Introduction to Linear Response

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Outline

1. Linear response
2. Micro-macro connection

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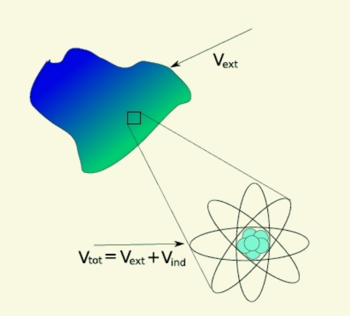
Response functions

External perturbation V_{ext} applied on the sample
$\rightarrow V_{tot}$ acting on the electronic system



Potentials

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

$$\delta V_{ind} = v \delta \rho$$

Dielectric function

$$\epsilon = \frac{\delta V_{ext}}{\delta V_{tot}} = 1 - v \frac{\delta \rho}{\delta V_{tot}}$$

$$\epsilon^{-1} = \frac{\delta V_{tot}}{\delta V_{ext}} = 1 + v \frac{\delta \rho}{\delta V_{ext}}$$

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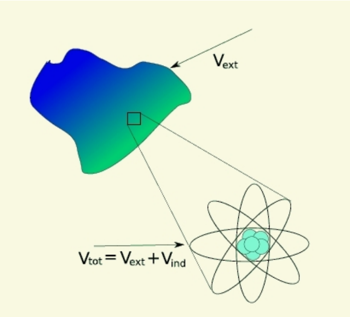

Dielectric function

$$\epsilon = \frac{\delta V_{ext}}{\delta V_{tot}} = 1 - vP$$

$$\epsilon^{-1} = \frac{\delta V_{tot}}{\delta V_{ext}} = 1 + v\chi$$

$$P = \frac{\delta \rho}{\delta V_{tot}} \qquad \chi = \frac{\delta \rho}{\delta V_{ext}}$$

$$\chi = P + Pv\chi$$

Linear response

Linear response

- For a sufficiently small perturbation, the response of the system can be expanded into a Taylor series with respect to the perturbation.
- We consider only the (first order) linear response.
- The linear response to the perturbation is independent of the perturbation and depends only on the properties of the sample.
- Strong field interaction (laser field for instance) not covered by linear response.

$$\delta\rho(\mathbf{r}_1, t_1) = \int d\mathbf{r}_3 dt_3 \chi(\mathbf{r}_1, \mathbf{r}_3, t_1 - t_3) V_{ext}(\mathbf{r}_3, t_3)$$

Linear response: Kubo formula

- $\hat{H}$ is the many-body Hamiltonian and $\hat{H}_1(t)$ a time-dependent perturbation.

$$\hat{H}_{tot} = \hat{H} + \hat{H}_1(t) \quad \text{with} \quad \hat{H}_1(t) = \int d\mathbf{r}_1 F(\mathbf{r}_1, t)\hat{P}(\mathbf{r}_1, t)$$

  Typically the perturbation is an electromagnetic field coupled with densities or currents.

- The first-order variation of the observable $\langle\hat{O}\rangle$ due to $\hat{H}_1$ is

$$\delta\langle\hat{O}(1)\rangle = -i\theta(t_1 - t_2)\int d2\langle N|[\hat{O}(1), \hat{H}_1(2)]|N\rangle$$

  where 1 stands for $\mathbf{r}_1 t_1 \sigma_1$ and $|N\rangle$ is the ground-state wavefunction.

- In linear-response theory one considers small variations δF:

$$\delta\langle\hat{O}(1)\rangle = \int d2\chi_{OP}(1,2)\delta F(2)$$

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- In linear-response theory one considers small variations δF:

$$\delta\langle\hat{O}(1)\rangle = \int d2\chi_{OP}(1,2)\delta F(2)$$

  $\chi_{OP}(1,2) = -i\theta(t_1 - t_2)\langle N|[\hat{O}(1), \hat{P}(2)]|N\rangle = \delta\langle\hat{O}(1)\rangle/\delta F(2)$
  is a (causal or retarded) response function.

Linear response: Kubo formula

Linear response

$$\chi_{OP}(1,2) = -i\theta(t_1 - t_2)\langle N|[\hat{O}(1), \hat{P}(2)]|N\rangle = \frac{\delta\langle \hat{O}(1)\rangle}{\delta F(2)}$$

Examples

$$\chi_{\rho\rho} \quad \chi_{\mathbf{jj}} \quad \chi_{\mathbf{j}\rho} \quad \chi_{\sigma\sigma} \ \cdots$$

G.F. Giuliani and G. Vignale, Quantum theory of the electron liquid, Ch. 3

Linear response

Linear response

$$\chi_{OP}(1,2) = -i\theta(t_1 - t_2)\langle N|[\hat{O}(1), \hat{P}(2)]|N\rangle = \delta\langle\hat{O}(1)\rangle/\delta F(2)$$

Lehmann representation

By inserting a completeness relation and taking the Fourier transform, the response function can be written in the Lehmann representation as:

$$\chi_{OP}(\mathbf{r}_1, \mathbf{r}_2, \omega) = \sum_s \left[\frac{O_s(\mathbf{r}_1)P_s^*(\mathbf{r}_2)}{\omega + E_0 - E_s + i\eta} - \frac{O_s^*(\mathbf{r}_1)P_s(\mathbf{r}_2)}{\omega + E_s - E_0 + i\eta}\right]$$

where:

$$O_s(\mathbf{r}_1) = \langle N|\hat{O}(\mathbf{r}_1)|N, s\rangle \quad \text{and} \quad P_s^*(\mathbf{r}_s) = \langle N, s|\hat{P}(\mathbf{r}_2)|N\rangle$$

The response function has poles at the excitation energies $\pm(E_0 - E_s)$, corresponding to transitions between the ground state $|N\rangle$ and the excited state $|N, s\rangle$ of the unperturbed Hamiltonian $\hat{H}$. The first term is given by resonant transitions, the second by antiresonant transitions.

Linear response

Linear response

$$\chi_{OP}(1,2) = -i\theta(t_1 - t_2)\langle N|[\hat{O}(1), \hat{P}(2)]|N\rangle = \delta\langle \hat{O}(1)\rangle / \delta F(2)$$

Kramers-Kronig relations

As a consequence of its causality character, the response function $\chi_{OP}(\omega)$ is analytic in the complex upper half-plane.
Thanks to this, the real and imaginary parts of $\chi_{OP}(\omega)$ are related through the Kramers-Kronig relations:

$$\mathrm{Re}\chi_{OP}(\omega) = \frac{1}{\pi}\int_{-\infty}^{+\infty} d\omega' \frac{\mathrm{Im}\chi_{OP}(\omega')}{\omega' - \omega}$$

$$\mathrm{Im}\chi_{OP}(\omega) = -\frac{1}{\pi}\int_{-\infty}^{+\infty} d\omega' \frac{\mathrm{Re}\chi_{OP}(\omega')}{\omega' - \omega}$$

Outline

1 Linear response

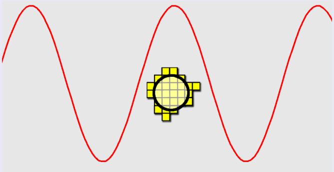
2 Micro-macro connection

Micro-macro connection

Observation

At long wavelength, external fields are slowly varying over the unit cell:

- dimension of the unit cell for silicon: 0.5 nm
- visible radiation 400 nm < λ < 800 nm



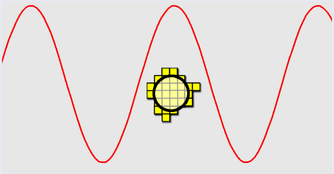
Total and induced fields are rapidly varying: they include the contribution from electrons in all regions of the cell.
Large and irregular fluctuations over the atomic scale.

Micro-macro connection

Observation

One usually measures quantities that vary on a macroscopic scale. When we calculate microscopic quantities we need to average over distances that are

- large compared to the cell parameter
- small compared to the wavelength of the external perturbation.



The differences between the microscopic fields and the averaged (macroscopic) fields are called the crystal local fields.

Suppose that we are able
to calculate the microscopic dielectric function ϵ,
how do we obtain the macroscopic dielectric function ϵ_M
that we measure in experiments ?

Micro-macro connection

Fourier transform

In a periodic medium, every function $V(\mathbf{r}, \omega)$ can be represented by the Fourier series

$$V(\mathbf{r}, \omega) = \sum_{\mathbf{qG}} V(\mathbf{q} + \mathbf{G}, \omega) e^{i(\mathbf{q}+\mathbf{G})\mathbf{r}}$$

or:

$$V(\mathbf{r}, \omega) = \sum_{\mathbf{q}} e^{i\mathbf{qr}} \sum_{\mathbf{G}} V(\mathbf{q} + \mathbf{G}, \omega) e^{i\mathbf{Gr}} = \sum_{\mathbf{q}} e^{i\mathbf{qr}} V(\mathbf{q}, \mathbf{r}, \omega)$$

where:

$$V(\mathbf{q}, \mathbf{r}, \omega) = \sum_{\mathbf{G}} V(\mathbf{q} + \mathbf{G}, \omega) e^{i\mathbf{Gr}}$$

$V(\mathbf{q}, \mathbf{r}, \omega)$ is periodic with respect to the Bravais lattice and hence is the quantity that one has to average to get the corresponding macroscopic potential $V_M(\mathbf{q}, \omega)$.

Micro-macro connection

Averages

$$V_M(\mathbf{q},\omega) = \frac{1}{\Omega_c}\int d\mathbf{r}\, V(\mathbf{q},\mathbf{r},\omega)$$

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$$V(\mathbf{q},\mathbf{r},\omega) = \sum_{\mathbf{G}} V(\mathbf{q}+\mathbf{G},\omega)e^{i\mathbf{G}\mathbf{r}}$$

Therefore:

$$V_M(\mathbf{q},\omega) = \sum_{\mathbf{G}} V(\mathbf{q}+\mathbf{G},\omega)\frac{1}{\Omega_c}\int d\mathbf{r}e^{i\mathbf{G}\mathbf{r}} = V(\mathbf{q}+\mathbf{0},\omega)$$

The macroscopic average V_M corresponds to the $\mathbf{G} = 0$ component of the microscopic V.

Example

$$V_{ext}(\mathbf{q},\omega) = \epsilon_M(\mathbf{q},\omega)V_{tot,M}(\mathbf{q},\omega)$$

Micro-macro connection

Fourier transforms

Fourier transform of a function $f(\mathbf{r},\mathbf{r}',\omega)$:

$$f(\mathbf{q}+\mathbf{G},\mathbf{q}+\mathbf{G}',\omega) = \int d\mathbf{r}d\mathbf{r}' e^{-i(\mathbf{q}+\mathbf{G})\mathbf{r}} f(\mathbf{r},\mathbf{r}',\omega) e^{+i(\mathbf{q}+\mathbf{G}')\mathbf{r}'} \equiv f_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega)$$

Micro-macro connection

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Therefore the relation

$$V_{tot}(\mathbf{r}_1, \omega) = \int d\mathbf{r}_2 \epsilon^{-1}(\mathbf{r}_1, \mathbf{r}_2, \omega) V_{ext}(\mathbf{r}_2, \omega)$$

in the Fourier space becomes:

$$V_{tot}(\mathbf{q}+\mathbf{G}, \omega) = \sum_{\mathbf{G}'} \epsilon^{-1}_{\mathbf{G},\mathbf{G}'}(\mathbf{q}, \omega) V_{ext}(\mathbf{q}+\mathbf{G}', \omega)$$

Micro-macro connection

Example

$$V_{tot,M}(\mathbf{q},\omega) = \epsilon_M^{-1}(\mathbf{q},\omega)\,V_{ext}(\mathbf{q},\omega)$$

Macroscopic dielectric function

$$V_{tot}(\mathbf{q}+\mathbf{G},\omega) = \sum_{\mathbf{G}'} \epsilon^{-1}_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega)\,V_{ext}(\mathbf{q}+\mathbf{G}',\omega)$$

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V_{ext} is a macroscopic quantity:

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Micro-macro connection

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Micro-macro connection

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Micro-macro connection

Macroscopic dielectric function

$$V_{ext}(\mathbf{q}+\mathbf{G},\omega)=\sum_{\mathbf{G}'}\epsilon_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega)V_{tot}(\mathbf{q}+\mathbf{G}',\omega)$$

Micro-macro connection

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Remember: V_{ext} is a macroscopic quantity:

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$$V_{ext}(\mathbf{q},\omega) = \epsilon_{\mathbf{G}=0,\mathbf{G}'=0}(\mathbf{q},\omega) V_{tot,M}(\mathbf{q},\omega) + \sum_{\mathbf{G}'\neq 0} \epsilon_{\mathbf{G}=0,\mathbf{G}'}(\mathbf{q},\omega) V_{tot}(\mathbf{q}+\mathbf{G}',\omega)$$

$$V_{ext}(\mathbf{q},\omega) = \epsilon_M(\mathbf{q},\omega) V_{tot,M}(\mathbf{q},\omega)$$

$$\epsilon_M(\mathbf{q},\omega) \neq \epsilon_{\mathbf{G}=0,\mathbf{G}'=0}(\mathbf{q},\omega)$$

Micro-macro connection

Spectra

$$\epsilon_M(\mathbf{q}, \omega) = \frac{1}{\epsilon^{-1}_{\mathbf{G}=0,\mathbf{G}'=0}(\mathbf{q}, \omega)}$$

Micro-macro connection

Spectra

$$\epsilon_M(\mathbf{q},\omega) = \frac{1}{\epsilon^{-1}_{\mathbf{G}=0,\mathbf{G}'=0}(\mathbf{q},\omega)}$$

$$\mathrm{Abs}(\omega) = \lim_{\mathbf{q}\to 0} \mathrm{Im}\,\epsilon_M(\mathbf{q},\omega) = \lim_{\mathbf{q}\to 0} \mathrm{Im}\frac{1}{\epsilon^{-1}_{\mathbf{G}=0,\mathbf{G}'=0}(\mathbf{q},\omega)}$$

$$\mathrm{EELS}(\omega) = -\lim_{\mathbf{q}\to 0} \mathrm{Im}\,\epsilon^{-1}_M(\mathbf{q},\omega) = -\lim_{\mathbf{q}\to 0} \mathrm{Im}\,\epsilon^{-1}_{\mathbf{G}=0,\mathbf{G}'=0}(\mathbf{q},\omega)$$

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