Second order harmonic generation from bulk, interfaces and surfaces: an *ab initio* study

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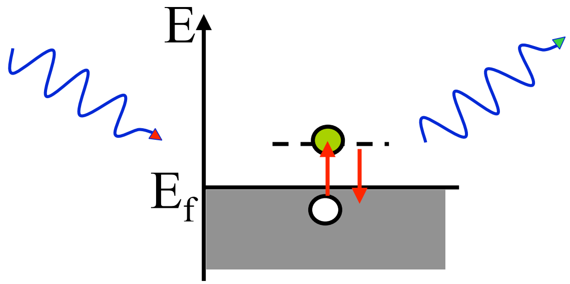
Response to a perturbation

Linear optics

The response depends linearly on the electric field

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

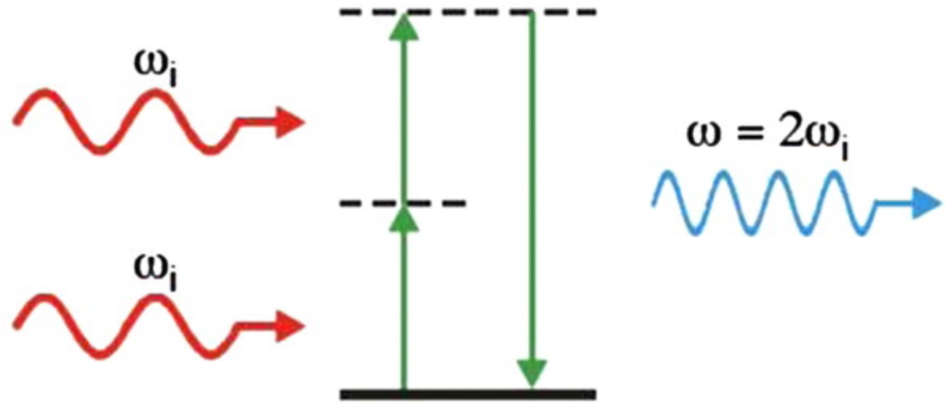


Nonlinear optics

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

First nonlinear term

but…

Symmetry $\quad$ Centro-symmetric materials $\quad \chi^{(2)} = 0$

The first non-vanishing term is $\chi^{(3)}$

Interest for Second Harmonic Generation:
in condensed matter

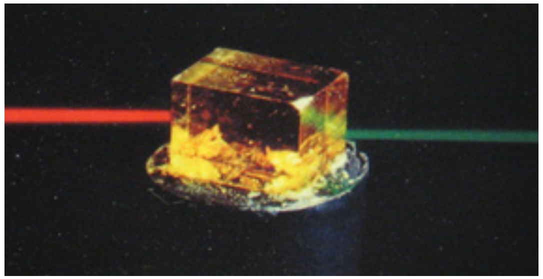
- Probe for materials :

  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

- Development and characterisation of new materials

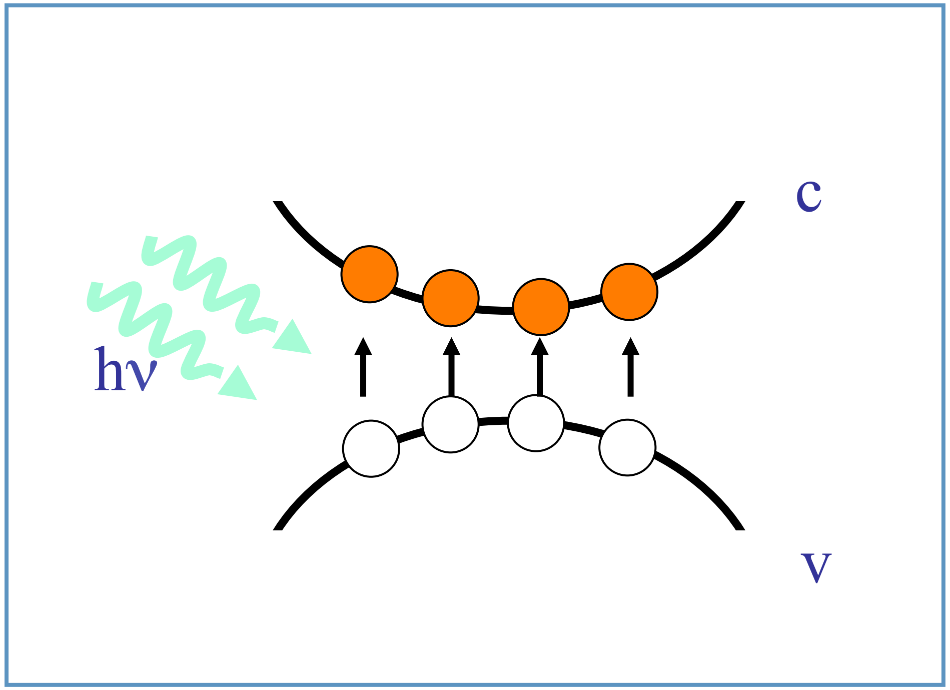
  New optical devices



Outline

- Introduction: nonlinear optics in solids
- How do we get the spectrum for SHG
- 4 applications :
  - GaAs
  - Silicon under constraint
  - Si_n/Ge_n superlattices
  - Surfaces

How do we get the spectrum for SHG



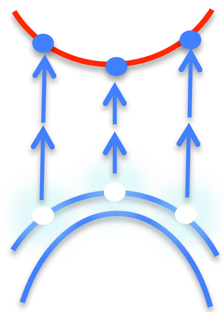
Independent particle approximation:

All the electrons make independent transitions

(IPA)

Fermi golden rule

How do we get the spectrum for SHG



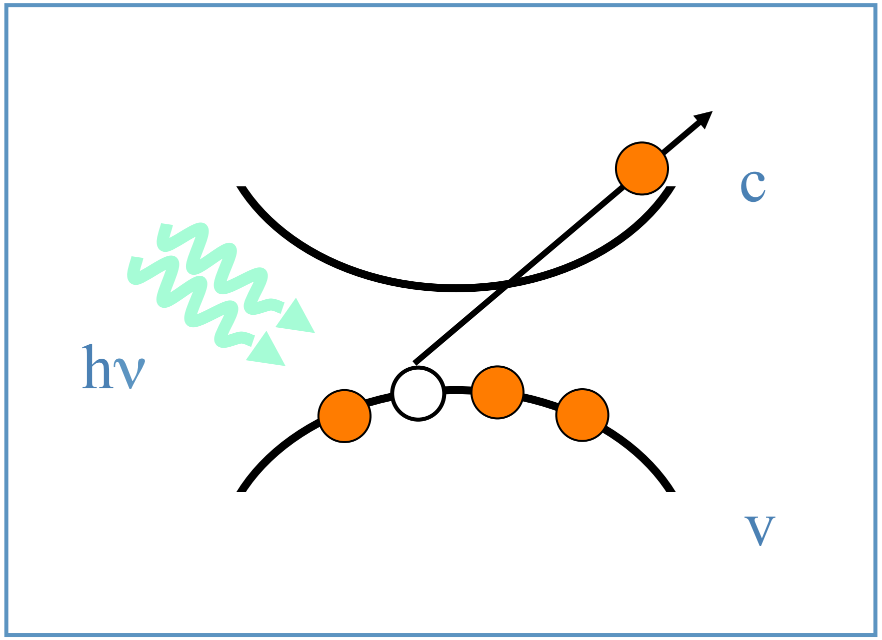
Second-order response

Independent Particle Approximation

$$\chi^{(2)}_{abc}(-2\omega,\omega,\omega)=\frac{-ie3}{\hbar^2 m^3\omega^3 V}\sum_{nml}\int d\vec{k}\,\frac{1}{E_m-E_n-2\omega-2i\eta}$$

$$\times\left[f_{nl}(\vec{k})\frac{p^a_{nm}(\vec{k})\left\{p^b_{ml}(\vec{k})p^c_{\ln}(\vec{k})\right\}}{E_l-E_n-\omega-i\eta}+f_{ml}(\vec{k})\frac{p^a_{nm}(\vec{k})\left\{p^b_{ml}(\vec{k})p^c_{\ln}(\vec{k})\right\}}{E_m-E_l-\omega-i\eta}\right]$$

Additional effect : screening



GW approximation:
Hedin's equations (1965)

⇒Shift of the conduction bands

⇒Opening of the gap

Scissor operator

See B. Mendoza's talk

Screening: *Hole- (N-1) electrons*

Additional effects : local fields

From Microscopic to Macroscopic polarization …

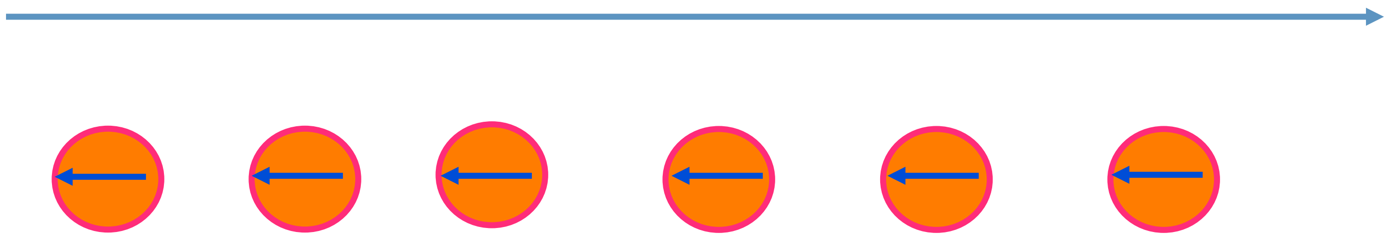
See L. Mochan's talk

Perturbation= external macroscopic field

Induces a microscopic response (polarisation of the atoms)

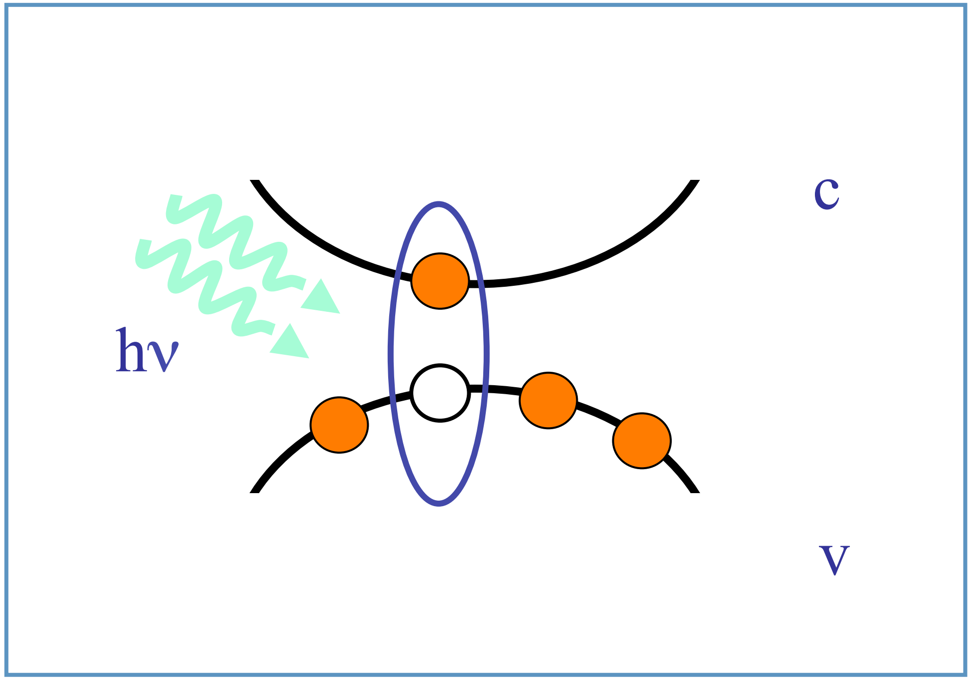
Perturbation=external macroscopic + induced microscopic

has to be taken into account in a self consistent way



« Local field »

Additional effects: exciton



Electron-hole interaction
(excitonic effect)

Bethe Salpeter Equation
(2-particles equation)
or
Time-Dependent
Density-Functional Theory
(TDDFT)

Scheme of the derivation of the $\chi^{(2)}$

First step: microscopic polarisation in terms of the external electric field
Second order time-dependent perturbation theory
valid for low intensity

Second step: macroscopic polarisation in terms of
- the total electric field
- second-order response functions

R. Del Sole and E. Fiorino and PRB **29** (1984)

Third step: calculation of the response functions
within time-dependent density functional theory

Macroscopic response and excitons

$$\chi^{(2)}_{xyz}(2\mathbf{q},2\omega) = -\frac{i}{12 q_x q_y q_z}\left[\varepsilon_M^{LL}(\mathbf{q},\omega)\right]^2\left[\varepsilon_M^{LL}(2\mathbf{q},2\omega)\right]\chi_{\rho\rho\rho}(2\mathbf{q},\mathbf{q},\mathbf{q},\omega,\omega)$$

Evaluated in the long wavelength limit q ➔ 0

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

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

2light

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Some results for GaAs

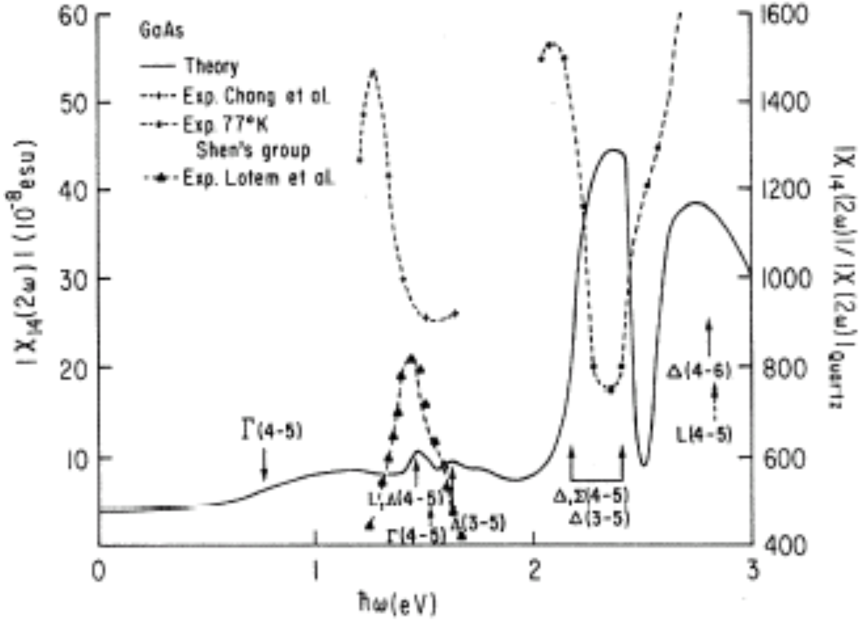
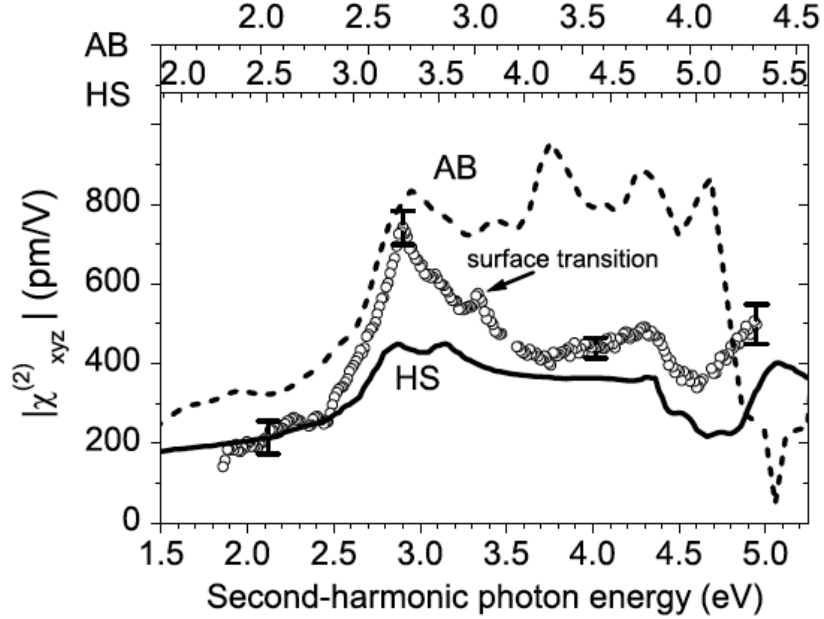


FIG. 3. Comparison of $|\chi^{(2)}_{14}(2\omega)|$ of GaAs with available experimental data.

C. Y. Fong Y. R. Shen PRB (1975)

Dilation and translation of the energy scale

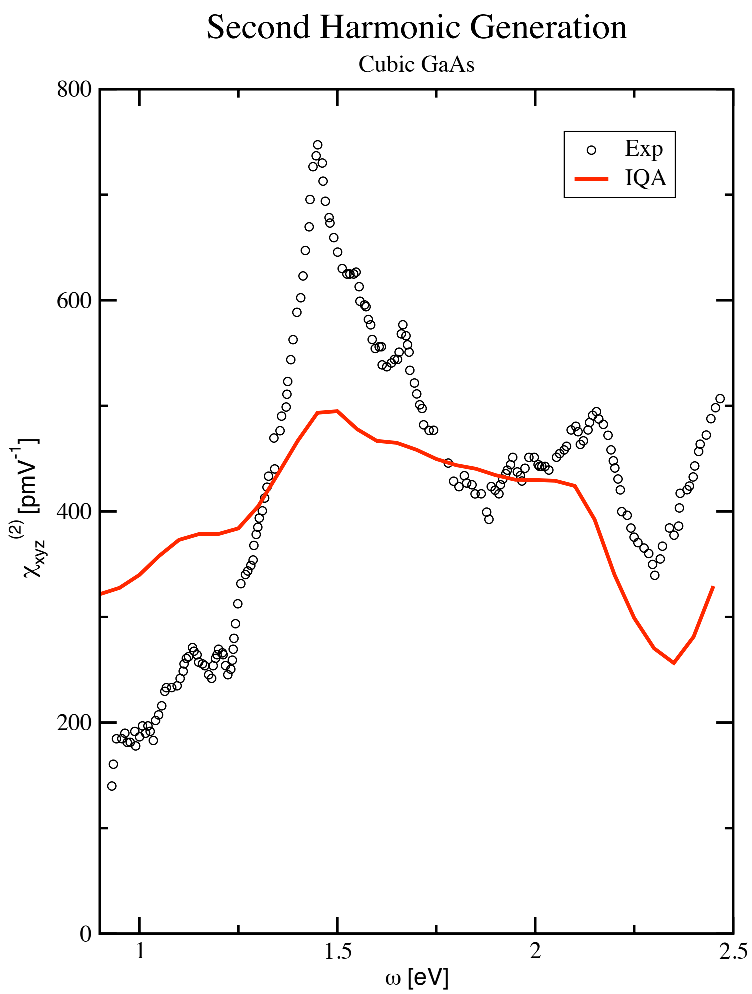


S. Bergfeld and W. Daum, PRL (2003)

J. Hugues and J. Sipe, PRB (1996)

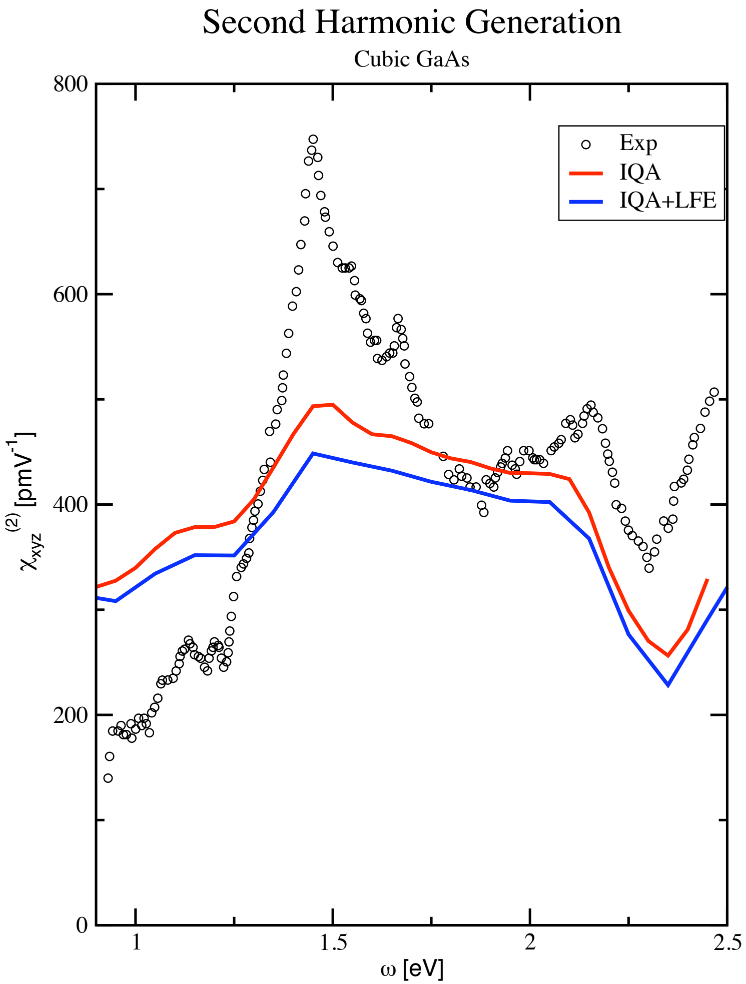
B. Adolph and F. Bechstedt, PRB (1998)

$\chi^{(2)}$ for GaAs



Screening

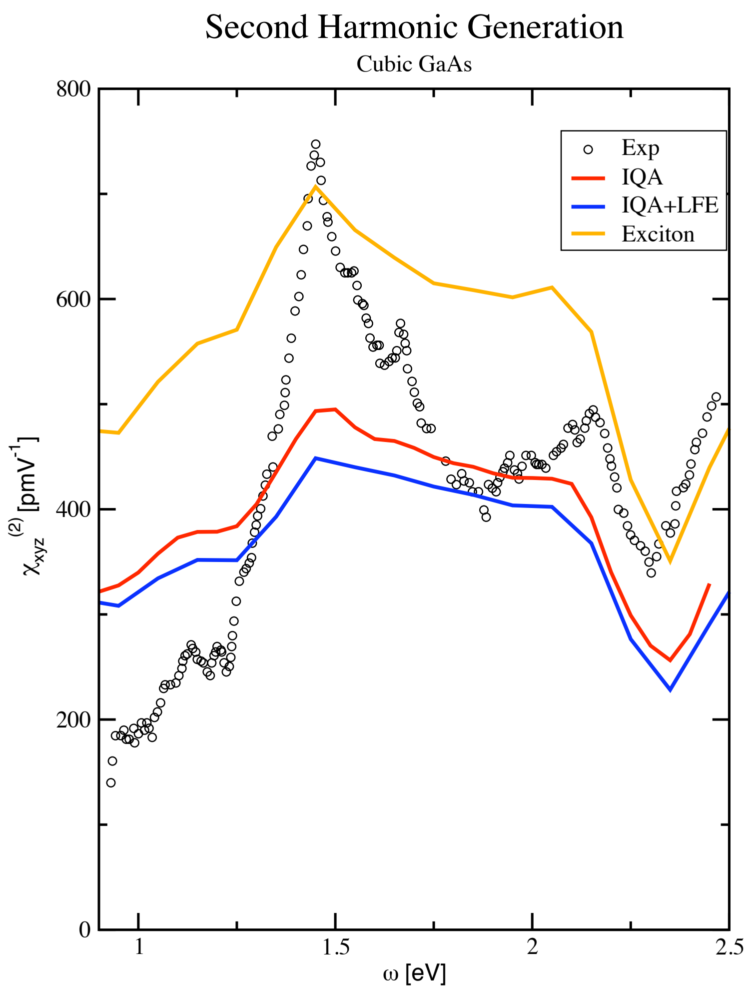
$\chi^{(2)}$ for GaAs



Screening

Screening and local fields

$\chi^{(2)}$ for GaAs



Full calculation

Screening

Screening and local fields

Exciton (Long range kernel)

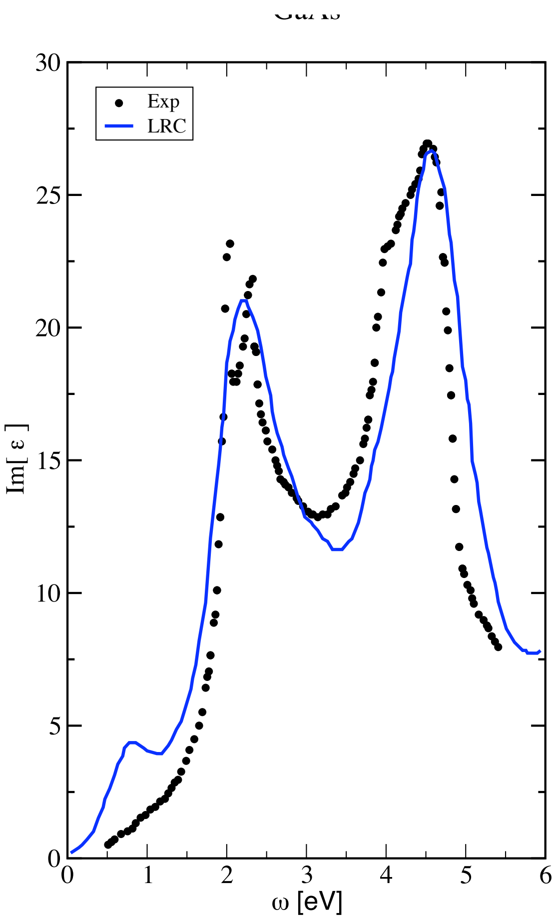
$$f_{xc} = \frac{\alpha}{q^2}$$

ε_M for GaAs

$$\chi^{(2)}_{xyz}(2\mathbf{q},2\omega) = -\frac{i}{12 q_x q_y q_z}\left[\varepsilon_M^{LL}(\mathbf{q},\omega)\right]^2\left[\varepsilon_M^{LL}(2\mathbf{q},2\omega)\right]\chi_{\rho\rho\rho}(2\mathbf{q},\mathbf{q},\mathbf{q},\omega,\omega)$$

ε_M for GaAs

$$\chi^{(2)}_{xyz}(2\mathbf{q},2\omega) = -\frac{i}{12 q_x q_y q_z}\left[\varepsilon_M^{LL}(\mathbf{q},\omega)\right]^2\left[\varepsilon_M^{LL}(2\mathbf{q},2\omega)\right]\chi_{\rho\rho\rho}(2\mathbf{q},\mathbf{q},\mathbf{q},\omega,\omega)$$

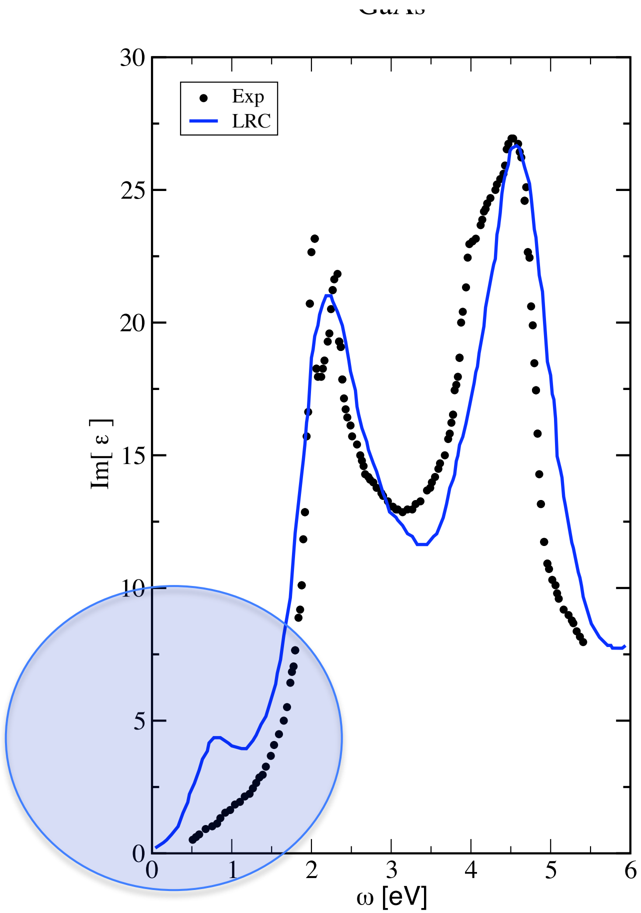


Linear dielectric function

- TDDFT (Long rang kernel)
- Similar results with BSE

ε_M for GaAs

$$\chi^{(2)}_{xyz}(2\mathbf{q},2\omega) = -\frac{i}{12q_xq_yq_z}\left[\varepsilon_M^{LL}(\mathbf{q},\omega)\right]^2\left[\varepsilon_M^{LL}(2\mathbf{q},2\omega)\right]\chi_{\rho\rho\rho}(2\mathbf{q},\mathbf{q},\mathbf{q},\omega,\omega)$$

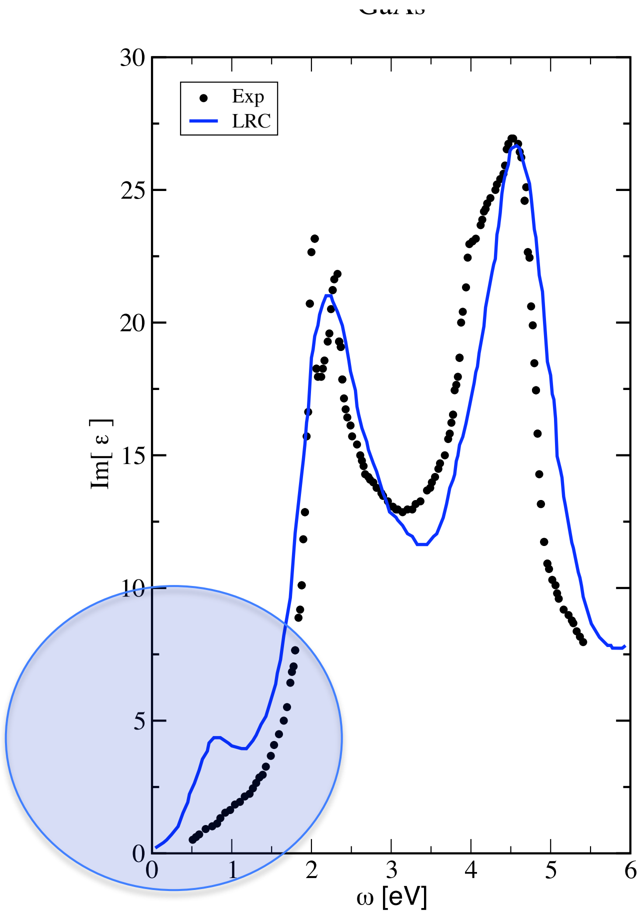


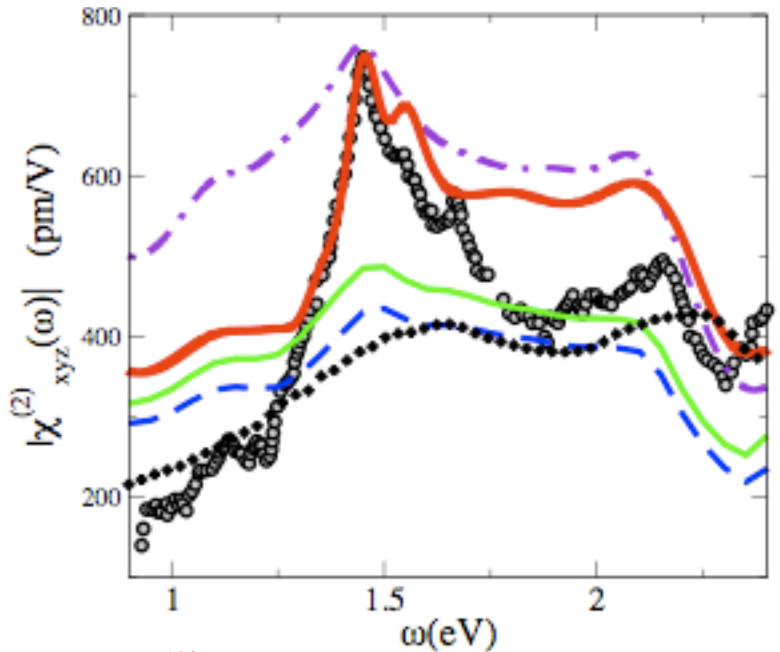
Linear dielectric function

- TDDFT (Long rang kernel)
- Similar results with BSE

$\chi^{(2)}$ and ε_M for GaAs

$$\chi^{(2)}_{xyz}(2\mathbf{q},2\omega) = -\frac{i}{12q_x q_y q_z}\left[\varepsilon_M^{LL}(\mathbf{q},\omega)\right]^2\left[\varepsilon_M^{LL}(2\mathbf{q},2\omega)\right]\chi_{\rho\rho\rho}(2\mathbf{q},\mathbf{q},\mathbf{q},\omega,\omega)$$





$\chi^{(2)}$ evaluated with the experimental dielectric functions

Good agreement with the experiment

The desription of the exciton should be improved in this region

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Silicon under constraint

- Microelectronic devices
- Multiple optical functionalities
- Industrial processes

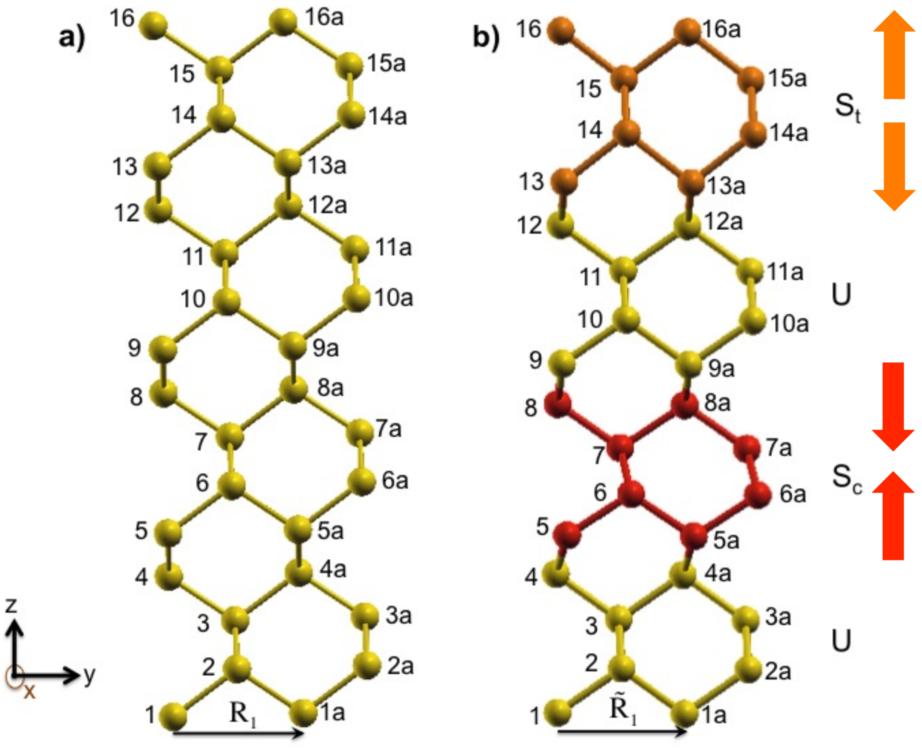
But : due to the centro-symetry of the crystal, $\chi^{(2)}$=0 in the dipole approximation

The first non-vanishing susceptbility : $\chi^{(3)}$

- Requires important optical power
- Competition with other nonlinear processes

  (Two-photon absorption)

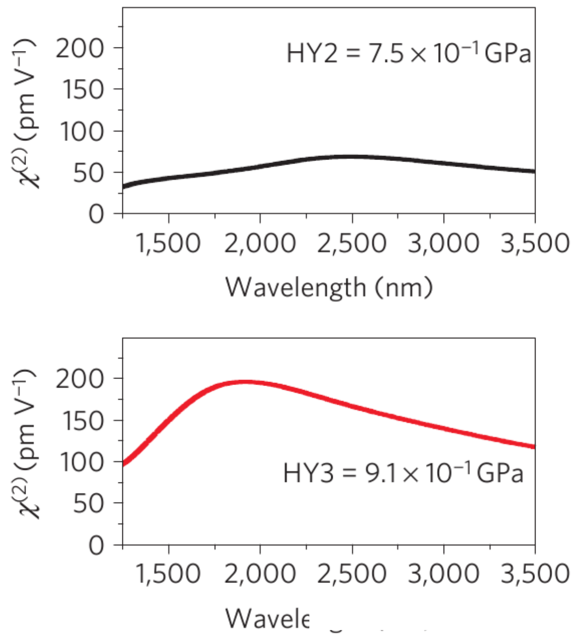
Silicon under constraint



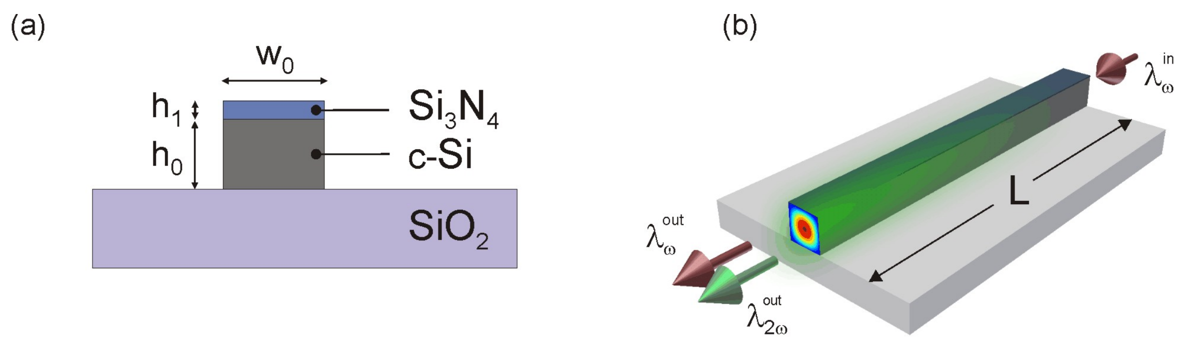
Supercell without constraint $\chi^{(2)}=0$

Supercell with constraint

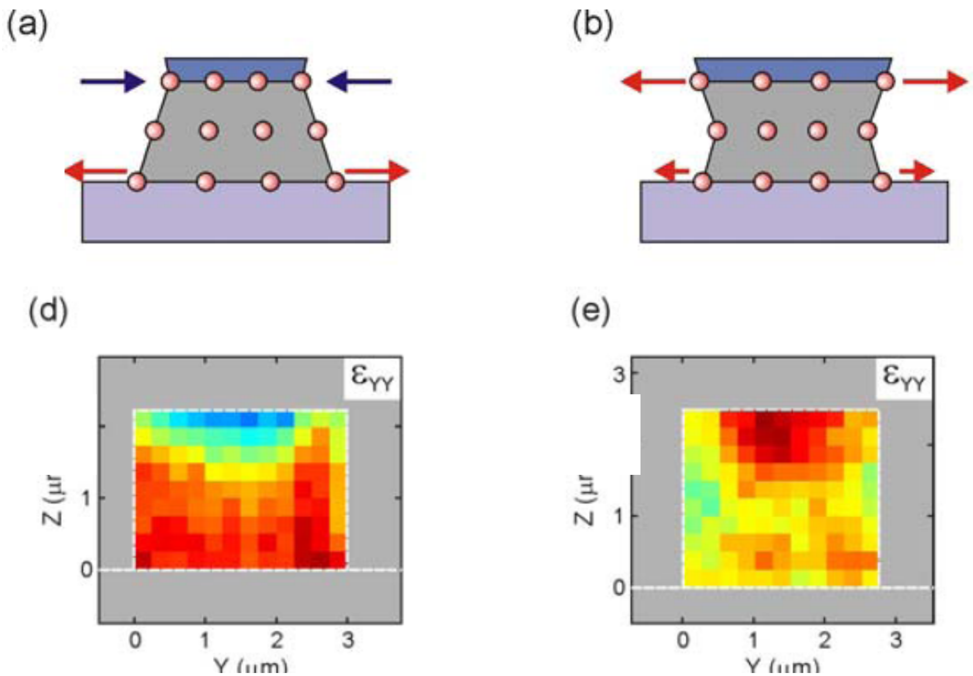
- Uniaxial constraint (001) $\chi^{(2)} \neq 0$, $\chi^{(2)}<0.5$pm/V
- Biaxial constraint $\chi^{(2)}\approx200$pm/V
- The more the lattice is distorded, the larger is $\chi^{(2)}$



Silicon under constraint



Experiment :
Silicon wave guide under constraint



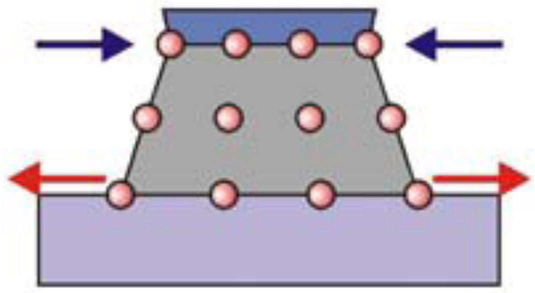
Micro-Raman spectroscopy

L. Pavesi, M. Cazzanelli,
F. Bianco, E. Borga, University of Trento
G. Pucker and M. Ghulinyan, Advanced Photonics
& Photovoltaics Unit, Trento
D. Modotto and S. Wabnitz, University of Brescia
R. Pierobon, CIVEN, Venezia

Silicon under constraint

The most favorable situation : biaxial compressive-tensile

Nature Materials (2012)



Theory

- $\chi^{(2)}$=200 pm/V

  (GaAs $\chi^{(2)}$ =700 pm/V)

- Silicon surface $\chi^{(2)} \approx$3 pm/V
- Si/SiO_2 $\chi^{(2)}$ <1pm/V

Experiment

- The signal is linked to the inhomogeneity and to the amplitude of the constraint
- Similar to $LiNbO_3$

(considered as a good nonlinear crystal)

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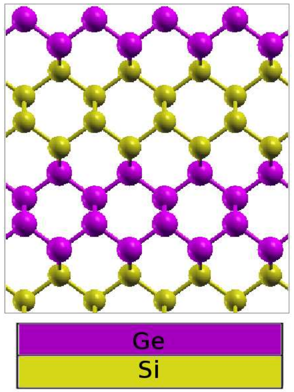
Si_n/Ge_n superlattices

- Role of the confinement in silicon-based structures
- Multilayers
- Nonlinear optical properties

Si and Ge are centrosymmetric



If n is even (Si_4/Ge_4), the crystal is centrosymmetric

$$\chi^{(2)} = 0$$

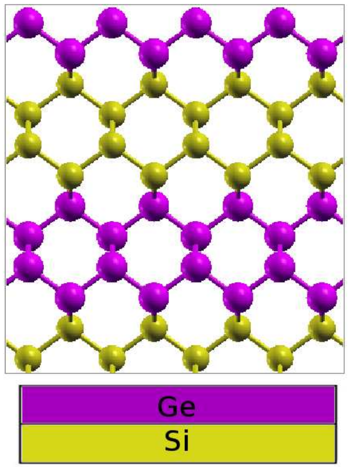
If n is odd, the nonlinear response is allowed and the signal can be large

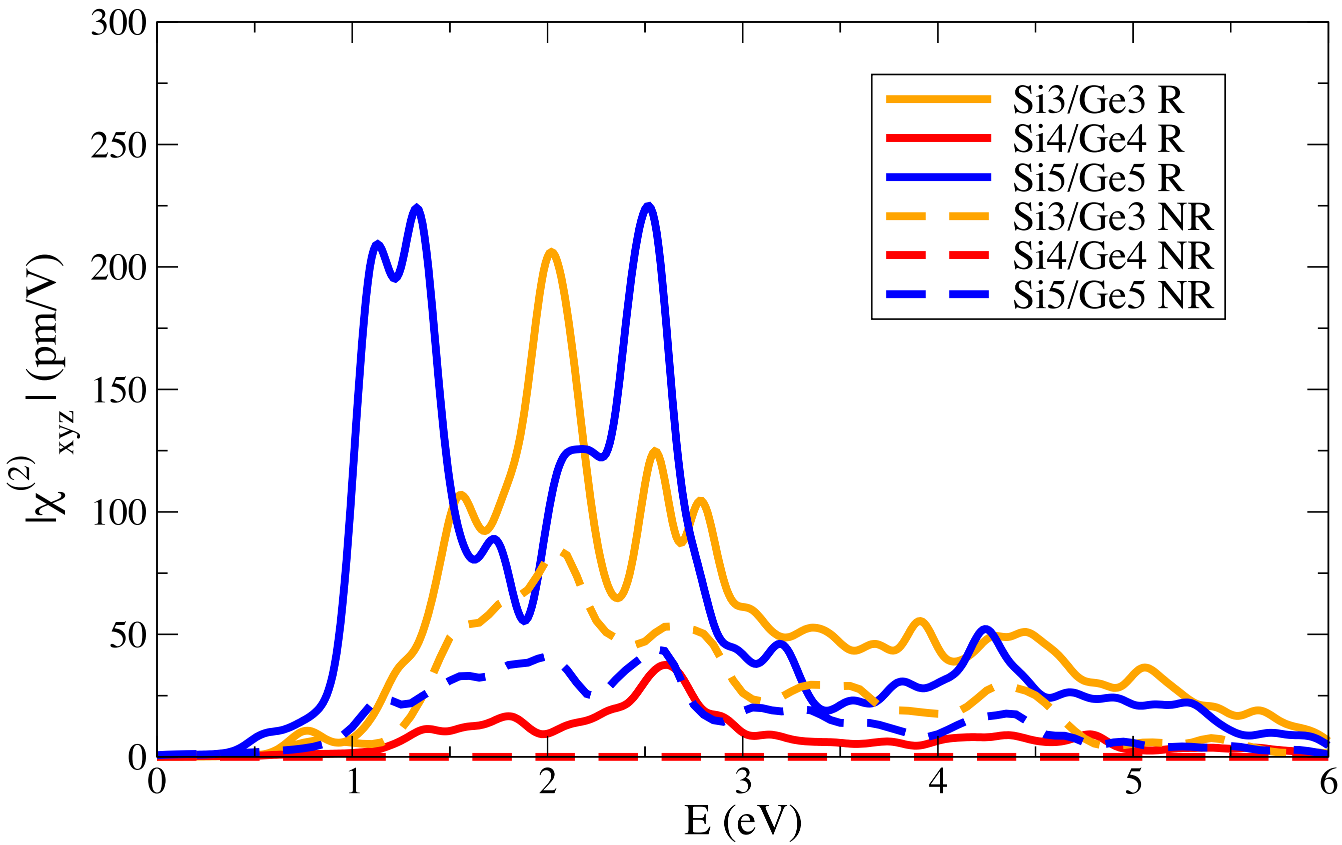
Experimentally, it seems not to be the case!

- Mixture of odd and even layers ?
- Nonuniformity of the layer thickness ?
- Strained interface ?

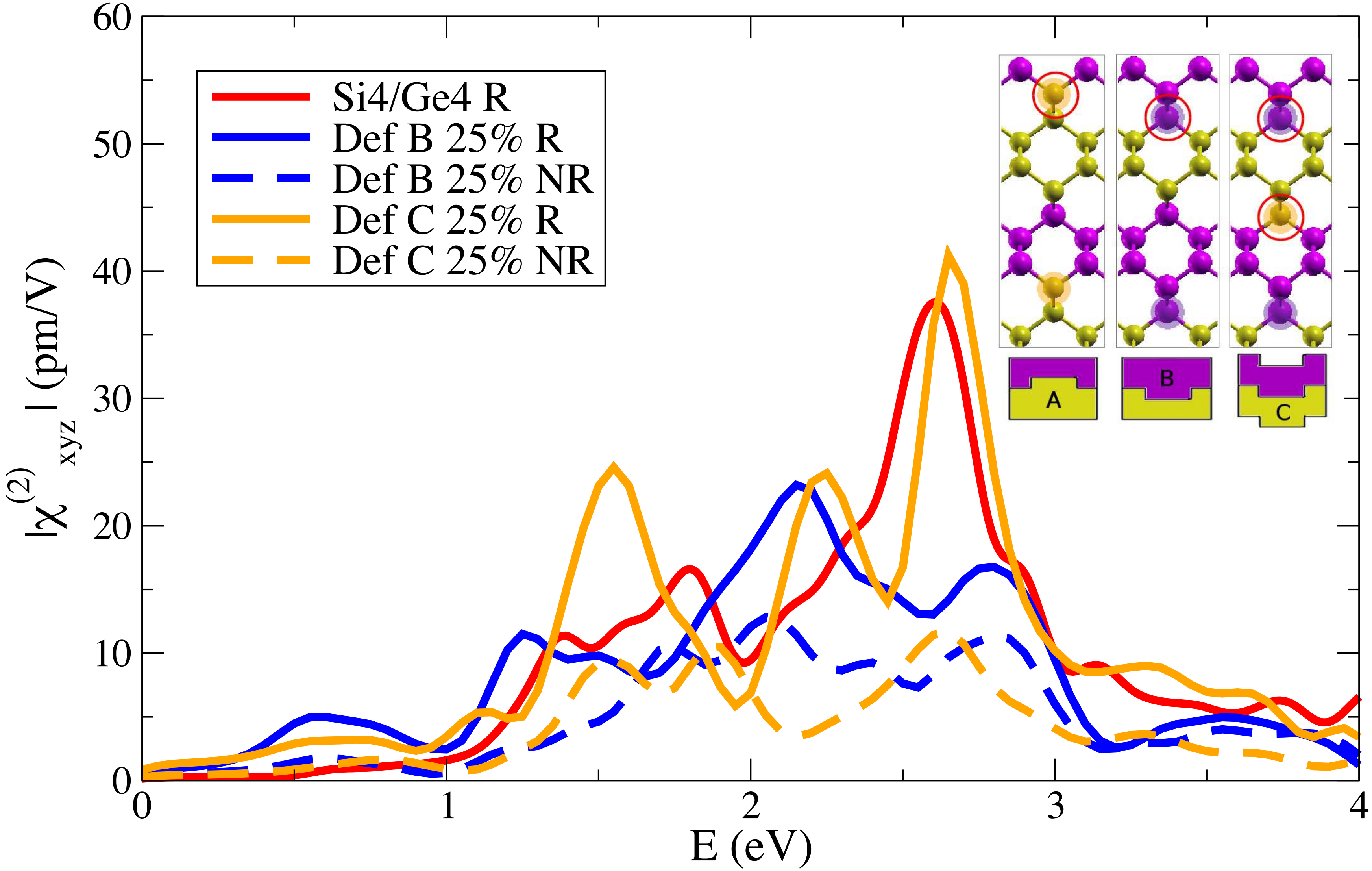
Si_n/Ge_n superlattices

Strain at the interface (relaxation effects)





Si_n/Ge_n superlattices



Si_n/Ge_n superlattices

- In all superlattices, strain enhances SHG
- Even superlattices: defects enhance SHG
- Odd superlattices : defects decrease SHG

Odd superlattices	even superlattices
↕	↕
Substitutional defects	strain

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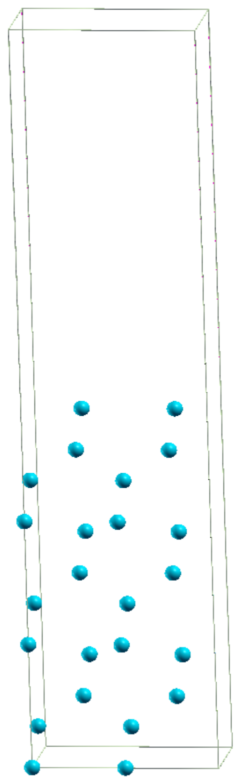
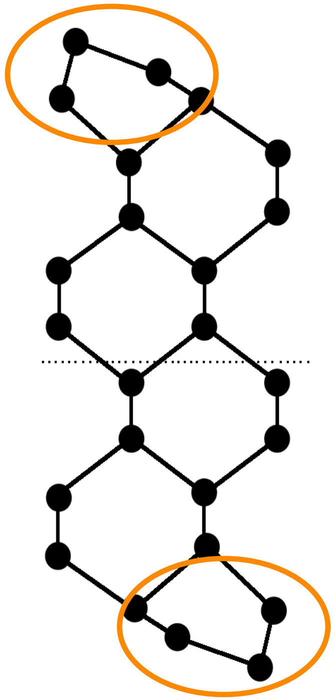
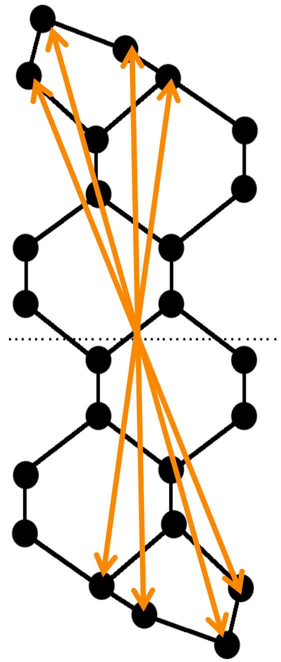
Surfaces







Construction of a supercell (atoms + vacuum)

System with 2 surfaces

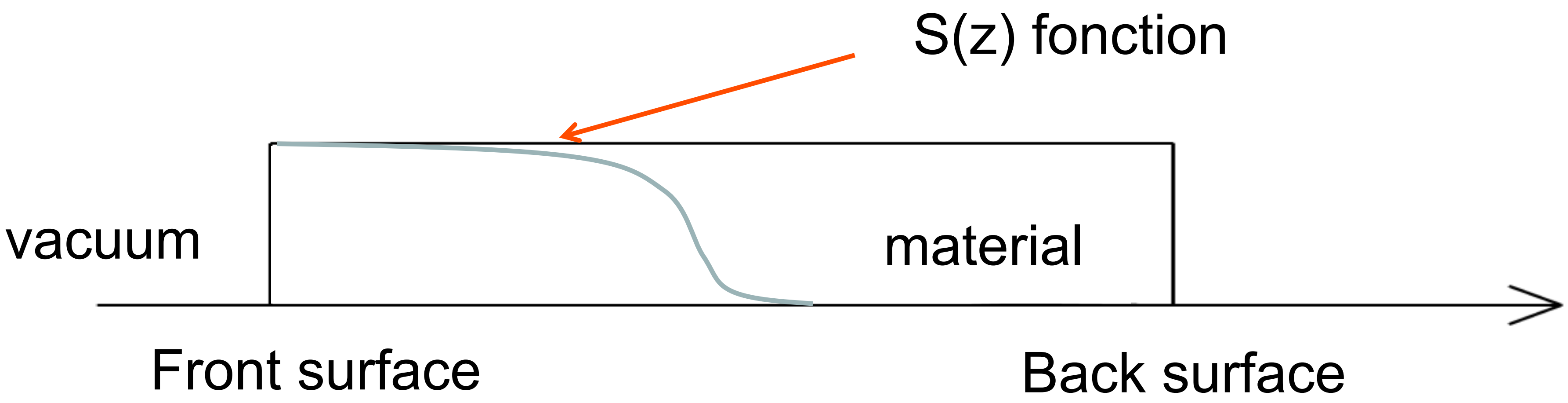
Inversion symmetry

$$\chi^{(2)} = 0$$

Signal from only one surface

It is possible to extract the signal from only one surface, using a new operator *p*, instead of p [1]

$$\mathcal{p} = \frac{1}{2}\left\{ \mathrm{p} S(z) + S(z)\mathrm{p} \right\} \qquad \mathrm{p} = i\left[H, r \right]$$



[1] L. Reining et al, Phys. Rev. B 50 8411 (1994)

Signal from only one surface

Interpretation:

S(z) is introduced to screen the field inside the material

Two approaches are possible:

Screen the two incoming fields at ω [1]

Screen the outgoing field at 2ω [2]

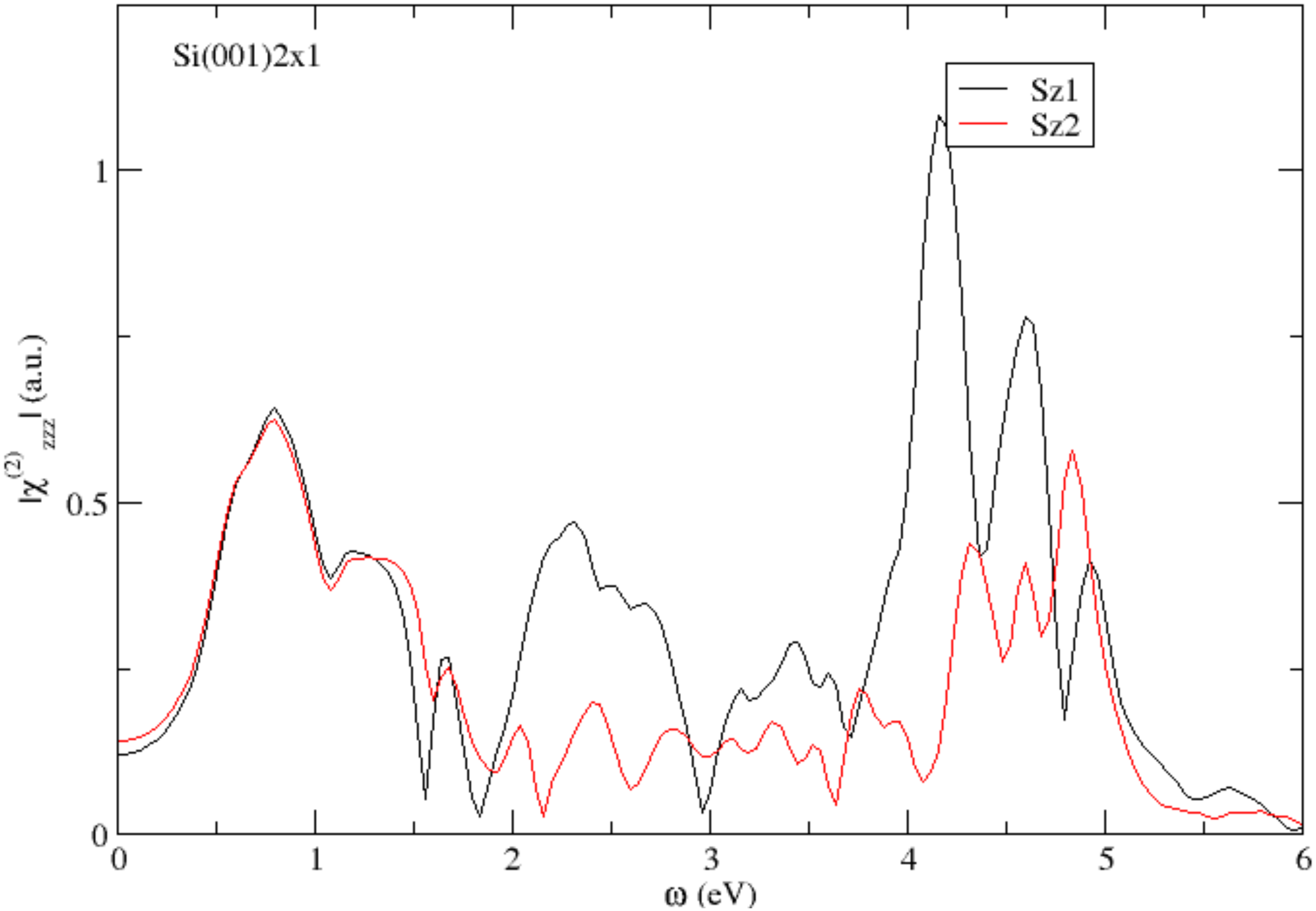
$$\chi^{(2)}_{abc} = \frac{-i}{\omega^3 V} \sum_{nml} \int d\vec{k} \frac{1}{E_m - E_n - 2\omega - 2i\eta} \left[f_{nl}(\vec{k}) \frac{p^a_{nm}(\vec{k}) p^b_{ml}(\vec{k}) p^c_{\ln}(\vec{k})}{E_l - E_n - \omega - i\eta} + \ldots \right]$$

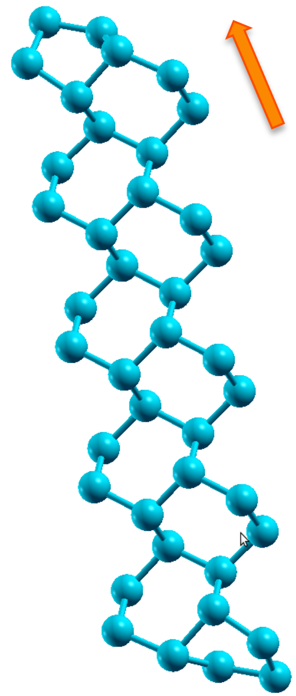
[1] L. Reining et al, Phys. Rev. B 50 8411 (1994)

[2] B. Mendoza et al, Phys. Rev. Lett. 81, 3781 (1998)

Signal from only one surface

Comparison between the two approaches





Tight binding calculation
72 Si atoms
2X1 surface

Signal from only one surface

Two approaches are possible:

Screen the two impinging fields at ω [1]

Screen the outgoing field at 2ω [2]

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

No divergence at ω=0

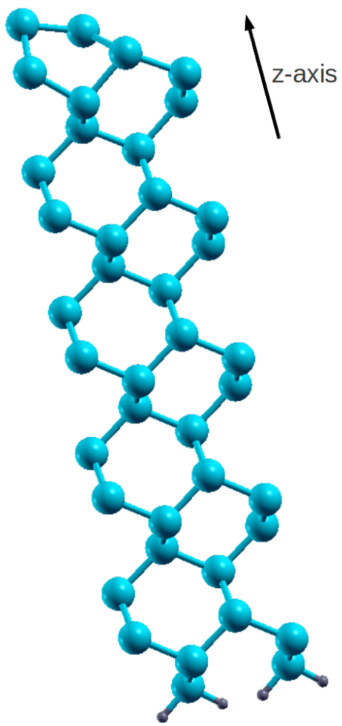
Related to Gauge invariance

[1] L. Reining et al, Phys. Rev. B 50 8411 (1994)

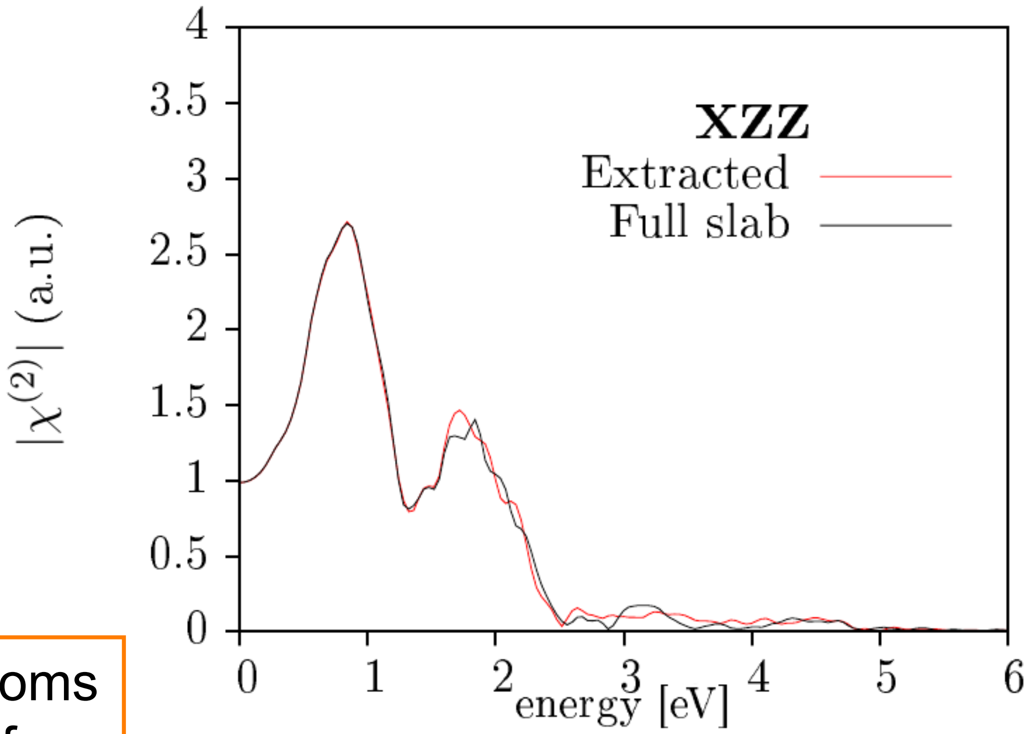
[2] B. Mendoza et al, Phys. Rev. Lett. 81, 3781 (1998)

Surfaces : numerical results

Non-reconstructed surface : *xxz; yyz; zxx; zyy; zzz*
Reconstructed surface (Asymmetric dimers) :
yyx; xyy; yyz; zyy; xxx; zxx; xxz; xzz; zzx; zzz



72 Si atoms
2X1 surface

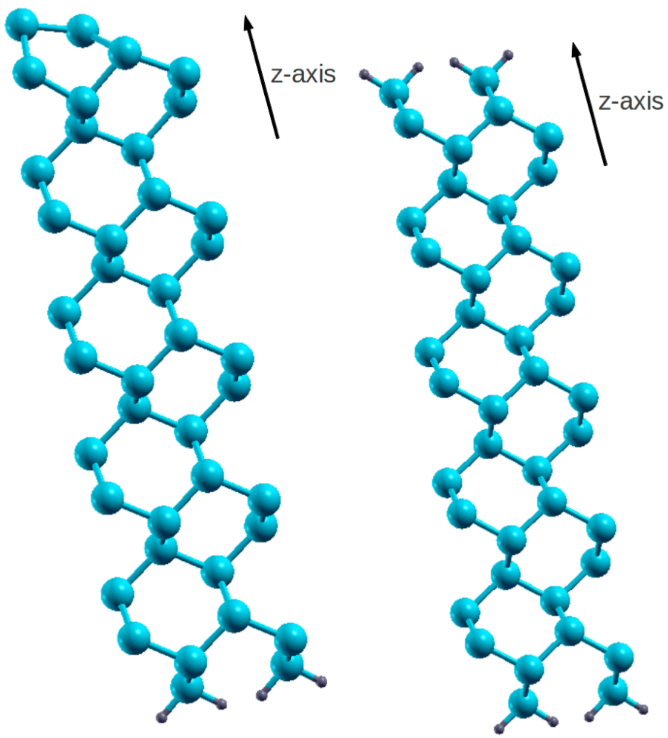


Surfaces : numerical results

Non-reconstructed surface : *xxz; yyz; zxx; zyy; zzz*

Reconstructed surface (Asymmetric dimers) :

yyx; xyy; yyz; zyy; xxx; zxx; xxz; xzz; zzx; zzz



72 Si atoms
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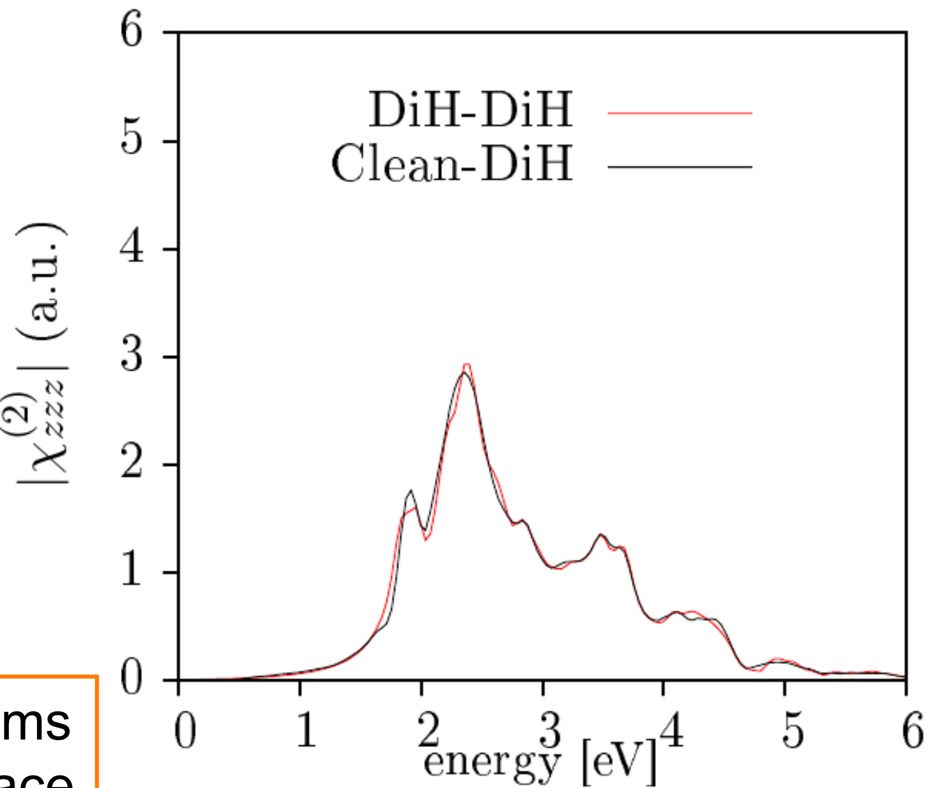
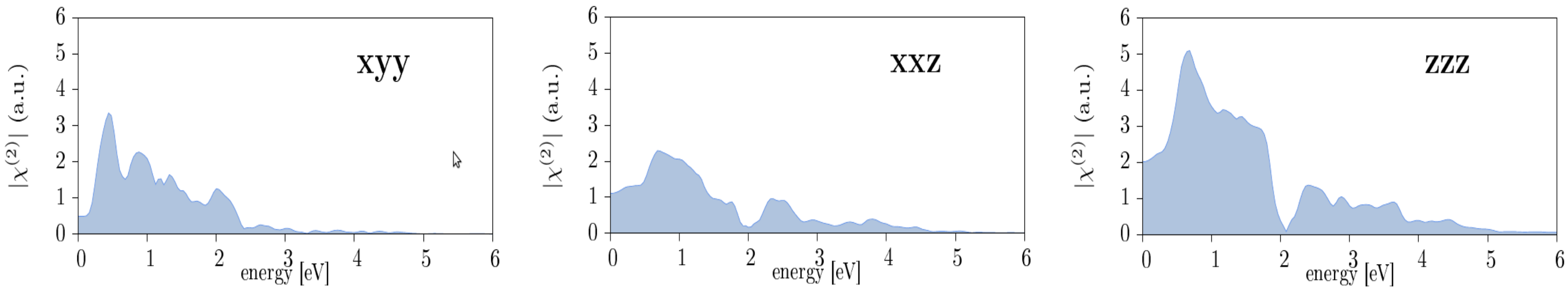


Surfaces : what's next?

Apply the method to an ab initio calculation (work in progress)

THE CHALLENGE : Local field effects

the Dyson equation has to be strongly
modified, to take into account only the half slab.



Casting

Formalism and GaAs : E. Luppi and H. Hübener (PhD)
LSI, Ecole Polytechnique

Si under contraint:
Exp : L. Pavesi, M. Cazzanelli, F. Bianco, E. Borga, University of Trento. G. Pucker and M. Ghulinyan, Advanced Photonics & Photovoltaics Unit, Trento. D. Modotto and S. Wabnitz, University of Brescia. R. Pierobon, CIVEN, Venezia
Theory : E. Degoli, S. Ossicini (University of Modena e Reggio Emilia), E. Luppi (Berkeley)

Si/Ge : M. Bertocchi (PhD), E. Luppi (LCT, Paris 6),
E. Degoli, S. Ossicini (University of Modena e Reggio Emilia)

Surfaces : N. Tancogne-Dejean (PhD)
LSI, Ecole Polytechnique

Thank you for your attention