

Challenges and Perspectives from (TD) Density Functional Theory: From Low-Dimensional Structures to Real Materials

Angel Rubio

*NanoBio Spectroscopy Group and ETSF Scientific Development Centre
Dpto. Física de Materiales, Universidad del País Vasco,
Centro Física de Materiales CSIC-UPV/EHU San Sebastián, Spain
and FHI Max-Planck-Gesellschaft, Berlin, Germany*

<http://nano-bio.ehu.es> E-mail: angel.rubio@ehu.es



The Conference covers **DFT/TDDFT**, Quantum Chemistry, Quantum Monte Carlo, Many-body Perturbation Theory, Dynamical Mean-Field Theory, etc

Review talks:

- | | |
|------------------------|--|
| Lucia Reining | Many-Body Perturbation Theory: |
| Silke Biermann | Dynamical Mean Field Theory |
| Roberto Car | Electron Transport at the Molecular Scale: |
| Matthew Foulkes | Quantum Monte Carlo Methods: |



OUTLINE

Introduction:

DFT: some (bias non exhaustive) open problems

- * long range potential
- * dispersion forces: vdW, etc.
- * band-gap problem: local, vs non-local potentials
Hybrids.....

Excitations: TDDFT Application to finite systems:

Linear Response applications :

“small clusters, phenolates and porphyrines”

Spectroscopy of Solids:

Problems with standard XC functionals:

link to DFT polarisation theory

Applications to 1D: Linear chains and polymer



DFT Success “~chemical accuracy”

Structural properties, stability, phonons

Phase transitions

Surface catalysis and chemical reactivity

Biomodeling



Allows large scale simulations BUT.....

.....present XC-functionals usually fail in describing:

LEVEL ALIGNMENT (KS): DFT-Gap

Long-range potential (atom/molecule)

Dispersion forces VdW, Solvation

Charge-transfer, multiple excitations

Memory effects; Dissipation; lifetime; de-coherence

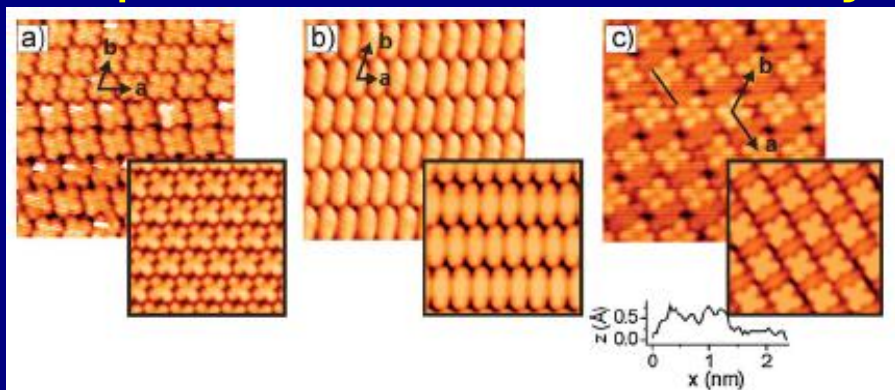
Open shell systems and Open quantum systems

Correlated Materials

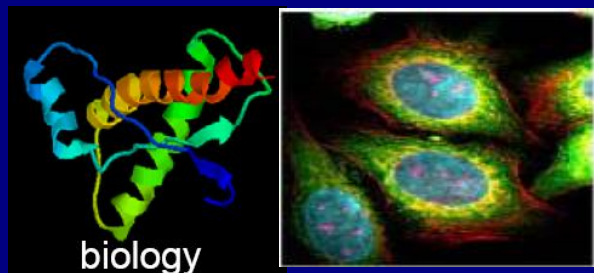


LEVEL ALIGNMENT, Dispersion forces VdW

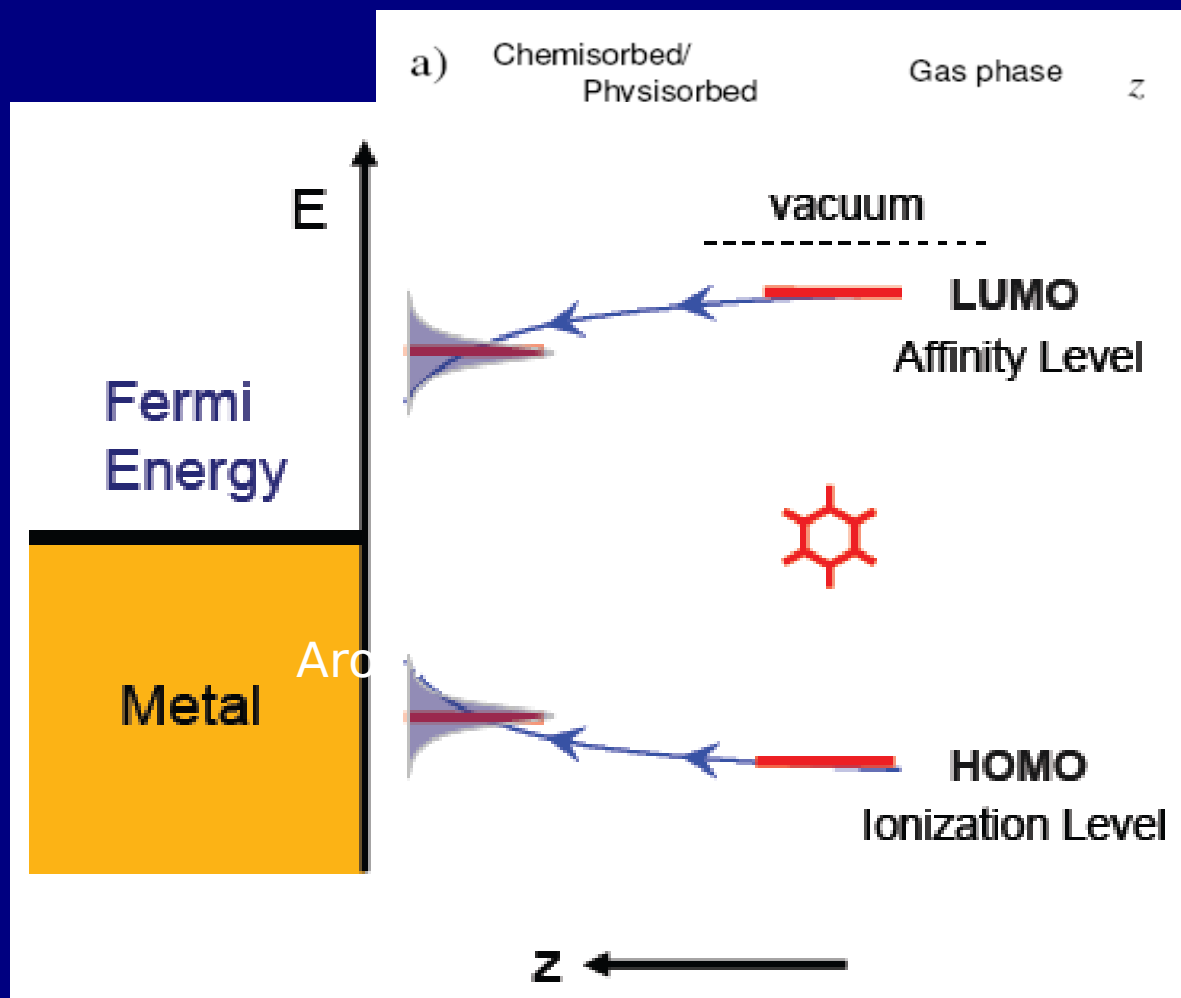
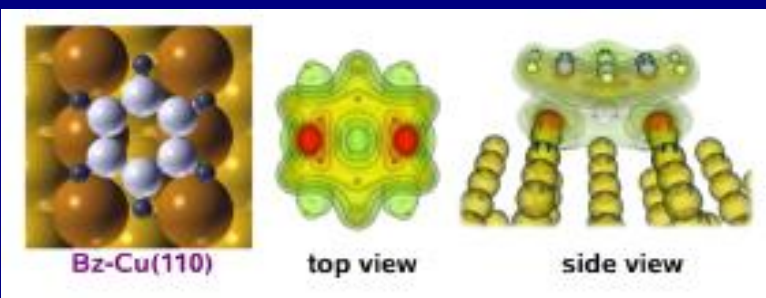
Supramolecular chemistry



Biophysics



Molecular Transport

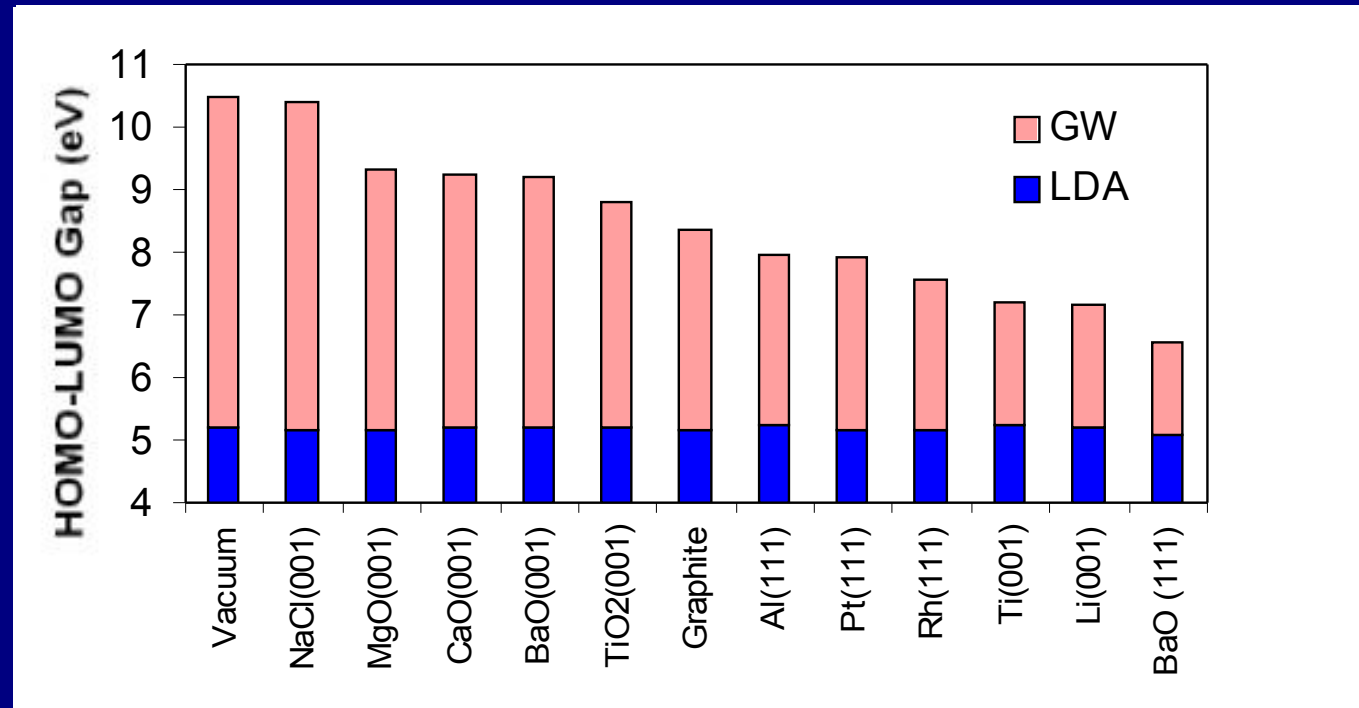
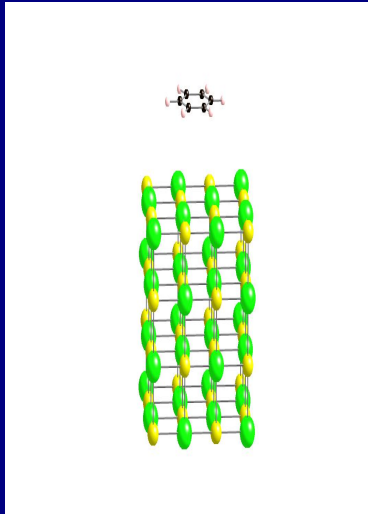


N. Atodiresei, S.Blugel et al, PRL **102**, 136809 (2009)

See the talk of P. Rinke for CO on surfaces

Challenges and Perspectives from (TD) Density Functional Theory
KITP, Santa Barbara, 2nd November 2009

Illustrative Example: physisorbed benzene



LDA gaps are independent of substrate and distance

Same result with other functionals (GGA, hybrid or exact exchange)

GW gaps show large variation across different surfaces

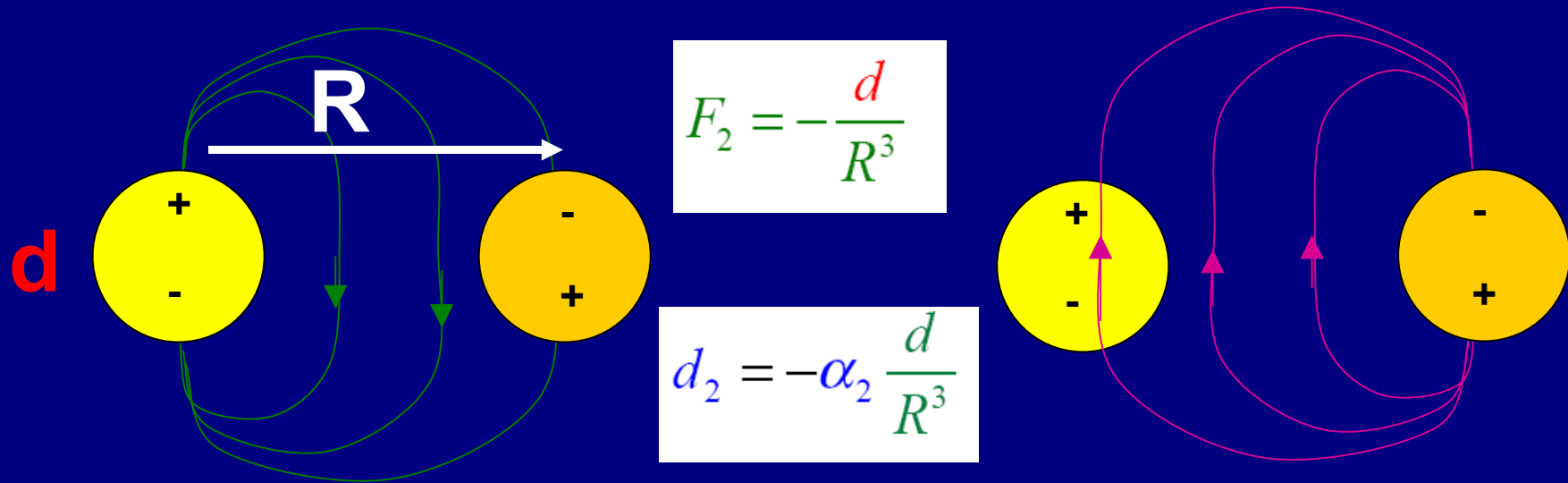
GW gap sensitive to atomistic details **screening is very important**



LONG-RANGED (vdW)

Weak but ubiquitous - additional to covalent, ionic bonds

Basic physics: long-range correlation "fluctuation dipoles"



$$E^{(2)} = -\frac{\alpha_2 \langle d^2 \rangle}{R^6} \approx -\frac{\alpha_2 \alpha_1 \hbar \omega_0}{R^6}$$

More accurate: $E = -C_6 R^{-6}$, $C_6 = \frac{3\hbar}{\pi} \int_0^\infty \alpha_1(iu) \alpha_2(iu) du$

A correlation effect, highly nonlocal so LDA & GGA FAIL



Adiabatic connection dissipation formalism (ACDFT)

$$E_C[n] = -\frac{1}{2} \int_0^1 d\lambda \int dr_1 dr_2 \frac{1}{r_{12}} \left[\frac{1}{\pi} \int_0^{+\infty} d\omega \left[\chi_\lambda(r_1, r_2; i\omega) - \chi_{KS}(r_1, r_2; i\omega) \right] \right]$$

System	Present	Standard
1D metals ^a	$-\mathbf{D}^{-2}(\ln(\mathbf{KD}))^{-3/2}$	$-D^{-5}$
1D insulators [9]	$-D^{-5}$	$-D^{-5}$
2D metals [10,11]	$-\mathbf{D}^{-5/2}$	$-D^{-4}$
π -conjugated layers ^a	$-\mathbf{D}^{-3}$	$-D^{-4}$
1 metallic, 1 π layer ^a	$-\mathbf{D}^{-3} \ln(\mathbf{D}/\mathbf{D}_0)$	$-D^{-4}$
2D insulators [6]	$-D^{-4}$	$-D^{-4}$
Thick metals or ins. [11]	$-D^{-2}$	$-D^{-2}$

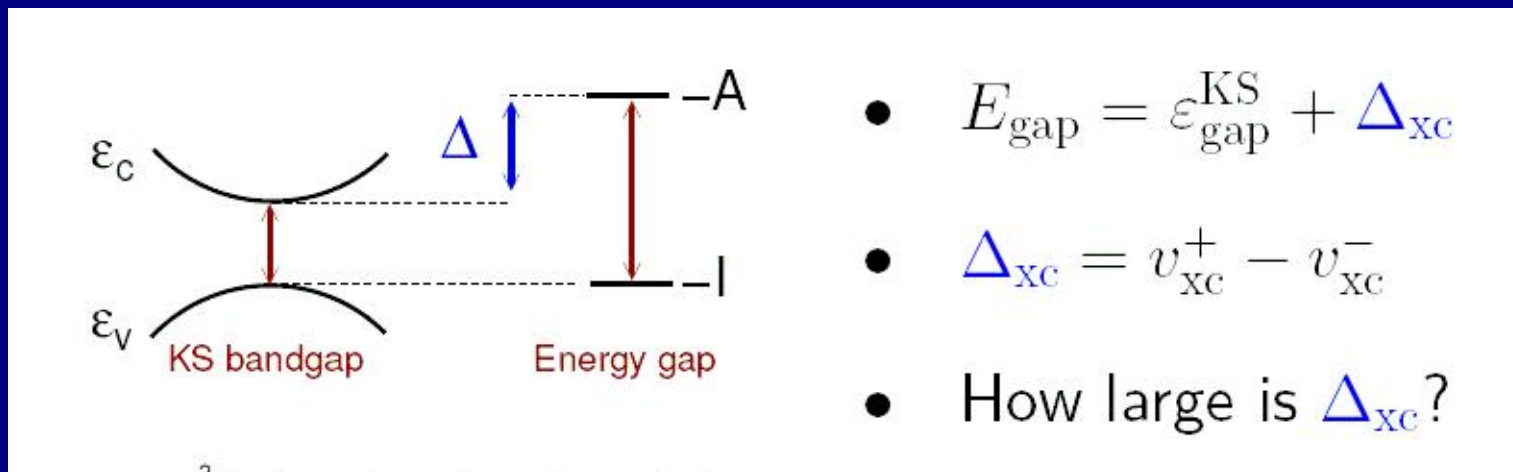
J. Dobson, A. White, AR PRL (2006);

Challenges and Perspectives from (TD) Density Functional Theory
KITP, Santa Barbara, 2nd November 2009



Band-gap of Solids: not the difference of KS eigenvalues?

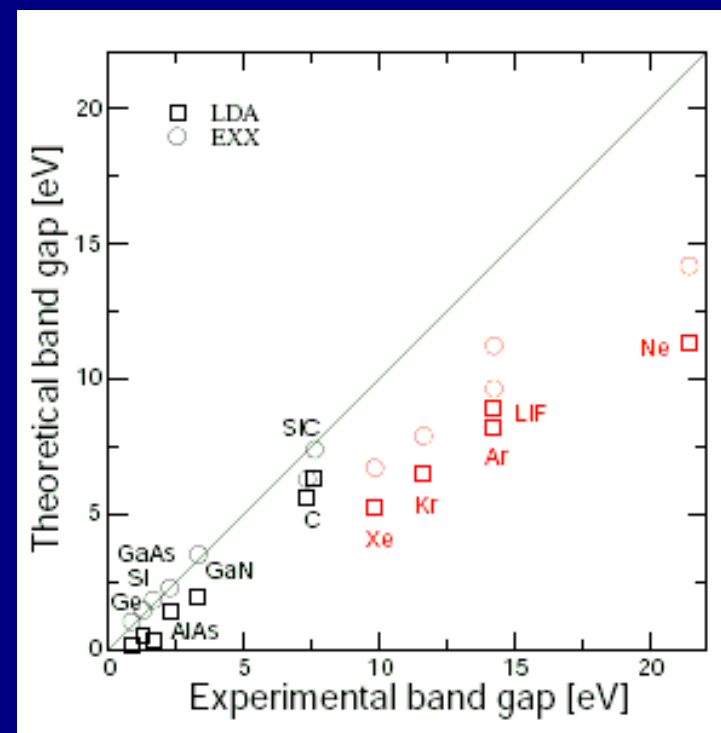
J.P. Perdew, M. Levy PRL 51, 1884 (1983); L.J. Sham, M. Schlüter PRL 51, 1888 (1983)



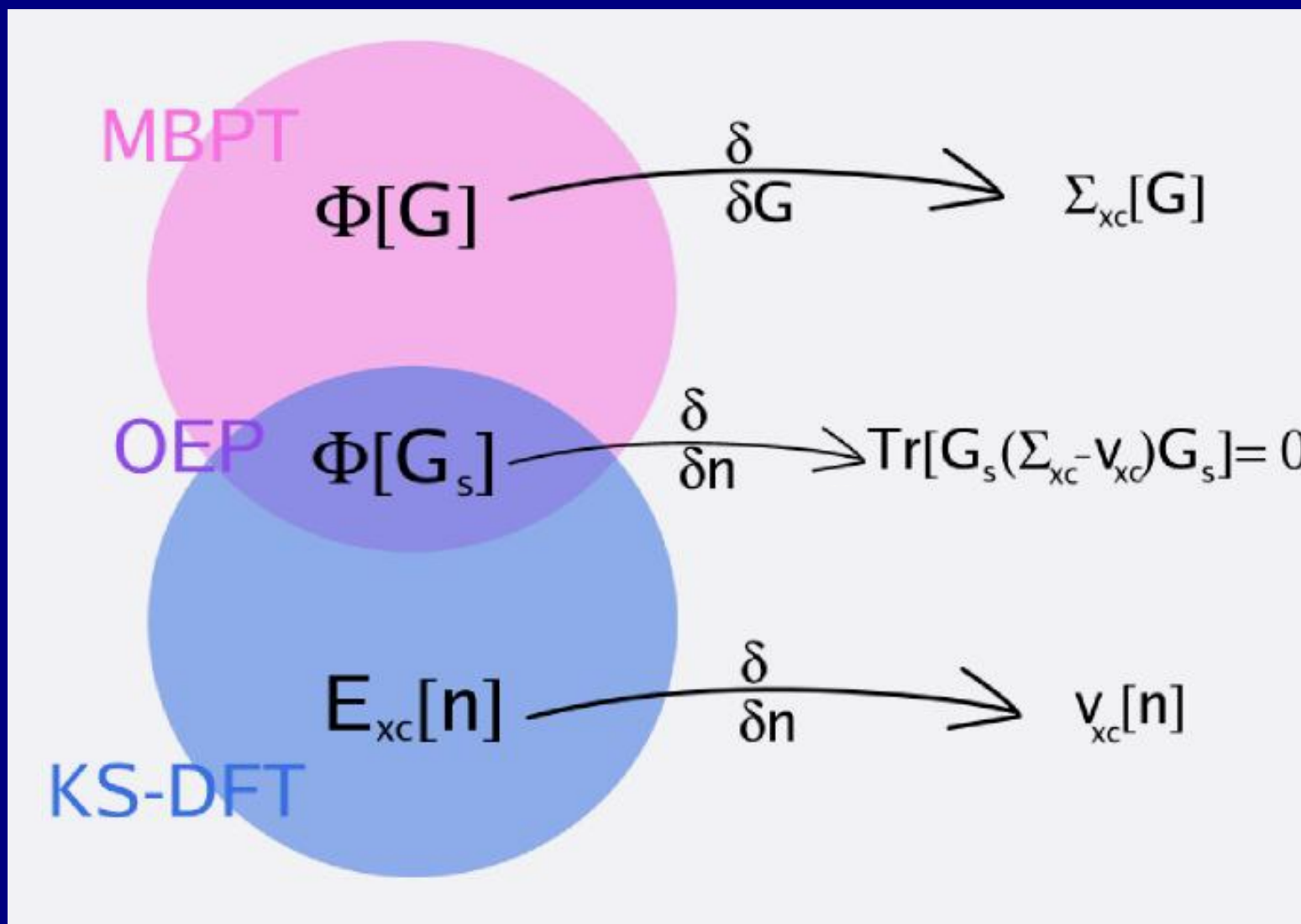
Problems of the EXX for wide-band-gap insulators Improved with new hybrid functionals

- Role of correlation?
 - ▷ LDA/GGA correlation not good
 - ▷ LDAx: part of correlation effects

Städele et al. PRB 59, 10031 (1999)
Magyar et al. PRB 69, 045111 (2004);
Sharma et al. PRL 95, 136402 (2005)



Accurate potentials can be obtained from MBPT expressions



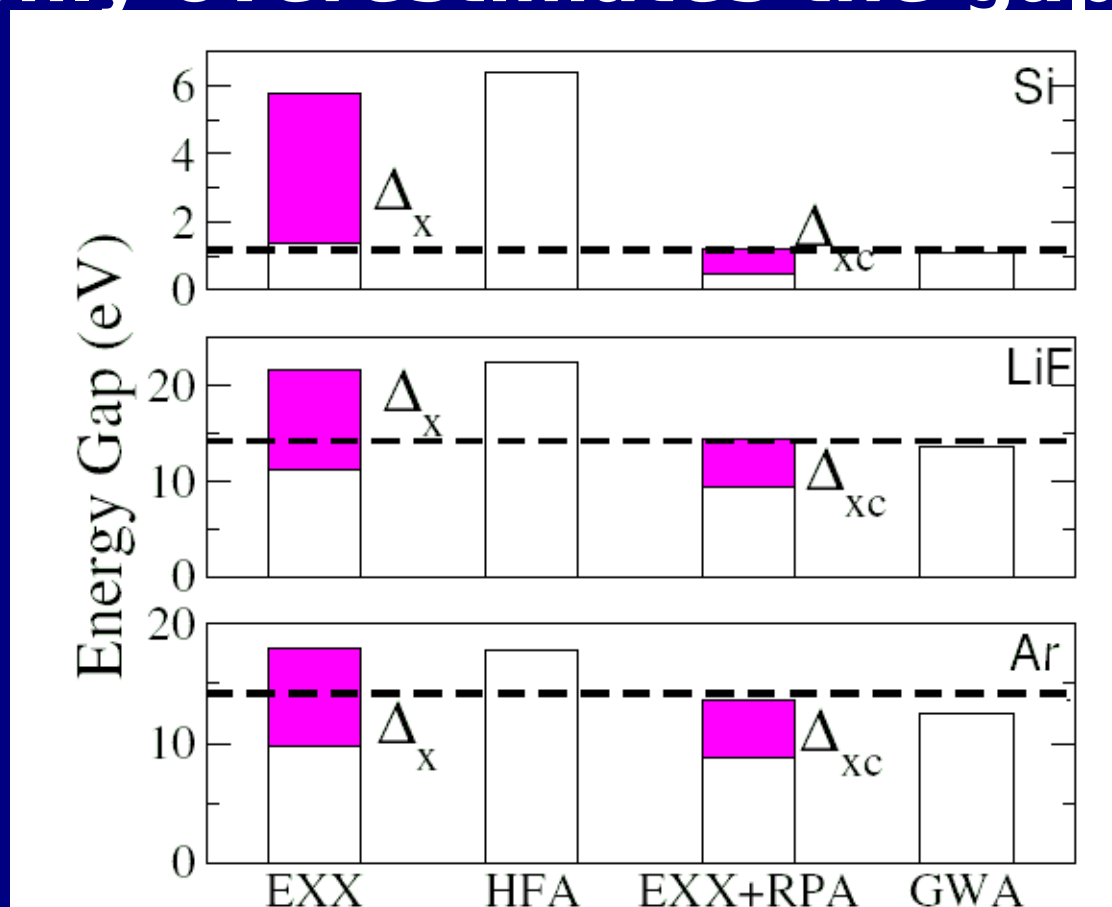
Linearised
Sham-Schlüter
equation



Estimate of the derivative discontinuity

30 to 50% comes from EXX+RPA

EXX only overestimates the gap (HF)



$$\Delta_{xc} = E_{\text{gap}} - E_{\text{gap}}^{\text{KS}} = \langle c | \sum_{xc} (\epsilon_c) - v_{xc} | c \rangle - \langle v | \sum_{xc} (\epsilon_v) - v_{xc} | v \rangle$$

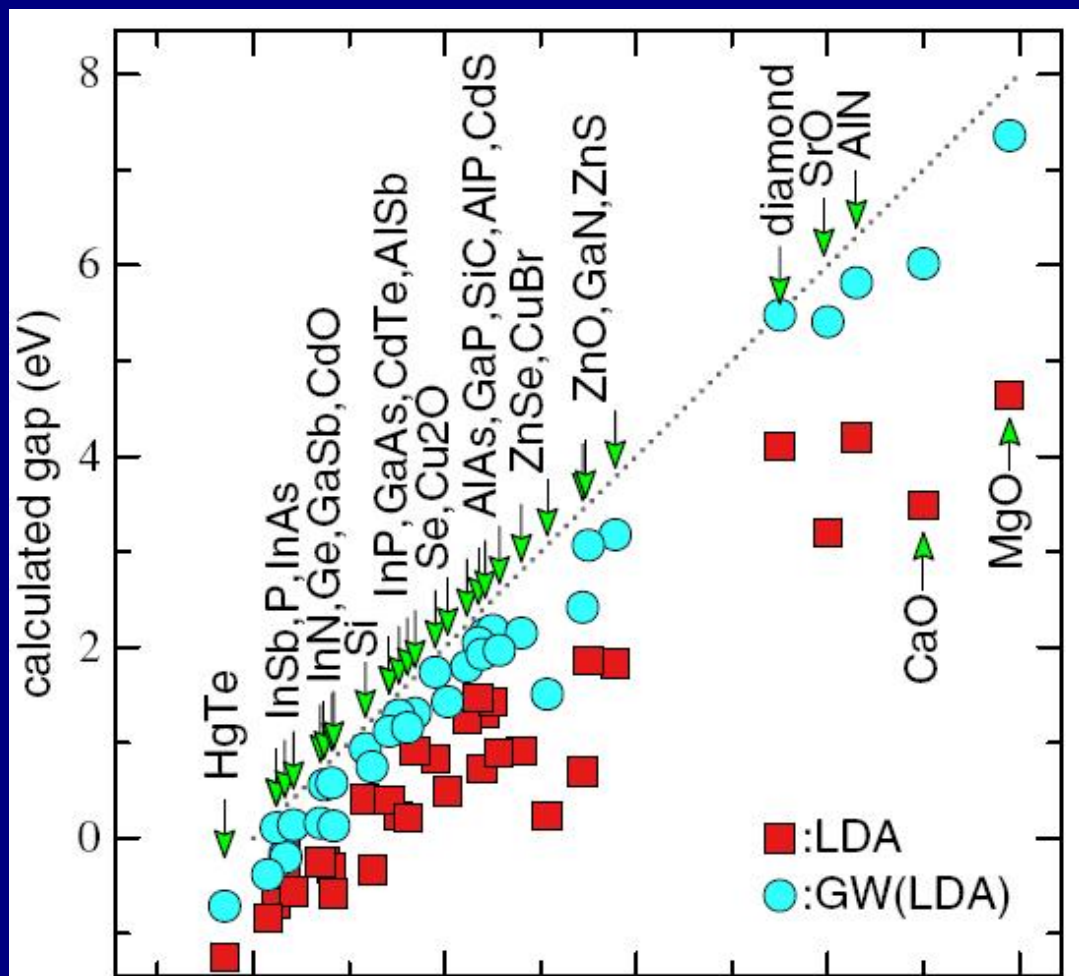
Grüning, Marini & Rubio JCP (2006); PRB(2007)

Challenges and Perspectives from (TD) Density Functional Theory
KITP, Santa Barbara, 2nd November 2009



Approximate the xc-non-local potential in terms of a real-GW selfenergy

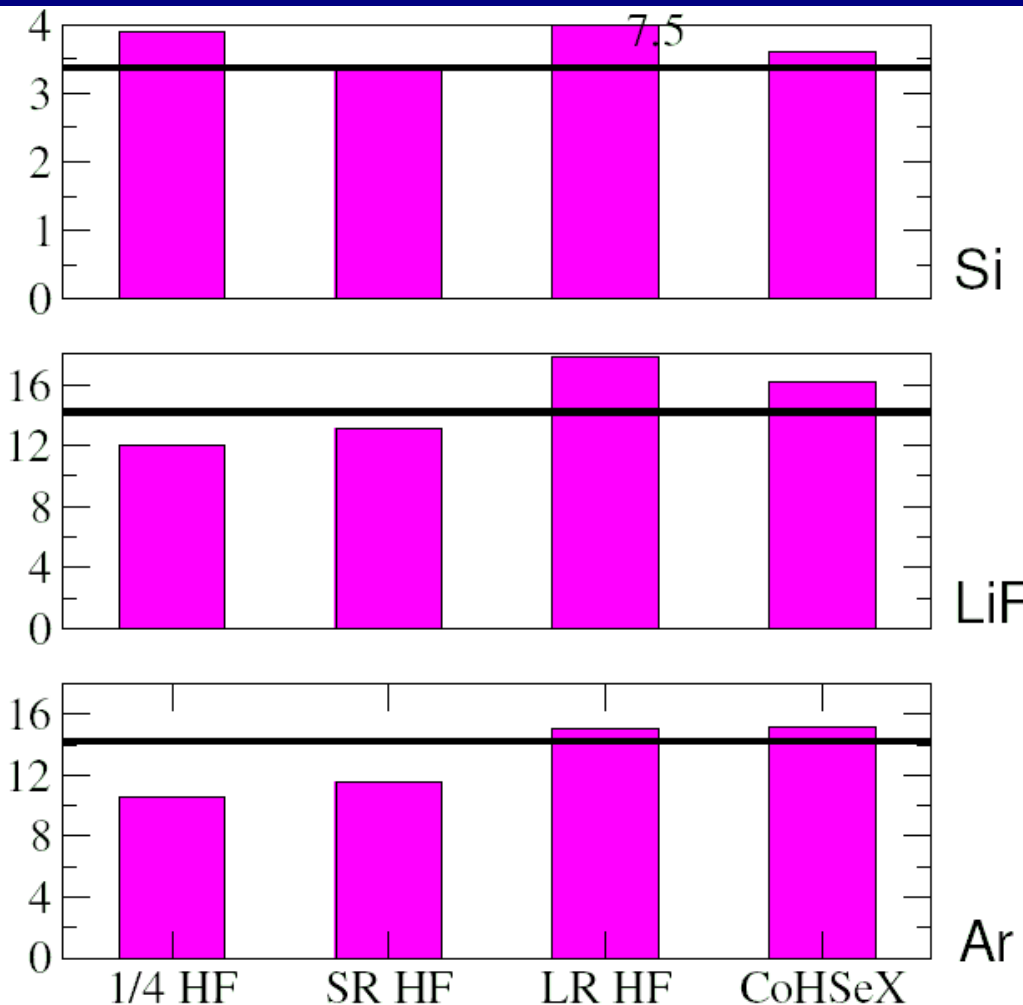
What is the best V_{xc} that reproduces the quasiparticle spectra?



Schilfgaarde, Kotani, and Faleev, PRL 96, 226402 (2006)



However, none of the mixing scheme gives good results for both semiconductors and insulators



$$E_{\text{xc}} = E_{\text{xc}}^{\text{den},\gamma}[n] + E_{\text{xc}}^{\text{orb},\gamma}[\{\psi_i\}]$$

$$E_{\text{xc}}^{\text{orb},\gamma} = -\frac{1}{4} \int d\mathbf{r} \int d\mathbf{r}' n(\mathbf{r}', \mathbf{r}) w^\gamma(\mathbf{r}, \mathbf{r}') n(\mathbf{r}, \mathbf{r}'),$$

$$w^\gamma(\mathbf{r}, \mathbf{r}') = \int d\mathbf{r}'' \frac{(\epsilon^\gamma)^{-1}(\mathbf{r}, \mathbf{r}'')}{|\mathbf{r}'' - \mathbf{r}'|}.$$

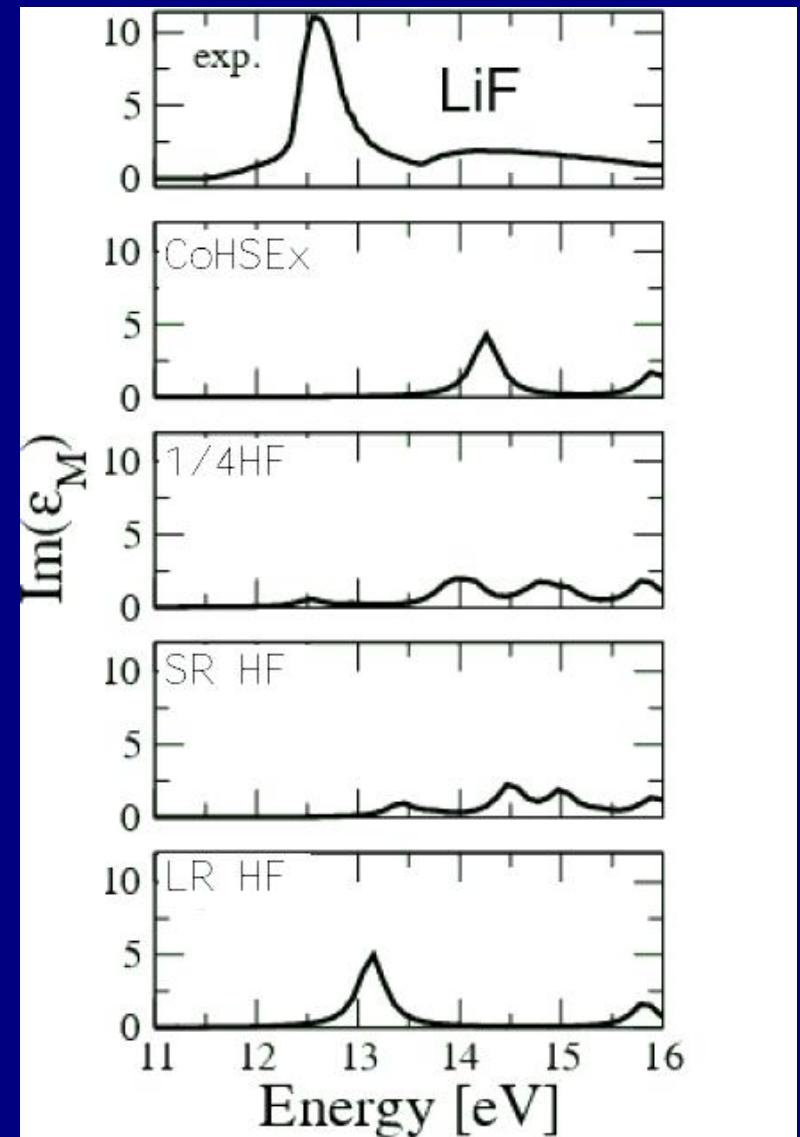
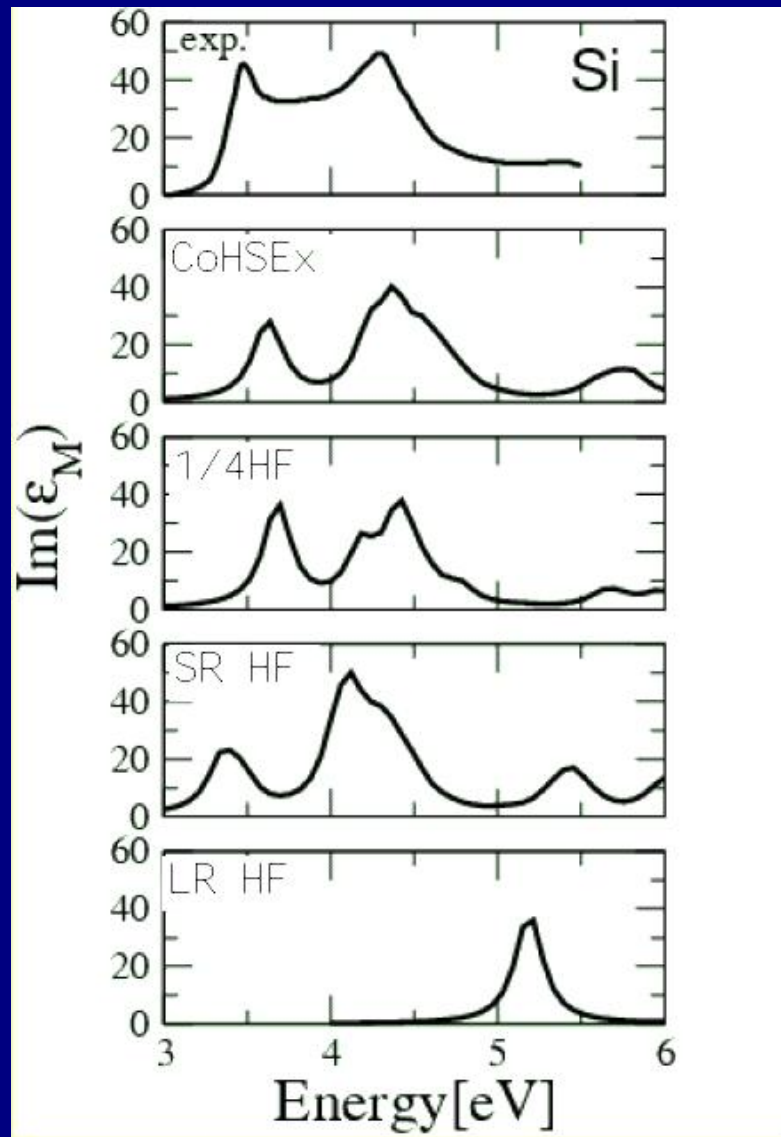
$$\text{1/4 HF: } (\epsilon^\gamma)^{-1}(\mathbf{r}, \mathbf{r}'') = \delta(\mathbf{r}' - \mathbf{r}'') \gamma$$

$$\text{SR HF: } (\epsilon^\gamma)^{-1}(\mathbf{r}, \mathbf{r}'') = \delta(\mathbf{r}' - \mathbf{r}'') e^{-\gamma(\mathbf{r}-\mathbf{r}'')}$$

$$\text{LR HF: } (\epsilon^\gamma)^{-1}(\mathbf{r}, \mathbf{r}'') = \delta(\mathbf{r}' - \mathbf{r}'') (1 - e^{-\gamma(\mathbf{r}-\mathbf{r}'')})$$



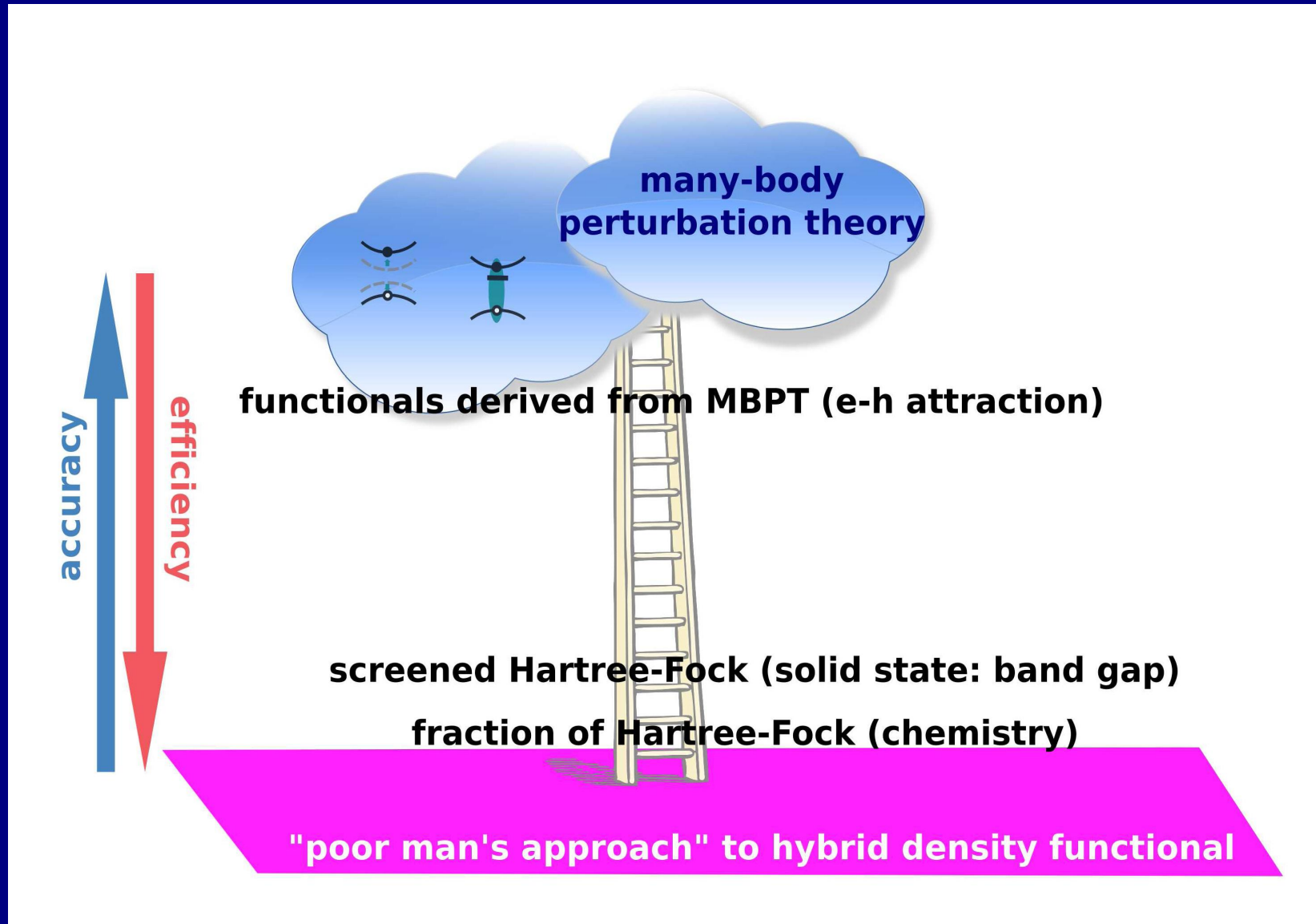
The mixing that is good for the Gap is not for optical spectra



The non-local potential corrects the gap (not exact) however screening is difficult to model properly



Density Functional versus Many-body perturbation theory (challenge)



EXACT ALTERNATIVE:

(Runge and Gross 1984):

Time Dependent Density Functional Theory

All observables are functionals of the TD density

One-to-one correspondence between the time-dependent density and the external potential, $v(r,t) \longleftrightarrow \rho(r,t)$

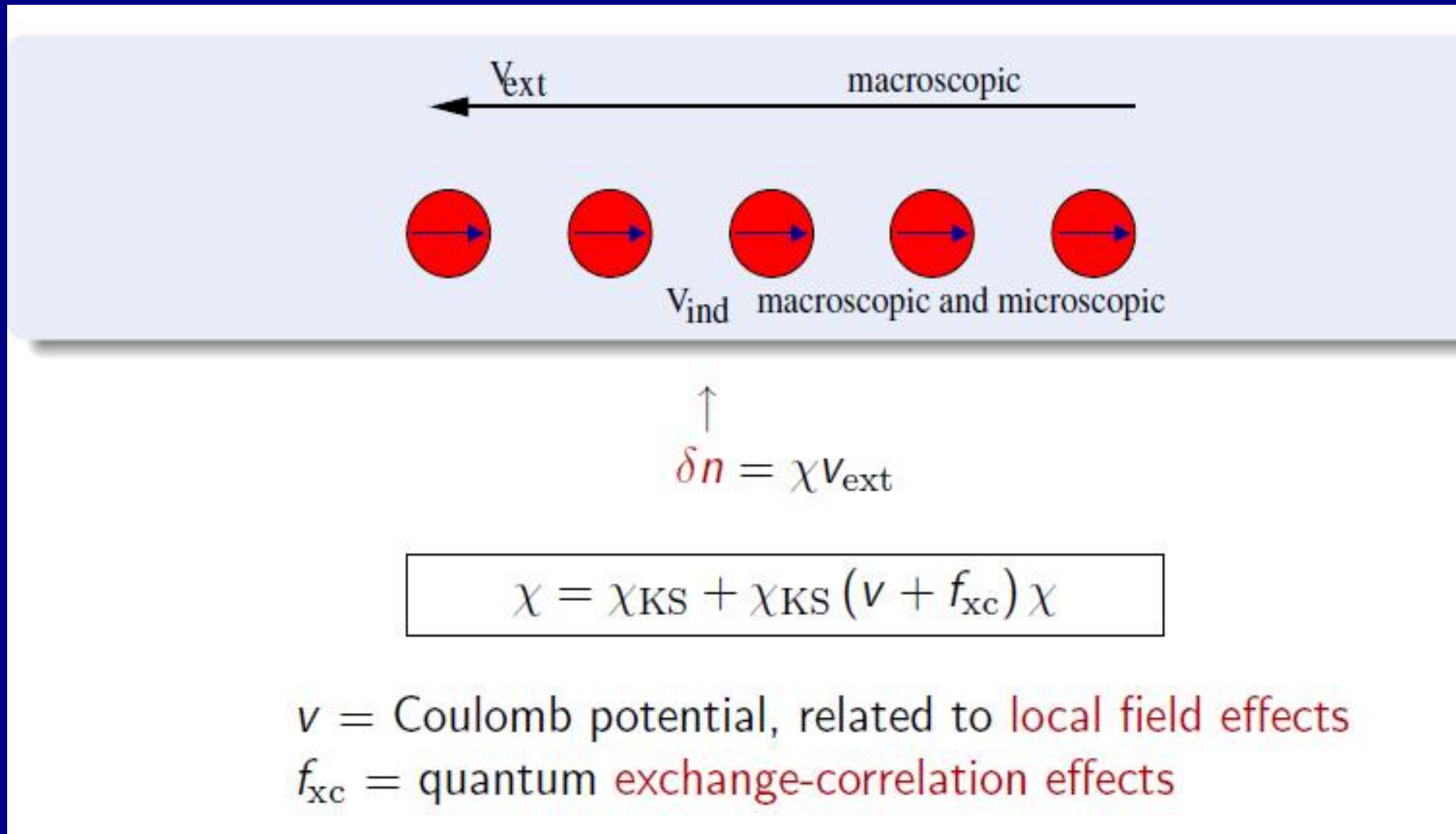
$$i\hbar \frac{d}{dt} \Phi = H \Phi \quad \rightarrow \quad i\hbar \frac{d}{dt} \psi_i = H_{KS}[\{\psi_j\}] \psi_i, \quad i=1, \dots, N$$

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

Time-Dependent Density Functional Theory, Lecture Notes in Physics, Vol. 706 (Springer, Berlin, 2006)



Linear Response



$$V_{\text{induced}} = \delta n v + \mathbf{f}_{\text{xc}} \delta n$$

Hartree

Challenges and Perspectives from (TD) Density Functional Theory
 KITP, Santa Barbara, 2nd November 2009



Linear Response

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

Lehmann representation of the density response function:

$$\chi(\mathbf{r}, \mathbf{r}', \omega) = \lim_{\eta \rightarrow 0^+} \sum_m \left[\frac{\langle 0 | \hat{n}(\mathbf{r}) | m \rangle \langle m | \hat{n}(\mathbf{r}') | 0 \rangle}{\omega - (E_m - E_0) + i\eta} - \frac{\langle 0 | \hat{n}(\mathbf{r}') | m \rangle \langle m | \hat{n}(\mathbf{r}) | 0 \rangle}{\omega + (E_m - E_0) + i\eta} \right]$$

χ (for a finite system) has poles at the excitation energies, $\Omega = E_m - E_0$, while χ_{KS} has poles at the KS eigenvalue differences, $\omega_{jk} = \epsilon_j - \epsilon_k$.

$$\chi_0(r, r', \omega) = \sum_{ij} (f_j - f_i) \frac{\psi_i^c(r) \psi_j(r) \psi_i(r') \psi_j^c(r')}{\epsilon_i - \epsilon_j - \omega}$$

$$f_{xc}(r, r', \omega) = \frac{\delta V_{xc}(r, \omega)}{\delta n(r, \omega)}$$



How to solve the linear response equations

(1) Sum over states:
$$\chi_0(\mathbf{r}, \mathbf{r}', \omega) = \sum_{ij} (f_j - f_i) \frac{\psi_i^c(\mathbf{r}) \psi_j(\mathbf{r}) \psi_i(\mathbf{r}') \psi_j^c(\mathbf{r}')}{\epsilon_i - \epsilon_j - \omega}$$

Leads to Casida equations e-h basis

(2) Time propagation

Apply E-perturbation $\delta v_{\text{ext}}(\mathbf{r}, t) = -\kappa z \delta(t) \rightarrow \psi_i(\mathbf{r}, t=0^+) = e^{ikz} \psi_i(\mathbf{r})$

Propagate ψ_i get dynamical polarizability $\alpha(\omega) = -k^{-1} \sum_i \langle \psi_i | z | \psi_i \rangle$

(3) Density Functional Perturbation Theory

Sternheimer equations

$$\left\{ H^{(0)} - \epsilon_k \pm \omega + i\eta \right\} |\psi_k^{(1)}(\omega)\rangle = - \left[\mathbf{r} + (v_c + f_{xc}) n^{(1)} \right] |\psi_k^{(0)}\rangle$$

Density variation

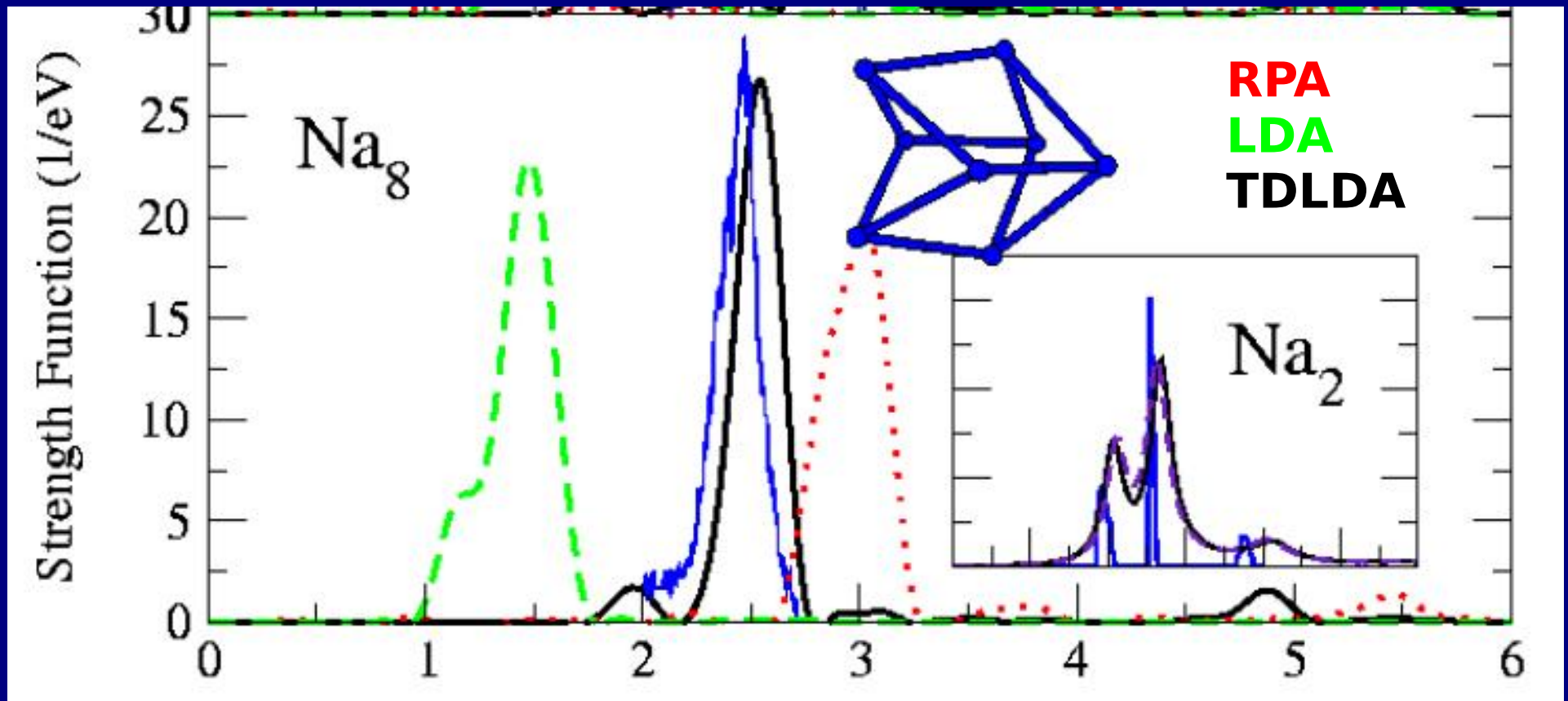
$$n^{(1)}(\mathbf{r}, \omega) = \sum_k f_k \left\{ \left(\psi_k^{(0)}(\mathbf{r}) \right)^* \psi_k^{(1)}(\mathbf{r}, \omega) + \left(\psi_k^{(1)}(\mathbf{r}, -\omega) \right)^* \psi_k^{(0)}(\mathbf{r}) \right\}$$

Challenges and Perspectives from (TD) Density Functional Theory

KITP, Santa Barbara, 2nd November 2009



Optical response

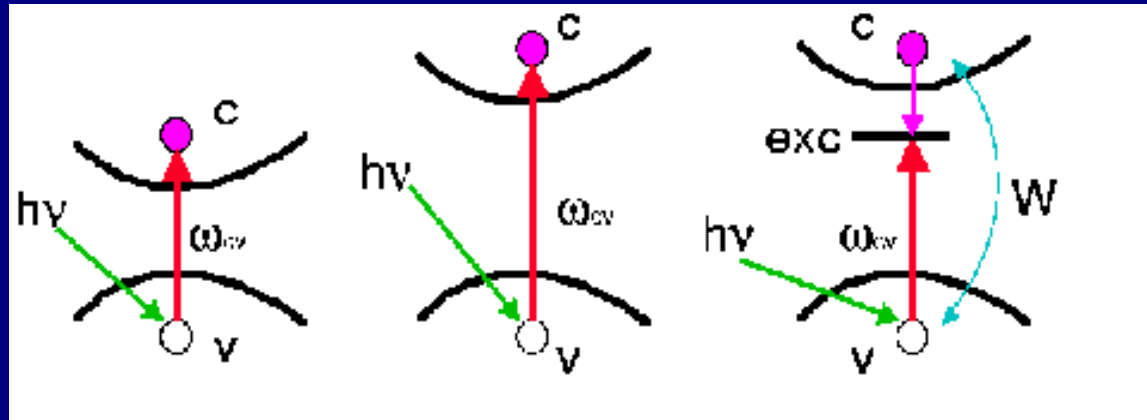


$$\chi(\omega) = \chi_0(\omega) + \chi_0(\omega) (\mathbf{v} + f_{xc}(\omega)) \chi(\omega)$$



Optical Spectroscopy

optical gap \neq transport gap \neq photoemission (QP) gap



Applications: (some)!

Charge transfer: phenolates and Photovoltaics

Chlorophylls: photosynthesis

Optical properties of 1D systems

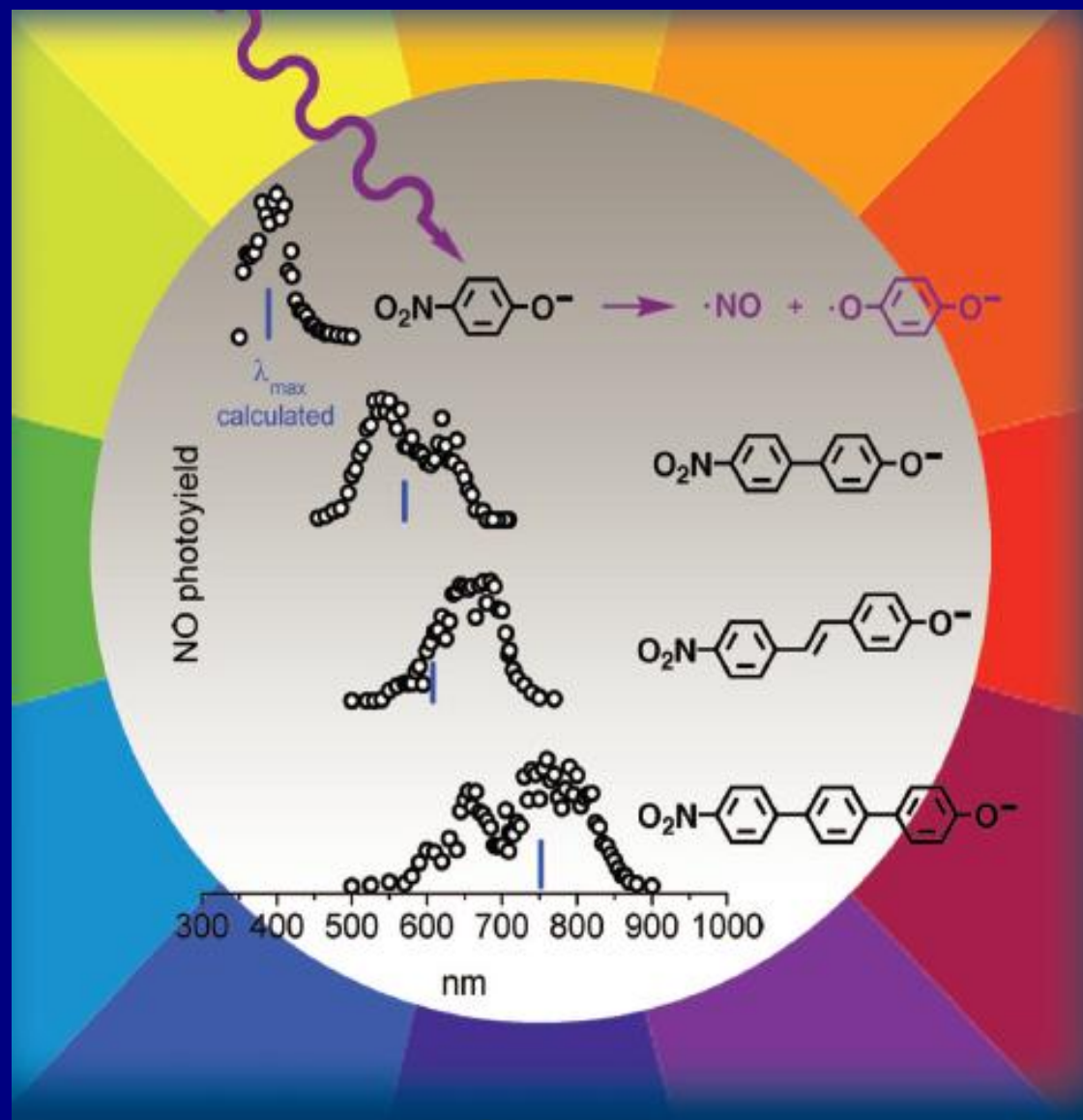


Charge Transfer excitations

Neepa, Kieron, frequency dependent kernel



Absorption Spectra of p-Nitrophenolate Ions *in Vacuo* as donor-acceptor molecules

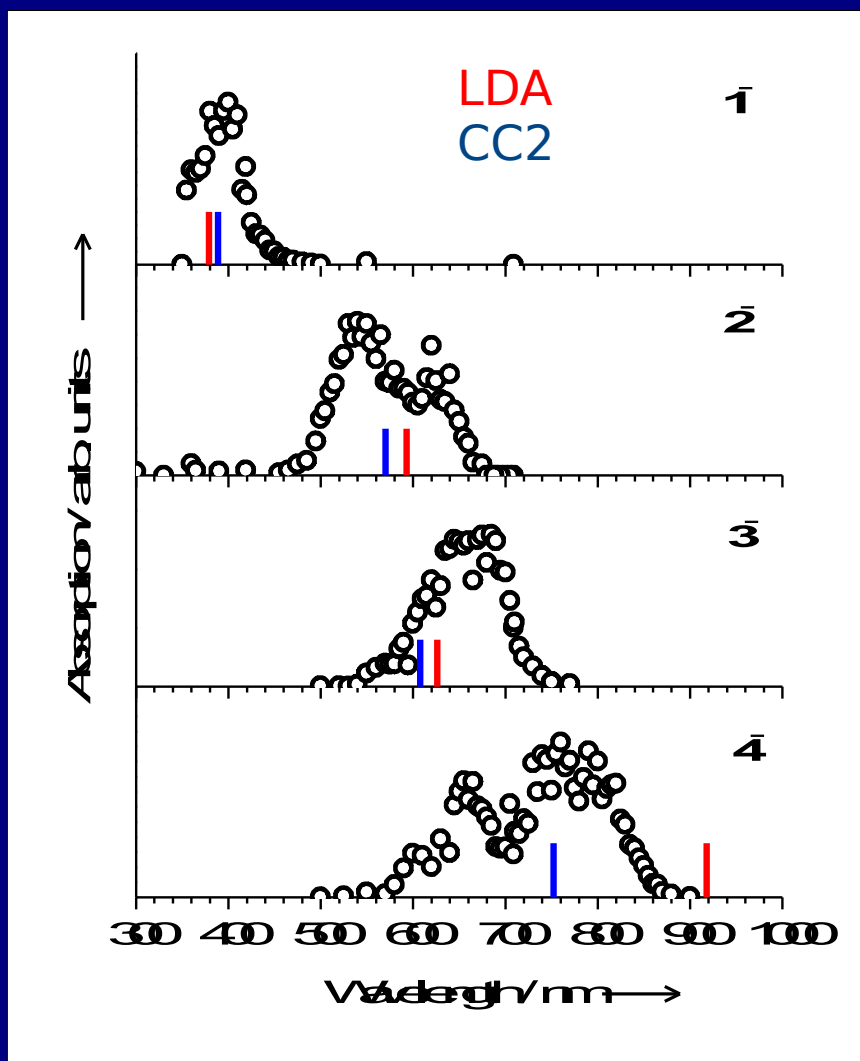


Steen Bronsted Nielsen et al, ChemPhysChem (2009)

Challenges and Perspectives from (TD) Density Functional Theory
KITP, Santa Barbara, 2nd November 2009

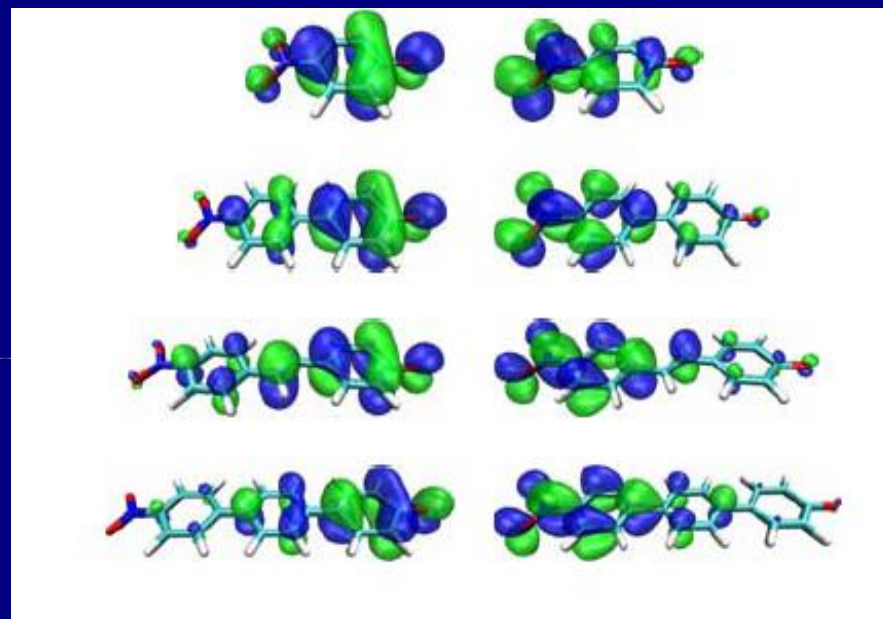


Absorption Spectra of p-Nitrophenolate Ions *in Vacuo*



HOMO

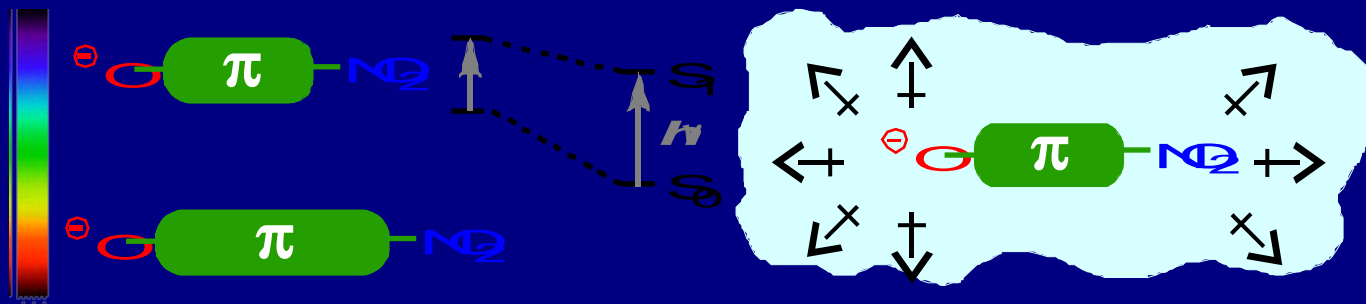
LUMO



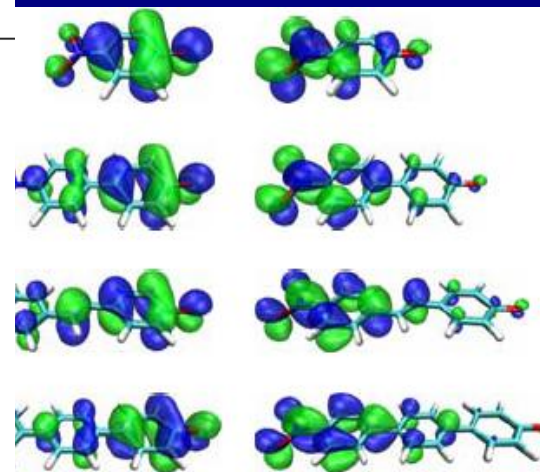
Steen Bronsted Nielsen et al, ChemPhysChem (2009)



Absorption Spectra of p-Nitrophenolate Ions in Solution



Compound	Solution (λ_{\max} / nm)				Gas phase (λ_{\max} / nm)	
	H ₂ O	MeOH	Toluene (+18C6)	MeCN	Exp	Theory CC2 TDDFT
1 ⁻	402 ^{b)}	387	408	430	392	389 379
2 ⁻	400 ^{c)}	406	472	507	541	570 593
3 ⁻		435	504	543	660	608 626
4 ⁻		377	445	466	775	752 918



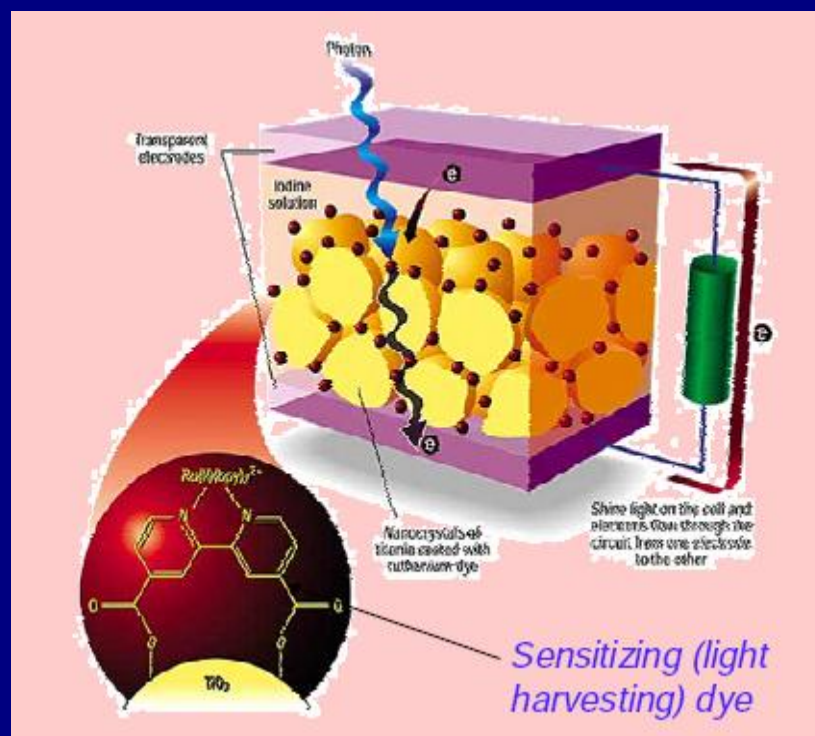
From blue to red: in vacuo they cover the full visible whereas in solution they absorb in a narrow energy region

The solvent shift is mainly due to counter ion and H-bond interactions, then the results do not correlate with solvent polarity

Challenges and Perspectives from (TD) Density Functional Theory
KITP, Santa Barbara, 2nd November 2009



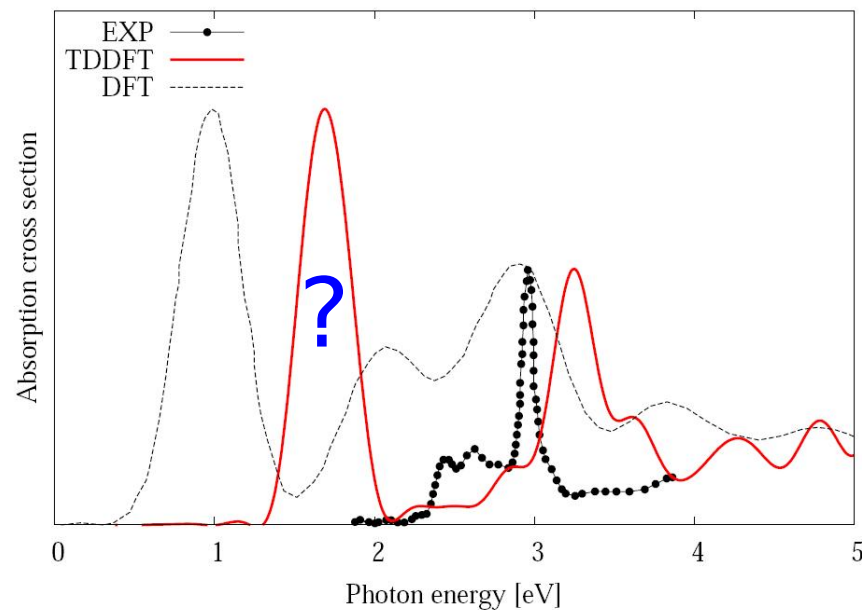
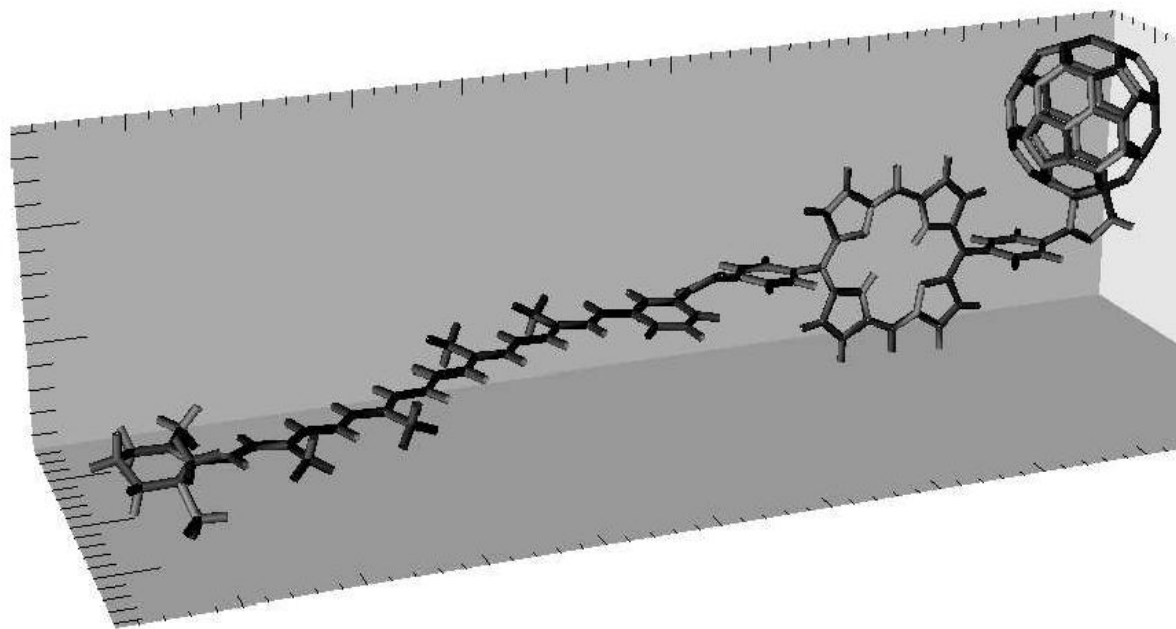
Photovoltaics Hybrids



Grätzel cells



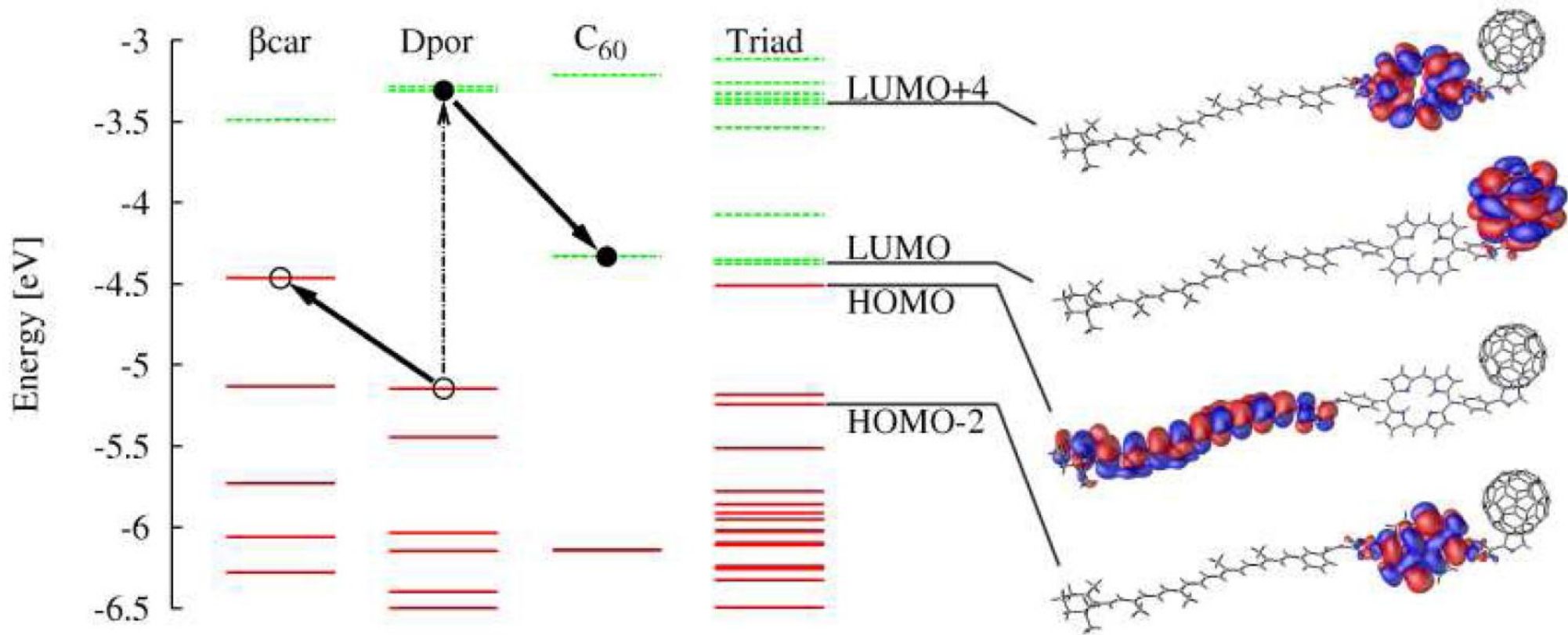
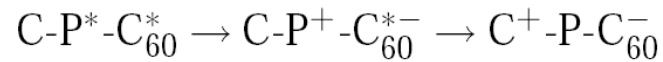
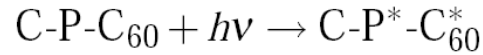
CT: Photo-excitation of the light-harvesting carotenoid-porphyrin-C60



N. Spallanzine et al, J. Phys. Chem. B, 2009, 113 (2009)



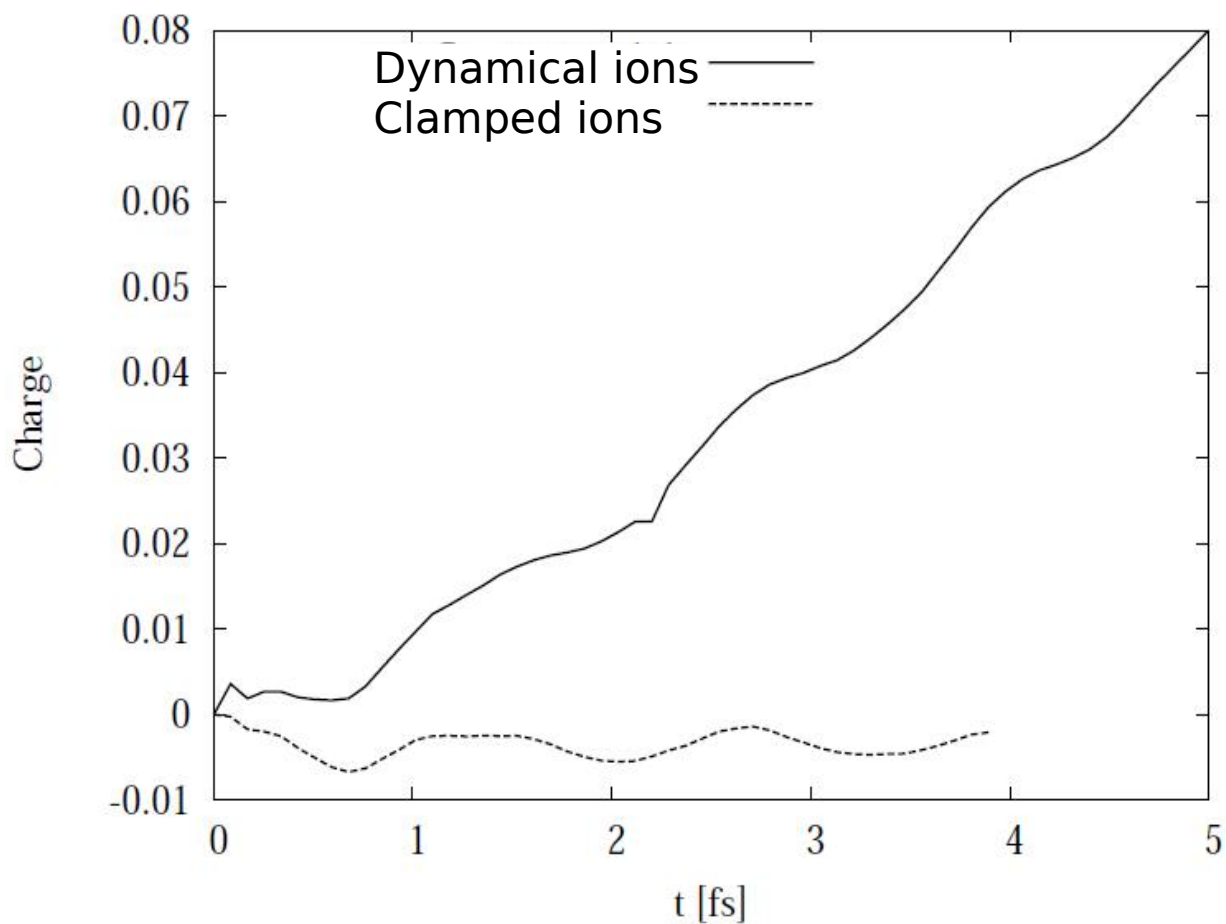
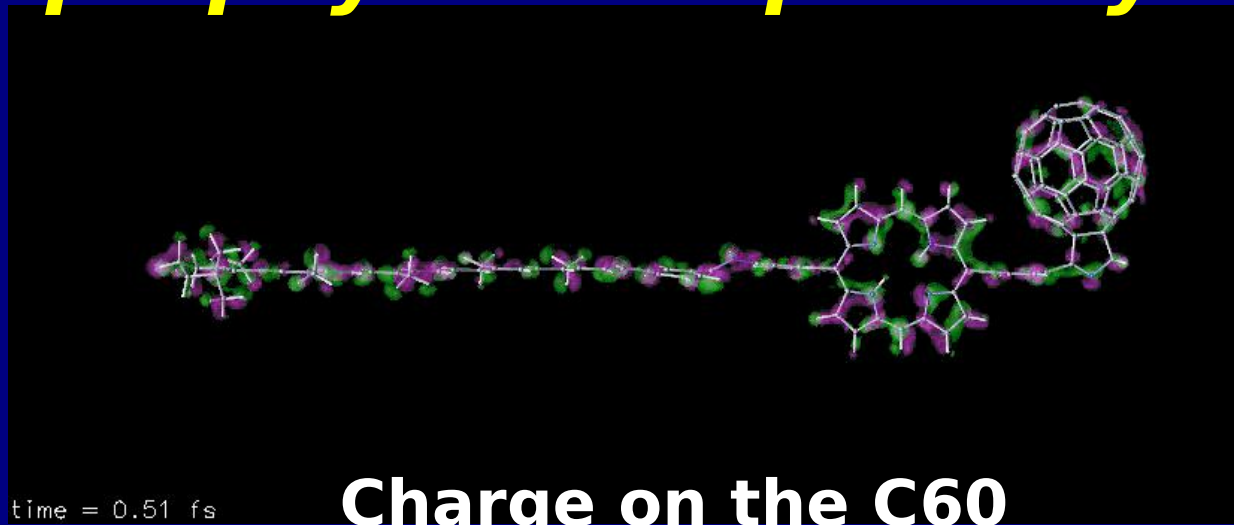
Photo-excitation of the light-harvesting carotenoid-porphyrin-C60



Challenges and Perspectives from (TD) Density Functional Theory
KITP, Santa Barbara, 2nd November 2009



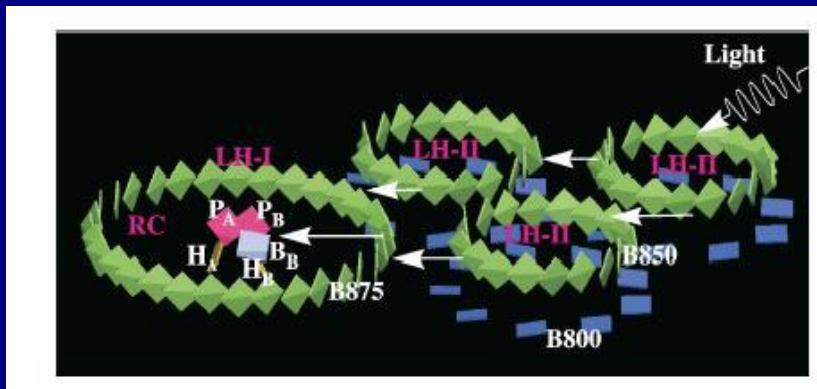
Carotenoid-porphyrin-C60 photodynamics



More biophysical processes

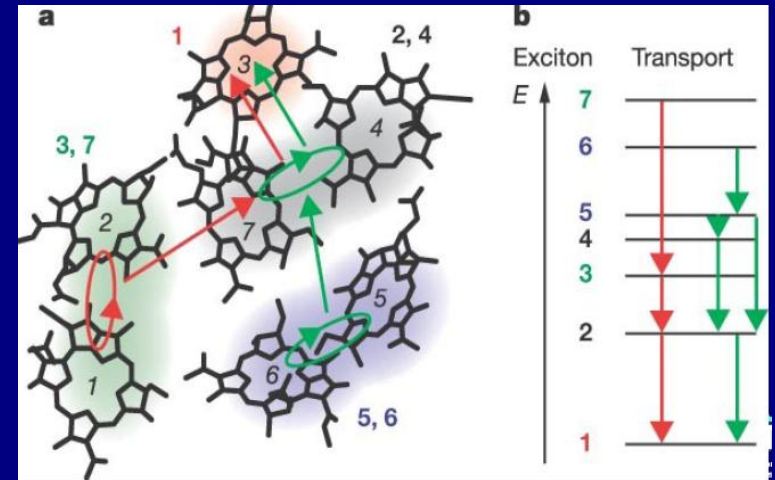
New studies to address the CT and environment in:

Chlorophyll : (*photosynthesis*)
(*K. Schulten et al*)



role of the porphyrine network:

(*Fleming et al*)



A) Large scale (massive) MD simulations: (build on CP)

Speeding up excite state dynamics (on-going)

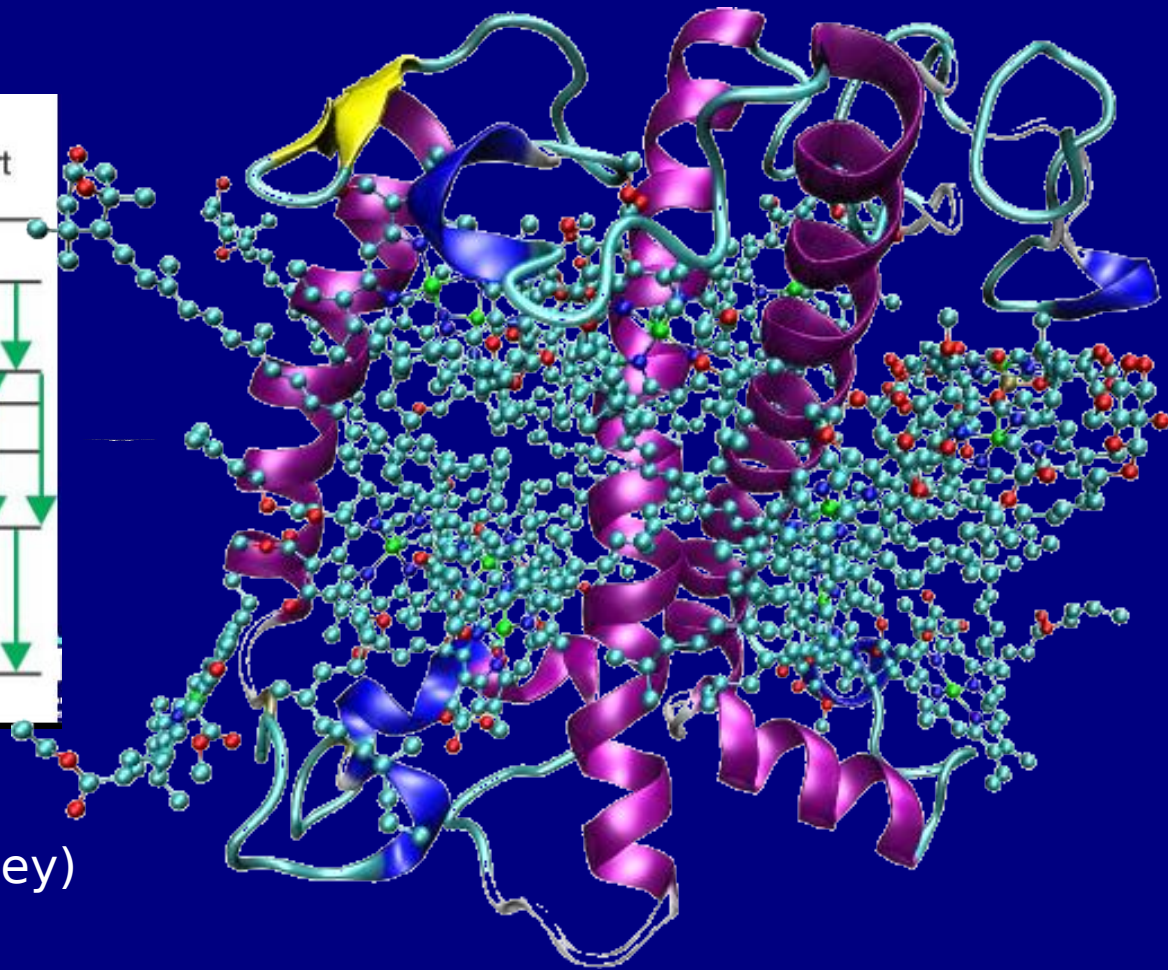
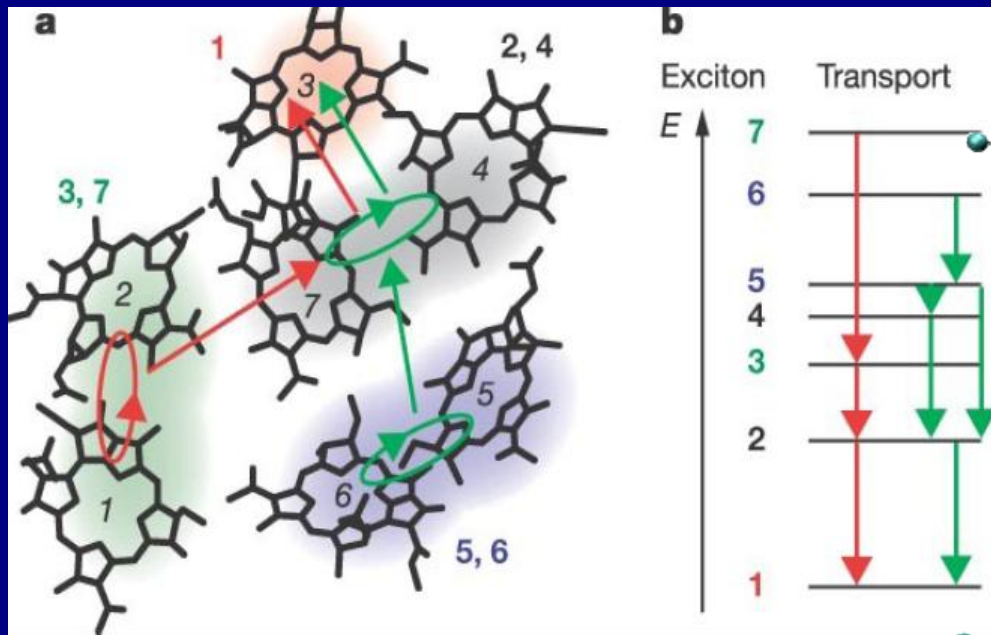
How to include non-adiabatic couplings?

J.L. Alonso, X. Andrade, P. Echenique, F. Falceto, D. Prada, AR PRL (2008)



Towards the color of plants:

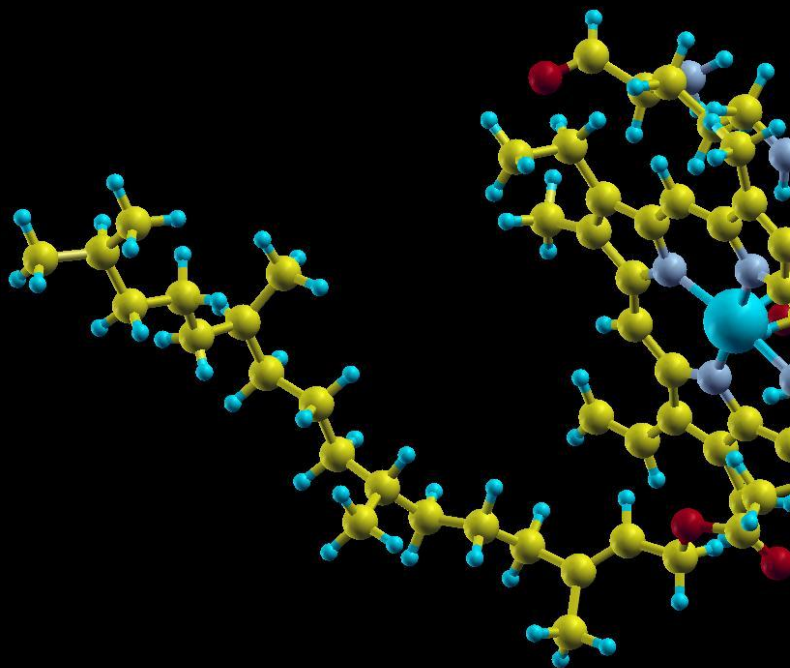
e.g. Spinach



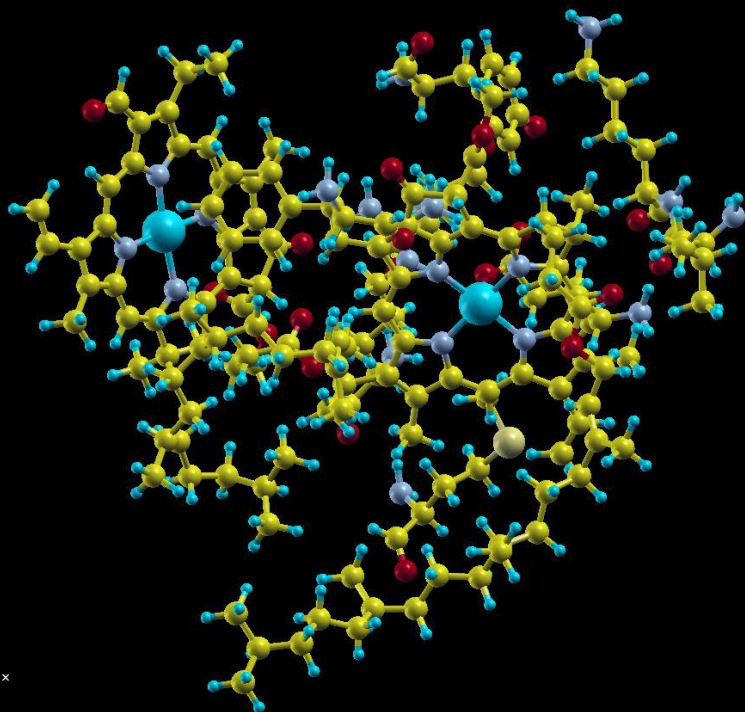
Fleming et al Nature (2005),.... (Berkeley)



Towards the color of plants:



Towards the color of plants:

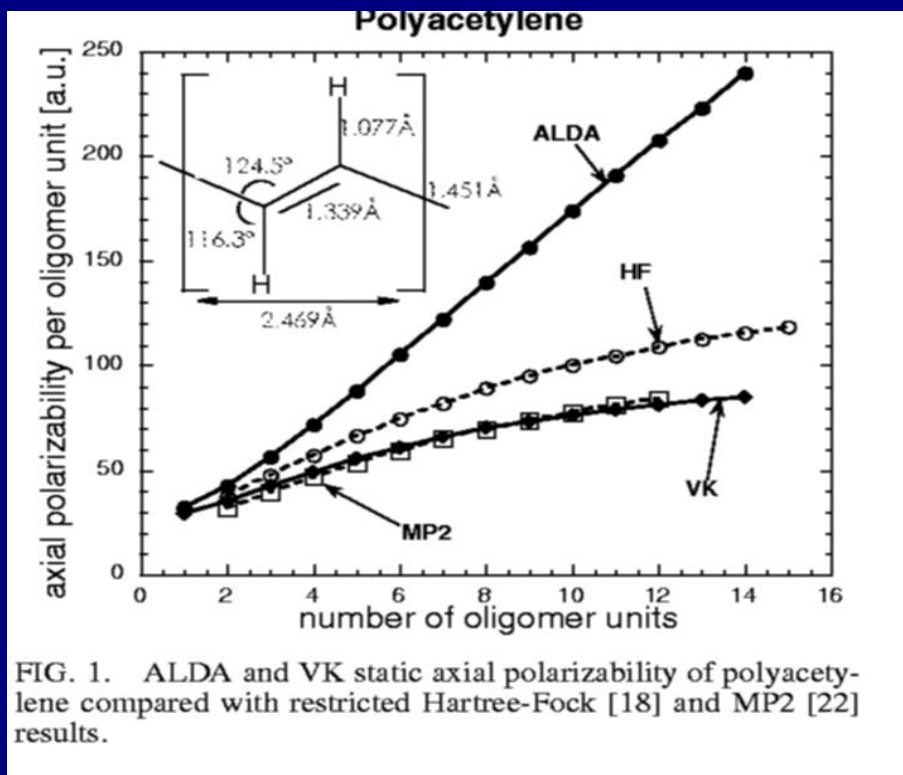


Challenge: proper treatment of the whole environment, including dissipation for very long simulations from fs to milliseconds and more.....

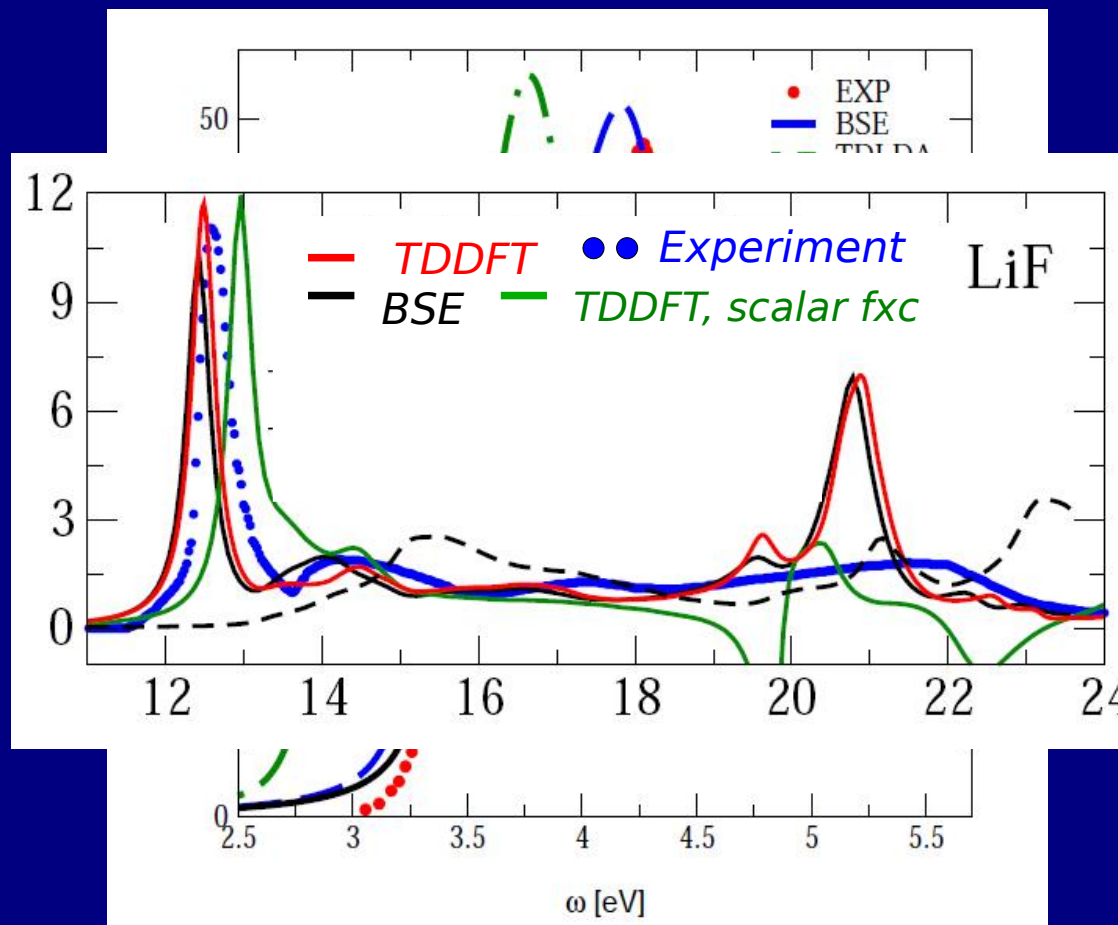


Problems with extended systems in finite fields?

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



M. van Faassen et al. PRL (2002)



Macroscopic Polarisation Theory and real-time simulation

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

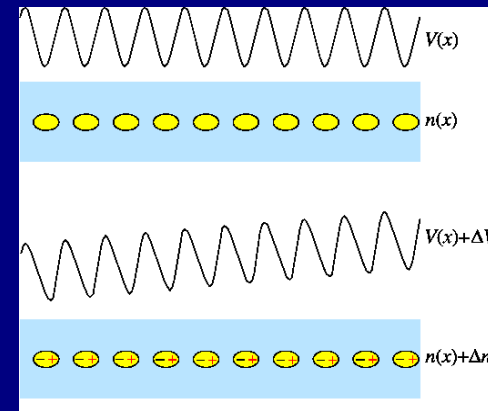
$$\vec{E} = \frac{-1}{c} \frac{d\vec{A}(t)}{dt}$$

$$A(t) = A_{ext}(t) + A_{ind}(t)$$

$$E_{mac} = 4\pi P(t)$$

$$H = H + H_{em}$$

$P = \text{polarisation}$



$$\frac{1}{4\pi} \frac{d^2 \vec{A}}{dt^2} = -e^2 \frac{n}{m} \vec{A} - c \frac{e}{V} \sum_i \langle \psi_i | \frac{\vec{p}}{m} | \psi_i \rangle = c^2 j_{mac}(t) = -c^2 \frac{d\vec{P}(t)}{dt}$$

What is the link to the “modern theory of polarisation”?
(see the recent review by Vanderbilt, Resta)

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



Macroscopic Polarisation Theory <--> real-time $\mathbf{A}(t)$

$$\vec{j}_{\text{mac}}(t) = -\frac{e}{c} \frac{1}{\Omega} \sum_{n\vec{k}} \int_{\Omega} d\vec{r} u_{n\vec{k}}^*(\vec{r}, t) \frac{-i\hbar}{m} \left(\vec{\nabla} + i\vec{k} + \frac{ie}{\hbar c} \vec{A}(t) \right) u_{n\vec{k}}(\vec{r}, t)$$

$$i\hbar \frac{\partial}{\partial t} u_{n\vec{k}}(\vec{r}, t) = \left\{ -\frac{\hbar^2}{2m} \left(\vec{\nabla} + i\vec{k} + \frac{ie}{\hbar c} \vec{A}(t) \right)^2 + V(\vec{r}, t) \right\} u_{n\vec{k}}(\vec{r}, t)$$

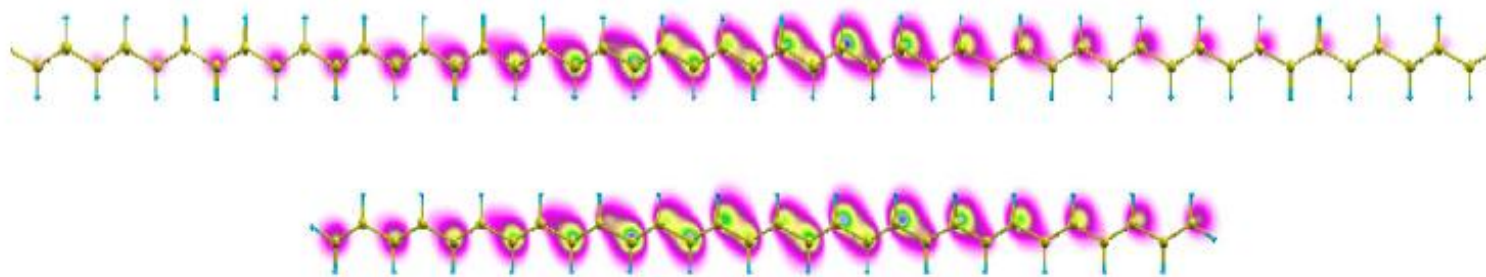
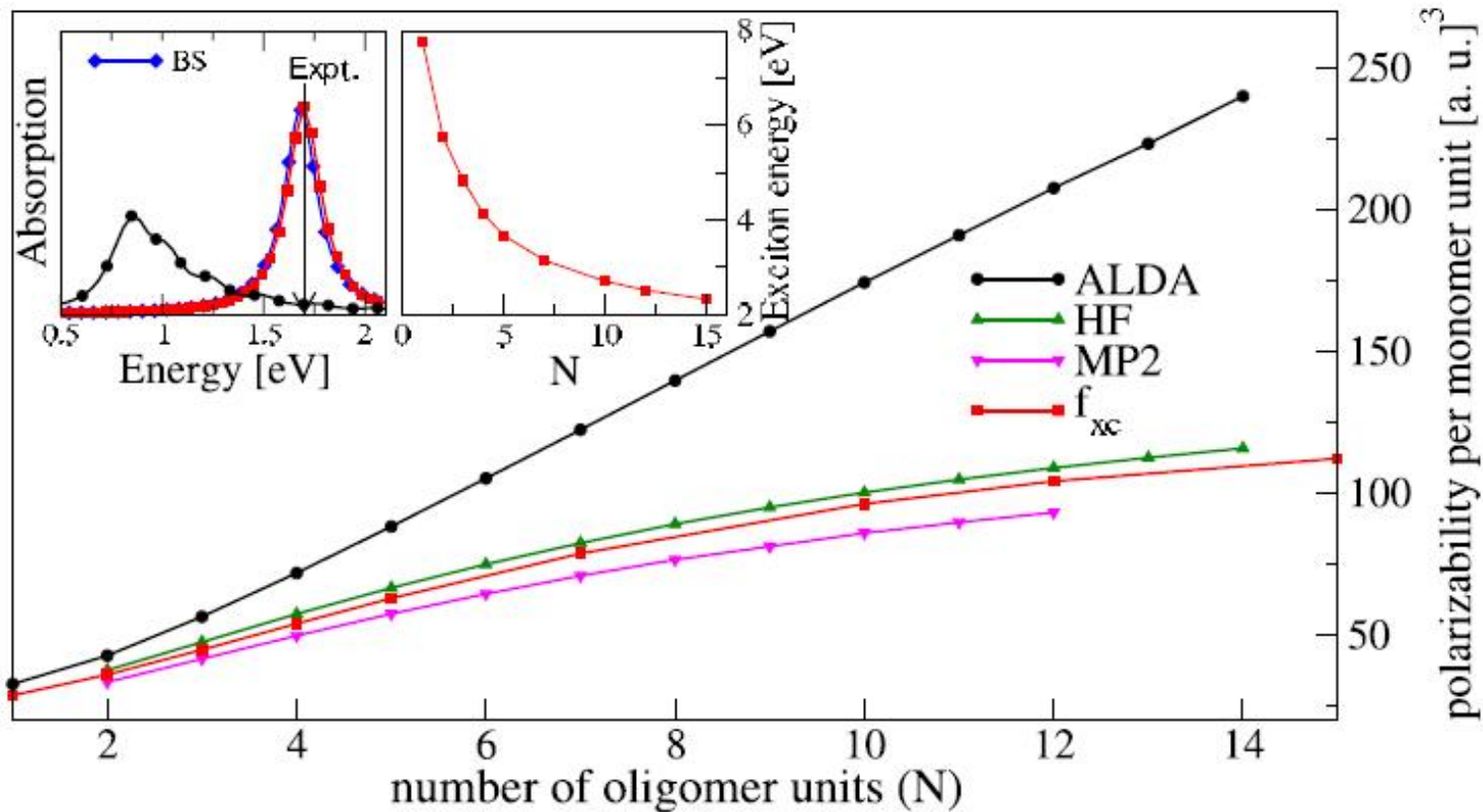
$$\frac{d\vec{P}(t)}{dt} = \frac{ie}{c} \frac{1}{\Omega} \int_{\Omega} d\vec{r} \sum_{n\vec{k}} \left\{ \frac{\partial u_{n\vec{k}}^*}{\partial t} \frac{\partial u_{n\vec{k}}}{\partial \vec{k}} + u_{n\vec{k}}^* \frac{\partial^2 u_{n\vec{k}}}{\partial t \partial \vec{k}} \right\}$$

$$\vec{P}(t) = \frac{ie}{c} \frac{1}{\Omega} \int_{\Omega} d\vec{r} \sum_{n\vec{k}} u_{n\vec{k}}^*(\vec{r}, t) \frac{\partial}{\partial \vec{k}} u_{n\vec{k}}(\vec{r}, t)$$

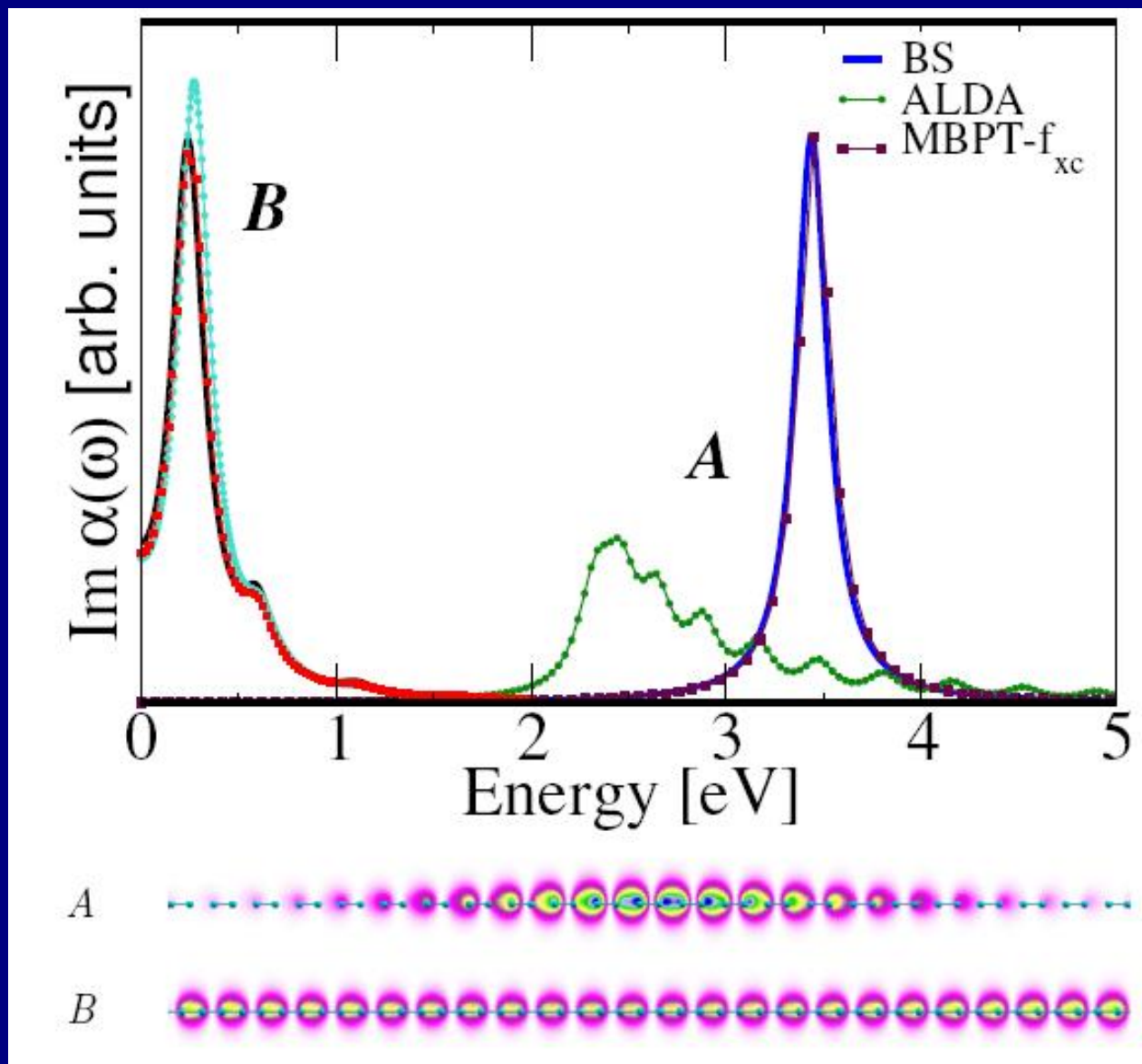
Berry Phase



Trans-polyacetylene (Organic Solids)



H₂ molecular chains (infinite long case)

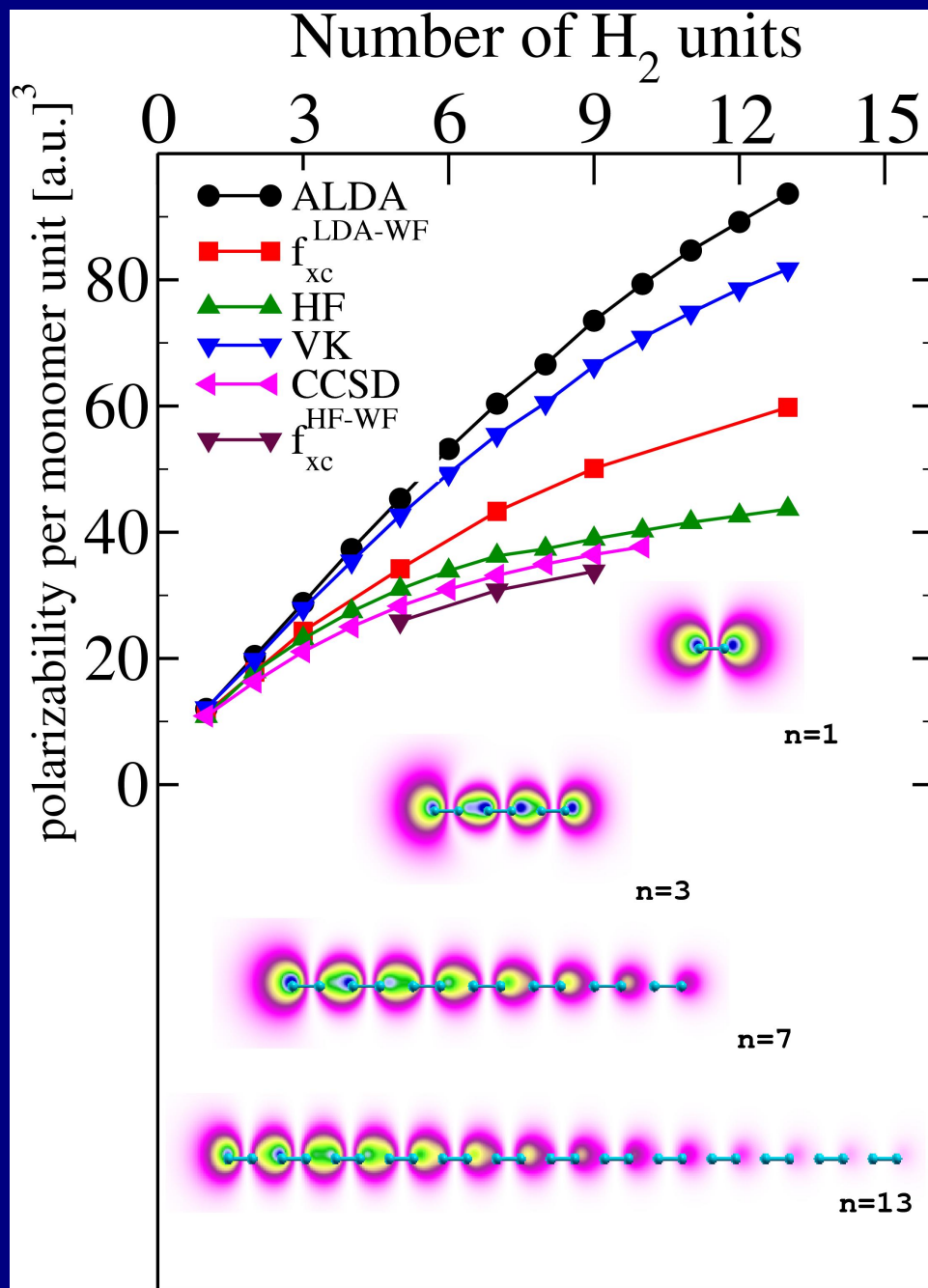


Metallic
versus
semiconducting

Dimerised
Equidistant (Mott!)

D. Varsano, A. Marini, AR PRL (2008)





Long-range effects

Exchange dominate
Exciton localisation
Polarisability saturation

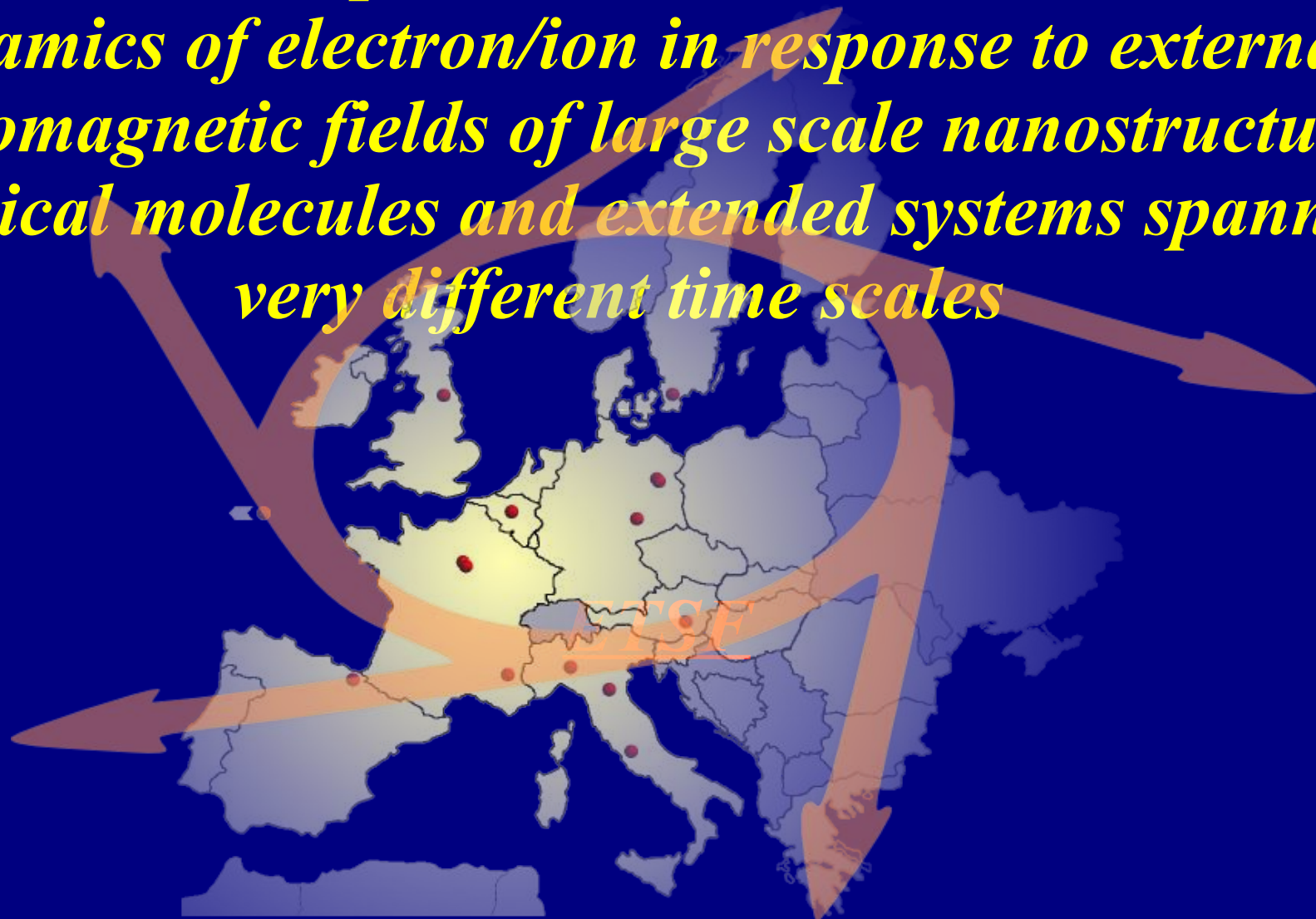
importance of the wfns in
the response and kernel

.....also for correlated
materials see Lucia's talk

eman ta zabal 2020



The combination of MBPT and (TD)DFT is a powerful tool to “predictive” describe the combined dynamics of electron/ion in response to external electromagnetic fields of large scale nanostructures, biological molecules and extended systems spanning very different time scales



Thank you!!!!

For more details see:
<http://nano-bio.ehu.es>
<http://etsf.eu>

