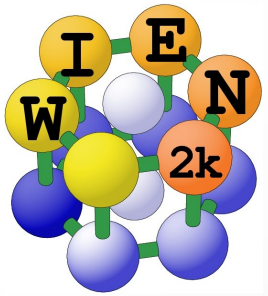
Optical properties by wien2k

Robert Laskowski

rolask@ihpc.a-star.edu.sg

Institute of High Performance Computing
Singapore



outline

- Basics, formalism
- What, how?
  - *optic*, *joint*, *tetra ….*
  - inputs / outputs, examples
- Beyond independent particle approximation
  - The Bethe-Salpeter equation

Introduction

- independent particles approximation (IPA)
- local field effects
- *matrix elements of momentum operator*
- dielectric function, dielectric tensor

Dielectric function

- photon propagates, external potential (V_{ext})
- Electrons respond, induce screening potential (V_s)

$$V(r,t) = V_{ext}(r,t) + V_s(r,t)$$

External potential

Screening potential

$$V_G^{ext} = \sum_{G'} \epsilon_{GG'} V_{G'}$$

dielectric constant ϵ_{GG}

- Dielectric constant (function) contains all information about the response

Light matter interaction

- single particle eigenstates (**IPA**) $\hat{H}_0 |nk\rangle = \varepsilon |nk\rangle$

- Time dependence in the linear regime: $V_{ext}, V_s, n \sim e^{i\omega t}$

- general form of the potential $V(r) = \frac{1}{\Omega} \sum_{q,G} V_G e^{-i(q+G)r}$

- Definition irreducible of polarizability: $P = \frac{\delta n}{\delta V}$ $\qquad V_G^s = \nu(q+B) n_G(q)$

$$n_G(q,\omega) = \sum_{G'} P^0_{GG'}(q,\omega) V_{G'}(q,\omega)$$

$$P^0_{GG'}(q,\omega) = \frac{1}{\Omega} \sum_{lmk} \frac{f_{m,k+q} - f_{l,k}}{\varepsilon_{m,k+q} - \varepsilon_{l,k} - \omega} [M^G_{lm}(k,q)]^* M^{G'}_{lm}(k,q)$$

$$M^G_{lm}(k,q) = \langle lk | e^{-i(q+G)r} | m, k+q \rangle$$

Light matter interaction

$$\epsilon_{GG'} = \delta_{GG'} - \nu(q+G) P^0_{GG'}(q,\omega)$$

random phase approximation (RPA)

with local field effects:

$$\epsilon_M(q,\omega) = \frac{1}{\epsilon^{-1}_{00}(q,\omega)}$$

$$V^{ext}_G(q) = \delta_{G,0} V_{ext}(q)$$

$$V^{ext}_G = \sum_{G'} \epsilon_{GG'} V_{G'} \quad V_0 = \varepsilon^{-1}_{00} V^{ext}_0$$

neglecting local field effects:

$$\epsilon_M(q,\omega) = \epsilon_{00}(q,\omega) = 1 - v(q) P_0(q,\omega)$$

Light matter interaction

$$\epsilon_M(q,\omega)=1-v(q)P_0(q,\omega)$$

Free electrons:
the Lindhard formula

$$\varepsilon(q,\omega)=1-\lim_{\eta\to 0}\frac{4\pi e^2}{q^2\Omega}\sum_k \frac{f(\varepsilon_{k+q})-f(\varepsilon_k)}{\varepsilon_{k+q}-\varepsilon_k-\omega-i\eta}$$

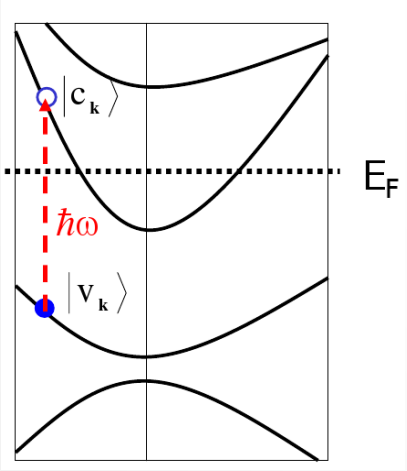
Bloch electrons:

$$\varepsilon(q,\omega)=1-\lim_{\eta\to 0}\frac{4\pi e^2}{q^2\Omega}\sum_k A^{l,l'}_{k,q}\frac{f(\varepsilon_{k+q})-f(\varepsilon_k)}{\varepsilon_{k+q}-\varepsilon_k-\omega-i\eta}$$

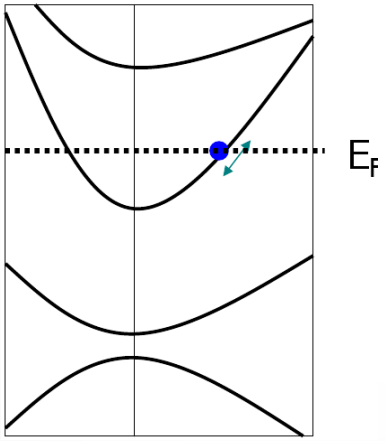
$$A^{l,l'}_{k,q}=\delta_{l,l'}+(1-\delta_{l',l})\frac{q^2}{m\omega^2_{l,l'}}|P_{l,l'}|^2$$

intra-band

inter-band



inter-band



intra-band

Long wave limit

With k·p method we find q $\rightarrow$ 0 limit of P

$$P^0(q\rightarrow 0,\omega)=4\pi\sum_{vck}\frac{\langle vk|p_i|ck\rangle\langle ck|p_j|vk\rangle}{(\varepsilon_{ck}-\varepsilon_{vk}-\omega)(\varepsilon_{ck}-\varepsilon_{vk})^2}$$

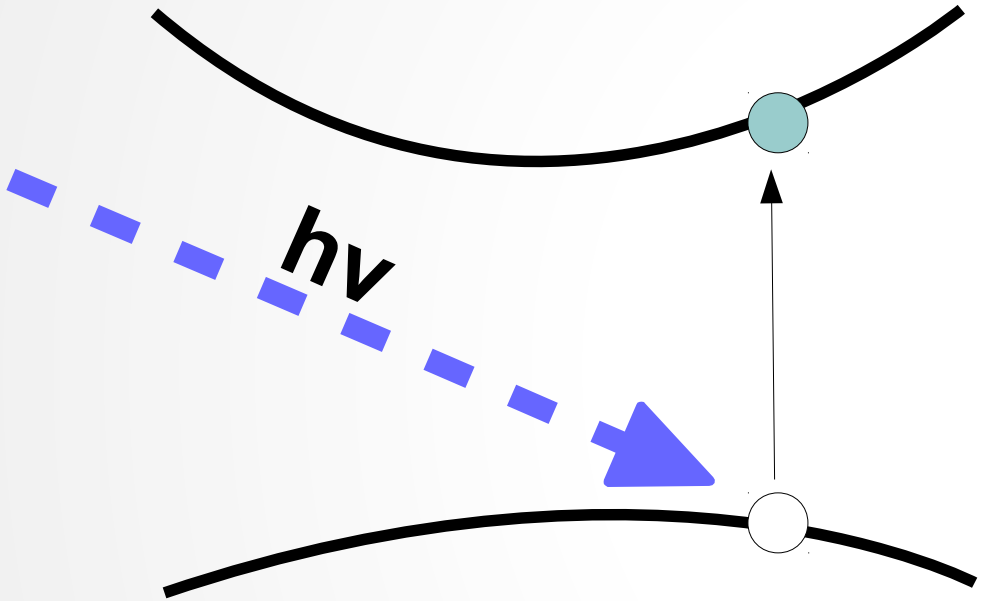
The expression for calculations of single particle excitation spectra

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

Key quantity is the momentum matrix (optic program):

$$\langle vk|p_i|ck\rangle$$

Interpretation



joint density of states

$$\sum_{vck} \delta(\varepsilon_{kc} - \varepsilon_{vk} - \omega)$$

transition probability

$$\mathrm{Im}\epsilon_{\alpha\beta}(\omega) = \frac{4\pi e^2}{m^2\omega^2} \sum_{c,v} \int d\mathbf{k} \, \langle c_\mathbf{k}|p^\alpha|v_\mathbf{k}\rangle\langle v_\mathbf{k}|p^\beta|c_\mathbf{k}\rangle \, \delta(\varepsilon_{c_\mathbf{k}} - \varepsilon_{v_\mathbf{k}} - \omega)$$

Momentum matrix elements

$$\langle vk | p_i | ck \rangle \sim \int \Psi_{vk} \frac{\partial}{\partial x_i} \Psi_{ck}$$

$$\Psi_{n,\mathbf{k}}(\mathbf{r}) = \begin{cases} \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} C_G^{n,\mathbf{k}} e^{i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}}, & \mathbf{r} \in I \\ \sum_{lm} W_{lm}^{n,\alpha,\mathbf{k}}(r) Y_{lm}(\hat{r}), & \mathbf{r} \in S_\alpha \end{cases}$$

The character of the state is hidden here

$$\begin{aligned} \nabla_0 \left(W(r) Y_{lm}(\hat{\mathbf{r}}) \right) &= F_+^0(lm) W_+(r) Y_{l+1,m} \\ &\quad + F_-^0(lm) W_-(r) Y_{l-1,m} \end{aligned}$$

Derivative of the wave function in ***z*** direction

$$\begin{aligned} W_+(r) &= \frac{\partial}{\partial r} W(r) - \frac{l}{r} W(r) \\ W_-(r) &= \frac{\partial}{\partial r} W(r) + \frac{l+1}{r} W(r) \end{aligned}$$

Interpretation

$$\langle vk | p_i | ck \rangle \sim \sum_L \langle W^L | W_{\pm}^{L\pm 1} \rangle$$

- ***L*** character of the **valence** state couples to ***L-1*** or ***L+1*** character of the ***conduction*** band

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

Symmetry

- triclinic

$$\begin{pmatrix} \mathrm{Im}\,\epsilon_{xx} & \mathrm{Im}\,\epsilon_{xy} & \mathrm{Im}\,\epsilon_{xz} \\ \mathrm{Im}\,\epsilon_{xy} & \mathrm{Im}\,\epsilon_{yy} & \mathrm{Im}\,\epsilon_{yz} \\ \mathrm{Im}\,\epsilon_{xz} & \mathrm{Im}\,\epsilon_{yz} & \mathrm{Im}\,\epsilon_{zz} \end{pmatrix}$$

- monoclinic ($\alpha, \beta = 90°$)

$$\begin{pmatrix} \mathrm{Im}\,\epsilon_{xx} & \mathrm{Im}\,\epsilon_{xy} & 0 \\ \mathrm{Im}\,\epsilon_{xy} & \mathrm{Im}\,\epsilon_{yy} & 0 \\ 0 & 0 & \mathrm{Im}\,\epsilon_{zz} \end{pmatrix}$$

- orthorhombic

$$\begin{pmatrix} \mathrm{Im}\,\epsilon_{xx} & 0 & 0 \\ 0 & \mathrm{Im}\,\epsilon_{yy} & 0 \\ 0 & 0 & \mathrm{Im}\,\epsilon_{zz} \end{pmatrix}$$

- tetragonal, hexagonal

$$\begin{pmatrix} \mathrm{Im}\,\epsilon_{xx} & 0 & 0 \\ 0 & \mathrm{Im}\,\epsilon_{xx} & 0 \\ 0 & 0 & \mathrm{Im}\,\epsilon_{zz} \end{pmatrix}$$

- cubic

$$\begin{pmatrix} \mathrm{Im}\,\epsilon_{xx} & 0 & 0 \\ 0 & \mathrm{Im}\,\epsilon_{xx} & 0 \\ 0 & 0 & \mathrm{Im}\,\epsilon_{xx} \end{pmatrix}$$

Optical functions

- Dielectric tensor

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

$$\Re \epsilon_{ij} = \delta_{ij} \frac{2}{\pi} P \int_0^\infty \frac{\omega' \Im \epsilon_{ij}(\omega')}{\omega'^2 - \omega^2} d\omega'$$

- Optical conductivity

$$\Re \sigma_{ij}(\omega) = \frac{\omega}{4\pi} \Im \epsilon_{ij}(\omega)$$

- Refractive index

$$n_{ii} = \sqrt{\frac{|\epsilon_{ii}(\omega)| + \Re \epsilon_{ii}(\omega)}{2}} \qquad k_{ii}(\omega) = \sqrt{\frac{|\epsilon_{ii}(\omega)| - \Re \epsilon_{ii}(\omega)}{2}}$$

- Reflectivity

$$R_{ii}(\omega) = \frac{(m_{ii} - 1)^2 + k_{ii}^2}{(n_{ii} + 1)^2 + k_{ii}^2}$$

- Absorption

$$A_{ii}(\omega) = \frac{2\omega k_{ii}(\omega)}{c}$$

- Loss function

$$L_{ii}(\omega) = -\Im\left(\frac{1}{\epsilon_{ii}(\omega)}\right)$$

Magneto-optics

- Cubic, no SOC

$$\begin{pmatrix} \mathrm{Im}\,\epsilon_{xx} & 0 & 0 \\ 0 & \mathrm{Im}\,\epsilon_{xx} & 0 \\ 0 & 0 & \mathrm{Im}\,\epsilon_{xx} \end{pmatrix} \xrightarrow{KK} \begin{pmatrix} \mathrm{Re}\,\epsilon_{xx} & 0 & 0 \\ 0 & \mathrm{Re}\,\epsilon_{xx} & 0 \\ 0 & 0 & \mathrm{Re}\,\epsilon_{xx} \end{pmatrix}$$

- Cubic, with SOC and magnetism along ***z***

$$\begin{pmatrix} \mathrm{Im}\,\epsilon_{xx} & 0 & 0 \\ 0 & \mathrm{Im}\,\epsilon_{xx} & 0 \\ 0 & 0 & \mathrm{Im}\,\epsilon_{zz} \end{pmatrix} \xrightarrow{KK} \begin{pmatrix} \mathrm{Re}\,\epsilon_{xx} & 0 & 0 \\ 0 & \mathrm{Re}\,\epsilon_{xx} & 0 \\ 0 & 0 & \mathrm{Re}\,\epsilon_{zz} \end{pmatrix}$$

$$\begin{pmatrix} 0 & \mathrm{Re}\,\epsilon_{xy} & 0 \\ -\mathrm{Re}\,\epsilon_{xy} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \xrightarrow{KK} \begin{pmatrix} 0 & \mathrm{Im}\,\epsilon_{xy} & 0 \\ -\mathrm{Im}\,\epsilon_{xy} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

Computing momentum matrix elements

- Run SCF (to get converged density)
- Generate potential (***x lapw0***)
- Generate dense k-mesh (***x kgen***)
- Generate eigenvectors (***x lapw1 -???***)
- Generate Fermi distribution (***x lapw2 -fermi -???***)
- Calculate momentum matrix elements (***x optic -???***)

$$\langle vk | p_i | ck \rangle \langle vk | p_j | ck \rangle$$

- compute imaginary part of the dielectric function (***x joint***)
- (***x kram***) for computing other optical constants

optic program – input, output

input

- ***case.inop***

800	1	number of k-points, first k-point
-5.0	5.0	energy window for matrix elements
3		number of cases (see choices)
1		Re <x><x>
3		Re <z><z>
7		Im <x><y>
OFF		write unsquared matrix elements to file?

Choices:
1.....Re<x><x>
2.....Re<y><y>
3.....Re<z><z>
4.....Re<x><y>
5.....Re<x><z>
6.....Re<y><z>
7.....Im<x><y>
8.....Im<x><z>
9.....Im<y><z>

output

- ***case.symmat***
  $\langle vk | p_i | ck \rangle \langle vk | p_j | ck \rangle$
- ***case.mommat*** (ON)
  $\langle vk | p_j | ck \rangle$

joint program – input, output

- ***x joint***, computes dielectric tensor components

$$\mathrm{Im}\epsilon_{\alpha\beta}(\omega) = \frac{4\pi e^2}{m^2\omega^2}\sum_{c,v}\int d\mathbf{k}\,\langle c_\mathbf{k}|p^\alpha|v_\mathbf{k}\rangle\langle v_\mathbf{k}|p^\beta|c_\mathbf{k}\rangle\,\delta(\varepsilon_{c_\mathbf{k}}-\varepsilon_{v_\mathbf{k}}-\omega)$$

input

- ***case.injoint***

1 18	lower and upper band index
0.000 0.001 1.000	Emin, dE, Emax [Ry]
ev	output units eV / Ry
4	switch
1	number of columns
0.1 0.2	broadening for Drude terms choose gamma for each case!

Switch:
0...JOINT DOS for each band combination
1...JOINT DOS sum over all band combinations
2...DOS for each band
3...DOS sum over all bands
4...Im(EPSILON) total
5...Im(EPSILON) for each band combination
6...intraband contributions
7...intraband contributions including band analysis

output

- ***case.joint***

kram program – input, output

input

- ***case.inkram*** (metal)

0.1	broadening gamma
0.0	energy shift (scissors operator)
1	add intraband contributions 1/0
12.6	plasma frequency
0.2	broadening for intraband part

- ***case.inkram*** (semiconductor)

0.05	broadening gamma
1.000	energy shift (scissors operator)
0	add intraband contributions 1/0

output

- ***case.epsilon***
- ***case.sigmak***
- ***case refraction***
- ***case.absorp***
- ***case.eloss***

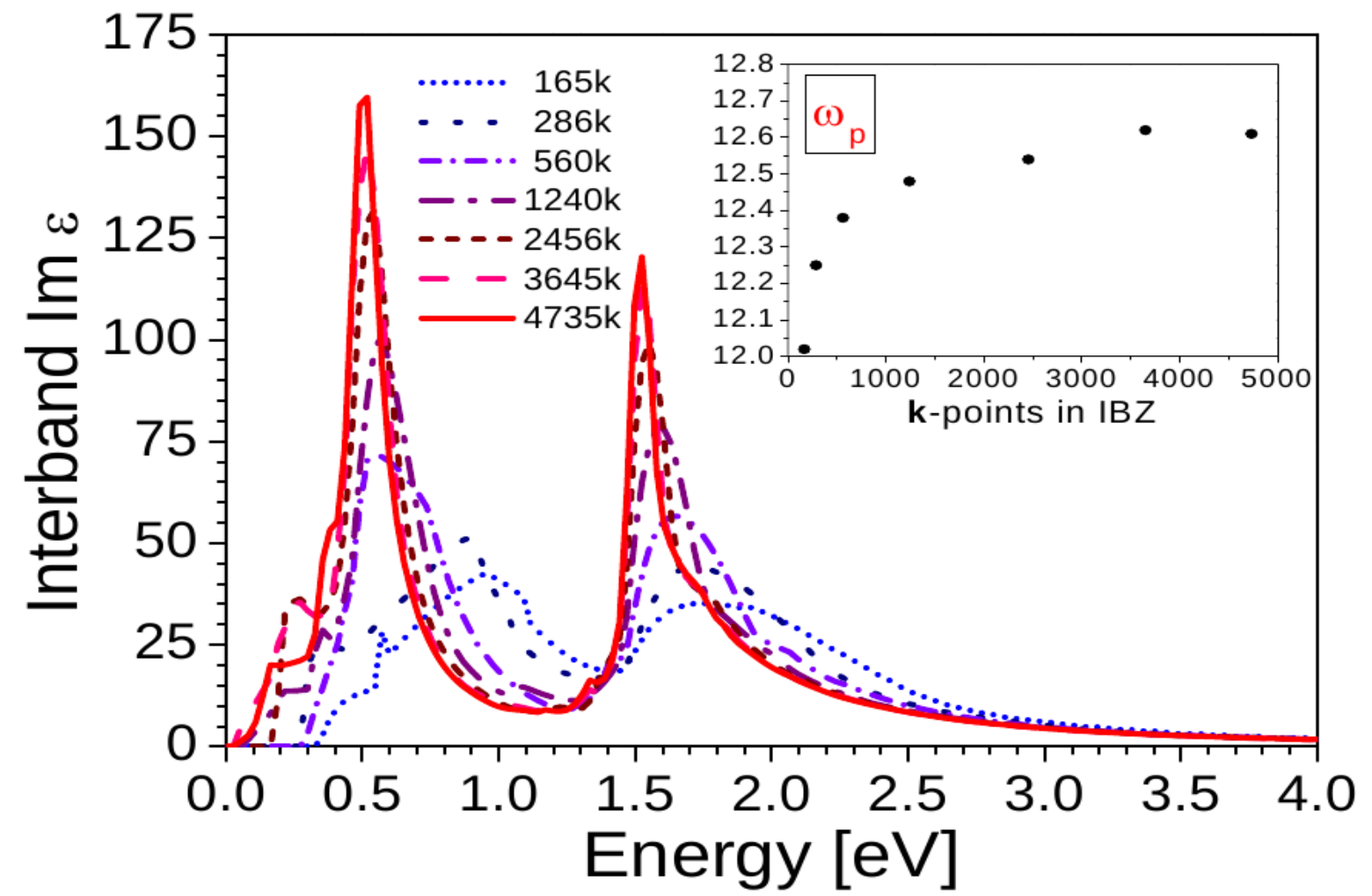
Intra-band contribution

$$\mathrm{Im}\,\epsilon_{\alpha\beta}(\omega) = \frac{4\pi N e^2}{m}\frac{\Gamma}{\omega(\omega^2+\Gamma^2)} = \frac{\Gamma\omega^2_{p,\alpha\beta}}{\omega(\omega^2+\Gamma^2)}$$

$$\mathrm{Re}\,\epsilon_{\alpha\beta}(\omega) = 1 - \frac{\omega^2_{p,\alpha\beta}}{(\omega^2+\Gamma^2)}$$

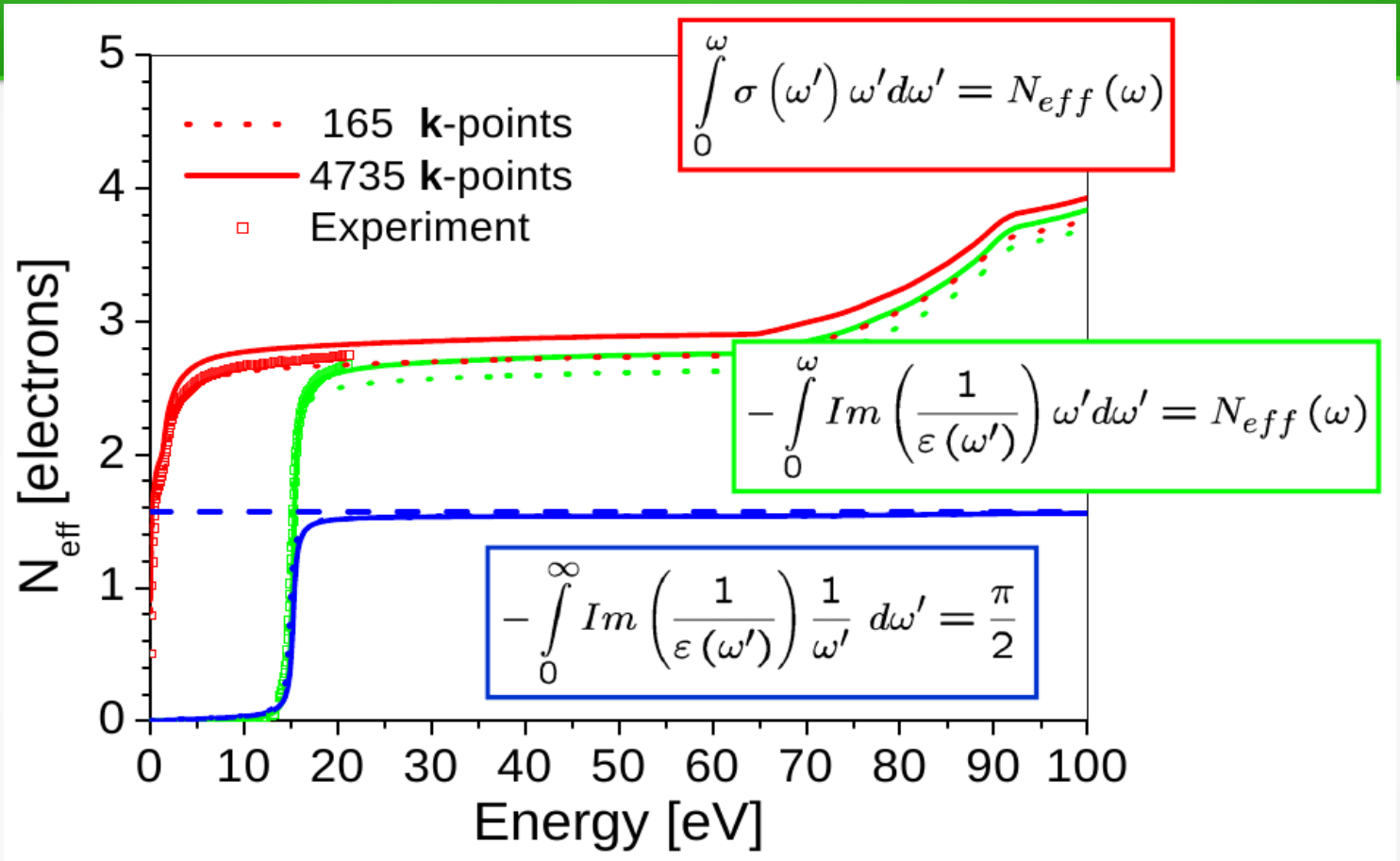
$$\omega^2_{p,\alpha\beta} = \frac{e^2}{m^2\pi^2}\sum_l \int d\mathbf{k}\ \langle l|p^\alpha|l\rangle_{\mathbf{k}}\langle l|p^\beta|l\rangle_{\mathbf{k}}\ \delta(\varepsilon_l - \varepsilon_F)$$

Example: Al, k-point convergence



- always check **k-point convergence** (use dense k-mesh !!!)

Example: Al, sumrules

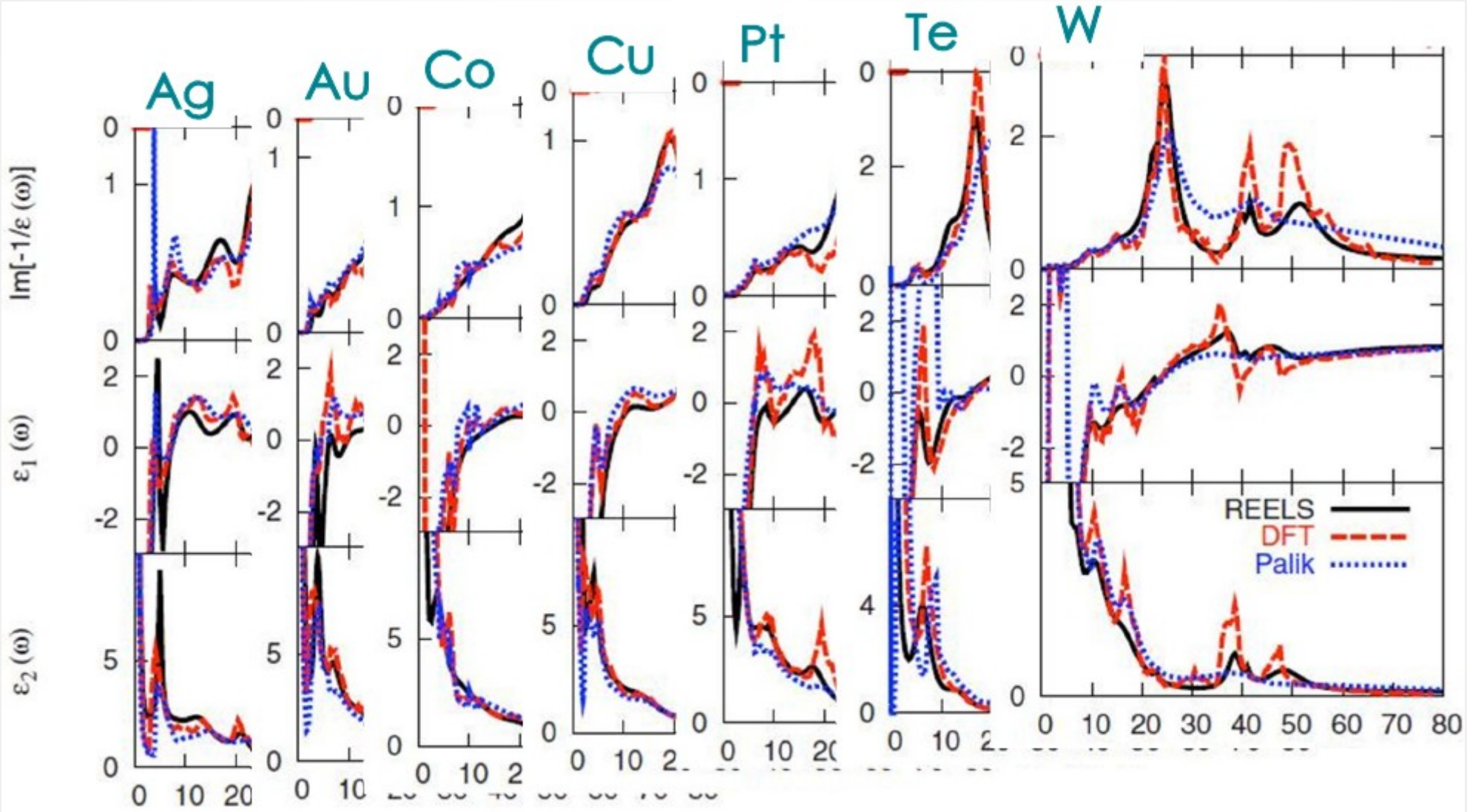


- for KK transformation you need *Im(ε)* in a wide energy range

$$\Re\,\epsilon_{ij} = \delta_{ij}\frac{2}{\pi} P \int_0^{\infty} \frac{\omega' \Im\,\epsilon_{ij}(\omega')}{\omega'^2 - \omega^2} d\omega'$$

- be aware that LAPW linearization breaks down for high conduction states !!!

Theory vs experiment



W. Werner, et al J. Phys. Chem. Ref. Data 38, 1013 (2009)

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).

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

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

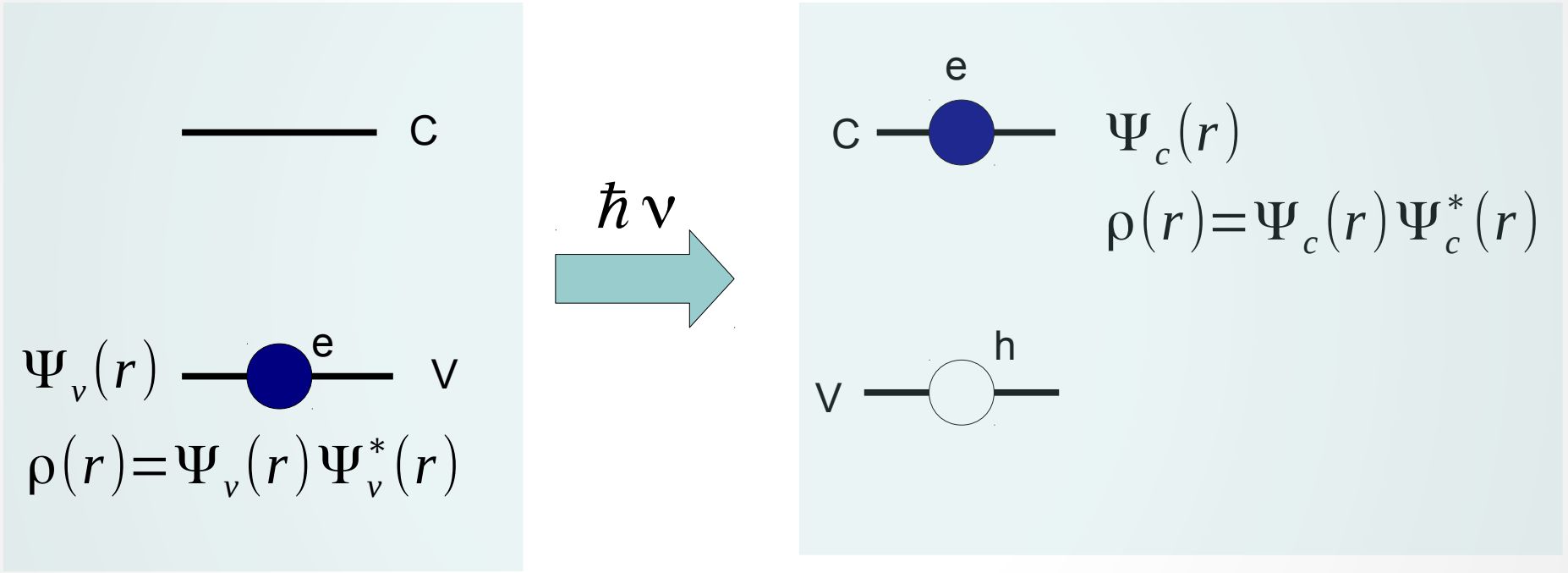
$$\varepsilon_{vk}^{QP} = \varepsilon_{vk}^{LDA}$$

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

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

non-locality of the self energy operator or scissor shift

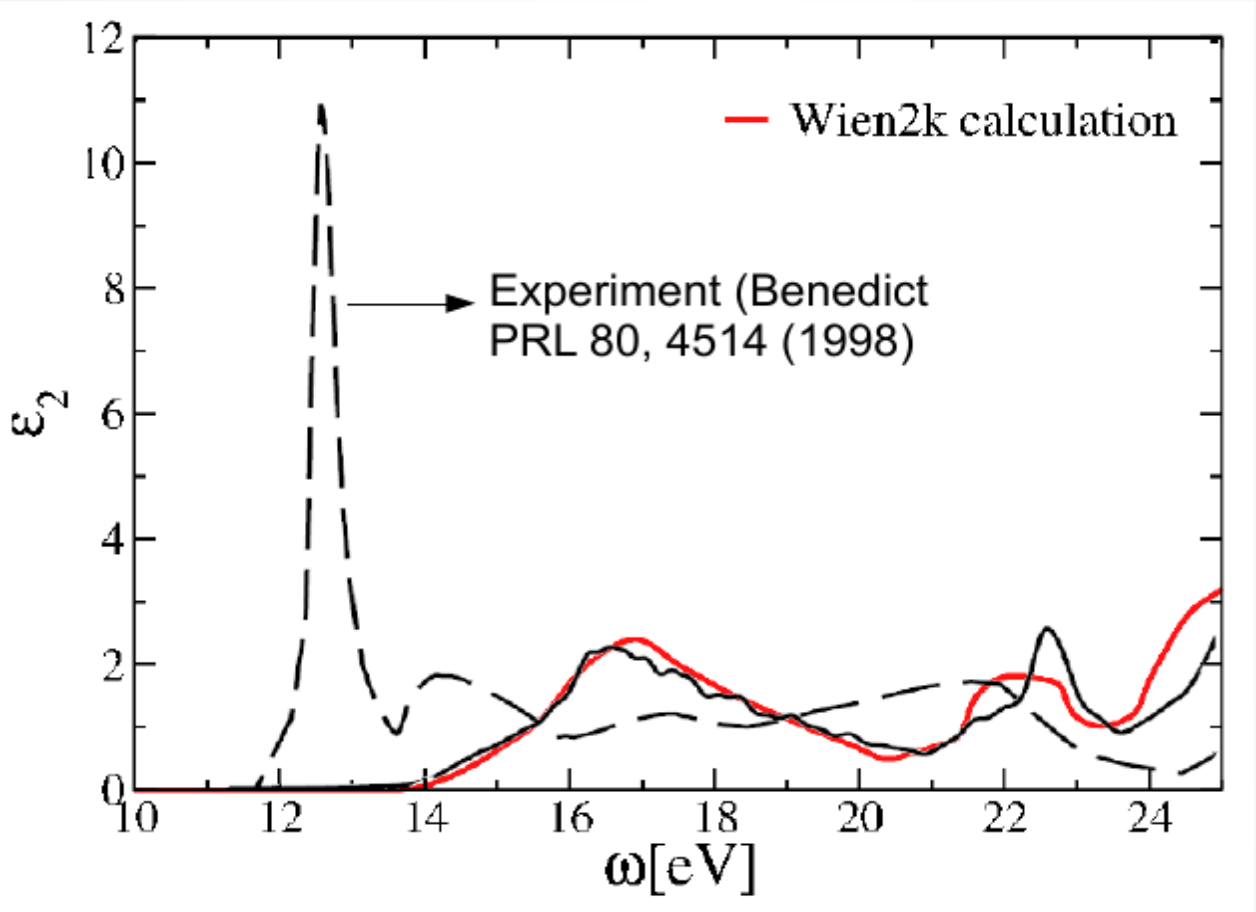
Beyond IPA

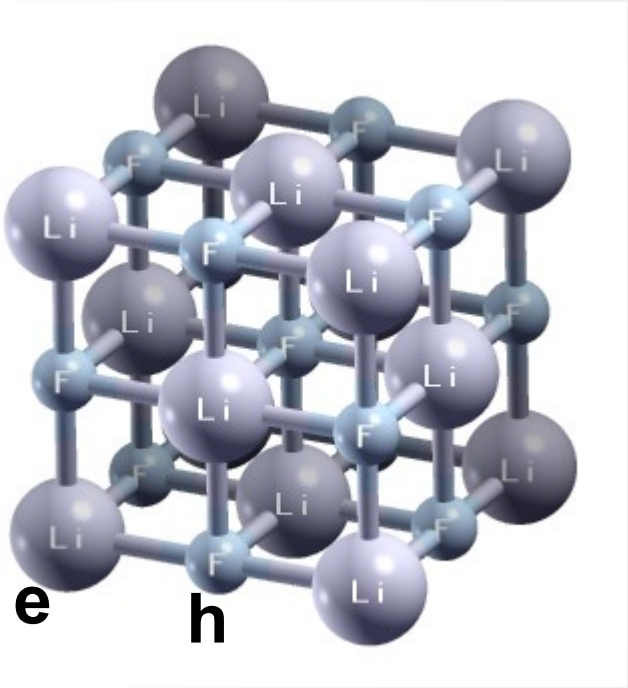


$$\rho_c(r) \neq \rho_v(r)$$

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

LiF absorption spectra



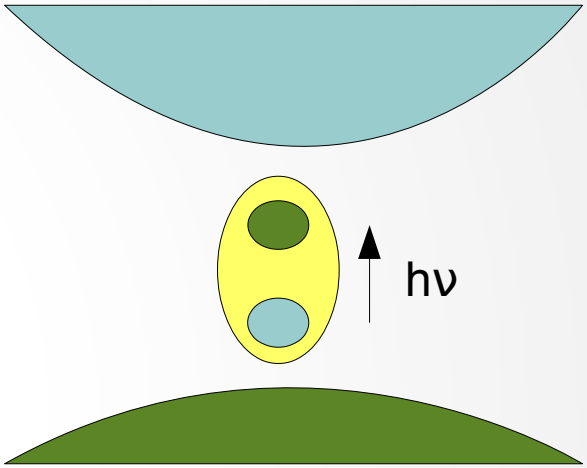


Bethe-Salpeter Equation

- 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.

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:

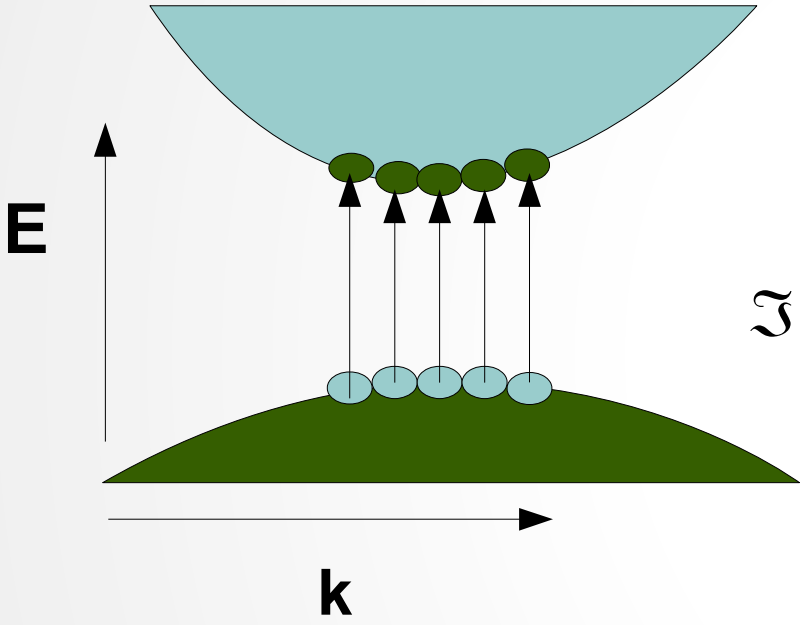
$$\langle vc|W^d(E_\lambda)|v'c'\rangle = \int dr\,dr'\,\psi_c^*(r)\psi_{c'}(r)\psi_v(r')\psi_{v'}^*(r')\frac{i}{2\pi}\int d\omega\, e^{i\omega 0^+} W(r,r',\omega)$$
$$\times\left[\frac{1}{E_\lambda-\omega-(E_{c'}-E_{v'})+iO^+}+\frac{1}{E_\lambda+\omega-(E_c-E_v)+iO^+}\right]$$

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

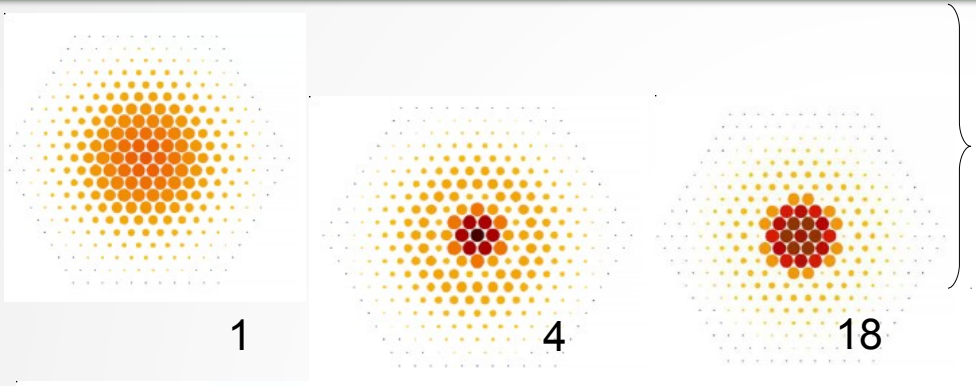


macroscopic dielectric function

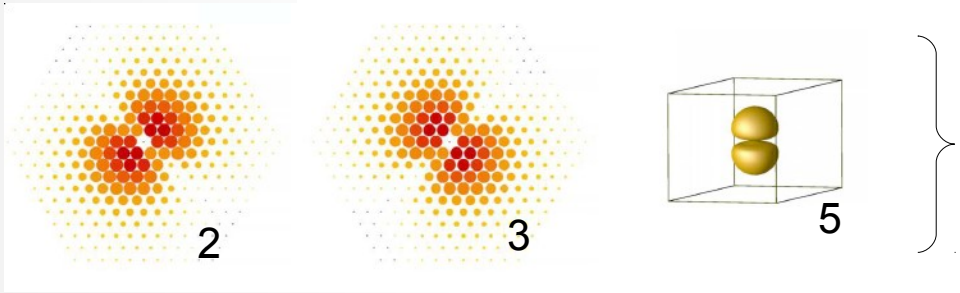
$$\Im\,\epsilon_M(\omega) = \sum_{\lambda} \left| \sum_{vck} A^{\lambda}_{vck} \frac{\langle vk|p|ck\rangle}{(\varepsilon_{ck} - \varepsilon_{vk})} \right|^2 \delta(E_\lambda - \hbar\omega)$$

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

Exciton envelope function in AlN



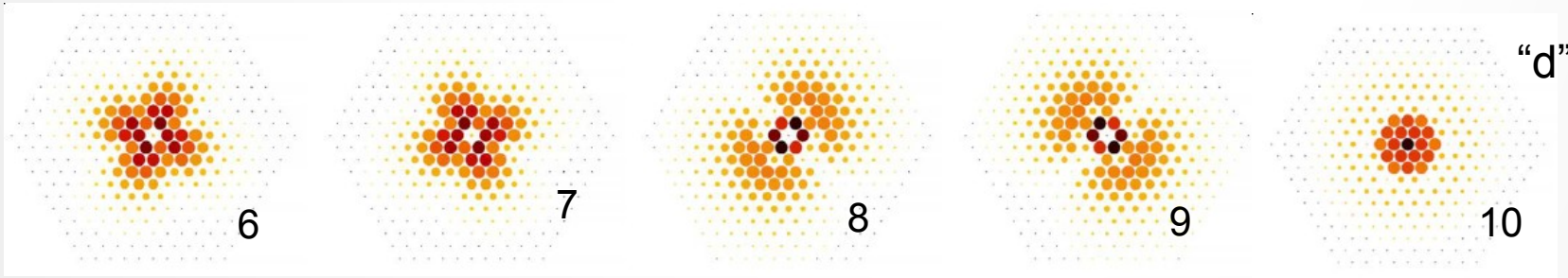
"s"- dipole active



"p"- dipole inactive

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

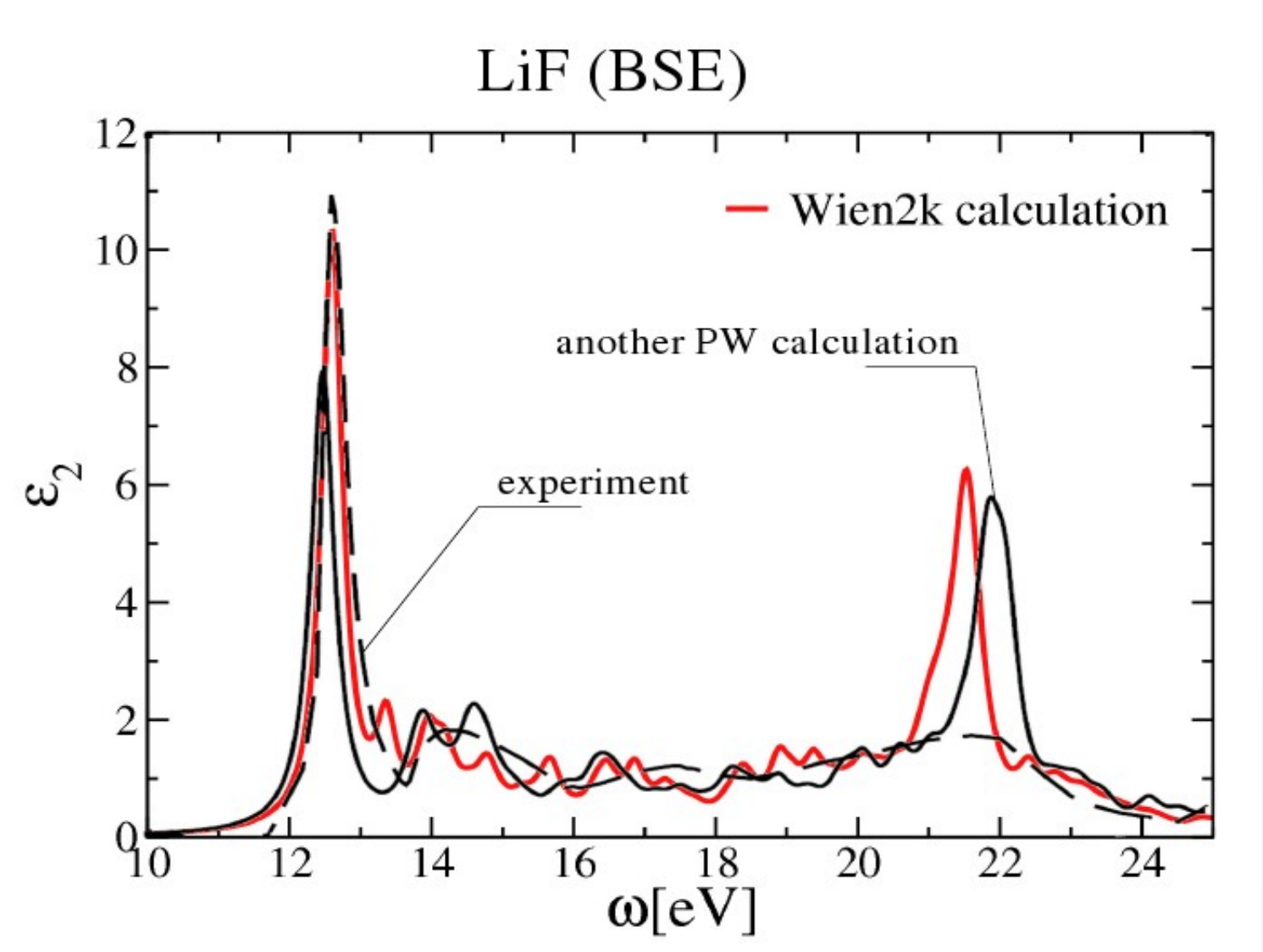
$$oscil.\,strength \sim \frac{1}{n^3}$$



"d" - dipole inactive

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

LiF absorption spectra



BSE in wien2k

- BSE is computationally very expensive
- available upon request

rolask@ihpc.a-star.edu.sg