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ICTP 40th Anniversary

**SMR 1564 - 4**

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

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# TDDFT THEORY:

# APPLICATIONS TO NANO AND BIO-STRUCTURES

## Optical Properties of Nanostructures:
## Illustration of the physics for nano- and bio structures

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

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

DONOSTIA INTERNATIONAL PHYSICS CENTER

# Optical properties of nanostrutures


## Angel Rubio

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*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 nanostrutures*

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

*Seeing bond breaking and formation!!!*

*Nanostructures: -small metal and semiconductor cluster*
*-carbon nanotubes: relaxation times*

*Bio-photoreceptors:*
*-Green-fluorescent protein*
*-Isomerisation and device applications of azobencene*

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

*Implementation:*

✔ Numerical description of functions: real space discretization (1D-3D).

✔ Auxiliary use of LCAO/ FFTs. QM/MM for biomolecular structures

✔ Electon-ion coupling: pseudopotentials. Spin-Orbit .....


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)*

# Time dependent multicomponent KS theorem

## transformation to a body-fixed coordinate frame required

T.Kreibig and E.K.U Gross PRL (2001)

*The densities , N of the interacting system can be calculated as densities of a non-interacting (KS) system*

$$\rho(r,t)=\sum_j\left|\varphi_j(r,t)\right|^2$$

$$N(R,t)=\left|\chi(R,t)\right|^2$$

$$i\partial_t\varphi_j(r,t)=\left(\frac{\hbar^2}{2\mu_e}\nabla_r^2+v_s[\rho,N](r,t)\right)\varphi_j(r,t)$$

$$i\partial_t\chi(R,t)=\left(\frac{\hbar^2}{2\mu_n}\nabla_R^2+W_s[\rho,N](R,t)\right)\chi(R,t)$$

$$v_s(r,t)=v_{laser}(r,t)+v_{ee}^H(r,t)+v_{en}^H(r,t)\ +\ \mathbf{v_{xc}[\rho,N](r,t)}$$

$$W_s(R,t)=W_{laser}(R,t)+\frac{Z_1Z_2}{R}+W_{en}^H(R,t)\ +\ \mathbf{W_{xc}[\rho,N](R,t)}$$

# The Electron Localisation Function (ELF) : Seeing Bonds!!! *(what is a bond?)*

Definition:

$$elf_\sigma = \frac{1}{1+\left[\frac{C_\sigma(r)}{C_\sigma^{uni}(r)}\right]^2}$$

*Becke, Edgecombe, JCP92, 5397 (1990)*

$$C_\sigma^{uni}(r) = \frac{3}{5}(6\pi^2)^{2/3}\rho_\sigma^{5/3}(r)$$

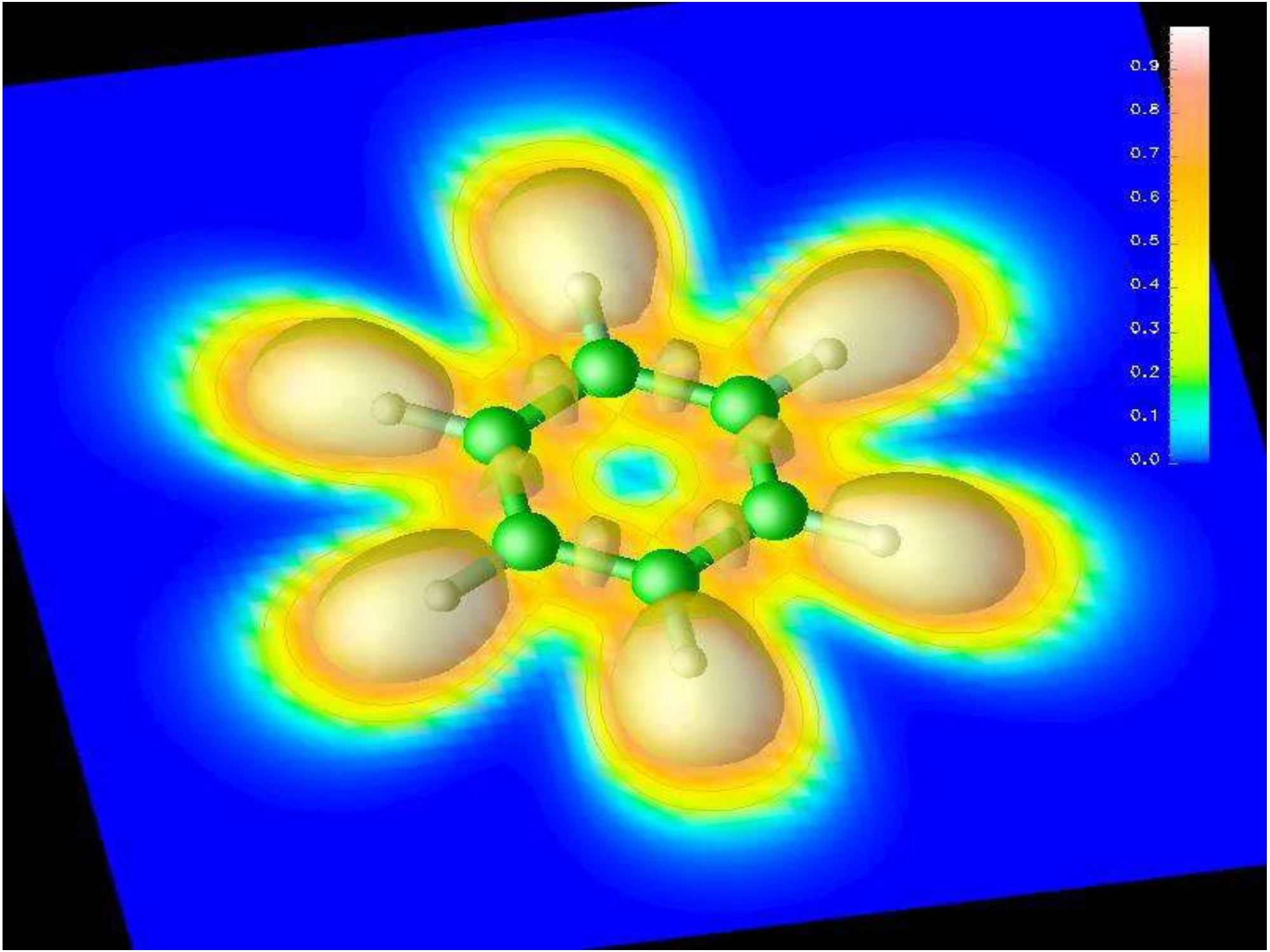
$0 < \text{elf} < 1$

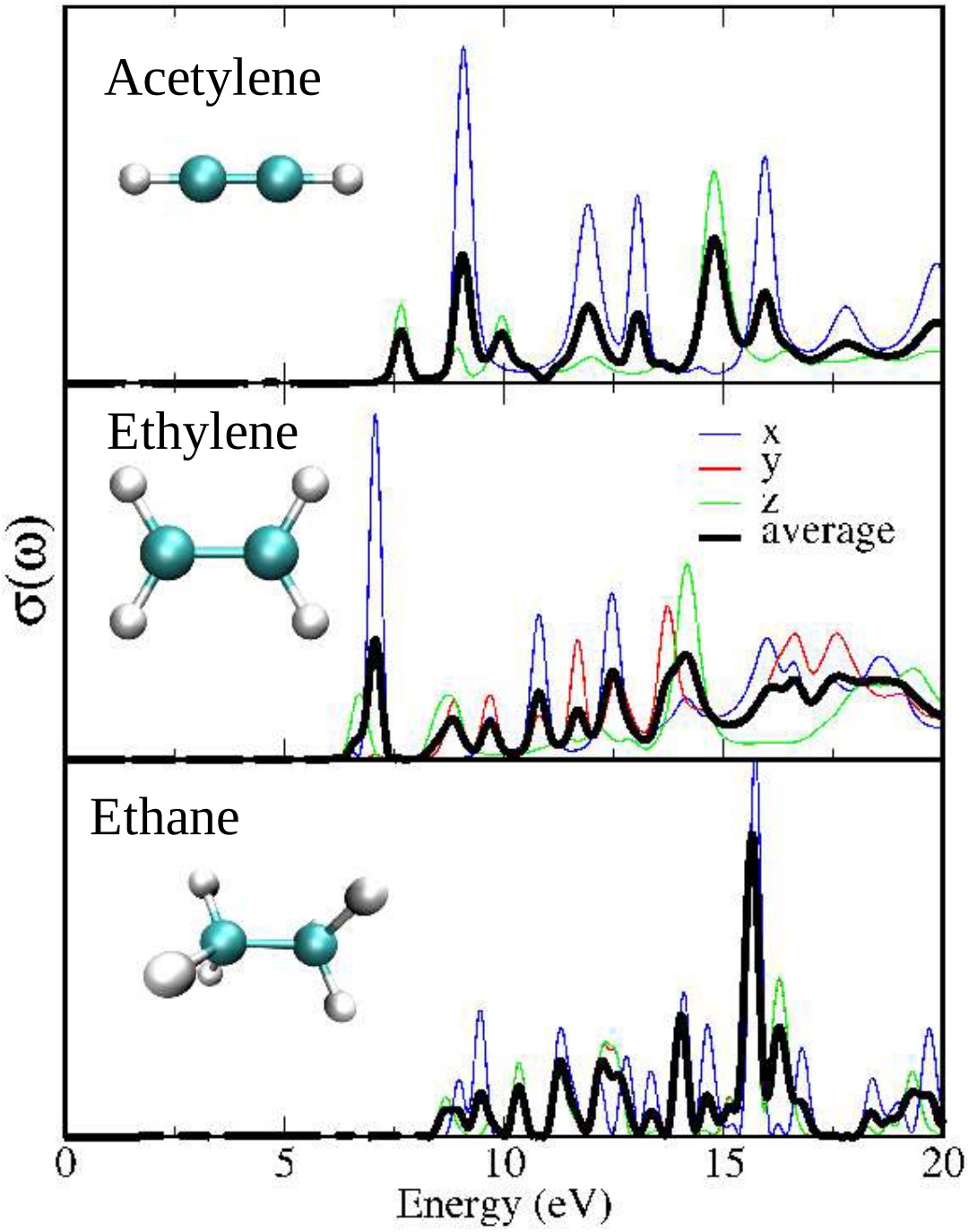
high localisation $\longrightarrow$ $C_\sigma \sim 0$ $\longrightarrow$ elf ~ 1

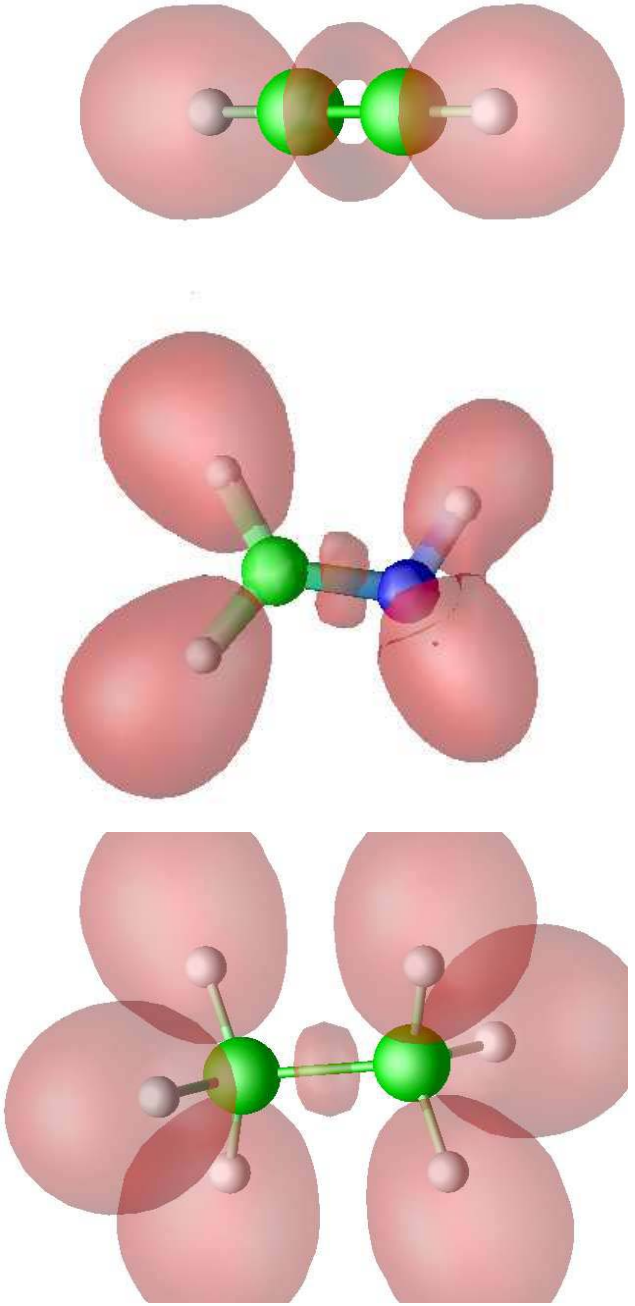
completely delocalised $\longrightarrow$ $C_\sigma \sim C_\sigma^{uni}$ $\longrightarrow$ elf ~ 1/2

When the wavefunction is a Slater determinant (in the time dependent case)

$$C_\sigma^{det}(r,t) = \sum_{i=1}^{N_\sigma} |\nabla \varphi_{i\sigma}(r,t)|^2 - \frac{1}{4}\frac{[\nabla \rho_\sigma(r,t)]^2}{\rho_\sigma(r,t)} - \frac{j\ (r,t)}{(r,t)}$$


0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0

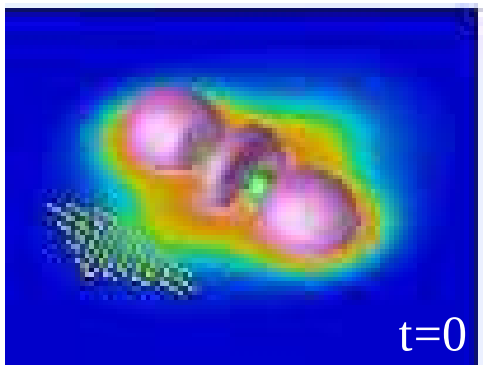

Acetylene
Ethylene
Ethane
x
y
z
average
σ(ω)
0
5
10
15
20
Energy (eV)

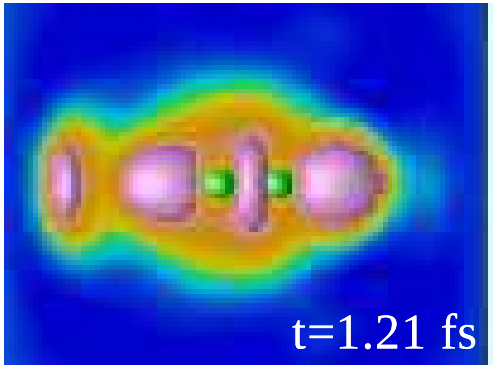


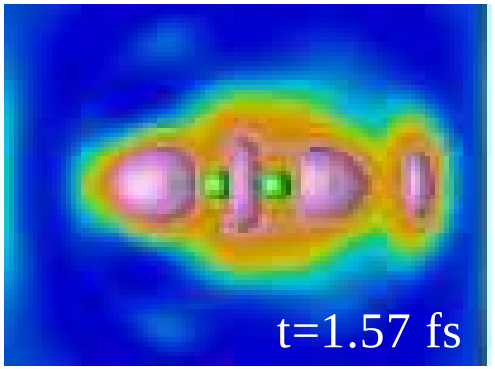
# Time-dependet case: acetylene $C_2H_2$ in a strong laser field

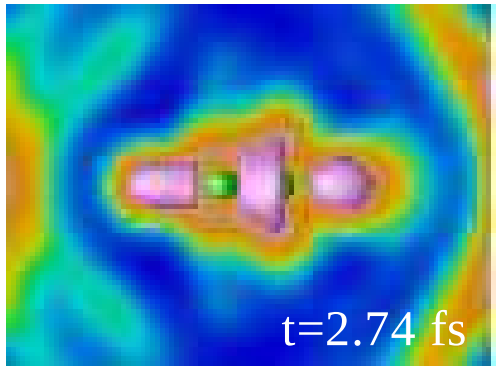
*=17eV, T= 8fs, I= 1.2x10$^{14}$ Wcm$^{-2}$*

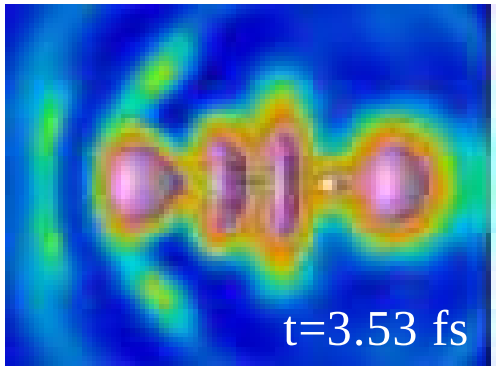
fast ionisation

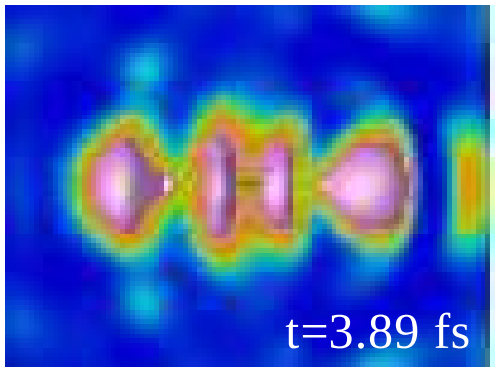



to *

T. Burnus, M.A.L.Marques, E.K.U Gross, (2004)

# Nano (bio-) structures

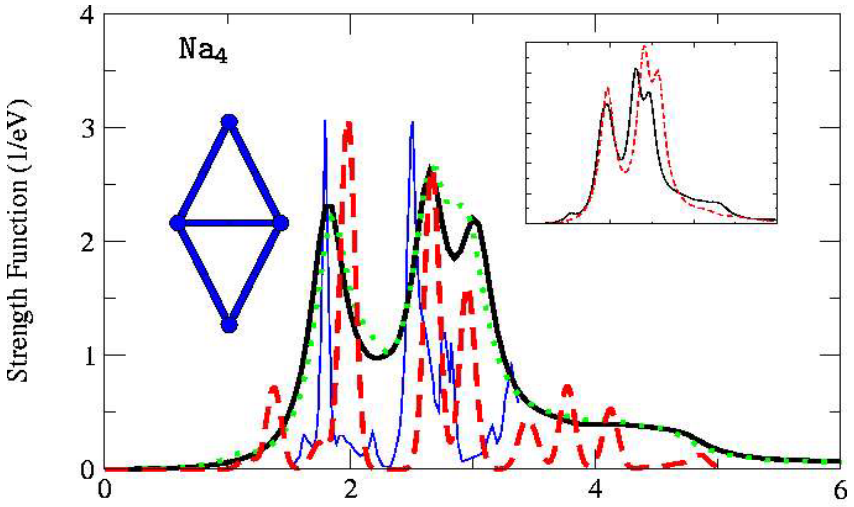
***How good is the performance of TDDFT and present DFT XC-functionals?***

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

# Linear optical response: general aspects

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

$$\chi_0(r,r',w)=\sum_{ij}(f_j-f_i)\frac{\varphi_i^c(r)\varphi_j(r)\varphi_i(r')\varphi_j^c(r')}{\epsilon_i-\epsilon_j-w}$$




$$[1-(v+f_{xc}(\omega))\chi_0(\omega)]\lambda(\omega)=0$$

Single-pole approximation $\Rightarrow$

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

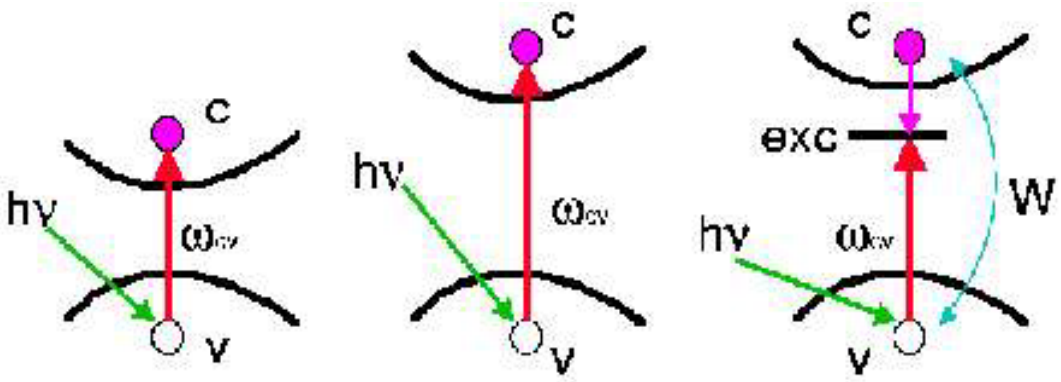
$$K\approx\int d^3r\int d^3r'\varphi_{j_0}(r)\varphi^*_{j_0}(r')\varphi_{k_0}(r')\varphi^*_{k_0}(r)\cdot\left(\frac{1}{|r-r'|}+f_{xc}(r,r')\right)$$

LDA- thick solid line

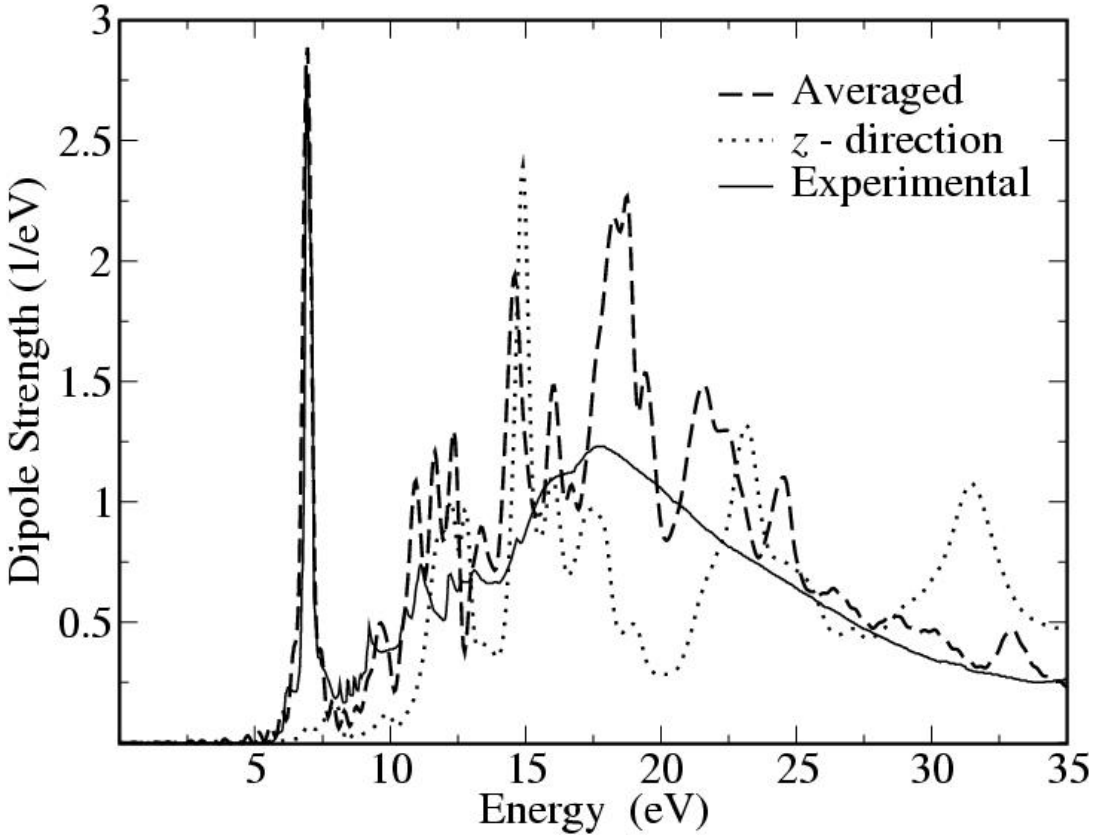
EXX- dotted line

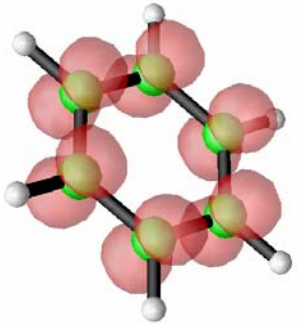
Bethe-Salpeter

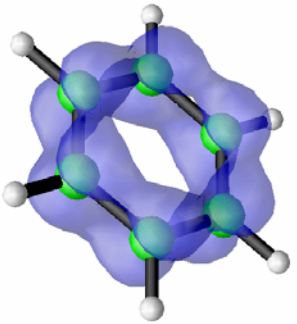
Experiments



# *Optical response:* (Benzene)





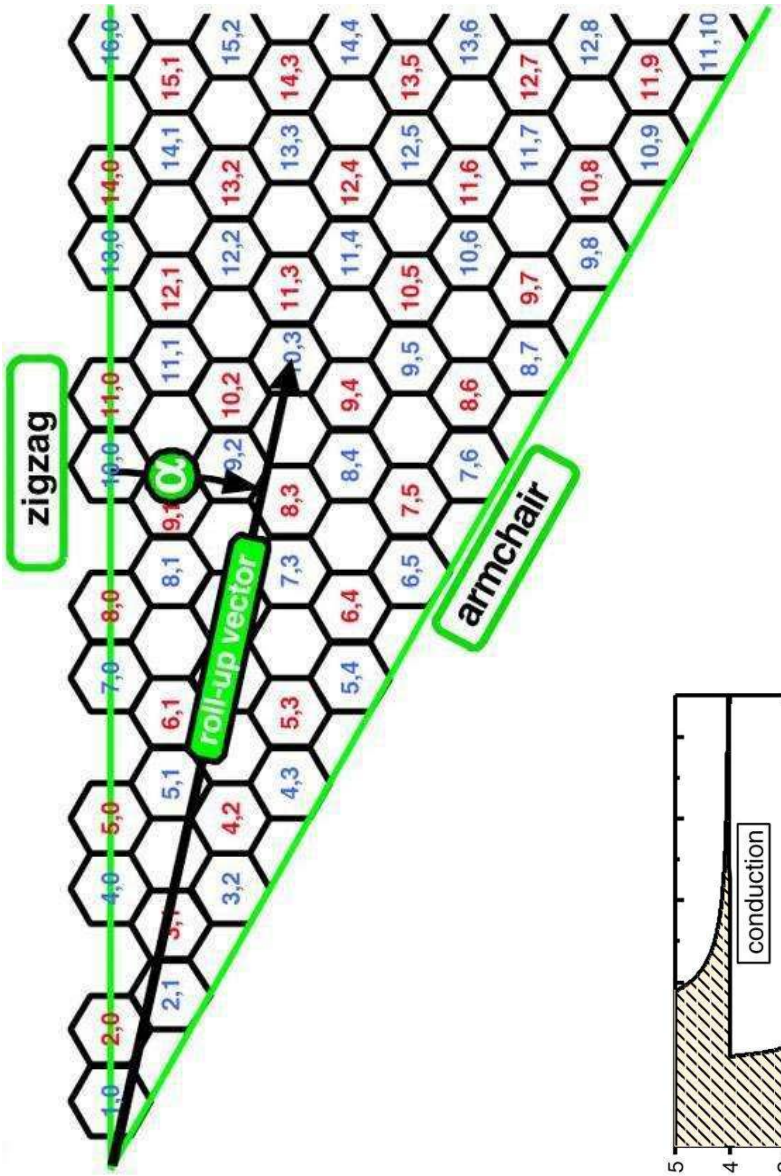
* (LUMO)

7eV

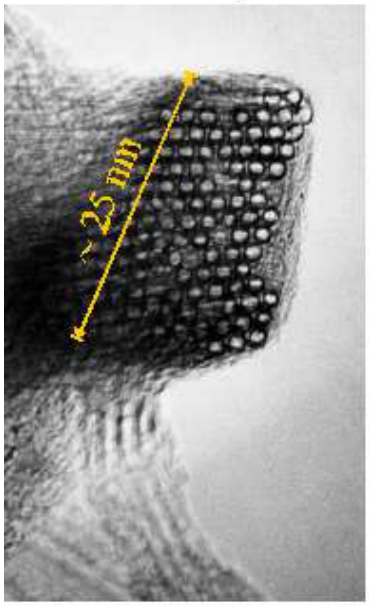
(HOMO)

*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)*

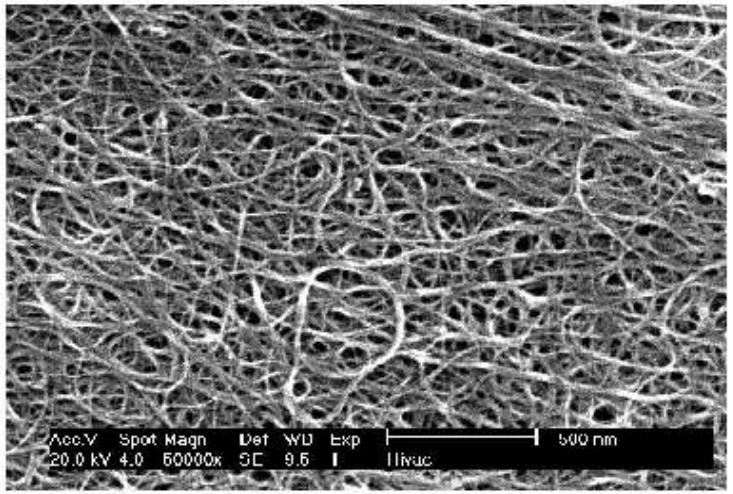
# Carbon nanotubes: Iijima (1991)

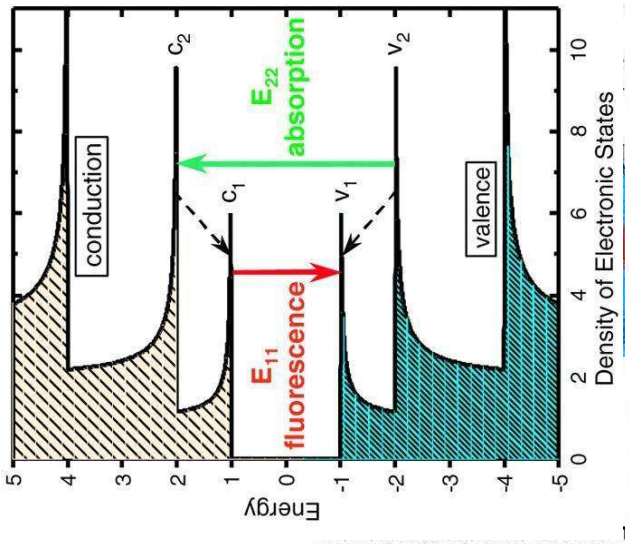


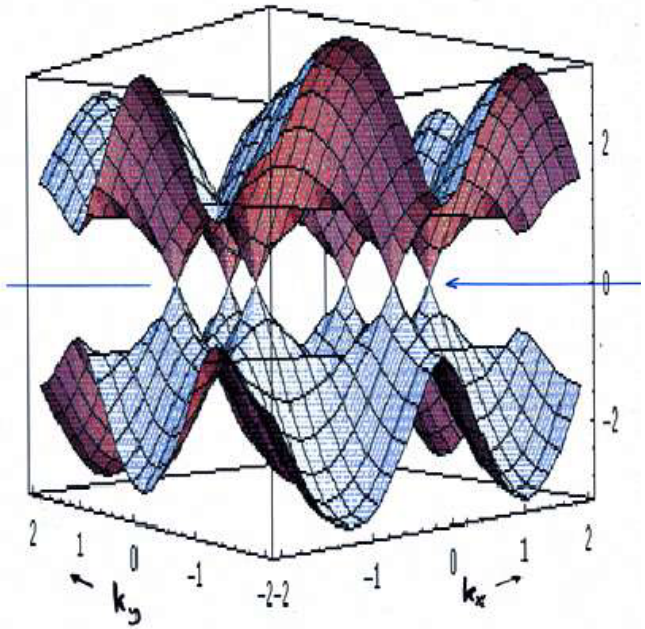

TEM of Rope



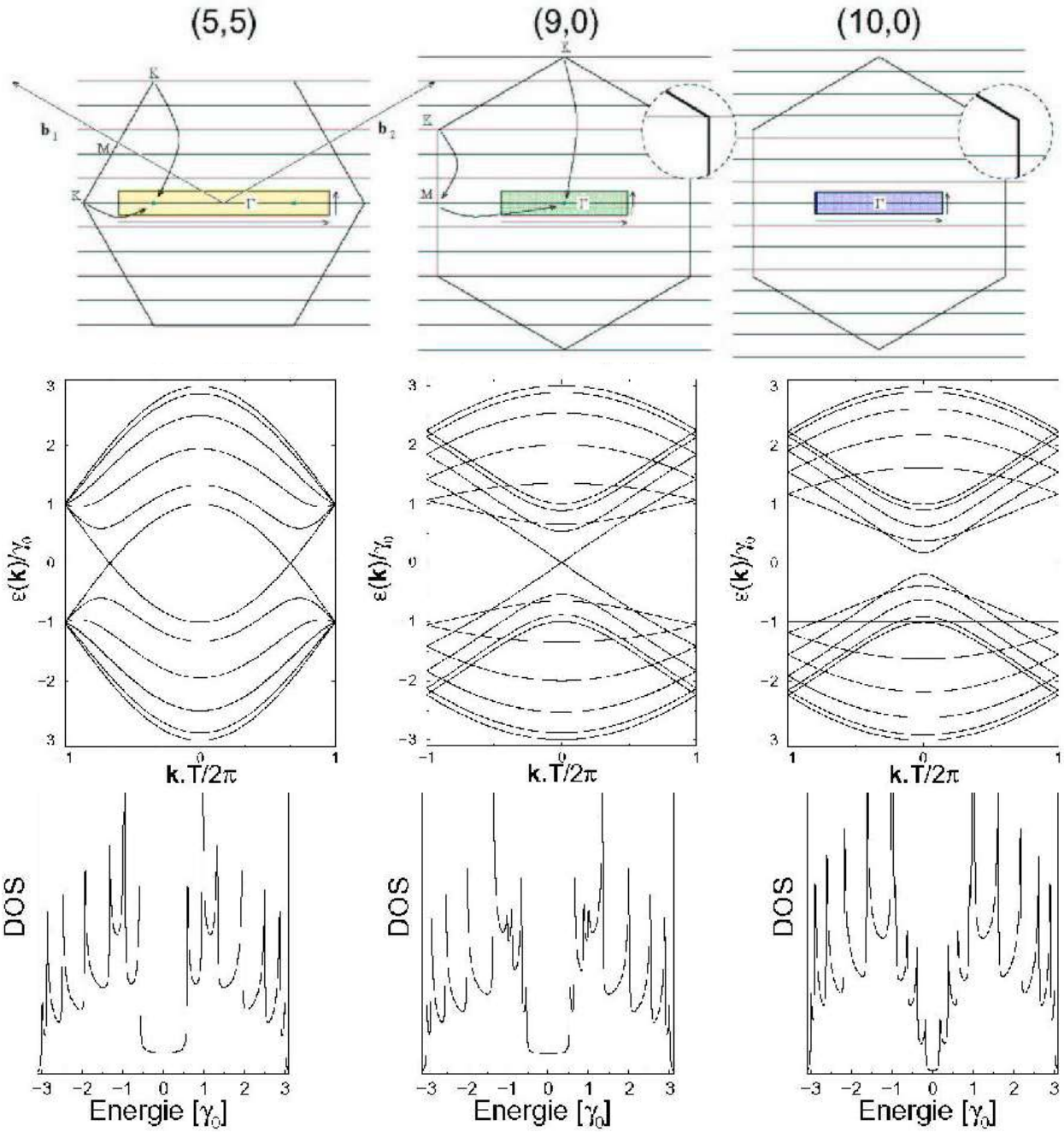

SEM: 'bucky-paper'

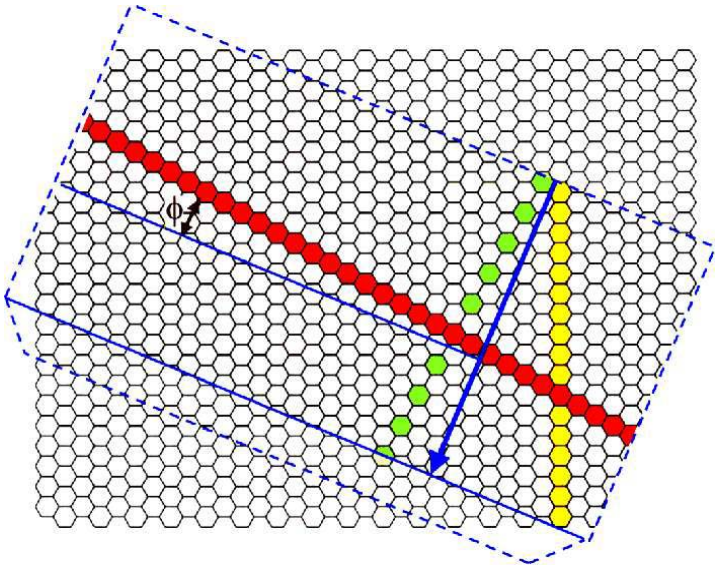


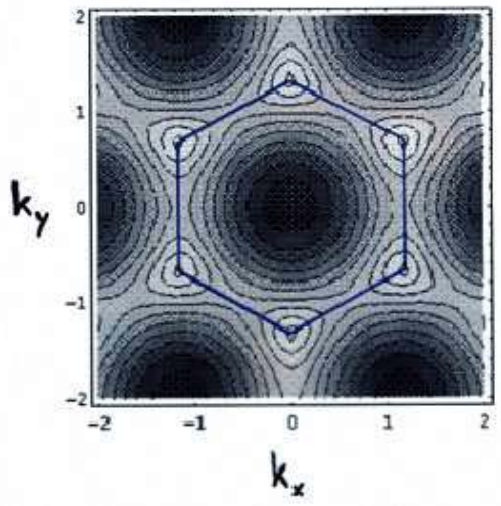



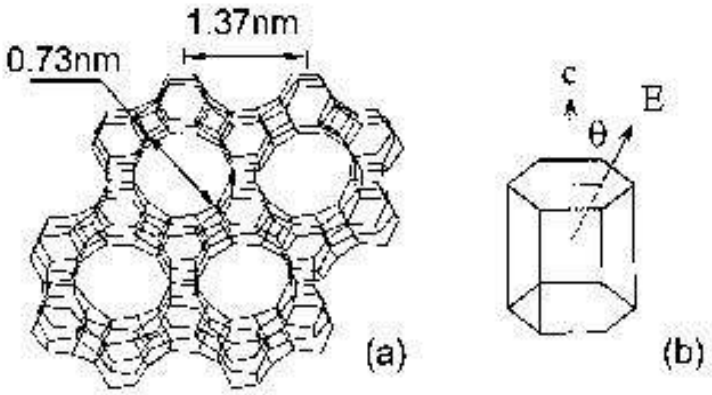
# Simple model for the electronic structure: TB of C-tubes



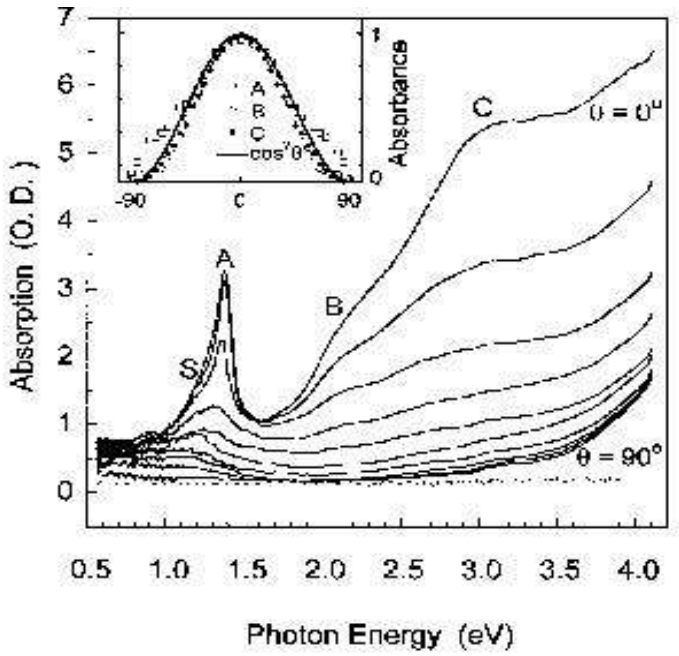



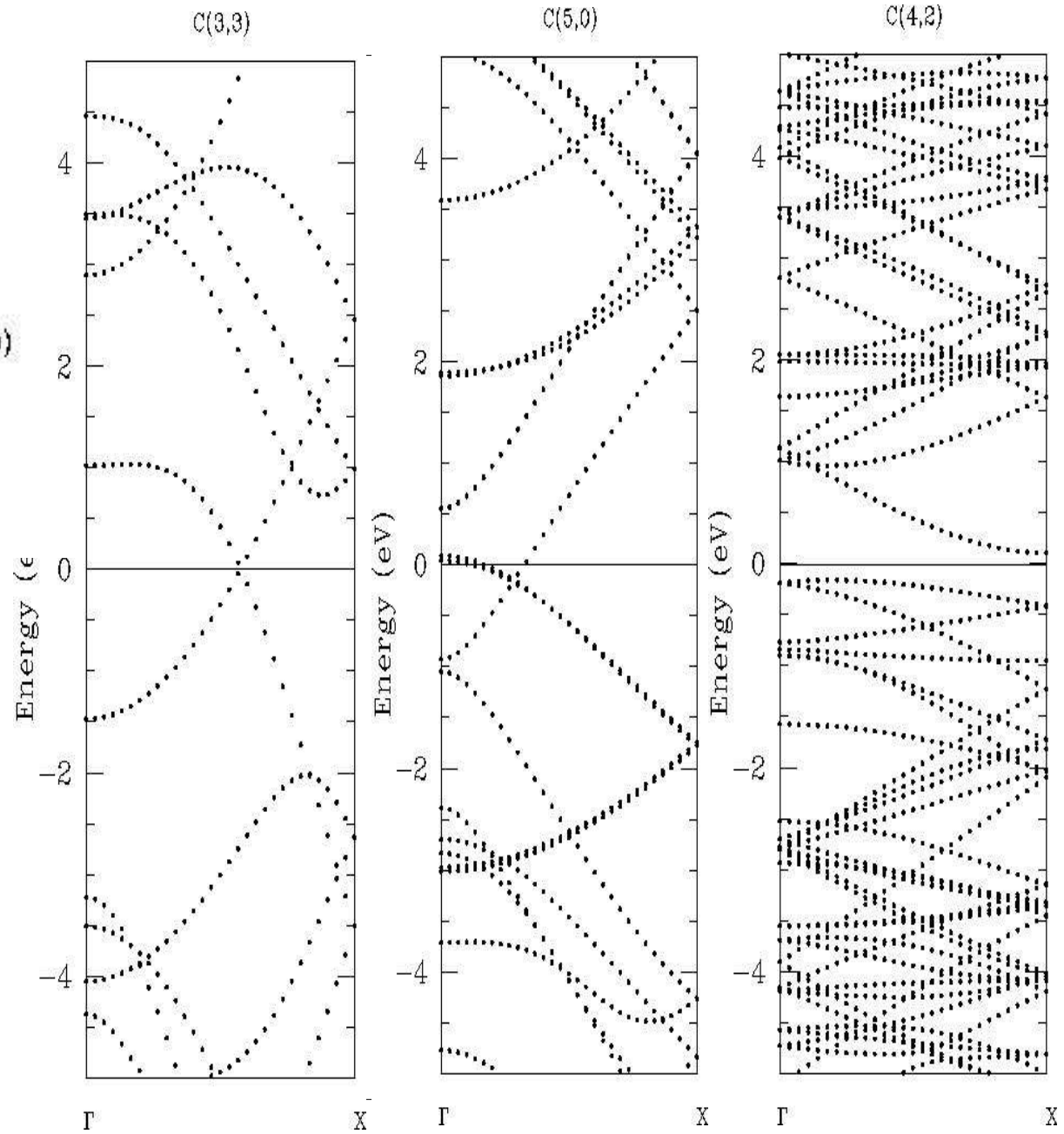
# Optical Properties of C-Tubes: A way to elucidate tube-chirality



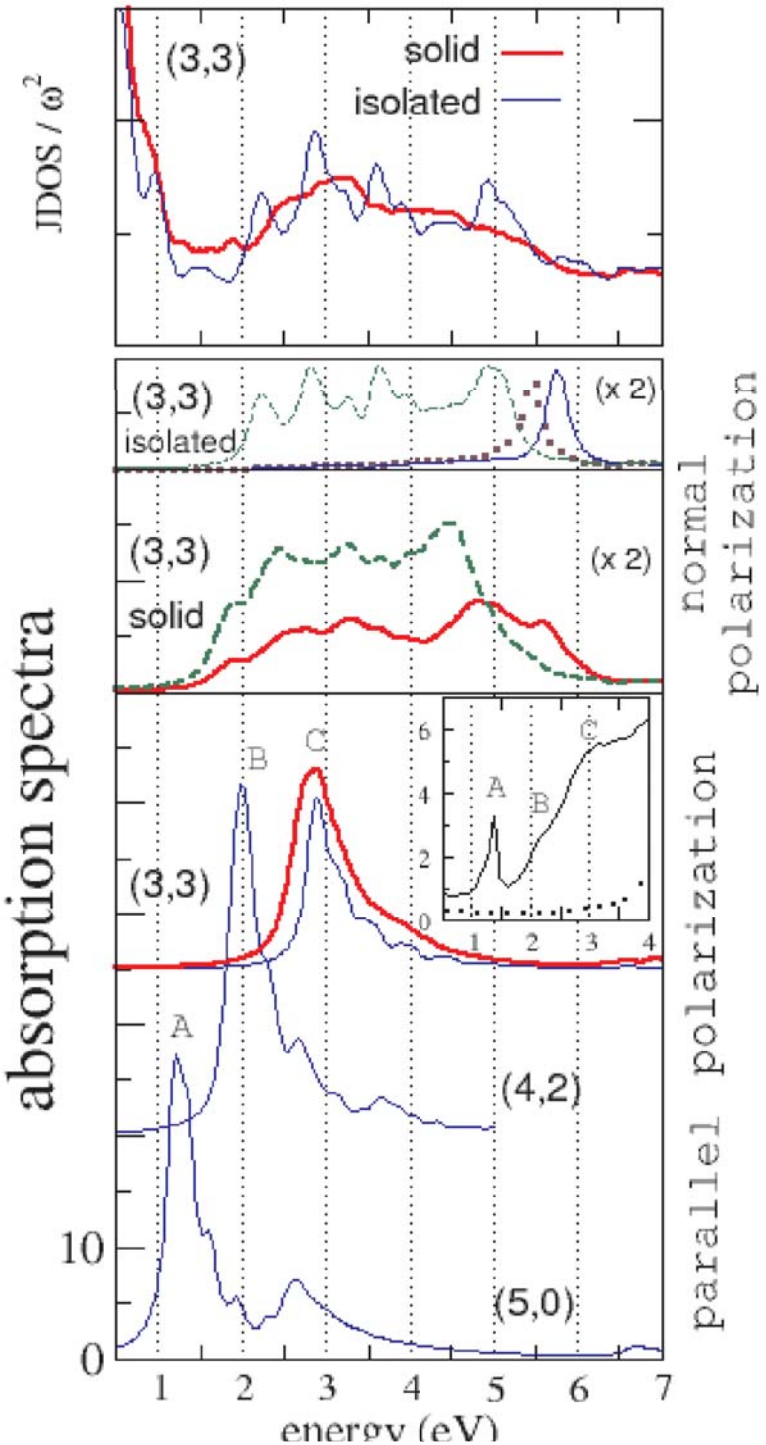

Zeolite type $AlPo_4$-5




*Z.M..Lie et al, PRL (2001)*



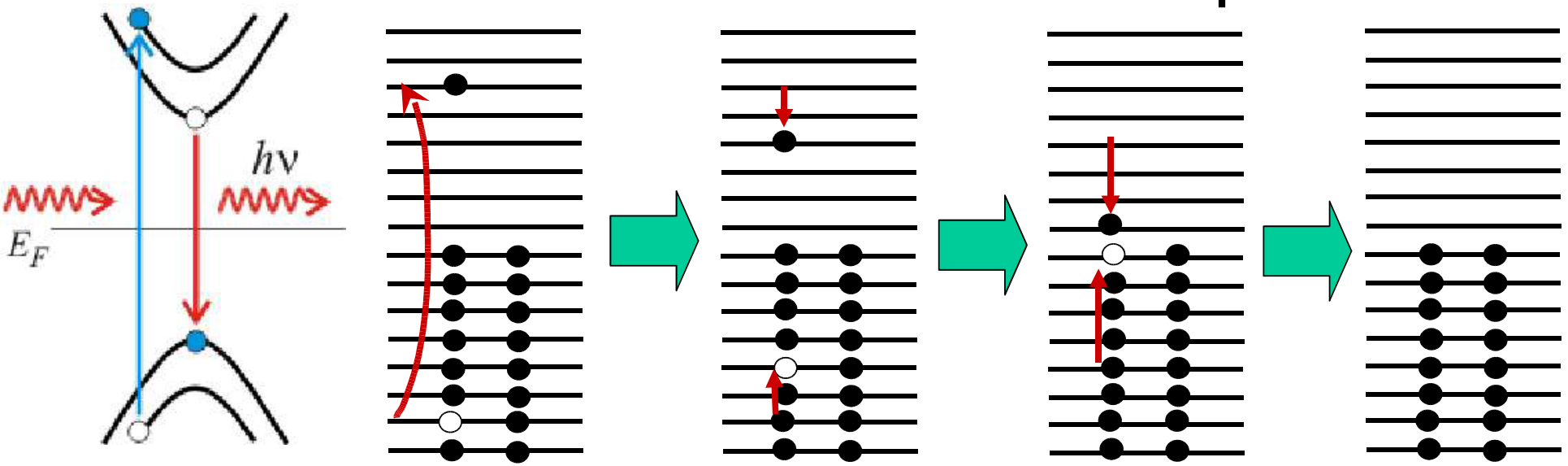

*A.G. Marinopoulus, L. Reining, A.R. PRL (2003)*




("*depolarization effects*")

# Hot carrier relaxation in nanotube

## Relaxation of hole and electron after photo-excitation




TDDFT-MD is parameter free and treats

* Time evolution of wave function with ionic motion: **electron phonon coupling**
*Time evolution of charge density:
**electron-electron coupling** within DFT
* excitonic effects!!!!!!

*Y. Miyamoto, D. Tomanek, AR (unpublished)*

**Ichida, et al., Physica B 323, 237 (2002)**

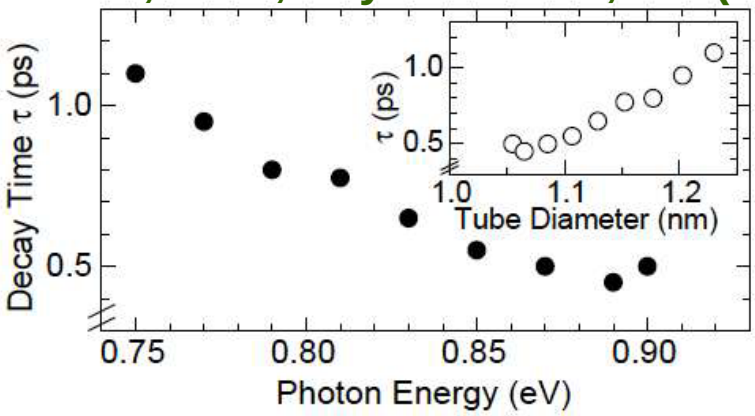
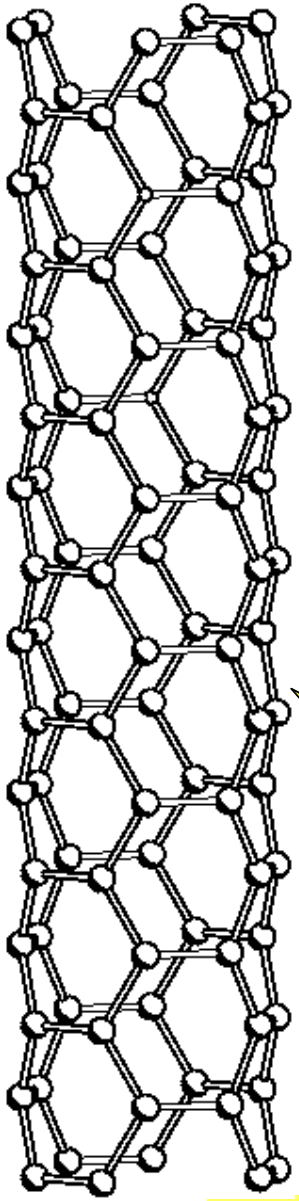



Fig. 2. Observed fast decay time as a function of probe photon energy. Inset: Tube diameter dependence of decay time.

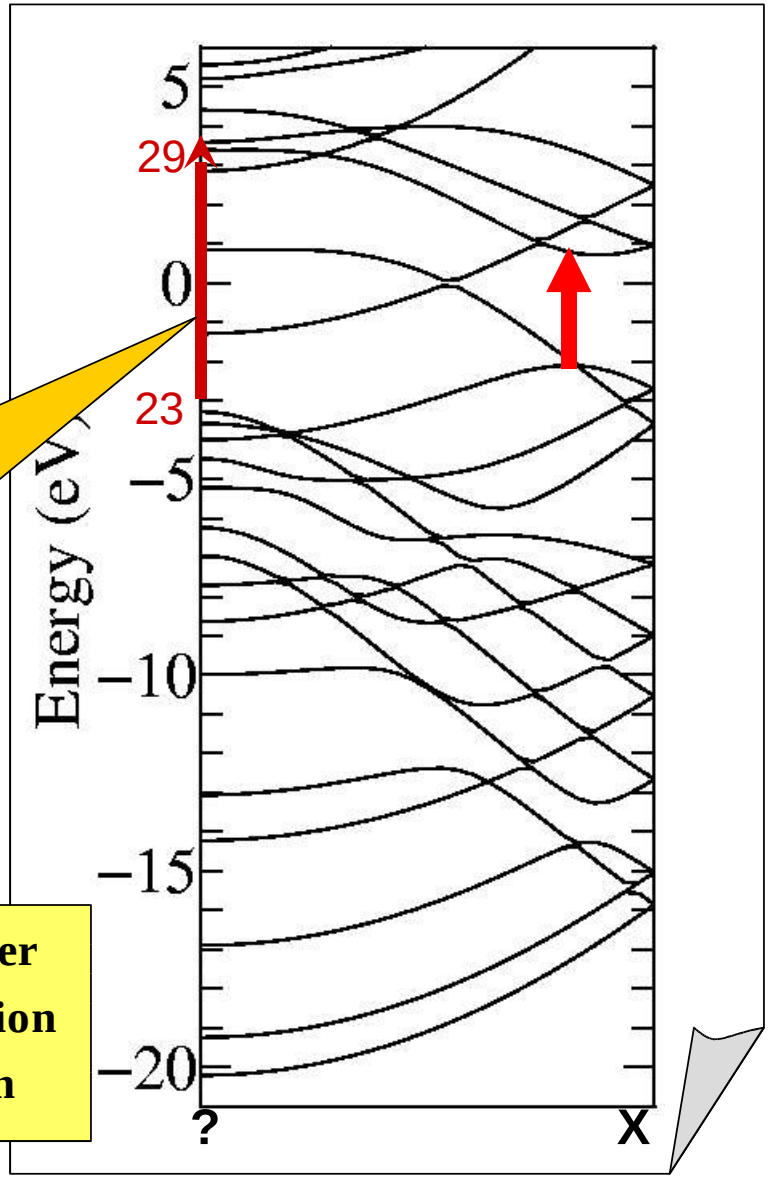
# Present case: (3,3) nanotube



Assigned excitation with experimental data

[Z. M. Li et al, Phys. Rev. Lett. 87, 127401 (2001).]

**Transition considered: Optically allowed, with E// (tube axis), but *not observed experimentally*!!**



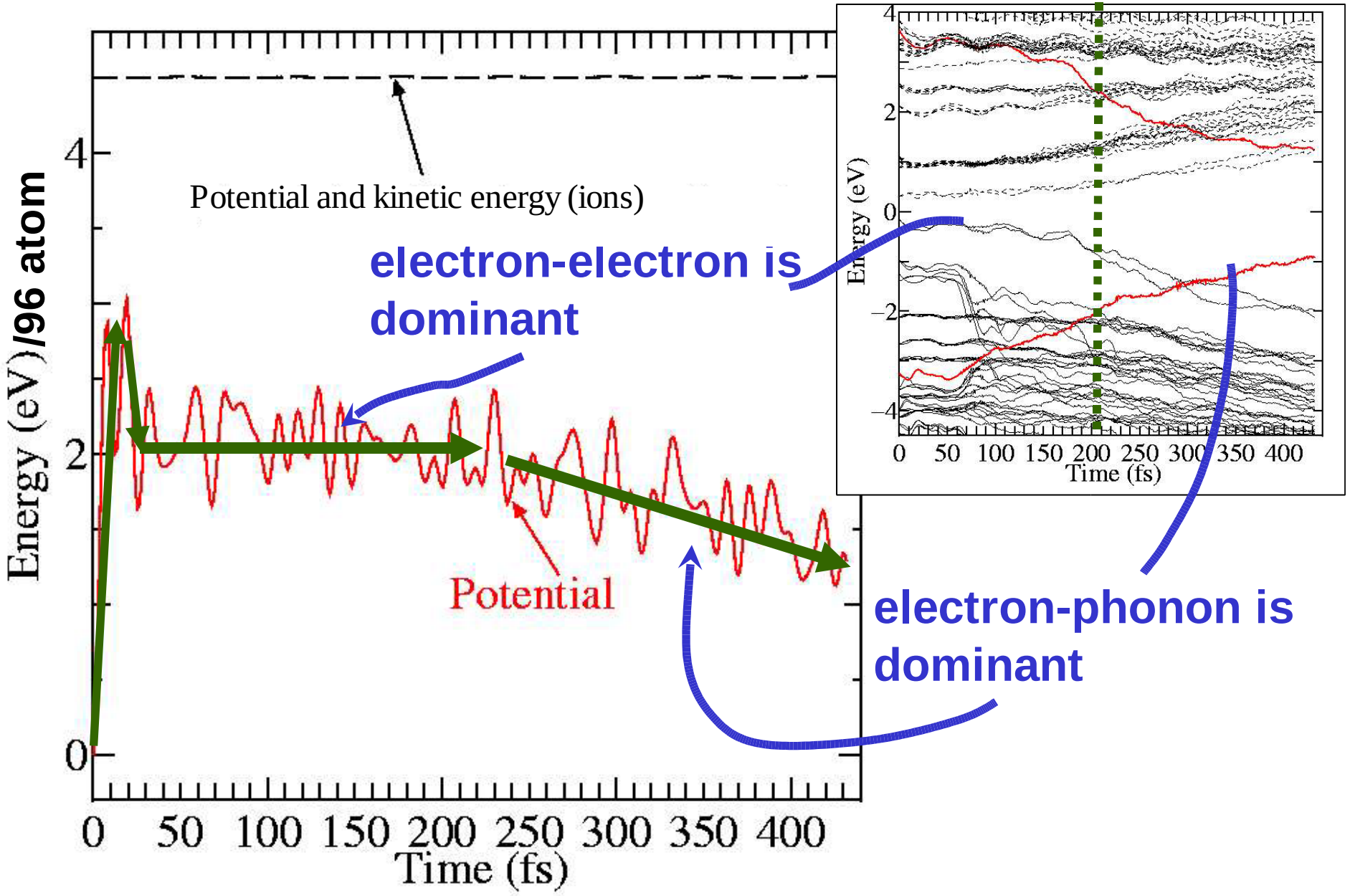

**Randomized ionic velocities under the Maxwell-Boltzmann distribution with 300K as an initial condition**

**Computational conditions: TDLDA (with adiabatic xc potential)**

**Time step: 0.08 a.u. (=0.0019 fs)**

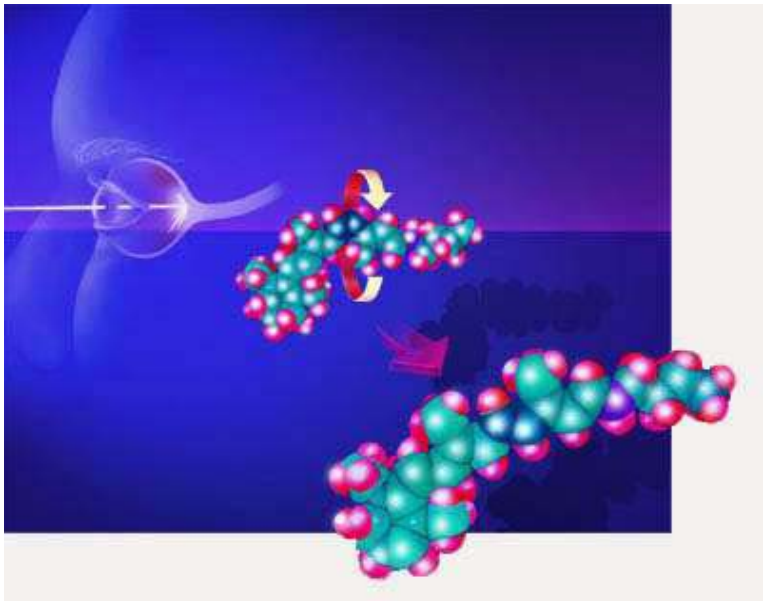
# Energy transfer with longer time-scale

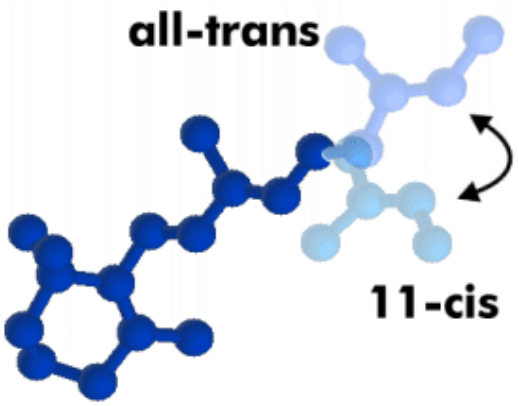
*electron-electron vs. electron-phonon interaction on real-time axis*

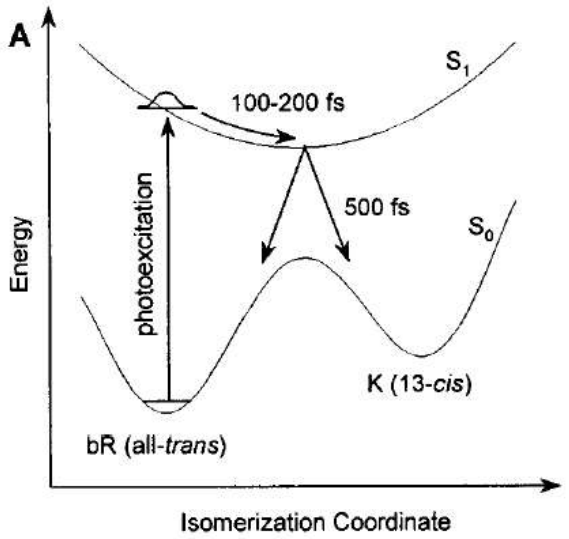


# Biological molecules: photoreceptors

*QM/MM + TDDFT approach*






**F. Gai et al. Science 279, 1886 (1998)**

*M.A.L Marques, X. Lopez, D. Varsano, A. Castro, and A. R. Phys. Rev. Lett.* ***90****, 158101 (2003)*

# Time Scales:

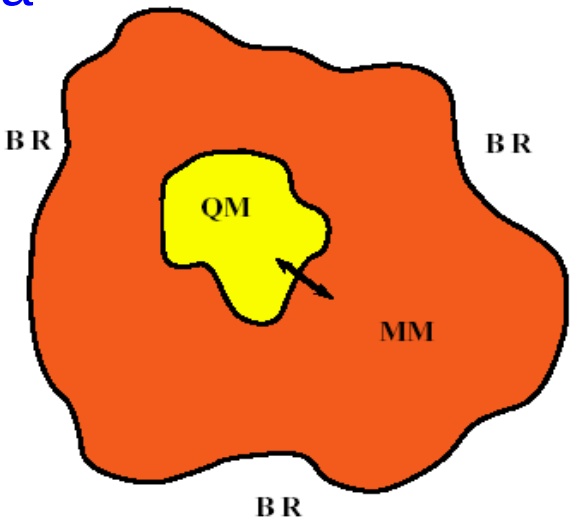
- Local Motions (0.01 to 5 Å, $10^{-15}$ to $10^{-1}$ s)
  - Atomic fluctuations
  - Sidechain Motions
  - Loop Motions
- Rigid Body Motions (1 to 10Å, $10^{-9}$ to 1s)
  - Helix Motions
  - Domain Motions (hinge bending)
  - Subunit motions
- Large-Scale Motions (> 5Å, $10^{-7}$ to $10^{4}$ s)
  - Helix coil transitions
  - Dissociation/Association
  - Folding and Unfolding

## QM/MM Hamiltonian

For Local Phenomena

$$\hat{H} = \hat{H}_{QM} + \hat{H}_{QM/MM} + \hat{H}_{MM} + \hat{H}_{boundary} + \hat{H}_{restraints}$$

$$\hat{H}_{QM/MM} = \hat{H}^{elec}_{QM/MM} + \hat{H}^{vdW}_{QM/MM} + \hat{H}^{bonded}_{QM/MM}$$





1. Warshel , A.; Levitt, M. J. Mol. Biol., **1976**, *103*, 227

2. Field, M.J.; Bash, P.A.; Karplus, M. J. Comp. Chem., **1990**, *11*, 700


## QM/MM Electrostatics

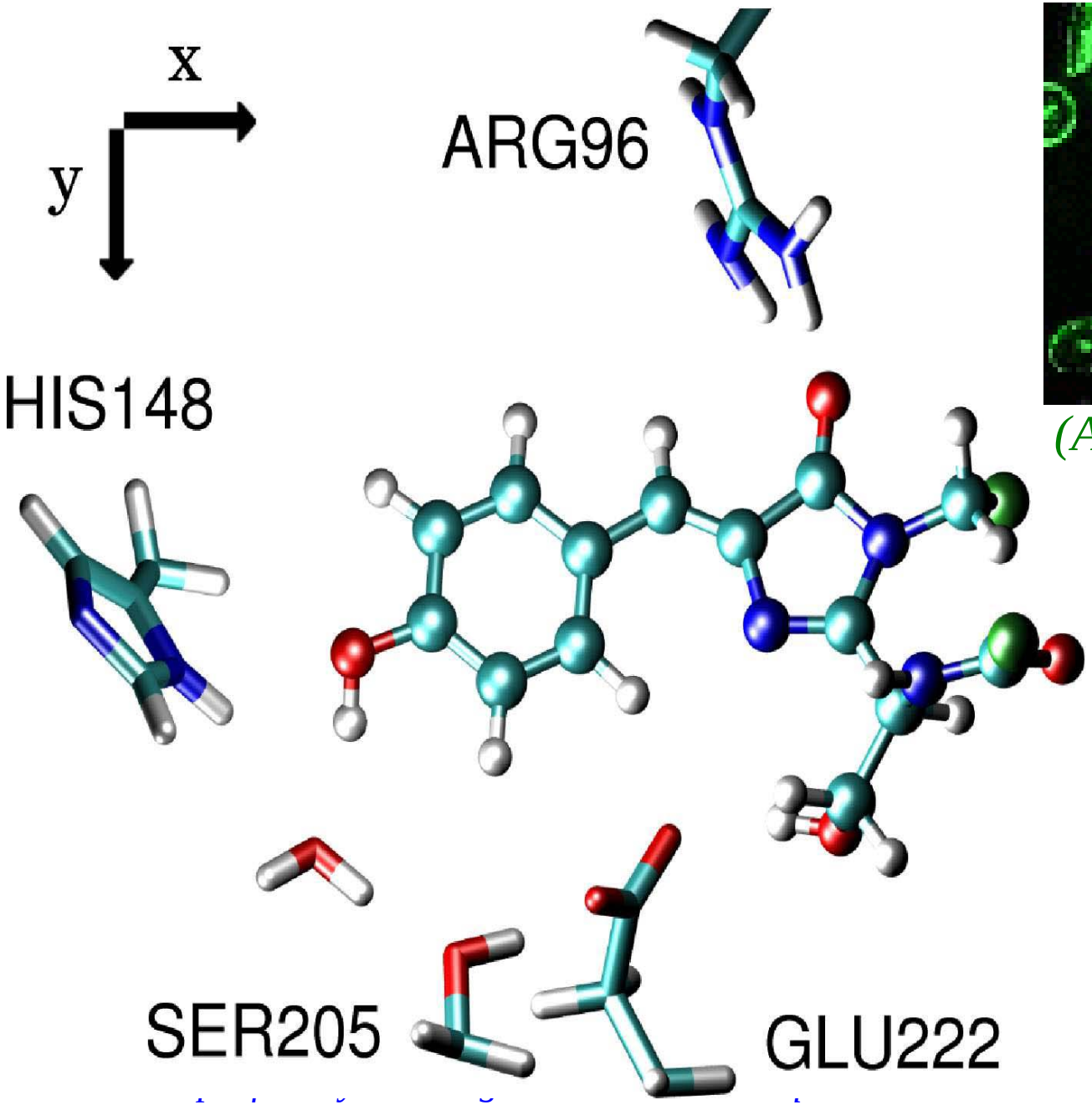
$$\hat{H}^{elec.}_{QM/MM} = -\sum_{i,M} \frac{q_M}{r_{iM}} + \sum_{\alpha,M} \frac{Z_\alpha q_M}{R_{\alpha M}}$$

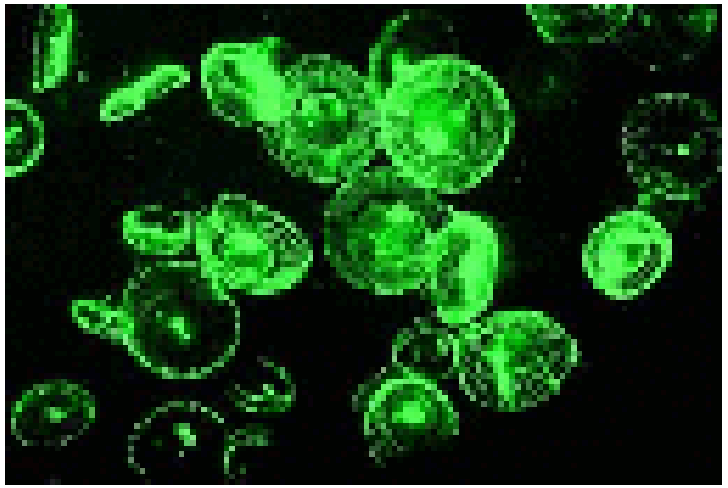
Van der Waals Interactions

$$\hat{H}^{v.d.Waals}_{QM/MM} = \sum_{\alpha,M} \left[ \frac{A_{\alpha M}}{R^{12}_{\alpha M}} - \frac{B_{\alpha M}}{R^{6}_{\alpha M}} \right]$$

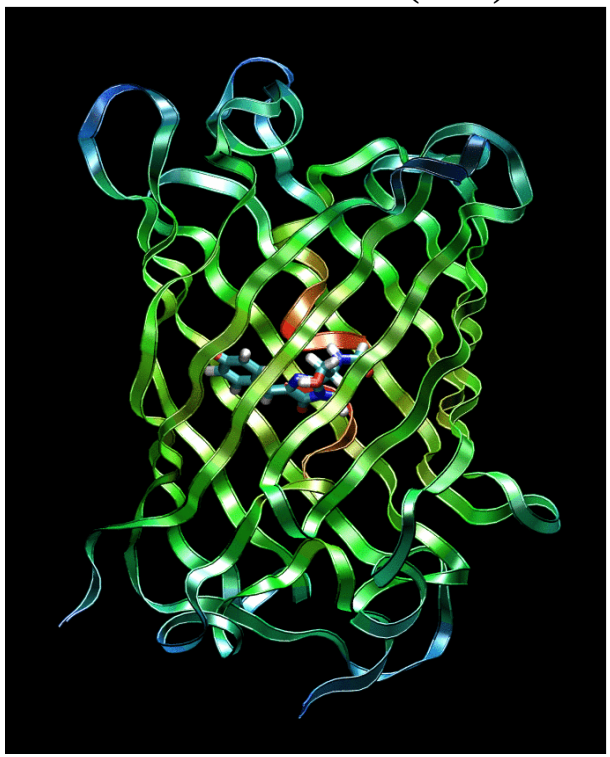
**SCF**

# *Towards understanding biomolecule colours*



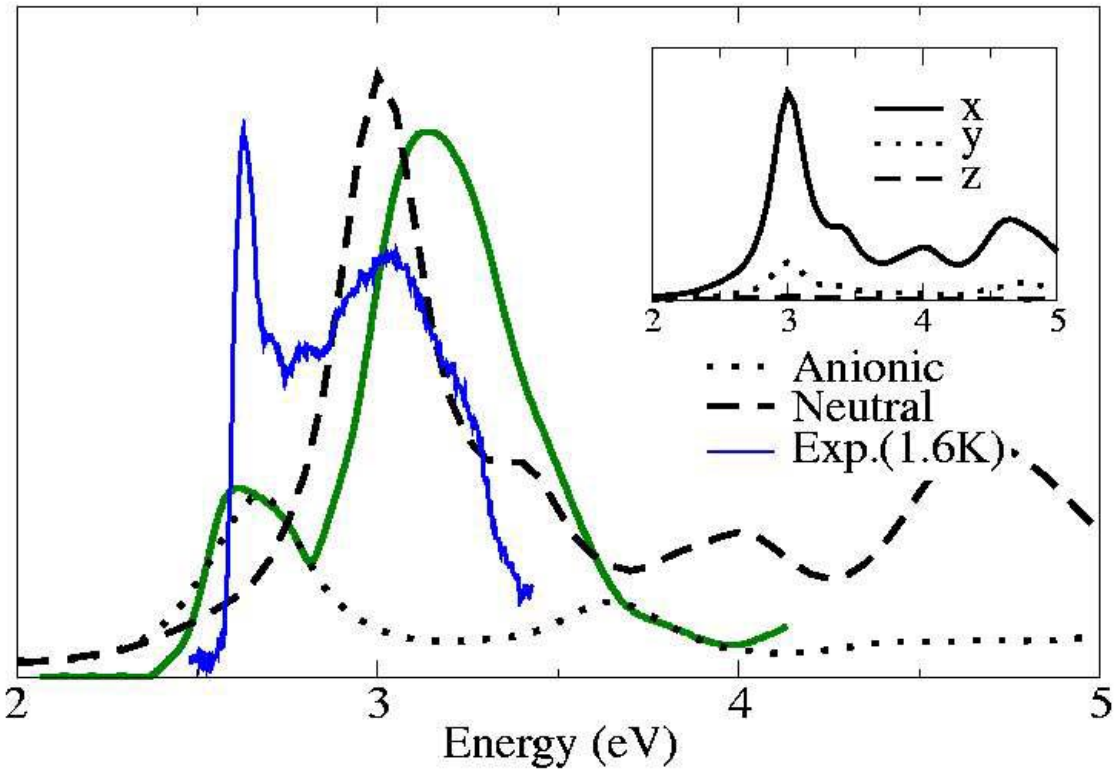



*(Aequorea victoria: jellyfish)*
Green Fluorescent Protein (GFP).

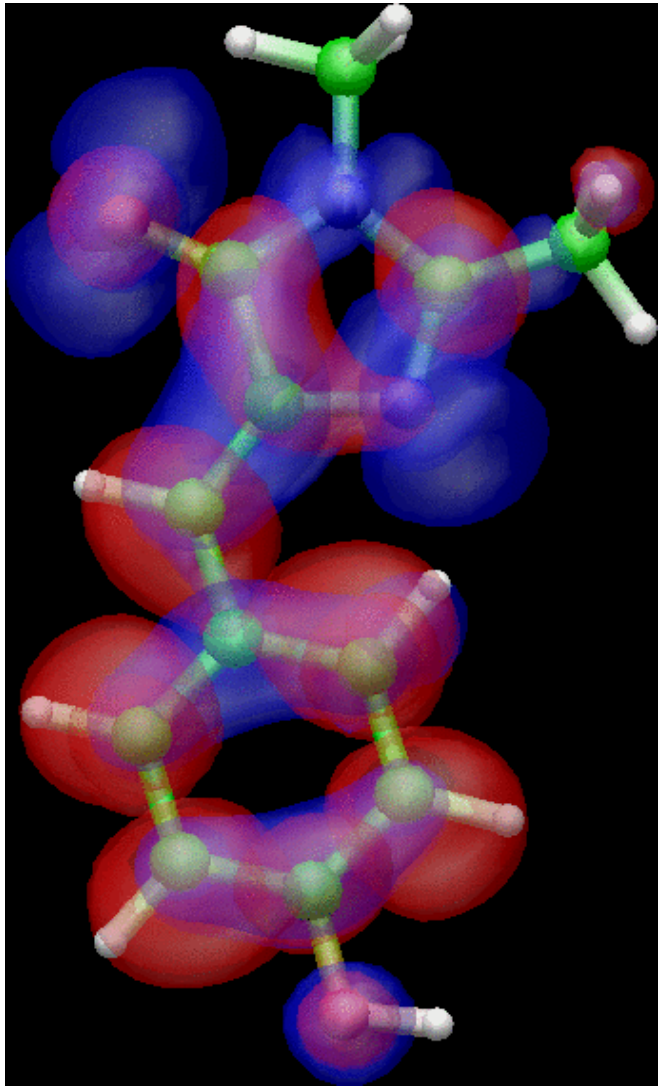


# *Towards understanding biomolecular colours: the GFP case*

HOMO-LUMO

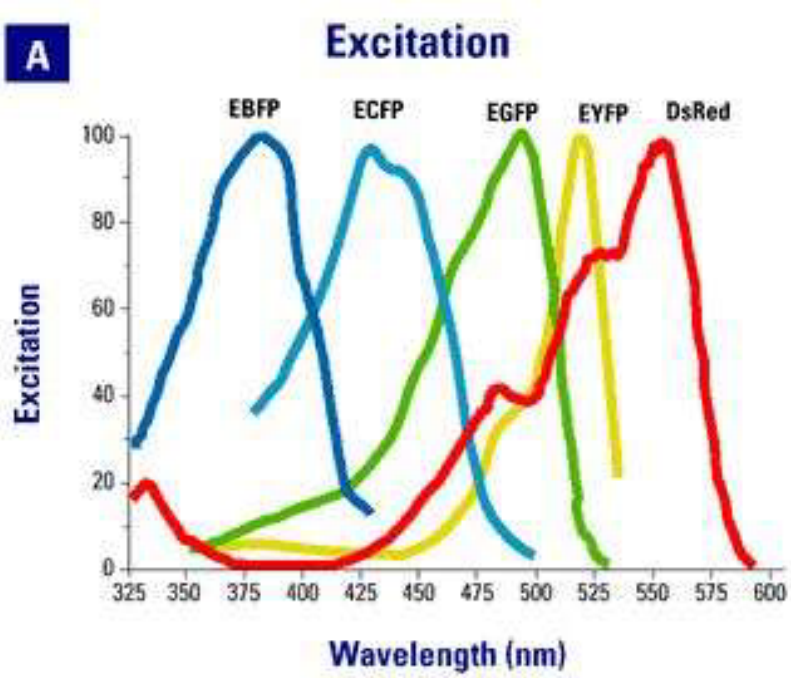


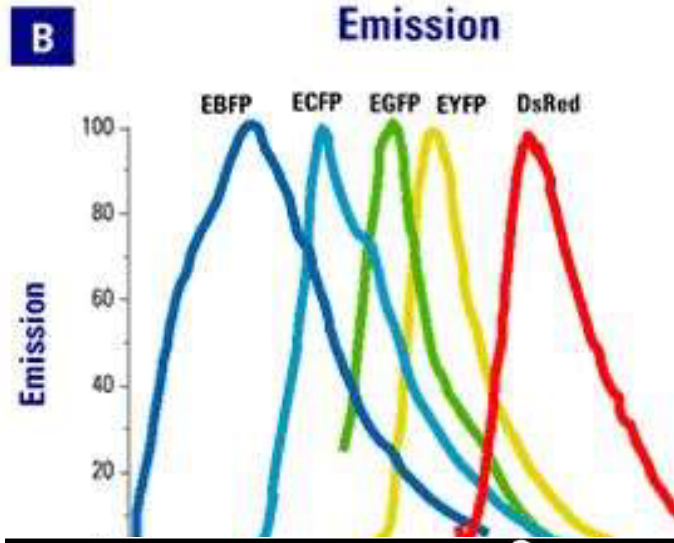

*T.M.H. Creemers et al, Proc. Natl. Acad. Sci.. USA (1999)*

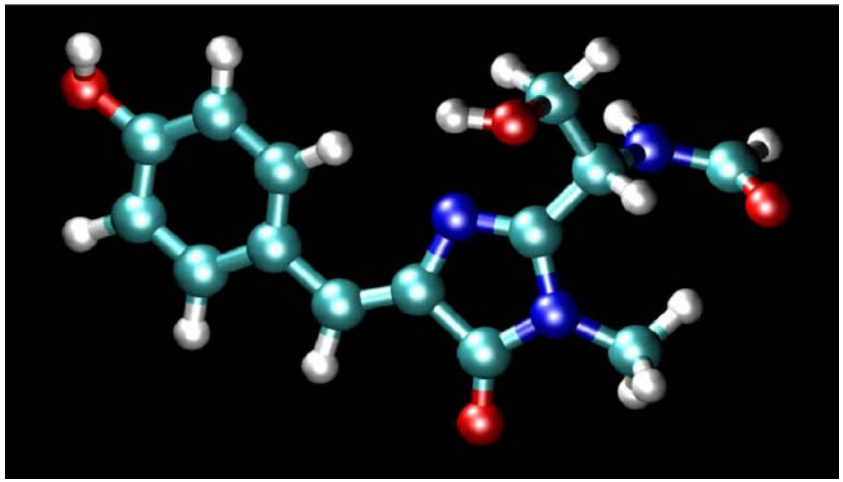


*QM/MM approach*

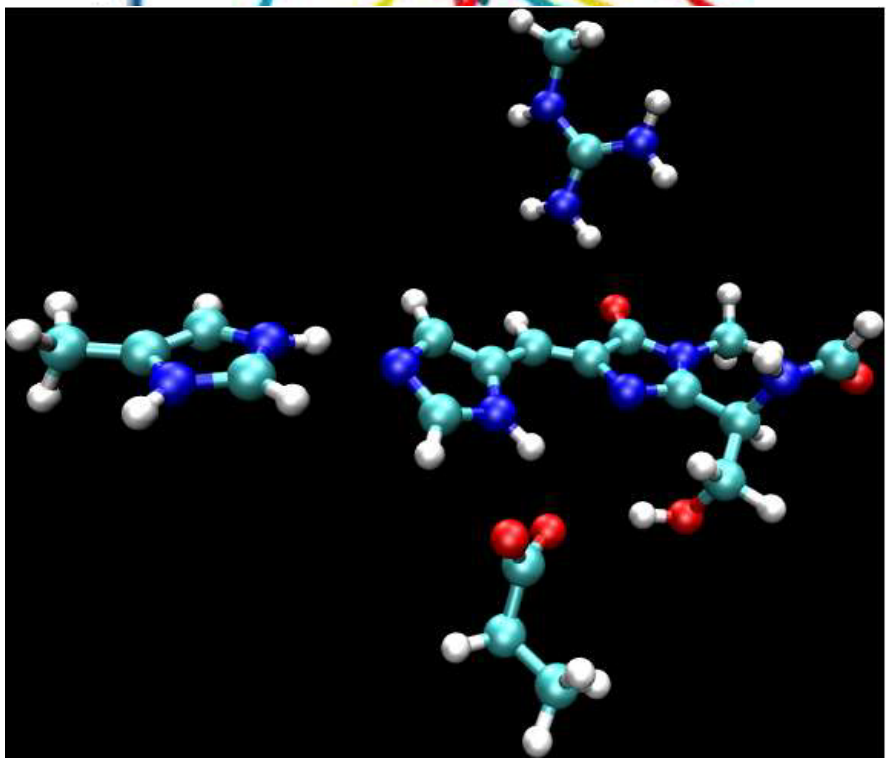
# Blue Fluorescent Protein- Mutants

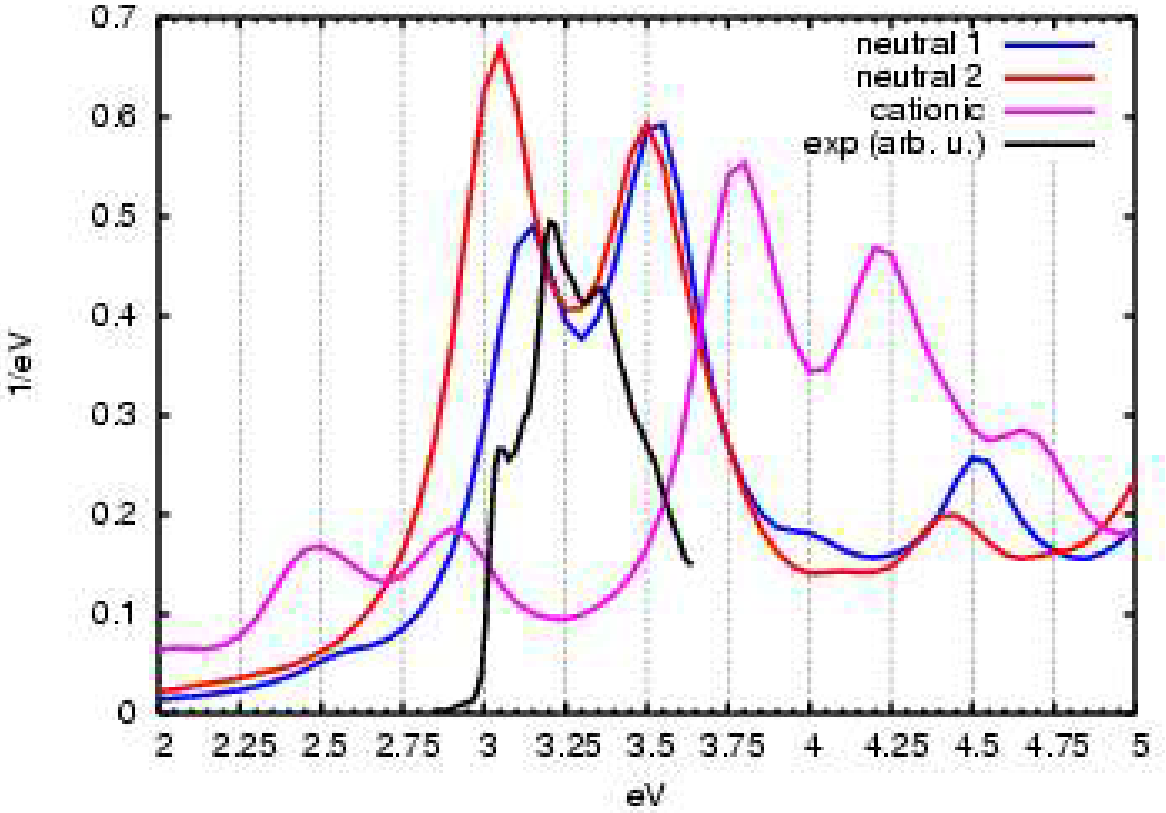


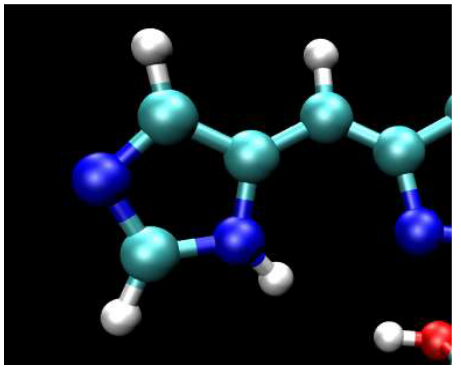



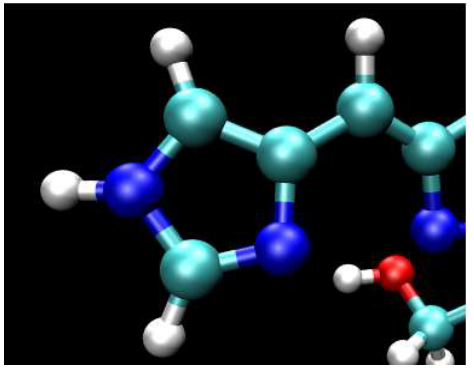
Green





Neutral



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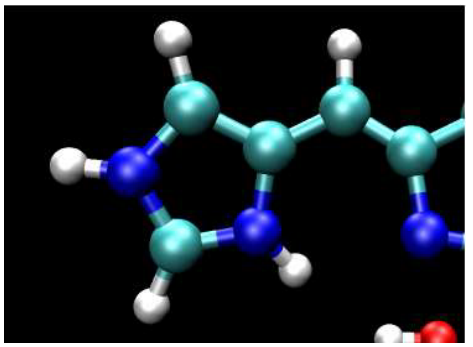
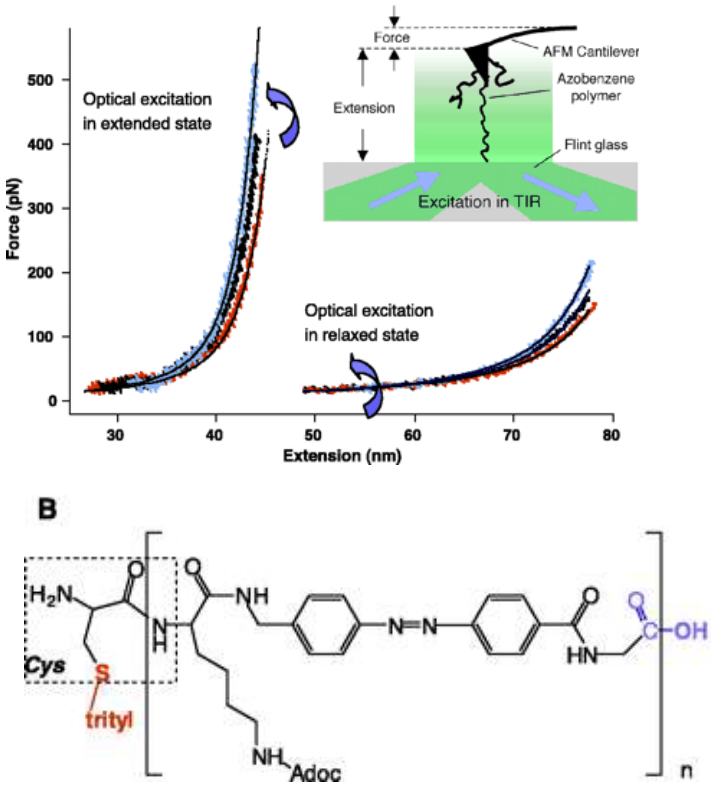


Cationic

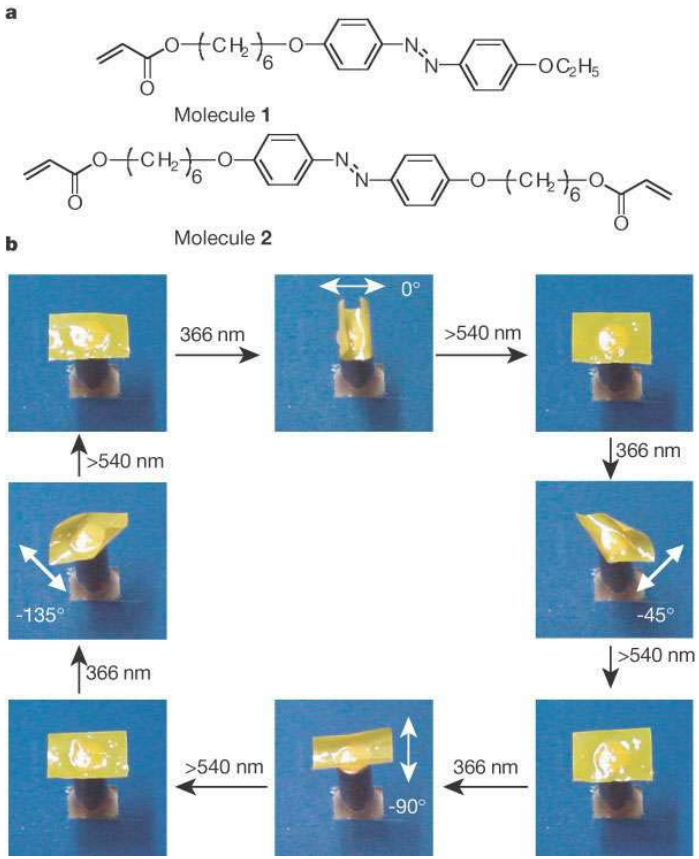
# Azobenzene: spectroscopy along femtosecond-laser induced photoisomerization

*Azobenzene dyes are known to isomerize at the central N-N bond within fractions of picoseconds at high quantum yield* [*T. Nägele et al, Chem. Phys. Lett.* ***272****, 489 (1997)*].

*One example is the APB optical trigger*: ***Single-Molecule Optomechanical Cycle***

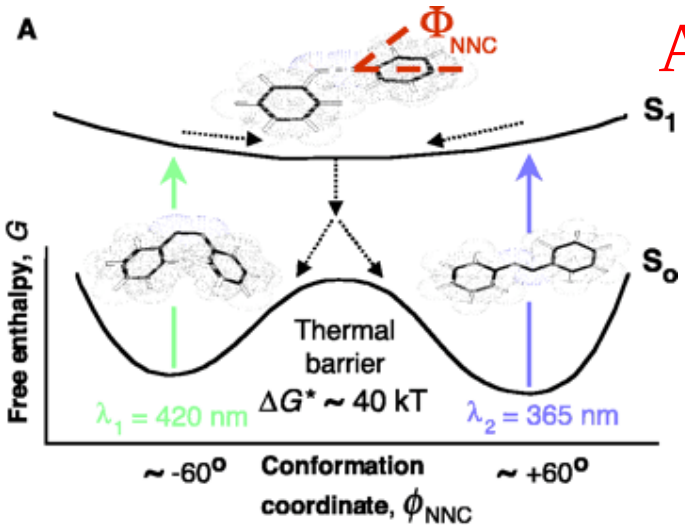


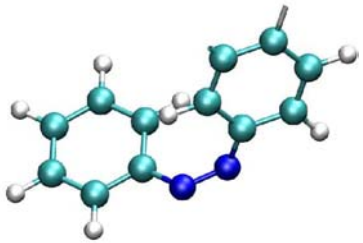

*T. Hugel et al, Science, 296, 1103 (2002)*

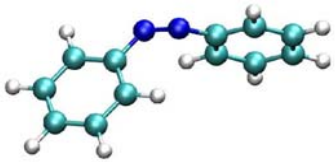



Y. Yu et al, Nature 425, 145 82003)

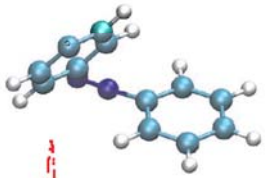
# Azobenzene: spectroscopy along femtosecond-laser induced photoisomerization

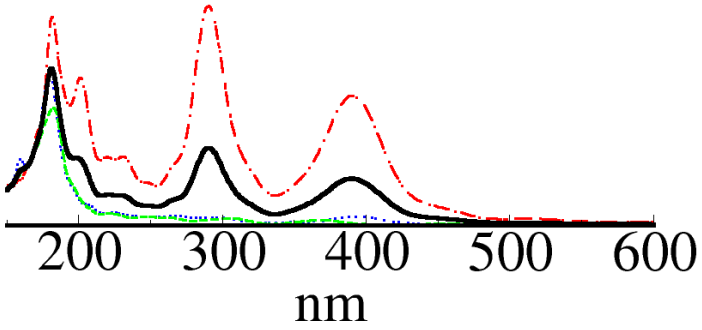


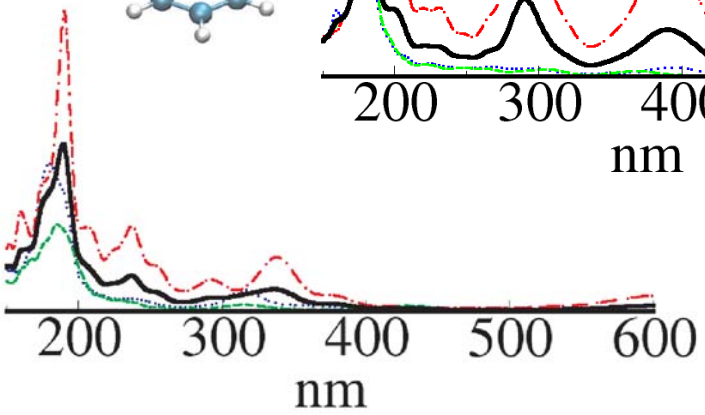



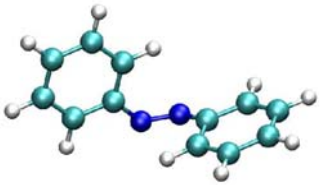


CIS



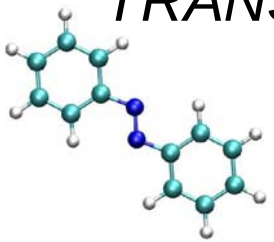





TRANS






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

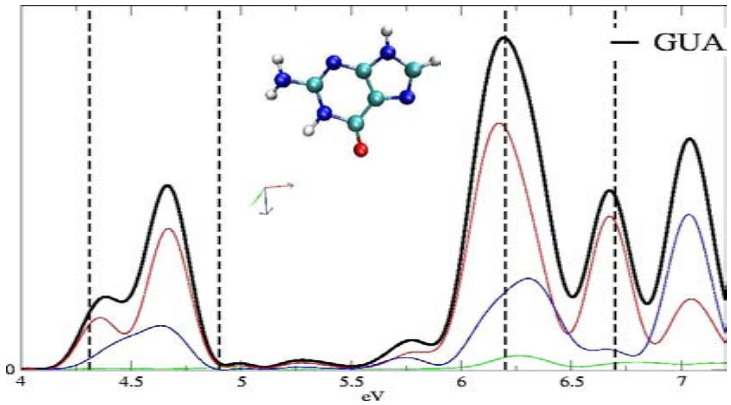
# *Optical Rotatory Power*

$$\Re_j(E) \propto \int_0^\infty dt\, e^{i(E+i\delta)t} L_j(t) \quad ; \quad \Re(E) = \Re_x + \Re_y + \Re_z$$

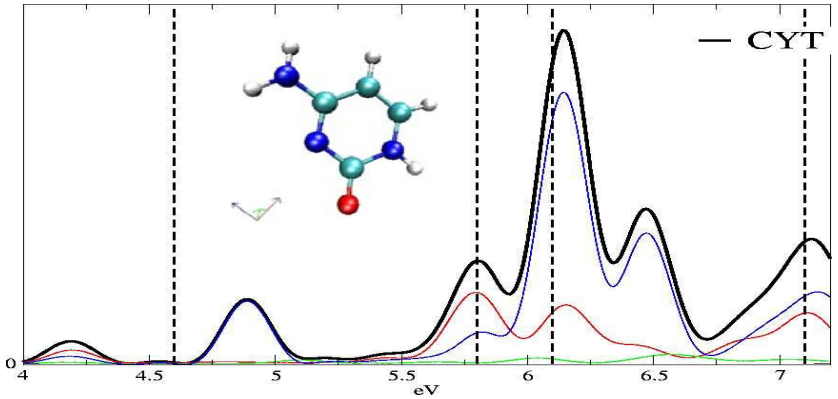
$$R(E) = \Im \frac{\Re(E)}{\pi}$$ rotational strenght function

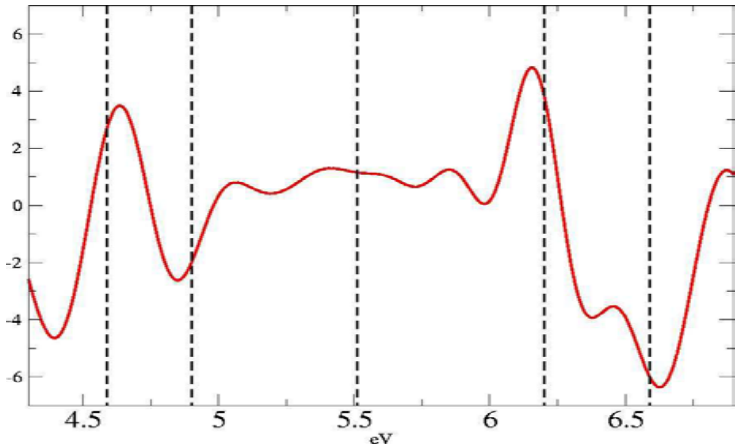
Guanine

Cytosine

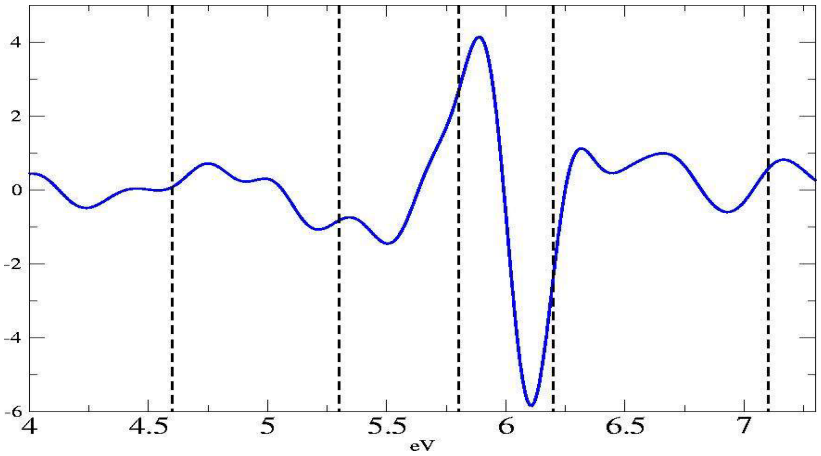



Absorption



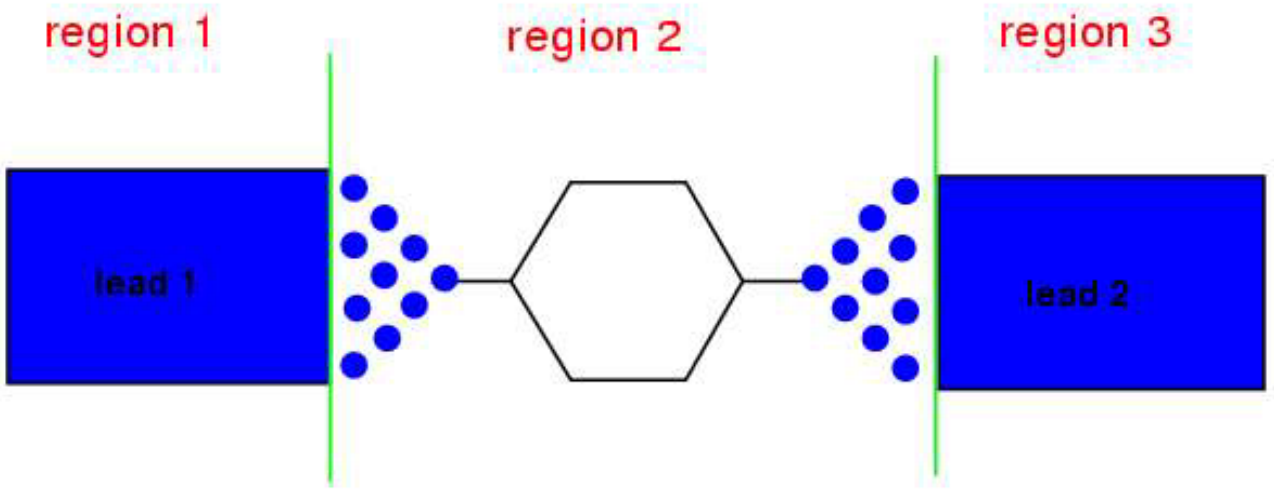




Circular dichroism



# *First principles description of Molecular transport ??????*

*In connection with Mark Ratner Lectures!*




- (Landauer): Non equilibrium Green's Functions

$$G = \frac{2e^2}{h} Tr\left[G^R(w)\Gamma_L(w)G^A(w)\Gamma_R(w)\right]$$

- *TDDFT? -----TD-Current-DFT*

*QUESTIONS?*

- ✔ Ground-state DFT?

  *J(r,t); virtual exc.*
- ✔ Temperature

  *e-phon coupling?*
- ✔ Dissipation??
- ✔ Finite bias (resonant)
- ✔ AC transport
- ✔ Role of contacts
- ✔ *MOLECULE*

*Friday*

## *III. Extended systems: problems and new developments*

# Calculation of optical properties

Optical absorption

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

$$\sigma_{abs}(\omega) \propto Im(\epsilon(\omega))$$

$$EELS \alpha \epsilon^{-1}(\omega) = 1 + v\chi$$

Dielectric function in Random Phase Approximation (RPA)

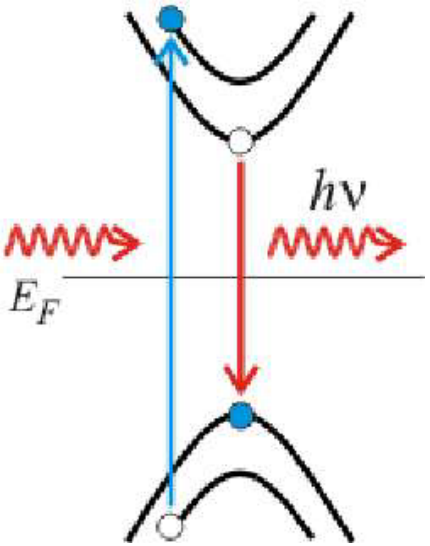
$$\epsilon_{RPA} = 1 - v_c \chi^{(0)}$$

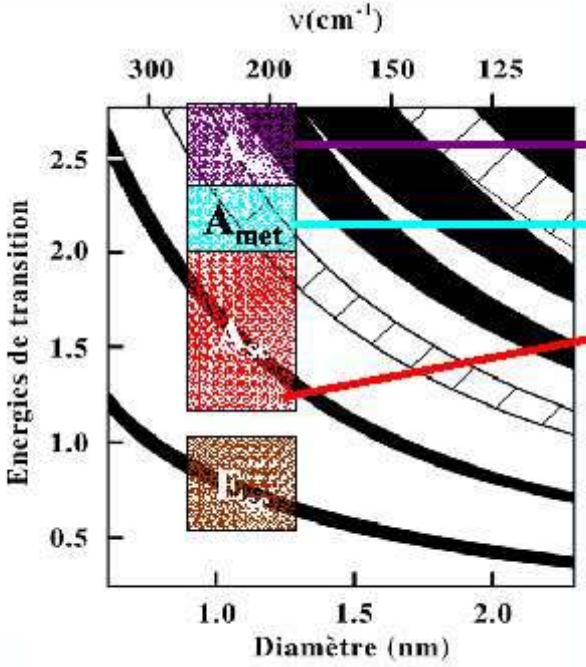
$$\chi^{(0)}(r, r', \omega) = 2\,\Sigma_{i \neq j}(f_i - f_j)\frac{\phi_i(r)\phi_j^*(r)\phi_i^*(r')\phi_j(r')}{\epsilon_i - \epsilon_j - \omega - i\eta}$$

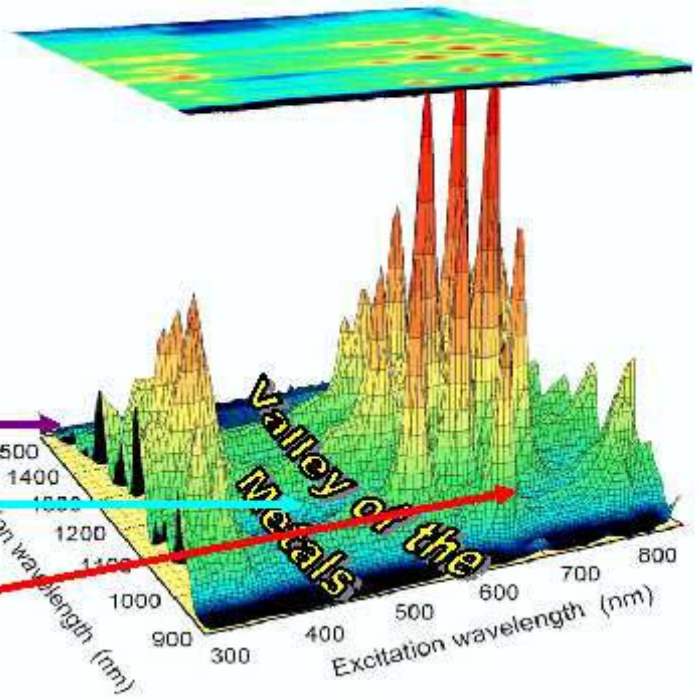
Macroscopic ε with local field effects (LFE):

$$\epsilon_M(\omega) = 1/\epsilon^{-1}_{G=G'=0}(q \to 0, \omega)$$

# Tube (n,m) characterisation

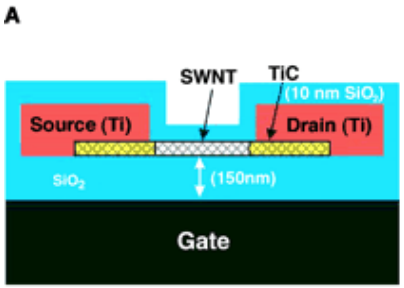


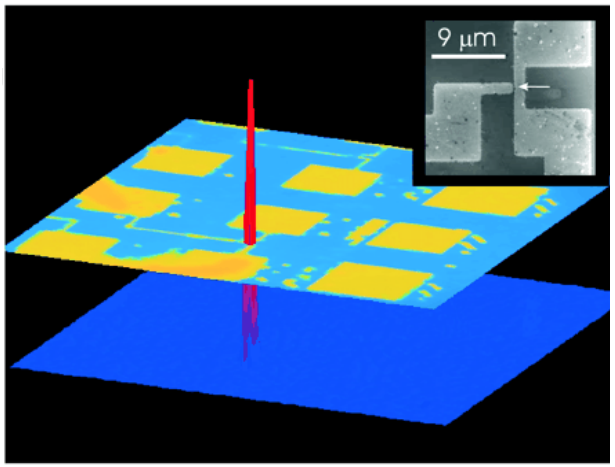




*Bachilo et al, Science 298, 2361 (2002)*

[Optical FET device!!!!!!]




*J. A. Misewich, et al Science 300, 783 (2003)*