Excited state properties
within WIEN2k

Claudia Ambrosch-Draxl, University of Leoben, Austria
Chair of Atomistic Modelling and Design of Materials

Beyond the ground state

Basics about light scattering

- The dielectric tensor

The WIEN2k code

- The program
- Input / output
- Examples

Outlook

- TDDFT versus manybody perturbation theory

Contents

Resonse to external electric field $\mathbf{E}$

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

Linear approximation

susceptibility χ $\quad \mathbf{P} = \chi \mathbf{E}$

conductivity σ $\quad \mathbf{J} = \sigma \mathbf{E}$

dielectric tensor ϵ $\quad \mathbf{D} = \epsilon \mathbf{E}$

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

Fourier transform

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

The dielectric tensor

- Free electrons: the Lindhard formula

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

- Bloch electrons

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

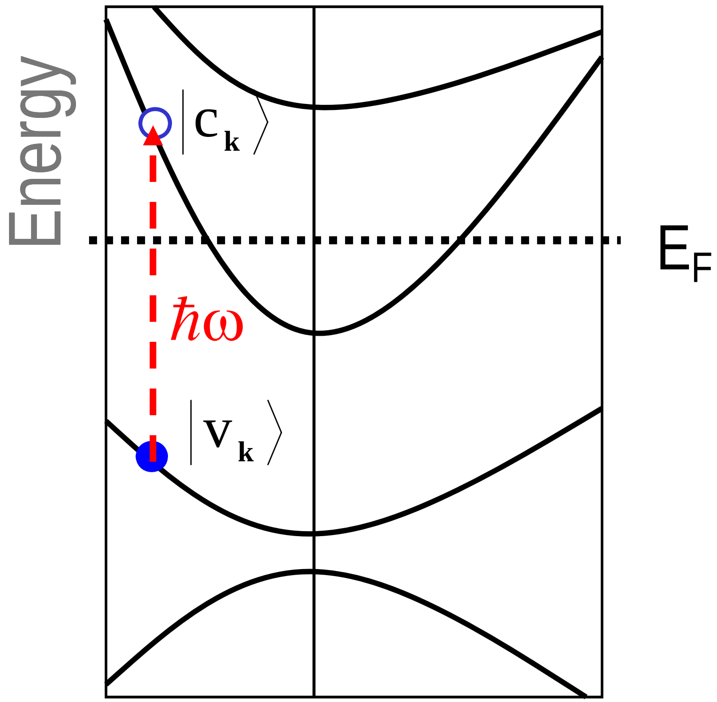
$$\lim_{q\to 0} |\mathbf{k}+\mathbf{q}, l'|\mathbf{k}, l|^2 = \delta_{l'l} + (1-\delta_{l'l})\frac{q^2}{m^2\omega_{l'l}^2}|P_{l',l}|^2$$

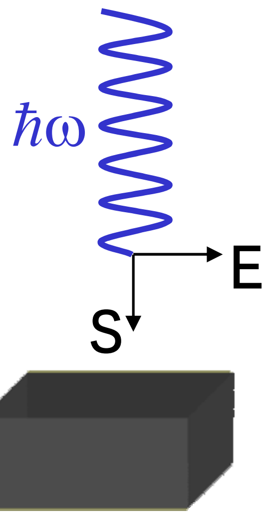
intraband | interband

Interband contributions

- Independent particle approximation

RPA





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

Optical *constants*

- Complex dielectric tensor

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

- Optical conductivity

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

- Complex refractive index

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

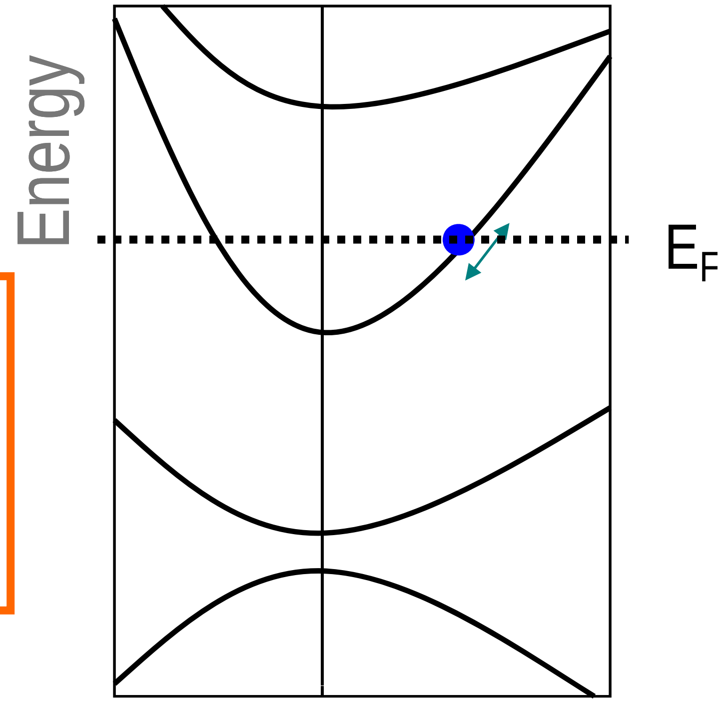
- Reflectivity
- Absorption coefficient
- Loss function

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

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

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

Intraband contributions



- Dielectric tensor

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

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

- Optical conductivity

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

Drude-*like* terms

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

plasma frequency

Sumrules

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

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

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

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: example

- 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 ‖z, spin-orbit coupling: tetragonal

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

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

The Program …

SCF cycle → converged potential

- x kgen → dense mesh
- x lapw1 → Kohn-Sham states (higher E_{max})
- x lapw2 -Fermi → Fermi distribution

optic package

- x optic → momentum matrix elements
- x joint → tensor components
- x kram → optical *constants*
  ↔ life time broadening
  ↔ *scissors* shift

The Program Flow

optic

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

- Al.inop

2000 1	number of k-points, first k-point
-5.0 2.2	energy window for matrix elements
1	number of cases (see choices)
1	Re <x><x>
OFF	write unsymmetrized matrix elements to file?

- Ni.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	

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

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

- 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 term(s)
	choose gamma for each case!

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	

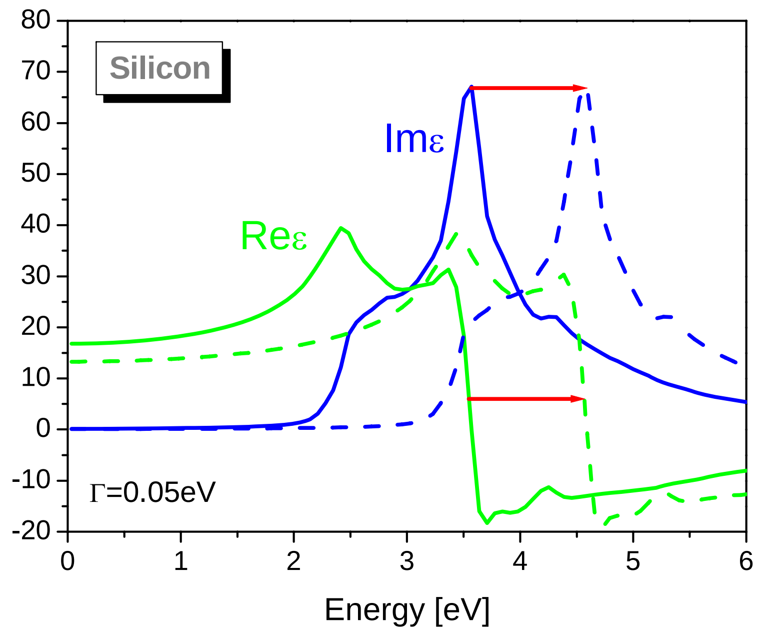
kram

Al.inkram

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

Si.inkram

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



Inputs

optic

- case.symmat
- case.mommat

joint

- case.joint

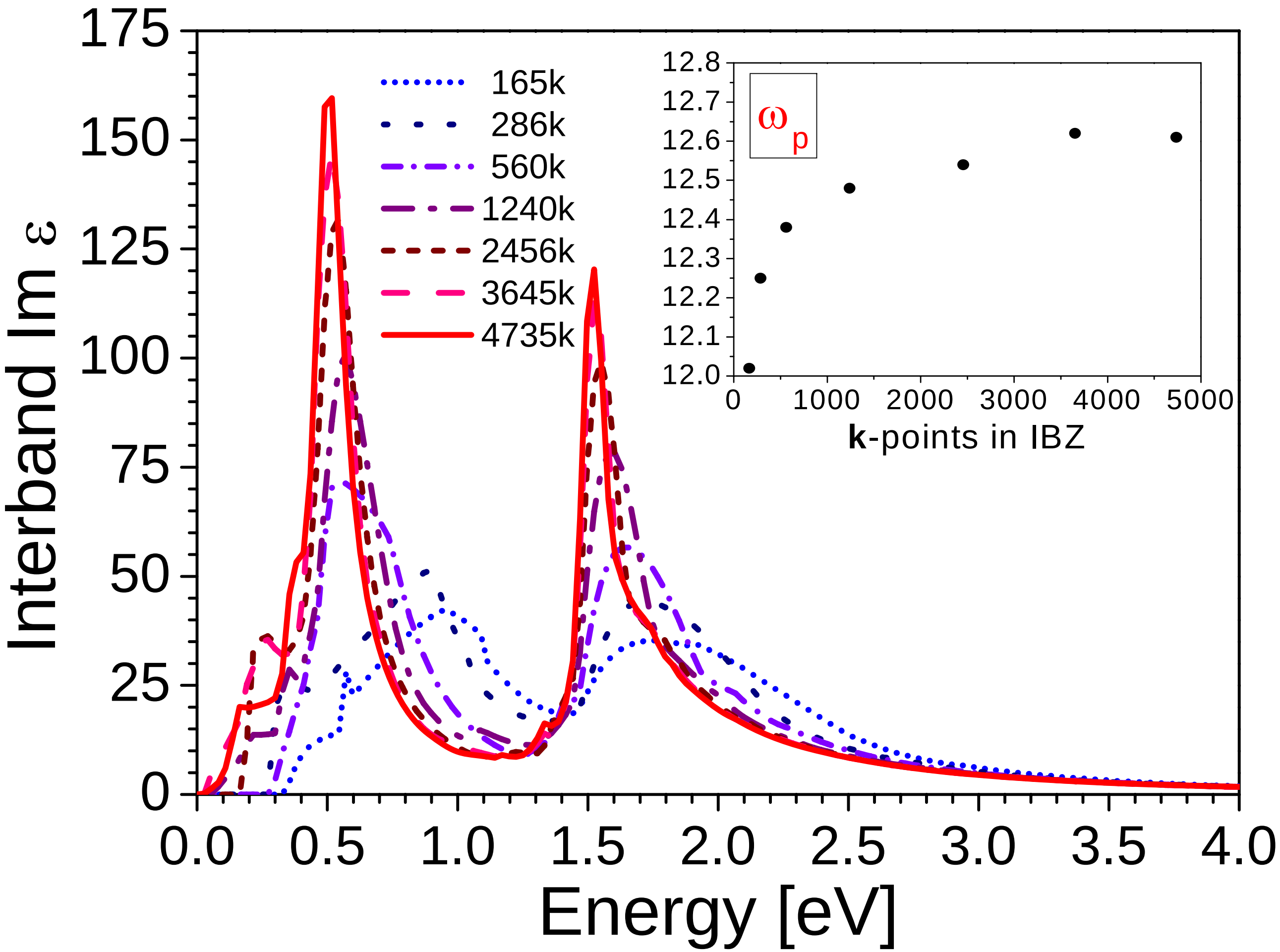
kram

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

Outputs

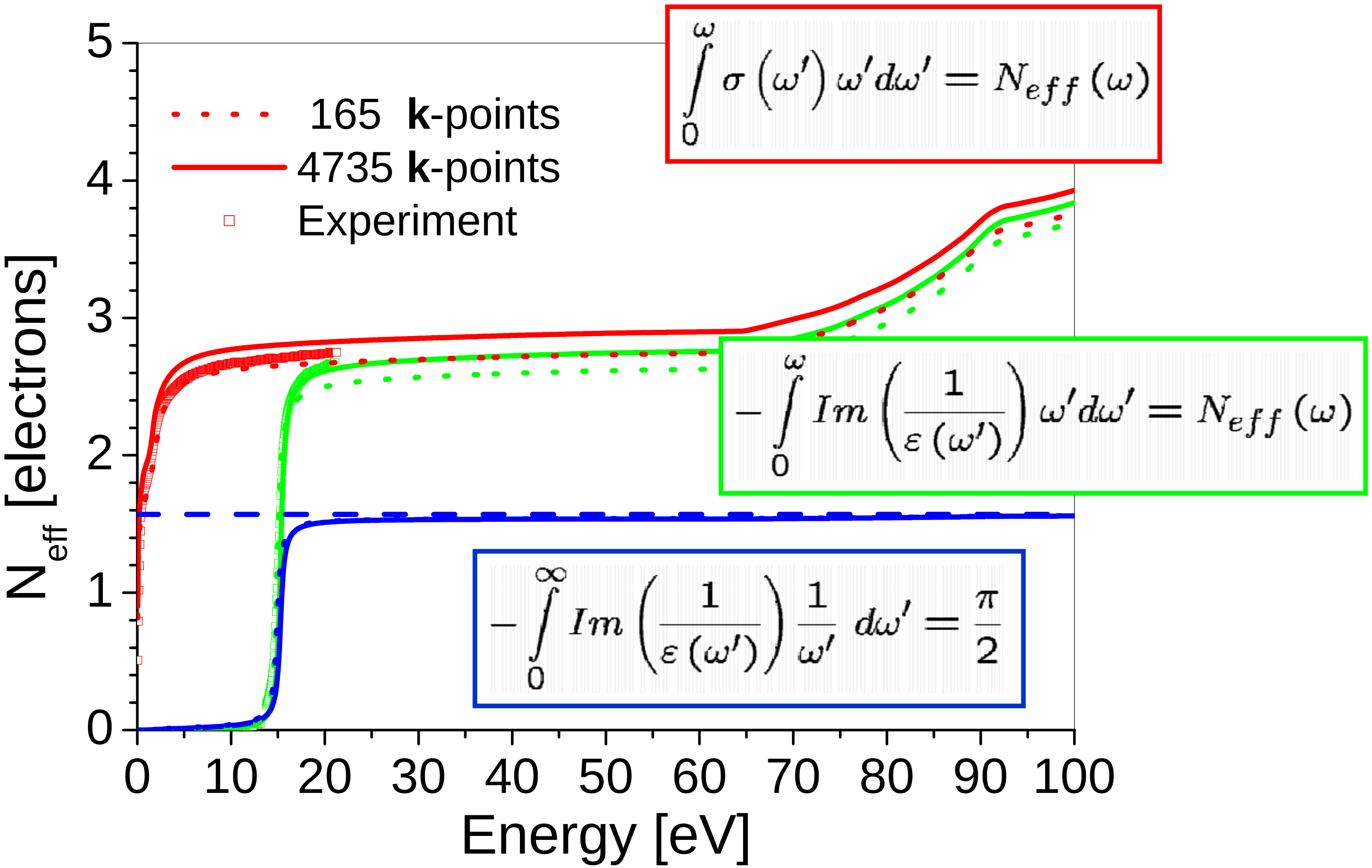
Results . . .

Convergence



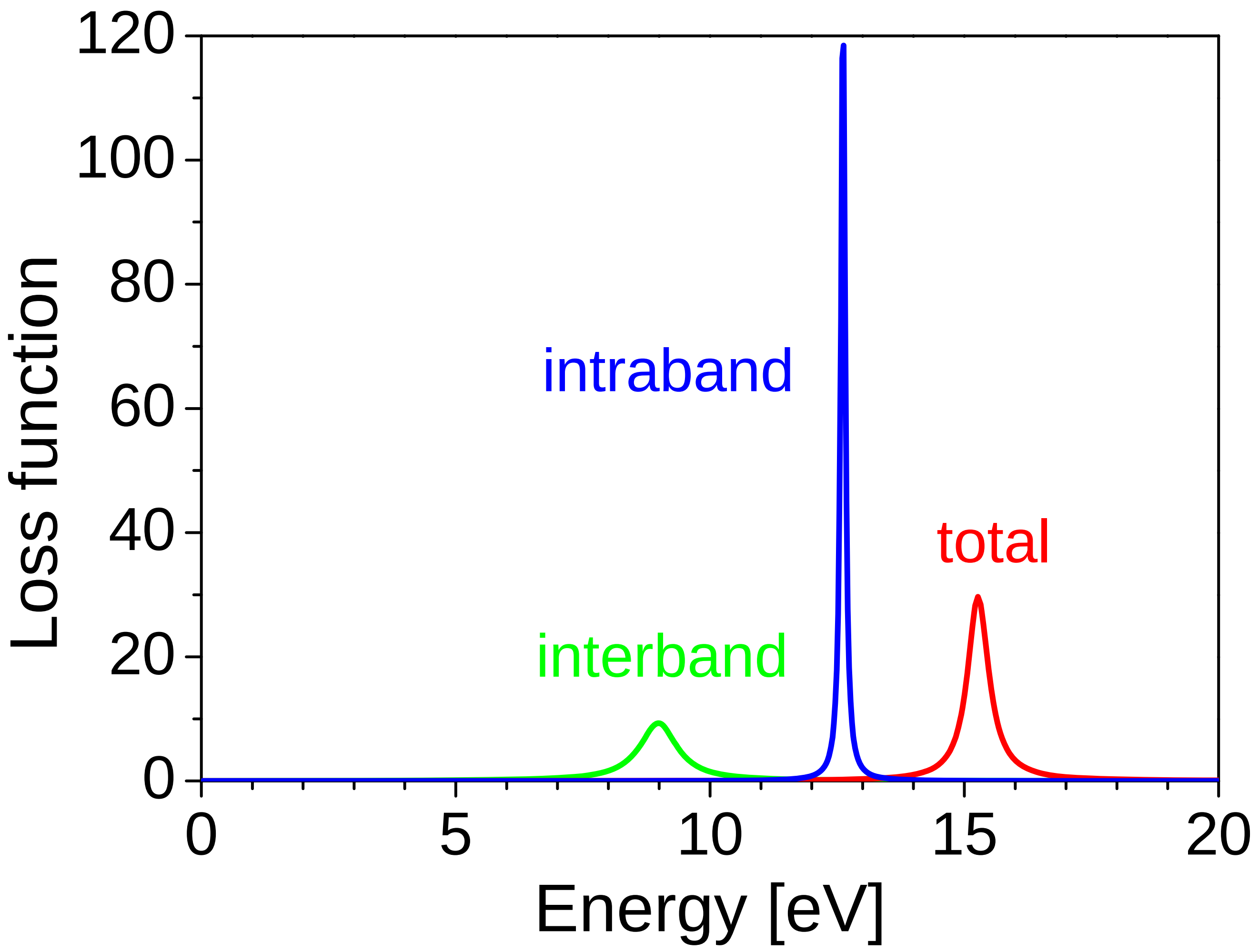
Example: Al

Sumrules



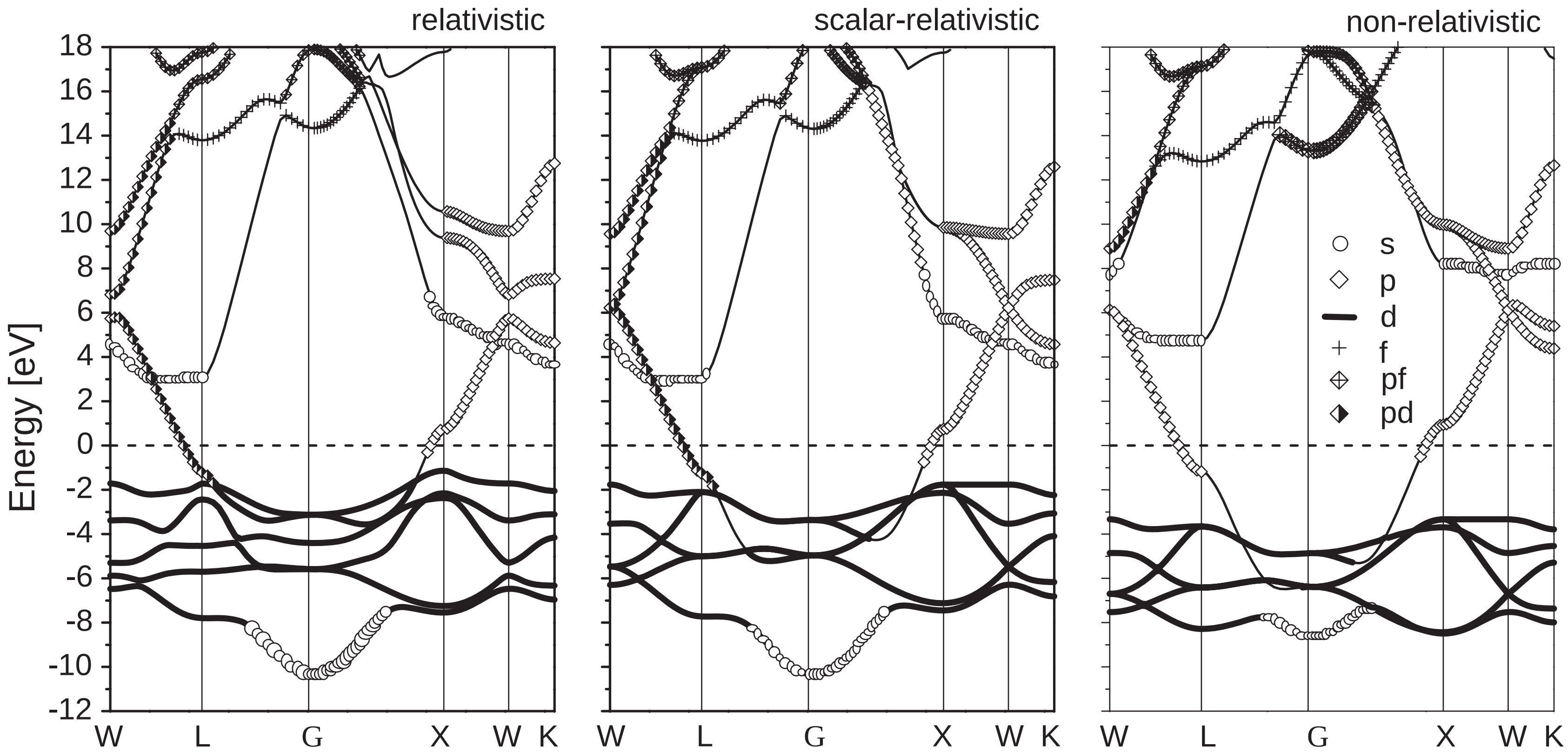
Example: Al

Loss function



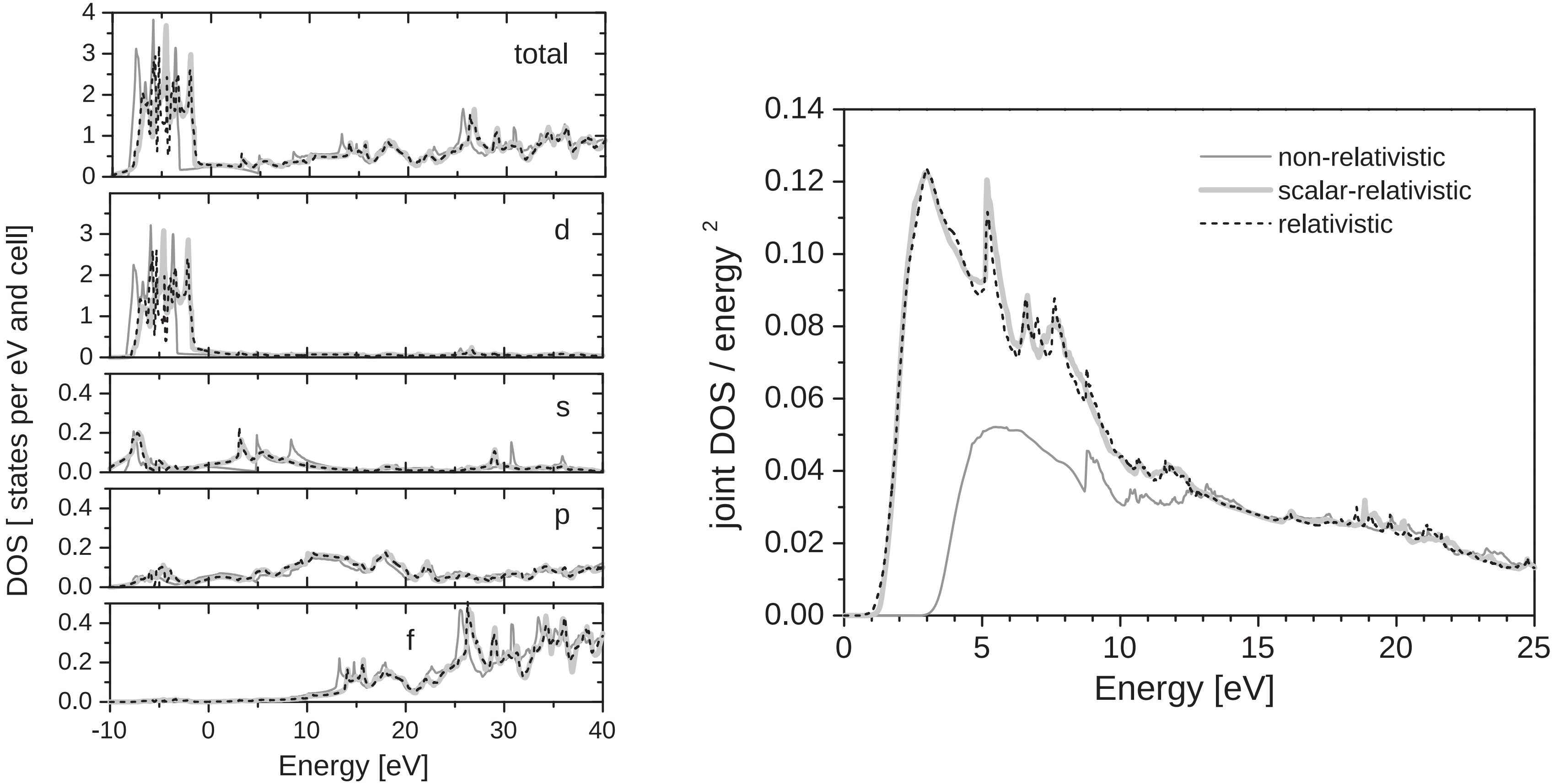
Example: Al

Band structure



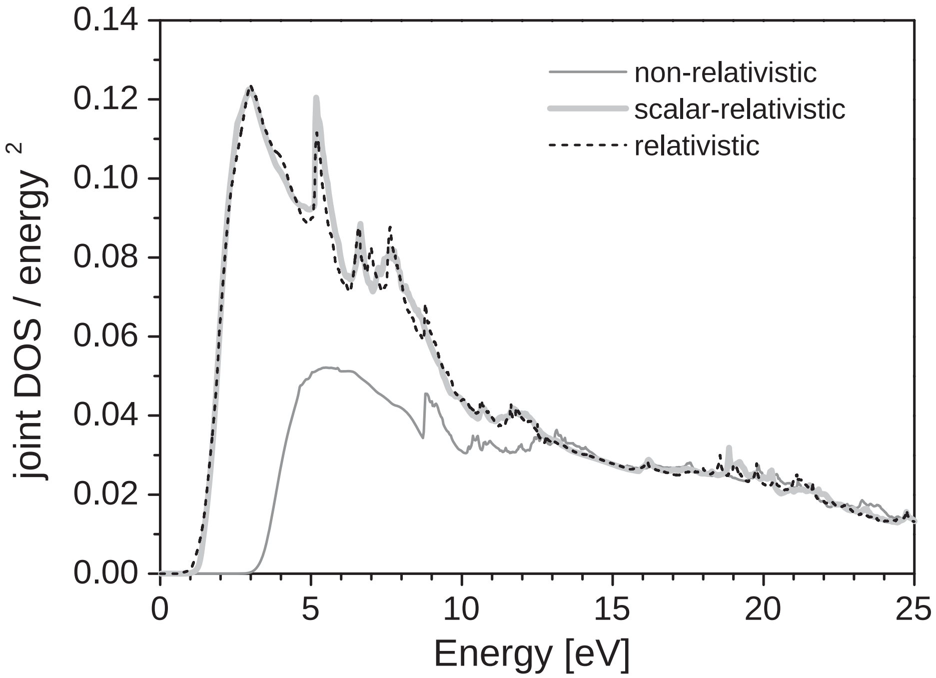
Example: Au

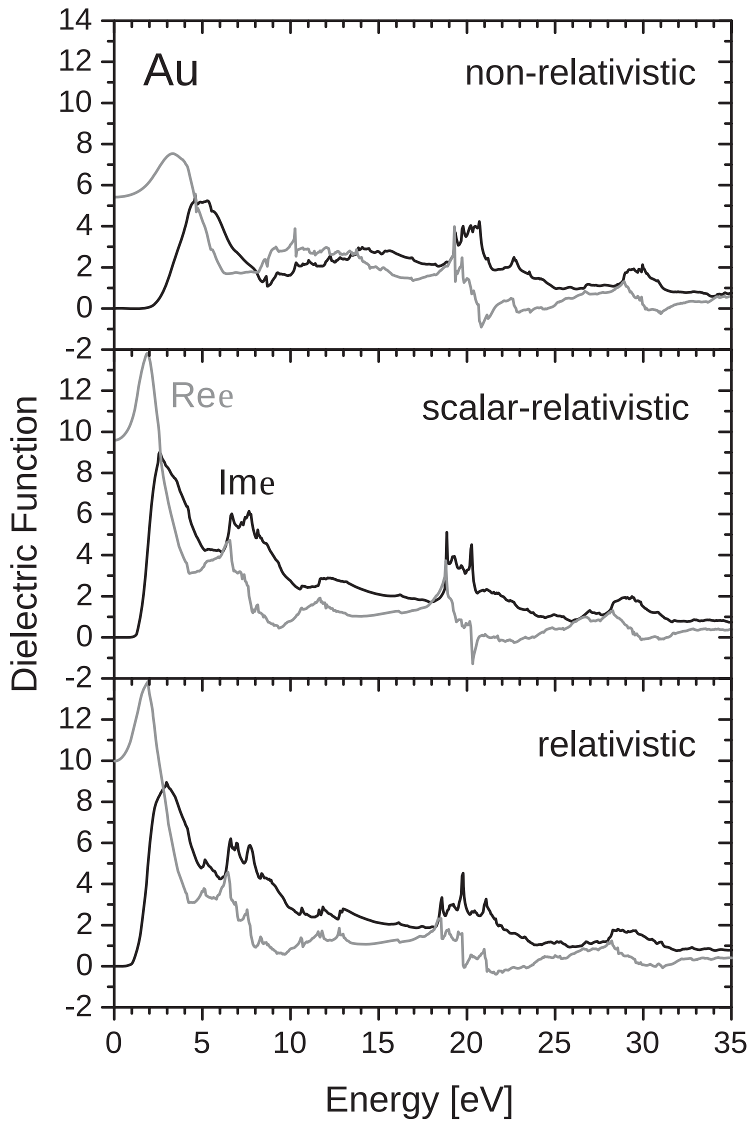
Density of states



Example: Au

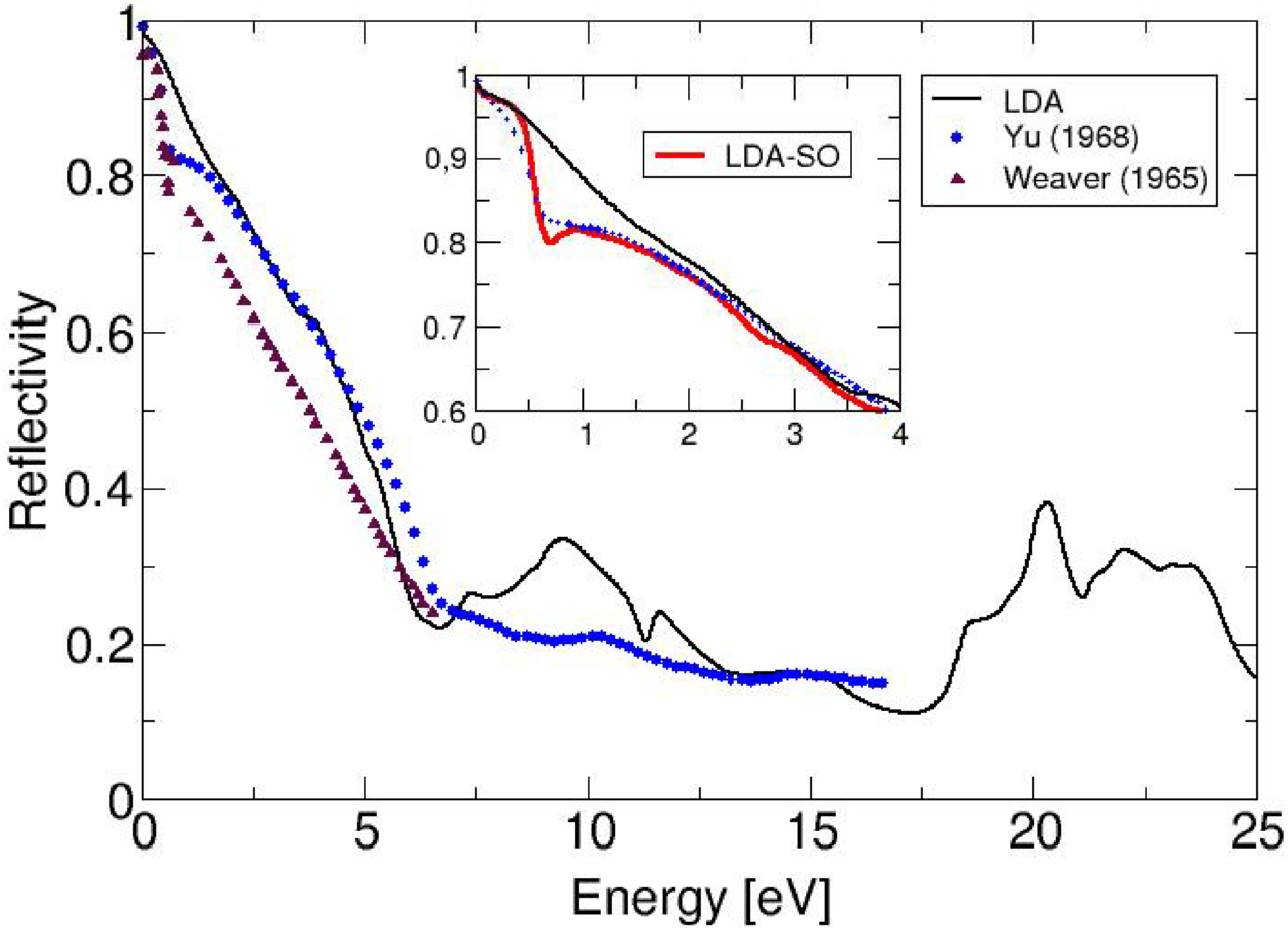
Dielectric tensor





Example: Au

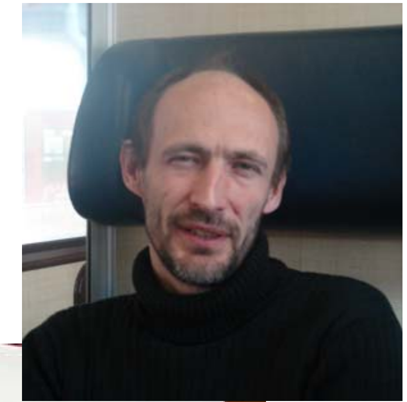
Theory versus experiment



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

Whom to ask?

Robert Abt



C. Ambrosch-Draxl and J. O. Sofo
Linear optical properties of solids within the full-potential linearized augmented planewave method
Comp. Phys. Commun. **175**, 1-14 (2006)

. . . and Beyond

Discrepancies

- Ground state

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

- Excited state

  Interpretation in terms of ground state properties

  Interpretation within one-particle picture

Response function

- Manybody treatment needed
- 2 routes

  Time-dependent DFT (TDDFT)

  Manybody perturbation theroy (MBPT)

MBPT

- mixing of concepts
- 4 point functions involved
- very demanding
- 2 steps: GW & BSE
- linear-response regime

TDDFT

- keeps spirit of DFT
- 2 point functions
- less demanding
- 1 functional needed
  in principle one step
  in practice: GW needed
- generally applicable
  linear-response regime
  strong laser fields etc.

G. Onida, L. Reining, and A. Rubio, Rev. Mod. Phys. 74, 601 (2002)