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ICTP 40th Anniversary

SMR 1564 - 3

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

TDDFT THEORY:

APPLICATIONS TO NANO AND BIO-STRUCTURES

Optical Properties of Nanostructures: Motivation. Basic Concepts. Foundations TDDFT

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Optical properties of nanostrutures

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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

I. Motivation. Basic concepts. Foundations TDDFT.

Introduction: experimental motivation
quasiparticle concept
quantum control of states: Quantum information
non linear response and time resolved properties
Techniques: Hartree-Fock, CI, DFT........ TDDFT
octopus project

TDDFT foundations:
basic theorems, excitation energies, nuclear motion,
excited state electron-ion dynamics

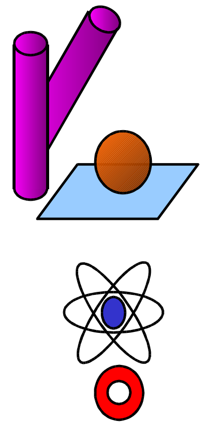
Nanoscience: different scales need to be bridged
(multicompnent simulations)

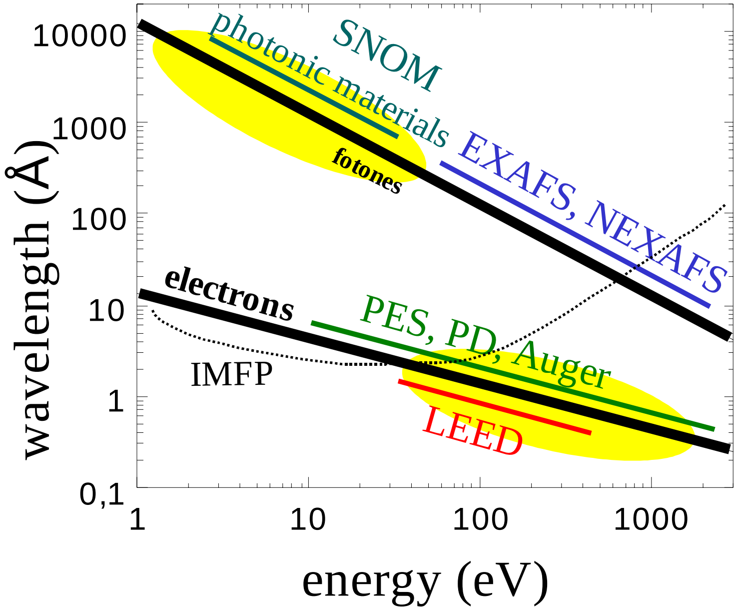
- spatial scale: 0D - 1D - 2D
  from molecule-nano-bio-meso-wires-leads

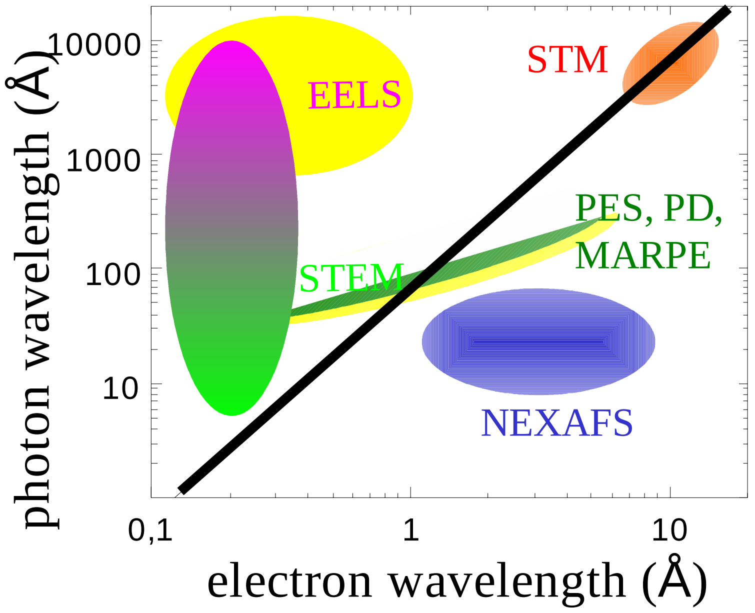
- time scale: femtosecond (electron excitations)
  picoseconds (fonon)
  nanosecond (charge-transfer)
  milisecond >>> bio-structural organisation
  growth; self assembly

FIRST PRINCIPLES TOOLS: SPECTROSCOPIES

Characterisation tools of the “nanoworld“
Need of the knowledge of response functions!!!!!







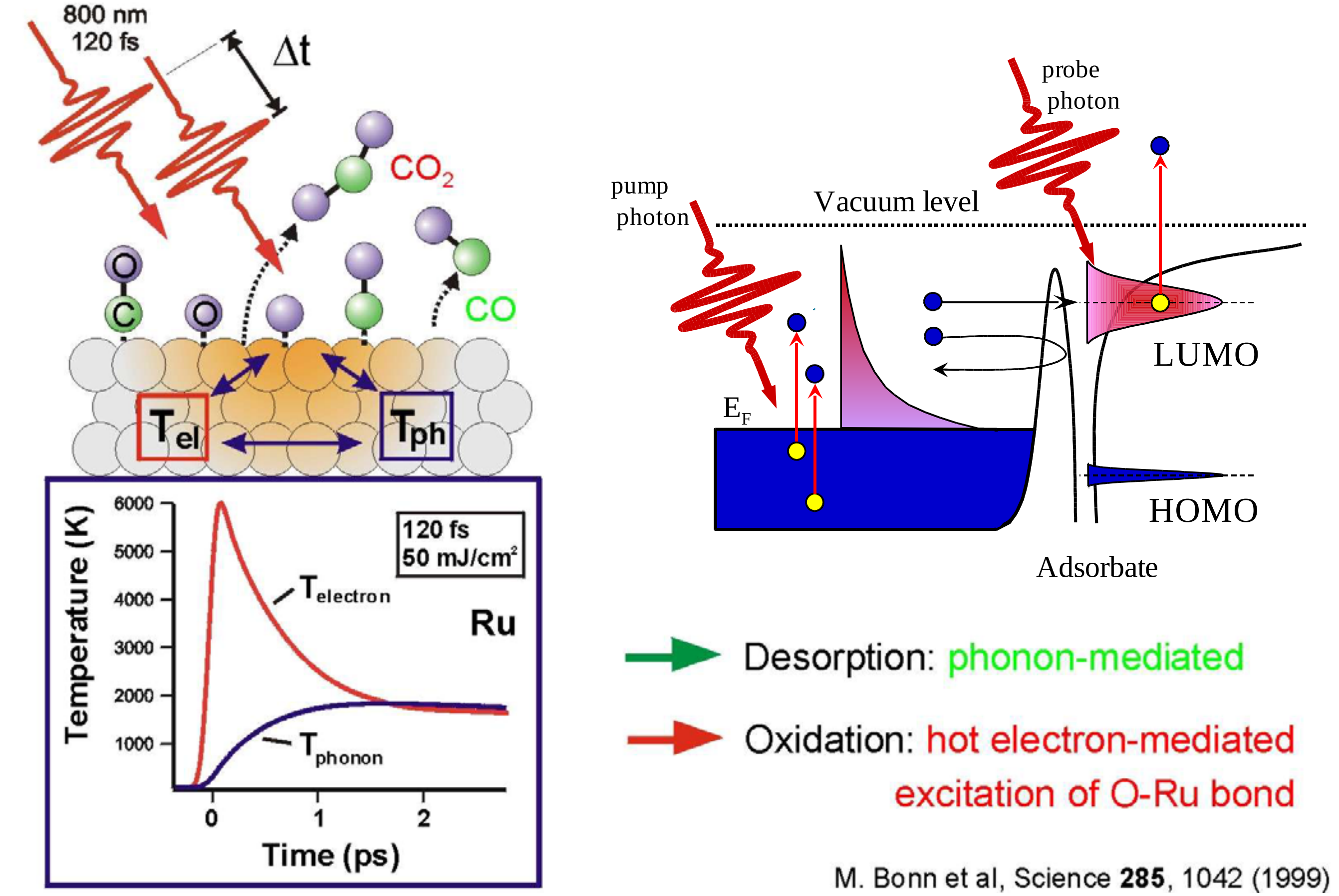
The spatial resolution depends on

- the wavelength,
- the spatial localization (STM, SNOM),
- the inelastic attenuation (PES, PD),
- the range of the interaction (EELS, MARPE)

Photochemistry:

Phonon- versus electron- mediated surface reactions:

Femtosecond photooxidation of CO on Ru(001)



Desorption: phonon-mediated

Oxidation: hot electron-mediated excitation of O-Ru bond

M. Bonn et al, Science **285**, 1042 (1999)

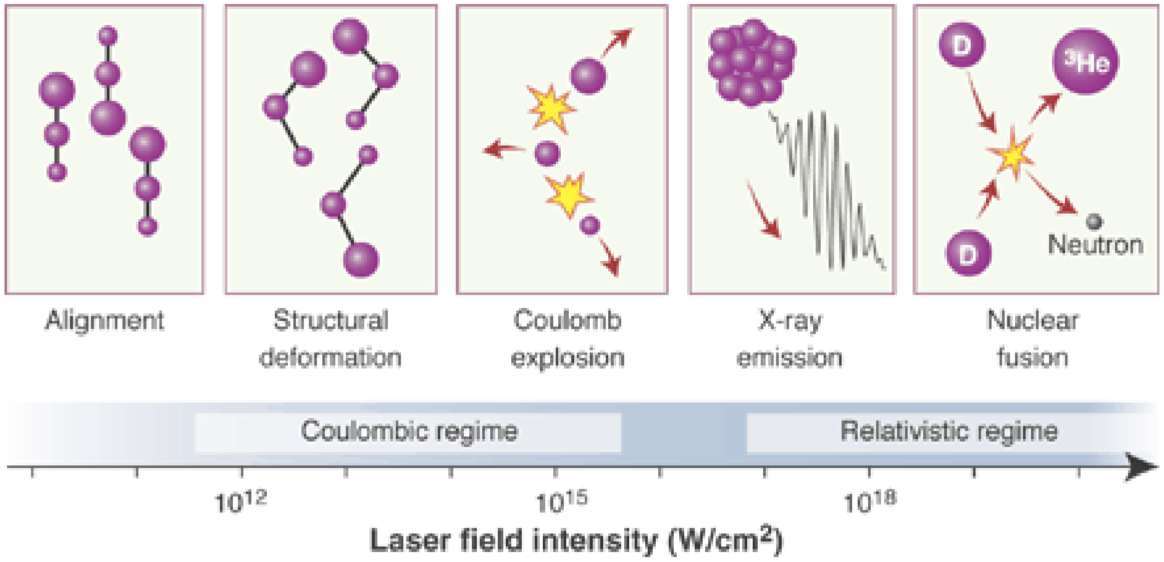
Electronic coupling between a solid and an adsorbate governs chemical dynamics at surfaces

The dynamics of electronic excitations play an important role in molecule-surface interactions and reactivity, as in laser-driven surface reactions, and are also critical to technological applications of electronic materials

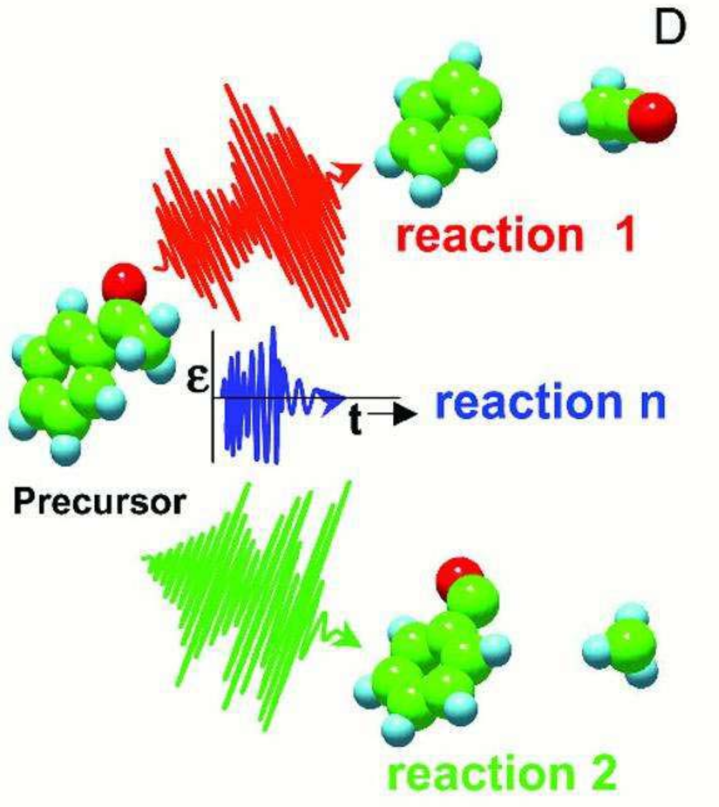
Motivation: non-linear phenomena and chemical reactivity

Quantum optimally controlled landscapes: time resolved dynamics

High-intense short-laser (fs) pulses

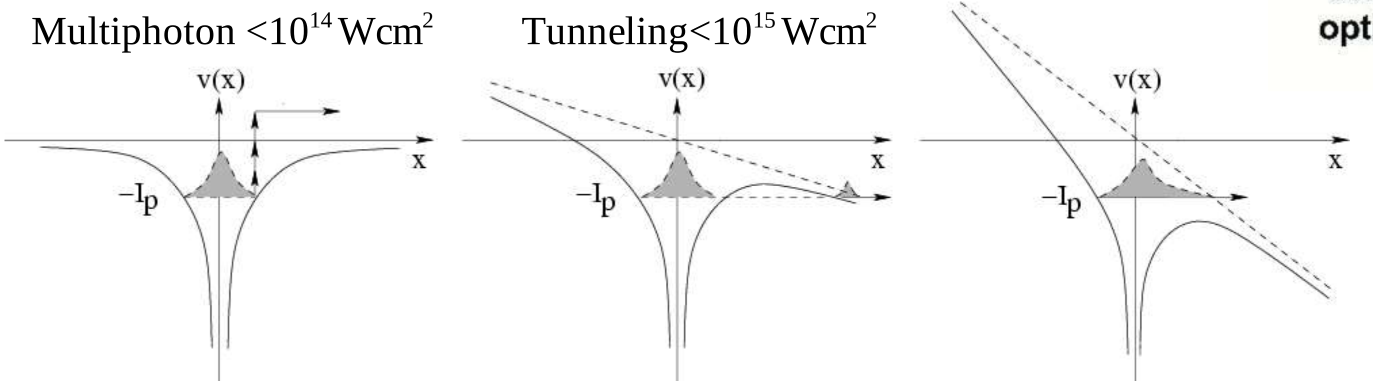


K. Yamanouchi, Science 295, 1659 (2002)



selective product formation using optimally-tailored, strong-field laser pulses: ~fs

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

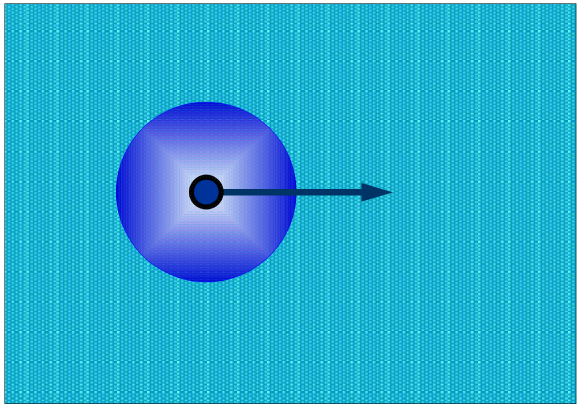

Multiphoton <10^{14} Wcm^2

Tunneling<10^{15} Wcm^2

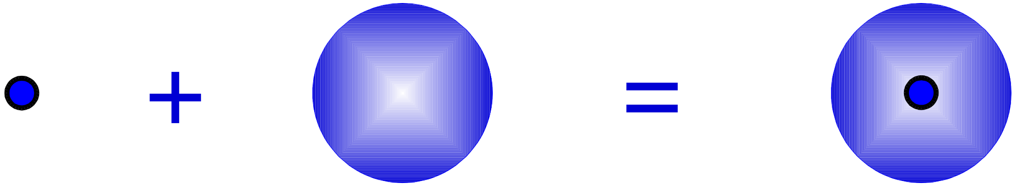
$$E = \frac{1}{4\pi\epsilon_0}\frac{e}{a_0^2} = 5.1 \times 10^9 \mathrm{V/m}$$

QUASIPARTICLES

- a fundamental concept in condensed-matter physics -



a system composed of interacting *real* bodies acts as if it were composed of weakly interacting *fictitous* bodies **(quasiparticles)**



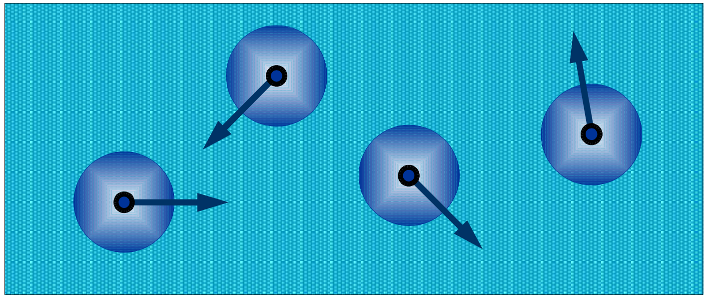
bare particle

Cloud of other particles

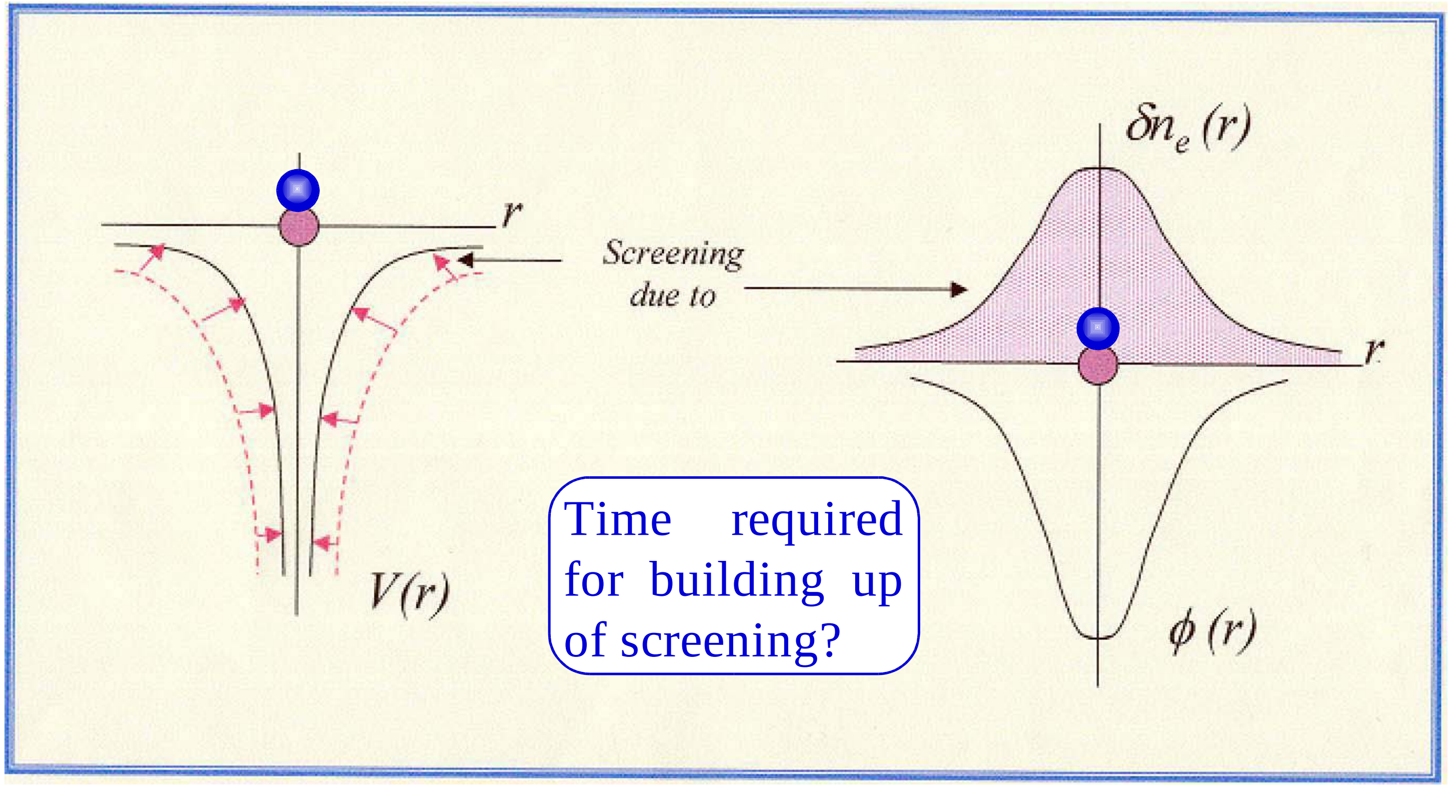
quasiparticle

one many-body problem ⇒ many one-body problems

Lifetime: relevance

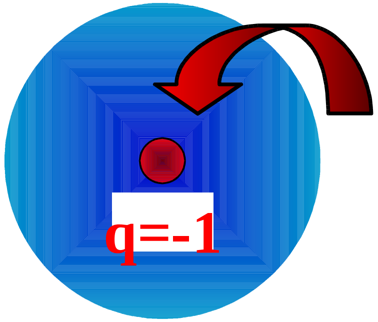


- screening and localisation
- electron-phonon coupling
- surface photochemistry
- electron transfer across interfaces
- electron dynamics and energy transfer



Time required for building up of screening?

‘Bare particles get dressed’
Huber *et al.*,
Nature **414**, 286 (2001)



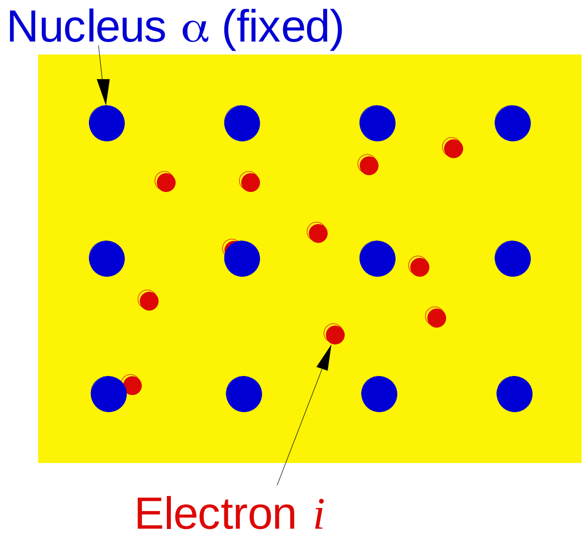
Introduding a negative bare charge q=-1 in a nanostructure: monitorise the time evolution of the electronic density (TDDFT calculation)

$$\delta n(\vec{r}) = \int d\vec{r}_1 \chi(\vec{r},\vec{r}_1)\delta v(\vec{r}_1)$$

where $\chi(\mathbf{r}_1,\mathbf{r}_2)$ is the *density-response function*. In general, the external perturbation can be time-dependent. Using the frequency representation, we have that

$$\delta n(\vec{r};\omega) = \int d\vec{r}_1 \chi(\vec{r},\vec{r}_1;\omega)\delta v(\vec{r}_1;\omega)$$

The Basic Problem and Formalism:



Hamiltonian of the coupled electron-ion system:

N ions, coordinates $\vec{R}_1,\ldots,\vec{R}_N \equiv \vec{R}$, momenta $\vec{P}_1,\ldots,\vec{P}_N \equiv \vec{P}$, charges $Z_1,\ldots,Z_N$, masses $M_I,\ldots,M_n$

N_e electrons, coordinates $\vec{r}_1,\ldots,\vec{r}_N \equiv \vec{r}$, momenta $\vec{p}_1,\ldots,\vec{p}_N \equiv \vec{p}$, mass m

$$\begin{aligned} H &= \sum_{I=1}^{N} \frac{\vec{P}_I^2}{2M_I} + \sum_{i=1}^{N_e} \frac{\vec{p}_i^2}{2m} + \sum_{i>j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \sum_{I>J} \frac{Z_I Z_J e^2}{|\vec{R}_i - \vec{R}_J|} - \sum_{i,I} \frac{Z_I e^2}{|\vec{R}_I - \vec{r}_i|} \\ &= T_N + T_e + V_{ee}(\vec{r}) + V_{NN}(\vec{R}) + V_{Ne}(\vec{r},\vec{R}) \end{aligned}$$

Schrödinger equation

$$[T_N + T_e + V_{ee}(\vec{r}) + V_{NN}(\vec{R}) + V_{Ne}(\vec{r},\vec{R})]\Phi(x,\vec{R}) = E\Phi(x,\vec{R})$$

$x \equiv (\vec{r},s)$ full set of electronic positions and spin variables

Quantum chemistry: Hartree, Hartree-Fock and post HF techniques

Hartree approximation $\Phi(\vec{x}_1,\vec{x}_2,\dots,\vec{x}_N)=\phi_1(\vec{x}_1)\phi_2(\vec{x}_2)\dots\phi_N(\vec{x}_N)$

- Pauli's exclusion principle is taken into account.

Does it really make sense to work with the many-body wavefunction????

come from the presence of an interaction. It is a pure quantum property, called *exchange*.

The *density matrix*: $\gamma(\vec{x}_1,\vec{x}_2)=\sum_{n=1}^{N}\phi_n^*(\vec{x}_1)\phi_n(\vec{x}_2)$ (note that $n(\vec{x})=\gamma(\vec{x},\vec{x})$)

$$\Sigma_X(\vec{x}_1,\vec{x}_2)=-\frac{\gamma(\vec{x}_1,\vec{x}_2)}{|\vec{r}_1-\vec{r}_2|}$$

exchange or Fock operator:

The total energy for the Slater derminant is

$$E(\Phi)=\sum_{n=1}^{N}\int d\vec{x}\phi_n^*(\vec{x})\left[-\frac{1}{2}\vec{\nabla}^2+v_{\text{ext}}(\vec{r})\right]\phi_n(\vec{x})+\frac{1}{2}\int d\vec{x}_1 d\vec{x}_2\left(\frac{n(\vec{x}_1)n(\vec{x}_2)}{|\vec{r}_2-\vec{r}_1|}+\Sigma_X(\vec{x}_1,\vec{x}_2)\gamma(\vec{x}_2,\vec{x}_1)\right)$$

The essence of DFT:

Hohenberg-Kohn (1964)

$$E[R_{ions}]=\min_{\Psi}\langle\Psi|H_e|\Psi\rangle$$

- The ground state energy of a many body system is a unique functional of the density i.e,

$$n(r)=n[\Psi]=\left\langle\sum_i \delta(r-r_i)\right\rangle$$

can be inverted

$$\Psi(r_{1,}r_{2,.}\ldots,r_N)=\Psi[n(r)]\rightarrow E[R_{ions}]=\min_n\langle\Psi H_e\Psi\rangle\equiv\min_n E[n]$$

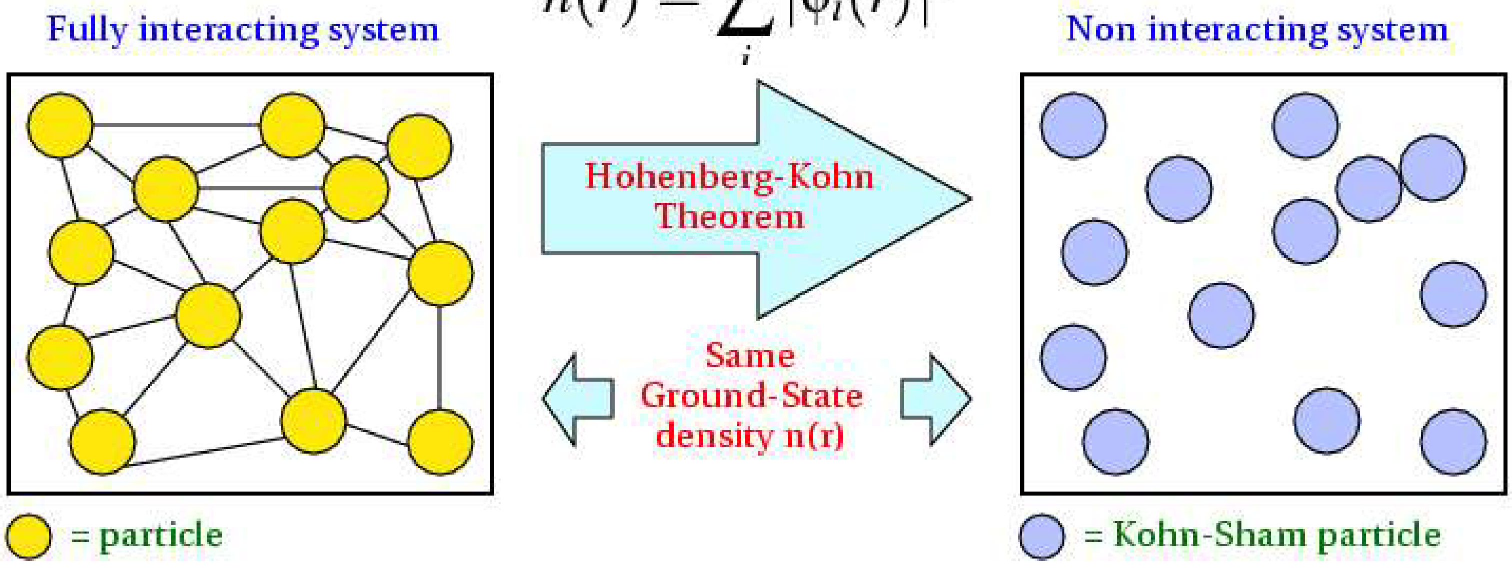
- The functional has a minimum at the 'equilibrium' density

Total-energy functional

$$E[n]=T[n]+E^H[n]+E^{xc}[n]+\int V(\vec{r})n(\vec{r})d^3r$$

Kohn-Sham approach (1965):

$$n(\vec{r}) = \sum_i |\phi_i(\vec{r})|^2$$



Fully interacting system

Hohenberg-Kohn Theorem

Non interacting system

Same Ground-State density n(r)

● = particle

● = Kohn-Sham particle

$$T_0[n] = \sum_i \int \phi_i^*(\vec{r}) \left(-\frac{\hbar^2}{2m}\nabla^2 \right) \phi_i(\vec{r}) d^3r$$

$T[n]$ ------- $T_0[n]$

Exc includes now the correlation contribution to T

$$\left\{ -\frac{\hbar^2}{2m}\nabla^2 + \underbrace{V(\vec{r}) + e^2 \int \frac{n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} d^3r + \mu_{xc}[n(\vec{r})]}_{V_{eff}(\vec{r})} \right\} \phi_i(\vec{r}) = \varepsilon_i \phi_i(\vec{r})$$

with the exchange-correlation potential

$$\mu_{xc}[n(\vec{r})] = \frac{\delta E_{xc}[n(\vec{r})]}{\delta n(\vec{r})} = \frac{\delta\{n(\vec{r})\varepsilon_{xc}[n(\vec{r})]\}}{\delta n(\vec{r})}$$

KS-equations

Some summary of DFT results for finite and extended systems

Property	LSDA	GGA
Exchange Energy	5% (not negative enough)	0.5%
Correlation Energy	100% (too negative)	5%
bond length	1% (short)	1% (long)
structure	favours close packing	improves
energy barrier	100% (too low)	30% (low)

Approx	Mean absolute error in the atomisation energy for 20 molecules
Unrestricted HF	3.1 eV (underbinding)
LSDA	1.3 eV (overbinding)
GGA	0.3 eV (mostly overbinding)
Chemical accuray	*0.05 eV*

J.P. Perdew and S. Kurth in A chemist's guide to density functional theory, W. Koch and M.C. Holthausen, (Wiley-VCH,, 2000)

Some Pathologies of the KS-DFT functional

Ban-gap problem
is discontinuous by a constant when an electron is added to the system
(Sham, Schlüter and Perdew, Levy (1983)

Widely separated open-shell atoms
Almbladh and von Barth 1985

Exchange correlation electric field in insulators

Godby and Sham 1984, Gonze, Ghosez and Godby 1995
(next Lecture for extended systems)

Time Dependent Density Functional Theory (Runge and Gross 1984)

Electron-dynamics first, then e-ion problem

HK-like theorem: v(r,t) <------> (r,t)

The time dependent density determines uniquely the time-dependent external potential and therefore all physical observables

Kohn-Sham formalism:

The time dependent density of the interacting system can be calculated as the density of an auxilary non-interacting system

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

?

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

Linear Response Theory:

$$\chi(r,r';\omega) = \lim_{\eta\to0^+}\sum_m\left(\frac{\langle 0|\hat\rho(r)|m\rangle\langle m|\hat\rho(r')|0\rangle}{\omega-(E_m-E_0)+i\eta} - \frac{\langle 0|\hat\rho(r')|m\rangle\langle m|\hat\rho(r)|0\rangle}{\omega+(E_m-E_0)+i\eta}\right)$$

The exact linear density response $(\ )\ =\ (V_{ext})(\ )$

has poles at the exact excitation energies $=E_m - E_n$

TDDFT does the job for you!!!

$(\ )\ =\ (V_{ext})(\ )$ however the KS system $(\ )\ =_0(\ )V_{eff}(\ )$

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

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

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

By virtue of time-dependent Hohenberg-Kohn theorem, ALL observables are funtionals of the TD density

some observables are easily expressed in terms of the density (no approximations involved)

e.g. TD dipole moment $d(t) = \int \rho(r, t) z d^3 r$

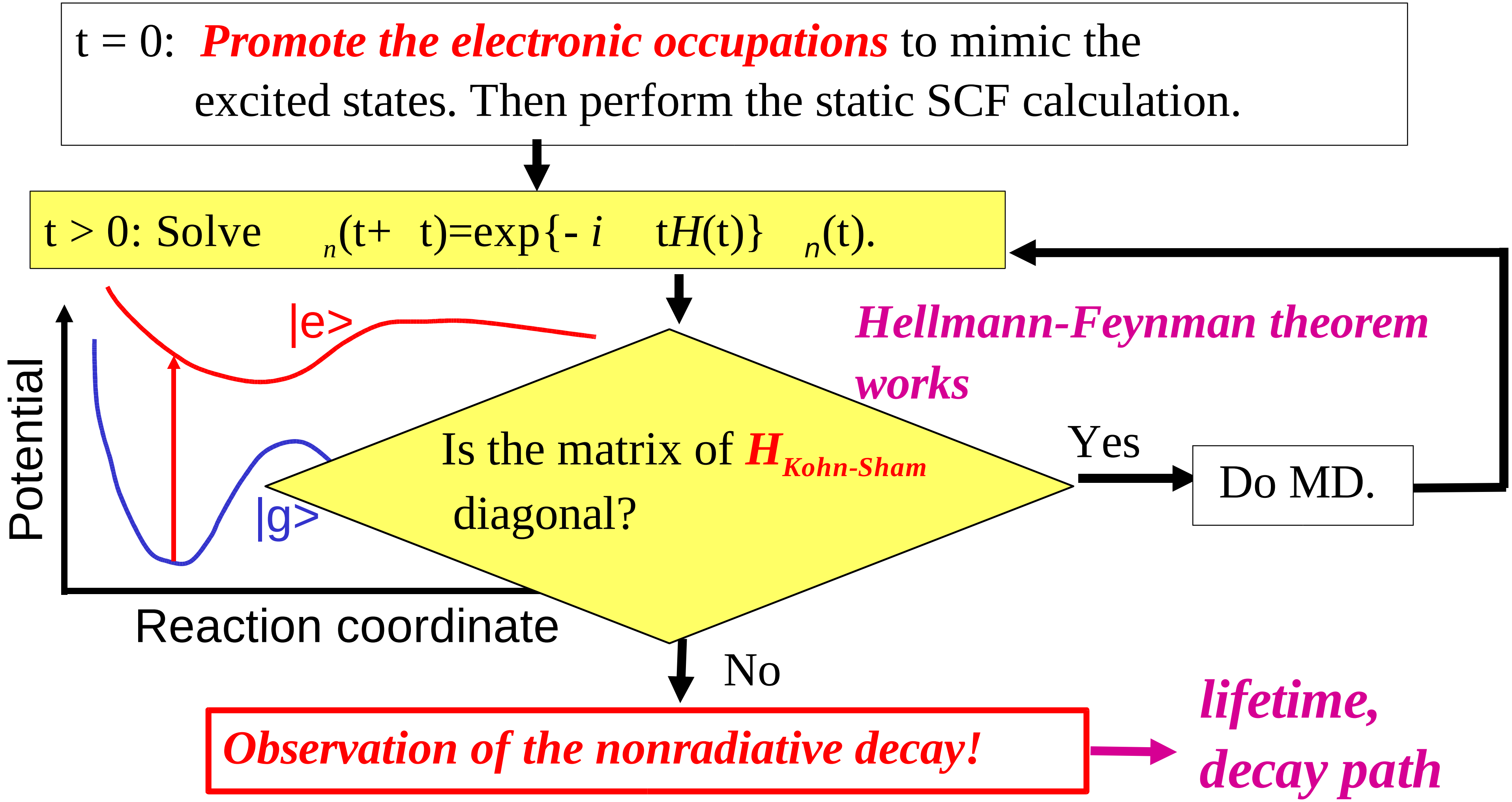
photon spectrum $\sim \left| d(\omega) \right|^2$

other observables are more difficult to express in terms of the density (involving further approximation)

e.g. ionization yields

Excited state electron-ion dynamics

Introduction: How to simulate excited state dynamics?



t = 0: ***Promote the electronic occupations*** to mimic the excited states. Then perform the static SCF calculation.

t > 0: Solve $_{n}$(t+ t)=exp{- i tH(t)} $_{n}$(t).

Is the matrix of ***$H_{Kohn\text{-}Sham}$*** diagonal?

Hellmann-Feynman theorem works

Yes

Do MD.

No

Observation of the nonradiative decay!

lifetime, decay path

1. No need of level assignment for a hole and an excited electron except at the beginning.
2. Automatic monitoring of the nonradiative decay (lifetime, decay path) without experiences.

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

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

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

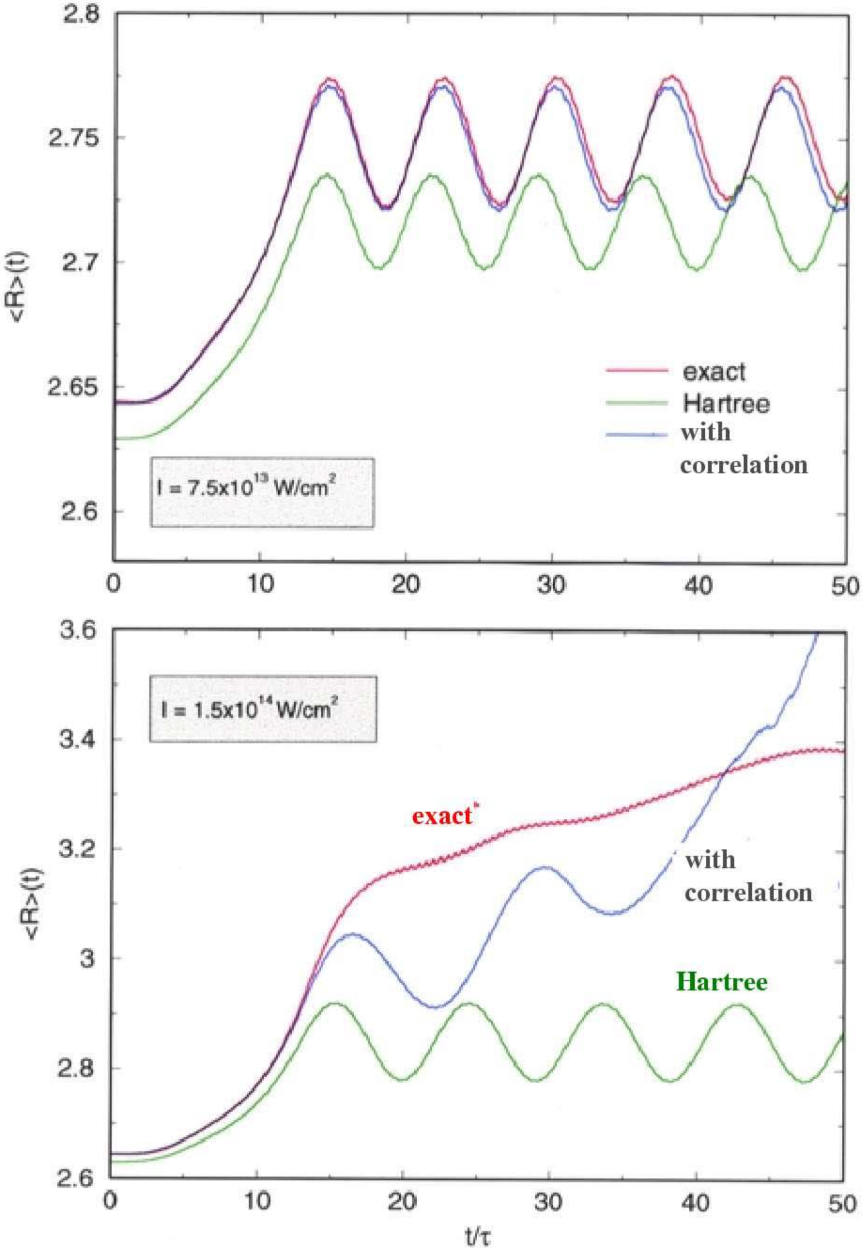
$$i\partial_t\varphi_j(r,t)=\left(\frac{\hbar^2}{2\mu_e}\nabla_r^2+v_s[\rho,N](r,t)\right)\varphi_j(r,t)$$

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

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

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

Nuclear Dynamics of H_2^+ in 1D in a 770 nm Laser pulse



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

*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).

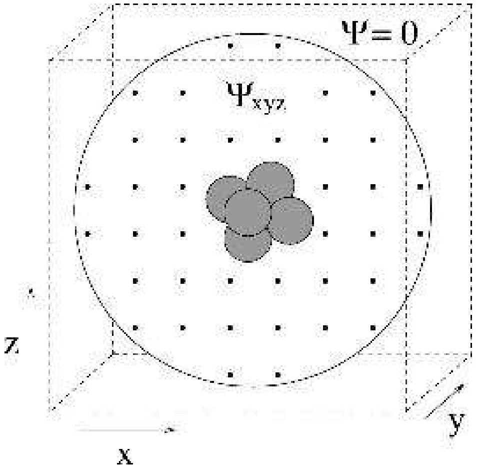
✔ Auxiliary use of LCAO/ FFTs. QM/MM for biomolecular structures

✔ 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)

Implementation

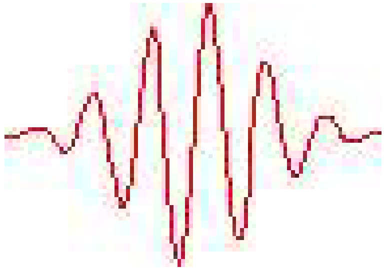


✔*High-order discretization* for the kinetic energy operator

$$\nabla^2 \Psi_i(x,y,z)=\frac{1}{h^2}\sum_{n=-N}^{n=N} C^2_{N,n}\left[\Psi_i(x+nh,y,z)+\Psi_i(x,y+nh,z)+\Psi_i(x,y,z+nh)\right]$$

✔Classical description of electromagnetic field.

$$\vec{E}(t)=\sqrt{\frac{I_0}{(8\pi)}}\, f(t)\sin(\omega t)\vec{e}\, D$$



(Absence of radiative-decay channel!)

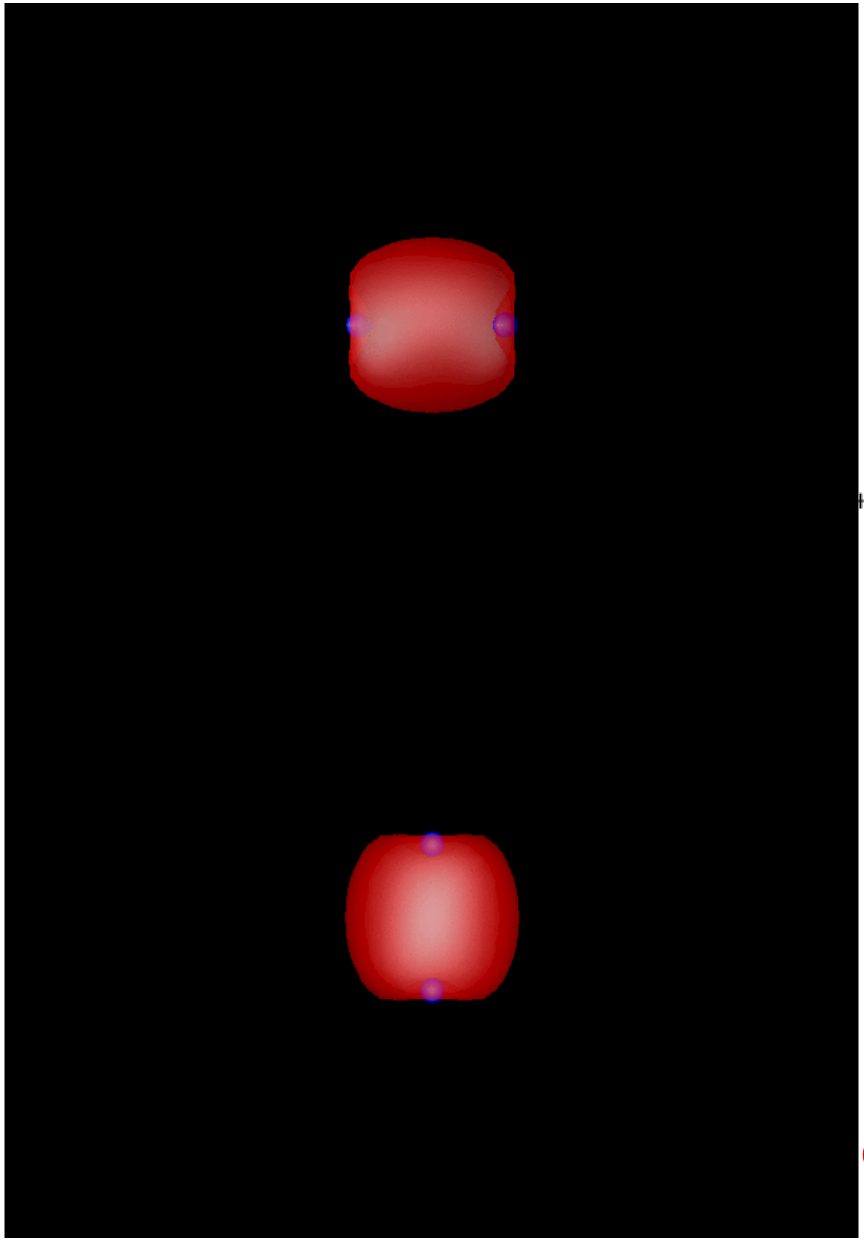
✔Classical description of nuclei (point particles): Ehrenfest path:

$$F_a(t)=-\left\langle \Phi(t)\middle|\nabla_a H\middle|\Phi(t)\right\rangle \qquad \Phi(t)=Det\{\Psi_i(t)\}$$

✔Solution of the TD-KS equations by unitary propagation schemes.

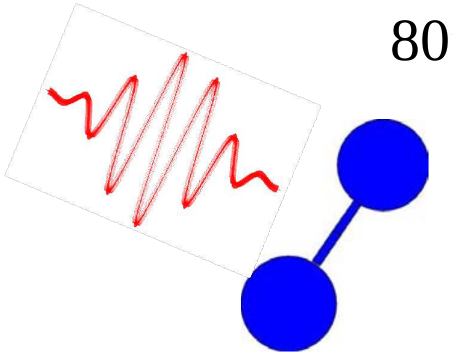
$$\Psi_i(t+\Delta t)=e^{-iH_{KS}(t+\Delta t)\,\Delta t/2}\, e^{-iH_{KS}(t)\,\Delta t/2}\,\Psi_i(t)$$

Femtosecond dynamics: *test photodissociation of a dimer (Na_2^+).*

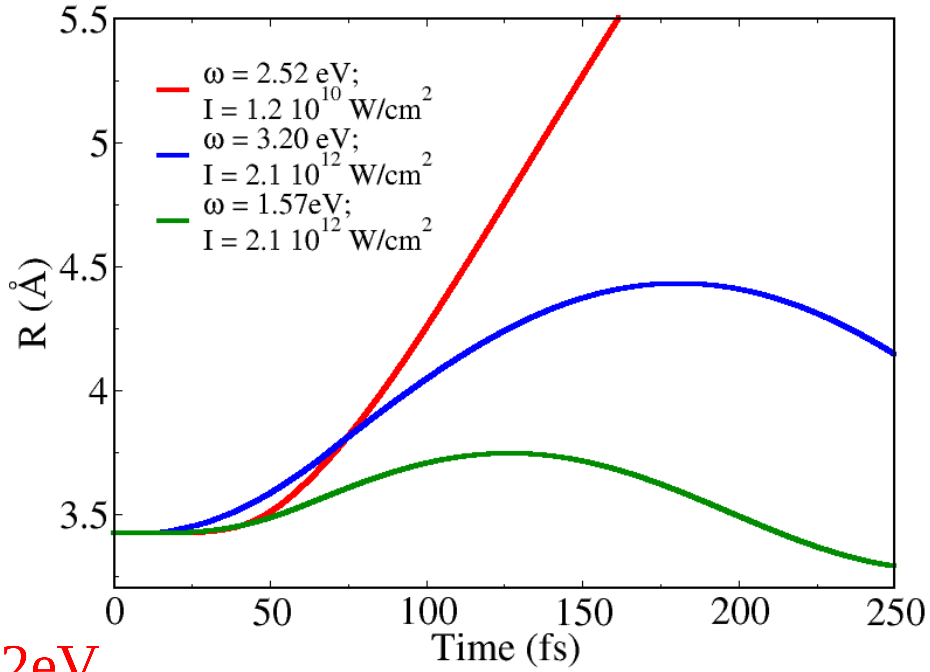


ω=2.5eV

ω=3.2eV



80fs



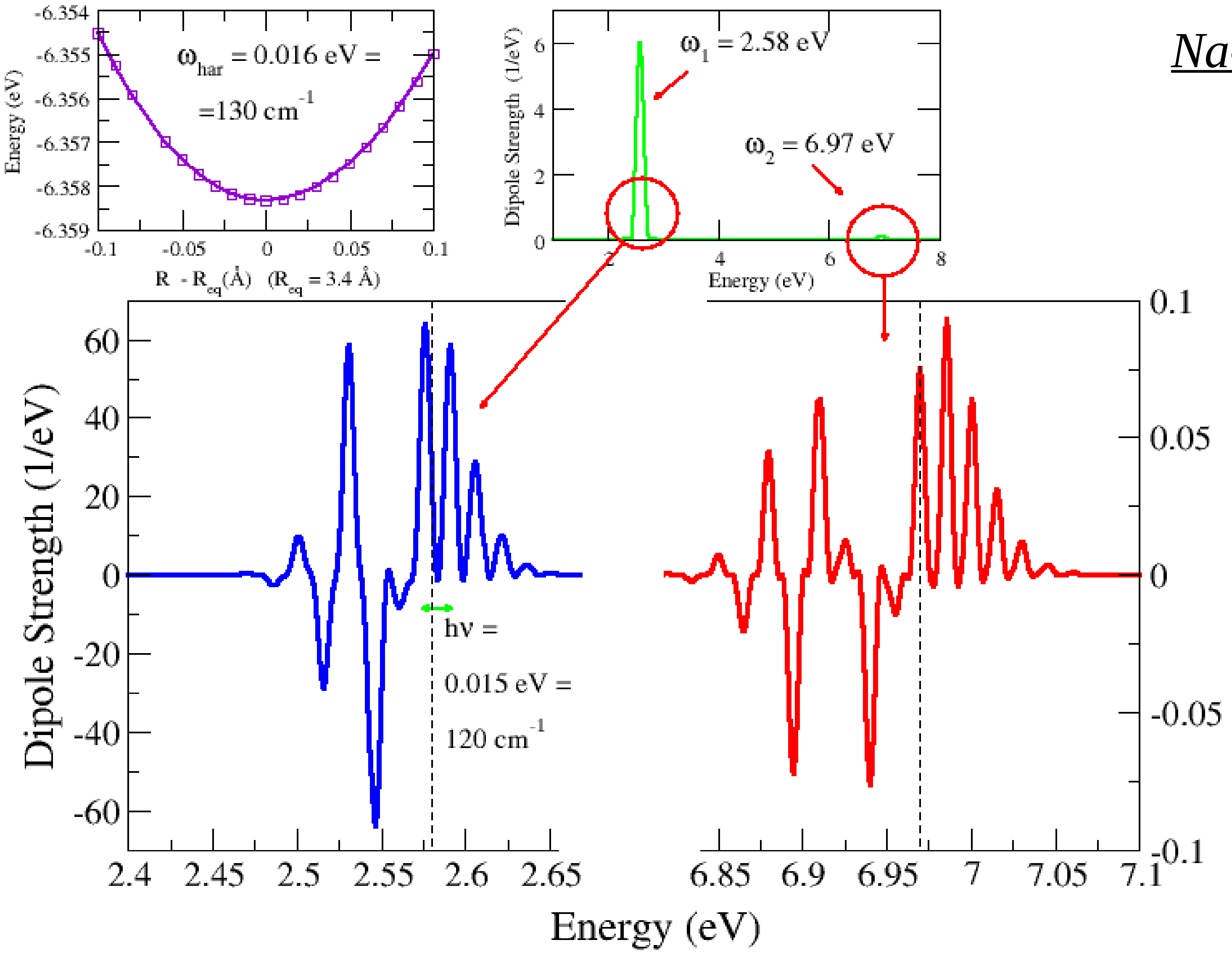
Time resolved Vibrational Spectroscopy: Raman

A. Castro, M.L. Marques. J.A. Alonso, G.F. Bertsch and AR (2003)

Femtosecond dynamics (*ongoing work!!!!*)

Time resolved Vibrational Spectroscopy: Raman & IR.

Na-dimer



The Electron Localisation Function (ELF) : Seeing Bonds!!!

Definition:

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

Becke, Edgecombe, JCP92, 5397 (1990)

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

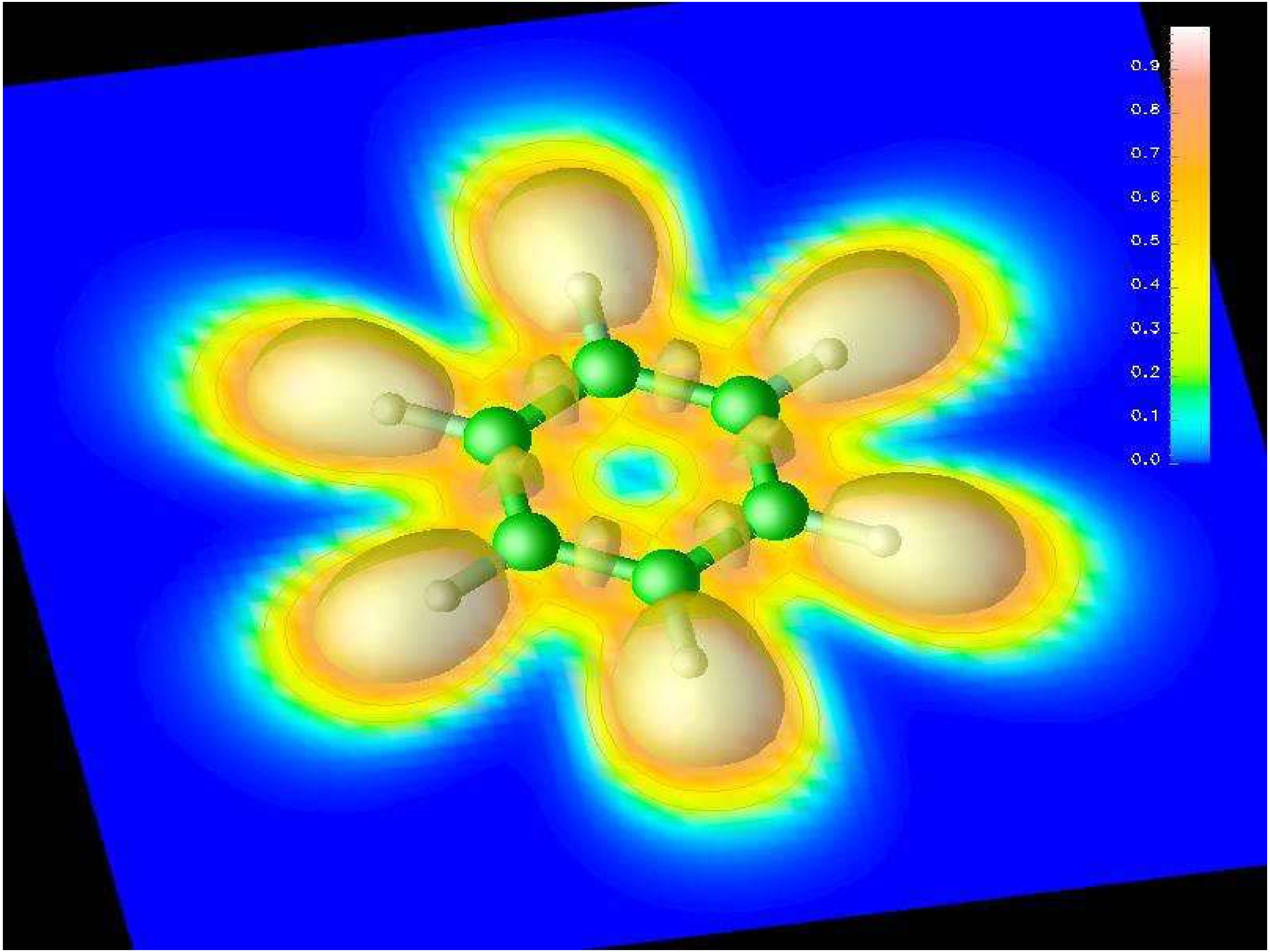
0 < elf < 1

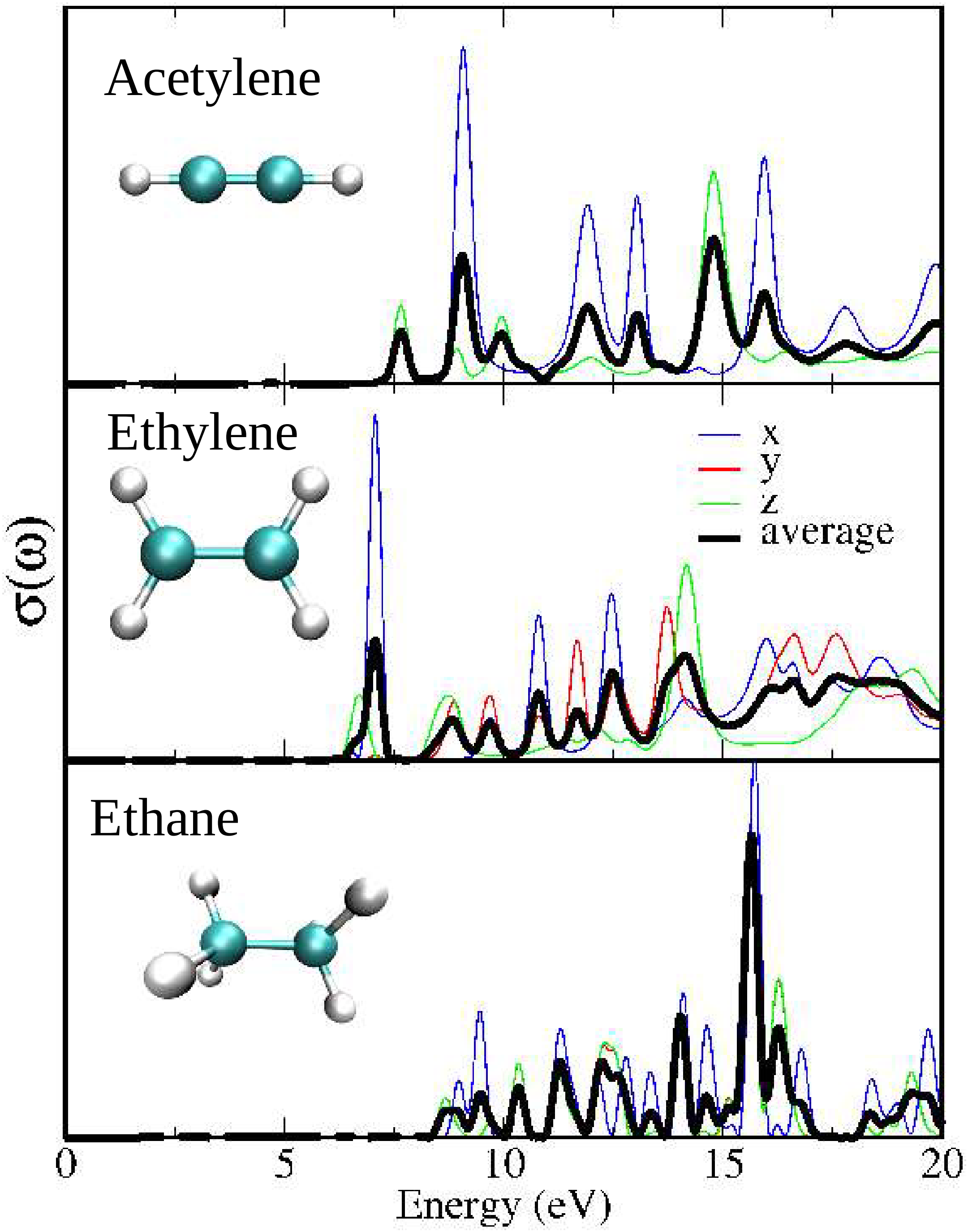
high localisation → $C_{\sigma}\sim 0$ → elf ~ 1

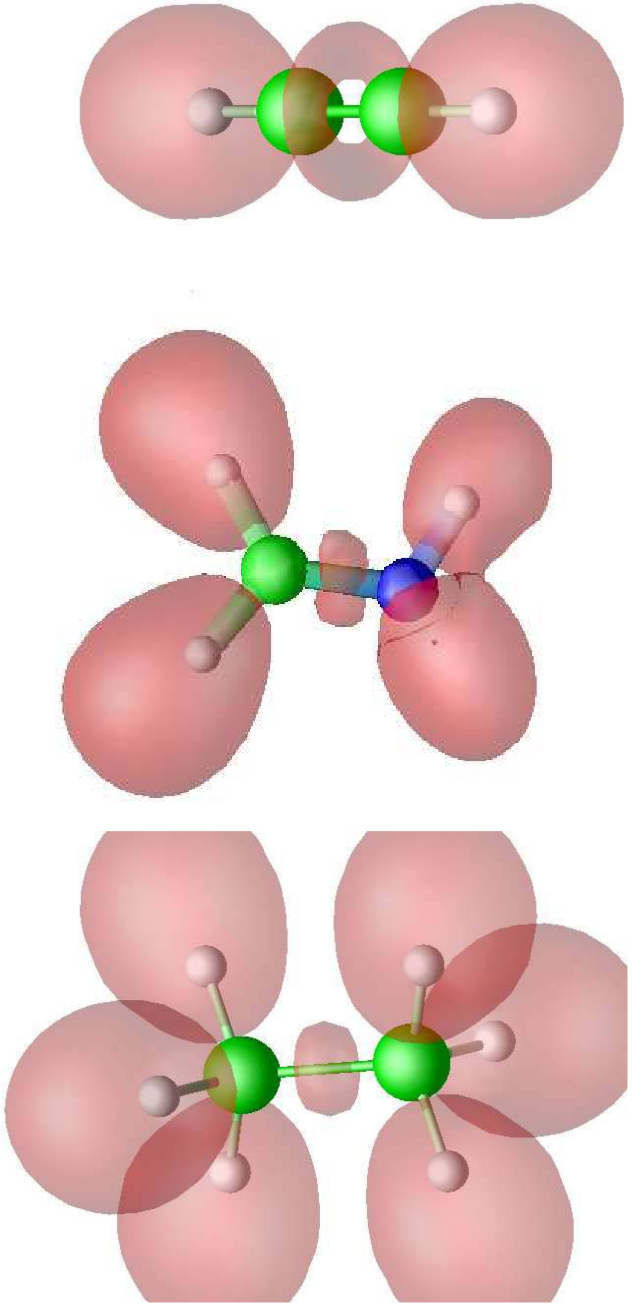
completely delocalised → $C_{\sigma}\sim C_{\sigma}^{uni}$ → elf ~ 1/2

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

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


0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0

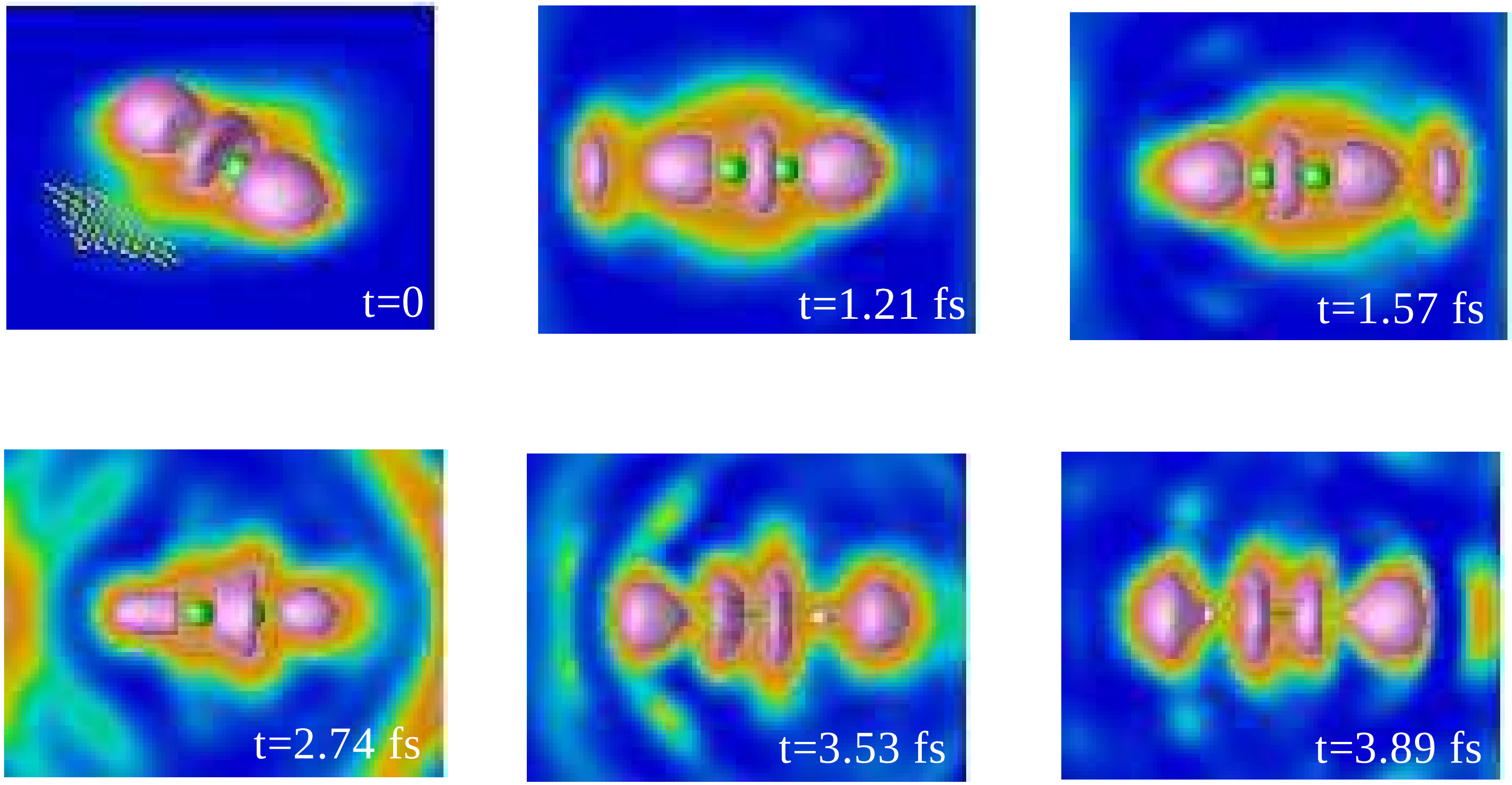

Acetylene
Ethylene
Ethane
x
y
z
average
σ(ω)
0
5
10
15
20
Energy (eV)



Time-dependet case: acetilene C_2H_2 in a strong laser field

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

fast ionisation



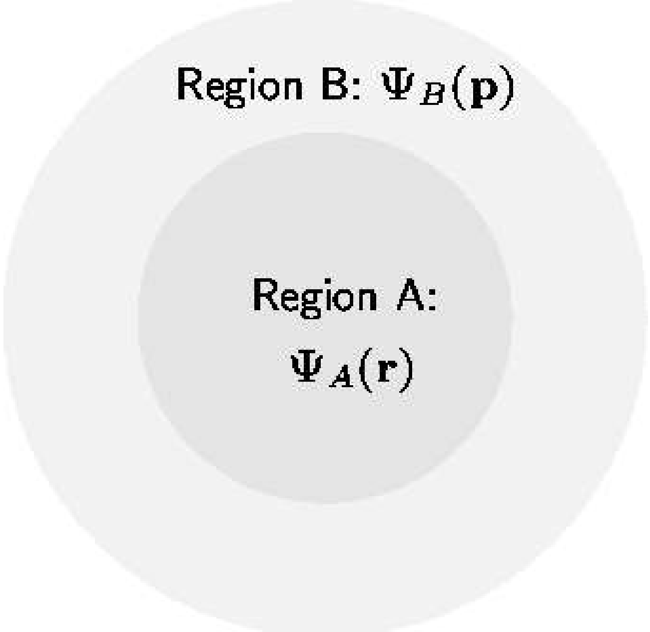
to *

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

Femtosecond dynamics: *Time-resolved photoelectron spectoscopy*

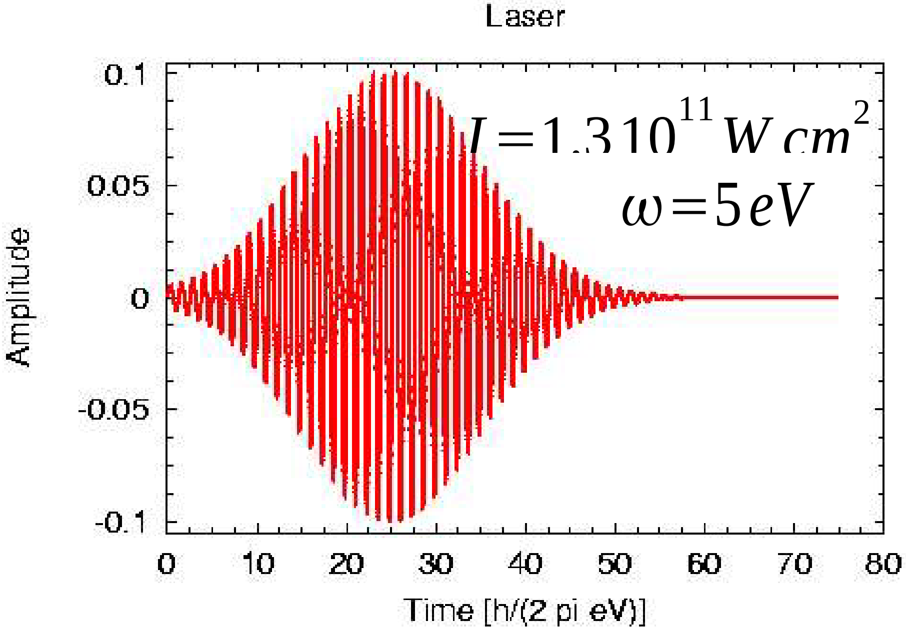
-The simulation region is divided in two parts: A and B, separated by a smooth mask function

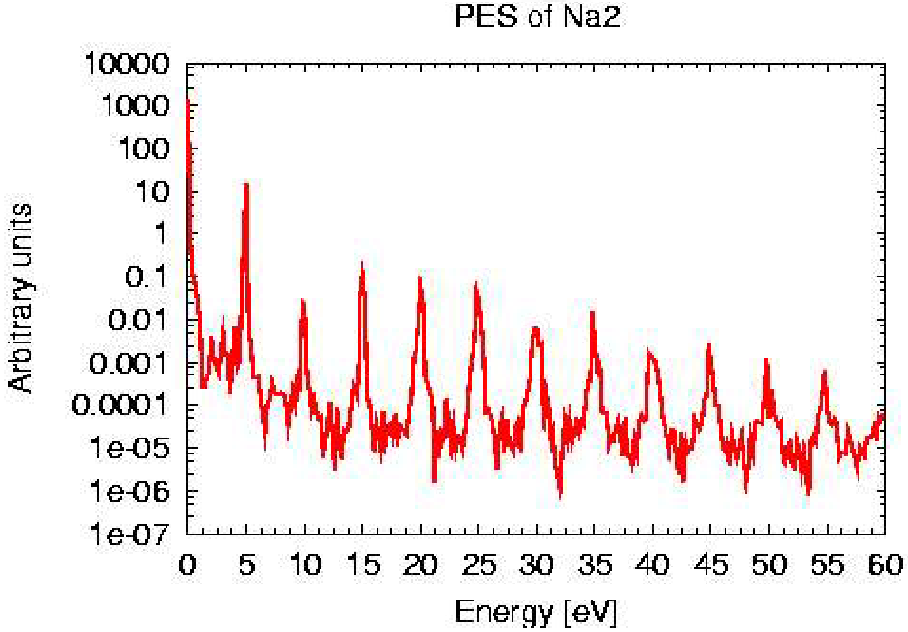
- *Electrons are not allowed to come back from B to A*



We write the photoelectron spectum as:

$$PES(p)=\sum_i \left|\Psi_i(p,t\to\infty)\right|^2$$





D. Varsano, M.A.L. Marques, H. Appel, E.K.U Gross and AR (to be published)