Second order harmonic generation from bulk, interfaces and surfaces: an \textit{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

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

Amplitude

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

but...

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

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

  - Surfaces
  - Thin films
  - Interfaces
  - Nanowires

- Development and characterisation of new materials

  New optical devices
• Introduction: nonlinear optics in solids

• How do we get the spectrum for SHG

• 4 applications:
  • GaAs
  • Silicon under constraint
  • \( \text{Si}_n/\text{Ge}_n \) 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

\[
\chi_{abc}^{(2)}(-2\omega, \omega, \omega) = \frac{-ie^3}{\hbar^2 m^3 \omega^3 V} \sum_{nml} \int d\mathbf{k} \frac{1}{E_m - E_n - 2\omega - 2i\eta} 
\]

\[
\times \left[ f_{nl}(\mathbf{k}) \frac{p_{nm}^a(\mathbf{k}) \{ p_{ml}^b(\mathbf{k}) p_{ln}^c(\mathbf{k}) \}}{E_l - E_n - \omega - i\eta} + f_{ml}(\mathbf{k}) \frac{p_{nm}^a(\mathbf{k}) \{ p_{ml}^b(\mathbf{k}) p_{ln}^c(\mathbf{k}) \}}{E_m - E_l - \omega - i\eta} \right] 
\]
Additional effect: screening

GW approximation: Hedin’s equations (1965)

⇒ Shift of the conduction bands

⇒ Opening of the gap

Scissor operator

Screening: Hole- (N-1) electrons

See B. Mendoza’s talk
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

Dyson equation for the density response function

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

Evaluated in the long wavelength limit \( q \to 0 \)

1st order

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

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

\[
g_{xc} = \frac{\partial^2 V_{xc}}{\partial \rho \partial \rho}
\]
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  • Siₙ/Geₙ superlattices
  • Surfaces
Some results for GaAs

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

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

Dilation and translation of the energy scale
\( \chi^{(2)} \) for GaAs

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

Second Harmonic Generation

Cubic GaAs

Screening

Screening and local fields
$\chi^{(2)}$ for GaAs

Full calculation

Screening

Screening and local fields

Exciton (Long range kernel)

$$ f_{xc} = \frac{\alpha}{q^2} $$
\[ \chi_{xyz}^{(2)}(2q,2\omega) = -\frac{i}{12q_x q_y q_z} \left[ \epsilon_{M}^{LL}(q,\omega) \right]^2 \left[ \epsilon_{M}^{LL}(2q,2\omega) \right] \chi_{\rho\rho\rho}(2q,q,q,\omega,\omega) \]
\[ \chi_{xyz}^{(2)}(2\mathbf{q}, 2\omega) = -\frac{i}{12q_x q_y q_z} \left[ \varepsilon_{LL}^{M} (\mathbf{q}, \omega) \right]^2 \left[ \varepsilon_{LL}^{M} (2\mathbf{q}, 2\omega) \right] \chi_{\rho\rho\rho}(2\mathbf{q}, \mathbf{q}, \mathbf{q}, \omega, \omega) \] for GaAs

**Linear dielectric function**

- TDDFT (Long range kernel)
- Similar results with BSE
\[ \chi_{xyz}^{(2)}(2q, 2\omega) = -\frac{i}{12q_x q_y q_z} \left[ \varepsilon_M^{LL}(q, \omega) \right]^2 \left[ \varepsilon_M^{LL}(2q, 2\omega) \right] \chi_{\rho\rho\rho}(2q, q, q, \omega, \omega) \]

**Linear dielectric function**

- TDDFT (Long rang kernel)
- Similar results with BSE
\( \chi^{(2)} \) and \( \varepsilon_M \) for GaAs

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

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

Good agreement with the experiment

The description 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-symmetry of the crystal, $\chi^{(2)} = 0$ in the dipole approximation

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

- Requires important optical power
- Competition with other nonlinear processes
  (Two-photon absorption)
Silicon under constraint

- **Uniaxial constraint (001)**
  \[ \chi^{(2)} \neq 0 \text{, } \chi^{(2)} < 0.5 \text{pm/V} \]
- **Biaxial constraint**
  \[ \chi^{(2)} \approx 200 \text{pm/V} \]
- The more the lattice is distorted, the larger is \( \chi^{(2)} \)
Experiment:

Silicon wave guide under constraint

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

Micro-Raman spectroscopy
The most favorable situation: biaxial compressive-tensile

**Theory**
- $\chi^{(2)} = 200 \text{ pm/V}$
- (GaAs $\chi^{(2)} = 700 \text{ pm/V}$)
- Silicon surface $\chi^{(2)} \approx 3 \text{ pm/V}$
- Si/SiO$_2$ $\chi^{(2)} < 1 \text{ pm/V}$

**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\textsubscript{n}/Ge\textsubscript{n} superlattices

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

Si and Ge are centrosymmetric

If \( n \) is even (\( \text{Si}_4/\text{Ge}_4 \)), 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?
\( \text{Si}_n/\text{Ge}_n \) superlattices

Strain at the interface (relaxation effects)

![Graph showing the \( \chi^{(2)} \) intensity for different \( n \) layers of Si and Ge in Si/Ge superlattices. The graph compares the SHG signal for different superlattices, illustrating the effect of strain at the interface. The signal intensity is shown as a function of energy for Si/Ge superlattices with varying thicknesses of Si and Ge layers.]
The intensity of the generated SHG signal is not linear with the defect percentage and the signal intensity, that is independent of any process, it is possible to deduce the total contribution due to any overlapping/combination/mixing process, non-planar deposition can be an important source of SHG in the measured systems.

In the left part of Fig. 3 a detailed study of the superlattices or diminish the signal in odd-periodicity has been observed also to the insertion of a non-vanishing odd component into the material. This proportionality has been observed also to the insertion of a non-vanishing odd component into the material. This proportionality has been observed also to the insertion of a non-vanishing odd component into the material. This proportionality has been observed also to the insertion of a non-vanishing odd component into the material.
Si$_n$/Ge$_n$ superlattices

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

Odd superlattices: Substitutional defects
Even superlattices: strain
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Surfaces

Construction of a supercell (atoms + vacuum)

System with 2 surfaces

Inversion symmetry $\chi^{(2)} = 0$
It is possible to extract the signal from only one surface, using a new operator $p$, instead of $p$ \[1\]

\[ p = \frac{1}{2} \{ pS(z) + S(z)p \} \quad p = i[H, r] \]

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 $\omega$ \[1\]
Screen the outgoing field at $2\omega$ \[2\]

$$\chi_{abc}^{(2)} = \frac{-i}{\omega^3 V} \sum_{nm\ell} \int d\vec{k} \frac{1}{E_m - E_n - 2\omega - 2i\eta} \left[ f_{nl}(\vec{k}) p^{a}_{nm}(\vec{k}) p^{b}_{ml}(\vec{k}) p^{c}_{ln}(\vec{k}) \right] + \ldots$$

Signal from only one surface

Comparison between the two approaches

$\chi^{(2)}_{zz}$

Si(001)2x1

- $S_{z1}$
- $S_{z2}$

Tight binding calculation
72 Si atoms
2X1 surface
Signal from only one surface

Two approaches are possible:
- Screen the two impinging fields at $\omega$ \[1\]
- Screen the outgoing field at $2\omega$ \[2\]

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

No divergence at $\omega=0$
 Related to Gauge invariance

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
2X1 surface
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 constraint:
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),
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Si/Ge: M. Bertocchi (PhD), E. Luppi (LCT, Paris 6),
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Surfaces: N. Tancogne-Dejean (PhD)
LSI, Ecole Polytechnique
Thank you for your attention