Regional School on Physics at the Nanoscale:
Theoretical and Computational Aspects
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Computer simulations beyond the electronic ground state

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International Atomic
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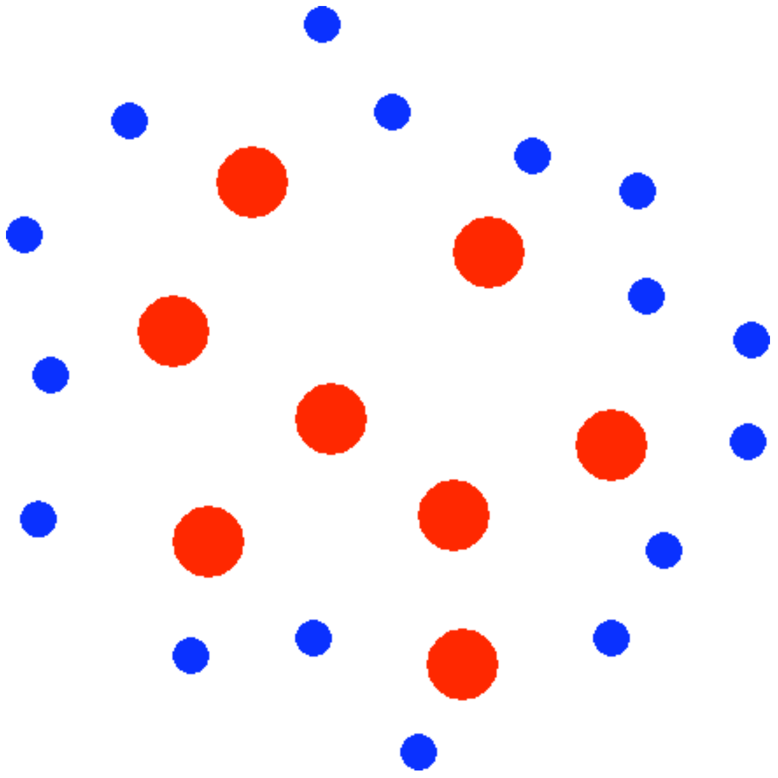
DEMOCRITOS
DEmocritos MOdeling Center for
Research In aTOmistic Simulation
INFM

Overview

- Computational atomistic nanoscience
- Short introduction to Density Functional Theory
- Going beyond the electronic ground state:
  Time-dependent density functional theory
  Foundations (Runge Gross theorem)
- TD-DFT in practice:
  Applications to linear and non-linear
  optical properties

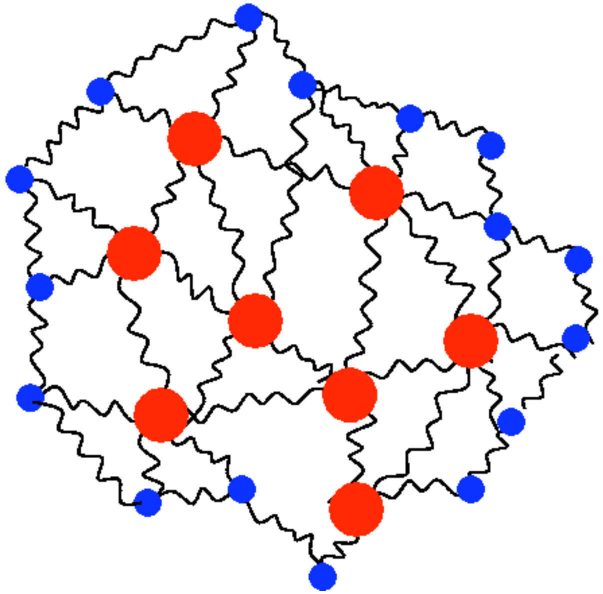
Computational Atomistic Nanoscience:



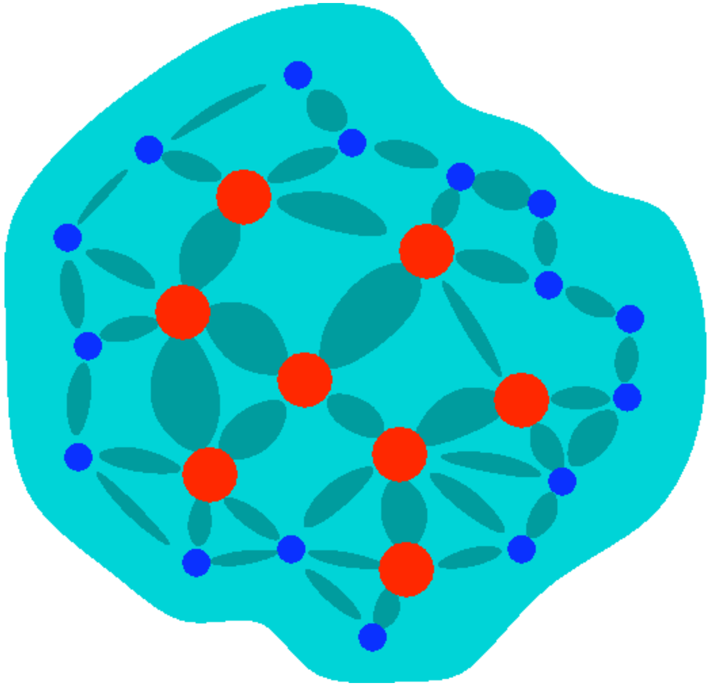
Treat nuclei as classical particles
(Born-Oppenheimer approx.)

Computational Atomistic Nanoscience: Two approaches

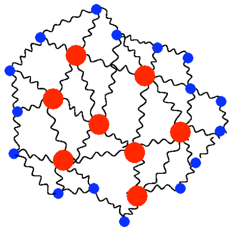
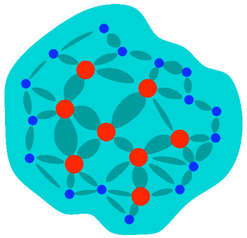
Classical Models



Quantum models



Computational Atomistic Nanoscience:
Two approaches

Classical Models	Quantum models
	
Can treat very large systems	Can treat relatively small systems
Problems with “chemistry”	Chemical bonding well described
Treat easily 10^4-10^5 atoms	Treat ≈ 100 atoms

One quantum approach:

Density Functional Theory (DFT)

- Treat the nuclei classicaly
- Solve the quantum problem for the electrons using DFT
- Avoid to deal many body wavefunctions (100s-1000s of e^-)
- Obtaining the electronic structure from DFT allows one to calculate forces, etc
- Opens the way to (Car-Parrinello) Molecular Dynamics, Phonon calculations, etc.

A short history of density-functional theory

1920s: Introduction of the Thomas-Fermi model.

1964: Hohenberg-Kohn paper proving existence of exact DF.

1965: Kohn-Sham scheme introduced.

1970s and early 80s: LDA. DFT becomes useful.

1985: Incorporation of DFT into molecular dynamics (Car-Parrinello)
(Now one of PRL’s top 10 cited papers).

1988: Becke and LYP functionals. DFT useful for some chemistry.

1998: Nobel prize awarded to Walter Kohn in chemistry for
development of DFT.

Basic ground-state DFT

Consider the charge density of an N-electron system as the expectation value of the **density operator**:

$$\hat{n}(\boldsymbol{r}) = \sum_{\sigma} \hat{n}_{\sigma}(\boldsymbol{r}), \qquad \hat{n}_{\sigma}(\boldsymbol{r}) = \hat{\psi}^{\dagger}_{\sigma}(\boldsymbol{r})\hat{\psi}_{\sigma}(\boldsymbol{r})$$

Hohenberg-Kohn theorem:

1. The **electron density** of an interacting system of electrons fully and uniquely **determines the external potential** v(r) that these electrons experience (and thus the Hamiltonian, and all observables of the system).

2. The ground-state energy of this system can be obtained by minimizing the total energy in terms of the density.

3. There exists a unique universal functional F[n] such that the total energy , E[n], can be written in the form

$$E[n] = F[n] + \int d^3r\, n(\boldsymbol{r}) v(\boldsymbol{r})$$

Basic ground-state DFT

For practical calculations: **Kohn-Sham framework**

$$n_\sigma(\boldsymbol{r}) = \sum_i^{N_\sigma} |\phi_{i\sigma}(\boldsymbol{r})|^2$$

The density is written in terms of Kohn-Sham orbitals which satisfy

$$\left[-\frac{\nabla^2}{2} + v_\sigma^{KS}[n_\uparrow, n_\downarrow](\boldsymbol{r})\right]\phi_{i\sigma}(\boldsymbol{r}) = \epsilon_{i\sigma}\phi_{i\sigma}(\boldsymbol{r})$$

$$v_\sigma^{KS}[n_\uparrow, n_\downarrow](\boldsymbol{r}) = v_\sigma(\boldsymbol{r}) + \int d^3r' \frac{n(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} + v_\sigma^{xc}[n_\uparrow, n_\downarrow](\boldsymbol{r})$$

$$v_\sigma^{xc}[n_\uparrow, n_\downarrow](\boldsymbol{r}) = \frac{\delta E_{xc}[n_\uparrow, n_\downarrow]}{\delta n_\sigma(\boldsymbol{r})}$$

Basic ground-state DFT

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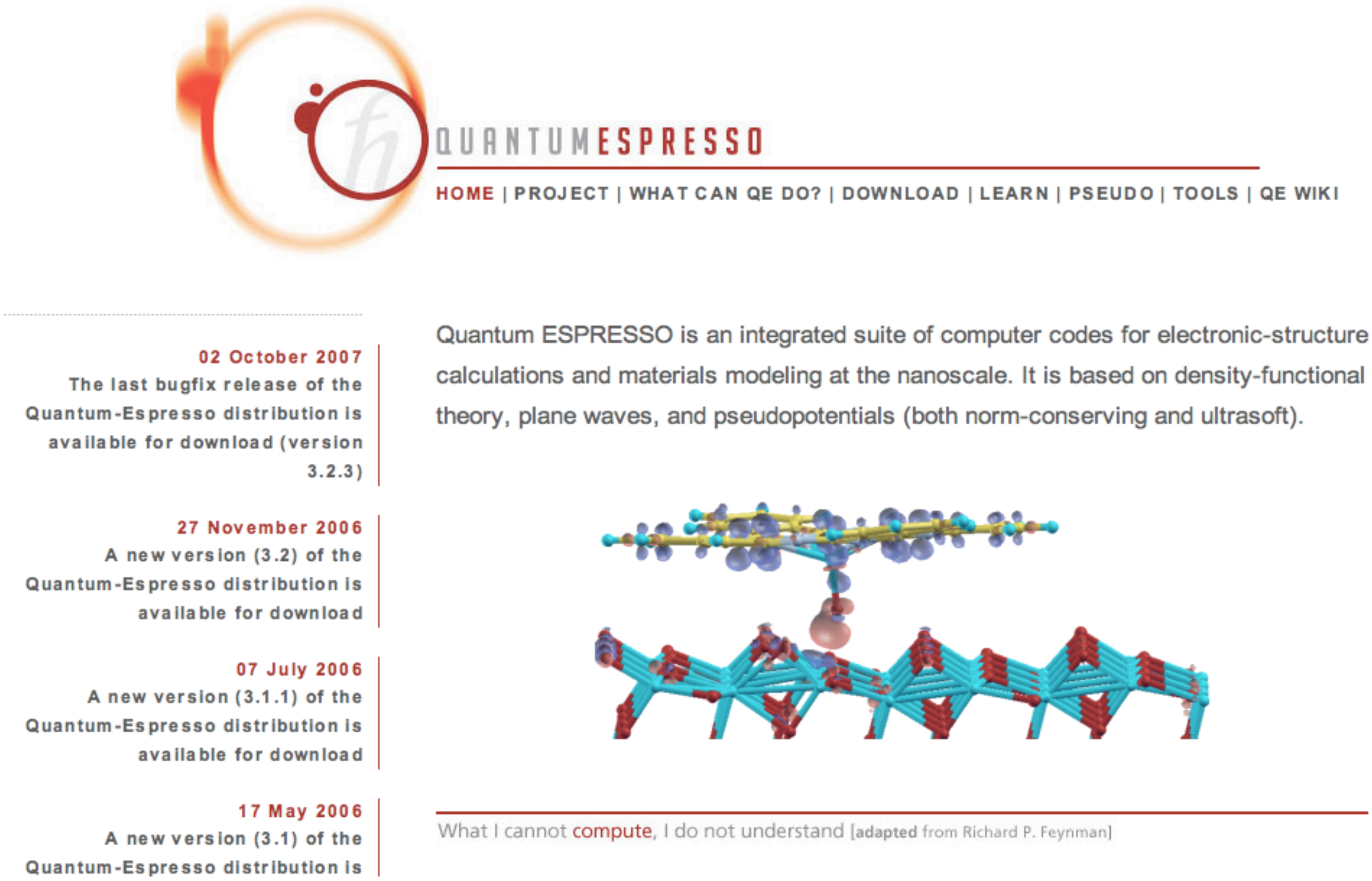
$$\boxed{\begin{aligned}
F[n_\uparrow, n_\downarrow] &= T_s[n_\uparrow, n_\downarrow] + E_{Hartree} + E_{xc}[n_\uparrow, n_\downarrow] \\
E_{Hartree} &= \frac{1}{2}\int d^3r \int d^3r' \frac{n(\boldsymbol{r})\, n(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \\
E_{xc}^{LDA} &= \int d^3r\, n(\boldsymbol{r}) \epsilon_{xc}^{unif}(n_\uparrow(\boldsymbol{r}), n_\downarrow(\boldsymbol{r}))
\end{aligned}}$$

One plane-wave based suite of codes:

http://www.quantum-espresso.org/



QUANTUMESPRESSO

HOME | PROJECT | WHAT CAN QE DO? | DOWNLOAD | LEARN | PSEUDO | TOOLS | QE WIKI

02 October 2007
The last bugfix release of the Quantum-Espresso distribution is available for download (version 3.2.3)

27 November 2006
A new version (3.2) of the Quantum-Espresso distribution is available for download

07 July 2006
A new version (3.1.1) of the Quantum-Espresso distribution is available for download

17 May 2006
A new version (3.1) of the Quantum-Espresso distribution is

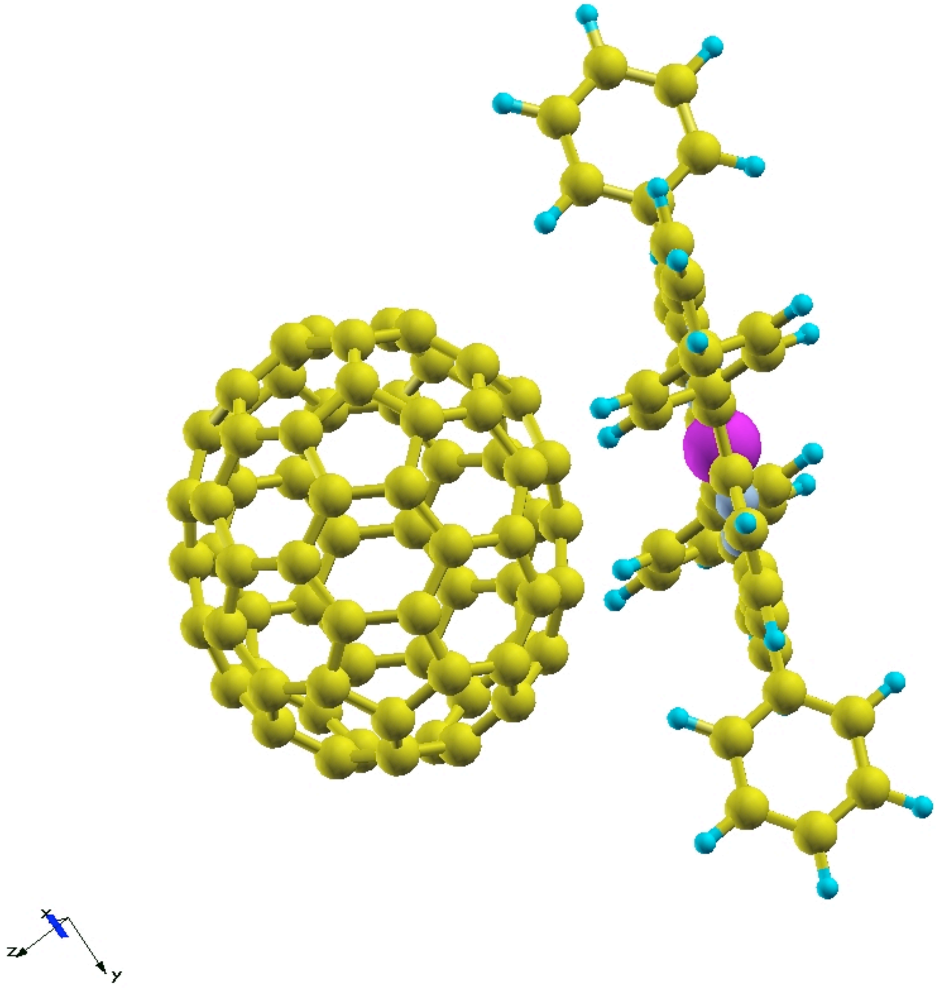
Quantum ESPRESSO is an integrated suite of computer codes for electronic-structure calculations and materials modeling at the nanoscale. It is based on density-functional theory, plane waves, and pseudopotentials (both norm-conserving and ultrasoft).

What I cannot compute, I do not understand [adapted from Richard P. Feynman]

Quantum espresso

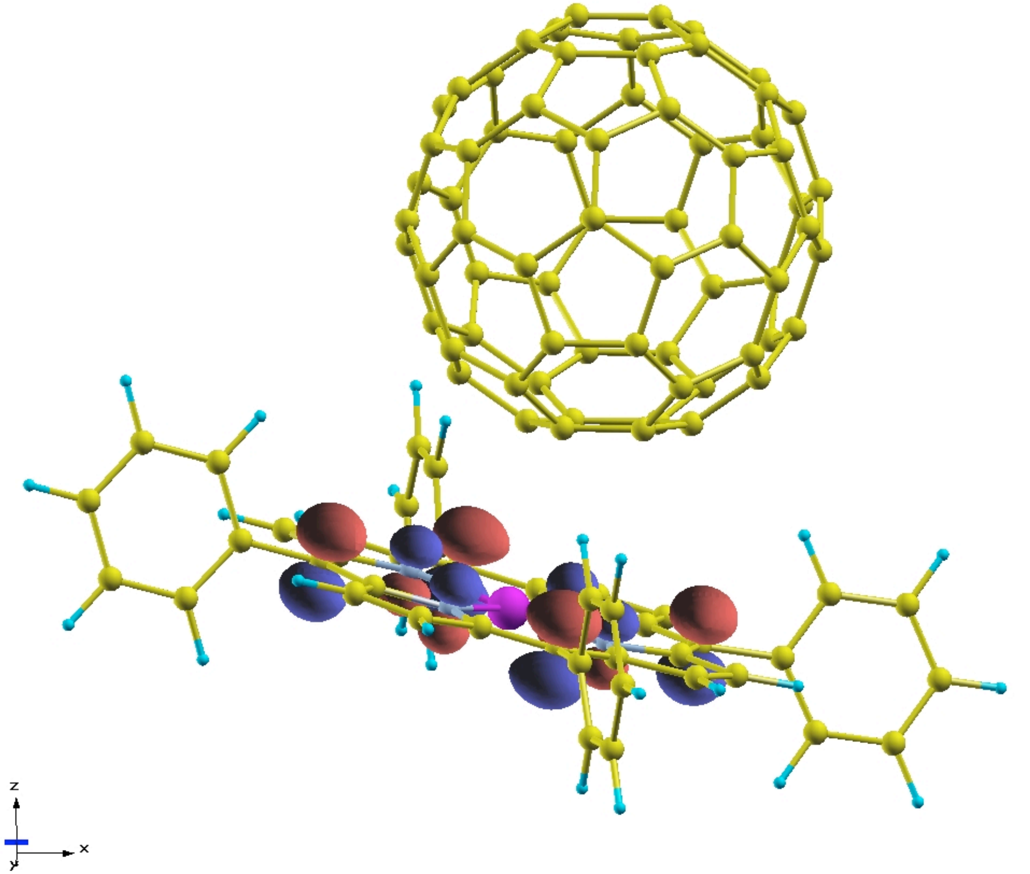
- Basic ground-state electronic structure
- Post-processing: Wannier Functions, Conductivities, etc..
- Linear response: Phonons, …
- Car-Parrinello Molecular Dynamics
- Rather large and active developer community

Example of a typical Nano-System treated with Quantum Espresso



Obtain equilibrium geometry

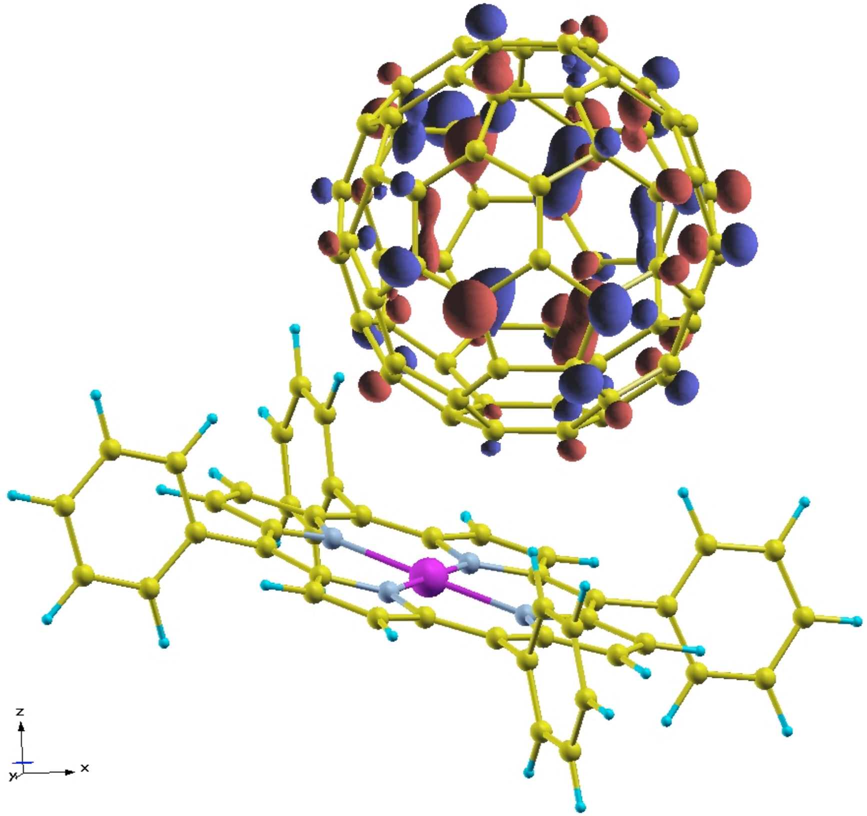
Energetics, electronic structure, …



HOMO

Obtain equilibrium geometry

Energetics, electronic structure, …



LUMO

The dark side:

Many well known failures of the approximate functionals

Important limitation: DFT is a ground state theory only

Particularly relevant for this audience:
Often one needs very fast (expensive) computers to treat the really interesting system sizes

Going to electronic excitations: Time-dependent DFT

1964: Hohenberg and Kohn: Density Functional Theory (DFT)

work in terms of electron density (instead of many-particle wavefunctions)

DFT is a **ground state** theory

1984: Runge and Gross: **Time-Dependent** Density Functional Theory (TDDFT)

$$\text{Given } |\Psi(t=0)\rangle : V(\boldsymbol{r},t) \Leftrightarrow n(\boldsymbol{r},t)$$

like DFT, TDDFT is **formally exact**

The Runge-Gross Theorem

Generalizing the HK theorem to time-dependent systems

There exists a one-to-one correspondence between the external v(r,t) and the electron density n(r,t), for systems evolving from a fixed many-body state.

Proof:

$$\begin{aligned} |\Psi(t_0)\rangle &= |\Psi'(t_0)\rangle \equiv |\Psi_0\rangle \\ n(\boldsymbol{r},t_0) &= n'(\boldsymbol{r},t_0) \equiv n^0(\boldsymbol{r}) \\ \boldsymbol{j}(\boldsymbol{r},t_0) &= \boldsymbol{j}'(\boldsymbol{r},t_0) \equiv \boldsymbol{j}^0(\boldsymbol{r}) \end{aligned}$$

Step 1: Different potentials v and v’ yield different current densities j and j’

Step 2: Different current densities j and j’ yield different densities n and n’

$$v(\boldsymbol{r},t) \neq v'(\boldsymbol{r},t) + c(t) \qquad \Rightarrow \qquad n(\boldsymbol{r},t) \neq n'(\boldsymbol{r},t)$$

Using TDDFT in practice

Finding an equivalent of the Kohn-Sham formalism

$$\mathrm{i}\frac{\partial}{\partial t}\varphi_{i\sigma}(\boldsymbol{r},t) = \hat{H}^{\mathrm{KS}}_{\sigma}(\boldsymbol{r},t)\varphi_{i\sigma}(\boldsymbol{r},t)$$

With a time-dependent Hamiltonian:

$$\hat{H}^{\mathrm{KS}}_{\sigma}(\boldsymbol{r},t) = -\frac{\nabla^2}{2} + v^{\mathrm{KS}}_{\sigma}[n_\uparrow, n_\downarrow](\boldsymbol{r},t)$$

Density and potentials are now defined like:

$$n_\sigma(\boldsymbol{r},t) = \sum_{i}^{N_\sigma} |\varphi_{i\sigma}(\boldsymbol{r},t)|^2$$

$$v^{\mathrm{KS}}_{\sigma}[n_\uparrow, n_\downarrow](\boldsymbol{r},t) = v_\sigma(\boldsymbol{r},t) + \int \mathrm{d}^3r' \, \frac{n(\boldsymbol{r}',t)}{|\boldsymbol{r}-\boldsymbol{r}'|} + v^{\mathrm{xc}}_{\sigma}[n_\uparrow, n_\downarrow](\boldsymbol{r},t)$$

Which functional to use ?

The easiest and probably most widely used functional is the

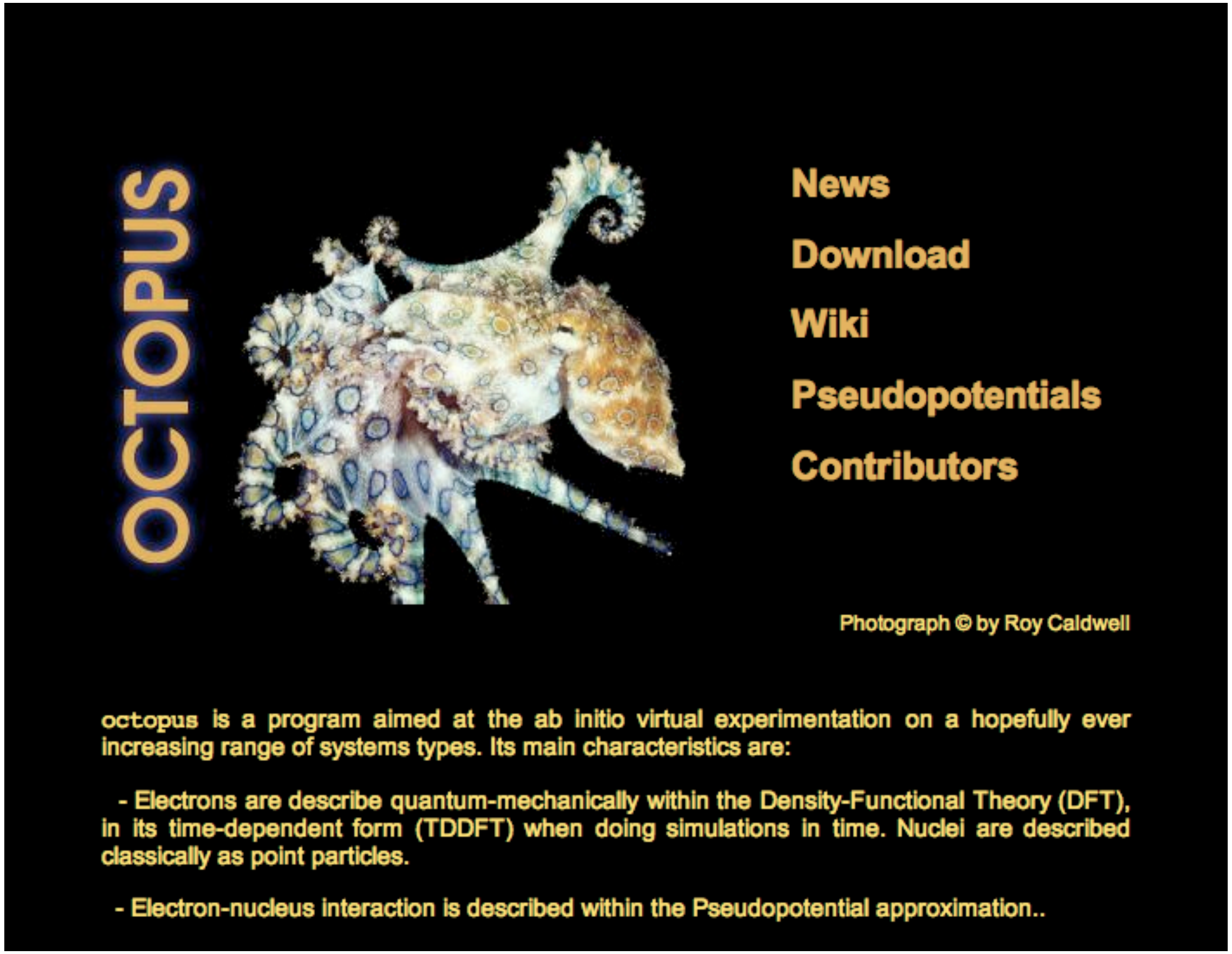
Adiabatic Local Density Approximation (ALDA)

$$v_\sigma^{\mathrm{xc\ ALDA}}(\boldsymbol{r},t) = \frac{\partial}{\partial n_\sigma}\left[n\,\varepsilon_{\mathrm{xc}}^{\mathrm{unif}}(n_\uparrow,n_\downarrow)\right]\Big|_{n_\alpha=n_\alpha(\boldsymbol{r},t)}$$

TDDFT in real time:

(1996:Bertsch; 2001: Octopus code)

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



Photograph © by Roy Caldwell

octopus is a program aimed at the ab initio virtual experimentation on a hopefully ever increasing range of systems types. Its main characteristics are:

- Electrons are describe quantum-mechanically within the Density-Functional Theory (DFT), in its time-dependent form (TDDFT) when doing simulations in time. Nuclei are described classically as point particles.

- Electron-nucleus interaction is described within the Pseudopotential approximation..

TDDFT in real time:

(1996:Bertsch; 2001: Octopus code)

- Consider a general time-dependent perturbation:

$$V_{pert}(\boldsymbol{r}, t)$$

- Obtain orbitals, charge density, and potentials by solving the Schrödinger equation explicitly in real time:

$$\psi_j(t+\Delta) = \exp\left(-iH(t+\frac{\Delta}{2})\Delta\right)\psi_j(t)$$

(*Nonlinear* TD Schrödinger equation)

- Can be used for *linear response* calculations, or for general TD *non-linear* problems.

How can we calculate optical spectra?

Consider a perturbation δV applied to the ground-state system:

$$\delta n(r,t) = \int d^3r' dt' \chi(r,r';t-t')\,\delta V(r',t')$$

The induced dipole is given by the induced charge density:

$$d(t) = \int d^3r\,\delta n(r,t)\hat{r}$$

Consider the perturbation due to an electric field:

$$\delta V(r,t) = -eE_{ext}(t)\cdot\hat{r}$$

How can we calculate optical spectra?

The dipole susceptibility is then given by:

$$d(t) = \int dt' \, \alpha(t - t') \, E_{ext}(t')$$

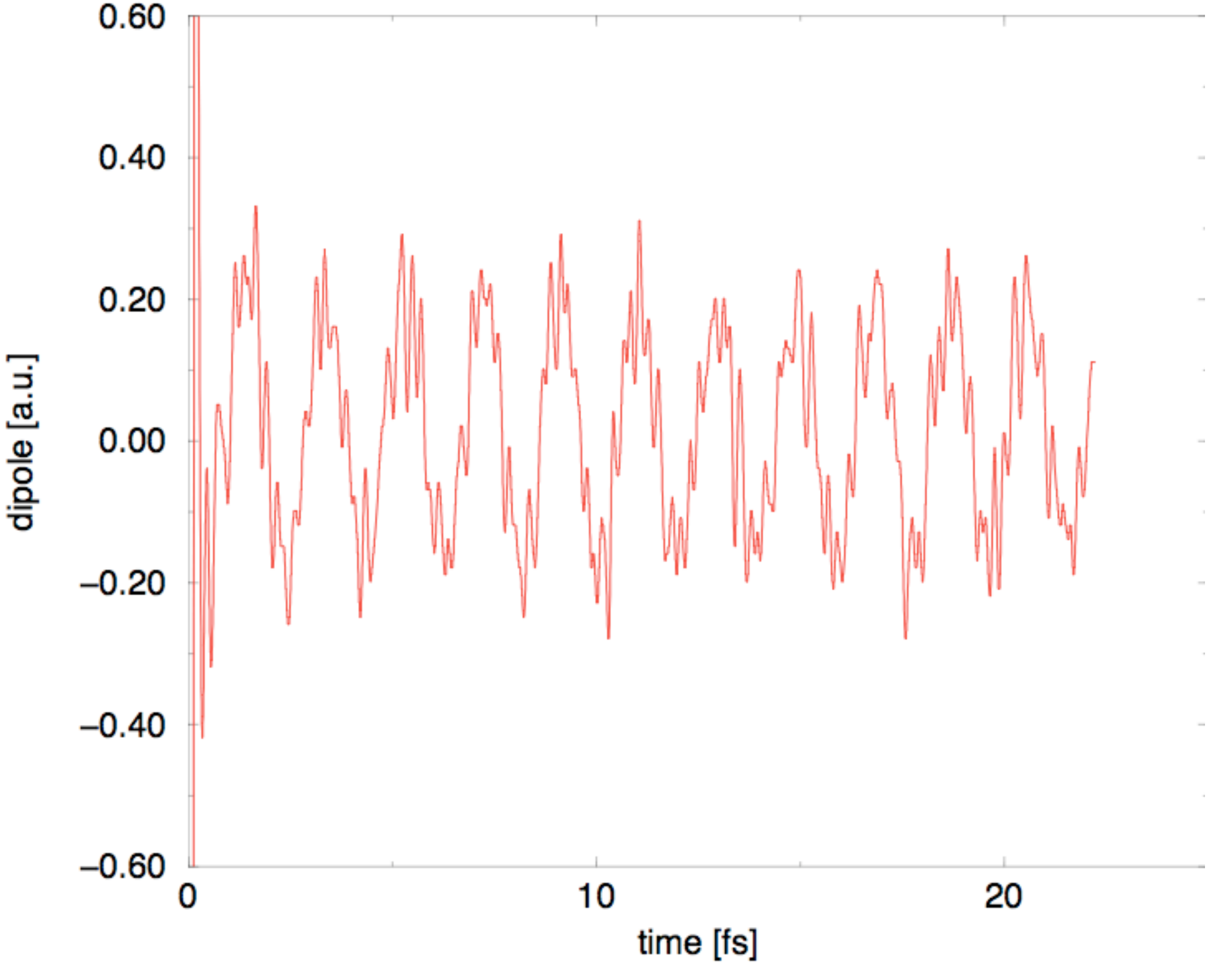
The experimentally measured strength function S is related to the Fourier transform of α:

$$S(\omega) = \frac{2m}{\pi e^2 \hbar} \, \omega \, \mathrm{Im} \, \alpha(\omega)$$

In practice: We take an E-field pulse $E_{ext} = E_0 \, \delta(t)$, calculate d(t), and obtain the spectrum $S(\omega)$ by calculating

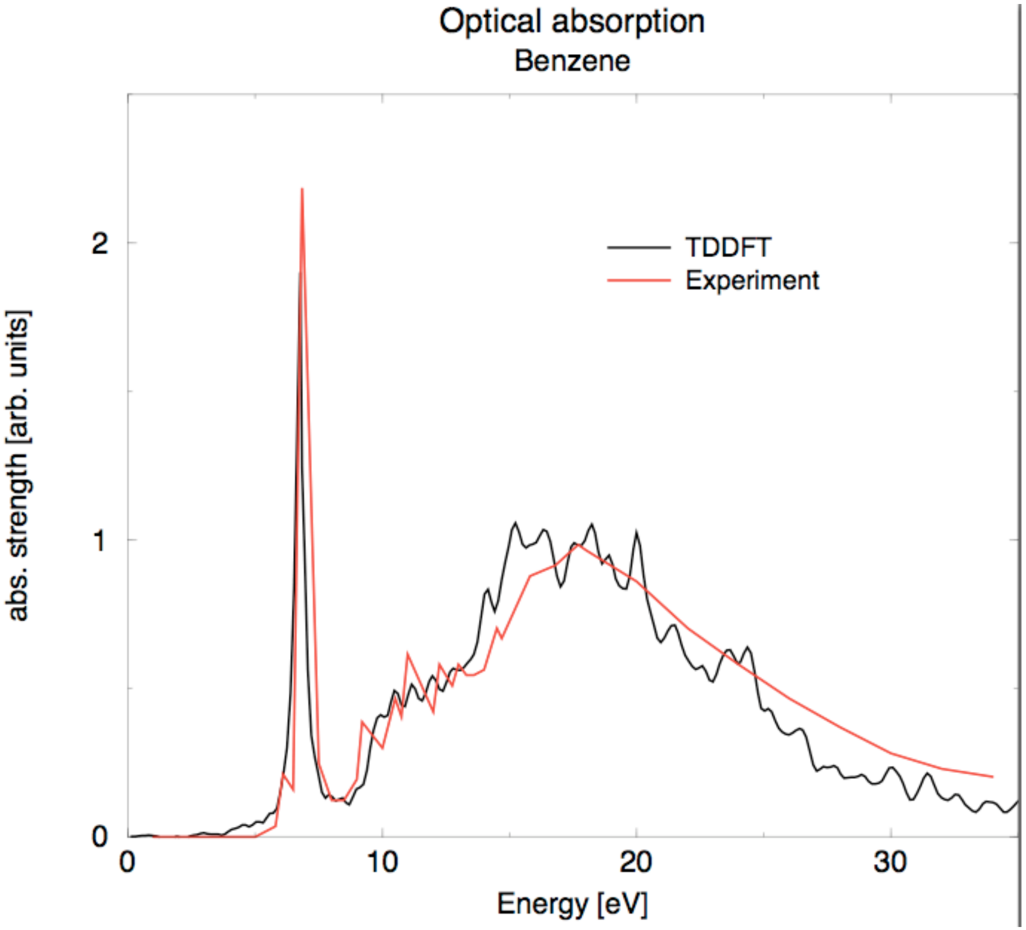
$$d(\omega) = \int_0^\infty dt \, e^{i\omega t - \delta t} \, d(t)$$

A typical dipole-function d(t) …



How well does it work?

Example: Optical absorption of Benzene



Experimental data from:
Koch, E.E., Otto, A.
Chem. Phys. Lett. **12**, 476 (1972)

A first application: Photochemistry

- Recent experimental progress made it possible to produce ultra-short intense laser pulses (few fs)
- This allows one to probe bond breaking/formation, charge transfer, etc. on the relevant time scales

- Nonlinear real-time TDDFT calculations can be a valuable tool to understand the physics of this kind of probe.

- Visualizing chemical bonds: Electron localization function

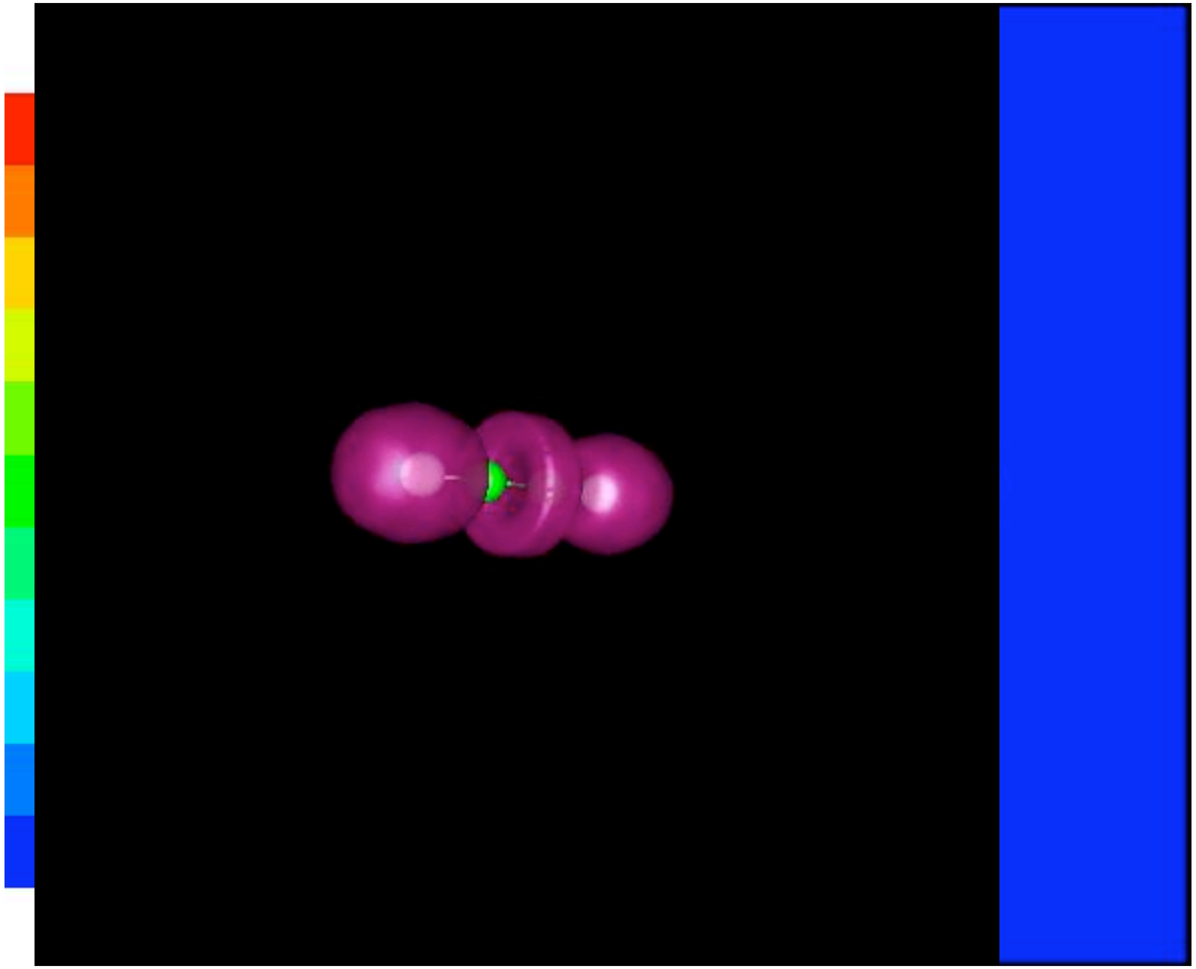
Nonlinear optical response

- Electron localization function:

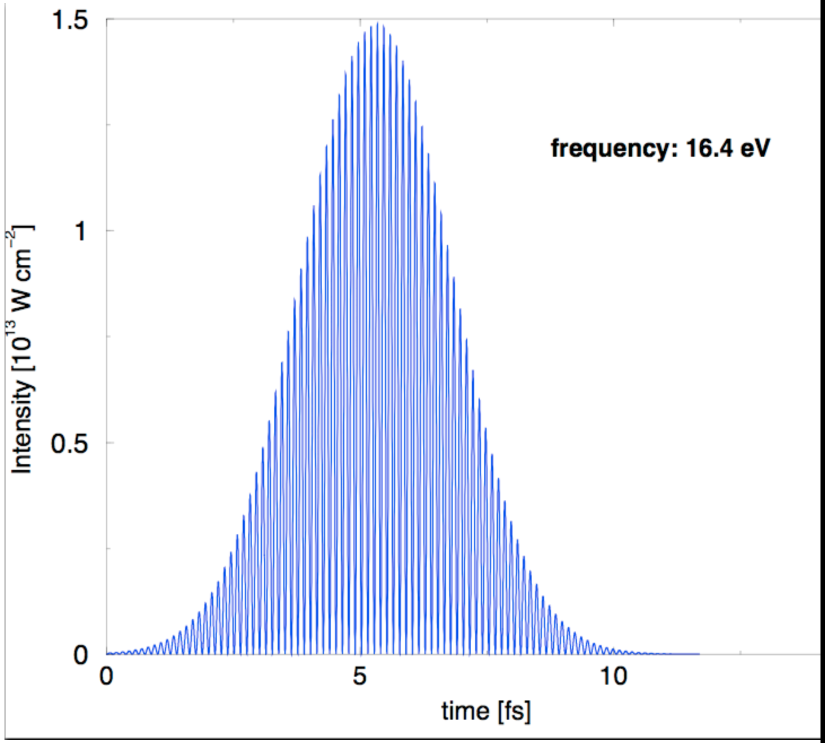
$$ELF(\boldsymbol{r},t) = \frac{1}{1+\left[D_\sigma(\boldsymbol{r},t)/D_\sigma^0(\boldsymbol{r},t)\right]^2}$$

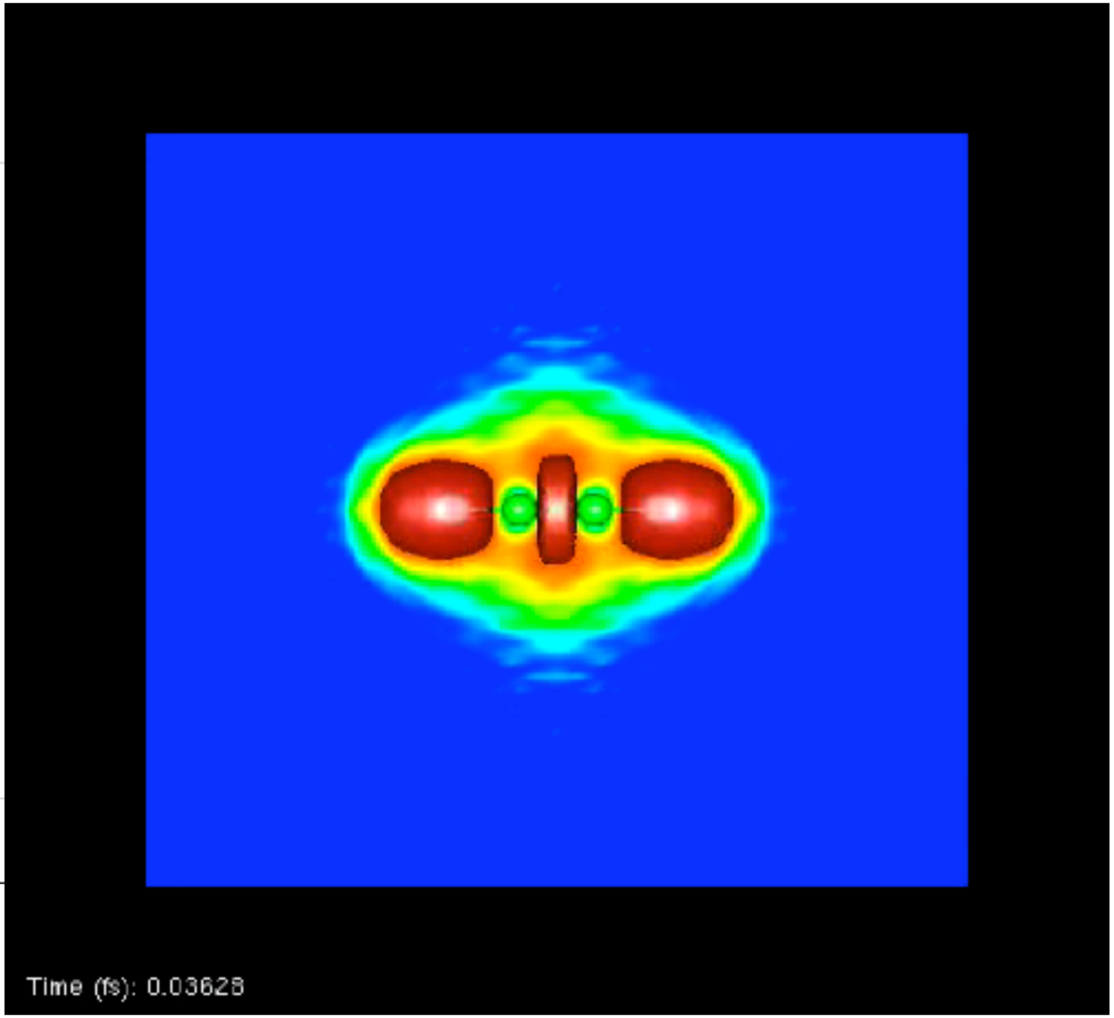
$$D_\sigma(\boldsymbol{r},t) = \tau_\sigma(\boldsymbol{r},t) - \frac{1}{4}\frac{\left[\nabla n_\sigma(\boldsymbol{r},t)\right]^2}{n_\sigma(\boldsymbol{r},t)} - \frac{j_\sigma^2(\boldsymbol{r},t)}{n_\sigma(\boldsymbol{r},t)}$$

Example: Ethyne C_2H_2



Example: Ethyne C_2H_2





Linear response formalism in TDDFT:

- Calculate the system's ground state using DFT
- Consider a monochromatic perturbation:

$$V_{pert}(\boldsymbol{r},t) = V_0(\boldsymbol{r})\left(\exp(i\omega t) + \exp(-i\omega t)\right)$$

- Linear response: assume the time-dependent response:

$$\psi_j(t) = e^{-i\epsilon_j t}\left(\psi_j^0 + \delta\psi_j^+ e^{i\omega t} + \delta\psi_j^- e^{-i\omega t}\right)$$

$$\delta n(\boldsymbol{r},t) = \delta n^+(\boldsymbol{r})e^{i\omega t} + \delta n^-(\boldsymbol{r})e^{-i\omega t}$$

$$\delta V(\boldsymbol{r},t) = V_{pert}(\boldsymbol{r},t) + \delta V_{SCF}^+(\boldsymbol{r})e^{i\omega t} + \delta V_{SCF}^-(\boldsymbol{r})e^{-i\omega t}$$

- Put these expressions into the TD Schrödinger equation

Linear response formalism in TDDFT:

$$
\begin{aligned}
\omega\delta\psi_v^+(\boldsymbol{r}) &= \left(H_{KS}^0 - \epsilon_v^0\right)\delta\psi_v^+ + \hat{P}_v\left(\delta V_{SCF}^+(\boldsymbol{r}) + V_{pert}(\boldsymbol{r})\right)\psi_v^0(\boldsymbol{r}) \\
-\omega\delta\psi_v^-(\boldsymbol{r}) &= \left(H_{KS}^0 - \epsilon_v^0\right)\delta\psi_v^- + \hat{P}_v\left(\delta V_{SCF}^-(\boldsymbol{r}) + V_{pert}(\boldsymbol{r})\right)\psi_v^0(\boldsymbol{r})
\end{aligned}
$$

Now define the following linear combinations:

$$
\begin{aligned}
x_v(\boldsymbol{r}) &= \frac{1}{2}\left(\delta\psi_v^+(\boldsymbol{r}) + \delta\psi_v^-(\boldsymbol{r})\right) \\
y_v(\boldsymbol{r}) &= \frac{1}{2}\left(\delta\psi_v^+(\boldsymbol{r}) - \delta\psi_v^-(\boldsymbol{r})\right)
\end{aligned}
$$

$$(\omega - \mathcal{L})\,|\boldsymbol{x},\boldsymbol{y}\rangle = |\mathbf{0},\boldsymbol{v}\rangle \qquad\qquad \mathcal{L} = \begin{pmatrix} 0 & D \\ K & 0 \end{pmatrix}$$

With the following definitions:

$$\begin{aligned} D\,|\boldsymbol{x}\rangle &= \left\{\left(H^0_{KS} - \epsilon_i\right) x_i(\boldsymbol{r})\right\} \\ K\,|\boldsymbol{x}\rangle &= \left\{\left(H^0_{KS} - \epsilon_i\right) x_i(\boldsymbol{r}) + \psi^0_i(\boldsymbol{r}) \sum_j \int d\boldsymbol{r}' \;\; f_{Hxc}(\boldsymbol{r},\boldsymbol{r}')\psi^0_{i'}(\boldsymbol{r}')x_{i'}(\boldsymbol{r}')\right\} \end{aligned}$$

$$\begin{pmatrix} 0 & D \\ K & 0 \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix} = \omega \begin{pmatrix} x \\ y \end{pmatrix}$$

Advantages:

One obtains not only the frequency (and oscillator strength), but the fulll eigenvector of each elementary excitation.

[Info can be used for spectroscopic assignments, to calculate forces, etc]

Disadvantages:

One obtains not only the frequency (and oscillator strength), but the fulll eigenvector of each elementary excitation.

[Info is often not needed, all the information is immediately destroyed after computation]

Computationally extremely demanding (large matrices to be diagonalized)

Conclusions

DFT as an efficient way to compute electronic and structural properties in nanoscale systems

TDDFT as the extension for electronic non-groundstate properties

Possible applications range from linear to non-linear optical properties