Microscopic-Macroscopic connection
relating experiment and theory

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How to relate macroscopic and microscopic world?
<table>
<thead>
<tr>
<th>Outline</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td>4</td>
</tr>
<tr>
<td>5</td>
</tr>
</tbody>
</table>
Outline

1. Starting point: Maxwell’s equations
2. Averaging procedure
3. Macroscopic dielectric function in cubic crystals
4. Dielectric tensor for non-cubic symmetries
5. Summary
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 \( \mathbf{E} \),
- the polarization \( \mathbf{P} \),
- the electric displacement \( \mathbf{D} \).

The response of a dielectric material to an external **magnetic** field is characterized by three macroscopic vectors:

- the electric field strength \( \mathbf{H} \),
- the magnetization \( \mathbf{M} \),
- the magnetic flux density \( \mathbf{B} \).

The *macroscopic* vectors have *microscopic* counterparts.
Maxwell’s equations in presence of a medium

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

- \( \rho_{\text{ext}}, \mathbf{j}_{\text{ext}} \) = external (or free) charges and currents
- \( \rho_{\text{ind}}, \mathbf{j}_{\text{ind}} \) = induced (or bound) charges and currents
Maxwell’s equations in presence of a medium

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

- \( \rho_{\text{ext}}, \mathbf{j}_{\text{ext}} \) = external charges and currents

- Continuity equation: \( \nabla \cdot \mathbf{j}_{\text{ext}} + \frac{\partial \rho_{\text{ext}}}{\partial t} = 0 \)
In the linear response regime, for an isotropic medium:

\[ P = \chi_e E \]
\[ D = E + 4\pi P = \varepsilon E \]
\[ M = \chi_m H \]
\[ B = H + 4\pi M = \mu H \]

- electric permittivity \( \chi_e \)
- dielectric function \( \varepsilon \)
- magnetic susceptibility \( \chi_m \)
- magnetic permeability \( \mu \)
Linear response

Perturbation theory

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

- We will consider only the first order (linear) response, proportional to the perturbation.

- \( \neq \) strong field interaction (intense lasers for instance).

- The linear coefficient linking the response to the perturbation is called a response function. It is independent of the perturbation and depends only on the system.

- We will consider non-magnetic materials.

Example

Density-density response function: 
\[
\delta \rho(r, t) = \int dt' \int dr' \chi(r, t, r', t') v_{\text{ext}}(r', t')
\]
From Maxwell’s equations

Averages

Cubic symmetry

Non-cubic symmetries

Summary

Which quantities are measured?

Absorption coefficient

The general solution of Maxwell’s eqs in vacuum is \( \mathbf{E}(\mathbf{r}, t) = \mathbf{E}_0 e^{i(k \cdot \mathbf{r} - \omega t)} \). Defining the complex refractive index as \( \mathcal{N} = \sqrt{\epsilon} = \nu + i\kappa \), the electric field inside a medium is the damped wave:

\[
\mathbf{E}(\mathbf{x}, t) = \mathbf{E}_0 e^{i\omega \mathbf{c} \cdot \mathbf{x} \mathcal{N}} e^{-i\omega t} = \mathbf{E}_0 e^{i\omega \nu \mathbf{c} \mathbf{x}} e^{-\frac{\omega \mathbf{c} \kappa \mathbf{x}}{\nu}} e^{-i\omega t}
\]

\( \nu \) and \( \kappa \) are the refraction index and the extinction coefficient and they are related to the dielectric constant as

\[
\epsilon_1 = \nu^2 - \kappa^2 \quad \epsilon_2 = 2\nu\kappa
\]

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

\[
\alpha = \frac{\omega \epsilon_2}{\nu \mathbf{c}}
\]

(related to the optical skin depth \( \delta \)).
Which quantities are measured?

Reflectivity

Normal incidence reflectivity:

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

\[
R = \left| \frac{(1 - \nu)^2 + \kappa^2}{(1 + \nu)^2 + \kappa^2} \right|
\]

The knowledge of the optical constant implies the knowledge of the reflectivity, which can be compared with the experiment.
Which quantities are measured?

**Example: Photoabsorption cross section**

Rem: $\delta \rho(r, \omega) = \int dr' \chi(r, r', \omega) \nu_{\text{ext}}(r', \omega)$

$$\sigma_{\text{ph}}(\omega) = -\frac{4\pi \omega}{c} \text{Im} \int dr \int dr' z \chi(r, r', \omega) z'$$

with $\nu_{\text{ext}}(r', \omega) = -\kappa_0 z'$

$$\sigma_{\text{ph}}(\omega) = \frac{4\pi \omega}{c\kappa_0} \text{Im} \int dr z \delta \rho(r, \omega)$$
Which quantities are measured?

Example: Energy loss by a fast charged particle

Given an external charge density $\rho_{\text{ext}}$, one can obtained the external potential $v_{\text{ext}}$

$$k^2 v_{\text{ext,ind}}(k, \omega) = 4\pi \rho_{\text{ext,ind}}(k, \omega) \quad \text{(Poisson equation)}$$

The response of the system is an induced density, defined by the response function $\chi$

$$\rho_{\text{ind}}(k, \omega) = \chi(k, \omega) v_{\text{ext}}(k, \omega)$$

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

$$v_{\text{tot}}(k, \omega) = \left[ 1 + \frac{4\pi}{k^2} \chi(k, \omega) \right] v_{\text{ext}}(k, \omega) = \epsilon^{-1}(k, \omega) v_{\text{ext}}(k, \omega)$$
Which quantities are measured?

Energy loss by a fast charged particle: “classical” electron

Particle ($e^-$) with velocity $v$: $\rho_{\text{ext}}(r, t) = e\delta(r - vt); \rho_{\text{ext}}(k, \omega) = \frac{e}{(2\pi)^3} \delta(\omega - k \cdot v)$

The total electric field is $E_{\text{tot}}(r, t) = -\nabla_r V_{\text{tot}}(r, t)$ and the energy lost by the electron in unit time is

$$\frac{dW}{dt} = \int dr \, j \cdot E_{\text{tot}}$$

with the current density $j = -e v \delta(r - vt)$. We get

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

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

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

\[ \lambda = \frac{2\pi}{q} \gg V^{1/3} \]

where \( V \) is the volume per unit cell of the crystal.

Example
\( E_{\text{ext}}(r, t), A_{\text{ext}}(r, t), V_{\text{ext}}(r, t), \)

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

\[ \Rightarrow \text{Large and irregular fluctuations over the atomic scale.} \]

Example
\( E_{\text{tot}}(r, t), j_{\text{ind}}(r, t), \rho_{\text{ind}}(r, t), \ldots \)
Measurable quantities

One usually measures quantities that vary on a macroscopic scale. We have to average over distances:

- large compared to the cell diameter,
- small compared to the wavelength of the external perturbation.
Macrosopic average

Procedure

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

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

Procedure

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

\[ V(r, \omega) = \sum_{qG} V(q + G, \omega) e^{i(q+G) \cdot r} \]

where \( R \) is any vector of the Bravais lattice, \( q \) is in the first Brillouin zone and \( G \) is a reciprocal lattice vector.

It is equivalent to write

\[ V(r, \omega) = \sum_{q} V(r, q, \omega) e^{i q \cdot r} \]

where \( V(r; q, \omega) = \sum_{G} V(q + G, \omega) e^{i G \cdot r} \) is a periodic function, with respect to the Bravais lattice.
Macroscopic average

For a **monocromatic** field with wavevector $\mathbf{q}$

Spatial average over a unit cell:

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

$$ = e^{i\mathbf{q} \cdot \mathbf{R}} \frac{1}{\Omega} \int d\mathbf{r} \sum_{\mathbf{G}} V(\mathbf{q} + \mathbf{G}, \omega) e^{i \cdot \mathbf{G} \cdot \mathbf{r}} $$

$$ = e^{i\mathbf{q} \cdot \mathbf{R}} V(\mathbf{q} + \mathbf{0}, \omega) $$

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

A simple example

\[ \nu_{\text{ext}}(\mathbf{q} + \mathbf{G}, \omega) = \sum_{\mathbf{G}'} \epsilon_{\mathbf{GG}'}(\mathbf{q}, \omega) \nu_{\text{tot}}(\mathbf{q} + \mathbf{G}', \omega) \]

\( \nu_{\text{ext}} \) is a macroscopic quantity: \( \nu_{\text{ext}}(\mathbf{q} + \mathbf{G}, \omega) = \nu_{\text{ext}}(\mathbf{q}, \omega) \delta_{\mathbf{G}0} \)

This is not the case for \( \nu_{\text{tot}}(\mathbf{q} + \mathbf{G}, \omega) \).

Macroscopic average of \( \nu_{\text{ext}} \)

\[ \nu_{\text{ext}}(\mathbf{q}, \omega) = \sum_{\mathbf{G}'} \epsilon_{\mathbf{0G}'}(\mathbf{q}, \omega) \nu_{\text{tot}}(\mathbf{q} + \mathbf{G}', \omega) \]

\[ \neq \epsilon_{\mathbf{00}}(\mathbf{q}, \omega) \nu_{\text{tot}}(\mathbf{q}, \omega) \]

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

A simple example

We have also the relation

\[ v_{\text{tot}}(q + G, \omega) = \sum_{G'} \epsilon^{-1}_{GG'}(q, \omega) v_{\text{ext}}(q + G', \omega) \]

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

Macroscopic average of \( v_{\text{tot}} \)

\( v_{\text{ext}} \) is macroscopic \( \Rightarrow \)

\[ v_{\text{tot}}(q + G, \omega) = \epsilon^{-1}_{G0}(q, \omega) v_{\text{ext}}(q, \omega) \]

\[ v_{\text{tot}}(q, \omega) = \epsilon^{-1}_{00}(q, \omega) v_{\text{ext}}(q, \omega) \]

\[ v_{\text{ext}}(q, \omega) = \epsilon_{M}(q, \omega) v_{\text{tot}}(q, \omega) \Rightarrow \epsilon_{M}(q, \omega) = \frac{1}{\epsilon^{-1}_{00}(q, \omega)} \]
We have defined **microscopic** and **macroscopic** fields.

*Microscopic quantities have to be averaged to be compared to experiments.*

The dielectric function also has a **microscopic** expression and its **macroscopic** counterpart.

\[
\epsilon_M(q) = \frac{1}{\epsilon^{-1}_{00}(q)}
\]

- **Absorption** ↔ \( \text{Im} \{ \epsilon_M \} \) and **EELS** ↔ \(-\text{Im} \left\{ \frac{1}{\epsilon_M} \right\}\)
Macrosopic dielectric function

Question

\( \varepsilon_{00} \) is not the macroscopic dielectric function.
What is it then?

Answer

\( \varepsilon_{00} \) is the macroscopic dielectric function without crystal local fields.
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.

This issue will be addressed in the next lectures!!!
<table>
<thead>
<tr>
<th>Outline</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Starting point: Maxwell’s equations</td>
</tr>
<tr>
<td>2. Averaging procedure</td>
</tr>
<tr>
<td>3. Macroscopic dielectric function in cubic crystals</td>
</tr>
<tr>
<td>4. Dielectric tensor for non-cubic symmetries</td>
</tr>
<tr>
<td>5. Summary</td>
</tr>
</tbody>
</table>
Dielectric tensor for cubic symmetries

Macroscopic fields

\( \mathbf{q} \) defines the direction for the propagation: we assume \( \mathbf{q} \parallel \mathbf{x} \)

Longitudinal fields

\( \mathbf{E} \parallel \mathbf{q} \)

Coulomb gauge: \( \nabla \cdot \mathbf{A} = 0 \Rightarrow \)

Poisson equation: \( \nabla^2 \nu_{\text{ext}} = 4\pi \rho_{\text{ext}} \)

Transverse fields

\( \mathbf{E} \perp \mathbf{q} \)

Optical spectroscopy

Electrostatic interaction

Photons

EELS

Microscopic-Macroscopic connection
Dielectric tensor for cubic symmetries

Properties - Macroscopic quantities

Electric displacement $\mathbf{D}(\mathbf{q}, \omega) = \mathbf{\epsilon}^M(\mathbf{q}, \omega) \mathbf{E}^{\text{tot}}(\mathbf{q}, \omega)$

No symmetry

$$\mathbf{\epsilon}^M(\mathbf{q}, \omega) = \begin{pmatrix}
\epsilon_{LL} & \epsilon_{xy} & \epsilon_{xz} \\
\epsilon_{yx} & \epsilon_{yy} & \epsilon_{yz} \\
\epsilon_{zx} & \epsilon_{zy} & \epsilon_{zz}
\end{pmatrix}$$

Cubic symmetry

$$\mathbf{\epsilon}^M(\mathbf{q}, \omega) = \begin{pmatrix}
\epsilon_{LL} & 0 & 0 \\
0 & \epsilon_{TT} & 0 \\
0 & 0 & \epsilon_{TM}
\end{pmatrix}$$

Macroscopic quantities only:
A longitudinal perturbation induces a longitudinal response
A transverse perturbation induces a transverse response
Dielectric tensor for cubic symmetries

Longitudinal and transverse components

\[ \varepsilon_{LL}^M = \frac{1}{1 + \frac{4\pi}{q^2} \chi_{\rho\rho}(q, \omega)} \]

\[ \varepsilon_{TT}^M = \ldots \text{more complicated}^* \ldots \]


Dielectric tensor for cubic symmetries

In the limit $q \rightarrow 0$

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

We finally reach a familiar result!
<table>
<thead>
<tr>
<th></th>
<th>Outline</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Starting point: Maxwell’s equations</td>
</tr>
<tr>
<td>2</td>
<td>Averaging procedure</td>
</tr>
<tr>
<td>3</td>
<td>Macroscopic dielectric function in cubic crystals</td>
</tr>
<tr>
<td>4</td>
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</tr>
<tr>
<td>5</td>
<td>Summary</td>
</tr>
</tbody>
</table>
Non-Cubic symmetries

Properties - Macroscopic quantities

\[ \mathbf{D}(q, \omega) = \mathbf{\epsilon}_M(q, \omega) \mathbf{E}^{\text{tot}}(q, \omega) \]

\[ \mathbf{\epsilon}_M(q, \omega) = \begin{pmatrix}
\epsilon_{LL}^M & \epsilon_{LT}^M \\
\epsilon_{TL}^M & \epsilon_{TT}^M
\end{pmatrix} \]

Microscopic and macroscopic quantities

A **longitudinal** perturbation induces a **longitudinal** and a **transverse** response.
A **transverse** perturbation induces a **longitudinal** and a **transverse** response.
Non-Cubic symmetries

Dielectric tensor - General case

\[
\vec{\varepsilon}_M(q, \omega) = 1 + 4\pi \vec{\alpha}(q, q, \omega) \left[ 1 + 4\pi \frac{q}{q_1} \vec{\alpha}(q, q, \omega) \right]
\]

COMPLICATED! But one can show that the relation

\[
\varepsilon_{LL}^M = \frac{1}{1 + \frac{4\pi}{q} \chi_{\rho \rho}(q, \omega)}
\]

holds also for the non-cubic symmetries.

Non-cubic symmetries - Principal axis

Principal axis

In the limit \( q \to 0 \), one can find 3 axis \( n_1, n_2, n_3 \), defining a frame in which \( \epsilon_M \) is diagonal.

Applying a longitudinal field \( E^{\text{tot}}(q, \omega) \), parallel to one of these axis \( (q \parallel n_i) \) leads to

\[
\left\langle \epsilon \right\rangle_M(n_i, \omega) : E^{\text{tot}}(n_i, \omega) = \epsilon^{LL}_M(n_i, \omega)E^{\text{tot}}(n_i, \omega)
\]

Along these directions, a longitudinal perturbation induces a longitudinal response through the usual relation

\[
\lim_{q \to 0} \epsilon^{LL}_M(q, \omega) = \lim_{q \to 0} \frac{1}{1 + \frac{4\pi}{q^2} \chi_{\rho\rho}(q, \omega)}
\]
Non-cubic symmetries - Principal axis

Longitudinal and transverse dielectric functions

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

$$\epsilon^L_L(n_1, \omega), \epsilon^L_L(n_2, \omega) \text{ and } \epsilon^L_L(n_3, \omega)$$

Using the crystal symmetries, they can be used to define also the transverse dielectric functions (depending on the symmetry)

The full dielectric tensor for $\mathbf{q} \neq 0$ will not be addressed here!
Dielectric tensor for non-cubic symmetries

In conclusion, in the limit $q \to 0$

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

can also be true for non-cubic symmetries, provided that the correct reference frame is chosen and symmetries are used.
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Summary

- The key quantity is the \((\text{microscopic} \text{ and } \text{macroscopic})\) dielectric tensor.
- Relation between \textit{microscopic} and \textit{macroscopic} fields through averages.
- For \textit{cubic} crystals, \textit{the longitudinal dielectric function defines entirely the optical response in the long wavelength limit}.
- The situation is not so simple for \textit{non-cubic} crystals.