Second-Harmonic Generation from First Principles:

A Time-Dependent Density-Functional theory

Eleonora Luppi, Hannes Hübener and Valerie Véniard

Thanks to: Lucia Reining, Angel Rubio and Fridhelm Bechsted

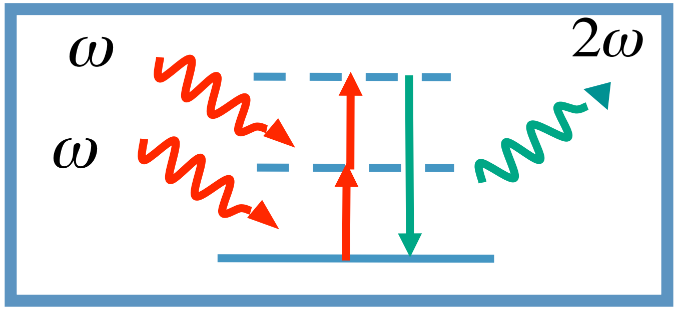
CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE

ÉCOLE POLYTECHNIQUE

ETSF France
Laboratoire des Solides Irradiés,
Ecole Polytechnique, CEA-DSM, CNRS,
91128 Palaiseau, France

Second-Harmonic Generation SHG

nonlinear optical process



Spectroscopy

Extreme sensitivity of SHG to the symmetry of the system (no inversion symmetry)

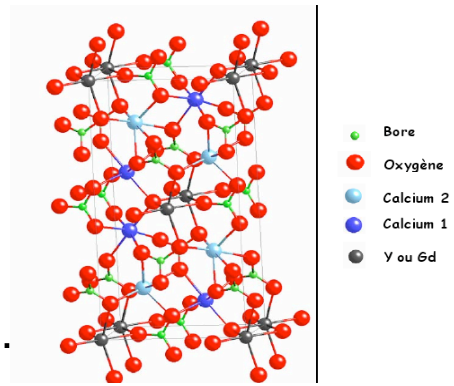
surfaces, interfaces
nanostructures:
carbon nanotubes …

New optical devices

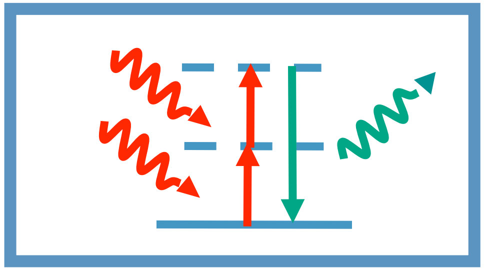
Optimisation of nonlinear optical materials

Self-doubling crystals

Oxoborate family:
GdCOB, YCOB …



SHG



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

Second-Order Susceptibility $\chi^{(2)}$

We have developed a First-Principle Theory based on TDDFT

exact and straightforward inclusion of the many-body effects

How we calculate

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

within our formalism ?

A Time-Dependent Density-Functional theory …

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

First Step:

second-order microscopic polarisation

Second Step:

second-order
macroscopic polarisation and response function

Third Step:

second-order response function within **TDDFT**

⇓

SHG spectrum ☺

Derivation of the $\chi^{(2)}$

Second-order time-dependent perturbation theory

J^{ind}

Polarization

Microscopic

$E^{P}(\vec{r},t)$

perturbing electric field

→

Macroscopic

$E^{TOT}(\vec{r},t)$

total electric field

Derivation of the $\chi^{(2)}$

Second-Order Displacement Vector

$$D(\mathbf{q},\omega) = \varepsilon_M \mathbf{E}^{tot}(\mathbf{q},\omega) + 4\pi \mathbf{P}_M^{(2)}$$

linear $\varepsilon_M = 1 + 4\pi\chi^{(1)}$

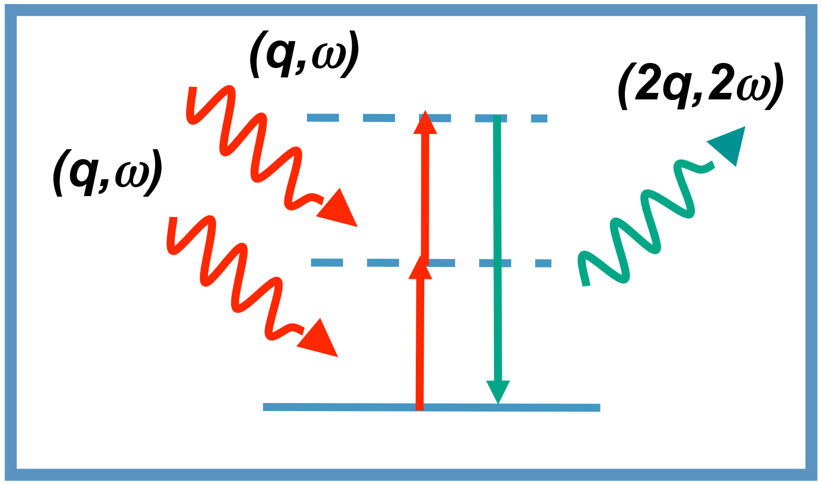
nonlinear $\mathbf{P}_M^{(2)} = \chi^{(2)} \mathbf{E}^{tot} \mathbf{E}^{tot}$

Derivation of the $\chi^{(2)}$

$$\chi^{(2)}(2\mathbf{q},2\omega)=\tilde{\alpha}^{(2)}(2\mathbf{q},\mathbf{q},\mathbf{q},\omega,\omega)\left[1+4\pi\frac{\mathbf{q}}{|q|}\frac{\mathbf{q}}{|q|}\frac{\tilde{\alpha}^{(1),L\rightarrow}(\mathbf{q},\mathbf{q},\omega)}{1-4\pi\tilde{\alpha}^{(1),LL}(\mathbf{q},\mathbf{q},\omega)}\right]^2\left[1+4\pi\frac{\mathbf{q}}{|q|}\frac{\mathbf{q}}{|q|}\frac{\tilde{\alpha}^{(1),L\rightarrow}(2\mathbf{q},2\mathbf{q},2\omega)}{1-4\pi\tilde{\alpha}^{(1),LL}(2\mathbf{q},2\mathbf{q},2\omega)}\right]$$

second order response function χ_{jjj}

?



Derivation of the $\chi^{(2)}$

Response Functions

Photons are described by transverse fields:

$\chi_{\vec{j}\vec{j}\vec{j}}$ current response function

- TDCFT: « Time-dependent current functional theory »

- Solved in the linear case for long wavelenght limit (q →0)

transverse components obtained from the longitudinal components

TDDFT (longitudinal)

Derivation of the $\chi^{(2)}$

$$\chi^{(2)}(2\mathbf{q},2\omega)=\tilde{\alpha}^{(2)}(2\mathbf{q},\mathbf{q},\mathbf{q},\omega,\omega)\left[1+4\pi\frac{\mathbf{q}}{|q|}\frac{\mathbf{q}}{|q|}\frac{\tilde{\alpha}^{(1),L\rightarrow}(\mathbf{q},\mathbf{q},\omega)}{1-4\pi\tilde{\alpha}^{(1),LL}(\mathbf{q},\mathbf{q},\omega)}\right]^2\left[1+4\pi\frac{\mathbf{q}}{|q|}\frac{\mathbf{q}}{|q|}\frac{\tilde{\alpha}^{(1),L\rightarrow}(2\mathbf{q},2\mathbf{q},2\omega)}{1-4\pi\tilde{\alpha}^{(1),LL}(2\mathbf{q},2\mathbf{q},2\omega)}\right]$$

long wavelenght limit link between $\alpha^{(2)}$ et $\chi_{\rho\rho\rho}$
TDDFT+symmetry properties

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

Cubic symmetry: zinc-blende

Macroscopic longitudinal dielectric function

Calculation of the response function $\chi_{\rho\rho\rho}$

Dyson equation for the second-order response function

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

Linear response

$$\chi_0^{(1)}$$

$$\chi^{(1)} = [1-\chi_0^{(1)} f_{uxc}]^{-1}\chi_0^{(1)}$$

$$f_{xc} = \frac{\delta V_{xc}}{\delta\rho}$$

Second-order response

$$\chi_0^{(2)}$$

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

New kernel

Calculation of the response function $\chi_{\rho\rho\rho}$

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

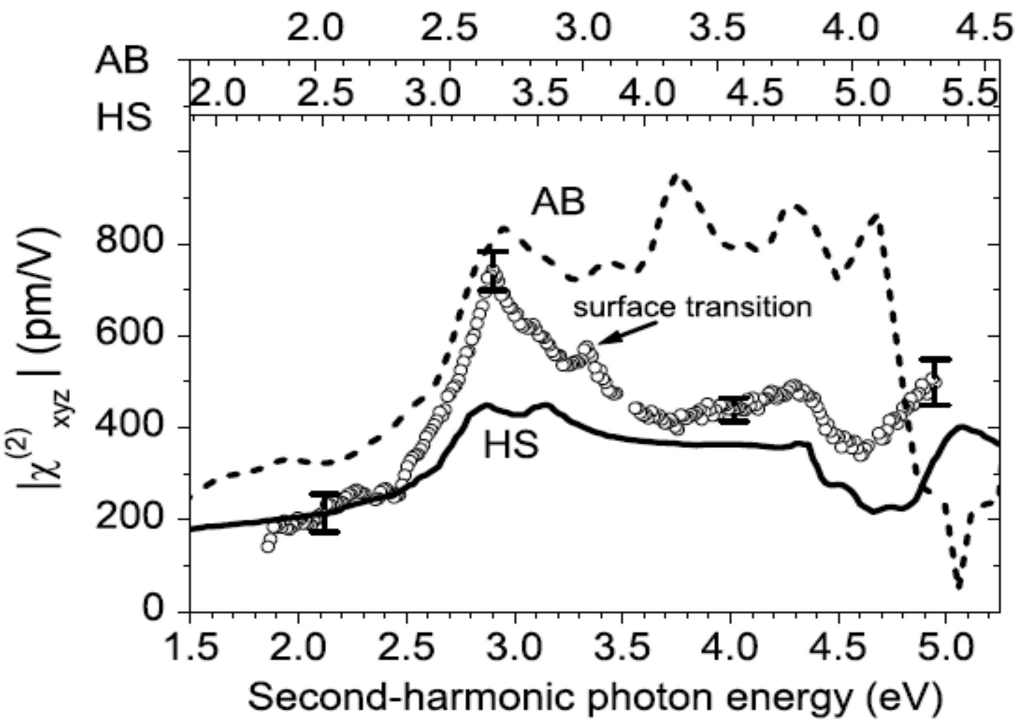
- Independent Particles Approximation (IPA)
- Quasiparticle band structure: SO or GW
- Local fields
- Excitons

Comparison with the experience:

GaAs semiconductor

Experiment in an higher energy range

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



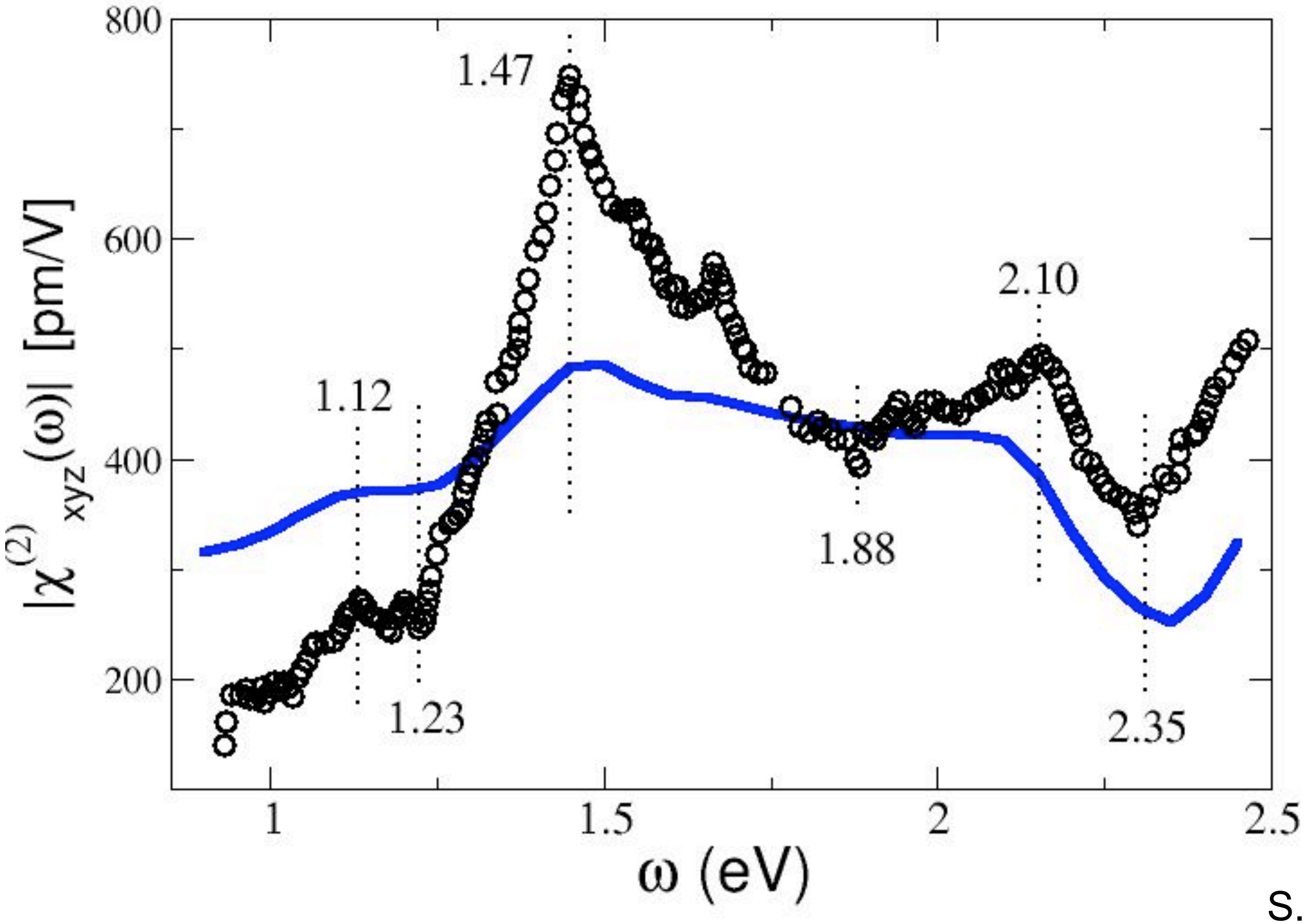
HS:Hughes and Sipe PRB (1996)

AB:Leitsmann et al. PRB(1998)

	$\chi^{(2)}_{xyz}(0)$	
Experiment		
Levine and Bethea APL (1972)	**180 ±10**	pm/V
Roberts JQE(1992)	**166**	pm/V
Eyres at *al.* APL(2001)	**172**	pm/V
Theory		
Chang et *al.* PRB(2001)	**224**	pm/V
Dal Corso et *al.* PRB(1996)	**205**	pm/V

Comparison with the experience:

GaAs



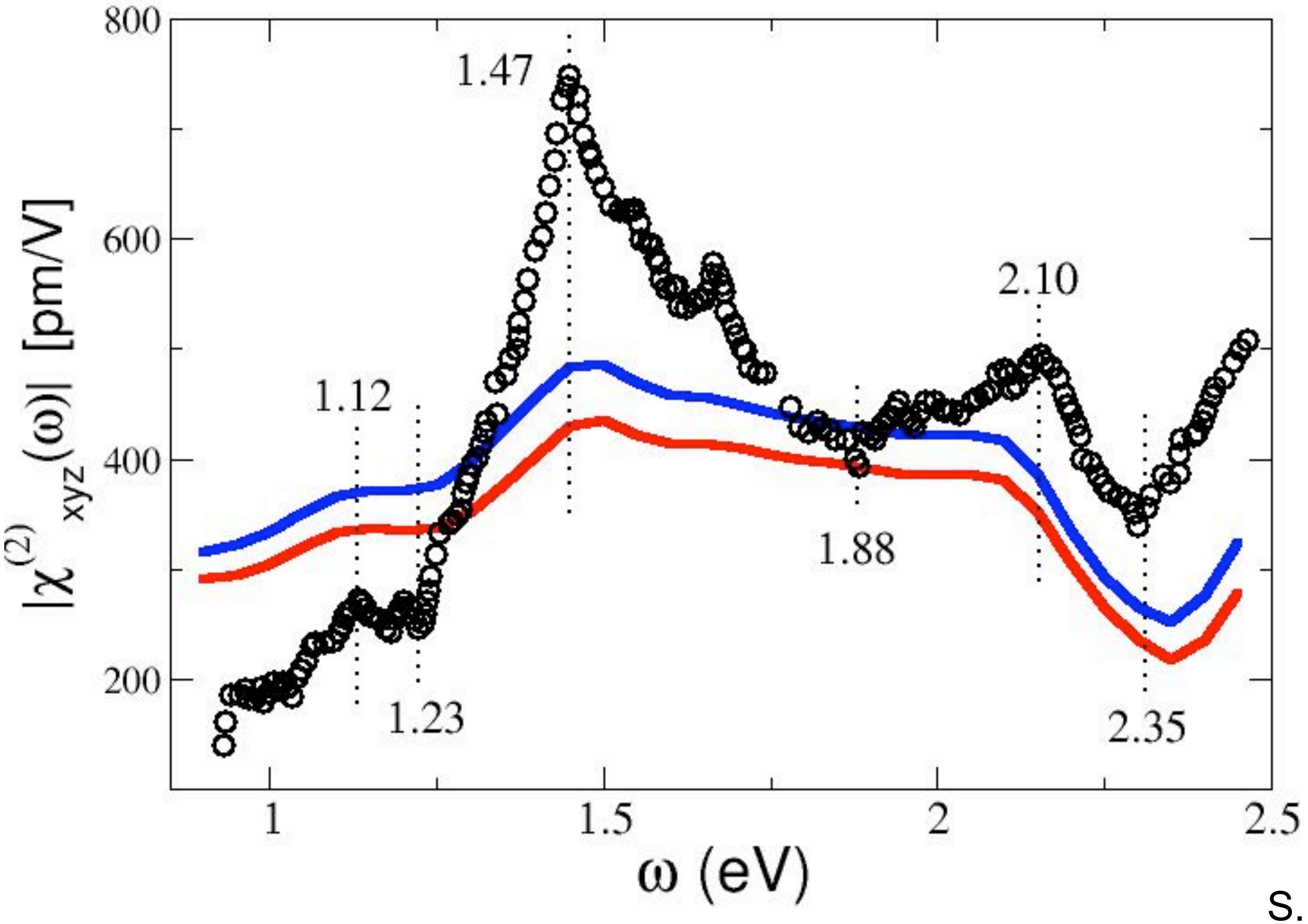
IPA

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

ENERGY POSITION of the PEAKS and VALLEYS are OK
but MAGNITUDE ?

Comparison with the experience:

GaAs



IPA

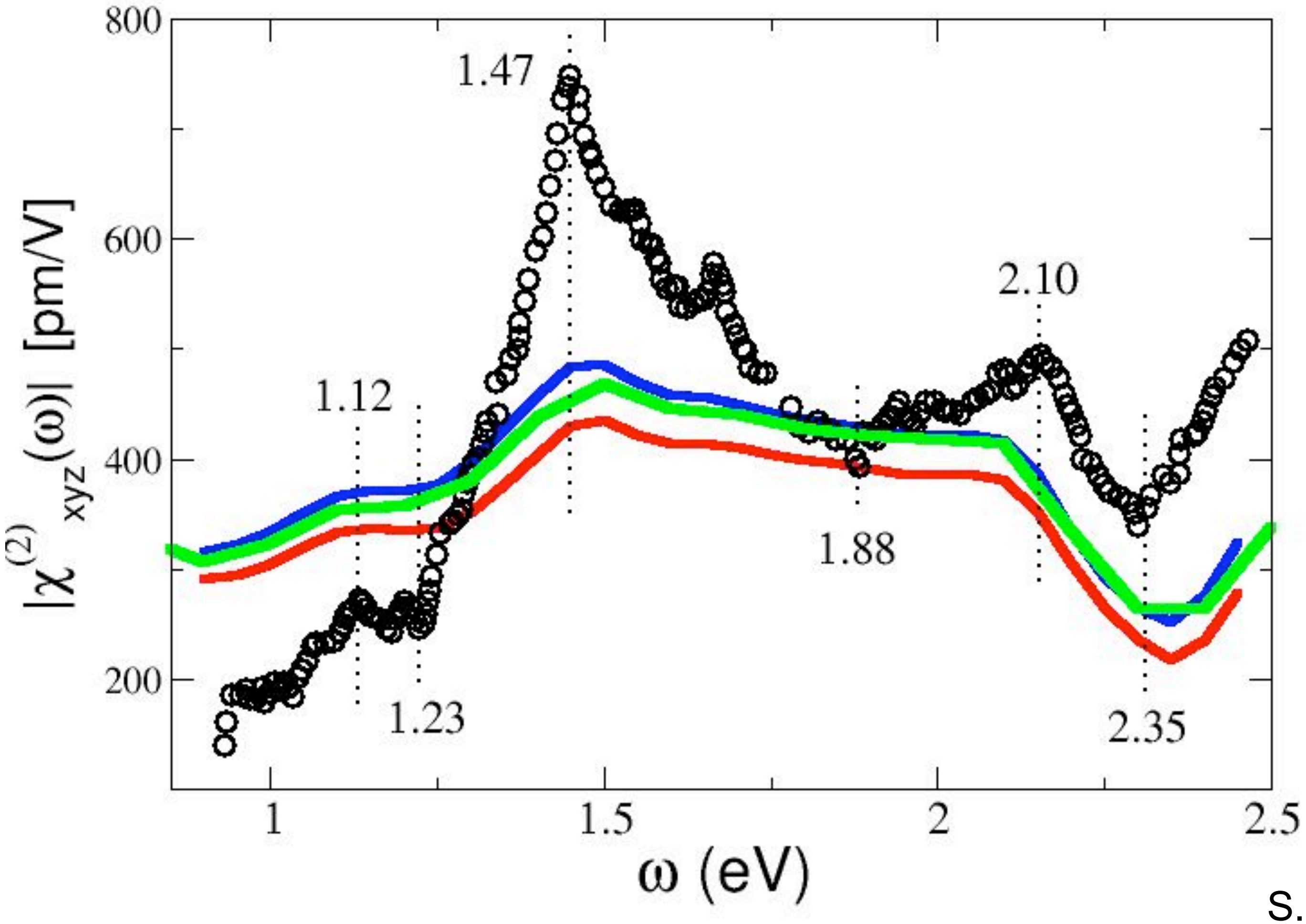
Local Fields

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

ENERGY POSITION of the PEAKS and VALLEYS are OK
but MAGNITUDE ?

Comparison with the experience:

GaAs



IPA

Local Fields

ALDA

Similar behaviour of the absorption spectra (linear response)

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

ENERGY POSITION of the PEAKS and VALLEYS are OK but MAGNITUDE ?

let's go back to linear ...

failure of f_{xc}^{ALDA} for absorption in solids: **short-range**

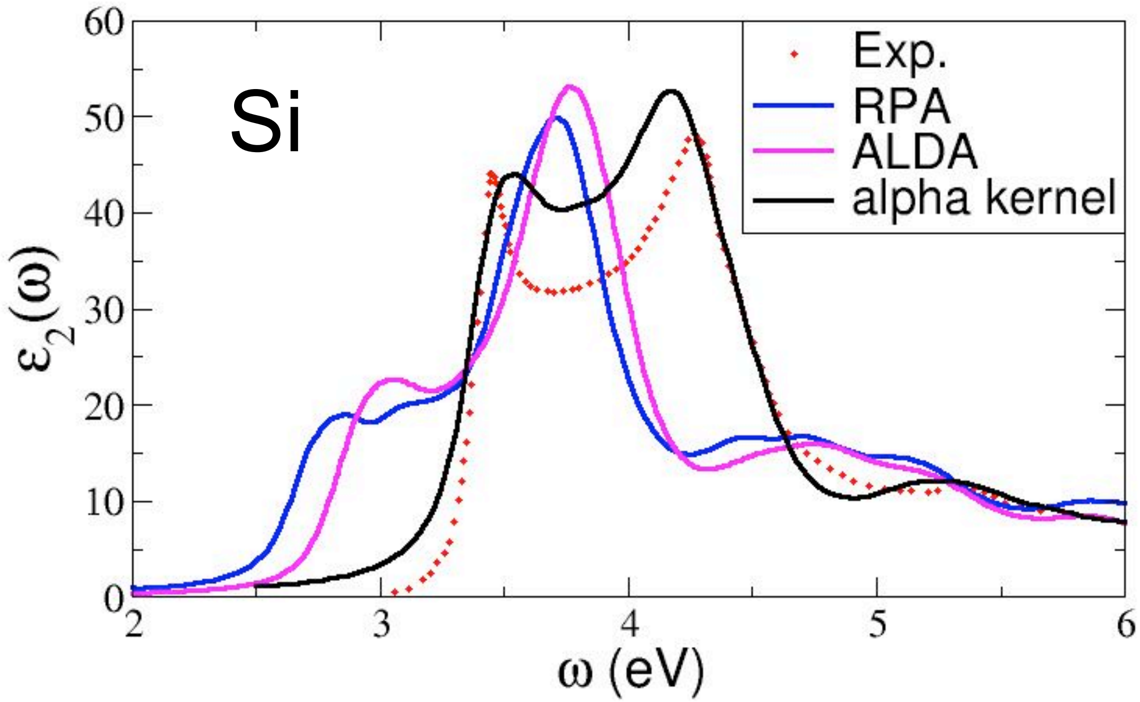
solution for TDDFT from Bethe-Salpeter equation

Reining *et al*, PRL 88, 66404 (2002)

long-range kernel

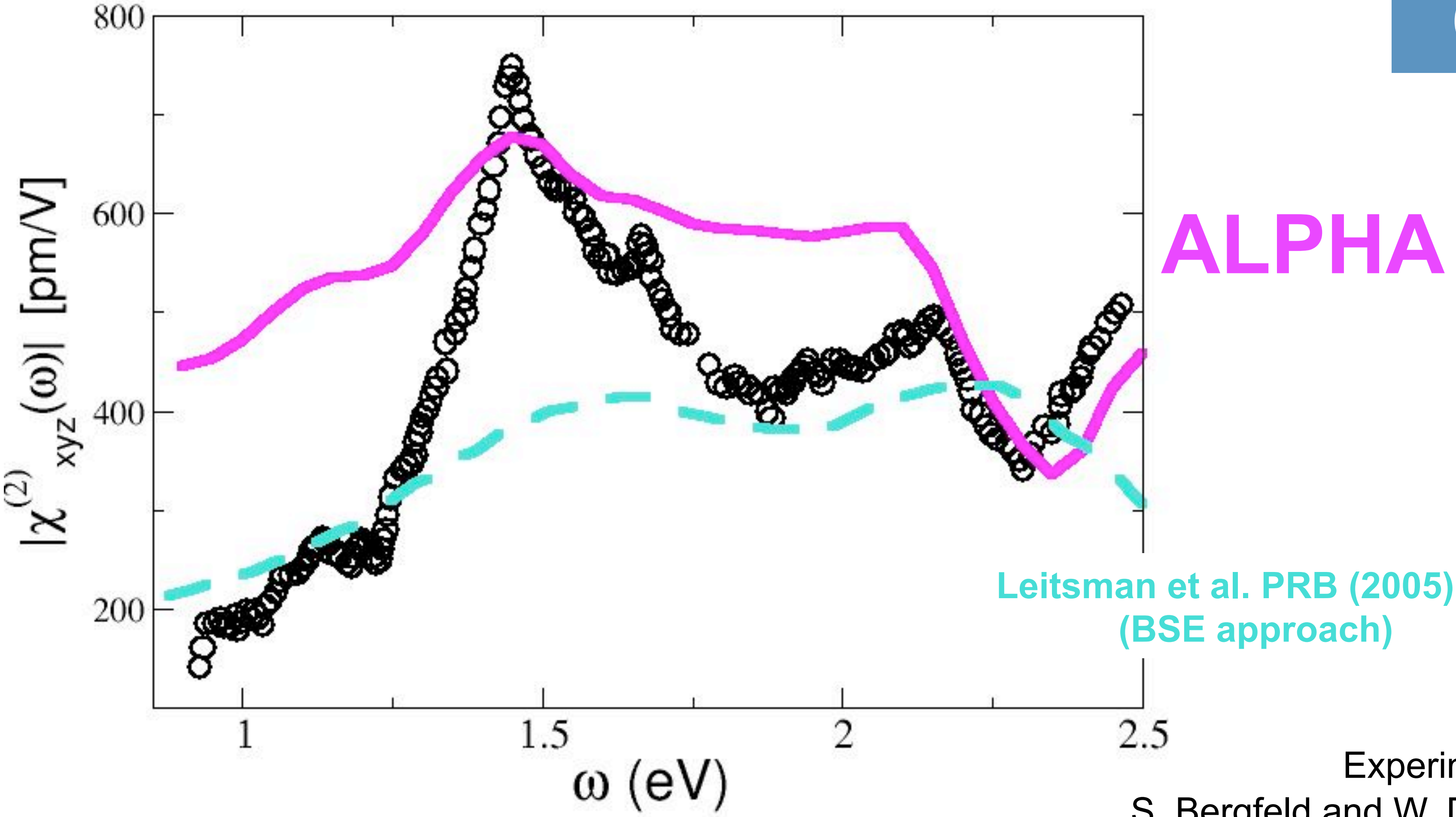
parameter to fit experiment

$$f_{xc}(q \to 0) = -\frac{\alpha}{q^2}$$



Comparison with the experience:

GaAs



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

ENERGY POSITION of the PEAKS and VALLEYS are OK

MAGNITUDE is OK

Conclusion:

- We have developed a first-principles theory in Time-Dependent Density Functional Theory for the macroscopic second-order susceptibility.

1) the exact relations between microscopic and macroscopic formulation of the second-order response function

2) a rigorous and straightforward inclusion of the many-body effects

- We have studied SHG for GaAs

1) good comparison with experimental results