
SPRING COLLEGE ON SCIENCE AT THE NANOSCALE
(24 May - 11 June 2004)

TDDFT THEORY:

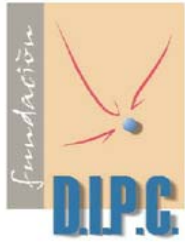
APPLICATIONS TO NANO AND BIO-STRUCTURES

Optical Properties of Nanostructures:
Extended systems: problems and new developments

A. RUBIO

Dept. de Fisica de Materiales, Univ. del Pais Vasco and Centro Mixto
CSIC-UPV/EHU, Donostia, San Sebastian, Spain

These are preliminary lecture notes, intended only for distribution to participants.



Optical properties of nanostructures

Angel Rubio

*Dpto. de Física de Materiales, Universidad del País Vasco, Donostia International Physics Center (DIPC),
and Centro Mixto CSIC-UPV/EHU, Donostia, Spain*

<http://dipc.ehu.es/arubio> E-mail: arubio@sc.ehu.es

I. Motivation. Basic concepts. Foundations TDDFT.

II. Illustration of the physics for nano- and bio structures

III. Extended systems: problems and new developments



ICTP Spring College on Science at the Nanoscale, Trieste May 24th -June 11th 2004

Optical properties of nanostructures

III. Extended systems: problems and new developments

Introduction:

how to handle the electron dynamics in extended systems under the influence of an external electromagnetic field?

TDDFT:

- Problems with standard exchange-correlation functionals*
- A new fxc derived from Many-body perturbation theory
proper description of excitonic effects!!!*
- Applications to polyacetylene as one-dimensional system*

G. Onida, L. Reining and AR, Rev. Mod. Phys. 74, 601 (2002)

ICTP Spring College on Science at the Nanoscale, Trieste May 24th -June 11th 2004

Time-dependent approach for extended systems: a gauge formalism

G.F. Bertsch, J.I. Iwata, AR, K. Yabana, PRB62, 7998 (2000)

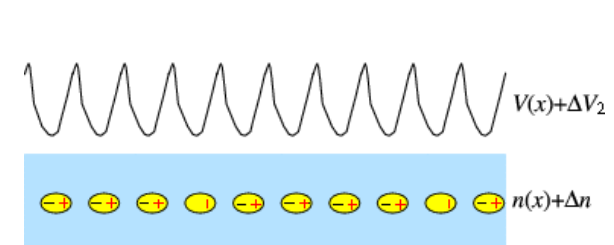
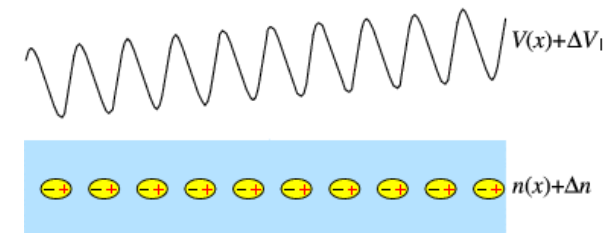
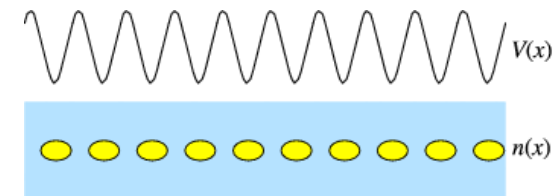
The Lagrangian of a periodic system in a volume V under a uniform field is

$$L = \sum_i \langle \psi_i | i \hbar \frac{\partial}{\partial t} - \frac{1}{2m} \left(\vec{p} + \frac{e}{c} \vec{A} \right)^2 - V_{ion} | \psi_i \rangle - E_{Hartree} - E_{xc} + \frac{V}{8\pi c^2} \left(\frac{d\vec{A}}{dt} \right)^2$$

The equation of motion are:

$$i \hbar \frac{\partial}{\partial t} \psi_i = \left[\frac{1}{2m} \left(\vec{p} + \frac{e}{c} \vec{A} \right)^2 + V_{ion} + V_H + V_{xc} \right] \psi_i$$

$$\frac{d^2 \vec{A}}{dt^2} = -4\pi e^2 \frac{n}{m} \vec{A} - 4\pi c \frac{e}{V} \sum_i \langle \psi_i | \frac{\vec{p}}{m} | \psi_i \rangle$$

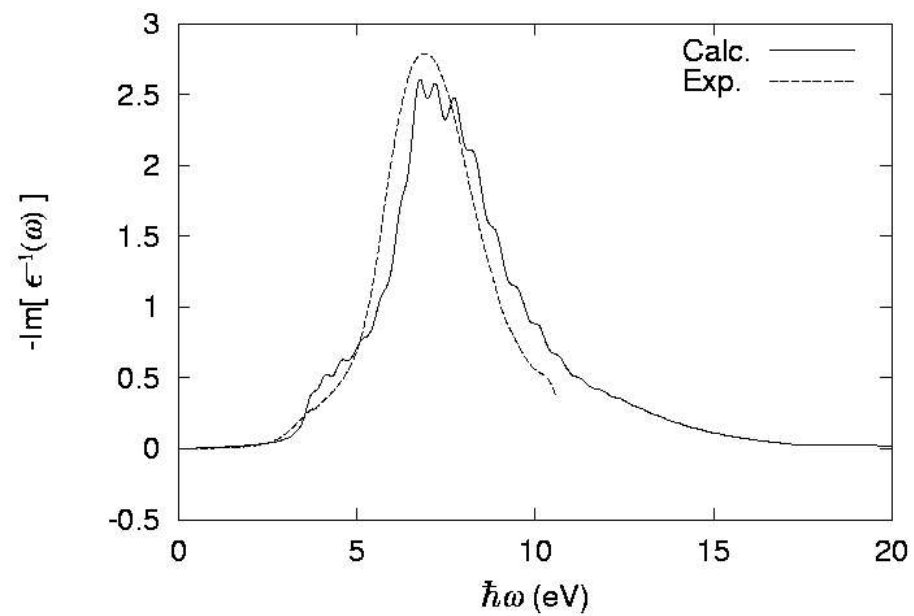
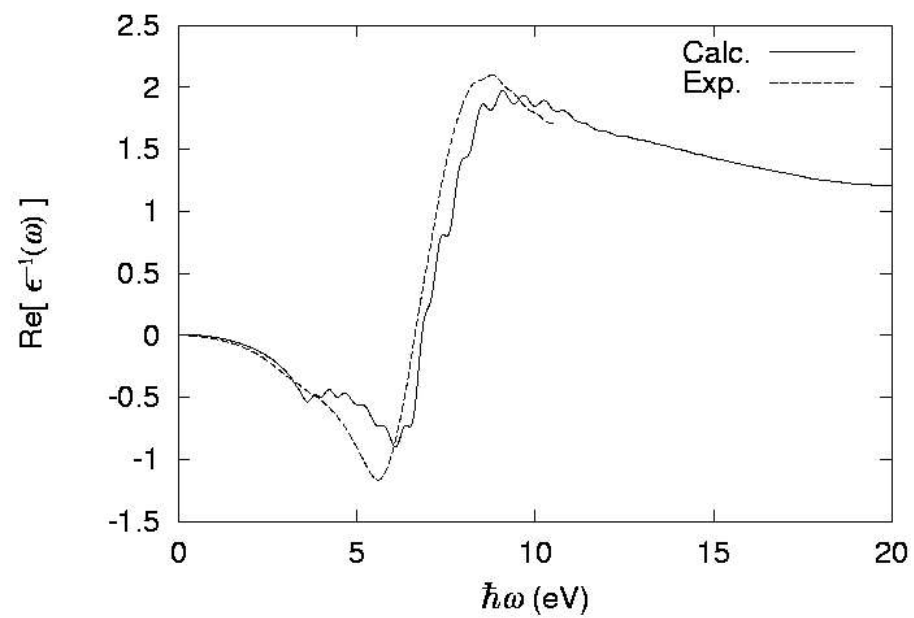


For the electric field is:

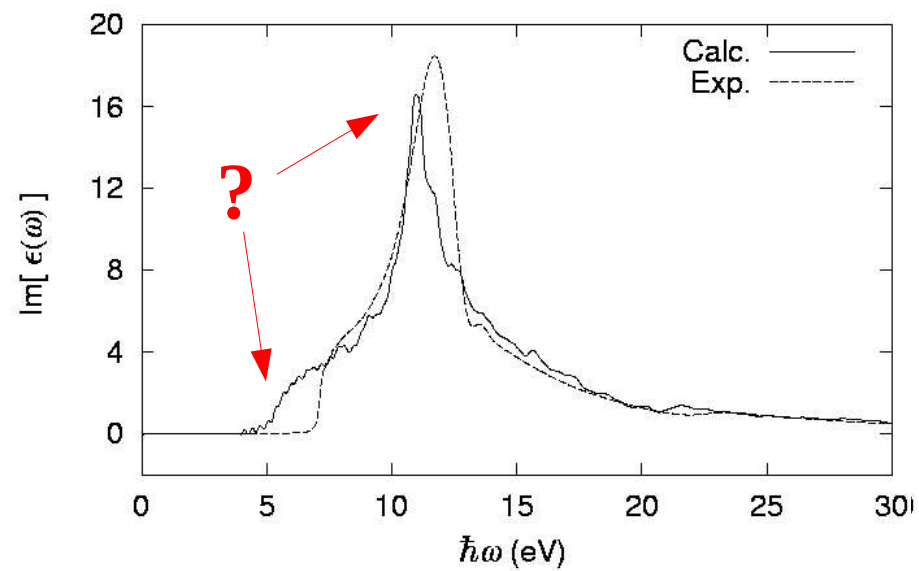
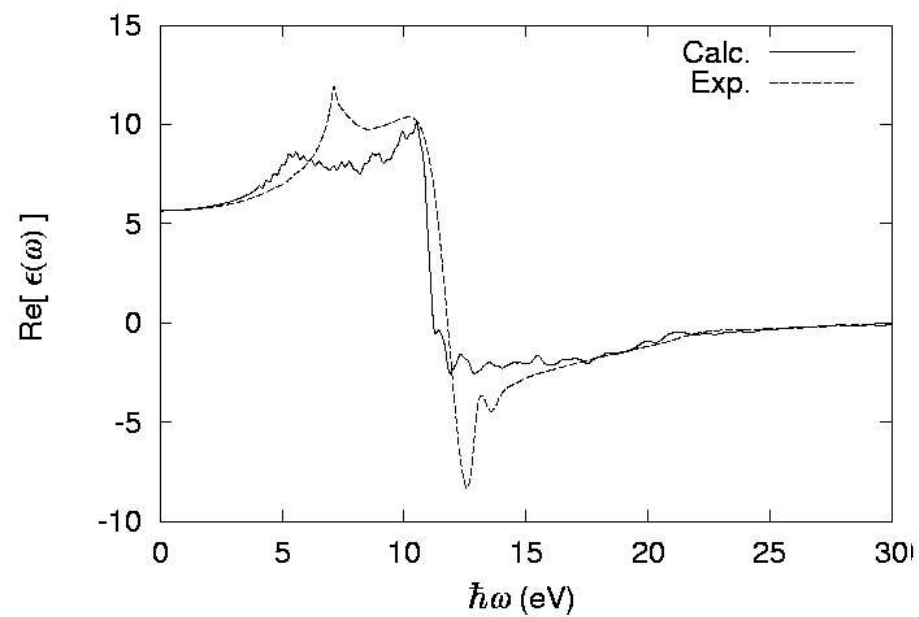
$$\vec{E}(t) = \frac{-1}{c} \frac{d\vec{A}}{dt}$$

$$\frac{d\vec{E}}{dt} = -4\pi \vec{j} \quad \text{and} \quad \vec{j} = \frac{-e}{V} \sum_i \langle \psi_i | \frac{\vec{p}}{m} | \psi_i \rangle - \frac{e^2}{c} n \vec{A}$$

Lithium

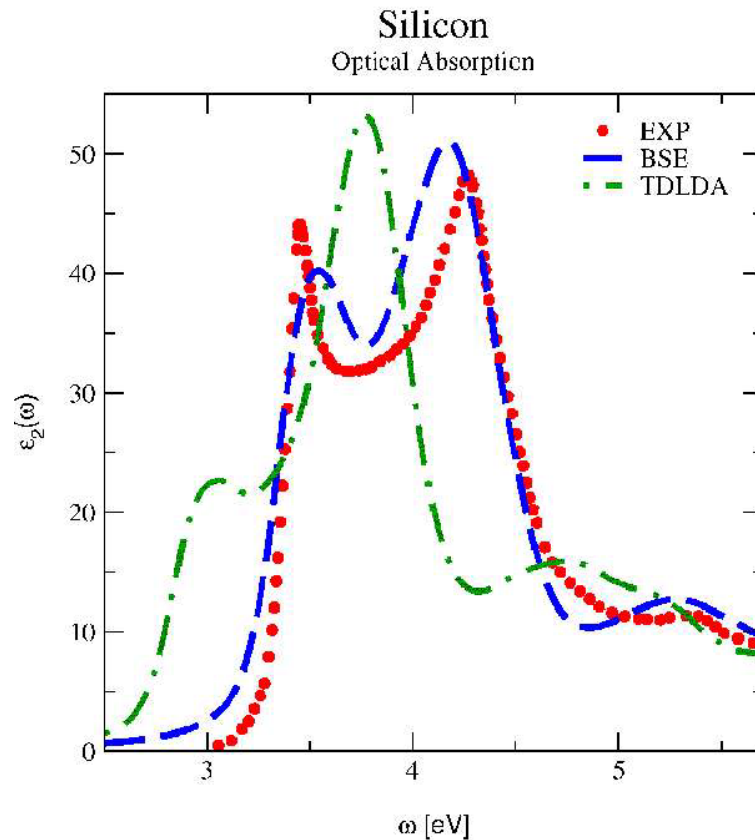


Diamond



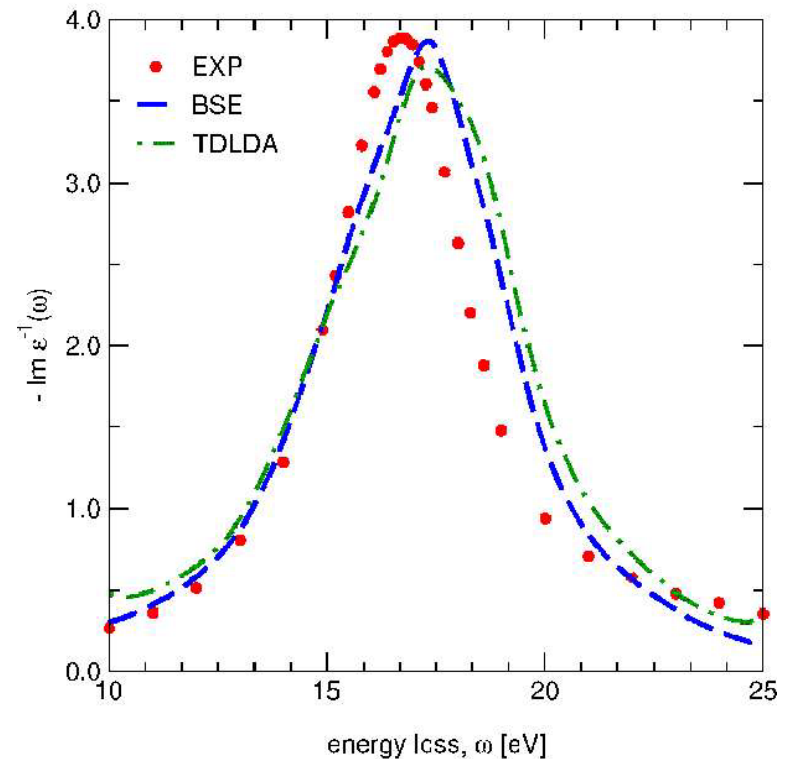
Non-local fxc for extended systems:

Motivation



The LDA Kernel is not able to reproduce Optical Properties in Solids

BSE vs TDLDA comparison on EEL



The LDA Kernel already offers a good representation of the Electron Energy Loss (EEL) spectrum in Solids

See for a review: G. Onida, L. Reining and AR, *Rev. Mod. Phys.* **74**, 601 (2002)

Why a non-local (static?) f_{xc} for extended systems:

- In the **EEL** spectra f_{xc} is added to the full coulomb that **already contains** a long range contribution

$$f_{xc} = -\alpha(\omega)/q^2$$

$$EEL \propto \epsilon^{-1}(\omega) = 1 + v\chi$$

$$\chi(\omega) = \chi_0(\omega) + \chi_0(\omega)(v + f_{xc}(\omega))\chi(\omega)$$

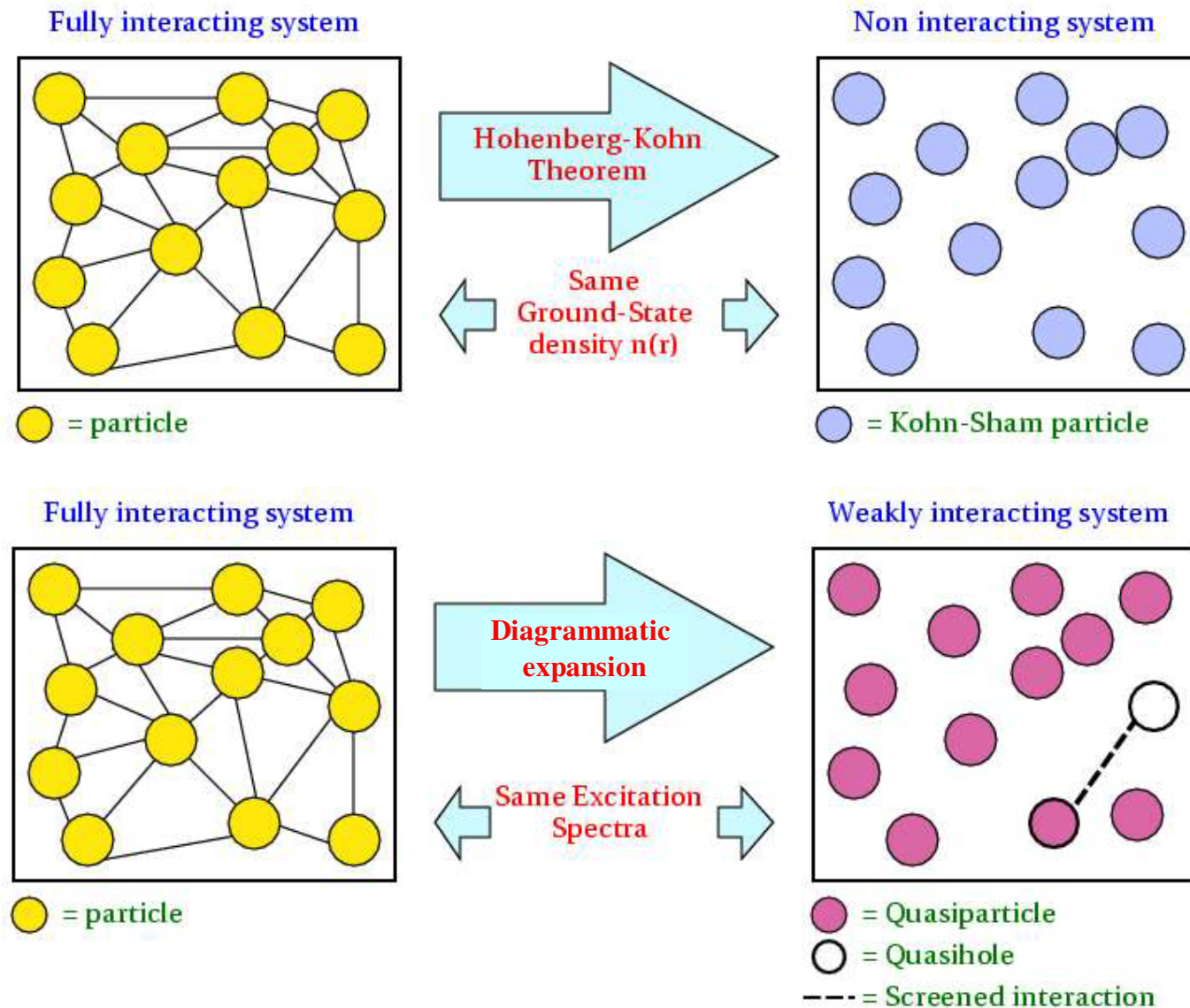
- In the **absorption** spectra f_{xc} is added to the full coulomb that **does not contains** the long range contribution ($q=0$)

$$\epsilon_M(\omega) = 1 - v\bar{\chi} \quad \epsilon_M^{RPA} \equiv 1/[1 - v\chi_0]_{G=G'=0}$$

$$\bar{\chi}(\omega) = \chi_0^{GW}(\omega) + \chi_0^{GW}(\omega)(\bar{v} + f_{xc}(\omega))\bar{\chi}(\omega)$$

The lack of a long range term in f_{xc}^{LDA} is relatively weightless in the EEL but is crucial in the absorption spectra!!!

Density Functional versus Many-body perturbation theory



Band-gap problem!!!!

Density Functional Theory and Many-Body Perturbation Theory

$$\left[-\frac{\nabla^2}{2} + V_{ext}(\mathbf{r}) + V_{Hartree}([n], \mathbf{r}) + V_{xc}([n], \mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

R. O. Jones and O. Gunnarsson, Rev. Mod. Phys. **61**, 689 (1989)

$$V_{xc}([n], \mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} \quad E_{xc}^{LDA}[n] = \int d\mathbf{r} n(\mathbf{r}) \epsilon_{xc}^{hom}([n]; \mathbf{r})$$

Density Functional Theory

Exchange-correlation Potential: Real, Local in space, Frequency independent

Self-Energy: Complex, Non-local in space, Frequency dependent

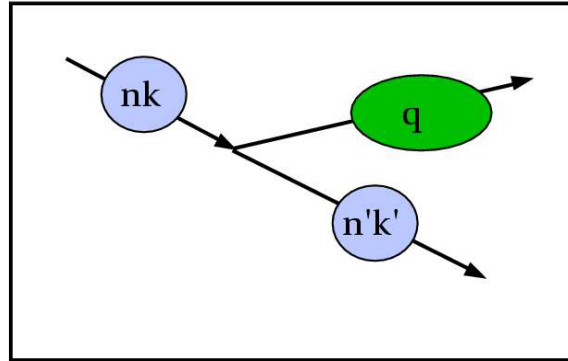
Many-Body Perturbation Theory

$$[\mathcal{H}_{KS} - V_{xc}(\mathbf{r})](\mathbf{r}) \phi_i(\mathbf{r}; E_\lambda) + \int d\mathbf{r}' \Sigma(\mathbf{r}, \mathbf{r}'; E_\lambda) \phi_i(\mathbf{r}'; E_\lambda) = E_\lambda(\omega) \phi_\lambda(\mathbf{r}, E_\lambda)$$

G. Onida, L. Reining and AR, Rev. Mod. Phys. **74**, 601 (2002)

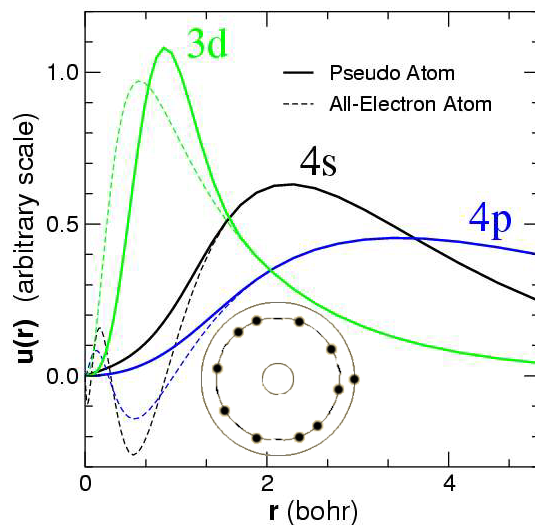
F. Aryasetiawan, Rep. Prog. Phys. **61**, 237-312 (1998)

The self-energy physics

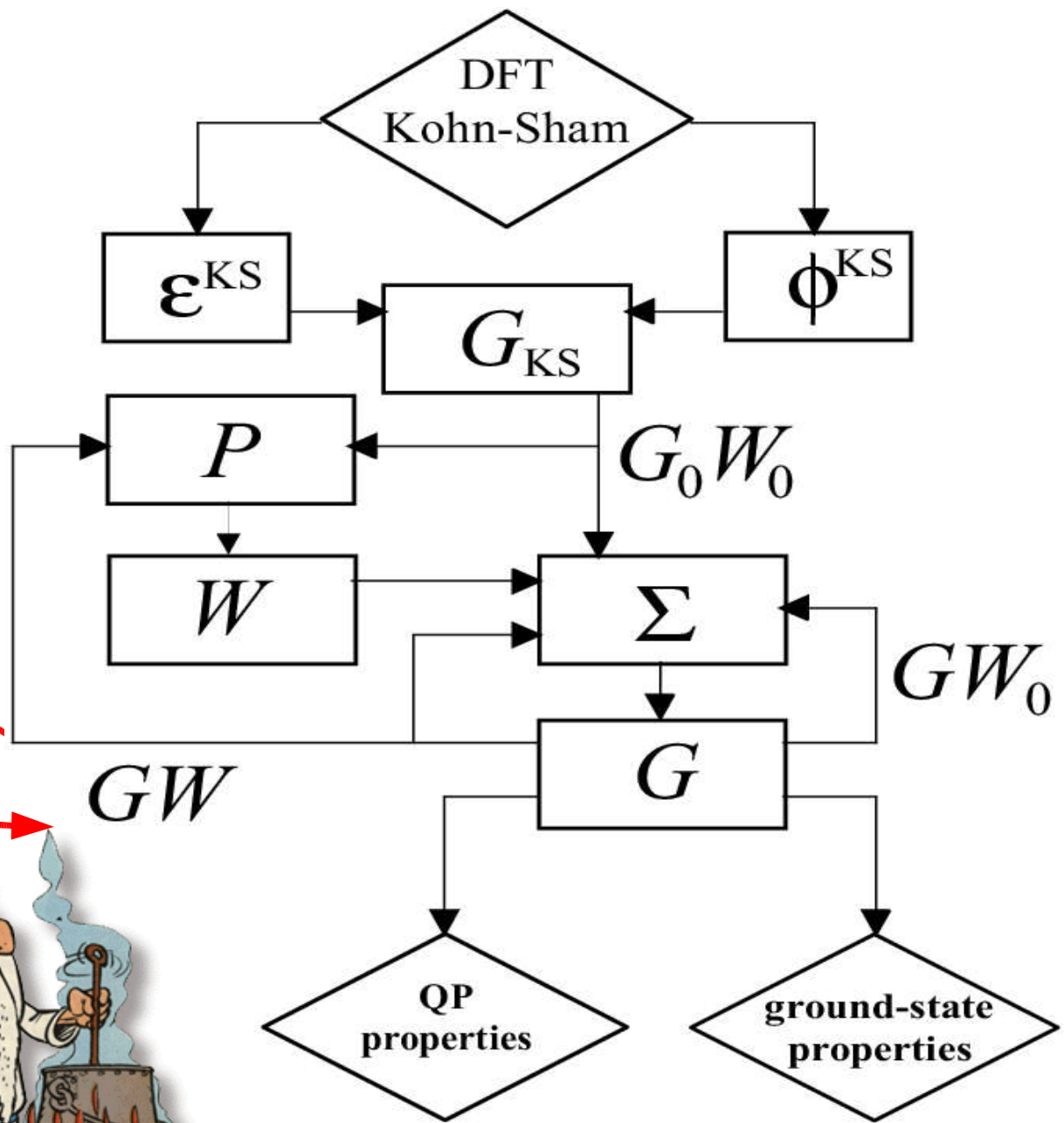


= Kohn-Sham states
 = Plasmons/Electron-hole states

The pseudopotential approach



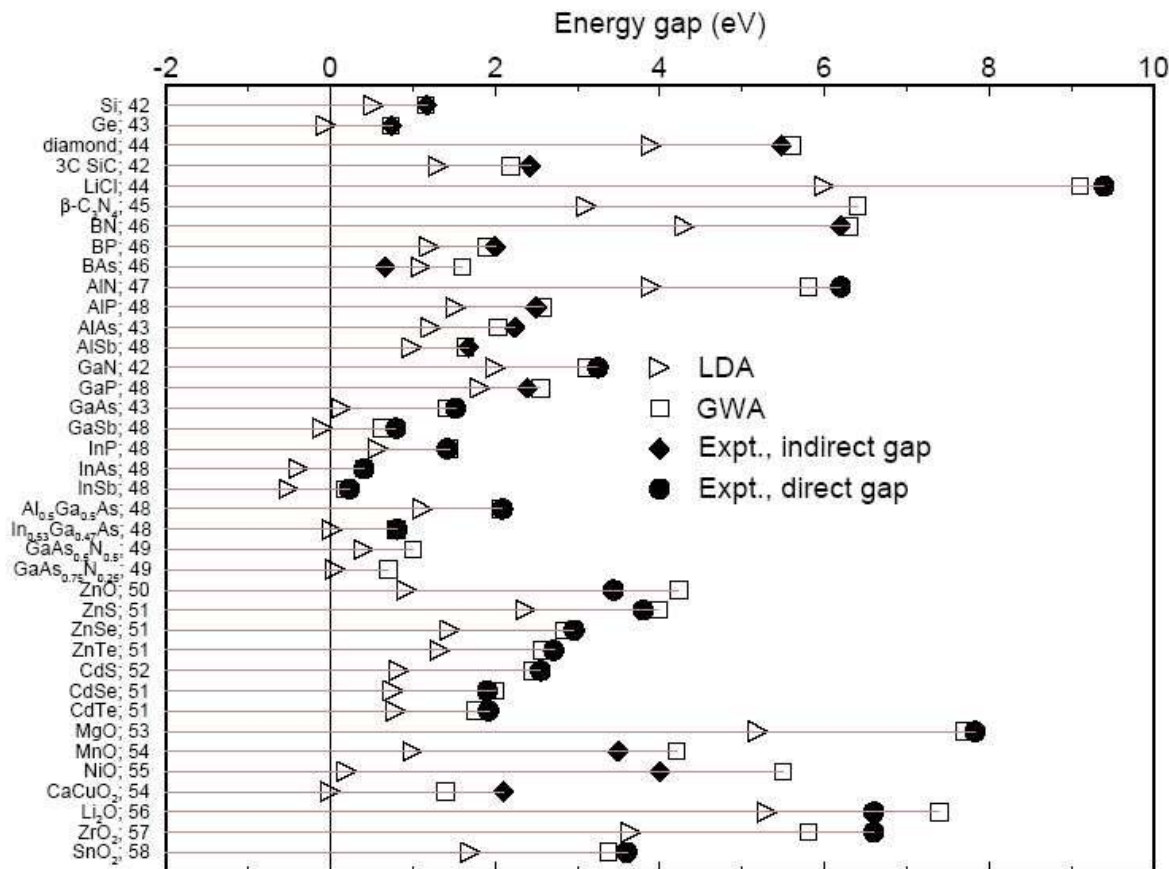
The GW "soup"



$$P(12) = -iG(12)G(21^+)$$

$$\Sigma(12) = iG(12^+)W(12)$$

G_0W_0 Band Structures of Insulators



$$E_n^{QP} \simeq \epsilon_n^{KS} + \langle \psi_n | \sum (\epsilon_n^{KS}) - v_{xc} | \psi_n \rangle$$

From "Quasiparticle calculations in solids", W.G. Aulbur, L. Jönsson and J.W. Wilkins, *Solid State Physics* 54 1 (2000),

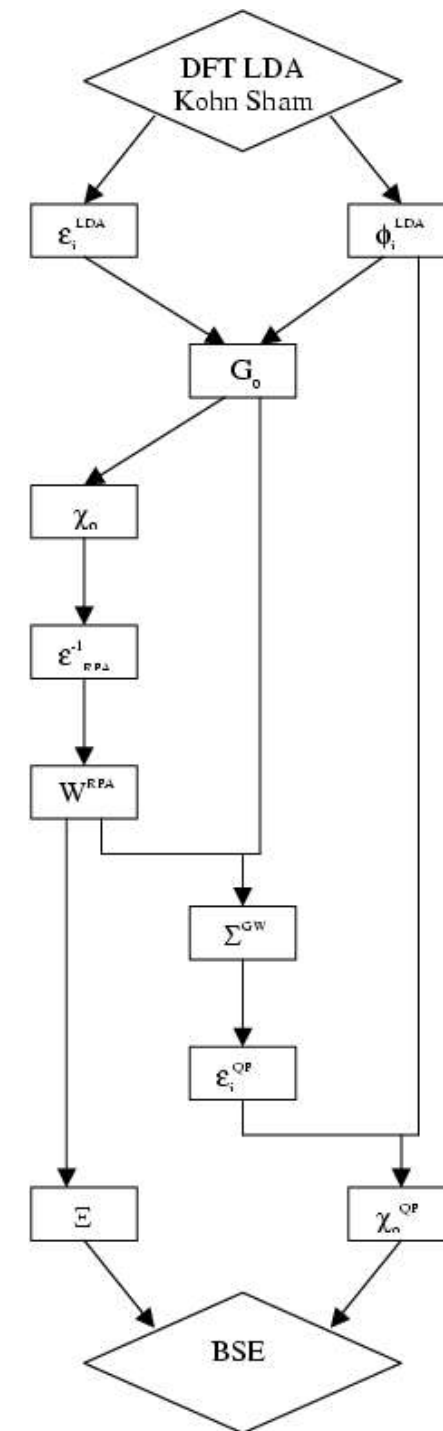
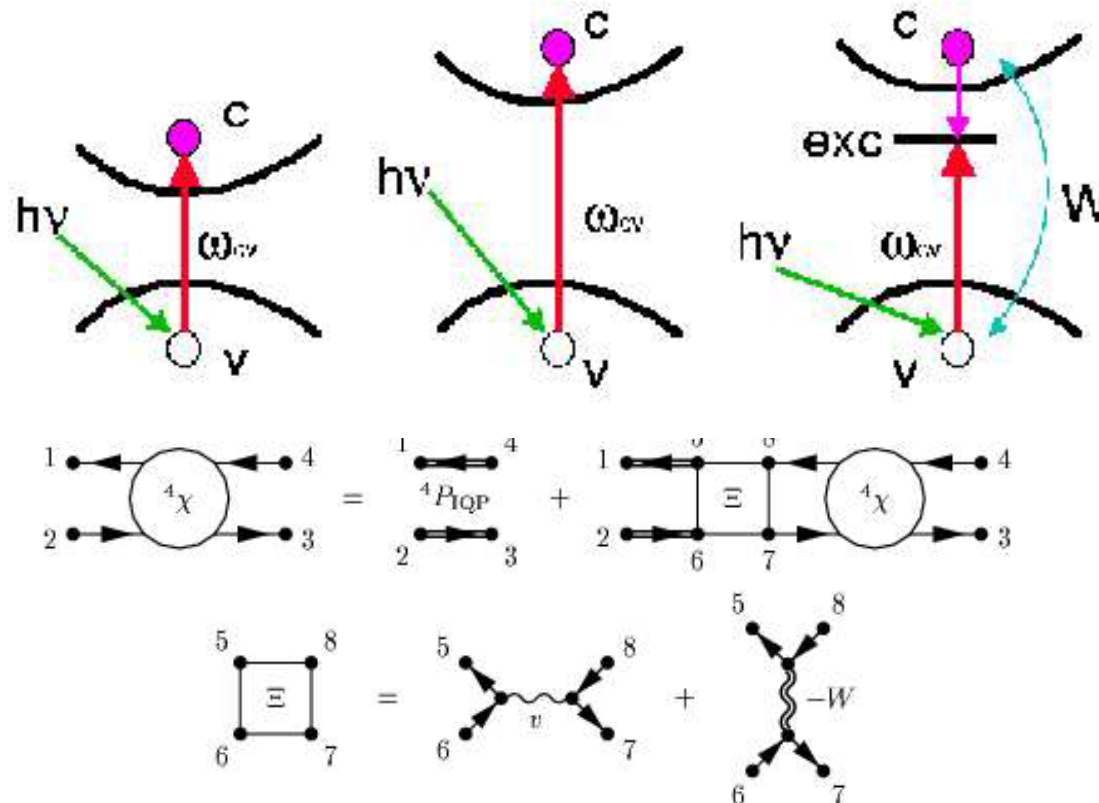
also available in preprint form at <http://www.physics.ohio-state.edu/~wilkins/vita/publications.html#reviews>

Bethe-Salpeter equation: excitonic effects

$$\Sigma = iG_0 W_0; W_0 = \epsilon_{RPA}^{-1} V$$

$$\epsilon_{RPA} = 1 - v_c \chi^{(0)}$$

$$\chi^{(0)}(r, r', \omega) = 2 \sum_{i \neq j} (f_i - f_j) \frac{\phi_i(r) \phi_j(r) \phi_i^*(r') \phi_j(r')}{\epsilon_i - \epsilon_j - \omega - i\eta}$$



TDDFT ...

$$t \left(\tilde{P}_{\mathbf{G}_1 \mathbf{G}_2}(t) \right) = \tilde{P}^0_{\mathbf{G}_1, \mathbf{G}_2}(t) + \tilde{P}^0_{\mathbf{G}_1, \mathbf{G}_3}(t - t_1) f^{xc}_{\mathbf{G}_3, \mathbf{G}_4}(t_1 - t_2) \tilde{P}_{\mathbf{G}_4 \mathbf{G}_2}(t_2)$$

$$\iint d\mathbf{r}_2 d\mathbf{r}_3 \chi_s(\mathbf{r}_1, \mathbf{r}_2; \omega) \left[\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + f^{xc}(\mathbf{r}_2, \mathbf{r}_3; \omega) \right] \xi(\mathbf{r}_3; \omega) = \lambda(\omega) \xi(\mathbf{r}_1; \omega) \quad \lambda(E_\lambda) = 1$$

$$t \left(\tilde{L}_{\mathbf{K}_1 \mathbf{K}_2}(t) \right) = \tilde{L}^0_{\mathbf{K}_1}(t) \delta_{\mathbf{K}_1 \mathbf{K}_2} + \sum_{\mathbf{K}_3} i \int dt_1 \left(\text{wavy line} \right) \tilde{L}_{\mathbf{K}_3 \mathbf{K}_2}(t_1) \quad \mathbf{K}_1 \equiv \{c_1, v_1, \mathbf{k}_1\}$$

$$\tilde{P}_{\mathbf{G}_1, \mathbf{G}_2}(\omega) \propto \sum_{\mathbf{K}_1, \mathbf{K}_2} \Phi_{\mathbf{K}_1}^*(\mathbf{G}_1) L_{\mathbf{K}_1, \mathbf{K}_2}(\omega) \Phi_{\mathbf{K}_2}(\mathbf{G}_2) \quad \Phi_{\mathbf{K}_1}(\mathbf{G}_1) = \langle c_1 \mathbf{k}_1 | e^{\mathbf{G}_1 \cdot \mathbf{r}} | v_1 \mathbf{k}_1 \rangle$$

$$\tilde{P}_{\mathbf{G}_1, \mathbf{G}_2}(\omega) \propto \sum_{\lambda} \frac{\Phi_{\lambda}^*(\mathbf{G}_1) \Phi_{\lambda}(\mathbf{G}_2)}{\omega - E_{\lambda}} \quad \mathbf{H}|\lambda\rangle = E_{\lambda}|\lambda\rangle \quad H_{\mathbf{K}_1, \mathbf{K}_2} = (\epsilon_{c_1 \mathbf{k}_1} - \epsilon_{v_1 \mathbf{k}_1}) \delta_{\mathbf{K}_1, \mathbf{K}_2} + iW_{\mathbf{K}_1, \mathbf{K}_2}$$

... and Many-Body Perturbation Theory

Many-Body approach to the Exchange-Correlation Kernel of TDDFT

A diagrammatic approach

Hypothesis

It exists a "many-body xc-kernel" such that
the TDDFT and Many-Body polarization
functions are identical

*Consequently TDDFT equation can be used as an equation for the xc-kernel
and as a formal solution can be found in terms of an iterative equation for
the n th order contribution*

Many-Body approach to the Exchange-Correlation Kernel of TDDFT

TDDFT

$$\tilde{\mathbf{P}}(\mathbf{q}, \omega) = \mathbf{P}^{(0)}(\mathbf{q}, \omega) + \mathbf{P}^{(0)}(\mathbf{q}, \omega) \mathbf{f}_{xc}(\mathbf{q}, \omega) \tilde{\mathbf{P}}(\mathbf{q}, \omega)$$

$$\tilde{P}_{\mathbf{G}_1, \mathbf{G}_2}(\mathbf{q}, \omega) = \text{const.} \sum_{\mathbf{K}_1, \mathbf{K}_2} \Phi_{\mathbf{K}_1}^*(\mathbf{q}, \mathbf{G}_1) \tilde{S}_{\mathbf{K}_1, \mathbf{K}_2}(\mathbf{q}, \omega) \Phi_{\mathbf{K}_2}(\mathbf{q}, \mathbf{G}_2)$$

MBPT

$$\tilde{\mathbf{S}}(\mathbf{q}, \omega) = \mathbf{S}^{(0)}(\mathbf{q}, \omega) + \mathbf{S}^{(0)}(\mathbf{q}, \omega) \mathbf{W}(\mathbf{q}) \tilde{\mathbf{S}}(\mathbf{q}, \omega)$$

$$\Phi_{\mathbf{K}}(\mathbf{q}, \mathbf{G}) = \langle c\mathbf{k} | e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} | v\mathbf{k} - \mathbf{q} \rangle \quad \mathbf{K} := (c v \mathbf{k})$$

Bethe-Salpeter Equation

$$\mathbf{f}_{xc}^{(n)}(\mathbf{q}, \omega) = \frac{1}{\mathbf{P}^{(0)}(\mathbf{q}, \omega)} \left[\delta \tilde{\mathbf{P}}^{(n)}(\mathbf{q}, \omega) \left(\mathbf{P}^{(0)}(\mathbf{q}, \omega) \right)^{-1} - \sum_{m=1, n-1} (-1)^m \delta \tilde{\mathbf{P}}^{(m)}(\mathbf{q}, \omega) \mathbf{f}_{xc}^{(n-m)}(\mathbf{q}, \omega) \right]$$

$$\mathbf{f}_{xc}(\mathbf{q}, \omega) = \sum_n \mathbf{f}_{xc}^{(n)}(\mathbf{q}, \omega) \quad \mathbf{f}_{xc}^{(0)}(\mathbf{q}, \omega) = 0$$

Iterative equation for $\mathbf{f}_{xc}$

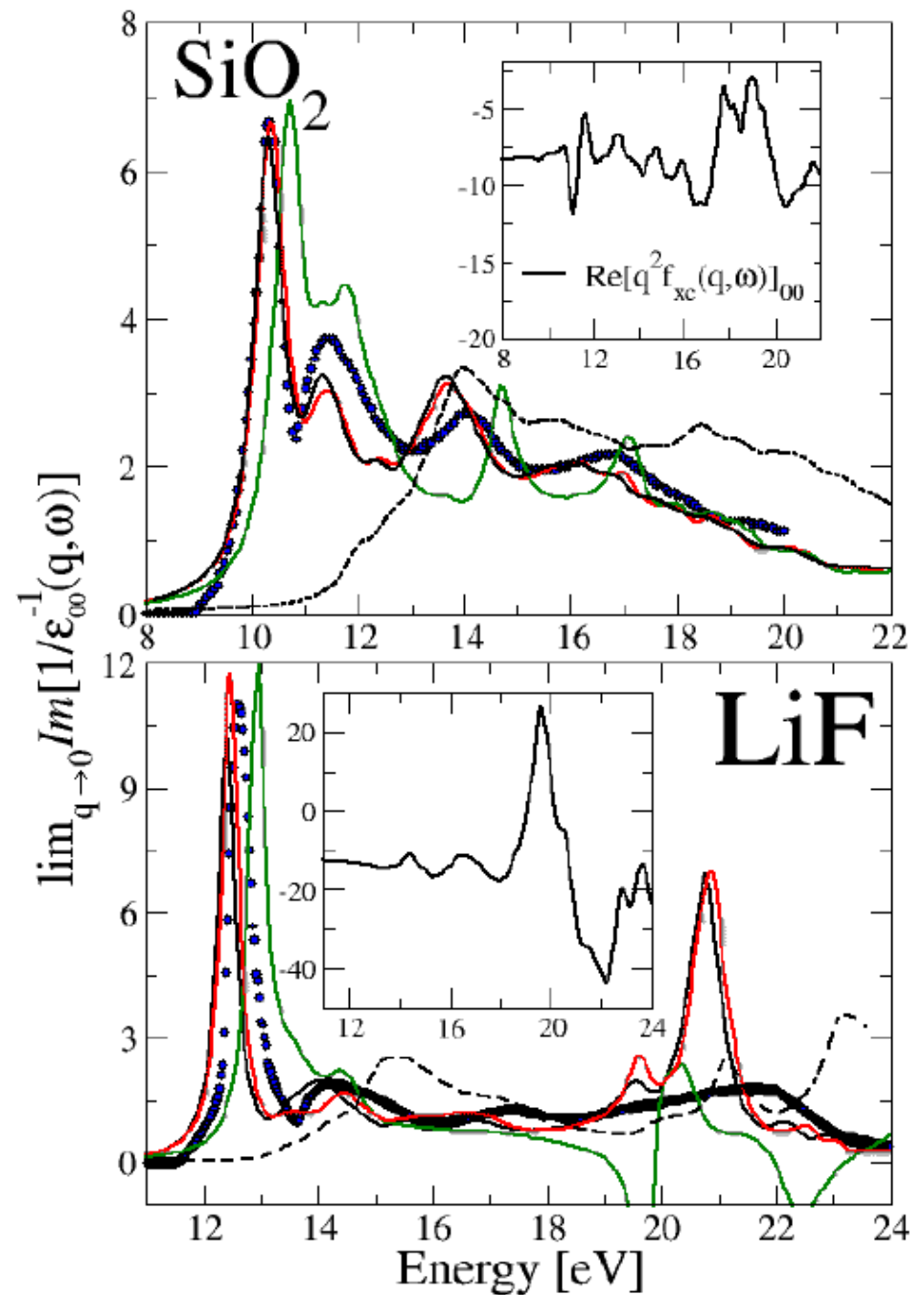
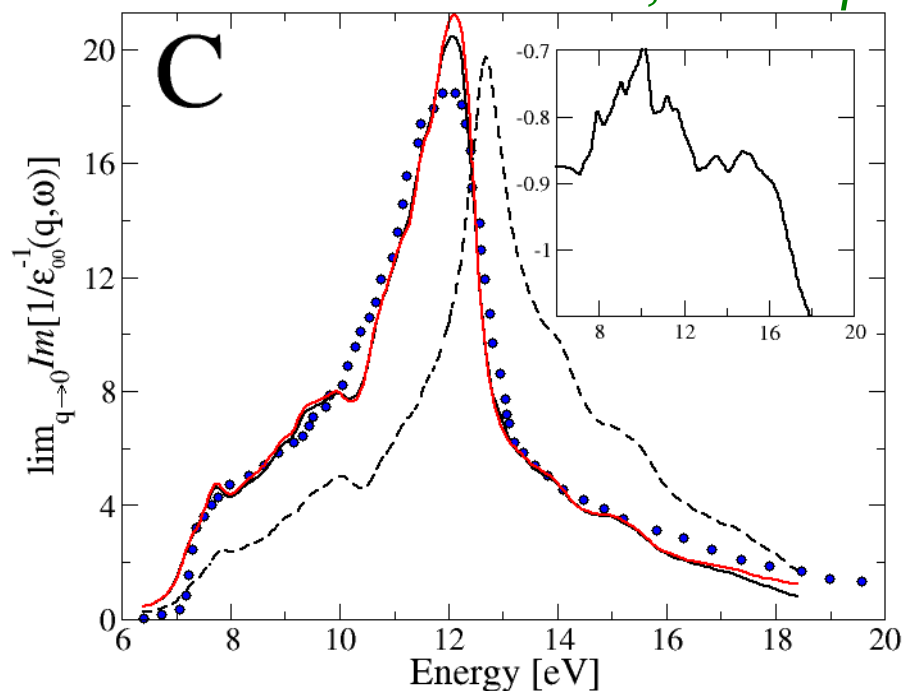
A. Marini, R. Del Sole and AR, PRL (2003)

Bound excitons in TDDFT

$$f_{xc}^{(1)}(\mathbf{q}, \omega) = \text{diagram}$$

$$\text{diagram} := [\mathbf{P}^{(0)}(\omega)]^{-1}$$

— *TDDFT* ●●● *Experiment*
— *BSE* — *TDDFT, scalar f_{xc}*



A. Marini, R. Del Sole and AR, PRL (2003)

How many terms ?

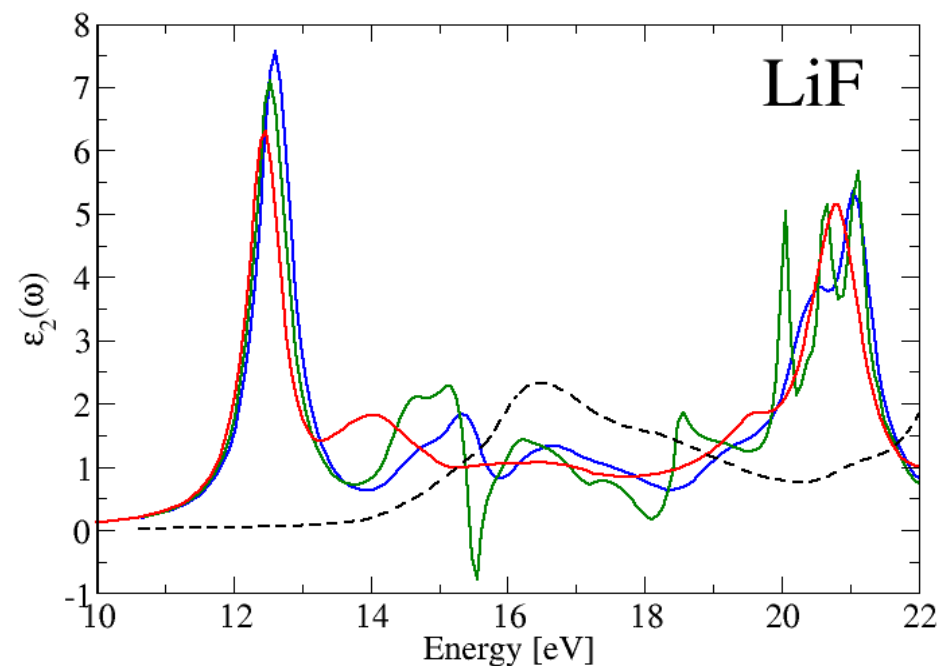
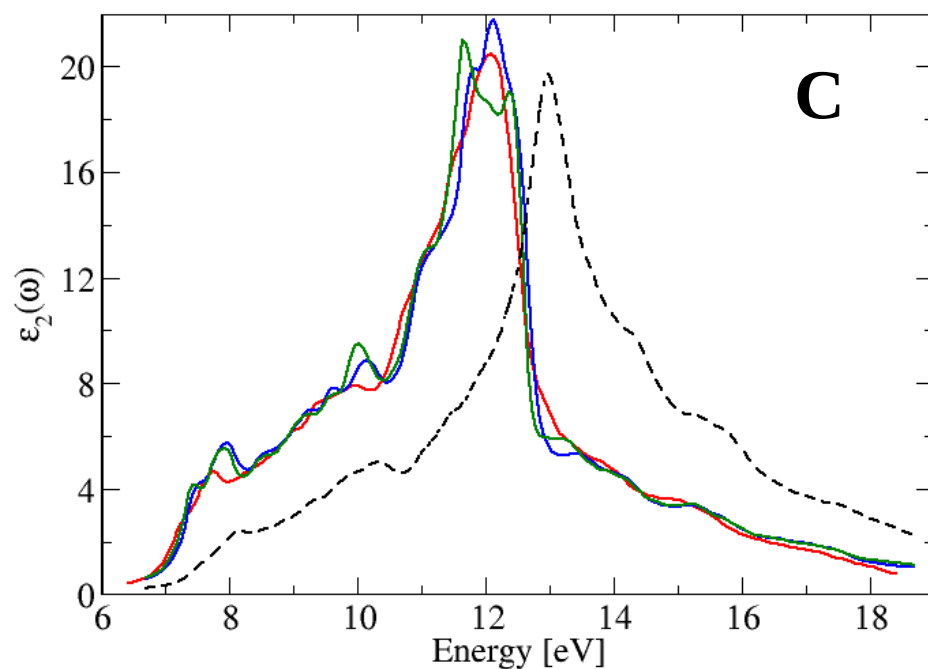
$$\mathbf{f}_{xc}^{(1)}(\mathbf{q}, \omega) = \text{diagram}$$

$$\mathbf{f}_{xc}^{(2)}(\mathbf{q}, \omega) = \text{diagram} - \text{diagram}$$

$$\mathbf{f}_{xc}^{(3)}(\mathbf{q}, \omega) = \text{diagram} + \text{diagram} - 2 \text{diagram}$$

$$\text{wavy line} := [\mathbf{P}^{(0)}(\omega)]^{-1}$$

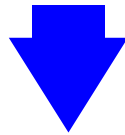
— *BSE* - - - *QP-RPA*



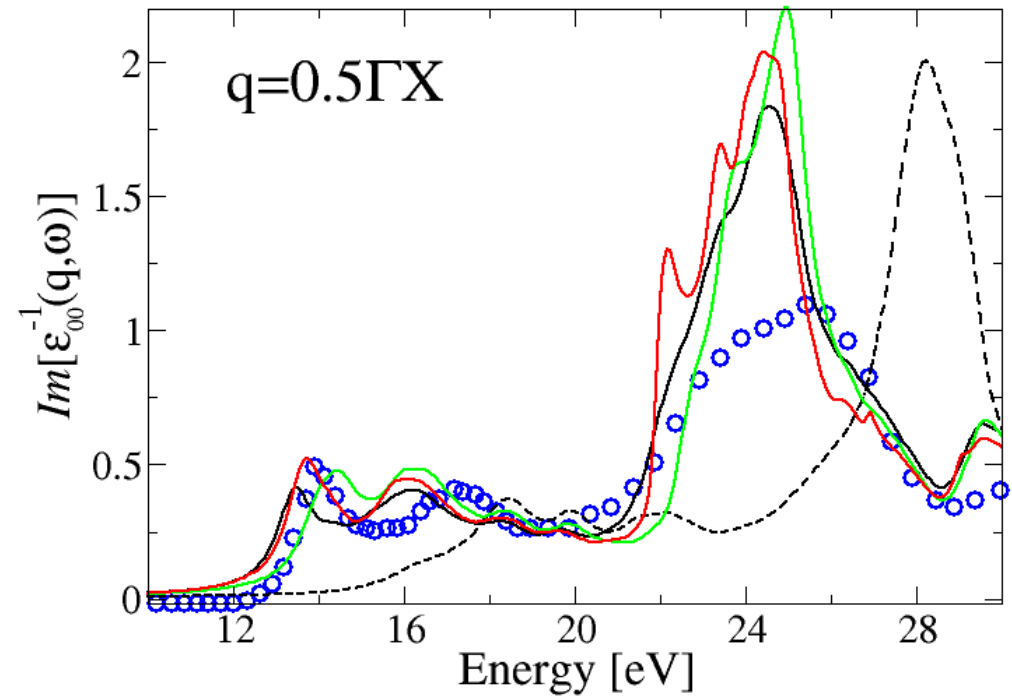
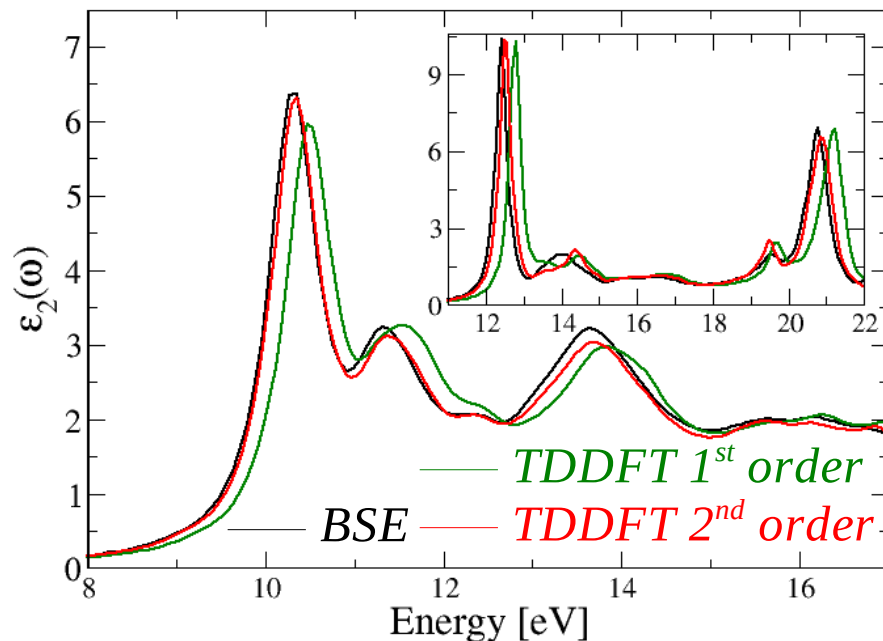
A many-body causal TDDFT kernel

$$\mathbf{f}_{xc}^{(n)}(\mathbf{q}, \omega) = \frac{1}{\mathbf{P}^{(0)}(\mathbf{q}, \omega)} \left[\delta \tilde{\mathbf{P}}^{(n)}(\mathbf{q}, \omega) \left(\mathbf{P}^{(0)}(\mathbf{q}, \omega) \right)^{-1} - \sum_{m=1, n-1} (-1)^m \delta \tilde{\mathbf{P}}^{(m)}(\mathbf{q}, \omega) \mathbf{f}_{xc}^{(n-m)}(\mathbf{q}, \omega) \right]$$

Causal/T-ordered



Causal/T-ordered f_{xc}



● Same agreement between BSE and TDDFT for the finite transferred momentum absorption spectra...

● ...and for the off-diagonal elements of the microscopic dielectric function

Low dimensional systems (1D): polyacetylene

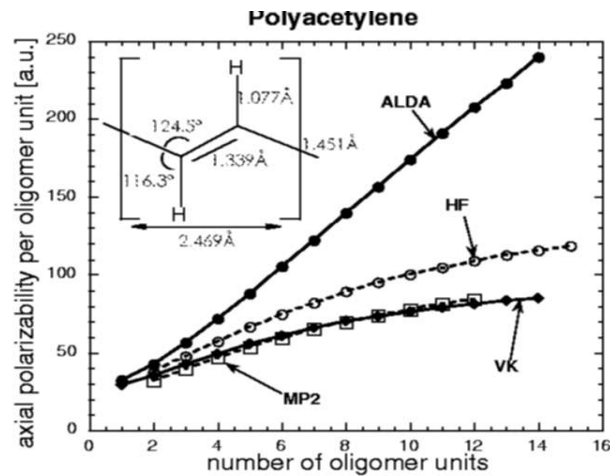


FIG. 1. ALDA and VK static axial polarizability of polyacetylene compared with restricted Hartree-Fock [18] and MP2 [22] results.

M. van Faassen et al. PRL **88** 186401 (2002)

Electric field dependence of the XC Potential in Molecular Chains

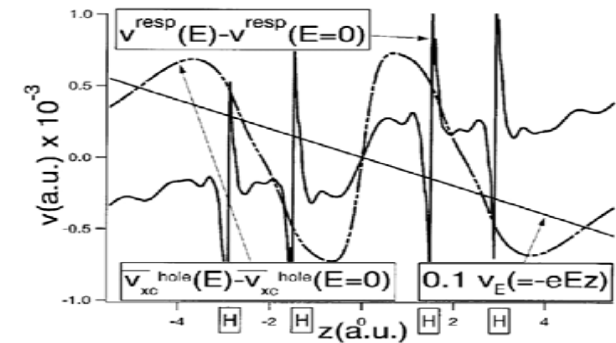


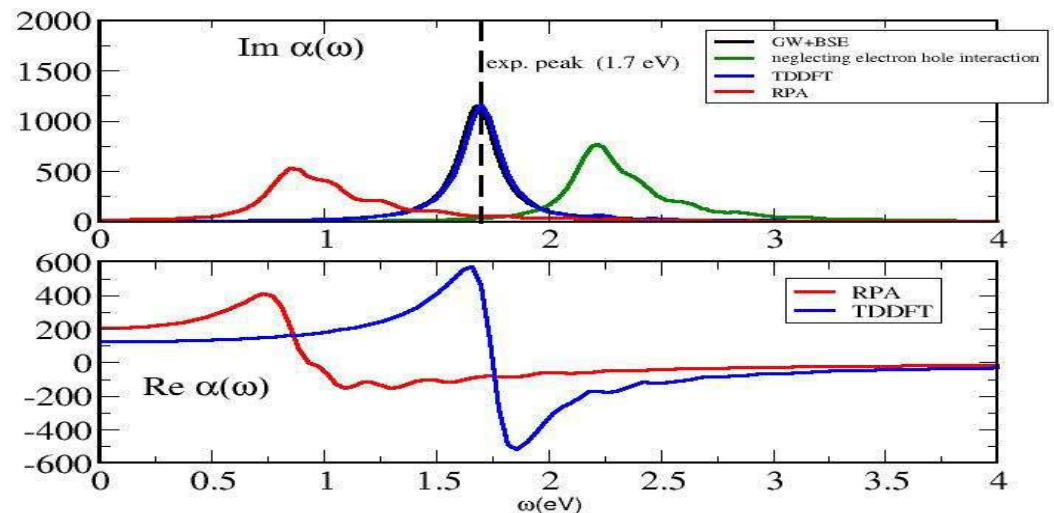
FIG. 2. Changes, due to an electric field of 0.001 a.u. in response and hole potentials for H₂-H₂, constructed from multireference CI singles doubles density with a large (cc-pV6Z without *d* and *f* functions) basis set, compared to the applied field (potential v_E).

S.J.A. Van Gisbergen PRL **83** 694 (1999)

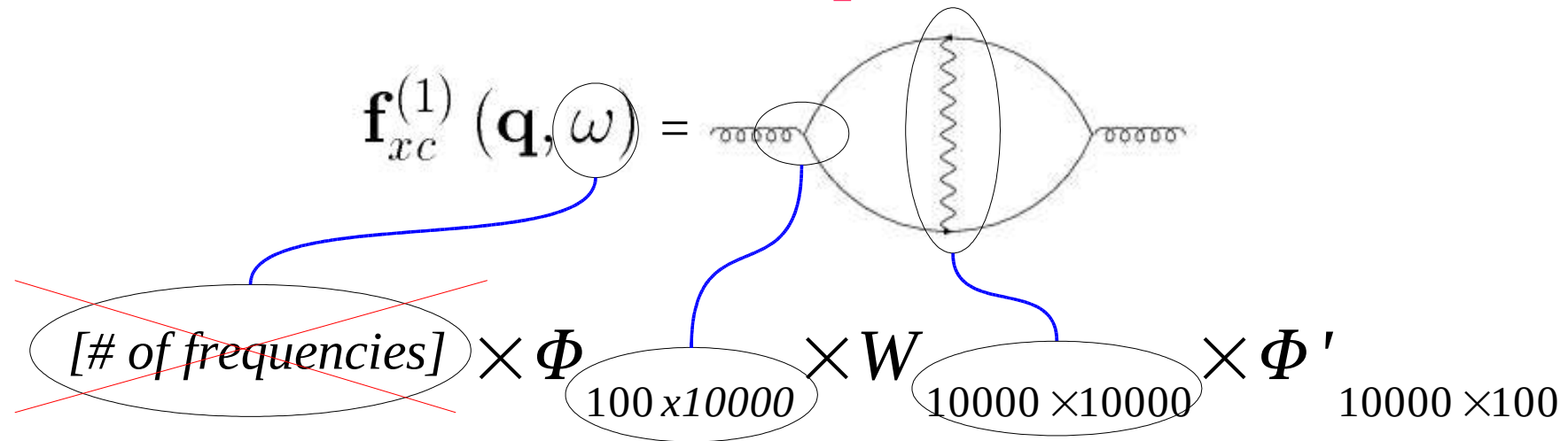
In LDA and GGA xc potential lack of a term counteracting the applied electric field

$$f_{xc}^{BSE}(r, r', \omega)$$

Isolated infinite Polyacetylene chain



Is TDDFT "fast" compared to the BSE ?



$$\mathbf{f}_{xc}^{(1)}(\mathbf{q}, \omega) = \frac{2}{\Omega N_k} \left[\mathbf{P}^{(0)}(\mathbf{q}, \omega - \Delta_{\mathbf{q}}) \right]^{-1} \sum_{\mathbf{K}} \left[\frac{\mathbf{R}_{\mathbf{K}}^{(\mathbf{q})} + \mathbf{R}_{\mathbf{K}}^{(\mathbf{q})\dagger}}{\omega - E_{\mathbf{K}}^{(\mathbf{q})} - \Delta_{\mathbf{q}} + i0^+} + \frac{\mathbf{Q}_{\mathbf{K}}^{(\mathbf{q})}}{(\omega - E_{\mathbf{K}}^{(\mathbf{q})} - \Delta_{\mathbf{q}} + i0^+)^2} \right] \left[\mathbf{P}^{(0)}(\mathbf{q}, \omega - \Delta_{\mathbf{q}}) \right]^{-1}$$

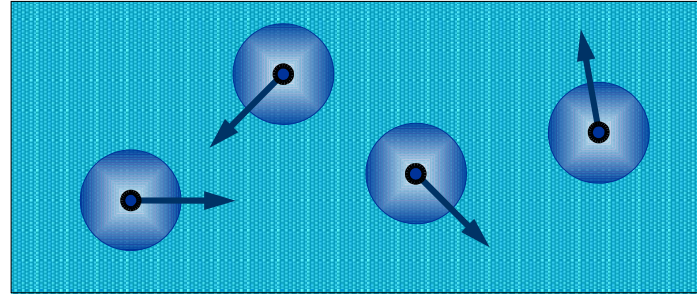
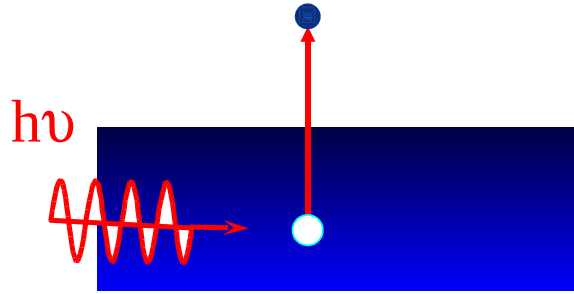
$$\left[R_{\mathbf{K}}^{(\mathbf{q})} \right]_{\mathbf{G}_1, \mathbf{G}_2} = \sum_{\mathbf{K}', E_{\mathbf{K}'}^{(\mathbf{q})} \neq E_{\mathbf{K}}^{(\mathbf{q})}} \frac{\Phi_{\mathbf{K}}^*(\mathbf{q}, \mathbf{G}_1) W_{\mathbf{K}, \mathbf{K}'}(\mathbf{q}) \Phi_{\mathbf{K}'}(\mathbf{q}, \mathbf{G}_2)}{E_{\mathbf{K}}^{(\mathbf{q})} - E_{\mathbf{K}'}^{(\mathbf{q})}} \quad \left[Q_{\mathbf{K}}^{(\mathbf{q})} \right]_{\mathbf{G}_1, \mathbf{G}_2} = \sum_{\mathbf{K}', E_{\mathbf{K}'}^{(\mathbf{q})} = E_{\mathbf{K}}^{(\mathbf{q})}} \Phi_{\mathbf{K}}^*(\mathbf{q}, \mathbf{G}_1) W_{\mathbf{K}, \mathbf{K}'}(\mathbf{q}) \Phi_{\mathbf{K}'}(\mathbf{q}, \mathbf{G}_2)$$

- When the only optical spectra is calculated TDDFT is as time consuming as BSE...
- ...but when the full dielectric matrix is needed TDDFT is more favorable than BSE

What about the description of decaying quasiparticle processes within TDDFT?

G. Onida, L. Reining and AR, Rev. Mod. Phys. 74, 601 (2002)

Lifetime of quasiparticles



interactions between quasiparticles limit how long the corresponding quantum states retain their identity, i.e., the **lifetime** of the excitation.

In combination with the velocity, this lifetime determines the **mean free path**, a measure of influence of the excitation

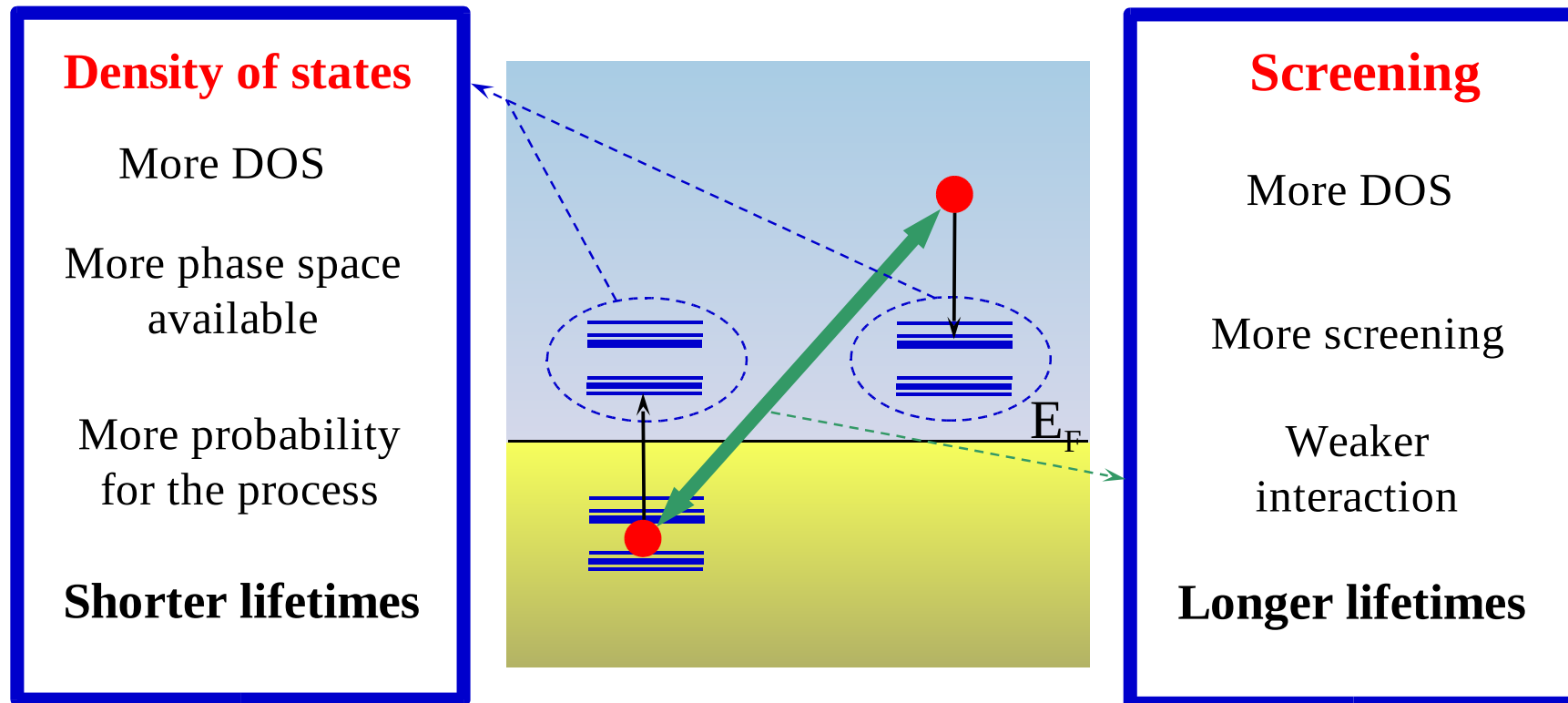
Importance of lifetime

- screening in an electron gas
- surface photochemistry
- electron-phonon coupling
- electron transfer across interfaces
- localization
- electron dynamics and energy transfer

PHYSICS OF LIFETIME

$$\tau^{-1} = 2 \sum \int d\mathbf{r} \int d\mathbf{r}' \phi_i^*(\mathbf{r}) \phi_f^*(\mathbf{r}') \text{Im}W(\mathbf{r},\mathbf{r}';\omega) \phi_i(\mathbf{r}') \phi_f(\mathbf{r})$$

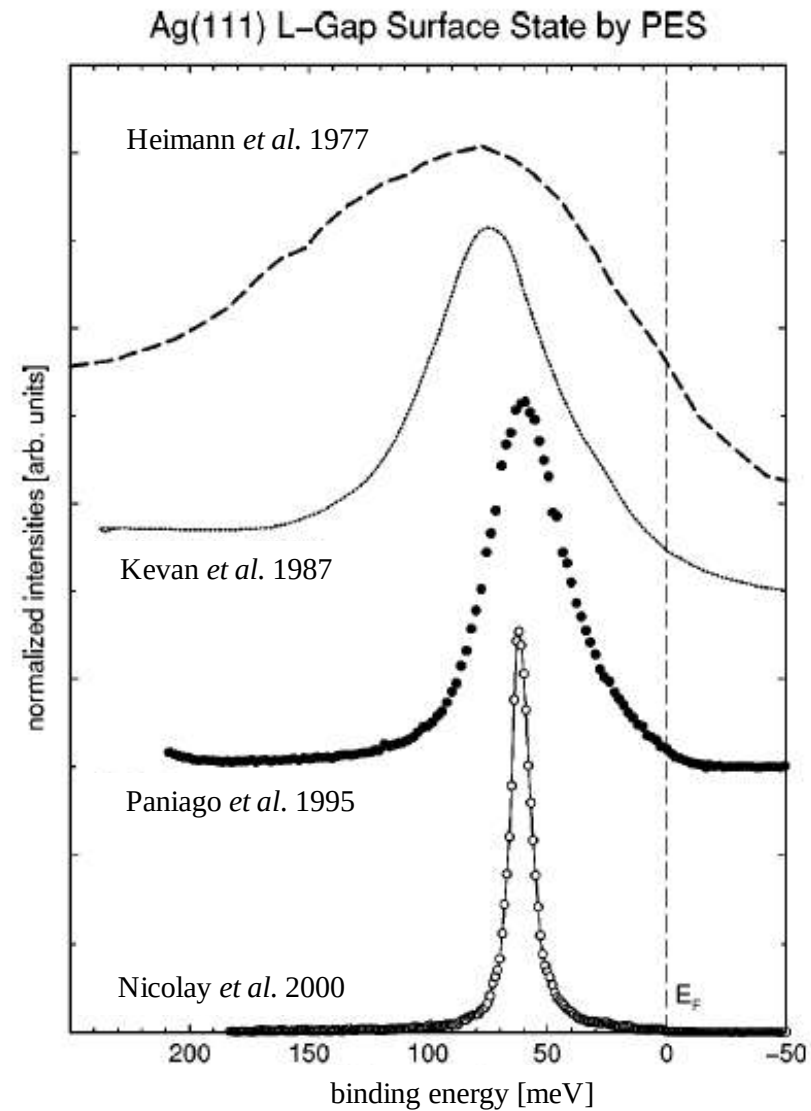
Density of States (DOS) versus Screening



Free electrons
Quinn (1962)

$$\tau \approx \frac{263 r_s^{-5/2}}{(E-E_F)^2} \propto \frac{n^{5/6}}{(E-E_F)^2}$$

Experimental lifetimes change quickly with time!



from F.Reinert *et al.*, PRB **63** (2001) 115415.

The 2-point vertex function

Suppose to have a good approximation for the (TD)DFT *potential*...

$$\hat{H} = \int d\mathbf{x} \hat{\psi}^\dagger(\mathbf{x}) [h_0(\mathbf{x}) + v_{xc}(\mathbf{x})] \hat{\psi}(\mathbf{x}) + H_{interaction} - \int d\mathbf{x} \hat{\psi}^\dagger(\mathbf{x}) v_{xc}(\mathbf{x}) \hat{\psi}(\mathbf{x})$$

$$\chi(1, 2) = \tilde{\chi}(1, 2) + \int d34 \tilde{\chi}(1, 2) [v(3, 4) + f_{xc}(3, 4)] \chi(4, 2)$$

$$f_{xc}(1, 2) \equiv \delta v_{xc}(1) / \delta \rho(2)$$

$$\tilde{\Gamma}(1, 2; 3) = \delta(1, 2) \delta(2, 3) + \int d4567 \Xi(1, 5; 2, 4) G(4, 6) G(7, 5) \tilde{\Gamma}(6, 7; 3)$$

$$\Xi(1, 4; 2, 3) \approx W(1, 2) \delta(1, 3) \delta(2, 4) - f_{xc}(1, 3) \delta(1, 2) \delta(3, 4)$$

$$\Sigma_{G_0 W_0} \rightarrow i \int d3 W^{TDDFT}(1^+, 3) \tilde{\Gamma}_{loc}(3, 2) G(1, 2) \quad \tilde{\Gamma}_{loc}(1, 2) = \int d3 \chi_0^{-1}(1, 3) \tilde{\chi}(3, 2)$$

No difference with GoWo using ALDA or similar approaches

PRL 62, 2718 (1989); PRB 49, 8024 (1994); PRB 56, 12832 (1997).

BUT IS $\tilde{\Gamma}(1, 2; 3) = \delta(1, 2) \delta(2, 3) + \tilde{\Gamma}_3(1, 2; 3) - \tilde{\Gamma}_{loc}(1, 3) \delta(1, 2) \sim \delta(1, 2) \delta(2, 3) ?$

● PRL 91, 056402 (2003); PRL 91, 256402 (2003). PRL 88, 066404 (2002) etc etc

The 3-point vertex function

$$\mathbf{f}_{xc}^{(1)}(\mathbf{q}, \omega) = \text{diagram} \quad \text{diagram} := [\chi_0(\omega)]^{-1}$$

$$\tilde{\chi}(1, 2) = \chi_0(1, 2) + \int d^3\mathbf{r} \chi_0(1, 3) \text{diagram} \quad \tilde{\chi}(4, 2) = -i \int d^3\mathbf{r} G(1, 3) G(4, 1) \tilde{\Gamma}_{TDDFT}^{(1)}(3, 4; 2)$$

If

$$\tilde{\Gamma}_{TDDFT}^{(1)}(1, 2; 3) \equiv \delta(1, 2) \delta(2, 3) + i W_0(1, 2) \int d^3\mathbf{r} G_0(1, 4) G_0(4, 2) \tilde{\Gamma}_{loc}(4, 3)$$

$$\tilde{\Gamma}_{TDDFT}^{(1)}(1, 2; 3) \equiv \delta(1, 2) \delta(2, 3) + i \text{diagram} \tilde{\chi}(4, 3)$$

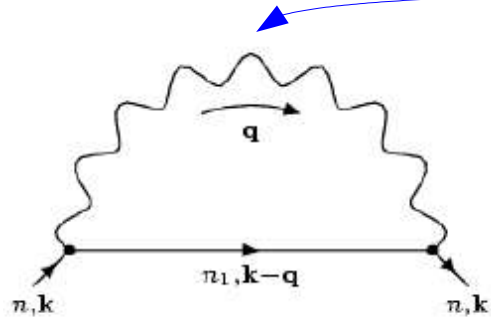
Closed expression for the "on mass-shell" electronic lifetime

$$\tau_{ck}^{-1} = \tau_{ck,0}^{-1} + \Delta\tau_{ck}^{-1}$$

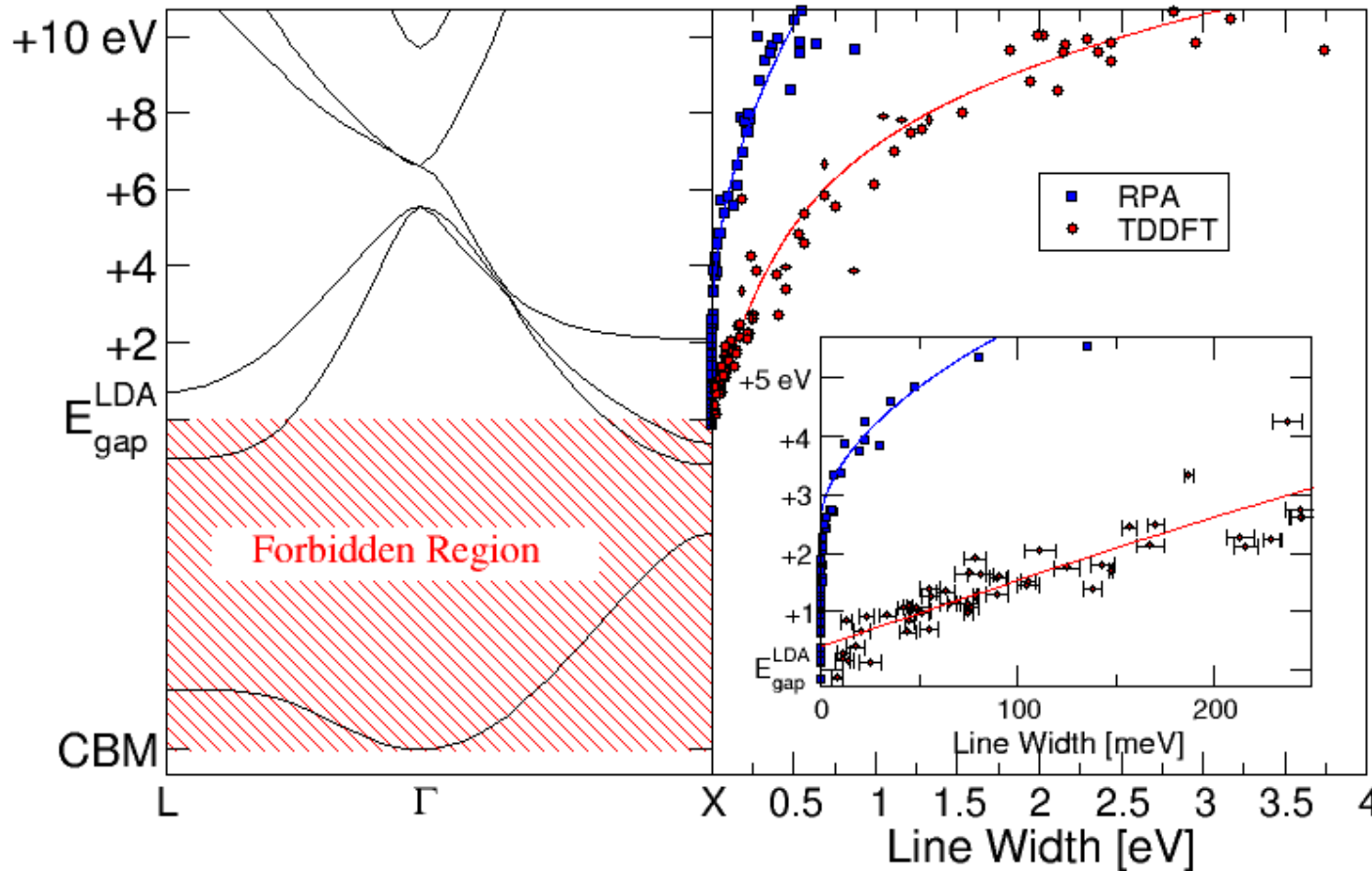
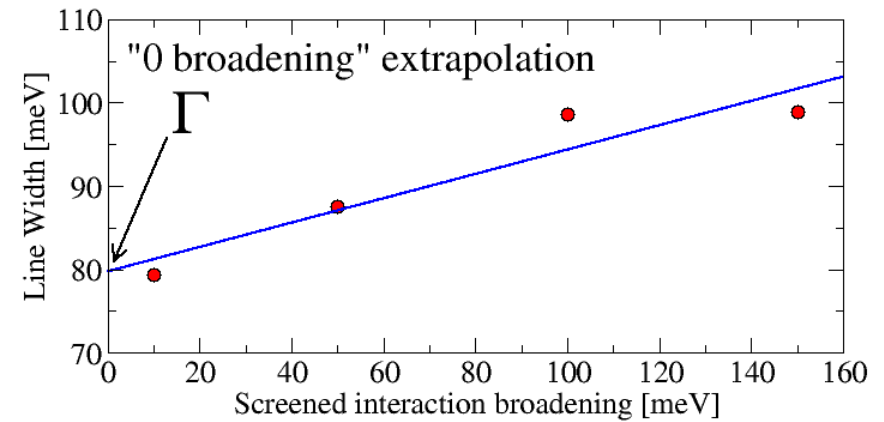
$$\tau_{ck,0}^{-1} = -2\Omega^{-1} \sum_{\mathbf{G}_1, \mathbf{G}_2} \sum_{\mathbf{q}, c'} \rho_{cc'}(\mathbf{k}\mathbf{q}\mathbf{G}_1) \rho_{cc'}^*(\mathbf{k}\mathbf{q}\mathbf{G}_2) \text{Im} [W_{\mathbf{G}_1\mathbf{G}_2}^{TDDFT}(\mathbf{q}, \epsilon_{c\mathbf{k}} - \epsilon_{c'\mathbf{k}-\mathbf{q}})] ,$$

$$\Delta\tau_{ck,0}^{-1} = -2\Omega^{-1} \sum_{\mathbf{G}_1, \mathbf{G}_2} \sum_{\mathbf{q}, c'} \text{Re} [(\Gamma_{cc'}^{cv}(\mathbf{k}\mathbf{q}\mathbf{G}_1) + \Gamma_{cc'}^{vc}(\mathbf{k}\mathbf{q}\mathbf{G}_1)) \rho_{cc'}^*(\mathbf{k}\mathbf{q}\mathbf{G}_2)] \text{Im} [W_{\mathbf{G}_1\mathbf{G}_2}^{TDDFT}(\mathbf{q}, \epsilon_{c\mathbf{k}} - \epsilon_{c'\mathbf{k}-\mathbf{q}})]$$

Excitonic effects (via TDDFT) on the lifetimes of LiF



- 10'000x10'000 BS kernel
- Up to 200 G-vectors dielectric function, 256 Q-points in the whole BZ
- Small broadening stability



- Linear behaviour
- Small penetration of the RPA "forbidden region"
- The f_{xc} kernel remains stable and robust even with a 10 meV broadening and energies up to 20 eV
- A BS-based calculation is, in this case, **enormously less convenient** than using TDDFT

Acknowledgements

A. Castro, A. Marini, X. López, L Wirtz, D. Varsano

Department of Material Physics, Centro Mixto CSIC-UPV, University of the Basque Country, and Donostia International Physics Center (DIPC), Donostia, Spain

M. A. L. Marques, C.A. Rozzi, and E. K. U. Gross

Institut für Theoretische Physik, Freie Universität, Berlin, Germany

L. Reining, V. Olevano

École Polytechnique, Palaiseau, France

R. Del Sole and G. Onida

Istituto Nazionale per la Fisica della Materia e Dipartimento di Fisica dell'Università di Roma ``Tor Vergata'', Roma, Italy

G.F. Bertsch, K. Yabana

Physics Department and Institute for Nuclear Theory University of Washington, Seattle (USA)

*It is one of the first duties of a professor, in any subject,
to exaggerate a little both the importance of his subject and his
own importance in it.*

G.H. Hardy (A Mathematician's Apology)

Thank you

<http://dipc.ehu.es/arubio>

E-mail: arubio@sc.ehu.es