Excitations in solids: Optical properties, XMCD, GW, and BSE in WIEN2k

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Basics about light scattering

- The dielectric tensor

Optics in the WIEN2k code

- The program
- Inputs / outputs
- Examples

Many-body perturbation theory

- The GW approach
- The Bethe-Salpeter equation

Exploring the core region

- Core excitons
- X-ray circular dichroism

Contents

Light-Matter Interaction

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 $\mathbf{P} = \chi \mathbf{E}$

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

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

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

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

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

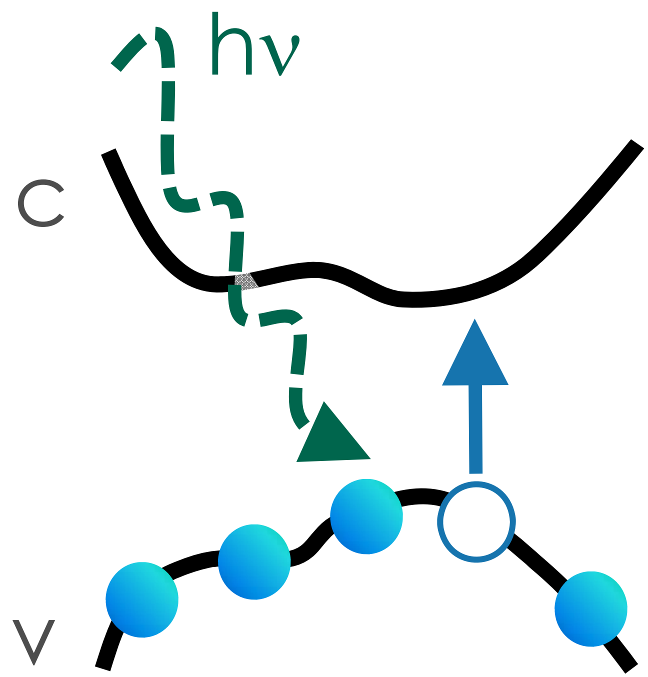
- Bloch electrons

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

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

Interband contributions

- Independent particle approximation



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

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

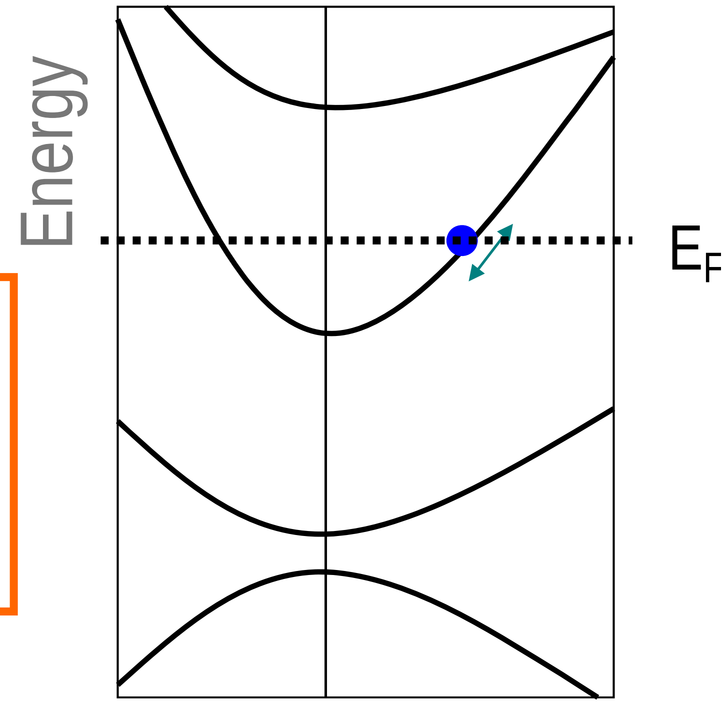
- Dielectric tensor

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

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

- Optical conductivity

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



Drude-*like* terms

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

plasma frequency

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

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

- monoclinic ($\alpha,\beta=90°$)

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

- orthorhombic

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

- tetragonal, hexagonal

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

- cubic

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

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 $\parallel z$, 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

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

- 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

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

- 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	

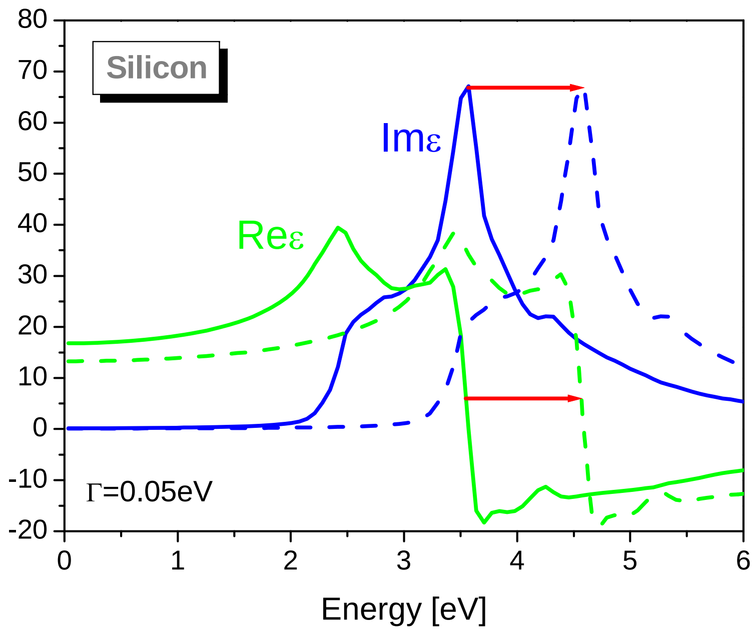
kram

- 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	
....	



optic

- case.symmat
- case.mommat

joint

- case.joint

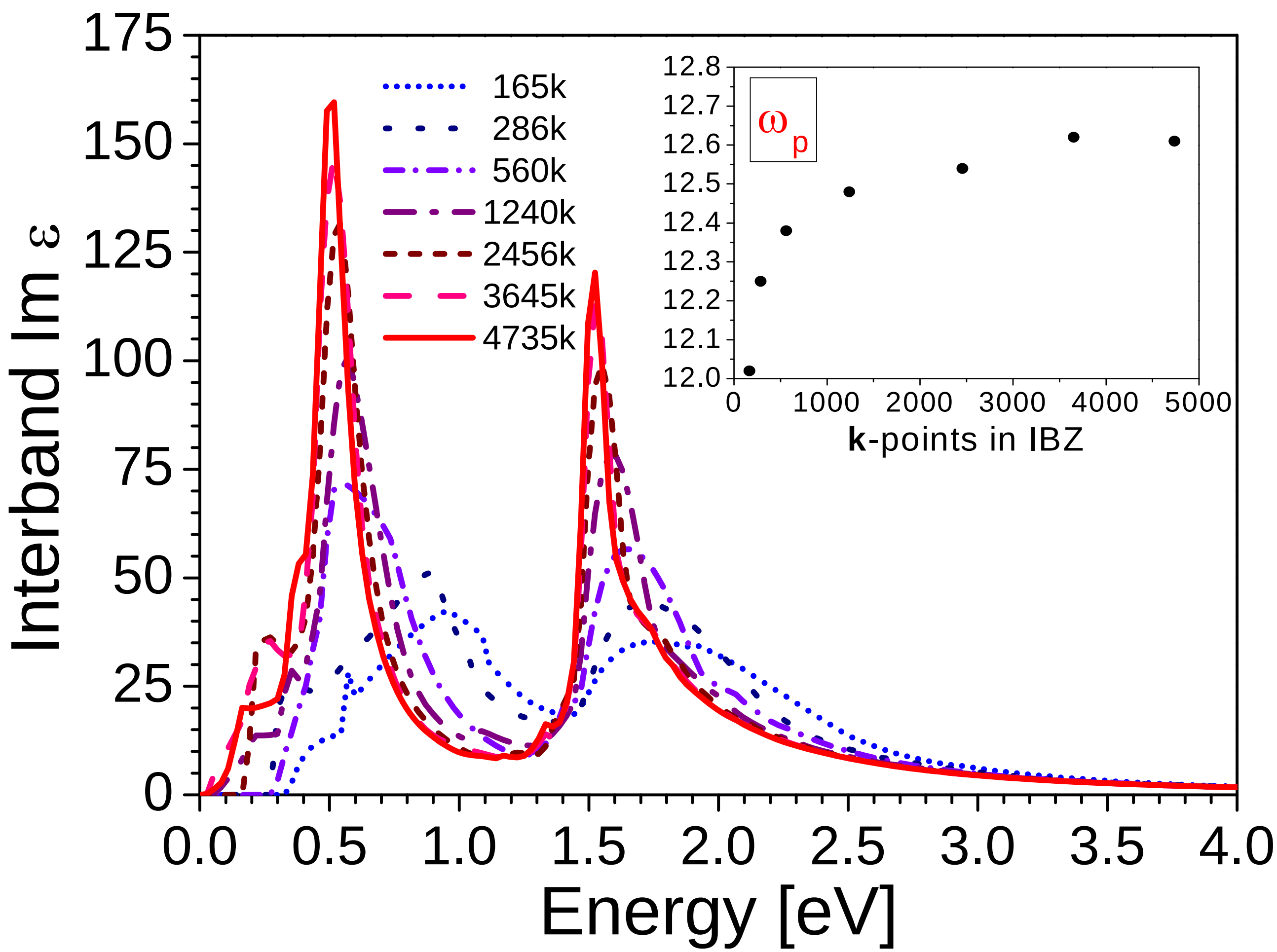
kram

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

Outputs

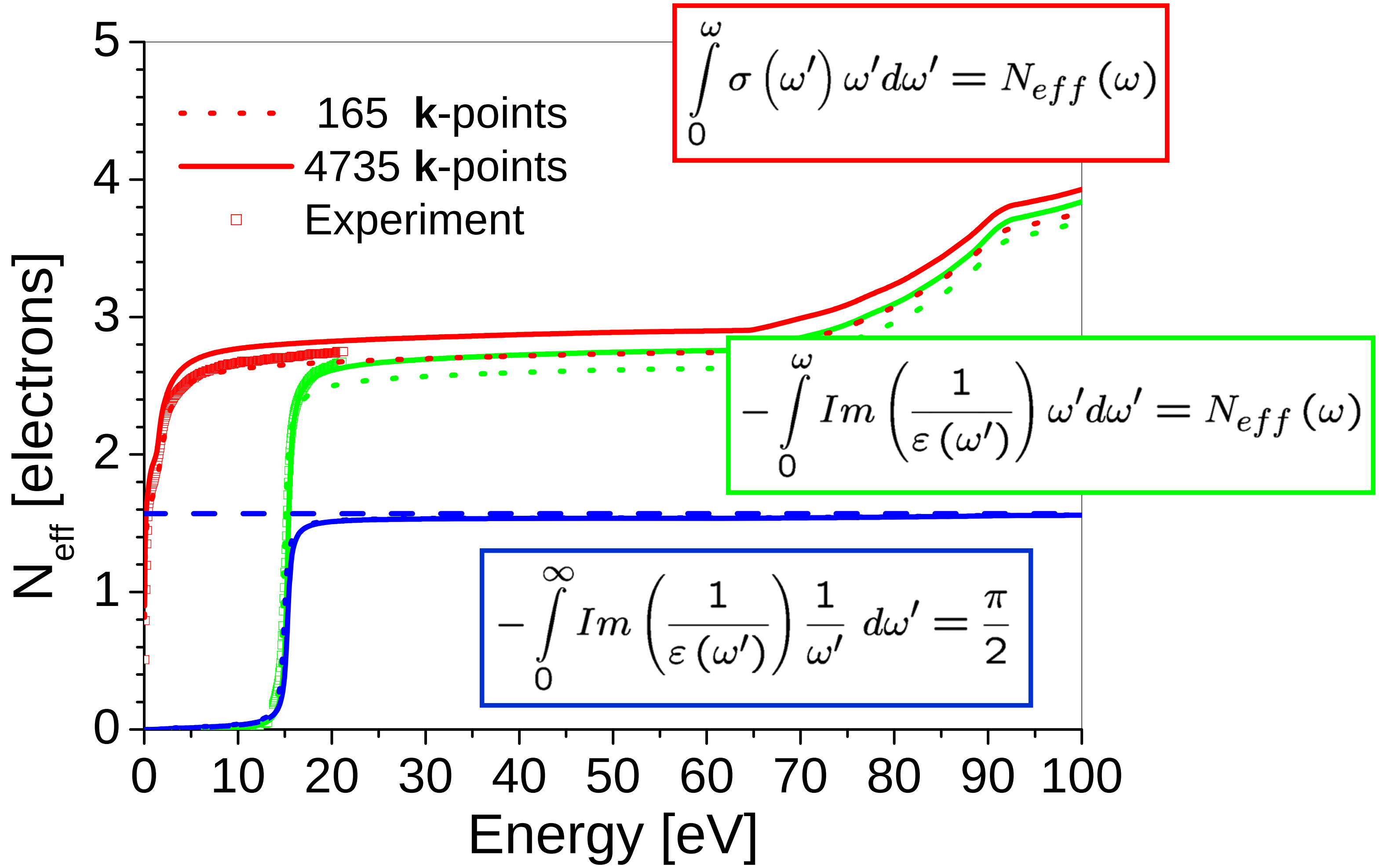
Results …

Convergence



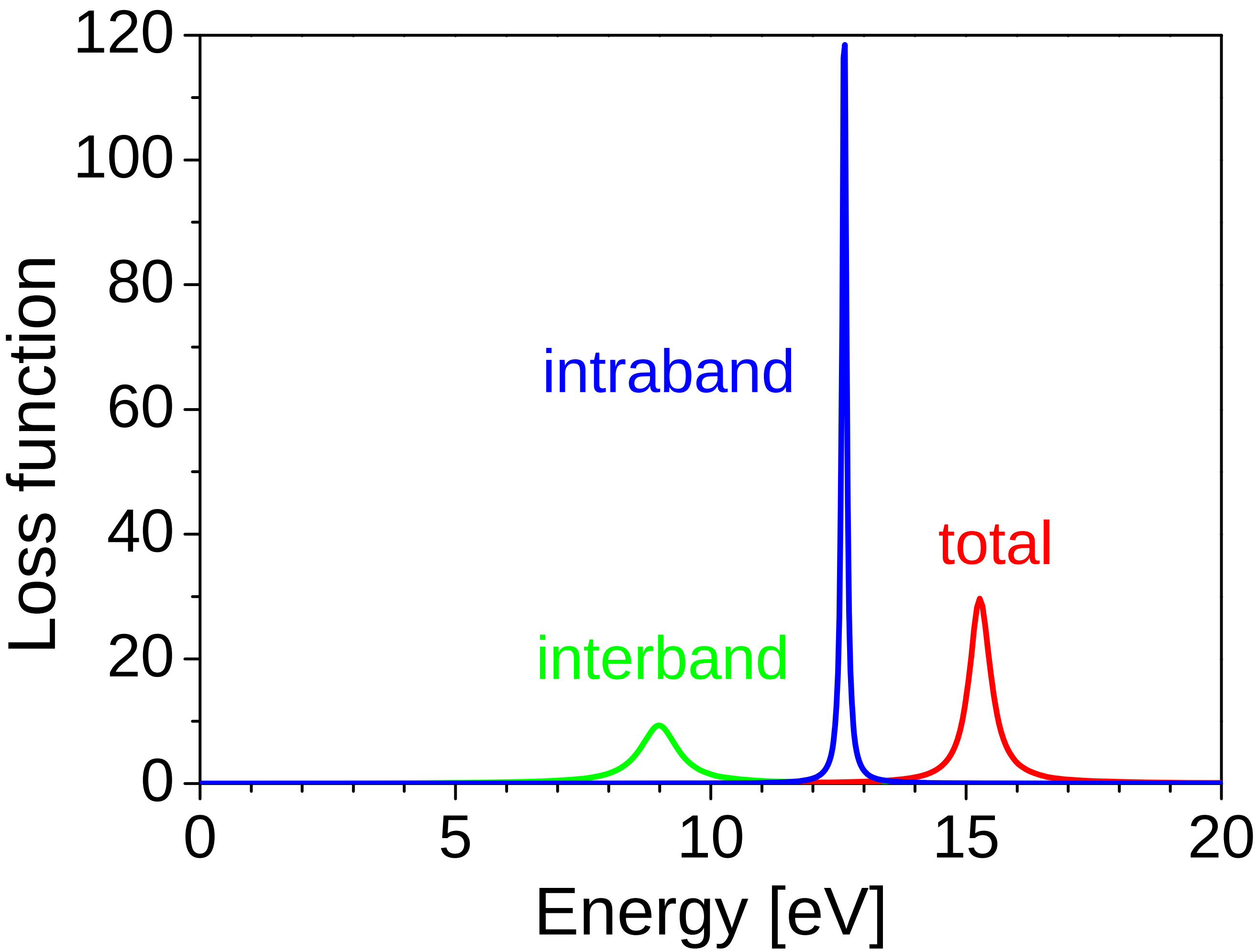
Example: Al

Sumrules



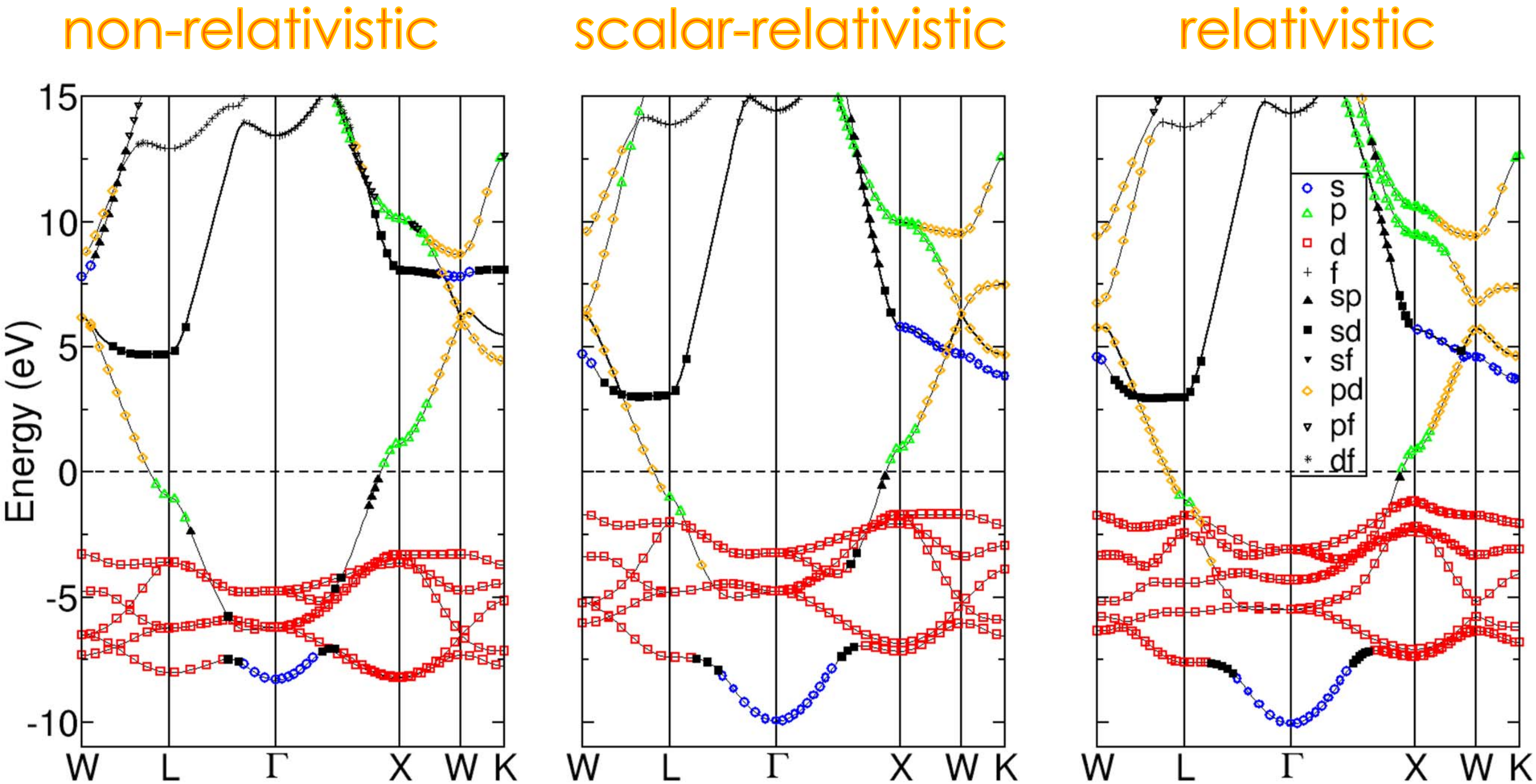
Example: Al

Loss function



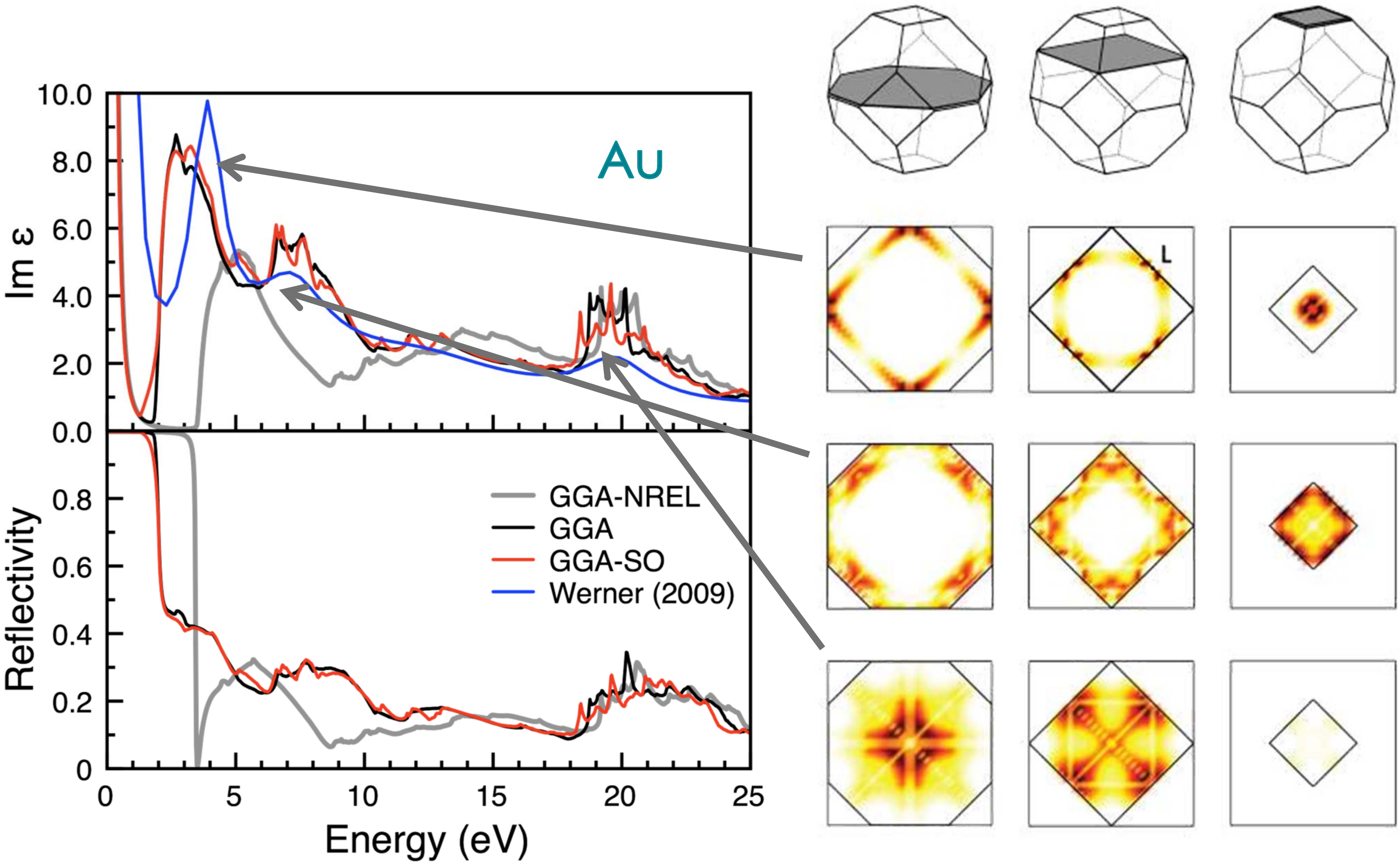
Example: Al

Relativistic effects



Example: Au

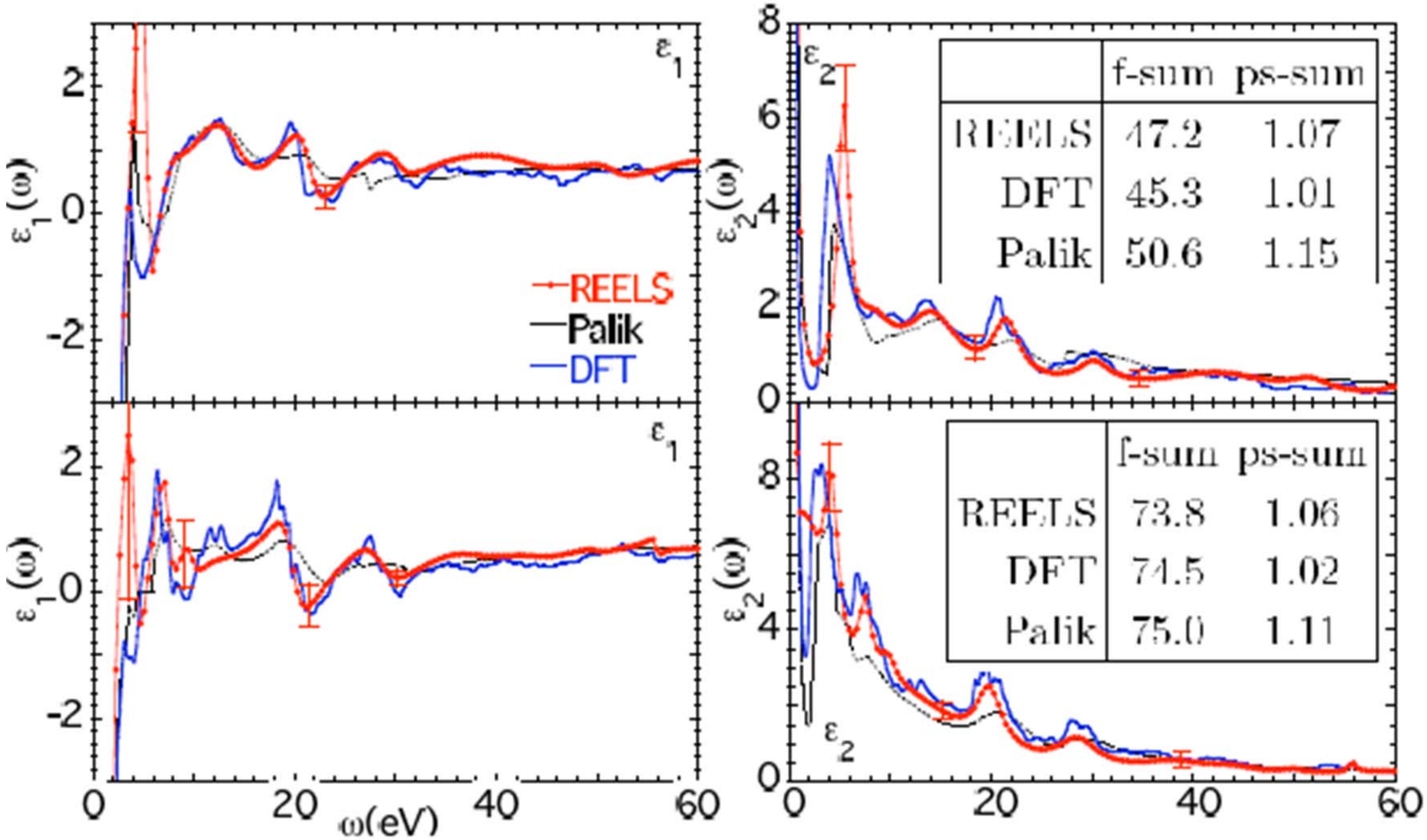
Relativistic effects



Example: Au

Theory versus experiment

- Ag
- Au



	f-sum	ps-sum
REELS	47.2	1.07
DFT	45.3	1.01
Palik	50.6	1.15

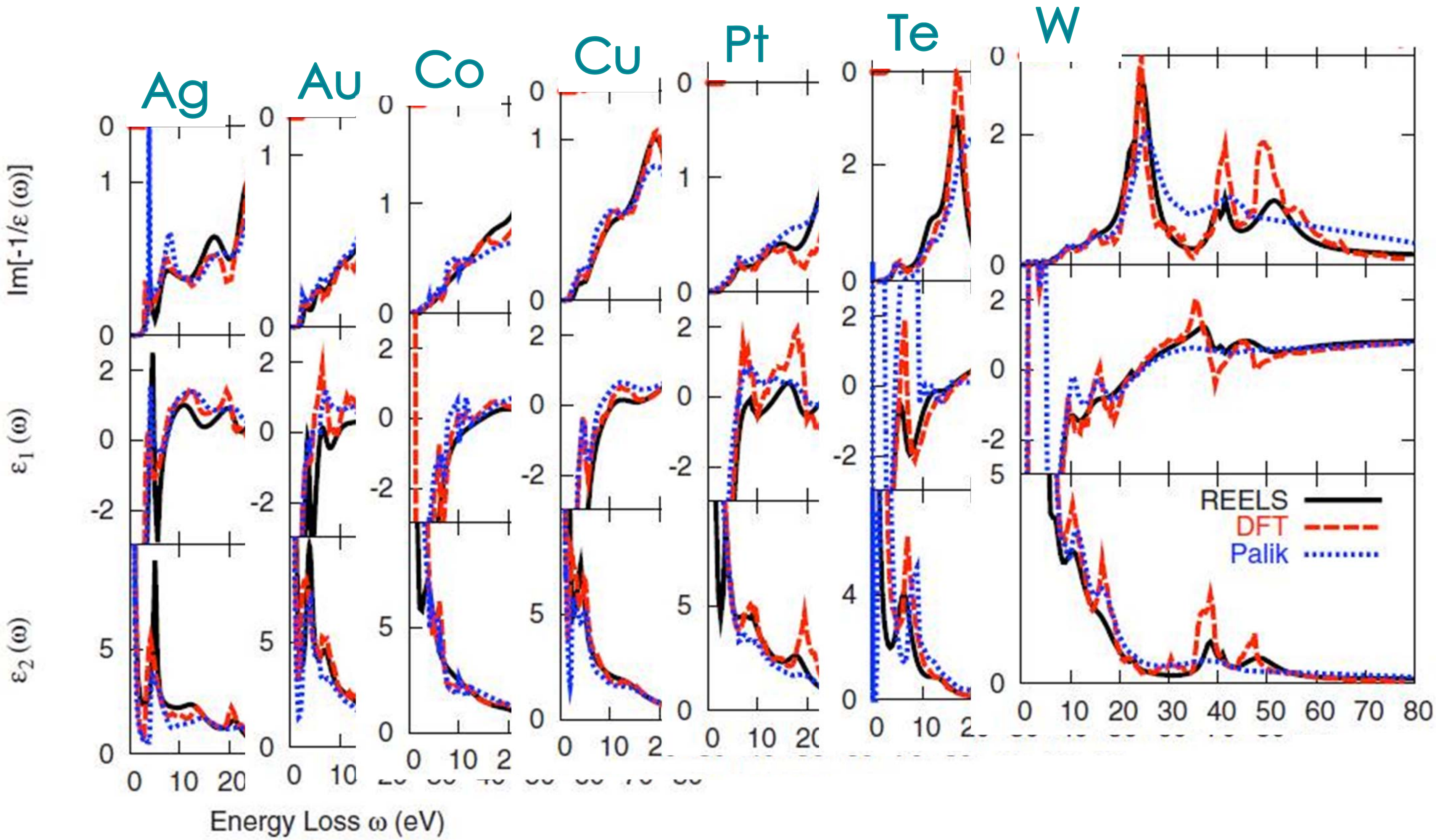
	f-sum	ps-sum
REELS	73.8	1.06
DFT	74.5	1.02
Palik	75.0	1.11

W. S. M. Werner, M. R. Went, M. Vos, K. Glantschnig, and C. Ambrosch-Draxl
Phys. Rev. B 77, 161404(R) (2008).

Examples: Ag, Au

Theory & experiment

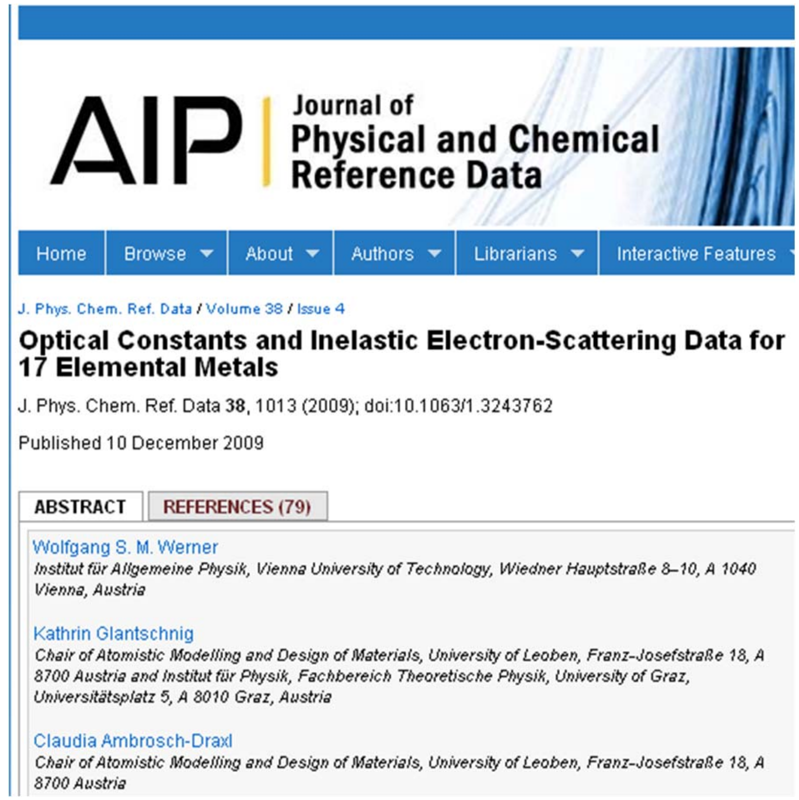
W. Werner, K. Glantschnig, and CAD
J. Phys. Chem. Ref. Data 38, 1013 (2009).



17 Elemental Metals

Theory & experiment

- Overall excellent agreement in the entire energy range (up to 100 eV)
- New REELS data agree much better with DFT
- Details of the band structure matter ….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J. Phys. Chem. Ref. Data / Volume 38 / Issue 4

Optical Constants and Inelastic Electron-Scattering Data for 17 Elemental Metals

J. Phys. Chem. Ref. Data **38**, 1013 (2009); doi:10.1063/1.3243762

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ABSTRACT | REFERENCES (79)

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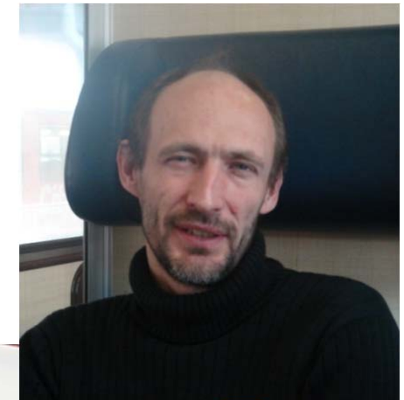
W. Werner, K. Glantschnig, and CAD
J. Phys. Chem. Ref. Data 38, 1013 (2009).

17 Elemental Metals

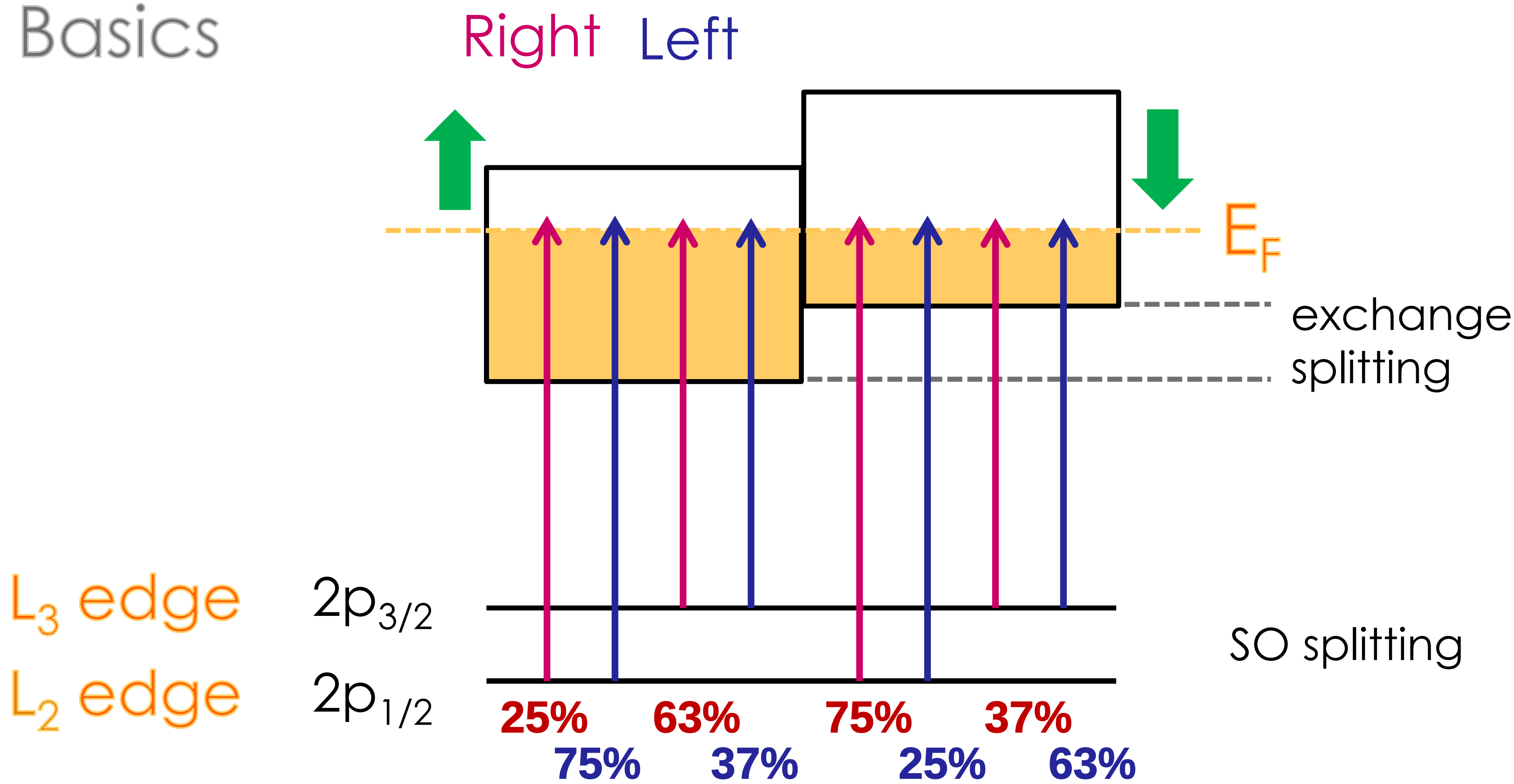
Whom to ask?

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).

Basics

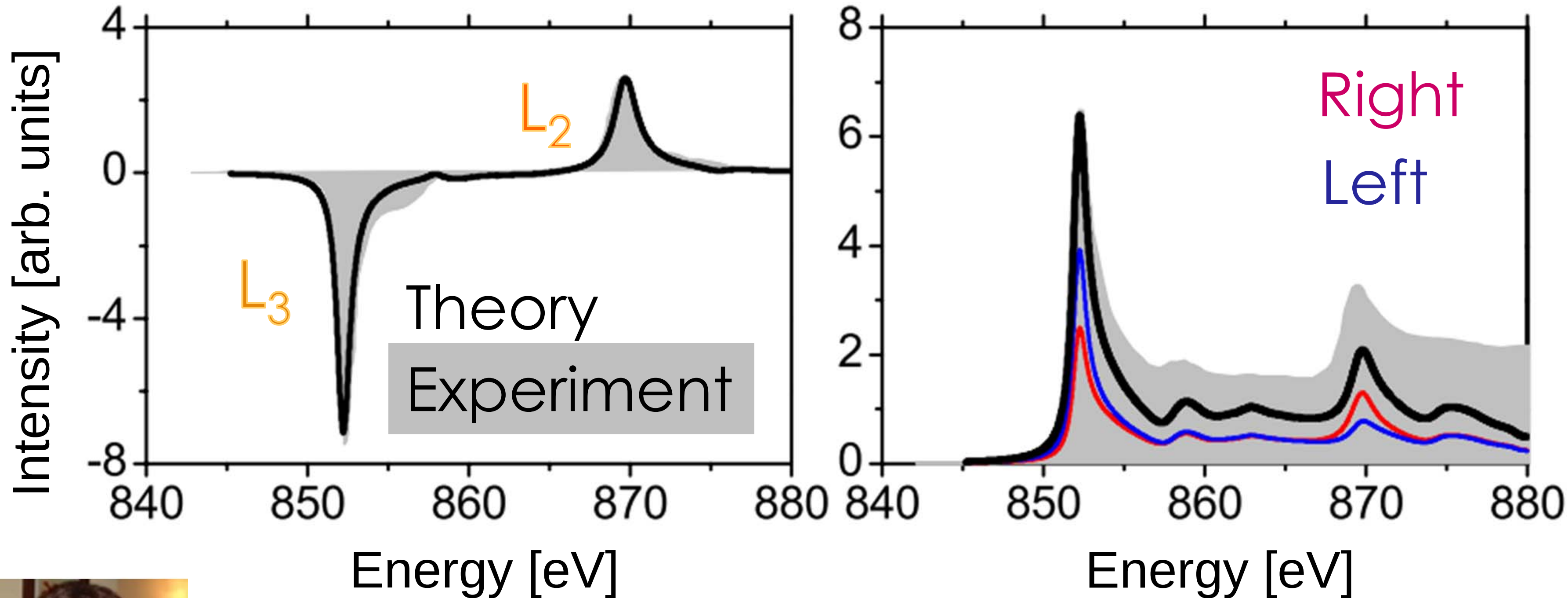


- A polarized photon beam excites electrons of different spin with different cross sections

Results: Ni

XMCD

Absorption

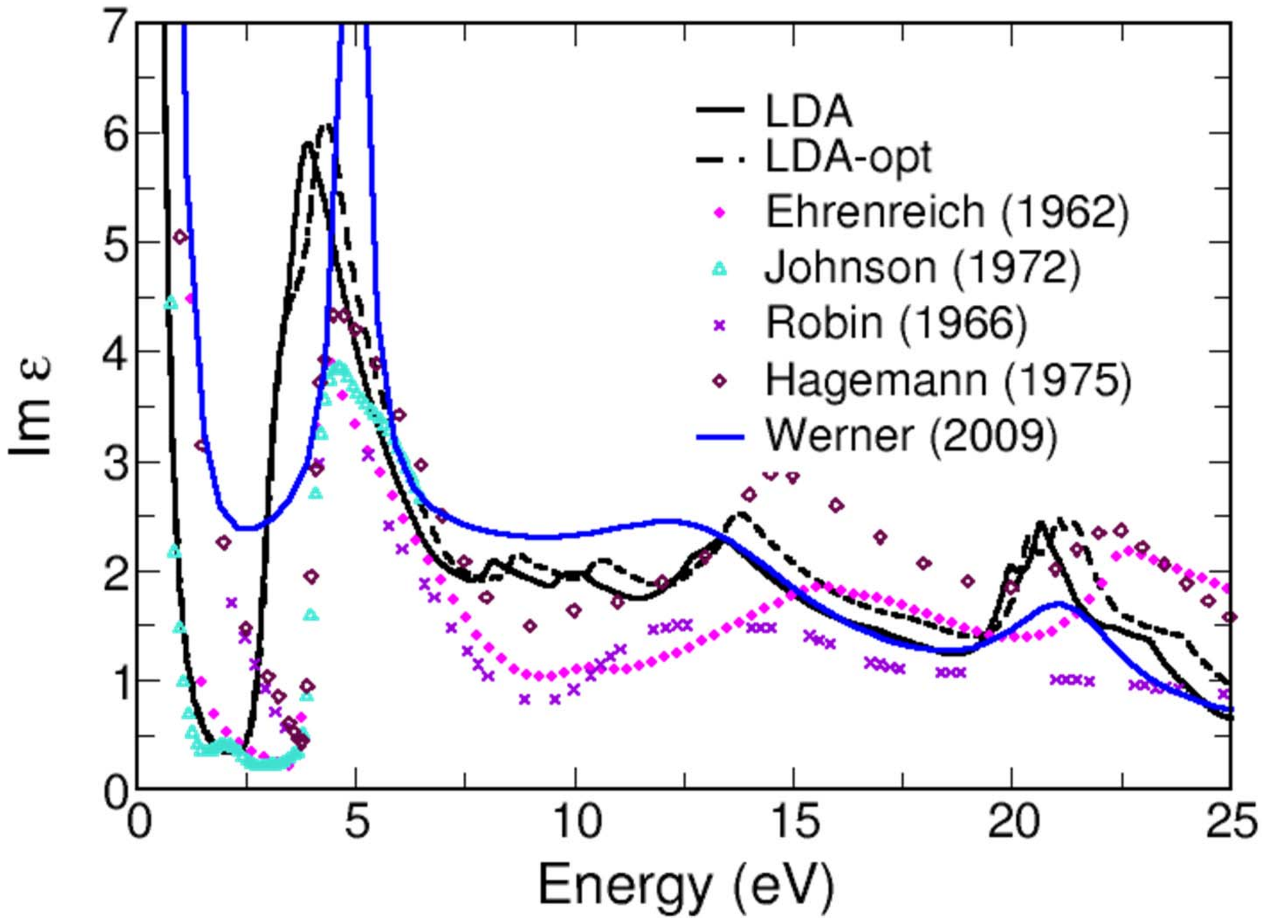


L. Pardini, F. Manghi, V. Bellini, and C. Ambrosch-Draxl,
in *Linear and Chiral Dichroism in the Electron Microscope*,
Edt. P. Schattschneider, 2011).

. . . Beyond

Details matter …

- Interband transition onset: *d* band position



Can Functionals Help?

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

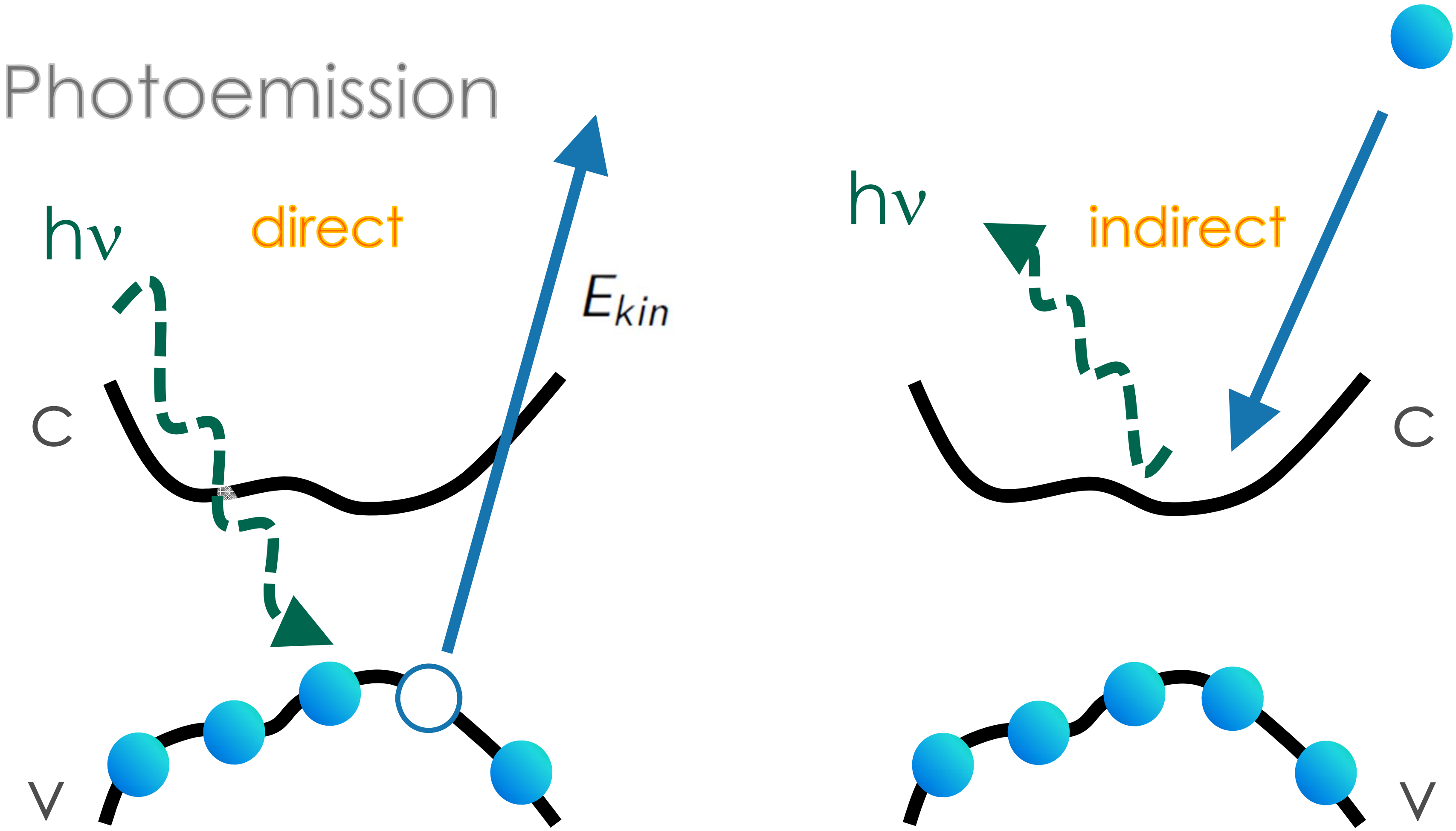
  Interpretation within one-particle picture

Response function

- Many-body treatment needed
- 2 routes

  Time-dependent DFT (TDDFT)

  Manybody perturbation theory (MBPT)



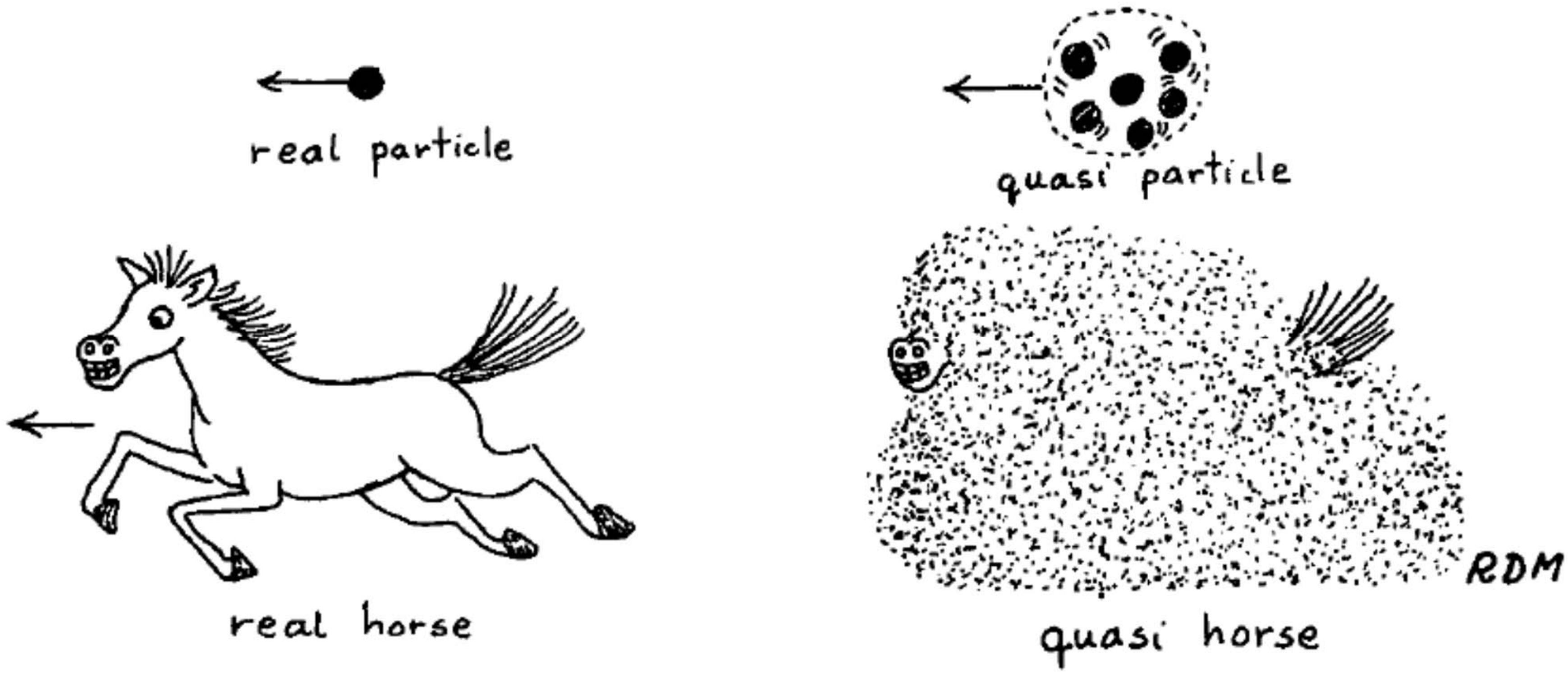
N-1 electrons

$$\epsilon_i = E(N) - E(N-1, i)$$

N+1 electrons

$$\epsilon_f = E(N+1, f) - E(N)$$

Probing Electronic States



The quasi horse according to Richard D. Mattuk

The Quasiparticle Concept

Where to start from?

$$\mathbf{G} = \mathbf{G_{KS}} + \ldots$$

- The quasiparticle equation

$$\left[T + V_{ext}(\mathbf{r}) + V_H(\mathbf{r})\right]\psi_i^{QP}(\mathbf{r}) + \int \boxed{\Sigma(\mathbf{r},\mathbf{r}',\epsilon_{\mathbf{i}})}\psi_i^{QP}(\mathbf{r})d^3\mathbf{r}' = \epsilon_i^{QP}\psi_i^{QP}(\mathbf{r})$$

- The Kohn Sham equation

$$\left[T + V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + \boxed{V_{xc}(\mathbf{r})}\right]\psi_i^{KS}(\mathbf{r}) = \epsilon_i^{KS}\psi_i^{KS}(\mathbf{r})$$

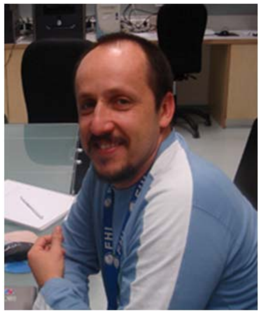
- G_0W_0

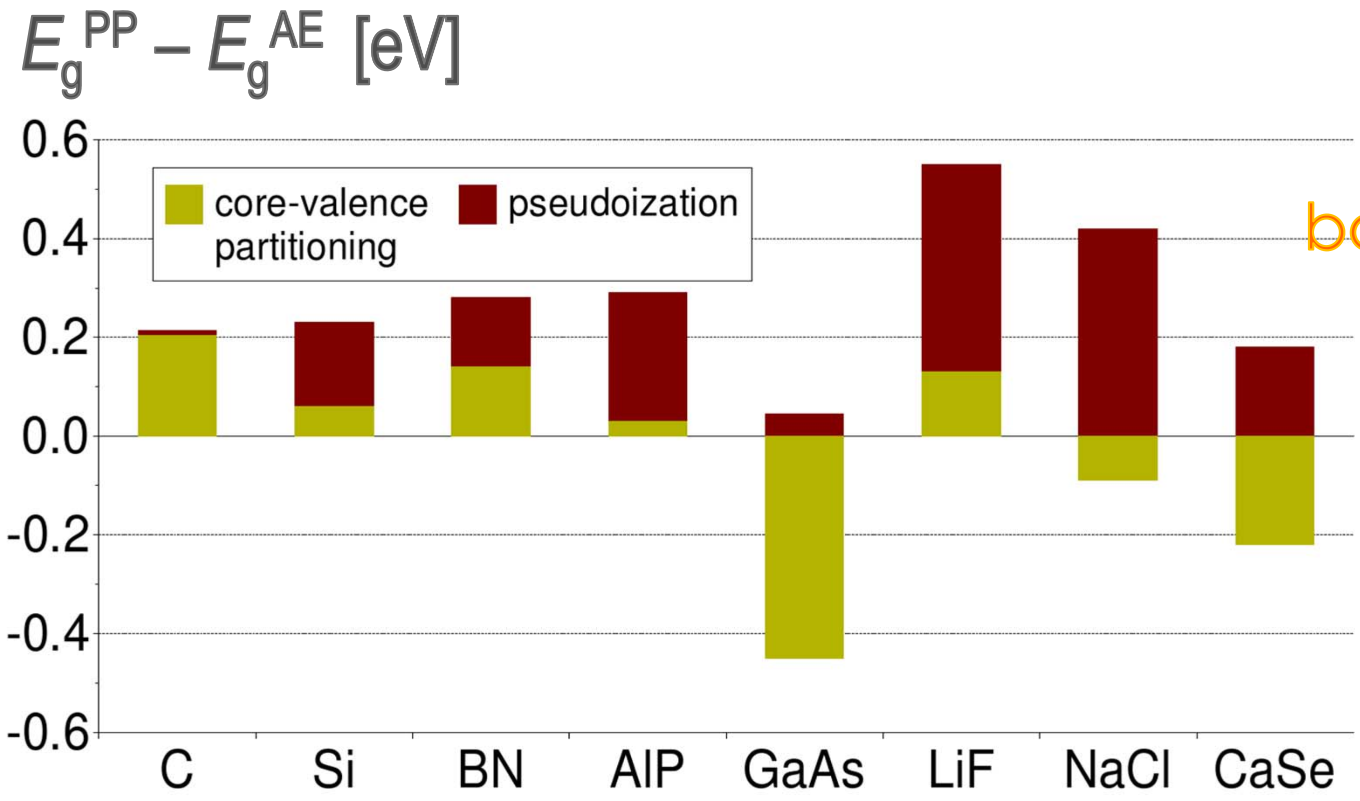
$$\mathbf{G_0} = \mathbf{G_{KS}}$$

$$\epsilon_{n\mathbf{k}}^{QP} = \epsilon_{n\mathbf{k}}^{DFT} - \left\langle n\mathbf{k}\middle|\Sigma(\epsilon_{n\mathbf{k}}^{QP}) - V_{xc}^{DFT}\middle|n\mathbf{k}\right\rangle$$

What is the precision?

- All-electron & pseudopotential results





G_0W_0
based on LDA

R. Gómez-Abal, X. Li, M. Scheffler, and CAD, PRL 101, 036402 (2008).

. . . Beyond

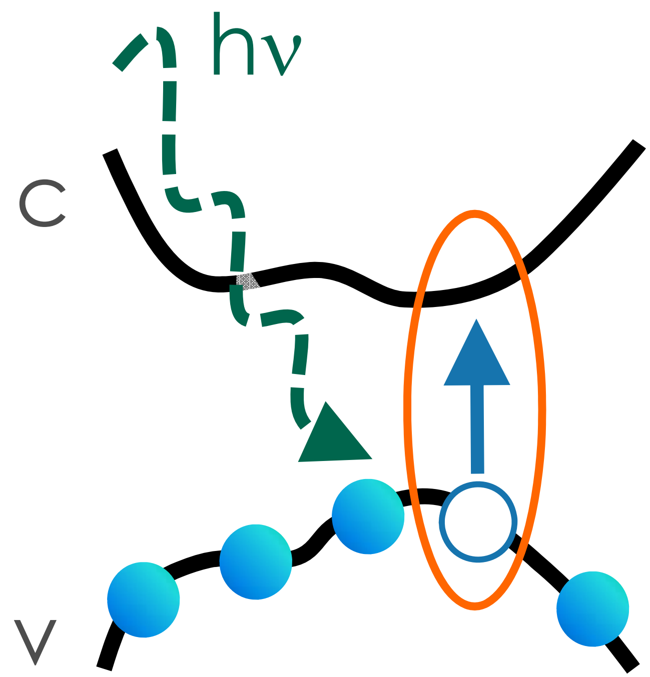
The electron-hole pair

- Effective H atom

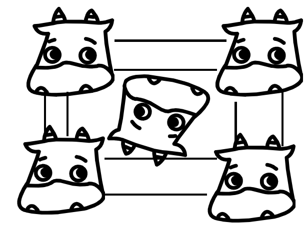
$$E_b \approx \frac{1}{m^* \varepsilon^2}$$

effective mass m^*

dielectric constant ε



The electron-hole pair



- Two-particle wavefunction

$$\Phi^{\lambda}(\mathbf{r_e},\mathbf{r_h}) = \sum_{\mathbf{vck}} \mathbf{A}^{\lambda}_{\mathbf{vck}}\psi^*_{\mathbf{vk}}(\mathbf{r_h})\psi_{\mathbf{ck}}(\mathbf{r_e})$$

KS states from GS calculation

- Effective two-particle Schrödinger equation

matrix form

$$\sum_{v'c'\mathbf{k}'} H^{e-h}_{vc\mathbf{k},v'c'\mathbf{k}'}\; A^{\lambda}_{v'c'\mathbf{k}'} = E_{\lambda}A^{\lambda}_{vc\mathbf{k}}$$

The eigenvalue problem

$$\sum_{v'c'\mathbf{k}'} H^{e-h}_{vc\mathbf{k},v'c'\mathbf{k}'}\ A^{\lambda}_{v'c'\mathbf{k}'} = E_\lambda A^{\lambda}_{vc\mathbf{k}}$$

- Diagonal term

$$H^{diag}_{vc\mathbf{k},v'c'\mathbf{k}'} = \left(\varepsilon_{c_\mathbf{k}} - \varepsilon_{v_\mathbf{k}}\right)\delta_{vv'}\delta_{cc'}\delta_{\mathbf{k}\mathbf{k}'}$$

- Direct term - attractive

$$H^{dir}_{vc\mathbf{k},v'c'\mathbf{k}'} = \int \psi_{v\mathbf{k}}(\mathbf{r})\psi^*_{c\mathbf{k}}(\mathbf{r}')\frac{\epsilon^{-1}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\psi^*_{v'\mathbf{k}'}(\mathbf{r})\psi_{c'\mathbf{k}'}(\mathbf{r}')d\mathbf{r}\,d\mathbf{r}'$$

- Exchange term - repulsive

$$H^{x}_{vc\mathbf{k},v'c'\mathbf{k}'} = \int \frac{\psi^*_{v'\mathbf{k}'}(\mathbf{r}')\psi^*_{c\mathbf{k}}(\mathbf{r})\psi_{v\mathbf{k}}(\mathbf{r})\psi_{c'\mathbf{k}'}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}\,d\mathbf{r}'$$

The dielectric function

$$\Phi_\lambda(\mathbf{r}_{el}, \mathbf{r}_{hole}) = \sum_{cv} A_\lambda^{cv} \psi_c(\mathbf{r}_{el}) \psi_v(\mathbf{r}_{hole})$$

- Bethe-Salpether equation (BSE)

$$\mathrm{Im}\varepsilon \sim \Sigma_\lambda \Sigma_{cv} \left| \frac{\langle c|\nabla|v\rangle A_\lambda^{cv}}{E_c - E_v} \right|^2 \delta(E_\lambda - \omega)$$

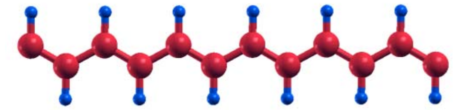
- Independet particle approximation (IPA)

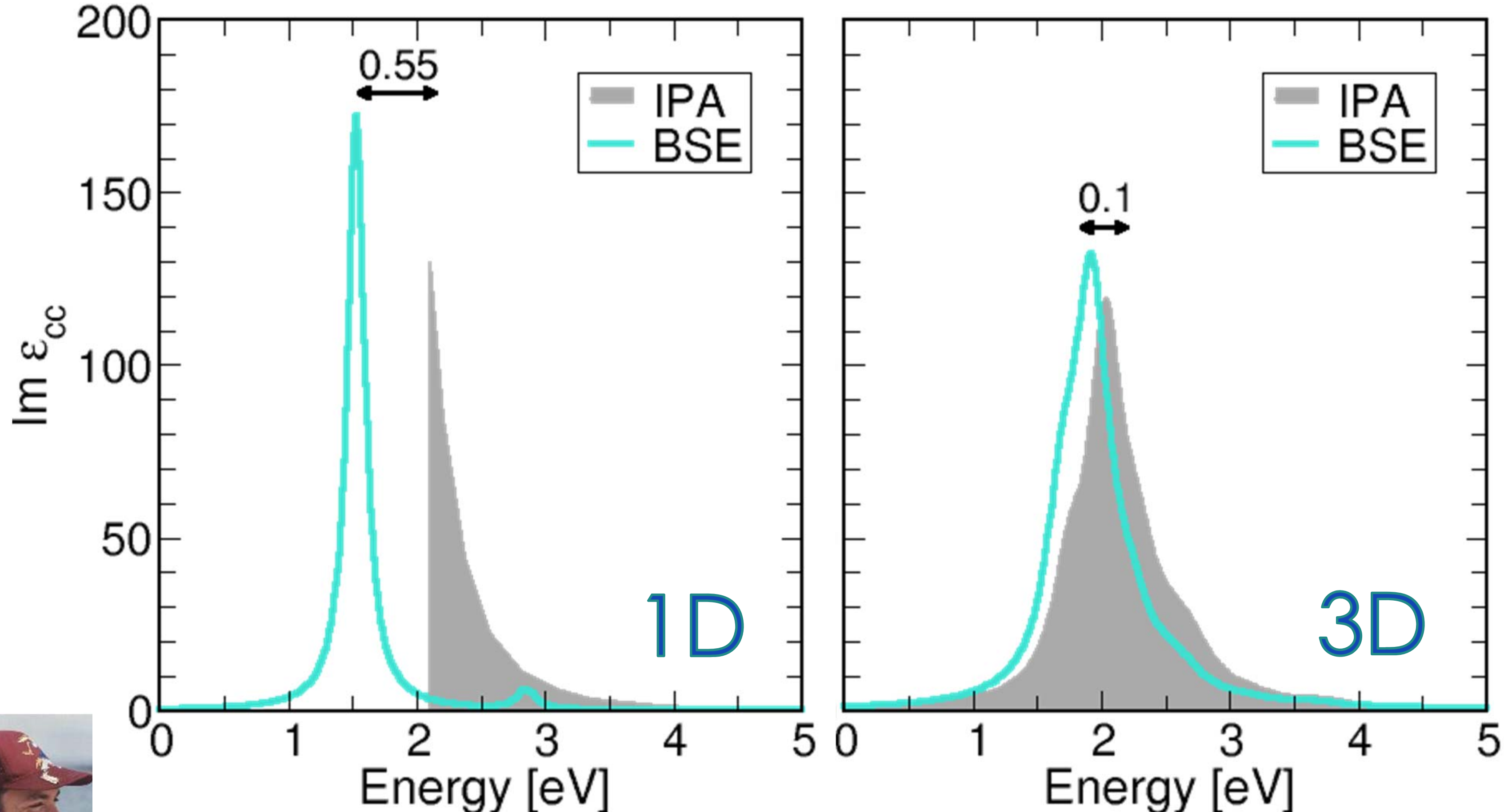
$$\mathrm{Im}\varepsilon \sim \Sigma_{cv} \left| \frac{\langle c|\nabla|v\rangle}{E_c - E_v} \right|^2 \delta(E_c - E_v - \omega)$$

oscillator strength

peak position

Polyacetylene





P. Puschnig and C. Ambrosch-Draxl, Phys. Rev. Lett. 89, 056405 (2002).
P. Puschnig and C. Ambrosch-Draxl, Phys. Rev. B 66, 165105 (2002).

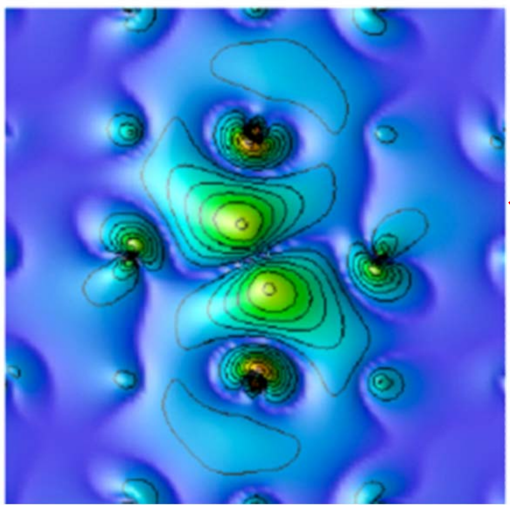
Core excitations

- Typical approach:
  Supercell including a core hole
- LAPW allows for a BSE treatment
  All-electron, full potential, no frozen core
- How well do both approaches compare?
- For deep core states they are basically equivalent

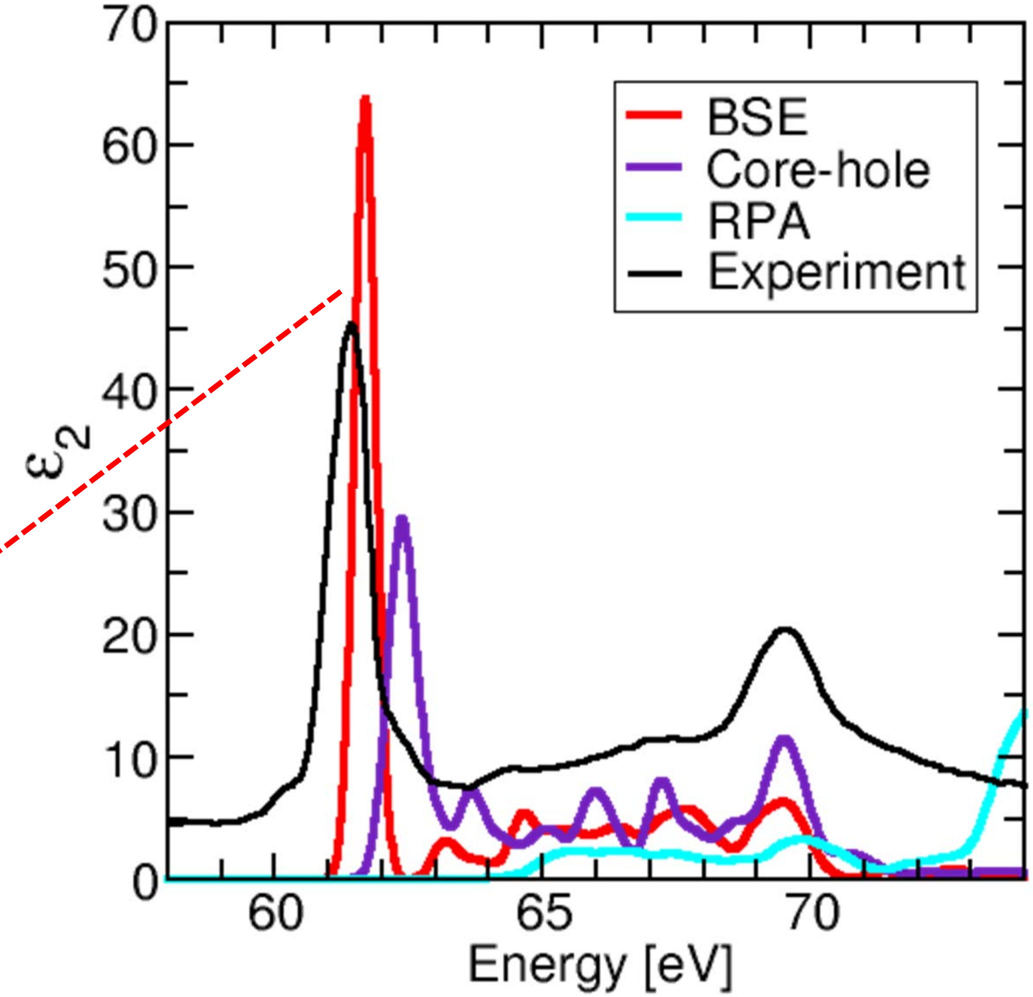
  J. J. Rehr, J. A. Soininen, and E. L. Shirley, Phys. Scr. T115, 207 (2005).
- **What about semi-core levels?**

XANES

- Li K edge in LiF



$\Phi^{\lambda}(\mathbf{r_e}, \mathbf{r_h})$



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- *GW*

  `FHI-gap` to be released

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- BSE

  http://amadm.unileoben.ac.at/software.html

  P. Puschnig and CAD, Phys. Rev. B 66, 165105 (2002).

Thanks for
your attention!