Microscopic-macroscopic connection

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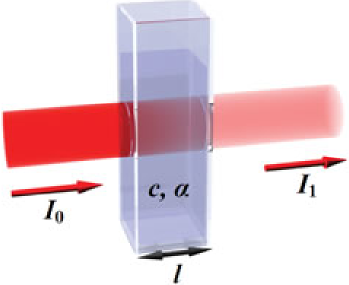
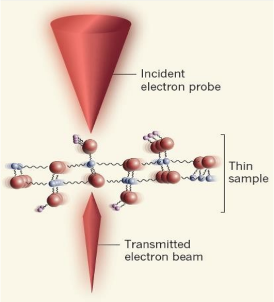
Motivation

We want to describe experimental observables, such as absorption spectroscopy, electron energy loss spectroscopy (EELS),....

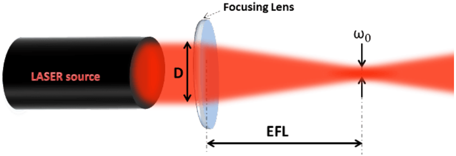




Experiments: macroscopical world

An experiment always measures averaged quantities over large distances compared to interatomic distances:

- Spot sizes are typically on the order of micrometers
- Wavelength of Ti:sapphire laser is 780nm
- Sample thickness ranges from a few nanometers to several millimeters



Quick estimate: $1\mu m$ spot size $\sim 4\times 10^6$ unit cells of Si (a$\sim 5\mathring{A}$).

Perturbation theory

- Only small perturbations (no strong-field interaction).
- The response can be expanded in powers of the perturbation.

Example: induced polarization in term of electric field

$$P_i = \sum_j \chi^{(1)}_{ij} E_j + \sum_{jk} \chi^{(2)}_{ijk} E_j E_k + \sum_{jkl} \chi^{(3)}_{ijkl} E_j E_k E_l + \dots$$

We consider only first order (linear response): the response is proportional to the perturbation.

Example: the response function $\chi^{(1)}$ describes the link between a perturbation V and the density response

$$n^{(1)}(\mathbf{r},t) = \int dt' \int d\mathbf{r} \chi^{(1)}_{ij}(\mathbf{r},\mathbf{r}',t,t') V(\mathbf{r}',t').$$

Dielectric function as key quantity

For optical linear response, the dielectric function ($\epsilon = \epsilon_1 + i\epsilon_2$) is the key quantity

The refractive index ν and extinction coefficient κ are related to the dielectric function

$$\epsilon_1 = \nu^2 - \kappa^2, \qquad \epsilon_2 = 2\nu\kappa.$$

Absorption coefficient α is the inverse distance over which intensity drops by a factor of $1/e$

$$\alpha = \frac{2\omega\kappa}{c} = \frac{\omega\epsilon_2}{\nu c}.$$

Reflection coefficient R at normal incidence

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

Energy loss by a fast particle

$$\frac{dW}{dt} = \int d^3\mathbf{r}\mathbf{j}.\,\mathbf{E}_{\text{tot}} = -\frac{e^2}{\pi^2}\int \frac{d^3\mathbf{r}}{k^2}\mathfrak{Im}\Big\{\frac{\omega}{\epsilon(\mathbf{k},\omega)}\Big\}.$$

Dielectric function as key quantity

The measured dielectric tensor is defined by the relation

$$\mathbf{D}_M(\omega) = \overset{\leftrightarrow}{\epsilon}_M(\omega)\mathbf{E}_M(\omega),$$

where $\mathbf{E}_M$ is the total *macroscopic* electric field.

Macroscopic quantity: does not depend on space.

From TDDFT, we can get:

$$\mathbf{D}(\mathbf{r},\omega) = \int d^3\mathbf{r}' \, \overset{\leftrightarrow}{\epsilon}(\mathbf{r},\mathbf{r}',\omega)\mathbf{E}(\mathbf{r},\omega).$$

This dielectric tensor is a *microscopic* quantity.

How to relate these two quantities?

Answer: macroscopic averaging

Maxwell's equations in matter

Maxwell equations reads in real space by

$$\boxed{\begin{aligned}
&\boldsymbol{\nabla}.\mathbf{D}(\mathbf{r},t) = 4\pi\rho(\mathbf{r},t), && \boldsymbol{\nabla}\times\mathbf{H}(\mathbf{r},t) - \frac{1}{c}\frac{\partial\mathbf{D}}{\partial t}(\mathbf{r},t) = \frac{4\pi}{c}\mathbf{J}(\mathbf{r},t),\\
&\boldsymbol{\nabla}.\mathbf{B}(\mathbf{r},t) = 0, && \boldsymbol{\nabla}\times\mathbf{E}(\mathbf{r},t) + \frac{1}{c}\frac{\partial\mathbf{B}}{\partial t}(\mathbf{r},t) = 0.
\end{aligned}}$$

$\mathbf{D}$ and $\mathbf{H}$: electric displacement and magnetic field.
Constitutive relations connecting $\mathbf{E}$ and $\mathbf{B}$ to $\mathbf{D}$ and $\mathbf{H}$:

$$\mathbf{D}(\mathbf{r},t) = \mathbf{E}(\mathbf{r},t) + 4\pi\mathbf{P}(\mathbf{r},t), \qquad \mathbf{H}(\mathbf{r},t) = \mathbf{B}(\mathbf{r},t) - 4\pi\mathbf{M}(\mathbf{r},t),$$

where $\mathbf{P}$ and $\mathbf{M}$ are respectively the *polarization* and *magnetization*.

Electric field in TDDFT/Maxwell's equations

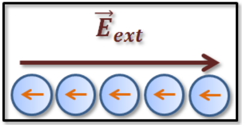
Question: which electric field is considered in Maxwell's equations and in TDDFT?

Local field effects

Applying an external electric field $\mathbf{E}_{\text{ext}}$ to a dielectric material → electric dipoles are created at a microscopic level.

Responsible for the appearance of an induced field $\mathbf{E}^{\text{ind}}$.

Total electric field felt by electrons is microscopic: $\mathbf{E} = \mathbf{E}^{\text{ext}} + \mathbf{E}^{\text{ind}}$.



Effects due to

- presence of the induced field
- density fluctuations
- any kind of microscopic inhomogeneities

must be taken into account.

These effects are often referred in solids as the *local-field effects*.

Macroscopic averaging

We now consider perfectly periodic crystals.
The unit of repetition is the unit cell.

If $\mathbf{R}$ is a translation from one unit cell to the next one, a periodic function fulfills

$$V(\mathbf{r} + \mathbf{R}; \omega) = V(\mathbf{r}; \omega)$$

In Fourier space this means that

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

where $\mathbf{G}$ are reciprocal lattice vectors.

Macroscopic averaging

Spatial average over a unit cell at $\mathbf{R}$ of a periodic function:

$$\begin{aligned} V(\mathbf{R};\omega) &= \langle V(\mathbf{r};\omega)\rangle \\ &= \frac{1}{\Omega}\int_\Omega \sum_{\mathbf{q},\mathbf{G}} V(\mathbf{q}+\mathbf{G};\omega)e^{i(\mathbf{q}+\mathbf{G}).\mathbf{r}} \quad (1) \\ &= \sum_{\mathbf{q}} V(\mathbf{q};\omega)e^{i(\mathbf{q}).\mathbf{r}} \quad (2) \end{aligned}$$

Macroscopic average corresponds to the component $\mathbf{G} = 0$.
Wave vector truncation: elimination of all wavevectors outside of the first Brillouin zone.

Macroscopic averaging

Let's try!

We have

$$\mathbf{D}(\mathbf{r},\omega) = \mathbf{E}(\mathbf{r},\omega) + 4\pi\mathbf{P}(\mathbf{r},\omega)$$

and

$$\mathbf{D}(\mathbf{r},\omega) = \int d^3\mathbf{r}'\epsilon(\mathbf{r},\mathbf{r}',\omega)\mathbf{E}(\mathbf{r}',\omega),$$

The polarization is the response to the total electric field.
The response function is the polarizability α

$$\mathbf{P}(\mathbf{r},\omega) = 4\pi\int d^3\mathbf{r}'\alpha(\mathbf{r},\mathbf{r}',\omega)\mathbf{E}(\mathbf{r}',\omega)$$

So

$$\mathbf{D}(\mathbf{r},\omega) = \mathbf{E}(\mathbf{r},\omega) + 4\pi\int d^3\mathbf{r}'\alpha(\mathbf{r},\mathbf{r}',\omega)\mathbf{E}(\mathbf{r}',\omega)$$

Macroscopic averaging

In Fourier space, this reads

$$\mathbf{D}(\mathbf{q}+\mathbf{G},\omega) = \mathbf{E}(\mathbf{q}+\mathbf{G},\omega) + 4\pi\sum_{\mathbf{G}'}\alpha(\mathbf{q}+\mathbf{G},\mathbf{q}+\mathbf{G}',\omega)\mathbf{E}(\mathbf{q}+\mathbf{G}',\omega)$$

Doing directly the macroscopic average

$$\mathbf{D}_M(\mathbf{q},\omega) = \mathbf{E}_M(\mathbf{q},\omega) + 4\pi\sum_{\mathbf{G}'}\alpha(\mathbf{q},\mathbf{q}+\mathbf{G}',\omega)\mathbf{E}(\mathbf{q}+\mathbf{G}',\omega)$$

does not give access to the macroscopic dielectric function!

$$\mathbf{D}_M(\mathbf{q},\omega) = \epsilon_M(\mathbf{q},\omega)\mathbf{E}_M(\mathbf{q},\omega)$$

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

Macroscopic averaging

Alternative approach:

The longitudinal dielectric function is given by

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

Its inverse is

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

The external field is macroscopic $\mathbf{E}^{\text{ext}}(\mathbf{q}+\mathbf{G}',\omega) = \mathbf{E}_M^{\text{ext}}(\mathbf{q},\omega)\delta_{\mathbf{G}'\mathbf{0}}$
Therefore

$$\mathbf{E}_M^{\text{tot}}(\mathbf{q},\omega) = \epsilon^{-1}(\mathbf{q},\mathbf{q},\omega)\mathbf{E}_M^{\text{ext}}(\mathbf{q},\omega)$$

$$\boxed{\epsilon_M(\mathbf{q},\omega) = \frac{1}{\epsilon^{-1}(\mathbf{q},\mathbf{q},\omega)} \neq \epsilon(\mathbf{q},\mathbf{q},\omega)} \tag{3}$$

Short summary

The dielectric function is the key quantity to describe linear response spectroscopies.

From macroscopic averaging of Maxwell equations, we showed that we need to compute the microscopic inverse dielectric function ϵ^{-1}

Dielectric matrix $\epsilon(\mathbf{q}+\mathbf{G},\mathbf{q}+\mathbf{G}',\omega)$ contains all the microscopic fluctuations of the field. We take the inverse and then the macroscopic average.

Interpretation: All microscopic components of the field couple together to produce the macroscopic response.

Next step

How to relate $\epsilon(\mathbf{q}+\mathbf{G},\mathbf{q}+\mathbf{G}',\omega)$ to response functions from TDDFT?

Longitudinal, transverse, and optical limit

Any vector field $\mathbf{E}$ can be decomposed into a longitudinal and a transverse part

$$\mathbf{E} = \mathbf{E}^L + \mathbf{E}^T$$

In real space, we have

$$\nabla \times \mathbf{E}^L = 0, \qquad \nabla . \mathbf{E}^T = 0$$

In reciprocal space

$$\begin{aligned} \mathbf{E}^L(\mathbf{k};\omega) &= \frac{\mathbf{k}}{k}\left(\mathbf{E}(\mathbf{k};\omega).\frac{\mathbf{k}}{k}\right), \\ \mathbf{E}^T(\mathbf{k};\omega) &= \mathbf{E}(\mathbf{k};\omega) - \mathbf{E}^L(\mathbf{k};\omega) = -\frac{\mathbf{k}}{k} \times \left(\frac{\mathbf{k}}{k} \times \mathbf{E}(\mathbf{k};\omega)\right). \end{aligned}$$

This is known as the Helmholtz decomposition.

Longitudinal, transverse, and optical limit

Dielectric tensor in the longitudinal-transverse basis

$$\overset{\leftrightarrow}{\epsilon}_M(\mathbf{q};\omega) = \begin{pmatrix} \epsilon_M^{LL}(\mathbf{q};\omega) & \epsilon_M^{LT}(\mathbf{q};\omega) \\ \epsilon_M^{TL}(\mathbf{q};\omega) & \epsilon_M^{TT}(\mathbf{q};\omega) \end{pmatrix}. \tag{4}$$

Equation of propagation of the electric field

$$|\mathbf{q}|^2\mathbf{E}^T(\mathbf{q};\omega) = \frac{\omega^2}{c^2}\overset{\leftrightarrow}{\epsilon}_M(\mathbf{q};\omega)\mathbf{E}(\mathbf{q};\omega), \tag{5}$$

$\mathbf{q}$ is the momentum of the photon.

Normal modes:

- Purely longitudinal field: condition of propagation of the plasmon, $\epsilon_M^{TL}(\mathbf{q};\omega) = 0$.
- Purely transverse electric field: dispersion relation of the photon, $|\omega^2\overset{\leftrightarrow}{\epsilon}{}_M^{TT}(\mathbf{q};\omega) - c^2q^2\overset{\leftrightarrow}{\mathbb{1}}| = 0$.

This yields the dispersion relation for transverse electromagnetic waves (photons) and longitudinal electromagnetic waves (plasmons).

Longitudinal, transverse, and optical limit

A photon is a transverse field, which cannot be represented by a scalar potential.

TDDFT can only deal with scalar potentials as perturbation.

Solution 1: Take the optical limit

Solution 2: Use Time-Dependent Current Density Functional Theory (TDCDFT)

Longitudinal, transverse, and optical limit

Optical limit (or long-wavelength limit, dipole approximation):
The scale of the variation of the field is very large compared to the characteristic size of the system.

Consequence: at any instant in time, the field can be considered uniform in the system.

Valid if $\lambda \to \infty$. Equivalent to the limit $\mathbf{q} \to 0$.

Quick estimate: If we take $a_0 \sim 0.5$nm as characteristic length scale, then $\lambda > 10a_0$ corresponds to photon energies below $22.5eV$.

Limitation

If the external field is not macroscopic, this does not work.
The averaging procedure has no meaning.

One needs another definition of the averaging, based on the statistical and quantum mechanical sense. (Beyond the scope of this lecture.)

Examples:

- x-ray spectroscopy (very short wavelength)
- EELS with atomic resolution

Optical limit for cubic materials

For cubic materials

$$\overset{\leftrightarrow}{\epsilon}_M(\mathbf{q};\omega) = \begin{pmatrix} \epsilon_M^{LL}(\mathbf{q};\omega) & 0 \\ 0 & \epsilon_M^{TT}(\mathbf{q};\omega) \end{pmatrix}.$$

Longitudinal perturbation induces a longitudinal response.
Transverse perturbation induces a transverse response.

In the optical limit

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

Knowledge of the longitudinal response to a longitudinal perturbation is enough!

This can be readily generalized to other symmetries, except monoclinic and triclinic.

Connecting with TDDFT

Approach by Del Sole and Fiorino[1].
Consider a perturbing field $\mathbf{E}^P$

$$\mathbf{E}^P = \mathbf{E}^{\text{ext}} + \mathbf{E}^{\text{ind},T} = \mathbf{E} - \mathbf{E}^{\text{ind},L},$$

Why? $\mathbf{E}^P$ is macroscopic !
One can show that

$$\mathbf{E}^T(\mathbf{q}+\mathbf{G};\omega) = \frac{\omega^2}{c^2|\mathbf{q}+\mathbf{G}|^2}\mathbf{D}^T(\mathbf{q}+\mathbf{G};\omega) \tag{6}$$

In the optical limit, $\frac{\omega^2}{c^2} \ll \frac{1}{|\mathbf{q}+\mathbf{G}|^2}$ for $\mathbf{G} \neq \mathbf{0}$.

Microscopic components of the transverse induced field are negligible in the optical limit.

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[1] Phys. Rev. B 29, 4631 (1984)

Connecting with TDDFT

Consider a perturbing field $\mathbf{E}^P = \mathbf{E} - \mathbf{E}^{\mathrm{ind},L}$.

Polarization is related to induced electric field via a quasi-polarizability $\overset{\leftrightarrow}{\tilde{\alpha}}$

$$\mathbf{P}(\mathbf{q}+\mathbf{G};\omega) = \sum_{\mathbf{G}'} \left[\overset{\leftrightarrow}{\tilde{\alpha}} (\mathbf{q};\omega)\right]_{\mathbf{G}\mathbf{G}'} \mathbf{E}^P(\mathbf{q}+\mathbf{G}';\omega)$$

$$\mathbf{E}^{\mathrm{ind}}(\mathbf{q};\omega) = -4\pi \mathbf{P}(\mathbf{q};\omega)$$

Combining these equations give

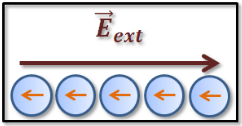
$$\mathbf{P}(\mathbf{q};\omega) = \left[\overset{\leftrightarrow}{\tilde{\alpha}} (\mathbf{q};\omega)\right]_{\mathbf{0}\mathbf{0}} \mathbf{E}(\mathbf{q};\omega) + 4\pi \left[\overset{\leftrightarrow}{\tilde{\alpha}} (\mathbf{q};\omega)\right]_{\mathbf{0}\mathbf{0}} \frac{\mathbf{q}}{q}\frac{\mathbf{q}}{q} \mathbf{P}(\mathbf{q};\omega).$$

Polarization on both sides: self-consistent equation

Connecting with TDDFT

Self consistent equation: directly linked to local-field effects

$$\begin{aligned}\mathbf{P}(\mathbf{q};\omega) &= \left[\overset{\leftrightarrow}{\tilde{\alpha}}(\mathbf{q};\omega)\right]_{\mathbf{00}}\mathbf{E}(\mathbf{q};\omega)\\ &\quad +4\pi\left[\overset{\leftrightarrow}{\tilde{\alpha}}(\mathbf{q};\omega)\right]_{\mathbf{00}}\frac{\mathbf{q}}{q}\frac{\mathbf{q}}{q}\mathbf{P}(\mathbf{q};\omega).\end{aligned}$$



After some algebra

$$\overset{\leftrightarrow}{\epsilon}_M(\mathbf{q};\omega) = \overset{\leftrightarrow}{\mathbb{1}} + 4\pi\left[\overset{\leftrightarrow}{\tilde{\alpha}}(\mathbf{q};\omega)\right]_{\mathbf{00}}\left[\overset{\leftrightarrow}{\mathbb{1}} + 4\pi\frac{\mathbf{q}}{q}\frac{\mathbf{q}}{q}\frac{\left[\overset{\leftrightarrow}{\tilde{\alpha}}(\mathbf{q};\omega)\right]_{\mathbf{00}}}{1-4\pi\left[\tilde{\alpha}^{LL}(\mathbf{q};\omega)\right]_{\mathbf{00}}}\right].$$

Connecting with TDDFT

We only need the longitudinal-longitudinal part

$$\epsilon_M^{LL}(\mathbf{q};\omega) = \frac{1}{1 - 4\pi\left[\tilde{\alpha}^{LL}(\mathbf{q};\omega)\right]_{\mathbf{00}}}$$

One can show that

$$\left[\tilde{\alpha}^{LL}(\mathbf{q};\omega)\right]_{\mathbf{00}} = -\frac{\left[\chi_{\rho\rho}(\mathbf{q};\omega)\right]_{\mathbf{00}}}{q^2}.$$

where $\chi_{\rho\rho}$ the density-density response function from TDDFT.

Putting everything together:

$$\boxed{\epsilon_M^{LL}(\mathbf{q};\omega) = \frac{1}{1 + 4\pi/q^2\left[\chi_{\rho\rho}(\mathbf{q};\omega)\right]_{\mathbf{00}}}.}$$

Link with quantum electrodynamics (QED)

In quantum electrodynamics,[2] both matter and photon field are quantized and treated within one Hamiltonian.

Taking the non-relativistic limit (Pauli-Fiertz Hamiltonian) and assuming no back-reaction of light on matter, one arrives at the coupled (self-consistent) Schrödinger-Maxwell equations.

Assuming linear response, one can further decouple Maxwell and Schrödinger equations.

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[2] Ruggenthaler, Tancogne-Dejean, Flick, Appel, Rubio, Nature Reviews Chemistry 2, 0118 (2018)

Comparison to Lorentz model

Classical model for the local-field correction.
The local field: sum of the applied external field and an induced field created by neighboring dipoles

$$\mathbf{E}^{\text{loc}}(\omega) = \mathbf{E}^{\text{ext}}(\omega) + \mathbf{E}^{\text{dip}}(\omega),$$

with $\mathbf{E}^{\text{dip}}(\omega) = \frac{4\pi}{3}\mathbf{P}(\omega)$ for a cubic media.
We get

$$\epsilon_{\text{Lorentz}}(\omega) = \frac{1}{1 - \frac{4\pi}{3}\alpha(\omega)}.$$

Exact result

$$\epsilon_M^{LL}(\mathbf{q};\omega) = \frac{1}{1 - 4\pi\left[\tilde{\alpha}^{LL}(\mathbf{q};\omega)\right]_{\mathbf{00}}}$$

Some references

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Summary

- The key quantity is the dielectric tensor
- Relation between microscopic and macroscopic fields
- The longitudinal part is enough to describe the full optical response in the long wavelength limit ($\mathbf{q} \to 0$)
- How to connect with response function from TDDFT

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