The Bethe-Salpeter Equation

Preliminary

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Outline

1. Linear Response and (solid state) Spectroscopies
   - Absorption Spectroscopy
   - Loss Spectroscopy
   - Inelastic X-ray Scattering
   - Importance of the dielectric function
2. Micro-Macro Connection
   - Micro-Macro :: the loss function
   - Micro-Macro :: the absorption

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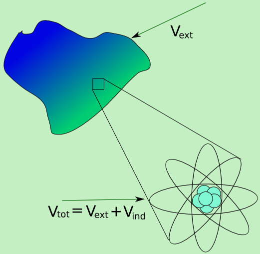
Linear Response Approach

System submitted to an external perturbation



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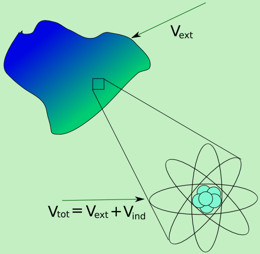

$$V_{tot} = \varepsilon^{-1} V_{ext}$$

$$V_{tot} = V_{ext} + V_{ind}$$

Linear Response Approach

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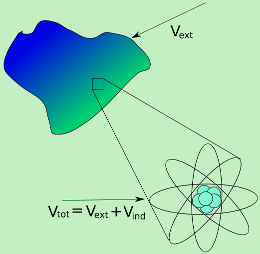

$$V_{tot} = \varepsilon^{-1} V_{ext}$$

$$V_{tot} = V_{ext} + V_{ind}$$

$$\mathbf{E} = \varepsilon^{-1}\mathbf{D}$$

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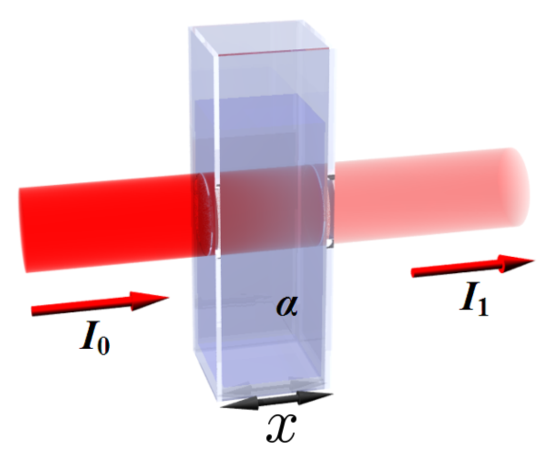
Absorption

Beer Law

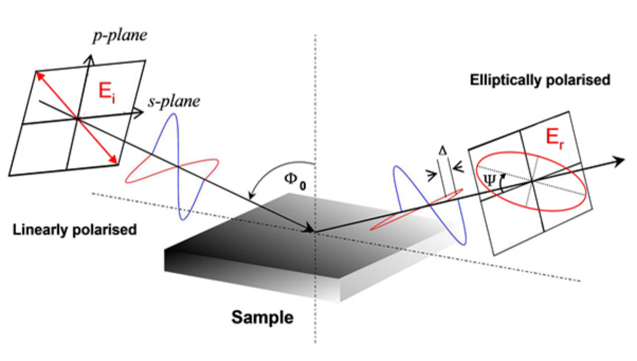
$$I(x) = I_0 e^{-\alpha x}$$

$$\alpha \Longleftrightarrow \varepsilon$$



Absorption

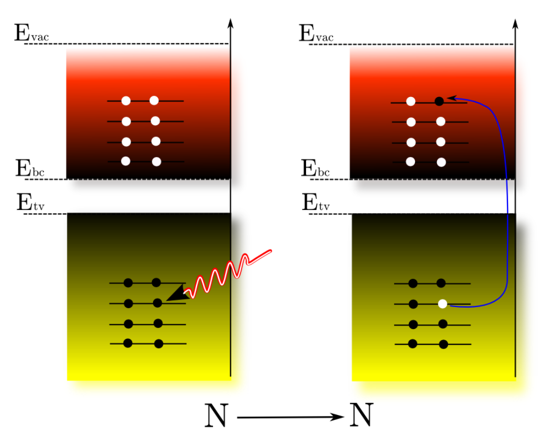
Ellipsometry Experiments



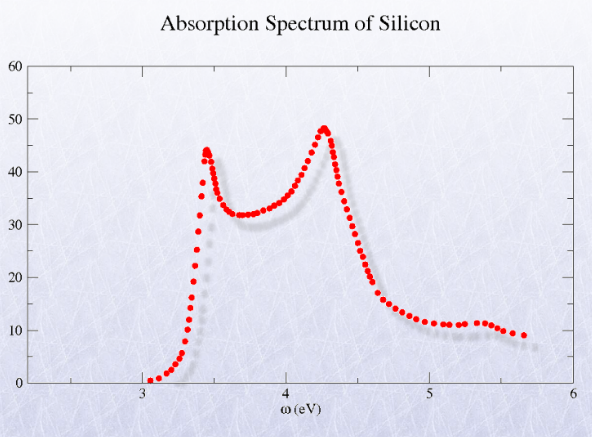
$$\varepsilon = sin^2\Phi + sin^2\Phi tan^2\Phi \left(\frac{1 - \frac{E_r}{E_i}}{1 + \frac{E_r}{E_i}} \right)$$

Absorption

Creation of an electron-hole pair

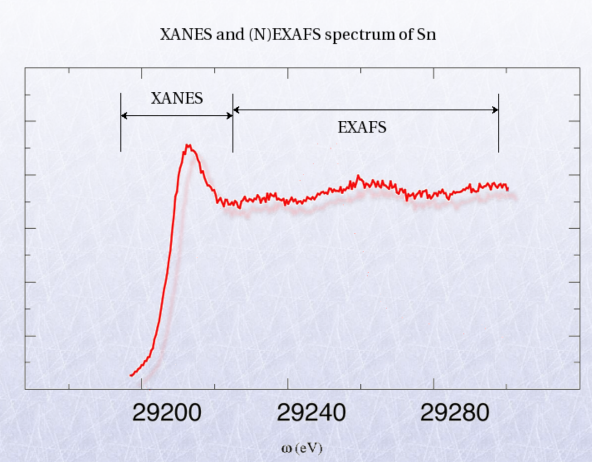


Absorption



Lautenschlager *et al.*, PRB **36**, 4821 (1987)

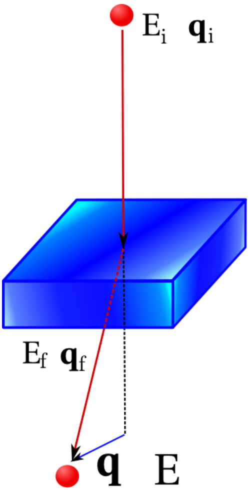
Absorption



Izumi *et al.*, Anal.Chem. **77**, 6969 (2005)

Outline

Spectroscopy: Electron Scattering

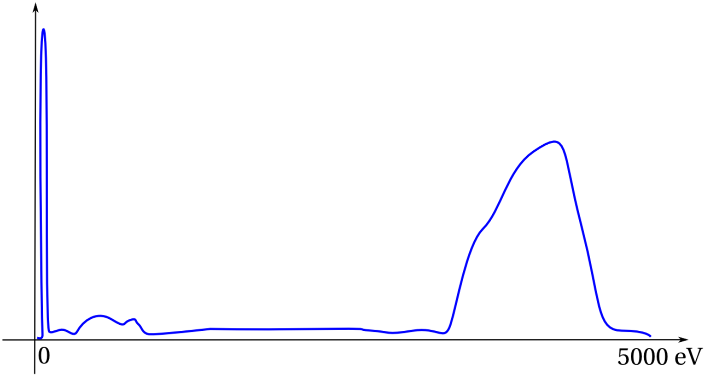


Spectroscopy: Electron Scattering

Energy Loss Function

$$\frac{d^2\sigma}{d\Omega dE} \propto \mathrm{Im}\left\{\varepsilon^{-1}\right\}$$

Spectroscopy: Electron Scattering



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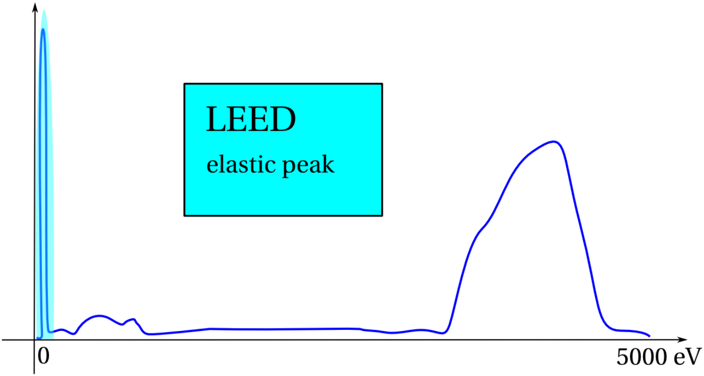
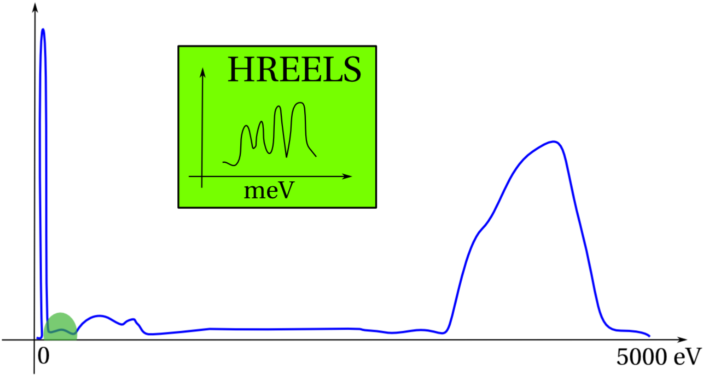
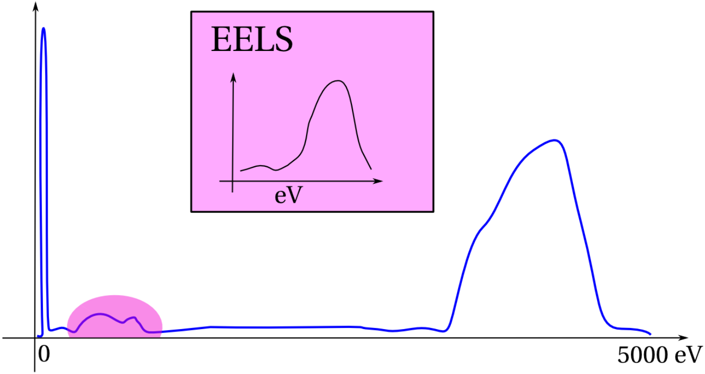


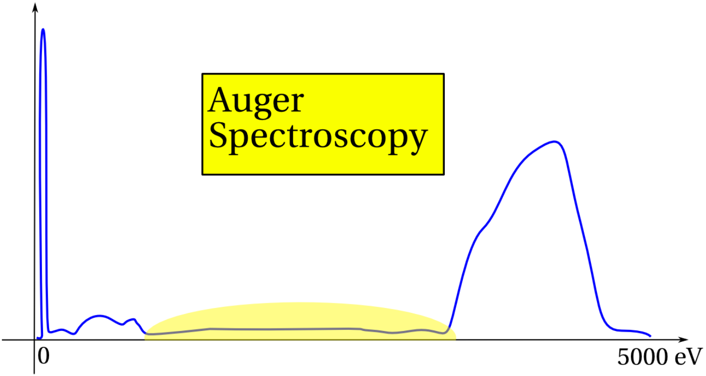
Spectroscopy: Electron Scattering



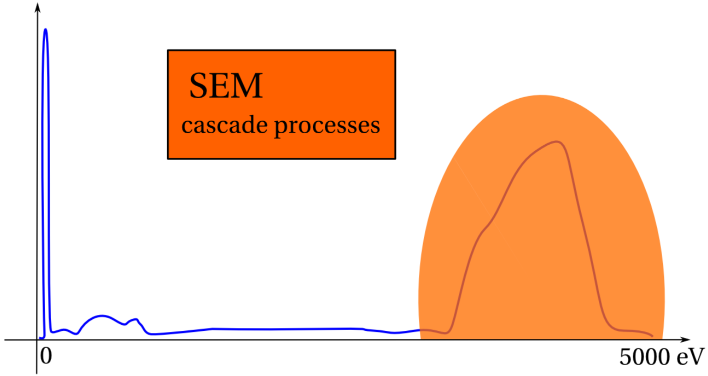
Spectroscopy: Electron Scattering



Spectroscopy: Electron Scattering



Spectroscopy: Electron Scattering



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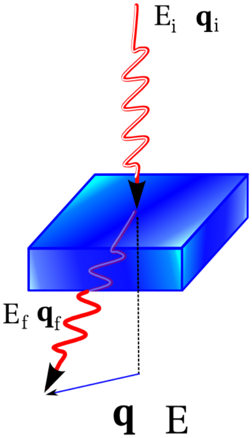
Spectroscopy: X-ray Scattering



Spectroscopy: X-ray Scattering

Energy Loss Function

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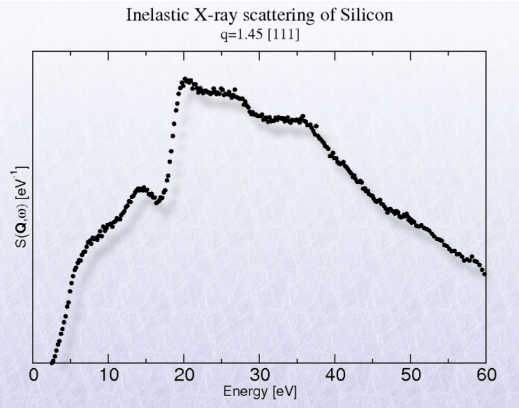

Weissker *et al.*, PRL **97**, 237602 (2006)

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Importance of dielectric function ε

- Absorption (reflectivity, refraction index)
- EELS
- IXS, RIXS, CIXS
- Compton Scattering
- Surface analysis (RAS, SDR, etc.)

Importance of dielectric function ε

- Absorption (reflectivity, refraction index)
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- Surface analysis (RAS, SDR, etc.)

- Photo-emission (GW)

Linear Response Approach

Definition of polarizability

$$\varepsilon^{-1} = 1 + v\chi$$

χ is the polarizability of the system

Linear Response Approach

Polarizability

interacting system $\delta n = \chi \delta V_{ext}$

non-interacting system $\delta n_{n-i} = \chi^0 \delta V_{tot}$

Linear Response Approach

Polarizability

interacting system $\delta n = \chi \delta V_{ext}$

non-interacting system $\delta n_{n-i} = \chi^0 \delta V_{tot}$

Single-particle polarizability

$$\chi^0 = \sum_{ij} \frac{\phi_i(\mathbf{r})\phi_j^*(\mathbf{r})\phi_i^*(\mathbf{r}')\phi_j(\mathbf{r}')}{\omega - (\epsilon_i - \epsilon_j)}$$

hartree, hartree-fock, dft, etc.

G.D. Mahan *Many Particle Physics* (Plenum, New York, 1990)

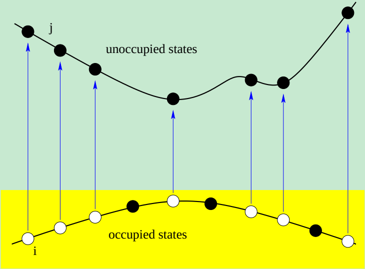
Linear Response Approach

Polarizability

interacting system $\delta n = \chi \delta V_{ext}$

non-interacting system $\delta n_{n-i} = \chi^0 \delta V_{tot}$

$$\chi^0 = \sum_{ij} \frac{\phi_i(\mathbf{r})\phi_j^*(\mathbf{r})\phi_i^*(\mathbf{r}')\phi_j(\mathbf{r}')}{\omega - (\epsilon_i - \epsilon_j)}$$



Linear Response Approach

Polarizability

interacting system $\delta n = \chi \delta V_{ext}$

non-interacting system $\delta n_{n-i} = \chi^0 \delta V_{tot}$

$\Updownarrow$

Density Functional Formalism

$$\delta n = \delta n_{n-i}$$

$$\delta V_{tot} = \delta V_{ext} + \delta V_H + \delta V_{xc}$$

Polarizability in DFT + Linear Response

$$\chi \delta V_{ext} = \chi^0 \left(\delta V_{ext} + \delta V_H + \delta V_{xc} \right)$$

$$\chi = \chi^0 \left(1 + \frac{\delta V_H}{\delta V_{ext}} + \frac{\delta V_{xc}}{\delta V_{ext}} \right)$$

Polarizability in DFT + Linear Response

$$\chi \delta V_{ext} = \chi^0 \left(\delta V_{ext} + \delta V_H + \delta V_{xc} \right)$$

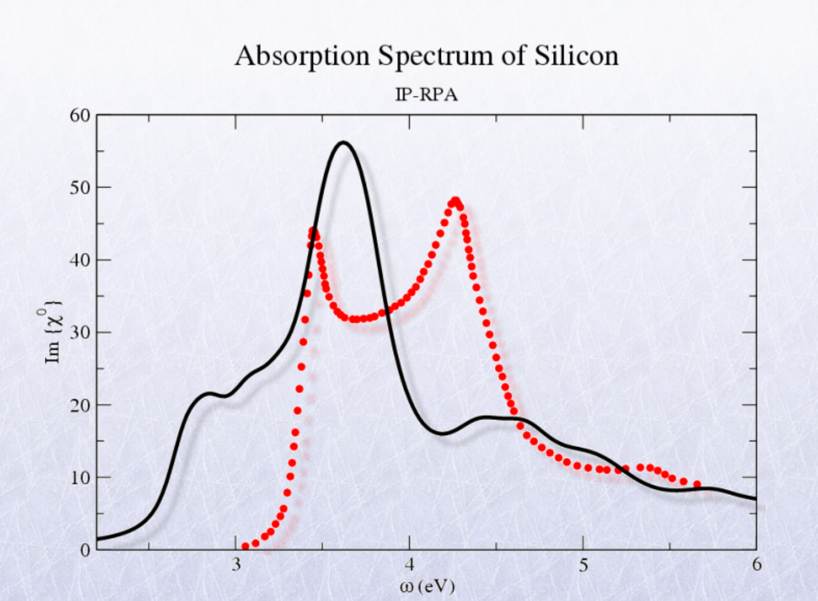
$$\chi = \chi^0 \left(1 + \frac{\delta V_H}{\delta V_{ext}} + \frac{\delta V_{xc}}{\delta V_{ext}} \right)$$

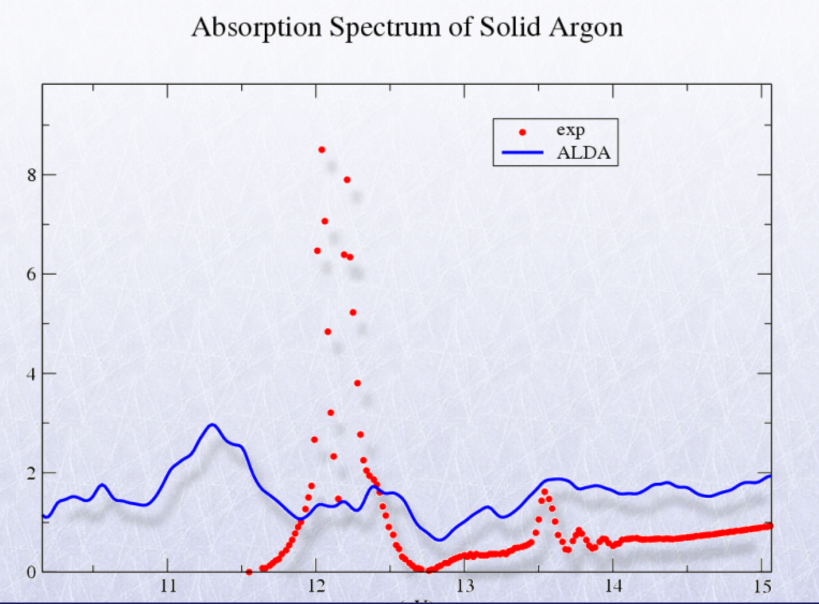
$$\frac{\delta V_H}{\delta V_{ext}} = \frac{\delta V_H}{\delta n} \frac{\delta n}{\delta V_{ext}} = v\chi$$

$$\frac{\delta V_{xc}}{\delta V_{ext}} = \frac{\delta V_{xc}}{\delta n} \frac{\delta n}{\delta V_{ext}} = f_{xc}\chi$$

$$\chi = \chi^0 + \chi^0 \left(v + f_{xc} \right) \chi$$

with $f_{xc} = \frac{\delta V_{xc}}{\delta n}$ **exchange-correlation kernel**
with $v = \frac{\delta V_H}{\delta n}$ **coulomb interaction**

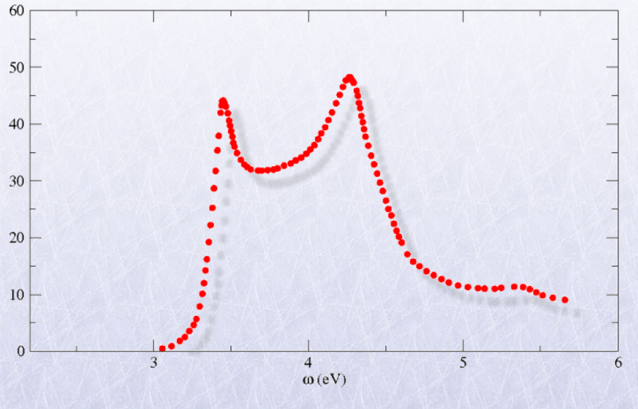

Absorption Spectrum of Silicon
IP-RPA
Im {χ⁰}
ω (eV)
0
10
20
30
40
50
60
3
4
5
6


Absorption Spectrum of Solid Argon
exp
ALDA
0
2
4
6
8
11
12
13
14
15

Microscopic (calculation) | Macroscopic (measurement)

$$\varepsilon^{-1}(\mathbf{r}, \mathbf{r}', \omega)$$

$$\chi(\mathbf{r}, \mathbf{r}', \omega)$$



Outline

Solids

Reciprocal Space - Frequency domain

$$f(\mathbf{r}) \to f_{\mathbf{G}}(\mathbf{q}) = \frac{1}{\Omega}\int d\mathbf{r} f(\mathbf{r}) e^{\imath(\mathbf{q}+\mathbf{G})\dot{\mathbf{r}}}$$

$\mathbf{G}$ =reciprocal lattice vector

$\mathbf{q} \in 1BZ$ momentum transfer of the perturbation

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Reciprocal Space - Frequency domain

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$\mathbf{G}$ =reciprocal lattice vector

$\mathbf{q} \in 1BZ$ momentum transfer of the perturbation

$$\chi^0(\mathbf{r},\mathbf{r}',\omega) \longrightarrow \chi^0_{\mathbf{GG}'}(\mathbf{q},\omega)$$

$$\chi^0_{\mathbf{GG}'}(\mathbf{q},\omega) = \sum_{vc\mathbf{k}} \frac{\left\langle \phi_{v\mathbf{k}} \middle| e^{\imath(\mathbf{q}+\mathbf{G})\mathbf{r}} \middle| \phi^*_{c\mathbf{k}+\mathbf{q}} \right\rangle \left\langle \phi_{c\mathbf{k}+\mathbf{q}} \middle| e^{-\imath(\mathbf{q}+\mathbf{G}')\mathbf{r}'} \middle| \phi^*_{v\mathbf{k}} \right\rangle}{\omega - (\epsilon_{c\mathbf{k}+\mathbf{q}} - \epsilon_{v\mathbf{k}}) + \imath\eta}$$

Outline

Micro-Macro :: the loss function

$$
\begin{aligned}
\varepsilon^{-1}(\mathbf{r}, \mathbf{r}', \omega) &= \int d\mathbf{q} \sum_{\mathbf{G},\mathbf{G}'} e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} \varepsilon^{-1}_{\mathbf{G}\mathbf{G}'}(\mathbf{q}, \omega) e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'} \\
&= \int d\mathbf{q} e^{-i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')} \sum_{\mathbf{G},\mathbf{G}'} e^{-i\mathbf{G}\cdot\mathbf{r}} \varepsilon^{-1}_{\mathbf{G}\mathbf{G}'}(\mathbf{q}, \omega) e^{i\mathbf{G}'\cdot\mathbf{r}'} \\
&= \int d\mathbf{q} e^{-i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')} \varepsilon^{-1}(\mathbf{q}, \mathbf{r}, \mathbf{r}', \omega).
\end{aligned}
$$

Micro-Macro :: the loss function

$$\varepsilon^{-1}(\mathbf{r},\mathbf{r}',\omega) = \int d\mathbf{q} \sum_{\mathbf{G},\mathbf{G}'} e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} \varepsilon^{-1}_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}$$

$$= \int d\mathbf{q} e^{-i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')} \sum_{\mathbf{G},\mathbf{G}'} e^{-i\mathbf{G}\cdot\mathbf{r}} \varepsilon^{-1}_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) e^{i\mathbf{G}'\cdot\mathbf{r}'}$$

$$= \int d\mathbf{q} e^{-i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')} \varepsilon^{-1}(\mathbf{q},\mathbf{r},\mathbf{r}',\omega).$$

$$\varepsilon^{-1}_M(\mathbf{q},\omega) = \int d\mathbf{r} d\mathbf{r}' \varepsilon^{-1}(\mathbf{q},\mathbf{r},\mathbf{r}',\omega)$$

$$= \int d\mathbf{r} d\mathbf{r}' \sum_{\mathbf{G},\mathbf{G}'} e^{-i\mathbf{G}\cdot\mathbf{r}} \varepsilon^{-1}_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) e^{i\mathbf{G}'\cdot\mathbf{r}'}$$

$$= \varepsilon^{-1}_{00}(\mathbf{q},\omega).$$

Micro-Macro :: the loss function

The Macroscopic inverse dielectric function is the head ($\mathbf{G} = \mathbf{G}' = 0$ component) of the inverse dielectric matrix.

$$\varepsilon_{\mathrm{M}}^{-1}(\mathbf{q},\omega) = \varepsilon_{00}^{-1}(\mathbf{q},\omega)$$

Micro-Macro :: the loss function

Reciprocal Space - Frequency domain

$$\chi_{\mathbf{GG}'}(\mathbf{q},\omega) = \left[1 - \chi^0 \left(v + f_{xc}\right)\right]^{-1}_{\mathbf{GG}''} \chi^0_{\mathbf{G}''\mathbf{G}'}$$

Micro-Macro :: the loss function

Reciprocal Space - Frequency domain

$$\chi_{\mathbf{GG'}}(\mathbf{q},\omega) = \left[1 - \chi^0 \left(v + f_{xc}\right)\right]^{-1}_{\mathbf{GG''}} \chi^0_{\mathbf{G''G'}}$$

$$\varepsilon^{-1}_{\mathbf{GG'}}(\mathbf{q},\omega) = \delta_{\mathbf{GG'}} + v_{\mathbf{G}}(\mathbf{q})\chi_{\mathbf{GG'}}(\mathbf{q},\omega)$$

Micro-Macro :: the loss function

Reciprocal Space - Frequency domain

$$\chi_{\mathbf{GG'}}(\mathbf{q},\omega) = \left[1 - \chi^0\left(v + f_{xc}\right)\right]^{-1}_{\mathbf{GG''}} \chi^0_{\mathbf{G''G'}}$$

$$\varepsilon^{-1}_{\mathbf{GG'}}(\mathbf{q},\omega) = \delta_{\mathbf{GG'}} + v_{\mathbf{G}}(\mathbf{q})\chi_{\mathbf{GG'}}(\mathbf{q},\omega)$$

$$\mathrm{ELS}(\mathbf{q},\omega) = -\mathrm{Im}\{\varepsilon^{-1}_{\mathrm{M}}(\mathbf{q},\omega)\} = -\mathrm{Im}\{\varepsilon^{-1}_{00}(\mathbf{q},\omega)\}$$

Outline

The case of absorption

- $\mathbf{q} \to 0$

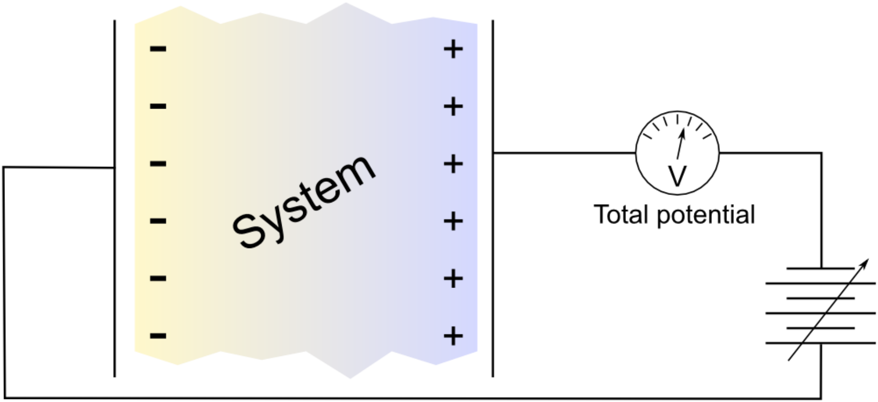
The case of absorption

- $\mathbf{q} \to 0$
- $\lambda >>$ system

The case of absorption

- $\mathbf{q} \to 0$
- $\lambda >> $ system
- perturbing potential is not (only) the external potential

The case of absorption



$$\mathbf{D} = \varepsilon_{\mathrm{M}} \mathbf{E}$$

The case of absorption

Macro :: $$\mathbf{D}(\mathbf{q},\omega) = \varepsilon_M(\mathbf{q},\omega)\mathbf{E}(\mathbf{q},\omega).$$

micro :: $$\mathbf{E}_{\mathbf{G}}(\mathbf{q},\omega) = \varepsilon^{-1}_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega)\mathbf{D}_{\mathbf{G}'}(\mathbf{q},\omega)$$

The case of absorption

$$\text{Macro} :: \qquad \mathbf{D}(\mathbf{q},\omega) = \varepsilon_M(\mathbf{q},\omega)\mathbf{E}(\mathbf{q},\omega).$$

$$\text{micro} :: \qquad \mathbf{E}_0(\mathbf{q},\omega) = \varepsilon_{00}^{-1}(\mathbf{q},\omega)\mathbf{D}_0(\mathbf{q},\omega)$$

The case of absorption

$$\text{Macro} :: \qquad \mathbf{D}(\mathbf{q},\omega) = \varepsilon_M(\mathbf{q},\omega)\mathbf{E}(\mathbf{q},\omega).$$

$$\text{micro} :: \qquad \mathbf{E}_0(\mathbf{q},\omega) = \varepsilon^{-1}_{00}(\mathbf{q},\omega)\mathbf{D}_0(\mathbf{q},\omega)$$

$$\varepsilon_{\mathrm{M}}(\mathbf{q},\omega) = \frac{1}{\varepsilon^{-1}_{00}(\mathbf{q},\omega)}$$

Micro-Macro :: the absorption

The Macroscopic dielectric function is the inverse of the head ($\mathbf{G} = \mathbf{G}' = 0$ component) of the inverse dielectric matrix.

$$\varepsilon_{\mathrm{M}}(\mathbf{q}, \omega) = \frac{1}{\varepsilon^{-1}_{00}(\mathbf{q}, \omega)}$$

Micro-Macro :: the absorption

- What about ε_{00} ?

Micro-Macro :: the absorption

- What about ε_{00} ?
- ε_{00} is the macroscopic dielectric function **without local fields**

Micro-Macro :: the absorption

Can we exploit the definition of perturbing potential $(V_{ext} + V_{tot}^{macr})$ to obtain a response function that would avoid all this inversion of the inverse ??

Micro-Macro :: the absorption

Can we exploit the definition of perturbing potential ($V_{ext} + V_{tot}^{macr}$) to obtain a response function that would avoid all this inversion of the inverse ??

Polarizability

$$\varepsilon^{-1} = 1 + v\chi \qquad ; \quad \delta n = \chi V_{ext}$$

Micro-Macro :: the absorption

Can we exploit the definition of perturbing potential $(V_{ext} + V_{tot}^{macr})$ to obtain a response function that would avoid all this inversion of the inverse ??

Modified Polarizability

$$\varepsilon^{-1} = 1 + v\chi \qquad ; \qquad \delta n = \chi V_{ext}$$

$$\varepsilon = 1 - v\bar{\chi} \qquad ; \qquad \delta n = \bar{\chi}\left(V_{ext} + V_{tot}^{macr}\right)$$

Micro-Macro :: the absorption

Modified Polarizability :: two consequences

- $\bar{\varepsilon} = 1 - v\bar{\chi} \quad ; \quad \delta n = \bar{\chi}\left(V_{ext} + V_{tot}^{macr}\right)$

$$\varepsilon_{\mathrm{M}} = \bar{\varepsilon}_{00}$$

Micro-Macro :: the absorption

Modified Polarizability :: two consequences

- $\bar{\varepsilon} = 1 - v\bar{\chi} \quad ; \quad \delta n = \bar{\chi}\left(V_{ext} + V_{tot}^{macr}\right)$

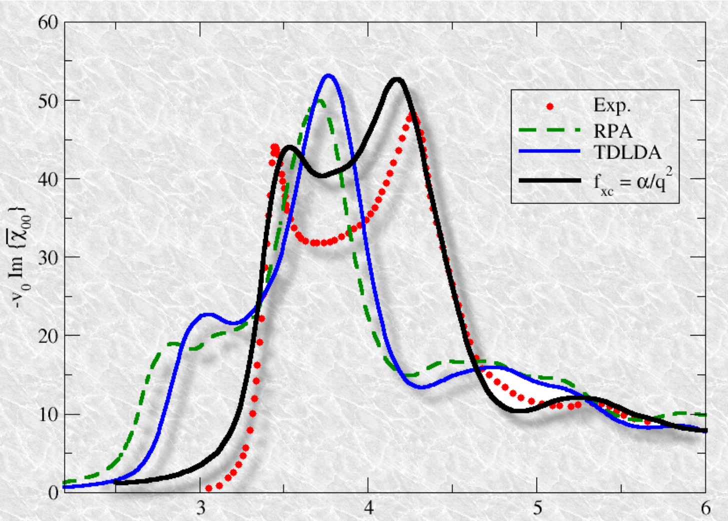
$$\varepsilon_M = \bar{\varepsilon}_{00}$$

- $\bar{\chi} = \chi^0 + \chi^0\left(\bar{v} + \Xi\right)\bar{\chi}$

$$\bar{v} = \begin{cases} 0 & \mathbf{G} = 0 \\ v_{\mathbf{G}} = \frac{1}{|\mathbf{q}+\mathbf{G}|^2} & \mathbf{G} \neq 0 \end{cases}$$

No long range component in v for the absorption.

Micro-Macro :: the absorption



Summary

- We need to calculate the macroscopic dielectric function, related to many spectroscopies (optical properties, loss function, refraction index, Compton scattering, IXS, etc.)
- average procedure

$$\begin{aligned} \mathrm{Loss}(\omega) &= -\mathrm{Im}\ \varepsilon_{\mathrm{M}}^{-1}(\mathbf{q},\omega) = -v_0\ \mathrm{Im}\ \chi_{00}(\mathbf{q},\omega) \\ \mathrm{Abs}(\omega) &= \mathrm{Im}\ \varepsilon_{\mathrm{M}}(\mathbf{q},\omega) = -v_0\ \mathrm{Im}\ \bar{\chi}_{00}(\mathbf{q},\omega) \end{aligned}$$

- We need to go beyond ALDA, towards BSE, for accurate results.