Electronic and optical properties of nanostructures and biomolecules from first-principles

Daniele Varsano

Department of Physics
University of Rome "La Sapienza"

daniele.varsano@roma1.infn.it

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"Roma La Sapienza"
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SAPIENZA
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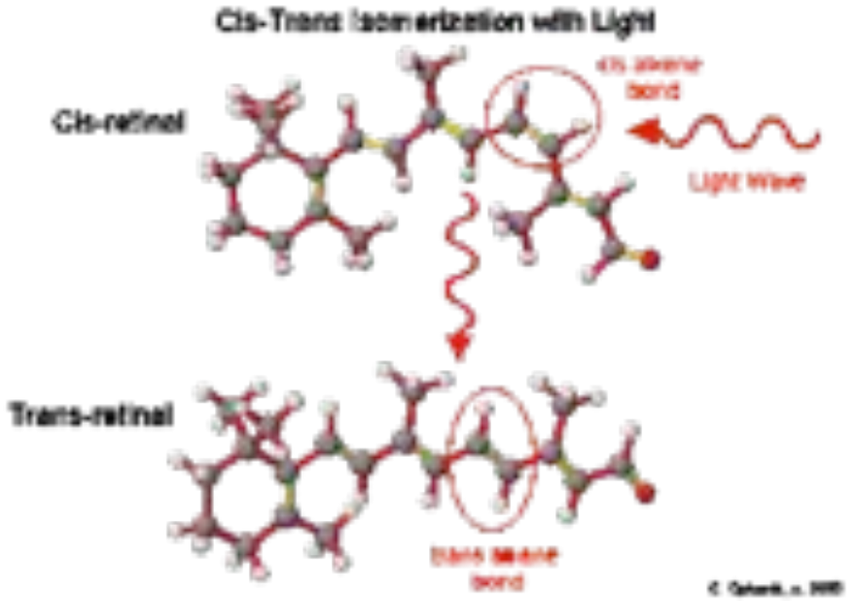
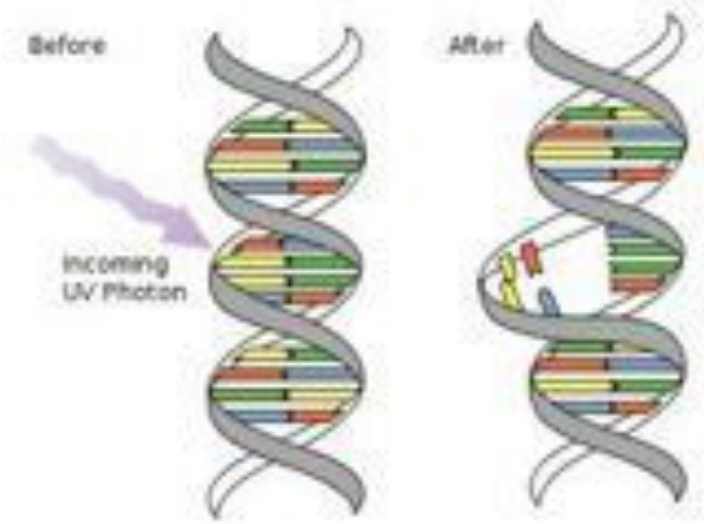
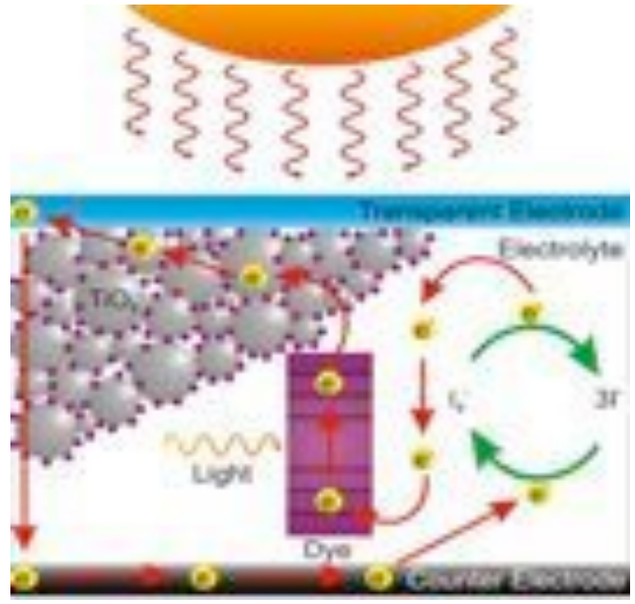
Overview

Theoretical understanding of electronic properties and light-matter interactions from <u>first principle</u>

Fundamental processes occurring in biosystems and new technological devices







occurs at nanoscale

Quantum mechanical description is needed

$$i\hbar\frac{\partial\Psi(\mathbf{r},t)}{\partial t} = H\Psi(\mathbf{r},t)$$

$\Psi(\mathbf{r},t)$ very complicate object

Theoretical approach

Density Functional Theory (DFT) (W. Kohn Nobel Prize 1998)

Density instead of wave function as fundamental variable.

Correlation effects approximated by effective potentials

Ground state properties: Electronic structure, reliable geometries

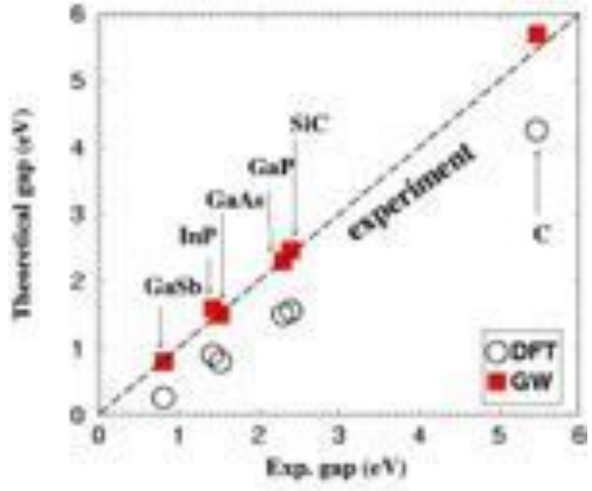
Time Dependent Density Functional Theory (TDDFT) (Runge, Gross 1984)

Extension of DFT for time-varying external potential

Excited state properties: Absorption spectrum

Very good compromise between computational efficiency and accuracy.

Approximations of correlation effects can be critical



Many Body Perturbation Theory (Hedin 1965)

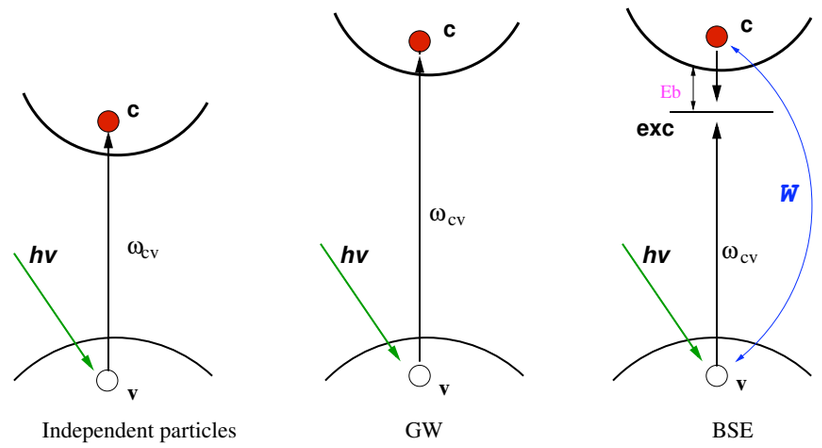
Perturbation theory around non interacting Hamiltonian

Green function as a fundamental variable

Quasi-particle energies (GW)

Absorption spectra: inclusion of **electrons-holes** interaction (BSE)

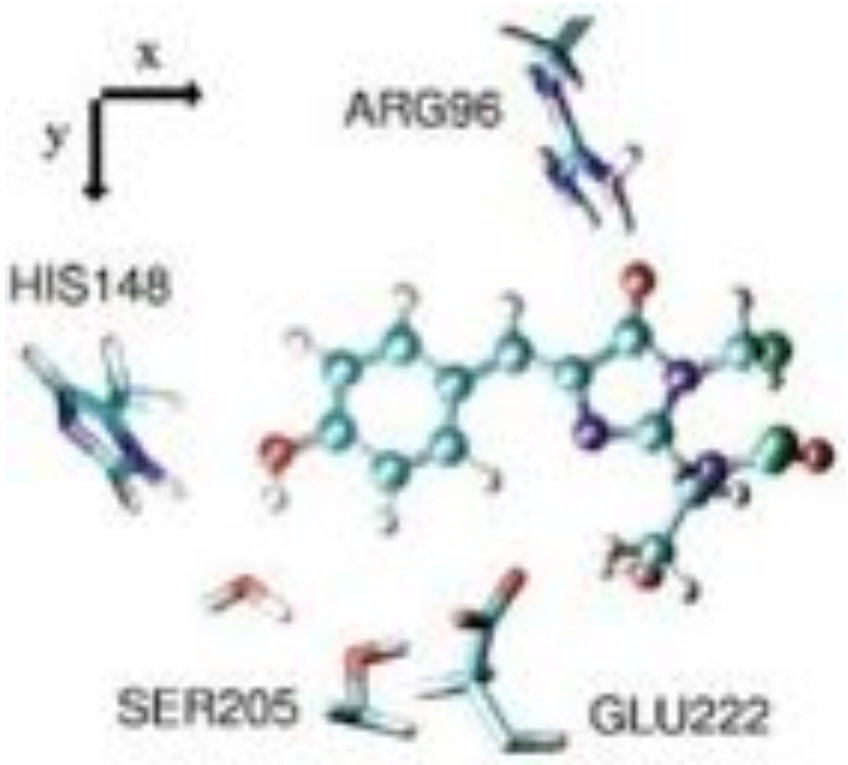
Accurate but computationally demanding



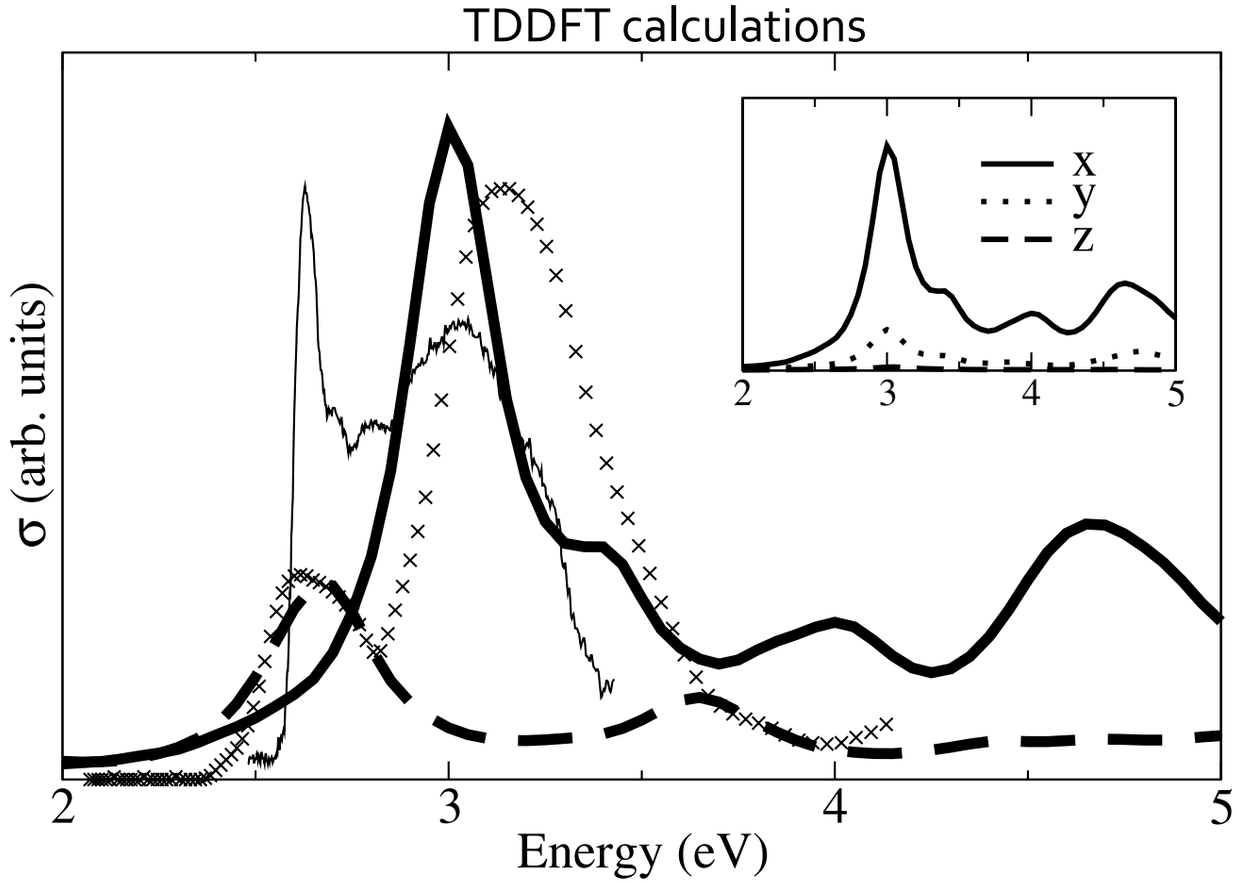
TDDFT and MBPT permits the study of excited state properties of matter.

Computational ab-initio spectroscopy

Interpretation and theoretical assistance to experiments



GFP Nobel Prize (2008)

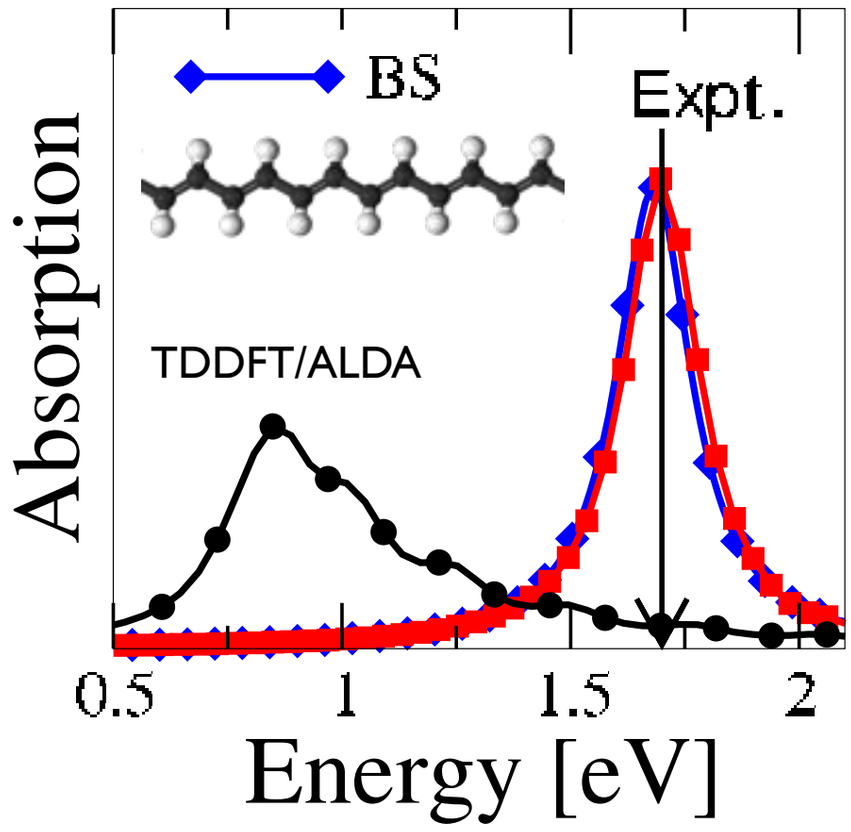


Exp. by S. B. Nielsen *et al.*, Phys. Rev. Lett. **87,** 228102 (2001).
T. M. H. Creemers *et al.*, Proc. Natl. Acad. Sci. U.S.A. **97,** 2974 (2000)

M. Marques, X. Lopez, D.Varsano, A. Castro and A. Rubio Phys. Rev. Lett. **90**, 258101 (2003)

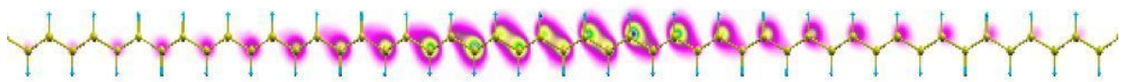
Exciton confinement in molecular chains

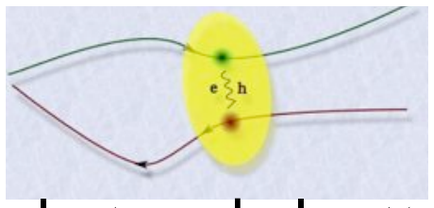
Polyacetylene polymer



exciton localization from BSE solution

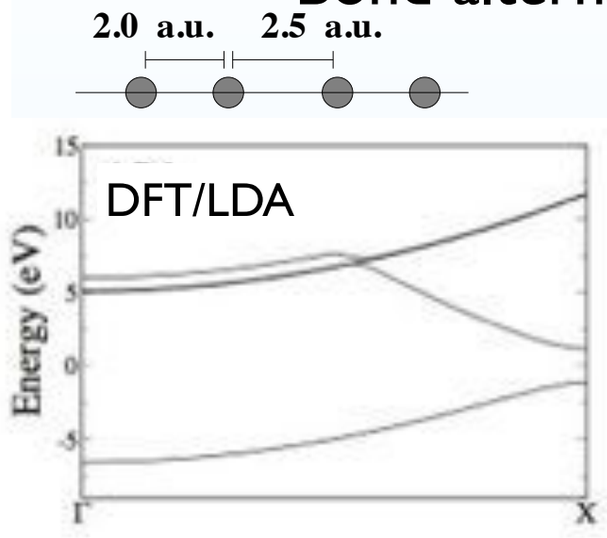
$$\Psi_S(\mathbf{r_h}, \mathbf{r_e}) = \sum_{v,c} A_s^{(vc)} \phi_v^*(\mathbf{r_h}) \phi_c(\mathbf{r_e})$$

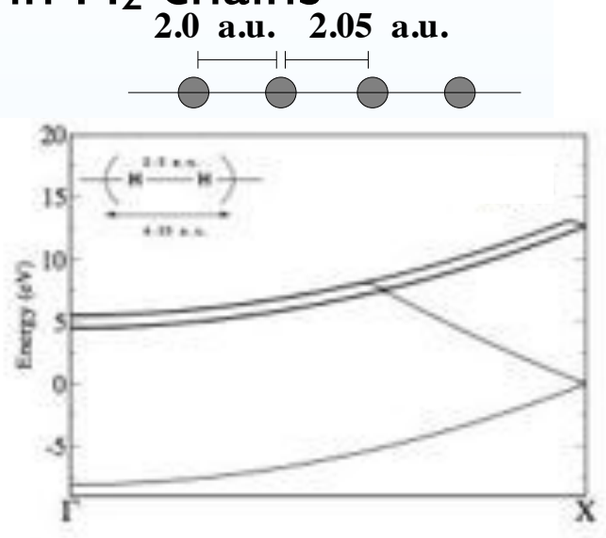


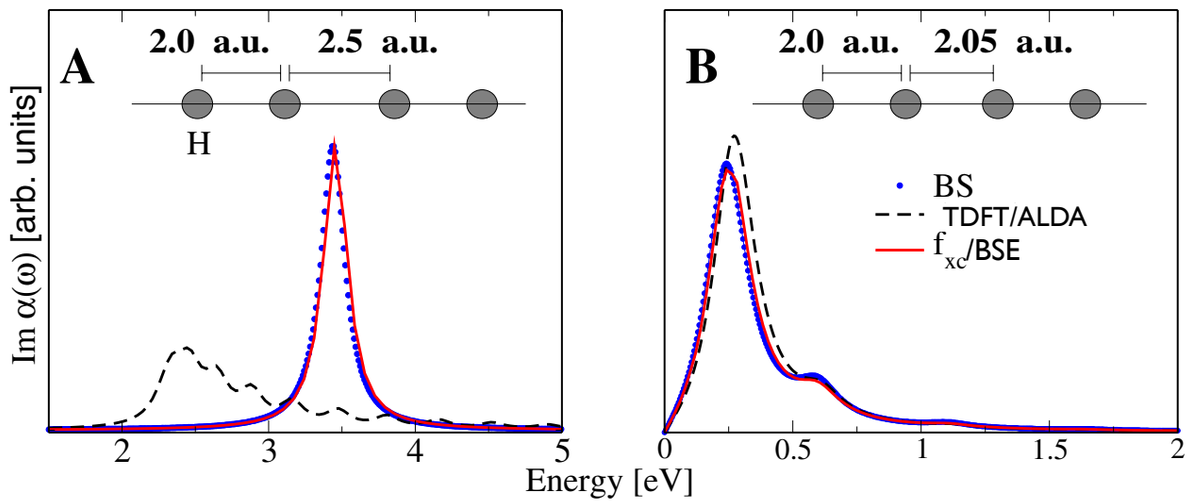


Role played by electron-hole attraction is not captured by TDDFT in simple approximations

Bond alternation in H_2 chains





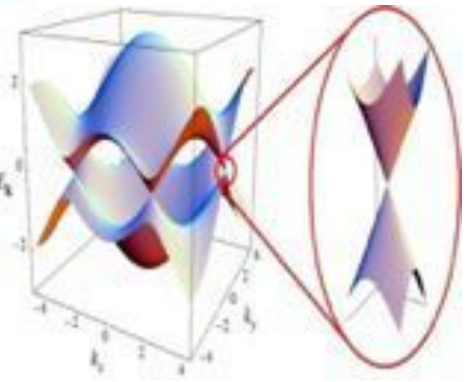


D. Varsano, A. Marini and A. Rubio Phys. Rev. Lett. 101, 133002 (2008)

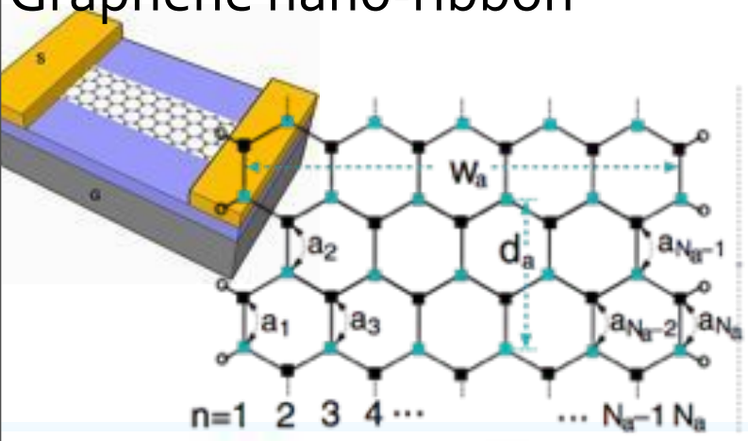
Excitonic effects in graphene nanostructures (nanoribbons)

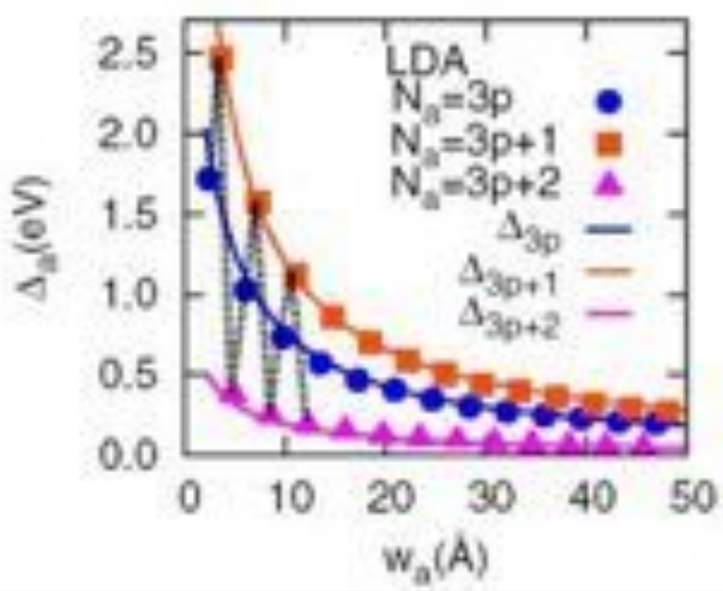
Graphene

Nobel Prize 2010

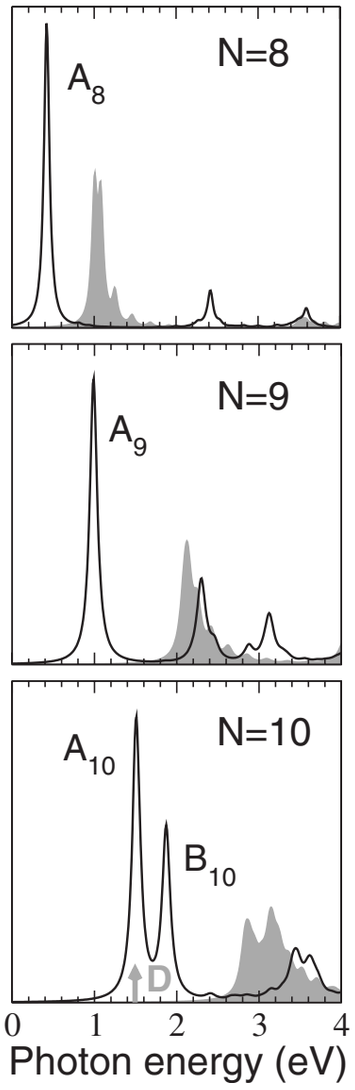


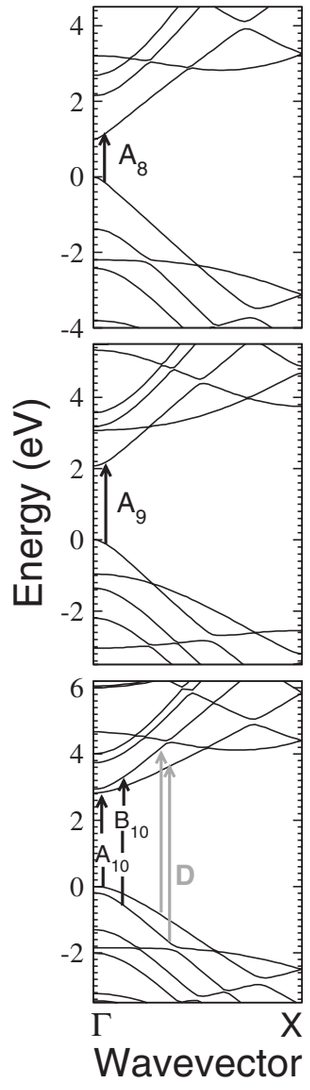
Graphene nano-ribbon



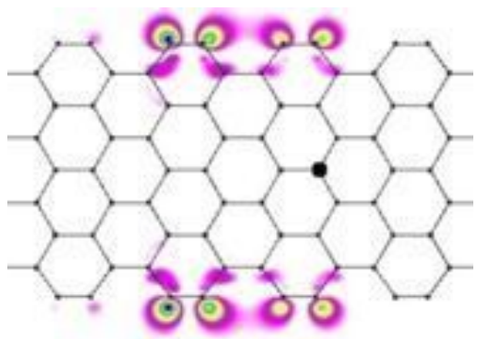


Son et al. PRL 97, 216803 (2006)

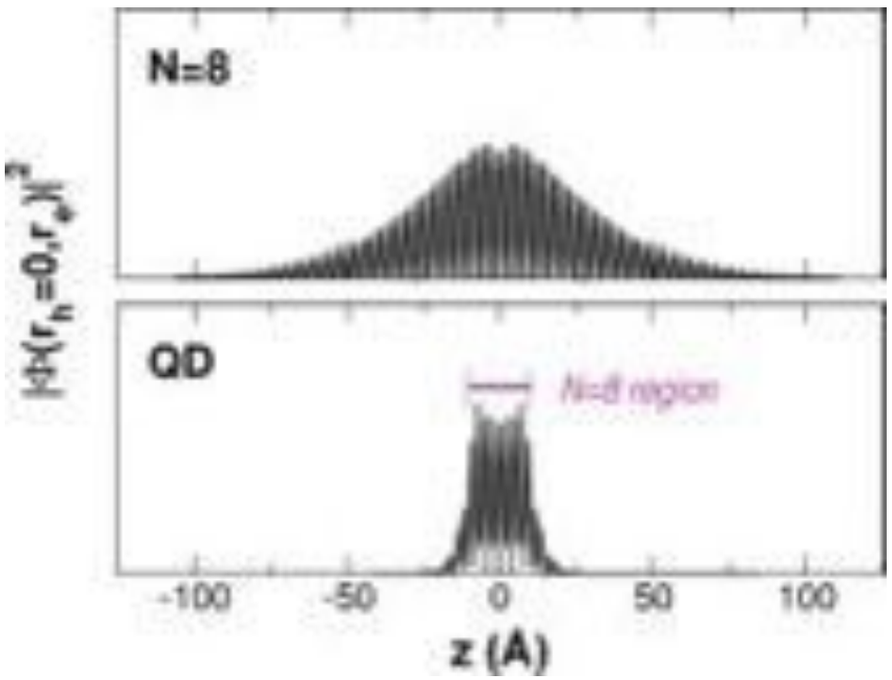




Binding energy depends on ribbon family: tunable optoelectronic features



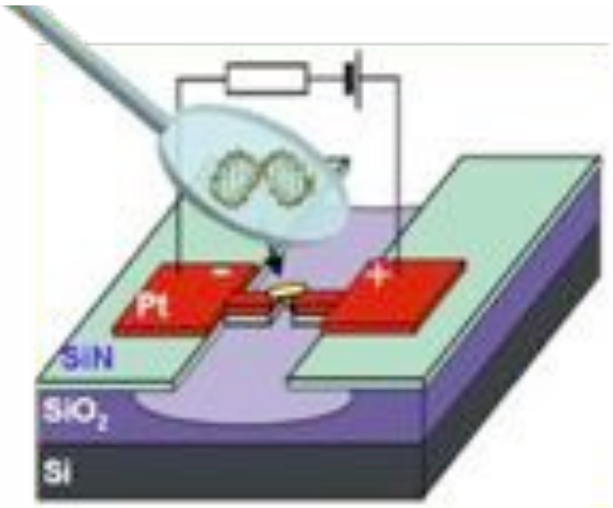
Modulated GNR



addition or removal of single dimeric line permits confinement of electrons and holes

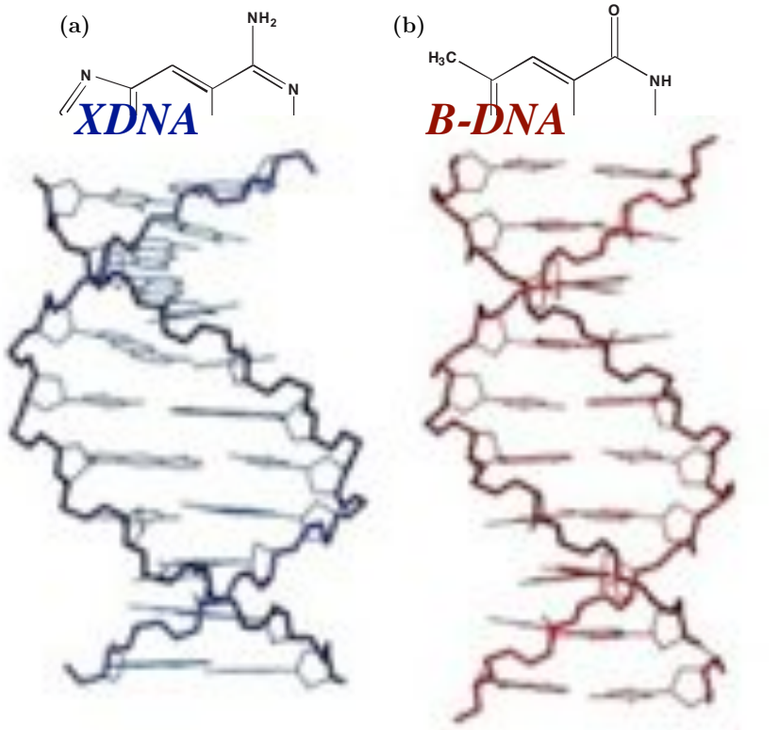
D. Prezzi, D. Varsano et al. Phys. Rev. B **77** 041404 (R) 2008
D. Prezzi, D. Varsano et al. Phys. Rev. B **84** 041401 (R) 2011

DNA for biomolecular electronics



DNA molecule presents great properties of structuring and recognition but poor conductivity for long (>40nm) molecules deposited on substrates

- Improve measurement setup:
- Exploring DNA derivatives that could improve intrinsic conductivity:

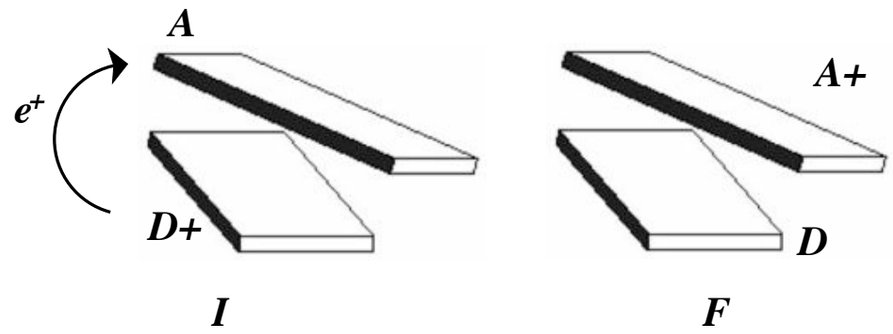


Liu, S. Lynch, E. Kool, JACS 126, 6900 (2004)

Larger diameter
Reduced inter-stacking distance
Enhanced inter-stacking interaction
Hhypochromism

$$k = \frac{2\pi}{\hbar} |V_{IF}|^2 \frac{e^{-\frac{(\lambda+\Delta G^0)^2}{4k_B T\lambda}}}{\sqrt{4\pi k_B T\lambda}}$$

Hole transfer in DNA



xGC-xGC	GC-GC	xAT-xAT	AT-AT
0.205	0.075	0.054	0.008

Net increase upon size expansion

Importance of structural fluctuations

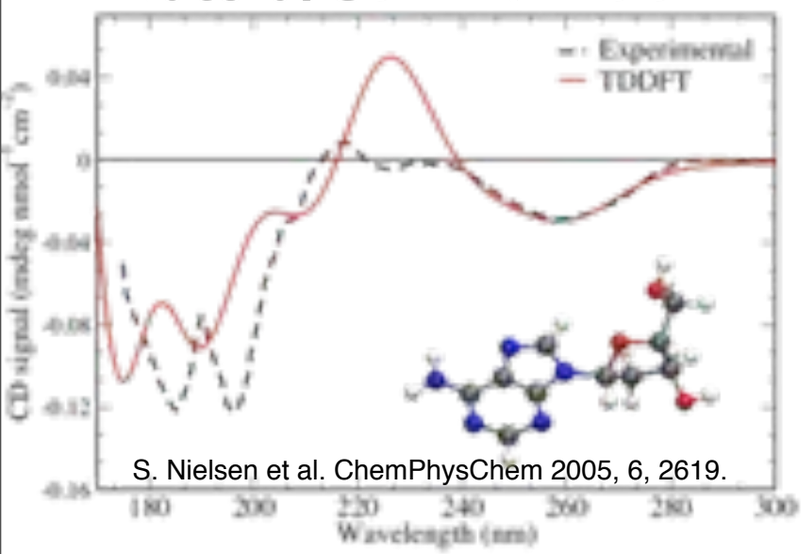
D. Varsano, R. Di Felice, M. Marques, A. Rubio J. Phys Chem B,**110,** 7129 (2006)
D. Varsano, A. Garbesi and R. Di Felice J. Phys Chem B **111,** 14012 (2007)
A. Migliore, S. Corni, D. Varsano, M. Klein and R. Di Felice J. Phys. Chem. B **2009,** 113, 9402–9415

Optical activity in DNA nucleotides and base pairs

Development of a first principle scheme based on real time TDDFT for calculation of circular dichroism

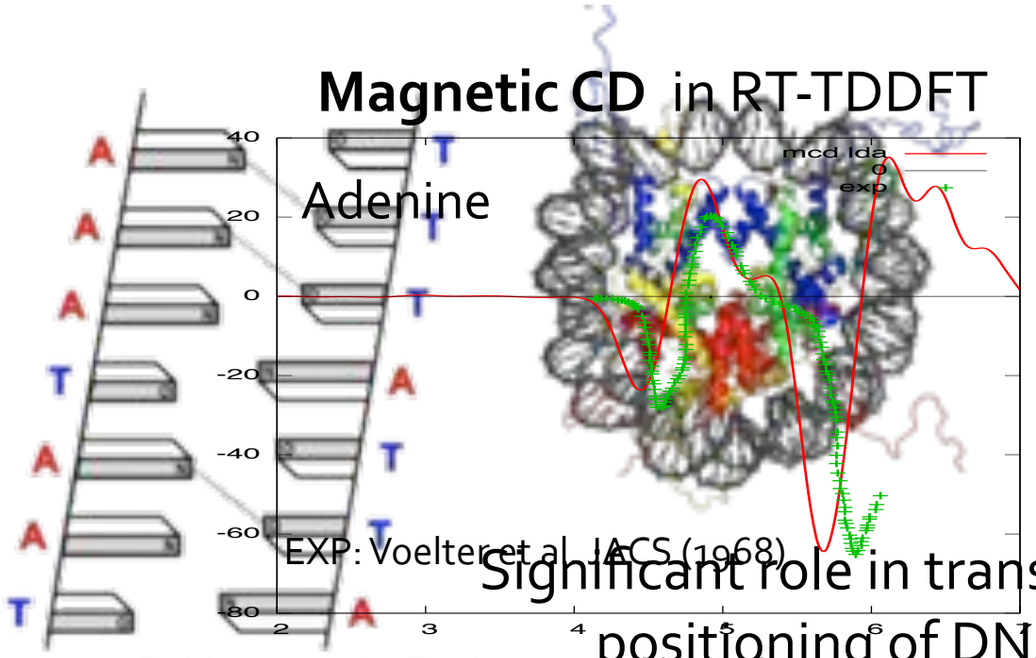
D. Varsano et al. PCCP **11**, 4481 (2009)

Natural CD in RT-TDDFT



S. Nielsen et al. ChemPhysChem 2005, 6, 2619.

Magnetic CD in RT-TDDFT



EXP: Voelter et al. JACS (1968)

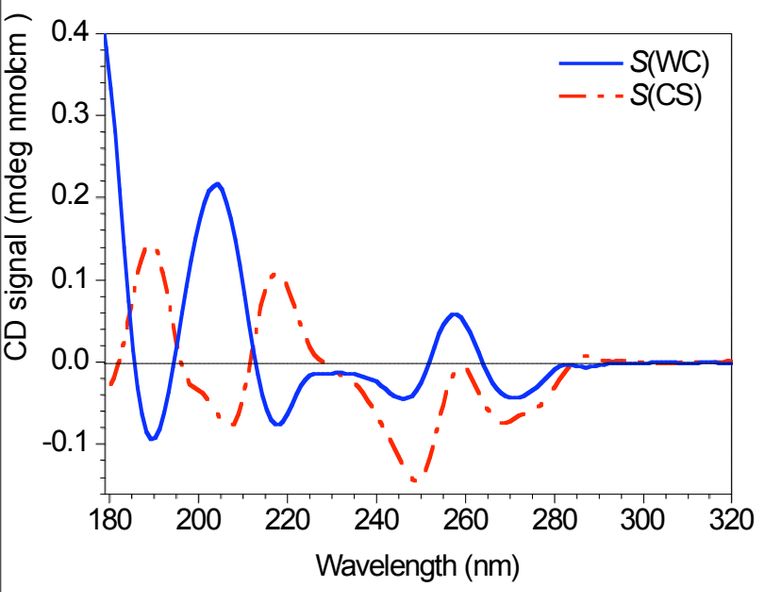
A-tracts have smaller bp/turns and axial rise than random DNA and alternating $(AT:TA)_n$

Significant role in translational and rotational positioning of DNA in nucleosomes.

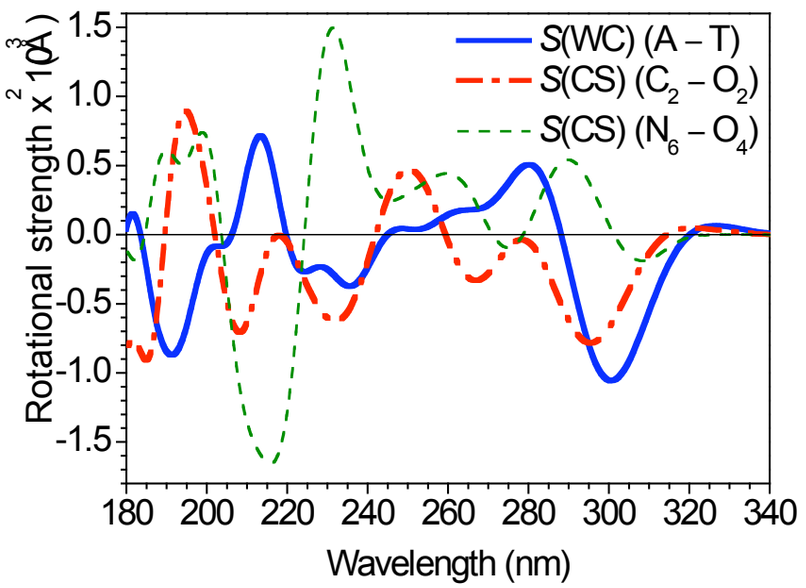
D. Varsano, L. Espinosa and A. Rubio, in preparation (2012)

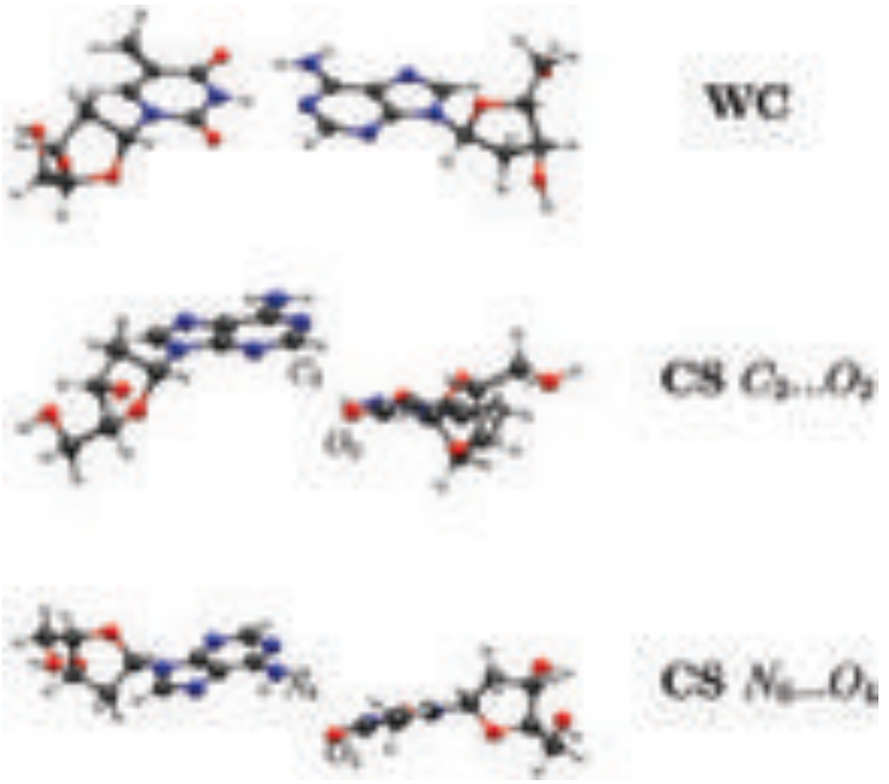
E. Segal and J. Widom, Curr. Op. in Structural Biology **19**, 65 (2009)

Synchrotron radiation circular dichroism experiments



TDDFT calculations

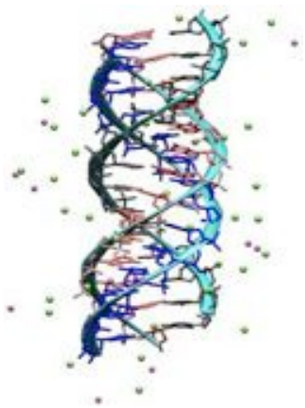


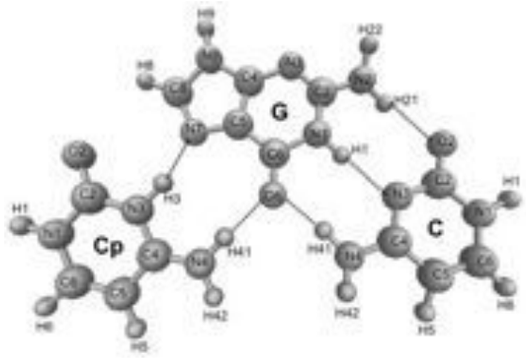


L. Nielsen, A. Holm, D. Varsano et al. , J. Phys. Chem. B **113**, 9614 (2009)

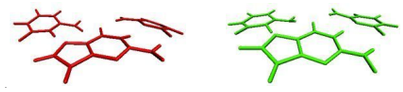
Optical properties and structural effects on DNA derivatives

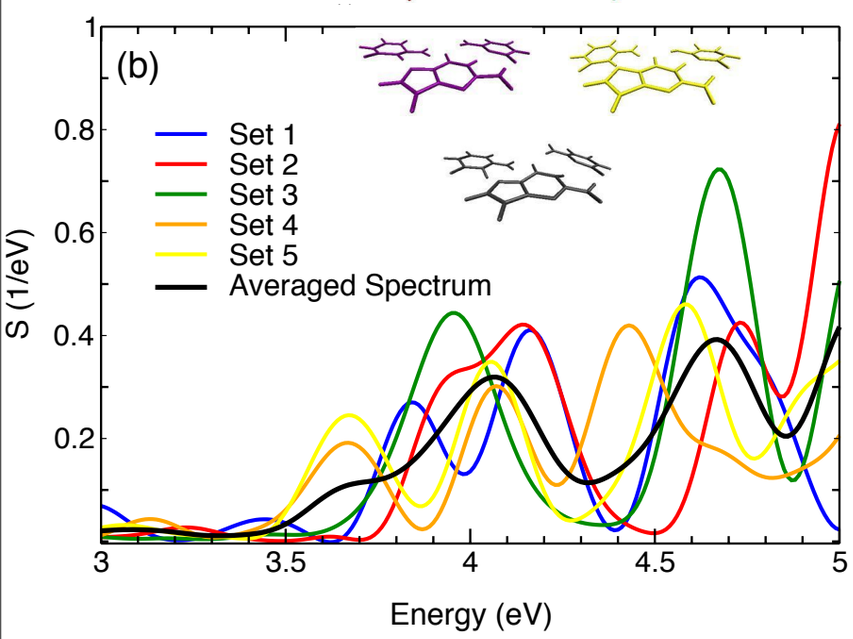
DNA-Triplex:





agents for alter gene expression
sequence specific tool for potential gene therapy



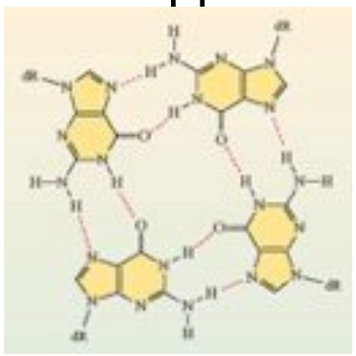


- Stability by classical MD
- Fingerprint of Hoogsteen H-bonding in optical spectra

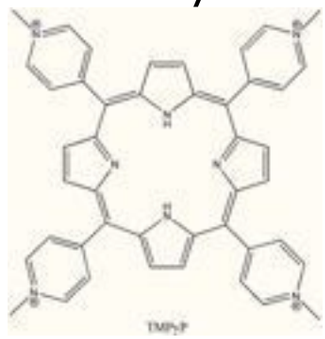
T. Ghane, D. Varsano, and R. Di Felice submitted to JPCB (2012)

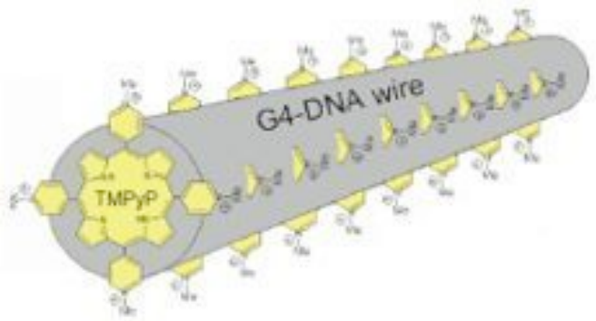
G4/porphyrins intercalation

G4 plane

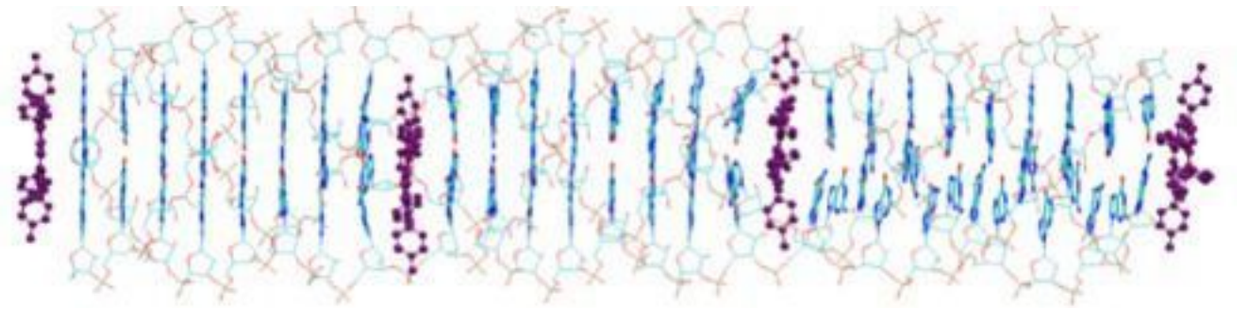


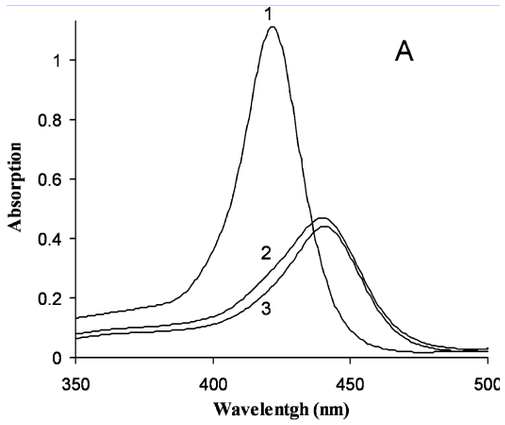
TMPyP

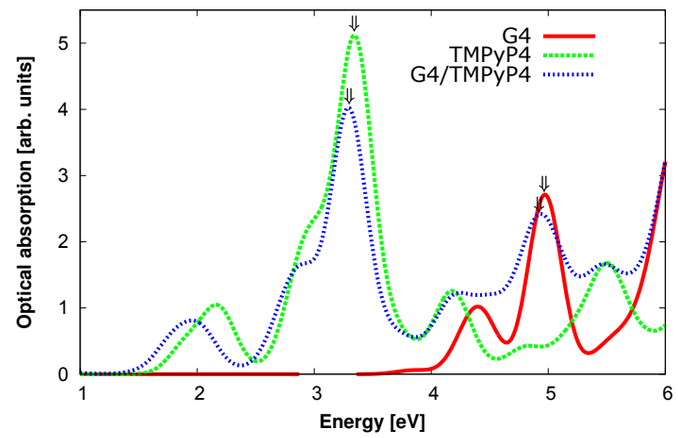




compound that stabilize G4 in DNA telomers can be potential candidates for anti-tumor drugs





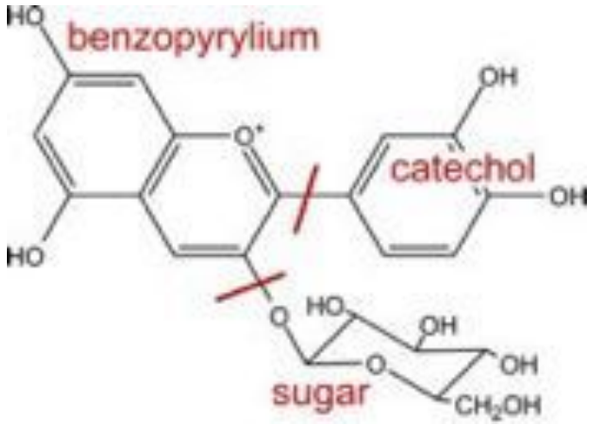


I. Lubitz et al. Biochemistry, **46**,12925 (2007)

L.A. Espinosa-Leal, D. Varsano et al. to be submitted (2012)

Optical properties of natural dyes

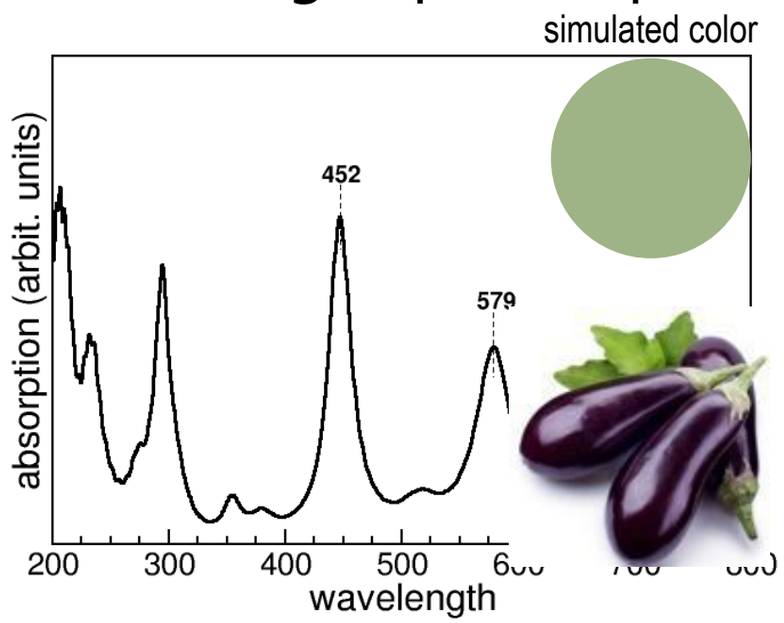
Cyanin: Natural dye in plants and fruits



Food industry, pharmaceutical, solar cell applications

what makes things look the color they have

TDDFT (PBE) gas-phase spectrum

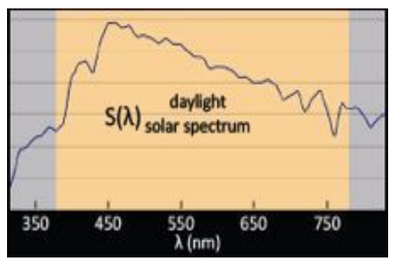


Reasonable agreement of absorption peaks with experiments, but:

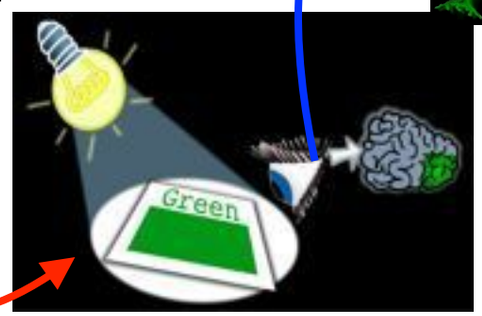
What about the color?

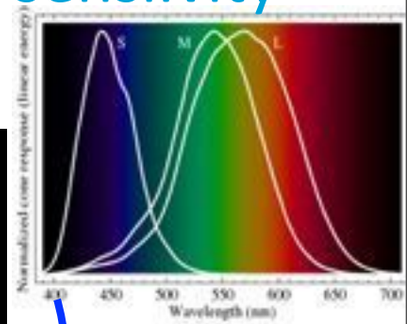
A. Calzolari, D. Varsano et al.
J. Phys.Chem A **113**, 8801 (2009)

stimulus = illuminant × trasmission × sensilvity



incident radiation (*illuminant*)

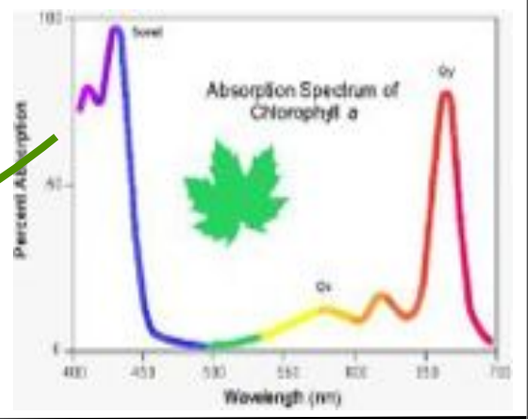




$$T(x,\lambda) = S(\lambda)e^{-\alpha(\lambda)x}$$

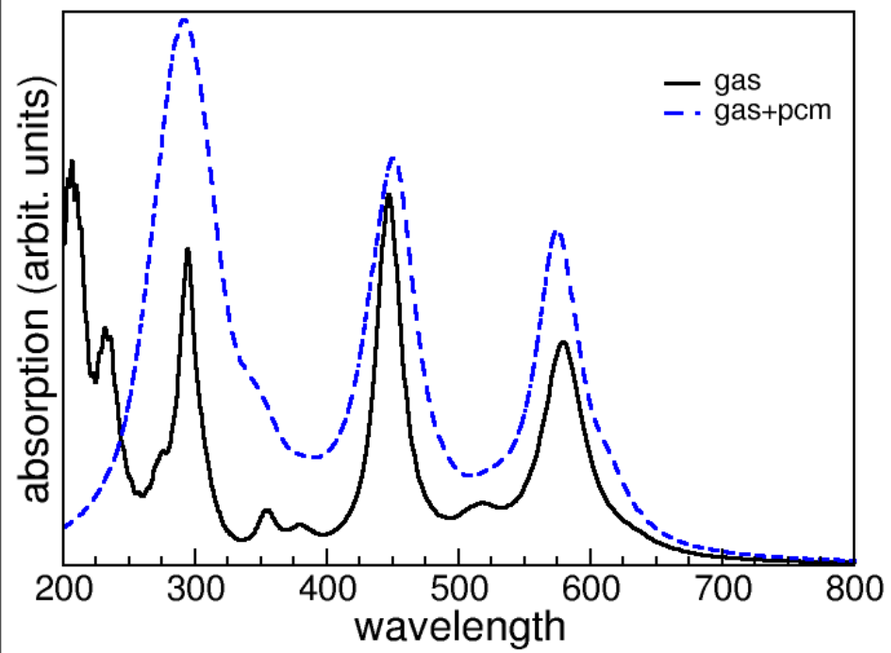
color perceived by human eye

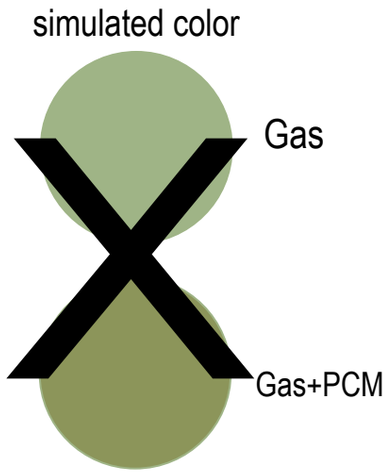
$$\mathrm{R\ G\ B}(x) = \int S(\lambda)e^{-\alpha(\lambda)x}\mathrm{r\ g\ b}(\lambda)d\lambda$$



Optical properties of natural dyes

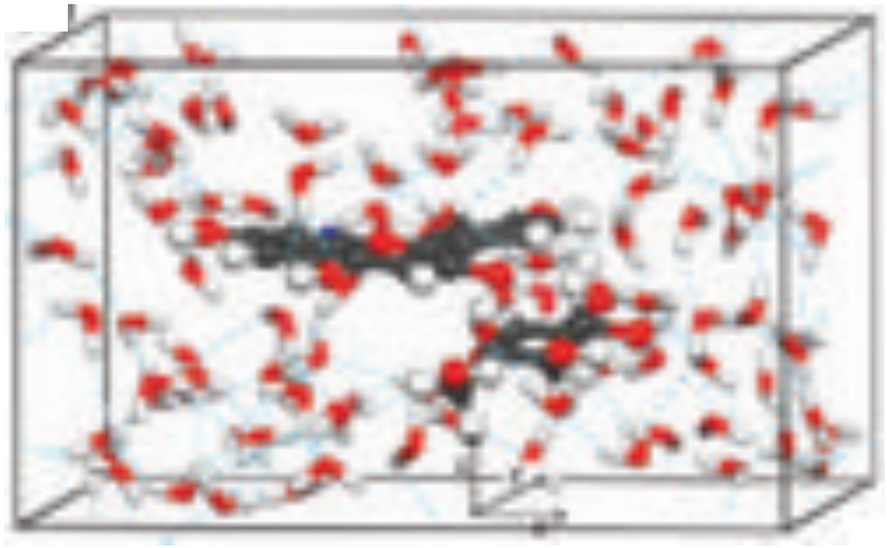
solvation effect - implicit solvent (PCM)

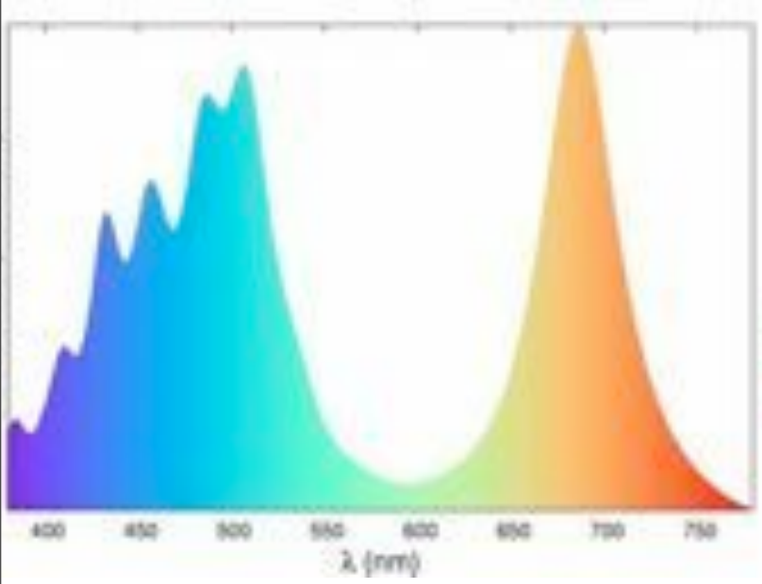


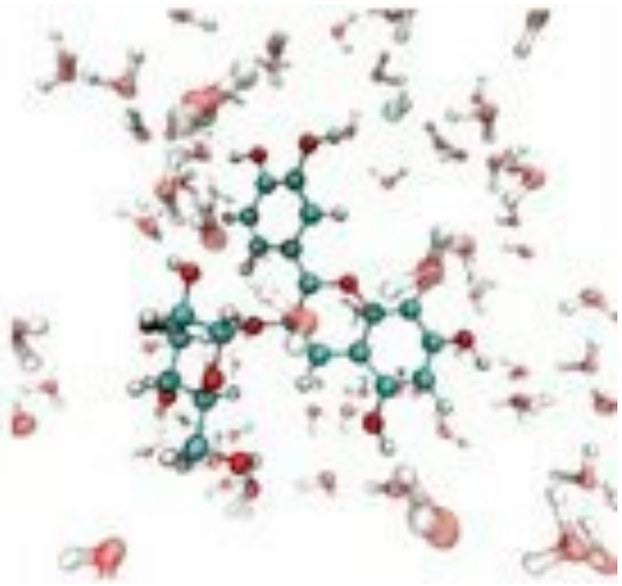


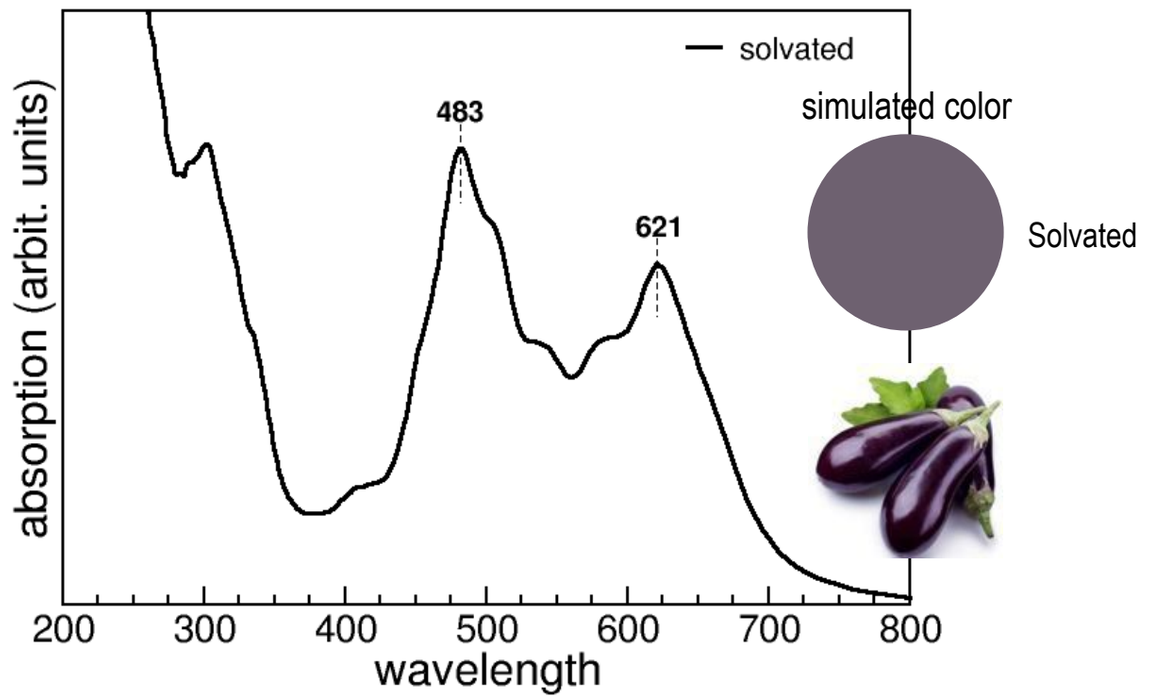
Explicit solvent: CP molecular dynamics

$C_{21}H_{21}O_{11}Cl@(H_2O)_{95}$









Optical effect of the solvent and **intramolecular motion**

O.B. Malcioğlu, A. Calzolari, R. Gebauer, D. Varsano, and S. Baroni, JACS **133**, 15425 (2011)

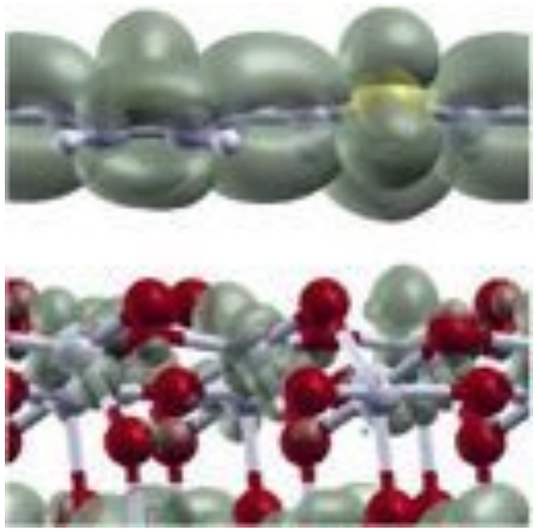
Future Research

Understanding fundamental processes in new generation photovoltaic hybrid materials by first principle techniques

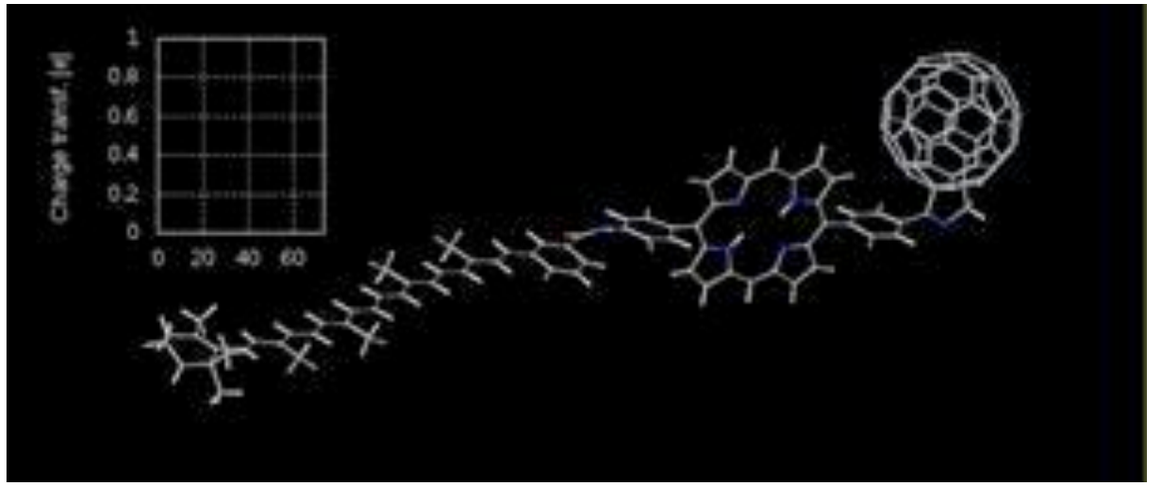
Multiscale approach to optical properties of biological chromophores

Understanding fundamental processes in new generation photovoltaic hybrid materials by first principle techniques

Catechol@SIC



α-PT/TiO_2



Molecular Triad

The principal mechanism affecting the efficiency of excitonic solar cell:
Photoabsorption of visible light by the dye and the subsequent **charge transfer** of the photoelectron to the semiconductor.

Electronic and excitonic properties by first principle calculations of the molecule (polymer)/semiconductor interfaces

- Nanoscale modeling of the dye(polymer)/semiconductor interfaces.
- Optical and electronic properties of the interfaces.

Many Body Perturbation Theory can provide accurate quasiparticle energy levels, exciton binding energy, excitation character

- Charge dynamic of the electron-hole excitation

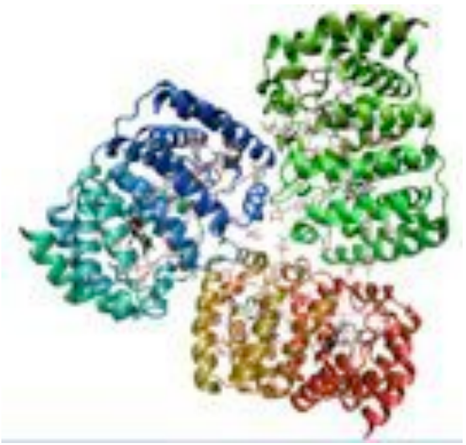
Optical properties of biological chromophores in photoactive proteins

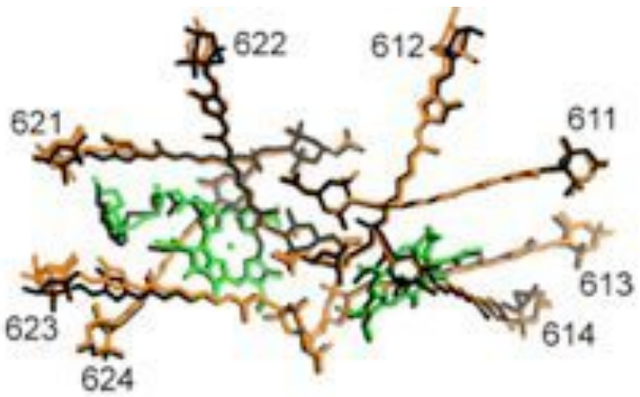
Specific interaction of the surrounding protein environment determines functionality and efficiency of the chromophores

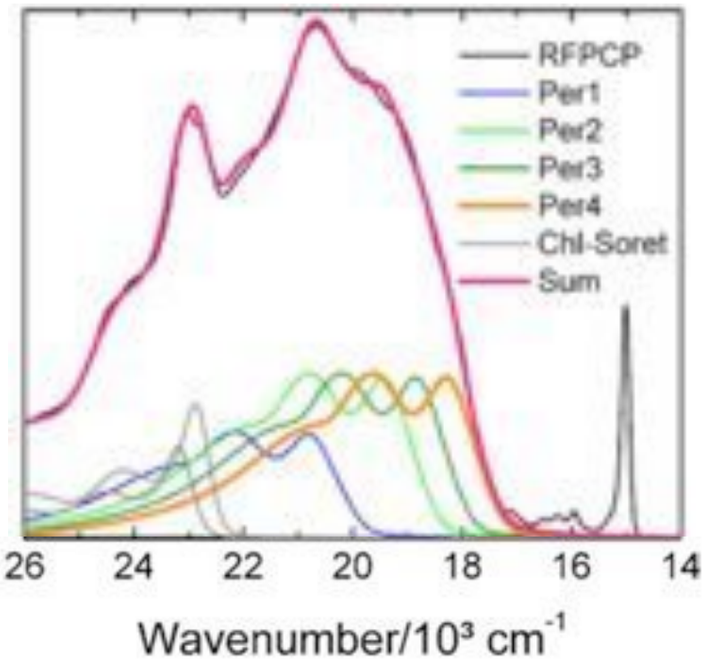
The Peridinin-Chlorophyll-Protein (PCP) complex

a light harvesting complex that feeds energy to PSII in dinoflagellates.

Amphidinium

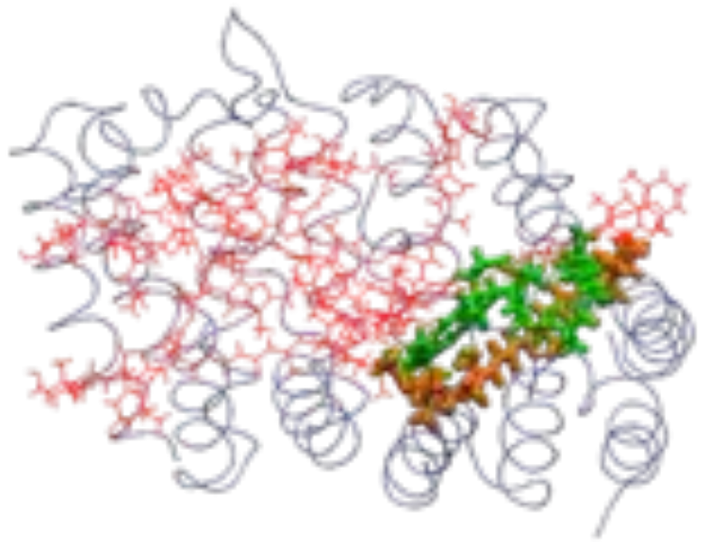






*T. Schulte et al. PNAS 106, 20764 (**2009**)*

Exploration of the optical properties of biological chromophores in their natural environment, by high accuracy quantum mechanical first principle methods focusing on a reliable description of the environment



- Mixed QM/MM methods: *Many Body Perturbation Theory for optics and QMC for structural optimization (in collaboration with L.Guidoni (L'Aquila)*
- Distinguish between geometry and external field effects: *e.g. the role of the bond length alternation in the excitation of polyene chains*
- Systems of interests: PCP, GFP, Rhodopsin:

*GFP chemical shift in TDDFT: M. Marques, X. Lopez, D.Varsano, A. Castro and A. Rubio Phys. Rev. Lett. **90**, 258101 (2003)*

Conclusion

- First-principle calculations: a powerful and predictive tool for nanoscale system characterization and interpretation and guidance of experiments

- My research combines different ab-initio methods for the study of electronic and optical properties with application in

★ Biological systems

★ Energy conversion materials

★ Molecular electronics