Theoretical Spectroscopy
relating theory and experiment

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# Outline

1. **Spectroscopy**

2. **Starting point: Maxwell’s equations**

3. **Averaging procedure**

4. **Macroscopic dielectric function in cubic crystals**

5. **Macroscopic dielectric tensor for non-cubic symmetries**

6. **Summary**
Outline

1 Spectroscopy

2 Starting point: Maxwell’s equations

3 Averaging procedure

4 Macroscopic dielectric function in cubic crystals

5 Macroscopic dielectric tensor for non-cubic symmetries

6 Summary
How to relate macroscopic and microscopic world?
Energy range

Energy Level Transition
Nuclear and electron spin
Molecular rotations
Molecular vibrations
Valence electrons
Middle-shell electrons
Inner-shell electrons
Nuclear

Energy
Joules

Wavelength
nm

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

Theoretical spectroscopy
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Energy range

Theoretical spectroscopy

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Scattering

- Elastic Scattering: $E_i = E_f$
- Inelastic Scattering: $E_i \neq E_f$
Scattering

**Elastic Scattering**

- The **differential cross section** is defined by the probability to observe a scattered particle into a solid angle unit if the target is irradiated by a flux of one particle by surface unit:

\[
\frac{d\sigma}{d\Omega} = \frac{\text{Scattered flux} / \text{Unit of solid angle}}{\text{Incident flux} / \text{Unit of surface}}
\]

**Inelastic Scattering**

- The **double differential cross section** \(\frac{d^2\sigma}{d\Omega dE}\) is defined as the differential cross section within an energy range unit.
Electronic excitations:

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

Creation of an electron-hole pair
Absorption

Beer’s law:

\[ I(x) = I_0 e^{-\alpha_a x} \]

\[ \alpha_a(\omega) \propto \sigma(\omega) \]

\[ \alpha_a(\omega) \leftrightarrow \text{Im} \{\varepsilon(\omega)\} \propto \text{Im} \{\alpha(\omega)\} \]
Absorption

Lautenschlager et al., PRB 36, 4821 (1987)
Electron scattering
Electron scattering
Electron scattering

LEED elastic peak

0 5000 eV
Electron scattering

HREELS

meV

0

5000 eV
Electron scattering
Electron scattering
Electron scattering
X-ray scattering
X-ray scattering

Energy Loss Function

\[ \frac{d^2 \sigma}{d\Omega dE} \propto \text{Im} \left\{ \varepsilon^{-1} \right\} \]

Weisser et al., PRL 97, 237602 (2006)
Photo-emission spectroscopy

UPS, XPS, ARPES

Photoemission spectra ↔ density of states
(careful with strongly interacting electrons)
Photo-emission spectroscopy

Investigation of **occupied bands**
Spectroscopy: Photo-emission Spectroscopy

Zhou et al., PRB 71, 161403 (2005)
Inverse photo-emission spectroscopy

ARIPES
Inverse photo-emission spectroscopy

Investigation of empty bands
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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 magnetic 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

\[ \nabla \cdot \mathbf{E}(r, t) = 4\pi \rho_{\text{ind}}(r, t) + 4\pi \rho_{\text{ext}}(r, t) \]

\[ \nabla \cdot \mathbf{B}(r, t) = 0 \]

\[ \nabla \times \mathbf{E}(r, t) = -\frac{1}{c} \frac{\partial \mathbf{B}(r, t)}{\partial t} \]

\[ \nabla \times \mathbf{B}(r, t) = \frac{4\pi}{c} \left[ j_{\text{ind}}(r, t) + j_{\text{ext}}(r, t) \right] + \frac{1}{c} \frac{\partial \mathbf{E}(r, t)}{\partial t} \]

\[ \rho_{\text{ext}}, j_{\text{ext}} = \text{external (or free) charges and currents} \]

\[ \rho_{\text{ind}}, j_{\text{ind}} = \text{induced (or bound) charges and currents} \]
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: \( \nabla \cdot \mathbf{j}_{\text{ext}} + \frac{\partial \rho_{\text{ext}}}{\partial t} = 0 \)
Constitutive relations

In the linear response regime, for an isotropic medium:

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

- electric permittivity \( \chi_e \)
- dielectric function \( \epsilon \)
- magnetic susceptibility \( \chi_m \)
- magnetic permeability \( \mu \)
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: \( \delta \rho(r, t) = \int dt' \int dr' \chi_{\rho \rho}(r, t, r', t') v_{\text{ext}}(r', t') \)

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

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

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

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

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

\[
\alpha_a = \frac{\omega \epsilon_2}{\nu c}
\]

(related to the optical skin depth \( \delta = 2/\alpha_a \)).
Which quantities are measured?

Reflectivity

Normal incidence reflectivity:

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

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

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

Photoabsorption cross section

Remind: \( \delta \rho(r, \omega) = \int d\mathbf{r}' \chi(r, \mathbf{r}', \omega) \nu_{\text{ext}}(\mathbf{r}', \omega) \)

\[
\sigma_{\text{ph}}(\omega) = -\frac{4\pi \omega}{c} \text{Im} \{ \alpha(\omega) \} = -\frac{4\pi \omega}{c} \text{Im} \left\{ \int d\mathbf{r} \int d\mathbf{r}' z \chi(\mathbf{r}, \mathbf{r}', \omega) z' \right\}
\]

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

\[
\sigma_{\text{ph}}(\omega) = \frac{4\pi \omega}{c \kappa_0} \text{Im} \left\{ \int d\mathbf{r} z \delta \rho(\mathbf{r}, \omega) \right\}
\]
Which quantities are measured?

Energy loss by a fast charged particle

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

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

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

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

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

$$v_{\text{tot}}(q, \omega) = \left[ 1 + \frac{4\pi}{q^2} \chi(q, \omega) \right] v_{\text{ext}}(q, \omega) = \epsilon^{-1}(q, \omega) v_{\text{ext}}(q, \omega)$$
Energy loss by a fast charged particle

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

The total electric field is $\mathbf{E}_{\text{tot}}(r, t) = -\nabla_r \mathbf{v}_{\text{tot}}(r, t)$.

The energy lost by the electron in unit time is

$$\frac{dW}{dt} = \int d\mathbf{r} j \cdot \mathbf{E}_{\text{tot}}$$

with the current density $j = -e\mathbf{v}\delta(r - vt)$, yielding

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

We define loss function $-\text{Im} \left\{ \frac{1}{\epsilon(q, \omega)} \right\}$.
Which quantities 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

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

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

Typical values:
- \( a_{\text{cell}} \approx 0.5 \text{ nm} \)
- \( 400 \text{ nm} \leq \lambda \leq 800 \text{ nm} \) (visible)

### Microscopic quantities

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

⇒ Large and irregular fluctuations over the atomic scale.

#### Example

- \( E_{\text{tot}}(r, t), j_{\text{ind}}(r, t), \rho_{\text{ind}}(r, t), \ldots \)

- \( E_{\text{ext}}(r, t), A_{\text{ext}}(r, t), v_{\text{ext}}(r, t), \ldots \)
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 the 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

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

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

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

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

For a monochromatic field with wavevector \( \mathbf{q} \), the spatial average over a unit cell is:

\[
V(R, \omega) = \langle V(r; q, \omega) \rangle_R e^{i \mathbf{q} \cdot R} \\
= e^{i \mathbf{q} \cdot R} \frac{1}{\Omega} \int d\mathbf{r} \sum_{\mathbf{G}} V(\mathbf{q} + \mathbf{G}, \omega) e^{i \mathbf{G} \cdot \mathbf{r}} \\
= e^{i \mathbf{q} \cdot R} V(\mathbf{q} + \mathbf{0}, \omega)
\]

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

A simple example

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

\( \nu_{\text{ext}} \) is a macroscopic quantity: \( \nu_{\text{ext}}(q + G, \omega) = \nu_{\text{ext}}(q, \omega) \delta_{G0} \)

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

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

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

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

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

Macroscopic average of $v_{tot}$

We have also the relation

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

$v_{ext}$ is macroscopic $\Rightarrow$ $v_{tot}(q + G, \omega) = \epsilon^{-1}_{G0}(q, \omega) v_{ext}(q, \omega)$

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

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

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

Question
Is the macroscopic averaging always meaningful?

Answer
- If the external applied field has a very short wavelength 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.

This issue will be addressed in the next lecture!
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:

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

- Absorption \( \leftrightarrow \) \( \text{Im} \{\epsilon_M\} \) and EELS \( \leftrightarrow \) \(-\text{Im} \left\{ \frac{1}{\epsilon_M} \right\} \)
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Dielectric tensor for cubic symmetries

**Macroscopic fields**

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

**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 field**

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 \textit{longitudinal} and \textit{transverse} components

\[ \mathbf{V}(q) = \mathbf{V}^L(q) + \mathbf{V}^T(q), \]

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

In terms of transverse and longitudinal components:

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

\[
\begin{pmatrix}
D^L \\
D^T
\end{pmatrix}
= \begin{pmatrix}
\epsilon_{LL}^M & \epsilon_{LT}^M \\
\epsilon_{TL}^M & \epsilon_{TT}^M
\end{pmatrix}
\begin{pmatrix}
E^L \\
E^T
\end{pmatrix}
\]
Dielectric tensor for cubic symmetries

**Question**

How can we make the link between

- the *microscopic* dielectric tensor

\[
D(q + G, \omega) = \sum_{G'} \langle \epsilon(q + G, q + G', \omega) \rangle E^{tot}(q + G', \omega)
\]

- and the *macroscopic* dielectric tensor

\[
D(q, \omega) = \langle \epsilon_M(q, \omega) \rangle E^{tot}(q, \omega)
\]
Dielectric tensor for cubic symmetries

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

No symmetry

\[ \overleftrightarrow{\epsilon}_M(\mathbf{q}, \omega) = \begin{pmatrix} \epsilon^{LL} & \epsilon^{xy} & \epsilon^{xz} \\ \epsilon^{yx} & \epsilon^{yy} & \epsilon^{yz} \\ \epsilon^{zx} & \epsilon^{zy} & \epsilon^{zz} \end{pmatrix} \]

Cubic symmetry

\[ \overleftrightarrow{\epsilon}_M(\mathbf{q}, \omega) = \begin{pmatrix} \epsilon^{LL} & 0 \\ 0 & \epsilon^{TT} \end{pmatrix} \]

Macroscopic quantities only:
A longitudinal perturbation induces a longitudinal response
A transverse perturbation induces a transverse response
Cubic symmetries with $q \to 0$

**Longitudinal dielectric function**

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

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

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

**Transverse dielectric function**

$$\lim_{q \to 0} \epsilon_{TT}^M(q, \omega) = \epsilon_{LL}^M(\omega)$$
Cubic symmetries with $q \to 0$

In the limit $q \to 0$

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

Dielectric tensor

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

$$\epsilon_{M}(\omega) = \epsilon_{LL}^M(\omega)$$

We finally reach the familiar result!
Cubic symmetries with $q \neq 0$

**Longitudinal dielectric function**

One can show that the relation

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

holds also when $q \neq 0$.

**Transverse dielectric function and mixed components**

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

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

There is no easy way to compute these elements of the dielectric tensor. Further approximations are needed.
Cubic symmetries

Summary

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

- In the long wavelength limit ($q \to 0$) only a **scalar** dielectric function is needed:

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

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


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Non-Cubic symmetries

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

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

Even for \( q \to 0 \):

A longitudinal perturbation induces a longitudinal and a transverse response.

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

In the general case:

\[
\varepsilon_M(q, \omega) = 1 + 4\pi \tilde{\alpha}(q, q, \omega) \left[ 1 + 4\pi \frac{q}{q} \frac{q \cdot \tilde{\alpha}(q, q, \omega)}{1 - 4\pi \tilde{\alpha}_{LL}(q, q, \omega)} \right]
\]

COMPLICATED! But one can show that the relation

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

holds also for the non-cubic symmetries.

Non-Cubic symmetries

\( \vec{\tilde{\alpha}} \) is the quasi-polarizability:

\[
j_{\text{ind}}(q + G, \omega) = \sum_{G'} \vec{\tilde{\alpha}}(q + G, q + G', \omega) E_{\text{pert}}(q + G', \omega)
\]  \hspace{1cm} (1)

and for the longitudinal component one can write:

\[
\tilde{\alpha}^{LL}(q, q, \omega) = -\frac{1}{q^2} \chi_{\rho\rho}(q, \omega).
\]

Non-cubic symmetries for $q \to 0$

It can be proved that $\epsilon_M$ is an analytic function of $q$, then the limit $q \to 0$ does not depend on the direction of $q \Rightarrow \overrightarrow{\epsilon}_M(\omega)$

**Principal axes**

One can find 3 axes $n_1, n_2, n_3$ defining a frame in which $\overrightarrow{\epsilon}_M$ is diagonal. Applying a field $E^{tot}(q, \omega)$ parallel to one of these axes $n_i$ leads to

$$\overrightarrow{\epsilon}_M(n_i, \omega) : E^{tot}(n_i, \omega) = \epsilon_i(\omega)E^{tot}(n_i, \omega)$$

whatever the direction of $q$.

In particular, a longitudinal perturbation induces a longitudinal response:

$$\epsilon_i(\omega) = \epsilon^{LL}_M(n_i, \omega)$$

But the relation can also be used for a transverse dielectric function!
For \( \mathbf{q} \to 0 \), we have defined three quantities:

\[
\epsilon_{LL}^M(\mathbf{n}_1, \omega) , \quad \epsilon_{LL}^M(\mathbf{n}_2, \omega) , \quad \epsilon_{LL}^M(\mathbf{n}_3, \omega)
\]

with

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

Along the principal axes

For \( \mathbf{q} \to 0 \):

A **longitudinal** perturbation induces a **longitudinal** response.

A **transverse** perturbation induces a **transverse** response.
Non-cubic symmetries

Summary

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

- Using the crystal symmetries one can find the principal axes.
- The optical properties can be deduced from a longitudinal calculation.
- Keep in mind that the principal frame is not always orthogonal and for an arbitrary orientation of the field it is necessary to calculate the full tensor.
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Theoretical spectroscopy

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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.