Optical Properties of Solids

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Outline

Basics
- light scattering
- dielectric tensor in the RPA
- sumrules
- symmetry
- the band gap problem

Program
- program flow
- inputs
- outputs

Examples
- convergence
- results

Outlook
- applications
- beyond linear optics
- beyond RPA

Outline

Basics	light scattering dielectric tensor in the RPA sumrules symmetry the band gap problem
Program	program flow inputs outputs
Examples	convergence results
Outlook	applications beyond linear optics beyond RPA

Properties & Applications

Dielectric function
Optical absorption
Optical gap
Exciton binding energy
Photoemission spectra
Core level spectra
Raman scattering
Compton scattering
Positron annihilation
NMR spectra
Electron spectroscopy

Light emitting diodes
Lasers
Solar cells
Displays
Computer screens
Smart windows
Light bulbs
CDs & DVDs

understand physics
characterize materials
tailor special properties

Light - Matter Interaction

Response to external electric field $\boldsymbol{E}$

Polarizability: $P_\alpha = \sum_\beta \underline{\chi_{\alpha\beta}} E_\beta + \sum_{\beta\gamma} \chi_{\alpha\beta\gamma} E_\beta E_\gamma + \ldots$

Linear approximation:

$\mathbf{P} = \chi \mathbf{E}$	susceptibility χ
$\mathbf{J} = \sigma \mathbf{E}$	conductivity σ
$\mathbf{D} = \epsilon \mathbf{E}$	dielectric tensor ϵ

$$D_\alpha(\mathbf{r}, t) = \sum_\beta \int_{\mathbf{r}'} \int_{t'} \epsilon_{\alpha\beta}(\mathbf{r}, \mathbf{r}', t - t') E_\beta(\mathbf{r}', t')$$

Fourier transform:

$$D_\alpha(\mathbf{q} + \mathbf{G}, \omega) = \sum_\beta \sum_{\mathbf{G}'} \underline{\epsilon_{\alpha\beta}(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}', \omega)} E_\beta(\mathbf{q} + \mathbf{G}', \omega)$$

The Dielectric Tensor

Free electrons: Lindhard formula

$$\epsilon(\mathbf{q},\omega) = 1 - \lim_{\eta\to 0} \frac{4\pi e^2}{|\mathbf{q}|^2\Omega_c} \sum_{\mathbf{k}} \frac{f(\varepsilon_{\mathbf{k+q}}) - f(\varepsilon_{\mathbf{k}})}{\varepsilon_{\mathbf{k+q}} - \varepsilon_{\mathbf{k}} - \omega - i\eta}$$

Bloch electrons:

$$\epsilon(\mathbf{q},\omega) = 1 - \lim_{\eta\to 0} \frac{4\pi e^2}{|\mathbf{q}|^2\Omega_c} \sum_{\mathbf{k},l,l'} |\mathbf{k}+\mathbf{q},l'|\mathbf{k},l|^2 \frac{f(\varepsilon_{\mathbf{k+q}}) - f(\varepsilon_{\mathbf{k}})}{\varepsilon_{\mathbf{k+q}} - \varepsilon_{\mathbf{k}} - \omega - i\eta}$$

$$\lim_{q\to 0} |\mathbf{k}+\mathbf{q},l'|\mathbf{k},l|^2 = \delta_{l'l} + (1-\delta_{l'l}) \frac{q^2}{m^2\omega_{l'l}^2} |P_{l',l}|^2$$

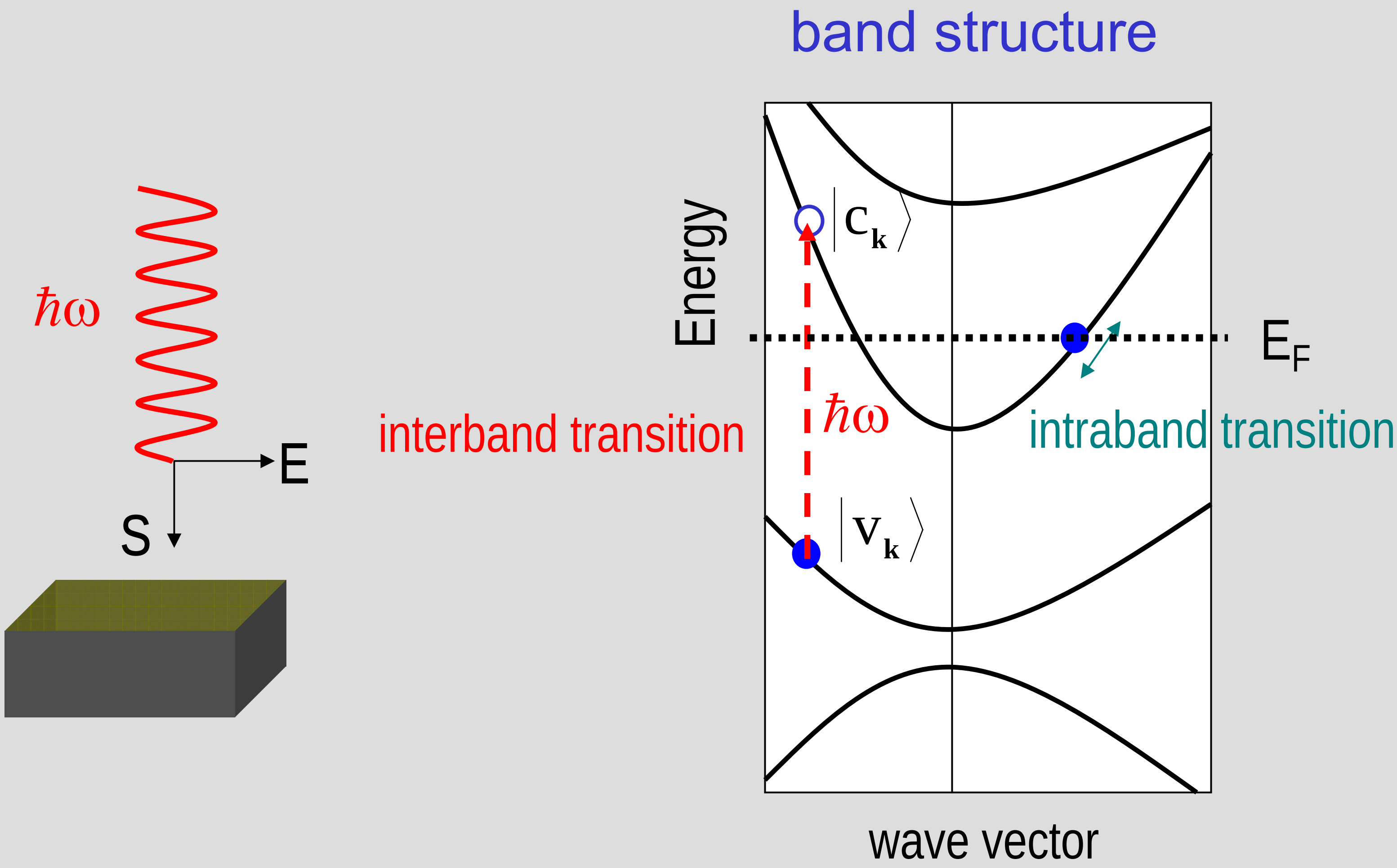
intraband interband

Interband contribution:

$$\mathrm{Im}\,\epsilon_{\alpha\beta}(\omega) = \frac{4\pi e^2}{m^2\omega^2} \sum_{l,l'} \int d\mathbf{k}\, \langle l'|p^\alpha|l\rangle_{\mathbf{k}} \langle l|p^\beta|l'\rangle_{\mathbf{k}}\, (f(\varepsilon_l) - f(\varepsilon_{l'}))\, \delta(\varepsilon_{l'} - \varepsilon_l - \omega)$$

independent particle approximation, random phase approximation (RPA)

Light Scattering



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

Optical Properties

Optical "Constants"

Complex dielectric tensor:

Kramers-Kronig relations

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

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

Optical conductivity:

$$\mathrm{Re}\,\sigma_{\alpha\beta}(\omega) = \frac{\omega}{4\pi} \mathrm{Im}\, \epsilon_{\alpha\beta}(\omega)$$

Complex refractive index:

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

Reflectivity:

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

Absorption coefficient:

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

Loss function:

$$L_{\alpha\alpha}(\omega) = -\mathrm{Im}\left(\frac{1}{\varepsilon_{\alpha\alpha}(\omega)}\right)$$

Intraband Contributions

Dielectric Tensor:

Drude-like terms

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

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

Optical conductivity:

$$\text{Re}\,\sigma_{\alpha\beta}(\omega) = \frac{\omega}{4\pi}\,\text{Im}\,\epsilon_{\alpha\beta}(\omega) = \frac{\omega^2_{p,\alpha\beta}}{4\pi}\frac{\Gamma}{\omega^2+\Gamma^2}$$

Plasma frequency:

$$\omega^2_{p,\alpha\beta} = \frac{4\pi e^2}{\Omega^2}\left(\frac{n}{m}\right)_{\alpha\beta} = \frac{e^2}{m^2\pi^2}\sum_l \int d\mathbf{k}\,\langle l|p^\alpha|l\rangle_{\mathbf{k}}\langle l|p^\beta|l\rangle_{\mathbf{k}}\,\delta(\varepsilon_l-\varepsilon_F)$$

Metals

Sumrules

$$\int_0^{\omega} \sigma\left(\omega'\right) \omega' d\omega' = N_{eff}(\omega)$$

$$-\int_0^{\omega} Im\left(\frac{1}{\varepsilon\left(\omega'\right)}\right) \omega' d\omega' = N_{eff}(\omega)$$

$$-\int_0^{\infty} Im\left(\frac{1}{\varepsilon\left(\omega'\right)}\right) \frac{1}{\omega'}\, d\omega' = \frac{\pi}{2}$$

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

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

Magneto-optics

without magnetic field, spin-orbit coupling: cubic

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

with magnetic field H ıı z, spin-orbit coupling: tetragonal

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

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

Example: Ni

Be careful ....

Wavefunction vs. Density

Hartree-Fock:

ε_i ionization energies

$$\varepsilon_i = E(n_1, n_2, \ldots, n_i, \ldots, n_N) - E(n_1, n_2, \ldots, n_{i-1}, \ldots, n_N)$$

Koopman's theorem

DFT:

ε_i Lagrange parameters

$$\varepsilon_i(n_1, n_2, \ldots, n_i, \ldots, n_N) = \frac{dE}{dn_i}$$

Janak's theorem

$\psi_i(\mathbf{r})$ auxiliary functions $\rho(\mathbf{r}) = \sum_i f_i \; |\psi_i(\mathbf{r})|^2$

Open Questions

Approximations used:

Ground state:

$$V_{xc}(\mathbf{r}) = \frac{dE_{xc}\left(\rho(\mathbf{r})\right)}{d\rho(\mathbf{r})}$$

Local Density Approximation (LDA)

Generalized Gradient Approximation (GGA)

Excited state:

Interpretation within one-particle picture
Interpretation of excited states in terms of ground state properties
Electron-hole interaction ignored (RPA)

Where do possible errors come from?
How to treat excited states ab initio?

The Band Gap Problem

Ionization energy $\varepsilon_N(N) = -I$

Electro-affinity $\varepsilon_{N+1}(N+1) = -A$

Band gap $E_g = I - A = \varepsilon_{N+1}(N+1) - \varepsilon_N(N)$

$$E_g = \underbrace{\varepsilon_{N+1}(N) - \varepsilon_N(N)}_{\varepsilon_g} + \underbrace{\varepsilon_{N+1}(N+1) - \varepsilon_{N+1}(N)}_{\Delta_{xc}}$$

$$\boxed{E_g = \varepsilon_g + \Delta_{xc}}$$

$\boxed{\Delta_{xc}}$ shift of conduction bands: scissors operator

many-body perturbation theory: GW approach

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Program Flow

SCF cycle	converged potential
kgen	dense mesh
lapw1	eigenstates
lapw2	Fermi distribution
optic	momentum matrix elements
joint	dielectrix tensor components
kram	$\mathrm{Re}\,\varepsilon \longleftrightarrow \mathrm{Im}\,\varepsilon$ optical coefficients, broadening, scissors operator

Optics in WIEN2k

"optic"

al.inop

2000 1	number of k-points, first k-point
-5.0 2.2	E_{min}, E_{max}: energy window for matrix elements
1	number of cases (see choices below)
1	Re <x><x>
OFF	unsymmetrized matrix elements written to file?

ni.inop (magneto-optics)

800 1	number of k-points, first k-point
-5.0 5.0	Emin, Emax: energy window for matrix elements
3	number of cases (see choices below)
1	Re <x><x>
3	Re <z><z>
7	Im <x><y>
OFF	

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>

"joint"

al.injoint

1 18	lower and upper band index
0.000 0.001 1.000	E_{min}, dE, Emax [Ry]
eV	output units eV / Ry
4	switch
1	number of columns to be considered
0.1 0.2	broadening for Drude model
	choose gamma for each case!

SWITCH

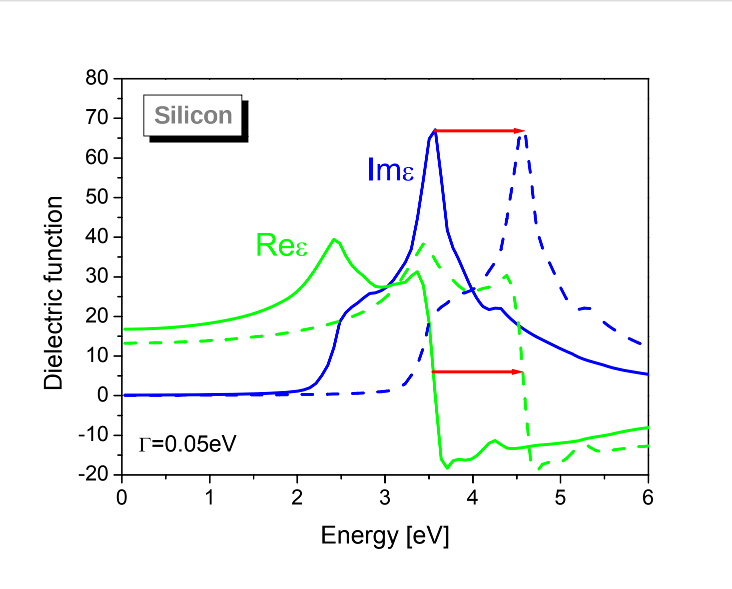
0...JOINT DOS	for each band combination
1...JOINT DOS	sum over all band combinations
2...DOS	for each band
3...DOS	sum over all bands
4...Im(EPSILON)	total
5...Im(EPSILON)	for each band combination
6...INTRABAND	contributions
7...INTRABAND	contributions including band analysis

"kram"

al.inkram

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

as number of colums
as number of colums



si.inkram

0.05	broadening gamma
1.00	energy shift (scissors operator)
0	
….	

Inputs

optic

case.symmat	momentum matrix elements, symmetrized
case.mommat	analysis, NLO

joint

case.joint	Im ε	SWITCH 4

kram

case.epsilon	complex dielectric tensor
case.sigmak	optical conductivity
case.refraction	refractive index
case.absorp	absorption coefficient
case.eloss	loss function

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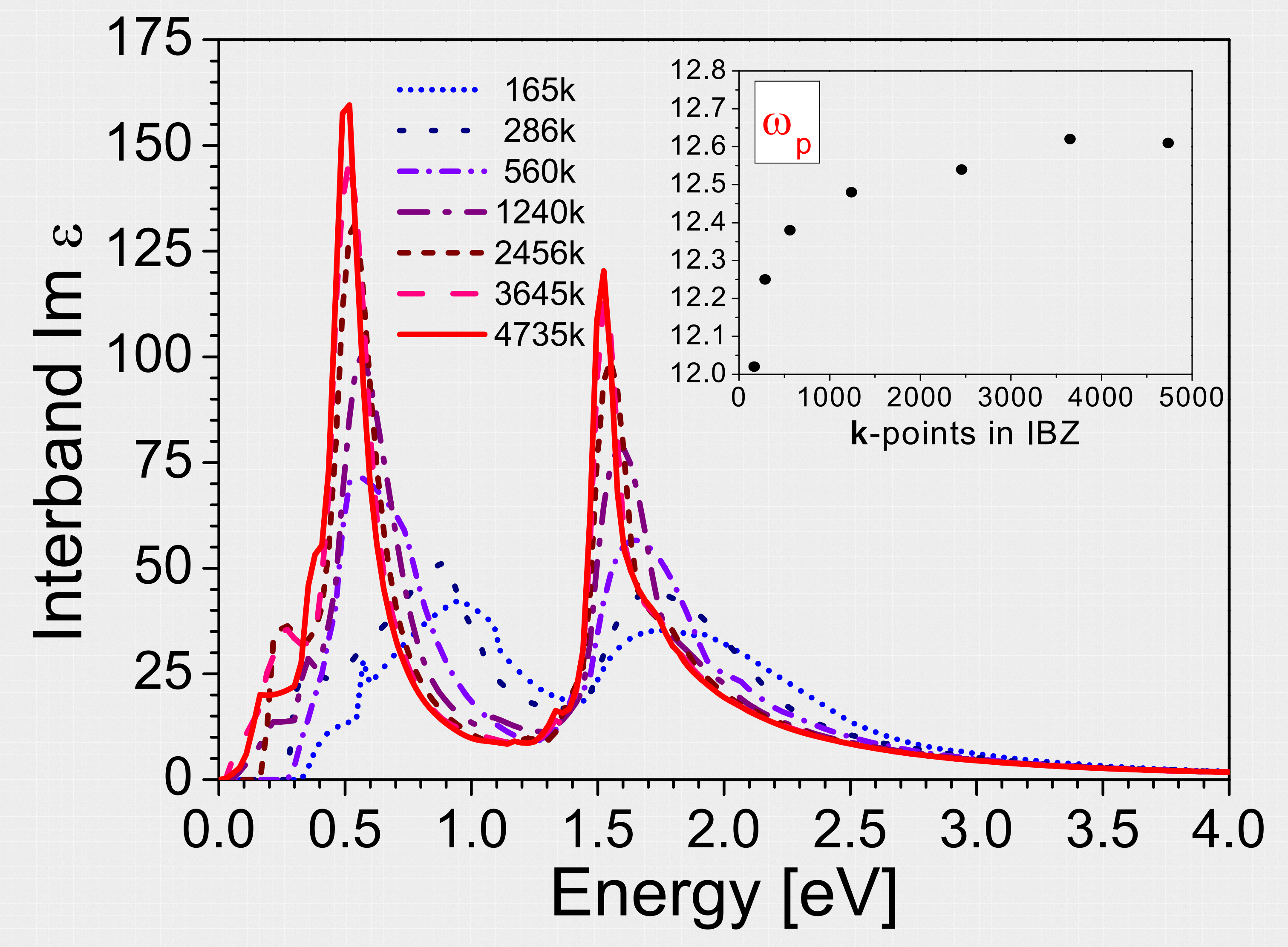
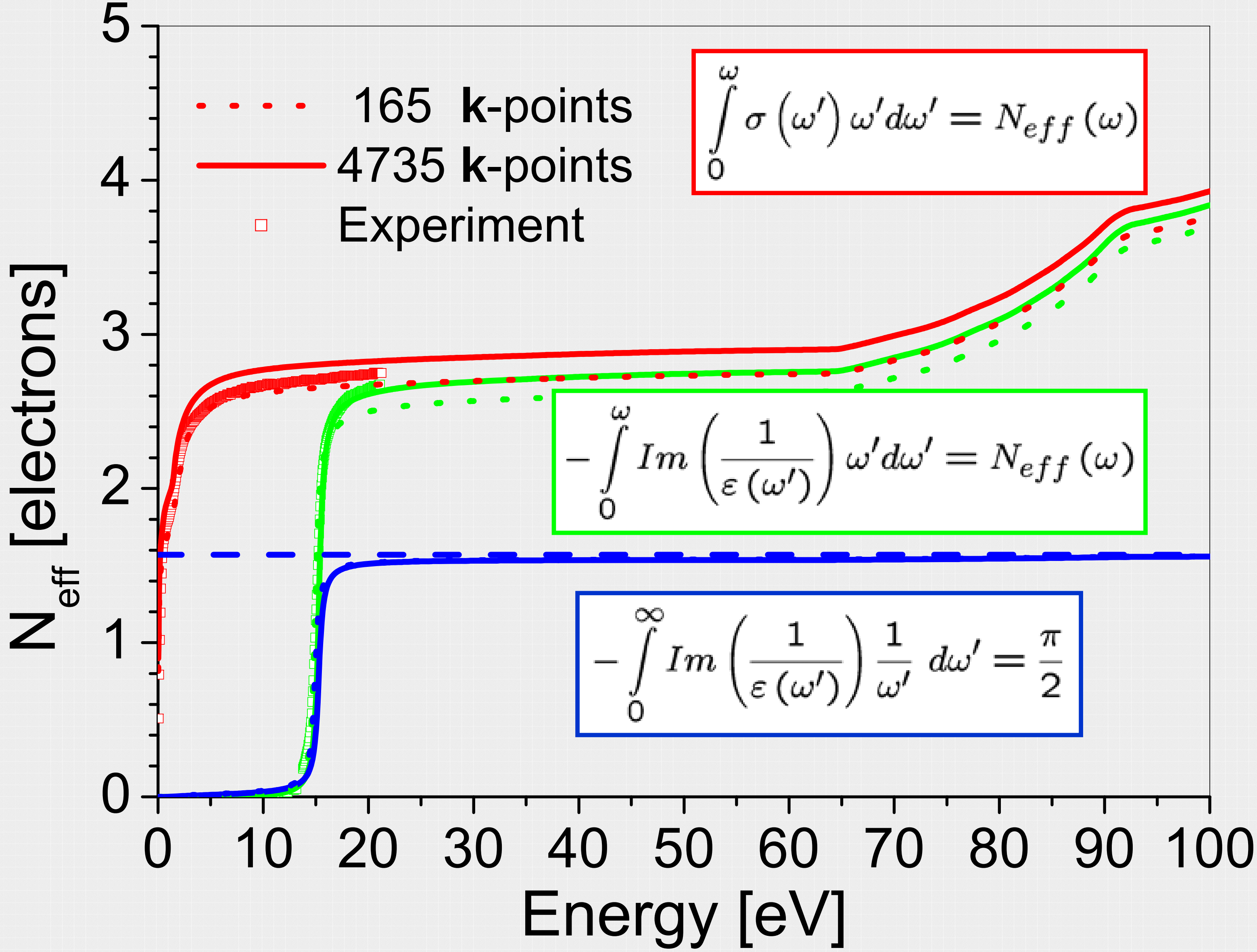
Results ....

Convergence



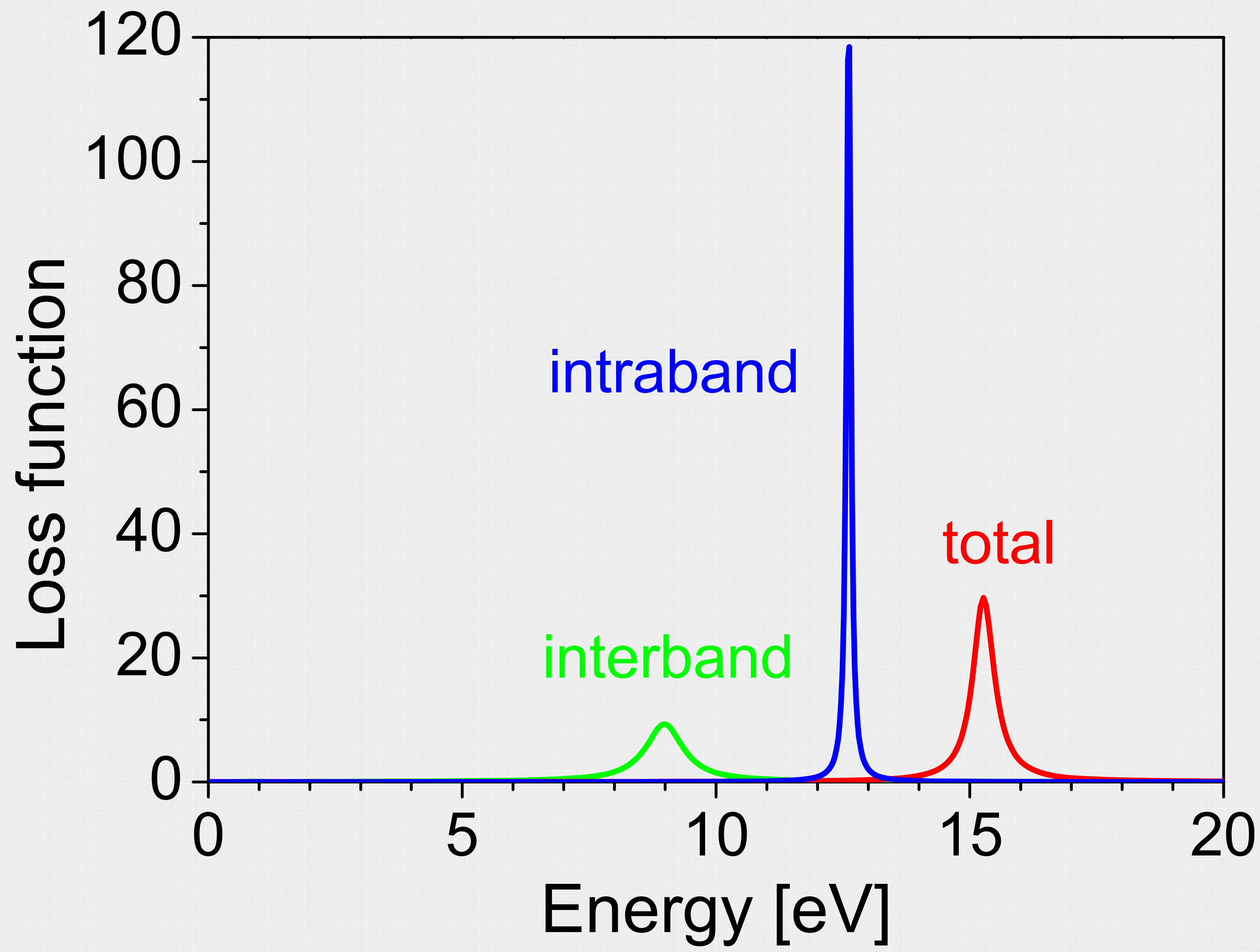
Example: Al

Sumrules



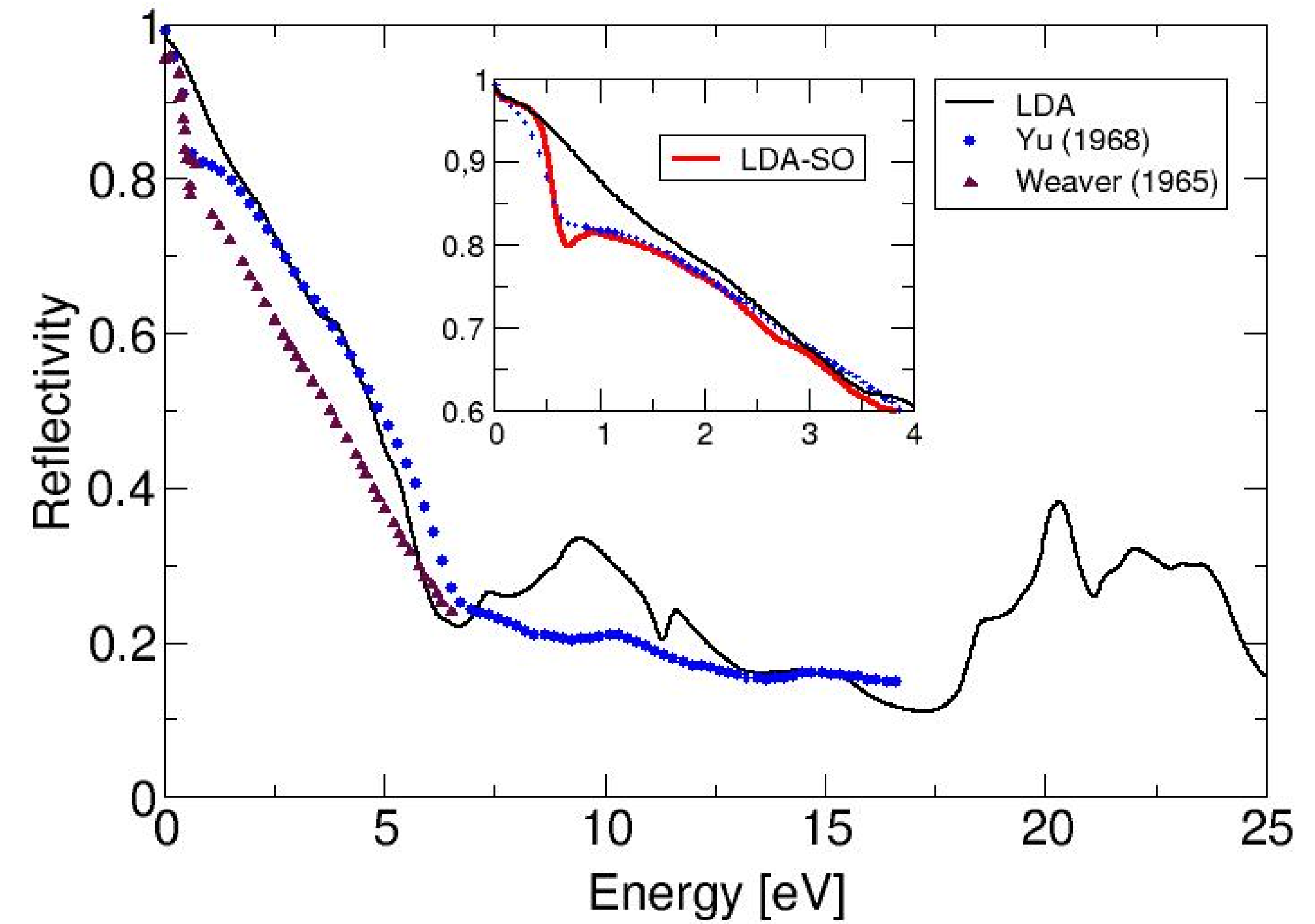
Example: Al

Loss Function



Example: Al

Theory - Experiment



K. Glantschnig, and C. Ambrosch-Draxl, (preprint).

Example: Platinum

C. Ambrosch-Draxl and J. O. Sofo
Comp. Phys. Commun., in print