Nanoquanta Network of Excellence

ETSF

A TDDFT formalism for linear and non-linear response of nanostructures and solids

Angel Rubio

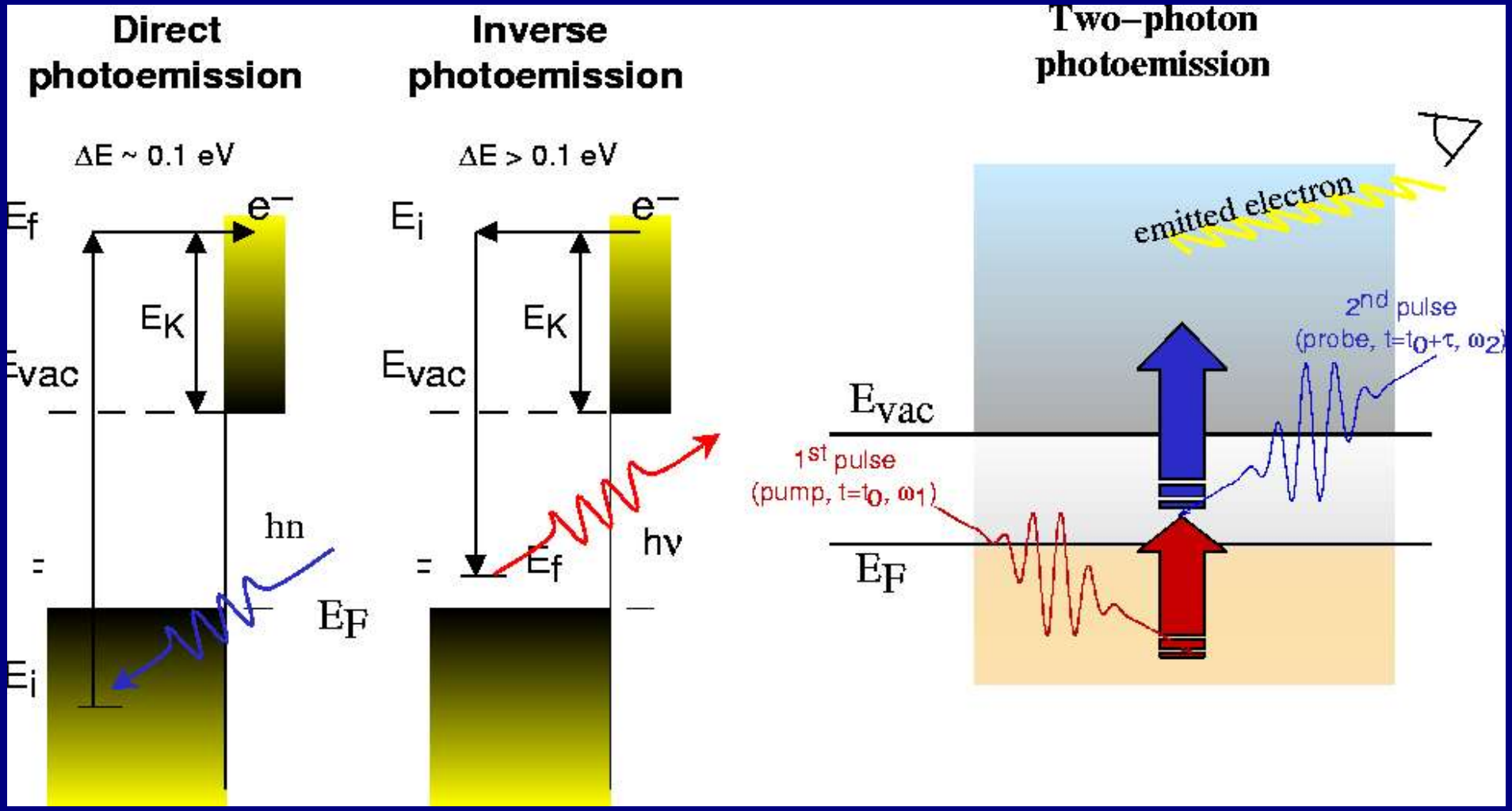
DONOSTIA INTERNATIONAL PHYSICS CENTER

Dpto. 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

eman ta zabal zazu
euskal herriko unibertsitatea
universidad del país vasco



Physical Processes: Spectroscopies



Time-dependent approach: TDDFT?

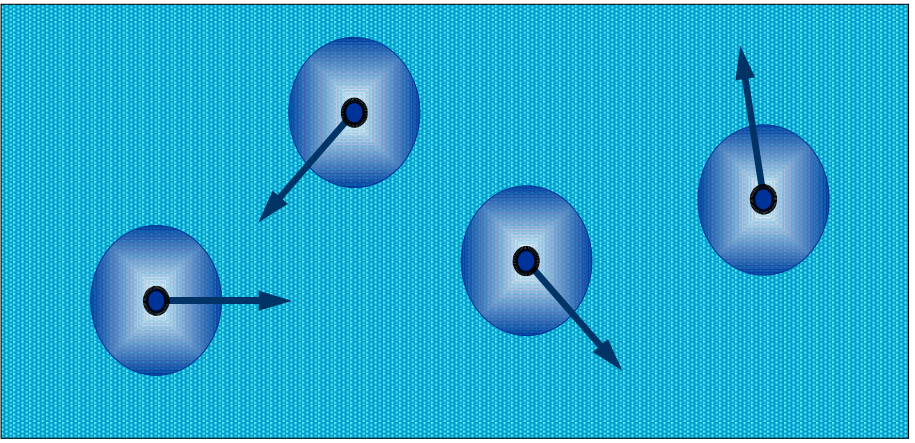
OUTLINE

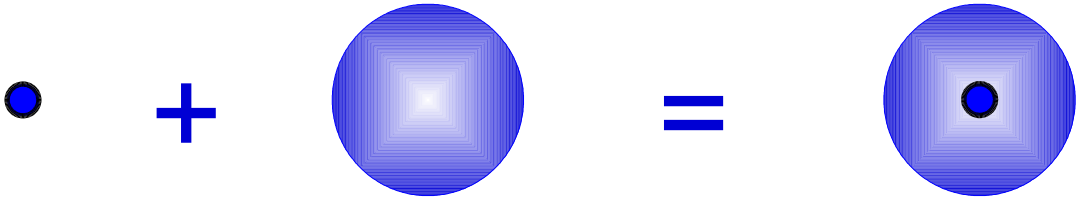
- Introduction:
  - Quasiparticle concept
  - Basic DFT and TDDFT: *octopus project*
- Application to finite systems:
  - Linear Response applications : benzene, clusters
  - Non-linear regime: Femtosecond dynamics: Sodium dimer
- Spectroscopy of Solids: optics and EELS
  - TDDFT and Many-body perturbation theory
    - *Problems with standard exchange-correlation functionals*
    - *New fxc : Bound excitons*
  - Applications to 1D: Linear chains and polymers
    - Nanotubes

QUASIPARTICLES

- a fundamental concept in condensed-matter physics - MBPT-

a system composed of interacting *real* bodies acts as if it were composed of weakly interacting *fictitous* bodies **(quasiparticles)**





bare particle

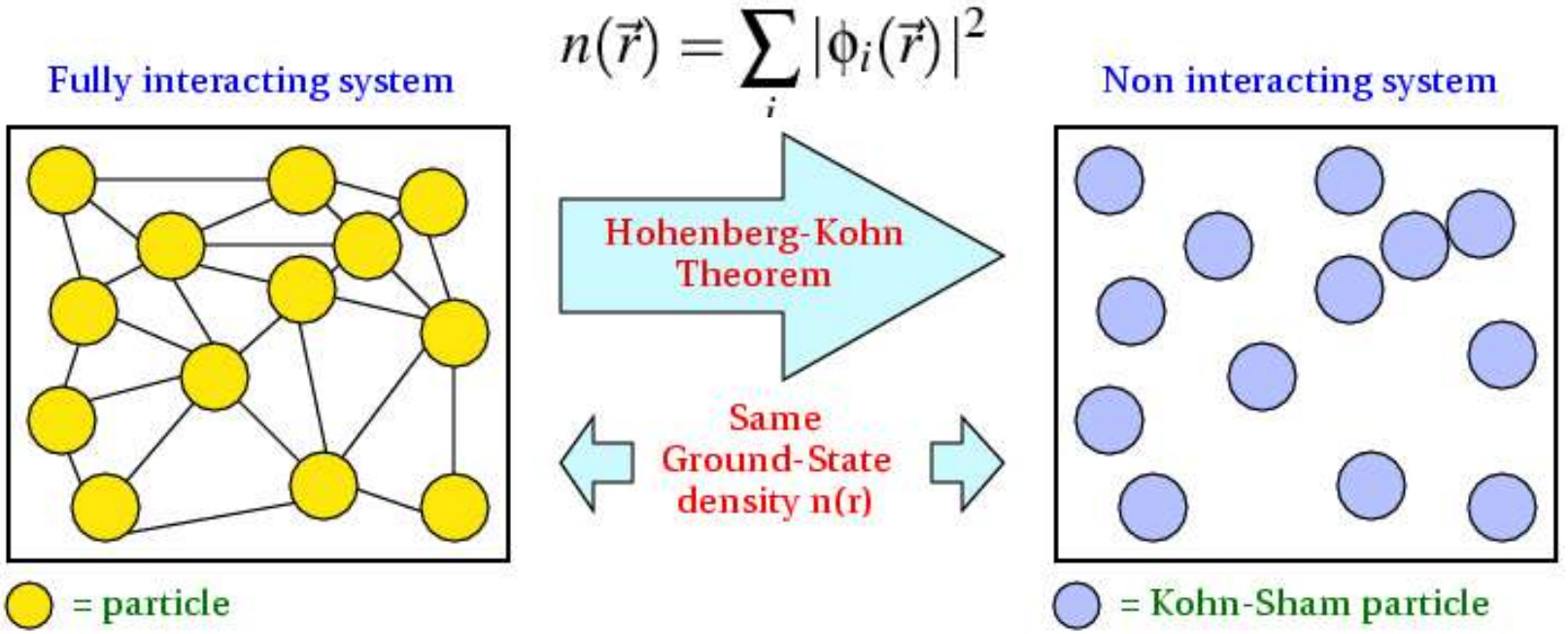
Cloud of other particles

quasiparticle

one many-body problem ⇒ many one-body problems

DFT Kohn-Sham approach (1965):

$$n(\vec{r}) = \sum_i |\phi_i(\vec{r})|^2$$



T[n] ------- $T_0[n]$

$$T_0[n] = \sum_i \int \phi_i^*(\vec{r}) \left(-\frac{\hbar^2}{2m} \nabla^2 \right) \phi_i(\vec{r}) d^3r$$

Exc includes now the correlation contribution to T

$$\left\{ -\frac{\hbar^2}{2m}\nabla^2 + \underbrace{V(\vec{r}) + e^2 \int \frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|} d^3r + \mu_{xc}[n(\vec{r})]}_{V_{eff}(\vec{r})} \right\} \phi_i(\vec{r}) = \varepsilon_i \phi_i(\vec{r})$$

KS-equations

with the exchange-correlation potential

$$\mu_{xc}[n(\vec{r})] = \frac{\delta E_{xc}[n(\vec{r})]}{\delta n(\vec{r})} = \frac{\delta\{n(\vec{r})\varepsilon_{xc}[n(\vec{r})]\}}{\delta n(\vec{r})}$$

Some summary of DFT results for finite and extended systems

Property	LSDA	GGA
Exchange Energy	5% (not negative enough)	0.5%
Correlation Energy	100% (too negative)	5%
bond length	1% (short)	1% (long)
structure	favours close packing	improves
energy barrie	100% (too low)	30% (low)

Approx	Mean absolute error in the atomisation energy for 20 molecules
Unrestricted HF	3.1 eV (underbinding)
LSDA	1.3 eV (overbinding)
GGA	0.3 eV (mostly overbinding)
Chemical accuray	*0.05 eV*

J.P. Perdew and S. Kurth in A chemist's guide to density functional theory, W. Koch and M.C. Holthausen, (Wiley-VCH,, 2000)

Density Functional Theory vs 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)

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

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

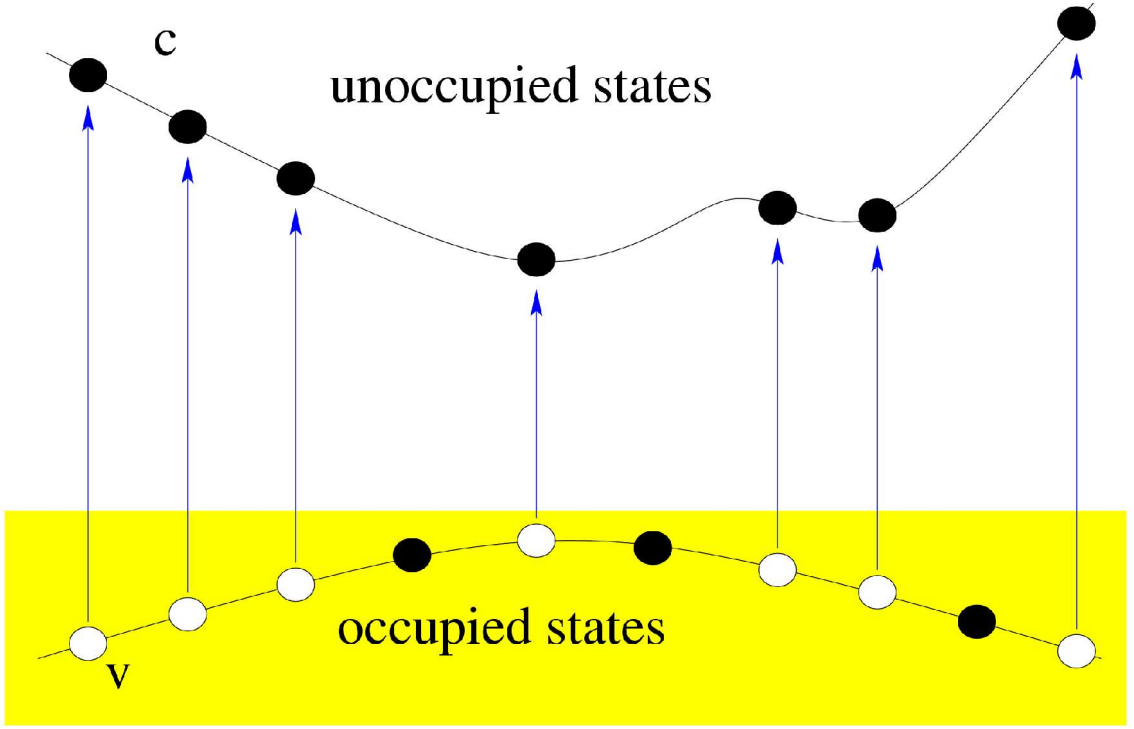
$$[\mathcal{H}_{KS} - V_{xc}(\mathbf{r})](\mathbf{r})\,\phi_i(\mathbf{r};E_\lambda) + \int d\mathbf{r}'\Sigma(\mathbf{r},\mathbf{r}';E_\lambda)\,\phi_i(\mathbf{r}';E_\lambda) = E_\lambda(\omega)\,\phi_\lambda(\mathbf{r},E_\lambda)$$

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

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

Screening effects: $\varepsilon = 1 - v\,P$ polarisation

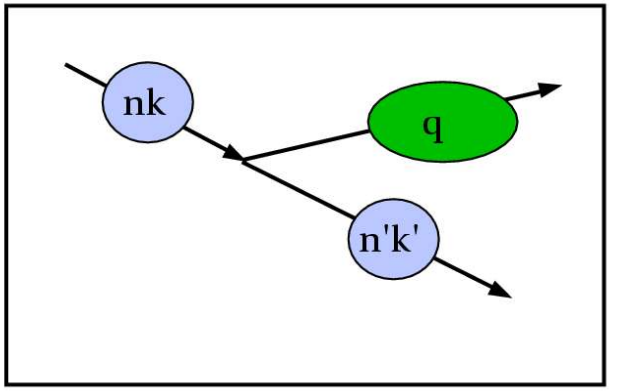
Independent Electrons (KS!)



$$P = P^0 \propto \sum_{vc} \frac{|\langle \phi_c | e^{i\mathbf{q}\cdot\mathbf{r}} | \phi_v \rangle|^2}{\omega - (\epsilon_c - \epsilon_v) + i\eta}$$

$$\sum_{vc} |\langle \phi_c | e^{i\mathbf{q}\cdot\mathbf{r}} | \phi_v \rangle|^2 \, \delta\big(\omega - (\epsilon_c - \epsilon_v)\big)$$

Hedin's GW (1965)



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

$$P(1\,2) = -iG(1\,2)\,G\left(2\,1^{+}\right)$$

$$\Sigma(1\,2) = iG\left(1\,2^{+}\right)W(1\,2)$$

Hedin Equation's (1965)

$$P(1\,2) = -\mathrm{i}\int \mathrm{d}(3\,4)\, G(1\,3)\, G\left(4\,1^{+}\right)\Gamma(3\,4,2)$$

$$W(1\,2) = v(1\,2) + \int \mathrm{d}(3\,4)\, W(1\,3)\, P(3\,4)\, v(4\,2)$$

$$\Sigma(1\,2) = \mathrm{i}\int \mathrm{d}(3\,4)\, G\left(1\,4^{+}\right) W(1\,3)\,\Gamma(4\,2,3)$$

$$G(1\,2) = G_0(1\,2) + \int \mathrm{d}(3\,4)\, G_0(1\,3)\left[\Sigma(3\,4) - \delta(3\,4)\, v_{\mathrm{xc}}(4)\right] G(4\,2)$$

$$\Gamma(1\,2,3) = \delta(1\,2)\,\delta(1\,3) + \int \mathrm{d}(4\,5\,6\,7)\,\frac{\delta\Sigma(1\,2)}{\delta G(4\,5)} G(4\,6)\, G(7\,5)\,\Gamma(6\,7,3)$$

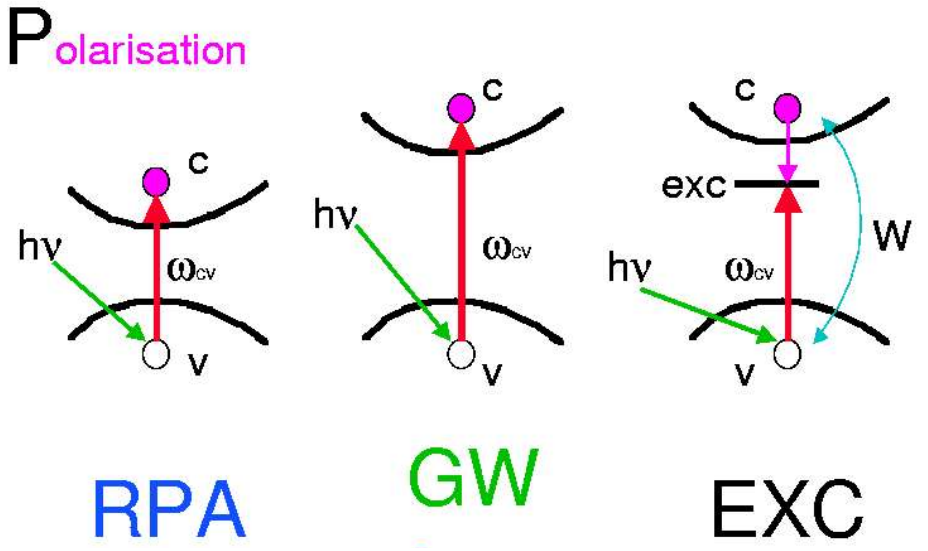
The GW "soup"

$$P(1\,2) = -\mathrm{i}G(1\,2)\, G\left(2\,1^{+}\right)$$

$$\Sigma(1\,2) = \mathrm{i}G\left(1\,2^{+}\right) W(1\,2)$$

Beyond DFT:

MBQFT: Exciton and Bethe-Salpeter equation



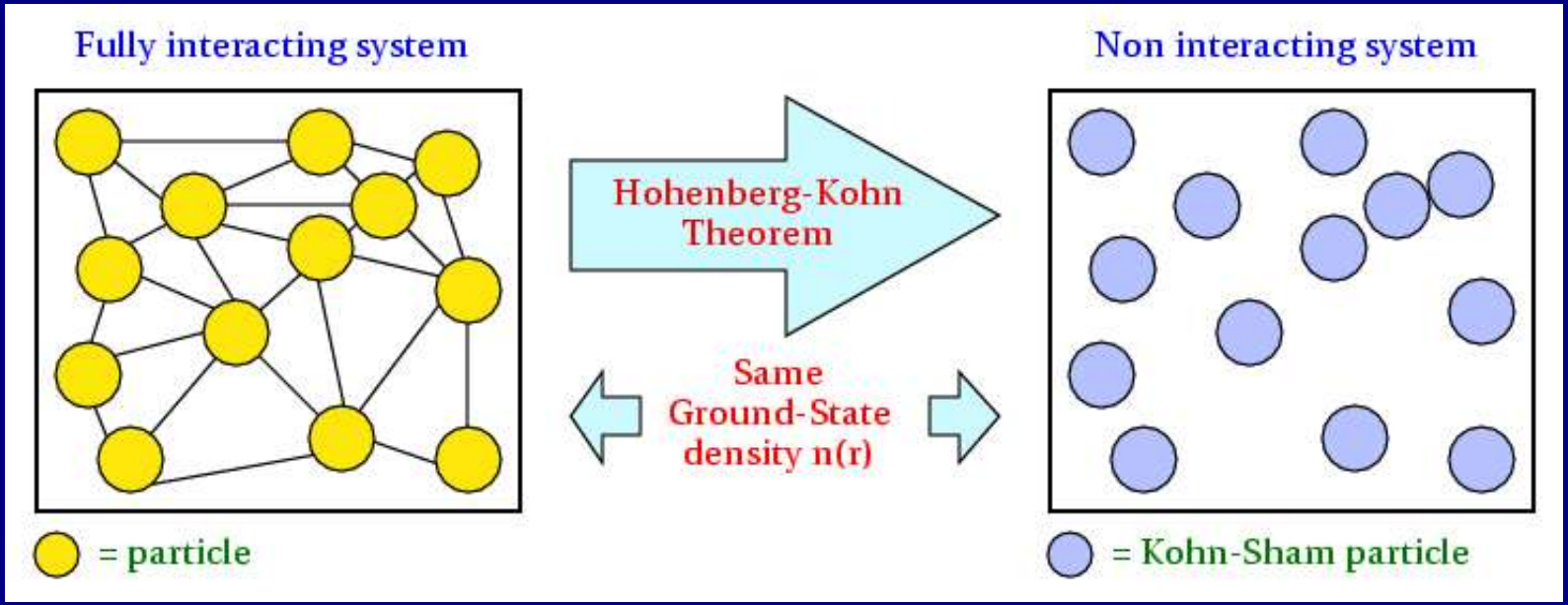
$$\mathrm{Im}\,[\varepsilon(\omega)] \sim \Sigma_{vc} |\langle v|D|c\rangle|^2 \; \delta(E_c - E_v - \omega)$$

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

Bethe-Salpeter equation: $(\epsilon_{c\mathbf{k}} - \epsilon_{v\mathbf{k}}) A^S_{vc\mathbf{k}} + \sum_{\mathbf{k}' v' c'} \langle vc\mathbf{k}|K^{eh}|v'c'\mathbf{k}'\rangle A^S_{v'c'\mathbf{k}'} = \Omega^S A^S_{vc\mathbf{k}}$

Dimensionality effects: nanotubes as quasi-1D structure

Density Functional versus Many-body perturbation theory



ground state

What about excited-state properties: electron-ion dynamics, spectroscopies

Time Dependent Density Functional Theory (Runge and Gross 1984)

Electron-dynamics first, then e-ion problem

HK-like theorem: $v(r,t) \leftrightarrow \rho(r,t)$

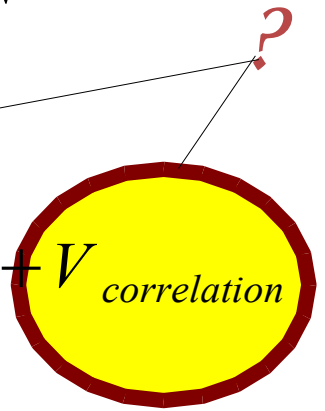
The time dependent density determines uniquely the time-dependent external potential and therefore all physical observables

Kohn-Sham formalism:

The time dependent density of the interacting system can be calculated as the density of an auxilary non-interacting system

$$i\hbar\frac{d}{dt}\Phi = H\Phi \quad \rightarrow \quad i\hbar\frac{d}{dt}\psi_i = H_{KS}\left[\{\psi_j\}\right]\psi_i, \quad i = 1,\cdots N$$

$$H_{KS} = \frac{\hbar^2}{2m}\left(i\nabla - \frac{e}{c\hbar}\left(A + A_{xc}\right)\right)^2 + V_{external} + V_{hartree} + V_{exchange} + V_{correlation}$$



By virtue of time-dependent Hohenberg-Kohn theorem, ALL observables are funtionals of the TD density

some observables are easily expressed in terms of the density (no approximations involved)

e.g. TD dipole moment $d(t) = \int \rho(r, t) z d^3 r$

photon spectrum $\sim \left| d(\omega) \right|^2$

other observables are more difficult to express in terms of the density (involving further approximation)

e.g. ionization yields

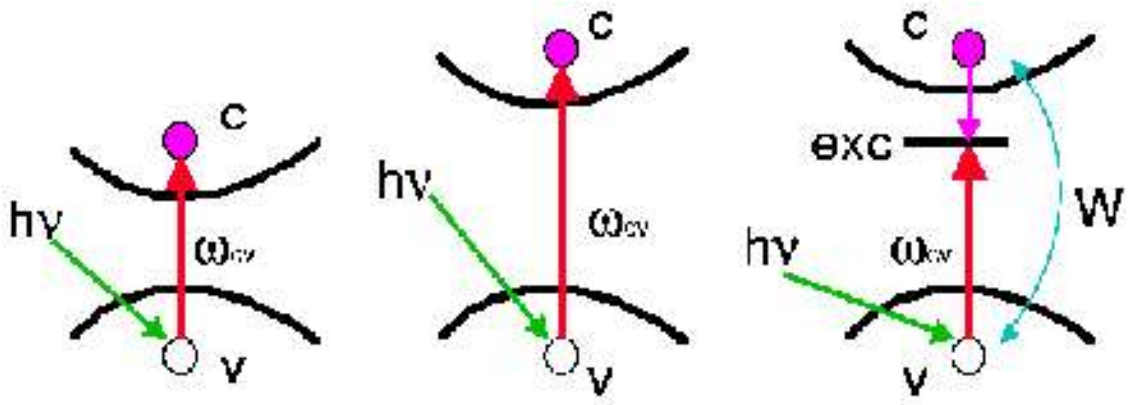
*The **octopus project** is aim to the first principle description of the excite state electron-ion dynamics of nanostructures and extended systems within TDDFT*

http://www.tddft.org/programs/octopus

M.A.L. Marques, A. Castro, G. Bertsch, AR Comp.Phys.Comm. (2002)
C. Rozzi, M.A.L. Marques, A. Castro, E.K.U. Gross A. R. (to be published)

- Applications to finite systems:
  - Linear Response applications : benzene, clusters
  - Biological photoreceptors

Linear optical response: general aspects



$$K_{ij} = \int dr\, \rho_i(r) \frac{d V_{xc}(r)}{d \rho(r)} \rho_j(r)$$

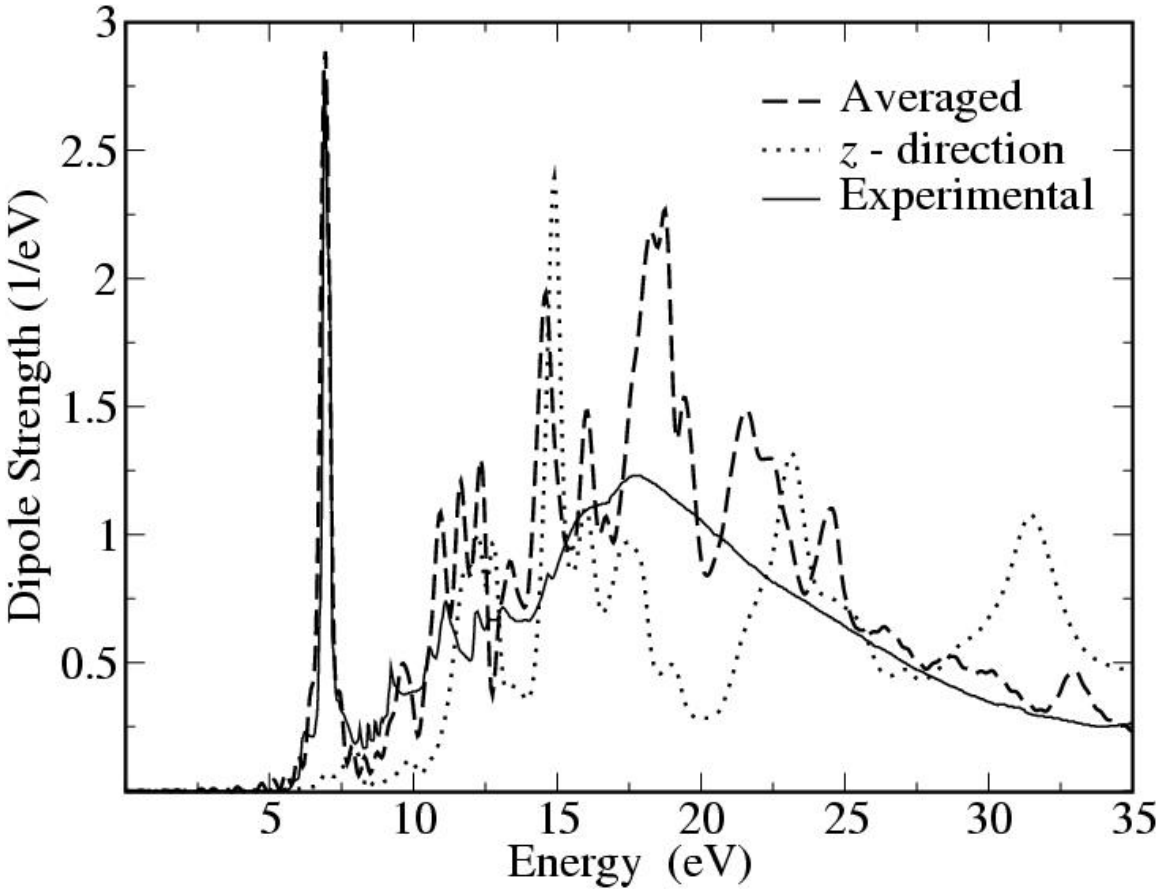
$$f_{xc}^{ALDA}(r,r',\omega) = \delta(r-r') \frac{d^2}{dn^2} \left(n\varepsilon_{xc}^{hom} \right) \Big|_{\rho(r)}$$

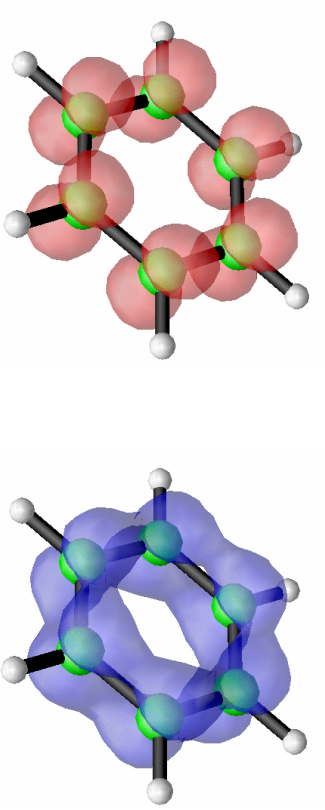
Single-pole approximation $\Rightarrow$

$$\Omega = \left(\varepsilon_{j_0} - \varepsilon_{k_0} \right) + K$$

$$K \approx \int d^3r \int d^3r' \varphi_{j_0}(r) \varphi_{j_0}^*(r') \varphi_{k_0}(r') \varphi_{k_0}^*(r) \cdot \left(\frac{1}{|r-r'|} + f_{xc}(r,r') \right)$$

Optical response: Benzene

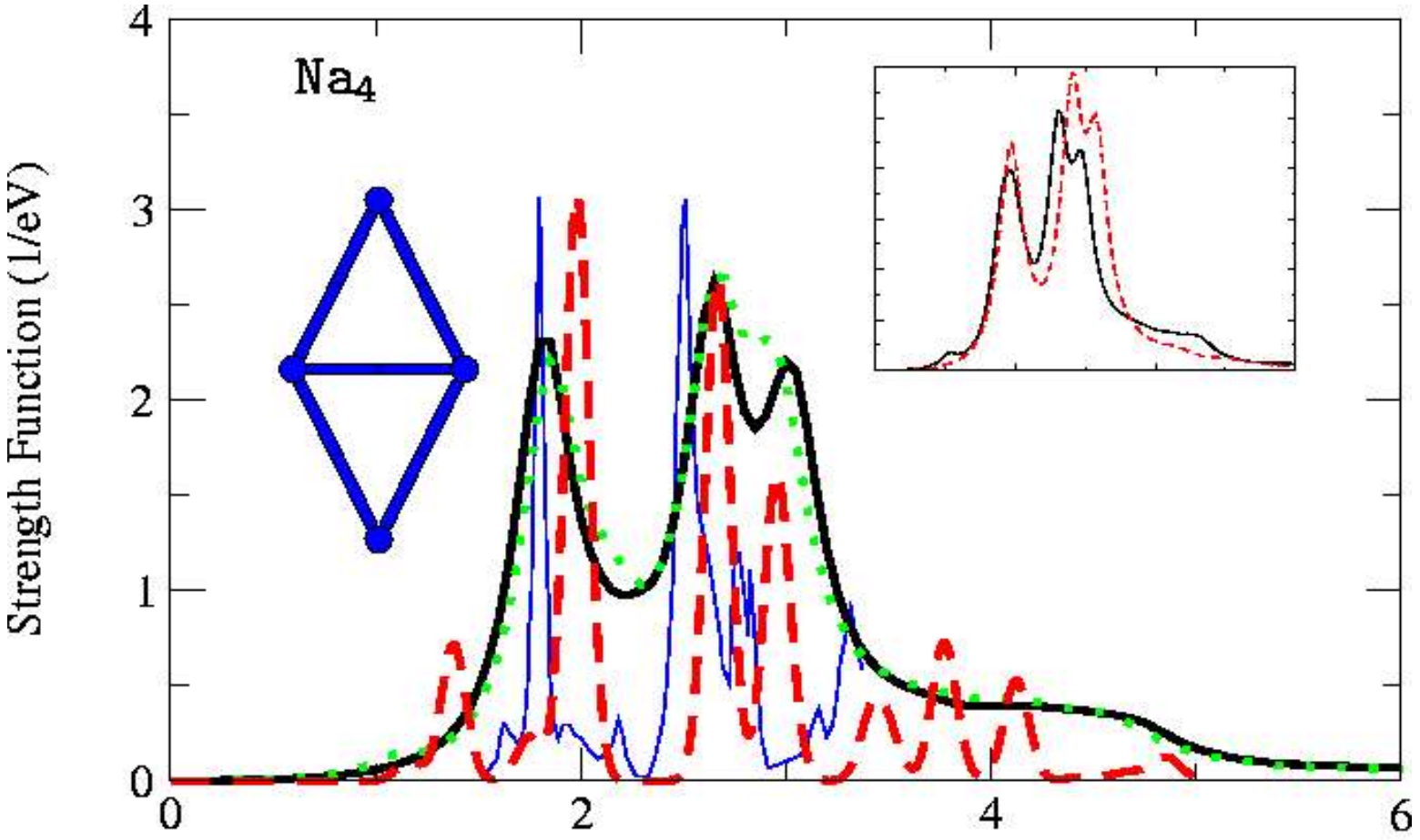




π* (LU

M.A.L Marques, A. Castro, G.F. Bertsch and AR, Comp. Phys. Comm. (2002);
K. Yabana and G. F. Bertsch, Int. J. Quantum Chem. 75, 55 (1999)

Assessment of xc-functionals in TDDFT



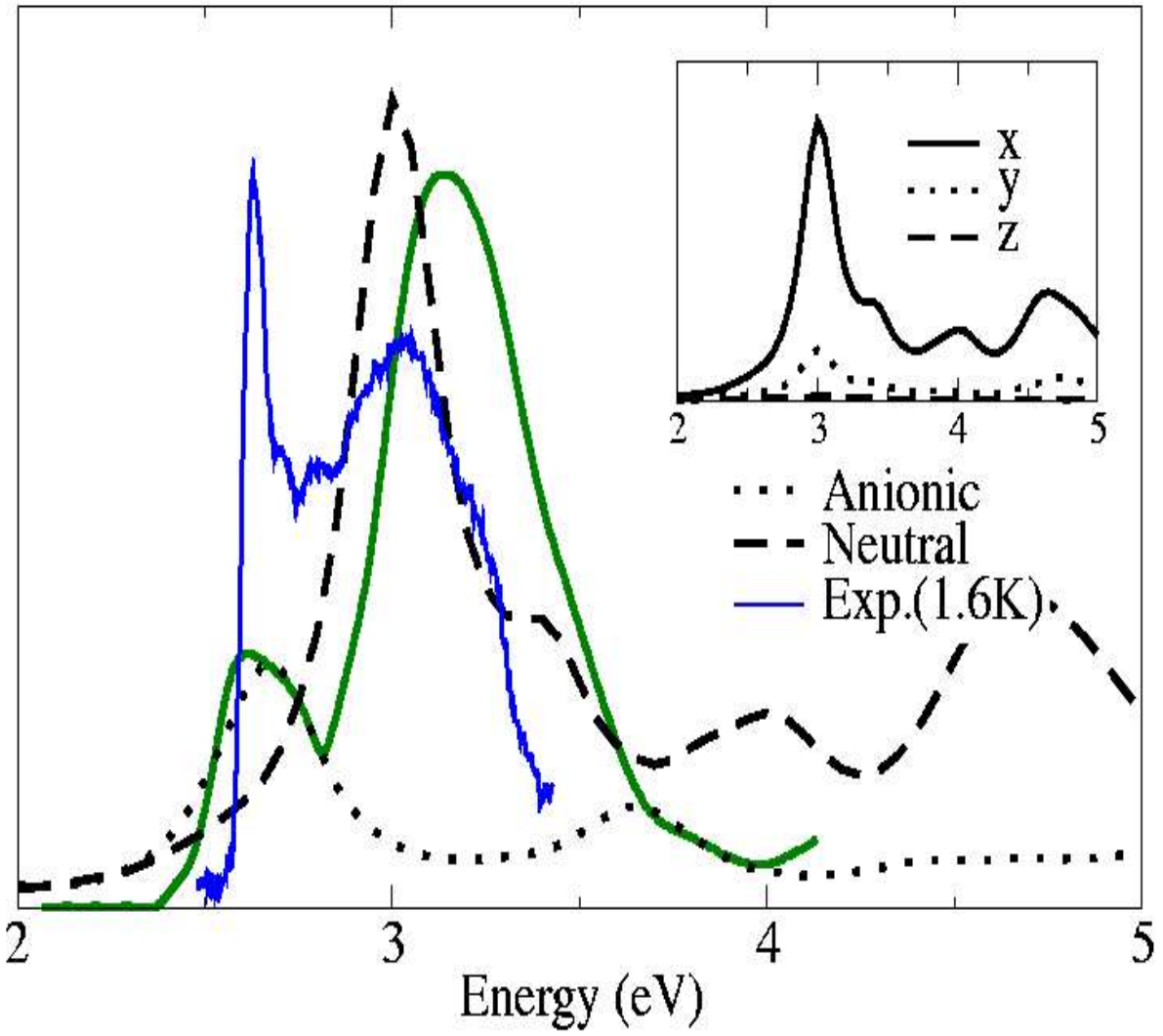
EXX- dotted line
Bethe-Salpeter
Experiments

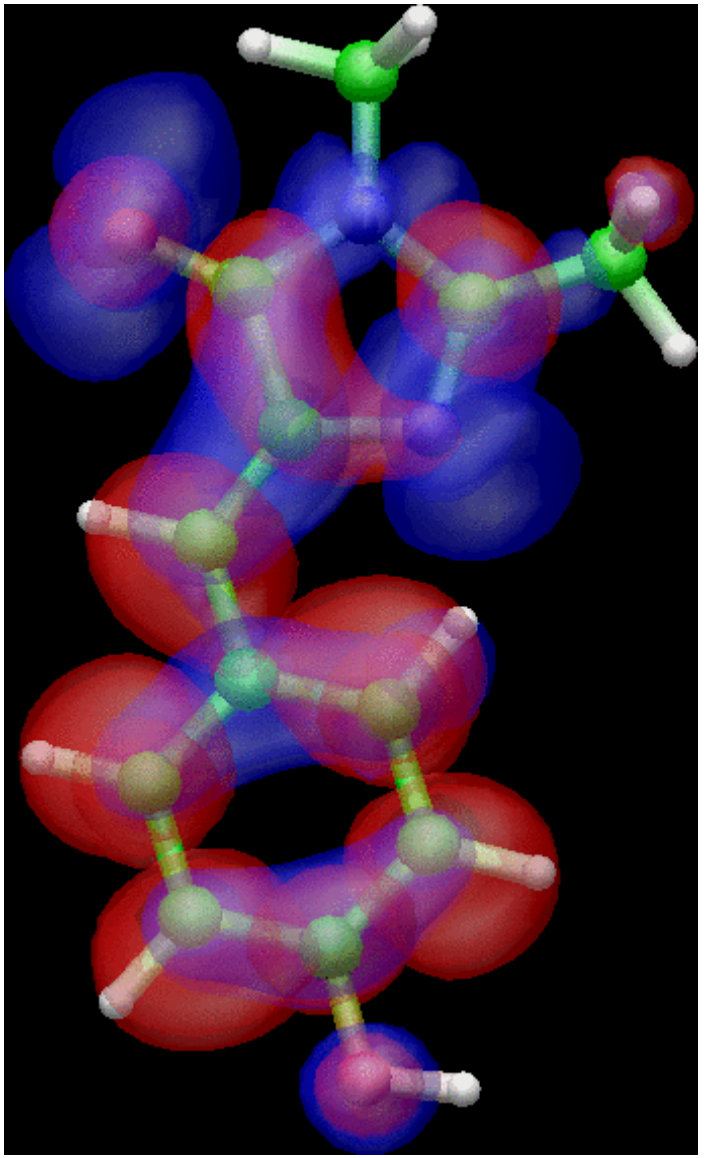
M.A.L. Marques, A. Castro and AR, J. Chem. Phys. ***115****, 3006 (2001)*

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

Biological molecules: photoreceptors

HOMO LUMO

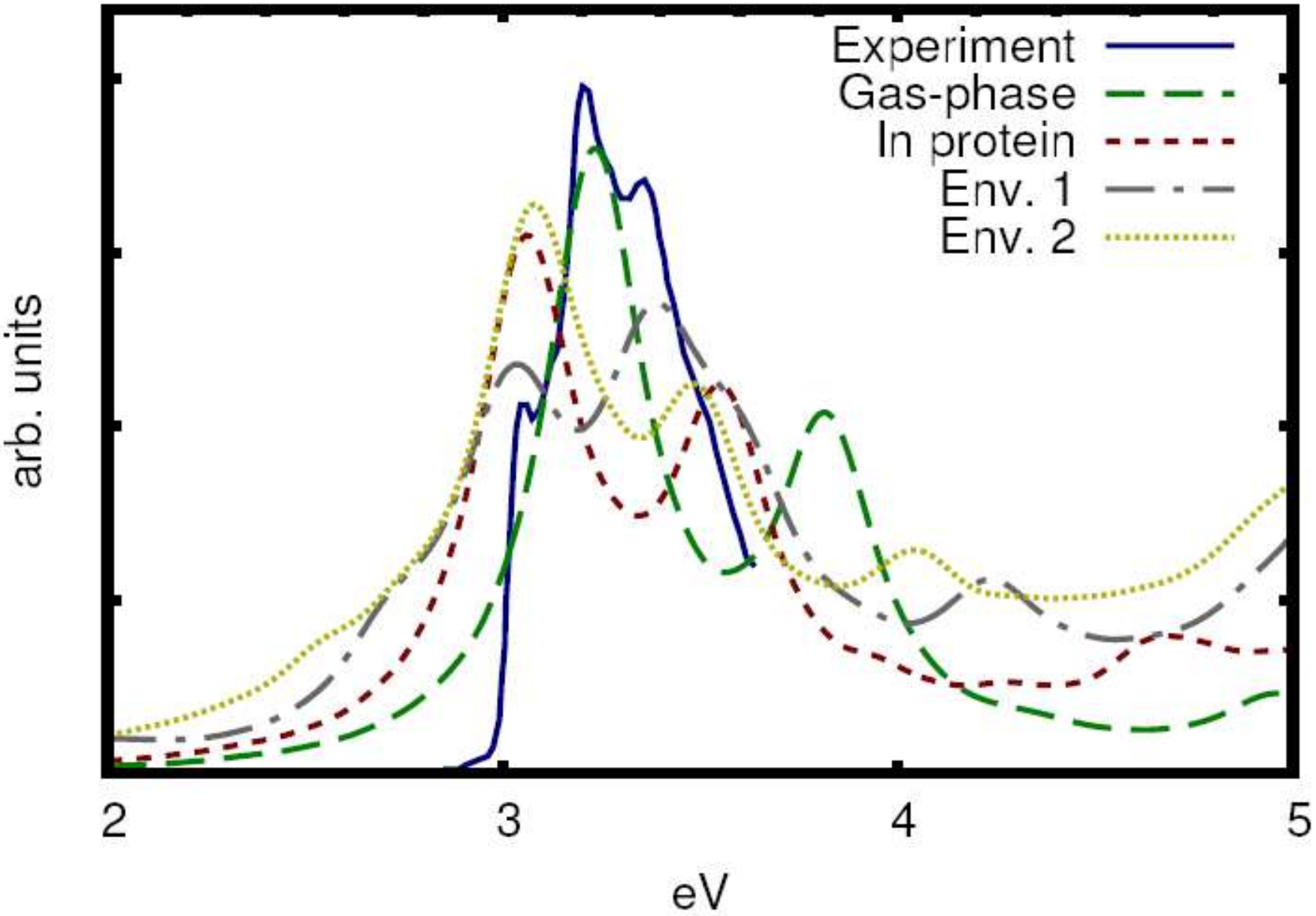




T.M.H. Creemers et al, Proc. Natl. Acad. Sci.. USA (1999)

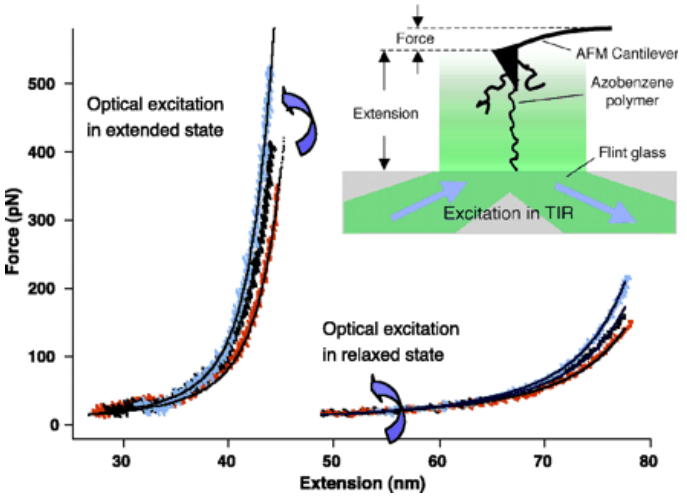
M.A.L Marques, X. Lopez, D. Varsano, A. Castro, and A. R. Phys. Rev. Lett. 90, 136101 (2003)

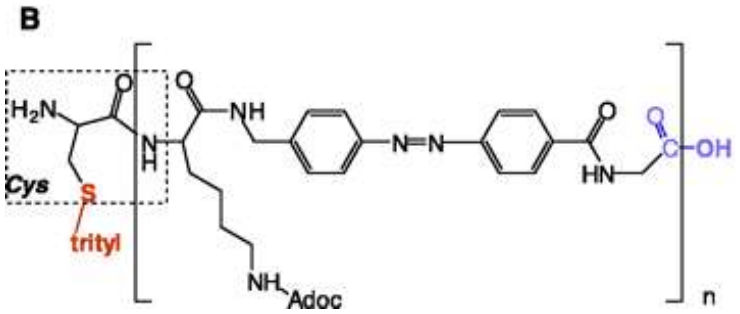
Blue Fluorescent Protein - Mutants

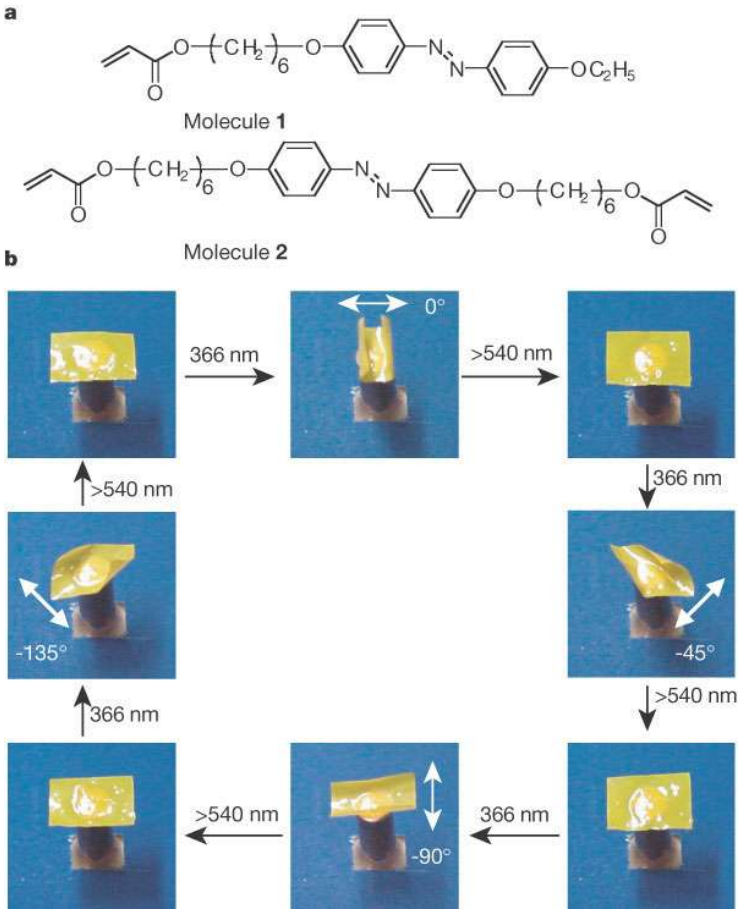


Azobenzene: spectroscopy along femtosecond-laser induced photoisomerization

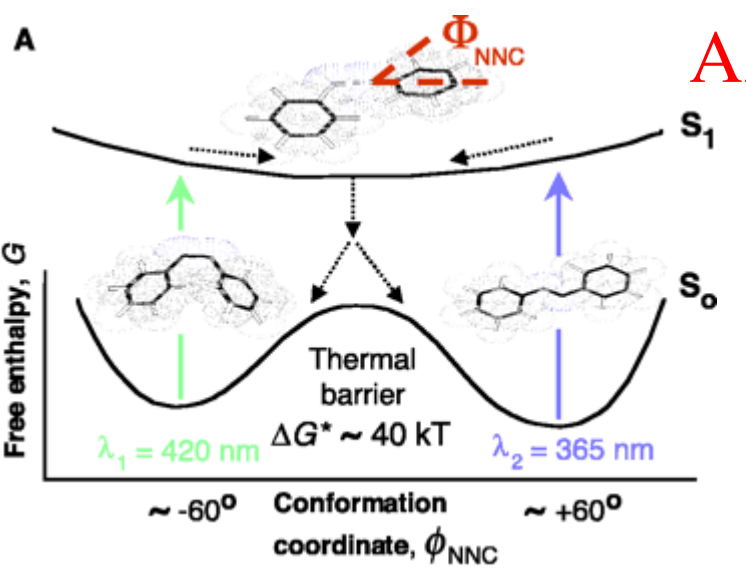
APB optical trigger ***Single-Molecule Optomechanical Cycle***

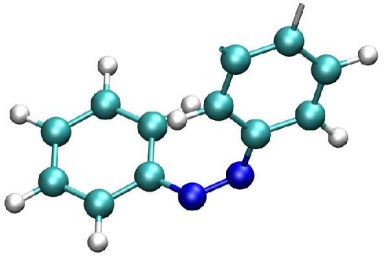


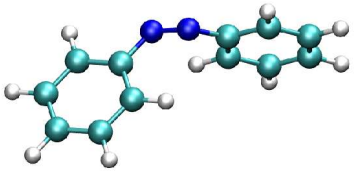


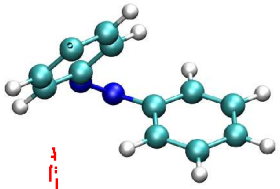


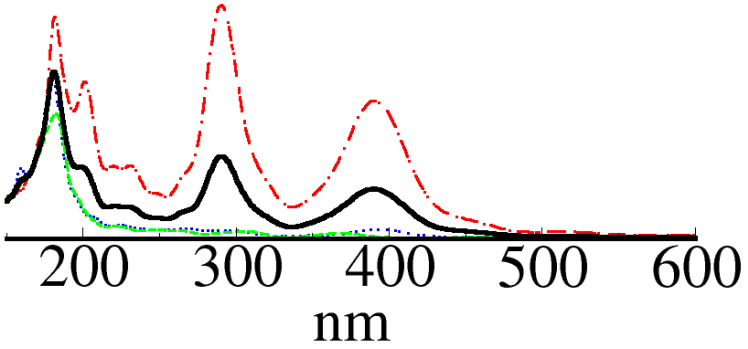
Azobenzene: spectroscopy along femtosecond-laser induced photoisomerization

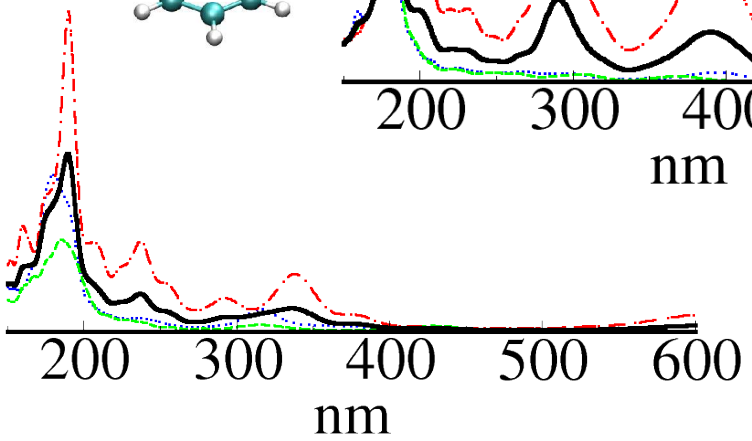


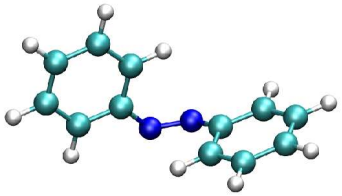


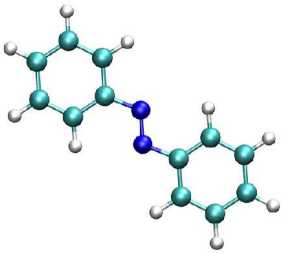












Next step: QM/MM calculation of the chromophore+peptide system

Optical absorption and electron energy loss spectroscopy of extended systems

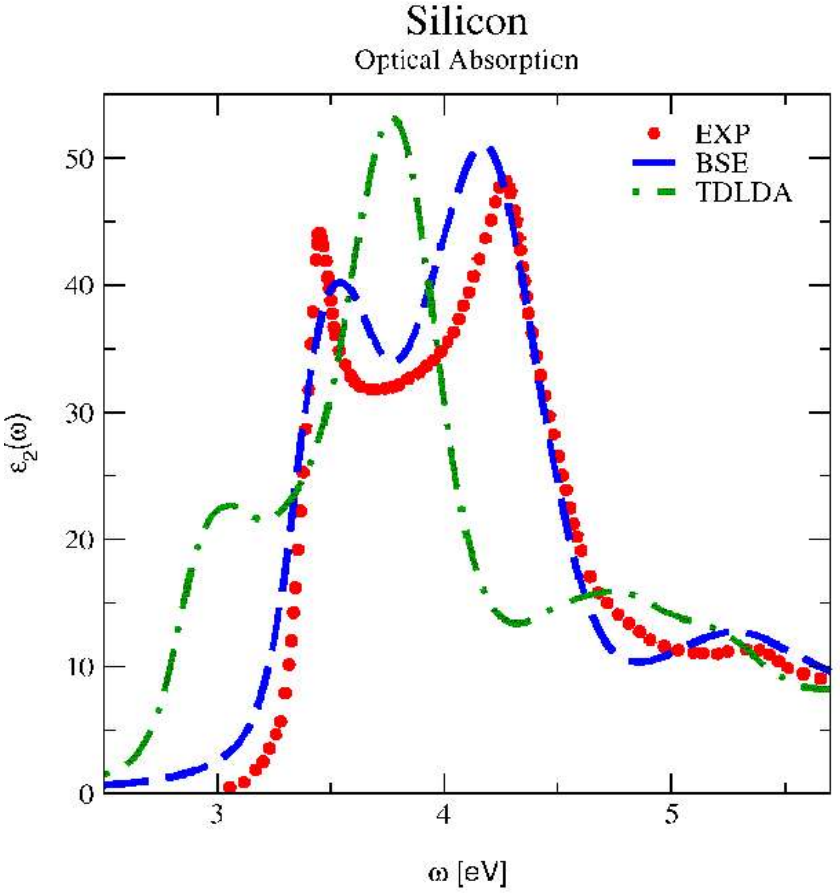
TDDFT:

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

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

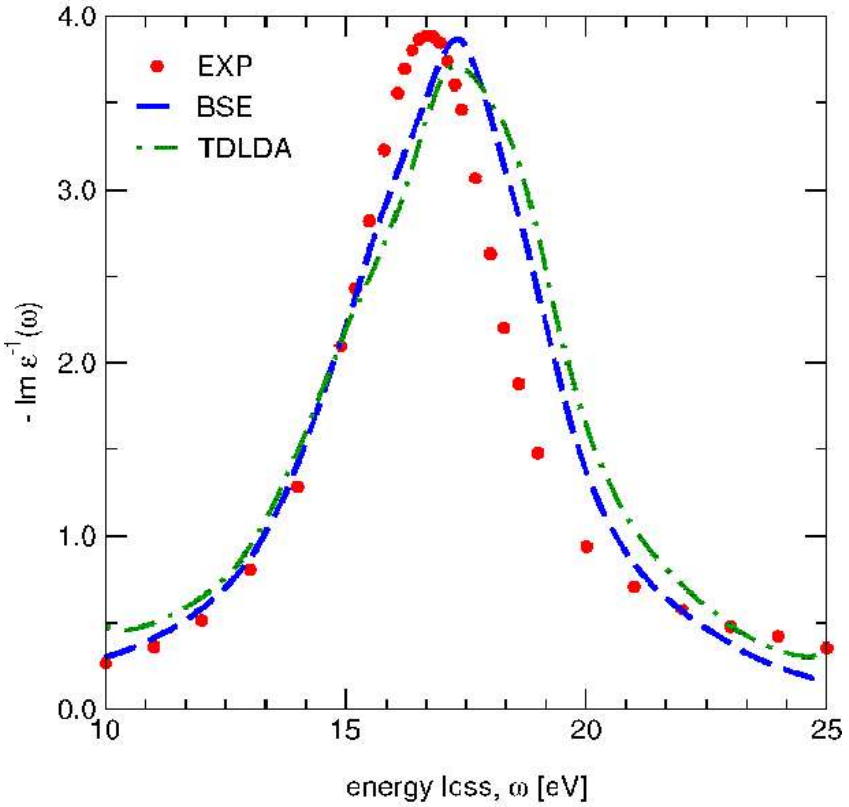
Non-local fxc for extended systems:

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)*

Low dimensional systems (1D): polyacetylane

Electric field dependence of the XC Potential in Molecular Chains

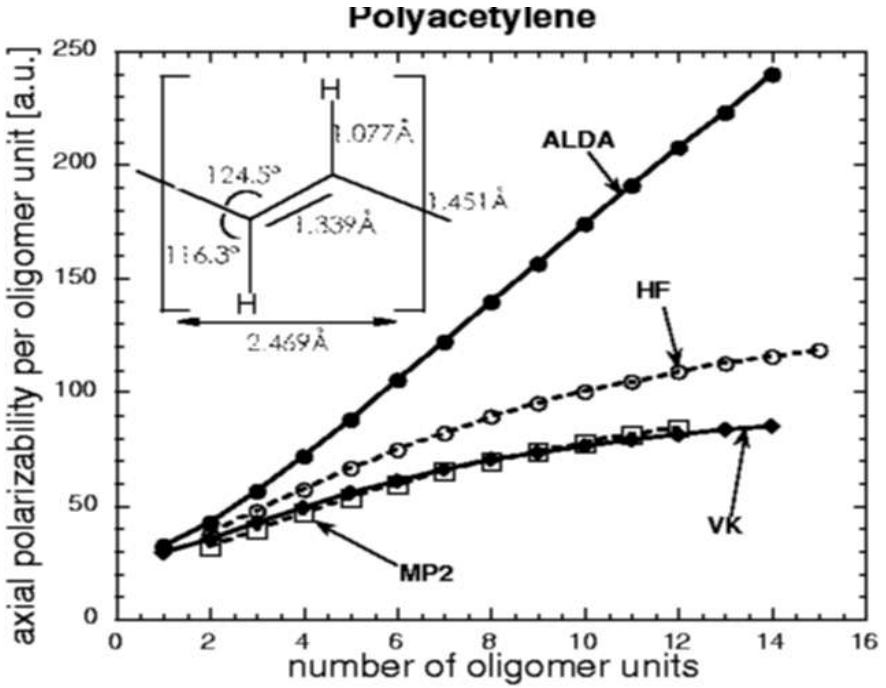


FIG. 1. ALDA and VK static axial polarizability of polyacetylene compared with restricted Hartree-Fock [18] and MP2 [22] results.

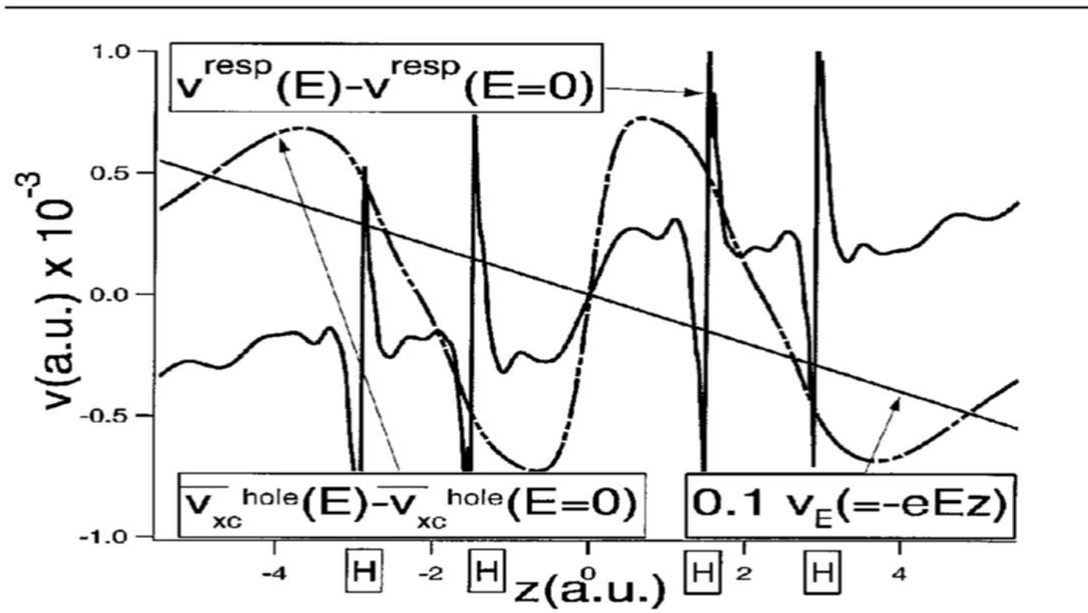


FIG. 2. Changes, due to an electric field of 0.001 a.u. in response and hole potentials for H_2-H_2, constructed from multireference CI singles doubles density with a large (cc-pV6Z without *d* and *f* functions) basis set, compared to the applied field (potential v_E).

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

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

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

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 nth order contribution

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

4-point equations!!!!

$$\text{BSE} \Leftrightarrow \left[\Delta E + < v > - < W > \right] A_\lambda = E_\lambda A_\lambda$$

$$\text{TDDFT} \Leftrightarrow \left[\Delta E + < v > + < f_{xc} > \right] A_\lambda = E_\lambda A_\lambda$$

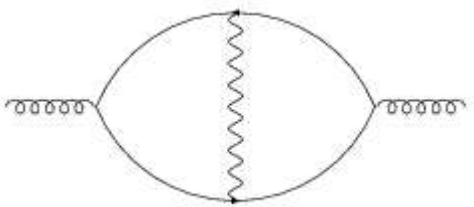
$$< v > = \int d\mathbf{r} d\mathbf{r}' \quad \phi_v(\mathbf{r}) \phi_c^*(\mathbf{r}) \quad v(\mathbf{r}, \mathbf{r}') \quad \phi_{v'}^*(\mathbf{r}') \phi_{c'}(\mathbf{r}')$$

L. Reining, V. Olevano, AR, G. Onida, PRL88, 0664041 (2002);
F. Sottile et al, PRL (2004) ; S. Botti et al, PRB (2004).

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

Bound excitons in TDDFT

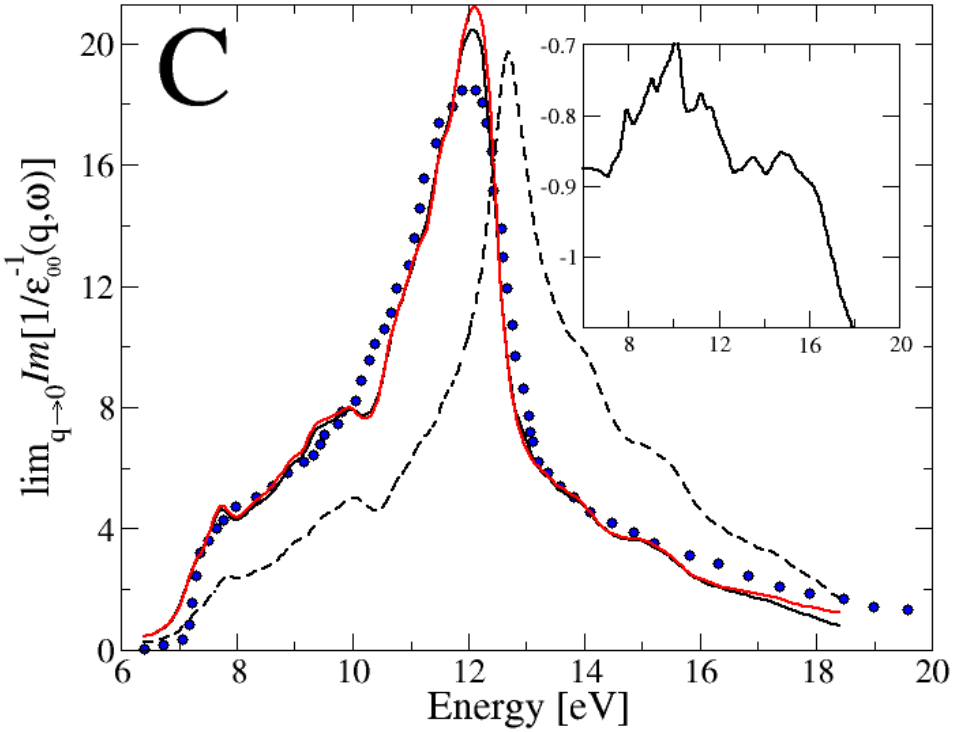
$$\mathbf{f}_{xc}^{(1)}(\mathbf{q},\omega)$$

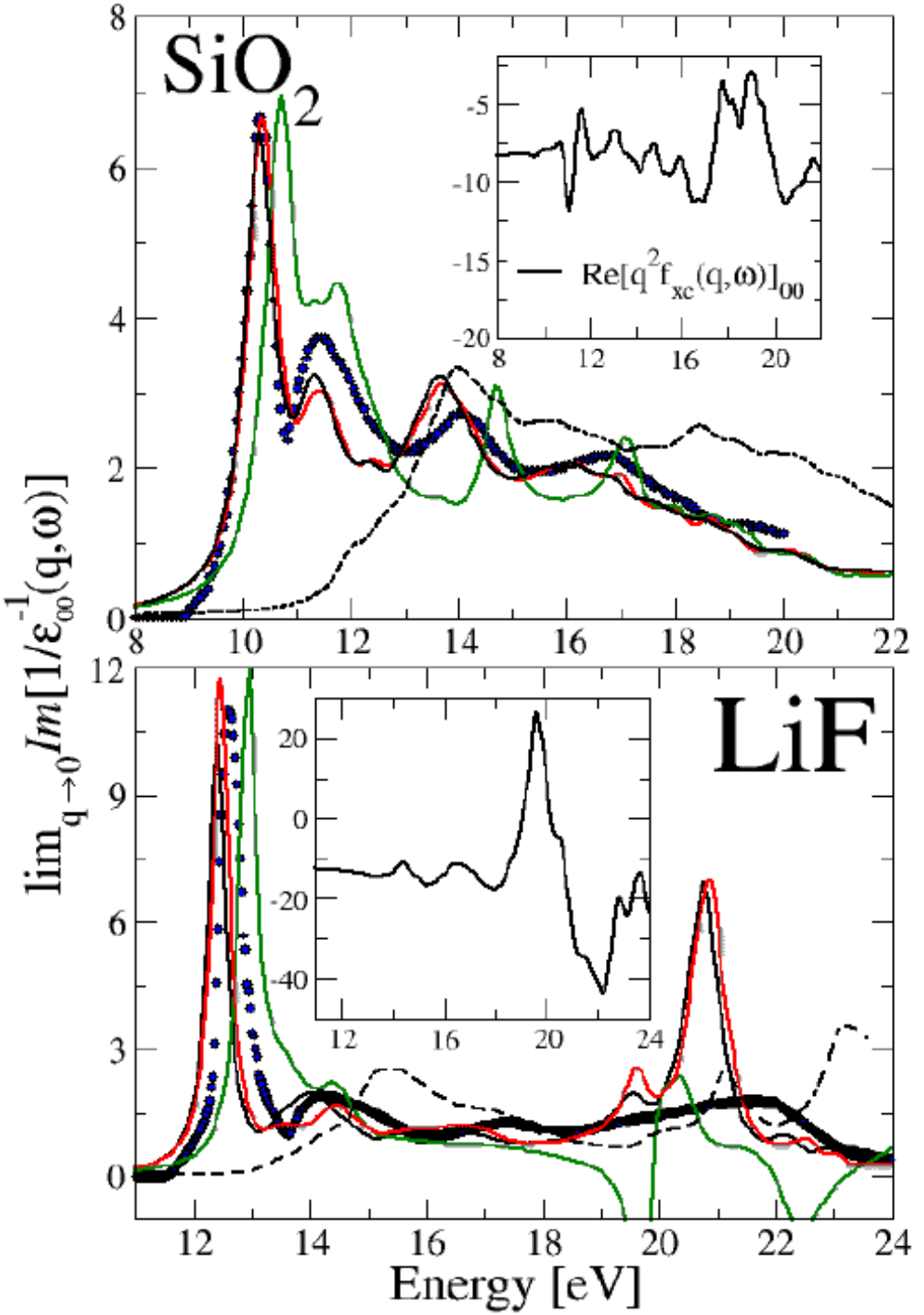


$$:= \left[\mathbf{P}^{(0)}(\omega)\right]^{-1}$$

— *TDDFT* ●●● *Experiment*

— *BSE* — *TDDFT, scalar fxc*



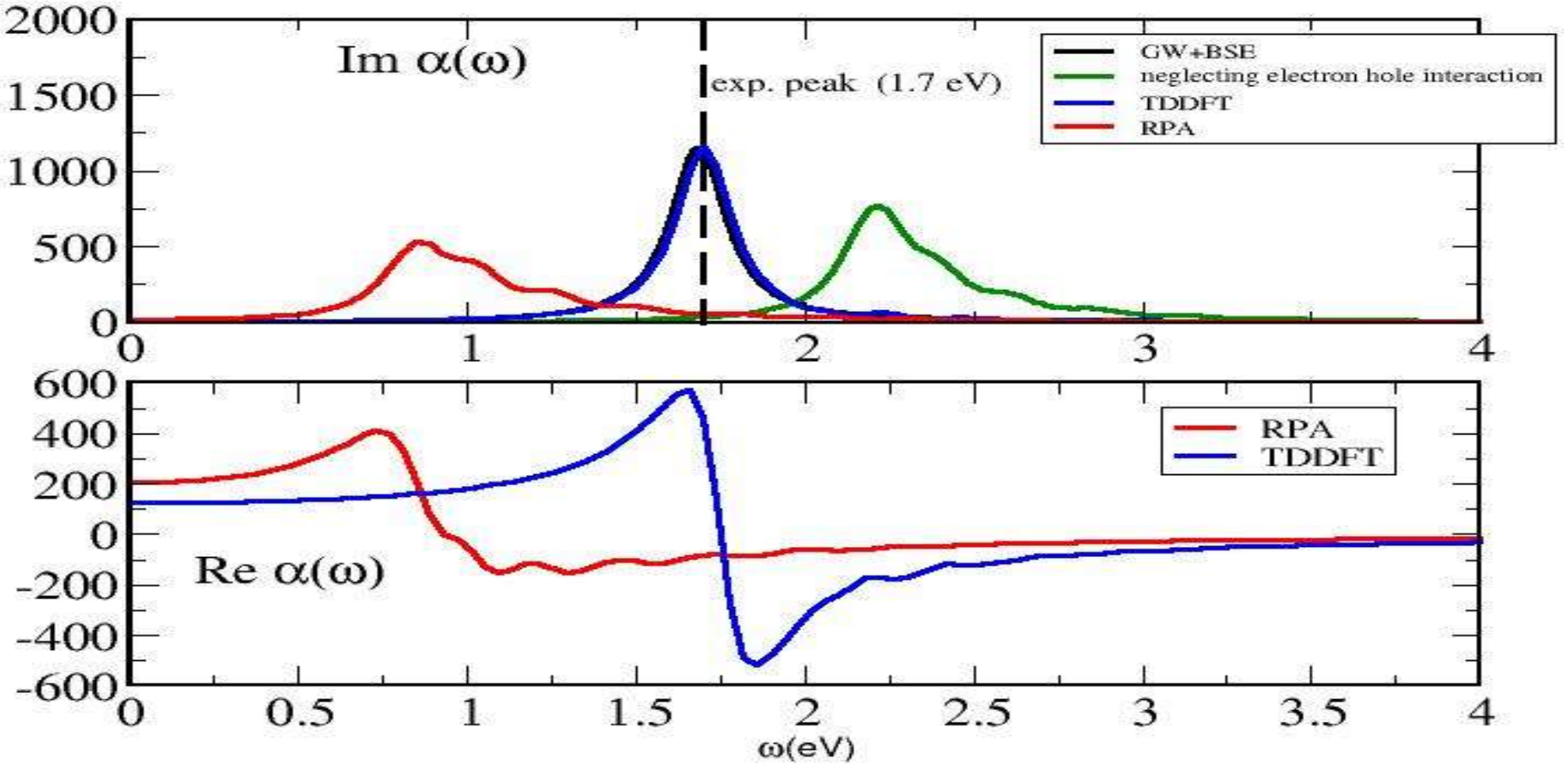


A. Marini, R. Del Sole and AR, PRL (2003)

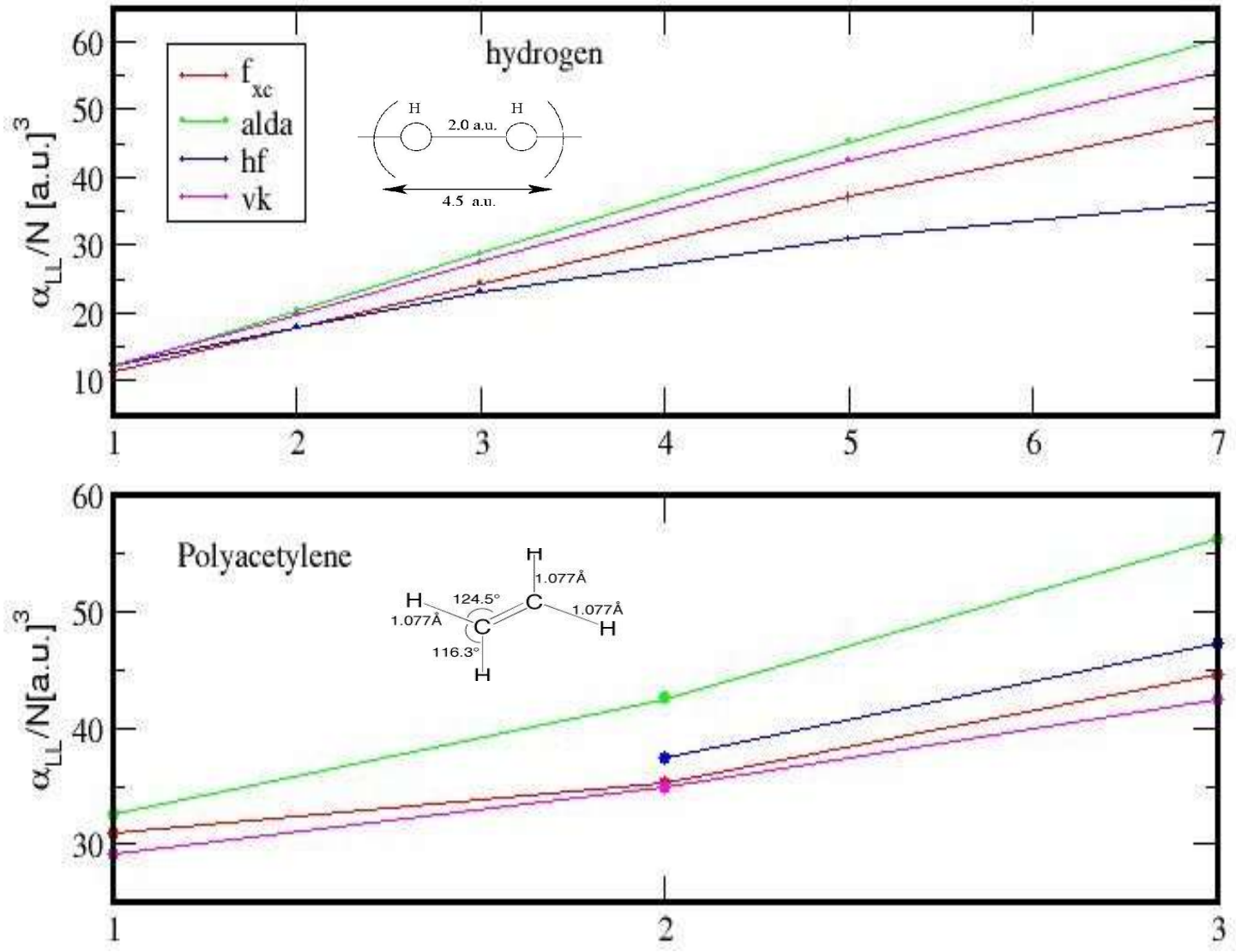
Low dimensional sytems (1D): polyacetylane

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

Isolated infinite Polyacetylene chain



Longitudinal polarizabilty per Monomer



Low dimensional sytems (1D): polyacetylane

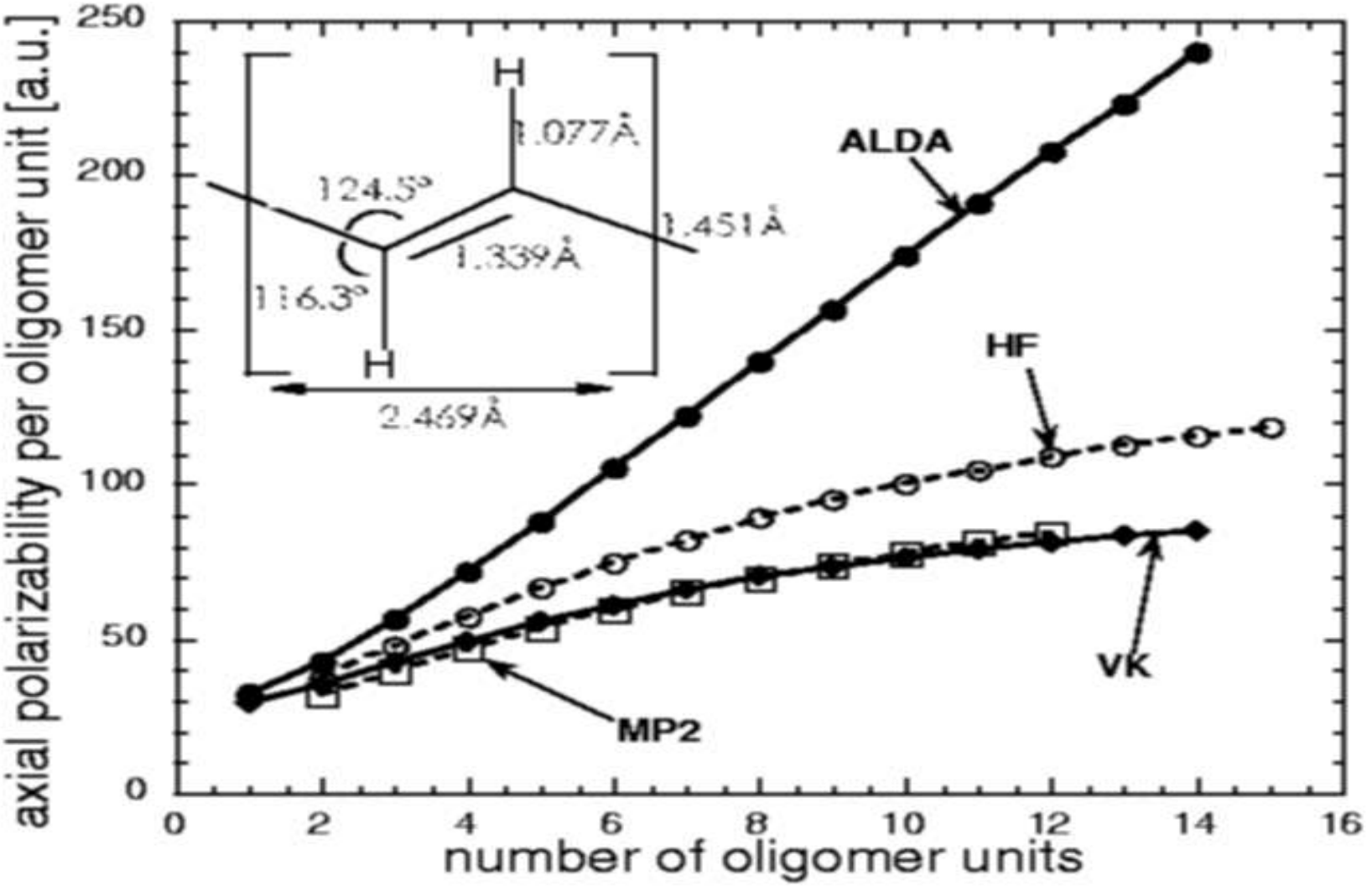
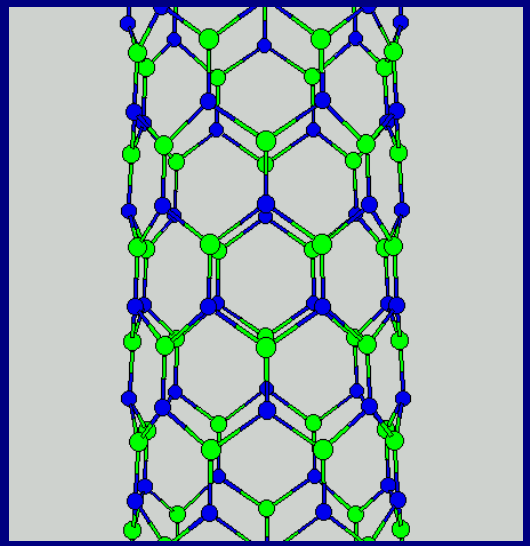


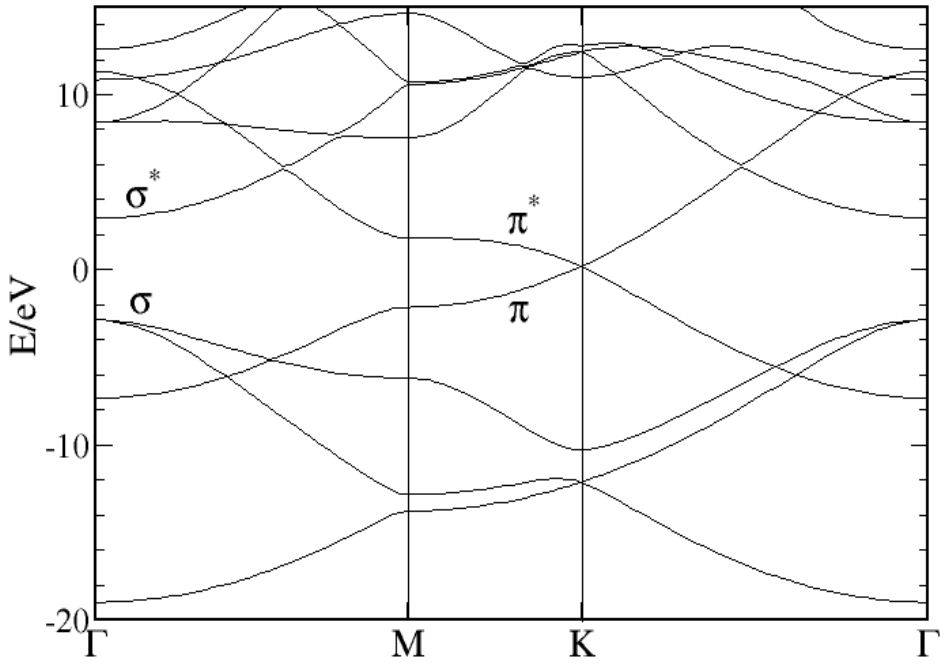
FIG. 1. ALDA and VK static axial polarizability of polyacetylene compared with restricted Hartree-Fock [18] and MP2 [22] results.

Bound Excitons in BN nanotubes (also relevant for C)

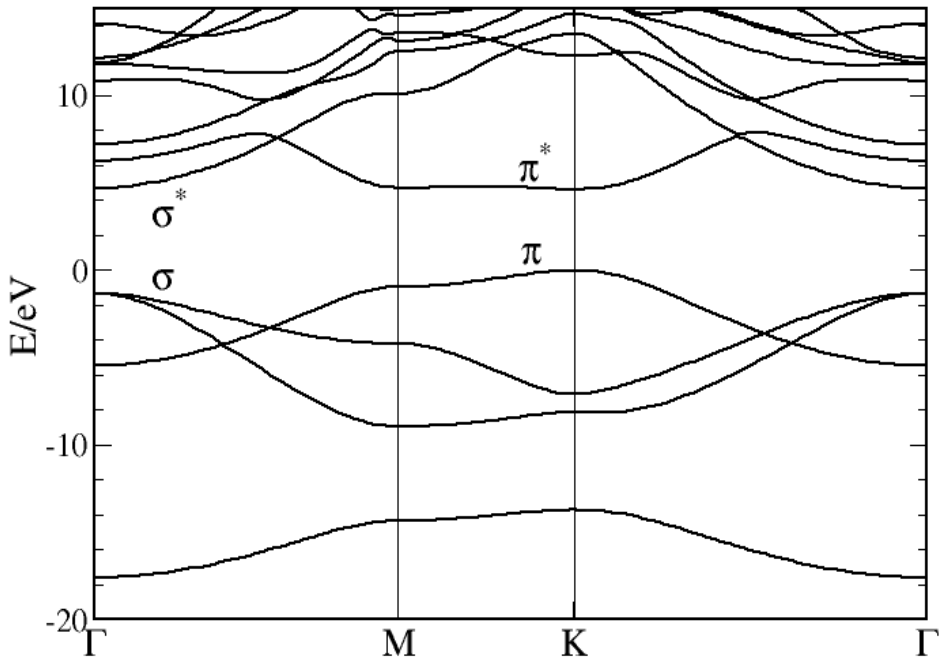


dimensionality efffects

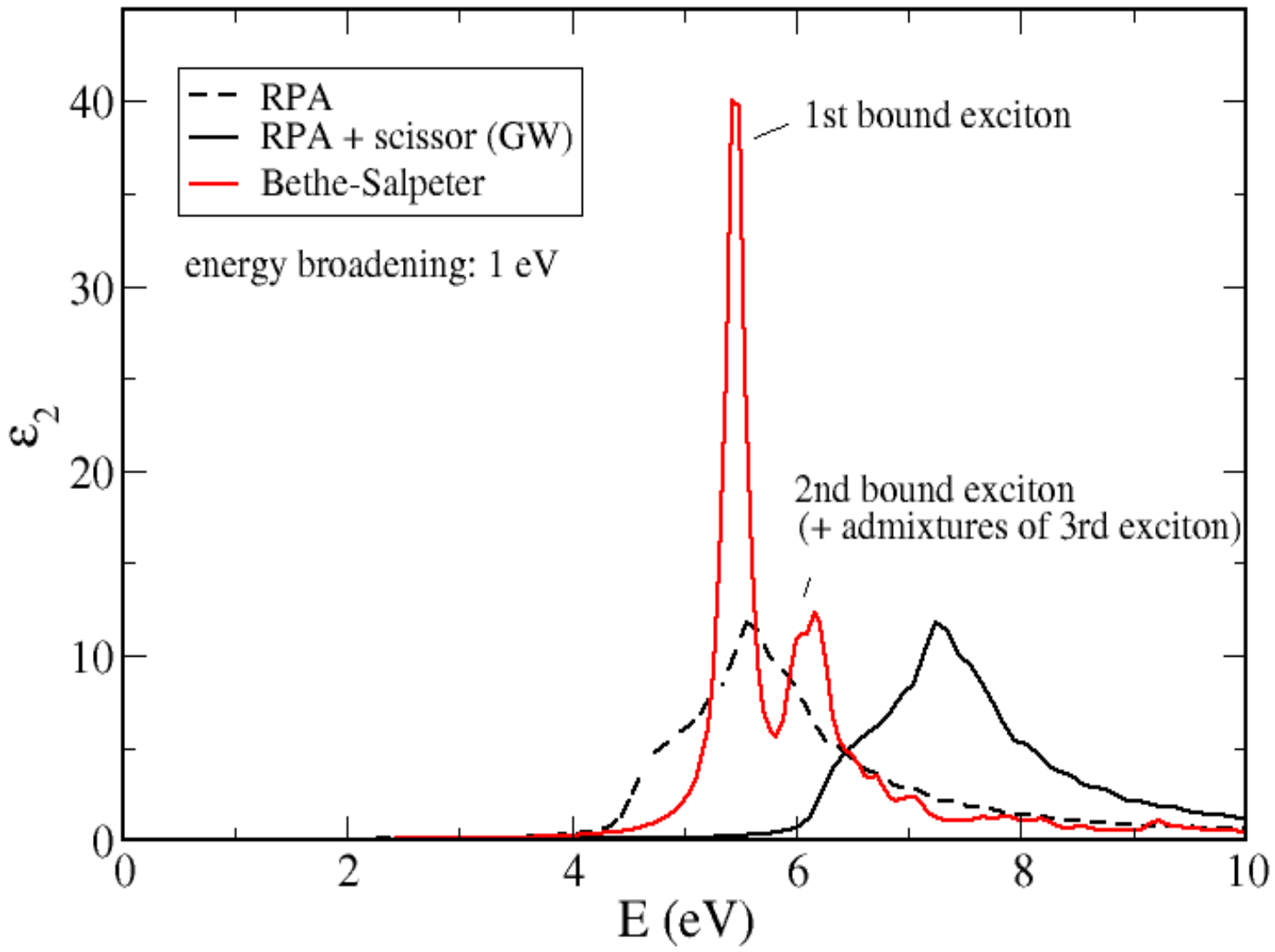
graphite (black)



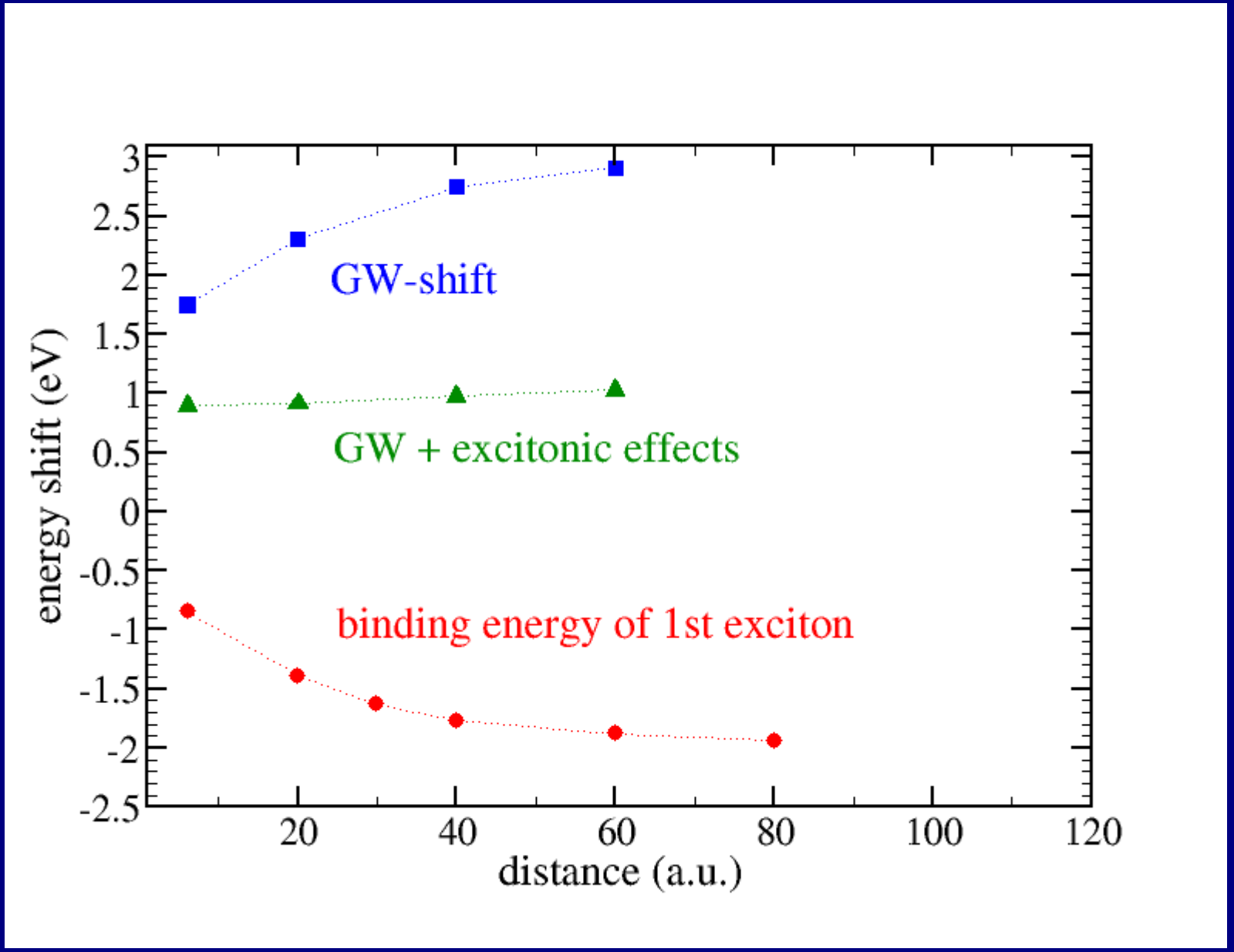
BN-sheet (transparent)



Bound excitons in bulk h-BN

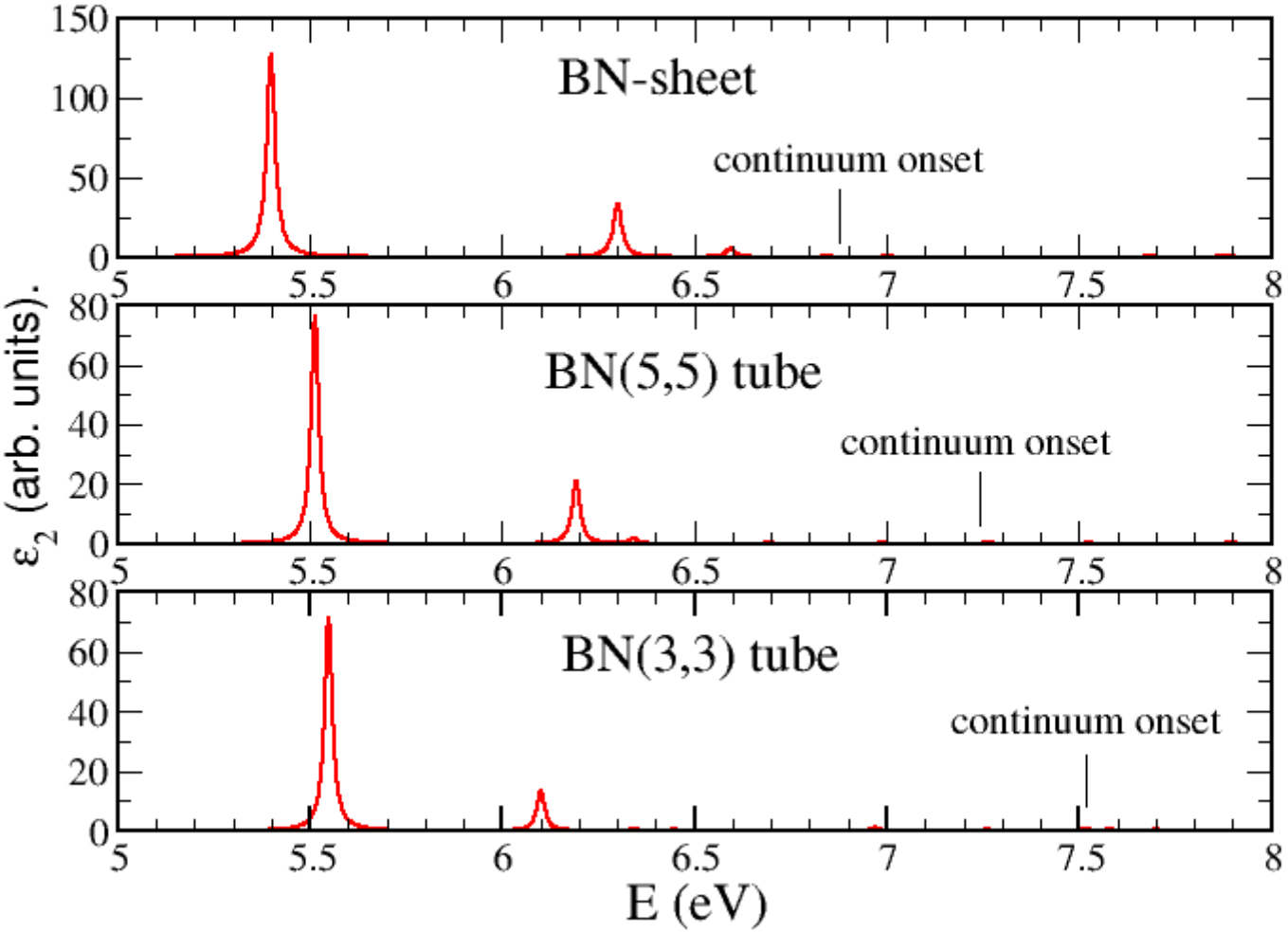


Combined effect of GW-shift and excitons



1st absorption peak remains (almost) at constant position.....

Dimensionality effect: Exciton in (quasi-) 1-D, 2-D, 3-D



Position of first absorption peak almost unchanged

Distance between the peaks and the continuum changes

Summary

- TDDFT is a powerful tool to handle the combined dynamics of electron/ion in response to external electromagnetic fields of nanostructures, biological molecules and extended systems.

- Problem: we need better fxc functionals based on either DFT (or current-DFT) or MBPT approaches

Ongoing work on applications to:

- T*ime-resolved spectroscopies: pump-probe simulations.*
- *High-harmonic generation from quantum dots.*
- *QM/MM: for excited-state dynamics in biomolecules: photoisomerisation*
- *Control chemical reactivity:Pulse optimization in laser induced reaction*
- *Non-linear effects in One-dimensional systems*
- *Time-dependent Molecular transport !!!!!!!!*
- *Quantum nuclei, etc.....*

www.tddft.org/programs/octopus

Acknowledgments

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

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, S. Botti, F. Sottile, V. Olevano

École Polytechnique, Palaiseau, France

S.G. Louie and M.L. Cohen

Department of Physics, University of California at Berkeley, USA

G.F. Bertsch

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

R. Del Sole and G. Onida

INFM e Dipartimento di Fisica dell'Università di Roma ``Tor Vergata'', Roma, Italy

Thank you

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