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ICTP 40th Anniversary

SMR 1564 - 4

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

TDDFT THEORY:

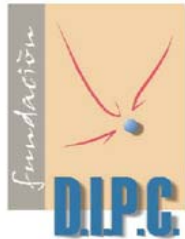
APPLICATIONS TO NANO AND BIO-STRUCTURES

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

A. RUBIO

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



Optical properties of nanostructures

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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 nanostructures

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

$$\rho(\mathbf{r}, t) = \sum_j |\varphi_j(\mathbf{r}, t)|^2$$

$$N(\mathbf{R}, t) = |\chi(\mathbf{R}, t)|^2$$

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

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

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

$$W_s(\mathbf{R}, t) = W_{\text{laser}}(\mathbf{R}, t) + \frac{Z_1 Z_2}{R} + W_{en}^H(\mathbf{R}, t) + \mathbf{W}_{xc}[\rho, N](\mathbf{R}, t)$$

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)

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

$$0 < elf < 1$$

high localisation



$$C_{\sigma} \sim 0$$



$$elf \sim 1$$

completely delocalised



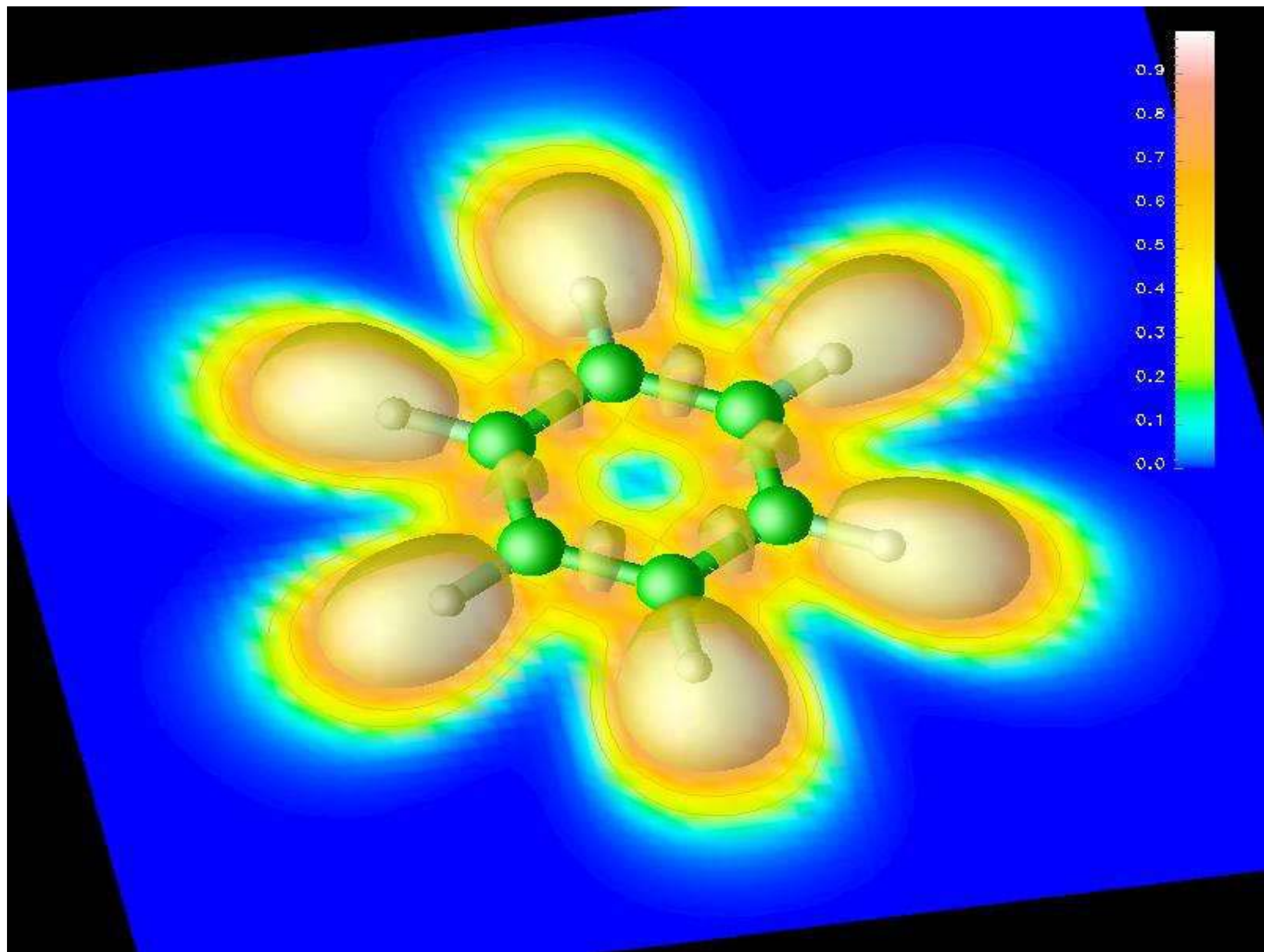
$$C_{\sigma} \sim C_{\sigma}^{uni}$$

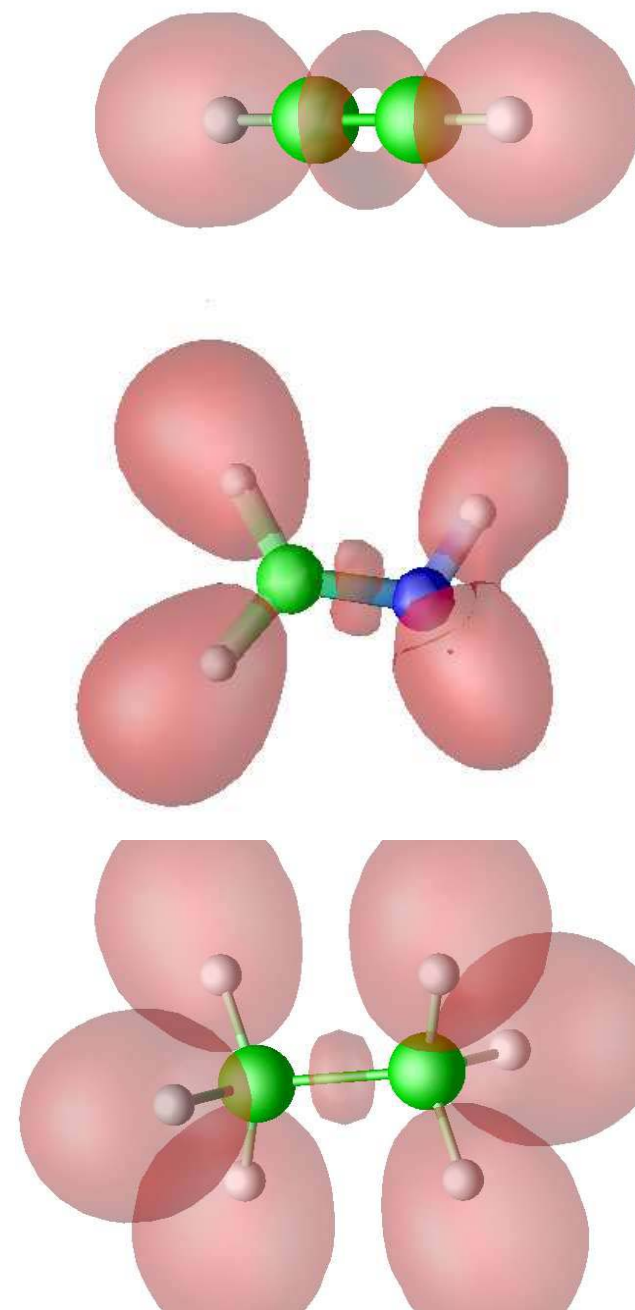
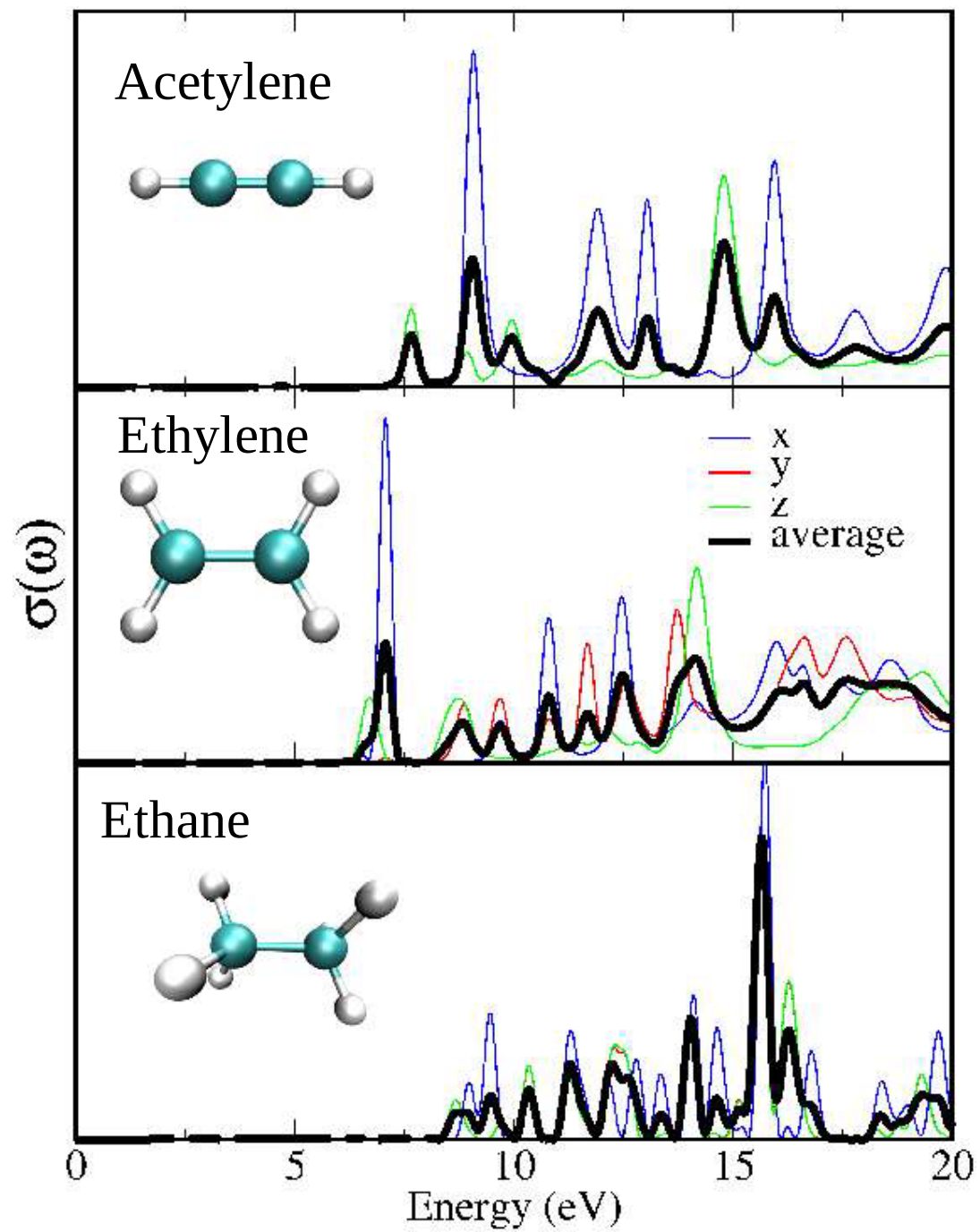


$$elf \sim 1/2$$

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

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

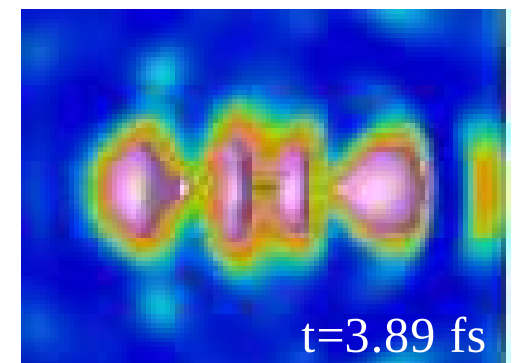
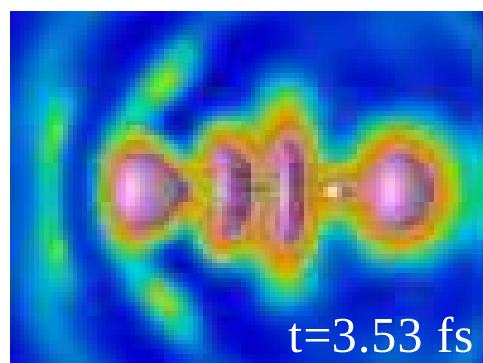
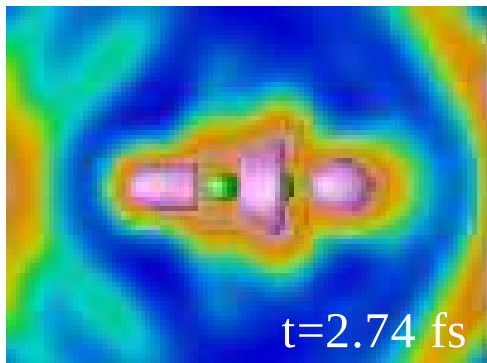
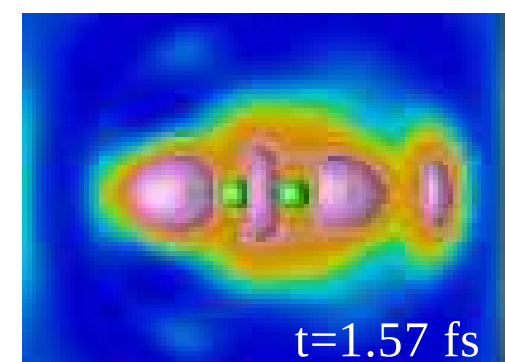
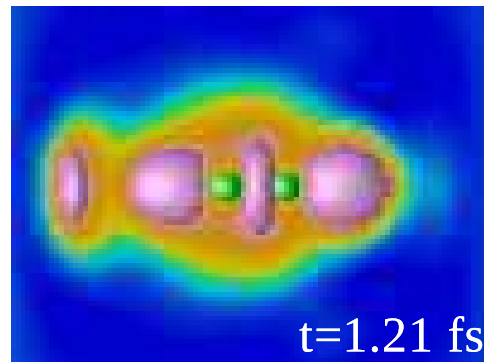
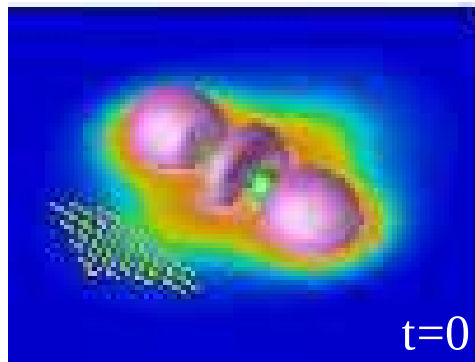




Time-dependent case: acetylene C_2H_2 in a strong laser field

$=17\text{eV}$, $T=8\text{fs}$, $I=1.2\times 10^{14}\text{ Wcm}^{-2}$

fast ionisation



to *

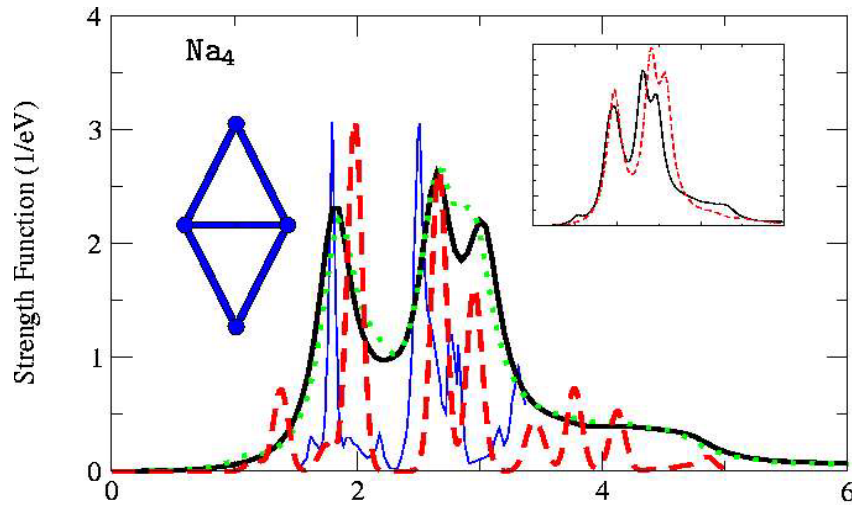
Nano (bio-) structures

*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

$$\chi(\omega) = \chi_0(\omega) + \chi_0(\omega)(v + f_{xc}(\omega))\chi(\omega) \quad \chi_0(r, r', \omega) = \sum_{ij} (f_j - f_i) \frac{\varphi_i^c(r) \varphi_j(r) \varphi_i(r') \varphi_j^c(r')}{\epsilon_i - \epsilon_j - \omega}$$



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

Single-pole approximation $\Rightarrow$

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

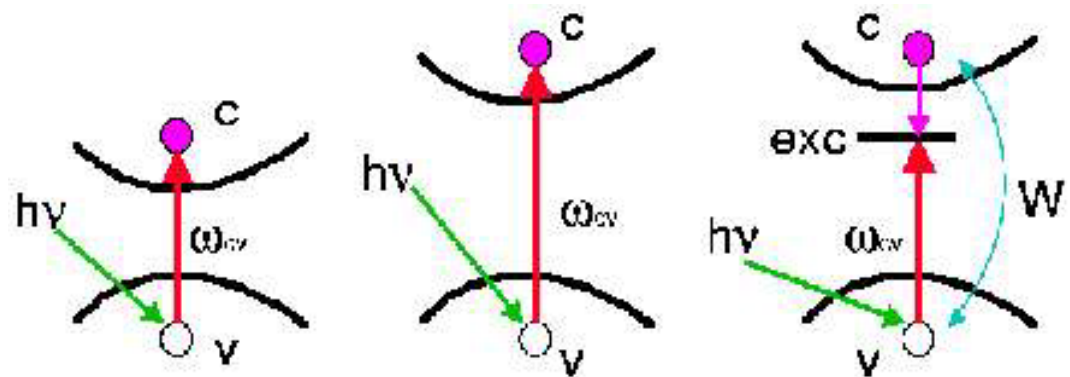
$$K \approx \int d^3r \int d^3r' \varphi_{j_0}(r) \varphi_{j_0}^*(r') \varphi_{k_0}(r') \varphi_{k_0}^*(r) \cdot \left(\frac{1}{|r-r'|} + f_{xc}(r, r') \right)$$

LDA- thick solid line

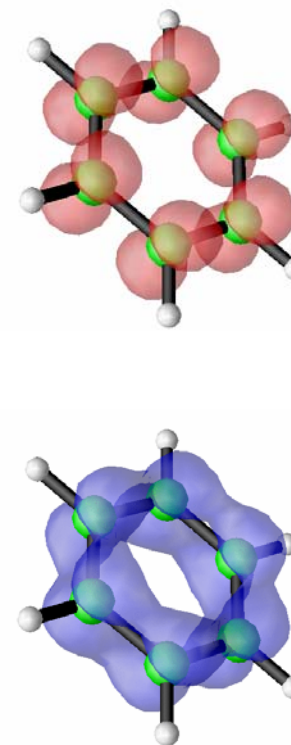
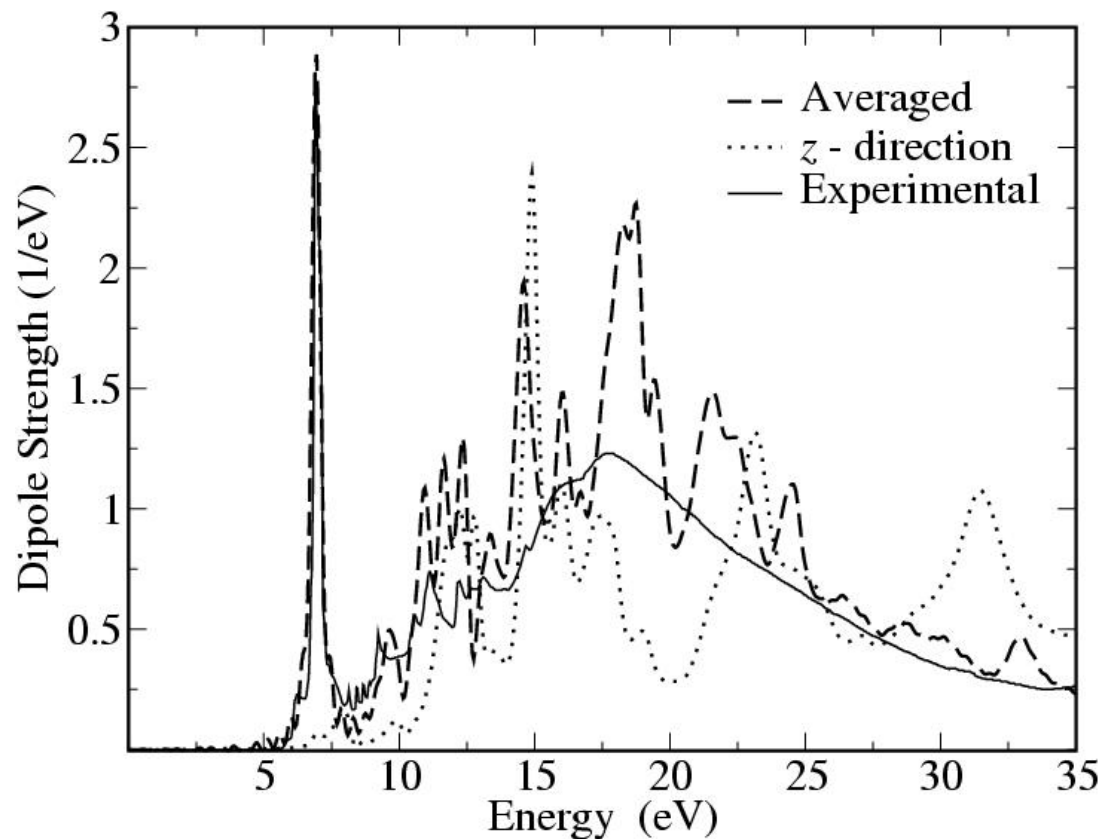
EXX- dotted line

Bethe-Salpeter

Experiments



Optical response: (Benzene)



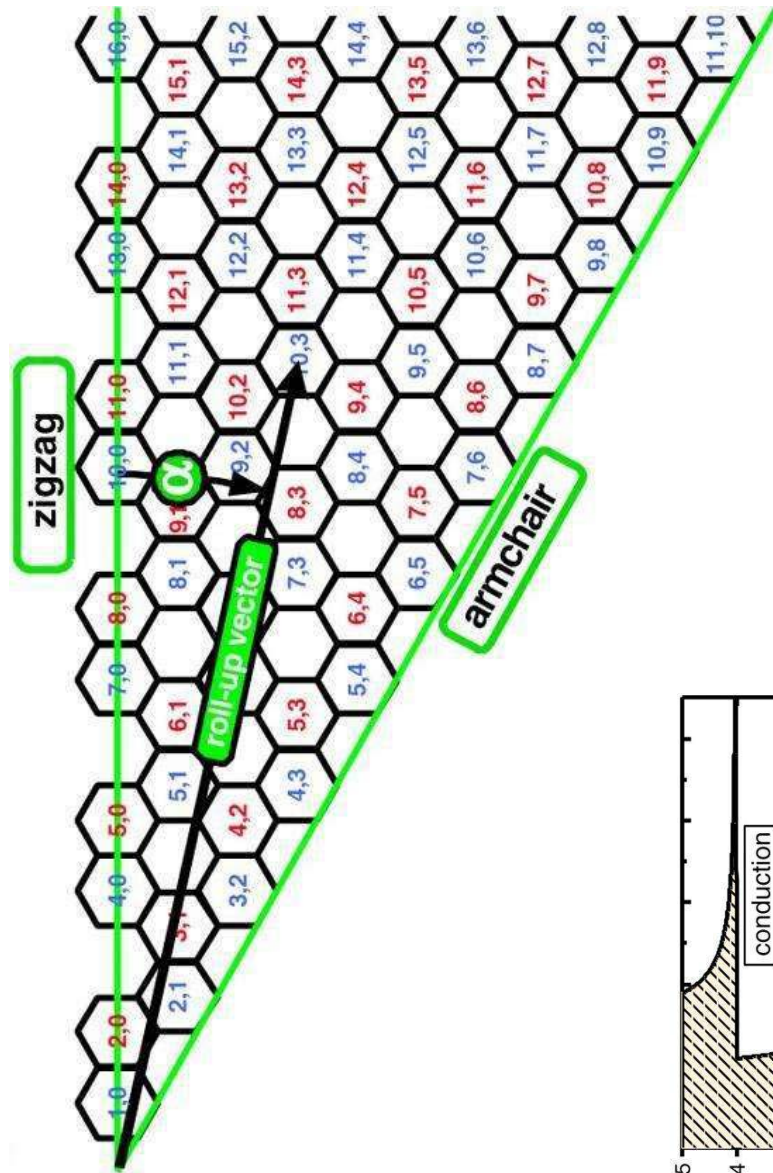
* (LUMO)

7eV

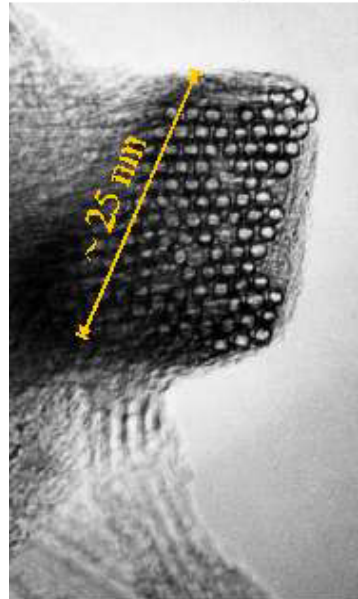
(HOMO)

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)

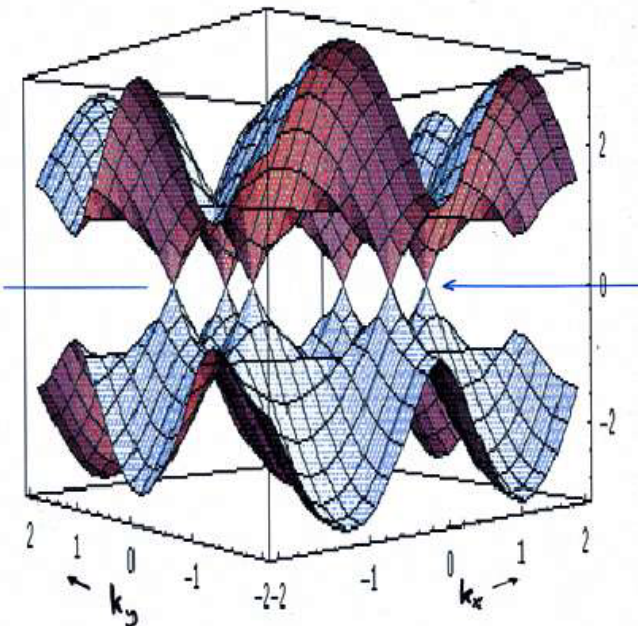
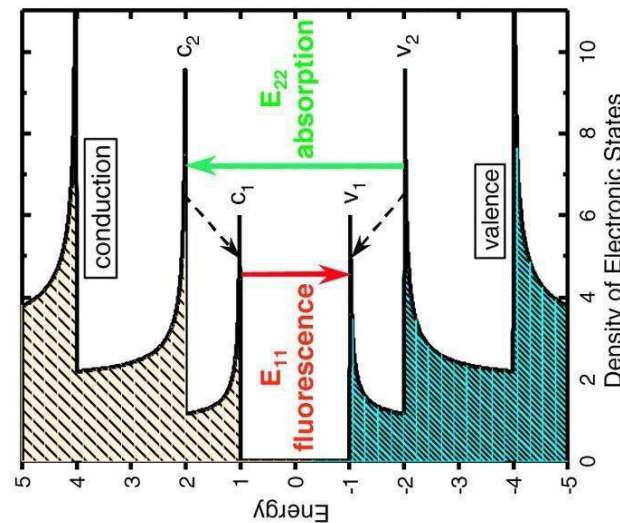
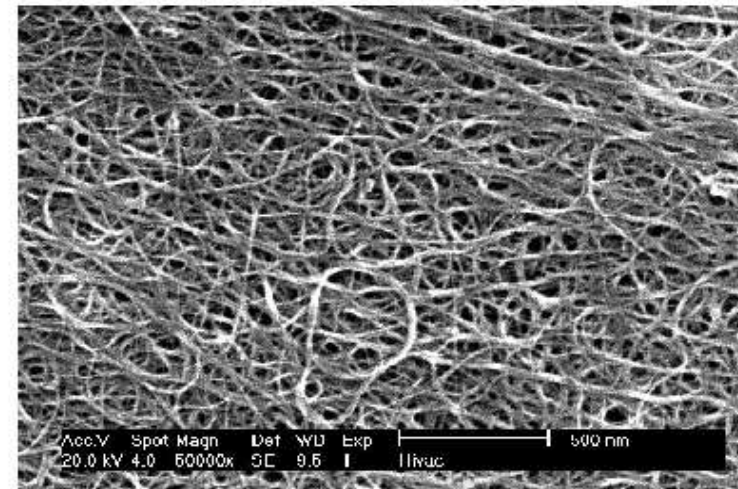
Carbon nanotubes: Iijima (1991)



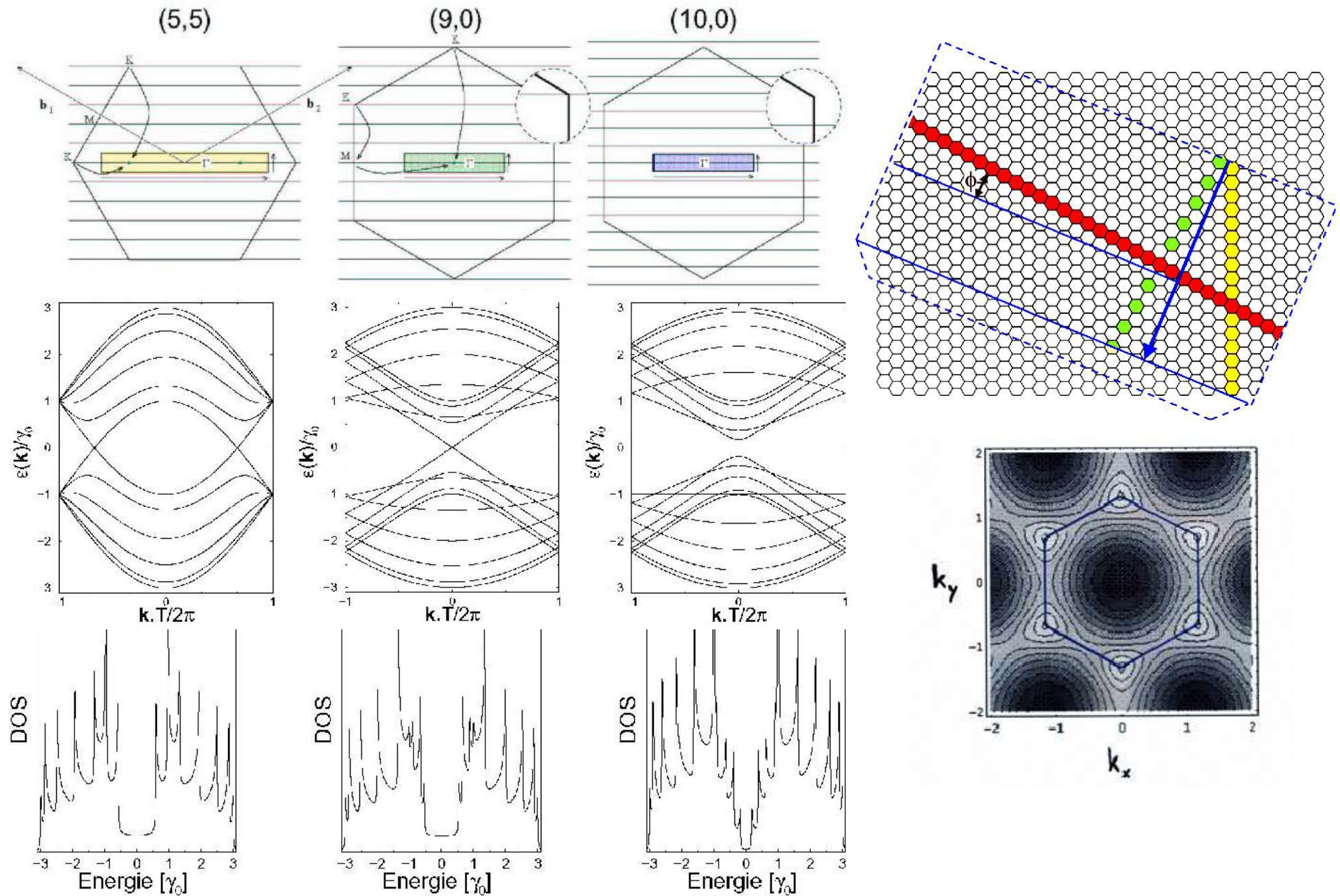
TEM of Rope



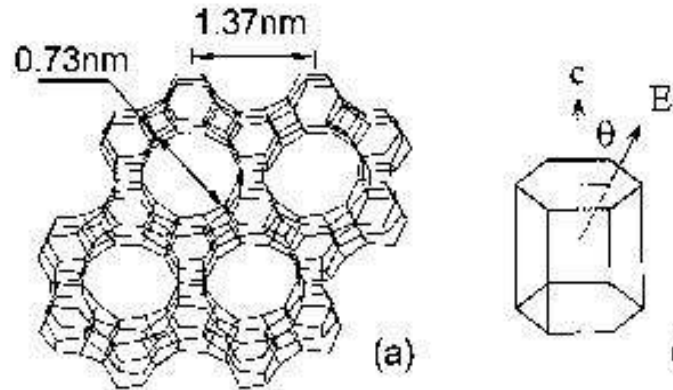
SEM: 'bucky-paper'



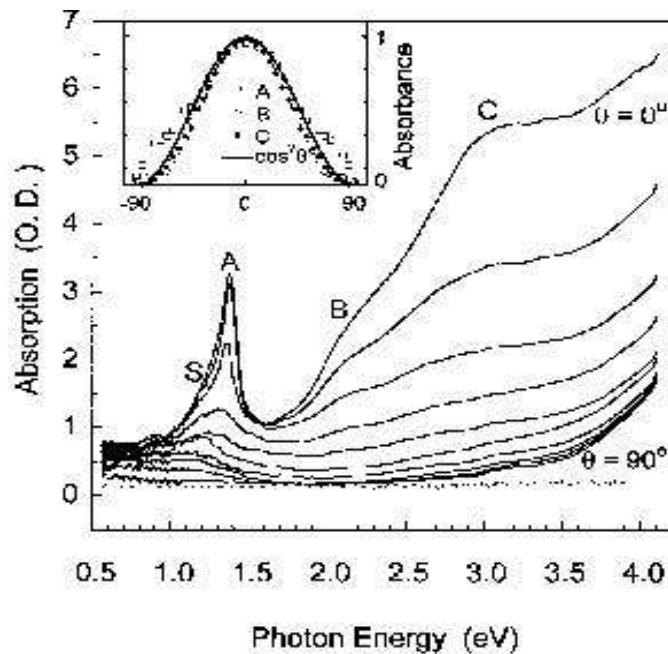
Simple model for the electronic structure: TB of C-tubes



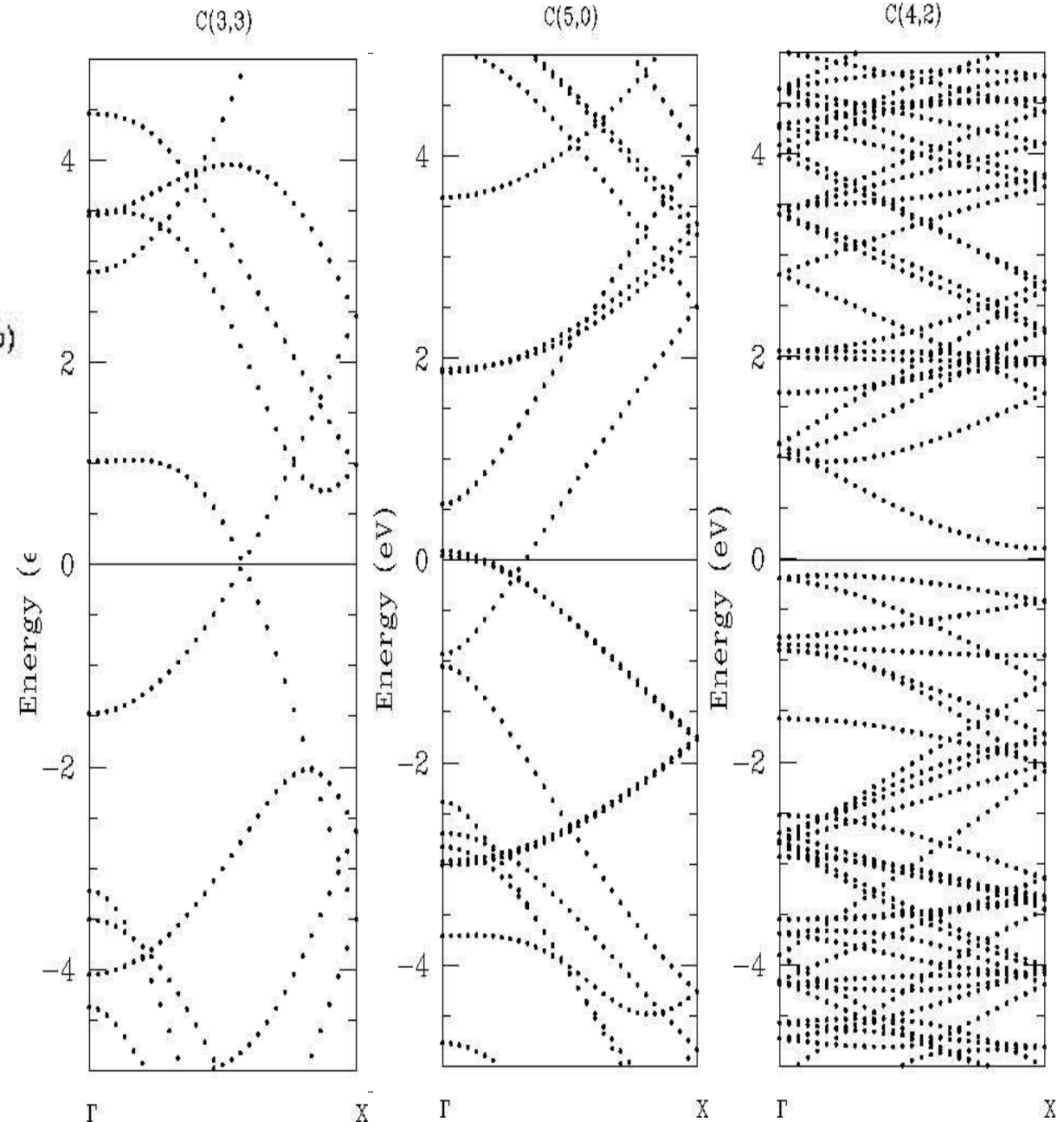
Optical Properties of C-Tubes: A way to elucidate tube-chirality



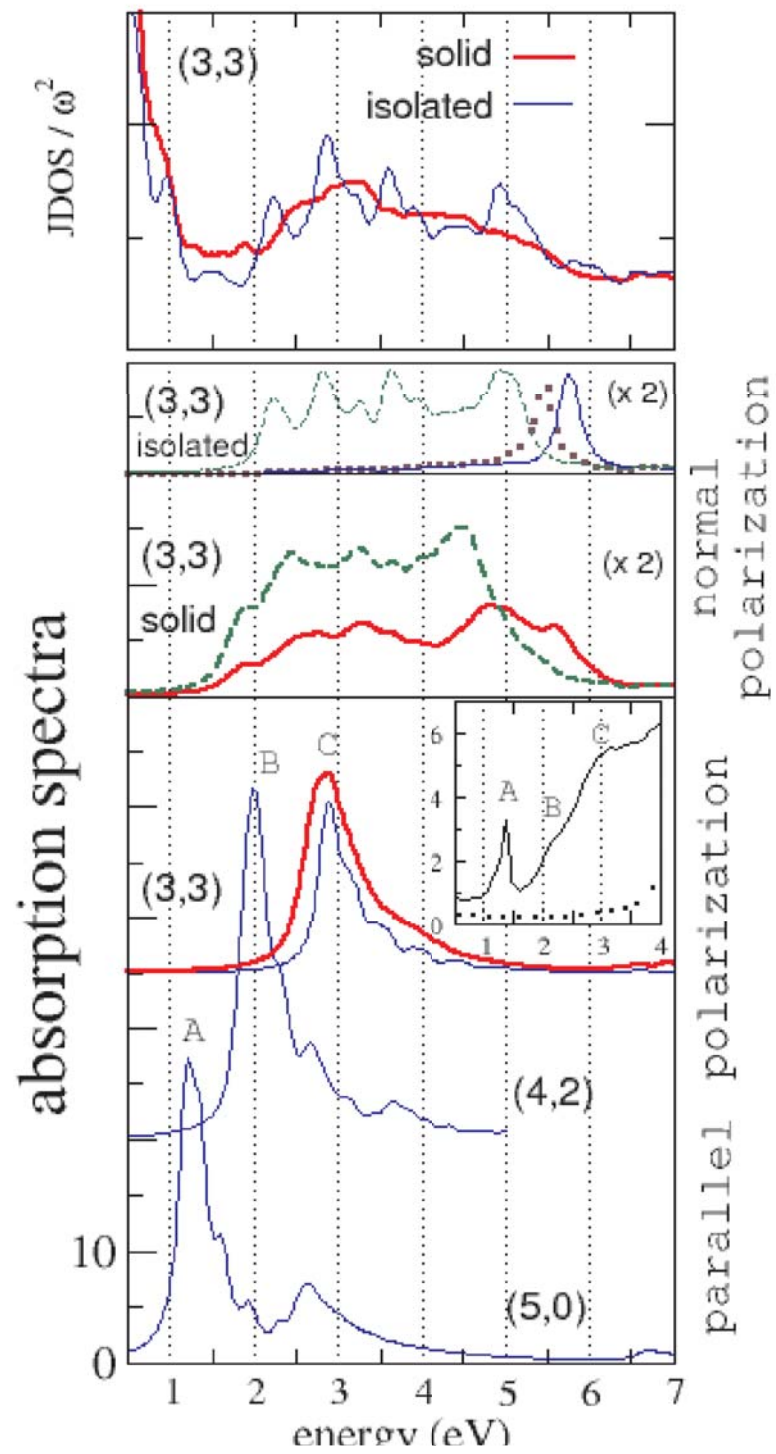
Zeolite type AlPo_4 -5



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



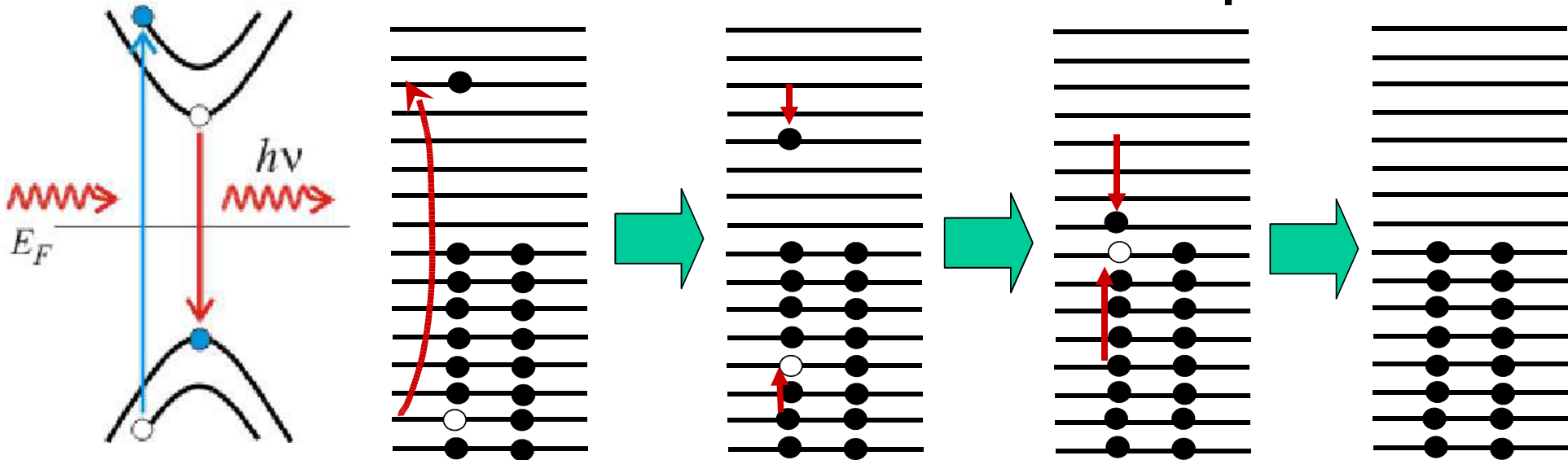
A.G. Marinopoulos, L. Reining, A.R. PRL (2003)



(“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)

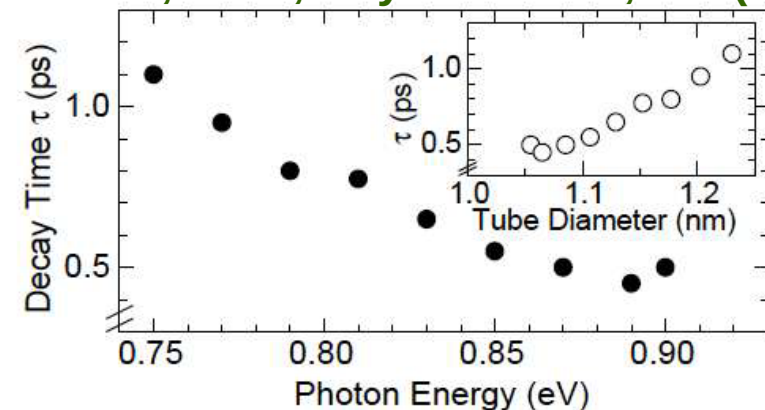
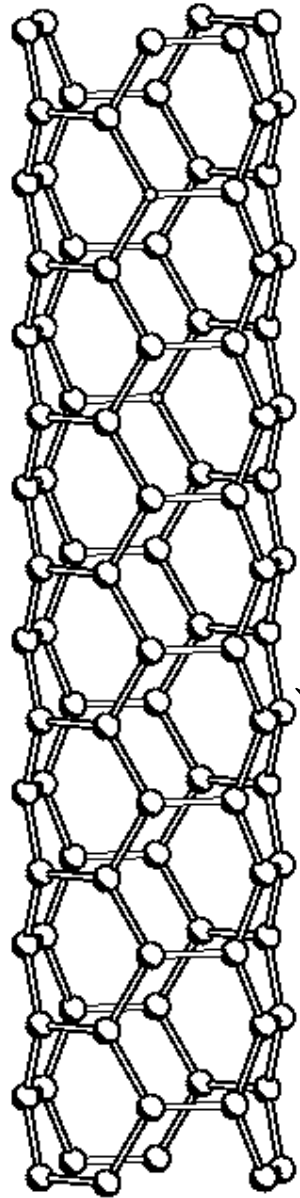


Fig. 2. Observed fast decay time as a function of probe photon energy. Inset: Tube diameter dependence of decay time.

Present case: (3,3) nanotube

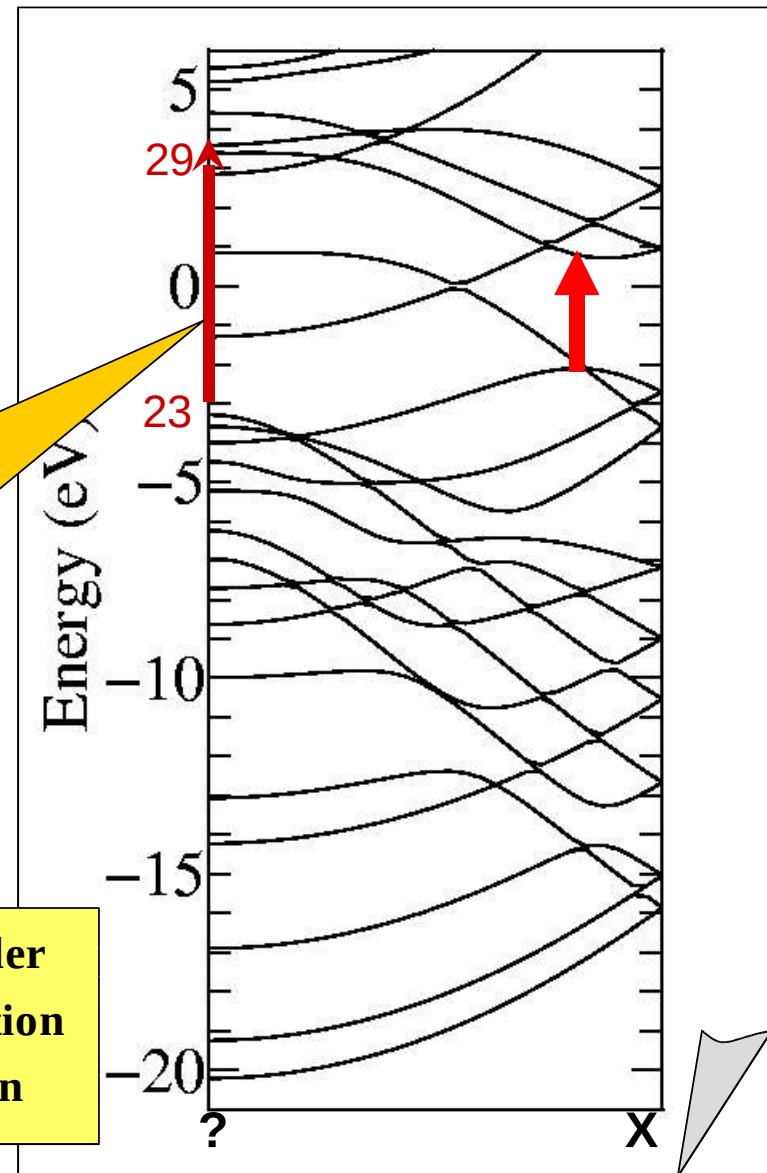


Assigned excitation with experimental data

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

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

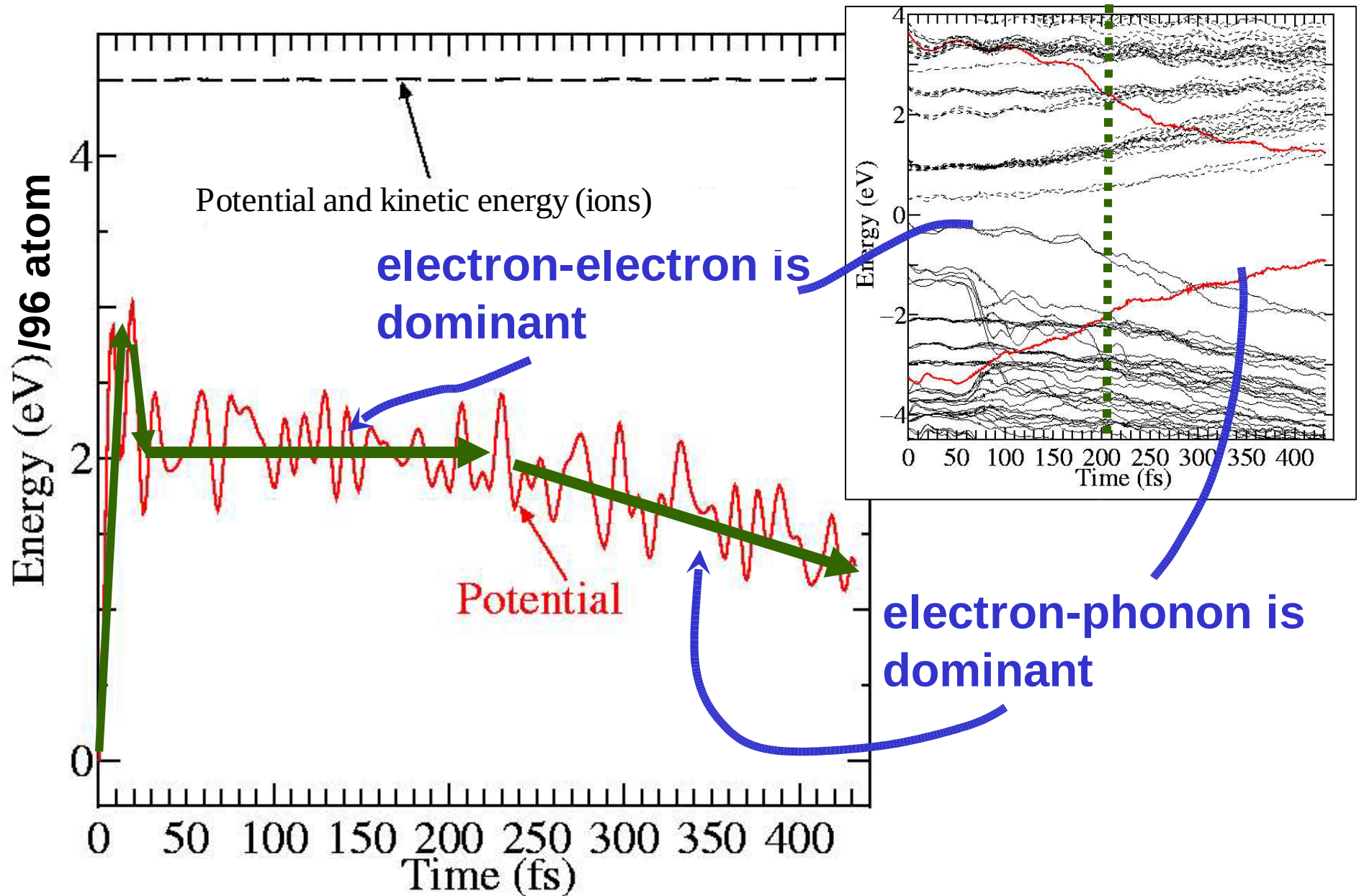
Randomized ionic velocities under the Maxwell-Boltzmann distribution with 300K as an initial condition



Computational conditions: TDLDA (with adiabatic xc potential)

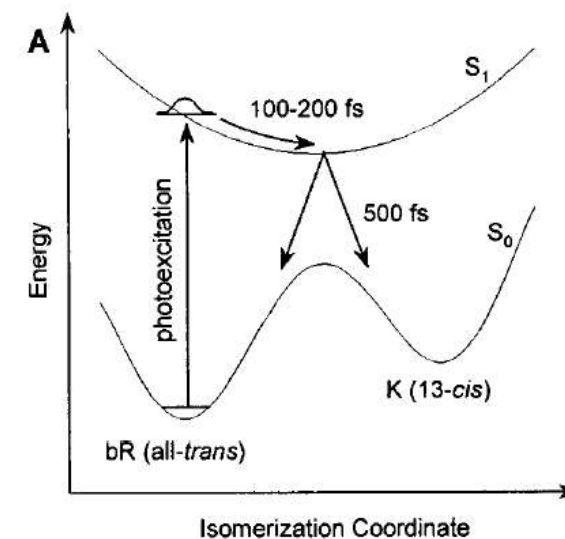
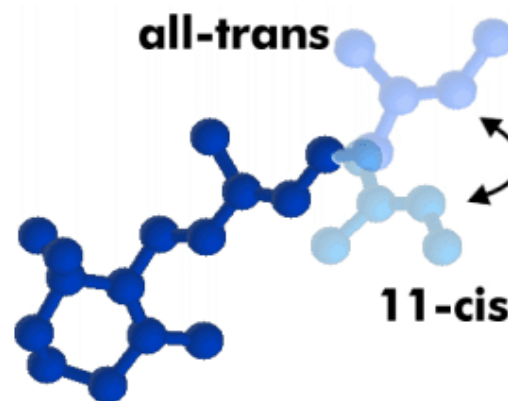
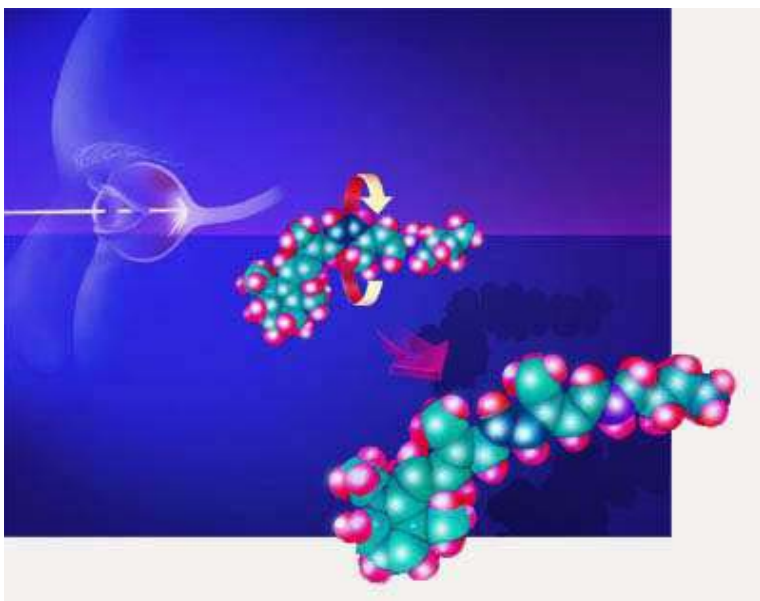
Time step: 0.08 a.u. (=0.0019 fs)

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:

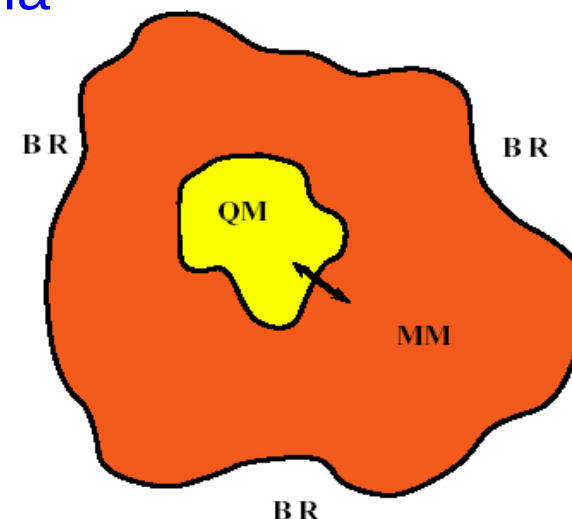
- Local Motions (0.01 to 5 Å, 10^{-15} to 10^{-1} s)
 - Atomic fluctuations
 - Sidechain Motions
 - Loop Motions
- Rigid Body Motions (1 to 10Å, 10^{-9} to 1s)
 - Helix Motions
 - Domain Motions (hinge bending)
 - Subunit motions
- Large-Scale Motions ($> 5\text{Å}$, 10^{-7} to 10^4 s)
 - Helix coil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

QM/MM Hamiltonian

For Local Phenomena

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

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



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

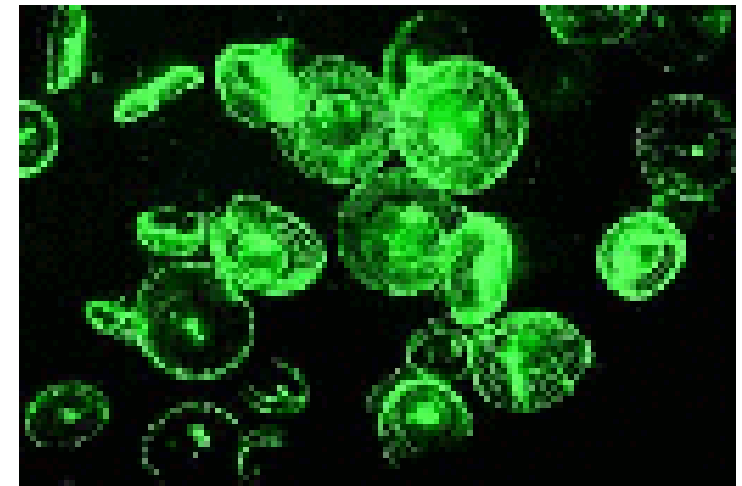
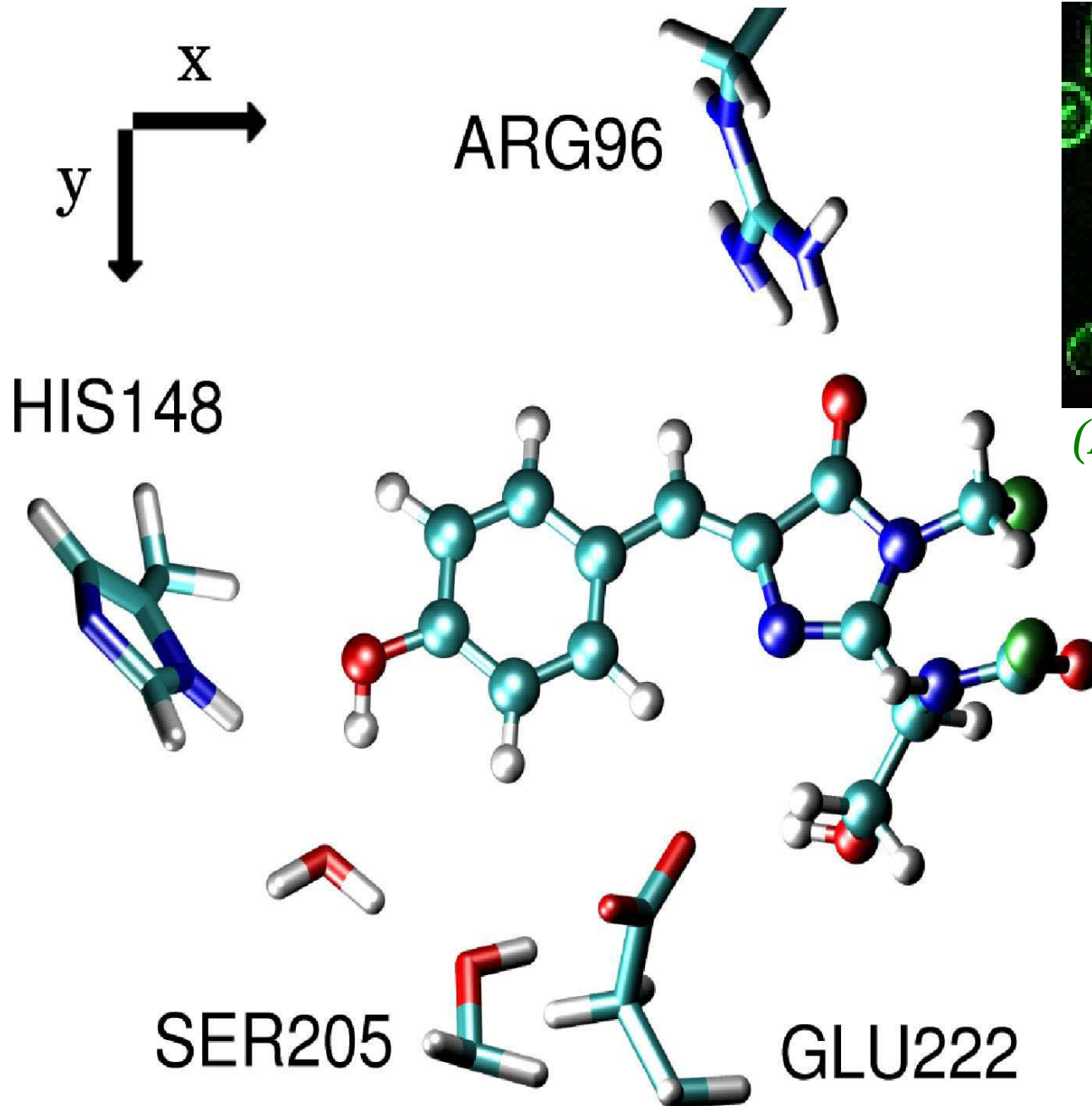
$$\hat{H}_{QM/MM}^{elec.} = - \sum_{i,M} \frac{q_M}{r_{iM}} + \sum_{\alpha,M} \frac{Z_{\alpha} q_M}{R_{\alpha M}}$$

Van der Waals Interactions

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

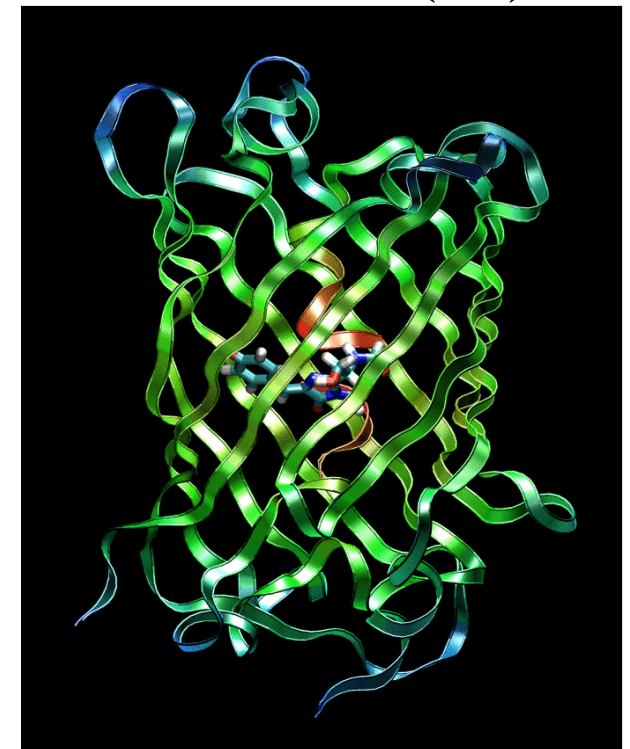
SCF

Towards understanding biomolecule colours



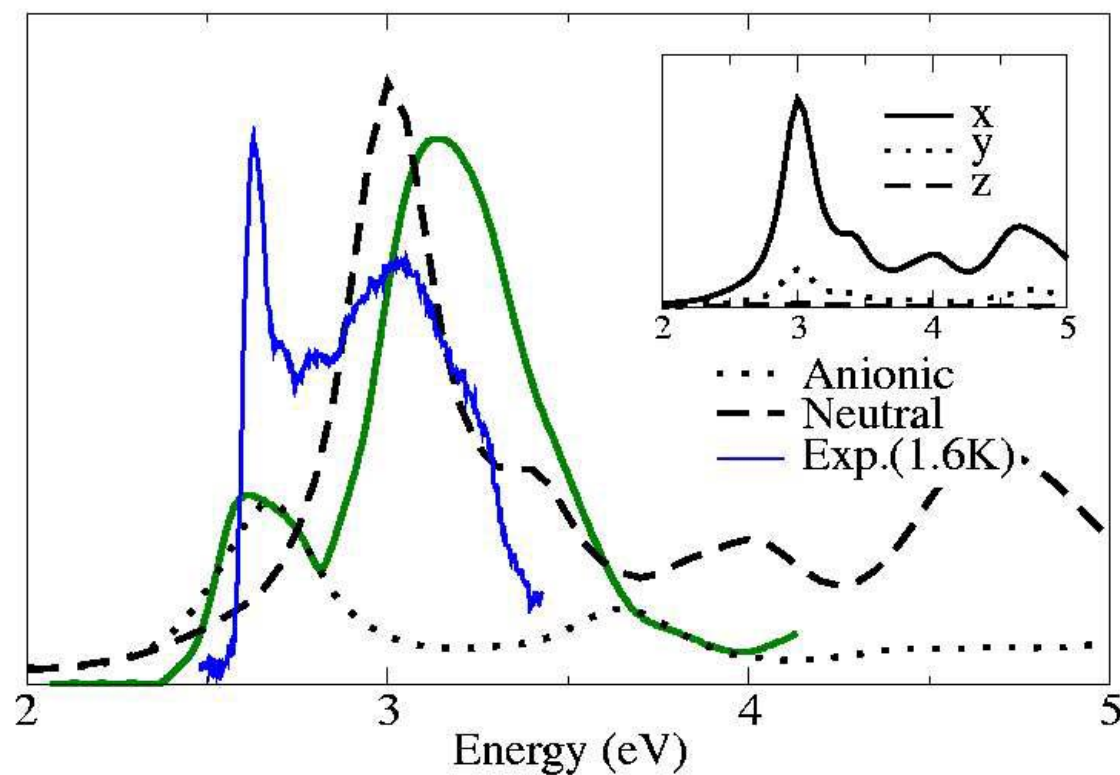
(Aequorea victoria: jellyfish)

Green Fluorescent Protein (GFP).



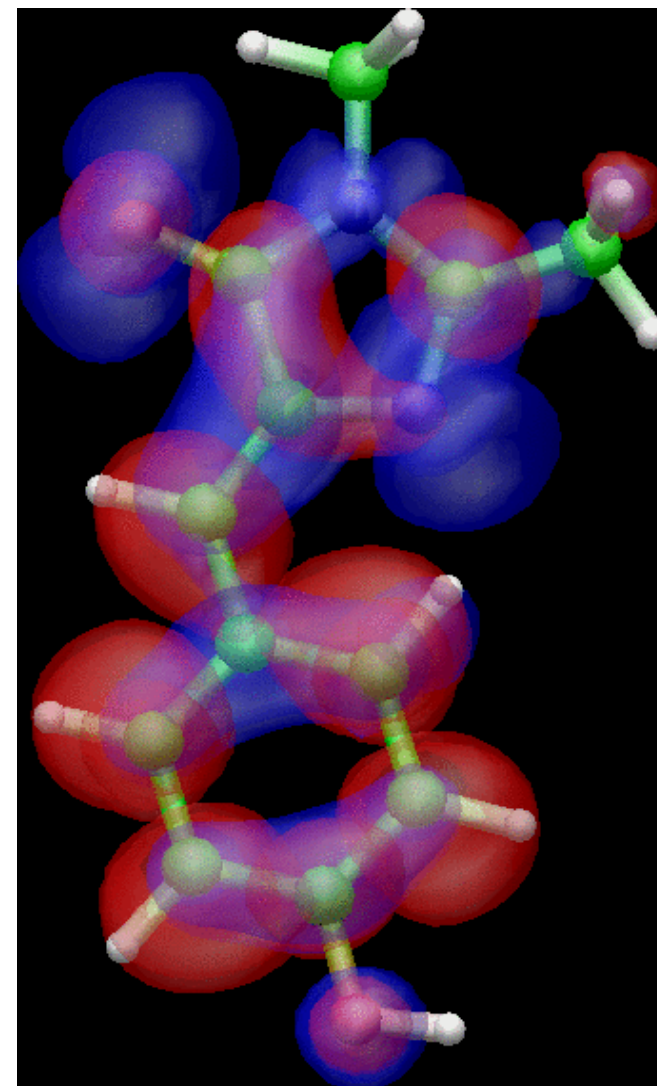
Towards understanding biomolecular colours: the GFP case

HOMO-LUMO

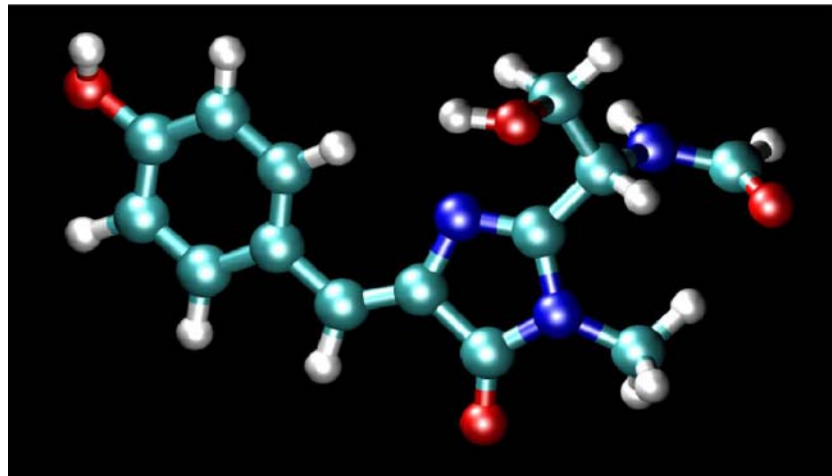
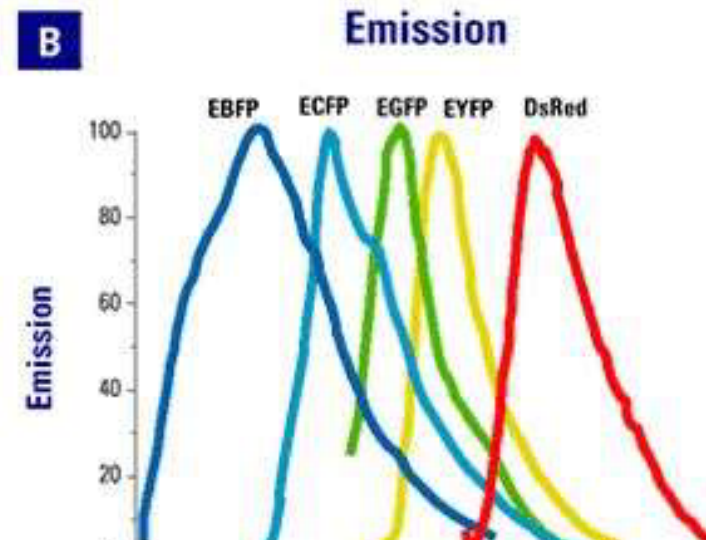
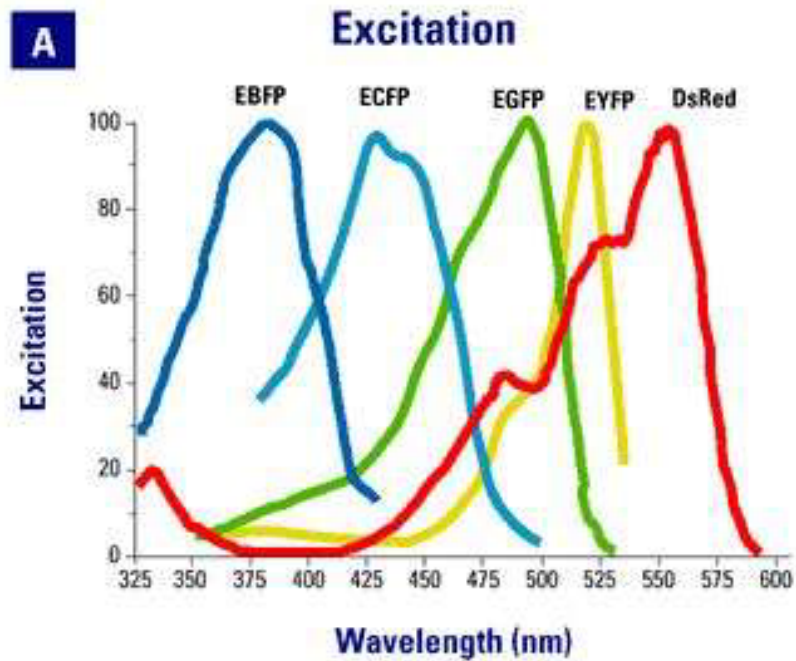


T.M.H. Creemers et al, Proc. Natl. Acad. Sci.. USA (1999)

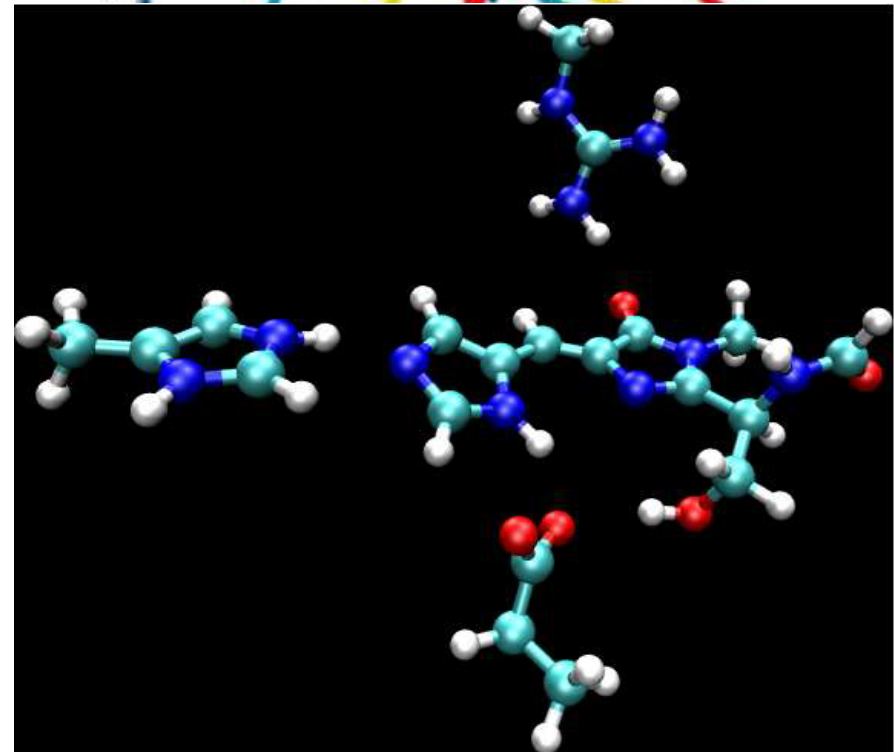
QM/MM approach

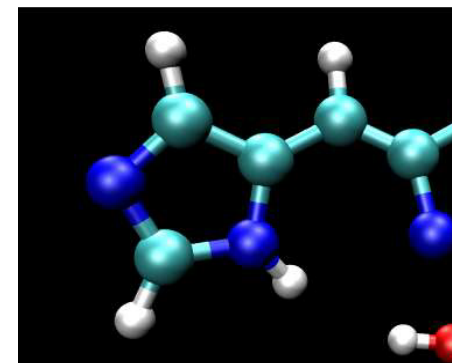
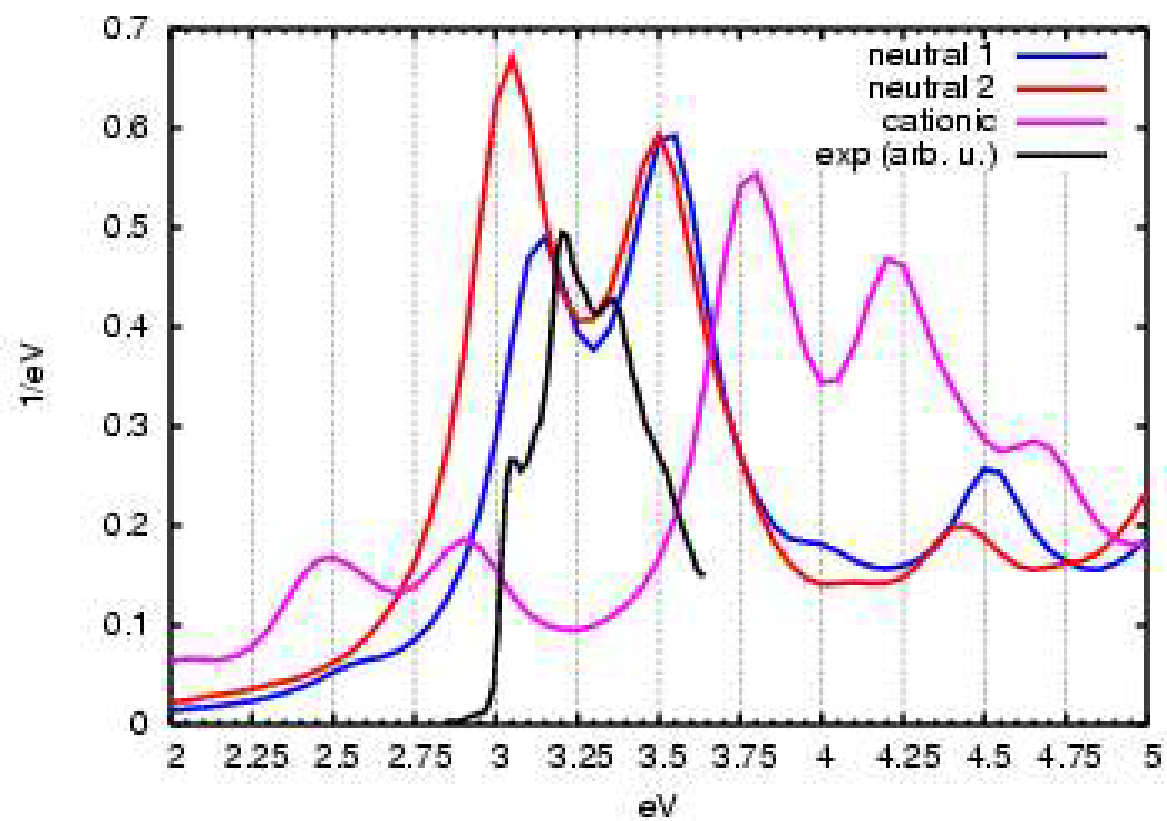


Blue Fluorescent Protein- Mutants

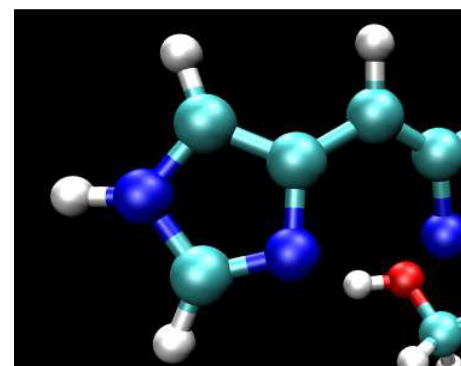


Green

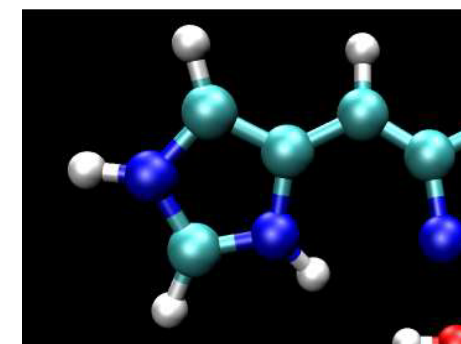




Neutral



Neutral

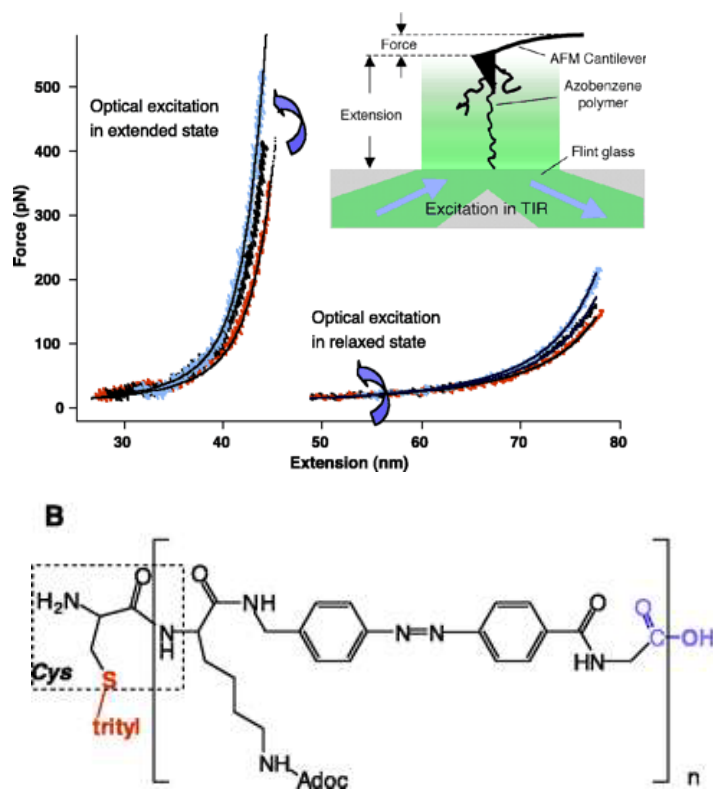


Cationic

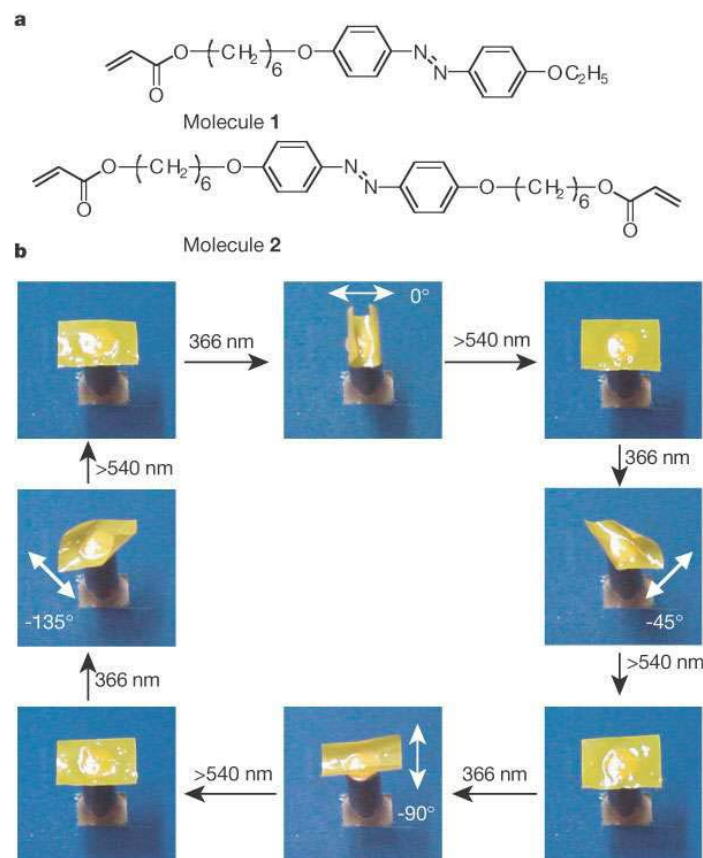
Azobenzene: spectroscopy along femtosecond-laser induced photoisomerization

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**

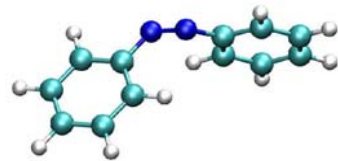
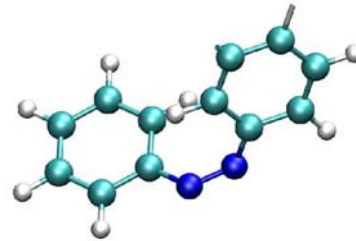
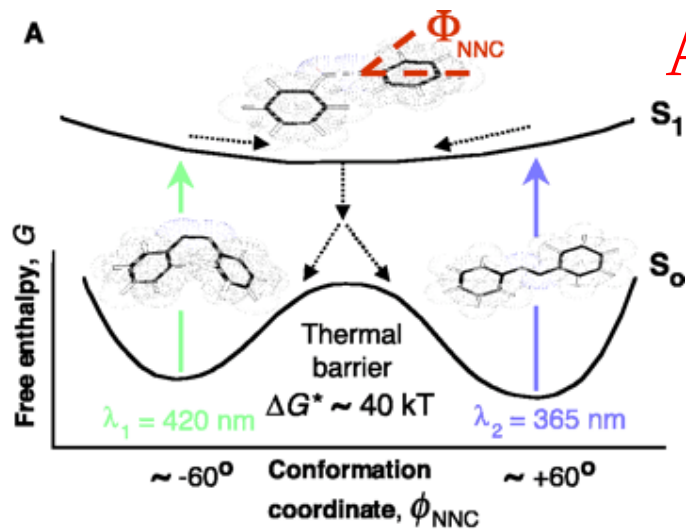


T. Hugel et al, Science, 296, 1103 (2002)

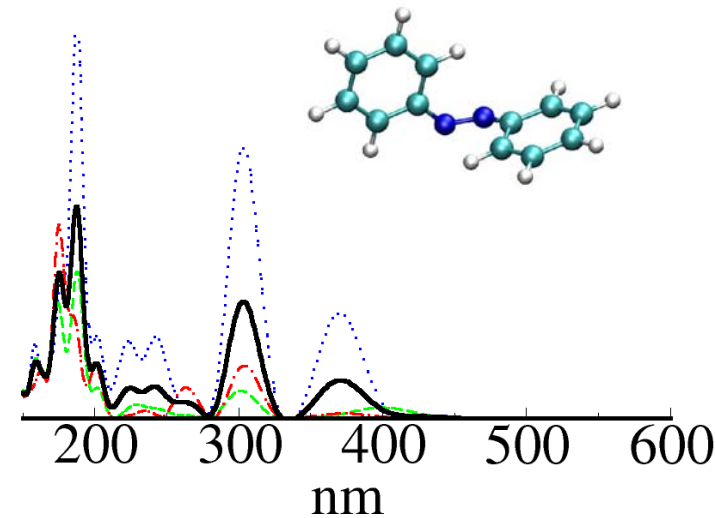
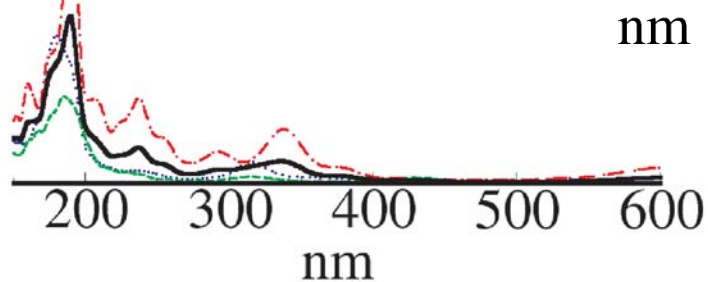
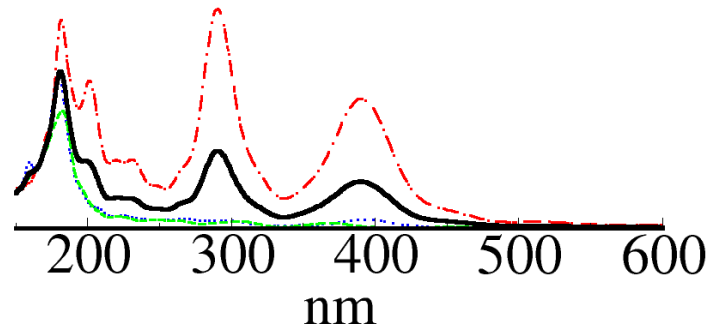
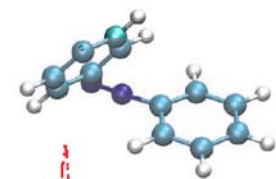


Y. Yu et al, Nature 425, 145 82003)

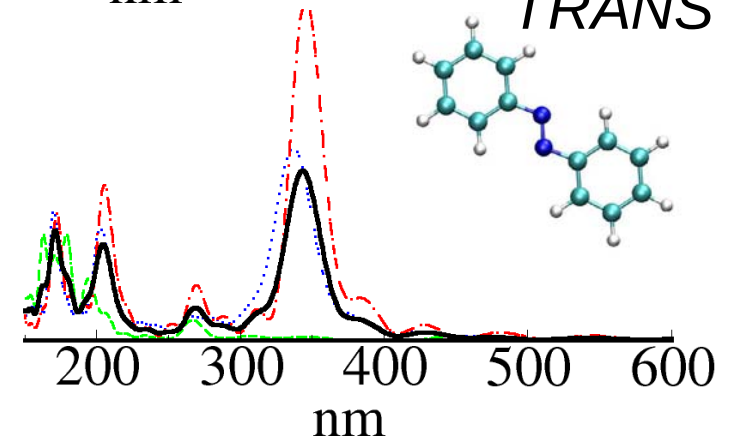
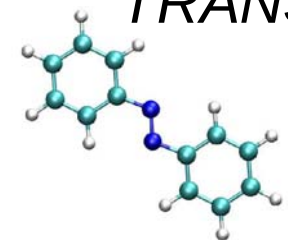
Azobenzene: spectroscopy along femtosecond-laser induced photoisomerization



CIS



TRANS



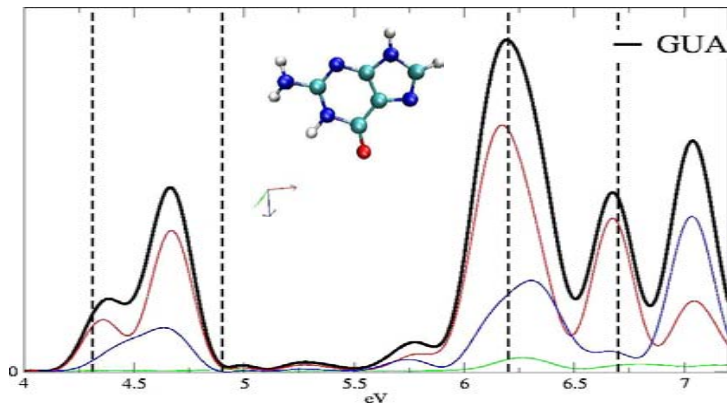
Next step: QM/MM calculation of the chromophore+peptide system

Optical Rotatory Power

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

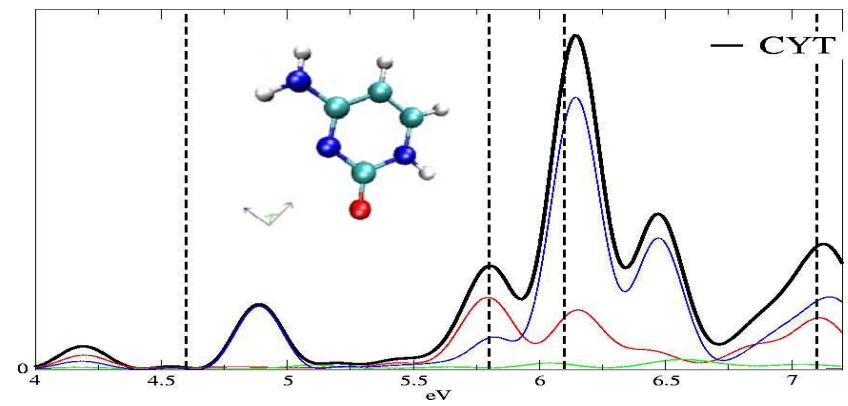
$$R(E) = \Im \frac{\Re(E)}{\pi} \quad \text{rotational strength function}$$

Guanine

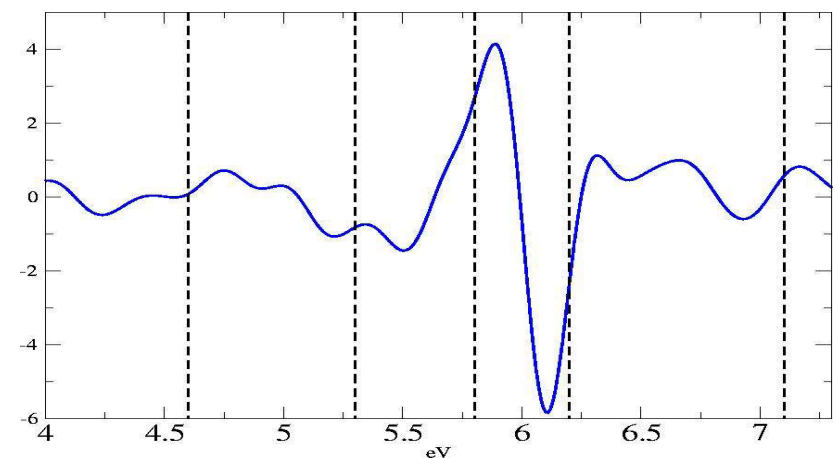
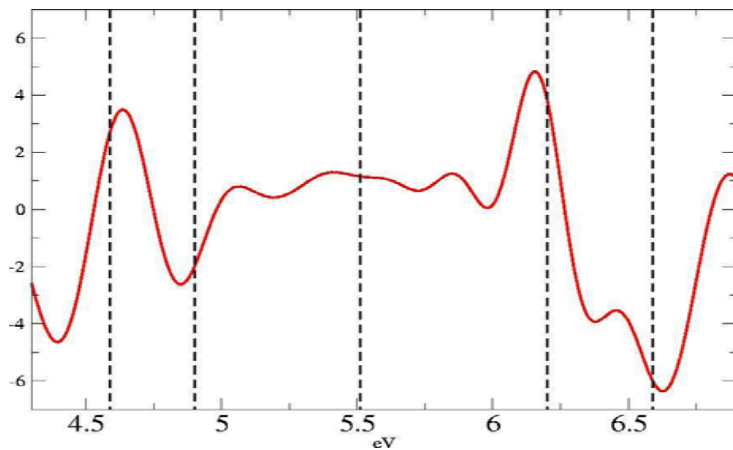


Absorption

Cytosine

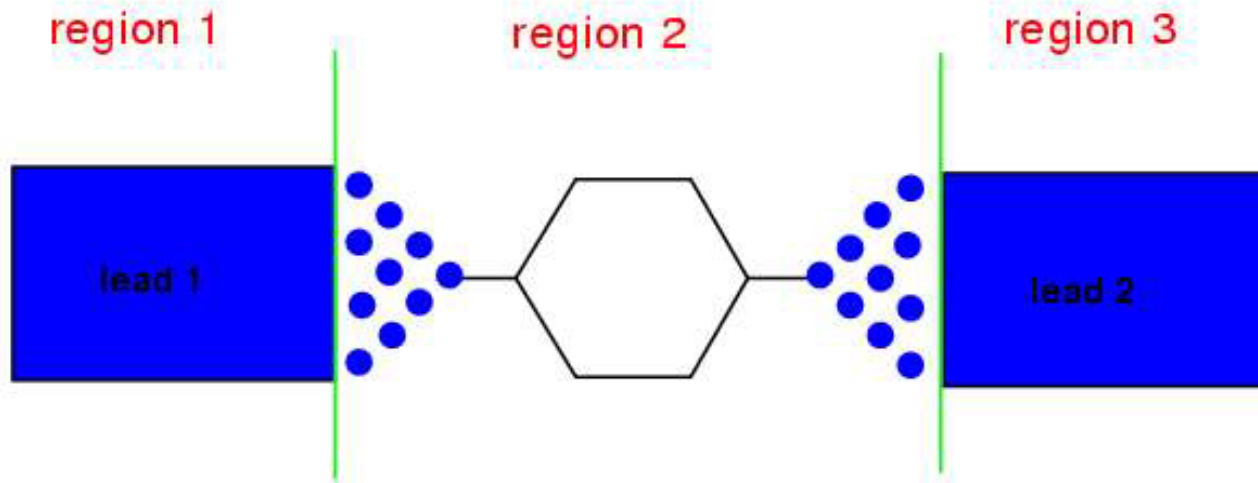


Circular dichroism



First principles description of Molecular transport ??????

In connection with Mark Ratner Lectures!



- (Landauer): Non equilibrium Green's Functions

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

- 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

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

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

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

Dielectric function in Random Phase Approximation (RPA)

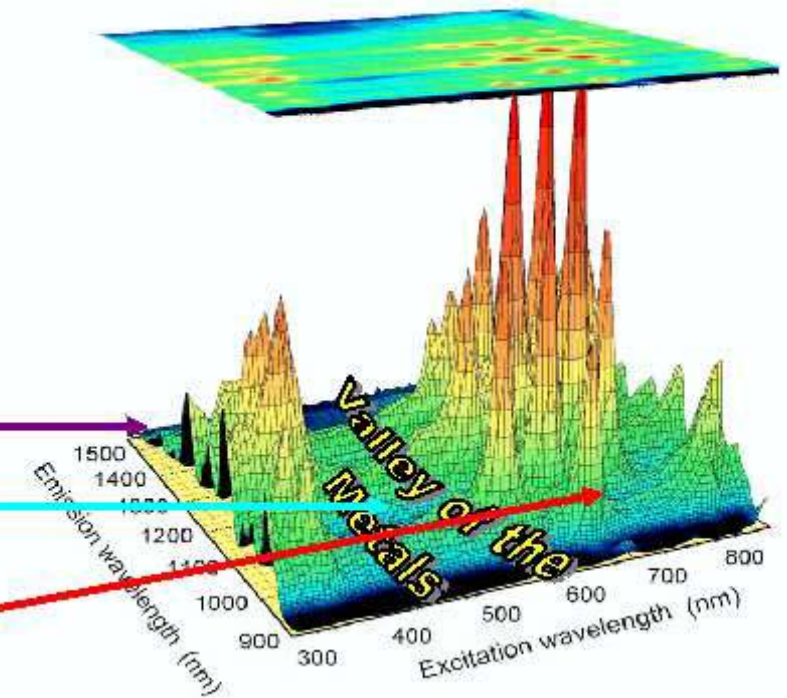
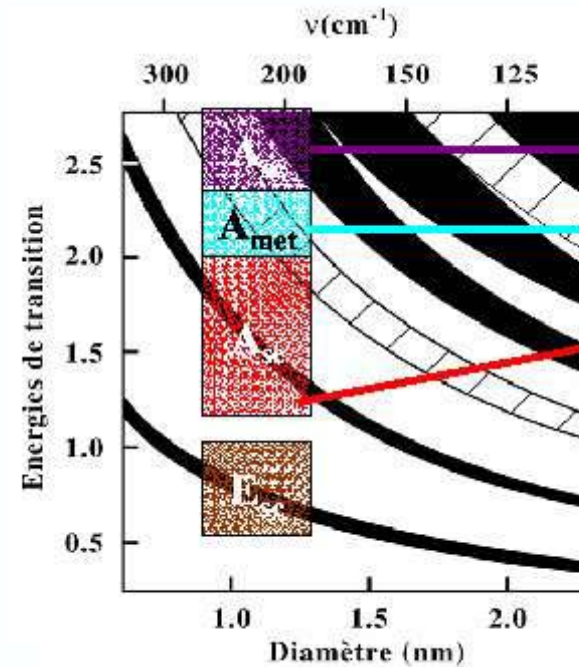
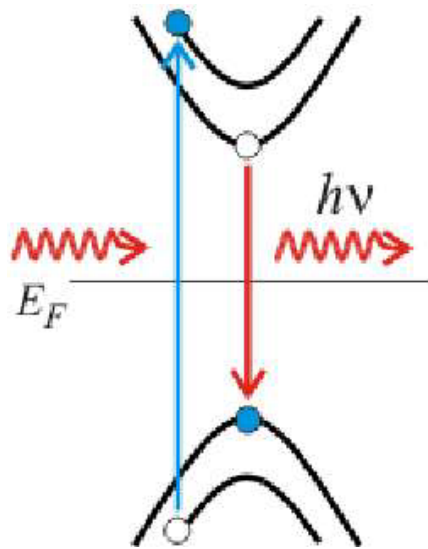
$$\epsilon_{RPA} = 1 - v_c \chi^{(0)}$$

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

Macroscopic ϵ with local field effects (LFE):

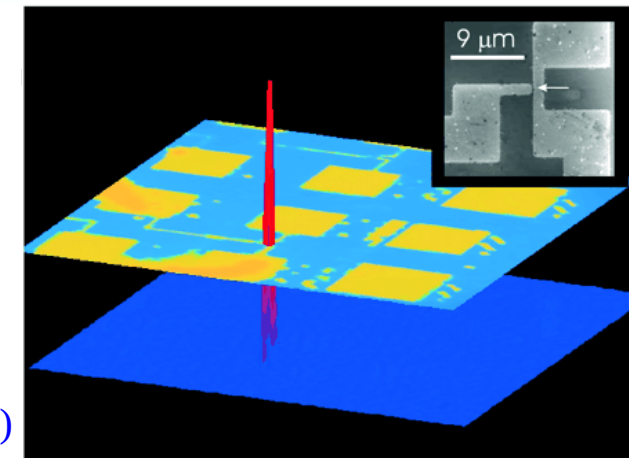
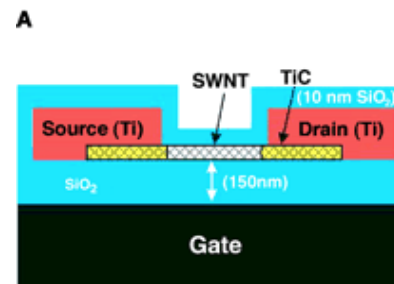
$$\epsilon_M(\omega) = 1 / \epsilon_{G=G'=0}^{-1}(q \rightarrow 0, \omega)$$

Tube (n,m) characterisation



Bachilo et al, Science 298, 2361 (2002)

Optical FET device!!!!!!



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