Local field effects for optical linear and nonlinear properties of surfaces

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Response to a perturbation

**Linear optics**

The response depends linearly on the electric field

\[ P^a = \chi^{(1)}_{ab} E^b \]

**Nonlinear optics**

for higher light intensities, higher order terms can be important

\[ P^a = \chi^{(1)}_{ab} E^b + \chi^{(2)}_{abc} E^b E^c + \chi^{(3)}_{abcd} E^b E^c E^d + \ldots \]
Second Harmonic Generation

Amplitude

\[ \chi^{(3)} E^3 \ll \chi^{(2)} E^2 \ll \chi^{(1)} E \]

but...

Symmetry

Centro-symmetric materials

\[ \chi^{(2)} = 0 \]

in the dipole approximation (Long wavelength limit)
What can we learn from linear optics?  
(in condensed matter)

- Absorption and refraction
- Birefringence
- Luminescence
- Photoconductivity
- Photocatalysis  ...
What can we learn from Second Harmonic Generation? (in condensed matter)

• Probe for materials:
  Sensitivity to local symmetries and selection rules for electronic transitions in $\chi^{(2)}$
  $\Rightarrow$ gives access to states with different symmetries, compared to linear optics

• Development and characterisation of new materials

New optical devices

• Surfaces
  • Thin films
  • Interfaces
  • Nanowires
  • defects
What about surfaces?

How optical properties of materials are modified by the presence of a surface?

- Nano-scaled objects
- Photo-catalysis
- Molecules deposited on a surface
• Introduction: linear and nonlinear optics in solids
• How do we compute an optical spectrum for a solid?
• Response of the surface
Starting point: band theory

Independent particle approximation:
*All the electrons make independent transitions (IPA)*

Fermi golden rule
Starting point: band theory

Linear response

Independent Particle Approximation

\[ \varepsilon_{ab}(\omega) = \delta_{ab} + \frac{8\pi e^2}{\hbar m^2 \omega^2 V} \sum_{nm} \int d\vec{k} f_{nm}(\vec{k}) \left( \frac{p^a_{nm}(\vec{k}) p^b_{mn}(\vec{k})}{E_m - E_n - \omega - i\eta} \right) \]

(Reciprocal space)
Starting point: band theory

Second-order response

Independent Particle Approximation

\[
\chi_{abc}^{(2)}(-2\omega, \omega, \omega) = \frac{-ie^3}{\hbar^2 m^3 \omega^3 V} \sum_{nml} \int d\vec{k} \frac{1}{E_m - E_n - 2\omega - 2i\eta} \\
\times \left[ f_{nl}(\vec{k}) \frac{p_{nm}^a(\vec{k}) \left\{ p_{ml}^b(\vec{k}) p_{ln}^c(\vec{k}) \right\}}{E_l - E_n - \omega - i\eta} + f_{ml}(\vec{k}) \frac{p_{nm}^a(\vec{k}) \left\{ p_{ml}^b(\vec{k}) p_{ln}^c(\vec{k}) \right\}}{E_m - E_l - \omega - i\eta} \right]
\]

(Reciprocal space)
Additional effects
Additional effects

• Screening

GW approximation: *Hedin’s equations (1965)*

⇒ Shift of the conduction bands

⇒ Opening of the gap
Additional effects

- Screening
- Excitonic effects

Bethe Salpeter Equation
(2-particles)

or

Time-Dependent Density-Functional Theory (TDDFT)
Additional effects

- Screening
- Excitonic effects

- Local fields (macroscopic response)

  Expected to be very important for surfaces
Additional effects: local fields (1)

From Microscopic to Macroscopic polarization …

**Perturbation** = external macroscopic field

Induces a microscopic response (polarisation of the atoms)

**Perturbation** = external macroscopic + induced microscopic

*has to be taken into account in a self consistent way*
Additional effects : local fields (2)

From Microscopic to Macroscopic polarization …

How to obtain a macroscopic measurable quantity?

- Large compared to the cell dimension
- Small compared to the wavelength of the external perturbation

average over distances

Local fields = difference between micro and macro

Macroscopic response
Macroscopic response (local fields)

Linear and Second-order Response Function in the framework of TDDFT

Dyson equation:

1st order

\[ \left[ 1 - \chi_0^{(1)} \nu \right] \chi^{(1)} = \chi_0^{(1)} \]

2nd order

\[ [1 - \chi_0^{(1)}(2\omega)\nu] \chi^{(2)}(2\omega, \omega) = \chi_0^{(2)}(2\omega, \omega) [1 + \nu \chi^{(1)}(\omega)]^2 \]

\( \chi_0^{(1)}, \chi_0^{(2)} \) Independent particle response functions

DP code: \( \chi^{(1)} \)

linear response

2light \( \chi^{(2)} \)

Second harmonic generation
Macroscopic response (local fields)

Crystal $\Rightarrow$ 3D periodicity $\Rightarrow$ reciprocal space (plane waves)

1st order

$$
\left[ 1 - \chi_0^{(1)} v \right] \chi^{(1)} = \chi_0^{(1)}
$$

$$
\sum_{G''} \left[ \delta_{G,G''} - \chi_0^{(1)} \left( \vec{q} + \vec{G}, \vec{q} + \vec{G}'', \omega \right) v(\vec{q} + \vec{G}'') \right] \chi^{(1)}(\vec{q} + \vec{G}'', \vec{q} + \vec{G}', \omega) = \\
\chi_0^{(1)}(\vec{q} + \vec{G}, \vec{q} + \vec{G}', \omega)
$$

$$
\epsilon_M(\vec{q}) = \frac{1}{1 + v(\vec{q}) \chi^{(1)}(\vec{q}, \vec{q})}
$$
• Introduction: linear and nonlinear optics in solids
• How do we get a spectrum for a solid?
• Response of the surface
Crystalline Solid

3D periodicity

Unit Cell

Surface

2D periodicity

Super-cell
(atoms + vacuum)

Si(001) 2x1

Requirement: Results should not depend on the amount of vacuum introduced in the cell
Effect of the vacuum on the spectra

Silicon surface (001)2×1

Void 1

Void 2

Void 3

Vacuum
Optical Response of Surfaces - IPA

\[ \varepsilon_{ab}(\omega) = \delta_{ab} + \frac{8\pi e^2}{\hbar m^2 \omega^2 V} \sum_{nm} \int d\vec{k} f_{nm}(\vec{k}) \frac{p_{nm}(\vec{k}) p_{mn}(\vec{k})}{E_m - E_n - \omega - i\eta} \]

V: volume of the super-cell

In-plane

Out-of-plane
Optical Response of Surfaces – local fields

In-plane

Including local field effects (LFE)
Optical Response of Surfaces – local fields

Out-of-plane

- Position of the peak
- Change of scale

- Strong LFE
- Position of the peak depends on the size of the vacuum
Optical Response of Surfaces – local fields

Out-of-plane

- Strong LFE
- Position of the peak depends on the size of the vacuum
Optical properties in Real Space

\[ \chi^{(0)}(\mathbf{r}, \mathbf{r}', \omega) = 2 \sum_{i,j} (f_i - f_j) \frac{\phi_i(\mathbf{r}) \phi_j^*(\mathbf{r}) \phi_i^*(\mathbf{r}') \phi_j(\mathbf{r}')}{{E_i - E_j - \omega - i\eta}} \]

Independent Particles (IPA)

\[ \epsilon(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r}, \mathbf{r}') - \int d\mathbf{r}'' V(\mathbf{r}, \mathbf{r}'') \chi_0(\mathbf{r}'', \mathbf{r}') \]

(No Local Field Effects)

Local Field Effects included

\[ \chi(\mathbf{r}, \mathbf{r}') = \chi^{(0)}(\mathbf{r}, \mathbf{r}') + \int \int \chi^{(0)}(\mathbf{r}, \mathbf{r}_1) v(\mathbf{r}_1 - \mathbf{r}_2) \chi(\mathbf{r}_2, \mathbf{r}') + \int d\mathbf{r}'' V(\mathbf{r}, \mathbf{r}'') \chi(\mathbf{r}'', \mathbf{r}') \]

\[ \epsilon^{-1}(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r}, \mathbf{r}') + \int d\mathbf{r}'' V(\mathbf{r}, \mathbf{r}'') \chi(\mathbf{r}'', \mathbf{r}') \]

\[ \epsilon_M \text{ from Macroscopic average} \]

Tiago, et al. PRB 73, 205334 (2006)
The system is periodic in x and y-directions.

We define a mixed space

\[(x, y, z) \rightarrow (q_x + G_x, q_y + G_y, z) \rightarrow (q_{//} + G_{//}, z)\]

**Approximation**: we neglect in-plane local field effects

\[G_{//} = 0 \quad (x, y, z) \rightarrow (q_{//}, z)\]
Local Field effects from real space

Out-of-plane IPA/LFE comparison
Local Field effects from real space

**Question**: Why is the real space approach different from the reciprocal space approach?

**Answer**: The density is localized on the material.

**Real space**: Contribution to the integrals in the Dyson equation comes only from the region where the density spreads (independent of the vacuum size).

**Reciprocal space**: Integrals are replaced by sums over G-vectors, defined according to the size of the super-cell (depends on the vacuum size).
Alternative approach in reciprocal space

One must solve the Dyson equation with:

- The subset of $G$-vectors corresponding to the matter

Super-cell: $G_n^{cell} = \frac{2\pi}{L_{cell}} n$

Material slab: $G_n^{slab} = \frac{2\pi}{L_{slab}} n$

- Normalize to the volume of matter

No approximation for the in-plane Local Fields
Selected G approach

![Graph showing selected G approach]
Results: Linear Spectrum

\[ \text{Im}\{\epsilon(\omega)\} \]

- \( \epsilon_{\parallel} \)
- \( \epsilon_{\perp} \)
- Bulk
Results: Second harmonic generation
Real-space calculation

Reciprocal space: based on the super-cell approach (takes advantage of the 2-D periodicity of the system)

Linear spectroscopy:
- In-plane local fields are negligible (Reflectance anisotropy spectroscopy “RAS”)
- Out-of-plane local fields are important (non-grazing light incidence)

SHG for surfaces: all components seem to be affected (work in progress)
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Thank you for your attention
Macroscopic response (local fields)

Dyson equation for the density response function

1st order

\[
\left(1 - \chi^{(1)}_0 (v + f_{xc})\right) \chi^{(1)}_{\rho\rho} = \chi^{(1)}_0
\]

\[
f_{xc} = \frac{\partial V_{xc}}{\partial \rho}
\]

2nd order

\[
\left[1 - \chi^{(1)}_0 (2\omega) f_{xc}(2\omega)\right] \chi^{(2)}_{\rho\rho}(2\omega,\omega) = \chi^{(2)}_0 (2\omega,\omega) \left[1 + f_{xc}(\omega) \chi^{(1)}_{\rho\rho}(\omega)\right]^2
\]

\[
+ \chi^{(1)}_0 (\omega) g_{xc}(\omega) \chi^{(1)}_{\rho\rho}(\omega) \chi^{(1)}_{\rho\rho}(\omega)
\]

New kernel

\[
g_{xc} = \frac{\partial^2 V_{xc}}{\partial \rho \partial \rho}
\]

DP code
Roadmap for computing $\varepsilon_M$

- DP code: $\chi^{(0)}_{G,G'}(q, \omega)$
- Real Space code: $\chi^{(0)}(z, z'; q_\parallel)$
- 1D Dyson-like equation: $\chi(z, z'; q_\parallel)$
- Macroscopic Average: $\varepsilon_{IPA}^M(q, \omega)$, $\varepsilon_{RPA}^M(q, \omega)$