Ab initio calculations of electronic response: ingredients, results and challenges

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ETSF European Theoretical Spectroscopy Facility

Electronic response.....

1) .....importance and challenge

2) Induced potentials: Hartree

*** Example: plasmon dispersion in graphene, tubes**

3) Induced potentials: xc

*** Example: IXS for silicon**

4) Honey or balls? GW+BSE

5) Frontiers I: localisation, correlation

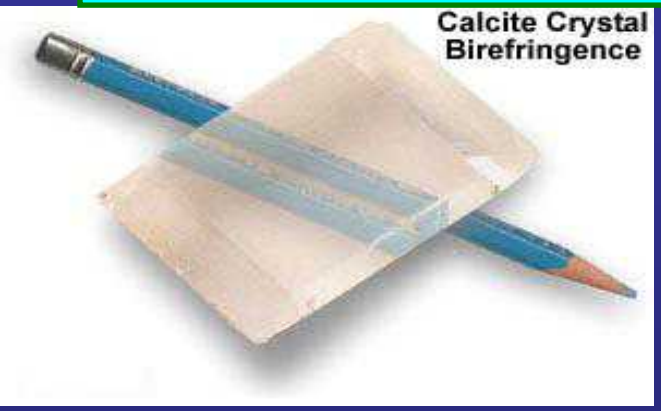
***Examples: TMO, CIS**

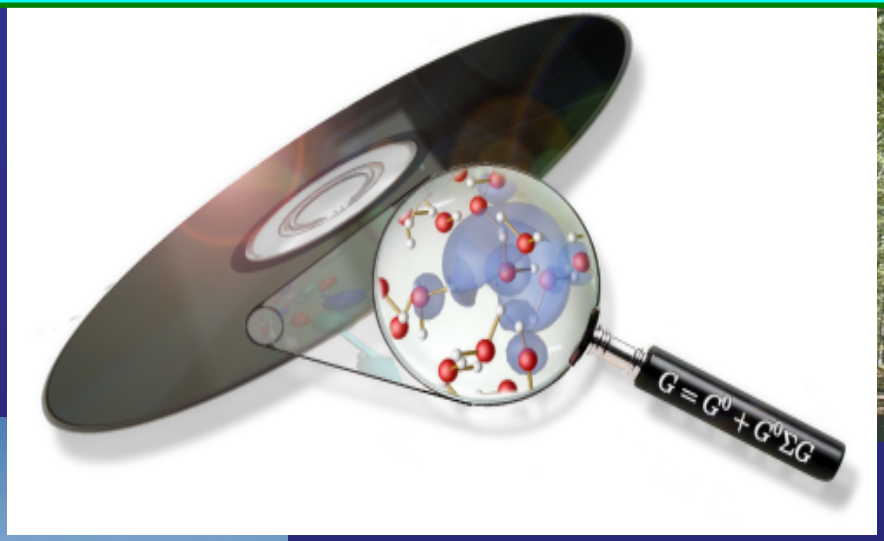
6) Frontiers II: merge

7) Frontiers III: compromise

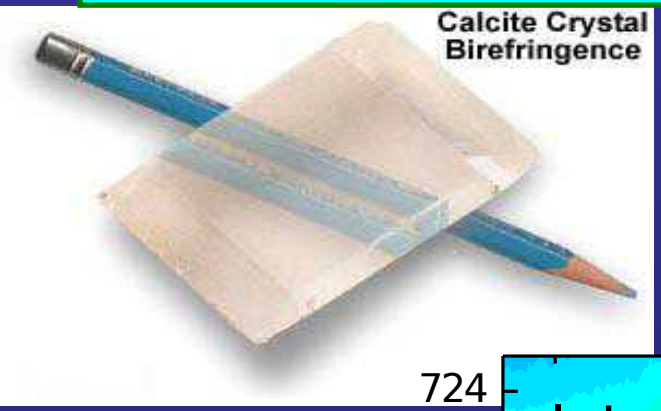
8) Summary

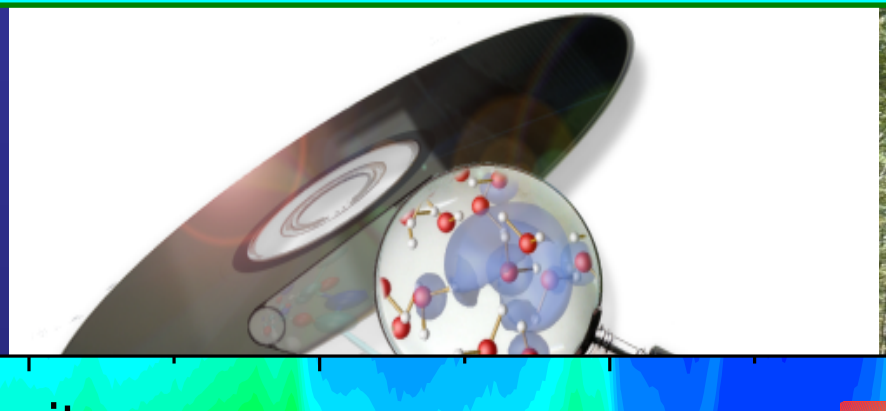
Electronic response.....

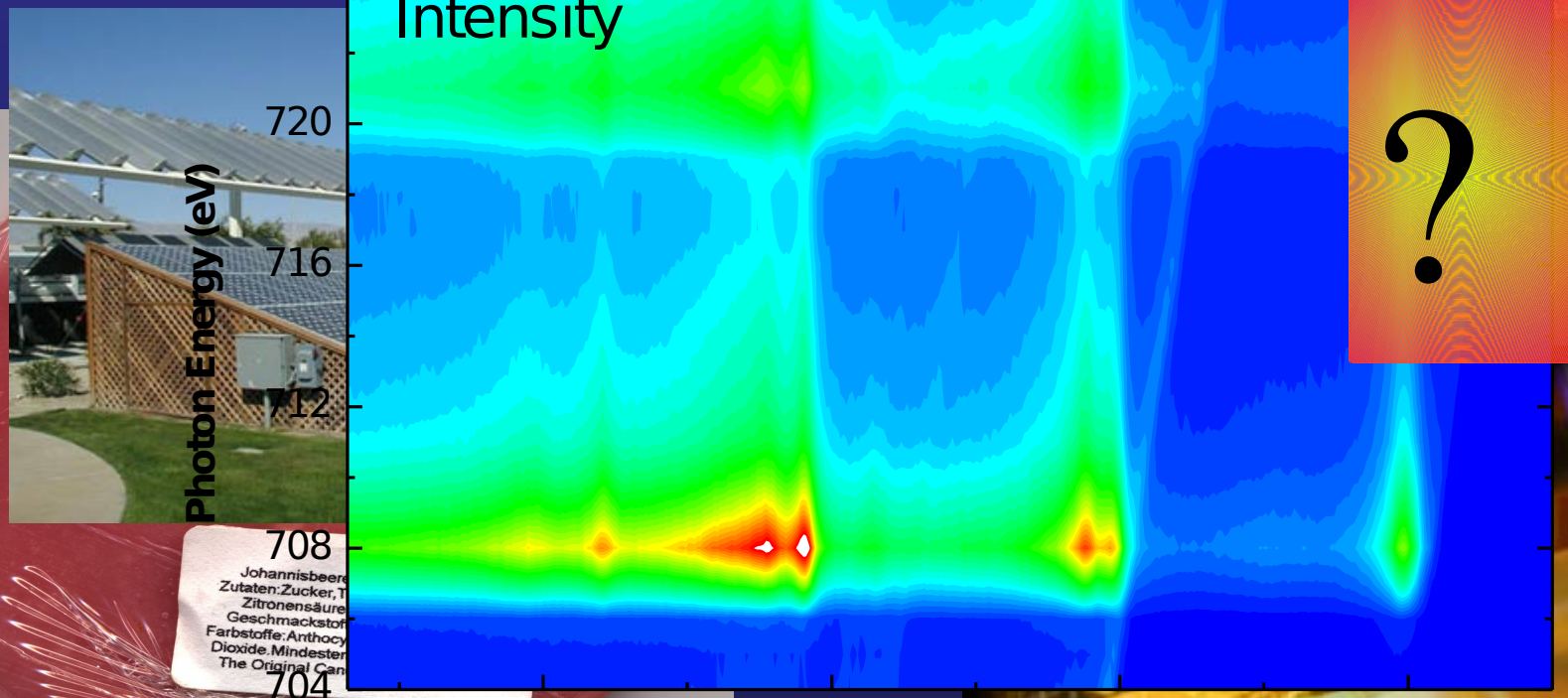




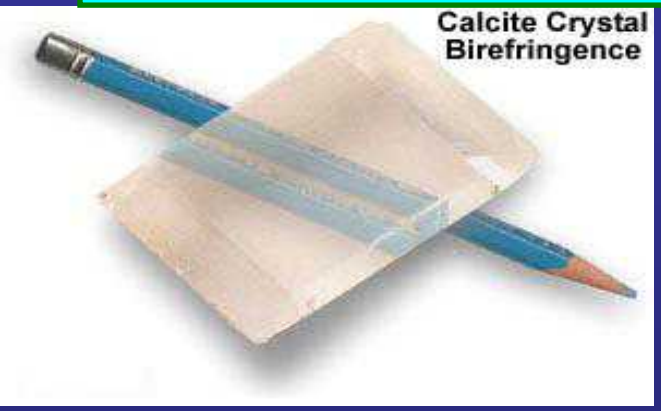
Electronic response.....

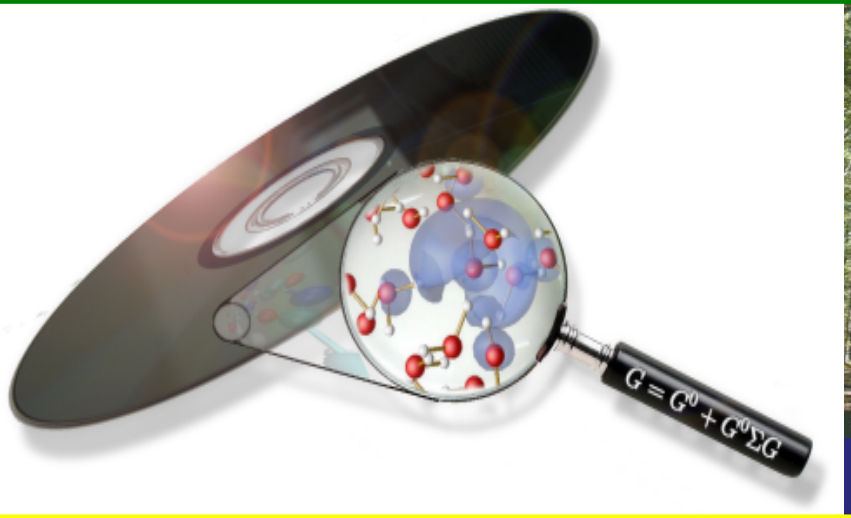




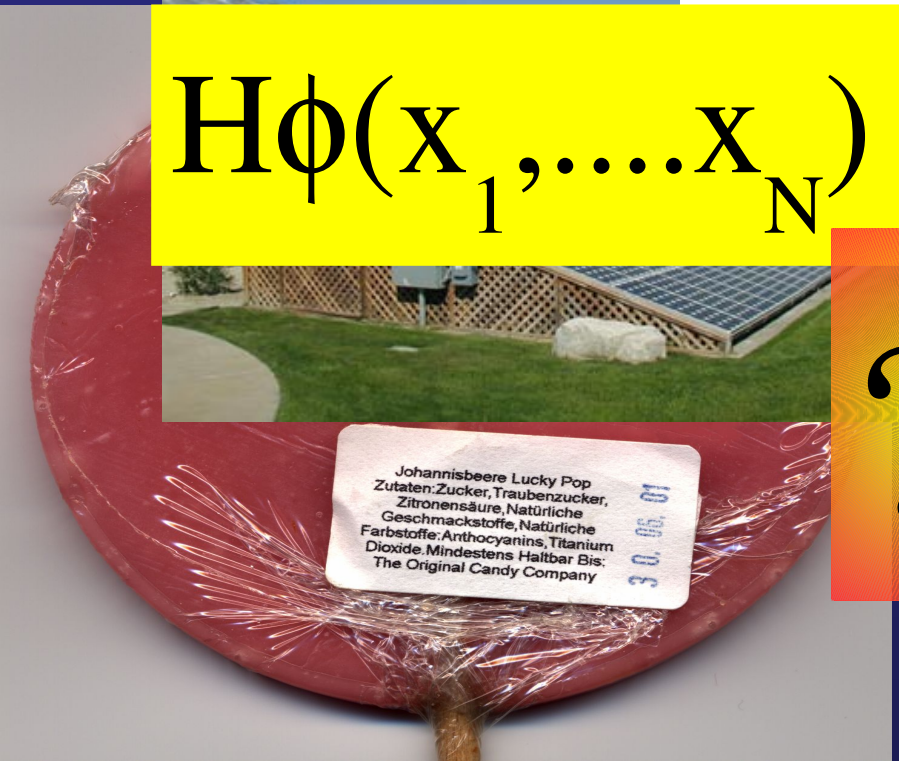


Electronic response.....





$$H\phi(x_1,\ldots.x_N) = E\,\phi(x_1,\ldots.x_N)$$



?

Electronic response.....

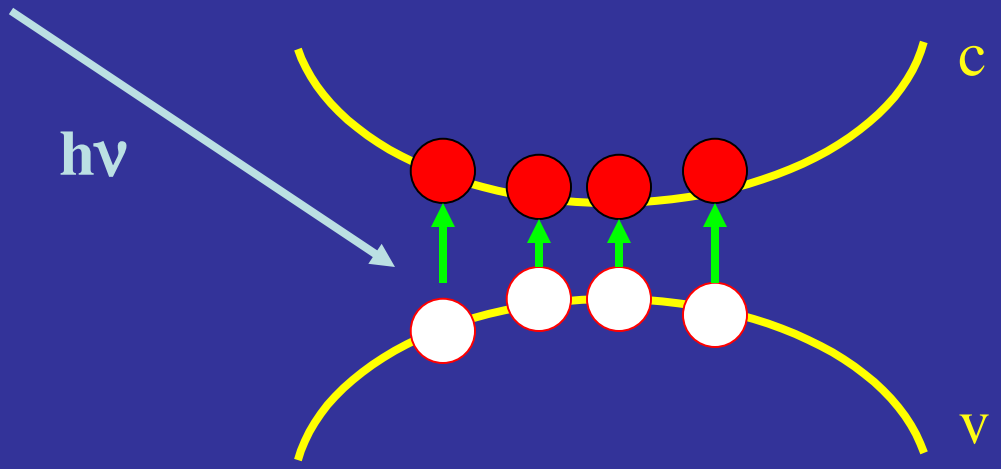
realistic

feasible

Calculations

easy to interpret

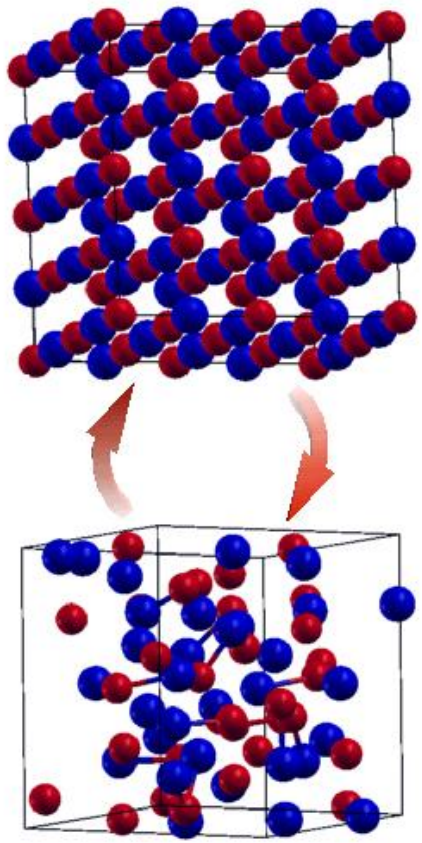
Independent electrons and transitions



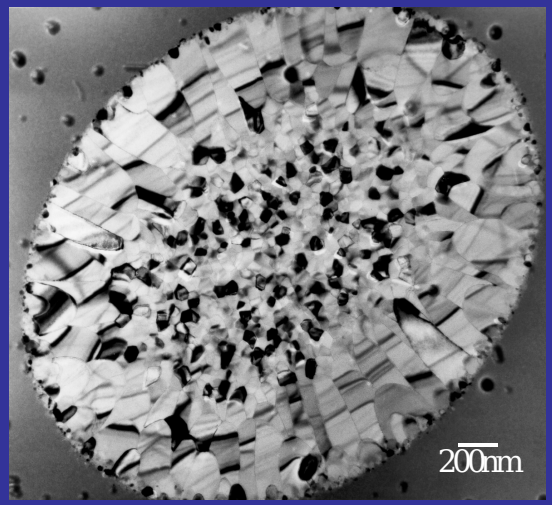
$$\mathrm{Im}\,[\chi_0] \sim \Sigma_{vc} \,|\langle v|D|c\rangle|^2\, \delta\,(E_c - E_v - \omega)$$

Energies and wavefunctions often from DFT – Kohn Sham

PCM: Reversible phase transition



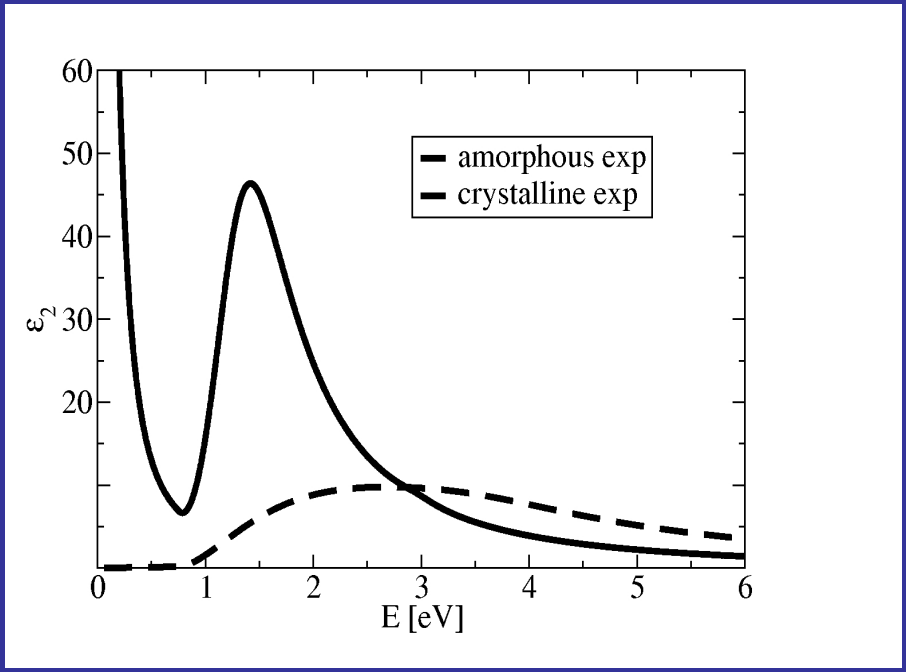
GeSbTe alloys:

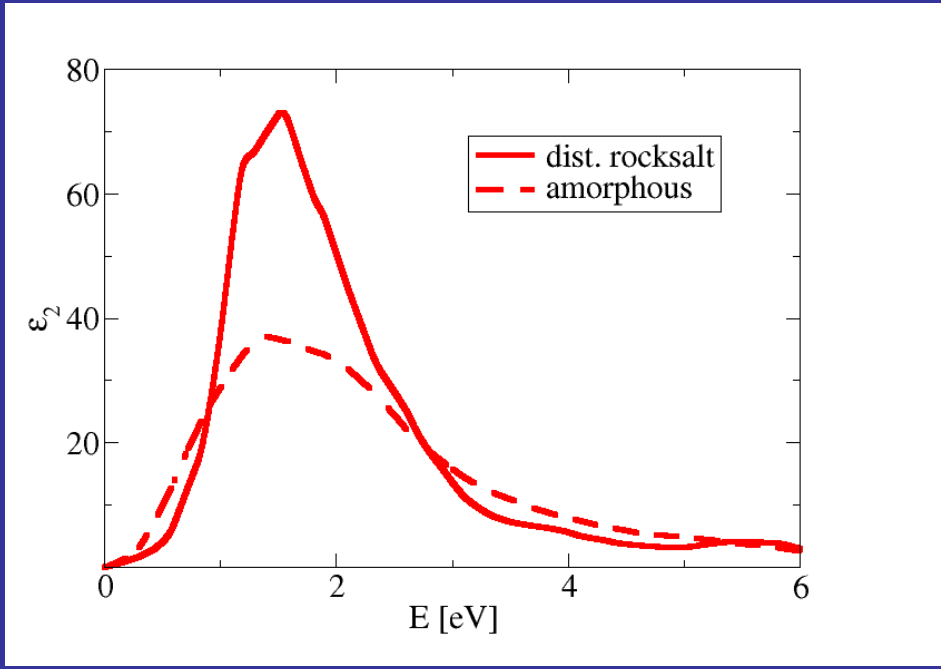


- rapid transition: ~10-100ns
- large optical & electric contrast
- although already applied still not well understood

calculations & experiment

- spectroscopy on polycrystalline thin films of GeTe
- optical spectra calculations (RPA)



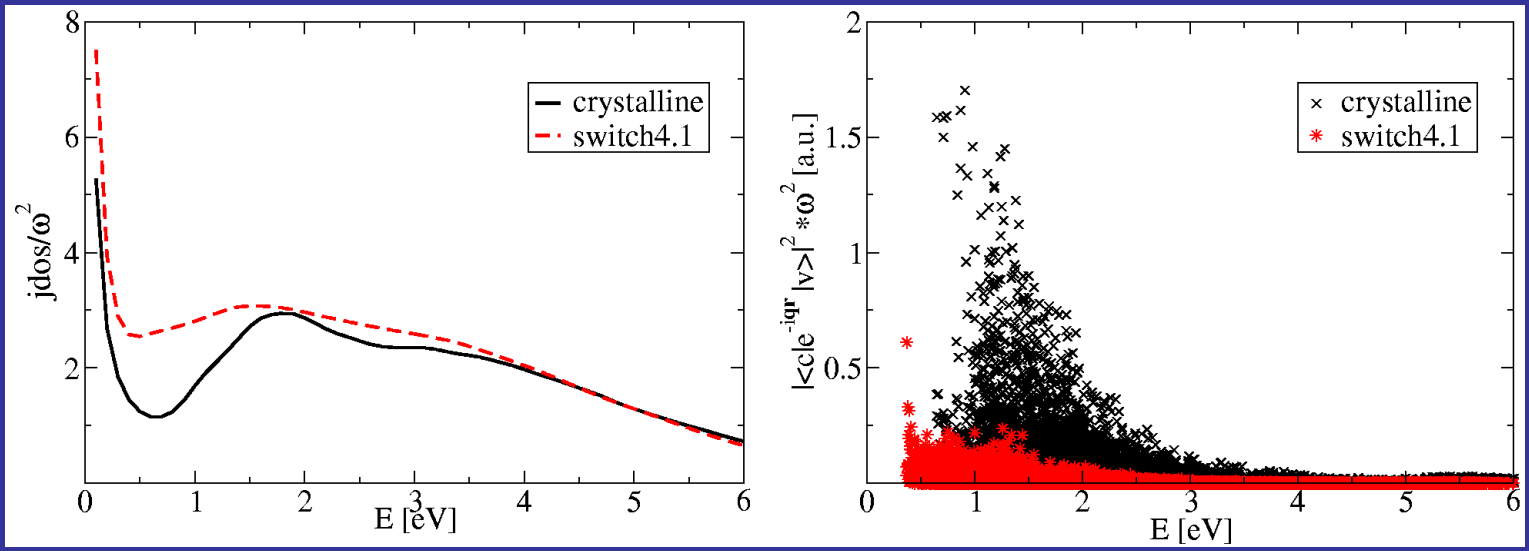


change in local order results in change of optical absorption.

Origin of strong change in absorption

Absorption given by Fermi's golden rule:

$$Im(\varepsilon_M(\omega)) = 2\pi \lim_{\mathbf{q}\to 0} v_0(\mathbf{q}) \sum_{vc} \left|\left\langle c \left| e^{-i\mathbf{q}\cdot\mathbf{r}} \right| v \right\rangle\right|^2 \delta(\omega - (\epsilon_c - \epsilon_v))$$



No significant changes in jdos

Matrix elements define optical contrast!

W. Welnic, S. Botti, L. Reining, and M. Wuttig,, Phys. Rev. Lett. **98**, 236403 (2007)

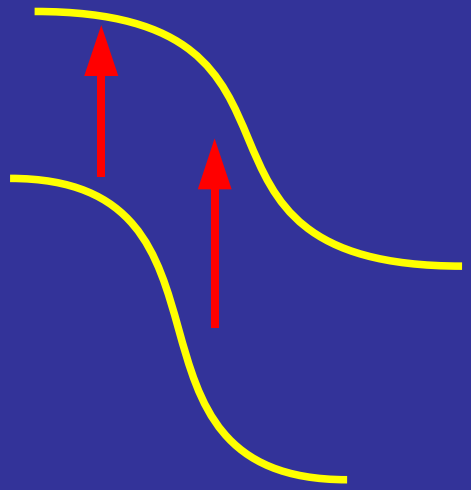
PFlop:

→ from model short range amorphous to realistic material

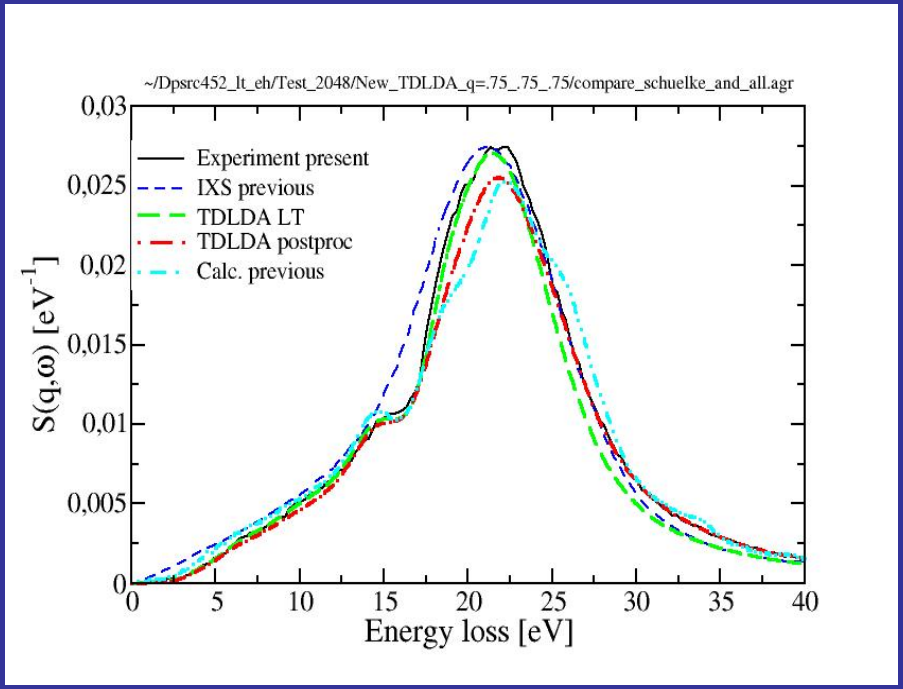
→ defects

→ many body effects for localized states

Silicon:



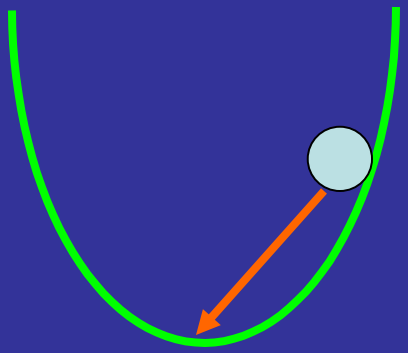
3 – 5 eV



20 eV

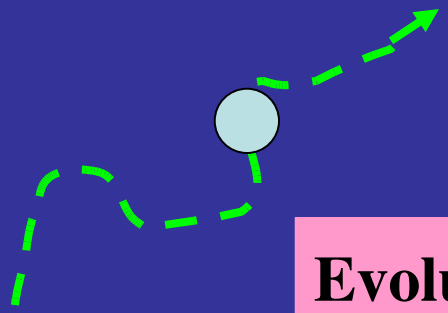
Time-Dependent Density Functional Theory

Equilibrium position: minimization of E



Ground state: DFT min[E]

Density propagation

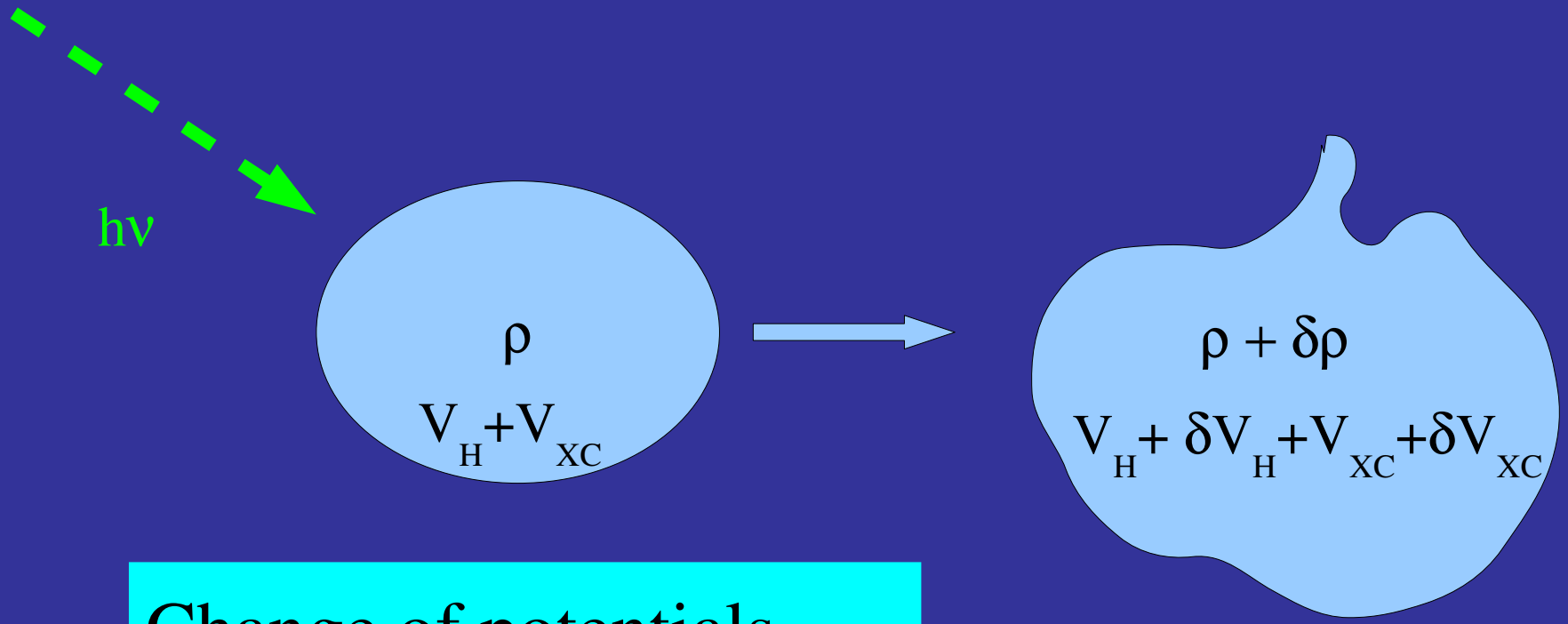


Trajectory: extrema of the action A

Evolution of the system (its density) due to external field: TD-DFT [A]

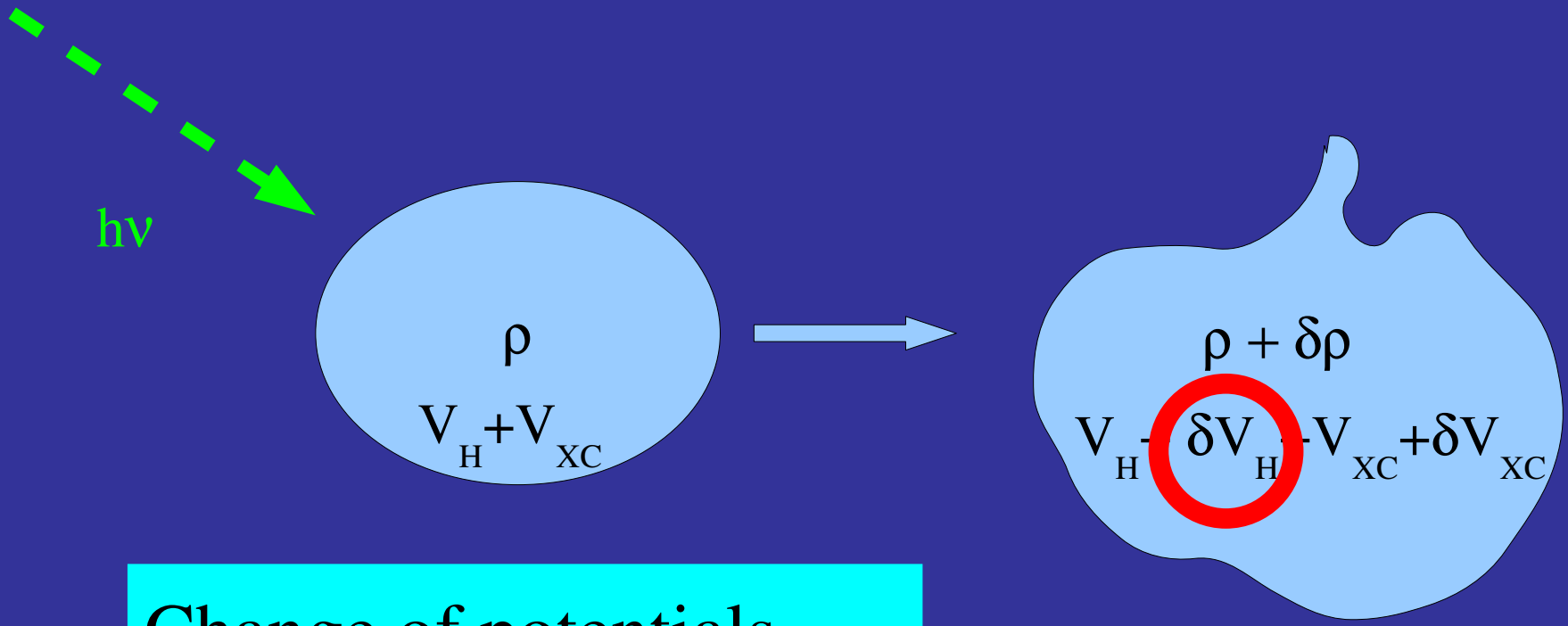
Runge and Gross 1984

Excitation ?



Change of potentials

Excitation ?



Change of potentials

Induced Hartree: long-range and local field effects

RPA

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

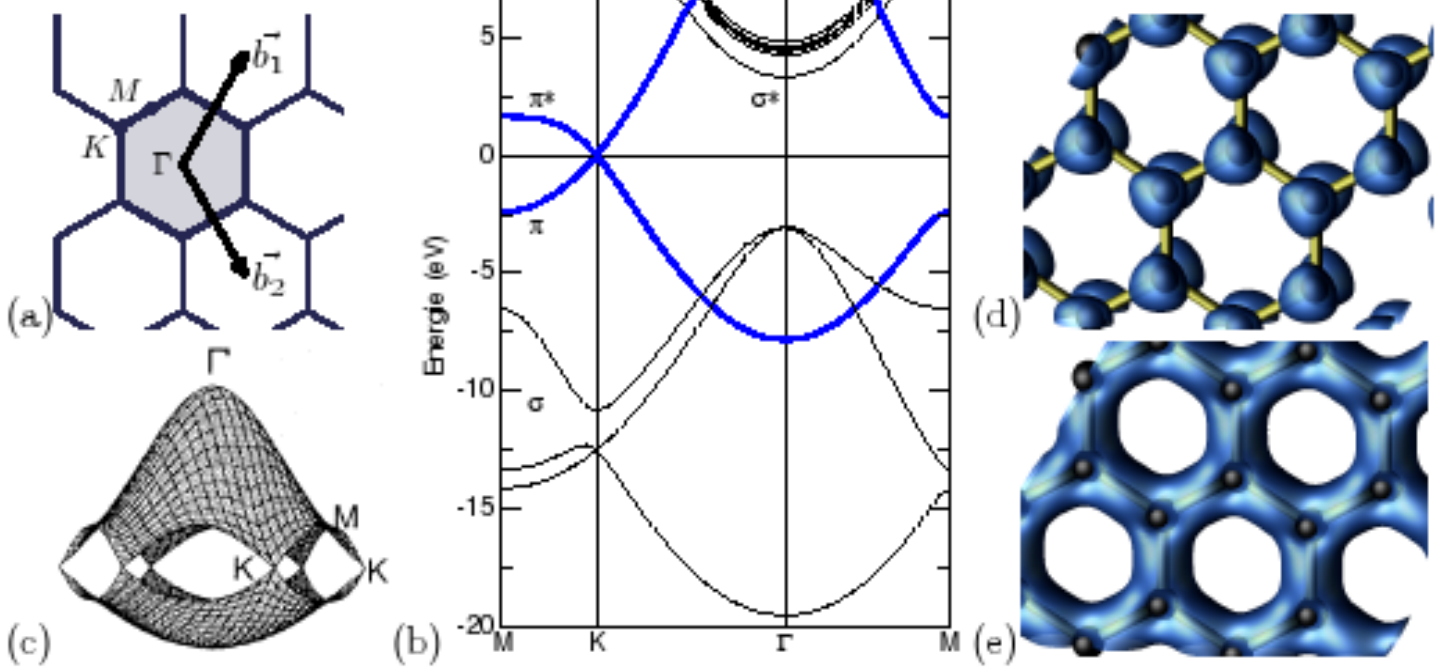
TDDFT-RPA: $\chi = \chi_0 + \chi_0 [\, v \,] \chi$

$v\,(q+G) \sim 1/|q+G|^2$

$G=0 \rightarrow$ plasmon

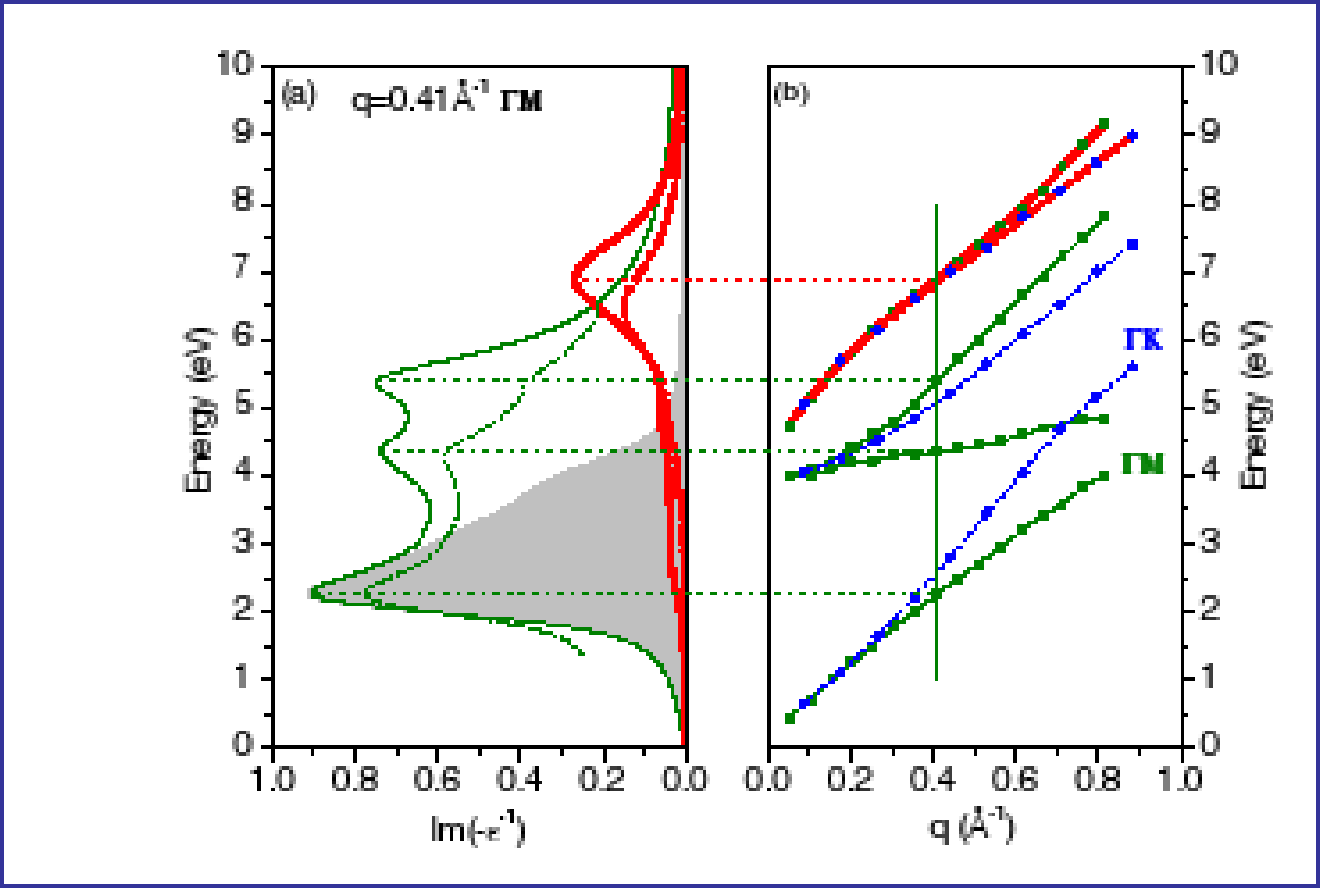
$G \neq 0 \rightarrow$ crystal local field effects

Graphene, π plasmon



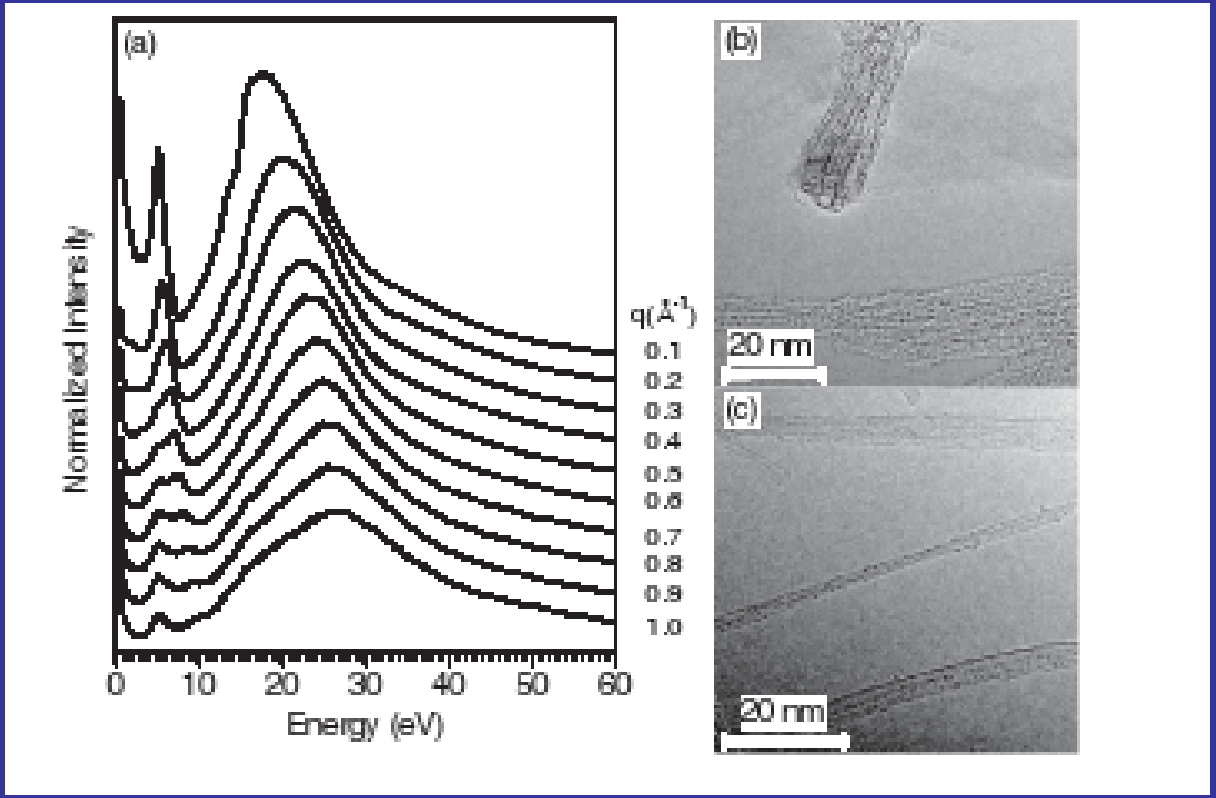
R. Hambach, Diplomarbeit

Graphene, π plasmon



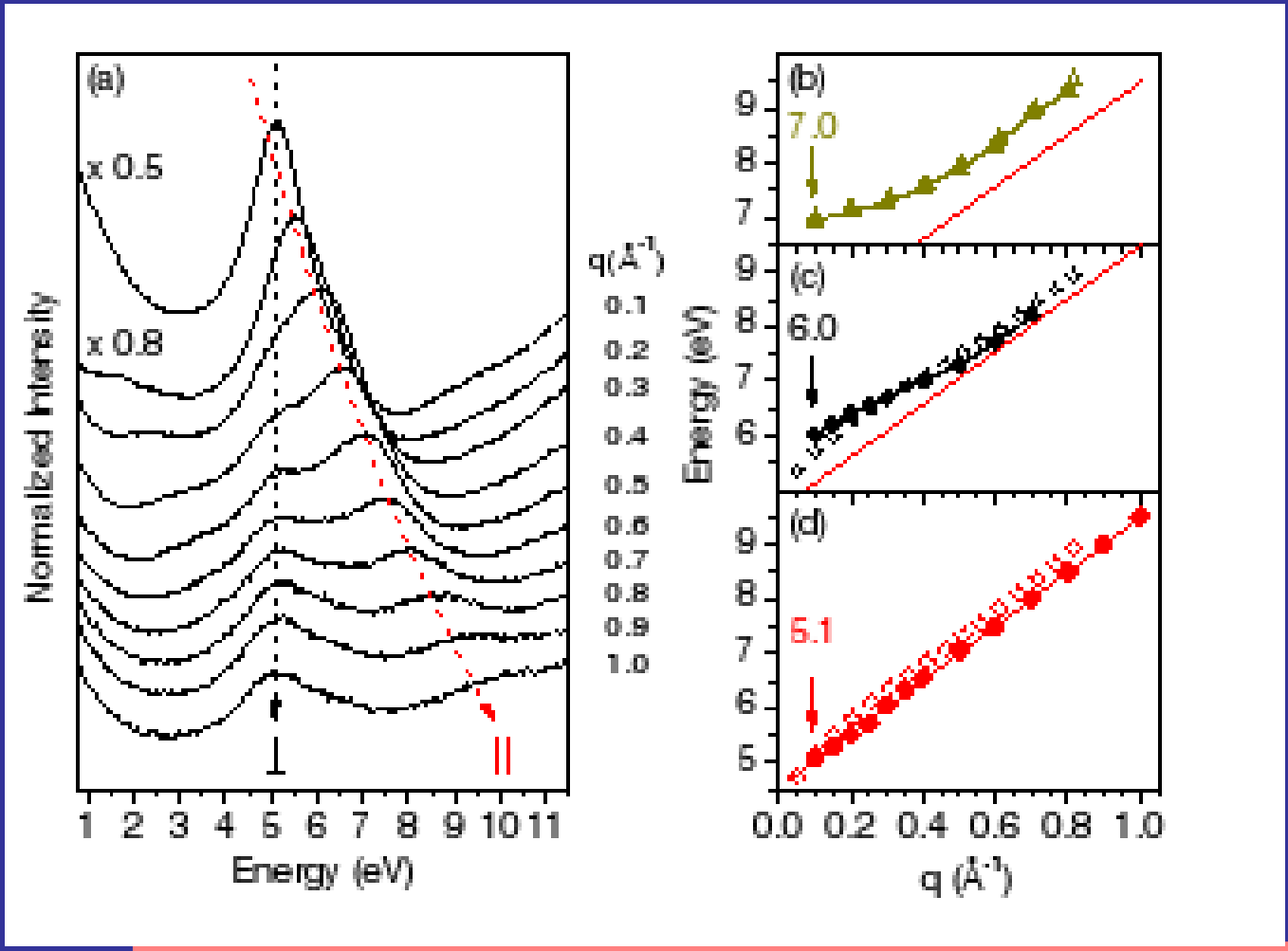
C. Kramberger, R. Hambach et al., PRL in press (2008)

Isolated carbon nanotube, π plasmon



C. Kramberger et al., PRL 100, 196803 (2008)

Nanotubes and graphene, π plasmon dispersion



C. Kramberger et al., PRL 100, 196803 (2008)

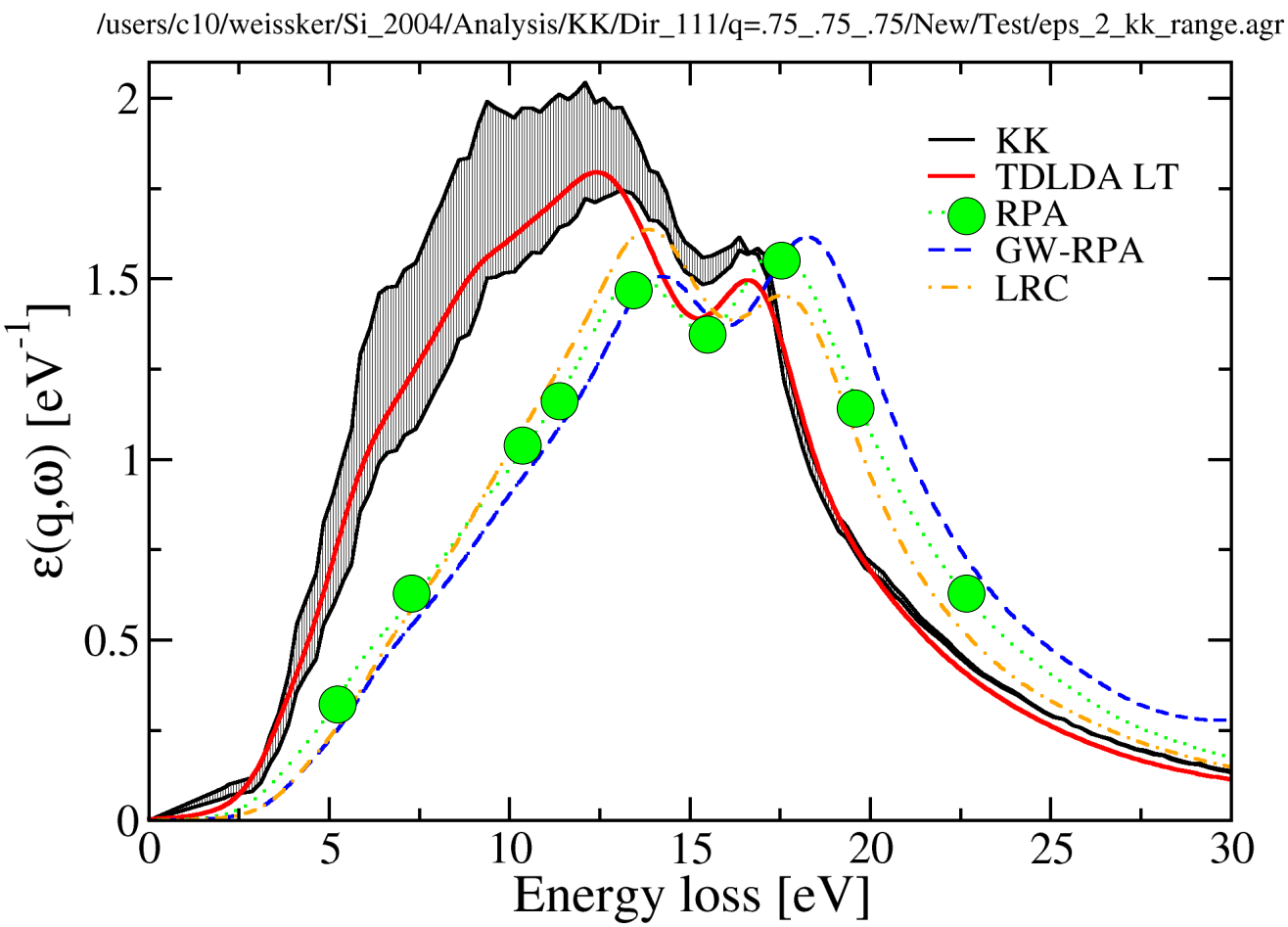
PFlop:

→ larger nanotubes

→ multiwall

→ doping

More quantitatively?



H. Weissker et al., Phys. Rev. Lett. **97**, 237602 (2006)

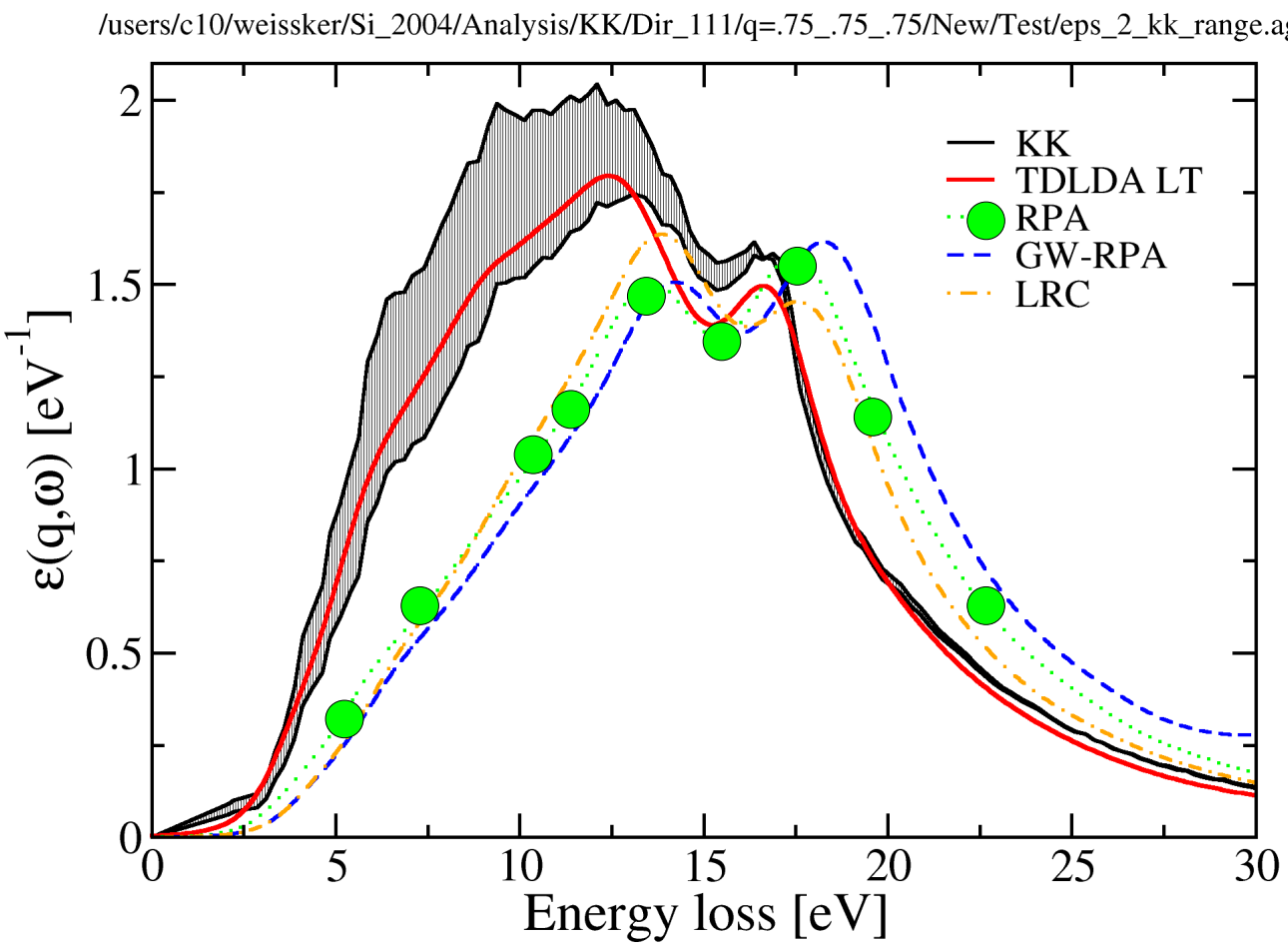
Collaboration LSI – ESRF (ID16)

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

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

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

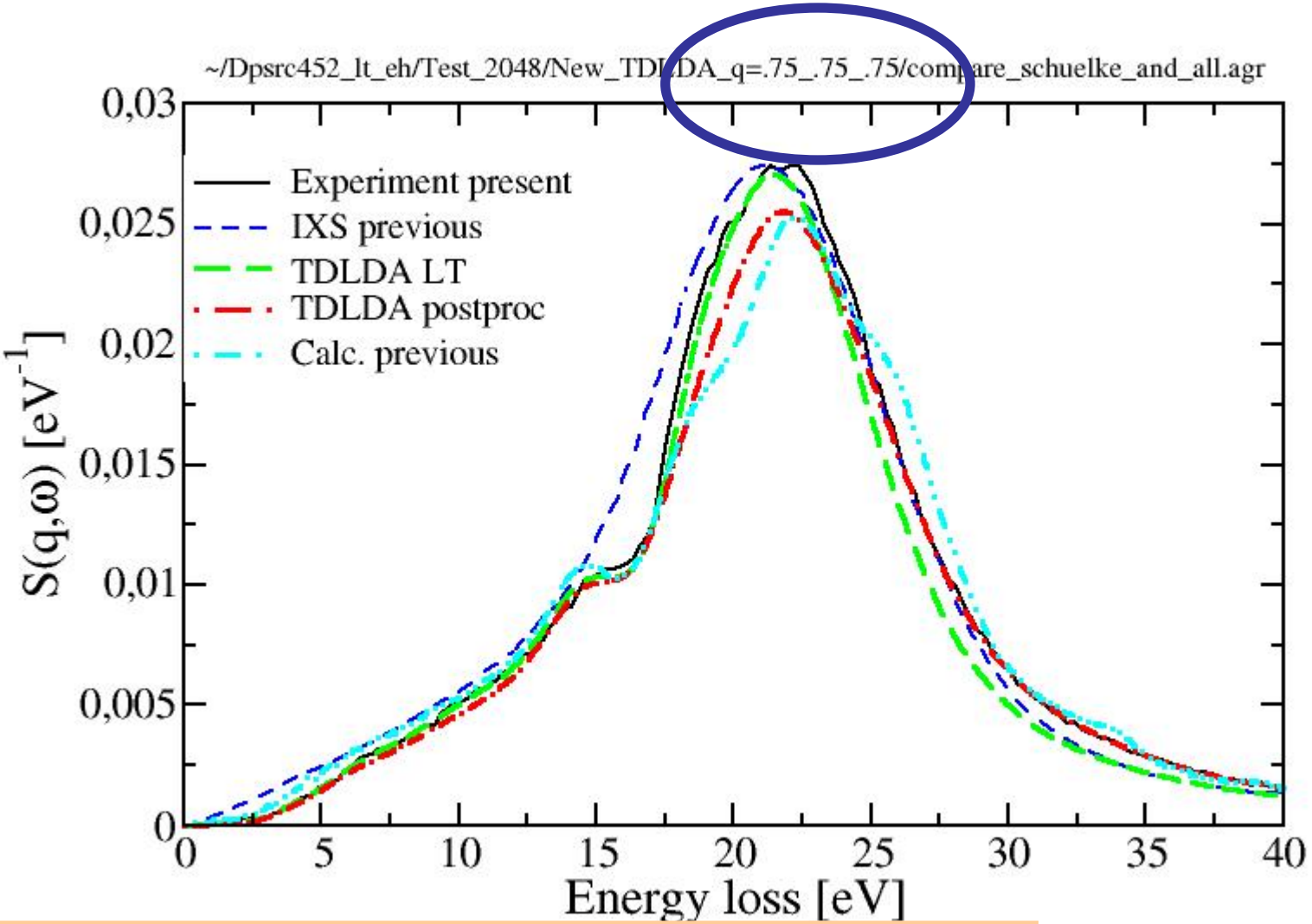
TDLDA: $\delta V_{xc}^{LDA}(r,t)/ \delta\rho(r',t') = \delta(r-r')\delta(t-t')dV_{xc}/d\rho$



H. Weissker et al., Phys. Rev. Lett. **97**, 237602 (2006)

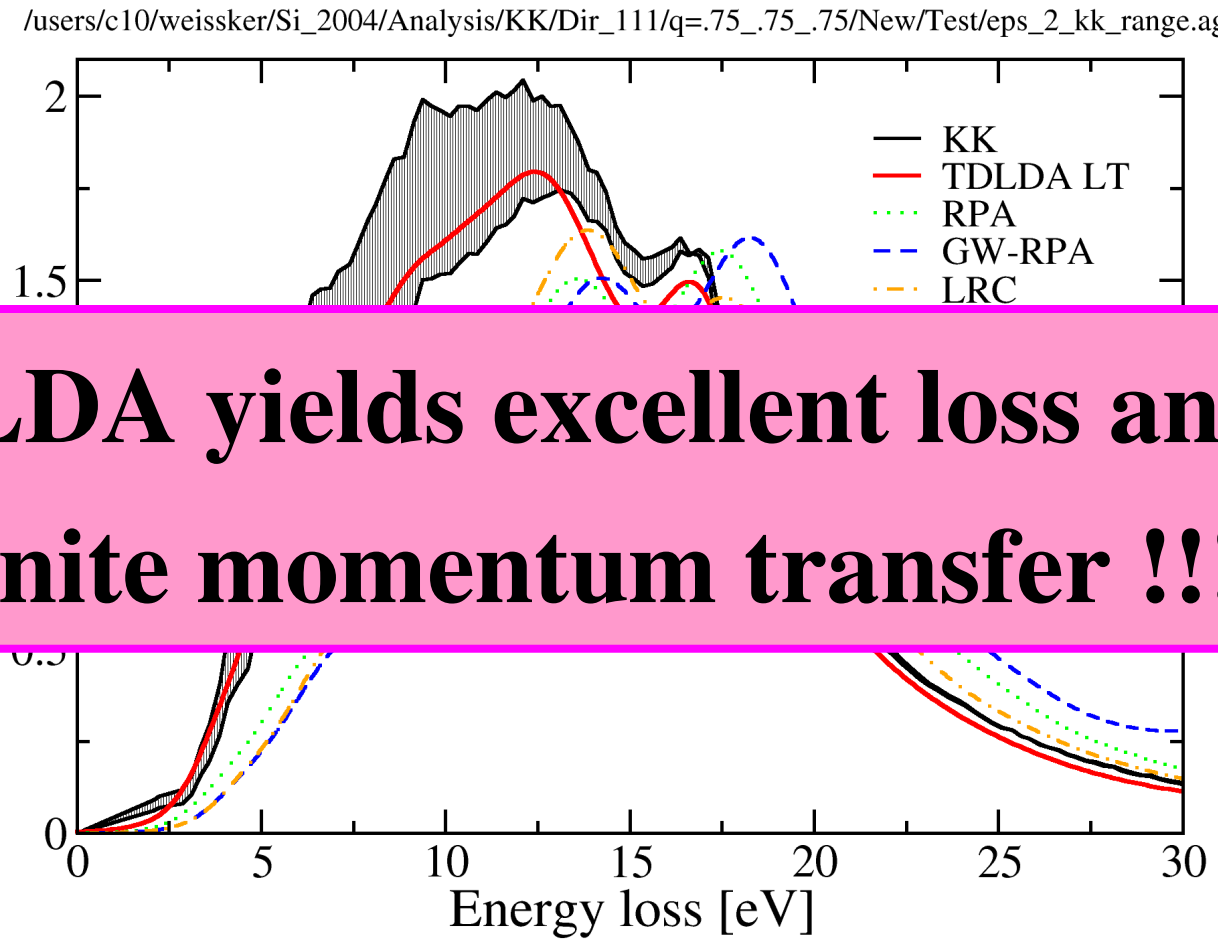
Collaboration LSI – ESRF (ID16)

Fortunately.....TDLDA often works



H. Weissker et al., Phys. Rev. Lett. **97**, 237602 (2006)

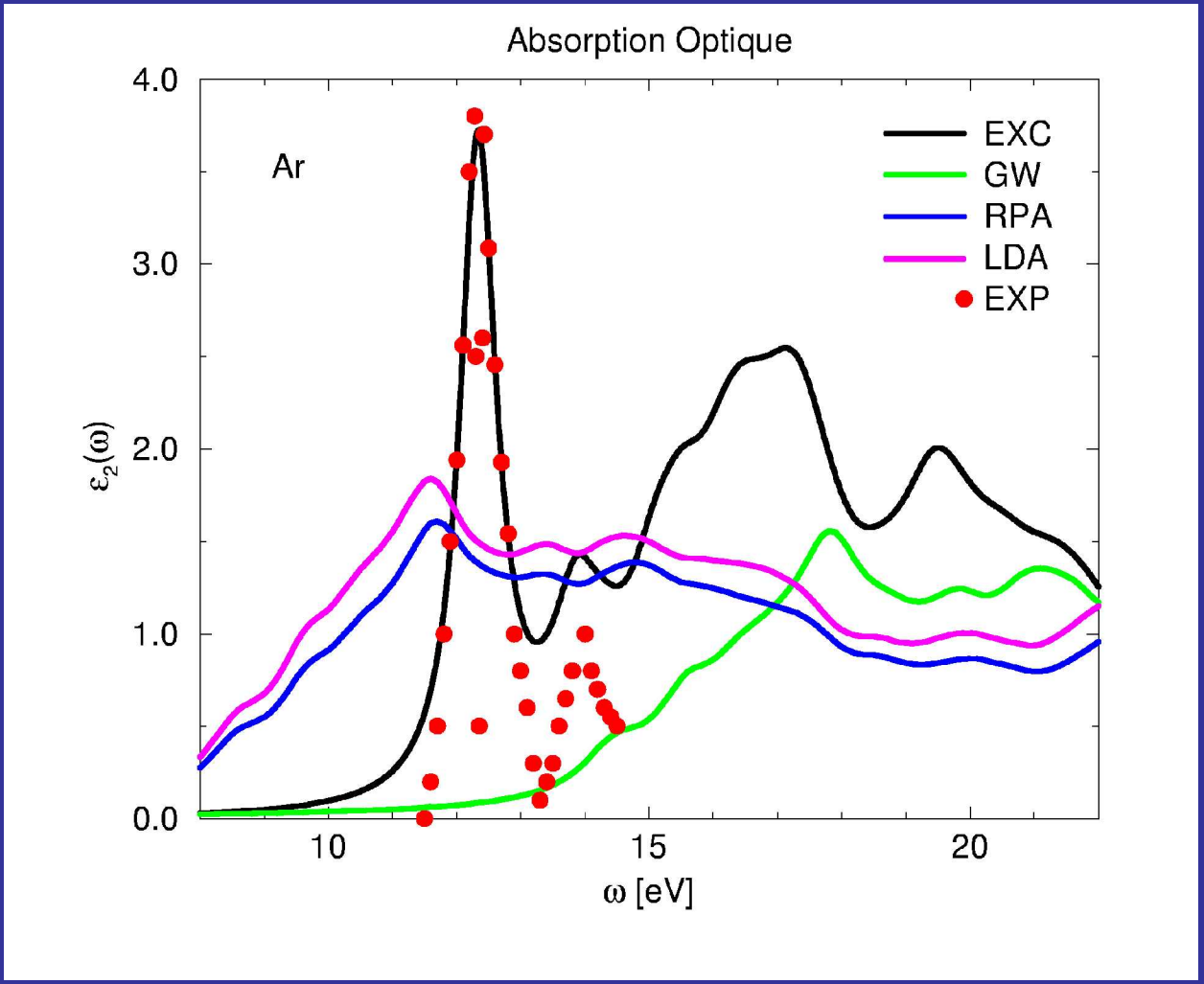
Collaboration LSI – ESRF (ID16)



TD-LDA yields excellent loss and Im(ε) for finite momentum transfer !!!

H. Weissker et al., Phys. Rev. Lett. **97**, 237602 (2006)

Collaboration LSI – ESRF (ID16)



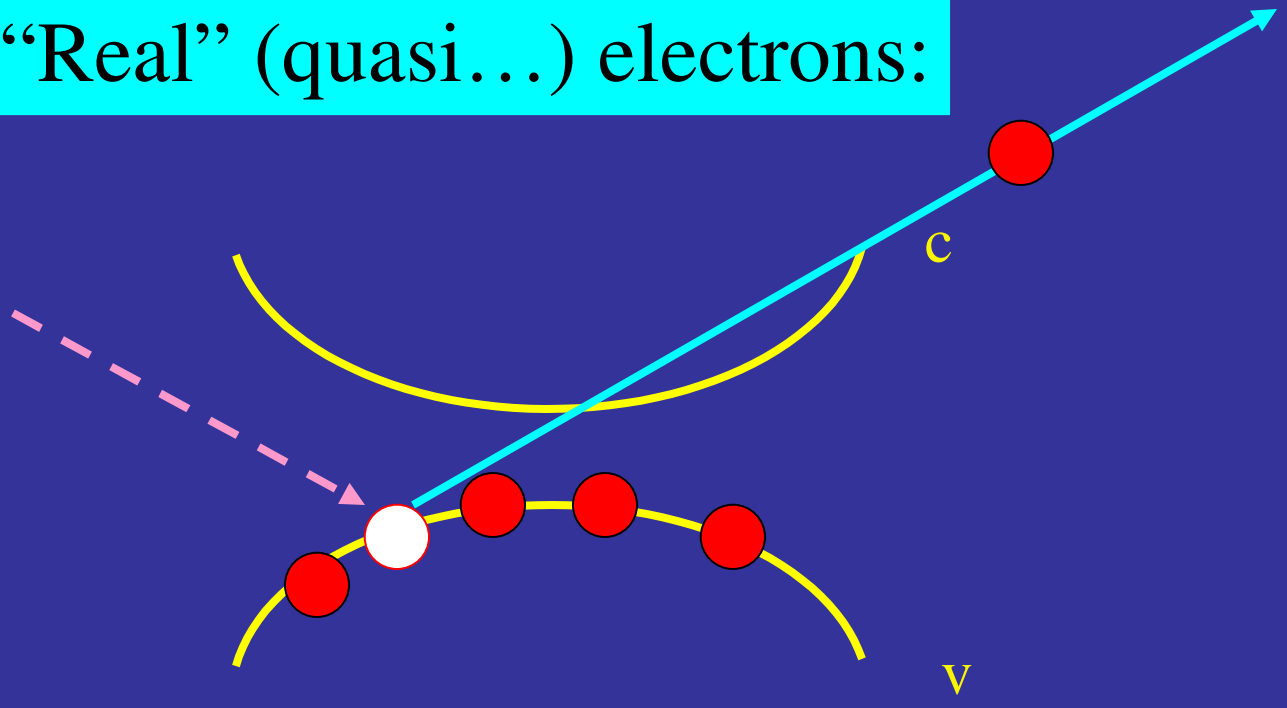
RPA and TDLDA: sometimes quite wrong!

E_c-E_v (minimum, eV)

	DFT-KS	Exp.
Silicon	0.55	1.17
Diamond	4.26	5.48
MgO	5.3	7.83
Ar	8.2	14.2

KS underestimates gaps (transition energies)

“Real” (quasi…) electrons:



Hole - (N-1) electrons

Exchange

Relaxation - dynamical correlations

$$(-\nabla^2/2 + V_{ext} + V_H + V_{xc}(r))\,|n\rangle = E_n\,|n\rangle$$

$$(-\nabla^2/2 + V_{ext} + V_H + \Sigma)\,|n\rangle = E_n\,|n\rangle$$

$V_{xc}(r)$ to $\Sigma(r,r',E_n)$

$W=\varepsilon^{-1}v$!!!

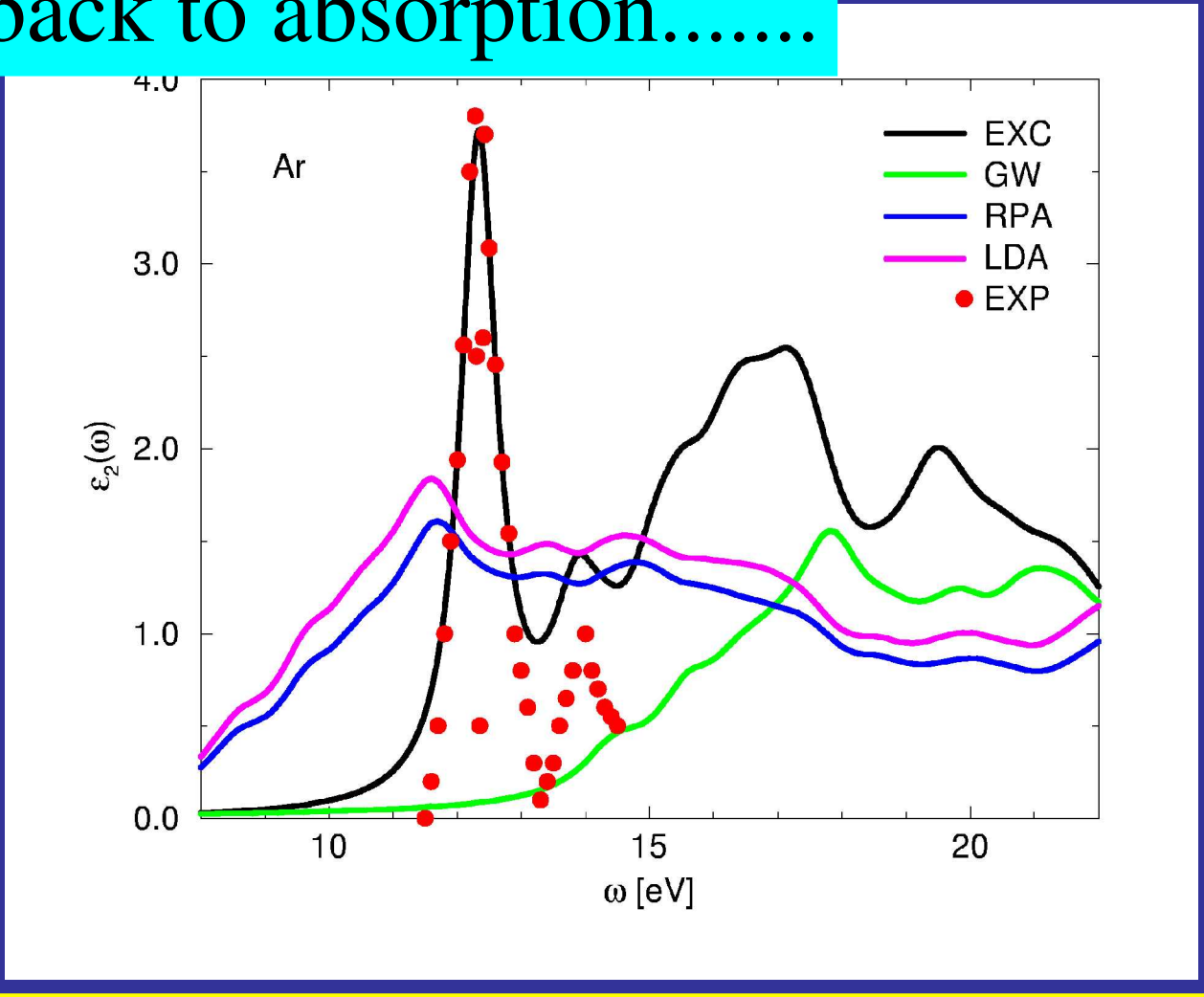
$\Sigma = iGW$ L. Hedin, PR 1965

E_c-E_v (minimum, eV)

	DFT-KS	Σ=iGW	Exp.
Silicon	0.55	1.19	1.17
Diamond	4.26	5.64	5.48
MgO	5.3	7.8	7.83
Ar	8.2	14.0	14.2

GW contains screening of hole (or electron)→ correct energies

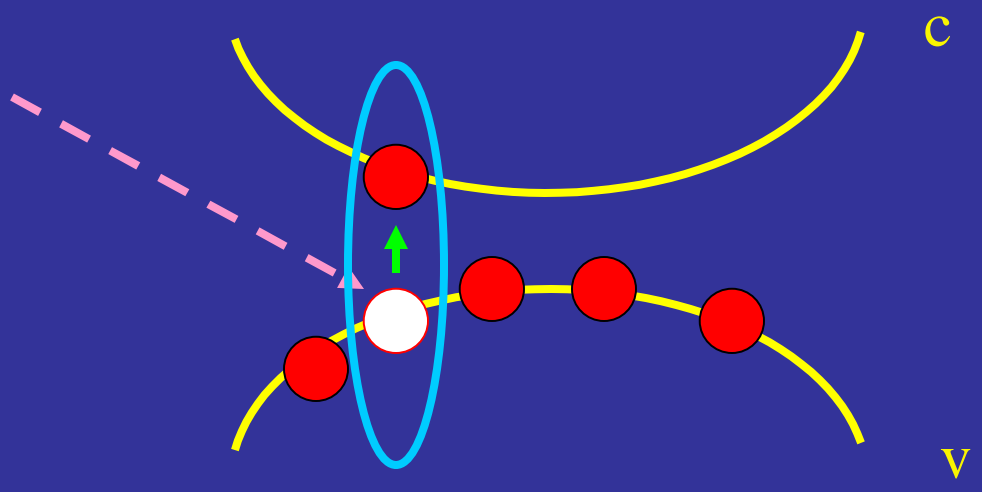
But back to absorption.....



Even good bandstructure

→ sometimes quite wrong!

Absorption ?



Electron-hole interaction

Excitonic effects

Bethe-Salpeter Equation

GW + Bethe Salpeter Equation

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

$$\mathrm{Im}\,[\varepsilon] \sim \Sigma_{vc} |\langle v|D|c\rangle|^2 \qquad \delta\,(E_c - E_v - \omega)$$

$$\mathrm{Im}\,[\varepsilon] \sim \Sigma_\lambda |\, \Sigma_{vc} \langle v|D|c\rangle\, A_\lambda^{vc}|^2\, \delta\,(E_\lambda - \omega)$$

->Mixing of transitions

->Modification of excitation energies

From $\delta V_H/\delta\rho + \delta\Sigma/\delta G$

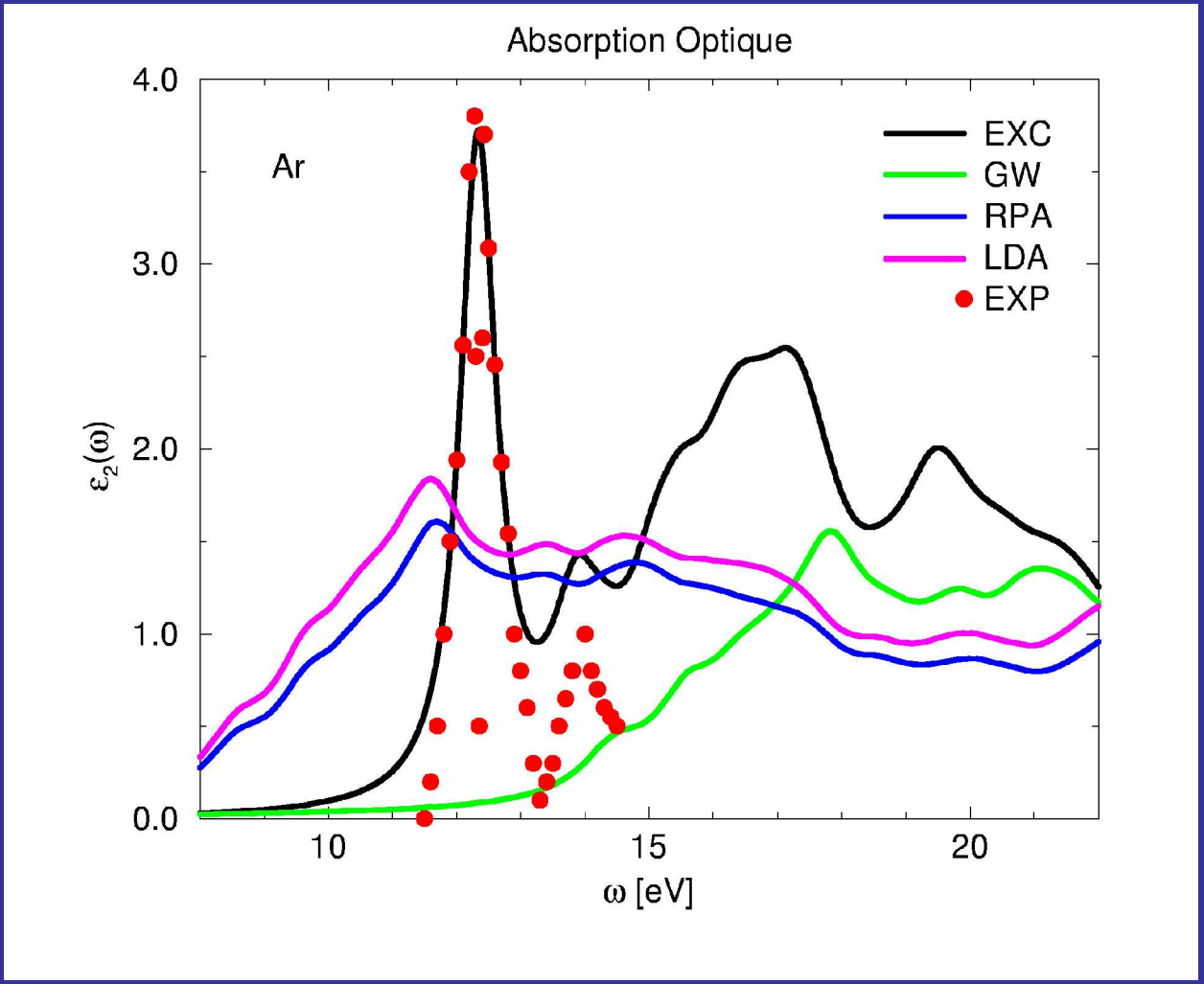
$$(H_{el} + H_{hole} + H_{el\text{-}hole})\, A_\lambda = E_\lambda\, A_\lambda$$

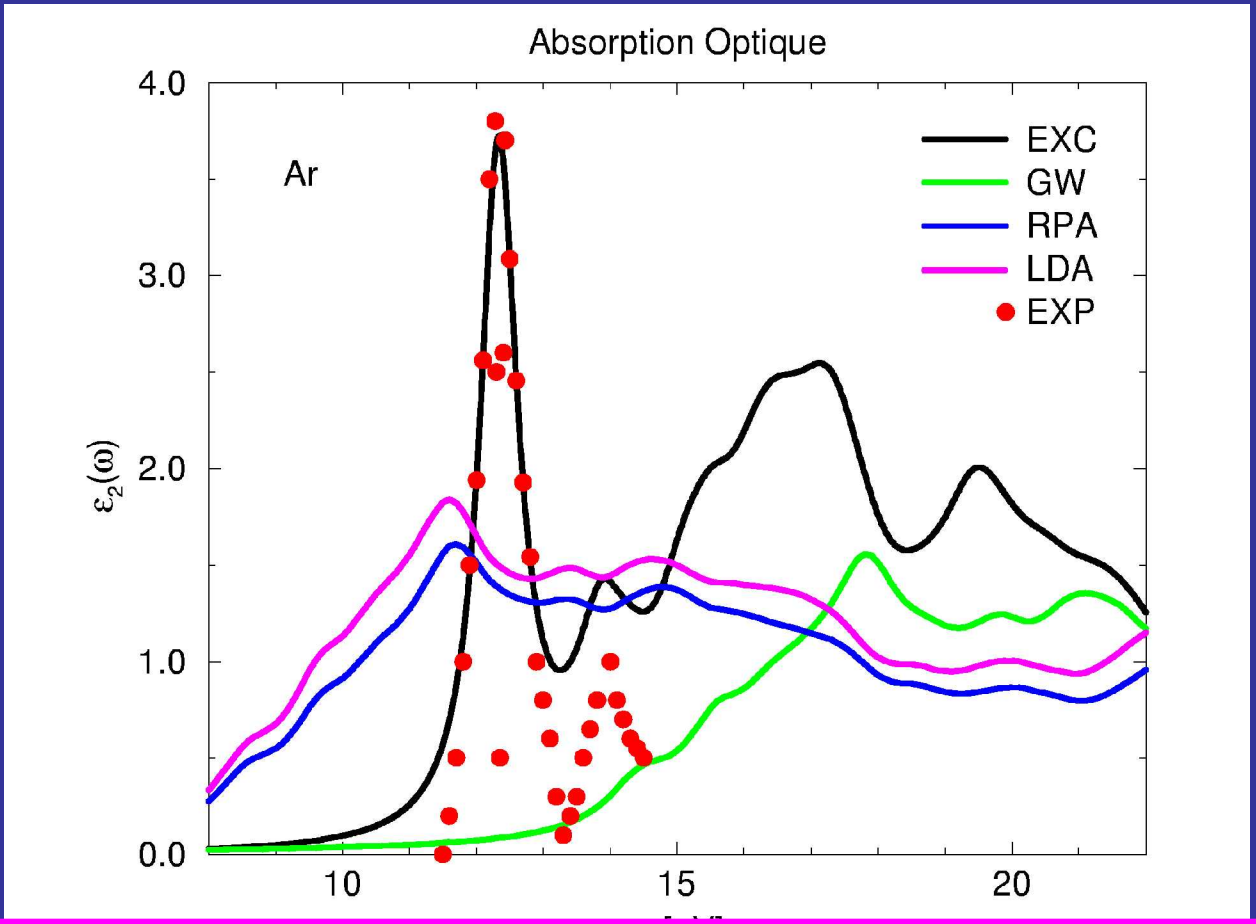
$$\mathrm{Im}\,[\varepsilon] \sim \Sigma_{vc} |\langle v|D|c\rangle|^2 \qquad \delta\,(E_c - E_v - \omega)$$

$$\mathrm{Im}\,[\varepsilon] \sim \Sigma_\lambda |\, \Sigma_{vc} \langle v|D|c\rangle\, A_\lambda^{vc}|^2\, \delta\,(E_\lambda - \omega)$$

->Mixing of transitions

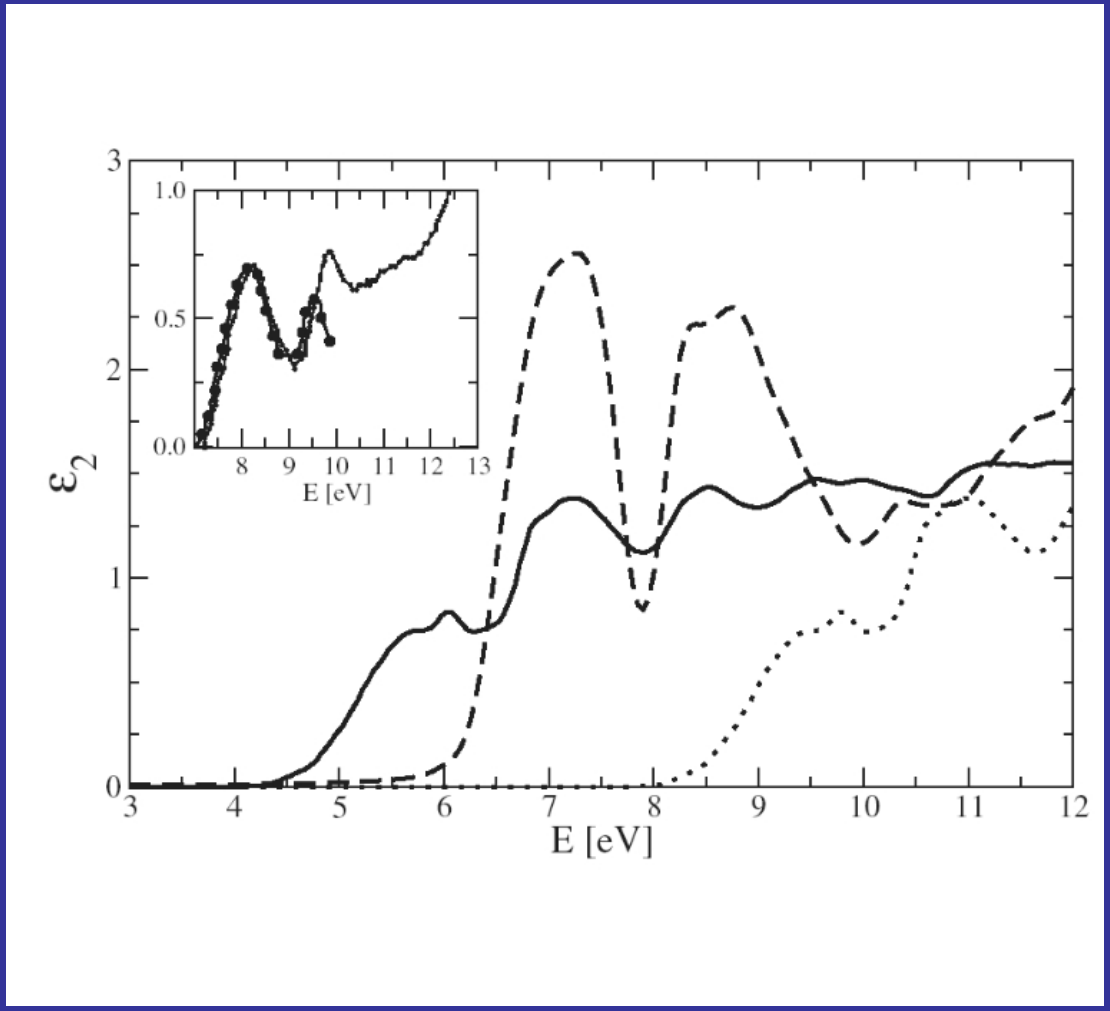
->Modification of excitation energies


Absorption Optique
Ar
EXC
GW
RPA
LDA
EXP
$\varepsilon_2(\omega)$
ω [eV]
0.0
1.0
2.0
3.0
4.0
10
15
20



Electron-hole interaction for good absorption spectra

Excitons in water



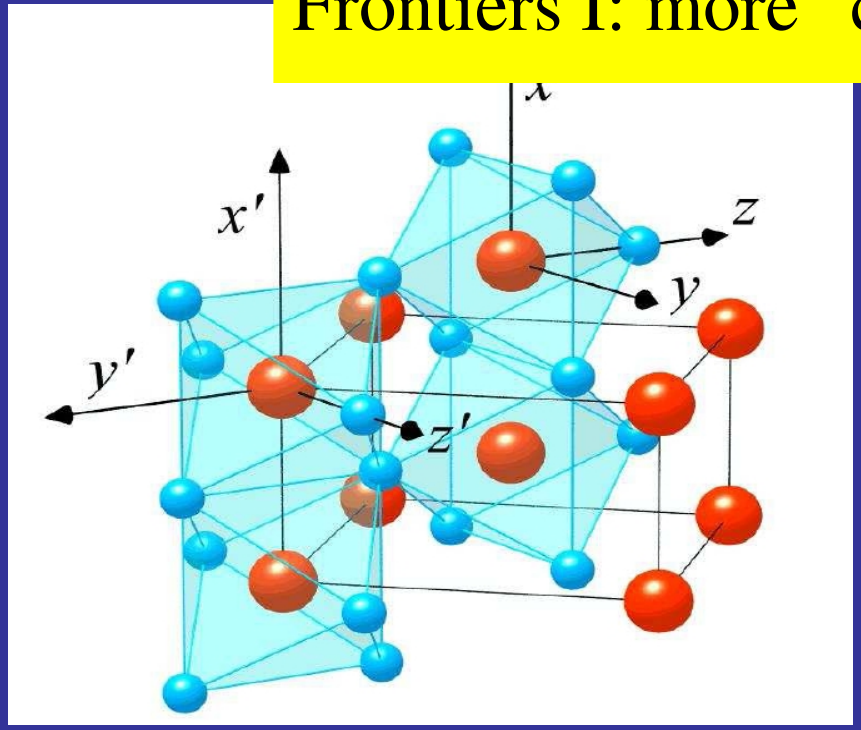
V. Garbuio, et al., PRL. **97**, 137402 (2006)

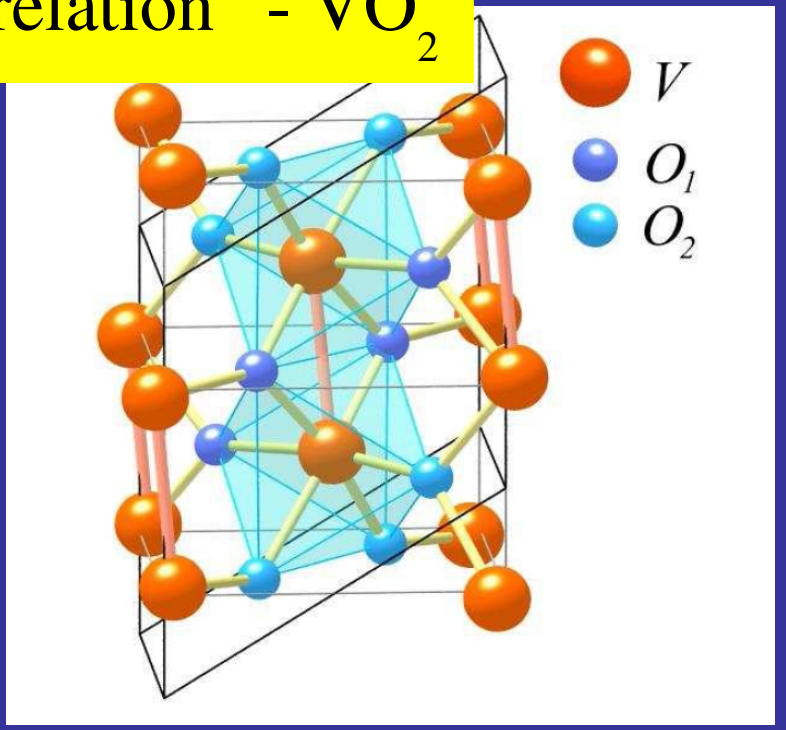
PFlop:

→ from model liquid to different phases of water

→ molecules in solution

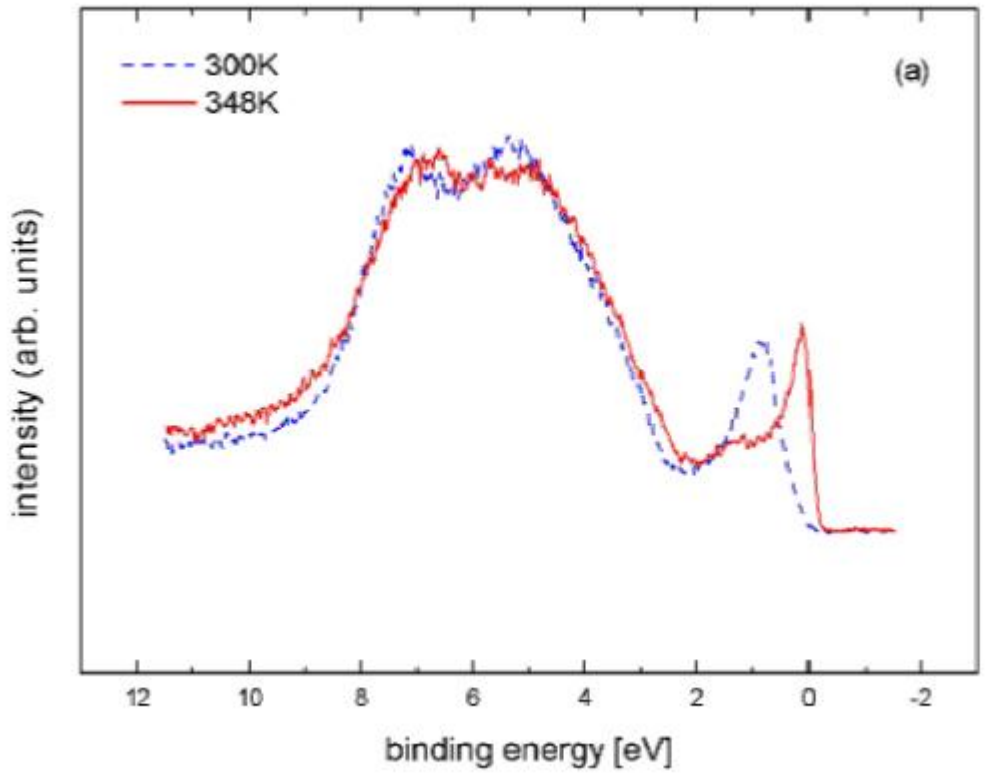
Frontiers I: more “correlation” - VO_2



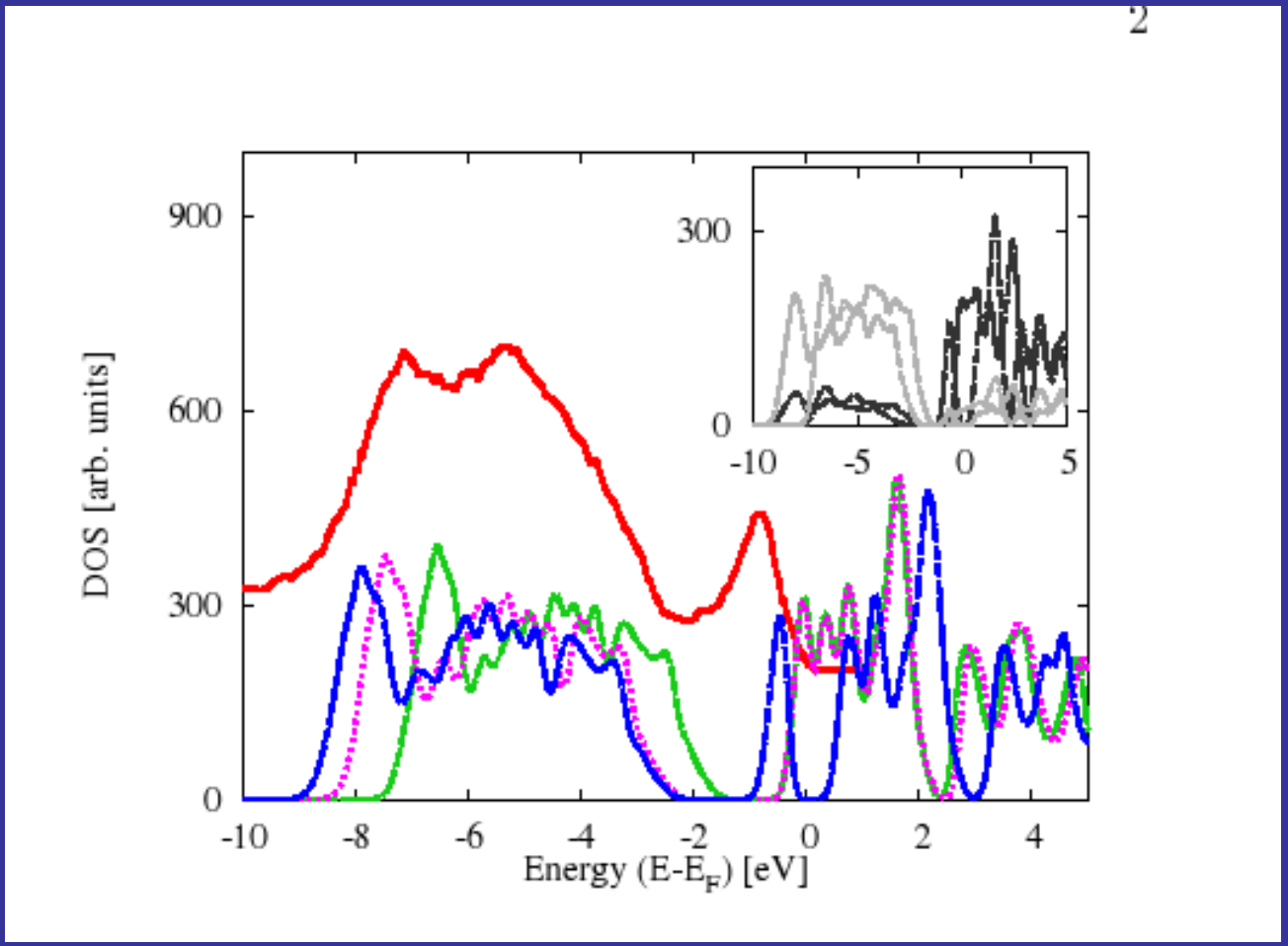


rutile

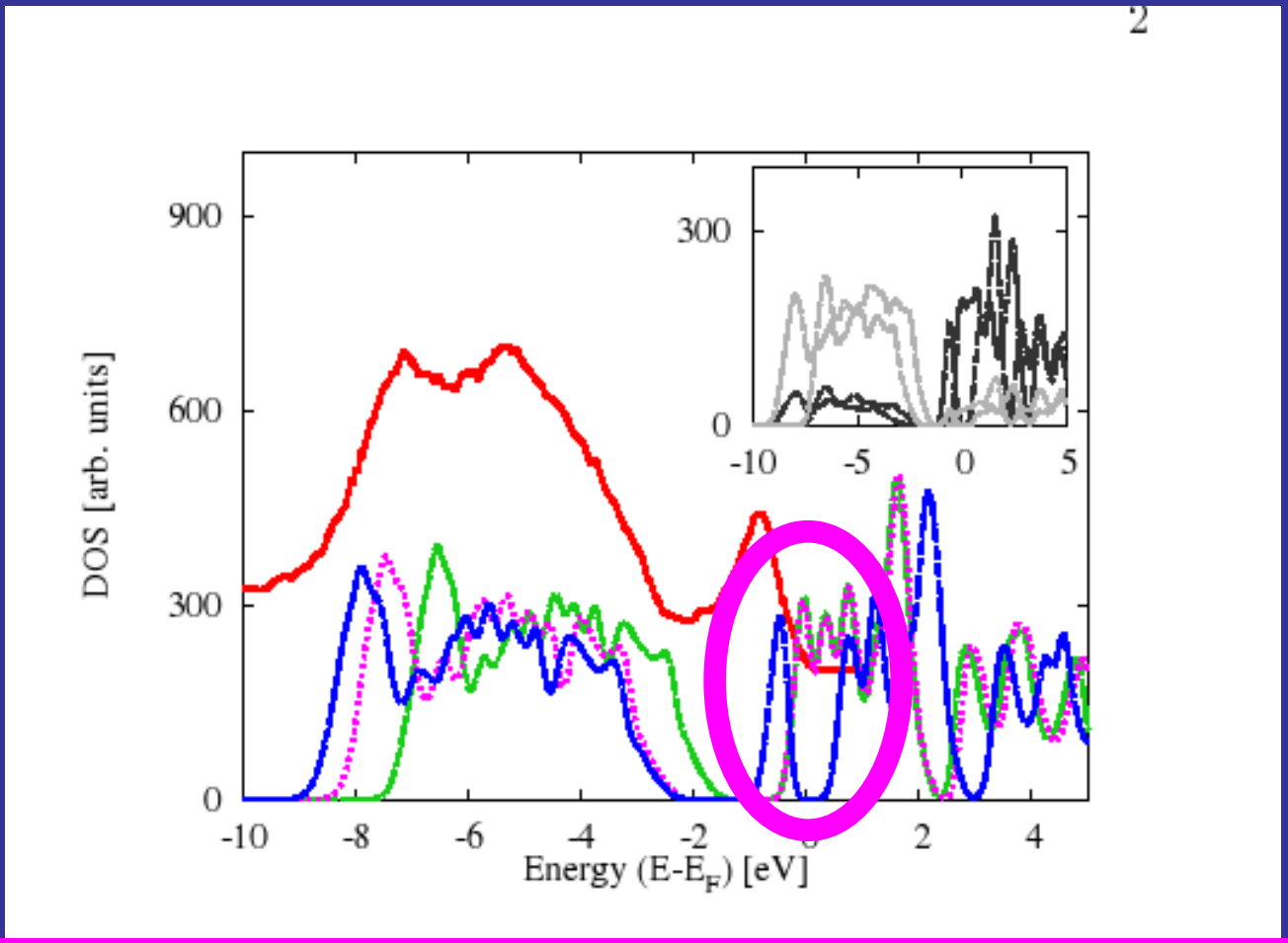
monoclinic



T. C. Koethe et al., Phys. Rev. Lett. 97, 116402 (2006).



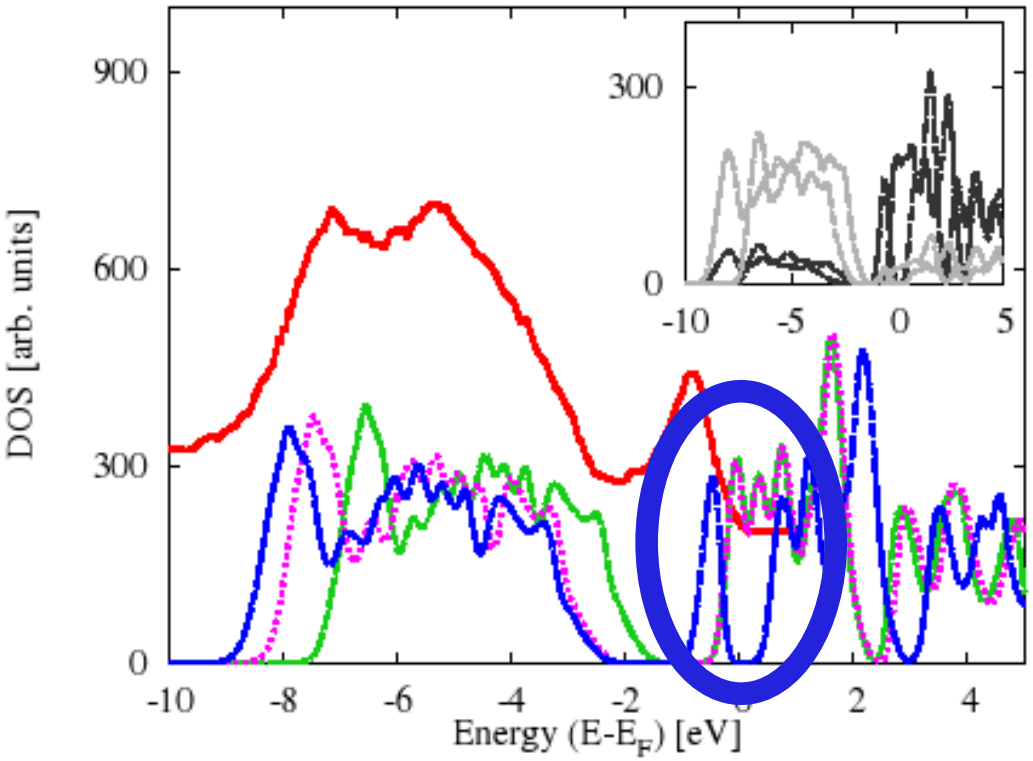
M. Gatti, F. Bruneval, V. Olevano and L. Reining, Phys. Rev. Lett. **99**, 266402 (2007)



No G_0W_0 gap

M. C

Phys. Rev. Lett. 99, 266402 (2007)



Self consistency opens gap

M. C

Phys. Rev. Lett. 99, 266402 (2007)

Away from the LDA starting point!

→ S. V. Faleev, M. van Schilfgaarde, and T. Kotani, PRL 93, 126406 (2004).

→ F. Bruneval, N. Vast, and L. Reining, Phys. Rev. B 74, 045102 (2006).

→ F. Fuchs, et al., Phys. Rev. B 76, 115109 (2007).

Away from the LDA starting point!

...of practical importance: example photovoltaics

Beyond Standard GW

Quasiparticle energies within sc-GW for CIS

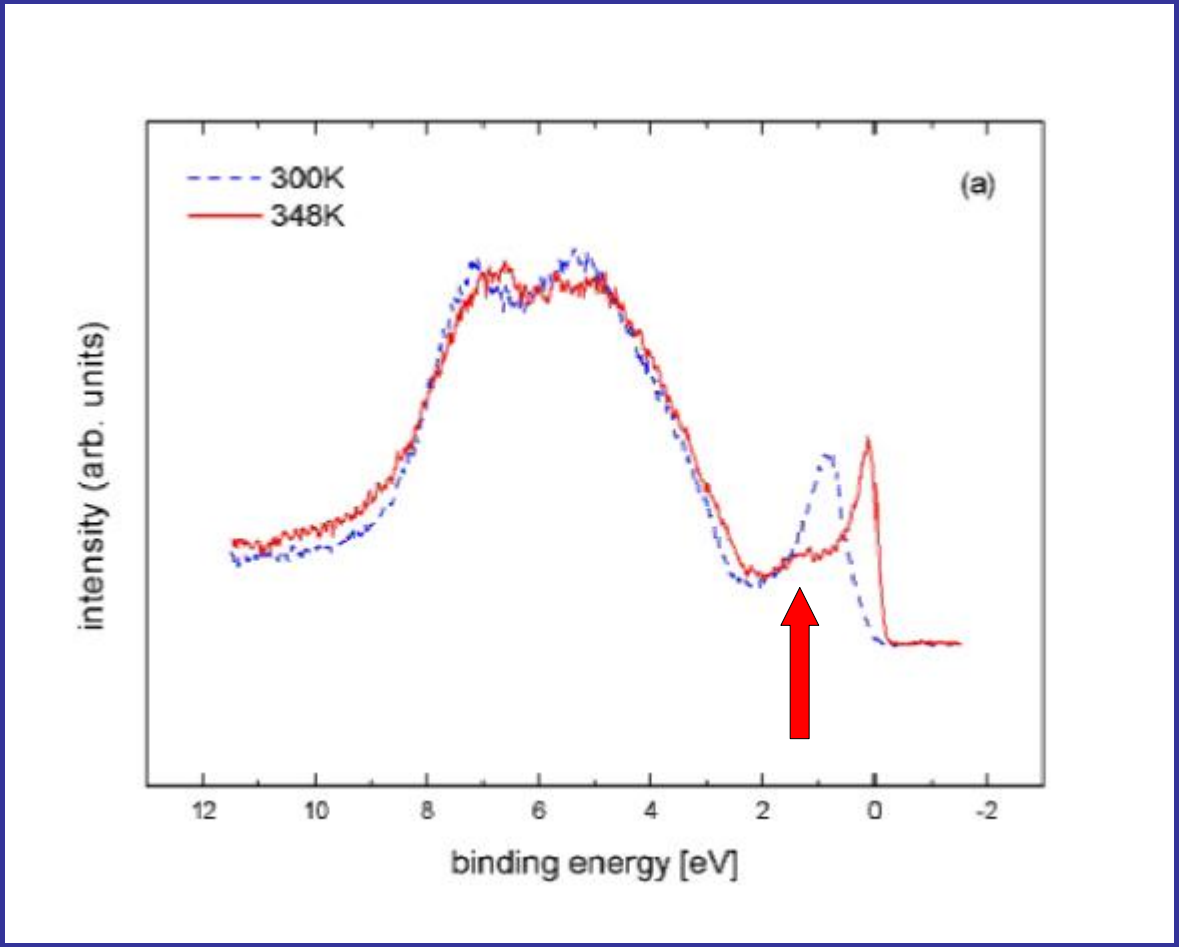
	$CuInS_2$			
	DFT-LDA	G_0W_0	sc-GW	exp.
E_g	-0.11	0.28	1.48	1.54
In-(S,Se)	6.5	6.9	7.0	6.9
(Se,S) s band	12.4	13.0	13.6	12.0
In 4 d band	14.6	16.4	18.2	18.2

	$CuInSe_2$			
	DFT-LDA	G_0W_0	sc-GW	exp.
E_g	-0.29	0.25	1.14	1.05 (+0.2)
In-(S,Se)	5.8	6.15	6.64	6.5
(Se,S) s band	12.6	12.9	13.6	13.0
In 4 d band	14.7	16.2	17.8	18.0

J. Vidal et al., collaboration EDF (2008)

CNRS ETSF

VO_2



T. C. Koethe et al., Phys. Rev. Lett. 97, 116402 (2006).

PFlop:

→ spectral functions with good precision

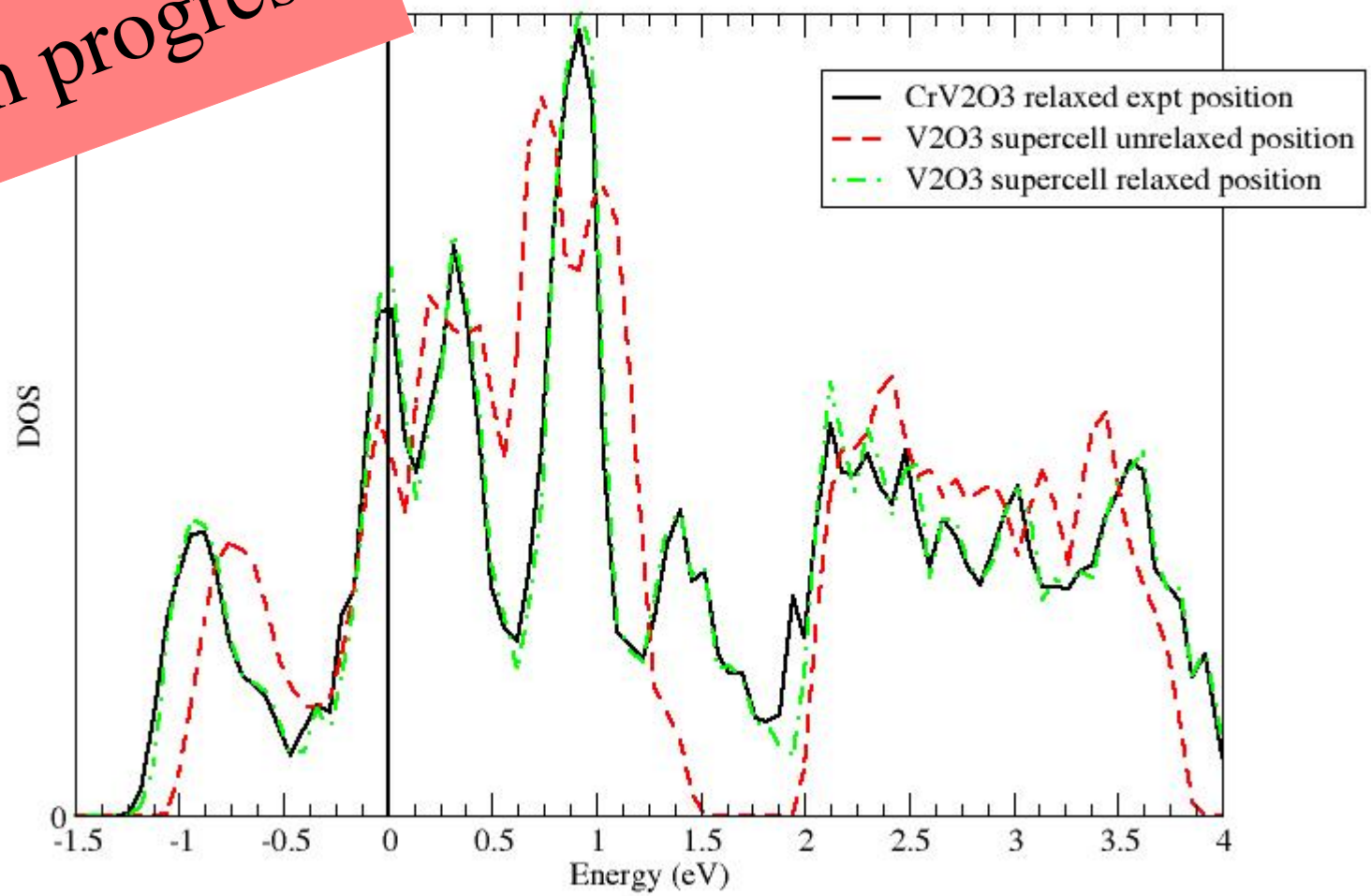
→ spectral functions beyond GW

→ defects, doping

V_2O_3

HF always large gap (12 eV) – scCOHSEX always metal

Work in progress!



PFlop:

→ doped material with advanced ground state calculation

→ spectral functions GW

→ beyond GW: better W

→ beyond GW: GWΓ, e.g. self-screening correction

Frontiers II: merge the 2 pictures:

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

$$\text{BSE } {}^4\chi = {}^4\chi_0 + {}^4\chi_0 [\, v + \delta\Sigma_{xc}/\delta G] \, {}^4\chi$$

(Waiting for PFlop....)

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

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

BSE $^4\chi = {}^4\chi_0 + {}^4\chi_0 [v + \delta\Sigma_{xc}/\delta G] {}^4\chi$

Introduce DF concept into MBPT

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

BSE $^4\chi = {}^4\chi_0 + {}^4\chi_0 [v + \delta\Sigma_{xc}/\delta G] \, {}^4\chi$

Introduce DF concept into MBPT

$\delta\Sigma_{xc}(1,2) / \delta G(3,4) \rightarrow \delta\Sigma_{xc}(1,2) / \delta\rho(3)$

This leads directly to equation for χ

Bruneval, Sottile, Olevano, Del Sole, Reining, PRL 94, 186402 (2005)

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

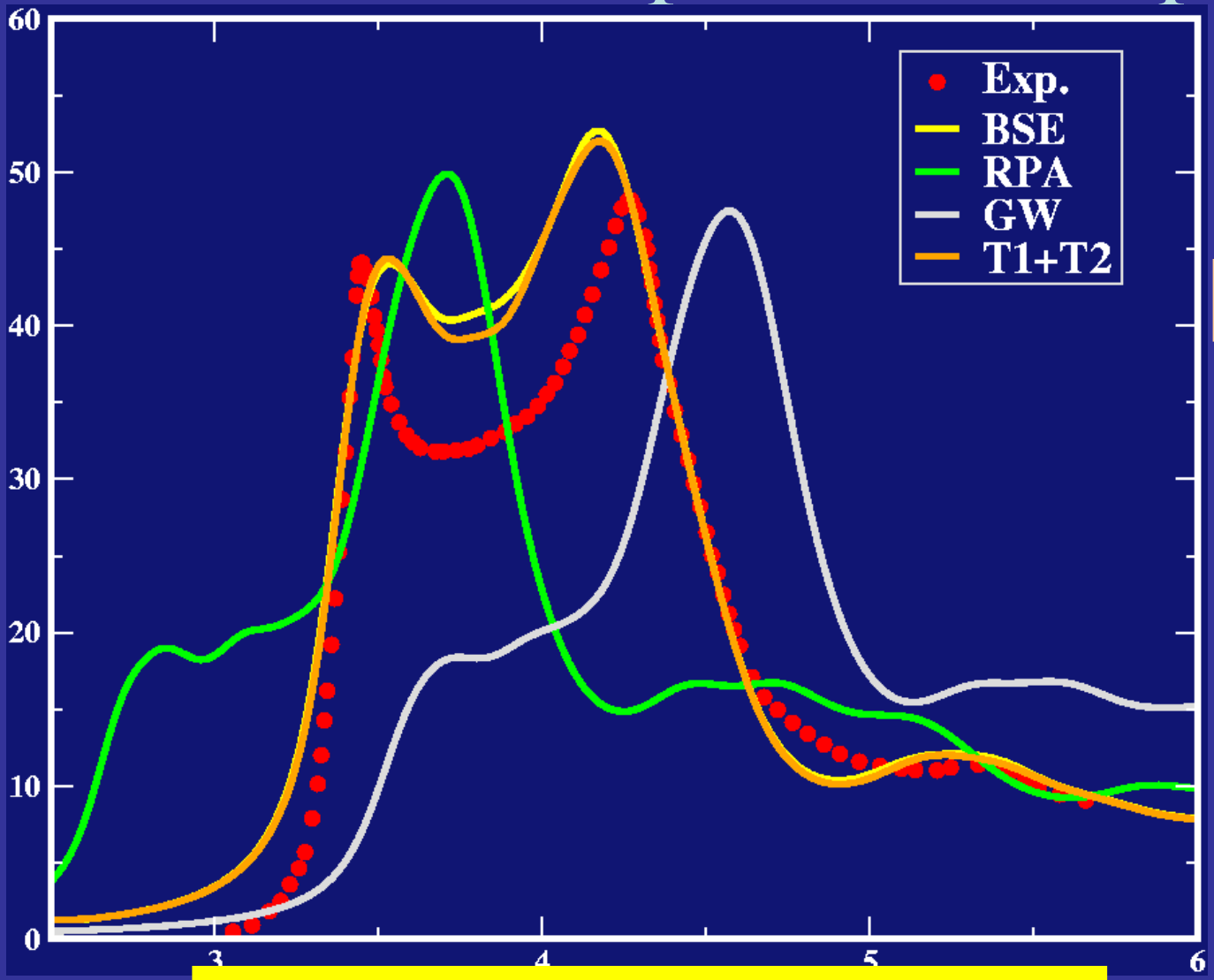
TDDFT $\chi = \chi_0 + \chi_0 [v + f_{xc}] \chi$

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

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

f_{xc} from BSE: ~ shift + $\chi_0^{-1}GGWGG\chi_0^{-1}$

Silicon: Optical Absorption



F. Sottile PhD thesis

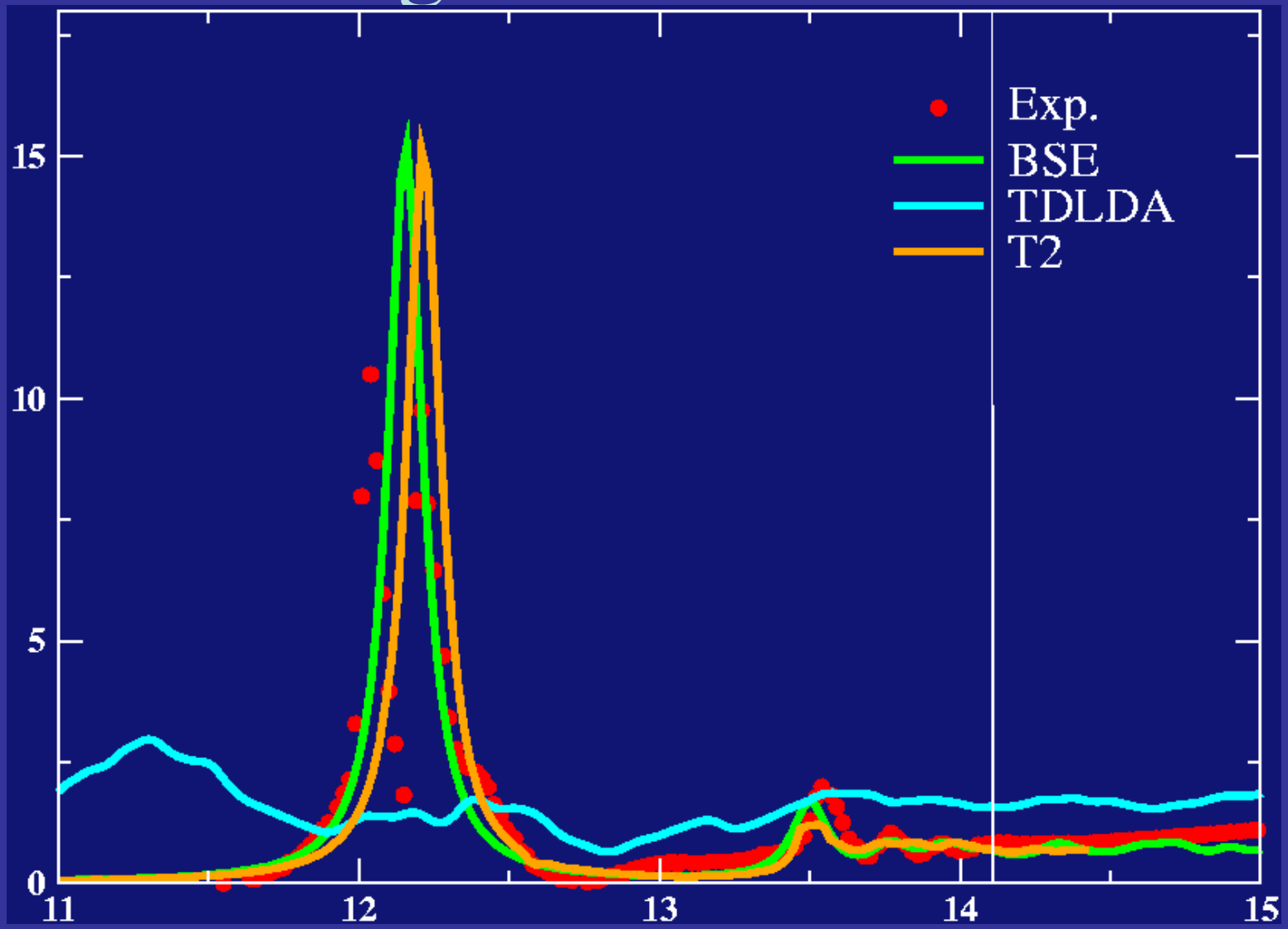
Hanke and Sham

Albrecht et al.

Benedict et al.

BSE and TDDFT: nice result

Solid Argon: Bound Excitons



- Francesco Sottile, PhD thesis (2003)

TDDFT including excitons:

Reining et al, PRL 88, 066404 (2002);
Sottile PhD thesis and Sottile et al, PRL 91, 056402 (2003)

Bruneval PhD thesis and
Bruneval, Sottile, Olevano, Del Sole, Reining, PRL (2005)

Adragna PhD thesis and Adragna et al,PRB 68, 165108 (2003),
Marini et al PRL 91, 256402 (2003)

Stubner, Tokatly, Pankratov, PRB 70, 245119 (2004)
and Ref. therein

von Barth, Dahlen, van Leeuwen, Stefanucci,
PRB 72, 235109 (2005)

Still:

- calculation of full spectral function delicate

+ long

- satellite masked by absence of vertex in Σ

(W screens classical charge)

Frontiers III: compromise?

$V_{xc}([\rho];r)\delta(r-r')$ → $\rho(r)$ *no spectrum, no gap*

$V_{xc}([\rho]; r,t)\delta(r-r')\delta(t-t')$ → $\rho(r,t)$ *spectrum, optical gap*

$\Sigma(r,r',t,t')$ → $G(r,r',t,t')$ *QP gap, ARPES, propagation,…*

Gatti, Olevano, Reining, Tokatly, submitted (2007)

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→ $Im[G(r,r,\omega)]$ *QP gap, XPS*

Gatti, Olevano, Reining, Tokatly, submitted (2007)

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$\Sigma(r,r',t,t')$ → $G(r,r',t,t')$ *QP gap, ARPES, propagation,…*

$V_{SF}(r,\omega)$

→ $Im[G(r,r,\omega)]$ *QP gap, XPS*

$V_{SF}(r,\omega)$ *is real and local in space*

Gatti, Olevano, Reining, Tokatly, Phys. Rev. Lett. ***99****, 057401 (2007)*

6) Summary

δV makes.....

* crystal local field effects
* anomalous angular dependence of IXS spectra
* excitons
* satellites
*.....

Most profitable to take different points of view !!!!

6) Summary

We need.....

* crystal local field effects
* anomalous angular dependence of IXS spectra
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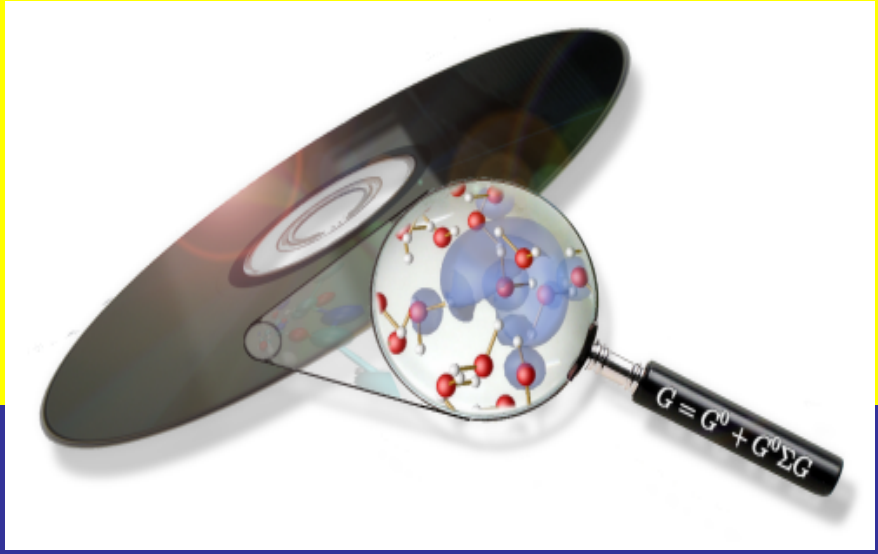
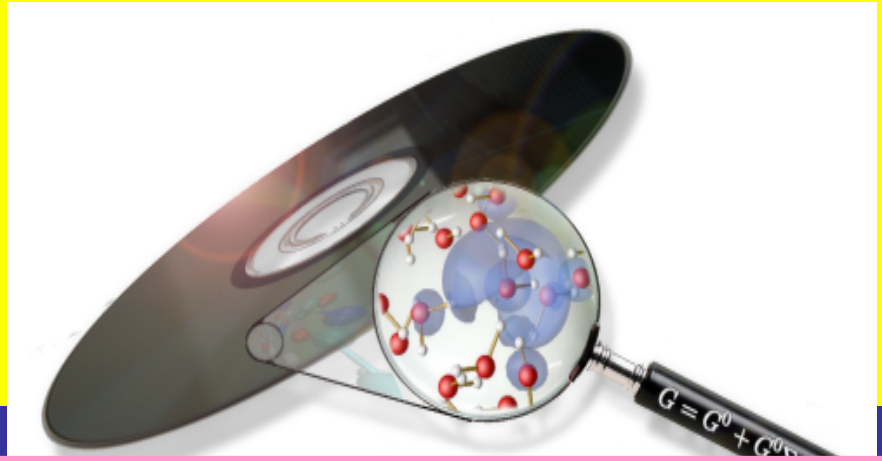
* satellites
*.....



6) Summary

We need.....

* crystal local field effects
* anomalous angular dependence of IXS spectra
* excitons
* satellites
*.....



More thoughts and more computers !!!!

Ab initio calculations of electronic response: ingredients, results and challenges

http://www.etsf.eu
http://etsf.polytechnique.fr

Experimentalists

Nanoquanta Network of Excellence

ETSF European Theoretical Spectroscopy Facility

http://www.etsf.eu