Spectroscopie théorique: décrire et comprendre les excitations électronique

Laboratoire des Solides Irradiés

OUTLINE

Matteo Gatti

Theoretical Spectroscopy
ETSF

Different type of spectroscopies:
Photoemission

Eleonora Luppi

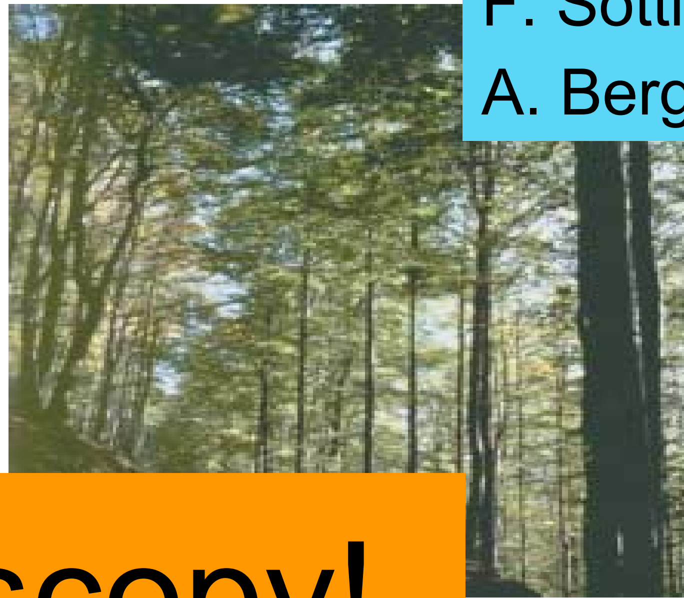
Absorption, Energy Loss

Beyond the linear response…



W. Welnic

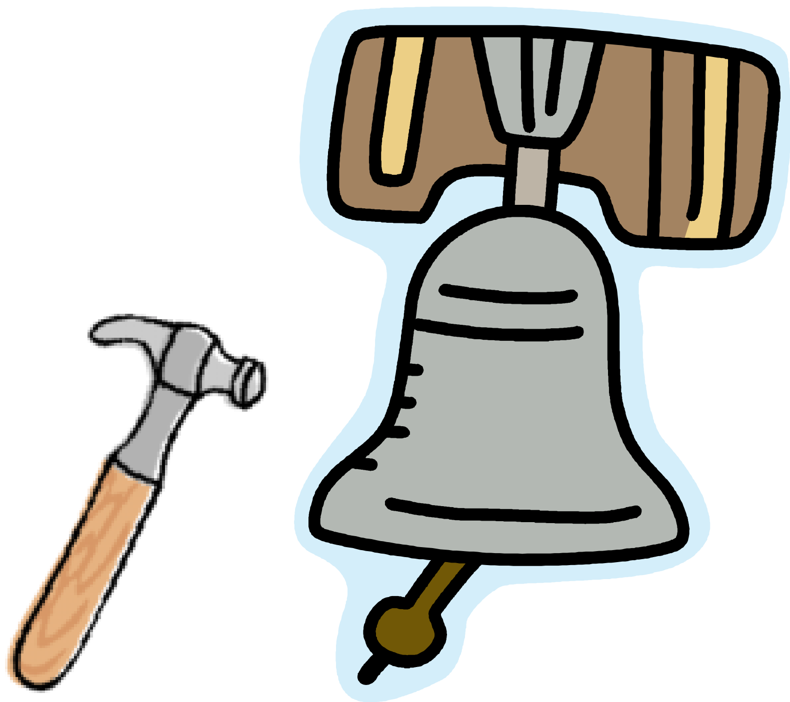
F. Sottile
A. Berger



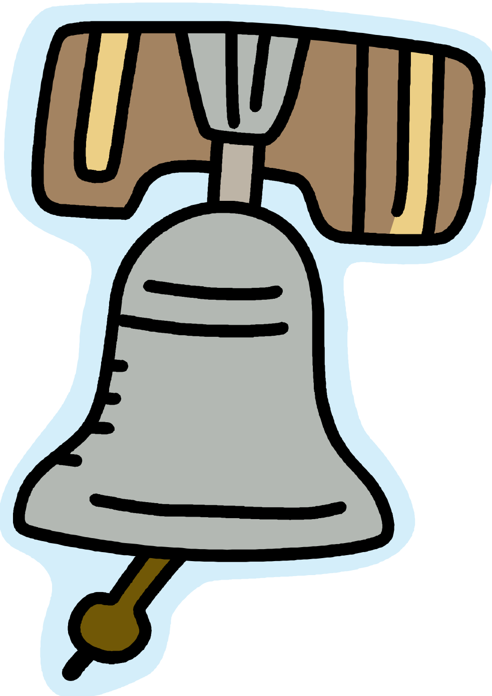
Spectroscopy!

J. Vidal

Spectroscopy



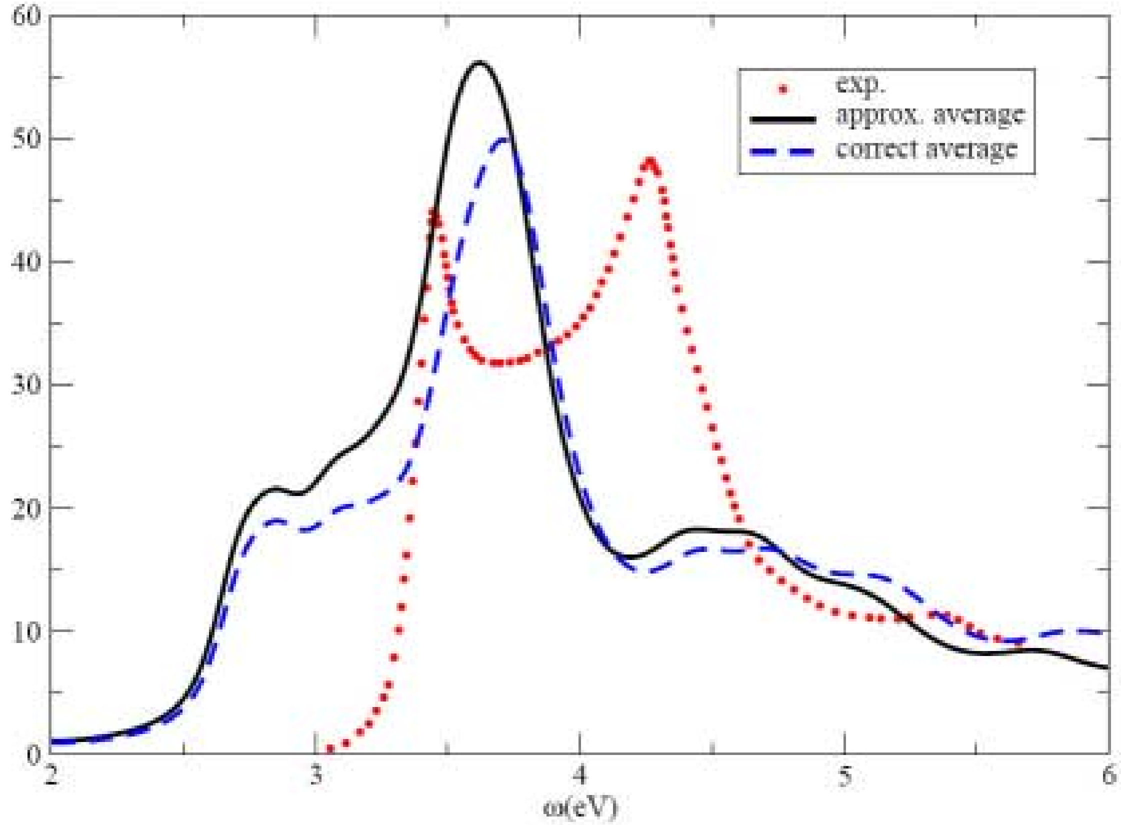
Spectroscopy

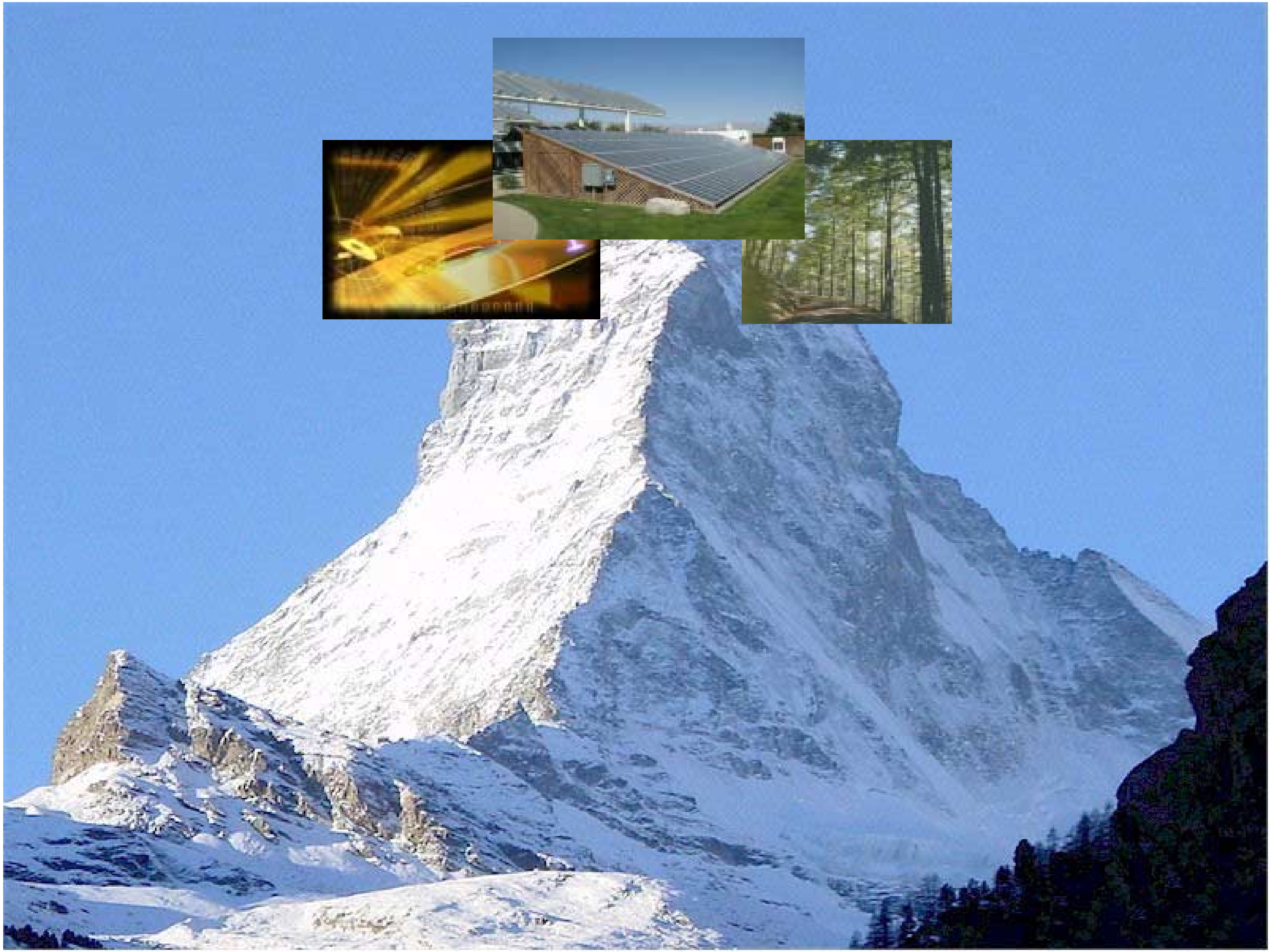


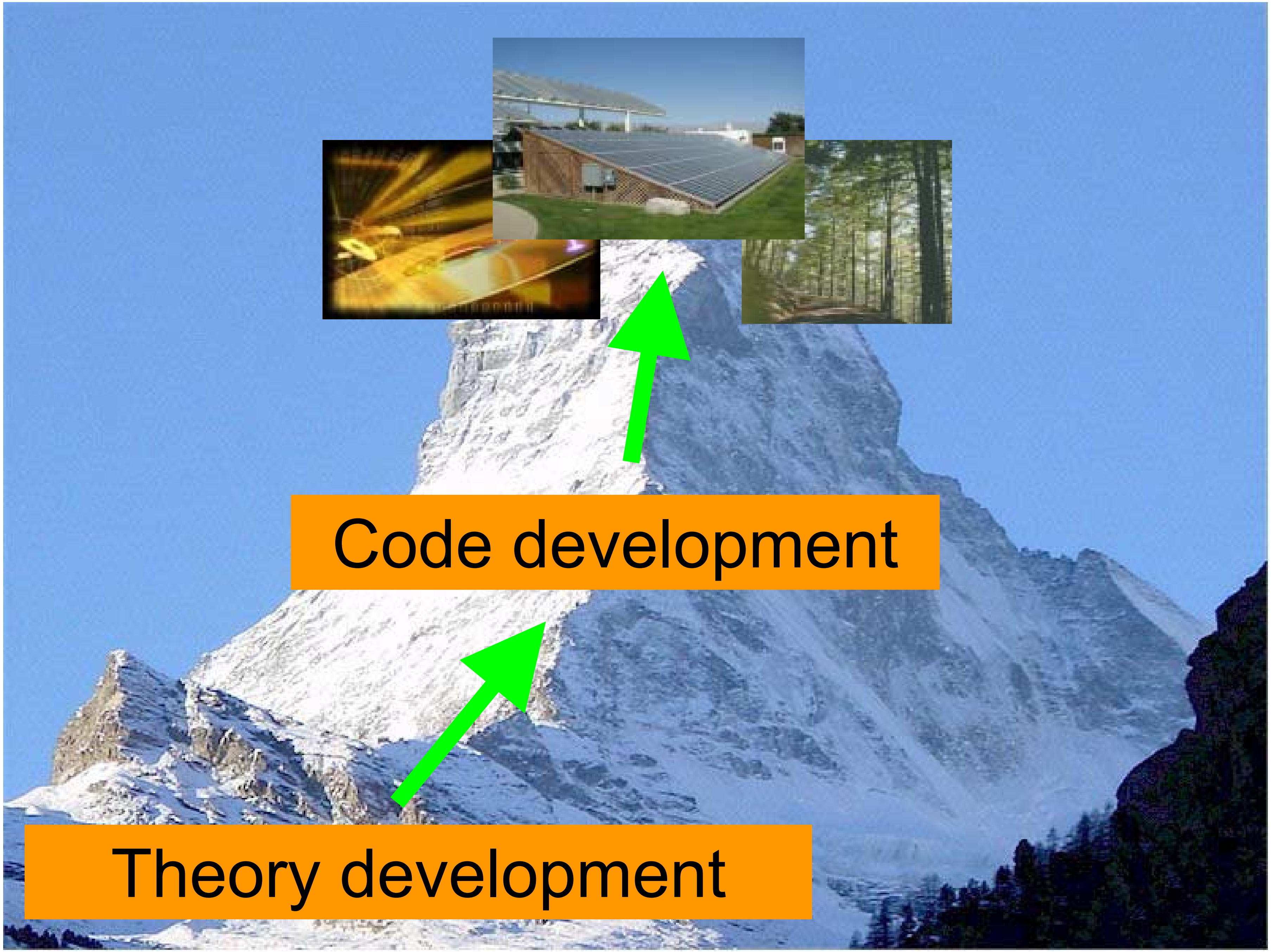
Perturbation   Excitation   Response

Beyond DFT

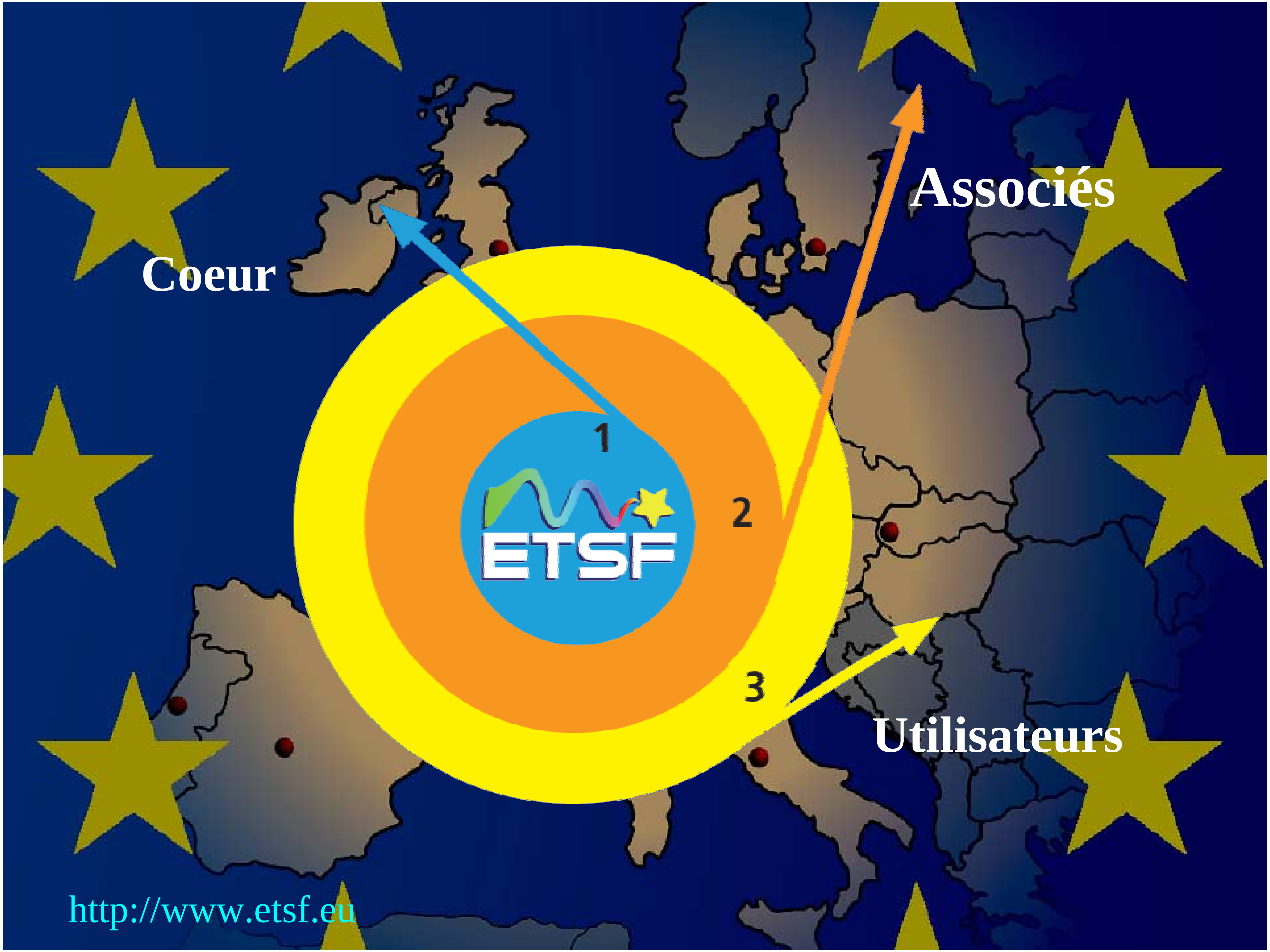
Silicon: absorption spectrum






Code development
Theory development


http://www.etsf.eu


Coeur
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(Theoretical) spectroscopy

- Photoemission (PES/IPES, UPS, ARUPS, ...)
- Absorption (optical, XAS, XANES, NEXAFS,...)
- Reflectance (RAS, SDR, ...)
- Energy loss (EELS, IXS, ...)
- Raman, Auger, ...

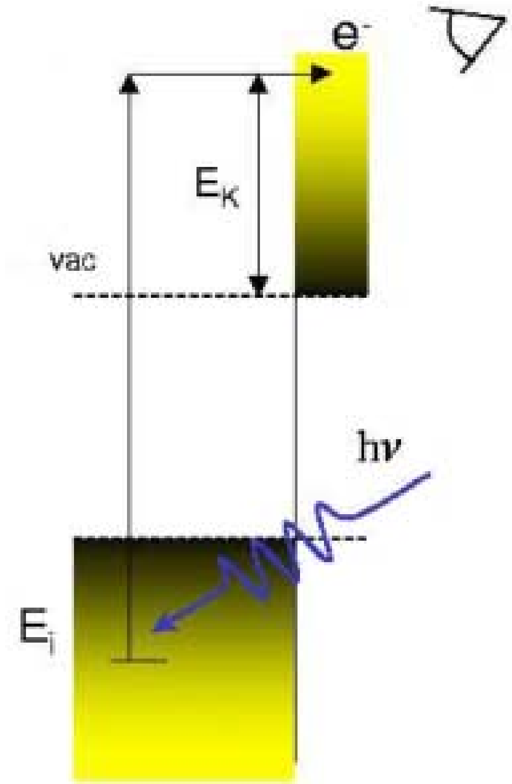
G. Bruant

http://www.etsf.eu

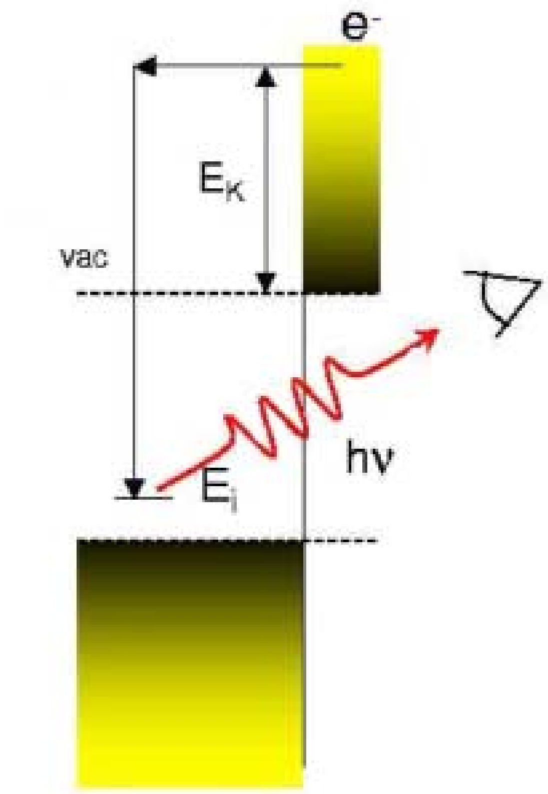
ETSF
European Theoretical Spectroscopy Facility

Photoemission

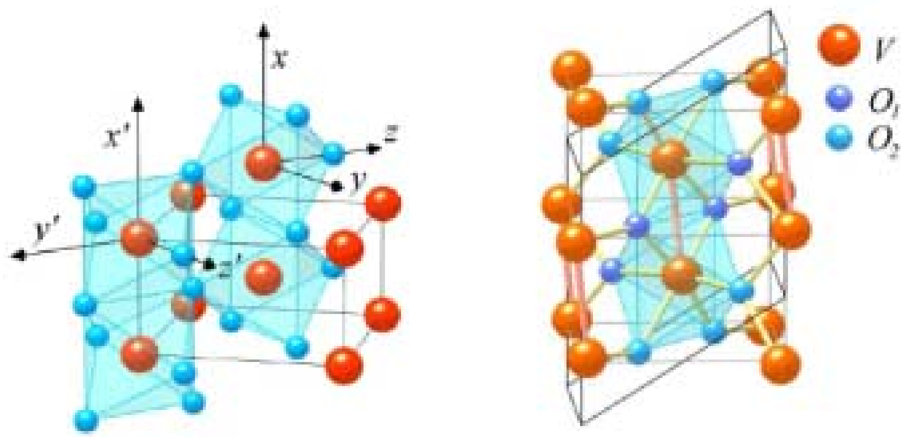
Direct photoemission



Inverse photoemission

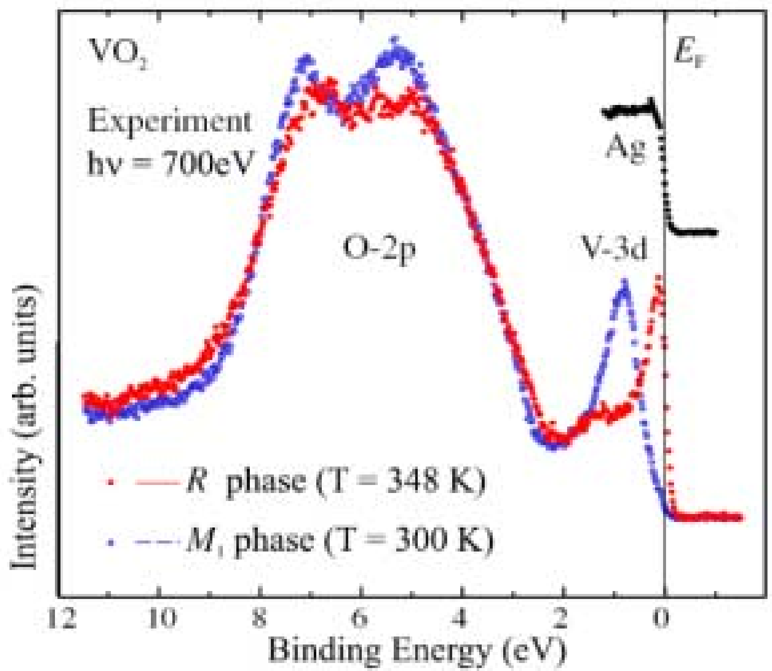


Photoemission spectra of VO_2: a case study



for $T > T_c$
Rutile + Metal

for $T < T_c$
Monoclinic + Insulator

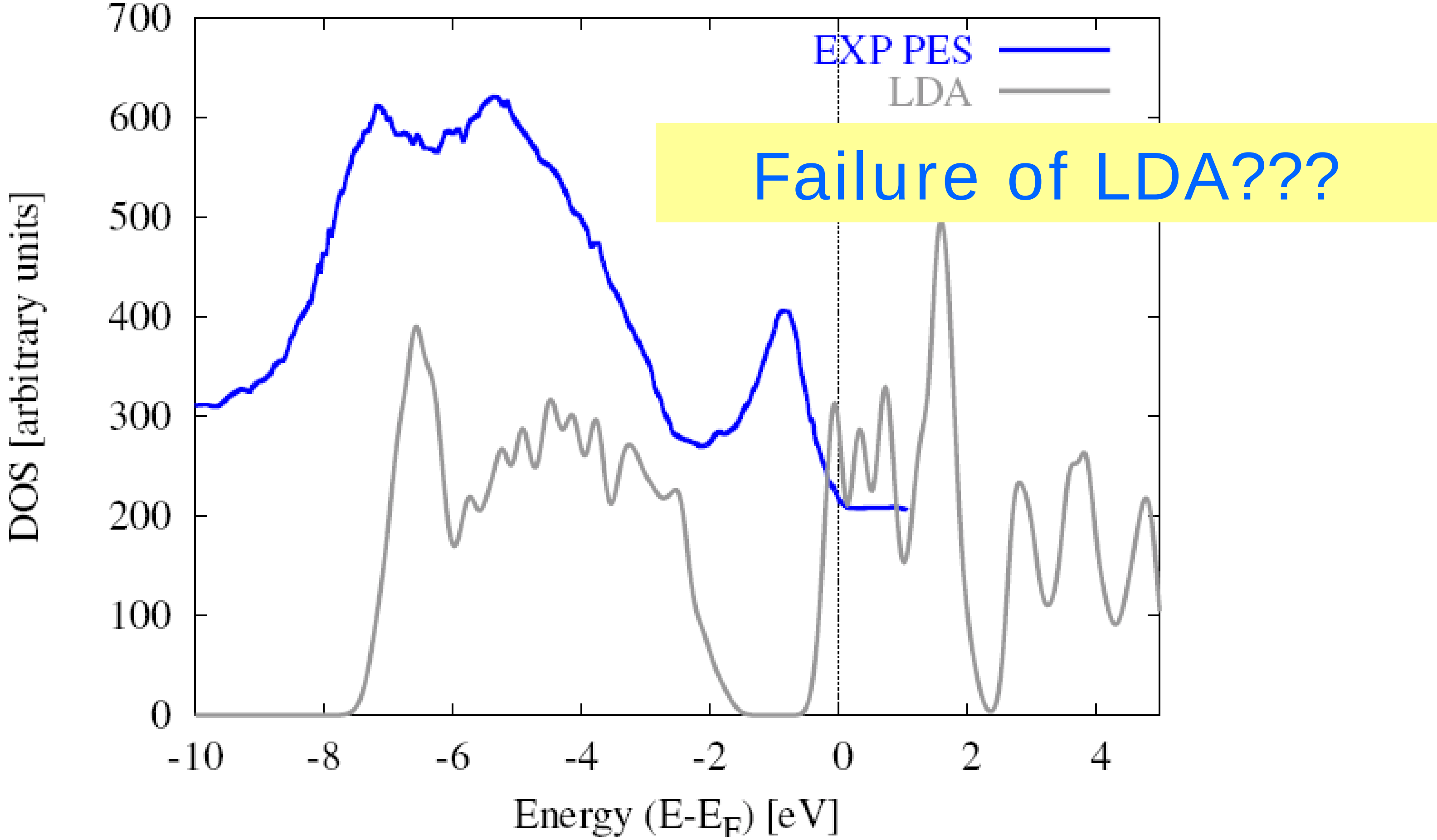


Mechanism?
Role of electronic correlation?

From: Koethe *et al*. PRL 97 (2006)

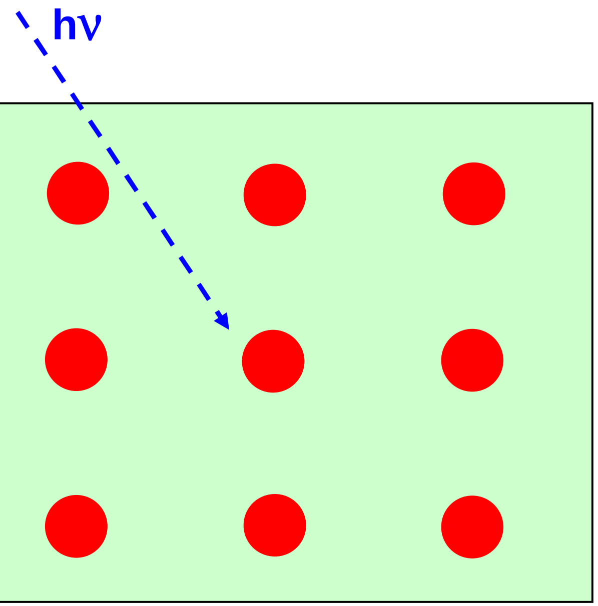
Photoemission: Beyond DFT

VO_2: Insulating phase

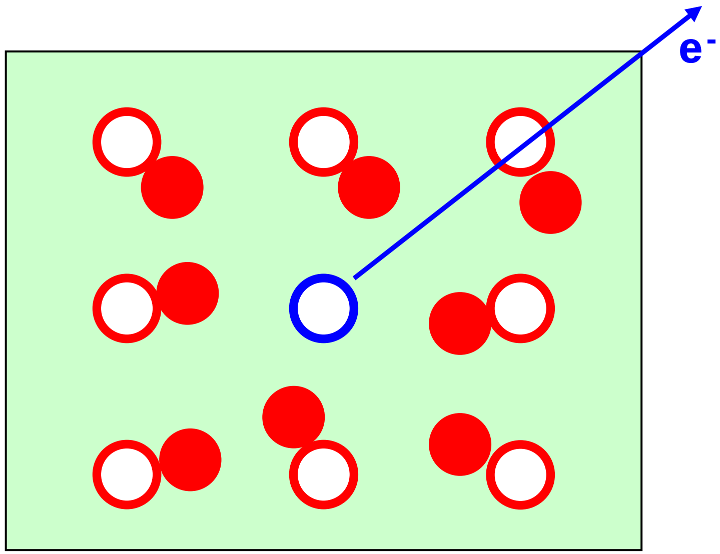


Lattice parameters and phase stability in LDA are OK

Green's function and self-energy



Green's function and self-energy



Green's function G = propagation of an extra-particle

self-energy Σ = nonlocal, complex, frequency dependent operator

= exchange, correlation and dynamical relaxation

Standard G_0W_0 band structure

Kohn-Sham equation:

$$H_0(r)\varphi_{\rm KS}(r) + V_{xc}(r)\varphi_{\rm KS}(r) = \epsilon_{\rm KS}\varphi_{\rm KS}(r)$$

Quasiparticle equation:

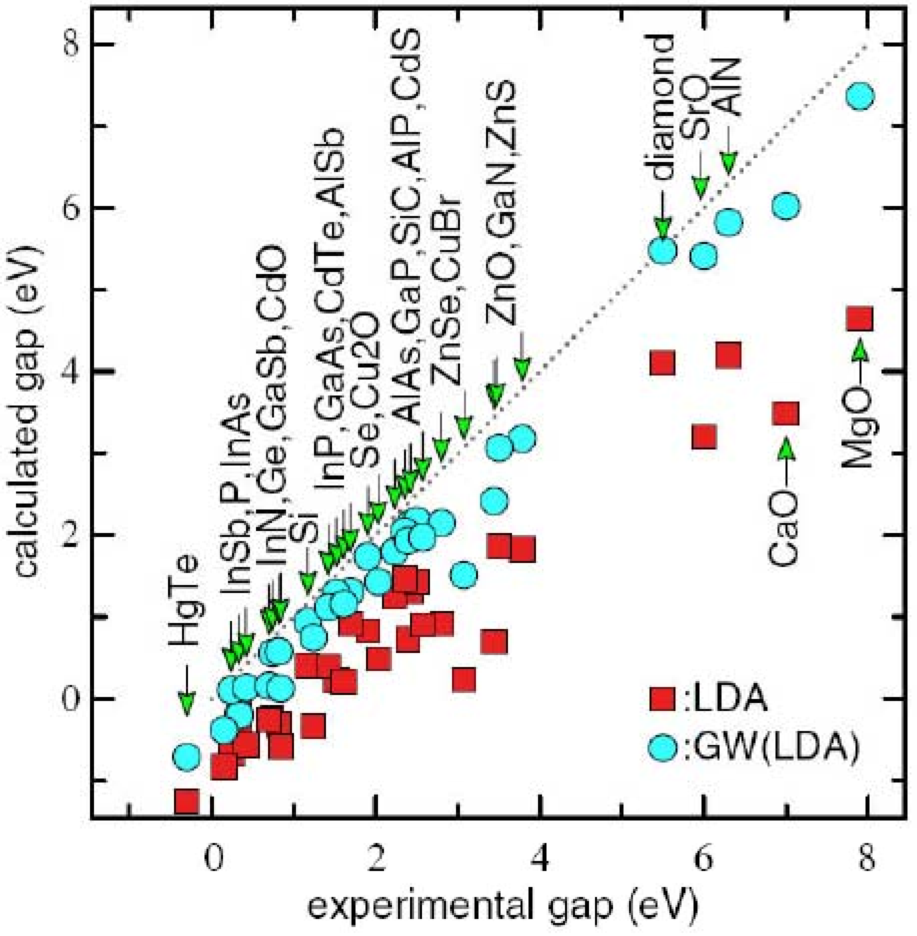
$$H_0(r)\phi_{\rm QP}(r) + \int dr'\ \Sigma(r, r', \omega = E_{\rm QP})\ \phi_{\rm QP}(r') = E_{\rm QP}\,\phi_{\rm QP}(r)$$

Quasiparticle energies = 1st order perturbative corrections

$$E_{\rm QP} - \epsilon_{\rm KS} = \langle\varphi_{\rm KS}|\Sigma - V_{xc}|\varphi_{\rm KS}\rangle$$

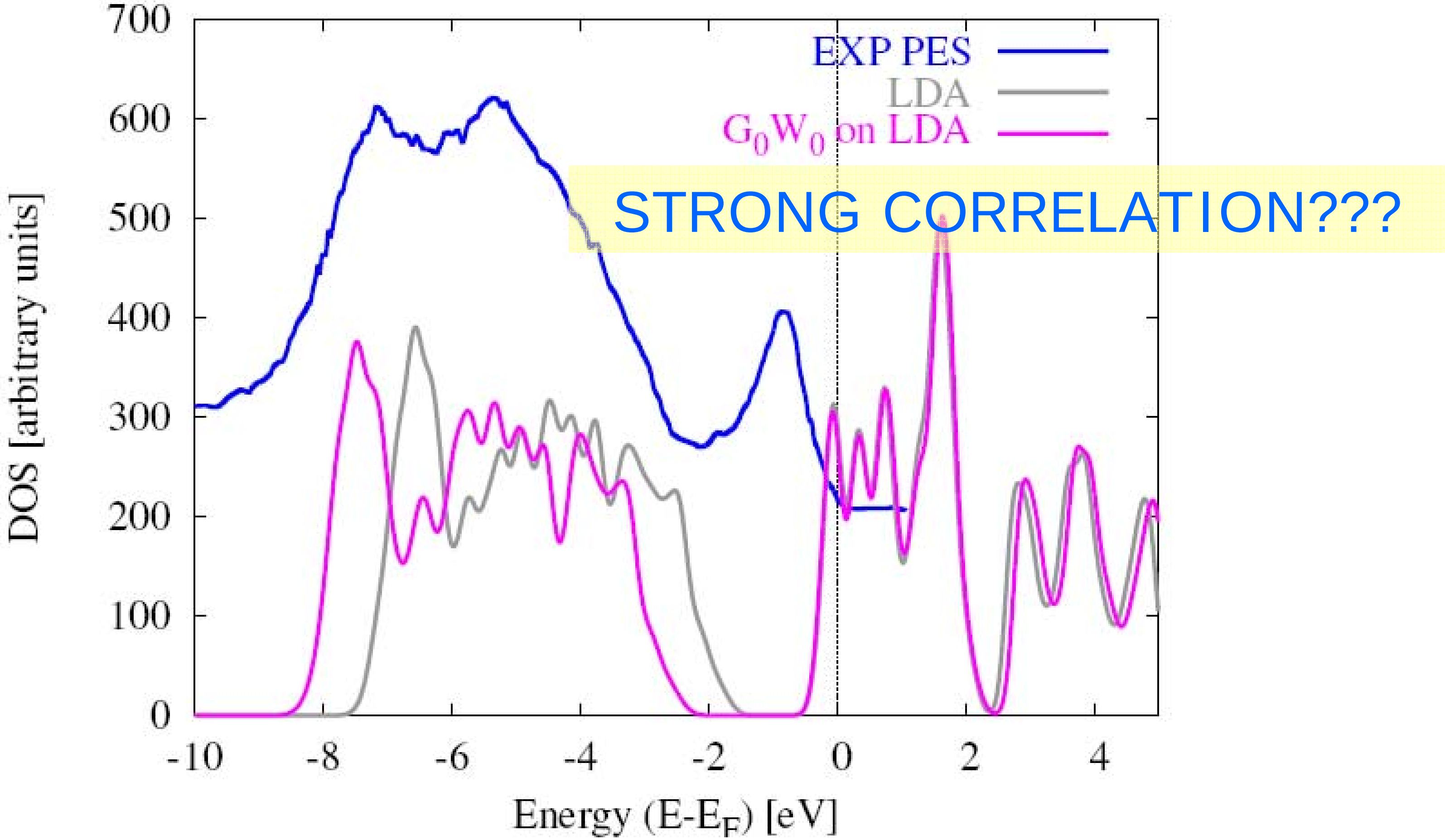
See: M. Hybersten and S.G. Louie, PRB 34 (1986);
R.W. Godby, M Schlüter and L.J. Sham, PRB 37 (1988)

Standard G_0W_0 band structure



From: van Schilfgaarde *et al.*, PRL 96 (2006)

Photoemission of VO_2



Standard G_0W_0 band structure

Beyond standard G_0W_0!

Kohn-Sham equation:

$$H_0(r)\varphi_{\mathrm{KS}}(r) + V_{xc}(r)\varphi_{\mathrm{KS}}(\ldots \;\ldots_{\mathrm{KS}}(r)$$

Quasiparticle equation:

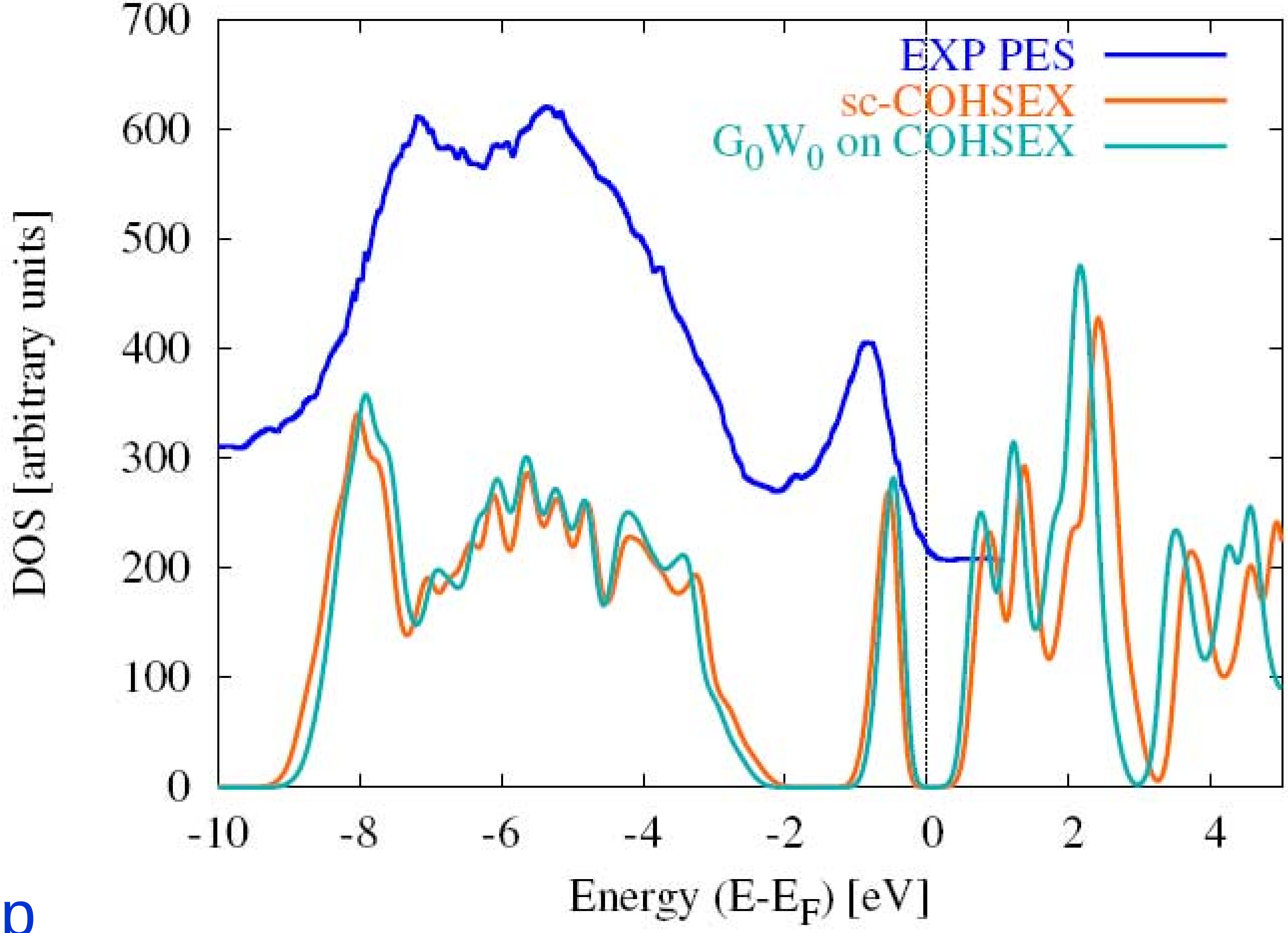
$$H_0(r)\phi_{\mathrm{QP}}(r) + \int \ldots , \omega = E_{\mathrm{QP}})\; \phi_{\mathrm{QP}}(r') = E_{\mathrm{QP}}\,\phi_{\mathrm{QP}}(r)$$

Quasip… …ergies = 1st order perturbative corrections

$$E_{\mathrm{QP}} - \epsilon_{\mathrm{KS}} = \langle \varphi_{\mathrm{KS}} | \Sigma - V_{xc} | \varphi_{\mathrm{KS}} \rangle$$

See: M. Hybersten and S.G. Louie, PRB 34 (1986);
R.W. Godby, M Schlüter and L.J. Sham, PRB 37 (1988)

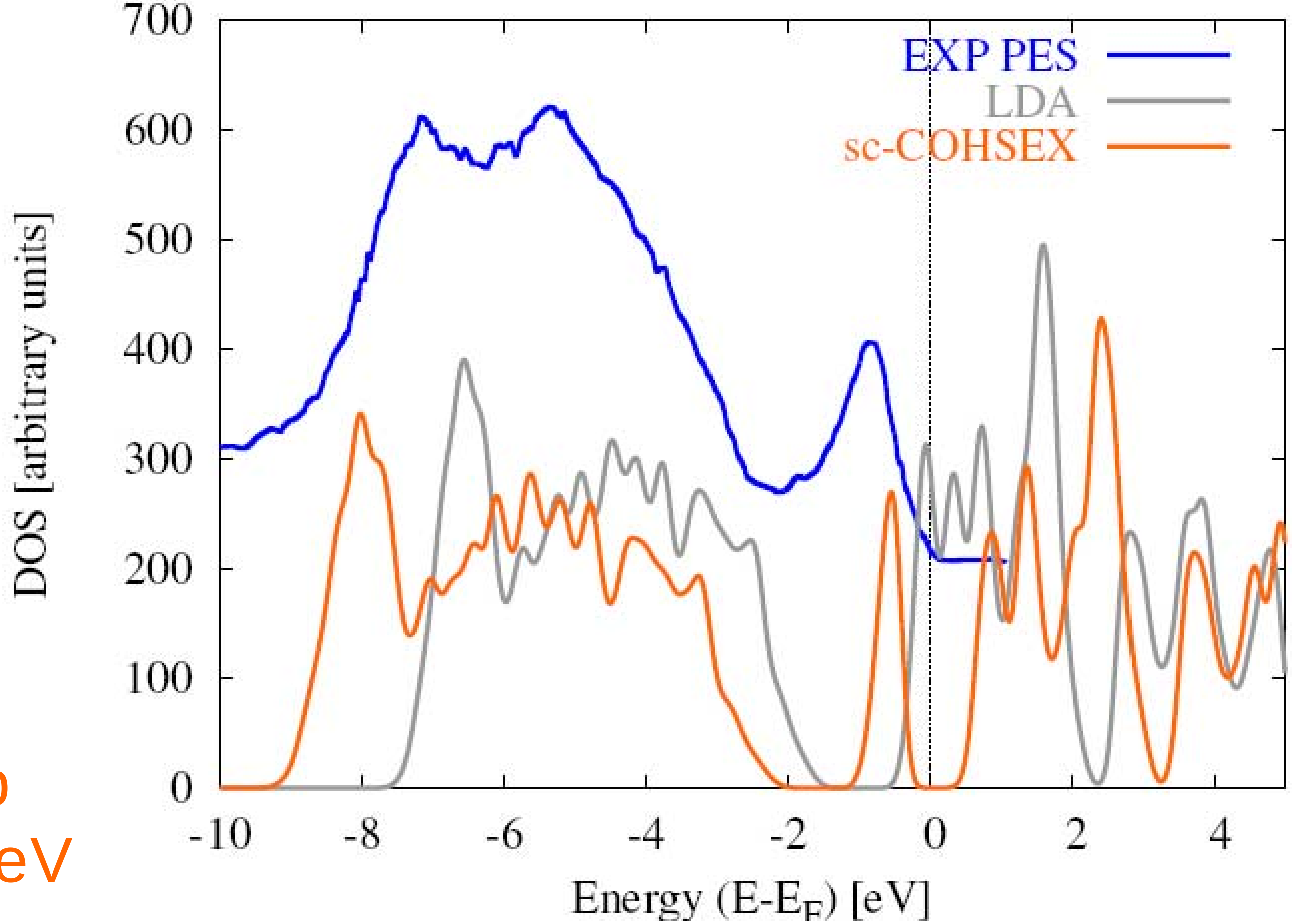
Photoemission of VO_2



Gap
0.65 eV

From: M. Gatti, F. Bruneval, V. Olevano and L. Reining, PRL 99 (2007)

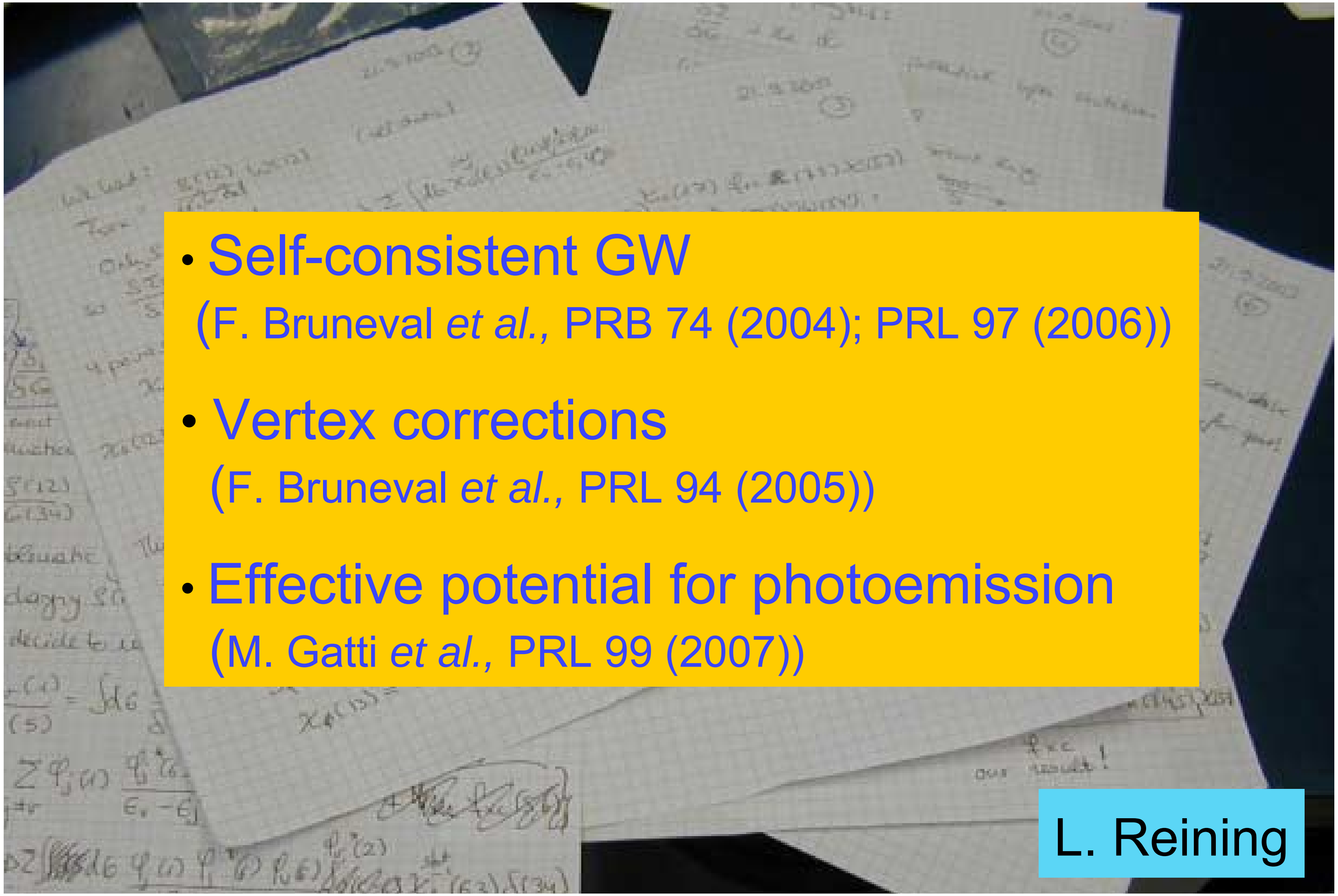
Photoemission of VO_2



Gap
0.78 eV

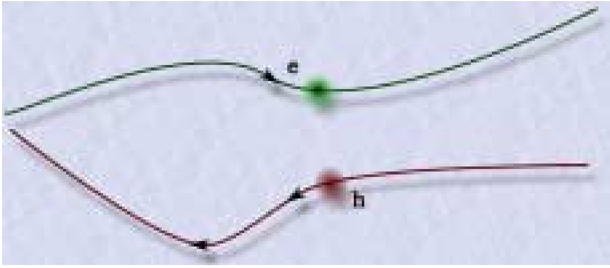
COHSEX = static approximation to GW (Hedin '65)

Theory development: beyond GW

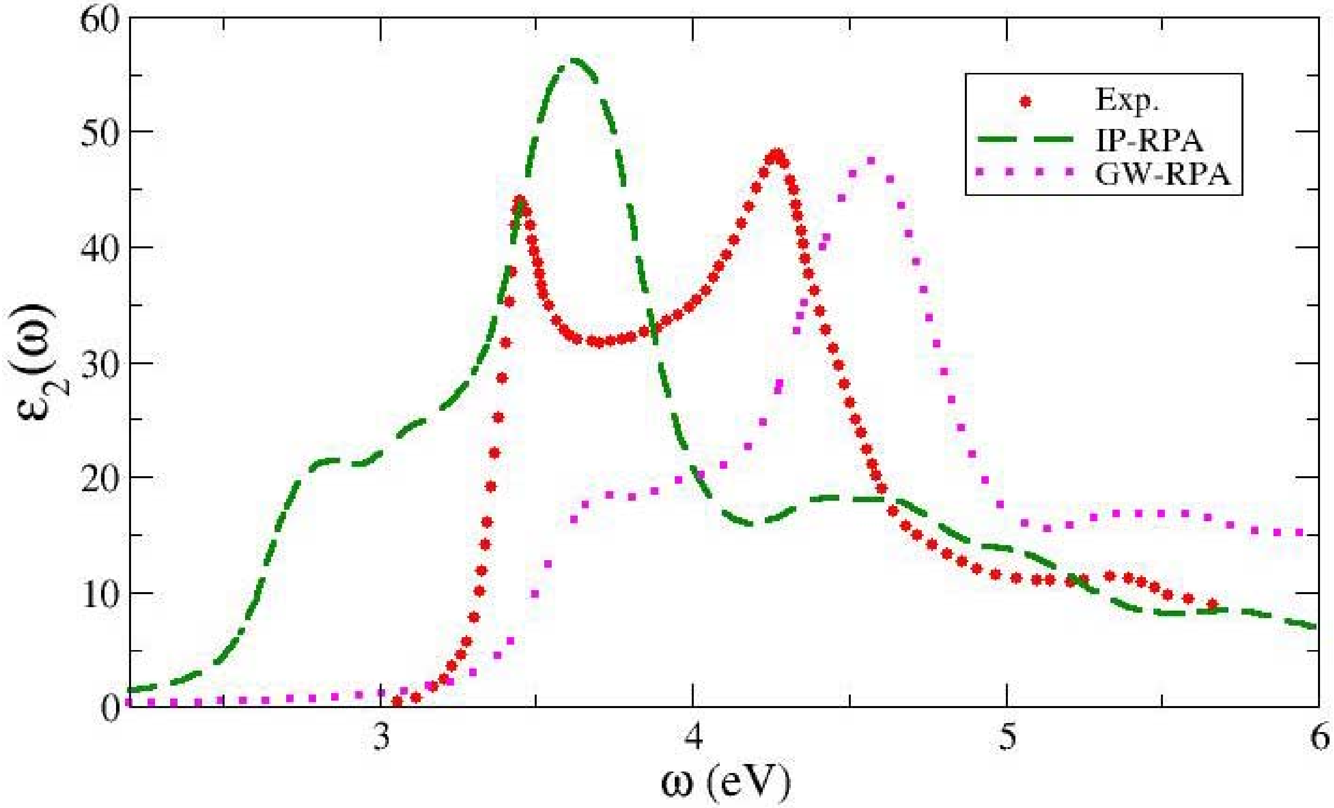


- Self-consistent GW
  (F. Bruneval *et al.*, PRB 74 (2004); PRL 97 (2006))
- Vertex corrections
  (F. Bruneval *et al.*, PRL 94 (2005))
- Effective potential for photoemission
  (M. Gatti *et al.*, PRL 99 (2007))

L. Reining



Silicon



Even good bandstructure

→ sometimes quite wrong absorption spectra!

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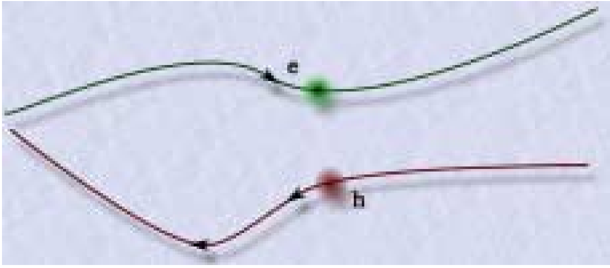
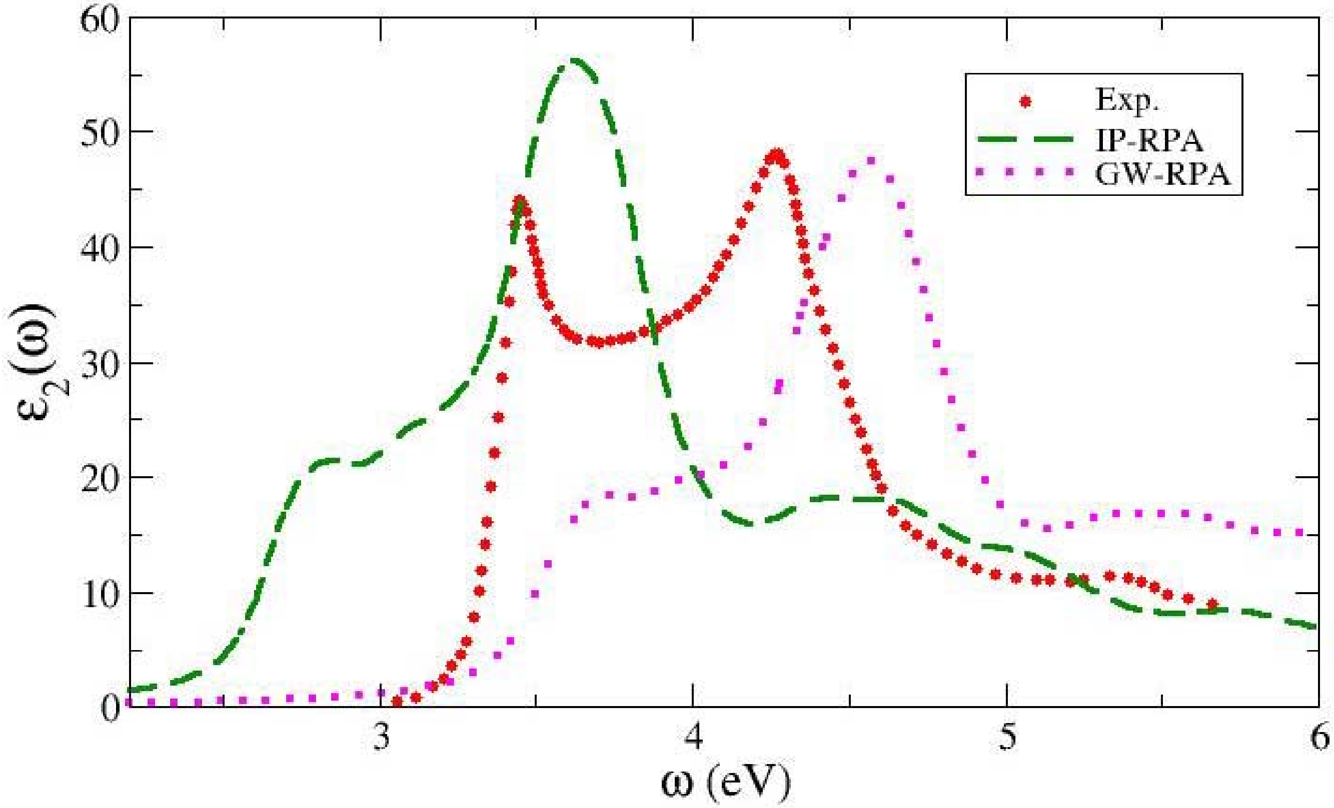
Absorption, Energy Loss

Beyond the linear response…



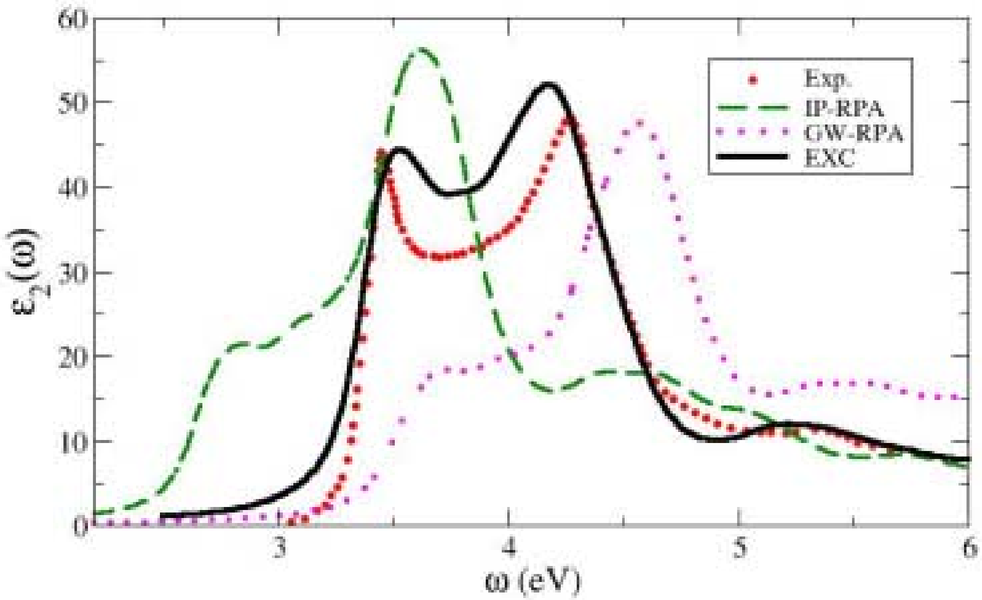
Silicon



Even good bandstructure

→ sometimes quite wrong absorption spectra!

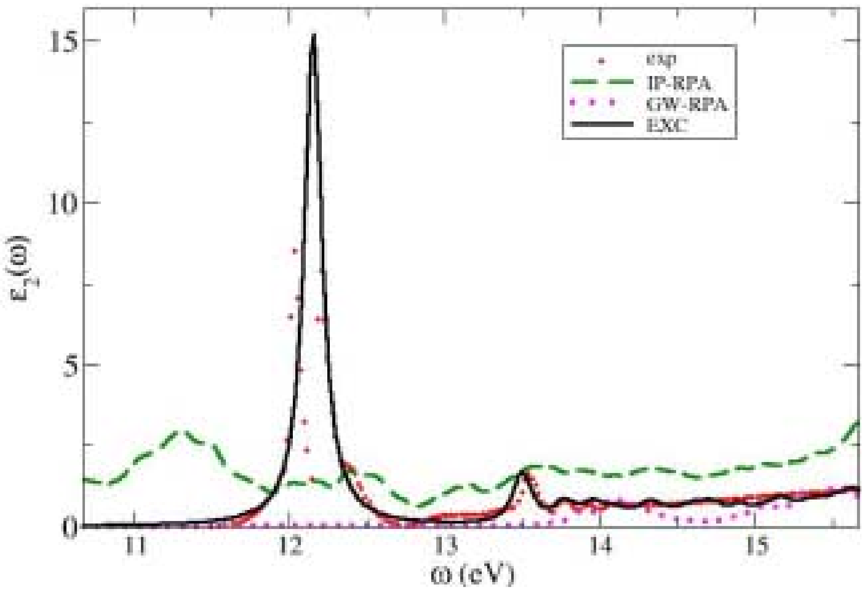
Neutral Excitations: Absorption spectra…



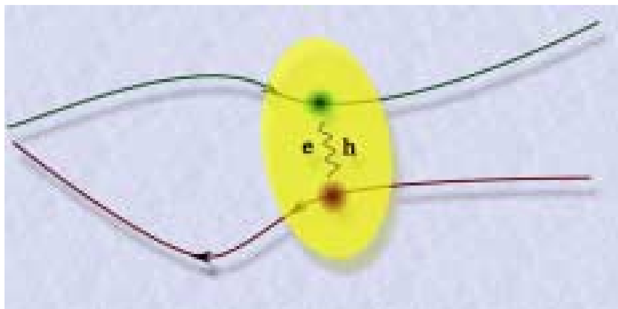
Silicon

Francesco Sottile et *al*.
PRL **91**, 56402(2003)
PRB **76,**161103(2007)

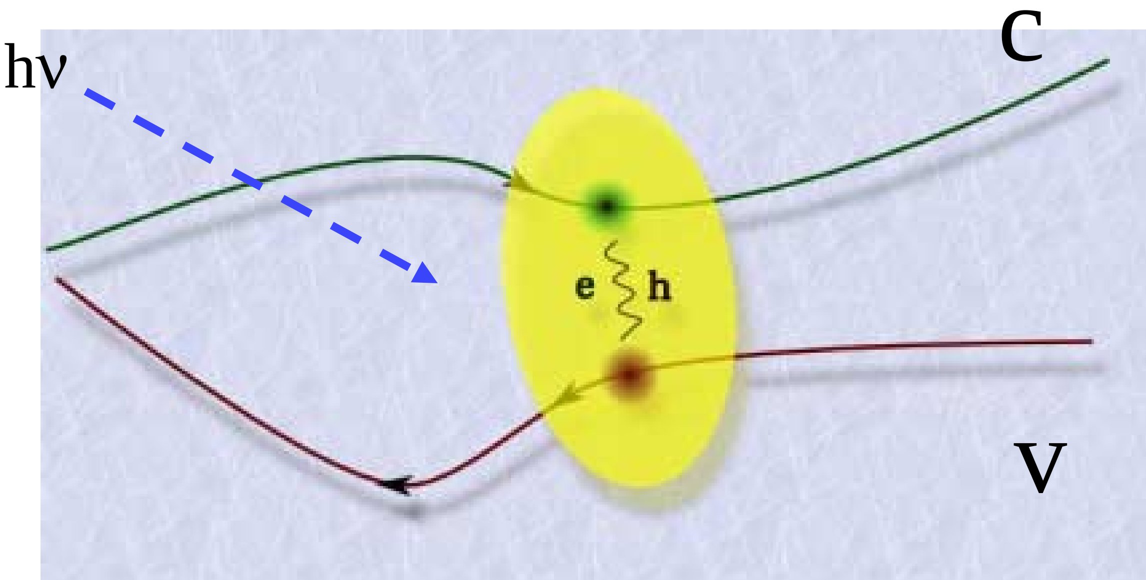
Argon



EXC =



EXC ?



Electron-hole interaction

Excitonic effects

⇓

Bethe-Salpeter Equation

GW + Bethe Salpeter Equation

$$(H_{el} + H_{hole} + H_{el\text{-}hole}) A_\lambda = E_\lambda A_\lambda$$

RPA

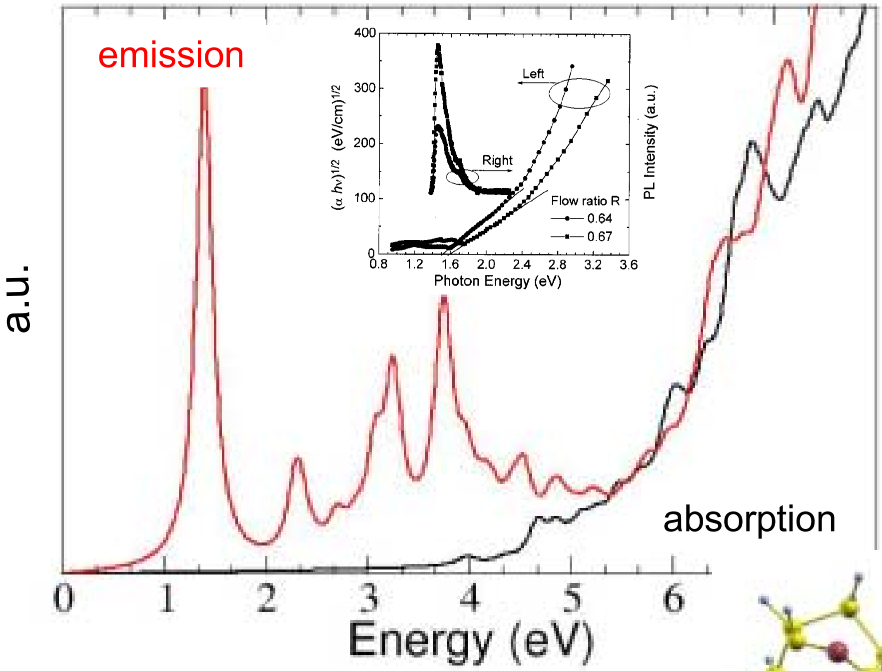
$$\text{Abs} \sim \Sigma_{vc} |\langle v|D|c\rangle|^2 \qquad \delta\,(E_c - E_v - \omega)$$

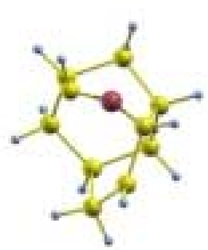
$$\text{Abs} \sim \Sigma_\lambda | \Sigma_{vc} \langle v|D|c\rangle A_\lambda^{vc}|^2 \,\delta\,(E_\lambda - \omega)$$

Mixing of transitions

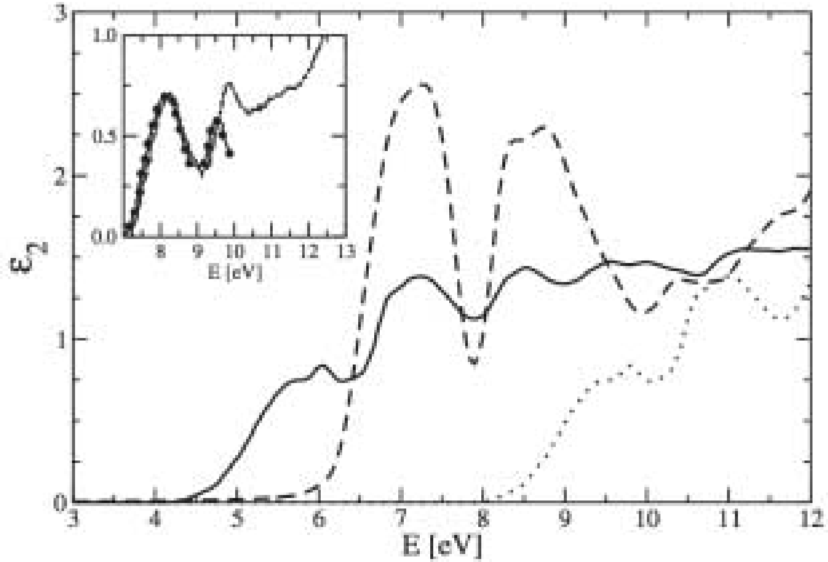
Modification of excitation energies

$$(H_{el} + H_{hole} + H_{el\text{-}hole}) A_\lambda = E_\lambda A_\lambda$$





The nature of luminscence
Eleonora Luppi PRB **75**,0333 (2006)



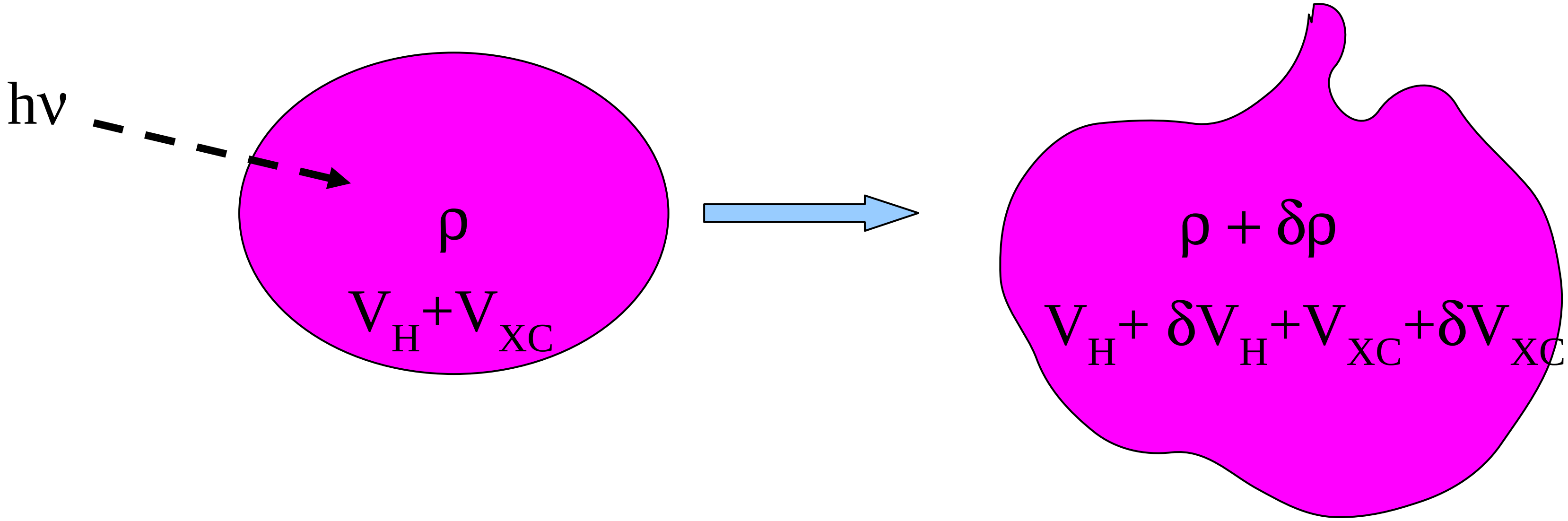
Absorption spectrum of liquid water
Viviana Garbuio, Lucia Reining et *al.*
PRL **97**,137402 (2006)

BSE usually nice but 2 particle problem!

Can we use: $\rho(r,t)$?

Time Dependent Density Functional Theory

Absorption ?



Change of potentials

Electron, hole and excitonic effects

TDDFT $\chi = \chi_0 + \chi_0 [v + f_{xc}] \chi$

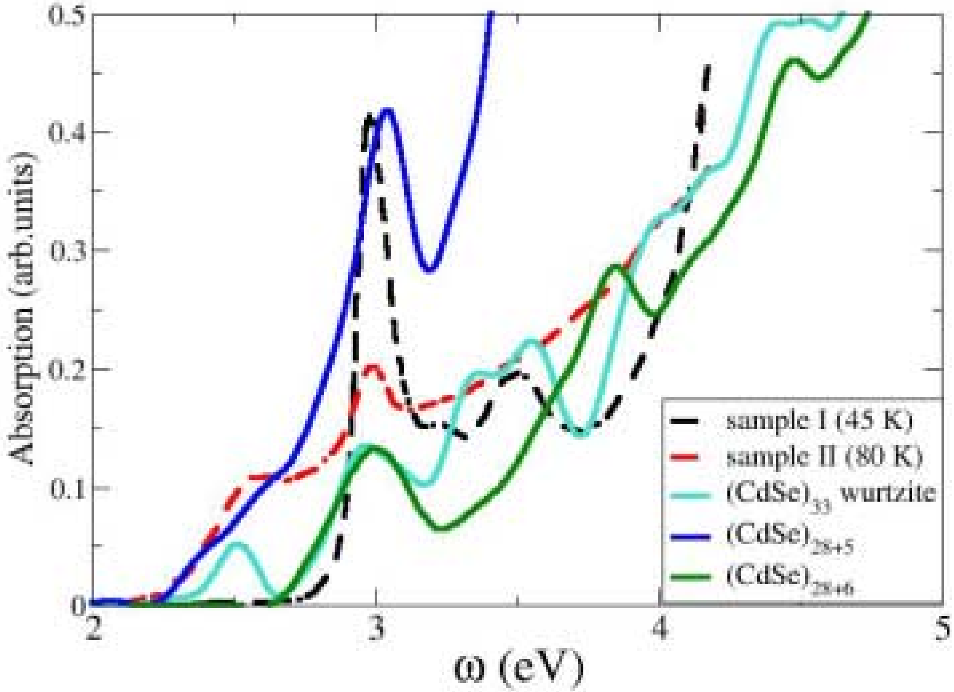
$\delta V_{xc}/\delta\rho$

TDLDA

- $\delta V_{xc}^{LDA}(r,t)/ \delta\rho(r',t') = \delta(r-r')\delta(t-t') dV_{xc}/d\rho$

Silvana Botti PRB **75**, 035311(2007)

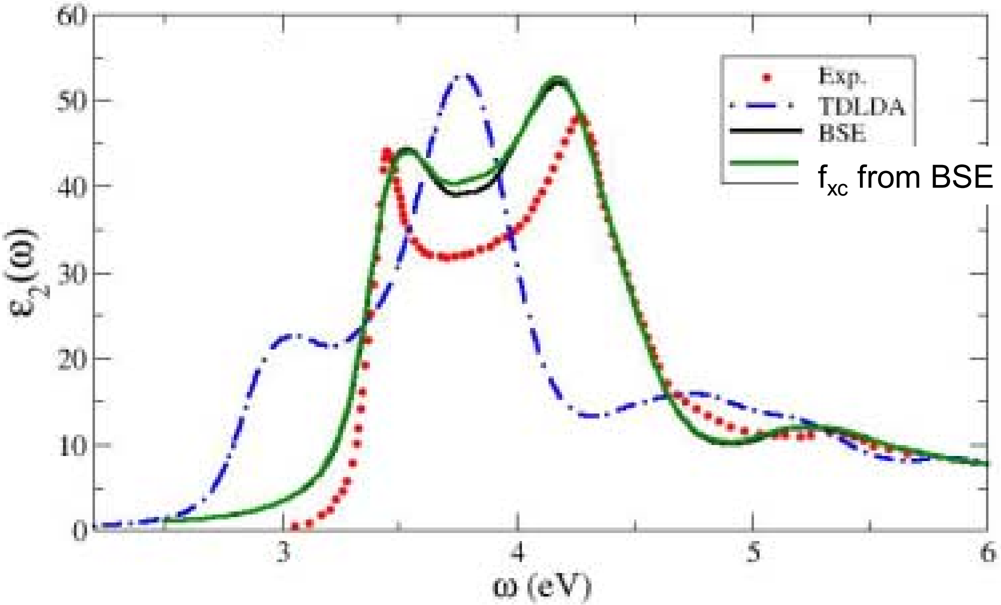
FINITE SYSTEMS **YES**



Identification of CdSe nanoparticles

INFINITE SYSTEMS ***NO***

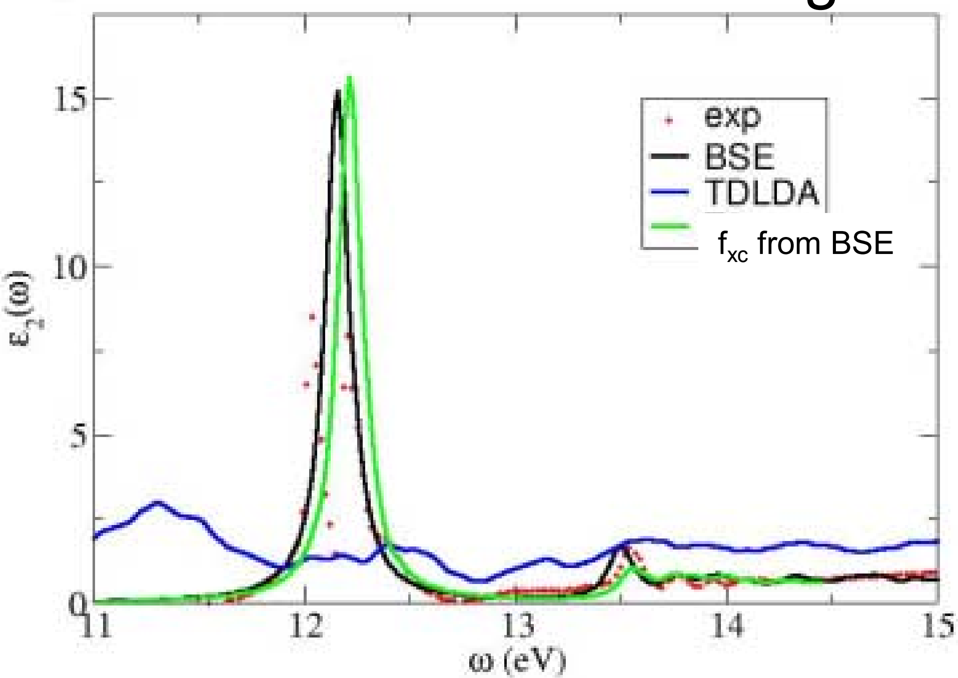
Faulire of TDLDA for infinite systems …



Silicon

Francesco Sottile et *al*.
PRB **76,**161103(2007)

Argon



f_{xc} from BSE:

$$\sim \text{shift} + \chi_0^{-1} GGWGG \chi_0^{-1}$$

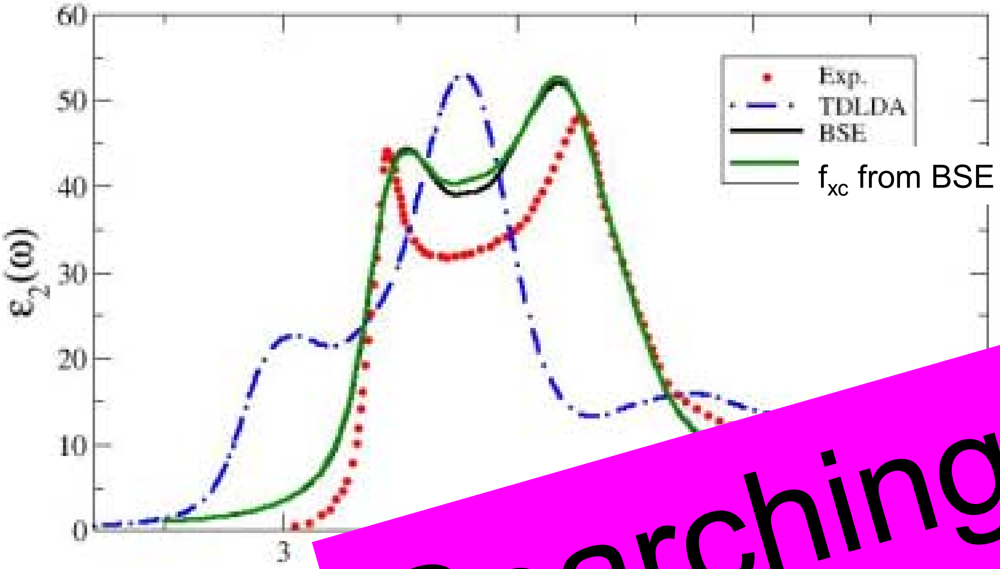
Reining et al. Phys.Rev.Lett. 88, 66404 (2002)
Long-range kernel

Sottile et al. Phys.Rev.Lett. 91, 56402 (2003)
Full many-body kernel. Mapping Theory

Sottile et al. Phys.Rev.B 68, 205112 (2003)
Long-range and contact exciton

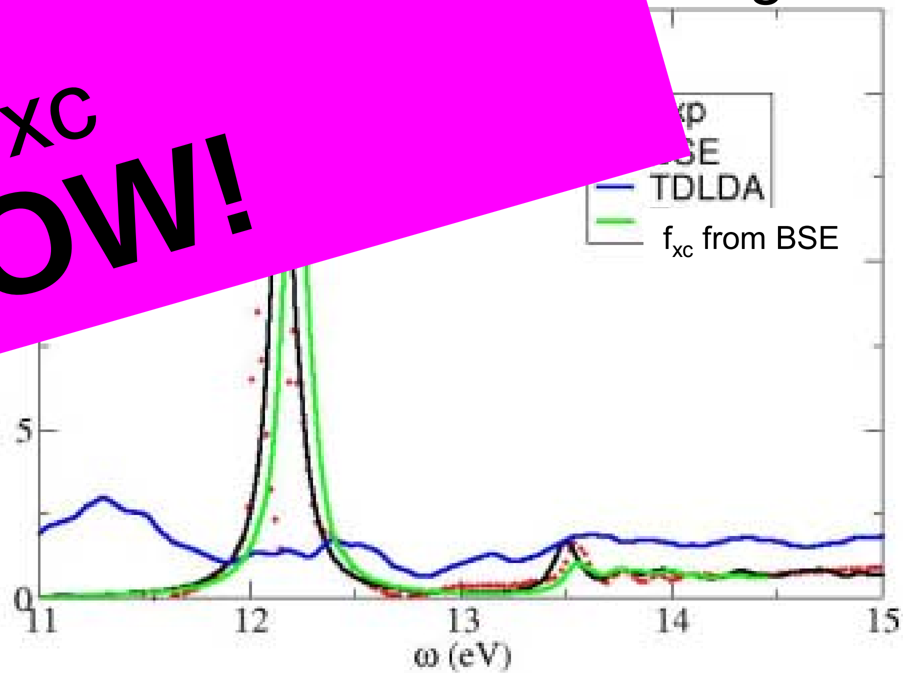
Botti et al. Phys. Rev. B 72, 125203 (2005)
Dynamic long-range component

Faulire of TDLDA for infinite systems …



co Sottile et *al*.
161103(2007)

Argon



f_x

~ shift + χ

Searching for new f_{xc} NOW!

Reining et al. Phys.Rev.Lett
Long-range kernel

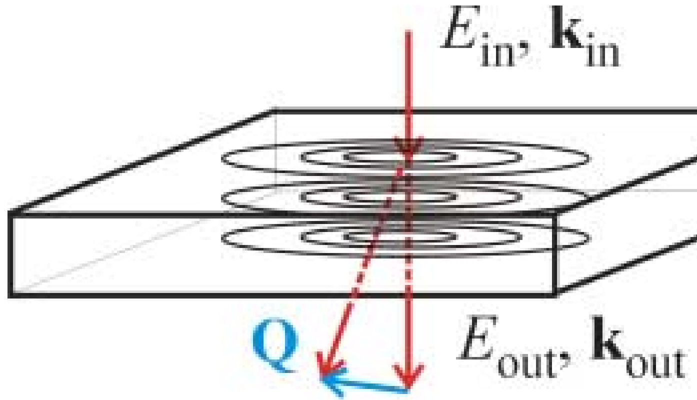
Sottile et al. Phys.Rev.Lett. 91
Full many-body kernel. Mapp

Sottile et al. Phys.Rev.B 68, 205112 (2003)
Long-range and contact exciton

Botti et al. Phys. Rev. B 72, 125203 (2005)
Dynamic long-range component

But .... TDLDA often works:

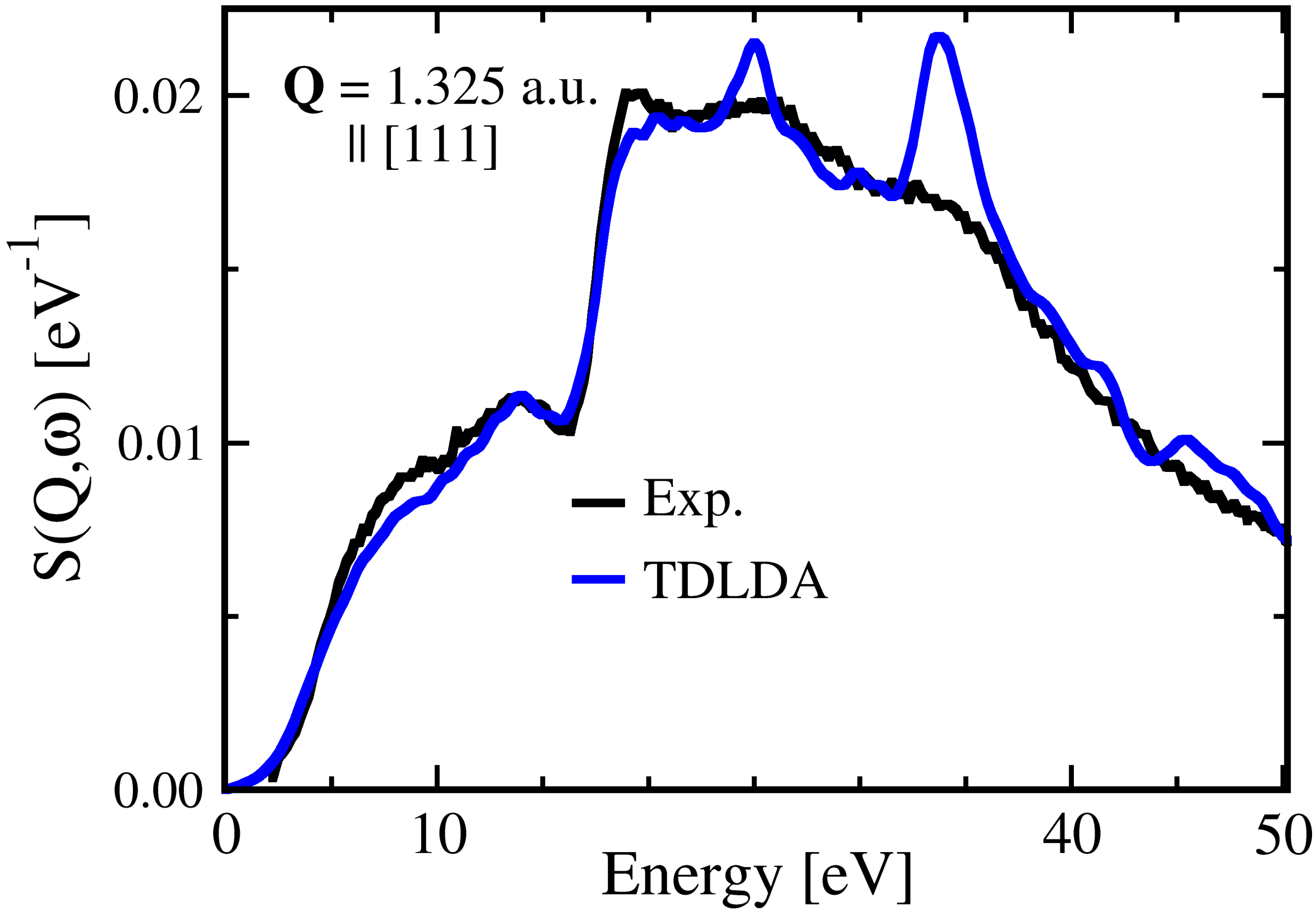
Inelastic X-ray scattering



Collective excitations Plasmons

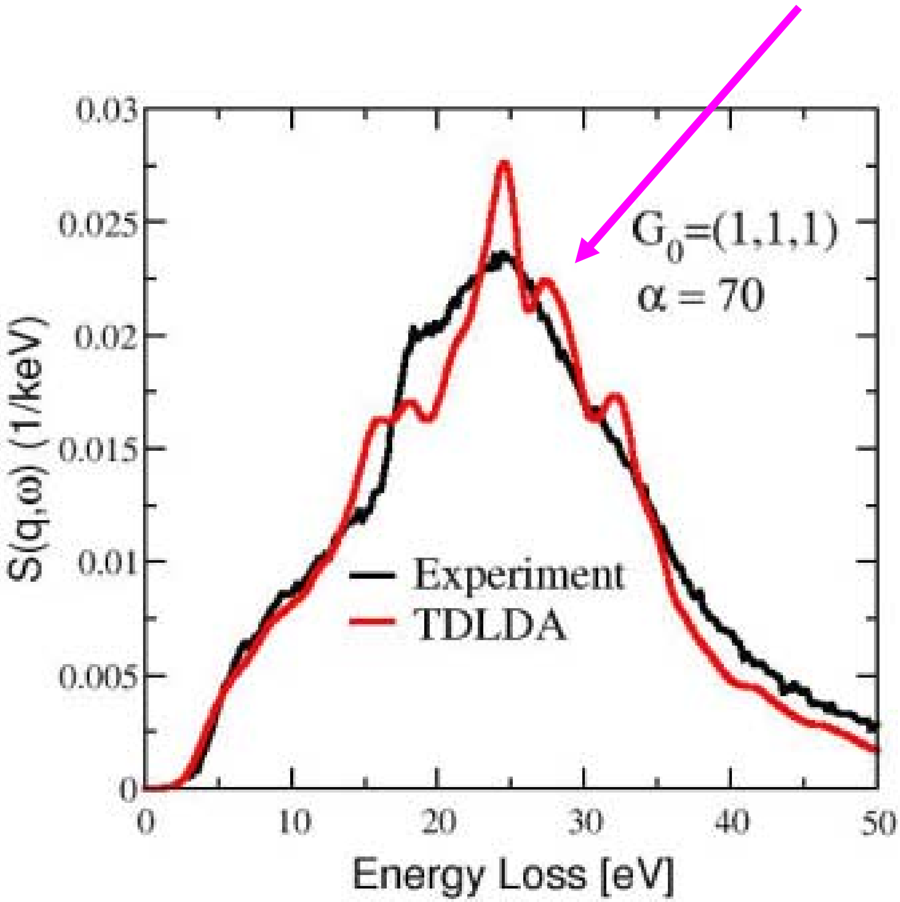
$$S(Q,\omega) \propto -\mathrm{Im}\frac{1}{\varepsilon_M(Q,\omega)}$$

TDLDA



H. Weissker et al., Phys. Rev. Lett. **97**, 237602 (2006)
Collaboration LSI – ESRF (Grenoble)

But some discrepancies along the [111] reflection

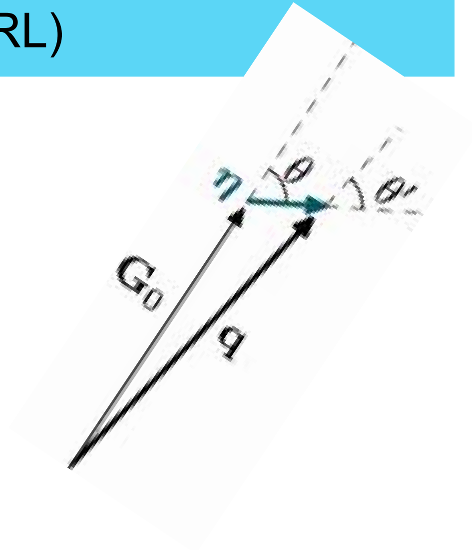


Idea from the graphite

Ralph Hambach, Christine Giorgetti

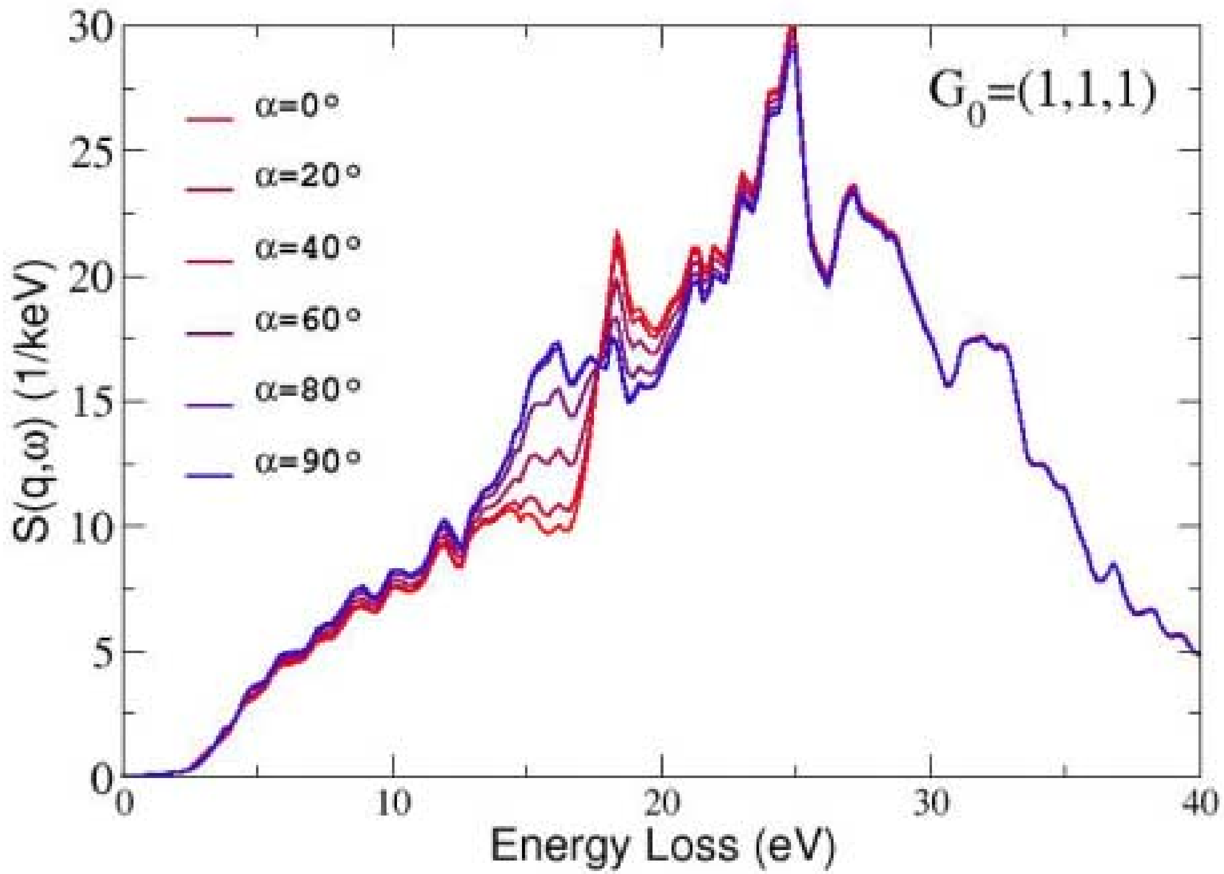
(submitted to PRL)

α=angle between the momentum transfer q and the deviation η



Strong anomaly angular dependence of the loss function

Anisotropy for isotropic materials ?



Silicon

Application for beam time at ESRF, Experimental Method

(Ralph Hambach, H.-C. Weissker, Christine Giorgetti 2008)

H.-C. Weissker *et al., PRL 97, 237602 (2006)*

OUTLINE

Matteo Gatti

Theoretical Spectroscopy ETSF

Different type of spectroscopies: Photoemission

Eleonora Luppi

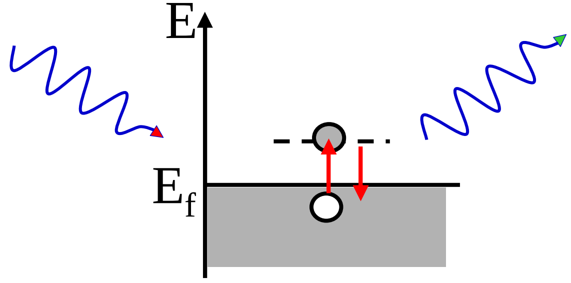
Absorption, Energy Loss

Beyond the linear response…

Linear Optic

Propagation of light in a medium:

The response of the medium
depends linearly on the electric field E



$$P^a(\omega) = \chi_{ab}^{(1)}(\omega) E^b(\omega)$$

(first order in E)

Nonlinear Optic

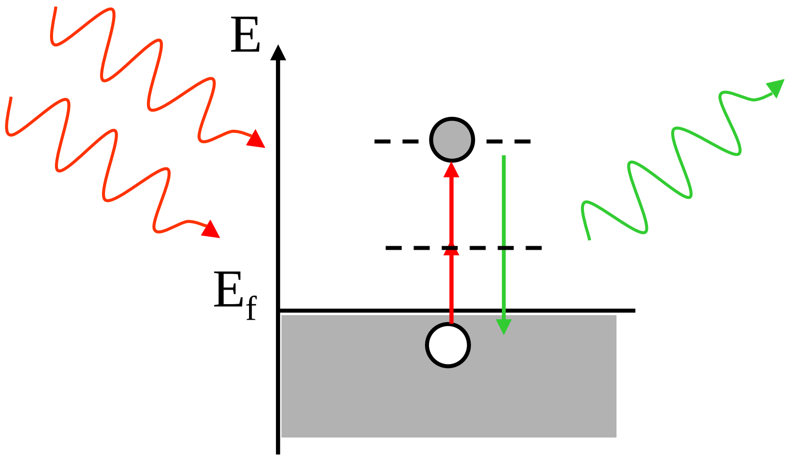
For higher light intensities, we have to take
into account superior orders

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

Génération de seconde harmonique

Second order response function χ^2

Eleonora Luppi, Hannes Hübener and Valerie Véniard

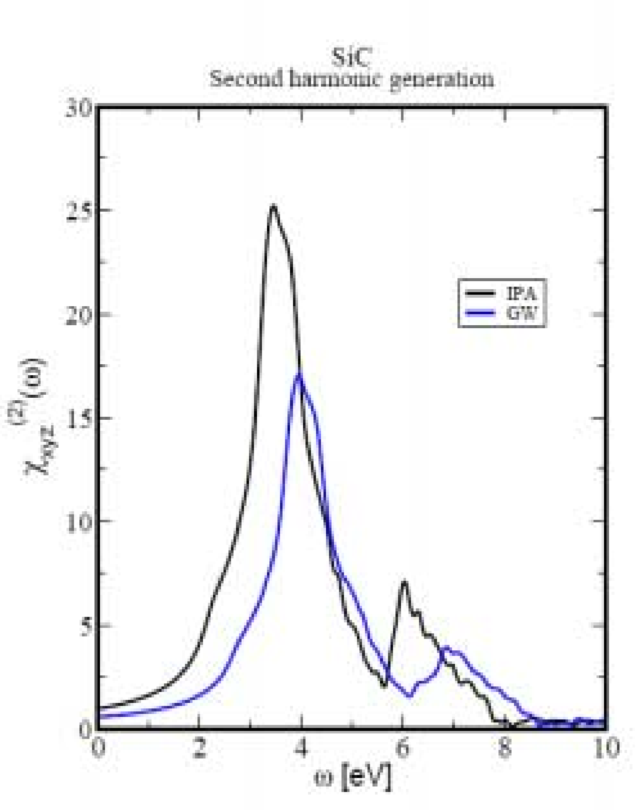


- sensitivity to local symmetry (probe)
- different selection rules and system resonances for e^- transitions in χ^2 respect with linear optic

Developments on several levels

Step 1: Microscopic Polarization

Second order response function:
second order time-dependent perturbation theory



Step 2: Macroscopic Polarization

Calcul des Champs locaux: équations de Maxwell

Step 3: TDDFT

Excitonic effects

Etape 4: Implémentation numérique

Now

Perspectives:

- Interaction with high energy photons
- Higher order process

Lucia Reining
Valérie Véniard
Christine Giorgetti
Silvana Botti
Francesco Sottile
Hans-Christian Weissker
Eleonora Luppi
Xochitl Lopez-Lozano
Arjan Berger
Wojciech Welnic
Alberto Zobelli
Federico Iori
Matteo Gatti
Julien Vidal
Hannes Hübener
Ralf Hambach
Gaëlle Bruant **ETSF Administrator**
Andrea Cucca **System Manager**

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Irene Aguilera
Noel Haddad
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