Optical Properties with Wien2k

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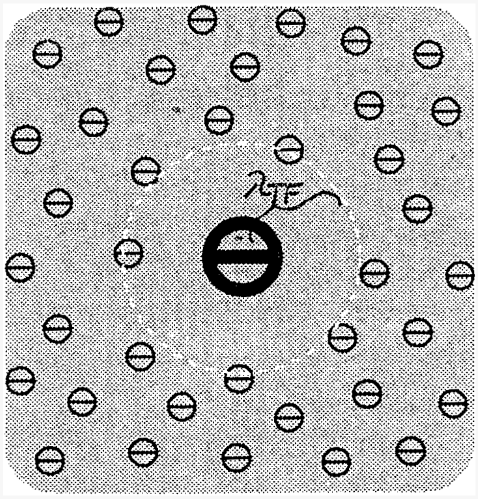
Ambrosch-Draxl and Sofo, Comp. Phys. Commun. 175, 1 (2006)

Appetizer

$$\operatorname{Im}\varepsilon_{ij}(\omega) \Rightarrow \begin{cases} \text{optical conductivity} & \operatorname{Re}\sigma_{ij} = \dfrac{\omega}{4\pi}\operatorname{Im}\varepsilon_{ij} \\ \text{refractive index} & n_{ii} = \sqrt{(|\varepsilon_{ii}| + \operatorname{Re}\varepsilon_{ii})/2} \\ \text{extinction coefficient} & k_{ii} = \sqrt{(|\varepsilon_{ii}| - \operatorname{Re}\varepsilon_{ii})/2} \\ \text{absorption coefficient} & \alpha_{ii} = 2\omega k/c \\ \text{energy loss function} & L_{ij} = -\operatorname{Im}(\varepsilon^{-1})_{ij} \\ \text{reflectivity} & R_{ii} = \dfrac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \\ \text{sum rules} & N_{\text{eff}} = \displaystyle\int_0^{\omega} \mathrm{d}\omega' \operatorname{Im}\varepsilon(\omega') \end{cases}$$

Screening



Consider a test charge Q in a solid:

$$V(\boldsymbol{r}-\boldsymbol{r}') = \frac{-Q}{|\boldsymbol{r}-\boldsymbol{r}'|} \longleftrightarrow V(\boldsymbol{q}) = -\frac{4\pi Q}{\boldsymbol{q}^2}$$

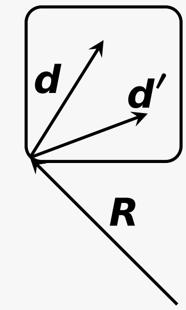
e^- will move to screen the charge
⇝ effective potential W;
dielectric function "$V = \varepsilon W$"

Simplest model: Thomas-Fermi

$$W(\boldsymbol{r}) = \frac{e^{-\boldsymbol{k}_{\text{TF}}\boldsymbol{r}}}{\boldsymbol{r}} \longleftrightarrow W(\boldsymbol{q}) = \frac{4\pi}{\boldsymbol{k}_{\text{TF}}{}^2 + \boldsymbol{q}^2}$$

$$\boldsymbol{k}_{\text{TF}}^2 = 4\pi\mathcal{N}(E_{\text{F}})$$

Ansatz for W



$\boldsymbol{r} = \boldsymbol{R} + \boldsymbol{d}$

$$W \sim \int \mathrm{d}\boldsymbol{r}' \mathrm{d}t \, \varepsilon^{-1}(\boldsymbol{r}';t) V(\boldsymbol{r}-\boldsymbol{r}';t-t')$$

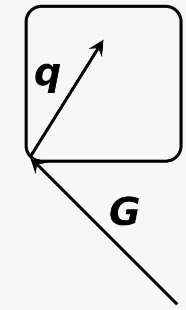
Bare $V(\boldsymbol{r},\boldsymbol{r}';t,t') = V(\boldsymbol{r}-\boldsymbol{r}')\delta(t-t')$ is translation invariant and instantaneous

Response depends on position in unit cell, is retarded

$$\rightsquigarrow \; W_{\boldsymbol{R}}(\boldsymbol{d},\boldsymbol{d}';t) = \sum_{\tilde{\boldsymbol{R}}} \int \mathrm{d}\boldsymbol{d}_1 \mathrm{d}\boldsymbol{d}_2 \; {\varepsilon^{-1}}_{\tilde{\boldsymbol{R}}}(\boldsymbol{d}_1,\boldsymbol{d}_2;t)$$

$$\cdot V(\boldsymbol{R}+\boldsymbol{d}-\boldsymbol{d}'-[\boldsymbol{d}_1-\boldsymbol{d}_2-\tilde{\boldsymbol{R}}])$$

The Dielectric Function



$\boldsymbol{k} = \boldsymbol{G} + \boldsymbol{q}$

$$W_G(\boldsymbol{q},\omega) = \sum_{\boldsymbol{G}'} {\varepsilon^{-1}}_{\boldsymbol{G}\boldsymbol{G}'}(\boldsymbol{q},\omega) \; V_{\boldsymbol{G}'}(\boldsymbol{q},\omega)$$

light is long-wavelength:

$$W_G(\boldsymbol{q},\omega) \approx {\varepsilon^{-1}}_{\boldsymbol{G}\boldsymbol{0}}(\boldsymbol{q},\omega) \; V_{\boldsymbol{0}}(\boldsymbol{q},\omega)$$

$\boldsymbol{G}' = \boldsymbol{0}, \; \boldsymbol{q} \to \boldsymbol{0}$

“macroscopic” ε (u.c. average):

$$W(\boldsymbol{q},\omega) = {\varepsilon^{-1}}_{\boldsymbol{0}\boldsymbol{0}}(\boldsymbol{q},\omega) \; V_{\boldsymbol{0}}(\boldsymbol{q},\omega)$$

$$\varepsilon_{\mathrm{M}}(\boldsymbol{q},\omega) = \frac{1}{{\varepsilon^{-1}}_{\boldsymbol{0}\boldsymbol{0}}(\boldsymbol{q},\omega)}$$

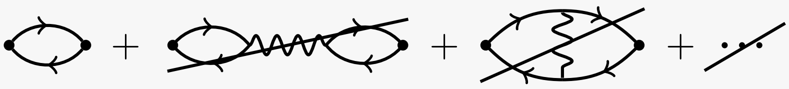
neglect local-field effects:

$$\varepsilon_{\mathrm{M}}(\boldsymbol{q},\omega) \approx \varepsilon_{\boldsymbol{0}\boldsymbol{0}}(\boldsymbol{q},\omega)$$

Calculating ε: The RPA

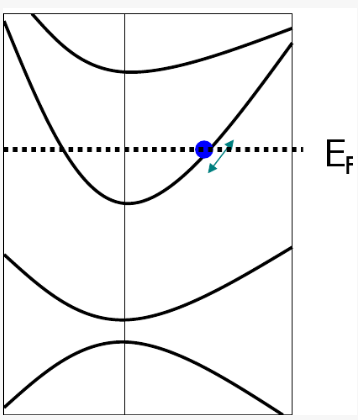
$$V(\boldsymbol{q}) = \varepsilon(\boldsymbol{q},\omega)\, W(\boldsymbol{q},\omega)$$

- Poisson: $\boldsymbol{q}^2 W = 4\pi\,(-Q + \delta n) \quad \longleftrightarrow \quad W = V + \frac{4\pi}{\boldsymbol{q}^2}\delta n$
- linear response: $\delta n = \cancel{\chi V}\, P\, W \quad \rightarrow \quad V = (1 - \frac{4\pi}{\boldsymbol{q}^2}P)\, W$
- “random-phase” approximation: P to lowest order

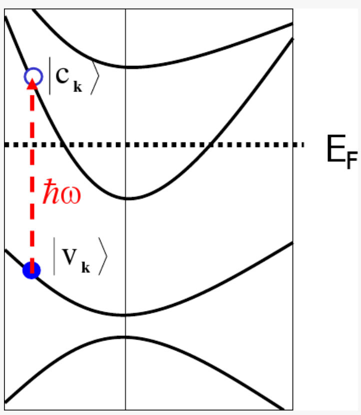
$P =$ 

$\sim G^0(1,2)\, G^0(2,1)$

Intra- and Interband transitions



intraband



interband

free e⁻: Lindhard formula

$$P = \frac{4\pi}{\boldsymbol{q}^2\Omega} \sum_{\boldsymbol{k}} \frac{f(\epsilon_{\boldsymbol{k}+\boldsymbol{q}}) - f(\epsilon_{\boldsymbol{k}})}{\epsilon_{\boldsymbol{k}+\boldsymbol{q}} - \epsilon_{\boldsymbol{k}} - \omega}$$

Bloch e⁻:

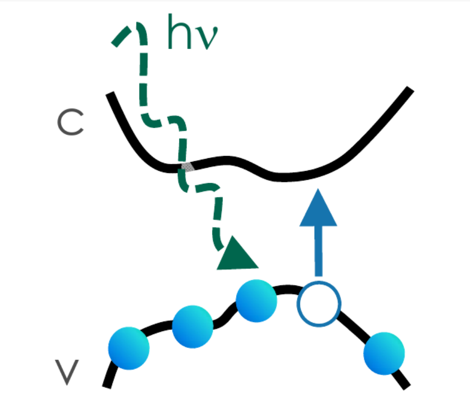
$$P = \frac{4\pi}{\boldsymbol{q}^2\Omega} \sum_{\boldsymbol{k}nn'} A^{nn'}_{\boldsymbol{kq}} \frac{f(\epsilon_{\boldsymbol{k}+\boldsymbol{q}}) - f(\epsilon_{\boldsymbol{k}})}{\epsilon_{\boldsymbol{k}+\boldsymbol{q}} - \epsilon_{\boldsymbol{k}} - \omega}$$

Intra- and Interband transitions

intraband: Drude model,
(ω_p: plasma frequency)

$$\mathrm{Im}\,\varepsilon^{\mathrm{intra}} = \frac{\Gamma {\omega_\mathrm{p}}^2}{\omega\,(\omega^2 + \Gamma^2)}$$

interband:



joint density of states:

$$\rho(\omega) = \sum_{c,v} \int \mathrm{d}\boldsymbol{k}\; \delta\Big(\epsilon_c(\boldsymbol{k}) - \epsilon_v(\boldsymbol{k}) - \omega\Big)$$

v-*c* transition probability
("selection rules") given by
momentum matrix elements

$$\mathrm{Im}\,\varepsilon_{ij}(\omega, \mathbf{0}) \propto \frac{1}{\omega^2} \sum_{c,v} \int \mathrm{d}\boldsymbol{k}\; \delta\Big(\epsilon_c(\boldsymbol{k}) - \epsilon_v(\boldsymbol{k}) - \omega\Big)\; \langle c\boldsymbol{k}|\widehat{p}_i|v\boldsymbol{k}\rangle\, \langle v\boldsymbol{k}|\widehat{p}_j|c\boldsymbol{k}\rangle$$

Symmetry Constraints

$\varepsilon_{ij} = \varepsilon_{ji}$ is always symmetric.

Additional constraints from crystal symmetry:

$$\varepsilon = U^{-1}\,\varepsilon\,U$$

cubic $\begin{pmatrix} 1 & 0 & 0 \\ & 1 & 0 \\ & & 1 \end{pmatrix}$

tetragonal, trigonal, hexagonal $\begin{pmatrix} 1 & 0 & 0 \\ & 1 & 0 \\ & & 3 \end{pmatrix}$

orthorhombic $\begin{pmatrix} 1 & 0 & 0 \\ & 2 & 0 \\ & & 3 \end{pmatrix}$

monoclinic $\begin{pmatrix} 1 & 4 & 0 \\ & 2 & 0 \\ & & 3 \end{pmatrix}$

triclinic $\begin{pmatrix} 1 & 4 & 5 \\ & 2 & 6 \\ & & 3 \end{pmatrix}$

Program Flow

`lapw1` Kohn-Sham eigenstates

`optic` momentum matrix elements (*case*.`symmat`)

`joint` imaginary part of dielectric tensor (`case.joint`)

`kram` derived quantities

- Kramers-Kronig

$$\mathrm{Re}\,\varepsilon_{ij} = \delta_{ij} + \tfrac{2}{\pi}\,\mathcal{P}\int_0^\infty \mathrm{d}\Omega\,\frac{\Omega}{\Omega^2-\omega^2}\,\mathrm{Im}\,\varepsilon_{ij}$$

⇝ all optical constants

`optic`: Momentum Matrix Elements

0 normal SCF run ⟶ converged density

1 x `kgen` ⟶ dense k-mesh (check convergence!)

2 x `lapw1` *-options* ⟶ eigenvectors on dense mesh

3 x `lapw2 -fermi` *-options* ⟶ *case*.`weight`

- metals: "`TETRA 101.0`" in *case*.`in2`

4 x `optic` *-options* ⟶ momentum matrix elements
case.`symmat`: $\langle c\boldsymbol{k}|\widehat{p}_i|v\boldsymbol{k}\rangle\,\langle v\boldsymbol{k}|\widehat{p}_j|c\boldsymbol{k}\rangle$

core-level spectra: Kevin Jorissen's lecture tomorrow 10:30

optic: Input and Output

case.inop

```
99999 1            #k-points,  1st k-point
-5.0 3.0 9999      Emin Emax [Ry],  NBvalMAX
2                  #indep. elements (symmetry/SOC)
1                  Re xx
3                  Re zz
OFF 3              write mommat2?, #spheres
1 2 3              spheres to sum over
```

symmetry

1: $\mathrm{Re}\langle xx\rangle$ 4: $\mathrm{Re}\langle xy\rangle$
2: $\mathrm{Re}\langle yy\rangle$ 5: $\mathrm{Re}\langle xz\rangle$
3: $\mathrm{Re}\langle zz\rangle$ 6: $\mathrm{Re}\langle yz\rangle$

spin-orbit

7: $\mathrm{Im}\langle xy\rangle$
8: $\mathrm{Im}\langle xz\rangle$
9: $\mathrm{Im}\langle yz\rangle$

case.symmat

$\langle v\boldsymbol{k}|\widehat{p}_i|c\boldsymbol{k}\rangle\,\langle c\boldsymbol{k}|\widehat{p}_j|v\boldsymbol{k}\rangle$

case.mommat2 (if ON)

$\langle v\boldsymbol{k}|\widehat{p}_i|c\boldsymbol{k}\rangle$

joint: Im(ε), (Joint) Density of States

case.injoint

```
1 9999 9999      lower, upper, upper-val bandindex
0.0 .001 1.0     Emin (≥ 0), dE, Emax [Ry]
eV               units [eV / ryd  / cm-1]
4                mode
2                #indep. elements
0.1 0.1          broadenings Γ for Drude (mode=6,7)
```

case.joint

$$\left.\begin{matrix}\mathrm{Im}\,\varepsilon_{ij}\\ \rho\end{matrix}\right\} \sim \sum_{c,v}\int \mathrm{d}\boldsymbol{k}\,\delta\big(\epsilon_c(\boldsymbol{k})-\epsilon_v(\boldsymbol{k})-\omega\big)\left\{\begin{matrix}\langle c\boldsymbol{k}|\widehat{p}_i|v\boldsymbol{k}\rangle\,\langle v\boldsymbol{k}|\widehat{p}_j|c\boldsymbol{k}\rangle\\ 1\end{matrix}\right.$$

`joint`: Modes of Operation

"physical" (all bands)

- 1 joint DOS
- 3 regular DOS
- 4 $\mathrm{Im}\,\varepsilon$ interband
- 6 $\mathrm{Im}\,\varepsilon$ intraband (Drude)

band analysis

- 0 joint DOS
- 2 DOS
- 5 interband
- 7 intraband

$$\mathrm{Im}\,\varepsilon_{ij} \sim \sum_{c,v,\boldsymbol{k}} \delta\big(\epsilon_c(\boldsymbol{k}) - \epsilon_v(\boldsymbol{k}) - \omega\big)\, \langle c\boldsymbol{k}|\widehat{p}_i|v\boldsymbol{k}\rangle\, \langle v\boldsymbol{k}|\widehat{p}_j|c\boldsymbol{k}\rangle$$

"sphere analysis"

$$|c\boldsymbol{k}\rangle = \sum_{\alpha}^{\mathrm{MT,I}} |c\boldsymbol{k}\rangle_\alpha$$

NB: cross-terms are missed!

***case*`.inop`**

```
OFF 3   mommat2?, #spheres
1 2 3   spheres to sum over
```

`kram`: Kramers-Kronig Analysis

***case*`.inkram`**

```
0.1         interband broadening
0.0         energy shift (scissors operator)
1           add intraband contributions?  1/0
12.6 12.6   plasma frequencies  (joint, mode=6)
 0.1  0.1   broadenings Γ for Drude models
```

output

- *case*`.epsilon` — $\mathrm{Re}\,\varepsilon, \mathrm{Im}\,\varepsilon$
- *case*`.absorp` — $\mathrm{Re}\,\sigma, \alpha$
- *case*`.reflectivity` — R
- *case*`.sigmak` — $\mathrm{Re}\,\sigma, \mathrm{Im}\,\sigma$
- *case*`.eloss` — loss function
- *case*`.refraction` — n, k
- *case*`.sumrules`

More Stuff You May Need to Know

spin-polarized calculations

Kramers-Kronig is not additive.

1. `x joint -up && x joint -dn`
2. `addjoint-updn`
3. `x kram`

procedure for metals

1. `x joint (mode=6)` $\longrightarrow$ plasma frequencies $\omega_{\mathrm{p}_{ij}}$
2. `x joint (mode=4)` $\longrightarrow$ interband $\mathrm{Im}\,\varepsilon$
3. `x kram (intra=1,` insert ω_{p}`)`

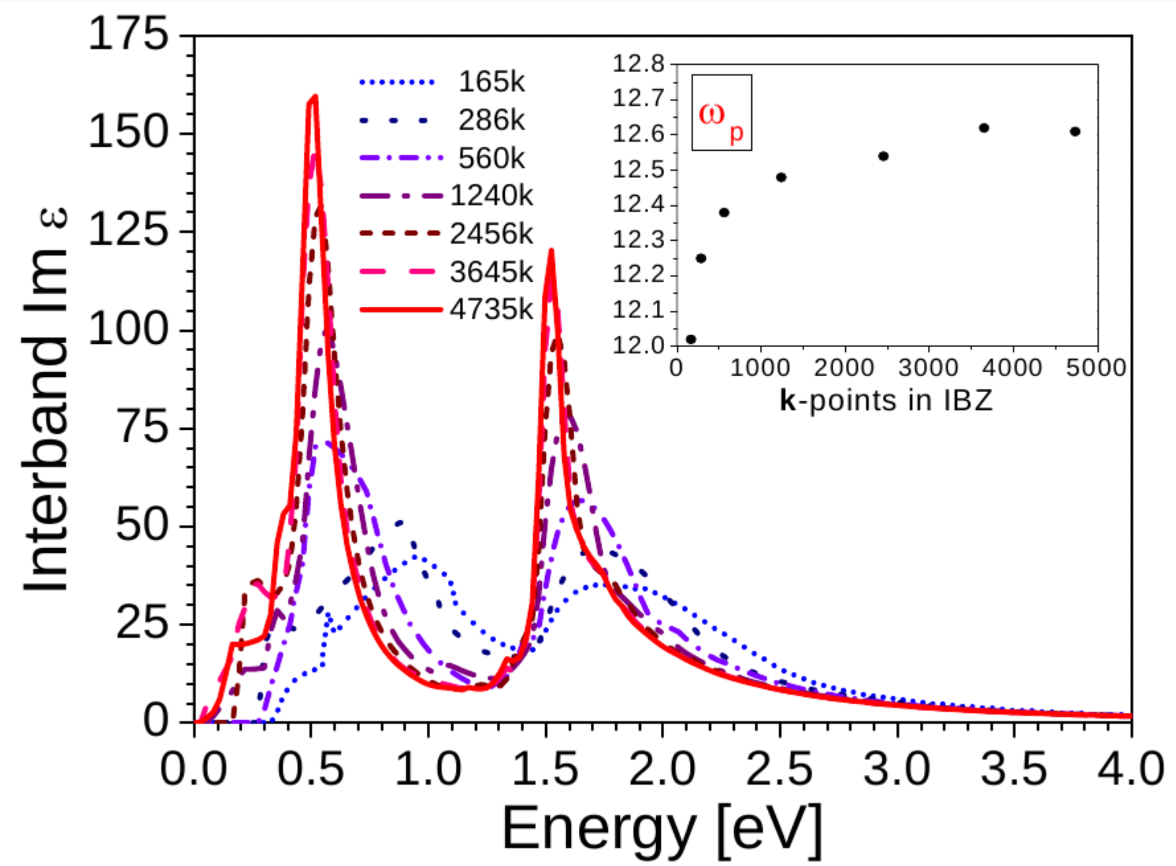
$$\mathrm{Im}\,\varepsilon^{\mathrm{intra}} = \frac{\Gamma {\omega_{\mathrm{p}}}^2}{\omega\,(\omega^2+\Gamma^2)}, \qquad \mathrm{Re}\,\varepsilon^{\mathrm{intra}} = 1 - \frac{{\omega_{\mathrm{p}}}^2}{\omega^2+\Gamma^2}$$

Kramers-Kronig needs $\mathrm{Im}\,\varepsilon$ in a large energy range

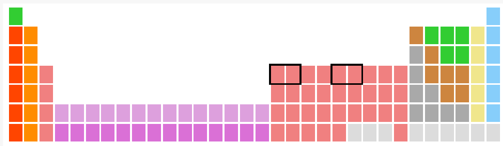
Some Limitations

- linear optical properties only
  - $W = \varepsilon^{-1(1)} V + \cancel{\varepsilon^{-1(2)} V^2 + \cdots}$
- Kohn-Sham eigenstates interpreted as excited states
  - ⇝ "scissors" operator: $\epsilon_c(\boldsymbol{k}) \to \epsilon_c^{\mathrm{LDA}}(\boldsymbol{k}) + \Delta$
- independent-particle approx. (no e^-– h^+ interaction)
  - ⇝ Bethe-Salpeter (BSE) → Peter Blaha's lecture (13:00)
- LDA/GGA are not exact
  - ⇝ hybrid DFT, effective potentials → Peter Blaha
  - ⇝ DFT+U, LDA+DMFT → my lecture (tomorrow 9:00)

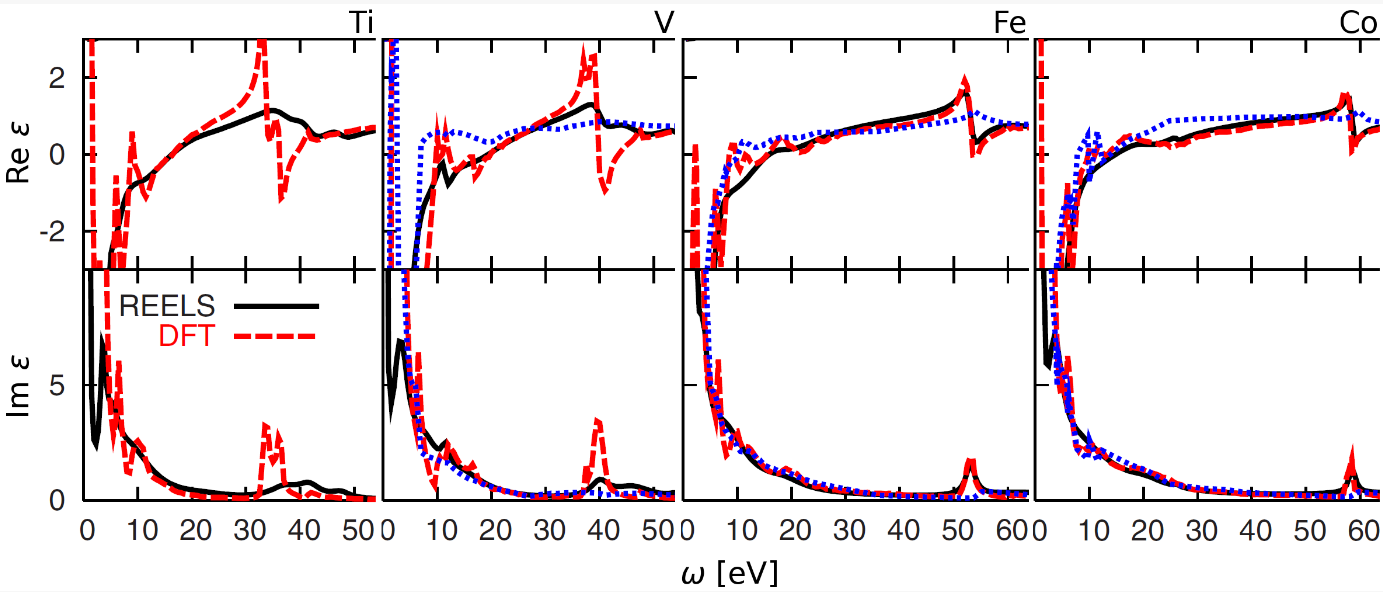
Example: Al, k-Mesh Convergence



Comparison to Experiment



REELS = reflection electron energy loss spectroscopy



Optical Constants for 17 Elemental Metals
Werner *et al.*, Phys. Chem. Ref. Data 38, 1013 (2009)

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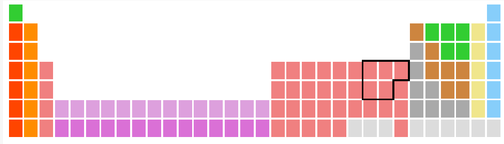

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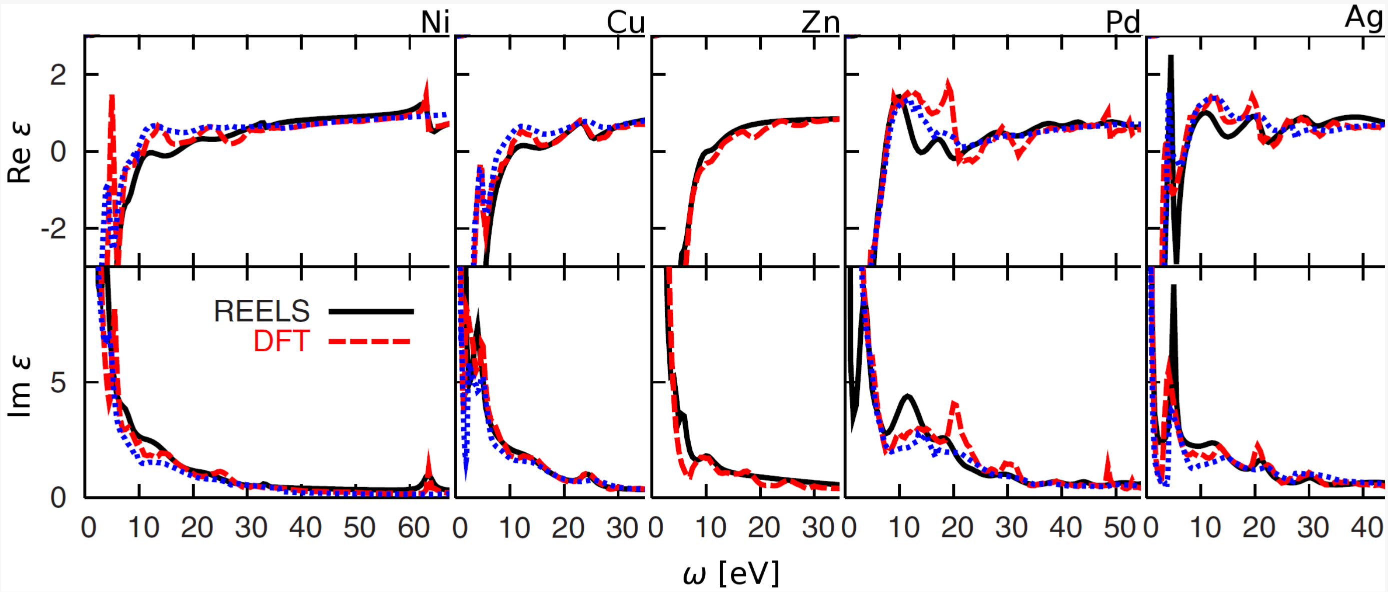

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