Theoretical Spectroscopy

relating theory and experiment

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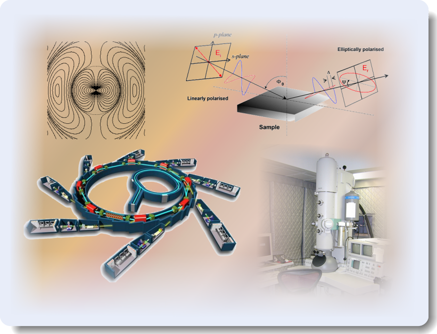
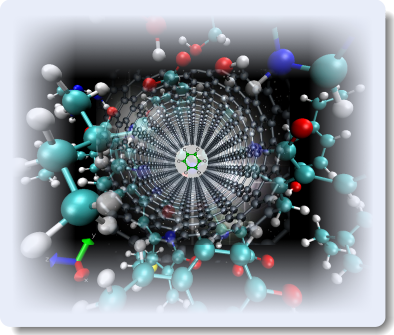
How to relate macroscopic and microscopic world?





You will find the content of these slides and more details in

S. Botti and M. Gatti
The microscopic description of a macroscopic experiment,
in "Fundamentals of Time-Dependent Density Functional Theory",
Chapter 3 (2011).

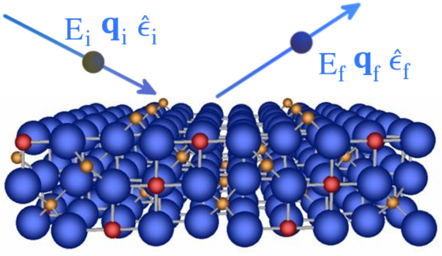
Outline

1. Theoretical spectroscopy
2. Starting point: Maxwell's equations
3. Averaging procedure
4. Macroscopic dielectric tensor

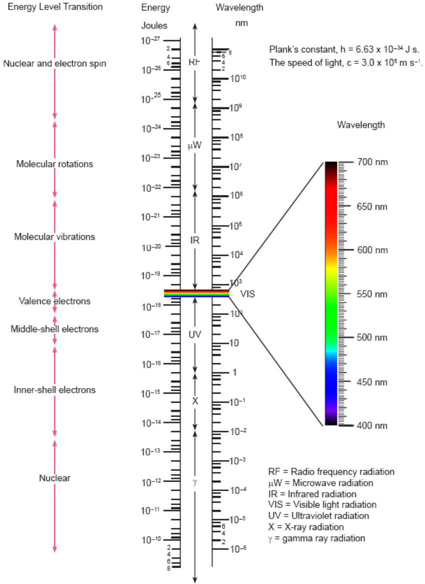
Outline

From Spectroscopy to Theoretical Spectroscopy

- Study of the properties of matter by investigating how it responds to a perturbation (photons, electrons, neutrons, . . .).
- A plot of the response as a function of wavelength – or more commonly frequency – is referred to as a spectrum.



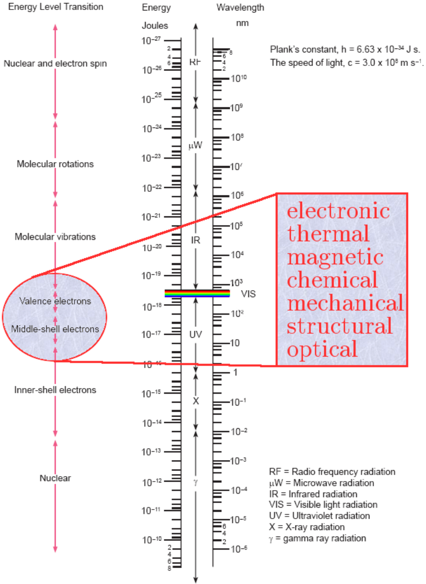
Energy range



Plank's constant, $h = 6.63 \times 10^{-34}$ J s.
The speed of light, $c = 3.0 \times 10^{8}$ m s^{-1}.

RF = Radio frequency radiation
μW = Microwave radiation
IR = Infrared radiation
VIS = Visible light radiation
UV = Ultraviolet radiation
X = X-ray radiation
γ = gamma ray radiation

Energy range



electronic
thermal
magnetic
chemical
mechanical
structural
optical

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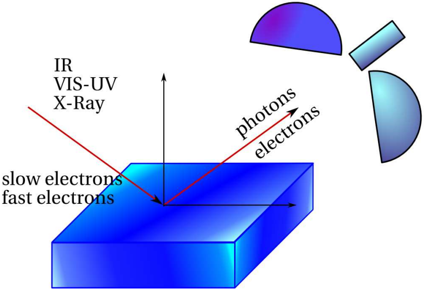
Gaining information on electronic excitations



- Optical absorption
- Electron energy loss
- Inelastic X-ray scattering
- Photoemission
- Inverse photoemission
- . . .

Absorption

Beer's law:

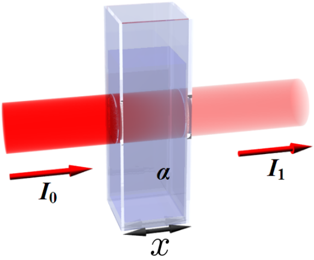
$$I(x) = I_0 e^{-\alpha_{\mathrm{abs}} x}$$

the absorption coefficient and the photoabsorption cross section are proportional:

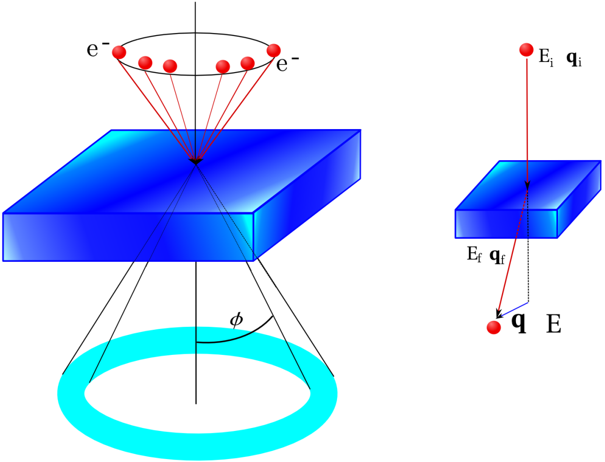
$$\alpha_{\mathrm{abs}}(\omega) \propto \sigma(\omega)$$

Also the imaginary part of the dielectric function and the dynamical polarizability describe the same process:

$$\alpha_{\mathrm{abs}}(\omega) \leftrightarrow \mathrm{Im}\{\epsilon(\omega)\} \propto \mathrm{Im}\{\alpha(\omega)\}$$



Electron scattering

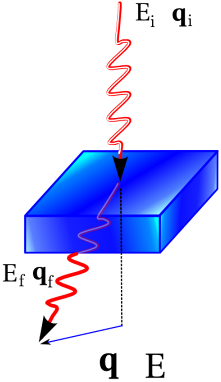


Electron energy loss

Energy Loss Function

$$\frac{d^2\sigma}{d\Omega dE} \propto \mathrm{Im}\left\{\varepsilon^{-1}(\mathbf{q},\omega)\right\}$$

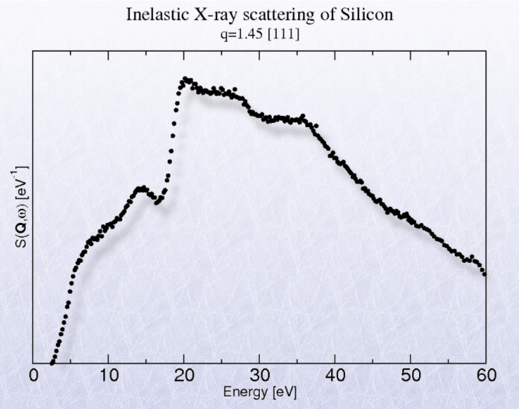
X-ray scattering



Inelastic X-ray scattering

Dynamic structure factor

$$\frac{d^2\sigma}{d\Omega dE} \propto \mathrm{Im}\left\{\varepsilon^{-1}(\mathbf{q},\omega)\right\}$$



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

Outline

1. Theoretical spectroscopy
2. Starting point: Maxwell's equations
3. Averaging procedure
4. Macroscopic dielectric tensor

How to study optical processes?

- The propagation of electromagnetic waves in materials is described by the Maxwell's equations, supplemented by appropriate constitutive equations.
- The optical phenomena (reflection, propagation, transmission) can be quantified by a number of parameters that determine the properties of the medium at the macroscopic level.
- Microscopic (semiclassical) models and averaging procedures yield these macroscopic parameters.

The response of a dielectric material to an external **electric** field

is characterized by three macroscopic vectors:

- the electric field strength **E**,
- the polarization **P**,
- the electric displacement **D**.

The response of a dielectric material to an external **magnetic** field

is characterized by three macroscopic vectors:

- the magnetic field strength **H**,
- the magnetization **M**,
- the magnetic flux density **B**.

The *macroscopic* vectors have *microscopic* counterparts.

Maxwell's equations in presence of a medium

$$
\begin{aligned}
\nabla \cdot \mathbf{E}(\mathbf{r}, t) &= 4\pi\rho_{\text{ind}}(\mathbf{r}, t) + 4\pi\rho_{\text{ext}}(\mathbf{r}, t) \\
\nabla \cdot \mathbf{B}(\mathbf{r}, t) &= 0 \\
\nabla \times \mathbf{E}(\mathbf{r}, t) &= -\frac{1}{c}\frac{\partial \mathbf{B}(\mathbf{r}, t)}{\partial t} \\
\nabla \times \mathbf{B}(\mathbf{r}, t) &= \frac{4\pi}{c}\left[\, \mathbf{j}_{\mathrm{ind}}(\mathbf{r}, t) + \mathbf{j}_{\mathrm{ext}}(\mathbf{r}, t)\right] + \frac{1}{c}\frac{\partial \mathbf{E}(\mathbf{r}, t)}{\partial t}
\end{aligned}
$$

- $\rho_{\text{ext}}, \mathbf{j}_{\mathrm{ext}}$ = external (or *free*) charges and currents
- $\rho_{\text{ind}}, \mathbf{j}_{\mathrm{ind}}$ = induced (or *bound*) charges and currents

Maxwell's equations in presence of a medium

$$\nabla \cdot \mathbf{D}(\mathbf{r}, t) = 4\pi \rho_{\text{ext}}(\mathbf{r}, t)$$
$$\nabla \cdot \mathbf{B}(\mathbf{r}, t) = 0$$
$$\nabla \times \mathbf{E}(\mathbf{r}, t) = -\frac{1}{c}\frac{\partial \mathbf{B}(\mathbf{r}, t)}{\partial t}$$
$$\nabla \times \mathbf{H}(\mathbf{r}, t) = \frac{4\pi}{c}\mathbf{j}_{\mathrm{ext}}(\mathbf{r}, t) + \frac{1}{c}\frac{\partial \mathbf{D}(\mathbf{r}, t)}{\partial t}$$

- $\rho_{\text{ext}}, \mathbf{j}_{\mathrm{ext}}$ = external charges and currents
- Continuity equation: $\nabla \cdot \mathbf{j}_{\mathrm{ext}} + \frac{\partial \rho_{\text{ext}}}{\partial t} = 0$

Constitutive relations

In the linear response regime, for an isotropic medium:

$$\mathbf{P} = \chi_{\mathrm{e}}\mathbf{E}$$

$$\mathbf{D} = \mathbf{E} + 4\pi\mathbf{P} = \epsilon\mathbf{E}$$

$$\mathbf{M} = \chi_{\mathrm{m}}\mathbf{H}$$

$$\mathbf{B} = \mathbf{H} + 4\pi\mathbf{M} = \mu\mathbf{H}$$

- electric permittivity χ_{e}
- dielectric function ϵ
- magnetic susceptibility χ_{m}
- magnetic permeability μ

Linear response

- For a sufficiently small perturbation, the response of the system can be expanded into a Taylor series with respect to the perturbation.
- The linear coefficient linking the response to the perturbation is called **response function**. It is independent of the perturbation and depends only on the system.
- We will consider only the first order (linear) response.
- We will not consider strong field interaction (e.g. intense lasers).
- We will consider non-magnetic materials.

Example

Density-density response function: $\delta\rho(\mathbf{r},t) = \int dt' \int d\mathbf{r}' \chi_{\rho\rho}(\mathbf{r},t,\mathbf{r}',t') v_{\mathrm{ext}}(\mathbf{r}',t')$

Dielectric tensor: $\mathbf{D}(\mathbf{r},t) = \int dt' \int d\mathbf{r}' \epsilon(\mathbf{r},t,\mathbf{r}',t') \mathbf{E}(\mathbf{r}',t')$

Physical quantities that are measured

More about response functions, their relations and sum rules:

- N. W. Ashcroft and N. D. Mermin "Solid state physics"
- G. Grosso and G. Pastori Parravicini "Solid state physics"

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Macroscopic average

Macroscopic quantities

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

$$\lambda = \frac{2\pi}{q} >> V_{\mathrm{cell}}^{1/3}$$

Typical values:

- $a_{\mathrm{cell}} \simeq 0.5\,\mathrm{nm}$
- $400\,\mathrm{nm} \leq \lambda \leq 800\,\mathrm{nm}$ (visible)

Example

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

Microscopic quantities

Total and induced fields are rapidly varying: they include the contribution from electrons in all regions of the cell.

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

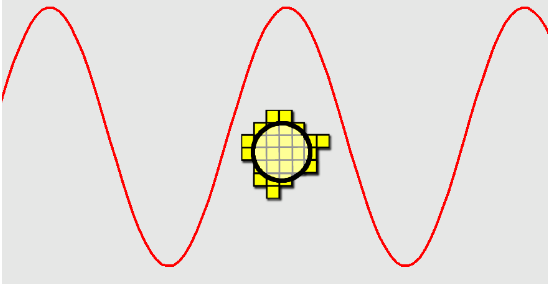
Example

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

Macroscopic average

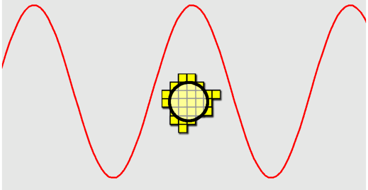
One usually measures quantities that vary on a macroscopic scale. When we calculate microscopic quantities we need to average over distances that are

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



Averaging procedure

- Average the microscopic quantities over a unit cell whose origin is at point **R**;
- Regard **R** as the new continuous coordinate appearing in Maxwell's equations.



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

Macroscopic average

In a periodic medium, every function can be represented by the Fourier series

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

where **R** is any vector of the Bravais lattice, **G** is a reciprocal lattice vector and **q** is in the first Brillouin zone.
This is equivalent to write

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

where $V(\mathbf{r};\mathbf{q},\omega) = \sum_{\mathbf{G}} V(\mathbf{q}+\mathbf{G},\omega) e^{i\mathbf{G}\cdot\mathbf{r}}$ has the periodicity of the Bravais lattice.

Macroscopic average

For a monochromatic field with wavevector **q**, the spatial average over a unit cell is:

$$\begin{aligned} V(\mathbf{R},\omega) &= < V(\mathbf{r};\mathbf{q},\omega) >_R \\ &= \frac{1}{\Omega}\int d\mathbf{r} \sum_{\mathbf{G}} V(\mathbf{q}+\mathbf{G},\omega) e^{i\mathbf{G}\cdot\mathbf{r}} \\ &= V(\mathbf{q}+\mathbf{0},\omega) \end{aligned}$$

The macroscopic average corresponds to the $\mathbf{G}=\mathbf{0}$ component.
Macroscopic quantities have all their $\mathbf{G}\neq 0$ components equal to 0.

Macroscopic average

A simple example

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

v_{ext} is a macroscopic quantity : $v_{\mathrm{ext}}(\mathbf{q}+\mathbf{G},\omega)=v_{\mathrm{ext}}(\mathbf{q},\omega)\,\delta_{\mathbf{G}\mathbf{0}}$
This not the case for $v_{\mathrm{tot}}(\mathbf{q}+\mathbf{G},\omega)$.

Macroscopic average of v_{ext}

$$\begin{aligned}v_{\mathrm{ext}}(\mathbf{q},\omega)&=\sum_{\mathbf{G}'}\epsilon_{\mathbf{0}\mathbf{G}'}(\mathbf{q},\omega)v_{\mathrm{tot}}(\mathbf{q}+\mathbf{G}',\omega)\\&\neq\epsilon_{\mathbf{0}\mathbf{0}}(\mathbf{q},\omega)v_{\mathrm{tot}}(\mathbf{q},\omega)\end{aligned}$$

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

Macroscopic average

Macroscopic average of $v_{\rm tot}$

We have also the relation

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

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

$$v_{\rm tot}(\mathbf{q},\omega)=\epsilon^{-1}_{\mathbf{00}}(\mathbf{q},\omega)v_{\rm ext}(\mathbf{q},\omega)$$

$$v_{\rm ext}(\mathbf{q},\omega)=\epsilon_{\rm M}(\mathbf{q},\omega)v_{\rm tot}(\mathbf{q},\omega)\Rightarrow\epsilon_{\rm M}(\mathbf{q},\omega)=\frac{1}{\epsilon^{-1}_{\mathbf{00}}(\mathbf{q},\omega)}$$

The microscopic components of the induced field couple to produce the macroscopic response.

Macroscopic dielectric function

Question

ε_{00} is not the macroscopic dielectric function.
What is it then ?

Answer

ε_{00} is the macroscopic dielectric function without crystal local fields.

Macroscopic dielectric function

Question

Is the macroscopic averaging always meaningful?

Answer

- If the external applied field has a very short wavelength (is not macroscopic) the averaging procedure for the response function of the material has no meaning.
- When dealing with surfaces, the definition is unclear due to the lack of periodicity in the direction perpendicular to the surface.

Microscopic dielectric function

Question

How can we calculate the microscopic dielectric functions?

Answer

They are determined by the elementary excitations of the medium: interband and intraband transitions, as well as collective excitations, i.e. one can calculate them using TDDFT or GW+BSE.

You should have already found the answer in other lectures!

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 and its macroscopic counterpart:

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

- *Absorption* $\leftrightarrow \mathrm{Im}\left\{\epsilon_{\mathrm{M}}\right\}$ and *EELS* $\leftrightarrow -\mathrm{Im}\left\{\frac{1}{\epsilon_{\mathrm{M}}}\right\}$

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From the dielectric function to the dielectric tensor

Macroscopic fields

$\mathbf{q}$ defines the direction for the propagation: we assume $\mathbf{q} \parallel x$.

Longitudinal fields

$E(\mathbf{q})$ propagates along $\mathbf{q}$

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

Transverse fields

$E(\mathbf{q})$ propagates $\perp$ to $\mathbf{q}$

$$\nabla \cdot \mathbf{E}(\mathbf{r}) = 0 \quad \text{or} \quad \mathbf{q} \cdot E(\mathbf{q}) = 0$$

Longitudinal fields

Electrostatic interaction, plasmon oscillations, screening, electron energy loss.

Transverse fields

Photons, optical response of solids.

General properties of the dielectric tensor

Any vector can be split into longitudinal and transverse components

$$\mathbf{V}(\mathbf{q}) = \mathbf{V}^{\mathrm{L}}(\mathbf{q}) + \mathbf{V}^{\mathrm{T}}(\mathbf{q})\,,$$

such that $\mathbf{q} \times \mathbf{V}^{\mathrm{L}}(\mathbf{q}) = 0$ and $\mathbf{q} \cdot \mathbf{V}^{\mathrm{T}}(\mathbf{q}) = 0\,.$

In terms of transverse and longitudinal components:

$$\mathbf{D}(\mathbf{q},\omega) = \overleftrightarrow{\epsilon}_M(\mathbf{q},\omega)\mathbf{E}^{tot}(\mathbf{q},\omega)$$

$$\begin{pmatrix} D^{\mathrm{L}} \\ \\ D^{\mathrm{T}} \end{pmatrix} = \left(\begin{array}{c|c} \epsilon_{\mathrm{M}}^{\mathrm{LL}} & \epsilon_{\mathrm{M}}^{\mathrm{LT}} \\ \hline \epsilon_{\mathrm{M}}^{\mathrm{TL}} & \epsilon_{\mathrm{M}}^{\mathrm{TT}} \end{array}\right) \begin{pmatrix} E^{\mathrm{L}} \\ \\ E^{\mathrm{T}} \end{pmatrix}$$

From dielectric function to dielectric tensor

Question

How can we make the link between

- the microscopic dielectric tensor

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

- and the macroscopic dielectric tensor

$$\mathbf{D}(\mathbf{q},\omega)=\overleftrightarrow{\epsilon}_{\mathrm{M}}(\mathbf{q},\omega)\mathbf{E}^{tot}(\mathbf{q},\omega)\,?$$

Dielectric tensor for cubic symmetries

$$\mathbf{D}(\mathbf{q},\omega) = \overleftrightarrow{\epsilon}_M(\mathbf{q},\omega)\mathbf{E}^{tot}(\mathbf{q},\omega)$$

No symmetry

$$\overleftrightarrow{\epsilon}_M(\mathbf{q},\omega) = \left(\begin{array}{c|cc} \epsilon^{\mathrm{LL}} & \epsilon^{xy} & \epsilon^{xz} \\ \hline \epsilon^{yx} & \epsilon^{yy} & \epsilon^{yz} \\ \epsilon^{zx} & \epsilon^{zy} & \epsilon^{zz} \end{array}\right)$$

Cubic symmetry and $q \longrightarrow 0$

$$\overleftrightarrow{\epsilon}_M(\mathbf{q},\omega) = \left(\begin{array}{c|c} \epsilon_{\mathrm{M}}^{\mathrm{LL}} & 0 \\ \hline 0 & \epsilon_{\mathrm{M}}^{\mathrm{TT}} \end{array}\right)$$

Macroscopic quantities only:

A longitudinal perturbation induces a longitudinal response

A transverse perturbation induces a transverse response

Cubic symmetries with $q \longrightarrow 0$

Longitudinal dielectric function

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

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

$$\delta\rho(\mathbf{r}, t) = \int dt' \int d\mathbf{r}' \chi_{\rho\rho}(\mathbf{r}, t, \mathbf{r}', t') v_{\mathrm{ext}}(\mathbf{r}', t')$$

Transverse dielectric function

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

Cubic symmetries with $q \longrightarrow 0$

In the limit $\mathbf{q} \to 0$

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

Dielectric tensor

The dielectric tensor is diagonal $\Rightarrow$ scalar dielectric function:

$$\epsilon_{\mathrm{M}}(\omega) = \epsilon_{\mathrm{M}}^{\mathrm{LL}}(\omega) = \lim_{\mathbf{q}\to 0} \frac{1}{\epsilon_{00}^{-1}(\omega)}$$

We finally reach the familiar result!

Cubic symmetries with $q \neq 0$

Longitudinal dielectric function

One can show that the relation

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

holds also when $\mathbf{q} \neq 0$.

Transverse dielectric function and mixed components

$$\epsilon_{\mathrm{M}}^{\mathrm{TT}}(\mathbf{q},\omega) \neq \epsilon_{\mathrm{M}}^{\mathrm{LL}}(\mathbf{q},\omega)$$

$$\epsilon_{\mathrm{M}}^{\mathrm{LT}}(\mathbf{q},\omega) \neq 0 \quad , \quad \epsilon_{\mathrm{M}}^{\mathrm{TL}}(\mathbf{q},\omega) \neq 0$$

There is no easy way to compute these elements of the dielectric tensor. Current response functions and further approximations are needed.

Cubic symmetries

Summary

- We have defined the longitudinal and transverse components of the dielectric tensor.
- In the long wavelength limit ($q \rightarrow 0$) only a scalar dielectric function is needed:

$$\epsilon_{\mathrm{M}}(\omega) = \lim_{\mathbf{q}\rightarrow 0} \frac{1}{1 + \frac{4\pi}{q^2}\chi_{\rho\rho}(\mathbf{q},\omega)} \,.$$

- When $q \neq 0$ only $\epsilon_{\mathrm{M}}^{\mathrm{LL}}(\mathbf{q},\omega)$ has a simple expression in terms of the density-density response function.

References for cubic symmetries

- H. Ehrenrich, *Electromagnetic Transport in Solids*, 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, Phys. Rev. B **12**, 3428 (1975).
- S. L. Adler, Phys. Rev. **126**, 413 (1962).
- N. Wiser, Phys. Rev. **129**, 62 (1963).

Non-Cubic symmetries

$$\mathbf{D}(\mathbf{q},\omega) = \overleftrightarrow{\epsilon}_M(\mathbf{q},\omega)\mathbf{E}^{\mathrm{tot}}(\mathbf{q},\omega)$$

$$\overleftrightarrow{\epsilon}_M(\mathbf{q},\omega) = \left(\begin{array}{c|c} \epsilon_{\mathrm{M}}^{\mathrm{LL}} & \epsilon_{\mathrm{M}}^{\mathrm{LT}} \\ \hline \epsilon_{\mathrm{M}}^{\mathrm{TL}} & \epsilon_{\mathrm{M}}^{\mathrm{TT}} \end{array}\right)$$

Even for $q \to 0$:
A longitudinal perturbation induces longitudinal and transverse responses.
A transverse perturbation induces longitudinal and transverse responses.

Non-Cubic symmetries

In the general case:

$$\overleftrightarrow{\epsilon}_{\mathrm{M}}(\mathbf{q},\omega) = 1 + 4\pi\,\overleftrightarrow{\tilde{\alpha}}(\mathbf{q},\mathbf{q},\omega)\left[1 + 4\pi\frac{\mathbf{q}}{q}\,\frac{\frac{\mathbf{q}}{q}\cdot\overleftrightarrow{\tilde{\alpha}}(\mathbf{q},\mathbf{q},\omega)}{1 - 4\pi\tilde{\alpha}^{\mathrm{LL}}(\mathbf{q},\mathbf{q},\omega)}\right]$$

COMPLICATED! But one can show that the relation

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

holds also for the non-cubic symmetries.

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

Non-cubic symmetries for $q \longrightarrow 0$

It can be proved that ϵ_{M} is an analytic function of $\mathbf{q}$, then the limit $q \rightarrow 0$ does not depend on the direction of $\mathbf{q}$ $\Rightarrow$ $\epsilon_{\mathrm{M}}(\omega)$

Principal axes

One can find 3 axes $\mathbf{n}_1$,$\mathbf{n}_2$,$\mathbf{n}_3$ defining a frame in which $\overleftrightarrow{\epsilon}_{\mathrm{M}}$ is diagonal.
Applying a field $\mathbf{E}^{tot}(\mathbf{q}, \omega)$ parallel to one of these axes n_i leads to

$$\overleftrightarrow{\epsilon}_{\mathrm{M}}(\mathbf{n}_i, \omega) : \mathbf{E}^{tot}(\mathbf{n}_i, \omega) = \epsilon_i(\omega)\mathbf{E}^{tot}(\mathbf{n}_i, \omega)$$

whatever the direction of $\mathbf{q}$.
In particular, a longitudinal perturbation induces a longitudinal response:

$$\epsilon_i(\omega) = \epsilon_{\mathrm{M}}^{\mathrm{LL}}(\mathbf{n}_i, \omega)$$

But the relation can also be used for a transverse dielectric function!

Non-cubic symmetries - Principal axes

For $\mathbf{q} \longrightarrow 0$, we have defined three quantities:

$$\epsilon_{\mathrm{M}}^{LL}(\mathbf{n}_1, \omega)\ ,\ \epsilon_{\mathrm{M}}^{LL}(\mathbf{n}_2, \omega)\ ,\ \epsilon_{\mathrm{M}}^{LL}(\mathbf{n}_3, \omega)$$

with

$$\lim_{q \to 0,\ \mathbf{q} \| \mathbf{n}_i} \epsilon_{\mathrm{M}}^{\mathrm{LL}}(\mathbf{q}, \omega) = \lim_{q \to 0,\ \mathbf{q} \| \mathbf{n}_i} \frac{1}{1 + \frac{4\pi}{q^2} \chi_{\rho\rho}(\mathbf{q}, \omega)}$$

Along the principal axes

For $q \longrightarrow 0$:

A longitudinal perturbation induces a longitudinal response.

A transverse perturbation induces a transverse response.

Non-cubic symmetries

Summary

In the limit $\mathbf{q} \to 0$ for a non-cubic symmetry:

- Using the crystal symmetries one can find the principal axes.
- The optical properties can be deduced from longitudinal calculations
- Keep in mind that the principal frame is not always orthogonal and $\mathbf{q}$ could be different from $\mathbf{n}_i$.

If the principal frame is known, on can deduce the optical properties from a longitudinal calculation performed in this frame.

Final summary

- The key quantities are the microscopic and macroscopic dielectric tensors.
- It is possible to establish the relations between microscopic and macroscopic fields through averages.
- For cubic crystals, the longitudinal dielectric function defines entirely the optical response in the long wavelength limit.
- For non cubic crystals, the longitudinal dielectric functions calculated along the principal axes can be used to define the optical response in the long wavelength limit.
- For non-vanishing momentum, the situation is not so simple: we can easily access only the longitudinal response.