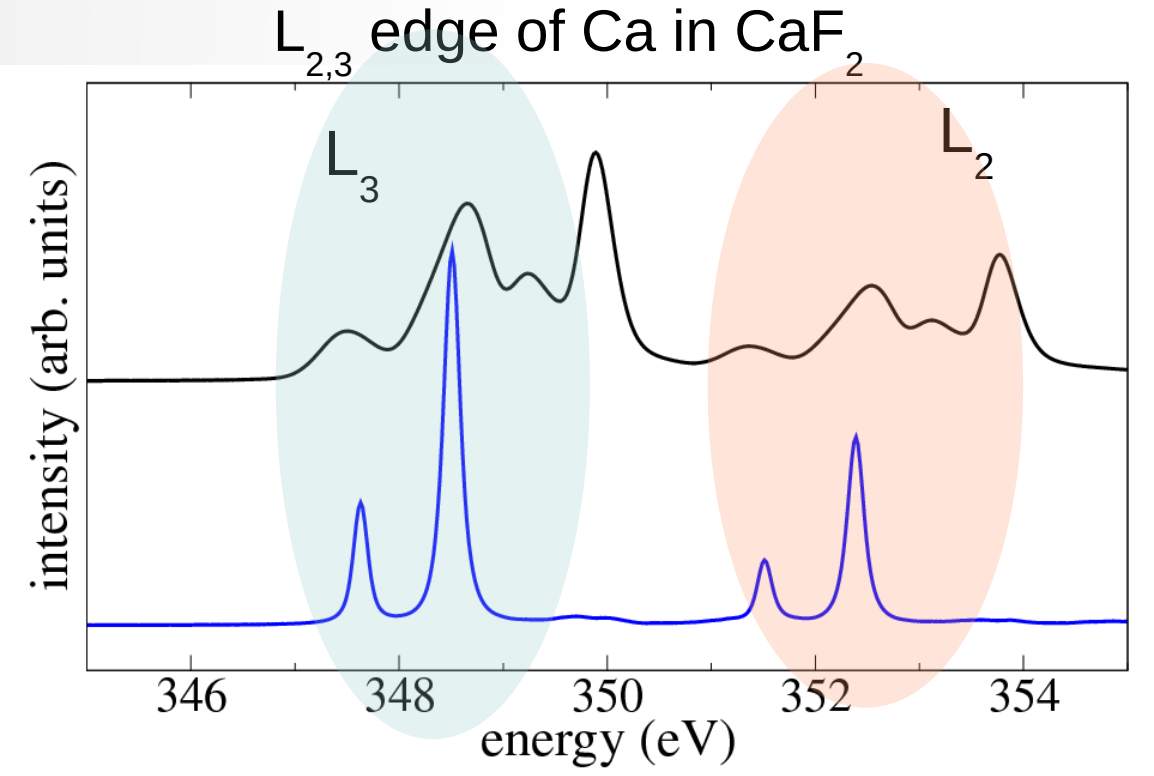
$\left| A_{vck}^{\lambda} \right|$ in BZ plotted for "s", "p" and "d" excitons

# X-ray absorption

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

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

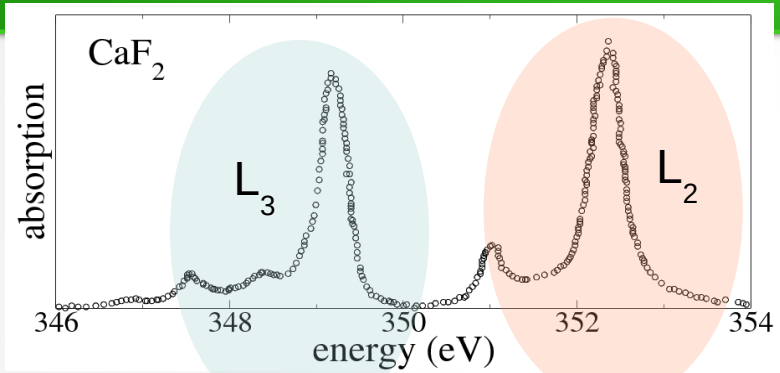
- branching ratio ($L_2/L_3$) is 1:2 (proportional to occupation of $2p_{1/2}$, $2p_{3/2}$)

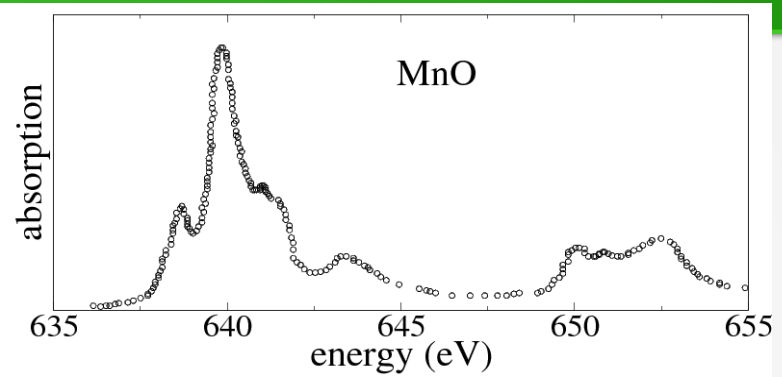


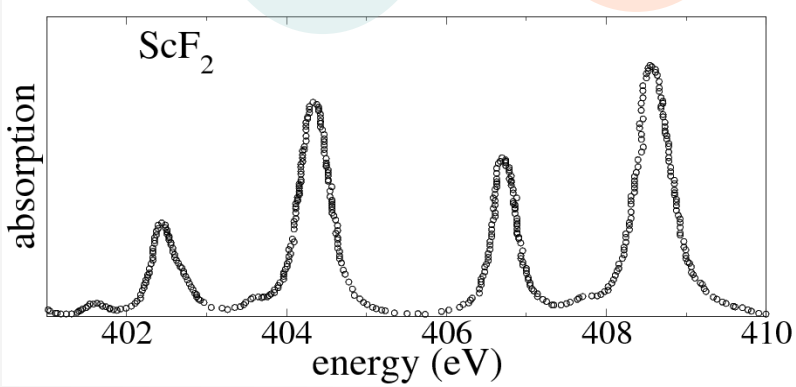

plain DFT

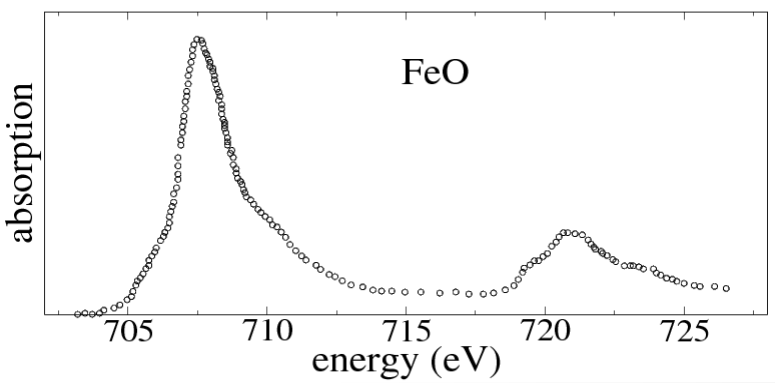
"core hole" DFT
(supercell with core hole on excited atom, wrong branching ratio)

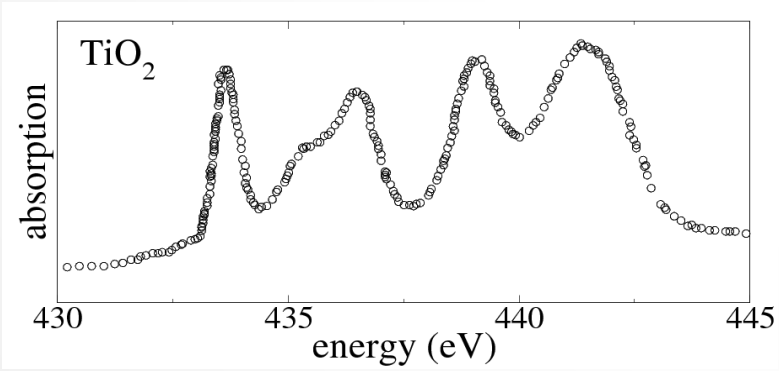
# Measured L edges of 3d metals

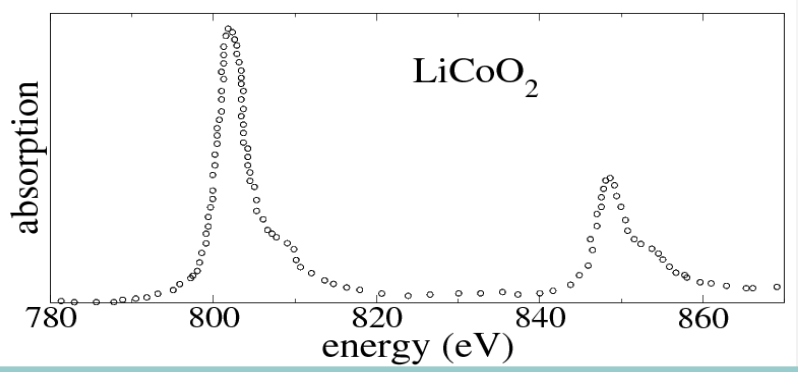


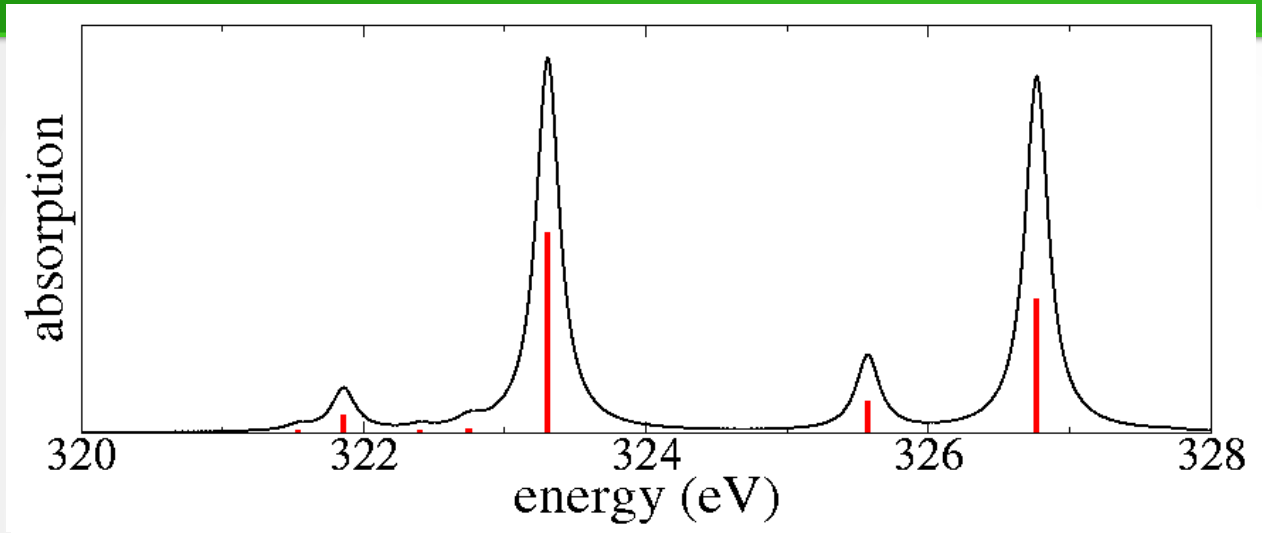



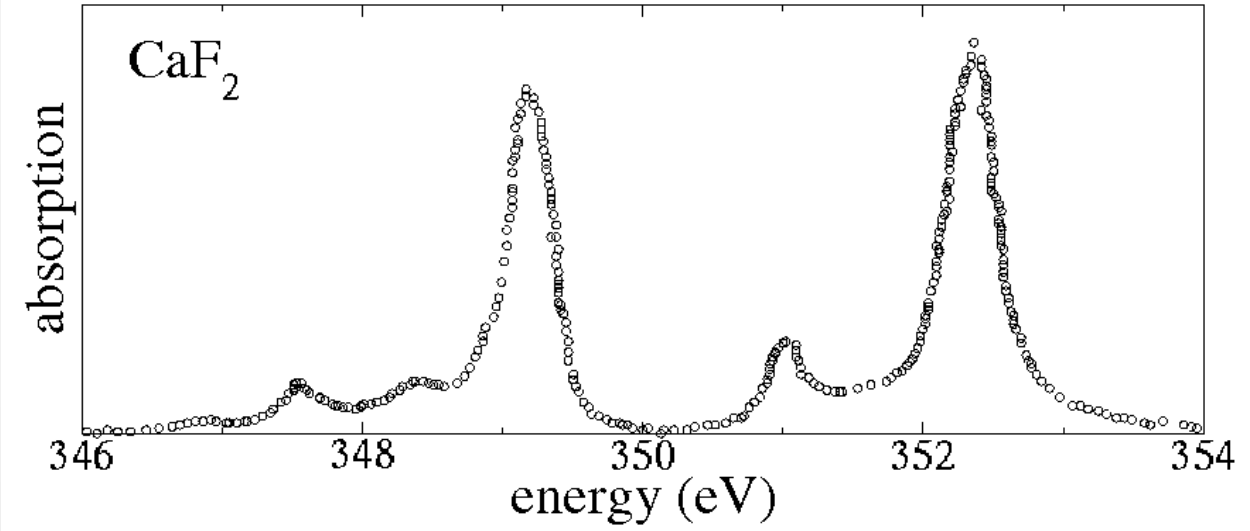




**BSE gives correct $L_2/L_3$ branching rations**

# $L_{2,3}$ 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 (thanks to Maciej P. Polak)

- 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
```

# BSE in wien2k

- BSE is computationally very expensive