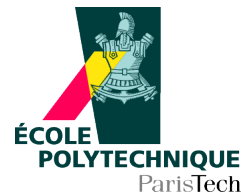# Microscopic-macroscopic connection

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Outline

Which quantities do we need?

Absorption coefficient

The general solution of the Maxwell's equations for the electric field is

$$\vec{E}(\vec{r},t) = \vec{E}_0 e^{i(kx-\omega t)}$$

$$k = \frac{\omega}{c}\sqrt{\varepsilon}$$

Defining the complex refractive index as $n = \sqrt{\varepsilon} = \nu + i\kappa$, the electric field inside a medium is the damped wave:

$$\vec{E}(\vec{r},t) = \vec{E}_0 e^{i\frac{\omega}{c}xn} e^{-i\omega t} = \vec{E}_0 e^{i\frac{\omega}{c}\nu x} e^{-\frac{\omega}{c}\kappa x} e^{-i\omega t}$$

ν and κ are the refraction index and the extinction coefficient and they are related to the dielectric constant ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) as

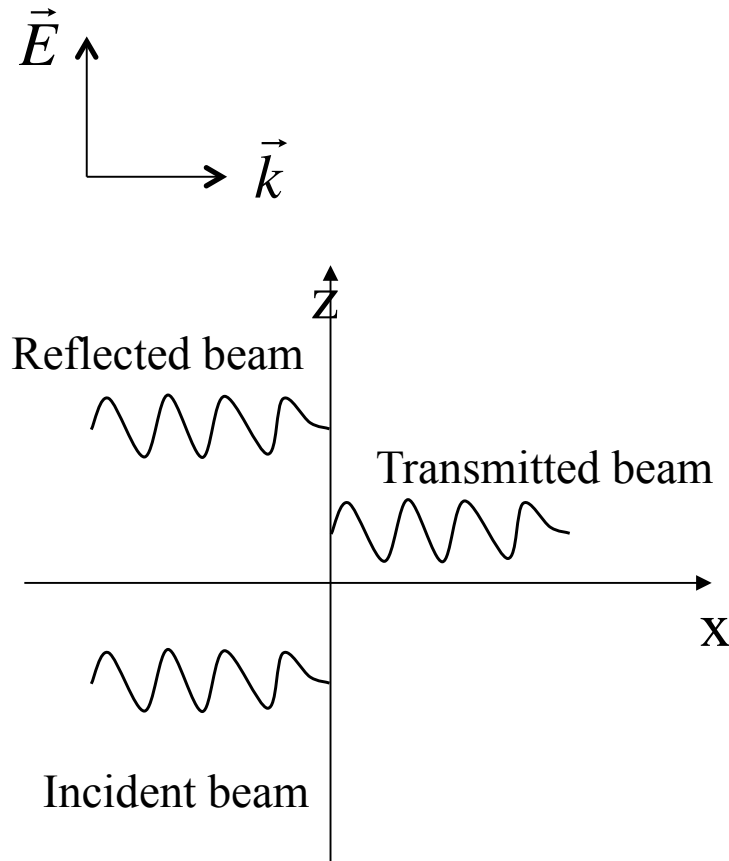$$\varepsilon_1 = \nu^2 - \kappa^2 \qquad \varepsilon_2 = 2\nu\kappa$$

The absorption coefficient α is the inverse distance where the intensity of the field is reduced by 1/e

(related to the optical skin depth δ).

$$\delta = \frac{c}{\omega\kappa}$$

$$\alpha = \frac{2\omega\kappa}{c} = \frac{\omega\varepsilon_2}{\nu c}$$

Which quantities do we need?

$\vec{E}$, $\vec{k}$

$\vec{z}$

Reflected beam

Transmitted beam

X

Incident beam

Reflectivity

Normal incidence reflectivity

$$R = \left| \frac{E_T}{E_i} \right|^2 < 1$$

Using the continuity of the tangential component of the electric field at the surface

$$R = \frac{(1-\nu)^2 + \kappa^2}{(1+\nu)^2 + \kappa^2}$$

The knowledge of the optical constant implies the knowledge of the absorption and of the reflectivity, which can be compared with the experiment.

Which quantities do we need?

Energy loss by a fast particle

Given an external charge density ρ_{ext}, one can obtained the external potential V_{ext}

$$k^2 V_{ext}(\vec{k}, \omega) = 4\pi \rho_{ext}(\vec{k}, \omega)$$ (Poisson equation)

The response of the system is an induced density, defined by the response function χ

$$\rho_{ind}(\vec{k}, \omega) = \chi(\vec{k}, \omega) V_{ext}(\vec{k}, \omega)$$

and the total (induced + external) potential acting on the system is

$$V_{tot}(\vec{k}, \omega) = \left[1 + \frac{4\pi}{k^2} \chi(\vec{k}, \omega\right] V_{ext}(\vec{k}, \omega) = \varepsilon^{-1}(\vec{k}, \omega) V_{ext}(\vec{k}, \omega)$$

Dielectric function: $$V_{ext}(\vec{k}, \omega) = \varepsilon(\vec{k}, \omega) V_{tot}(\vec{k}, \omega)$$

Which quantities do we need?

Energy loss by a fast particle

Charge density of a particle (e⁻) with velocity v : $\rho_{ext} = e\delta(\vec{r} - \vec{v}t)$

The total electric field is $\vec{E}_{tot} = -\vec{\nabla}_{\vec{r}} V_{tot}(\vec{r}, t)$

and the energy lost by the electron in unit time is

$$\frac{dW}{dt} = \int d\vec{r}\ \vec{j}.\vec{E}_{tot}$$

with the current density $\vec{j} = e\vec{v}\delta(\vec{r} - \vec{v}t)$

We get $$\frac{dW}{dt} = -\frac{e^2}{\pi^2}\int\frac{d\vec{r}}{k^2}\ \mathrm{Im}\left\{\frac{\omega}{\varepsilon(\vec{k},\omega)}\right\}$$

Electron Energy Loss Spectroscopy:

$$-\mathrm{Im}\left\{\frac{1}{\varepsilon(\vec{k},\omega)}\right\}$$

is called the loss function

Outline

Maxwell's equations

Maxwell's equations can be written either in vacuum or in a medium

$\mathbf{E}_{ext}(\mathbf{r}, t)$, $\mathbf{B}_{ext}(\mathbf{r}, t)$,

$\mathbf{j}_{ext}(\mathbf{r}, t)$, $\rho_{ext}(\mathbf{r}, t)$

$\mathbf{E}_{tot}(\mathbf{r}, t)$, $\mathbf{B}_{tot}(\mathbf{r}, t)$,

$\mathbf{j}_{tot}(\mathbf{r}, t)$, $\rho_{tot}(\mathbf{r}, t)$ with

$\rho_{tot=}\rho_{ext+}\rho_{ind}$, and

$\mathbf{j}_{tot=}\mathbf{j}_{ext+}\mathbf{j}_{ind}$

It is often more convenient to use D=$\mathbf{E}_{tot}$+4π $\mathbf{P}$ instead of $\mathbf{E}_{tot}$, as $\mathbf{D}$ is very close to the external field

$$\nabla.\mathbf{D} = \nabla.\mathbf{E}_{ext}$$

ρ_{ind} and j_{ind} are the induced charge and current density: they are not arbitrary, but reflect the spatial structure of the medium on a microscopic level and the motion of the particle in it, including also the response to an external field.

$$\vec{\nabla}.\vec{j}_{ind}(\vec{r},t)+\frac{\partial \rho_{ind}}{\partial t} = 0$$

Linear response

Perturbation theory

- For a sufficiently small perturbation, the response of the system can be extended into a taylor series, with respect to the perturbation.

- The first order (linear) response is proportional to the perturbation.

$$j_{ind}(\boldsymbol{r},\omega) = -\frac{e}{mc} <\rho> \boldsymbol{A}(\boldsymbol{r},\omega) - \frac{1}{c}\int d\vec{r}\,' \chi_{jj}(\boldsymbol{r},\boldsymbol{r}\,',\omega)\boldsymbol{A}(\boldsymbol{r}\,',\omega)$$
$$+\int d\vec{r}\,' \chi_{j\rho}(\boldsymbol{r},\boldsymbol{r}\,',\omega)V(\boldsymbol{r}\,',\omega)$$

$$\rho_{ind}(\boldsymbol{r},\omega) = -\frac{1}{c}\int d\vec{r}\,' \chi_{\rho j}(\boldsymbol{r},\boldsymbol{r}\,',\omega)\boldsymbol{A}(\boldsymbol{r}\,',\omega) + \int d\vec{r}\,' \chi_{\rho\rho}(\boldsymbol{r},\boldsymbol{r}\,',\omega)V(\boldsymbol{r}\,',\omega)$$

For simplicity, we will write

$$j_{ind} = -\frac{e}{mc} <\rho> -\frac{1}{c}\chi_{jj}\boldsymbol{A} + \chi_{j\rho}V$$

$$\rho_{ind} = -\frac{1}{c}\chi_{\rho j}\boldsymbol{A} + \chi_{\rho\rho}V$$

Linear response

The four response functions are not independent and using gauge invariance, one has

$$i\omega \chi_{j\rho} = \frac{\partial}{\partial \mathbf{r}'} \frac{e}{mc} <\hat{\rho}> \delta(\mathbf{r} - \mathbf{r}') - \frac{\partial}{\partial \mathbf{r}'} \chi_{jj}$$

$$\frac{\partial}{\partial \mathbf{r}'} \chi_{\rho j} = -i\omega \chi_{\rho\rho}$$

Only two quantities are needed, in terms of the electric field

$$\mathbf{j}_{ind} = \frac{ie}{m\omega} <\hat{\rho}> \mathbf{E} + \frac{i}{\omega} \chi_{jj} \mathbf{E} \qquad \rho_{ind} = \frac{i}{\omega} \chi_{\rho j} \mathbf{E}$$

Depending on the approximation, these response functions can be evaluated (IPA, RPA ...).

Linear response

Microscopic dielectric tensor

$$D(\boldsymbol{r},\omega) = \int d\vec{r}\,' \hat{\varepsilon}(\boldsymbol{r},\boldsymbol{r}',\omega) E_{tot}(\boldsymbol{r}',\omega)$$

In a perfect crystal

$$\hat{\varepsilon}(\boldsymbol{r}+\boldsymbol{R},\boldsymbol{r}'+\boldsymbol{R},\omega) = \hat{\varepsilon}(\boldsymbol{r},\boldsymbol{r}',\omega)$$

and Fourier components must satisfy

$$D(\boldsymbol{q}+\boldsymbol{G},\omega) = \sum_{G'} \hat{\varepsilon}(\boldsymbol{q}+\boldsymbol{G},\boldsymbol{q}+\boldsymbol{G}',\omega) E_{tot}(\boldsymbol{q}+\boldsymbol{G}',\omega)$$

q lies in the first Brillouin zone and **G** is a reciprocal lattice vector

Microscopic spatial fluctuations

- Infinite crystals → microscopic inhomogeneities (atomic scale)

- Semi-infinite crystals → presence of the surface

- Desorded medium → liquid

- Rough surfaces

Macroscopic average

We consider spatial fluctuations whose characteristic length scale is much smaller than the wavelength of light

Macroscopic quantities

Quantities that are slowly varying over the unit cells.

where V is the volume per unit cell of the crystal.

$$\lambda >> V^{1/3}$$

Examples

$E_{ext}(r, t), A_{ext}(r, t), V_{ext}(r, t),\ldots$

Typical values:
- dimension of the unit cell for silicon $a_{cell} \approx 0.5nm$
- Visible radiation $400\ nm < \lambda < 800\ nm$

Macroscopic average

Microscopic quantities

Total and induced fields are rapidly varying. They include the contribution
from electrons in all regions of the cell.
The contribution of electrons close to or far from the nuclei will be very different.

$\Rightarrow$ Large and irregular fluctuations over the atomic scale.

Examples

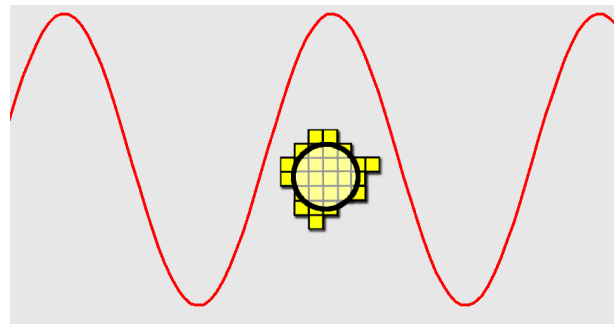$E_{tot}(r, t)$, $j_{ind}(r, t)$, $\rho_{ind}(r, t)$,...

Macroscopic average

Measurable quantities

One measures quantities that vary on a macroscopic scale.

In the long wavelength limit,
the macroscopic neighbourhood contains many particles

We have to average over distances :
- ✓ large compared to the cell diameter
- ✓ small compared to the wavelength of the external perturbation

Macroscopic average

Interpretation:

If we assume that the system is homogeneous : $\varepsilon(\mathbf{r}, \mathbf{r}', \omega) = \varepsilon(\mathbf{r} - \mathbf{r}', \omega)$

One has

$$\varepsilon(\mathbf{q+G}, \mathbf{q+G'}, \omega) = \delta_{GG'}\varepsilon(\mathbf{q+G}, \omega)$$

$$\mathbf{D}(\mathbf{q+G}, \omega) = \varepsilon(\mathbf{q+G}, \omega)\,\mathbf{E}(\mathbf{q+G}, \omega)$$

Measurable quantities : vary on a macroscopic scale

➔ the system is considered as homogeneous.

One has to transform

$$D(q+G) = \sum_{G'} \hat{\varepsilon}(q+G, q+G', \omega) E_{tot}(q+G, \omega)$$

into

$$D(q) = \hat{\varepsilon}(q, \omega) E_{tot}(q, \omega)$$

Macroscopic average

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

Complexity of the problem:

- Macroscopic external field $\Rightarrow$ induced fields
- The macroscopic procedure must take into account the fact that all the components of the induced fields will create the response.

Procedure:

- model for the system expressed in terms of an hamiltonian
- microscopic response of the system (linear-response theory for instance)
- $\Rightarrow$ Definition of the microscopic dielectric tensor $\boxed{\vec{D}(\vec{r},\omega) = \int d\vec{r}\,'\varepsilon(\vec{r},\vec{r}\,',\omega)E(\vec{r}\,',\omega)}$
- Averaging: definition of ε_M which relates the average parts of D and E

Outline

Macroscopic average

General definition:

We have to define two operators $\hat{P}_a$ and $\hat{P}_f$ which extract the average component and the fluctuation component of any function F

$$\hat{P}_f = \hat{1} - \hat{P}_a \qquad \begin{aligned} F_a &= \hat{P}_a F \\[1em] F_f &= \hat{P}_f F \end{aligned}$$

$\hat{P}_a$ and $\hat{P}_f$ have the following properties:

1) $\hat{P}_a^2 = \hat{P}_a \qquad \hat{P}_f^2 = \hat{P}_f$ and $\hat{P}_a \hat{P}_f = \hat{P}_f \hat{P}_a = 0$ $\Rightarrow$ Projectors

2) $\hat{P}_a$ commutes with the time and space differential operators

The average part of the field must obey
the macroscopic Maxwell's equations

Macroscopic average

- Ensemble-average $\qquad F_a(\lambda) = \sum_c P_c F_c(\lambda)$

    P_c : probability of finding the system in the configuration c of the ensemble
    F_c: value of the function in this configuration.

- Spatial average $\qquad F_a(\boldsymbol{r}) = \int d\boldsymbol{r}' P_a(\boldsymbol{r} - \boldsymbol{r}') F(\boldsymbol{r}')$
    $P_a(\boldsymbol{r})$: weight function

- Wave-vector truncation $\qquad F_a(\boldsymbol{q}) = P_a(\boldsymbol{q}) F_a(\boldsymbol{q})$

    $P_a(\boldsymbol{q})$: cut-off for the high wave-vector components

Macroscopic average

Notations
$$F = F_a + F_f \rightarrow \begin{pmatrix} F_a \\ F_f \end{pmatrix}$$

Microscopic Dielectric Tensor

$$\begin{pmatrix} D_a \\ D_f \end{pmatrix} = \begin{pmatrix} \hat{\varepsilon}_{aa} & \hat{\varepsilon}_{af} \\ \hat{\varepsilon}_{fa} & \hat{\varepsilon}_{ff} \end{pmatrix} \begin{pmatrix} E_a \\ E_f \end{pmatrix} \qquad \hat{O}_{\alpha\beta} = P_\alpha \hat{O} P_\beta$$

The problem of finding the macroscopic dielectric tensor is to decouple $\mathbf{D}_a$ and $\mathbf{D}_f$, by finding a relationship between $\mathbf{D}_{f \text{ and}}$ $\mathbf{E}_f$ to get

$$D_a = \hat{\varepsilon}_M E_a$$

Note: we suppose that we know the full dielectric tensor

Macroscopic average

Infinite crystals

Functions having the crystal symmetries V(**r**+ **R**)=V(**r**), where **R** is any vector of the Bravais lattice, can be represented by the Fourier series

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

It can be also written as

$$V(\vec{r},\omega) = \sum_{q} V(r;\vec{q},\omega)e^{i\vec{q}\vec{r}}$$

where $\quad V(\vec{r};\vec{q},\omega) = \sum_{G} V(\vec{q}+\vec{G},\omega)e^{i\vec{G}\vec{r}}$

is a periodic function, with respect to the Bravais lattice.
Varies strongly even if the original wave is a long wave and nearly constant within each cell (contains all the G-harmonics of the field).

Infinite crystals

Spatial average over a cell of the periodic part

$$V(\vec{R}, \omega) = \left\langle V(\vec{r}; \vec{q}, \omega) \right\rangle_R$$

$$= \frac{1}{\Omega} \int d\vec{r} \sum_G V(\vec{q} + \vec{G}, \omega) e^{i\vec{G}\vec{r}}$$

$$= V(\vec{q} + \vec{0}, \omega)$$

The macroscopic average corresponds to the G=0 component.
⇔ Truncation that eliminates all wave vectors outside the first Brillouin zone
(wave-vector truncation)

Macroscopic quantities have all their G components equal to 0,
except the G=0 component.

→ Satisfies the two criteria previously defined

Macroscopic average

• If the external applied field is not macroscopic, this averaging procedure
 for the response function of the material has no meaning.

Exemples: X-ray spectroscopy (very short wavelength)
                          EEL Spectroscopy with atomic resolution

Outline

Macroscopic average

A simple example: the longitudinal case

All the fields can be expressed in terms of potentials ($\mathbf{E}=-\mathbf{\nabla}V$)

The longitudinal dielectric function is defined as

$$V_{ext}(\vec{r},\omega) = \int d\vec{r}\,'\varepsilon(\vec{r},\vec{r}\,',\omega)V_{tot}(\vec{r}\,',\omega) \quad \text{(Real space)}$$

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

(Reciprocal space)

V_{ext} is a macroscopic quantity : $\quad V_{ext}(\vec{q}+\vec{G},\omega) = V_{ext}(q,\omega)\delta_{G0}$

This is not the case for $\quad V_{tot}(\vec{q}+\vec{G},\omega)$

Macroscopic average of V_{ext} :

$$V_{ext}(\vec{q},\omega) = \sum_{G'}\varepsilon_{0G'}(\vec{q},\omega)V_{tot}(q+G',\omega) \neq \varepsilon_{00}(\vec{q},\omega)V_{tot}(q,\omega)$$

The average of the product is not the product of the averages

Macroscopic average

A simple example: the longitudinal case

We have also

$$V_{tot}(\vec{q}+\vec{G},\omega) = \sum_{G'} \varepsilon_{GG'}^{-1}(\vec{q},\omega)V_{ext}(q+G',\omega)$$

where is $\varepsilon_{GG'}^{-1}$ the inverse dielectric function :

$$\sum_{G''} \varepsilon_{GG''}(\vec{q},\omega)\varepsilon_{G''G'}^{-1}(\vec{q},\omega) = \delta_{GG'}$$

Macroscopic average of V$_{tot}$:

V$_{ext}$ is macroscopic $\Rightarrow$ $\quad V_{tot}(\vec{q}+\vec{G},\omega) = \varepsilon_{G0}^{-1}(\vec{q},\omega)V_{ext}(q,\omega)$

$$V_{tot}(\vec{q},\omega) = \varepsilon_{00}^{-1}(\vec{q},\omega)V_{ext}(q,\omega)$$

Macroscopic average

Summary

- We have defined microscopic and macroscopic fields
- Microscopic quantities have to be averaged to be compared to experiments
- The dielectric function has
  - a microscopic expression (related to quantum mechanics)
  - a macroscopic expression (classical scheme - Maxwell's equations)
- We have defined a procedure

Outline

Dielectric tensor for cubic symmetries

Useful definitions

Longitudinal fields

$$\vec{\nabla} \times \vec{E}(\vec{r}) = 0 \quad \text{or} \quad \vec{k} \times \vec{E}(\vec{k}) = 0$$

E(k) propagates along **k**

Examples:
• plasmon oscillations
• sceening
• electron energy loss

Transverse fields

$$\vec{\nabla} . \vec{E}(\vec{r}) = 0 \quad \text{or} \quad \vec{k} . \vec{E}(\vec{k}) = 0$$

E(k) propagates perpendicular to **k**

Examples:
• photons
• optical properties of solids

Some definitions: $\vec{E}(\vec{r}) \leftrightarrow \vec{E}(\vec{k})$ (Fourier transform)

with $\vec{k} = \vec{q} + \vec{G}$ for crystals

(q is in the first Brillouin zone and G is a reciprocal lattice vector)

Dielectric tensor for cubic symmetries

Transverse-longitudinal decomposition:

Any vector field can be split into longitudinal and transverse components

$$\vec{E} = \vec{E}^L + \vec{E}^T \qquad \text{with} \qquad \vec{\nabla} \times \vec{E}^L = 0 \qquad \text{and} \qquad \vec{\nabla}.\vec{E}^T = 0$$

$$\vec{E}^L(\vec{k}) = \hat{k}\left[\hat{k}.\vec{E}(\vec{k})\right] \quad \text{and} \quad \hat{k} = \frac{\vec{k}}{k} \qquad \text{(In real space, the relations are nonlocal)}$$

Macroscopic dielectric tensor

The relation $\mathbf{D}(\mathbf{q},\omega) = \varepsilon_M(\mathbf{q},\omega)\,\mathbf{E}_{tot}(\mathbf{q},\omega)$ can be written in terms
of the longitudinal and transverse components

$$\begin{pmatrix} D^L \\ D^T \end{pmatrix} = \begin{pmatrix} \varepsilon_M^{LL} & \varepsilon_M^{LT} \\ \varepsilon_M^{TL} & \varepsilon_M^{TT} \end{pmatrix} \begin{pmatrix} E_{tot}^L \\ E_{tot}^T \end{pmatrix}$$

Dielectric tensor for cubic symmetries

Question:

How can we make the link between

- the microscopic dielectric tensor

$$\vec{D}(\vec{q} + \vec{G}, \omega) = \sum_{G'} \overleftrightarrow{\varepsilon}(\vec{q} + \vec{G}, \vec{q} + \vec{G}', \omega) E_{tot}(\vec{q} + \vec{G}', \omega)$$

Microscopic components of **D** and **E**$_{tot}$

- the macroscopic dielectric tensor

$$\vec{D}(\vec{q}, \omega) = \overleftrightarrow{\varepsilon}_M(\vec{q}, \omega) E_{tot}(\vec{q}, \omega)$$

Macroscopic components of **D** and **E**$_{tot}$

Dielectric tensor for cubic symmetries

No symmetry

$$\overset{\leftrightarrow}{\varepsilon}_M(\vec{q},\omega) = \begin{pmatrix} \varepsilon_M^{LL} & \varepsilon_M^{LT} \\ \varepsilon_M^{TL} & \varepsilon_M^{TT} \end{pmatrix}$$

A longitudinal (transverse) perturbation induces longitudinal and transverse responses.

Cubic symmetry with q→0

$$\overset{\leftrightarrow}{\varepsilon}_M(\vec{q},\omega) = \begin{pmatrix} \varepsilon_M^{LL} & 0 \\ 0 & \varepsilon_M^{TT} \end{pmatrix}$$

• A longitudinal perturbation induces a longitudinal response only.

• A transverse perturbation induces a transverse response only.

• Independent of the direction of **q**

This holds only for macroscopic quantities

The microscopic dielectric tensor has off-diagonal elements ε^{LT} and ε^{TL}

Cubic symmetries with q→0

Longitudinal dielectric function

$$\varepsilon_M^{LL}(\vec{q},\omega) = \lim_{q\to 0} \frac{1}{1 + \dfrac{4\pi}{q^2}\chi_{\rho\rho}(\vec{q},\omega)}$$

depends on the direcion of $\vec{q}$

where $\chi_{\rho\rho}(\mathbf{q},\omega)$ is the density-density response function (TDDFT), defined as

$$\rho_{ind}(\vec{q},\omega) = \chi_{\rho\rho}(\vec{q},\omega)V_{ext}(\vec{q},\omega)$$

Transverse dielectric function

$$\lim_{q\to 0}\varepsilon_M^{TT}(\vec{q},\omega) = \lim_{q\to 0}\varepsilon_M^{LL}(\vec{q},\omega)$$

Dielectric tensor

The tensor is diagonal and contains only one quantity $\varepsilon_M^{LL}(\vec{q},\omega)$

Cubic symmetries with q≠0

Longitudinal dielectric function

One can show that the relation

$$\varepsilon_M^{LL}(\vec{q},\omega) = \frac{1}{1 + \dfrac{4\pi}{q^2}\chi_{\rho\rho}(\vec{q},\omega)}$$

holds also when $\vec{q} \neq 0$

depends on $\vec{q}$

Transverse dielectric function

$$\varepsilon_M^{TT}(\vec{q},\omega) \neq \varepsilon_M^{LL}(\vec{q},\omega)$$

We have also $\varepsilon_M^{TL}(\vec{q},\omega) \neq 0$ $\varepsilon_M^{LT}(\vec{q},\omega) \neq 0$

These quantities are much more complicated
and need further approximation to be computed
(in principles they cannot be expressed in terms of TDDFT).

Cubic symmetries

Summary

- We have defined the longitudinal and transverse components of the dielectric tensor.

- In the long wavelength limit q→0 ,only one quantity is needed (optical isotropy)

$$\varepsilon_M^{LL}(\omega) = \varepsilon_M^{TT}(\omega) = \lim_{q \to 0} \frac{1}{1 + \dfrac{4\pi}{q^2} \chi_{\rho\rho}(\vec{q},\omega)}$$

- For q≠0, only $\varepsilon_M{}^{LL}$ has a simple expression in terms of the response function.

Cubic symmetries

Some references

✓ H. Ehrenreich, in the *Optical Properties of Solids*, Varenna Course XXXIV, edited by J. Tauc (Academic Press, New York, 1966), p. 106

✓ R. M. Pick, in *Advances in Physics*, Vol 19, p. 269.

✓ D. L. Johnson, Physical Review B, **12** 3428 (1975).

✓ S. L. Adler, Physical Review, **126** 413 (1962).

✓ N. Wiser, Physical Review, **129** 62 (1963).

✓ R. Del Sole and E. Fiorino, Phys. Rev. B **29**, 4631 (1984).

✓ W. L. Mochan and R. Barrera, Phys. Rev. B **32** 4984 (1985); ibid 4984 (1985).

Outline

Non-cubic symmetries

Properties of the macroscopic quantities

$$\ddot{\varepsilon}_M(\vec{q},\omega) = \begin{pmatrix} \varepsilon_M^{LL}(\vec{q},\omega) & \varepsilon_M^{LT}(\vec{q},\omega) \\ \varepsilon_M^{TL}(\vec{q},\omega) & \varepsilon_M^{TT}(\vec{q},\omega) \end{pmatrix}$$

Non-cubic symmetries

Dielectric tensor - General case

$$\vec{\vec{\varepsilon}}_M(\vec{q},\omega) = 1 + 4\pi\vec{\vec{\alpha}}(\vec{q},\vec{q},\omega)\left[1 + 4\pi\hat{q}\frac{\vec{\vec{\alpha}}(\vec{q},\vec{q},\omega)\hat{q}}{1 - 4\pi\alpha^{LL}(\vec{q},\vec{q},\omega)}\right]$$

Quasipolarisability α :

$$\vec{j}_{ind}(\vec{q}+\vec{G},\omega) = \sum_G \vec{\vec{\alpha}}(\vec{q}+\vec{G},\vec{q}+\vec{G}',\omega)\vec{E}_{pert}(\vec{q}+\vec{G}',\omega)$$

But one can show that the relation :
holds also for the non-cubic symmetries.

$$\varepsilon_M^{LL}(\vec{q},\omega) = \frac{1}{1 - 4\pi\alpha^{LL}(\vec{q},\vec{q}\,\omega)}$$

and we have

$$\alpha^{LL}(\vec{q},\vec{q},\omega) = -\frac{1}{q^2}\chi_{\rho\rho}(\vec{q},\vec{q},\omega)$$

Longitudinal-longitudinal
dielectric function

Outline

Non-cubic symmetries q→0

Main general result concerning ε_M : ε_M is an <u>analytic</u> function of $\vec{q}$

The limit q→0 does not depend on the direction of q

$\Rightarrow$ We can define $\varepsilon_M(\omega)$ as $\varepsilon_M(\omega) = \lim_{\vec{q}\to 0} \varepsilon_M(\vec{q},\omega)$

ε_M^{LL} is not analytic in the general case

Depending on the symmetry of the system, one can define the
3 principal axis, if they exist, ($\mathbf{n}_1$, $\mathbf{n}_2$,$\mathbf{n}_3$) defining a frame
in which $\varepsilon_M(\omega)$ is <u>diagonal</u>

If $\vec{E}_{tot}$ is parallel to one of these axis $\mathbf{n}_i$ $\boxed{\vec{\vec{\varepsilon}}_M(\omega)\vec{E}_{tot}(\omega) = \varepsilon_i(\omega)\vec{E}_{tot}(\omega)}$

$\varepsilon_i(\omega)$ can be calculated as a longitudinal dielectric function $\boxed{\varepsilon_i(\omega) = \varepsilon_M^{LL}(\vec{n}_i,\omega)}$

Non-cubic symmetries q→0

The distinction between longitudinal and transverse is not meaningful

The only important direction is the direction of the <u>electric field</u>

If q→ 0, the fields do not propagate

Existence of the principal frame ? ε_M is symmetric but complex …
No general answer
Use of geometrical arguments

Symmetries

- Cubic
- Hexagonal
- Orthorombic

- Monoclinic
- Triclinic

The optical axis are given
by the symmetry

The number of symmetry is
too low to get 3 optical axis

Shorter wavelength q≠0

Alternative:

We can use
$$\vec{\vec{\varepsilon}}_M(\vec{q},\omega) = 1 + 4\pi\vec{\vec{\alpha}}(\vec{q},\vec{q},\omega)\left[1 + 4\pi\hat{q}\frac{\hat{q}\vec{\vec{\alpha}}(\vec{q},\vec{q},\omega)}{1 - 4\pi\alpha^{LL}(\vec{q},\vec{q},\omega)}\right]$$

where
$$\vec{j}_{ind}(\vec{q}+\vec{G},\omega) = \sum_{G'}\vec{\vec{\alpha}}(\vec{q}+\vec{G},\vec{q}+\vec{G}',\omega)\vec{E}_{pert}(\vec{q}+\vec{G}',\omega)$$

The induced current can be evaluated through the
(Time-Dependent)-Density-Current Functional Theory (TD-DCFT)

Which quantities do we need?

Electron Energy Loss Spectroscopy: $-\text{Im}\left\{\dfrac{1}{\varepsilon(\vec{q},\omega)}\right\}$

In that case, $\boxed{\varepsilon(\vec{q},\omega) = \varepsilon_M^{LL}(\vec{q},\omega)}$

with $V_{ext}(\vec{q},\omega) = \varepsilon(\vec{q},\omega)V_{tot}(\vec{q},\omega)$

Is this correct? The perturbation is longitudinal.
What about the transverse response?

One can show that $\boxed{\vec{E}^T(\vec{q},\omega) = \dfrac{\omega^2}{c^2 q^2}\vec{D}^T(\vec{q},\omega) \quad \text{and} \quad \dfrac{\omega^2}{c^2 q^2} \approx \dfrac{v^2}{c^2}}$

In the nonrelativistic approximation, the transverse fields are negligible and the LL component of the dielectric tensor describes the energy loss of charged particles

Outline

Summary

✓ The key quantity is the <u>dielectric tensor</u>.

✓ Relation between microscopic and macroscopic fields.

✓ For cubic crystals, the longitudinal dielectric function $\varepsilon_M(\omega)$ defines entirely the optical response in the long wavelength limit $(q \rightarrow 0)$.

✓ For non-cubic crystals, the dielectric functions calculated along the principal axis can be used to define entirely the optical response in the long wavelength limit.

✓ For non-vanishing momentum, the situation is not so simple: $\varepsilon_M^{LL}(\mathbf{q}, \omega)$ only can be defined in a simple way.