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

TDDFT THEORY:

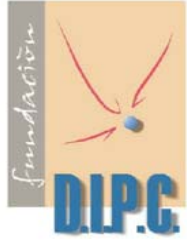
APPLICATIONS TO NANO AND BIO-STRUCTURES

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

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



Optical properties of nanostructures

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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 nanostructures

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

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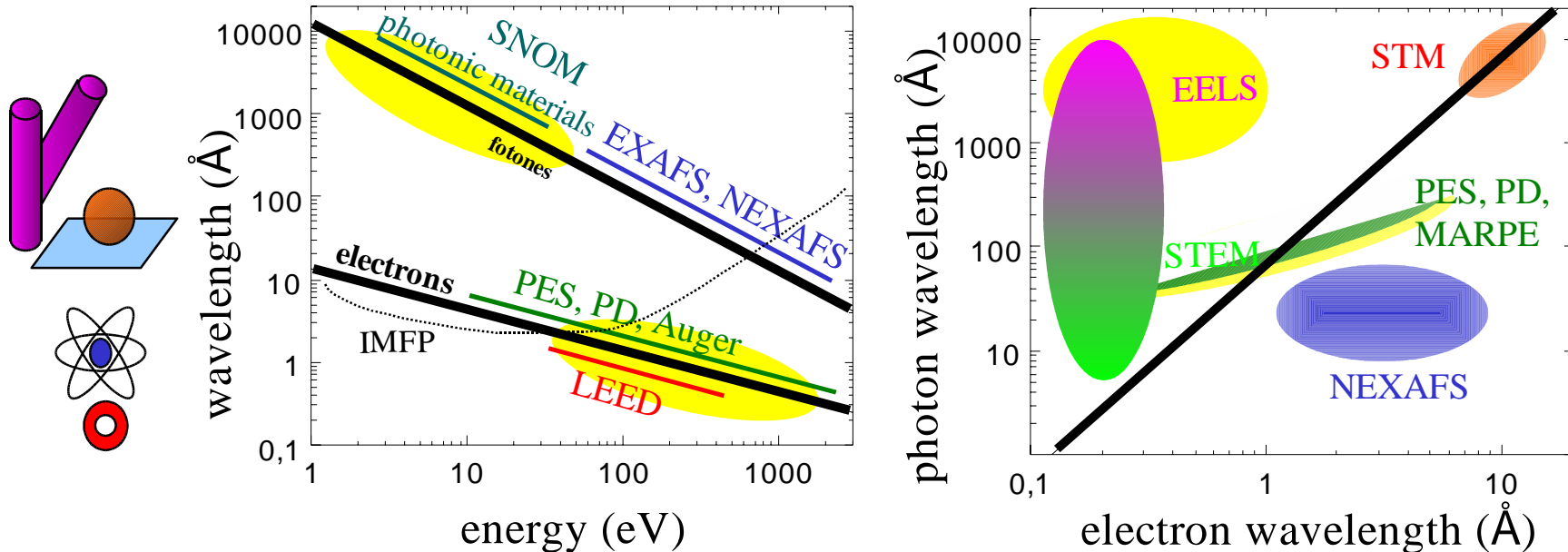
Nanoscience: different scales need to be bridged
(multicomponent simulations)

- spatial scale: 0D - 1D - 2D
from molecule-nano-bio-meso-wires-leads
- time scale: femtosecond (electron excitations)
picoseconds (phonon)
nanosecond (charge-transfer)
millisecond >>> bio-structural organisation
growth; self assembly

FIRST PRINCIPLES TOOLS: SPECTROSCOPIES

Characterisation tools of the “nanoworld”

Need of the knowledge of response functions!!!!

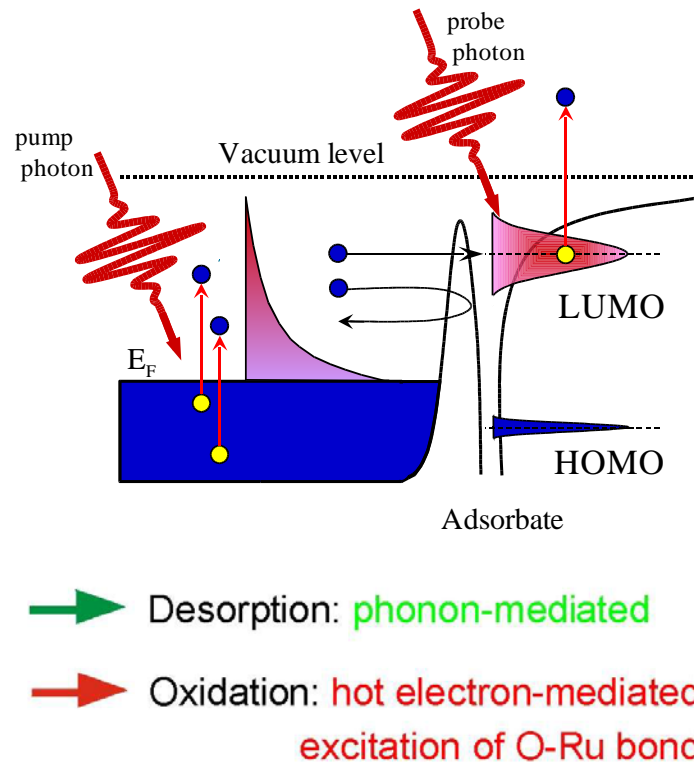
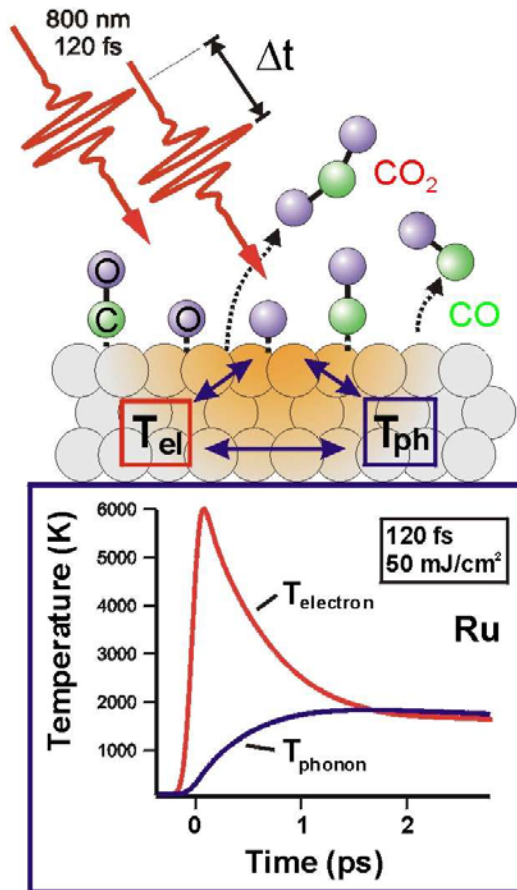


The **spatial resolution** depends on

- 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)



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

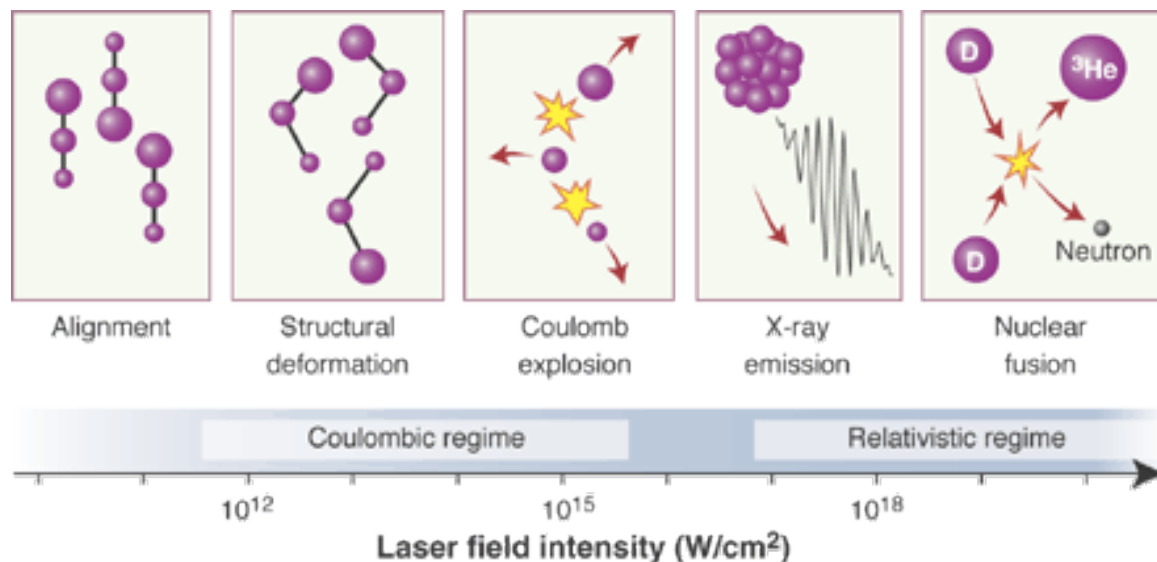
Electronic coupling between a solid and an adsorbate governs chemical dynamics at surfaces

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

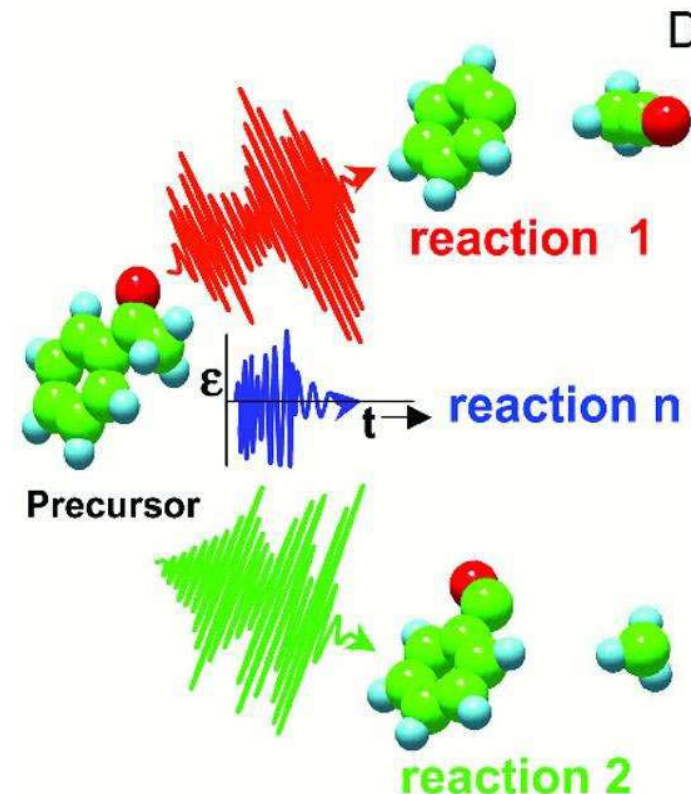
Motivation: non-linear phenomena and chemical reactivity

Quantum optimally controlled landscapes: time resolved dynamics

High-intense short-laser (fs) pulses



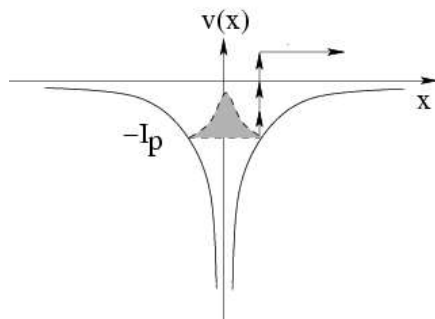
K. Yamanouchi, Science 295, 1659 (2002)



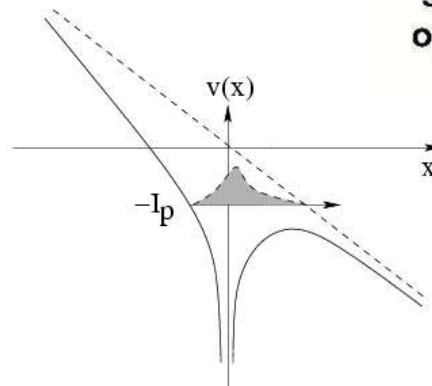
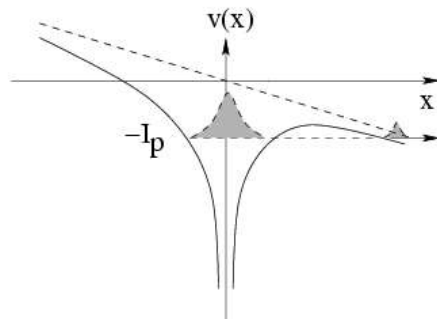
selective product formation using
optimally-tailored, strong-field laser
pulses: $\sim \text{fs}$

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

Multiphoton $< 10^{14} \text{ Wcm}^2$



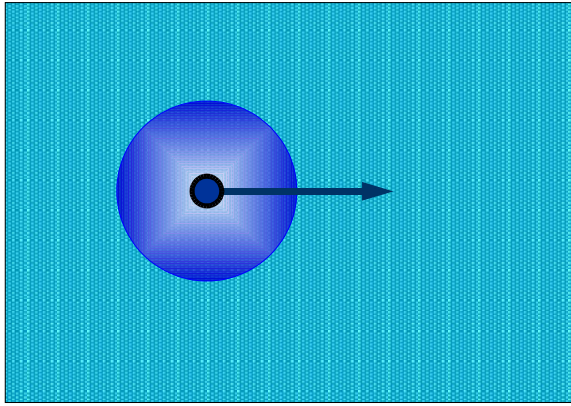
Tunneling $< 10^{15} \text{ Wcm}^2$



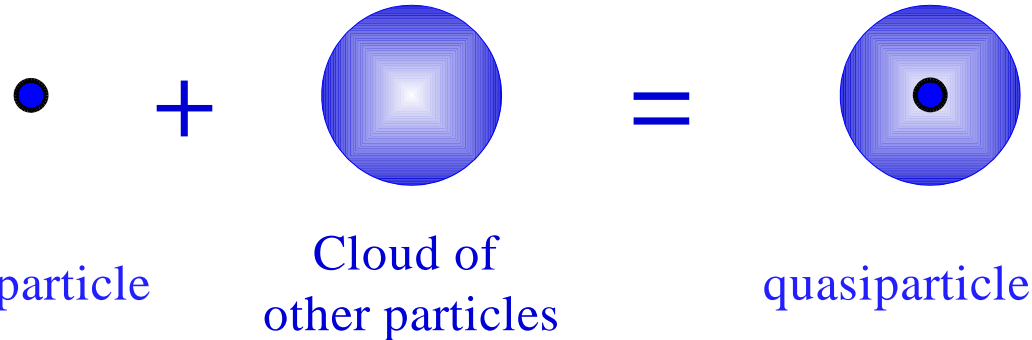
$$E = \frac{1}{4\pi\epsilon_0} \frac{e}{a_0^2} = 5.1 \times 10^9 \text{ V/m}$$


QUASIPARTICLES

- a fundamental concept in condensed-matter physics -

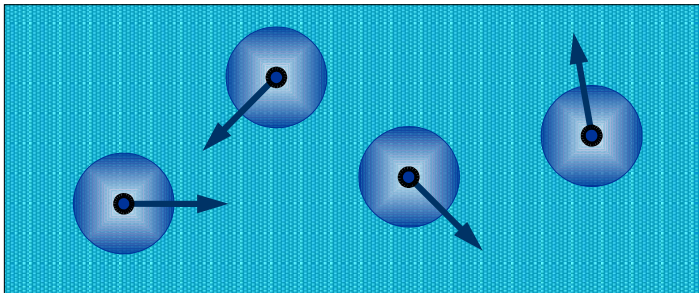


a system composed of interacting *real* bodies acts as if it were composed of weakly interacting *fictitious* bodies (**quasiparticles**)

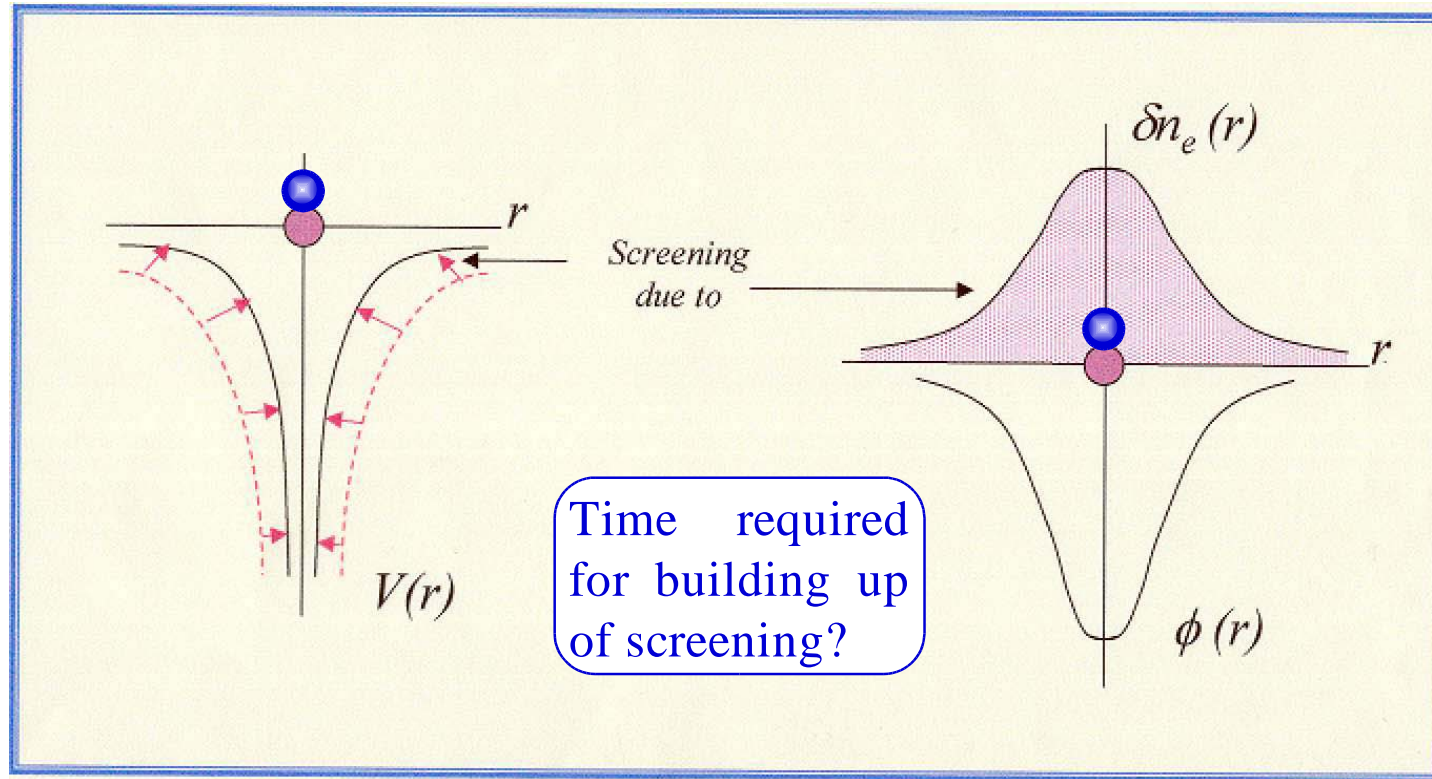


one many-body problem  many one-body problems

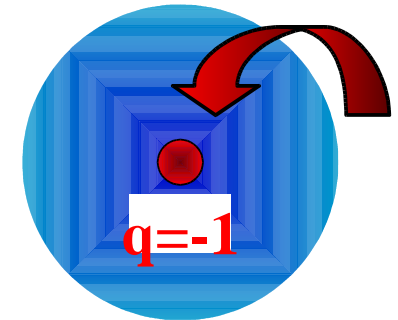
Lifetime: relevance



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



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



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

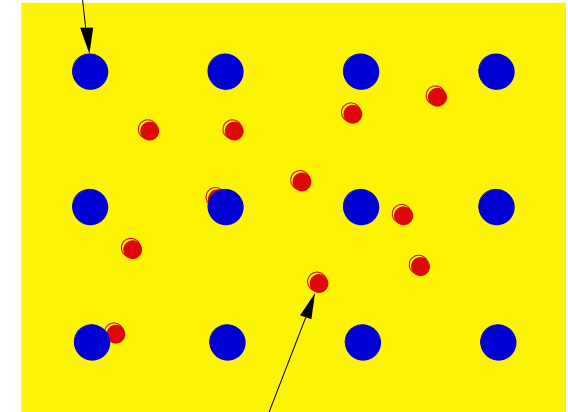
$$\delta n(\vec{r}) = \int d\vec{r}_1 \chi(\vec{r}, \vec{r}_1) \delta v(\vec{r}_1)$$

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:

Nucleus α (fixed)



Electron i

Hamiltonian of the coupled electron-ion system:

N ions, coordinates $\vec{R}_1, \dots, \vec{R}_N \equiv \vec{R}$, momenta $\vec{P}_1, \dots, \vec{P}_N \equiv \vec{P}$, charges Z_1, \dots, Z_N , masses M_1, \dots, M_N

N_e electrons, coordinates $\vec{r}_1, \dots, \vec{r}_{N_e} \equiv \vec{r}$, momenta $\vec{p}_1, \dots, \vec{p}_{N_e} \equiv \vec{p}$, 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 determinant 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)

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

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

$$n(\mathbf{r}) = n[\Psi] = \left\langle \sum_i \delta(\mathbf{r} - \mathbf{r}_i) \right\rangle$$

can be inverted

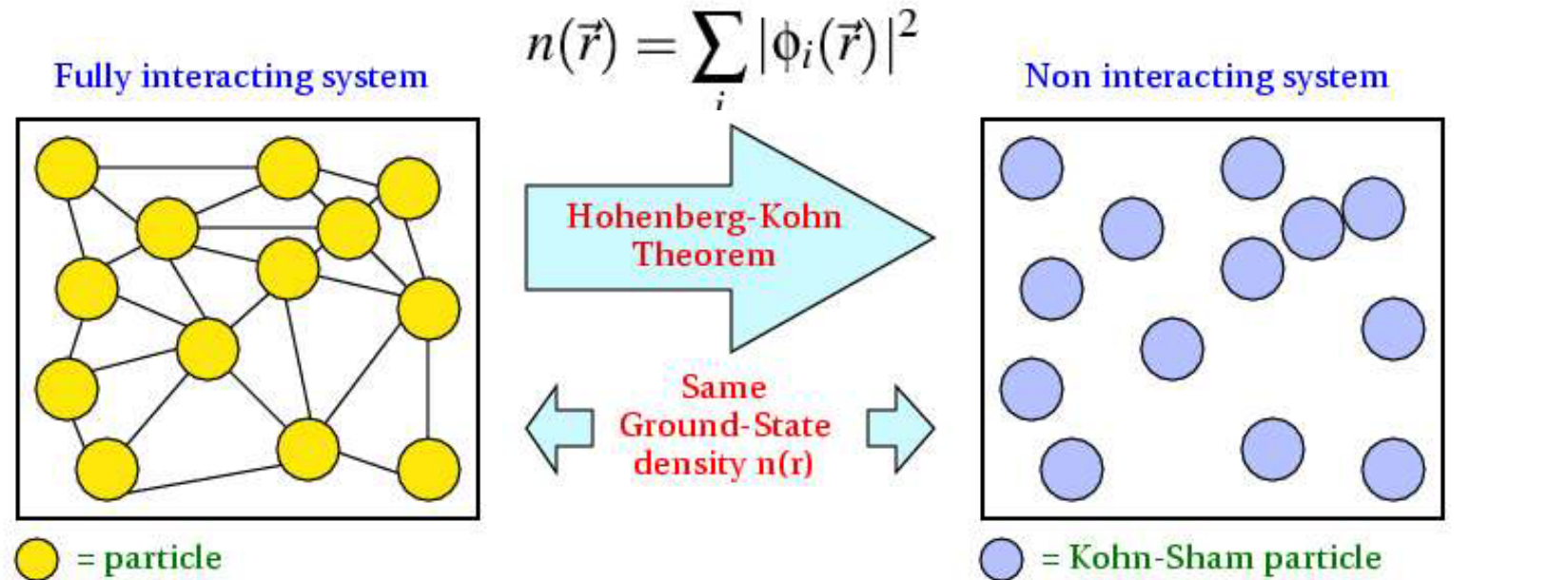
$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \Psi[n(\mathbf{r})] \rightarrow E[R_{\text{ions}}] = \min_n \langle \Psi | H_e | \Psi \rangle \equiv \min_n E[n]$$

- 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):



$$T[n] \text{ ----- } T_0[n]$$

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

Exc includes now the correlation contribution to T

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

with the exchange-correlation potential

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

KS-equations

Some summary of DFT results for finite and extended systems

<u>Property</u>	<u>LSDA</u>	<u>GGA</u>
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 accuracy *0.05 eV*

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

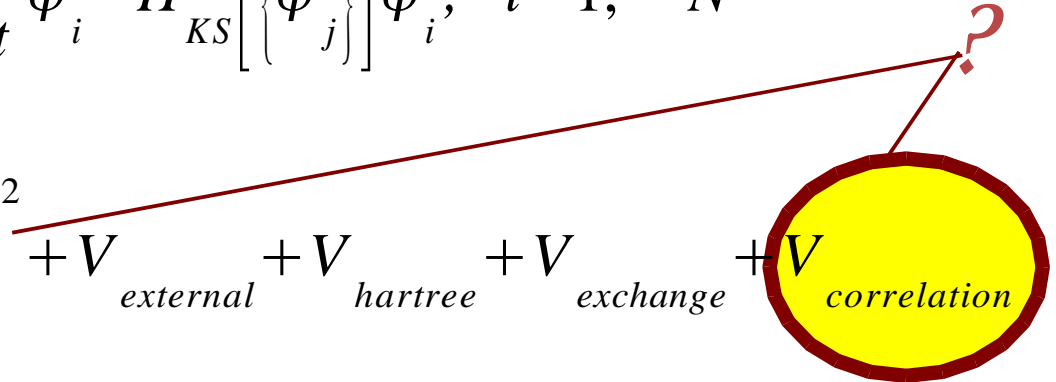
HK-like theorem: $v(\mathbf{r},t) \longleftrightarrow (\mathbf{r},t)$

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 auxiliary non-interacting system

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

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


Linear Response Theory:

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

The exact linear density response $\chi(r, r'; \omega)$ has poles at the exact excitation energies $E_m - E_n$

TDDFT does the job for you!!!

$\chi(r, r'; \omega) = \chi_0(r, r'; \omega) + \chi_0(r, r'; \omega) V_{\text{ext}}(r) \chi(r, r'; \omega)$ however the KS system $\chi_0(r, r'; \omega) = \chi_0(r, r'; \omega) V_{\text{eff}}(r) \chi_0(r, r'; \omega)$

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

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

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

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

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

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

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

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

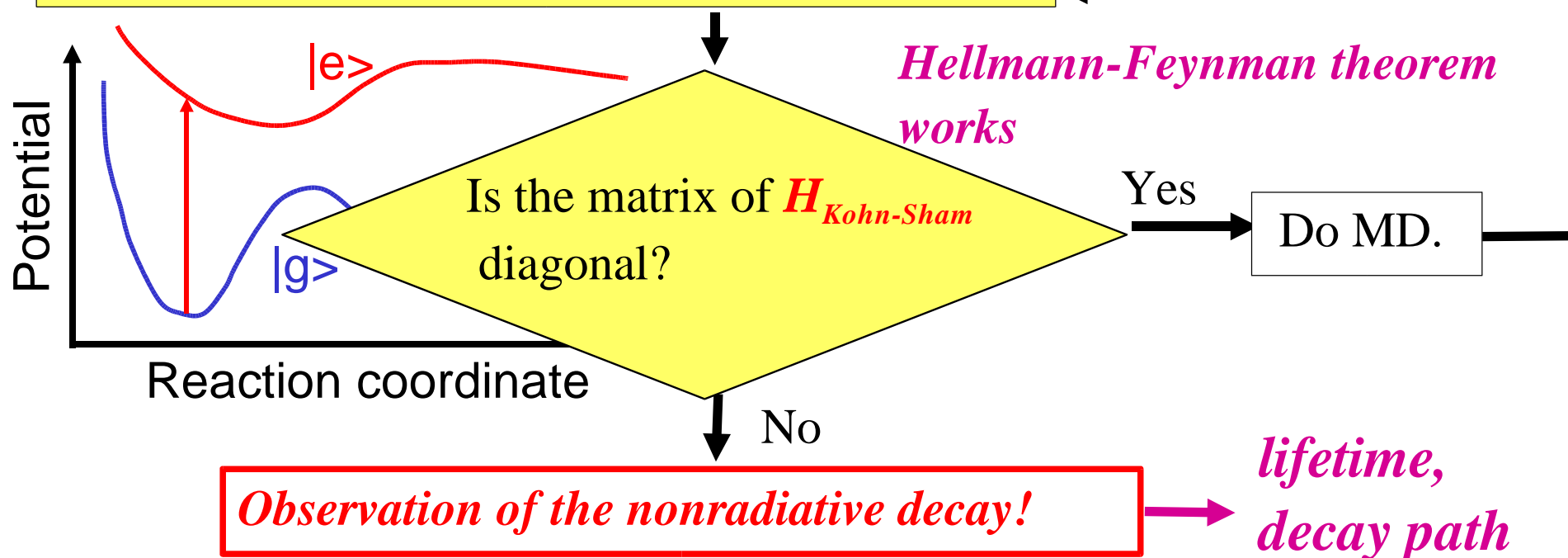
e.g. ionization yields

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 $\mathbf{n}(t + \Delta t) = \exp\{-i \Delta t \mathbf{H}(t)\} \mathbf{n}(t)$.



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

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

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

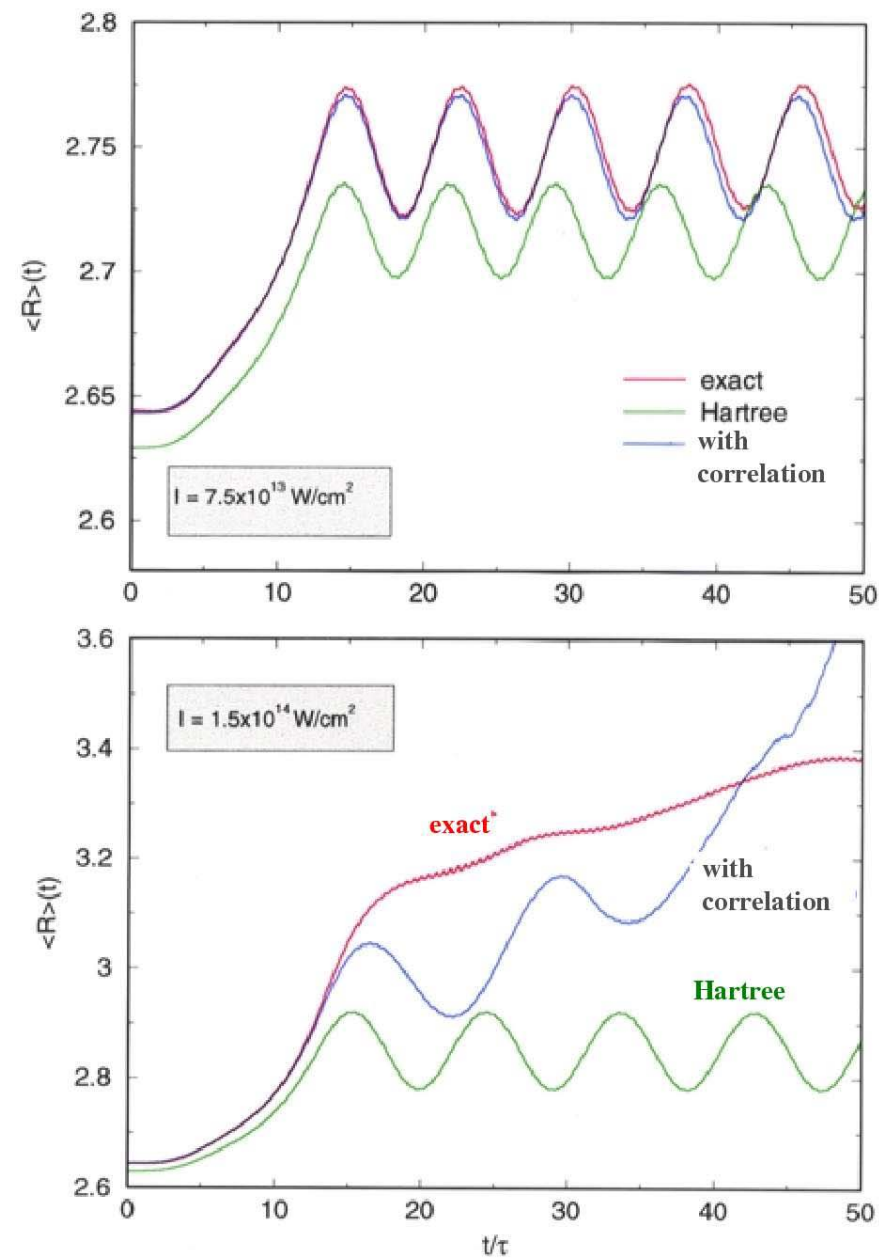
$$i\partial_t \varphi_j(\mathbf{r}, t) = \left(\frac{\hbar^2}{2\mu_e} \nabla_{\mathbf{r}}^2 + v_s[\rho, N](\mathbf{r}, t) \right) \varphi_j(\mathbf{r}, t)$$

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

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

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

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



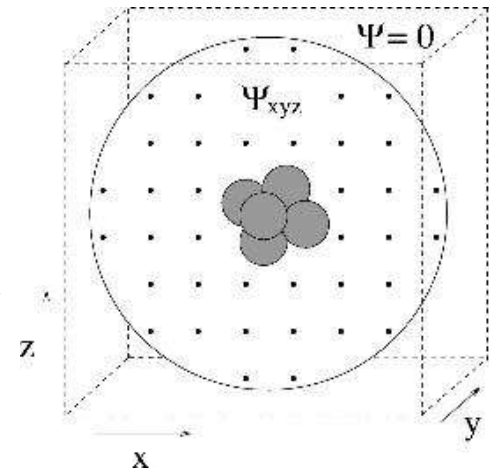
<http://www.tddft.org/programs/octopus>

*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

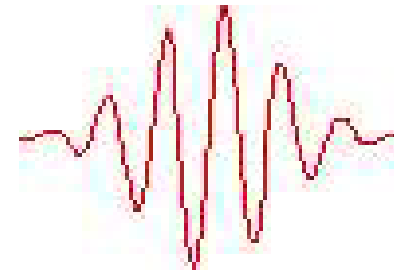
- ✓ *High-order discretization* for the kinetic energy operator

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



- ✓ Classical description of electromagnetic field.

$$\mathbf{E}(t) = \sqrt{\frac{I_0}{8\pi}} f(t) \sin(\omega t) \mathbf{e}_D$$



(Absence of radiative-decay channel!)

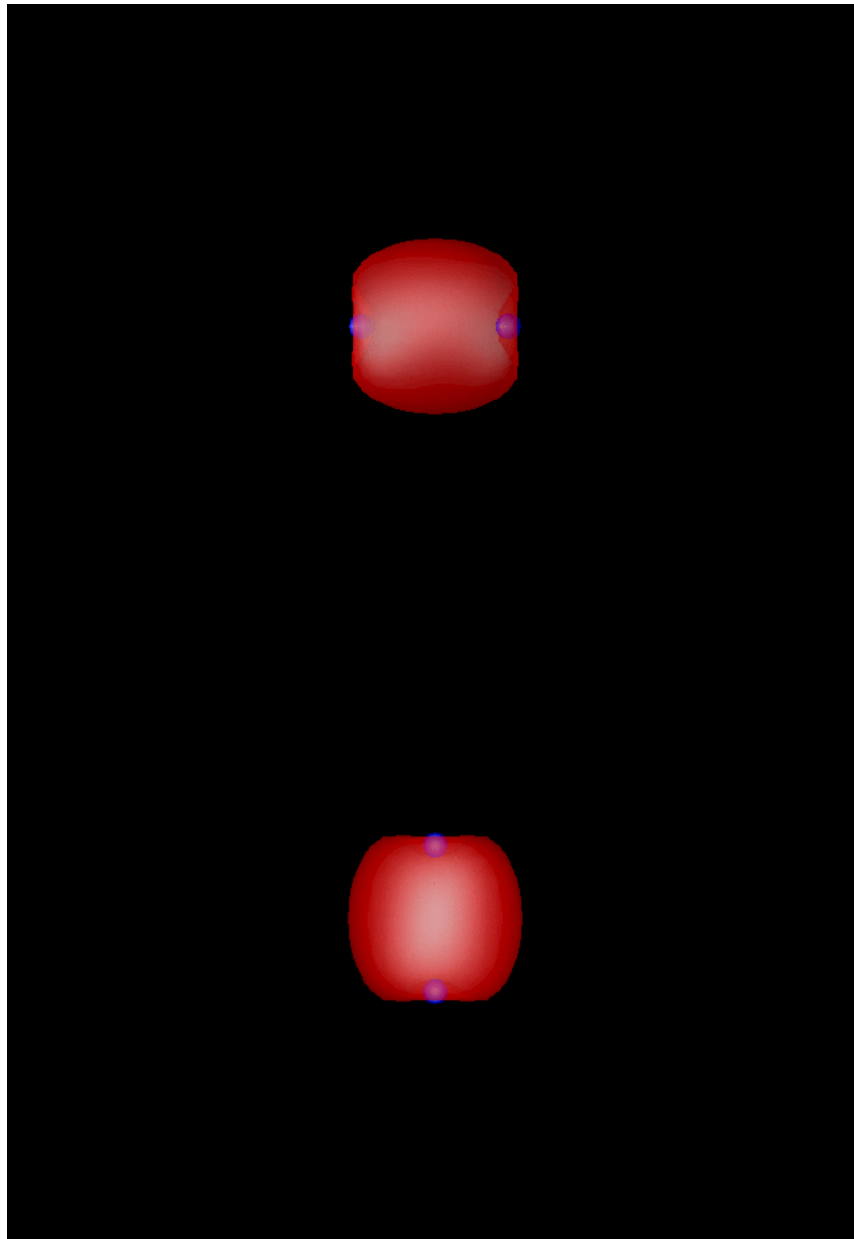
- ✓ Classical description of nuclei (point particles): **Ehrenfest path**:

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

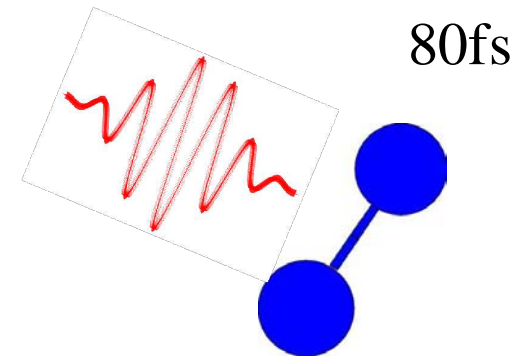
- ✓ Solution of the TD-KS equations by **unitary propagation schemes**.

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

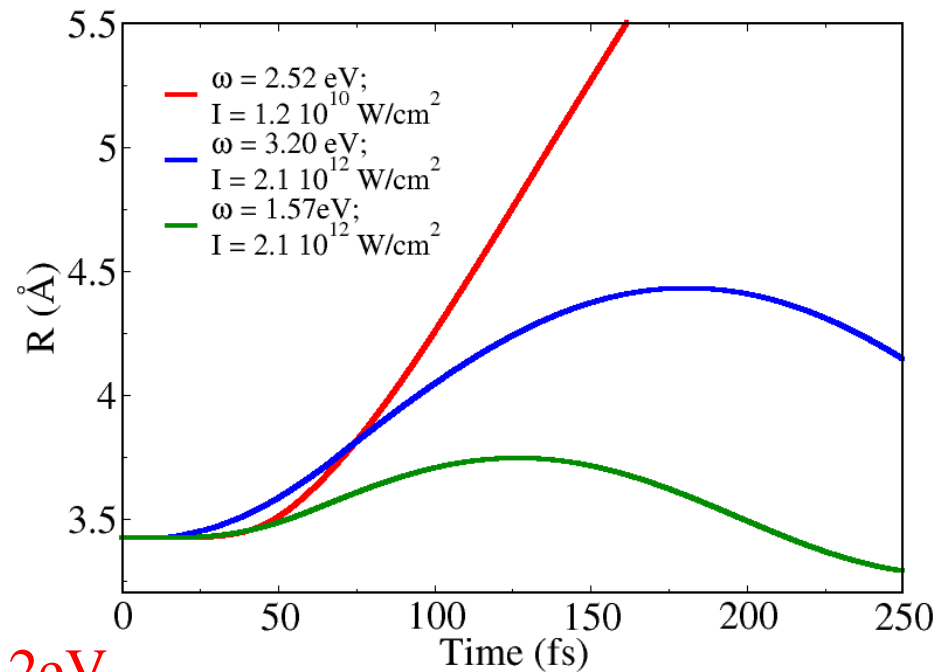
Femtosecond dynamics: *test photodissociation of a dimer (Na_2^+).*



$\omega = 2.5 \text{ eV}$



$\omega = 3.2 \text{ eV}$



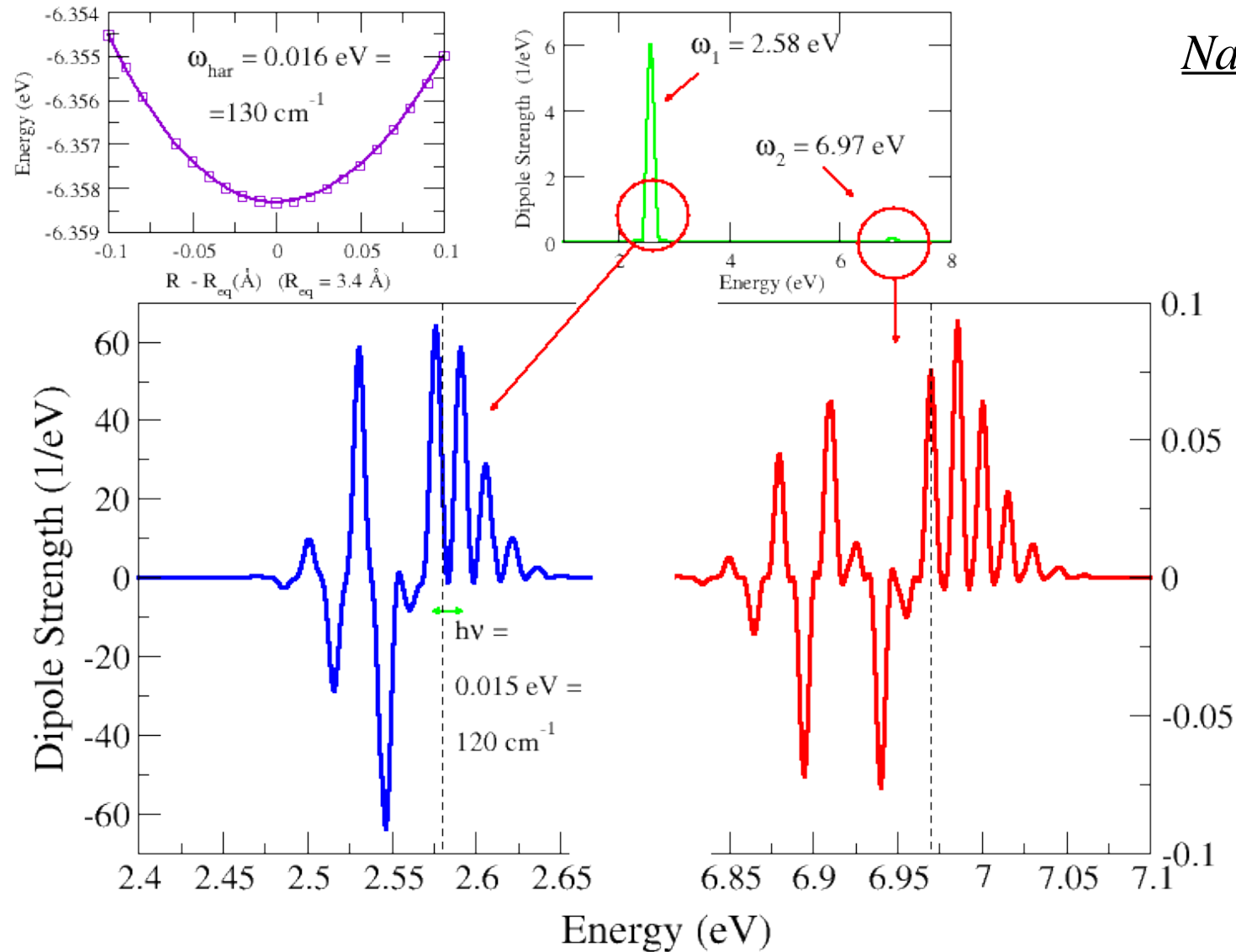
Time resolved Vibrational Spectroscopy: Raman

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)

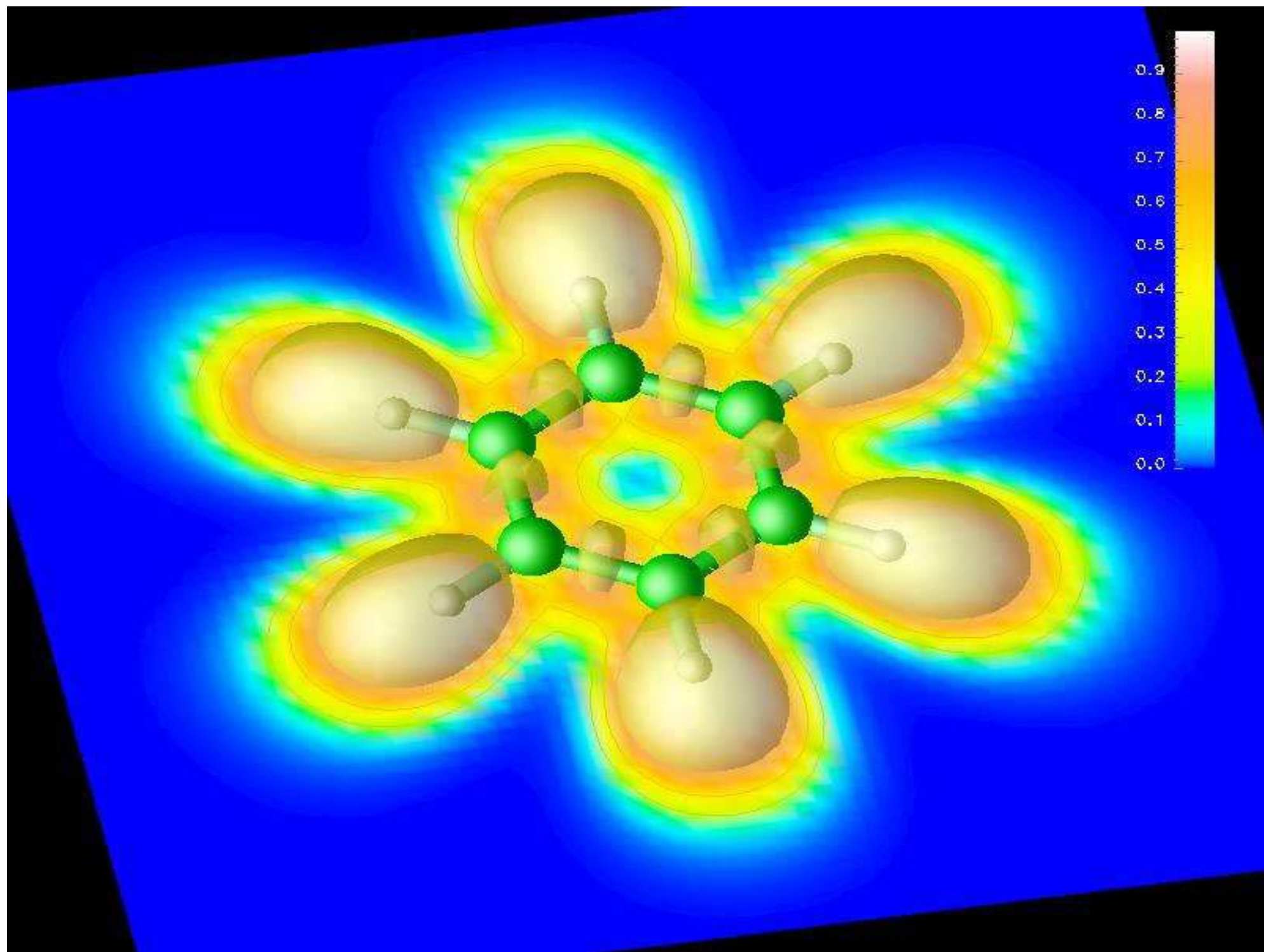
$$C_{\sigma}^{uni}(r) = \frac{3}{5} (6\pi^2)^{2/3} \rho_{\sigma}^{5/3}(r)$$

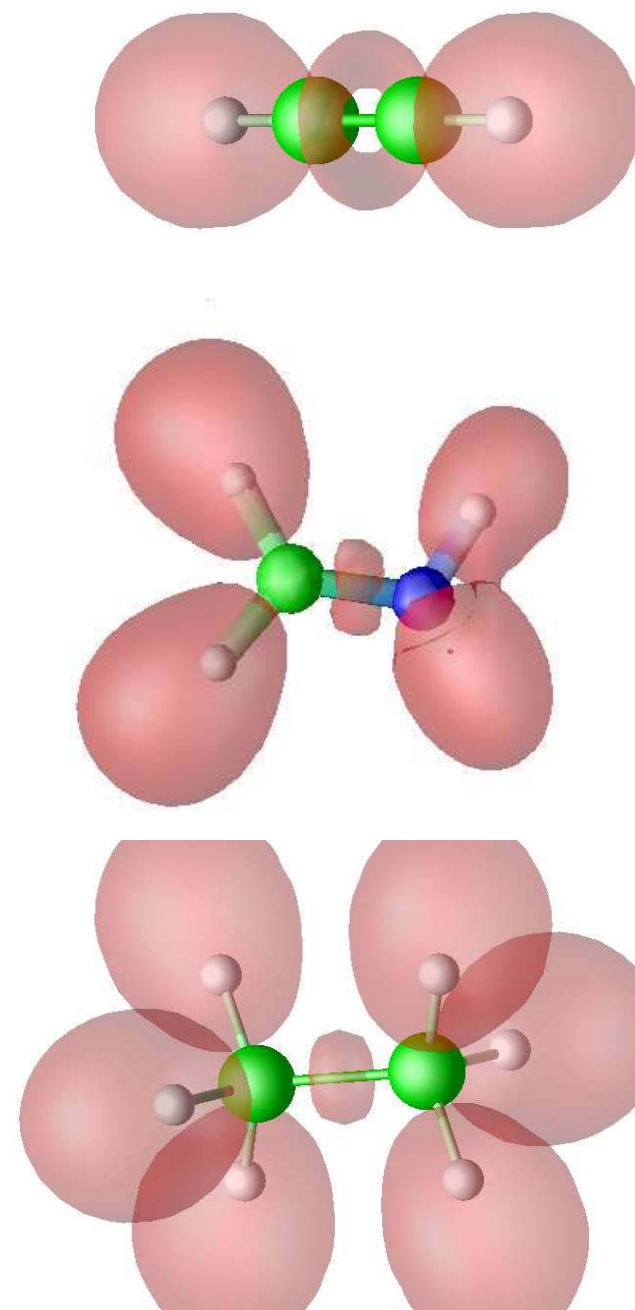
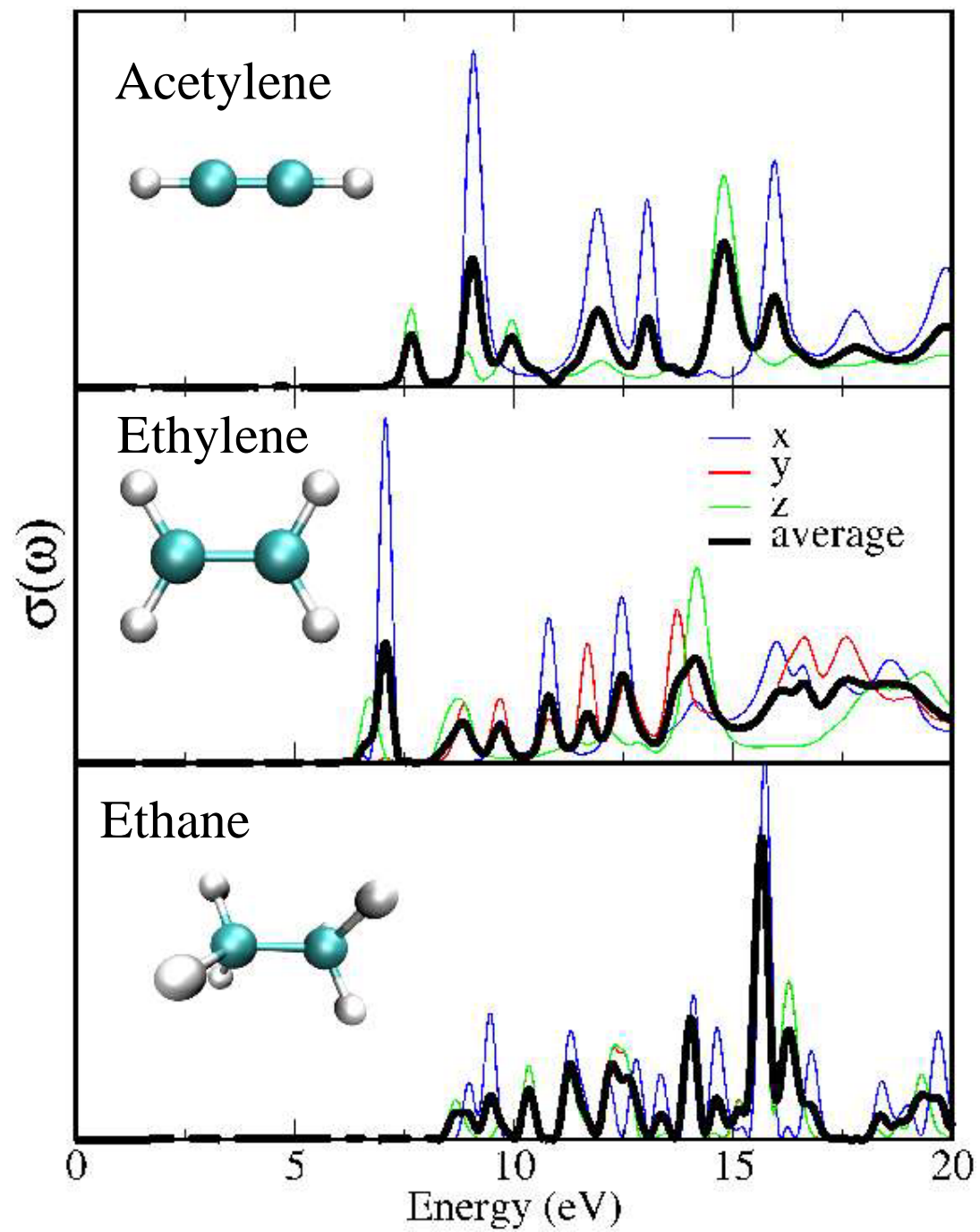
$$0 < elf < 1$$

high localisation	→	$C_{\sigma} \sim 0$	→	$elf \sim 1$
completely delocalised	→	$C_{\sigma} \sim C_{\sigma}^{uni}$	→	$elf \sim 1/2$

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

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

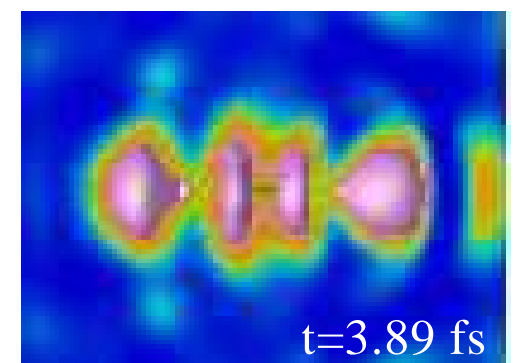
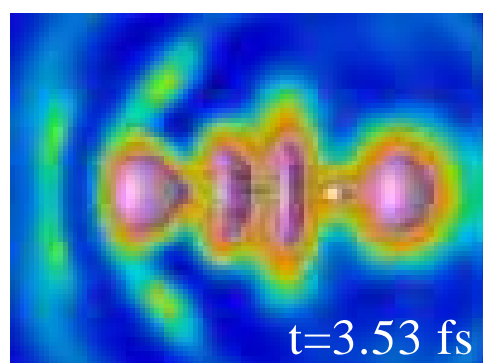
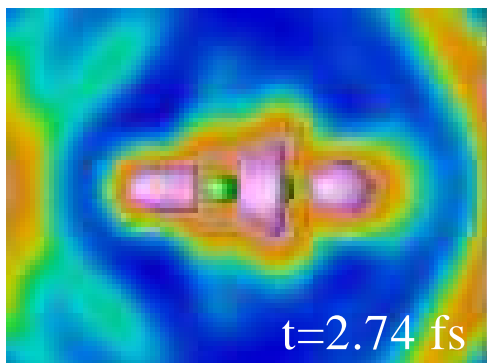
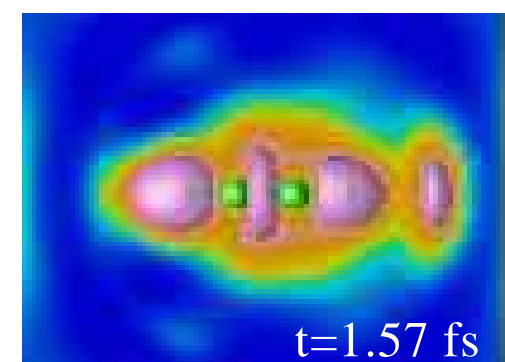
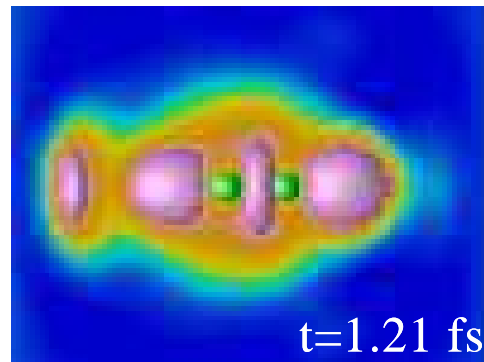
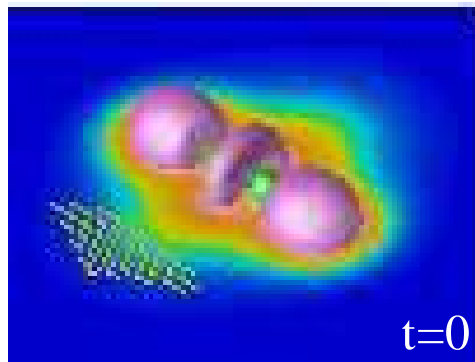




Time-dependent case: acetylene C_2H_2 in a strong laser field

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

fast ionisation



to *

Femtosecond dynamics: *Time-resolved photoelectron spectroscopy*

- 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 spectrum** as:

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

Laser

