

Microscopic-Macroscopic connection

relating experiment and theory

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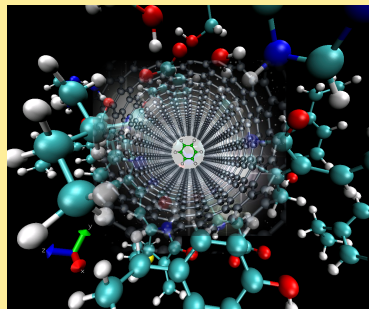
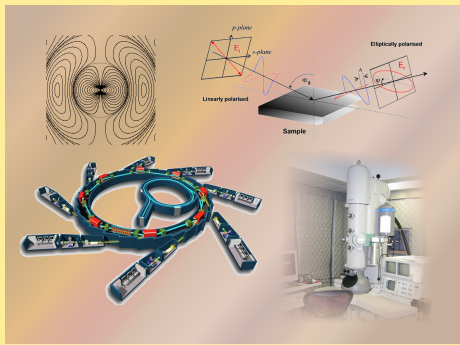
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June 27, 2007 – Queen's University, Belfast



How to relate macroscopic and microscopic world?



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

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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 electric 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

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

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

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

$$\nabla \times \mathbf{B}(\mathbf{r}, t) = \frac{4\pi}{c} (\mathbf{j}_{\text{ind}}(\mathbf{r}, t) + \mathbf{j}_{\text{ext}}(\mathbf{r}, t)) + \frac{1}{c} \frac{\partial \mathbf{E}(\mathbf{r}, t)}{\partial t}$$

- $\rho_{\text{ext}}, \mathbf{j}_{\text{ext}}$ = 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

$$\nabla \cdot \mathbf{D}(\mathbf{r}, t) = 4\pi\rho_{\text{ext}}(\mathbf{r}, t)$$

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

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

$$\nabla \times \mathbf{H}(\mathbf{r}, t) = \frac{4\pi}{c} \mathbf{j}_{\text{ext}}(\mathbf{r}, t) + \frac{1}{c} \frac{\partial \mathbf{D}(\mathbf{r}, t)}{\partial t}$$

- $\rho_{\text{ext}}, \mathbf{j}_{\text{ext}}$ = 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:

$$\mathbf{P} = \chi_e \mathbf{E}$$

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

$$\mathbf{M} = \chi_m \mathbf{H}$$

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

- electric permittivity χ_e
- dielectric function ϵ
- magnetic susceptibility χ_m
- magnetic permeability μ

Linear response

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: $\delta\rho(\mathbf{r}, t) = \int dt' \int d\mathbf{r}' \chi(\mathbf{r}, t, \mathbf{r}', t') v_{\text{ext}}(\mathbf{r}', t')$

Which quantities are measured?

Absorption coefficient

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

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

ν and κ are the refraction index and the extinction coefficient and they are related to the dielectric constant as

$$\epsilon_1 = \nu^2 - \kappa^2 \quad \epsilon_2 = 2\nu\kappa$$

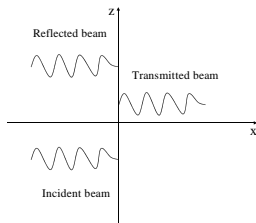
The absorption coefficient α is the inverse distance where the intensity of the field is reduced by 1/e:

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

(related to the optical skin depth δ).

Which quantities are measured?

Schematic diagram



Reflectivity

Normal incidence reflectivity:

$$R = \left| \frac{\mathbf{E}_T}{\mathbf{E}_i} \right|^2 < 1$$

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

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

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

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

$$\sigma_{\text{ph}}(\omega) = \frac{4\pi\omega}{c\kappa_0} \text{Im} \int d\mathbf{r} z \delta\rho(\mathbf{r}, \omega)$$

Which quantities are measured?

Example: Energy loss by a fast charged particle

Given an external charge density ρ_{ext} , one can obtain the external potential v_{ext}

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

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

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

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

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

Which quantities are measured?

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

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

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

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

with the current density $\mathbf{j} = -e\mathbf{v}\delta(\mathbf{r} - \mathbf{v}t)$. We get

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

$-\text{Im} \left\{ \frac{1}{\epsilon(\mathbf{k}, \omega)} \right\}$ 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

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

Microscopic quantities

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

⇒ Large and irregular fluctuations over the atomic scale.

Example

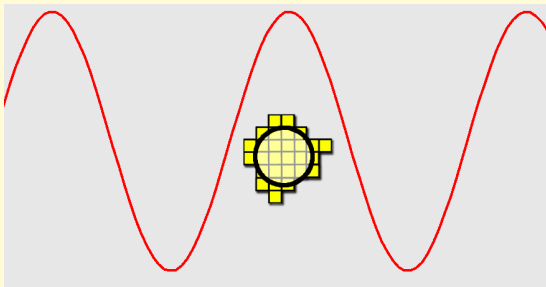
$$\mathbf{E}_{\text{tot}}(\mathbf{r}, t), \mathbf{j}_{\text{ind}}(\mathbf{r}, t), \rho_{\text{ind}}(\mathbf{r}, t), \dots$$

Macroscopic average

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.



Macroscopic 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

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

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

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

Macroscopic average

For a **monochromatic** field with wavevector \mathbf{q}

Spatial average over a unit cell:

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

The **macroscopic average** corresponds to the $\mathbf{G} = \mathbf{0}$ component.

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

Macroscopic average

A simple example

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

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

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

Macroscopic average of v_{ext}

$$v_{\text{ext}}(\mathbf{q}, \omega) = \sum_{\mathbf{G}'} \epsilon_{\mathbf{0}\mathbf{G}'}(\mathbf{q}, \omega) v_{\text{tot}}(\mathbf{q} + \mathbf{G}', \omega)$$

$$\neq \epsilon_{\mathbf{0}\mathbf{0}}(\mathbf{q}, \omega) v_{\text{tot}}(\mathbf{q}, \omega)$$

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

Macroscopic average

A simple example

We have also the relation

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

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

Macroscopic average of v_{tot}

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

$$v_{\text{tot}}(\mathbf{q}, \omega) = \epsilon_{\mathbf{0}\mathbf{0}}^{-1}(\mathbf{q}, \omega) v_{\text{ext}}(\mathbf{q}, \omega)$$

$$v_{\text{ext}}(\mathbf{q}, \omega) = \epsilon_M(\mathbf{q}, \omega) v_{\text{tot}}(\mathbf{q}, \omega) \Rightarrow \epsilon_M(\mathbf{q}, \omega) = \frac{1}{\epsilon_{\mathbf{0}\mathbf{0}}^{-1}(\mathbf{q}, \omega)}$$

Macroscopic average

Summary

- We have defined **microscopic** and **macroscopic** fields
- *Microscopic quantities have to be averaged to be compared to experiments*
- The dielectric function also has a **microscopic** expression and its **macroscopic** counterpart

$$\epsilon_M(\mathbf{q}) = \frac{1}{\epsilon_{00}^{-1}(\mathbf{q})}$$

- *Absorption* $\leftrightarrow \text{Im} \{ \epsilon_M \}$ and *EELS* $\leftrightarrow -\text{Im} \left\{ \frac{1}{\epsilon_M} \right\}$

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**.

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!!!

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Dielectric tensor for cubic symmetries

Macroscopic fields

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

Longitudinal fields

$$\mathbf{E} \parallel \mathbf{q}$$

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

Poisson equation: $\nabla^2 v_{\text{ext}} = 4\pi\rho_{\text{ext}}$

EELS

Electrostatic interaction

Transverse fields

$$\mathbf{E} \perp \mathbf{q}$$

Optical spectroscopy

Photons

Dielectric tensor for cubic symmetries

Properties - Macroscopic quantities

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

No symmetry

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

Cubic symmetry

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

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

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

$$\epsilon_M^{TT} = \dots \text{ more complicated}^* \dots$$



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

Dielectric tensor for cubic symmetries

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

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

We finally reach a familiar result!

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Non-Cubic symmetries

Properties - Macroscopic quantities

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

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

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

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

COMPLICATED! But one can show that the relation

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

holds also for the **non-cubic** symmetries.



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

Non-cubic symmetries - Principal axis

Principal axis

In the limit $\mathbf{q} \rightarrow 0$, one can find 3 axis $\mathbf{n}_1, \mathbf{n}_2, \mathbf{n}_3$, defining a frame in which ϵ_M is diagonal.

Applying a longitudinal field $\mathbf{E}^{tot}(\mathbf{q}, \omega)$, parallel to one of these axis ($\mathbf{q} \parallel \mathbf{n}_i$) leads to

$$\overleftrightarrow{\epsilon}_M(\mathbf{n}_i, \omega) : \mathbf{E}^{tot}(\mathbf{n}_i, \omega) = \epsilon_M^{LL}(\mathbf{n}_i, \omega) \mathbf{E}^{tot}(\mathbf{n}_i, \omega)$$

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

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

Non-cubic symmetries - Principal axis

Longitudinal and transverse dielectric functions

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

$$\epsilon_M^{LL}(\mathbf{n}_1, \omega), \epsilon_M^{LL}(\mathbf{n}_2, \omega) \text{ and } \epsilon_M^{LL}(\mathbf{n}_3, \omega)$$

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

The full dielectric tensor for $q \neq 0$ will not be addressed here!

Dielectric tensor for non-cubic symmetries

In conclusion, in the limit $\mathbf{q} \rightarrow 0$

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

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