# Microscopic-macroscopic connection

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# Outline

# Introduction

# Introduction: Which quantities do we need?

## Absorption coefficient

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

$$E(\mathbf{x}, t) = E_0 e^{\frac{i\omega}{c}\nu x} e^{-\frac{\omega}{c}\kappa x} e^{-i\omega t}$$

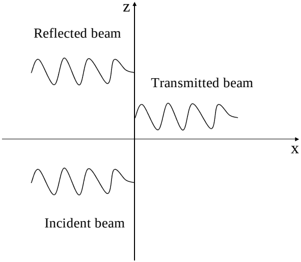
$\nu$=refraction index
$\kappa$ =extinction coefficient

They are related to the dielectric constant

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

$$\alpha = \frac{\omega \epsilon_2}{\nu c}$$

# Introduction: Which quantities do we measure?




## Reflectivity

Normal incidence reflectivity

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

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

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

# Introduction: Which quantities do we need?

## Energy loss by a fast charged particle

The energy lost by the electron in unit time is

$$\frac{dW}{dt} = -\frac{e^2}{\pi^2}\int \frac{d\mathbf{k}}{k^2} Im\left\{\frac{\omega}{\epsilon(\mathbf{k},\omega)}\right\}$$

## Electron Energy Loss Spectroscopy

$-Im\left\{\frac{1}{\epsilon(\mathbf{k},\omega)}\right\}$ is called the loss function

# Macroscopic average

# Maxwell's equations

Maxwell's equations can be written either in the medium or in vaccum

$\mathbf{E}_{tot}(\mathbf{r},t)$, $\mathbf{B}_{tot}(\mathbf{r},t)$, $\mathbf{j}_{tot}(\mathbf{r},t)$,$\rho_{tot}(\mathbf{r},t)$ with $\rho_{tot}=\rho_{ext}+\rho_{ind}$, and $\mathbf{j}_{tot}=\mathbf{j}_{ext}+\mathbf{j}_{ind}$

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

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

$\rho$ and $\mathbf{j}$ are not independent.
Continuity equation : $\nabla\mathbf{j}+\frac{\partial\rho}{\partial t}=0$

# Linear response

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

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

$$\mathbf{j}_{ind}(\mathbf{r},\omega) = -\frac{e}{mc} < \hat{\rho} > \mathbf{A}_{pert}(\mathbf{r},\omega) - \frac{1}{c}\int d\mathbf{r}'\chi_{\mathbf{jj}}(\mathbf{r},\mathbf{r}',\omega)\mathbf{A}_{pert}(\mathbf{r}',\omega) + \int d\mathbf{r}'\chi_{\mathbf{j}\rho}(\mathbf{r},\mathbf{r}',\omega)V_{pert}(\mathbf{r}',\omega)$$

$$\rho_{ind}(\mathbf{r},\omega) = -\frac{1}{c}\int d\mathbf{r}'\chi_{\rho\mathbf{j}}(\mathbf{r},\mathbf{r}',\omega)\mathbf{A}_{pert}(\mathbf{r}',\omega) + \int d\mathbf{r}'\chi_{\rho\rho}(\mathbf{r},\mathbf{r}',\omega)V_{pert}(\mathbf{r}',\omega)$$

For simplicity, we will write

$$\mathbf{j}_{ind} = -\frac{e}{mc} < \hat{\rho} > \mathbf{A}_{pert} - \frac{1}{c}\chi_{\mathbf{jj}}\mathbf{A}_{pert} + \chi_{\mathbf{j}\rho}V_{pert}$$

$$\rho_{ind} = -\frac{1}{c}\chi_{\rho\mathbf{j}}\mathbf{A}_{pert} + \chi_{\rho\rho}V_{pert}$$

# Linear response

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

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

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

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

$$\mathbf{j}_{ind} = \frac{ie}{m\omega} < \hat{\rho}(\mathbf{r}) > \mathbf{E}_{pert} + \frac{i}{\omega}\chi_{\mathbf{jj}}\mathbf{E}_{pert}$$

$$\rho_{ind} = \frac{i}{\omega}\chi_{\rho\mathbf{j}}\mathbf{E}_{pert}$$

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

# Linear response

## Microscopic dielectric tensor

$$\mathbf{D}(\mathbf{r},\omega) = \int d\mathbf{r}' \hat{\epsilon}(\mathbf{r},\mathbf{r}',\omega)\mathbf{E}_{tot}(\mathbf{r}',\omega)$$

In a perfect crystal

$$\hat{\epsilon}(\mathbf{r}+\mathbf{R},\mathbf{r}'+\mathbf{R},\omega) = \hat{\epsilon}(\mathbf{r},\mathbf{r}',\omega)$$

and Fourier components must satisfy

$$\mathbf{D}(\mathbf{q}+\mathbf{G},\omega) = \sum_{\mathbf{G}'} \hat{\epsilon}(\mathbf{q}+\mathbf{G},\mathbf{q}+\mathbf{G}',\omega)\mathbf{E}_{tot}(\mathbf{q}+\mathbf{G}',\omega)$$

**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

# Micro and macro

## Macroscopic quantities in the context of condensed matter

At long wavelength, external fields are slowly varying over the unit cells.

$$\lambda = \frac{2\pi}{q} >> V^{1/3}$$

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

## Example

$\mathbf{E}_{ext}(\mathbf{r}, t)$, $\mathbf{A}_{ext}(\mathbf{r}, t)$, $V_{ext}(\mathbf{r}, t)$,...

Typical values:

- dimension of the unit cell for silicon $a_{cell} \simeq 0.5nm$
- Visible radiation $400nm \leq \lambda \leq 800nm$
- X-ray range?

# Micro and macro

## 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.

## Example

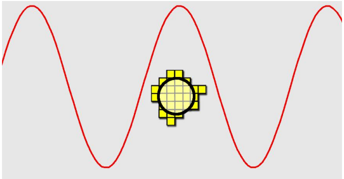
$\mathbf{E}_{tot}(\mathbf{r}, t)$, $\mathbf{j}_{ind}(\mathbf{r}, t)$, $\rho_{ind}(\mathbf{r}, t)$,...

# 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

If we assume that the system is homogeneous $\hat{\epsilon}(\mathbf{r},\mathbf{r}',\omega) = \hat{\epsilon}(\mathbf{r}-\mathbf{r}',\omega)$
one has $\hat{\epsilon}(\mathbf{q}+\mathbf{G},\mathbf{q}+\mathbf{G}',\omega) = \delta_{\mathbf{G}\mathbf{G}'}\hat{\epsilon}(\mathbf{q}+\mathbf{G},\omega)$
and

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

Measurable quantities : vary on a macroscopic scale
$\longrightarrow$ the system is considered as homogeneous.

One has to transform

$$\mathbf{D}(\mathbf{q}+\mathbf{G},\omega) = \sum_{\mathbf{G}'}\hat{\epsilon}(\mathbf{q}+\mathbf{G},\mathbf{q}+\mathbf{G}',\omega)\mathbf{E}_{tot}(\mathbf{q}+\mathbf{G}',\omega)$$

into $\quad \mathbf{D}(\mathbf{q},\omega) = \hat{\epsilon}(\mathbf{q},\omega)\mathbf{E}_{tot}(\mathbf{q},\omega)$

# 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 $\mathbf{D}(\mathbf{r},\omega) = \int d\mathbf{r}\epsilon(\mathbf{r},\mathbf{r}',\omega)\mathbf{E}(\mathbf{r}',\omega)$
- Averaging: definition of $\epsilon_M$ which relates the average parts of **D** and **E**

# Macroscopic average

## A simple example: the longitudinal case

All the fields can be expressed in terms of potential ($\mathbf{E} = \nabla V$) and the longitudinal dielectric function is defined as

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

Macroscopic average : cut-off of high wave vector

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

This not the case for $V_{tot}(\mathbf{q}+\mathbf{G},\omega)$.

Macroscopic average of $V_{ext}$ :

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

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

# Macroscopic average

## The longitudinal case

We have also

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

where $\epsilon^{-1}_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega)$ is the inverse dielectric function:

$$\sum_{\mathbf{G}''} \epsilon_{\mathbf{G}\mathbf{G}''}(\mathbf{q},\omega)\epsilon^{-1}_{\mathbf{G}''\mathbf{G}'}(\mathbf{q},\omega) = \delta_{\mathbf{G}\mathbf{G}',\omega}$$

Macroscopic average of $V_{tot}$:

$V_{ext}$ is macroscopic $\Rightarrow V_{tot}(\mathbf{q}+\mathbf{G},\omega) = \epsilon^{-1}_{\mathbf{G}\mathbf{0}}(\mathbf{q},\omega) V_{ext}(\mathbf{q},\omega)$

$$V_{tot}(\mathbf{q},\omega) = \epsilon^{-1}_{\mathbf{0}\mathbf{O}}(\mathbf{q},\omega) V_{ext}(\mathbf{q},\omega)$$

# Macroscopic average

## Macroscopic dielectric constant

$$V_{ext}(\mathbf{q},\omega) = \epsilon_M(\mathbf{q},\omega) V_{tot}(\mathbf{q},\omega) \Rightarrow \epsilon_M(\mathbf{q},\omega) = \frac{1}{\epsilon^{-1}_{\mathbf{00}}(\mathbf{q},\omega)}$$

- Inversion of the full dielectric matrix $\epsilon_{\mathbf{GG'}}(\mathbf{q},\omega) \rightarrow \epsilon^{-1}_{\mathbf{GG'}}(\mathbf{q},\omega)$
- We take the $\mathbf{G} = \mathbf{G}' = 0$ component of $\epsilon^{-1}_{\mathbf{GG'}}(\mathbf{q},\omega)$

## Interpretation

All the microscopic components of the induced field will couple together to produce the macroscopic response.

# Average quantities : procedure

Procedure proposed in : W. L. Mochan and R. G. Barrera, Phys. Rev. B **32** 4984 (1985); Phys. Rev. B **32** 4989 (1985)

General definition:
There are different averaging procedures, according to the specific characteristics of the system as well as the length scales involved. We formally define two operators $\hat{P}_a$ and $\hat{P}_f$ which extract the average component and the fluctuation component of any function F:

$$F_a = \hat{P}_a F \text{ and } F_f = \hat{P}_f F.$$

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

- $\hat{P}_a^2 = \hat{P}_a$.
- Thus $\hat{P}_f^2 = \hat{P}_f$ and $\hat{P}_a \hat{P}_f = \hat{P}_f \hat{P}_a = 0$.
- $\hat{P}_a$ commutes with the time and space differential operators: the average part of the fields must obey the Maxwell's equations

$\hat{P}_a$ and $\hat{P}_f$ are projector operators

# Average quantities

Specific examples :

1. Ensemble-average $F_a(\lambda) = \sum_c P_c F_c(\lambda)$
   $P_c$ : probability of finding the system in the configuration $c$ of the ensemble
   $F_c$: value of the function in this configuration.
2. Spatial average $F_a(\mathbf{r}) = \int d\mathbf{r}' P_a(\mathbf{r} - \mathbf{r}') F(\mathbf{r}')$
   $P_a(\mathbf{r})$ : weight function
3. Wave-vector truncation $F_a(\mathbf{q}) = P_a(\mathbf{q}) F(\mathbf{q})$
   $P_a(\mathbf{q})$: cut-off for the high wave-vector components

# Average quantities

Notations:

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

Microscopic Dielectric Tensor : $\mathbf{D} = \hat{\epsilon}\,\mathbf{E}_{tot}$

$$\begin{pmatrix} \mathbf{D}_a \\ \mathbf{D}_f \end{pmatrix} = \begin{pmatrix} \hat{\epsilon}_{aa} & \hat{\epsilon}_{af} \\ \hat{\epsilon}_{fa} & \hat{\epsilon}_{ff} \end{pmatrix} \begin{pmatrix} \mathbf{E}_a \\ \mathbf{E}_f \end{pmatrix} \qquad \hat{O}_{\alpha\beta} = \hat{P}_\alpha \hat{O} \hat{P}_\beta$$

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

$$\mathbf{D}_a = \hat{\epsilon}_M \mathbf{E}_a$$

Note: we suppose that we know the full dielectric tensor

# Average quantities

Going back to the Maxwell's equations,

$$\nabla \times \nabla \times \mathbf{E} = \frac{4i\pi\omega}{c^2}\mathbf{j}_{ext} + \frac{\omega^2}{c^2}\mathbf{D}$$

If the external current has no microscopic fluctuation ($\mathbf{j}_{ext,f} = 0$) :

$$[\hat{\epsilon}_{ff} - \frac{c^2}{\omega^2}(\hat{\nabla} \times \hat{\nabla}\times)_{ff}]\mathbf{E}_f = -\hat{\epsilon}_{fa}\mathbf{E}_a$$

Solving for $\mathbf{E}_f$, $\quad \mathbf{E}_f = -[\hat{\epsilon}_{ff} - \frac{c^2}{\omega^2}(\hat{\nabla} \times \hat{\nabla}\times)_{ff}]^{-1}\hat{\epsilon}_{fa}\mathbf{E}_a$
one has

$$\hat{\epsilon}_M = \hat{\epsilon}_{aa} - \hat{\epsilon}_{af}[\hat{\epsilon}_{ff} - \frac{c^2}{\omega^2}(\hat{\nabla} \times \hat{\nabla}\times)_{ff}]^{-1}\hat{\epsilon}_{fa}$$

This exact result shows that the macroscopic dielectric response is the sum of the average microscopic response and a correction due to the coupling between the average and the fluctuating fields.

# Longitudinal and transverse fields

## Longitudinal fields

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

$\mathbf{E}(\mathbf{k})$ propagates along $\mathbf{k}$.

In the Coulomb gauge, $\mathbf{E}(\mathbf{r})$ is related to a scalar potential $V$

## Transverse fields

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

$\mathbf{E}(\mathbf{k})$ propagates perpendicular to $\mathbf{k}$.

In the Coulomb gauge, $\mathbf{E}(\mathbf{r})$ is related to a vector potential $\mathbf{A}(\mathbf{r})$

# Microscopic spatial fluctuations

Characteristic length scale of the spatial fluctuations l $<< \lambda$ (wavelength of the radiation)

Longitudinal projector
$\hat{P}^L = \hat{\nabla}\hat{\nabla}^{-2}\hat{\nabla}$

Transverse projector
$\hat{P}^T = -\hat{\nabla} \times \hat{\nabla}^{-2}\hat{\nabla}\times$

$\hat{P}^L$ and $\hat{P}^T$ are also projectors and commute with $\hat{P}_a$ and $\hat{P}_f$
$\hat{\nabla} = i\mathbf{q}$ and $\hat{\nabla}^{-2} = -1/q^2$ in $q$-space

Projection of $\hat{\epsilon}_M = \hat{\epsilon}_{aa} - \hat{\epsilon}_{af}[\hat{\epsilon}_{ff} - \frac{c^2}{\omega^2}(\hat{\nabla} \times \hat{\nabla}\times)_{ff}]^{-1}\hat{\epsilon}_{fa}$ onto the longitudinal and transverse subspaces

$$[\hat{\epsilon}_{ff} - \frac{c^2}{\omega^2}(\hat{\nabla} \times \hat{\nabla}\times)_{ff}]^{-1} = \begin{pmatrix} \hat{\epsilon}_{ff}^{LL} & \hat{\epsilon}_{ff}^{LT} \\ \hat{\epsilon}_{ff}^{TL} & \hat{\epsilon}_{ff}^{TT} - \frac{c^2}{\omega^2}\hat{P}_f\hat{\nabla}^2\hat{P}^T\hat{P}_f \end{pmatrix}^{-1}$$

# Microscopic spatial fluctuations

Expansion in terms of $||\omega^2/c^2\hat{\nabla}^{-2}\hat{P}_f|| \approx l^2/\lambda^2$

$$[\hat{\epsilon}_{ff} - \frac{c^2}{\omega^2}(\hat{\nabla}\times\hat{\nabla}\times)_{ff}]^{-1} = \begin{pmatrix} (\hat{\epsilon}_{ff}^{LL})^{-1} & 0 \\ 0 & 0 \end{pmatrix} + \frac{\omega^2}{c^2}\hat{\nabla}^{-2}\hat{P}_f \begin{pmatrix} \cdots & \cdots \\ \cdots & \cdots \end{pmatrix}$$

Keeping only the first term

$$\hat{\epsilon}_M = \hat{\epsilon}_{aa} - \begin{pmatrix} \hat{\epsilon}_{af}^{LL} & \hat{\epsilon}_{af}^{LT} \\ \hat{\epsilon}_{af}^{TL} & \hat{\epsilon}_{af}^{TT} \end{pmatrix} \begin{pmatrix} (\hat{\epsilon}_{ff}^{LL})^{-1} & 0 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} \hat{\epsilon}_{fa}^{LL} & \hat{\epsilon}_{fa}^{LT} \\ \hat{\epsilon}_{fa}^{TL} & \hat{\epsilon}_{fa}^{TT} \end{pmatrix}$$

one gets

$$\hat{\epsilon}_M = \hat{\epsilon}_{aa} - \hat{\epsilon}_{af}(\hat{\epsilon}_{ff}^{LL})^{-1}\hat{\epsilon}_{fa}$$

The same calculation can be done with $\hat{\epsilon}_M^{-1}$:

$$\hat{\epsilon}_M^{-1} = \hat{\epsilon}_{aa}^{-1} - \hat{\epsilon}_{af}^{-1}((\hat{\epsilon}^{-1})_{ff}^{TT})^{-1}\hat{\epsilon}_{fa}^{-1}$$

# Interpretation

$$\hat{\epsilon}_M = \hat{\epsilon}_{aa} - \hat{\epsilon}_{af}(\hat{\epsilon}_{ff}^{LL})^{-1}\hat{\epsilon}_{fa}$$

The expansion corresponds to $\lambda^2/l^2 >> ||\hat{\epsilon}||$.

In case of a resonance , the procedure can be questioned (J. E. Sipe and J. van Kranendonk, Phys. Rev. A **9** 1806 (1974).)

The neglect of terms of the order of $l^2/\lambda^2$ is equivalent to the neglect of the transverse fluctuating electric field $E_f^T$.

# Infinite crystal

# Infinite crystal

Invariance : $\hat{\epsilon}(\mathbf{r}+\mathbf{R},\mathbf{r}'+\mathbf{R}) = \hat{\epsilon}(\mathbf{r},\mathbf{r}')$

$$\mathbf{D}(\mathbf{q}+\mathbf{G}) = \sum_{\mathbf{G}'} \hat{\epsilon}(\mathbf{q}+\mathbf{G},\mathbf{q}+\mathbf{G}')\mathbf{E}(\mathbf{q}+\mathbf{G}')$$

Longitudinal projector : $\hat{P}^L(\mathbf{q}+\mathbf{G},\mathbf{q}+\mathbf{G}') = \frac{\mathbf{q}+\mathbf{G}}{|\mathbf{q}+\mathbf{G}|}\cdot\frac{\mathbf{q}+\mathbf{G}}{|\mathbf{q}+\mathbf{G}|}\delta_{\mathbf{G}\mathbf{G}'}$

Average projector= truncation eliminating all wave vectors outside the first Brillouin zone $\hat{P}_a(\mathbf{q}+\mathbf{G},\mathbf{q}+\mathbf{G}') = \delta_{\mathbf{G}0}\delta_{\mathbf{G}'0}$

$$\hat{\epsilon}_M = \hat{\epsilon}_{00} - \sum_{\mathbf{G}\mathbf{G}'\neq 0} \hat{\epsilon}_{0\mathbf{G}} (\hat{\epsilon}_r^{LL})^{-1}_{\mathbf{G}\mathbf{G}'} \hat{\epsilon}_{G'0}$$

$$\hat{\epsilon}_M^{-1} = \hat{\epsilon}_{00}^{-1} - \sum_{\mathbf{G}\mathbf{G}'\neq 0} \hat{\epsilon}_{0\mathbf{G}}^{-1} \left[(\hat{\epsilon}^{-1})_r^{TT}\right]^{-1}_{\mathbf{G}\mathbf{G}'} \hat{\epsilon}_{G'0}^{-1}$$

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[0] Meaning of the subscript r: suppress the $\mathbf{G}=0$ component before doing the inversion

# Infinite crystal

The procedure can be simplified by defining the scalar operator $\hat{\epsilon}_{cc}$ :

$$\rho_{ext} = \hat{\epsilon}_{cc}\rho$$

$$(\hat{\epsilon}_M^{LL})^{-1} = (\hat{\epsilon}^{LL})_{00}^{-1} = (\hat{\epsilon}^{cc})_{00}^{-1}\hat{q}\hat{q}$$

$\hat{\epsilon}_{cc}$ can be calculated directly from the response of the system in the absence of transverse electric field.

Well-known result obtained first by Adler (1962) and Wiser (1963) using the random-phase-approximation(RPA) and neglecting longitudinal - transverse coupling

- does not depend on the microscopic theory used to obtain $\epsilon$
- Valid even in case of longitudinal - transverse coupling

# Calculation of $\hat{\epsilon}_M$

Starting point : microscopic dielectric tensor obtained in the linear response theory.

The hamiltonian $H$ is divided into two parts:

- a nonperturbed hamiltonian $H_0$
- a time-dependent perturbation $H_{pert}$

The induced current and induced density can be computed in terms of the perturbing field and the response functions are written in terms of the eigenfunctions of the unperturbed hamiltonian.

# Calculation of $\hat{\epsilon}_M$

Example: $\mathbf{E}_{tot} = \mathbf{E}_{ext} + \mathbf{E}^L_{ind} + \mathbf{E}^T_{ind}$

- $\mathbf{E}_{pert} = \mathbf{E}_{tot} \Rightarrow \mathbf{P} = \hat{\alpha}^{(0)}\mathbf{E}_{tot} \Rightarrow \hat{\epsilon} = 1 + 4\pi\alpha^{(0)}$
- $\mathbf{E}_{pert} = \mathbf{E}_{ext} \Rightarrow \mathbf{P} = \hat{\alpha}\mathbf{E}_{ext}$
  and
  $\mathbf{E}_{ext} = \left[\hat{\nabla} \times \hat{\nabla} \times + \frac{1}{c^2}\frac{\partial^2}{\partial^2}\right]^{-1} \left[\hat{\nabla} \times \hat{\nabla} \times + \frac{1}{c^2}\frac{\partial^2}{\partial t^2} + \frac{4\pi}{c^2}\frac{\partial}{\partial t}\hat{\sigma}\right] \mathbf{E}_{tot}$
  $\hat{\epsilon} = 1 + 4\pi\hat{\alpha}\left[\hat{\nabla} \times \hat{\nabla} \times + \frac{1}{c^2}\frac{\partial^2}{\partial^2}\right]^{-1} \left[\hat{\nabla} \times \hat{\nabla} \times + \frac{1}{c^2}\frac{\partial^2}{\partial t^2} + \frac{4\pi}{c^2}\frac{\partial}{\partial t}\hat{\sigma}\right]$
  $\hat{\sigma}$: conductivity

and we have

- $\hat{\alpha}^{(0)} =$ independent particle polarisability
- $\hat{\alpha}$ =full polarisability

$\Rightarrow$ Leads to the inversion of large matrices

# Calculation of $\hat{\epsilon}_M$

Example: $\mathbf{E}_{tot} = \mathbf{E}_{ext} + \mathbf{E}^L_{ind} + \mathbf{E}^T_{ind}$

- $\mathbf{E}_{pert} = \mathbf{E}_{ext} + \mathbf{E}^T_{ind}$

The former results cannot be directly applied: $\mathbf{E}_{pert}$ is not solution of any Maxwell's equations.
The formalism can be extended (R. Del Sole and E. Fiorino, Phys Rev B 29, 4631 (1984).)

$$\epsilon_M(\mathbf{q},\omega) = 1 + 4\pi\tilde{\alpha}(\mathbf{q},\mathbf{q},\omega).\left[1 + 4\pi\,\frac{\mathbf{q}}{q}\frac{\mathbf{q}}{q}\frac{\tilde{\alpha}(\mathbf{q},\mathbf{q},\omega)}{1-4\pi\tilde{\alpha}^{LL}(\mathbf{q},\mathbf{q},\omega)}\right]$$

with $\mathbf{P} = \tilde{\alpha}\,\mathbf{E}_{pert}$, $\tilde{\alpha}$ is the quasi-polarisability.

- Same assumption: $E^T(\mathbf{q}+\mathbf{G}) \approx 0$ for $\mathbf{G} \neq 0$
- Easier for practical calculation

# Calculation of $\hat{\epsilon}_M$: EELS

The charge density associated to an external classical charge $e$, with velocity $\mathbf{v}$ is given by $\rho_{ext}(\mathbf{r}, t) = e\delta(\mathbf{r} - \mathbf{v}t)$

$$\rho_{ext}(\mathbf{k}, \omega) = \frac{e}{V}\delta(\omega - \mathbf{k}\mathbf{v})$$

We assume that the potential created by the external charge is sufficiently smooth, so that it does not contain any microscopic component : $\mathbf{E}_{ext}(\mathbf{q}+\mathbf{G}, \omega) = \mathbf{E}_{ext}(\mathbf{q}, \omega)\delta_{\mathbf{G}0}$ with

$$\mathbf{E}_{ext}(\mathbf{q}, \omega) = -i\mathbf{q}V_{ext}(\mathbf{q}, \omega)$$

We know that the only nonvanishing component of the tranverse field corresponds to $\mathbf{G} = 0$, and we have

$$\mathbf{E}^T(\mathbf{q}) = \frac{\omega^2}{c^2|\mathbf{q}|^2}\mathbf{D}^T(\mathbf{q})$$

# Infinite crystal: EELS

With $\omega = \mathbf{qv}$ and in the nonrelativistic regime, $v << c$ :

$$\frac{\omega^2}{c^2|\mathbf{q}|^2} \approx \frac{v^2}{c^2} << 1$$

The transverse field $\mathbf{E}^T(\mathbf{q}) = \mathbf{E}^{i,T}(\mathbf{q})$ is negligible. With $E_{pert} = \mathbf{E}_{ext} + \mathbf{E}^T_{ind}$, the perturbing field is equal to the external longitudinal field and using

$$\mathbf{E}(\mathbf{q},\omega) = \left[1 - 4\pi \frac{\mathbf{q}}{|\mathbf{q}|}.\frac{\mathbf{q}}{|\mathbf{q}|}\tilde{\alpha}(\mathbf{q},\mathbf{q},\omega)\right] \mathbf{E}^P(\mathbf{q},\omega)$$

the total field is also longitudinal.
The calculation of the energy loss can be done using only scalar field and the loss function is $Im\left\{-1/\epsilon_M^{LL}(\mathbf{q},\omega)\right\}$

# Cubic symmetries with $q \longrightarrow 0$

## Longitudinal dielectric function

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

where $\chi_{\rho\rho}(\mathbf{q}, \omega)$ is the density-density response function (TDDFT), relating the induced density to the external potential

$$\rho_{ind}(\mathbf{q}, \omega) = \chi_{\rho\rho}(\mathbf{q}, \mathbf{q}, \omega) V^{ext}(\mathbf{q}, \omega)$$

## Transverse dielectric function

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

## Dielectric tensor

The dielectric tensor is diagonal (in terms of L and T) and contains only $\epsilon_M^{LL}(\omega)$

# Cubic symmetries with $q \neq 0$

## Longitudinal dielectric function

One can show that the relation

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

holds also when $q \neq 0$.

## Transverse dielectric functions

$$\epsilon_M^{TT}(\mathbf{q},\omega) \neq \epsilon_M^{LL}(\mathbf{q},\omega)$$

We have also $\epsilon_M^{LT}(\mathbf{q},\omega) \neq 0$ and $\epsilon_M^{TL}(\mathbf{q},\omega) \neq 0$
These quantities are much more complicated and need, in principle, further approximations to be computed.

# Non-cubic symmetries with $q \rightarrow 0$

- Main general result concerning $\hat{\epsilon}_M(\mathbf{q}, \omega)$ : $\hat{\epsilon}_M$ is an analytic function of $\mathbf{q}$ (R. Del Sole and E. Fiorino, Phys Rev B 29, 4631 (1984).)

  $\Longrightarrow$ The limit $\mathbf{q} \rightarrow 0$ does not depend on the direction of $\mathbf{q}$.

- We can define $\hat{\epsilon}_M$ as $\hat{\epsilon}_M(\omega) = \lim_{q \rightarrow 0} \hat{\epsilon}_M(\mathbf{q}, \omega)$

  $\hat{\epsilon}_M^{LL}(\mathbf{q}, \omega)$ is not analytic in the general case

- Depending on the symmetry of the system, one can define 3 principal axis (if they exist) ($\mathbf{n}_1$, $\mathbf{n}_2$,$\mathbf{n}_3$) defining a frame in which $\hat{\epsilon}_M(\omega)$ is diagonal.

  If $\mathbf{E}$ is parallel to one of these axis : $\hat{\epsilon}_M(\omega)\mathbf{E} = \epsilon_i(\omega)\mathbf{E}$

  $\epsilon_i$ can be calculated as $\epsilon_i^{LL}(\mathbf{n}_i, \omega)$

# Non-cubic symmetries with $q \rightarrow 0$

The distinction between longitudinal and transverse is not meaningful

The only important direction is the direction of the electric field

If $\mathbf{q} \rightarrow 0$ , the fields do not propagate

Calculation of $\hat{\epsilon}_M^{LL}$ and $\hat{\epsilon}_M^{TT}$ should lead to the same information.

$\epsilon_i$ can be seen as a longitudinal dielectric function

$$\epsilon_i = \epsilon_M^{LL}(\mathbf{n}_i, \omega)$$

but can also be used as a transverse dielectric function.

# Non-cubic symmetries with $q \to 0$

Existence of the principal frame ?

- $\epsilon_M$ is symmetric but complex $\Rightarrow$ No general answer
- To determine the principal axis, one needs $\hat{\epsilon}_M$ but $\epsilon_i$ can only be calculated in the optical (principal) frame.

Use of geometrical arguments

- cubic
- orthorombic
- hexagonal

  The optical axis are given by the symmetry

- monoclinic
- triclinic

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

# Non-cubic symmetries with $q \to 0$

## Dielectric tensor

As $\mathbf{q} \to 0$, $\hat{\epsilon}_M(\omega)$ is a tensor and in the (x,y,z)-basis has 6 independent component.

$\epsilon_{aa}$ is calculated as a longitudinal response (TDDFT) through the relation $\epsilon_{aa}(\omega) = \lim_{\mathbf{q}_a \to 0} \frac{1}{1+\frac{4\pi}{q_a^2}\chi_{\rho\rho}(\mathbf{q}_a,\mathbf{q}_a,\omega)}$ with $\mathbf{q}_a$ along $\mathbf{a}$, $\mathbf{a} = \mathbf{x}, \mathbf{y}, \mathbf{z}$

## Off-diagonal elements

$\epsilon_{ab}$ is defined as $\epsilon_{ab} = \mathbf{a}.\hat{\epsilon}_M.\mathbf{b}$

With the expression obtained for $\epsilon_M$, one gets

$$\epsilon_{ab} = 4\pi \frac{\mathbf{a}.\tilde{\alpha}(\mathbf{q}_a,\mathbf{q}_a).\mathbf{b}}{1-4\pi\tilde{\alpha}^{LL}(\mathbf{q}_a,\mathbf{q}_a)} \quad or \quad \epsilon_{ab} = 4\pi \frac{\mathbf{a}.\tilde{\alpha}(\mathbf{q}_b,\mathbf{q}_b).\mathbf{b}}{1-4\pi\tilde{\alpha}^{LL}(\mathbf{q}_b,\mathbf{q}_b)}$$

# Non-cubic symmetries with $q \to 0$

## Off-diagonal elements

One gets in terms of the usual response functions

$$\epsilon_{ab} = \frac{4\pi\epsilon_{aa}}{\omega^2}\mathbf{a}.\chi_{\mathbf{jj}}(\mathbf{q}_a, \mathbf{q}_a).\mathbf{b} \quad or \quad \epsilon_{ab} = \frac{4\pi\epsilon_{bb}}{\omega^2}\mathbf{a}.\chi_{\mathbf{jj}}(\mathbf{q}_b, \mathbf{q}_b).\mathbf{b}$$

Using the relations between the response functions

$$\epsilon_{ab} = \frac{4\pi\epsilon_{aa}}{\omega q_a}\chi_{\rho\mathbf{j}}(\mathbf{q}_a, \mathbf{q}_a).\mathbf{b} \quad or \quad \epsilon_{ab} = \frac{4\pi\epsilon_{bb}}{\omega q_b}\mathbf{a}.\chi_{\mathbf{j}\rho}(\mathbf{q}_b, \mathbf{q}_b)$$

Up to now, it cannot be related to $\chi_{\rho\rho}$

# Non-cubic symmetries with $q \to 0$

## Off-diagonal elements

Another way to get the off-diogonal terms

$$\begin{aligned}\epsilon_M(\mathbf{a}+\mathbf{b}) &= (\mathbf{a}+\mathbf{b})\hat{\epsilon}_M(\mathbf{a}+\mathbf{b}) \\ &= \epsilon_{aa}+\epsilon_{bb}+2\epsilon_{ab}\end{aligned}$$

Three independent calculations, based on a purely longitudinal approach, give access to $\epsilon_{ab}$

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