Perspectives

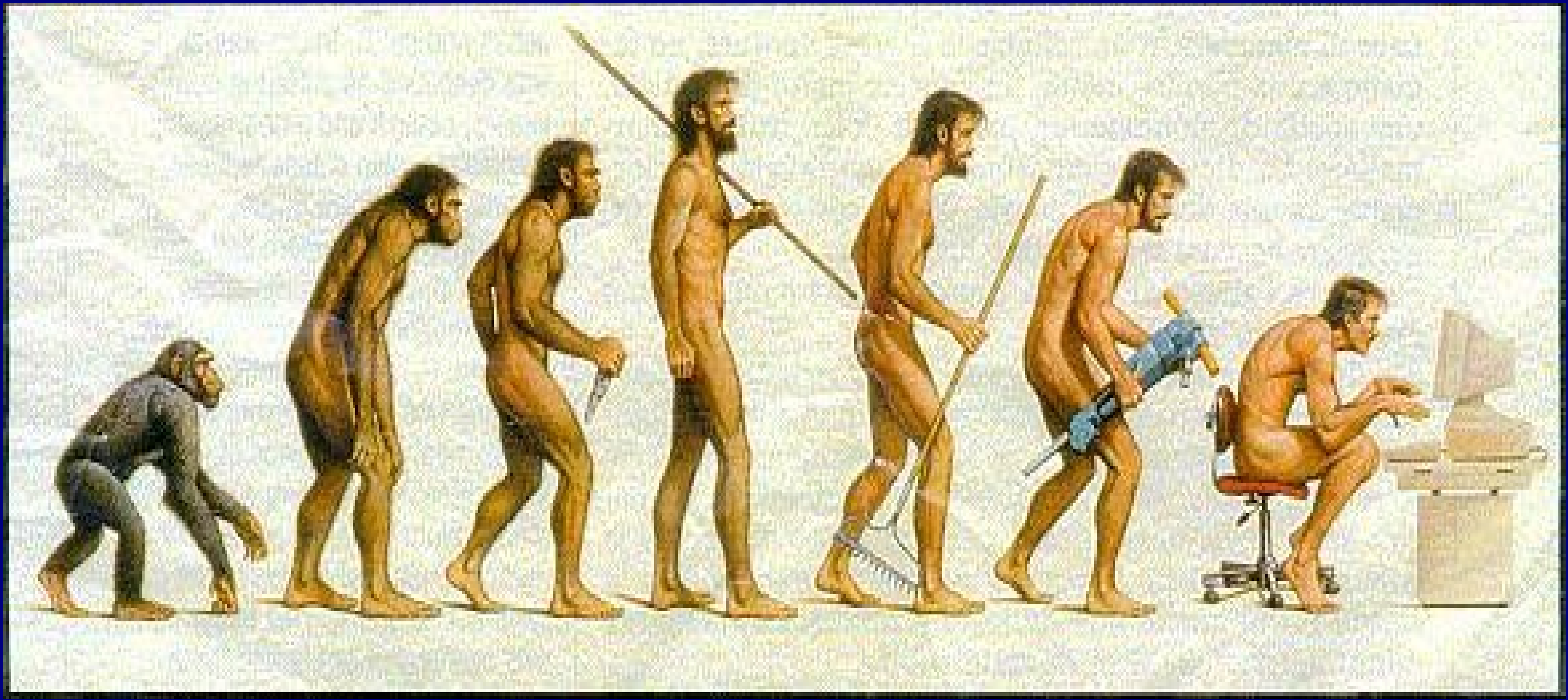
Open session about challenges and standing problems

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*





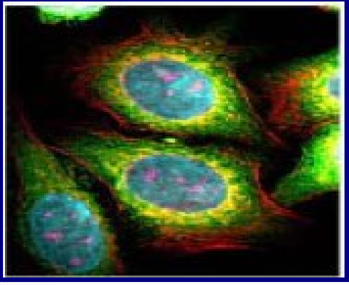
Nanotechnology: a higher form of evolution?
(Humility is perhaps appropriate…)

NEW CONCEPTS

Small is different: atoms and molecules as our building blocks

nano, bio and material science

Nanoelectronics + Nanoptics + Nanophononics



More is different: emergent properties of matter

Computational Science: insight into the fields of Physics, Chemistry, Materials Science, Medicine, Biology, Astrophysics, Earth science, Energy, transportation, Domotics, ...

Why Theoretical modeling

and

Theoretical Spectroscopy?

"Excitations" --- Interactions

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Open session about challenges and standing problems

TDDFT school, Benasque 4-17th January 2014

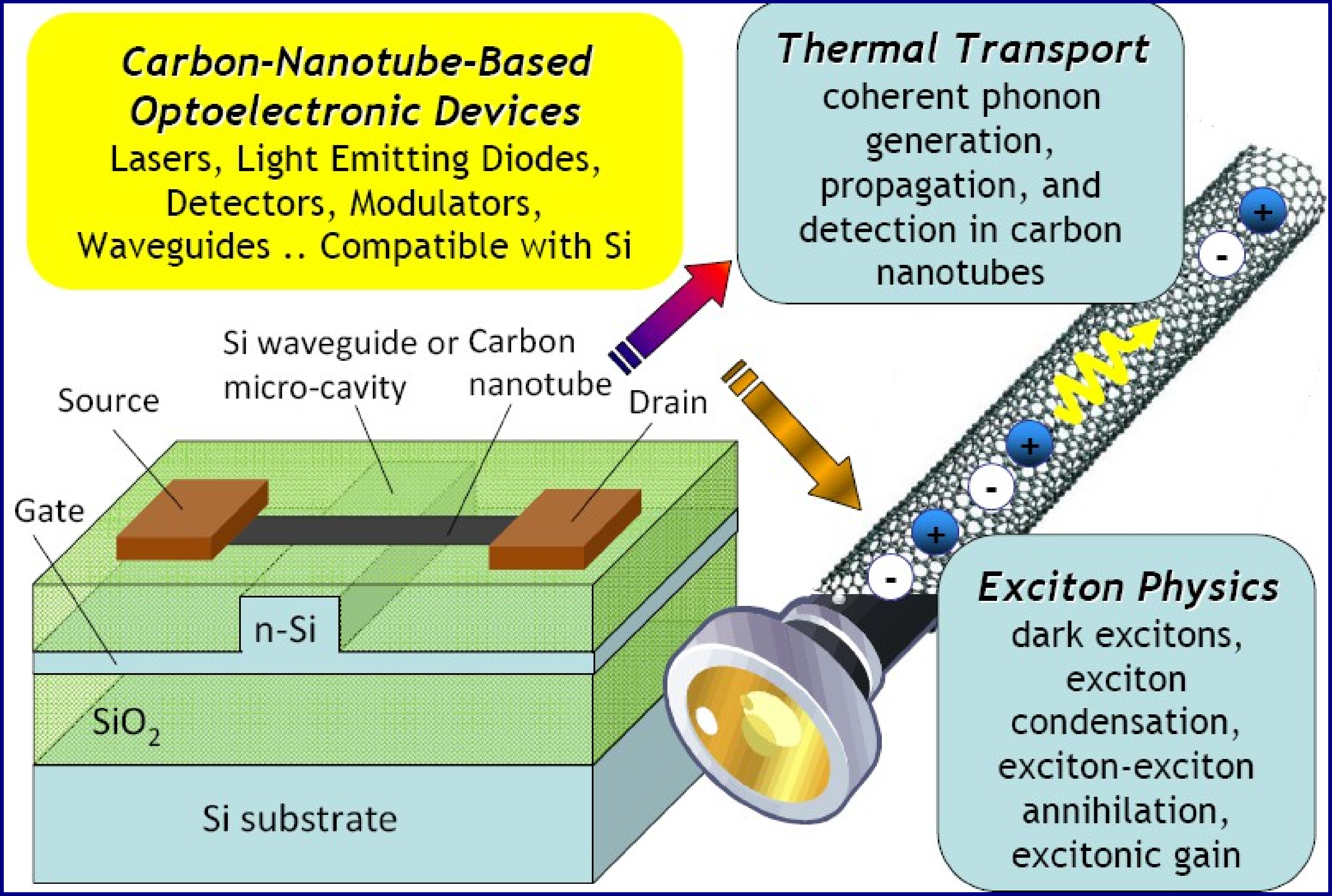
European Theoretical Spectroscopy Facility — ETSF

GROWTH

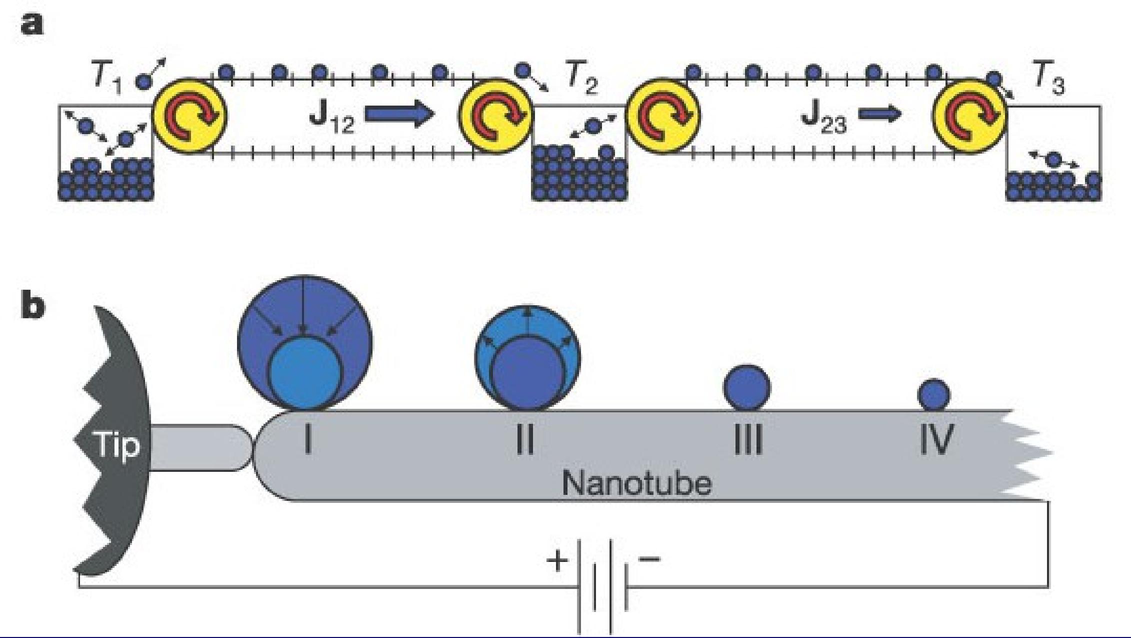
NEW CONCEPTS

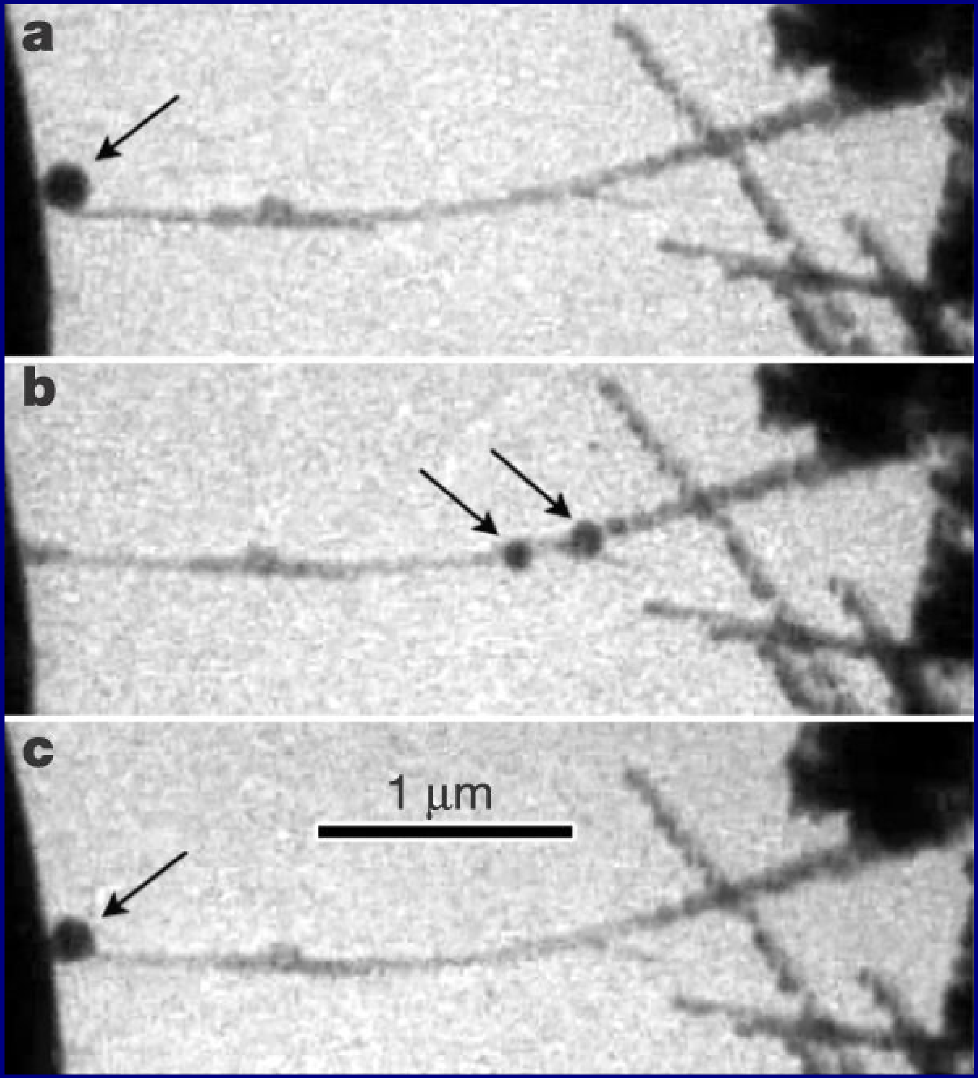
Small is different: atoms and molecules as our building blocks

Nanoelectronics + Nanoptics + Nanophononics



Nanotubos de carbono: transporte de masa

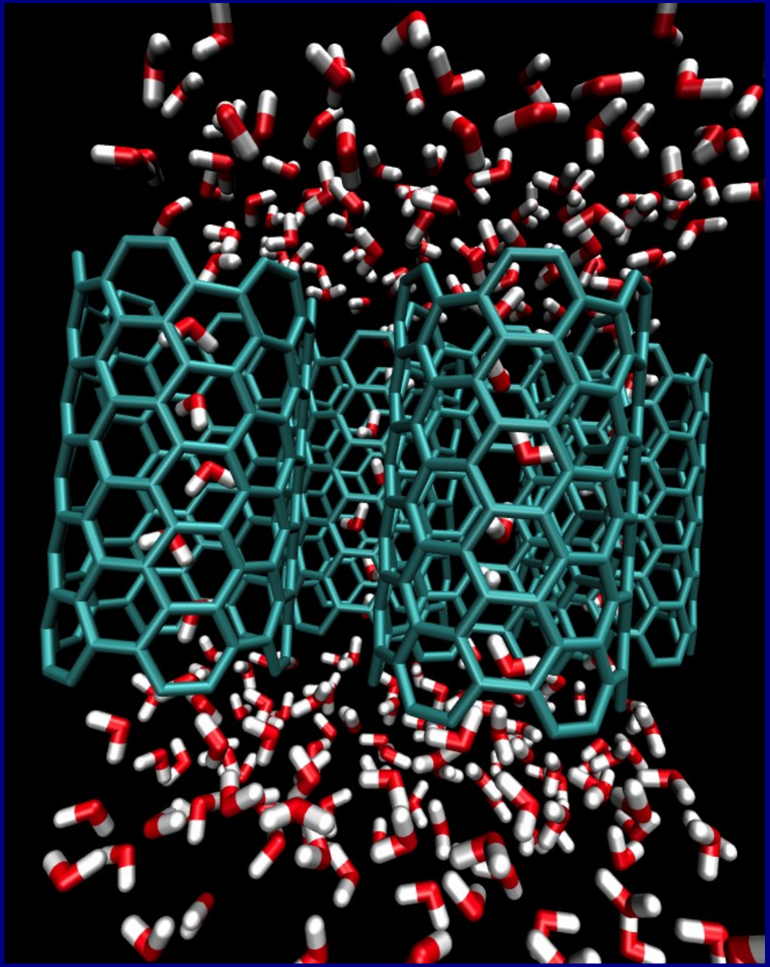


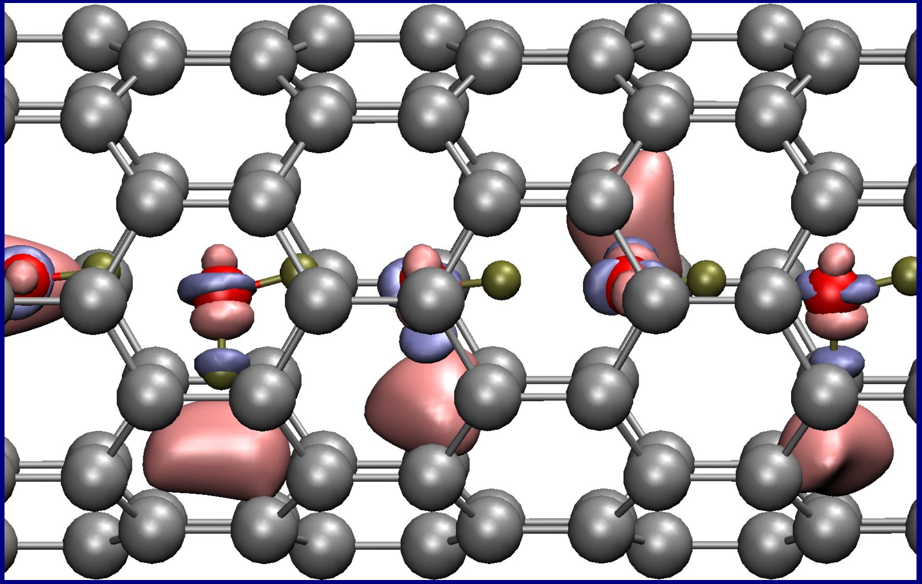


B.C. Regan et al, Nature 428, 924 (2004)

Nanocapillarity

Excited-state properties of confined water as it permeates through nanochannels: Nanosolvation





Why Theoretical modeling

and

Theoretical Spectroscopy?

“Excitations” --- Interactions

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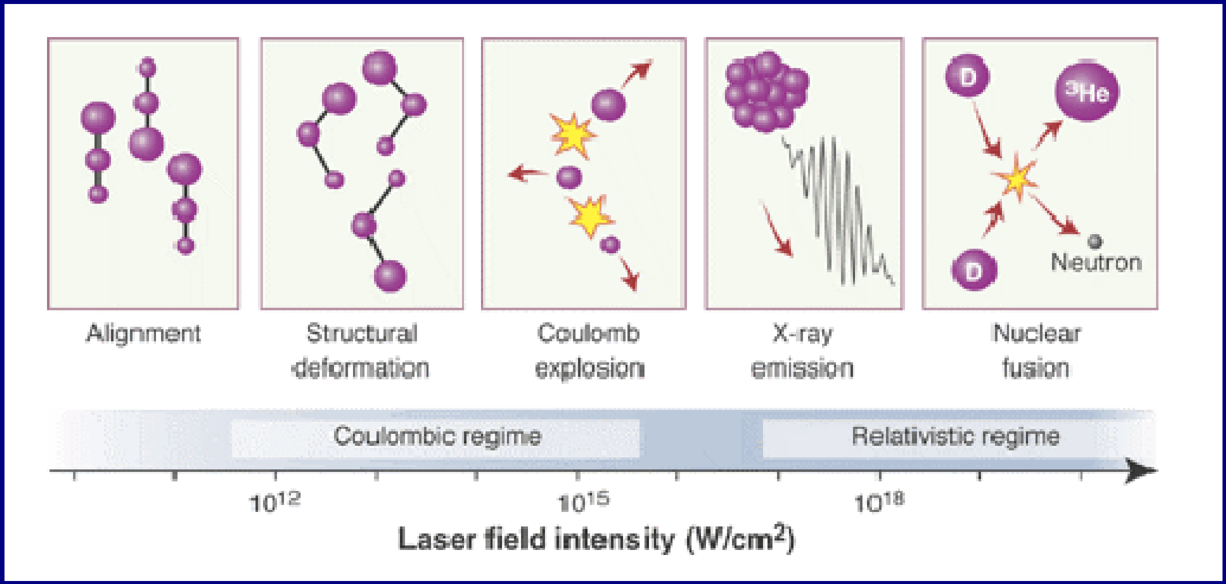
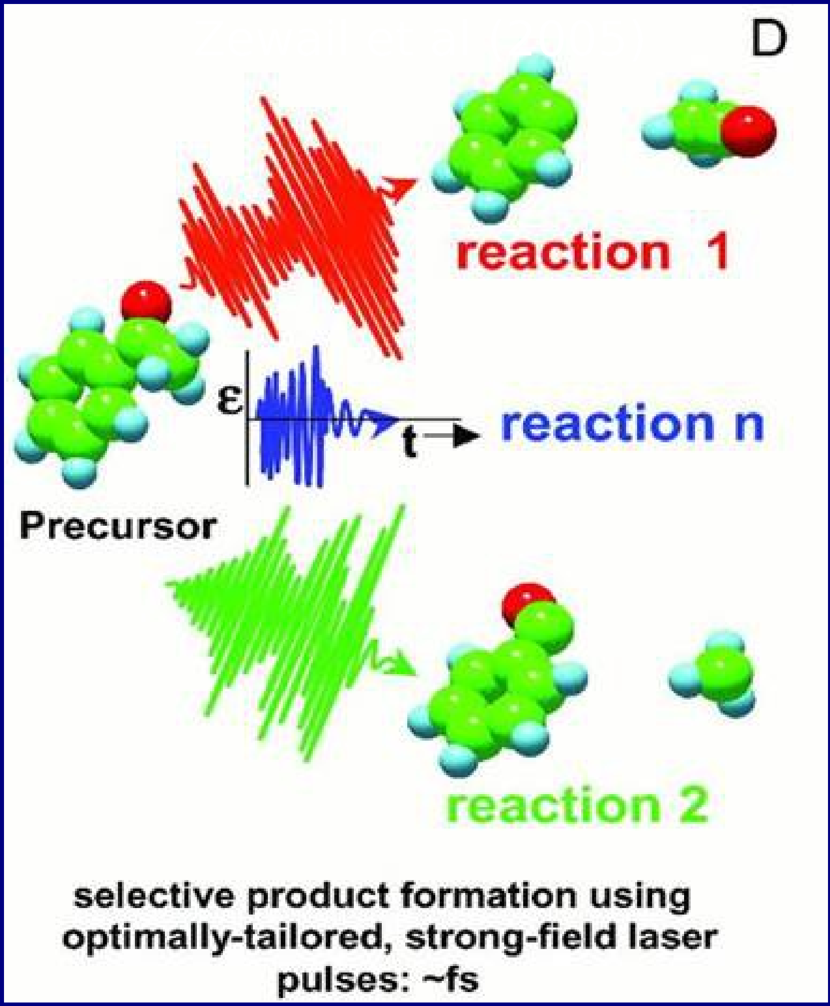
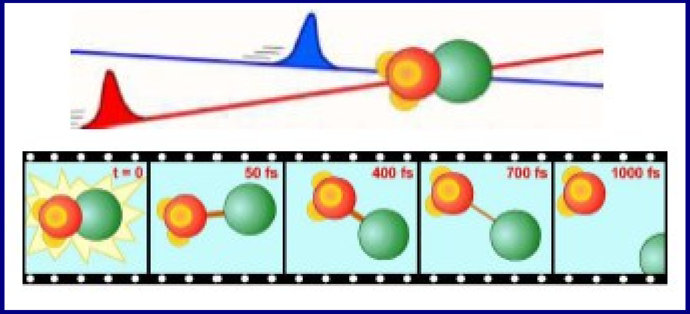
Quantum control



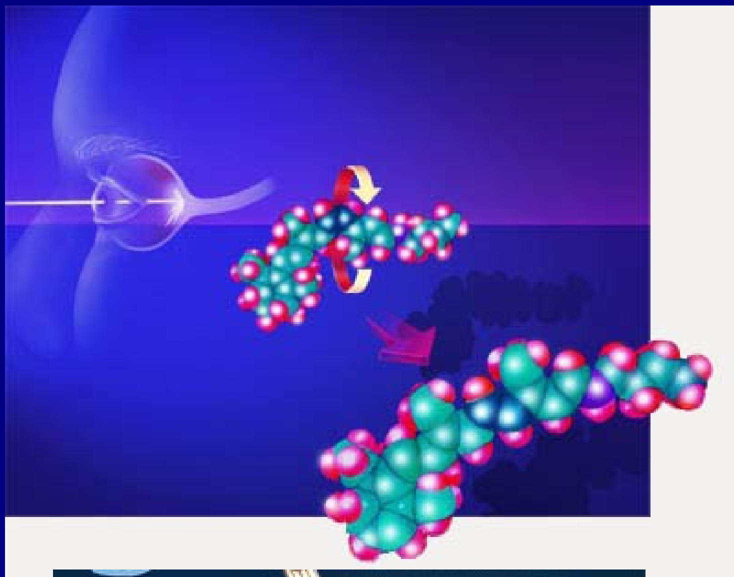


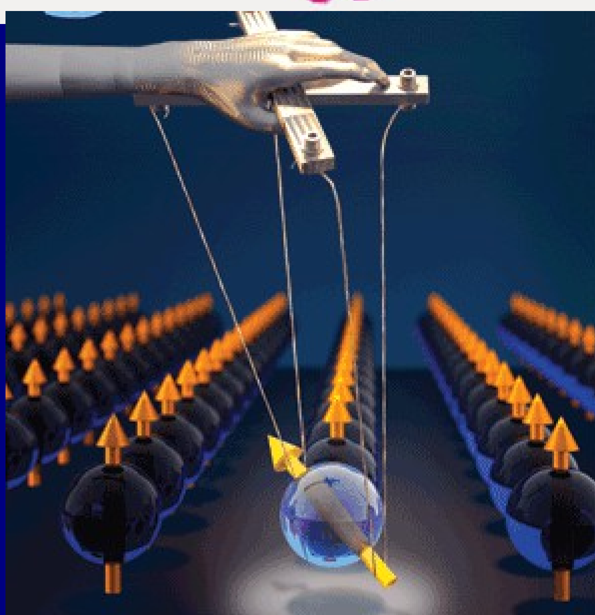
Time resolved pump-probe techniques

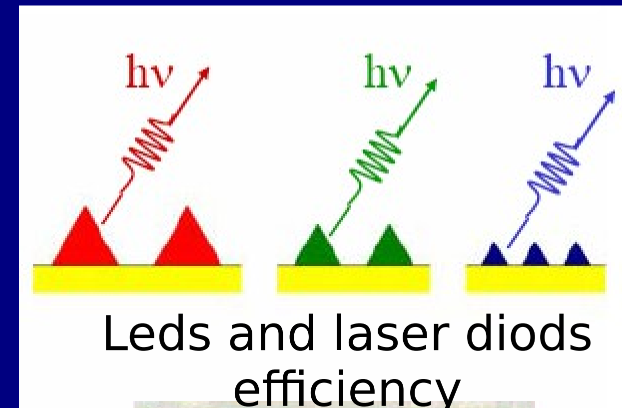


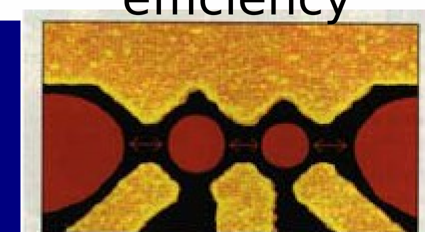
R. J. Levis *et al*, Science 292, 709 (2001)

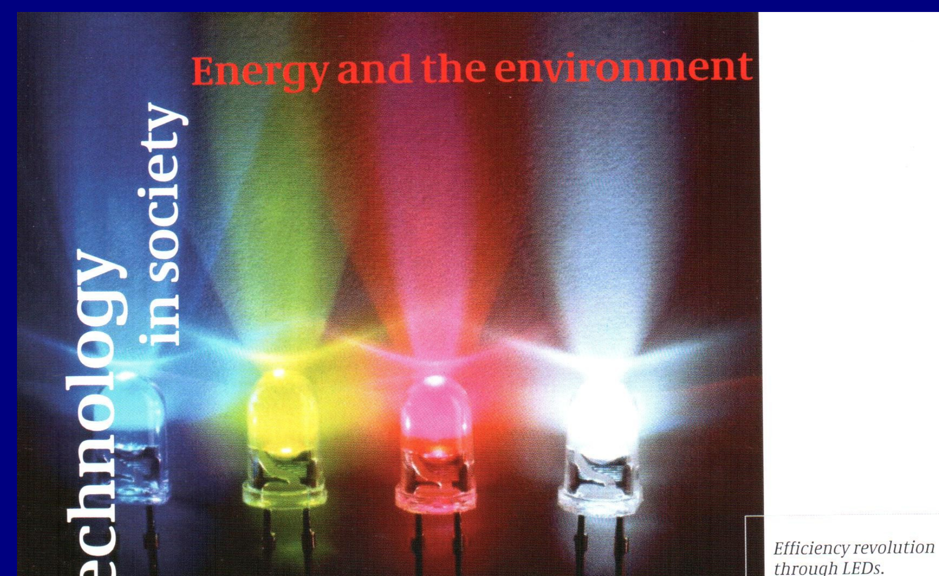
Seeing is believing**











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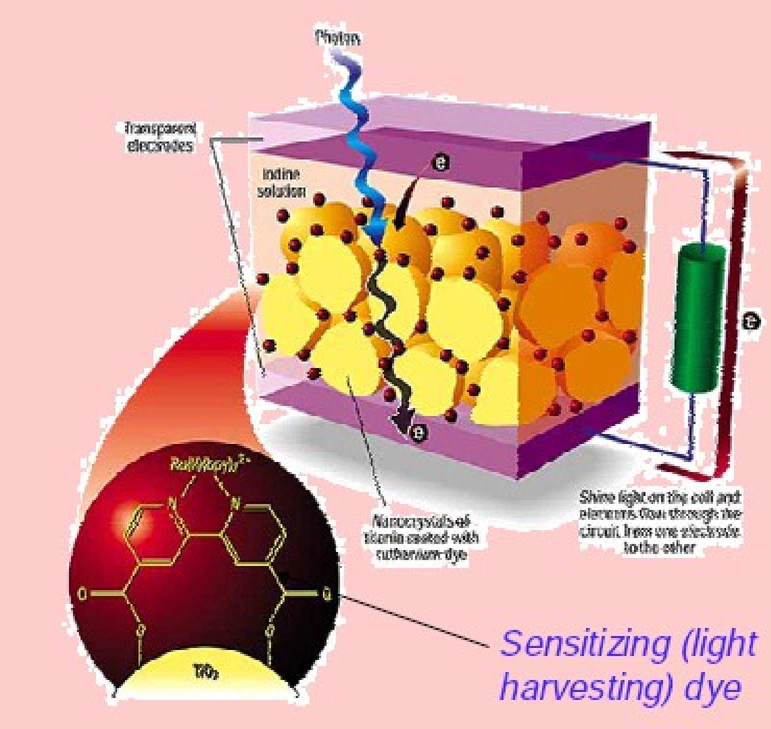
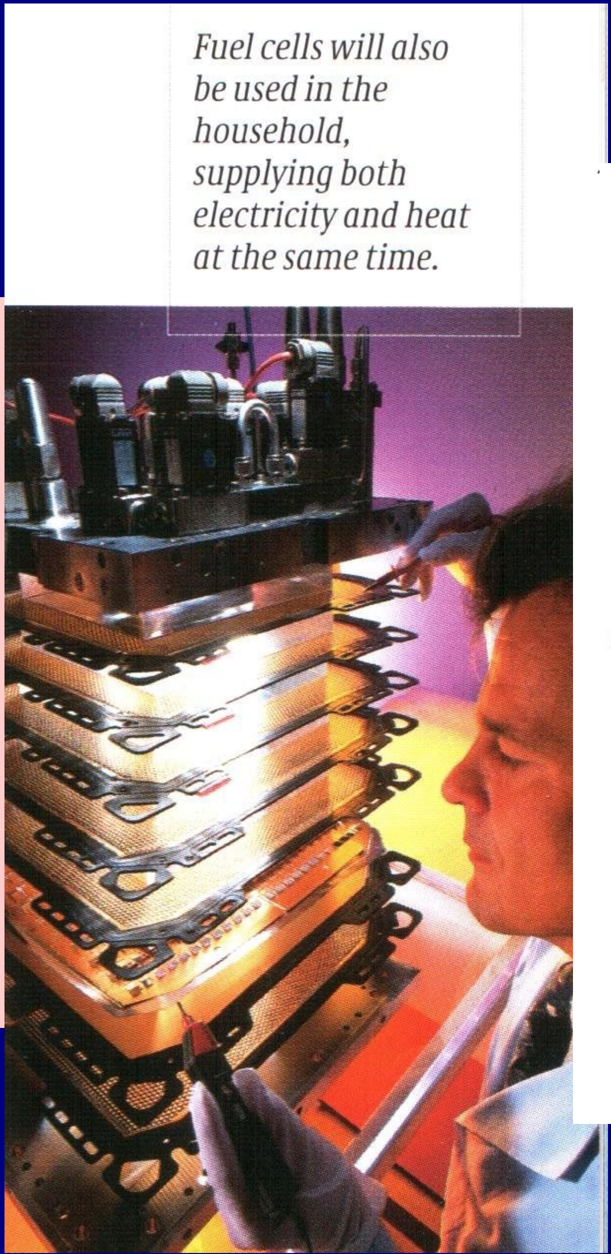
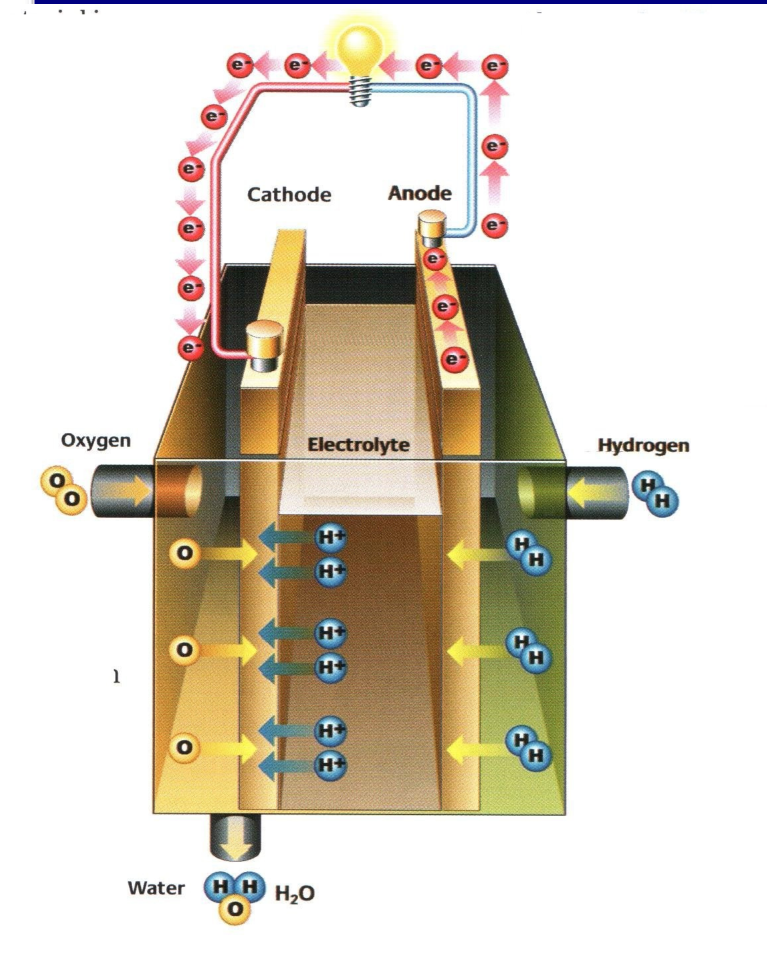
ENERGY APPLICATIONS

Grätzel cells
photovoltaics





Fuel cells



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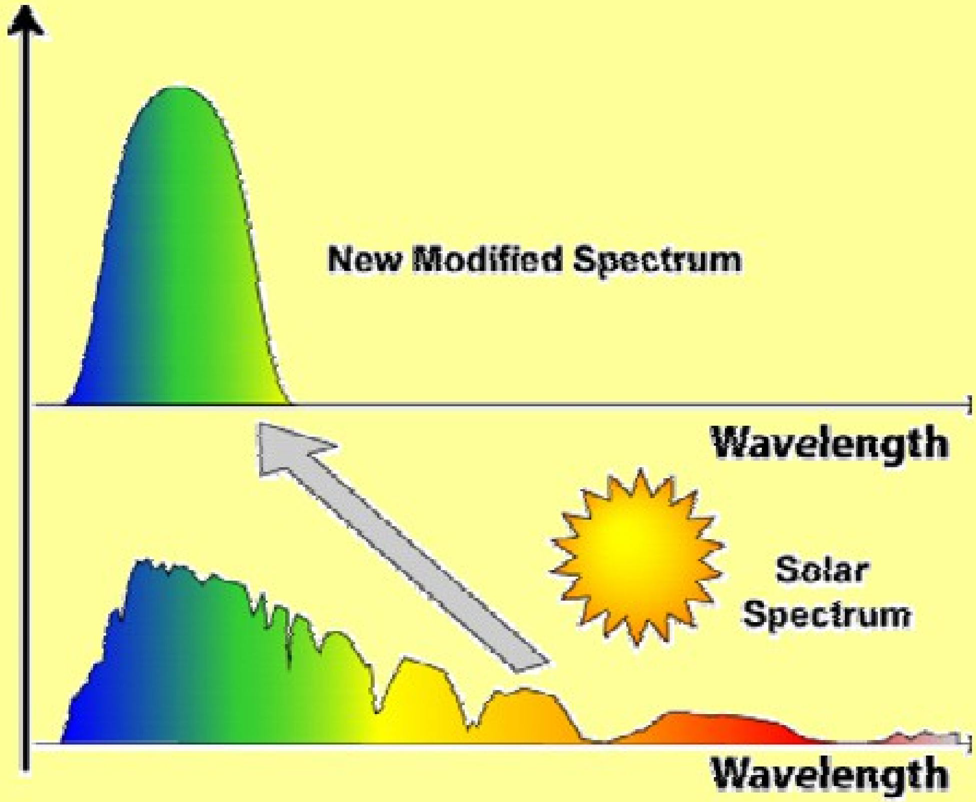
Revolutionary photovoltaics

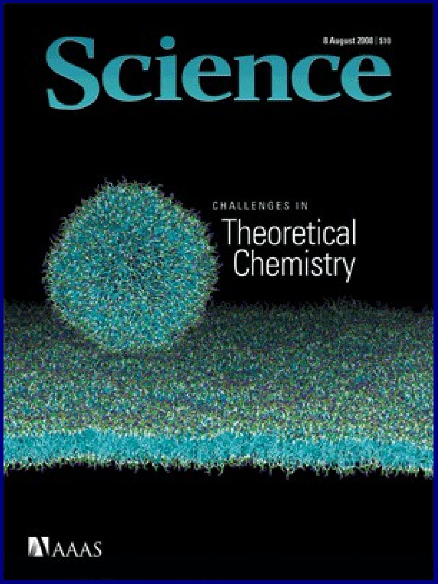
Photon management: converters



The solar spectrum can be "adapted" for a better quantum yield prior to the electron-hole excitation in the cell

Theoretical Framework

QM: (TD)DFT



$$H\ \Psi(r_1 \ldots\ldots\ldots r_N) = E\ \Psi(r_1 \ldots\ldots\ldots r_N)$$

Back to the ground

TDDFT school and workshop in Benasque

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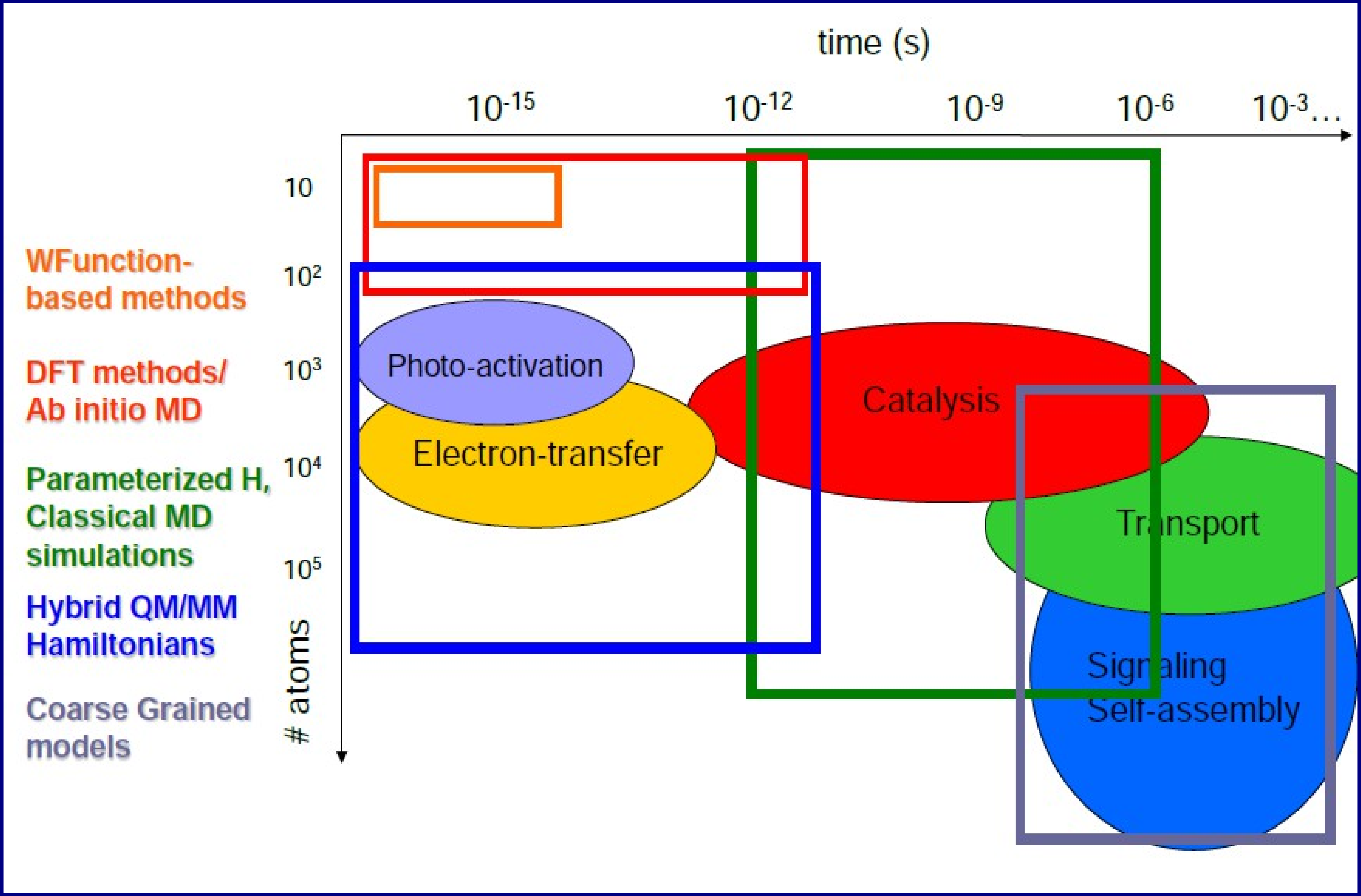
Time and size scales



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

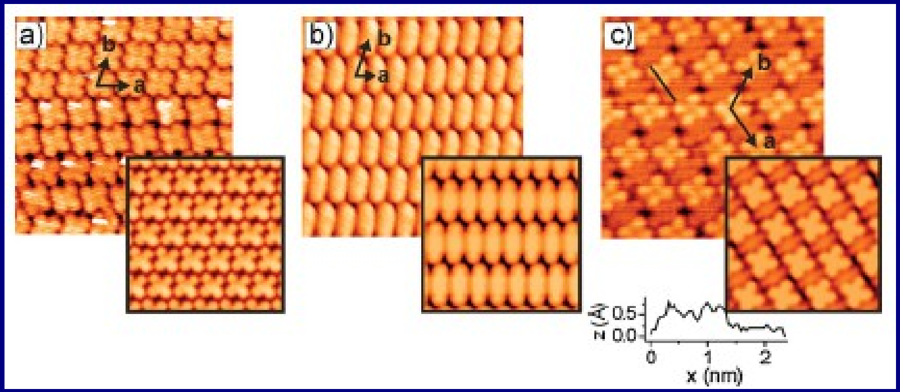
Memory effects; Dissipation; lifetime; de-coherence

Open shell systems and Open quantum systems

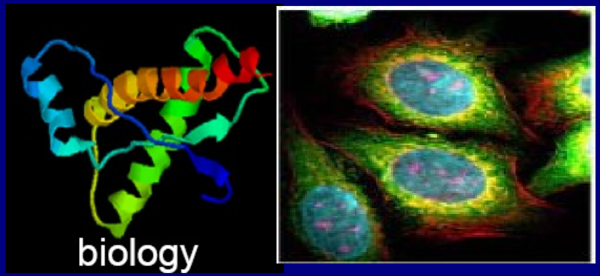
Correlated Materials ....

LEVEL ALIGNMENT,   Dispersion forces VdW

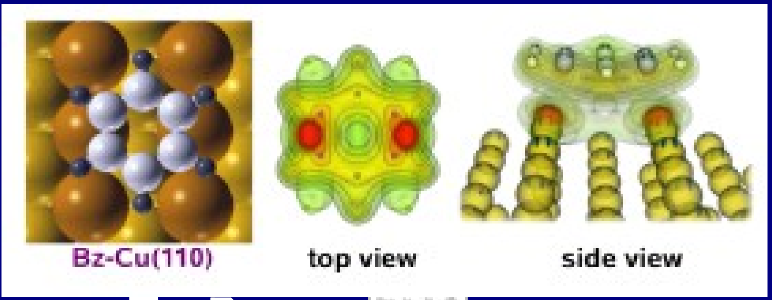
Supramolecular chemistry

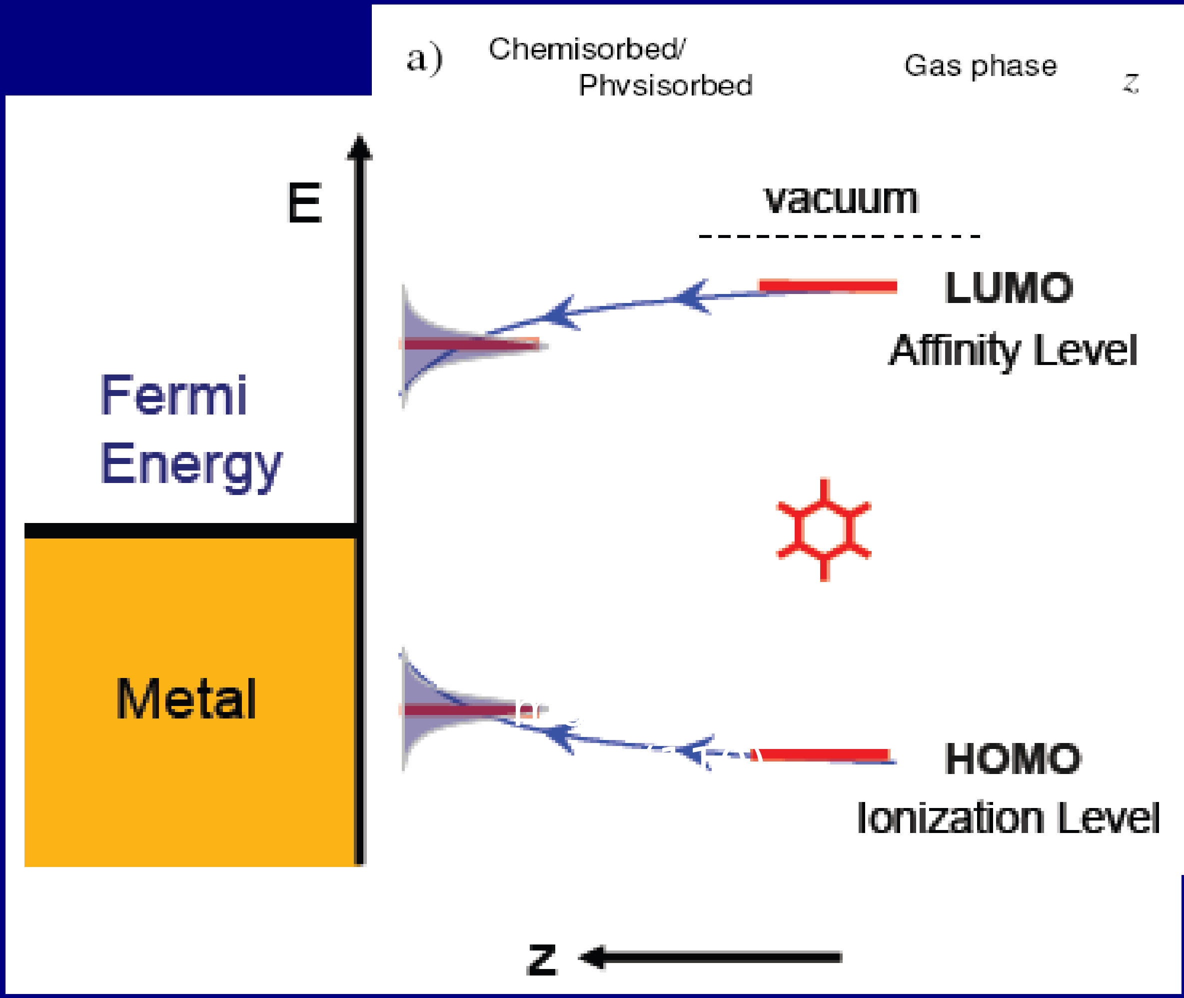


Biophysics ....



Molecular Transport

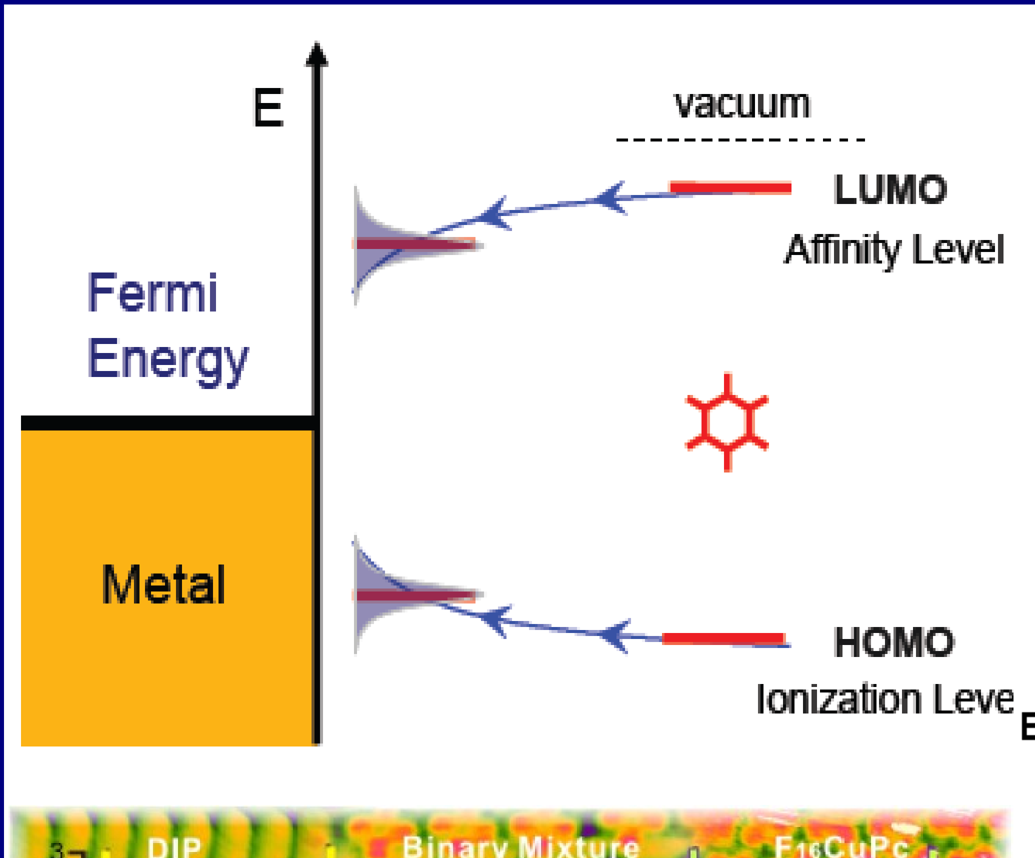


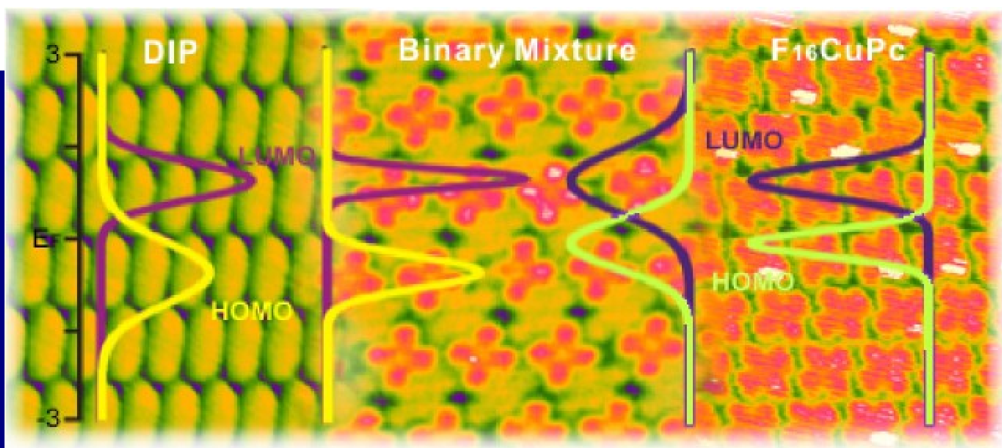


N. Atodiresei, S.Blugel et al, PRL **102**, 136809 (2009)

See the talk of P. Rinke for CO on surfaces

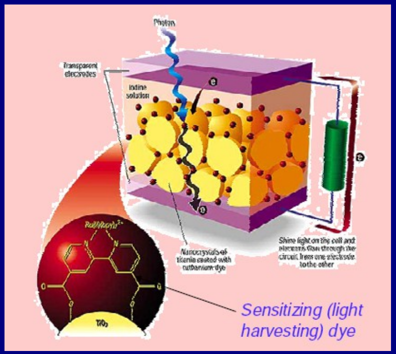
LEVEL ALIGNMENT, Dispersion forces VdW

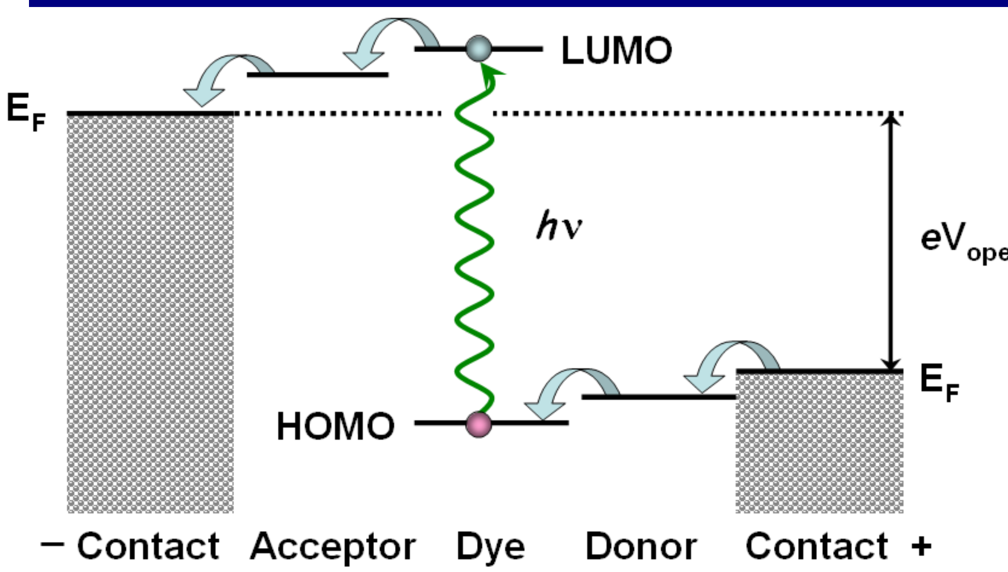




Charge Transfer excitations

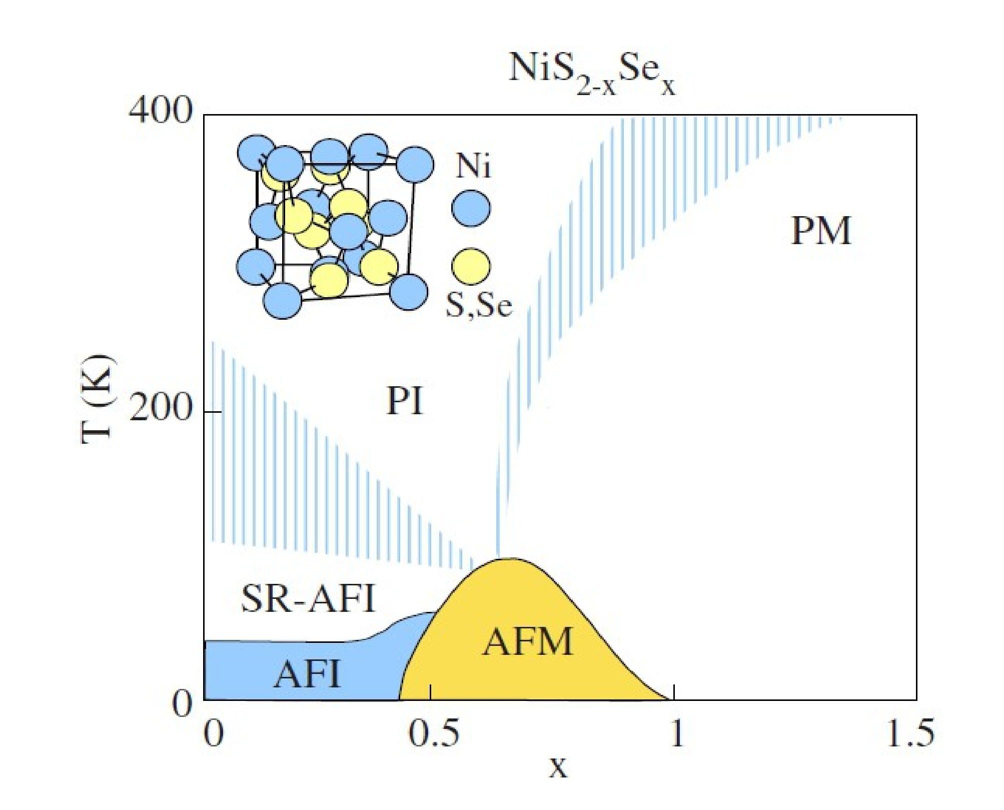
Photovoltaic Hybrids: Grätzell cells





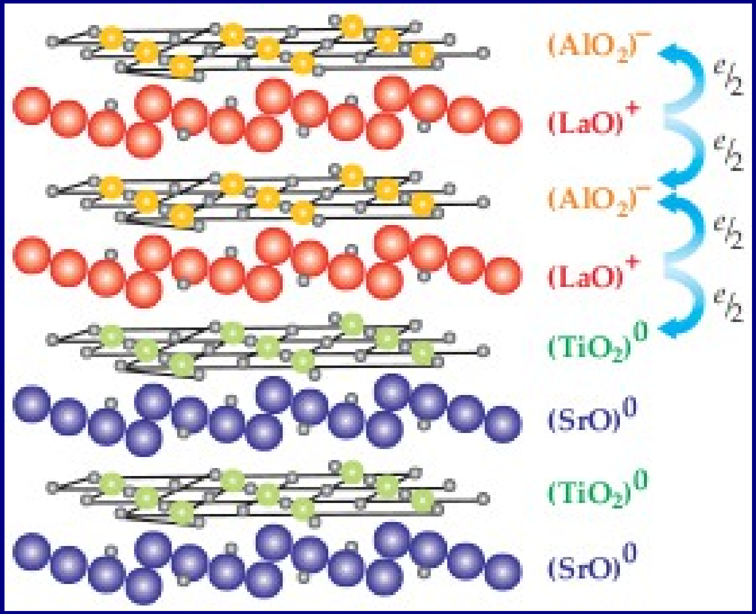
Road to Improving Efficiency: Controlling position of the frontier orbitals

Correlated materials



Sensitivity

Phase transitions with pressure doping or temperature



Emergence

Interface between correlated oxide insulators? It is metallic!

What is correlations and when a system is to be considered correlated?

...beyond LDA ? ... beyond HF?

How much of the "model hamiltonian" studies can be captured by present "advanced" functionals

ARTICLES

Collapse of magnetic moment drives the Mott transition in MnO

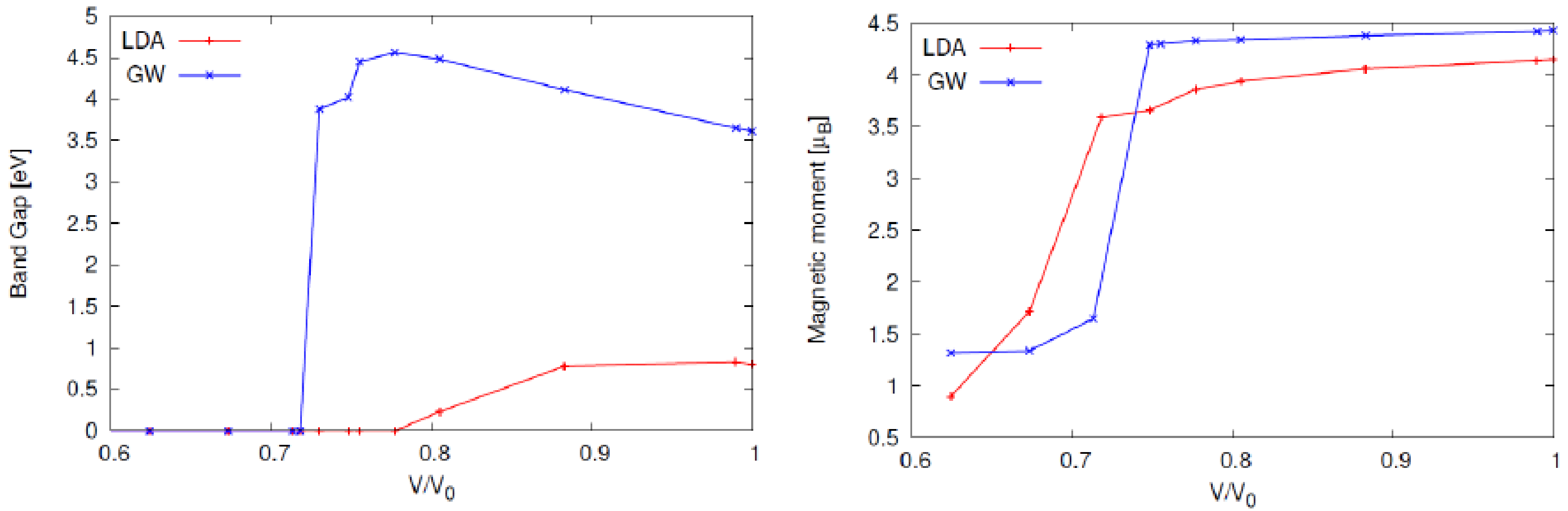
JAN KUNEŠ[1,2*], ALEXEY V. LUKOYANOV[3], VLADIMIR I. ANISIMOV[4], RICHARD T. SCALETTAR[5] AND WARREN E. PICKETT[5]

[1]Theoretical Physics III, Center for Electronic Correlations and Magnetism, Institute of Physics, University of Augsburg, Augsburg 86135, Germany
[2]Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnická 10, 162 53 Praha 6, Czech Republic
[3]Ural State Technical University-UPI, 620002 Yekaterinburg, Russia
[4]Institute of Metal Physics, Russian Academy of Sciences-Ural Division, 620041 Yekaterinburg GSP-170, Russia
[5]Department of Physics, University of California Davis, Davis, California 95616, USA
*e-mail: jan.kunes@physik.uni-augsburg.de

Published online: 3 February 2008; doi:10.1038/nmat2115

The metal–insulator transition in correlated electron systems, where electron states transform from itinerant to localized, has been one of the central themes of condensed-matter physics for more than half a century. The persistence of this question has been a consequence both of the intricacy of the fundamental issues and the growing recognition of the complexities that arise in real materials, when strong repulsive interactions play the primary role. The initial concept of Mott was based on the relative importance of kinetic hopping (measured by the bandwidth) and onsite repulsion of electrons. Real materials, however, have many further degrees of freedom that, as is recently attracting note, give rise to a rich variety of scenarios for a 'Mott transition'. Here, we report results for the classic correlated insulator MnO that reproduce a simultaneous moment collapse, volume collapse and metallization transition near the observed pressure, and identify the mechanism as collapse of the magnetic moment due to an increase of crystal-field splitting, rather than to variation in the bandwidth.

Mott transition in MnO: FCC model



LDA: metal at too large volume
magnetic moment decreases continuously

GW: metallization & magnetic moment collapse
are simultaneous: Mott transition

M. Gatti, AR (unpublished)

Strong correlation

- Conventional wisdom:

  "Strongly correlated materials are a wide class of materials that show unusual (...) electronic and magnetic properties (...) The essential feature that defines these materials is that the behaviour of their electrons cannot be described effectively in terms of non-interacting entities."

- In practise:

  Chemist's and physicist's approaches differ both in the class of materials and the definition of non-interacting entities!

- BUT: H chains are strongly correlated according to both communities

The metal-insulator "transition"

Single particle occupations

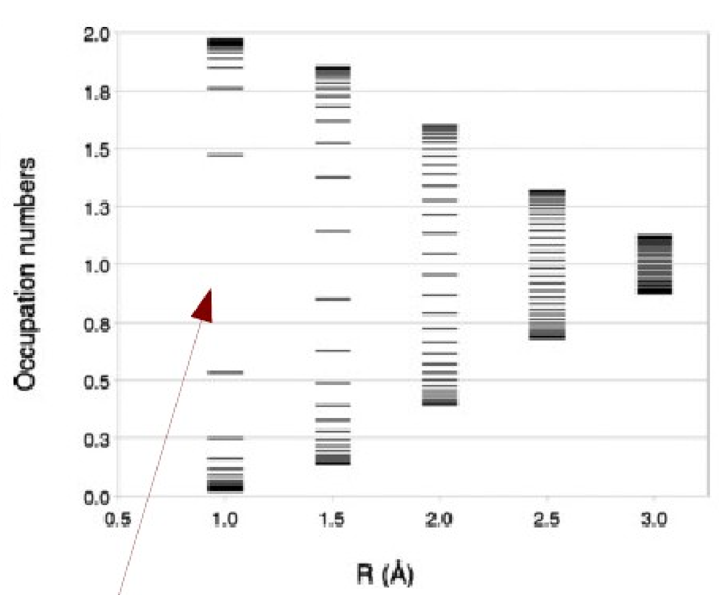


FIG. 3. The occupation numbers of the natural orbitals in H_{32}, as functions of interatomic distance R, are estimated by the 2-RDM method with DQG conditions.

Fermi's "surface"

Sinitskiy *et al.*(2010)

Long range correlation

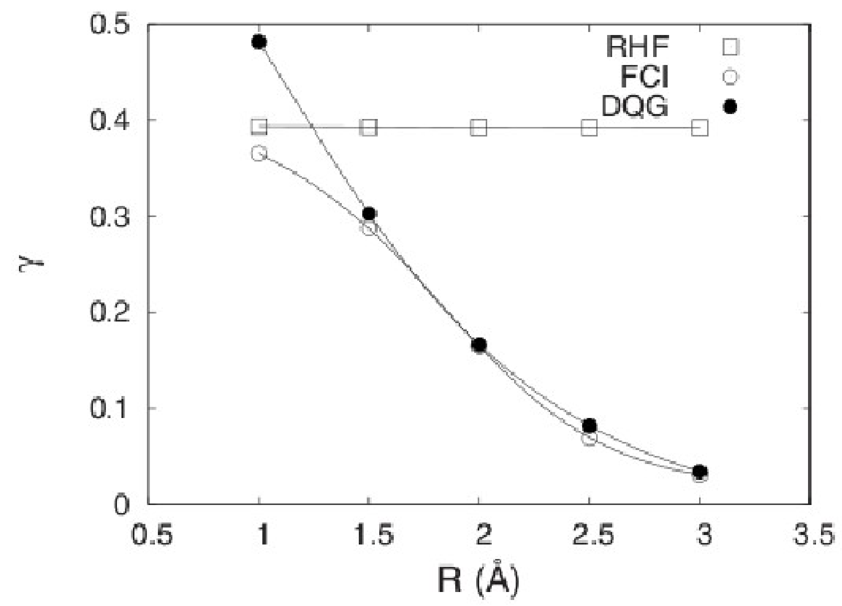


FIG. 4. Average of off-diagonal 1-RDM elements, which gives the correlations between atomic orbitals. This illustrates the metal-to-insulator transition in the linear chain of hydrogen atoms under the change of the distance R between the closest atoms.

Correlation

SIMPLE MODEL SYSTEMS

How to understand H_2
and
H-chain
(*Mott insulator in DFT*)

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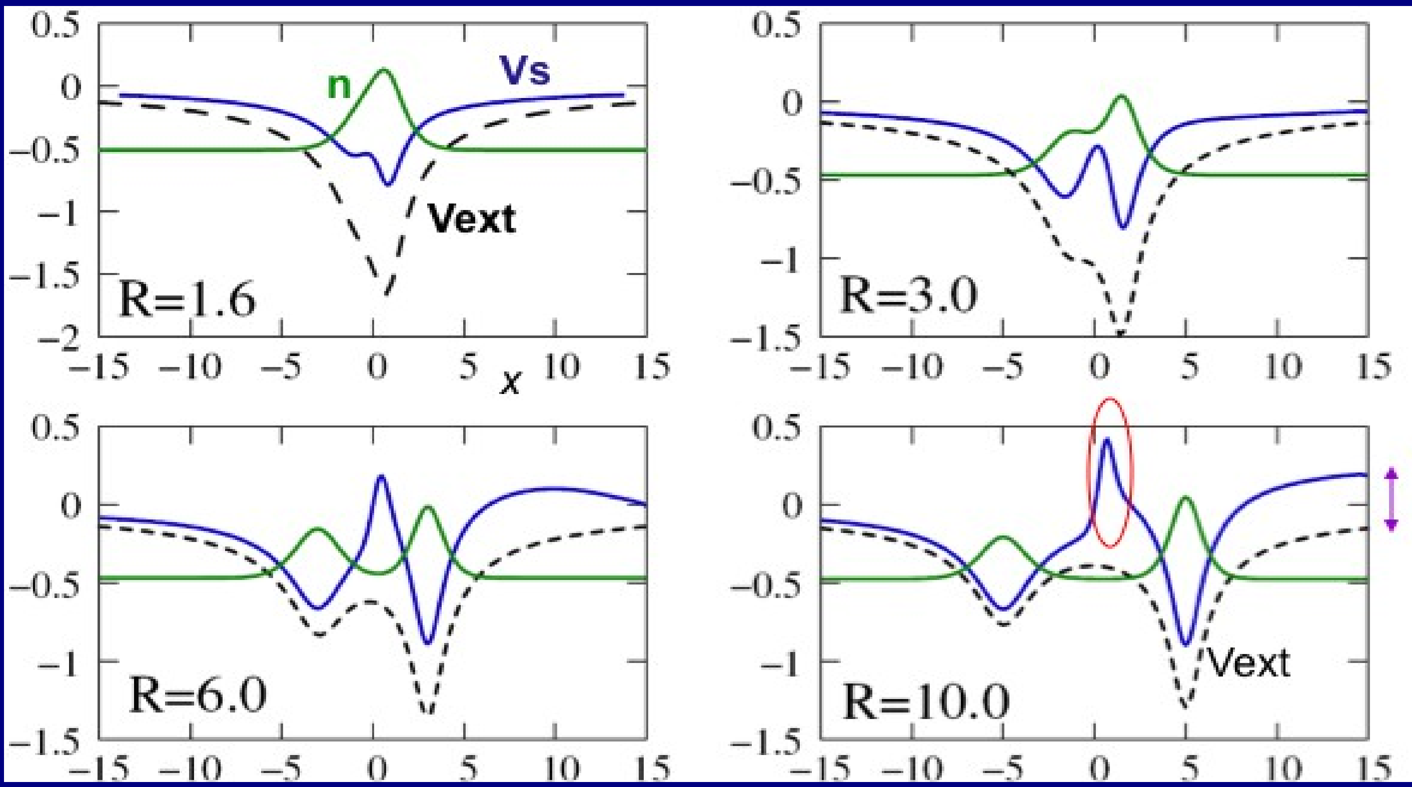
The step in KS potential

- Step aligns the atomic HOMOs
- Kohn-Sham system builds a ”wall“ to mimick the repulsion due to interaction and prevent tunneling

Prevents dissociation to unphysical fractional charges

- Step-height = difference between highest eigenvalues of the two wells

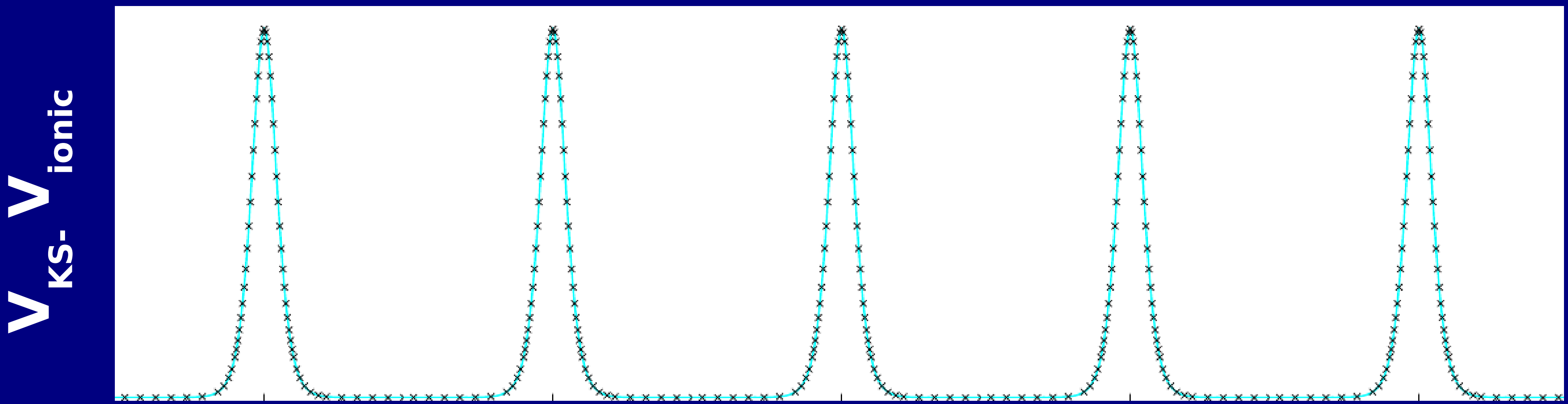


$$v_s(\mathbf{r}) = \frac{1}{2}\frac{\nabla^2\sqrt{n(\mathbf{r})}}{\sqrt{n(\mathbf{r})}} + \epsilon_1$$

“Peak” and “Step” structures

Early work of Perdew, Almbladh& von Barth, Gritsenko & Baerends
Recent work of Tempel, Martinez, Maitra, JCTC (2009) and N. Helbig, I. Tokatly, A. Rubio, JCP (2009)

H-chain Mott insulator: in DFT !!!



Clearly all local functionals and most orbital dependent functionals do not capture the step in the potential

The KS systems is metallic : fxc responsible for the gap

Open question

How to incorporate/model this effect into static and time-dependent DFT ?

(Some) Open questions

* Tunneling and/or CT processes at interfaces ???
  Open questions

* Related concepts:
    * Molecular dissociation: bumps in Vxc
    * Electron tunneling
    * Rabi Oscillations

* Dissipation; lifetimes; de-coherence, Non adiabatic couplings

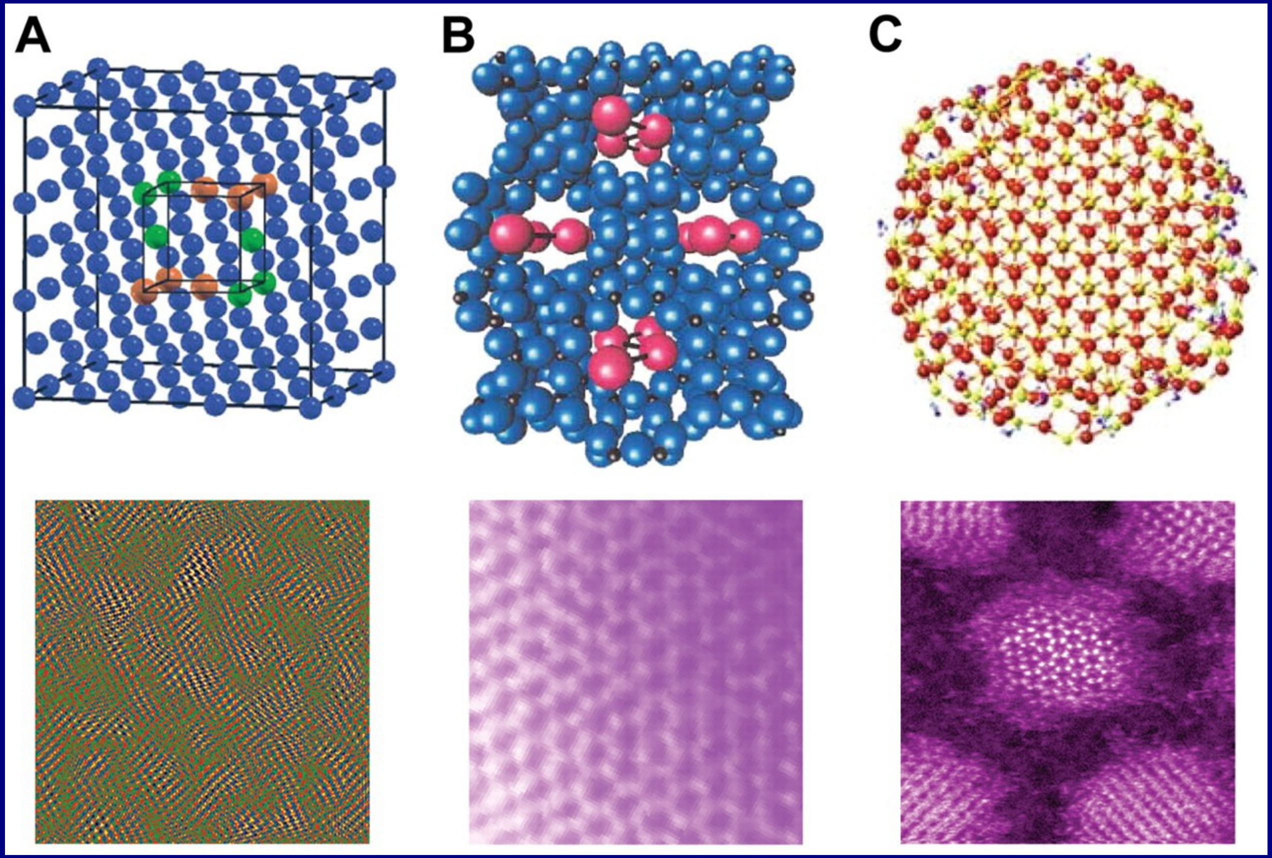
* Quantum control and open quantum systems

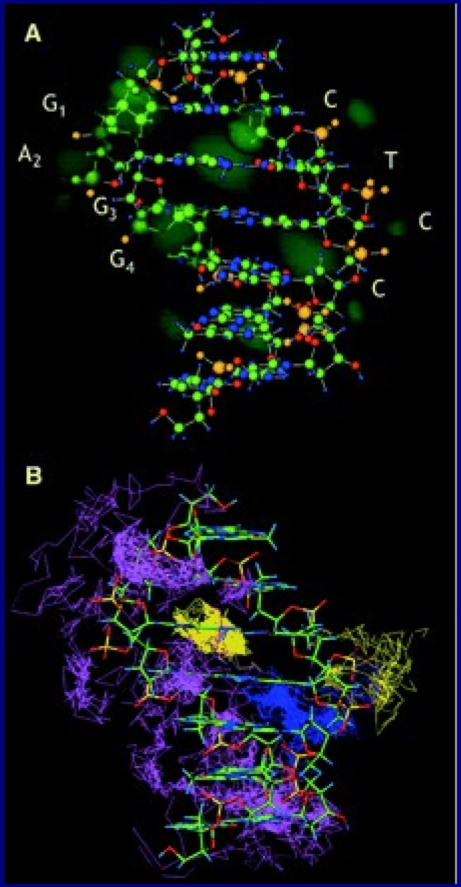
Work to be done:
"new spatial and frequency-dependent functionals"

Some active ? Fields for first principles modeling ??

The Problem with Determining Atomic Structure at the Nanoscale

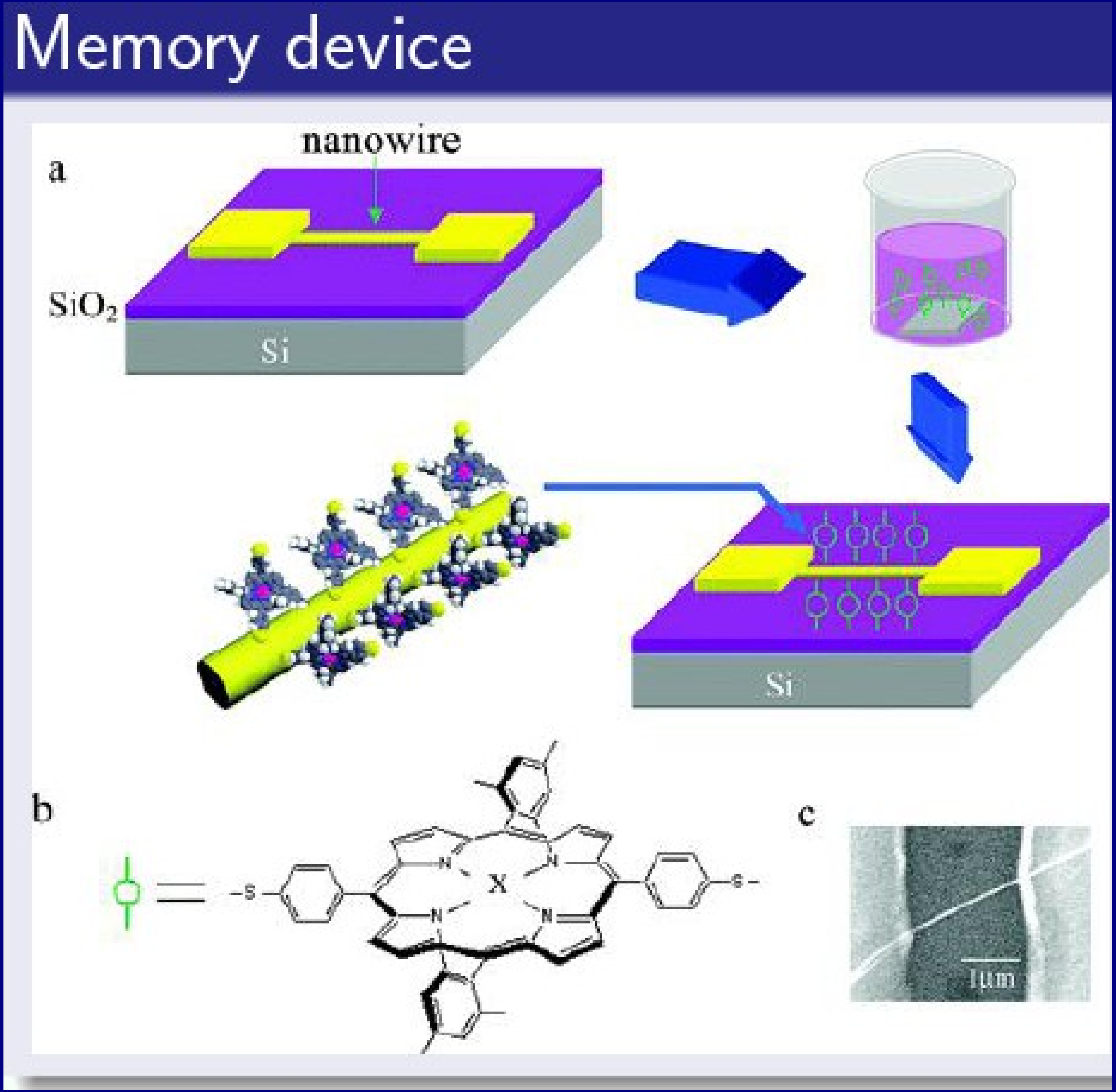
Science 27 April 2007 316: 561-565

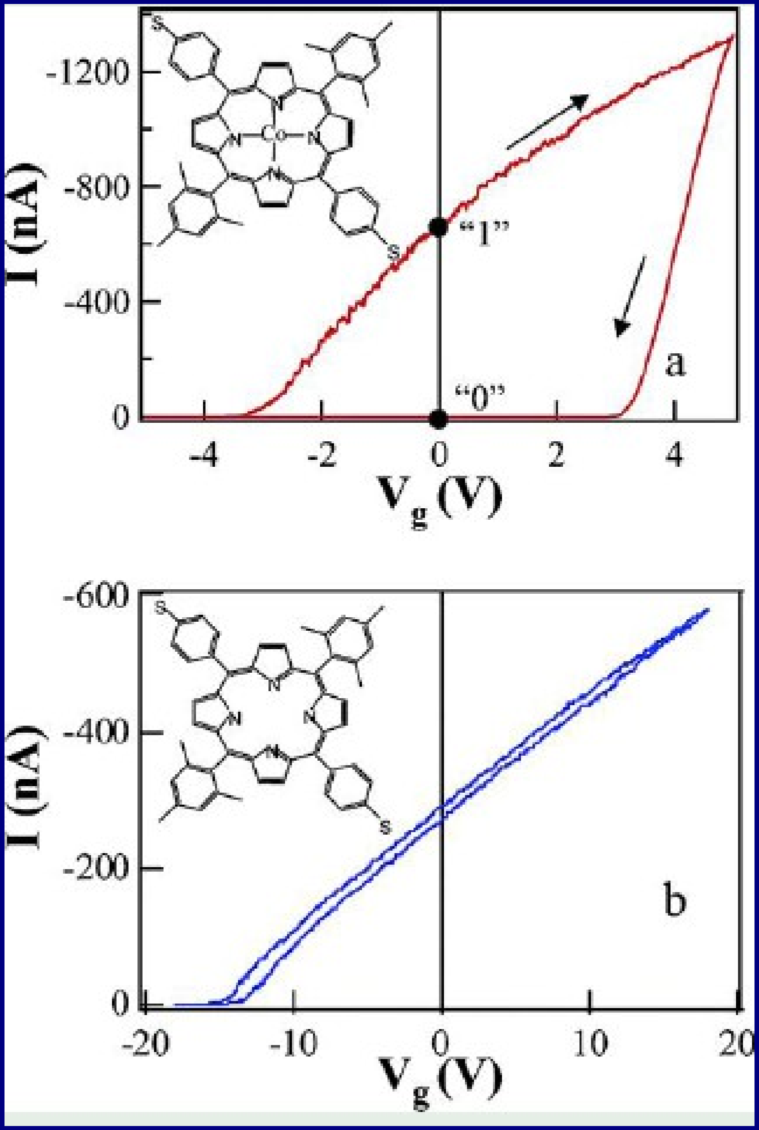




Examples of nanostructured materials. (A) Nanostructured bulk materials. (B) Intercalated mesoporous materials. (C) Discrete nanoparticles. In each case, ball-and-stick renditions of possible structures are shown on the top, and TEM images of examples are shown on the bottom.

Electron transfer processes in molecular devices



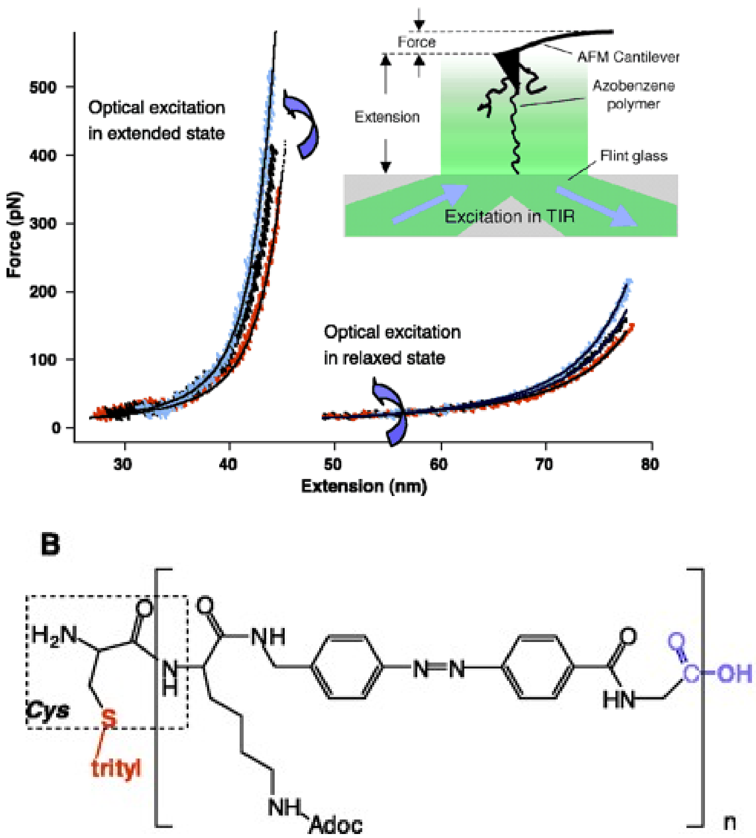


J.Phys.Chem.B 108, 9646, (2004)

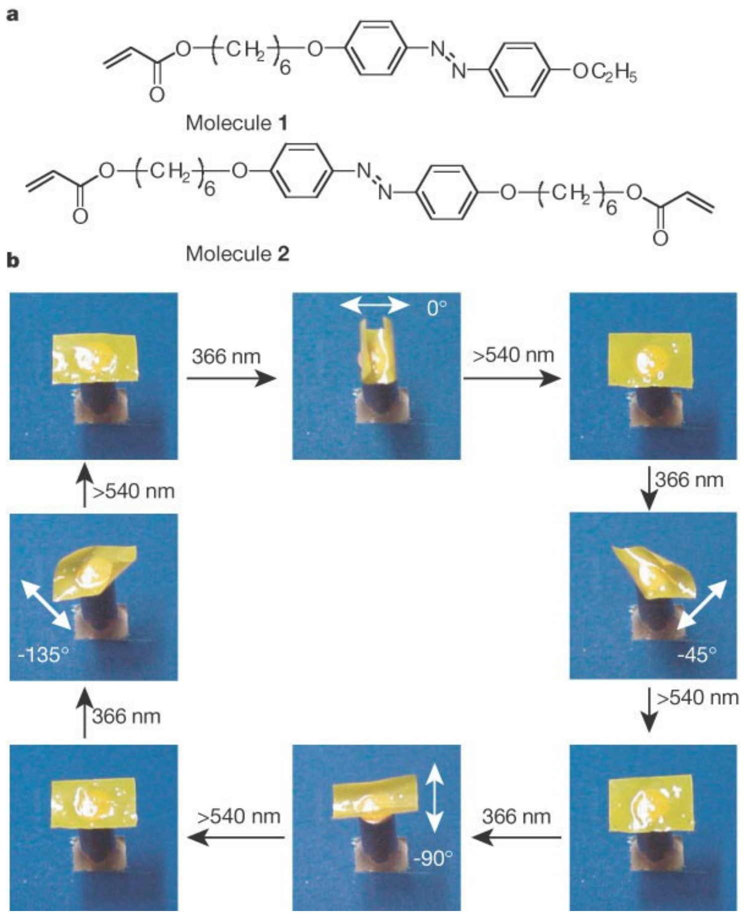
Azobenzene: spectroscopy along femtosecond laser induced photoisomerization

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)].*

Single-Molecule Optomechanical Cycle



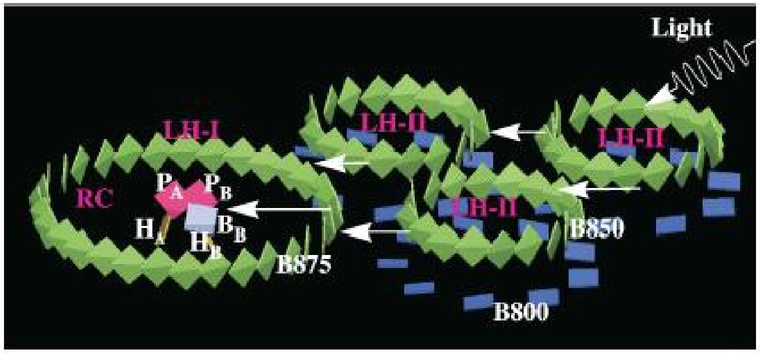
T. Hugel et al, Science, 296, 1103 (2002)

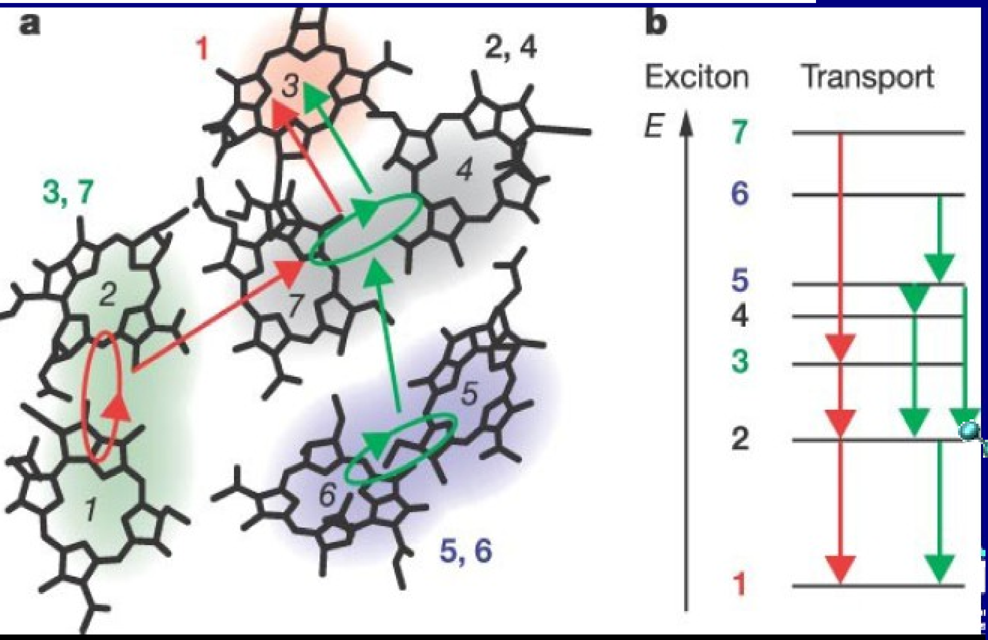


Y. Yu et al, Nature 425, 145 82003)

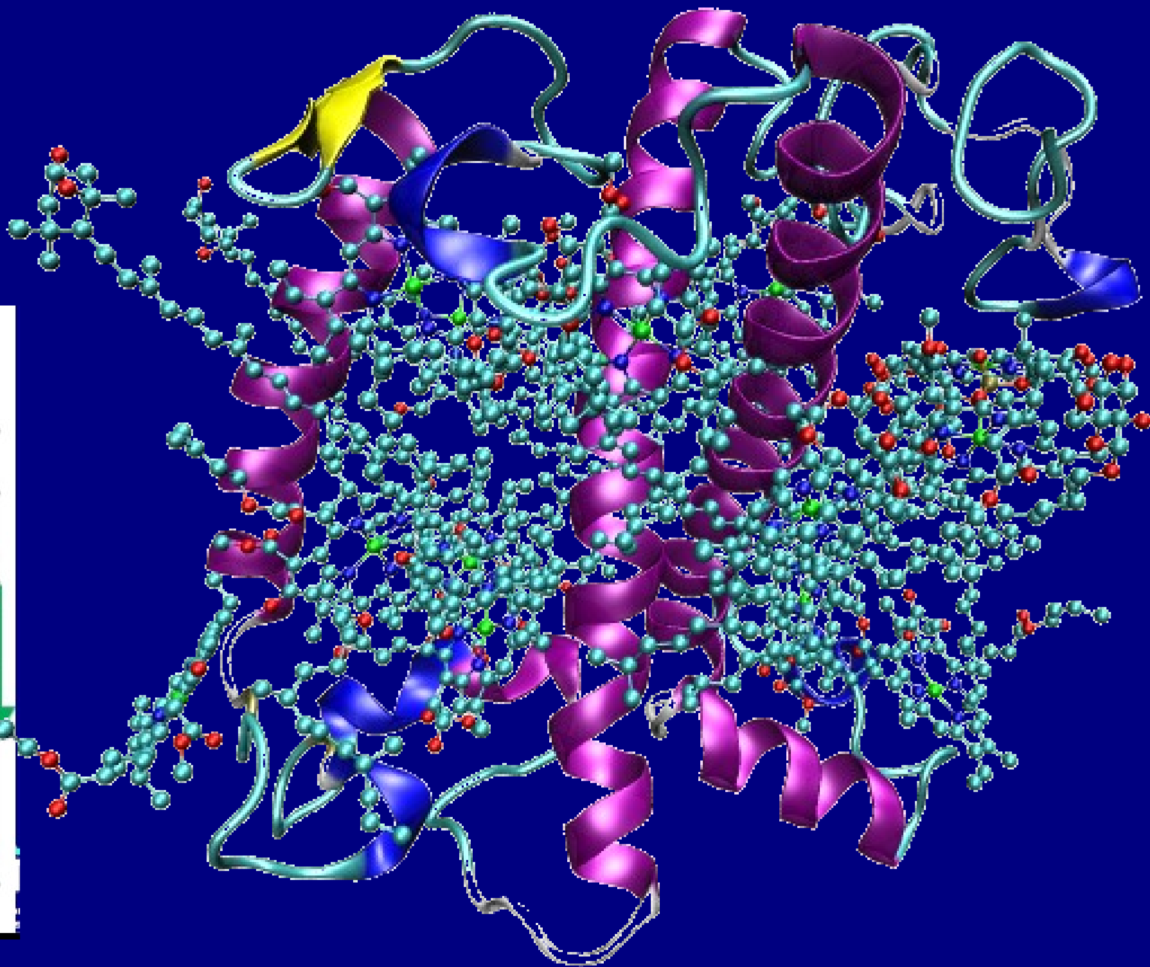
Quantum Biology: "artificial photosynthesis"

understand and controll energy transfer and the color of plants





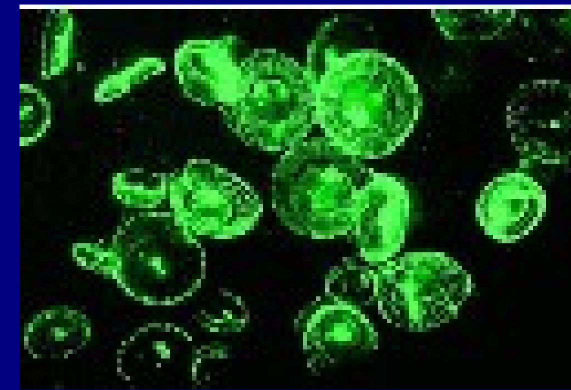
e.g. Spinach



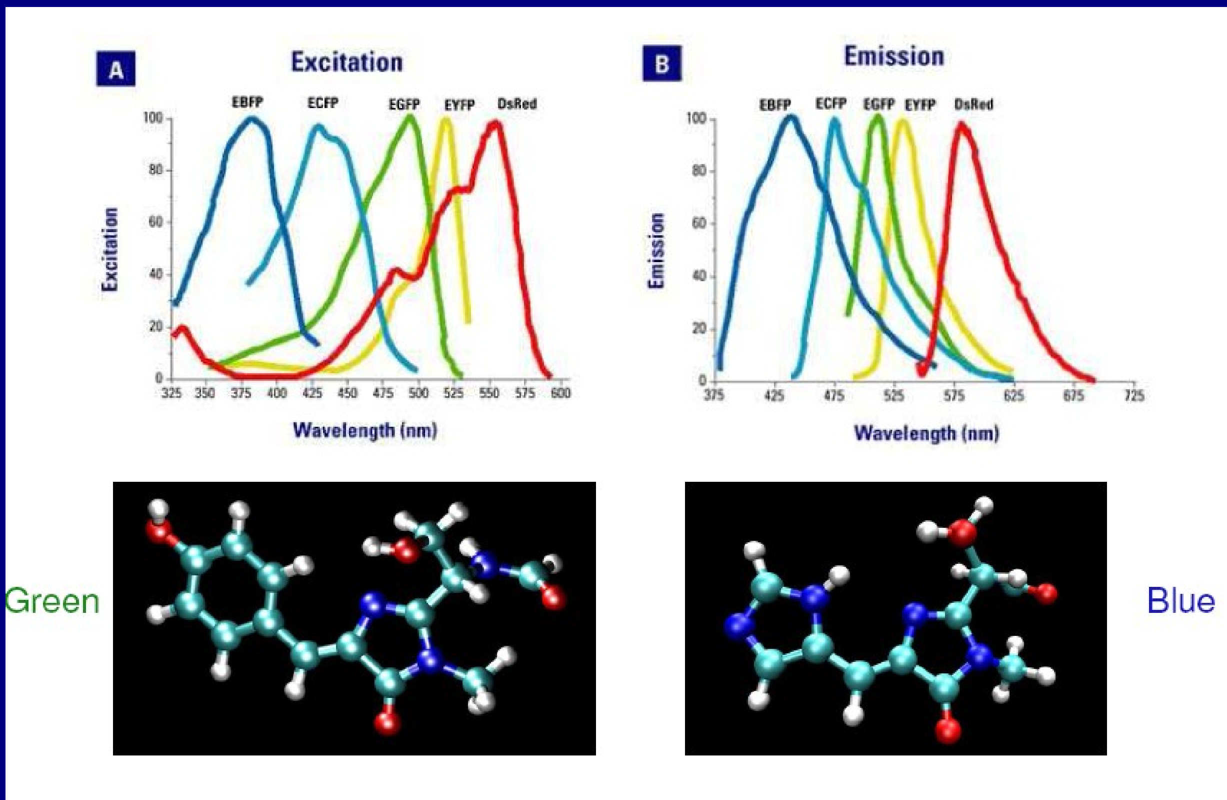
Fleming et al Nature (2005),…. (Berkeley)

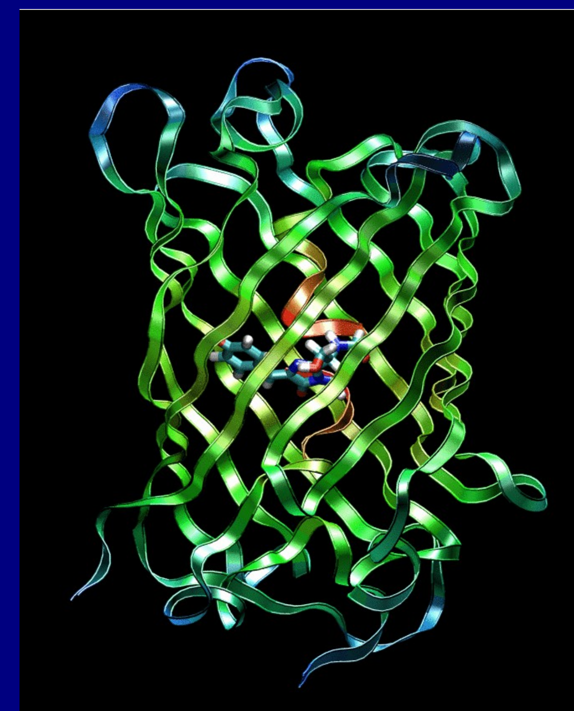
Some biophysical processes

Excitations in bio-systems: encouraging results!!
Green fluorescent protein and their mutants
(2008, Nobel prize in Chemistry)



(Aequorea victoria: jellyfish)

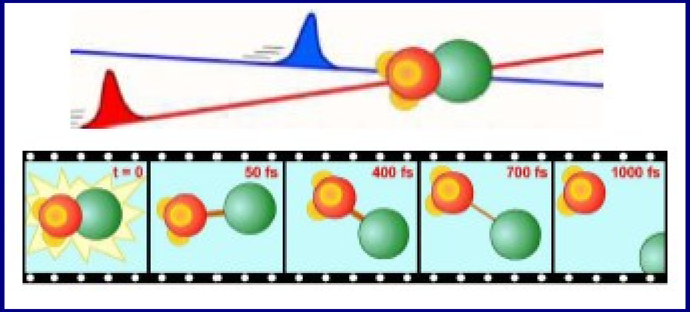


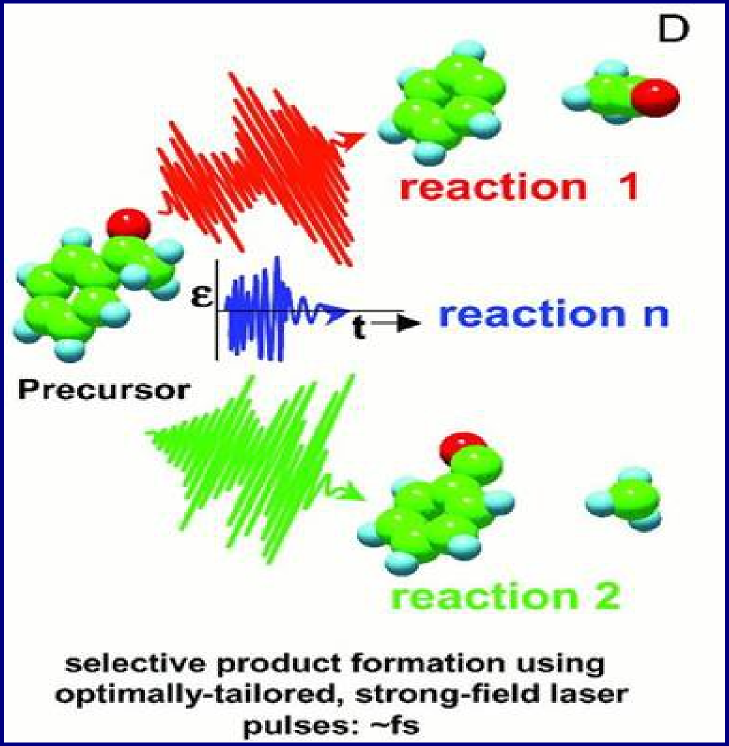


M.A.L Marques, X. Lopez, D. Varsano, A. Castro, and A. R.
Phys. Rev. Lett. ***90****, 158101 (2003)*

Quantum control

Time resolved pump-probe techniques





R. J. Levis *et al*, Science 292, 709 (2001)

Optimal control theory

Key question: What is the laser pulse that drives the system into a predefined goal?

Procedure: Define a target operator $\hat{O}$ and at the end of the laser interaction (t = T) maximize the functional

$$J_1[\Psi] = \langle \Psi(T) | \hat{O} | \Psi(T) \rangle = | \langle \Psi(T) | \Phi_\mathrm{F} \rangle |^2$$

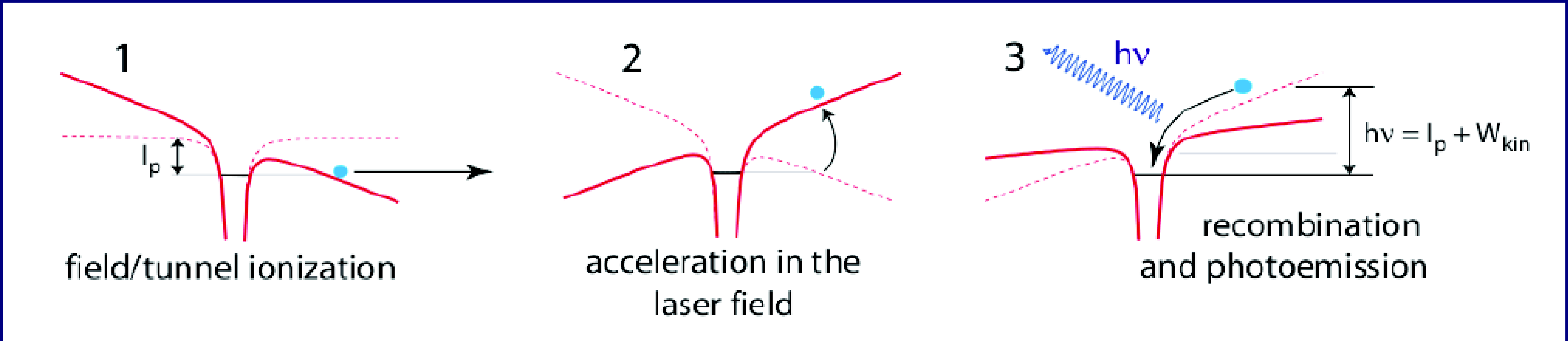
$\hat{O} = |\Phi_F\rangle\langle\Phi_F|$ target state

W. Zhu, J. Botina, H. Rabitz, JCP 108, 1953 (1998)

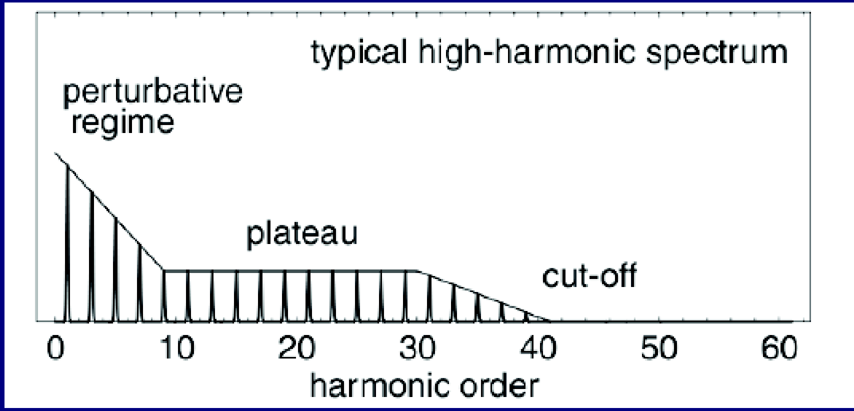
Example: High harmonic generation and selective bond-breaking

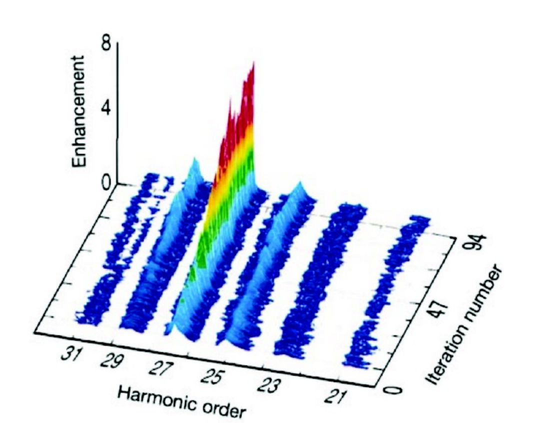
Tailoring HHG

HHG consists of the emission of integer multiples of the carrier frequency of a driving laser, due to its highly non-linear interaction with matter. It can be explained with the so-called 3-steps model:



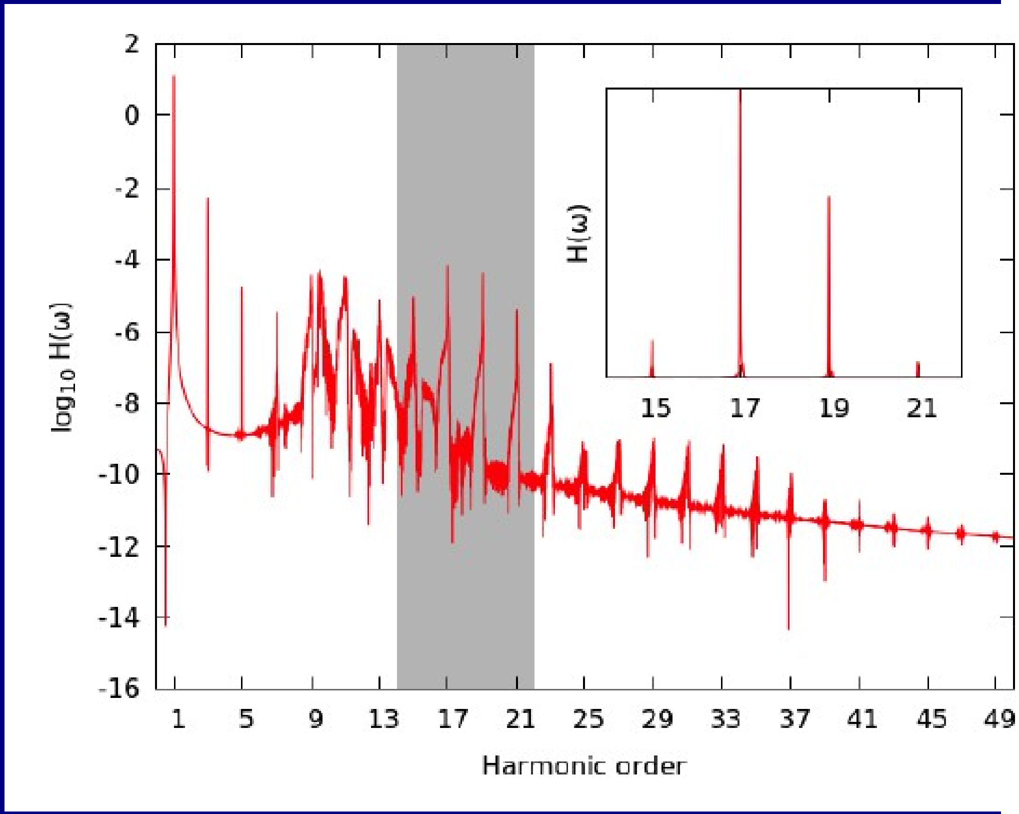
Typically, the HH spectrum (emission intensity vs. photon frequency) consists of a rapid intensity decrease, a plateau, and a cut-off.

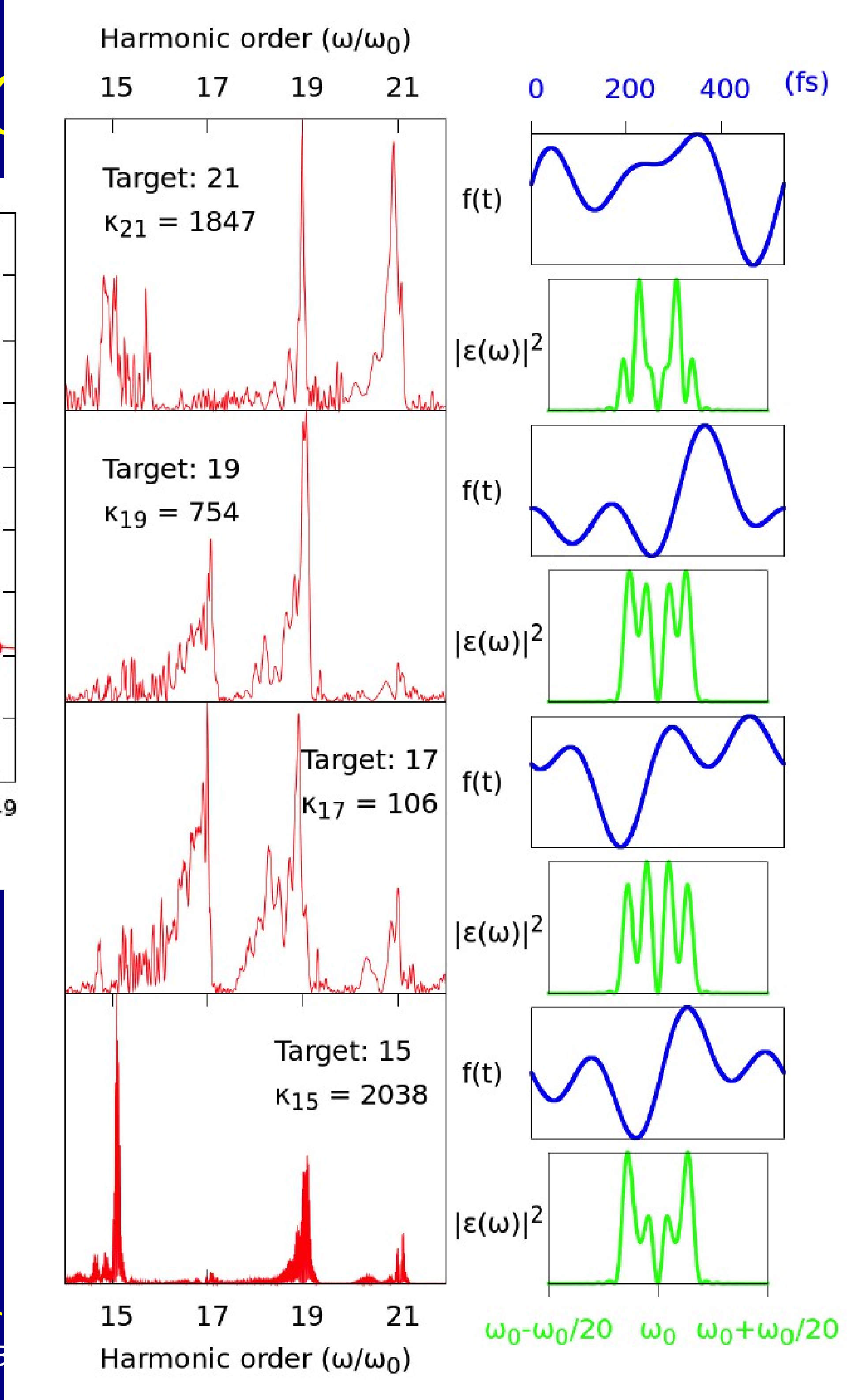




[R. Bartels *et al*, Nature **406**, 164 (2000)]

Tailoring HH





"enhancement factor"

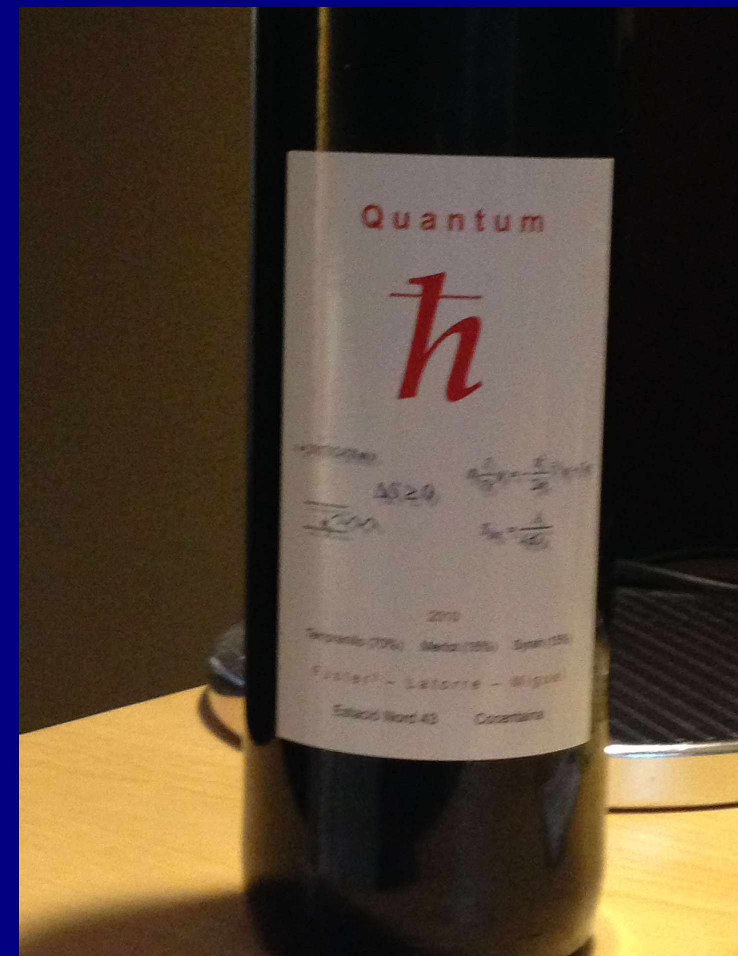
$$\kappa_j = \frac{\max_{\omega\in[k\omega_0-\beta,k\omega_0+\beta]}\{H[\varphi](\omega)\}}{H_{\rm ref}(j\omega_0)}$$

It is one of the first duties of a professor, for example, in any subject, to exaggerate a little both the importance of his subject and his own importance in it

G. H. Hardy (1940). A Mathematician's Apology.

CENTRO DE CIENCIAS DE BENASQUE PEDRO PASCUAL

See you in 2016



Open session about challenges and standing problems

TDDFT school, Benasque 4-17th January 2014

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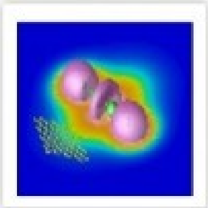

4th PEDRO PASCUAL POSTER PRIZE

Guillermo Albareda “Non Adiabatic dynamics..”

Tuomas Rossi “Quantum nanoplasmonics”

Johannes Flick “Real-time dynamics QED”

Yasumitsu Suzuki “Exact electron and nuclear TD-PES...”

HAS BEEN AWARDED THE PRIZE IN THE FOURTH PEDRO PASCUAL CONTEST FOR THE BEST POSTER PRESENTED DURING THE FOURTH SUMMER SCHOOL “6th TIME-DEPENDENT DENSITY-FUNCTIONAL THEORY: PROSPECTS AND APPLICATIONS” HELD IN BENASQUE FROM THE 2ND TO THE 15TH OF JANUARY 2014.

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