Time-dependent density-functional theory and its rôle in quantum control

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Quantum Control Conference, BIRS (Banff), April 4th-8th 2011

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Collaborators:
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Outline

1. Preamble
2. TDDFT
    - Density Matrices, Density Functionals
    - TDDFT: theoretical foundations
    - Some applications
    - Computational aspects
3. QOCT + TDDFT
    - Optimization for the TDKS system
    - Charge transfer in a 2D quantum dot system
    - Population of excited states to trigger isomerization
    - Mixed quantum-classical systems
4. Other (single electron) work

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The key QOCT equations

$$\hat{H}[u](t) = \hat{\mathcal{H}} + \epsilon[u](t)\hat{V}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\hat{\rho}[u](t) = -\mathrm{i}\left[\hat{H}[u](t), \hat{\rho}[u](t)\right]$$

$$\hat{\rho}[u](t_0) = \hat{\rho}_0$$

Problem: find the maximum of $G[u] = \mathrm{Tr}\left(\hat{\rho}[u](T)\hat{A}\right)$.

$$\frac{\partial G}{\partial u}[u] = -\mathrm{i}\int_{t_0}^{T}\mathrm{d}\tau\,\frac{\partial \epsilon}{\partial u}[u](\tau)\mathrm{Tr}\left[\hat{\rho}[u](\tau)\left[\hat{\chi}[u](\tau), \hat{V}\right]\right]\,.$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\hat{\chi}[u](t) = -\mathrm{i}\left[\hat{H}[u](t), \hat{\chi}[u](t)\right]$$

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The key QOCT equations

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$$\frac{\mathrm{d}}{\mathrm{d}t}|\psi[u](t)\rangle = -\mathrm{i}\hat{H}[u](t)|\psi[u](t)\rangle$$

$$|\Psi[u](t_0)\rangle = |\Psi_0\rangle$$

Problem: find the extrema of $G[u] = \langle\Psi[u](T)|\hat{A}|\Psi[u](T)\rangle$.

$$\frac{\partial G}{\partial u}[u] = 2\mathrm{Im}\int_{t_0}^{T}\mathrm{d}\tau\;\frac{\partial\epsilon}{\partial u}[u](\tau)\langle\chi[u](t)|\hat{V}|\psi[u](t)\rangle$$

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Non-equilibrium linear response

Kubo's formula:

$$\hat{H}(t) = \hat{H}_0 - f(t)\hat{V}$$

$$\delta A(t) = \mathrm{Tr}\left[\rho(T)\hat{A}\right] - \mathrm{Tr}\left[\rho^{(0)}(T)\hat{A}\right]$$

$$\delta A(T) = \int_{-\infty}^{\infty} \mathrm{d}\tau\, f(\tau)\chi(T,\tau)$$

$$\chi(T,\tau) = \frac{\mathrm{i}}{\hbar}\theta(T-\tau)\mathrm{Tr}\left[\hat{\rho}(t_0)\left[\hat{A}_I(T), \hat{V}_I(\tau)\right]\right]$$

for

$$\hat{X}_I(t) = \mathrm{e}^{i(t-t_0)\hat{H}_0}\hat{X}\mathrm{e}^{-i(t-t_0)\hat{H}_0}$$

“Generalized” non-equilibrium linear response

Kubo’s formula:

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$$\hat{X}_I(t) = \hat{U}_0^\dagger(t,t_0)\hat{X}\hat{U}(t,t_0)\,.$$

QOCT equations in the language of LRT

We can identify

$$G[u+\Delta u] - G[u] = \delta A(T)\,,$$

for

$$\begin{aligned}\hat{H}_0(t) &= \mathcal{H} + \epsilon[u](t)\hat{V} = \hat{H}[u](t)\\ -f(t)\hat{V} &= \Delta u \frac{\partial \epsilon}{\partial u}[u]\hat{V}\end{aligned}$$

And Kubo's formula gives:

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For pure systems:

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If $\hat{H}(t) = \mathcal{H} + \epsilon(t)\hat{V}$,

$$\frac{\delta G}{\delta \epsilon(t)} = 2\mathrm{Im}\langle\chi[\epsilon](t)|\hat{V}|\Psi[\epsilon](t)\rangle\,.$$

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Non-relativistic many-electron problem

$$\hat{\mathcal{H}}|\Phi\rangle = E|\Phi\rangle$$

$$\hat{\mathcal{H}} = \sum_{i=1}^{N} \hat{t}_i + \sum_{i=1}^{N} v_{\text{ext}}(\hat{\vec{r}}_i) + \sum_{i<j}^{N} \frac{1}{|\hat{\vec{r}}_i - \hat{\vec{r}}_j|}\,,$$

$$v_{\text{ext}}(\vec{r}) = \sum_{\alpha=1}^{N_{\text{nuclei}}} \frac{Z_\alpha}{|\vec{r} - \vec{R}_\alpha|}\,.$$

- In fact, what we really want are the values of the observables, and perhaps of matrix elements:

$$\mathcal{O}[\Phi] = \langle\Phi|\hat{\mathcal{O}}|\Phi\rangle\,.$$

For example, $\hat{\mathcal{O}} = \hat{\mathcal{H}}$, and we have the energy:

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The Variational Principle and the wave function approaches

- The variational equation is equivalent to Schrödinger's equation:

  $$\frac{\delta}{\delta\Phi}\{\langle\Phi|\hat{\mathcal{H}}|\Phi\rangle - E\langle\Phi|\Phi\rangle\} = 0\,,$$

  where the variational search is done over all *antisymmetric* N-electron wave functions.
- Fully unconstrained search is not possible in general. The wave function based approaches assume a certain form for the wave function: The Rayleigh-Ritz method finds the extrma in a restricted space of wave functions.
- The wave function is too big, and perhaps an unnecessary object. ("Inadmissible", W. Kohn). This is the key reasoning behind density-matrix functional theories, in particular density functional theory.

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Density Matrices

- Density matrix:

$$\rho(x'_1,\ldots,x'_N|x_1,\ldots,x_N) = \Phi^*(x'_1,\ldots,x'_N)\Phi(x_1,\ldots,x_N)$$

- Reduced density matrices:

$$\Gamma^{(k)}(x'_1,\ldots,x'_k|x_1,\ldots,x_k) = \binom{N}{k}\int \mathrm{d}x_{k+1}\ldots\mathrm{d}x_N\Phi^*(x'_1,\ldots,x'_k,x_{k+1},\ldots,x_N)\Phi(x_1,\ldots,x_k,x_{k+1},\ldots,x_N)\,.$$

- Expectation values of k-body operator:

$$\langle\Phi|\hat{\mathcal{O}}^k|\Phi\rangle = \int \mathrm{d}x_1\ldots\mathrm{d}x_k\hat{\mathcal{O}}^k[\Gamma^{(k)}(x'_1,\ldots,x'_k|x_1,\ldots,x_k)]\,.$$

- And most operators of interest are either one or two body operators:

$$\Gamma^{(1)}(x'_1|x_1) = N\int \mathrm{d}x_2\ldots\mathrm{d}x_N\Phi^*(x'_1,x_2,\ldots,x_N)\Phi(x_1,x_2,\ldots,x_N)\,.$$

$$\Gamma^{(2)}(x'_1,x'_2|x_1,x_2) = \binom{N}{2}\int \mathrm{d}x_3\ldots\mathrm{d}x_N\Phi^*(x'_1,x'_2,x_3,\ldots,x_N)\Phi(x_1,x_2,x_3\ldots,x_N)\,.$$

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The Energy as a functional of $\Gamma^{(2)}$.

The energy is an exact functional of the second order density matrix:

$$E[\Gamma^{(2)}] = \int \mathrm{d}x \left[\frac{1}{2}\nabla^2\Gamma^{(1)}(x|x')\right]_{x'=x} + \int \mathrm{d}x v_{\mathrm{ext}}(\vec{x})\gamma^{(1)}(x) + \int \mathrm{d}x \int \mathrm{d}x' \frac{1}{|\vec{r}-\vec{r}'|}\gamma^{(2)}(x,x')\,.$$

$$\gamma^{(1)}(x) = \Gamma^{(1)}(x|x)\,.$$
$$\gamma^{(2)}(x,x') = \Gamma^{(2)}(x,x'|x,x')\,.$$

Summing over spin in $\gamma^{(1)}$ one obtains the electronic density:

$$n(\vec{r}) = \sum_\sigma \gamma^{(1)}(\vec{r}\sigma)\,.$$

The Variational Principle and the representability problem

- If $E = E[\Gamma^{(k)}]$ is exact (or is a suitable approximation), then:

  $$\frac{\delta E}{\delta \Gamma^{(k)}} = 0\,.$$

  solves the many-electron problem. Since we have an exact functional for $k = 2$, we have an exact variational approach for two-point functions, instead of for the N-point wave function!!
- But... we must perform a constrained search: $\Gamma^{(k)}$ must be N-representable:
  $\Gamma^{(k)}$ is N-representable if it stems from a N-particle wavefunction.
  And the N-representability conditions for $k = 2$ are horribly difficult.
- The lower k, the easier the computational problem. Ideally, we would like to do a variational search over one-point functions, i.e. use a functional of the density:

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  solves the many-electron problem. Since we have an exact functional for $k = 2$, we have an exact variational approach for two-point functions, instead of for the N-point wave function!!
- But... we must perform a constrained search: $\Gamma^{(k)}$ must be N-representable:
  $\Gamma^{(k)}$ is N-representable if it stems from a N-particle wavefunction.
  And the N-representability conditions for $k = 2$ are horribly difficult.
- The lower k, the easier the computational problem. Ideally, we would like to do a variational search over one-point functions, i.e. use a functional of the density:

  $$E = E[n]\,.$$

Ground state density-functional theory

- First Hohenberg-Kohn theorem: there exists a one-to-one correspondence between electronic densities and external potentials. Therefore, the density determines the external potential, and for every observable there exists a functional of the density.
- Second Hohenberg-Konh theorem: there is an enery functional, $E = E[n]$, such that

  $$E[n] \geq E[n_0],$$

  for n_0 the ground state density, and such that

  $$E[n_0] = E_0,$$

  for E_0 the ground state energy.

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The time-dependent one-to-one mapping

- System $\mathcal{S}$: $\hat{H} = \hat{T} + \hat{W} + \hat{V}(t)$
  - $\hat{W} = \frac{1}{2}\sum_{i\neq j}\frac{1}{\hat{r}_{ij}}$ is the electronic interaction.
  - $\hat{V}(t) = \sum_i v(\hat{r}_i, t)$ is the external field seen by the electrons.
  - $|\Phi(t=0)\rangle = |\Phi_0\rangle \Rightarrow n(\vec{r},t) = \langle\Phi(t)|\hat{n}(\vec{r})|\Phi(t)\rangle$.
- System $\mathcal{S}'$: $\hat{H}' = \hat{T} + \hat{W}' + \hat{V}'(t)$
  - Question: Given $\hat{W}'$, is there any $v'(\vec{r},t)$ such that:

$$n'(\vec{r},t) = \langle\Phi'(t)|\hat{n}(\vec{r})|\Phi'(t)\rangle = n(\vec{r},t) \ \ ?$$

  - Answer: Yes, and it is unique.

[R. van Leeuwen, Phys. Rev. Lett. **82** 3863 (1999).]

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The Runge-Gross theorem, and the TDKS system

- Now assume that W'=W.
  $v'(\vec{r},t) = v(\vec{r},t)$ obviously, but the theorem also tells us that it is unique:
  There exists a unique relationship between time-dependent densities and external potentials.
  E. Runge and E. K. U. Gross, Phys. Rev. Lett. **52**, 997 (1984).
- And now assume that W'=0. I.e., we have a non-interacting system.

  There exists a potential $v'(\vec{r},t)$ for this non-interacting system such that it *reproduces* the density of the interacting system.

  This is the so-called time-dependent Kohn-Sham potential, $v_{\rm KS}(\vec{r},t)$. The evolution of the non-interacting system may be easily obtained by propagating single-particle equations (i.e. Runge-Gross or td Kohn-Sham equations):

$$\mathrm{i}\frac{\partial}{\partial t}\varphi_i(\vec{r},t) = -\frac{1}{2}\nabla^2\varphi_i(\vec{r},t) + v_{\rm KS}(\vec{r},t)\varphi_i(\vec{r},t)\,.$$

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Retrieval of observables in TDDFT

- The density of the *real*, interacting system, may be retrieved from the single-particle orbitals that solve the *auxiliary*, non-interacting system:

$$n(\vec{r},t) = \sum_{i=1}^{N} |\varphi_i(\vec{r},t)|^2 \,.$$

- The expectation value of any observable is a unique functional of the time-dependent density by virtue of the Runge-Gross theorem.
- Conclusion:

$$\cancel{\mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t}|\Psi(t)\rangle = \hat{H}(t)|\Psi(t)\rangle}$$

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But...

- RG is an *existence* theorem that is non-constructive: we do not know $v_{\rm KS}$.
- As in gs DFT, a smaller unknown part may be isolated:

$$v_{\rm KS}(\vec{r},t) = v(\vec{r},t) + u_{\rm Hartree}[n](\vec{r},t) + v_{\rm xc}[n](\vec{r},t)\,,$$

- Four decades of work on the development of *ground state* functionals have led to a `reasonable` success. For the time-dependent case, the *adiabatic approximation* is used, in which the ground-state functionals are used at each time. However, the true functional should have memory effects, and perhaps be relevant in the highly non-linear regime.

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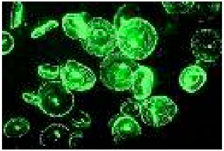
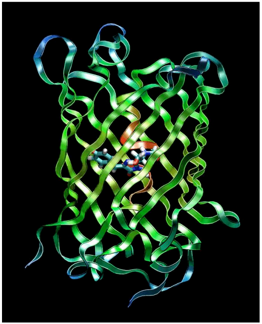
1. Optical absorption spectra (I)



Aequorea Victoria



- Problem: characterize the optical response of large nanosystems, such as proteins.
- Optical properties of the chromophore protected by the barrel structure.
- A small portion of the system exhibits “quantum” behaviour; the rest is classical.

1. Optical absorption spectra (II)

- We “kick” an atom/molecule with a sudden electric perturbation:

$$\mathbf{E}(t) = E_0\delta(t)\hat{\mathbf{z}} \Rightarrow \mathbf{E}(\omega) = E_0\hat{\mathbf{z}}$$

- If we calculate the evolution of the variation of the dipole moment, and obtain its Fourier transform, $\delta Z(\omega)$, we can easily obtain the dynamical polarizability:

$$\alpha_{zz}(\omega) = \frac{\delta Z(\omega)}{E_0}\,.$$

- The effect of this perturbation on the Kohn-Sham system is a phase shift at time zero: $\varphi_i(\vec{r}, t = 0^+) = e^{\mathrm{i}E_0 z}\varphi_i^{\mathrm{GS}}(\vec{r})$.
- The evolution is then followed by propagating the TDKS equations:

$$\begin{aligned} \mathrm{i}\frac{\partial}{\partial t}\varphi_i(\vec{r},t) &= -\frac{1}{2}\nabla^2\varphi_i(\vec{r},t) + v_{\mathrm{KS}}(\vec{r},t)\varphi_i(\vec{r},t)\,. \\ n(\vec{r},t) &= \sum_{i=1}^{N}|\varphi_i(\vec{r},t)|^2\,. \end{aligned}$$

$$\delta Z(t) = \int \mathrm{d}^3 r\, n(\vec{r},t) z - Z_0 \quad ; \quad \delta Z(\omega) = \int \mathrm{d}t e^{\mathrm{i}\omega t}\delta Z(t)\,.$$

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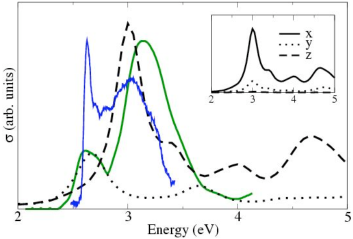


Phys. Rev. Lett. **90**, 258101 (2003).

- Experimental data are affected by solvent effects, and temperature; the key elements are the position of the peaks, and their relative strengths.
- Experimentally, both neutral and anionic configurations are present, probably at a 4:1 ration.
- Average over three spatial directions (the information about anisotropy is also accessible).
- TDLDA, for these molecules, and for this energy range, usually gives an error in the energies of about 0.1 - 0.2 eV.

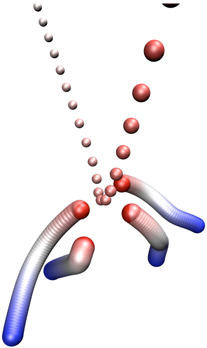
2. Mixed quantum-classical: non-adiabatic dynamics (I)

Many flavours of *ab initio* Molecular Dynamics (MD) based on (time-dependent) DFT.

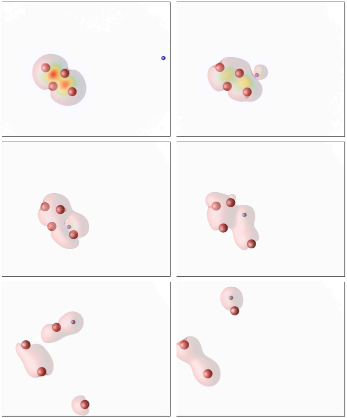
- “Traditional” Born-Oppenheimer MD.
- Car-Parrinello Molecular Dynamics.
- TDDFT Ehrenfest dynamics for the ground-state, possibly for excited states (J. L. Alonso, X. Andrade, P. Echenique, F. Falceto, D. Prada-Gracia, A. Rubio, 2008).
- Dynamics on excited potential energy surfaces: forces obtained through TDDFT linear response calculations
- Non-adiabatic couplings and transitions: surface hopping.
- Ehrenfest-path dynamics based on TDDFT: “mean field” or “most probable path” approach. Probes excited states, permits to study the effect of external laser fields.

2. Mixed quantum-classical: non-adiabatic dynamics (II)

$Li_4 + p$

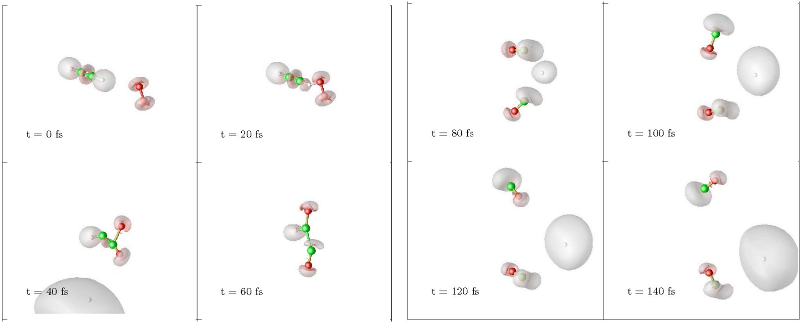


`http://arxiv.org/abs/1103.5306`



2. Mixed quantum-classical: non-adiabatic dynamics (III)

The so-called time-dependent electron localisation function can be used to monitor chemical bonds during chemical reactions.

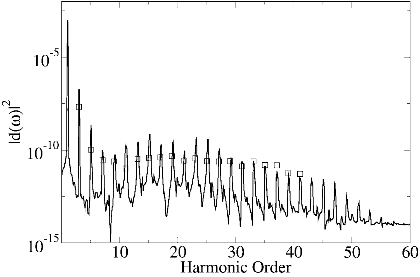


3. High harmonic generation

For large external perturbations (non-linear, or non-perturbative regime), one can directly propagate in time the TDKS equations. This permits, to obtain, e.g., harmonic spectra:

$$\sigma_{\rm emission} \propto \left| \int {\rm d}t e^{{\rm i}\omega t} \frac{\rm d}{{\rm d}t^2} d[n](t) \right|^2 ,$$

where $d[n](t)$ is the system dipole moment: $d[n](t) = \int {\rm d}^3 r n(\vec{r})(t) x$.



Harmonic spectrum for He at λ = 616 nm and I = 3.5 10^{14} W/cm^2. Calculations at the exact-exchange (within the KLI approximation) level of theory. [C. A. Ullrich, S. Erhard and E. K. U. Gross, 1996)]

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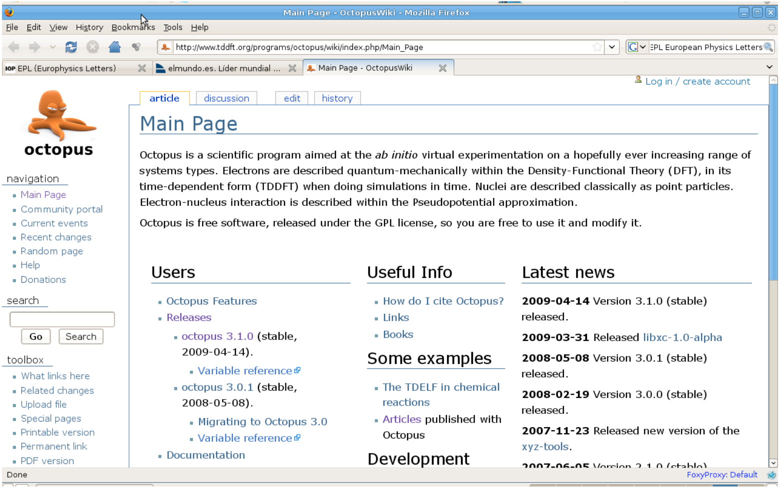
Computational



Main Page

Octopus is a scientific program aimed at the *ab initio* virtual experimentation on a hopefully ever increasing range of systems types. Electrons are described 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.

Octopus is free software, released under the GPL license, so you are free to use it and modify it.

Users

- Octopus Features
- Releases
  - octopus 3.1.0 (stable, 2009-04-14).
    - Variable reference
  - octopus 3.0.1 (stable, 2008-05-08).
    - Migrating to Octopus 3.0
    - Variable reference
- Documentation

Useful Info

- How do I cite Octopus?
- Links
- Books

Some examples

- The TDELF in chemical reactions
- Articles published with Octopus

Development

Latest news

2009-04-14 Version 3.1.0 (stable) released.

2009-03-31 Released libxc-1.0-alpha

2008-05-08 Version 3.0.1 (stable) released.

2008-02-19 Version 3.0.0 (stable) released.

2007-11-23 Released new version of the xyz-tools.

www.tddft.org/programs/octopus/

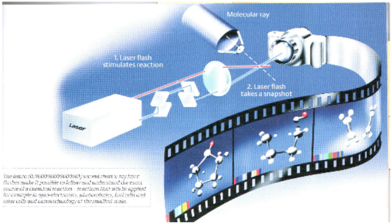
A. Castro et al, phys. stat. sol. (b) **243**, 2465 (2006).

Computational

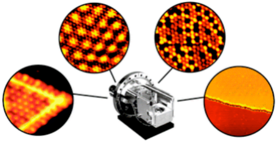
Theoretical Spectroscopy

New (expensive) experimental probes for matter:

Time resolved spectroscopies

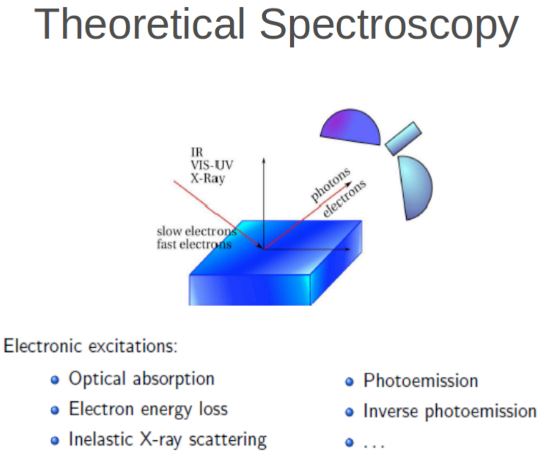


The femto ([illegible]) second short x-ray laser flashes make it possible to follow and understand the exact course of a chemical reaction – reactions that will be applied for example in opto-electronics, photovoltaics, fuel cells and solar cells and nanotechnology at the smallest scale.



Scanning probes

Computational

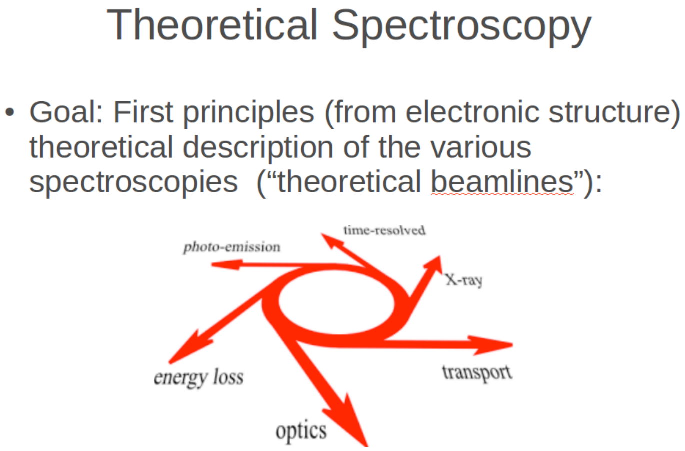


Theoretical Spectroscopy

Electronic excitations:

- Optical absorption
- Electron energy loss
- Inelastic X-ray scattering
- Photoemission
- Inverse photoemission
- ...

Computational



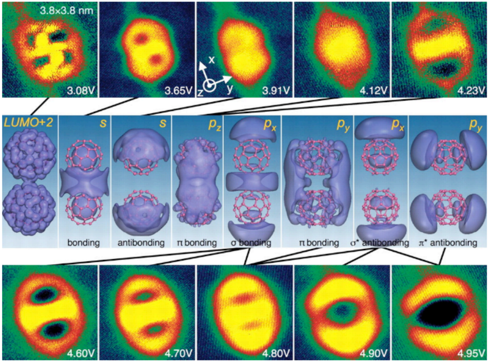
Theoretical Spectroscopy

- Goal: First principles (from electronic structure) theoretical description of the various spectroscopies ("theoretical beamlines"):

Computational

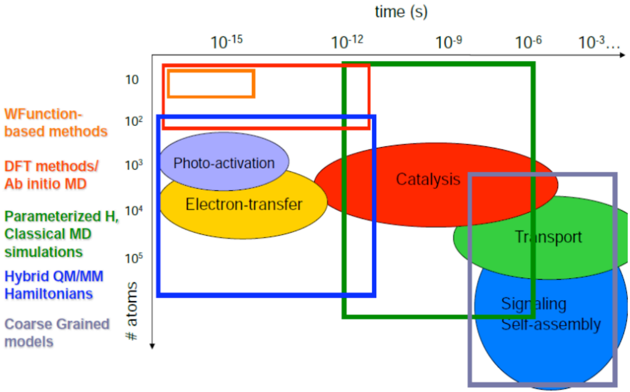
Theoretical Spectroscopy

Role: interpretation of (complex) experimental findings



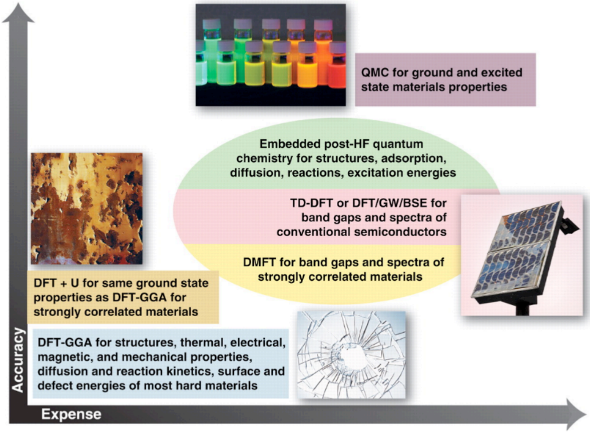
Computational

Theoretical Spectroscopy



Computational

Theoretical Spectroscopy



QMC for ground and excited state materials properties

Embedded post-HF quantum chemistry for structures, adsorption, diffusion, reactions, excitation energies

TD-DFT or DFT/GW/BSE for band gaps and spectra of conventional semiconductors

DMFT for band gaps and spectra of strongly correlated materials

DFT + U for same ground state properties as DFT-GGA for strongly correlated materials

DFT-GGA for structures, thermal, electrical, magnetic, and mechanical properties, diffusion and reaction kinetics, surface and defect energies of most hard materials

ETSF

- The octopus code is a member of the European Theoretical Spectroscopy Facility (ETSF, http://www.etsf.eu), which develops other platforms: abinit, yambo, exc, DP, etc.
- The targets of octopus are:
    - optical absorption spectra of molecules, clusters, nanostructures.
    - response to lasers (non-perturbative response to high intensity fields).
    - dichroism spectra, and other mixed (electric-magnetic) response.
    - adiabatic and non-adiabatic Molecular Dynamics (for e.g., infrared and vibrational spectra, photo-chemical reactions).
    - Quantum Optimal Control Theory.
    - . . .

Outline

1. Preamble
2. TDDFT
   - Density Matrices, Density Functionals
   - TDDFT: theoretical foundations
   - Some applications
   - Computational aspects
3. QOCT + TDDFT
   - Optimization for the TDKS system
   - Charge transfer in a 2D quantum dot system
   - Population of excited states to trigger isomerization
   - Mixed quantum-classical systems
4. Other (single electron) work

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Optimization for the TDKS system

- The optimization problem is first formulated for the real system of interacting electrons.
- Then, this optimization is substituted by an optimization for the fictitious system of Kohn-Sham electrons. This is exact if the target functional, initially a functional of the wave function of the real system, can be written exactly as a functional of the density.

$$F[\Psi] = \tilde{F}[n[\Psi]]$$

Optimization for the TDKS system

$$\boxed{\begin{aligned} \mathrm{i}\frac{\partial\varphi_i}{\partial t}(\vec{r}\sigma,t) &= -\frac{1}{2}\nabla^2\varphi_i(\vec{r}\sigma,t) + v_0(\vec{r})\varphi_i(\vec{r}\sigma,t) + \int \mathrm{d}^3r'\,\frac{n(\vec{r}',t)}{|\vec{r}'-\vec{r}|}\,\varphi_i(\vec{r}\sigma,t) \\ &\quad + \sum_{\tau} v_{\mathrm{xc}}^{\sigma\tau}[n_{\alpha\beta}]\varphi_i(\vec{r}\tau,t) + v_{\mathrm{ext}}(\vec{r},u,t)\varphi_i(\vec{r}\sigma,t)\,, \end{aligned}}$$

$$y = \begin{bmatrix} \varphi_1 \\ \dots \\ \varphi_N \end{bmatrix},$$

$$f[y(t),u,t] = -\mathrm{i}\begin{bmatrix} \hat{H}[n_{\alpha\beta}(t),u,t] & 0 & \dots & 0 \\ 0 & \hat{H}[n_{\alpha\beta}(t),u,t] & \dots & 0 \\ \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & \hat{H}[n_{\alpha\beta}(t),u,t] \end{bmatrix}\begin{bmatrix} \varphi_1(t) \\ \varphi_2(t) \\ \dots \\ \varphi_N(t) \end{bmatrix}$$

In condensed form:

$$\dot{\underline{\varphi}}(t) = -\mathrm{i}\underline{\hat{H}}[n(t),u,t]\underline{\varphi}(t)\,.$$

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In condensed form:

$$\dot{\underline{\varphi}}(t) = -\mathrm{i}\underline{\underline{\hat{H}}}[n(t),u,t]\underline{\varphi}(t)\,.$$

Optimization for the TDKS system (II)

- Definition of a target in terms of the Kohn-Sham orbitals:

$$F = F[\underline{\varphi}, u] \quad \Rightarrow \quad G[u] = F[\underline{\varphi}[u], u]$$

In usual cases, the target dependes only on the system at time T:

$$F[\underline{\varphi}[u], u] = J_1[\underline{\varphi}[u]] + J_2[u] = \langle \underline{\varphi}[u](T) | \hat{O} | \underline{\varphi}[u](T) \rangle + J_2[u]\,.$$

- Optimal control theory equations for this case:

$$\nabla_u G[u] = \nabla_u F[\underline{\varphi}[u], u] + 2\mathrm{Im}\left[\sum_{i=1}^{N} \int_0^T \mathrm{d}t\, \langle \lambda_i[u](t) | \nabla_u \hat{H}[n[u](t), u, t] | \varphi_i[u](t) \rangle \right]$$

$$\begin{aligned}
\dot{\underline{\varphi}}[u](t) &= -\mathrm{i}\underline{\underline{\hat{H}}}[n(t), u, t]\underline{\varphi}[u](t)\,, \\
\underline{\varphi}_u(0) &= \underline{\varphi}_0\,, \\
\dot{\underline{\lambda}}[u](t) &= -\mathrm{i}\left[\underline{\underline{\hat{H}}}[n(t), u, t] + \underline{\underline{\hat{K}}}[\underline{\varphi}[u](t)] \right] \underline{\lambda}[u](t)\,, \\
\underline{\lambda}[u](T) &= \frac{\delta F}{\delta \underline{\varphi}^*}[\underline{\varphi}[u](T), u]\,.
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$$\boxed{\dot{\underline{\lambda}}[u](t) = -\mathrm{i}\left[\underline{\underline{\hat{H}}}^{\dagger}[n[u](t),u,t] + \underline{\underline{\hat{K}}}[\underline{\varphi}[u](t)]\right]\underline{\lambda}[u](t)\,,}$$

$$\dot{\lambda}_i[u](t) = -\mathrm{i}\hat{H}^{\dagger}[n[u](t),u,t]\lambda_i[u](t) - \mathrm{i}\sum_{j=1}^{N}\hat{K}_{ij}[\underline{\varphi}[u](t)]\lambda_j[u](t)$$

$$\langle\vec{r}|\hat{K}_{ij}[\underline{\varphi}[u](t)]|\lambda_j[u](t)\rangle = -2\mathrm{i}\varphi_i[u](\vec{r},t)\mathrm{Im}\left[\int \mathrm{d}^3r'\,\lambda_j[u]^*(\vec{r}',t)f_{\mathrm{Hxc}}[n[u](t)](\vec{r},\vec{r}')\varphi_j[u](\vec{r}',t)\right]$$

$$f_{\mathrm{Hxc}}[n[u](t)](\vec{r},\vec{r}') = \frac{1}{|\vec{r}-\vec{r}'|} + f_{\mathrm{xc}}[n[u](t)](\vec{r},\vec{r}')$$

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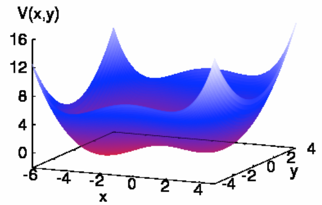
Charge transfer in a 2D quantum dot system

- System: double quantum dot, formed in a 2D electronic gas trapped in a semiconductor heterostructure.
- $V(x,y) = \frac{1}{64}x^4 - \frac{1}{4}x^2 + \frac{1}{32}x^3 + \frac{1}{2}y^2$



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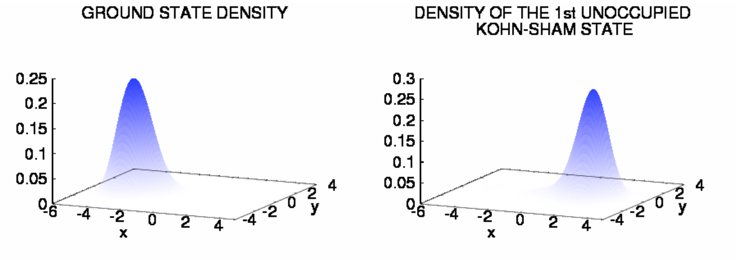


Charge transfer in a 2D quantum dot system (II)

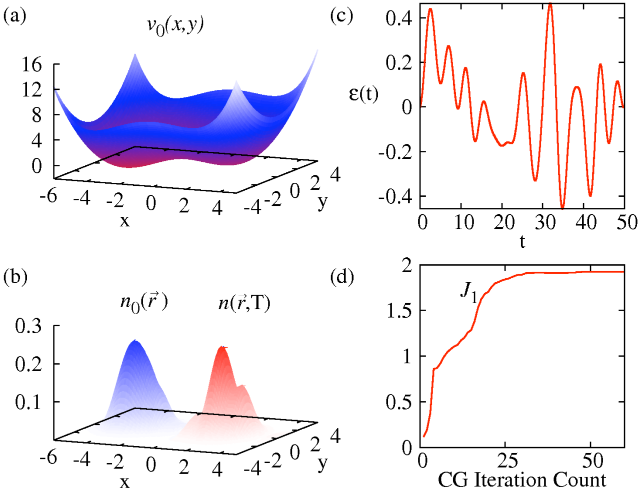
- Two electrons in a single orbital; LDA parameterisation of Attacalite *et al* [Attacalite et al,Phys. Rev. Lett. **88**, 256601 (2002)].
- Control: Electric field, expanded in a Fourier series:

$$\epsilon(t) = \sum_{n=1}^{N/2} a_n \sqrt{\frac{2}{T}}\cos(\frac{2\pi}{T}nt) + b_n \sqrt{\frac{2}{T}}\sin(\frac{2\pi}{T}nt)$$

- Target: transfer from one potential well to the other:

$$\begin{aligned} F[\underline{\varphi}, u = \{a, b\}] &= J_1[\underline{\varphi}] + J_2(\{a, b\})\,, \\ J_1[\underline{\varphi}] &= \int_{x>0} \mathrm{d}^2r\; n(\vec{r}, T)\,, \\ J_2(\{a, b\}) &= -\alpha \sum_{n=1}^{N/2} (a_n^2 + b_n^2) \end{aligned}$$

Charge transfer in a 2D quantum dot system (III)



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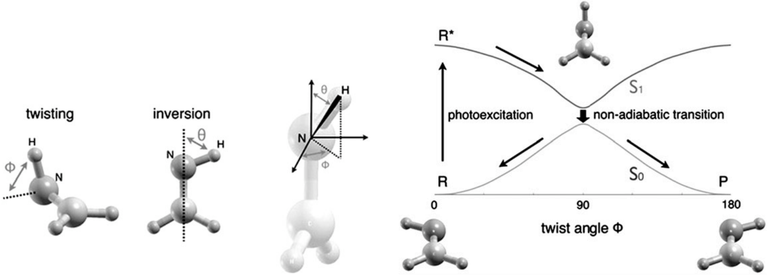
Isomerization

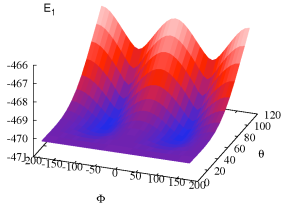
- System: formaldimine molecule, prototype of double bond rotation.

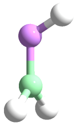


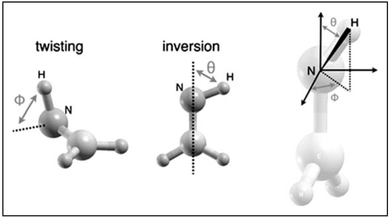
[Hirai and Sugino, PCCP **11**, 4421 (2009)]

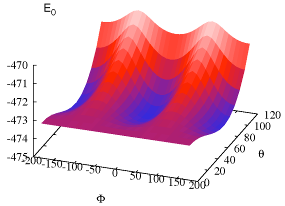
Isomerization (II)

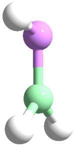
Potential energy surfaces (PBE / LDA kernel):











Isomerization (III)

- Target: population of the first excited state. The obvious choice would be to use the projection operator onto that state, but in TDDFT we do not have the state.
- Approximation of the target as a linear combination of Slater determinants:

$$|\Phi_I\rangle = \sum_{ia\sigma} c_{ia\sigma}\hat{a}^{\dagger}_{a\sigma}\hat{a}_{i\sigma}|\Phi_0\rangle$$

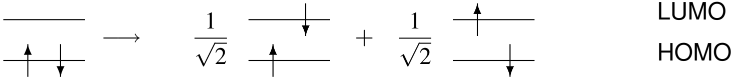
where:

  - $|\Phi_0\rangle$ is the ground state Kohn-Sham determinant.
  - $\{c_{ai\sigma}\}$ are the coefficients that result of the linear-response TDDFT computation for the I-th excitation:

$$\langle\Psi_0|\hat{X}|\Psi_I\rangle = \langle\Phi_0|\hat{X}|\Phi_I\rangle = \sum_{ai\sigma} c_{ia\sigma}\langle\phi^0_{i\sigma}|\hat{x}|\phi^0_{a\sigma}\rangle\,.$$

Isomerization (IV)

If the excitation is almost a pure HOMO-LUMO transition from a singlet spin unpolarized ground state:



The maximum possible population of this state is $\frac{1}{2}$!

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Optimization for a MQCS

$$\boxed{\begin{aligned} \dot{q}_i(t) &= \langle\Psi(t)|\frac{\partial\hat{H}}{\partial p_i}(q,p,u,t)|\Psi(t)\rangle\,, \\ \dot{p}_i(t) &= -\langle\Psi(t)|\frac{\partial\hat{H}}{\partial q_i}(q,p,u,t)|\Psi(t)\rangle\,. \\ |\dot{\Psi}(t)\rangle &= -\mathrm{i}\hat{H}(q,p,u,t)|\Psi(t)\rangle\,. \end{aligned}}$$

$$\hat{H}(q,p,u,t) = \hat{T}_Q + T_C(p) + \hat{V}(q,u,t)\,.$$

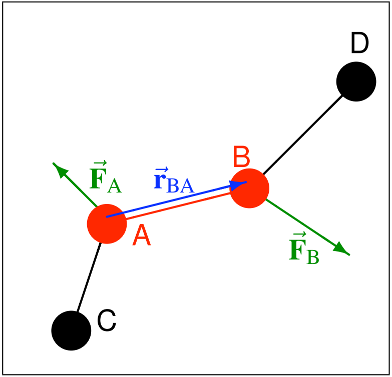
$$F[q,p,\Psi,u] = J_1[q(T),p(T),\Psi(T)] + J_2[u]\,.$$

Optimization for a MQCS

$$\begin{aligned}
\frac{\partial G}{\partial u_m}[u] \quad = \quad & \frac{\partial J_2}{\partial u_m}[u] + \int_0^T \mathrm{d}t\ \langle \Psi[u](t) | D(\tilde{q}[u](t), \tilde{p}[u](t)) \frac{\partial \hat{H}}{\partial u_m}[q[u](t), p[u](t), u, t] | \Psi[u](t) \rangle \\
& + 2\mathrm{Im} \int_0^T \mathrm{d}t\ \langle \chi(t) | \frac{\partial \hat{H}}{\partial u_m}[q[u](t), p[u](t), u, t] | \Psi[u](t) \rangle \, .
\end{aligned}$$

$$\begin{aligned}
\dot{\tilde{q}}_i(t) \quad &= \quad D(\tilde{q}(t), \tilde{p}(t)) \langle \Psi(t) | \frac{\partial \hat{H}}{\partial p_i}[q(t), p(t), u, t] | \Psi(t) \rangle - 2\mathrm{Re}\mathrm{i} \langle \chi(t) | \frac{\partial \hat{H}}{\partial p_i}[q(t), p(t), u, t] | \Psi(t) \rangle \, , \\
\dot{\tilde{p}}_i(t) \quad &= \quad -D(\tilde{q}(t), \tilde{p}(t)) \langle \Psi(t) | \frac{\partial \hat{H}}{\partial q_i}[q(t), p(t), u, t] | \Psi(t) \rangle + 2\mathrm{Re}\mathrm{i} \langle \chi(t) | \frac{\partial \hat{H}}{\partial q_i}[q(t), p(t), u, t] | \Psi(t) \rangle \, , \\
| \dot{\chi}(t) \rangle \quad &= \quad -\mathrm{i} \hat{H}^{\dagger}[q(t), p(t), u, t] | \chi(t) \rangle + D(\tilde{q}(t), \tilde{p}(t)) \hat{H}[q(t), p(t), u, t] | \Psi(t) \rangle \, . \\
\tilde{q}_i(T) \quad &= \quad -\frac{\partial J_1}{\partial p_i}[q(T), p(T), \Psi(T)] \, , \\
\tilde{p}_i(T) \quad &= \quad \frac{\partial J_1}{\partial q_i}[q(T), p(T), \Psi(T)] \, , \\
| \chi(x, T) \rangle \quad &= \quad \frac{\delta J_1}{\delta \Psi^*(x, T)} \, ,
\end{aligned}$$

Design of bond-breaking laser pulses



- If the AB bond is breaking,

$$\begin{aligned} \vec{\mathbf{r}}_{\mathrm{BA}} \cdot \vec{\mathbf{F}}_{\mathrm{B}} &> 0 \\ \vec{\mathbf{r}}_{\mathrm{BA}} \cdot \vec{\mathbf{F}}_{\mathrm{A}} &< 0 \end{aligned}$$

$$\Rightarrow$$

$$\begin{aligned} \vec{\mathbf{r}}_{\mathrm{BA}} \cdot \vec{\mathbf{F}}_{\mathrm{B}} - \vec{\mathbf{r}}_{\mathrm{BA}} \cdot \vec{\mathbf{F}}_{\mathrm{A}} &> 0 \Rightarrow \\ \vec{\mathbf{r}}_{\mathrm{BA}} \cdot \vec{\mathbf{F}}_{\mathrm{BA}} &> 0 \end{aligned}$$

$$(\vec{\mathbf{F}}_{\mathrm{BA}} = \vec{\mathbf{F}}_{\mathrm{B}} - \vec{\mathbf{F}}_{\mathrm{A}})$$

Design of bond-breaking laser pulses (III)

- Bond-breaking target:

$$J_1[\Psi] = \frac{1}{t_f - t_0} \int_{t_0}^{t_f} \mathrm{d}t \langle \Psi(t) | |\vec{\mathbf{r}}_{\mathrm{BA}}| |\hat{\vec{\mathbf{F}}}_{\mathrm{BA}}(t)| \left(1 + \vec{\mathbf{r}}_{\mathrm{BA}} \cdot \hat{\vec{\mathbf{F}}}_{\mathrm{BA}}(t) \right) | \Psi(t) \rangle \, .$$

- Within TDDFT, $\hat{\vec{\mathbf{F}}}_{\mathrm{A}}$ is a local density operator: the necessary expectation values can be written as simple density integrals.

$$\hat{\vec{\mathbf{F}}}_{\mathrm{A}}(t) = \int \mathrm{d}^3 r \, \hat{n}(\mathbf{r}) \, \nabla_{\vec{\mathbf{r}}_{\mathrm{A}}} v_{\mathrm{KS}}(\mathbf{r}, t) \, .$$

Design of bond-breaking laser pulses (III)

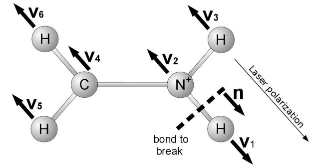
- Bond-breaking target:

$$J_1[\Psi] = \frac{1}{t_f - t_0}\int_{t_0}^{t_f} \mathrm{d}t \langle\Psi(t)| |\vec{\mathbf{r}}_{\mathrm{BA}}| |\hat{\vec{\mathbf{F}}}_{\mathrm{BA}}(t)| \left(1 + \vec{\mathbf{r}}_{\mathrm{BA}} \cdot \hat{\vec{\mathbf{F}}}_{\mathrm{BA}}(t)\right) |\Psi(t)\rangle \,.$$

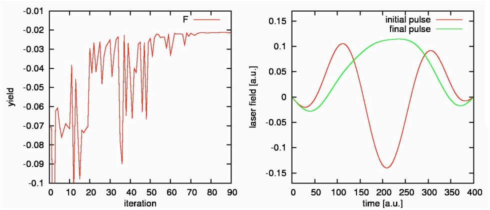
- Within TDDFT, $\hat{\vec{\mathbf{F}}}_{\mathrm{A}}$ is a local density operator: the necessary expectation values can be written as simple density integrals.

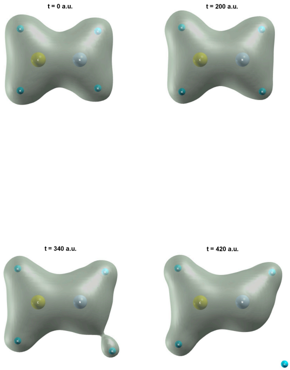
$$\hat{\vec{\mathbf{F}}}_{\mathrm{A}}(t) = \int \mathrm{d}^3 r \; \hat{n}(\mathbf{r}) \, \nabla_{\vec{\mathbf{r}}_{\mathrm{A}}} v_{\mathrm{KS}}(\mathbf{r}, t) \,.$$

Cleaving a NH bond



$$F = \mathbf{n} \cdot (\mathbf{v}_1 - \mathbf{v}_2) - 10 \sum_{i=1}^{6} |\mathbf{v}_i - \mathbf{v}_2|$$





Krieger et al., http://arxiv.org/abs/1102.3128.

Outline

1. Preamble
2. TDDFT
   - Density Matrices, Density Functionals
   - TDDFT: theoretical foundations
   - Some applications
   - Computational aspects
3. QOCT + TDDFT
   - Optimization for the TDKS system
   - Charge transfer in a 2D quantum dot system
   - Population of excited states to trigger isomerization
   - Mixed quantum-classical systems
4. Other (single electron) work

Control of currents in quantum rings

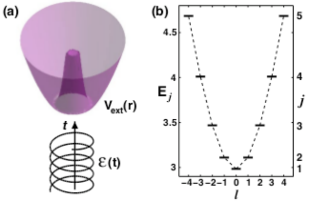


FIG. 1 (color online). (a) Shape of the external confining potential for a quantum ring and an example of a circularly polarized laser field. (b) Energy-level spectrum of a quantum ring. The transitions are allowed along the dashed line so that $\Delta l = \pm 1$.

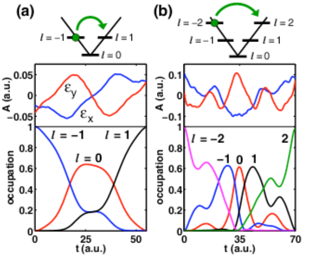


FIG. 4 (color online). Schematic picture of transitions from $l = -1$ to $l = 1$ (a) and from $l = -2$ to $l = 2$ (b) (upper panel), optimized fields for these transitions (middle panel), and the occupations of the states (lower panel).

E. Räsänen, AC, J. Werschnik, A. Rubio, and E. K. U. Gross, Phys. Rev. Lett. **98**, 157404 (2007).

Control of double quantum dots

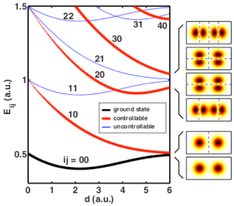


FIG. 1. (Color online) Left panel: lowest eigenenergies of a double quantum dot with $\omega_0=0.5$ as a function of the interdot distance. Black, red (thick), and blue (thin) curves mark the ground state, controllable states, and uncontrollable states, respectively. Right panel: densities of six lowest eigenstates at $d=5$. The dashed lines mark the nodes of the wave functions.

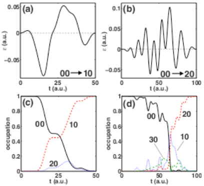
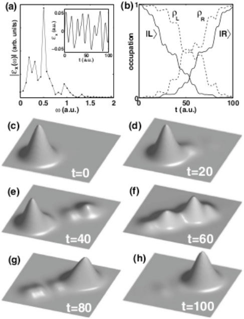


FIG. 3. (Color online) Upper panel: optimized pulses (x components) for transitions (a) $|00\rangle\rightarrow|10\rangle$ and (b) $|00\rangle\rightarrow|20\rangle$. The interdot distances are fixed to $d=3$ and 5 and the pulse lengths to $T=50$ and 100, respectively. Lower panel: occupations of states involved in the transitions.



E. Räsänen, AC, J. Werschnik, A. Rubio, and E. K. U. Gross, Phys. Rev. B **77**, 085324 (2008).

Acceleration of QOCT algorithms with mixing strategies

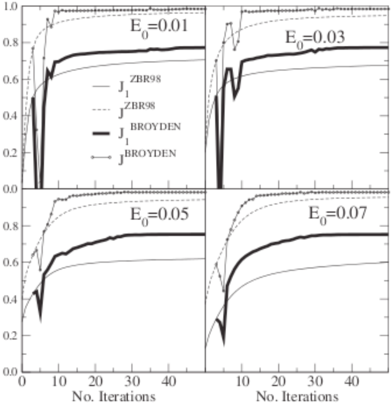


FIG. 3. Convergence histories for both the ZBR98 algorithm and the straight iteration scheme assisted with the modified Broyden mixing scheme. The modified Broyden scheme, however, is only applied after the third iteration.

AC and E. K. U. Gross, Phys. Rev. E **79**, 056704 (2009).

Ionization enhancement

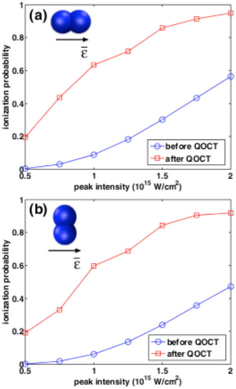


Fig. 1: (Color online) Ionization probability for the initial pulse (circles) and for the optimized pulse (squares) as a function of the peak intensity of the initial pulse. The polarization of the pulse is (a) parallel and (b) perpendicular to the molecule.

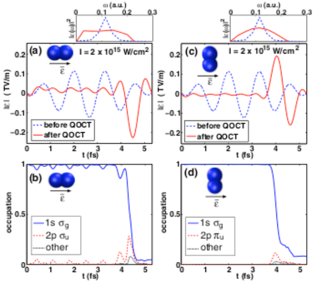


Fig. 2: (Color online) (a) Initial and optimized pulses (parallel polarization) and their power spectra (in arbitrary units) and (b) the occupation of selected single-electron states in the optimized ionization process, when $I = 2 \times 10^{15}$ W/cm^2. (c), (d) Same as (a), (b) but for perpendicular polarization.

AC, E. Räsänen, A. Rubio, and E. K. U. Gross, EPL **87**, 53001 (2009).

Conclusions

- TDDFT can be combined with QOCT, and the resulting equations are numerically tractable.
- This provides a scheme to perform QOCT calculations from first principles, in order to obtain tailored function-specific laser pulses capable of controlling the electronic state.
- Most of the previous applications of QOCT were targeted to control, with femto-second pulses, the motion of the nuclear wave packet on one or few potential energy surfaces, (scale of hundreds of femtoseconds). The approach presented here, on the other hand, controls the motion of the electronic degrees of freedom (sub-femto-second scale)
- Possibilities: shaping of the high harmonic generation spectrum, selective excitation of electronic excited states, control of the electronic current in molecular junctions, selective photo-chemistry, etc.
- arXiv:1009.2241v1 [physics.atm-clus]