Local field effects for optical linear and nonlinear properties of surfaces

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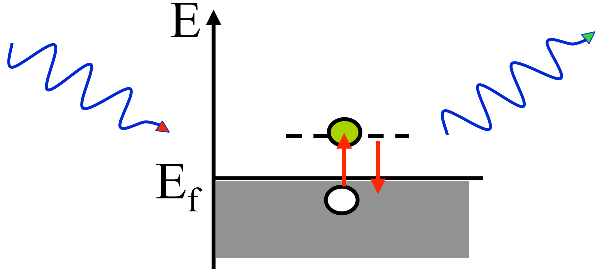
Response to a perturbation

Linear optics

The response depends linearly on the electric field

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

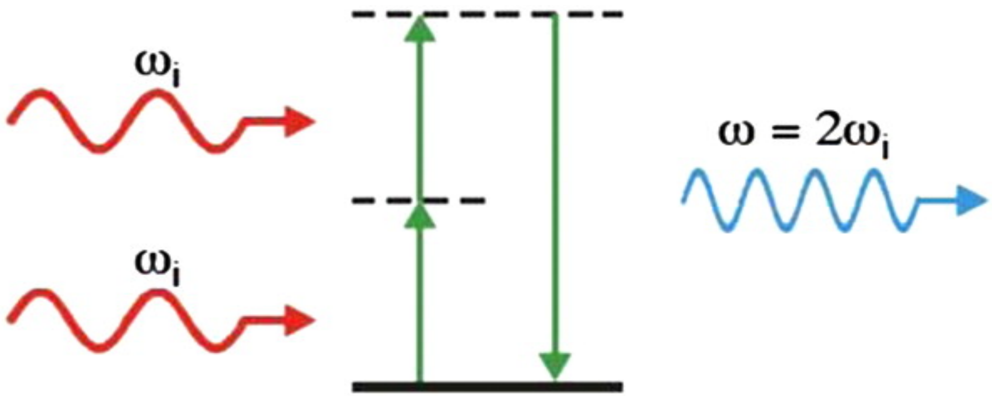


Nonlinear optics

for higher light intensities,
higher order terms can be important

$$P^a = \chi^{(1)}_{ab} E^b + \boxed{\chi^{(2)}_{abc} E^b E^c} + \chi^{(3)}_{abcd} E^b E^c E^d + \ldots$$

Second Harmonic Generation



Amplitude $\chi^{(3)}E^3 \ll \chi^{(2)}E^2 \ll \chi^{(1)}E$

First nonlinear term

but…

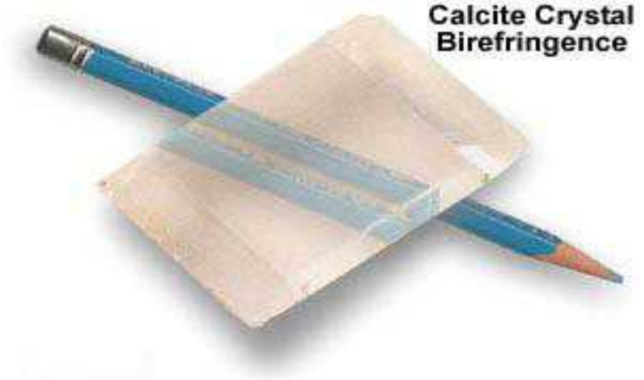
Symmetry

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 :**

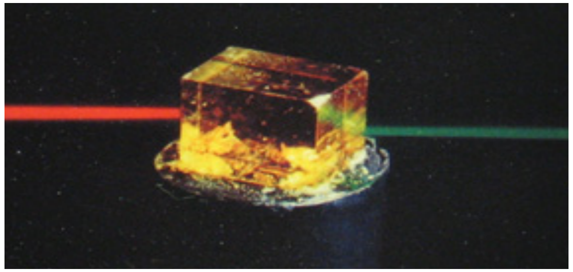
  Sensitivity to local symmetries and selection rules for electronic transitions in $\chi^{(2)}$

  $\Rightarrow$ gives access to states with different symmetries, compared to linear optics

  $\Rightarrow$
  - Surfaces
  - Thin films
  - Interfaces
  - Nanowires
  - defects

- **Development and characterisation of new materials**

  New optical devices



What about surfaces?

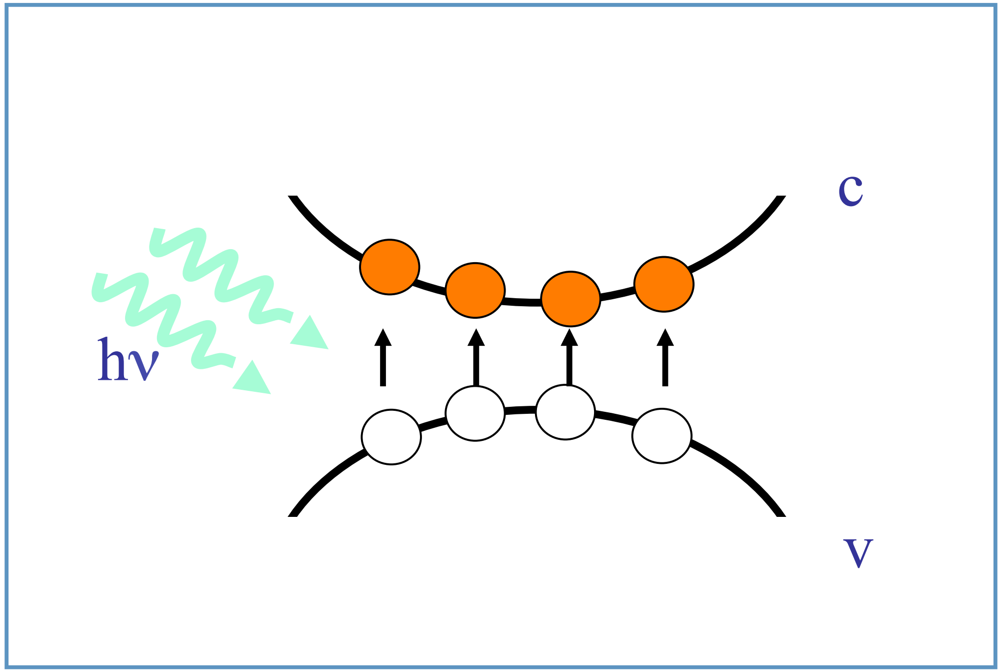
How optical properties of materials are modified by the presence of a surface?

- Nano-scaled objects
- Photo-catalysis
- Molecules deposited on a surface

Outline

- 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



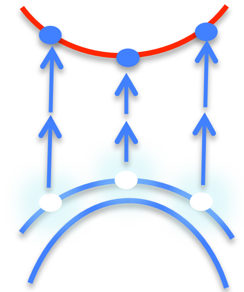
Independent particle approximation:

All the electrons make independent transitions

(IPA)

Fermi golden rule

Starting point: band theory



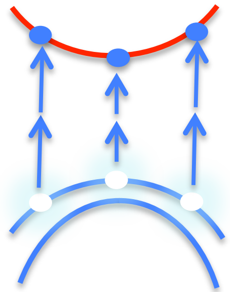
Linear response

Independent Particle Approximation

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

(Reciprocal space)

Starting point: band theory



Second-order response

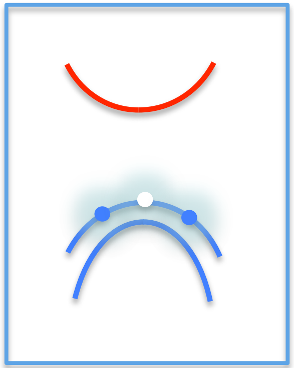
Independent Particle Approximation

$$\chi^{(2)}_{abc}(-2\omega,\omega,\omega)=\frac{-ie3}{\hbar^2 m^3\omega^3 V}\sum_{nml}\int d\vec{k}\,\frac{1}{E_m-E_n-2\omega-2i\eta}$$
$$\times\left[f_{nl}(\vec{k})\frac{p^a_{nm}(\vec{k})\left\{p^b_{ml}(\vec{k})p^c_{\ln}(\vec{k})\right\}}{E_l-E_n-\omega-i\eta}+f_{ml}(\vec{k})\frac{p^a_{nm}(\vec{k})\left\{p^b_{ml}(\vec{k})p^c_{\ln}(\vec{k})\right\}}{E_m-E_l-\omega-i\eta}\right]$$

(Reciprocal space)

Additional effects

Additional effects



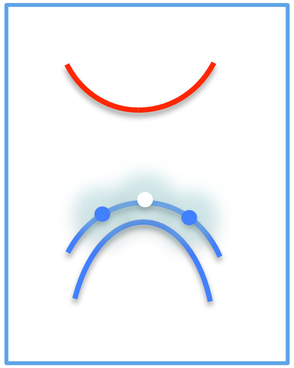
- Screening

  GW approximation:
  Hedin's equations (1965)

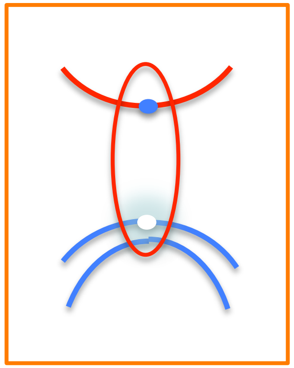
⇒Shift of the conduction bands

⇒Opening of the gap

Additional effects



- Screening
- Excitonic effects

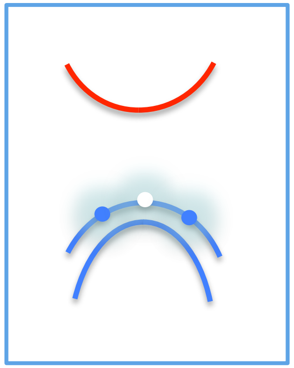


Bethe Salpeter Equation
(2-particles)

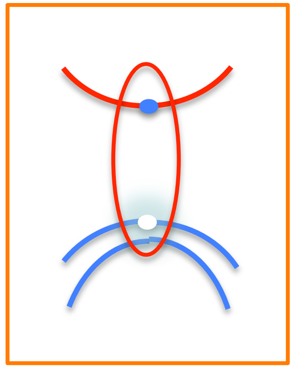
or

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)

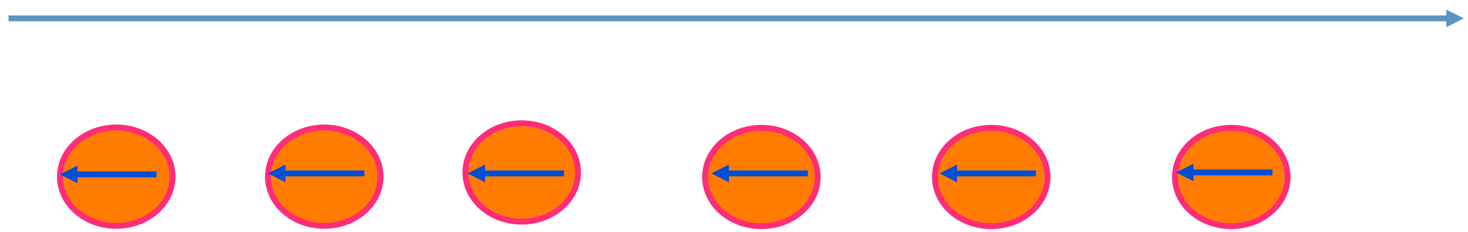
From Microscopic to Macroscopic polarization …

Perturbation= external macroscopic field

Induces a microscopic response (polarisation of the atoms)

Perturbation=external macroscopic + induced microscopic

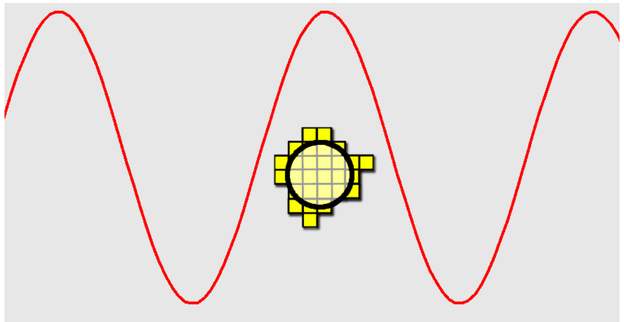
has to be taken into account in a self consistent way



Additional effects : local fields (2)

From Microscopic to Macroscopic polarization …

How to obtain a macroscopic measurable quantity ?



average over distances

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

→ Macroscopic response

Local fields = difference between micro and macro

Macroscopic response (local fields)

Linear and Second-order Response Function

in the framework of TDDFT

Time-dependent Density Functional Theory

Dyson equation:

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

2nd order
$$[1-\chi_0^{(1)}(2\omega)v]\chi^{(2)}(2\omega,\omega)=\chi_0^{(2)}(2\omega,\omega)\left[1+v\chi^{(1)}(\omega)\right]^2$$

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

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

linear response

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

Second harmonic generation

Macroscopic response (local fields)

Crystal ⇨ 3D periodicity ⇨ reciprocal space (plane waves)

1st order

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

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

$$\varepsilon_M(\vec{q})=\frac{1}{1+v(\vec{q})\chi^{(1)}(\vec{q},\vec{q})}$$

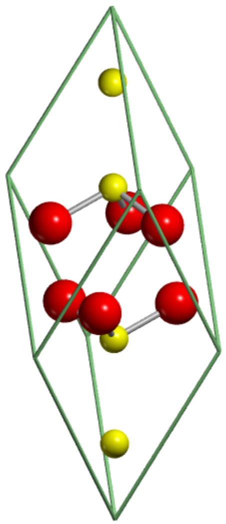
Outline

- Introduction: linear and nonlinear optics in solids
- How do we get a spectrum for a solid?
- Response of the surface

Crystalline Solid | Surface

3D periodicity

Unit Cell

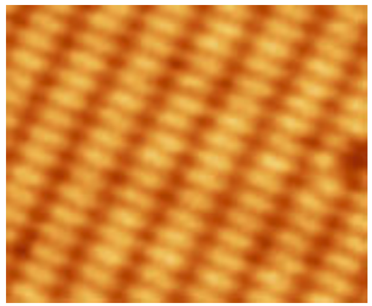


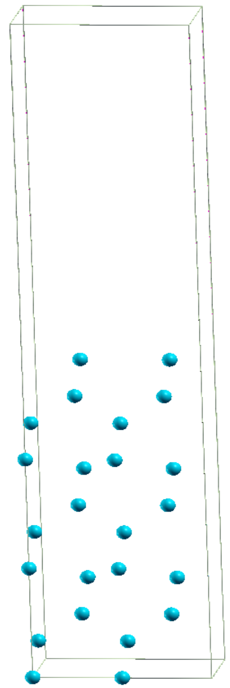
2D periodicity

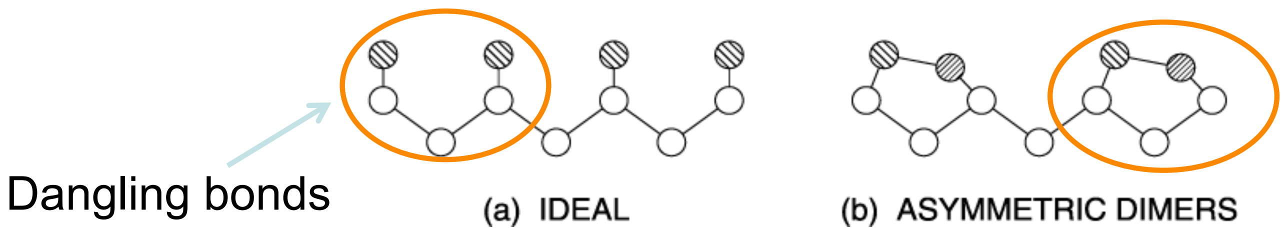
Super-cell

(atoms + vacuum)

Si(001) 2x1



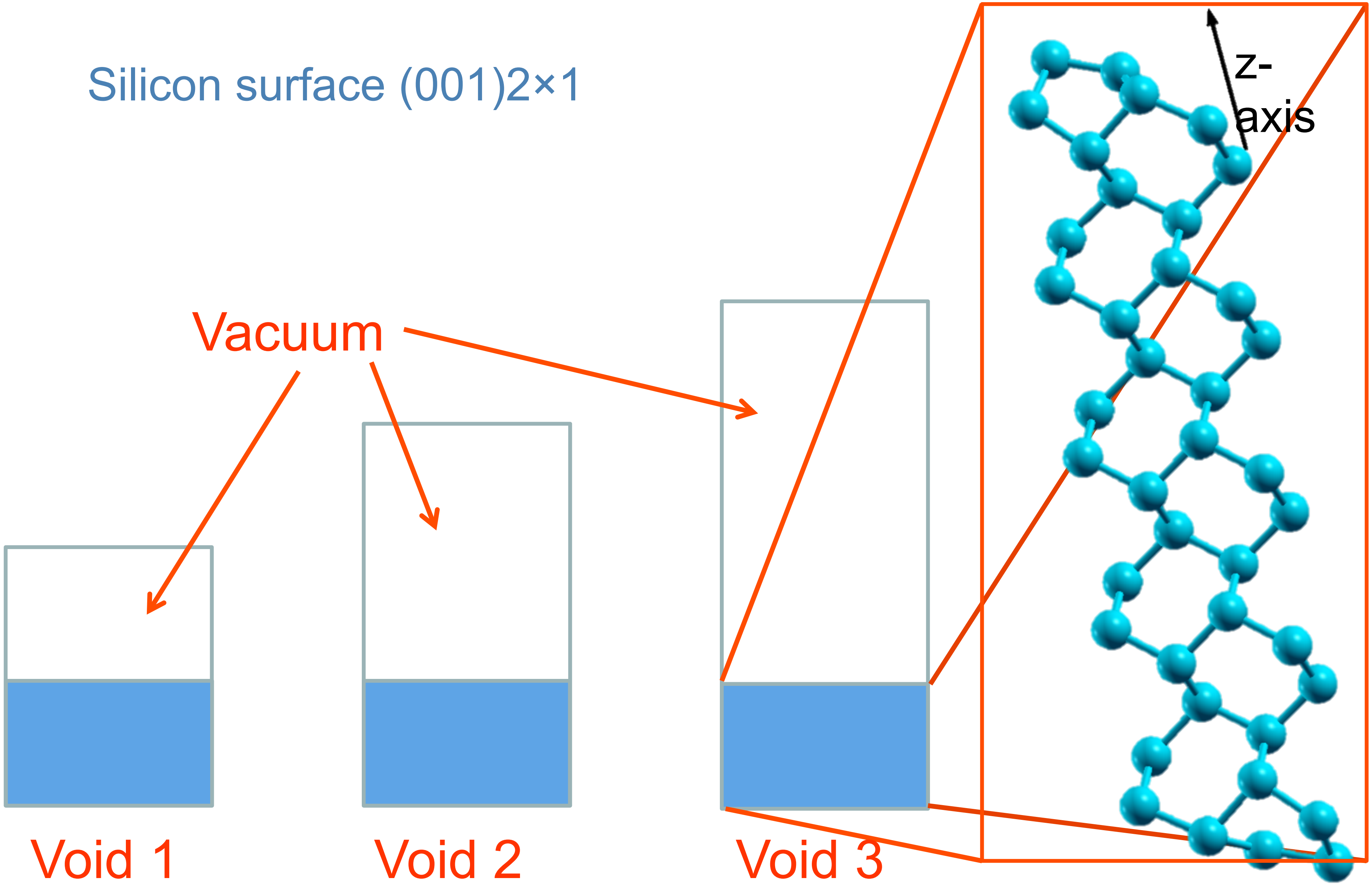




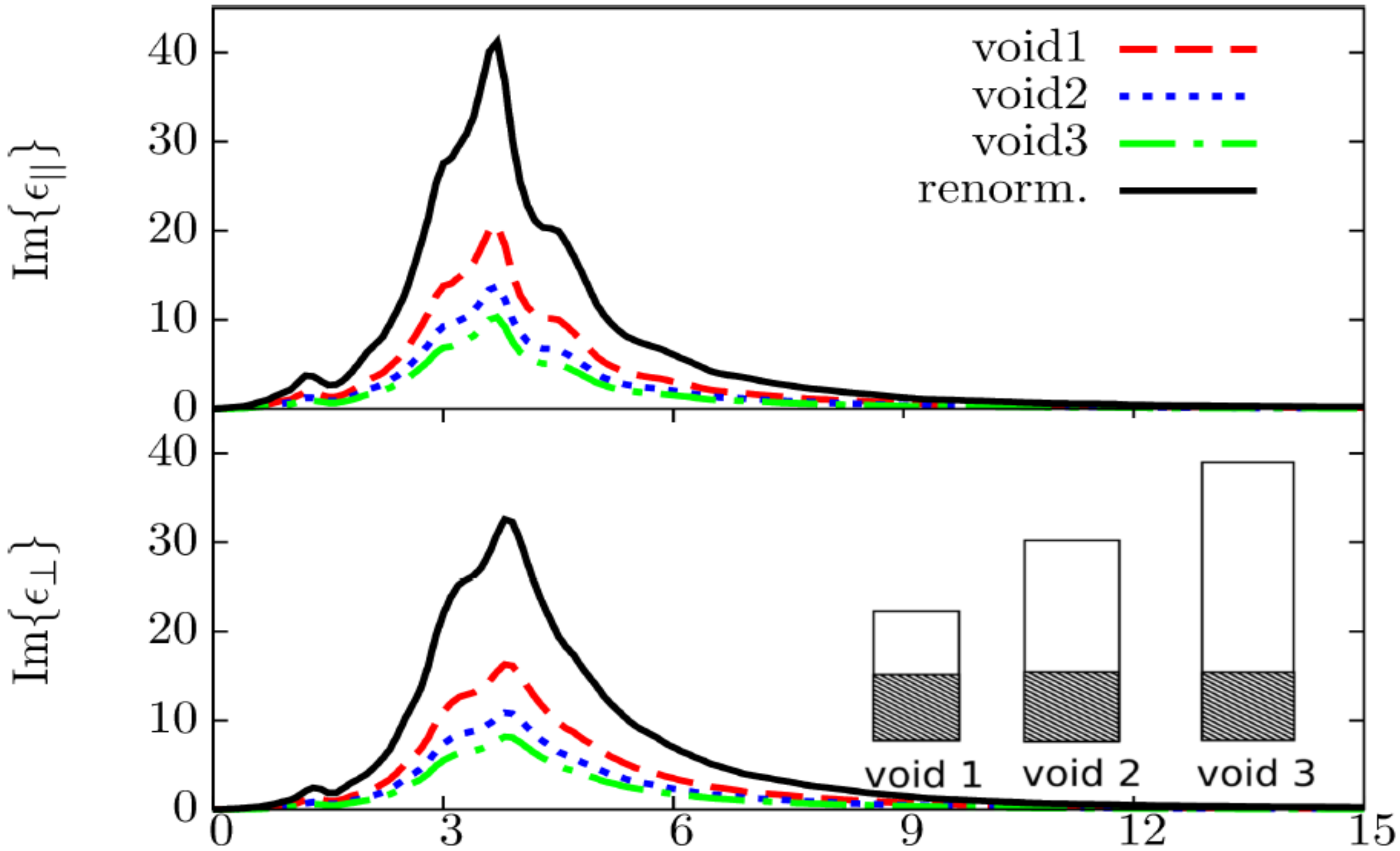
Requirement: Results should not depend on the amount of vaccum introduced in the cell

Effect of the vacuum on the spectra

Silicon surface (001)2×1



Optical Response of Surfaces - IPA



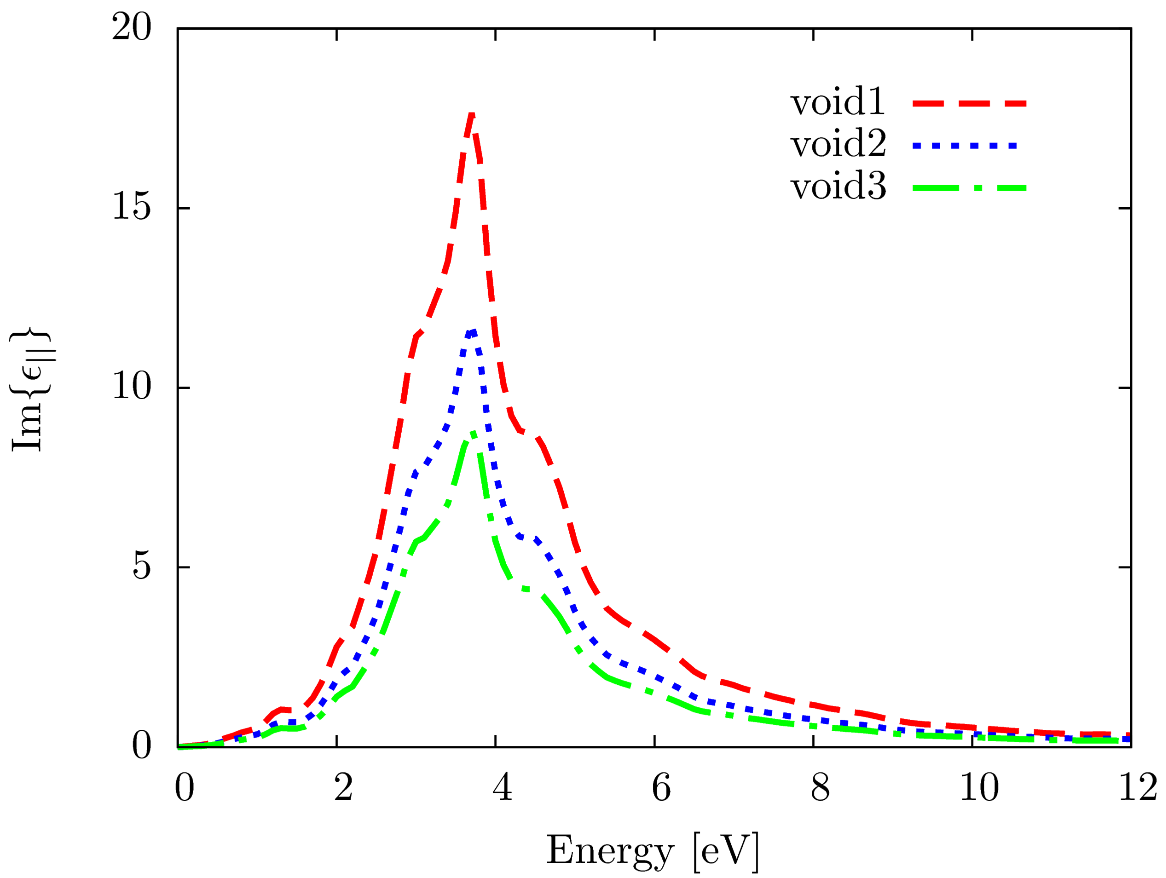
In-plane

Out-of-plane

V: volume
of the super-cell

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

Optical Response of Surfaces – local fields

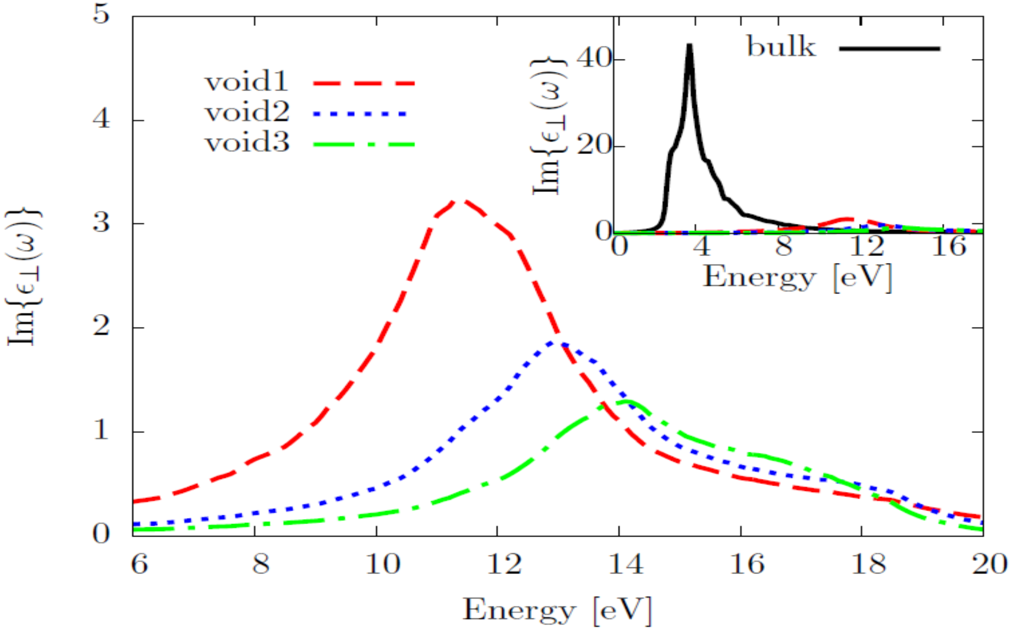


In-plane

Including
local field effects
(LFE)

Optical Response of Surfaces – local fields

Out-of-plane

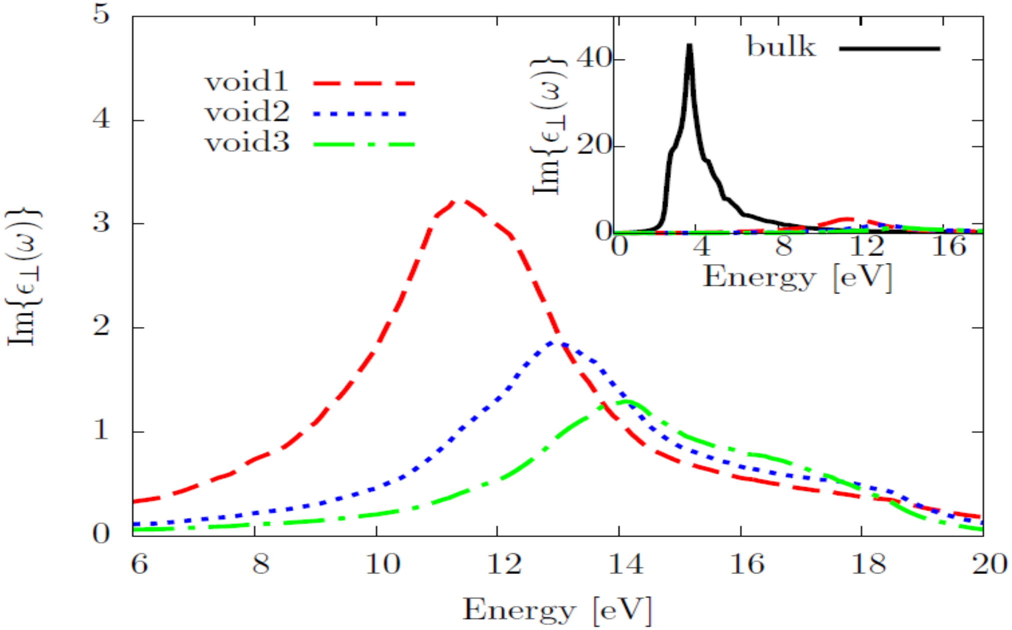


- Position of the peak
- Change of scale

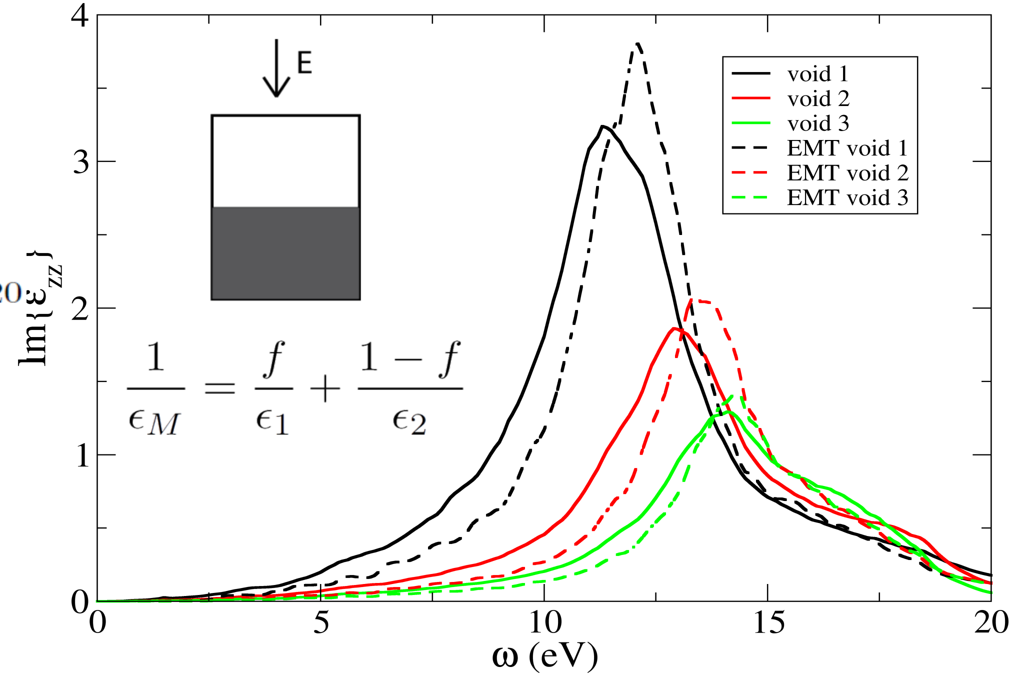
- Strong LFE
- Position of the peak depends on the size of the vacuum

Optical Response of Surfaces – local fields

Out-of-plane



Effective Medium Theory



$$\frac{1}{\epsilon_M} = \frac{f}{\epsilon_1} + \frac{1-f}{\epsilon_2}$$

- 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

$$\chi(\mathbf{r},\mathbf{r}') = \chi^{(0)}(\mathbf{r},\mathbf{r}') + \int\int \chi^{(0)}\mathbf{r},\mathbf{r}_1)v(\mathbf{r}_1 - \mathbf{r}_2)\chi(\mathbf{r}_2,\mathbf{r}')$$

+

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

Tiago, *et al.* PRB 73, 205334 (2006)
Ogut, *et al.* PRL 90, 127401 (2003)

ε_M from Macroscopic average

Real Space and Supercell

The system is periodic in x and y-directions.

We define a mixed space

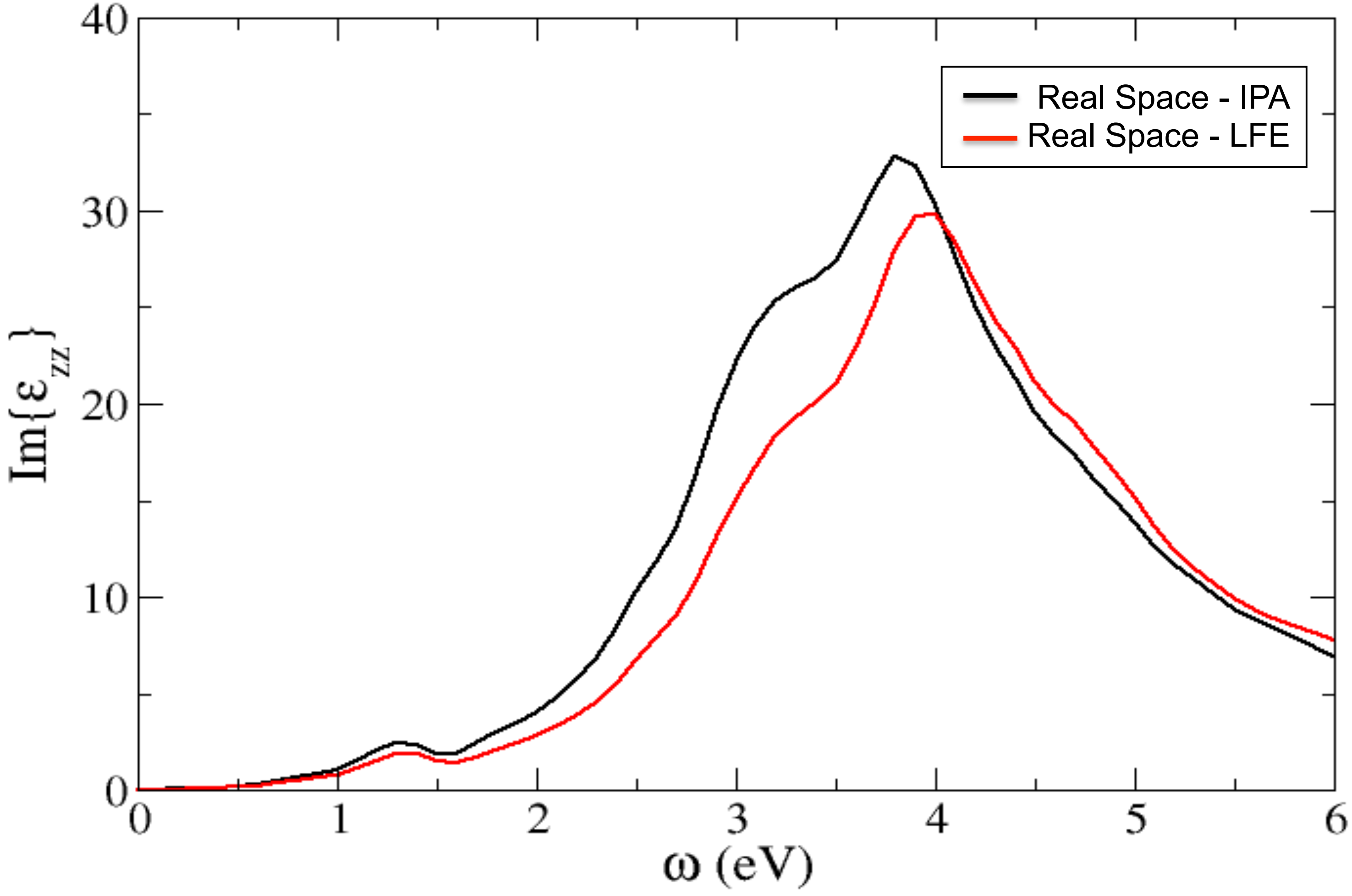
$(x,y,z) \rightarrow (q_x+G_x,q_y+G_y,z) \rightarrow (\mathbf{q}_{//}+\mathbf{G}_{//},z)$

Approximation : we neglect in-plane local field effects

$\mathbf{G}_{//}=0$ $\quad (x,y,z) \rightarrow (\mathbf{q}_{//}, z)$

Local Field effects from real space

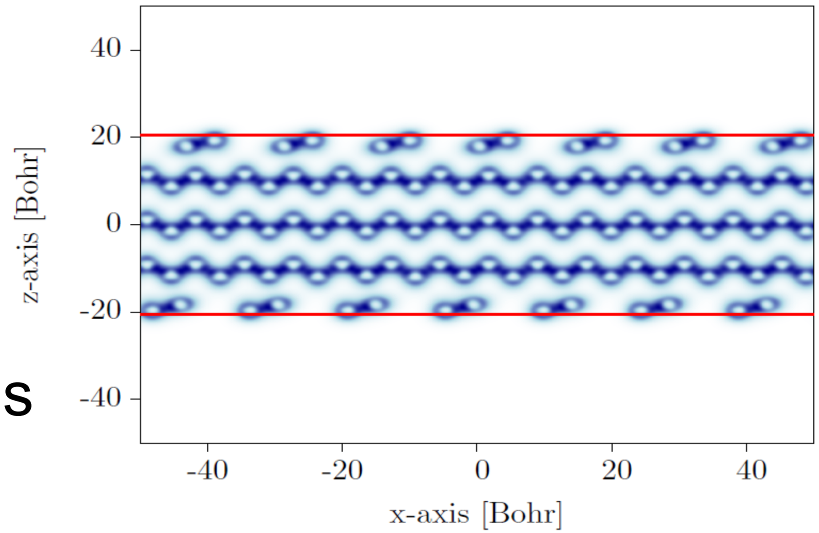
Out-of-plane IPA/LFE comparison



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 :

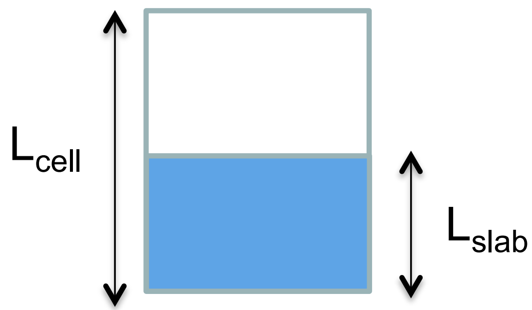
- The subset of G-vectors corresponding to the matter

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

G_0
G_1
G_2
G_3
G_4
.
.

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

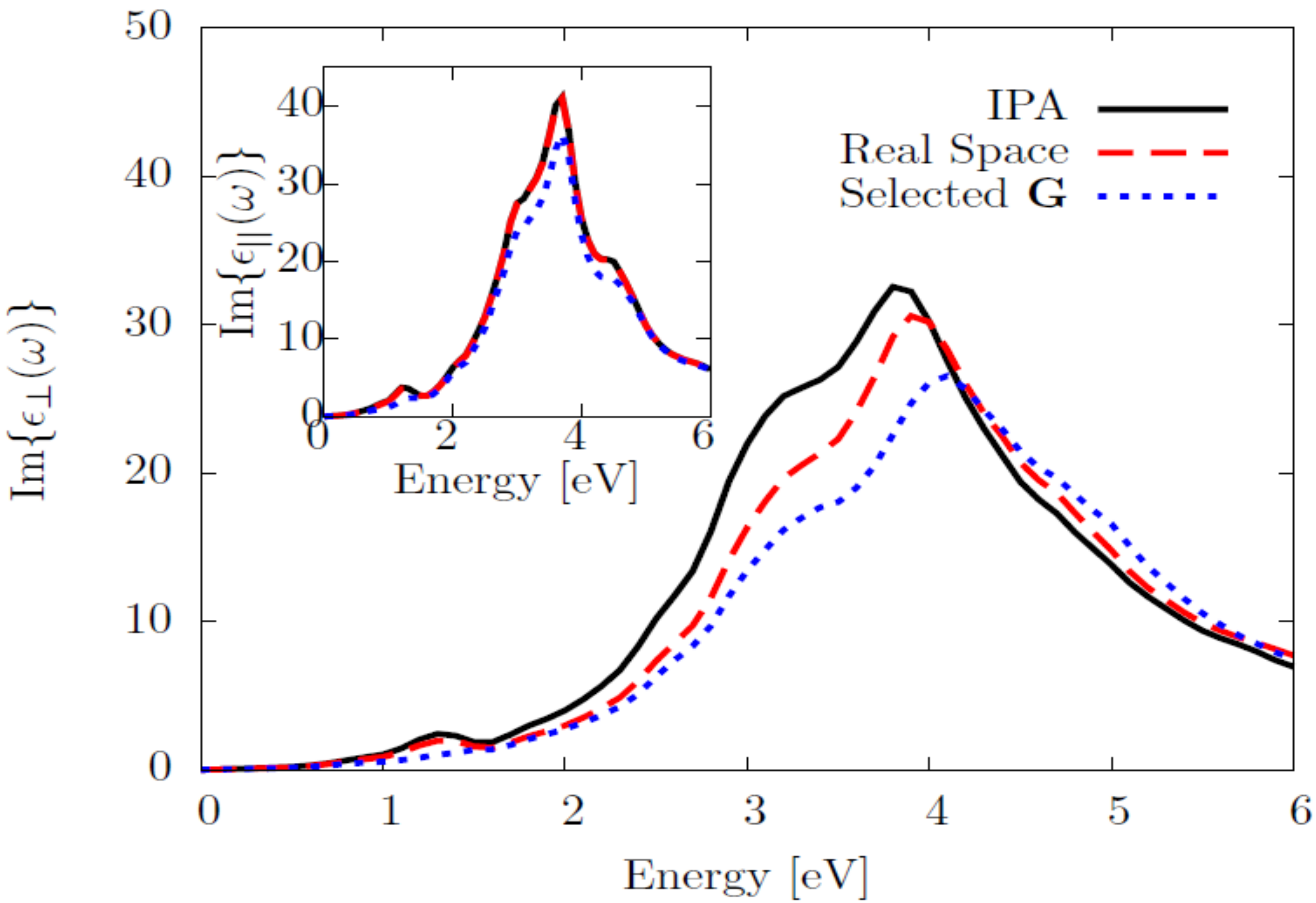
G_0
G_1
G_2
G_3
G_4
.
.



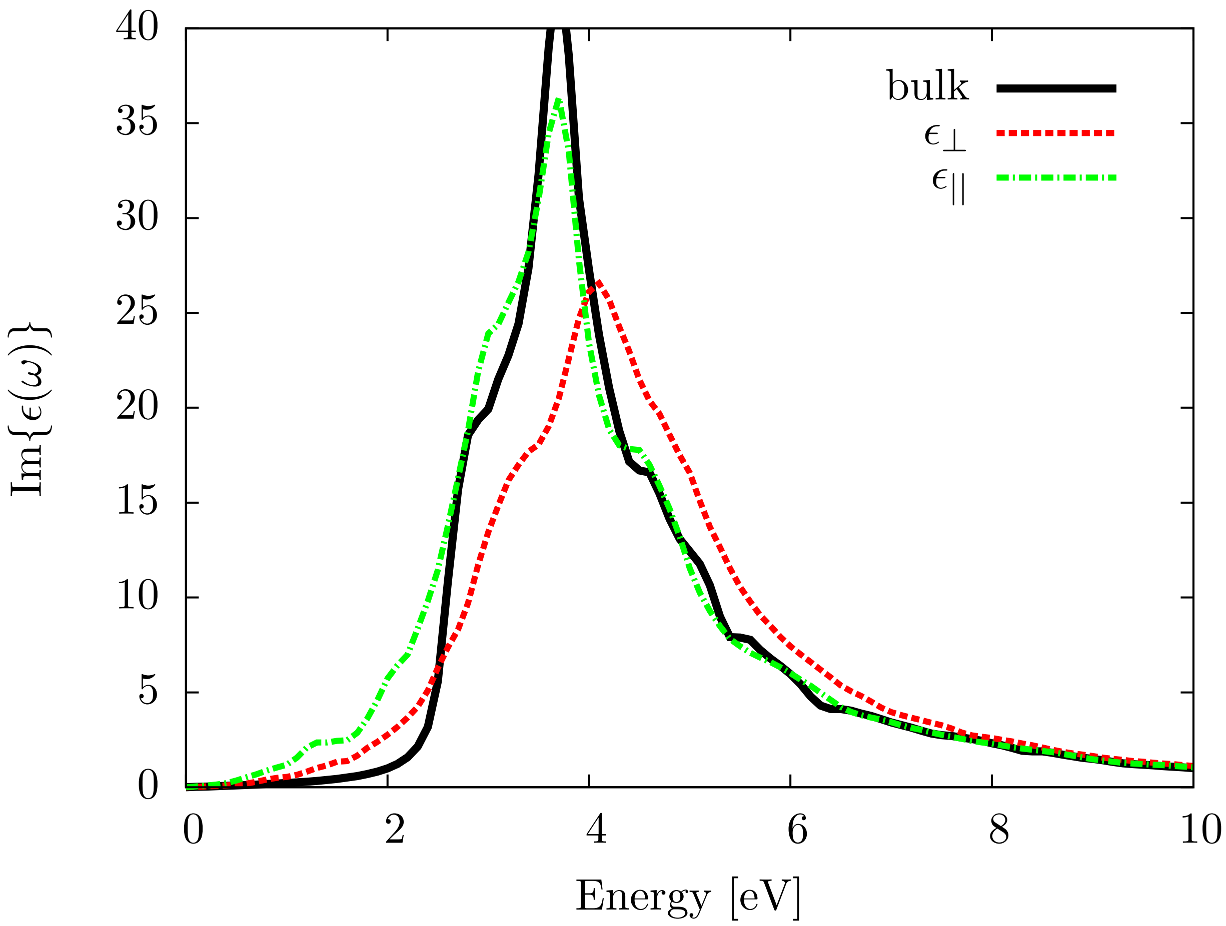
- Normalize to the volume of matter

No approximation for the in-plane Local Fields

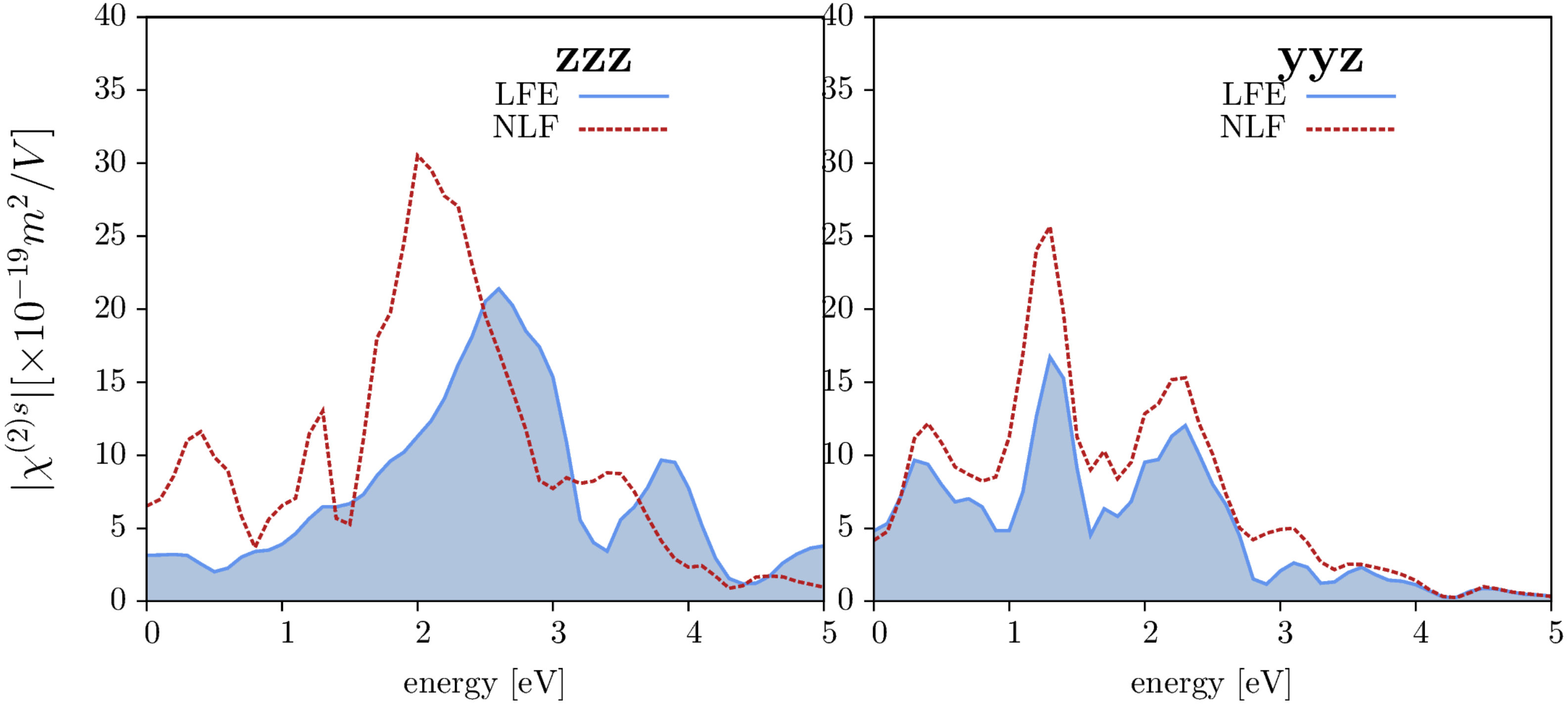
Selected G approach



Results: Linear Spectrum



Results: Second harmonic generation



Conclusions

- 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)

Acknowledgment

Theoretical spectroscopy group
Laboratoire des Solides Irradiés, Ecole Polytechnique

Thank you for your attention

Macroscopic response (local fields)

Dyson equation for the density response function

1st order

$$\left[1-\chi_0^{(1)}(v+f_{xc})\right]\chi_{\rho\rho}^{(1)} = \chi_0^{(1)} \qquad f_{xc}=\frac{\partial V_{xc}}{\partial \rho}$$

2nd order

$$[1-\chi_0^{(1)}(2\omega)f_{uxc}(2\omega)]\chi_{\rho\rho\rho}^{(2)}(2\omega,\omega) = \chi_0^{(2)}(2\omega,\omega)\left[1+f_{uxc}(\omega)\chi_{\rho\rho}^{(1)}(\omega)\right]^2 + \chi_0^{(1)}(\omega)g_{xc}(\omega)\chi_{\rho\rho}^{(1)}(\omega)\chi_{\rho\rho}^{(1)}(\omega)$$

New kernel

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

DP code

2light

Roadmap for computing ε_M

$\chi^{(0)}_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega)$

DP code

Real Space code

$\chi^{(0)}(z,z';\mathbf{q}_{||})$

1D Dyson-like equation

$\chi(z,z';\mathbf{q}_{||})$

Macroscopic Average

$\epsilon_M^{IPA}(\mathbf{q},\omega)$

$\epsilon_M^{RPA}(\mathbf{q},\omega)$