Time-dependent density functional theory

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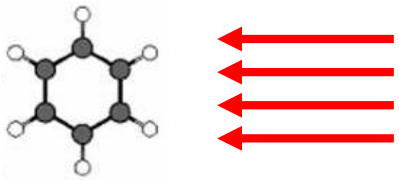
OUTLINE

- **Basics of TDDFT**
- **Linear response regime:**
  -- Calculation of excitation spectra
- **Beyond the linear regime:**
  -- TD Electron Localisation Function
  -- TD transport
  -- Demagnetization of ferromagnetic solids
  -- Control of harmonic generation

What do we want to describe?

System in laser field:
Generic situation



$$\hat{H}(t) = \hat{T}_e + \hat{W}_{ee} + \sum_{j,\alpha} - \frac{Z_\alpha e^2}{|r_j - R_\alpha|} + \vec{r}_j \cdot \vec{E}(t) \cdot \sin \omega t$$

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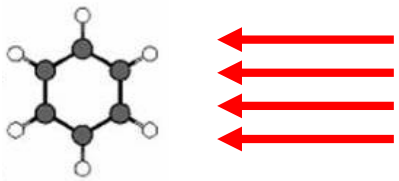

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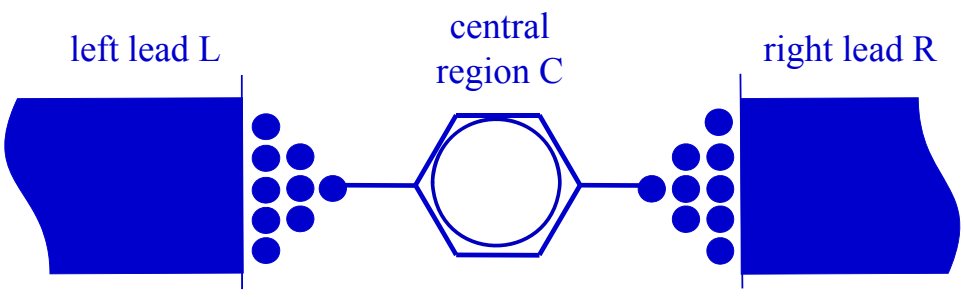
Electronic transport: Generic situation



Bias between L and R is turned on: U(t) ⟶ V

$$\hat{H}(t) = \hat{T}_e + \hat{W}_{ee} + \sum_{j,\alpha} - \frac{Z_\alpha e^2}{|r_j - R_\alpha|} + \vec{r}_j \cdot \vec{E}(t) \cdot \sin \omega t$$

Strong laser ($v_{laser}(t) \geq v_{en}$) :

Non-perturbative solution of full TDSE required

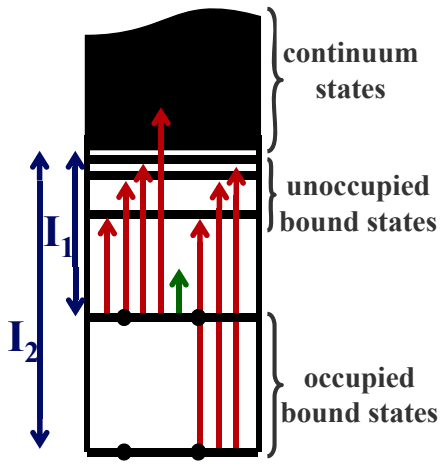
Weak laser ($v_{laser}(t) << v_{en}$) :

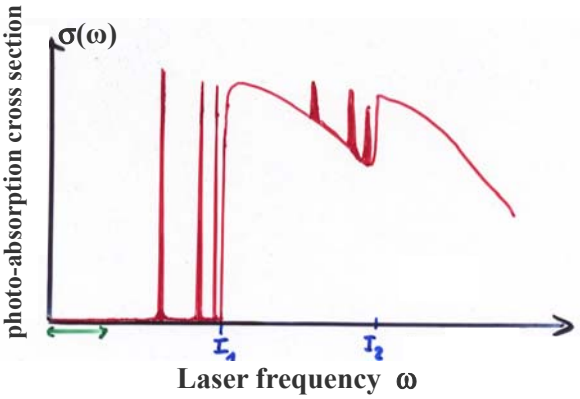
Calculate **1. Linear density response** $\rho_1(\vec{r}\,t)$

2. Dynamical polarizability $\alpha(\omega) = -\frac{e}{E}\int z\,\rho_1(\vec{r},\omega)\,d^3r$

3. Photo-absorption cross section $\sigma(\omega) = -\frac{4\pi\omega}{c}\,\mathrm{Im}\,\alpha$

Photo-absorption in weak lasers





Why don't we just solve the many-particle SE?

Example: Oxygen atom (8 electrons)

$\Psi(\vec{r}_1, \cdots, \vec{r}_8)$ depends on 24 coordinates

rough table of the wavefunction

10 entries per coordinate:	**$\Rightarrow 10^{24}$ entries**
1 byte per entry:	**$\Rightarrow 10^{24}$ bytes**
10^{10} bytes per DVD:	**$\Rightarrow 10^{14}$ DVDs**
10 g per DVD:	**$\Rightarrow 10^{15}$ g DVDs**
	$= 10^{9}$ t DVDs

ESSENCE OF DENSITY-FUNTIONAL THEORY

- **Every observable quantity of a quantum system can be calculated from the density of the system ALONE**
- **The density of particles interacting with each other can be calculated as the density of an auxiliary system of non-interacting particles**

Time-dependent density-functional formalism

(E. Runge, E.K.U.G., PRL 52, 997 (1984))

Basic 1-1 correspondence:

$$v(rt) \xleftrightarrow{1\text{-}1} \rho(rt)$$

The time-dependent density determines uniquely the time-dependent external potential and hence all physical observables for fixed initial state.

KS theorem:

The time-dependent density of the interacting system of interest can be calculated as density

$$\rho(rt) = \sum_{j=1}^{N} \left| \varphi_j(rt) \right|^2$$

of an auxiliary non-interacting (KS) system

$$i\hbar \frac{\partial}{\partial t} \varphi_j(rt) = \left(-\frac{\hbar^2 \nabla^2}{2m} + v_S[\rho](rt) \right) \varphi_j(rt)$$

with the local potential

$$v_S\left[\rho(r't')\right](rt) = v(rt) + \int d^3r' \frac{\rho(r't)}{|r-r'|} + v_{xc}\left[\rho(r't')\right](rt)$$

The functional $v_{xc}[\rho]$ is universal:

Curse or blessing?

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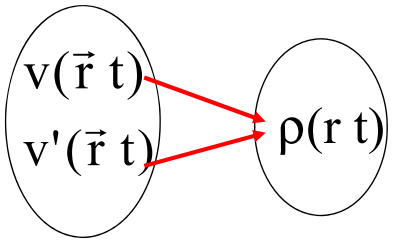
Functional can be systematically improved, i.e. results will improve -on average- for all systems. Systematic improvement for a single given system is not possible.

proof (basic idea):

to be shown that



is impossible

i.e. $v(\vec{r}\,t) \neq v'(\vec{r}\,t) + c(t) \Rightarrow \rho(\vec{r}\,t) \neq \rho'(\vec{r}\,t)$

$$v(\vec{r}\,t) \longrightarrow \vec{j}(\vec{r}\,t) \longrightarrow \rho(\vec{r}\,t)$$
$$v'(\vec{r}\,t) \longrightarrow \vec{j}'(\vec{r}\,t) \longrightarrow \rho'(\vec{r}\,t)$$

use $i\partial_t \vec{j}(\vec{r}\,t) = \left\langle \phi(t) \middle| \left[\hat{j}(\vec{r}), \hat{H}(t) \right] \middle| \phi(t) \right\rangle$

$$i\partial_t \vec{j}(\vec{r}\,t) = \left\langle \phi(t) \middle| \left[\hat{j}(\vec{r}), \hat{H}(t) \right] \middle| \phi(t) \right\rangle$$

equation of motion for $\vec{j}$

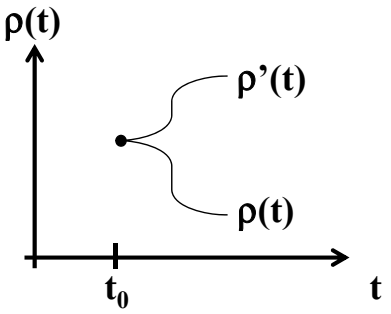
and

$$\frac{\partial \rho(\vec{r}t)}{\partial t} = -div\, \vec{j}(\vec{r}t)$$

continuity equation

to show that $\left.\frac{\partial \vec{j}}{\partial t}\right|_{t=t_0} \neq \left.\frac{\partial \vec{j}'}{\partial t}\right|_{t=t_0}$ **and** $\left.\frac{\partial^2 \rho}{\partial t^2}\right|_{t_0} \neq \left.\frac{\partial^2 \rho'}{\partial t^2}\right|_{t_0}$

$\Rightarrow$ **ρ and ρ' will become different from each other infinitesimally later than t_0**



Simplest possible approximation for $v_{xc}[\rho](\vec{r}t)$

Adiabatic Local Density Approximation (ALDA)

$$v_{xc}^{ALDA}(\vec{r}\,t) := v_{xc,stat}^{hom}(n)\Big|_{n=\rho(\vec{r}\,t)}$$

$v_{xc,stat}^{hom}$ **= xc potential of static homogeneous e-gas**

Approximation with correct asymptotic -1/r behavior: time-dependent optimized effective potential (TDOEP)

C. A. Ullrich, U. Gossmann, E.K.U.G., PRL 74, 872 (1995)

LINEAR RESPONSE THEORY

$t = t_0$: Interacting system in ground state of potential $v_0(r)$ with density $\rho_0(r)$

$t > t_0$: Switch on perturbation $v_1(r\,t)$ (with $v_1(r\,t_0)=0$).

Density: $\rho(r\,t) = \rho_0(r) + \delta\rho(r\,t)$

Consider functional $\rho[v](r\,t)$ defined by solution of interacting TDSE

Functional Taylor expansion of $\rho[v]$ around v_0:

$$\rho[v](r\,t) = \rho[v_0 + v_1](r\,t)$$

$$= \rho[v_0](r\,t) \longrightarrow \rho_0(r)$$

$$+ \int \frac{\delta\rho[v](r\,t)}{\delta v(r'\,t')}\Big|_{v_0} v_1(r'\,t')\,d^3r'\,dt' \longrightarrow \rho_1(r\,t)$$

$$+ \frac{1}{2}\int\int \frac{\delta^2\rho[v](r\,t)}{\delta v(r'\,t')\delta v(r''\,t'')}\Big|_{v_0} v_1(r',t')v_1(r'',t'')\,d^3r'\,d^3r''\,dt'\,dt'' \longrightarrow \rho_2(r\,t)$$

$$\vdots$$

$\rho_1(r,t)$ = linear density response of interacting system

$$\chi(r\,t, r'\,t') := \left.\frac{\delta \rho[v](r\,t)}{\delta v(r'\,t')}\right|_{v_0}$$ = density-density response function of interacting system

Analogous function $\rho_s[v_s](r\,t)$ for non-interacting system

$$\rho_S[v_S](r\,t) = \rho_S[v_{S,0} + v_{S,1}](r\,t) = \rho_S[v_{S,0}](r\,t) + \int \left.\frac{\delta \rho_S[v_S](r\,t)}{\delta v_S(r'\,t')}\right|_{v_{s,0}} v_{S,1}(r'\,t')\, d^3r'\, dt' + \cdots$$

$$\chi_S(r\,t, r'\,t') := \left.\frac{\delta \rho_S[v_S](r\,t)}{\delta v_S(r'\,t')}\right|_{v_{S,0}}$$ = density-density response function of non-interacting system

GOAL: Find a way to calculate $\rho_1(r\,t)$ without explicitly evaluating $\chi(r\,t, r'\,t')$ of the interacting system

starting point: Definition of xc potential

$$v_{xc}[\rho](r\,t) := v_S[\rho](r\,t) - v_{ext}[\rho](r\,t) - v_H[\rho](r\,t)$$

v_{xc} is well-defined through non-interacting/ interacting 1-1 mapping.

$$\left.\frac{\delta v_{xc}[\rho](r\,t)}{\delta\rho(r't')}\right|_{\rho_0} = \left.\frac{\delta v_S[\rho](r\,t)}{\delta\rho(r't')}\right|_{\rho_0} - \left.\frac{\delta v_{ext}[\rho](r\,t)}{\delta\rho(r't')}\right|_{\rho_0} - \frac{\delta(t-t')}{|r-r'|}$$

$$\left.\frac{\delta v_{xc}[\rho](r\,t)}{\delta\rho(r't')}\right|_{\rho_0} = \left.\frac{\delta v_S[\rho](r\,t)}{\delta\rho(r't')}\right|_{\rho_0} - \left.\frac{\delta v_{ext}[\rho](r\,t)}{\delta\rho(r't')}\right|_{\rho_0} - \frac{\delta(t-t')}{|r-r'|}$$

$\uparrow$ $\uparrow$ $\uparrow$ $\uparrow$

$f_{xc}(r\,t,r't')$ $\chi_S^{-1}(r\,t,r't')$ $\chi^{-1}(r\,t,r't')$ $W_C(r\,t,r't')$

$$\left.\frac{\delta v_{xc}[\rho](r\,t)}{\delta\rho(r't')}\right|_{\rho_0} = \left.\frac{\delta v_S[\rho](r\,t)}{\delta\rho(r't')}\right|_{\rho_0} - \left.\frac{\delta v_{ext}[\rho](r\,t)}{\delta\rho(r't')}\right|_{\rho_0} - \frac{\delta(t-t')}{|r-r'|}$$

$$\uparrow \qquad\qquad \uparrow \qquad\qquad \uparrow \qquad\qquad \uparrow$$

$$f_{xc}(r\,t,r't') \qquad \chi_S^{-1}(r\,t,r't') \qquad \chi^{-1}(r\,t,r't') \qquad W_C(r\,t,r't')$$

$$f_{xc} + W_C = \chi_S^{-1} - \chi^{-1}$$

$$\left.\frac{\delta v_{xc}[\rho](r\,t)}{\delta\rho(r't')}\right|_{\rho_0} = \left.\frac{\delta v_S[\rho](r\,t)}{\delta\rho(r't')}\right|_{\rho_0} - \left.\frac{\delta v_{ext}[\rho](r\,t)}{\delta\rho(r't')}\right|_{\rho_0} - \frac{\delta(t-t')}{|r-r'|}$$

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$$\chi_S \bullet \left| f_{xc} + W_C = \chi_S^{-1} - \chi^{-1} \right| \bullet \chi$$

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$$\chi_S (f_{xc} + W_C)\chi = \chi - \chi_S$$

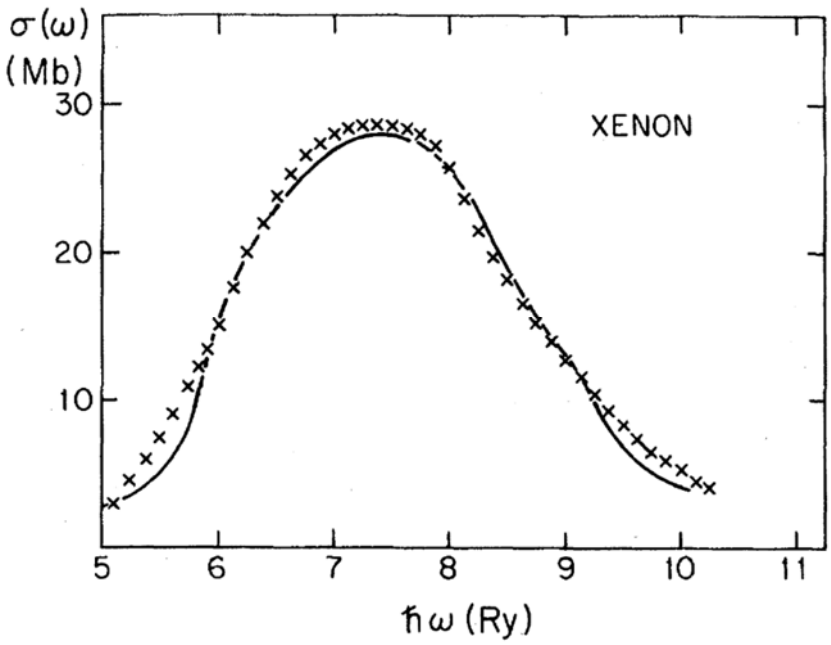
$$\chi = \chi_S + \chi_S (W_{ee} + f_{xc})\chi$$

Act with this operator equation on arbitrary $v_1(r\,t)$ and use $\chi\, v_1 = \rho_1$:

$$\rho_1(r\,t) = \int d^3r'dt' \chi_S(r\,t,r't') \left[v_1(r\,t) + \int d^3r''dt'' \{ W_{ee}(r't',r''t'') + f_{xc}(r't',r''t'') \} \rho_1(r''t'') \right]$$

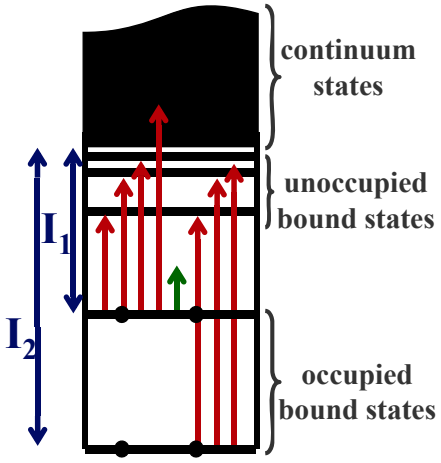
- Exact integral equation for $\rho_1(r\,t)$, to be solved iteratively
- Need approximation for $f_{xc}(r't',r''t'') = \left.\frac{\delta v_{xc}[\rho](r't')}{\delta\rho(r''t'')}\right|_{\rho_0}$
  (either for f_{xc} directly or for v_{xc})

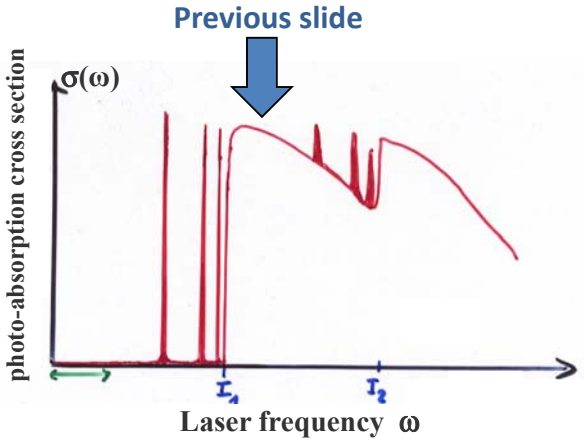
Total photoabsorption cross section of the Xe atom versus photon energy in the vicinity of the 4d threshold.



Solid line: self-consistent time-dependent KS calculation [A. Zangwill and P. Soven, Phys. Rev. A 21, 1561 (1980)]; crosses: experimental data [R. Haensel, G. Keitel, P. Schreiber, and C. Kunz, Phys. Rev. 188, 1375 (1969)].

Photo-absorption in weak lasers





Looking at those frequencies, Ω, for which $\rho_1(\omega)$ has poles, leads to the (non-linear) eigenvalue equation

(T. Grabo, M. Petersilka, EKUG, J. Mol. Struc. (Theochem) 501, 353 (2000))

$$\sum_{q'} \left(A_{qq'}(\Omega) + \omega_q \delta_{qq'} \right) \beta_{q'} = \Omega \beta_q$$

where

$$A_{qq'} = \alpha_{q'} \int d^3r \int d^3r' \, \Phi_q(r) \left(\frac{1}{|r - r'|} + f_{xc}(r, r', \Omega) \right) \Phi_{q'}(r')$$

$q = (j, a)$ double index

$\alpha_q = f_a - f_j$

$\Phi_q(r) = \varphi_a^*(r) \varphi_j(r)$

$\omega_q = \varepsilon_a - \varepsilon_j$

Atom	Experimental Excitation Energies $^1S \rightarrow {}^1P$ (in Ry)	KS energy differences $\Delta\epsilon_{KS}$ (Ry)	TDDFT
Be	0.388	0.259	0.391
Mg	0.319	0.234	0.327
Ca	0.216	0.157	0.234
Zn	0.426	0.315	0.423
Sr	0.198	0.141	0.210
Cd	0.398	0.269	0.391

from: M. Petersilka, U. J. Gossmann, E.K.U.G., PRL 76, 1212 (1996)

Excitation energies of CO molecule

State		Ω_{expt}	KS-transition	$\Delta\epsilon_{KS}$	TDDFT
A	$^1\Pi$	0.3127	$5\Sigma \rightarrow 2\Pi$	0.2523	0.3267
a	$^3\Pi$	0.2323			0.2238
I	$^1\Sigma^-$	0.3631	$1\Pi \rightarrow 2\Pi$	0.3626	0.3626
D	$^1\Delta$	0.3759			0.3812
a'	$^3\Sigma^+$	0.3127			0.3181
e	$^3\Sigma^-$	0.3631			0.3626
d	$^3\Delta$	0.3440			0.3404

T. Grabo, M. Petersilka and E.K.U. Gross, J. Mol. Struct. (Theochem) 501, 353 (2000)

approximations made: v_{xc}^{LDA} and f_{xc}^{ALDA}

Failures of ALDA in the linear response regime

- H_2 dissociation is incorrect:

$$E\left(^1\Sigma_u^+\right) - E\left(^1\Sigma_g^+\right) \xrightarrow[R\to\infty]{} 0 \quad \text{(in ALDA)}$$

(see: Gritsenko, van Gisbergen, Görling, Baerends, J. Chem. Phys. 113, 8478 (2000))

- response of long chains strongly overestimated

(see: Champagne et al., J. Chem. Phys. 109, 10489 (1998) and 110, 11664 (1999))

- in periodic solids, $f_{xc}^{ALDA}(q,\omega,\rho) = c(\rho)$ whereas,

for insulators, $f_{xc}^{exact} \xrightarrow[q\to 0]{} 1/q^2$ divergent.

- charge-transfer excitations not properly described

(see: Dreuw et al., J. Chem. Phys. 119, 2943 (2003))

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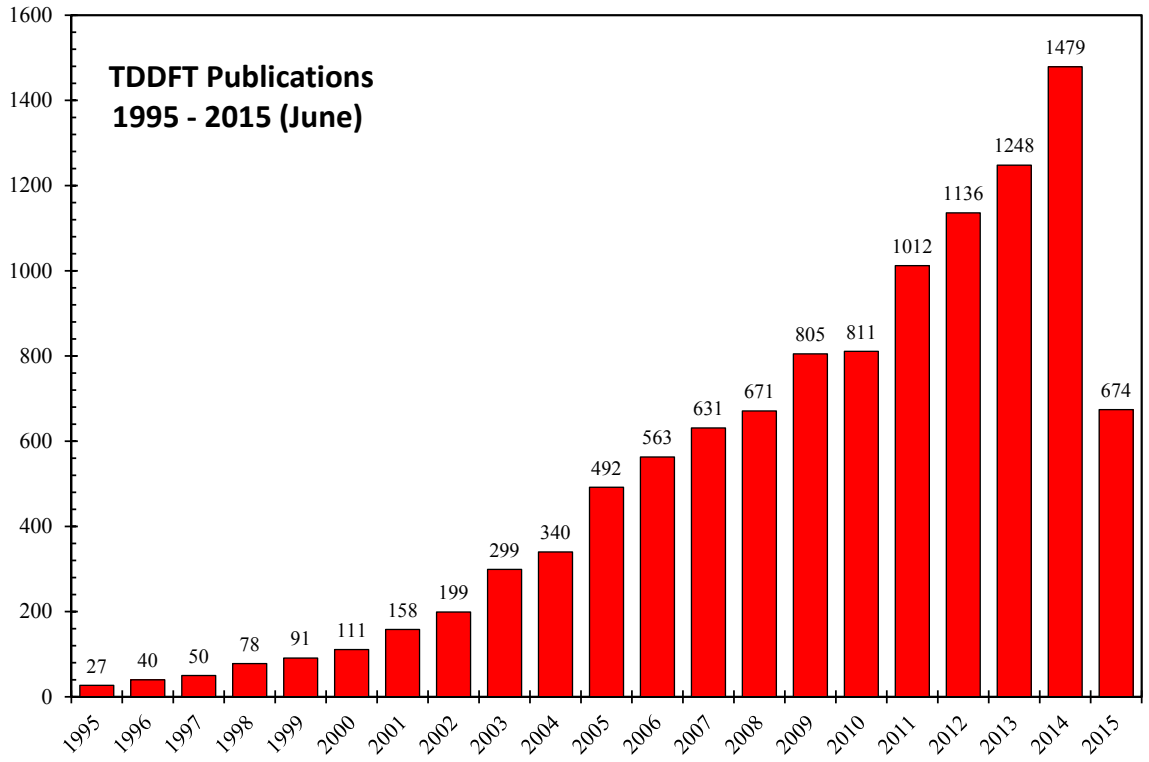
These difficulties have largely been solved by xc functionals more advanced than ALDA



Source: Web of Science as of June 2015

Time-Dependent Electron Localization Function

How can one give a rigorous mathematical meaning to chemical concepts such as

- **Single, double, triple bonds**
- **Lone pairs**

Note:

- Density $\rho_\sigma(\mathbf{r})$ is not useful!
- Orbitals are ambiguous (w.r.t. unitary transformations)

$$D_\sigma(\vec{r},\vec{r}') = \sum_{\sigma_3\sigma_4\ldots\sigma_N} \int d^3r_3 \ldots \int d^3r_N \left|\Psi(\vec{r}\sigma,\vec{r}'\sigma,\vec{r}_3\sigma_3\ldots,\vec{r}_N\sigma_N)\right|^2$$

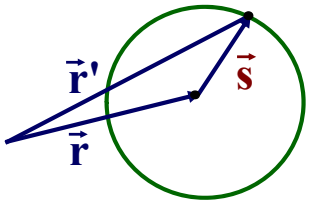
= **diagonal of two-body density matrix**

= **probability of finding an electron with spin σ at $\vec{r}$ and another electron with the same spin at $\vec{r}'$.**

$$P_\sigma(\vec{r},\vec{r}') := \frac{D_{\sigma\sigma}(\vec{r},\vec{r}')}{\rho_\sigma(\vec{r})}$$

= **conditional probability of finding an electron with spin σ at $\vec{r}'$ if we know with certainty that there is an electron with the same spin at $\vec{r}$.**

Coordinate transformation



If we know there is an electron with spin σ at $\vec{\mathbf{r}}$, then $P_\sigma\left(\vec{\mathbf{r}},\vec{\mathbf{r}}+\vec{\mathbf{s}}\right)$ is the (conditional) probability of finding another electron at $\vec{\mathbf{r}}+\vec{\mathbf{s}}$

Spherical average $$p_\sigma\left(\vec{r},|\vec{s}|\right)=\frac{1}{4\pi}\int_0^{\pi}\sin\theta d\theta\int_0^{2\pi}d\varphi P_\sigma\left(\vec{r},|\vec{s}|,\theta,\varphi\right)$$

If we know there is an electron with spin σ at $\vec{\mathbf{r}}$, then $p_\sigma\left(\vec{\mathbf{r}},\mathbf{s}\right)$ is the conditional probability of finding another electron at the distance **s** from .

Expand in a Taylor series:

$$p_\sigma\left(\vec{r},s\right)=\underbrace{p_\sigma\left(\vec{r},0\right)}_{0}+\underbrace{\left.\frac{dp_\sigma\left(\vec{r},s\right)}{ds}\right|_{s=0}}_{0}\cdot s+\frac{1}{3}C_\sigma\left(\vec{r}\right)s^2$$

The first two terms vanish.

$C_\sigma\left(\vec{\mathbf{r}}\right)$ is a measure of electron localization.

Why? $C_\sigma\left(\vec{r}\right)$, being the s^2-coefficient, gives the probability of finding a second like-spin electron very near the reference electron. If this probability very near the reference electron is low then this reference electron must be very localized.

$C_\sigma\left(\vec{r}\right)$ small means strong localization at $\vec{r}$

C_σ is always ≥ 0 (because p_σ is a probability) and $C_\sigma(\vec{r})$ is not bounded from above.

Define as a useful visualization of localization
(A.D. Becke, K.E. Edgecombe, JCP 92, 5397 (1990))

$$\mathrm{ELF} = \frac{1}{1+\left(\frac{C_\sigma(\vec{r})}{C_\sigma^{\mathrm{uni}}(\vec{r})}\right)^2}$$

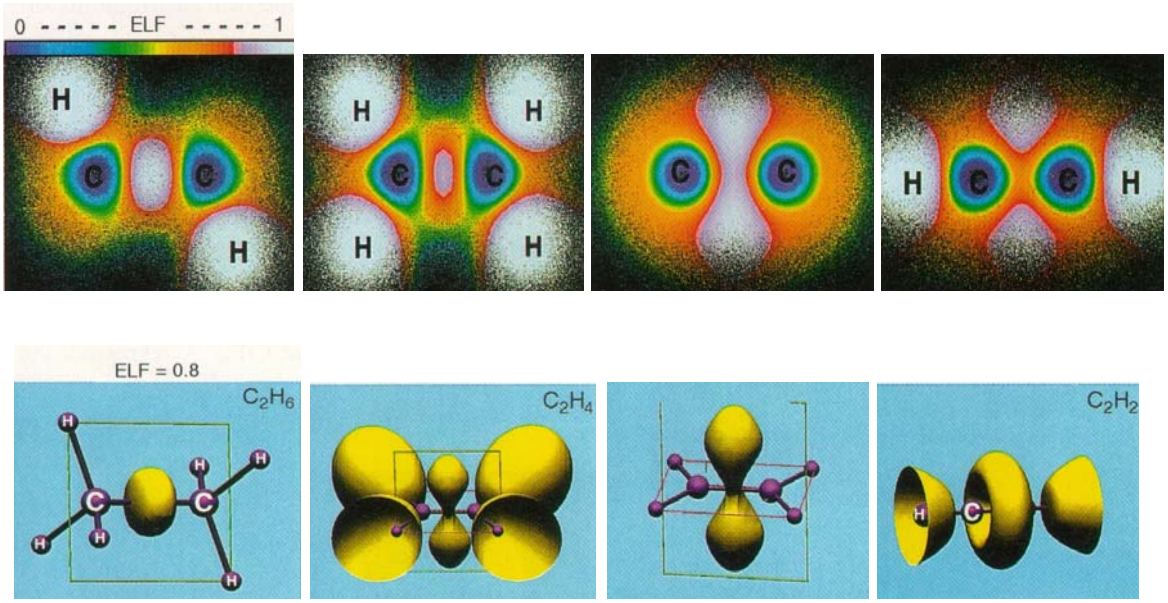
where

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

is the kinetic energy density of the uniform gas.

Advantage: ELF is dimensionless and $0 \leq \mathrm{ELF} \leq 1$

ELF



A. Savin, R. Nesper, S. Wengert, and T. F. Fässler, Angew. Chem. Int. Ed. 36, 1808 (1997)

For a determinantal wave function one obtains

in the static case:

$$C_\sigma^{\mathrm{det}}(\vec{r}) = \sum_{i=1}^{N_\sigma} \left|\nabla \varphi_{i\sigma}(\vec{r})\right|^2 - \frac{1}{4}\frac{\left(\nabla \rho_\sigma(\vec{r})\right)^2}{\rho_\sigma(\vec{r})}$$

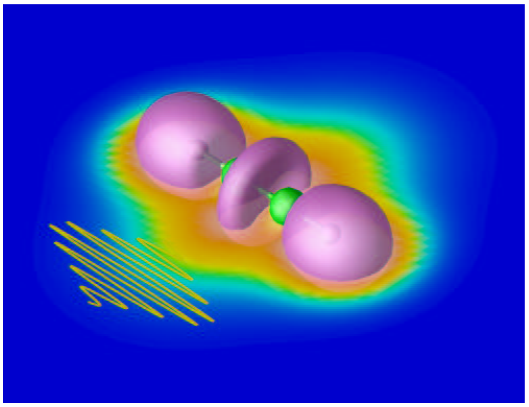
(A.D. Becke, K.E. Edgecombe, JCP 92, 5397 (1990))

in the time-dependent case:

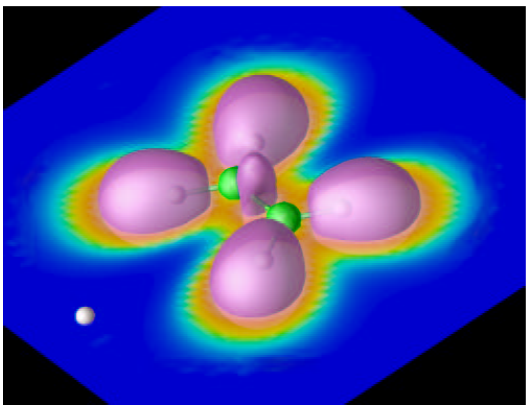
$$C_\sigma^{\mathrm{det}}(\vec{r},t) = \sum_{i=1}^{N_\sigma} \left|\nabla \varphi_{i\sigma}(\vec{r},t)\right|^2 - \frac{1}{4}\frac{\left(\nabla \rho_\sigma(\vec{r},t)\right)^2}{\rho_\sigma(\vec{r},t)} - j_\sigma(\vec{r},t)^2 \Big/ \rho_\sigma(\vec{r},t)$$

(T. Burnus, M. Marques, E.K.U.G., PRA (Rapid Comm) 71, 010501 (2005))

Acetylene in laser field
($\hbar\omega$ = 17.15 eV, I = 1.2×10^{14} W/cm^2)

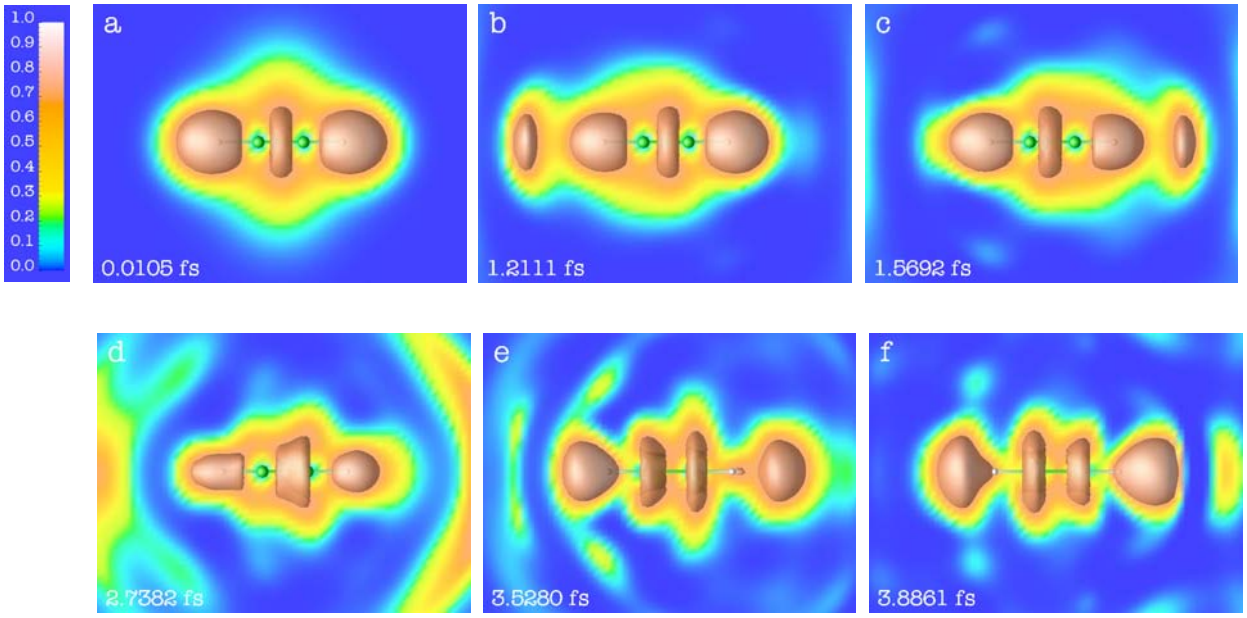


Scattering of a proton from ethylene
(E_{kin}(proton) = 2 keV)



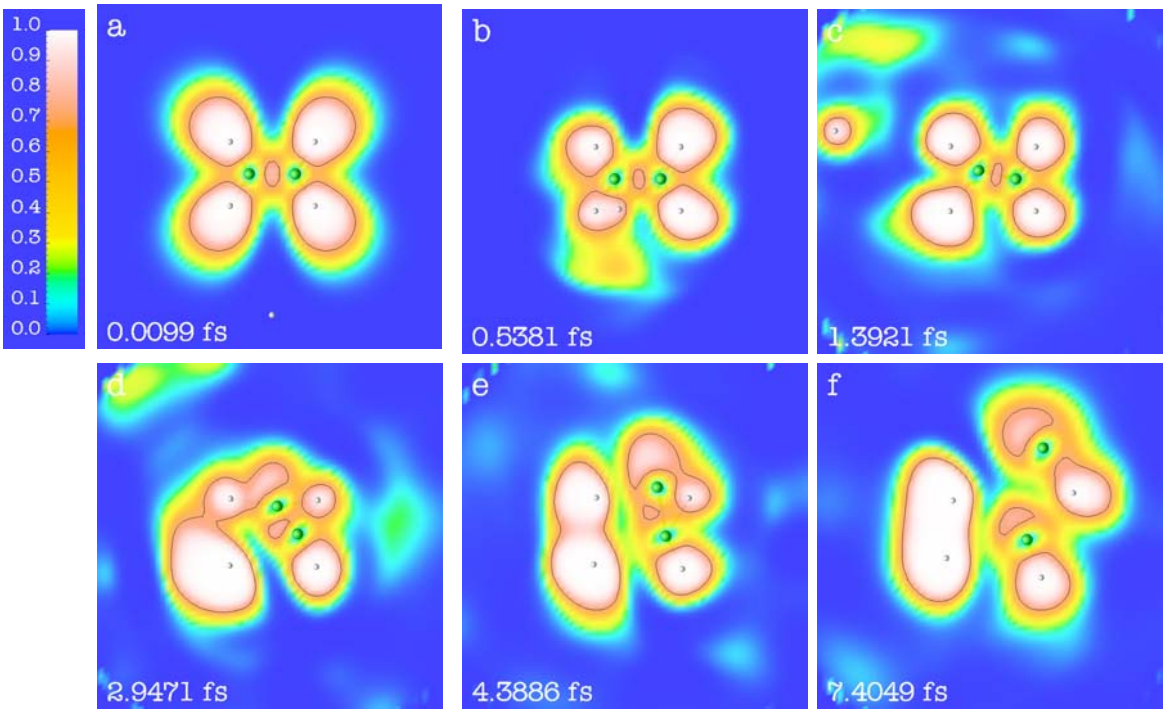
TDELF for acetylene in strong laser field

($\hbar\omega$ = 17.15 eV, I = 1.2×10^{14} W/cm^2)



TDELF for scattering process

2 keV proton colliding with ethylene



TDELF movies produced from TD Kohn-Sham equations

$$i\hbar\frac{\partial}{\partial t}\varphi_j(rt) = \left(-\frac{\hbar^2\nabla^2}{2m} + v_{KS}[\rho](rt)\right)\varphi_j(rt)$$

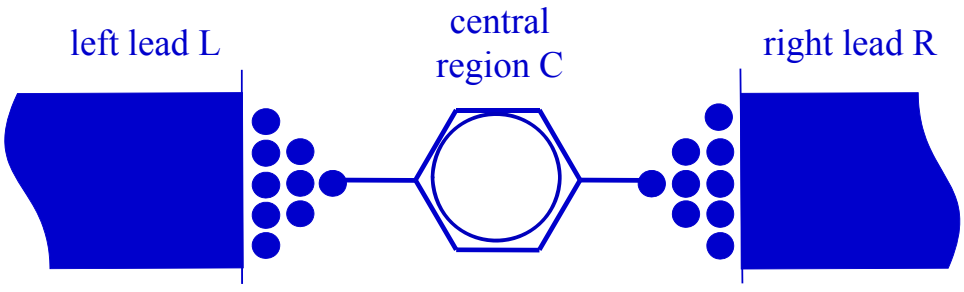
$$v_{KS}[\rho(r't')](rt) = v(rt) + \int d^3r' \frac{\rho(r't)}{|r-r'|} + v_{xc}[\rho\,(r't')](r\,t)$$

propagated numerically on real-space grid using `octopus` code

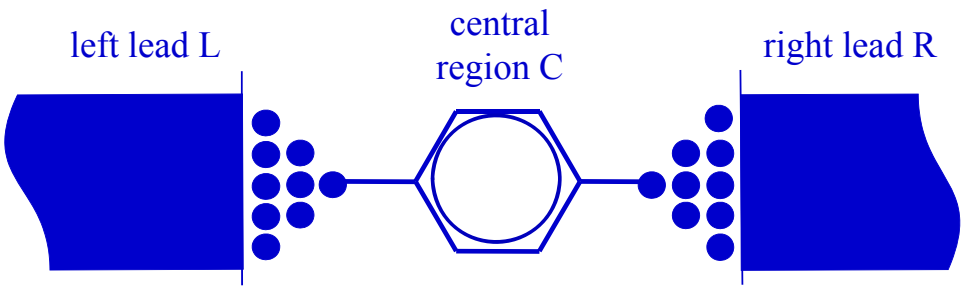
octopus: a tool for the application of time-dependent density functional theory,
A. Castro, M.A.L. Marques, H. Appel, M. Oliveira, C.A. Rozzi, X. Andrade, F. Lorenzen, E.K.U.G., A. Rubio, Physica Status Solidi 243, 2465 (2006).

T. Burnus, M. Marques, E.K.U.G, PRA (Rapid Comm) 71, 010501 (2005)

Electronic transport with TDDFT



Electronic transport with TDDFT

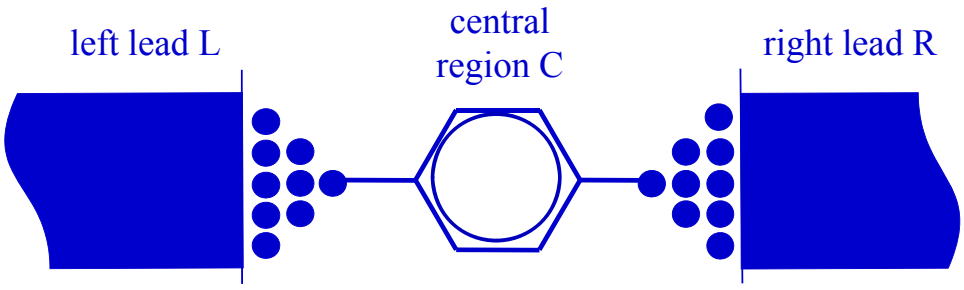


TDKS equation (E. Runge, EKUG, PRL **52**, 997 (1984))

$$i\hbar\frac{\partial}{\partial t}\varphi_j(rt)=\left(-\frac{\hbar^2\nabla^2}{2m}+v_{KS}[\rho](rt)\right)\varphi_j(rt)$$

$$v_{KS}[\rho(r't')](rt)=v(rt)+\int d^3r'\frac{\rho(r't)}{|r-r'|}+v_{xc}[\rho\,(r't')](r\,t)$$

Electronic transport with TDDFT



TDKS equation

$$i\frac{\partial}{\partial t}\begin{pmatrix}\varphi_L(t)\\ \varphi_C(t)\\ \varphi_R(t)\end{pmatrix}=\begin{pmatrix}H_{LL}(t) & H_{LC}(t) & H_{LR}(t)\\ H_{CL}(t) & H_{CC}(t) & H_{CR}(t)\\ H_{RL}(t) & H_{RC}(t) & H_{RR}(t)\end{pmatrix}\begin{pmatrix}\varphi_L(t)\\ \varphi_C(t)\\ \varphi_R(t)\end{pmatrix}$$

Effective TDKS Equation for the central (molecular) region only

S. Kurth, G. Stefanucci, C.O. Almbladh, A. Rubio, E.K.U.G.,
Phys. Rev. B 72, 035308 (2005)

$$i\frac{\partial}{\partial t}\varphi_C(t) = H_{CC}(t)\varphi_C(t) + \int_0^t dt'\left[H_{CL}G_L(t,t')H_{LC} + H_{CR}G_R(t,t')H_{RC}\right]\varphi_C(t') + iH_{CL}G_L(t,0)\varphi_L(0) + iH_{CR}G_R(t,0)\varphi_R(0)$$

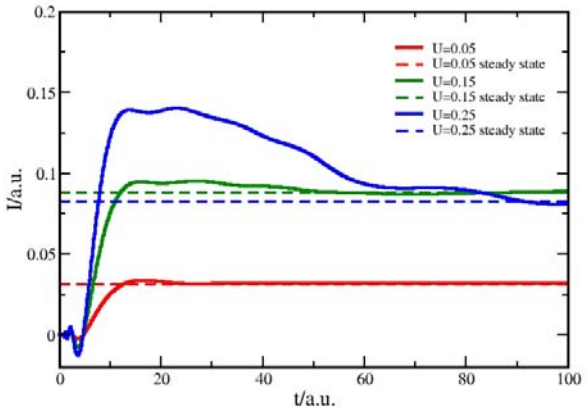
source term: $L \to C$ and $R \to C$ charge injection

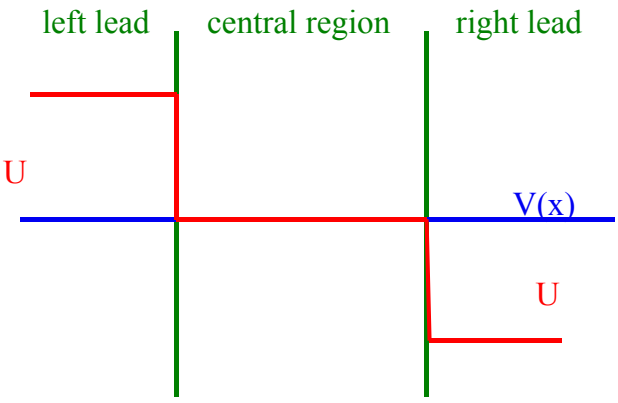
memory term: $C \to L \to C$ and $C \to R \to C$ hopping

Note: So far, no approximation has been made.

Numerical examples for non-interacting electrons

Recovering the Landauer steady state

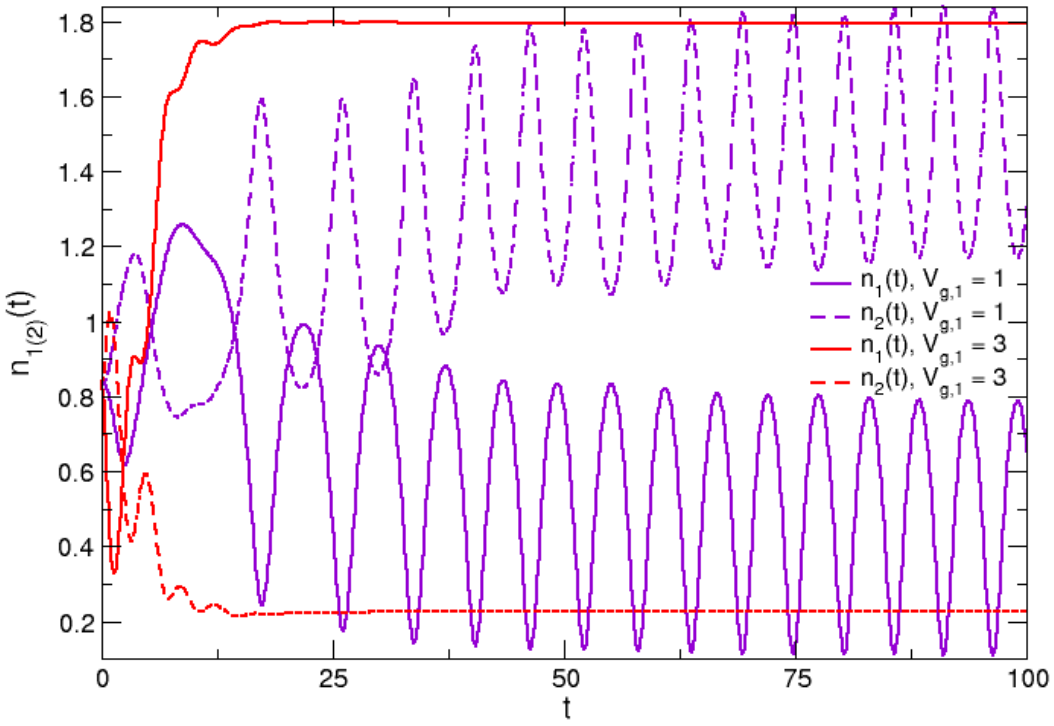




Time evolution of current in response to bias switched on at time t = 0,
Fermi energy $\varepsilon_F = 0.3$ a.u.
Steady state coincides with Landauer formula
and is reached after a few femtoseconds

Does one always reach a steady state after switching-on the bias?

Two-site Anderson model

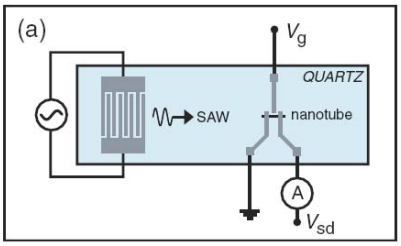


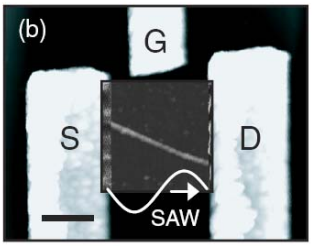
E. Khosravi, A.M. Uimonen, A. Stan, G. Stefanucci, S. Kurth, R. van Leeuwen, E.K.U. Gross, Phys. Rev. B 85, 075103 (2012)

ELECTRON PUMP

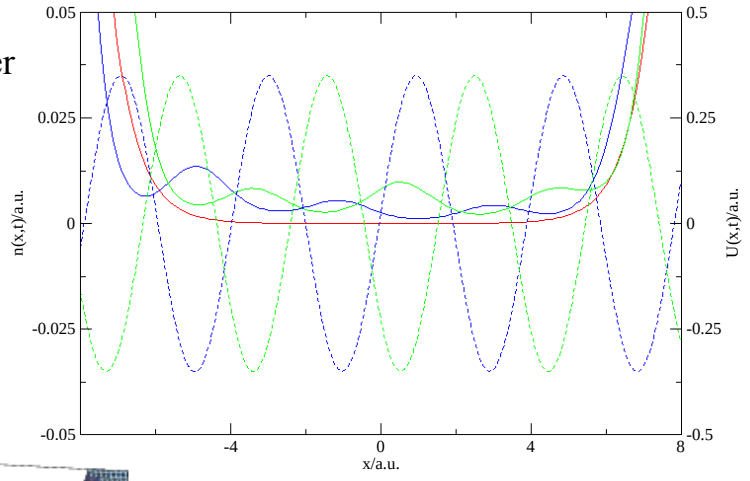
Device which generates a net current between two electrodes (with no static bias) by applying a time-dependent potential in the device region

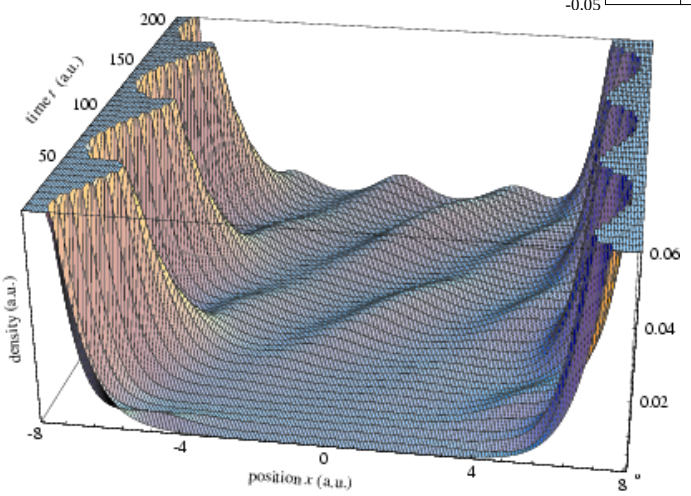
Experimental realization : Pumping through carbon nanotube by surface acoustic waves on piezoelectric surface (Leek et al, PRL 95, 256802 (2005))





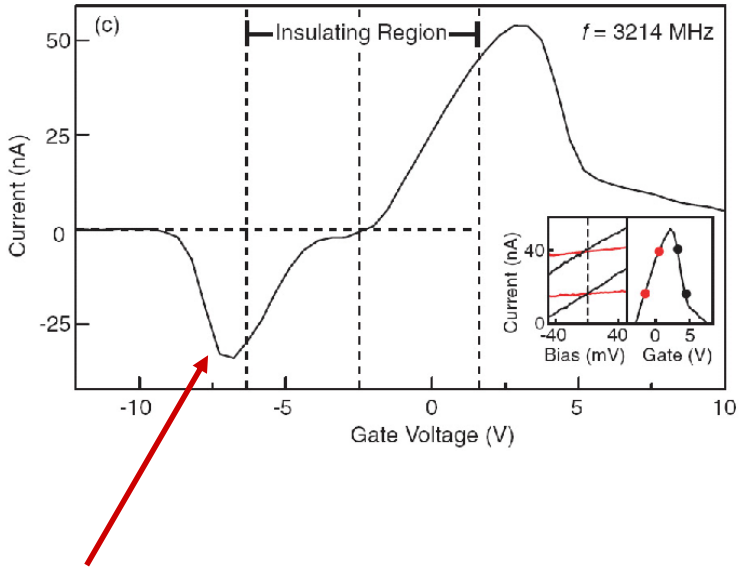
Pumping through a square barrier (of height 0.5 a.u.) using a travelling wave in device region
$U(x,t) = U_o \sin(kx-wt)$
(k = 1.6 a.u., w = 0.2 a.u.
Fermi energy = 0.3 a.u.)



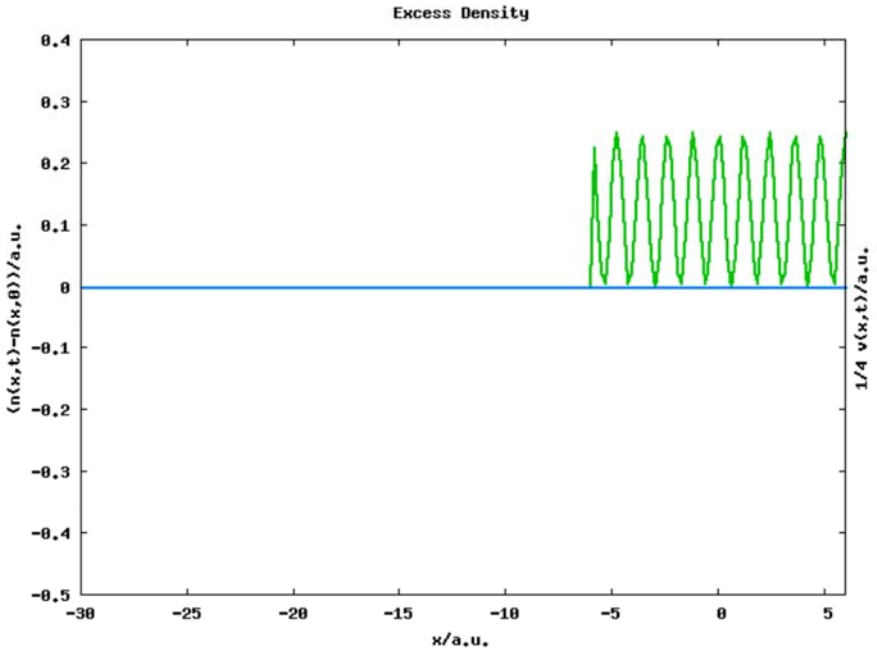


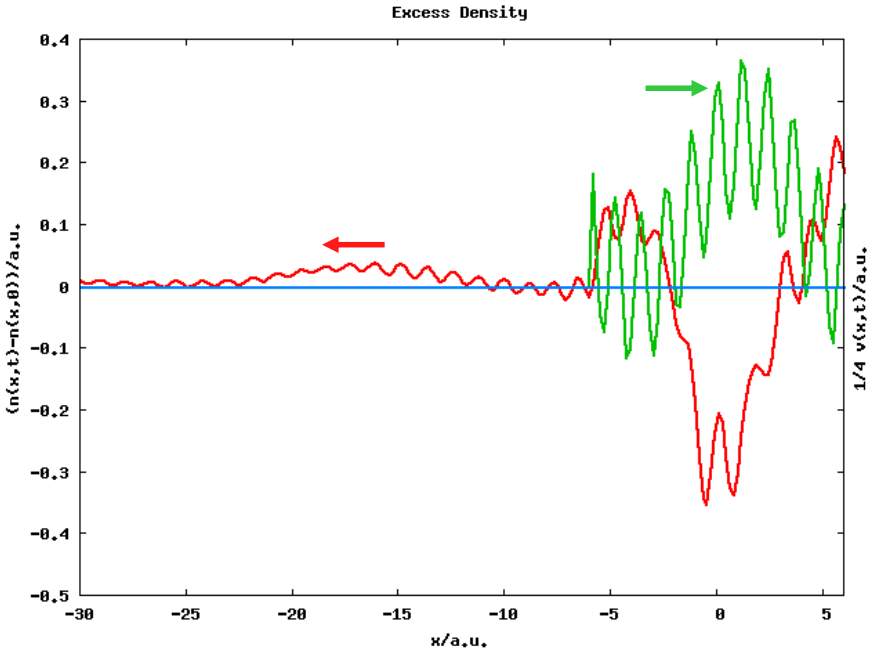
Patent: Archimedes (250 b.c.)

Experimental result:



Current flows in direction opposite to sound wave



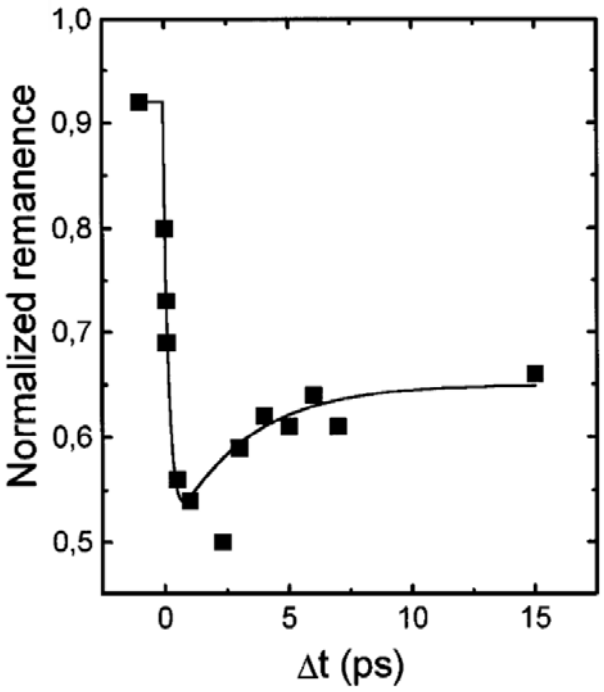


Current goes in direction opposite to the external field !!

G. Stefanucci, S. Kurth, A. Rubio, E.K.U. Gross, Phys. Rev. B 77, 075339 (2008)

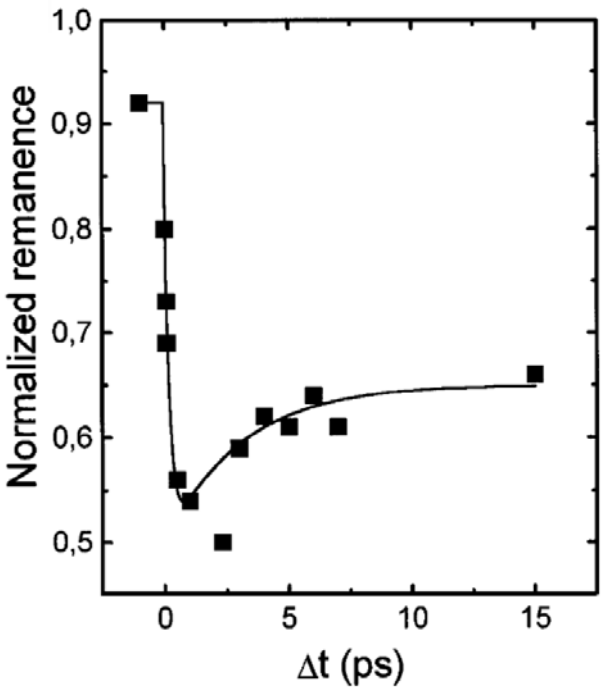
Laser-induced ultrafast demagnetization of solids: The first 100 femto-seconds

First experiment on ultrafast laser induced demagnetisation



Beaurepaire et al, PRL 76, 4250 (1996)

First experiment on ultrafast laser induced demagnetisation



Beaurepaire et al, PRL 76, 4250 (1996)

More recent experiments show demagnetization in less than 100 fs

Possible mechanisms for demagnetisation

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- Direct interaction of spins with the magnetic component of the laser
  Zhang, Huebner, PRL **85**, 3025 (2000)

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  Koopmans et al, PRL **95**, 267207 (2005)

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  Battiato, Carva, Oppeneer, PRL **105**, 027203 (2010)

- **Ab-initio (TDDFT) result for the first 50 fs:**
  Laser-driven charge excitation followed by spin-orbit-driven demagnetization of the localized d-electrons

  K. Krieger, J.K. Dewhurst, P.Elliott, S. Sharma, E.K.U. Gross, arXiv:1406.6607 (2014), to appear in JCTC (2015).

Theoretical approach: TDDFT with SOC

$$i\frac{\partial}{\partial t}\varphi_k(r,t) = \Big[\frac{1}{2}\big(-i\nabla - A_{laser}(t)\big)^2 + v_S[\rho,\boldsymbol{m}](r,t) - \mu_B\sigma\cdot B_S[\rho,\boldsymbol{m}](r,t) + \frac{\mu_B}{2c}\sigma\cdot\big(\nabla v_S[\rho,\boldsymbol{m}](r,t)\big)\times\big(-i\nabla\big)\Big]\varphi_k(r,t)$$

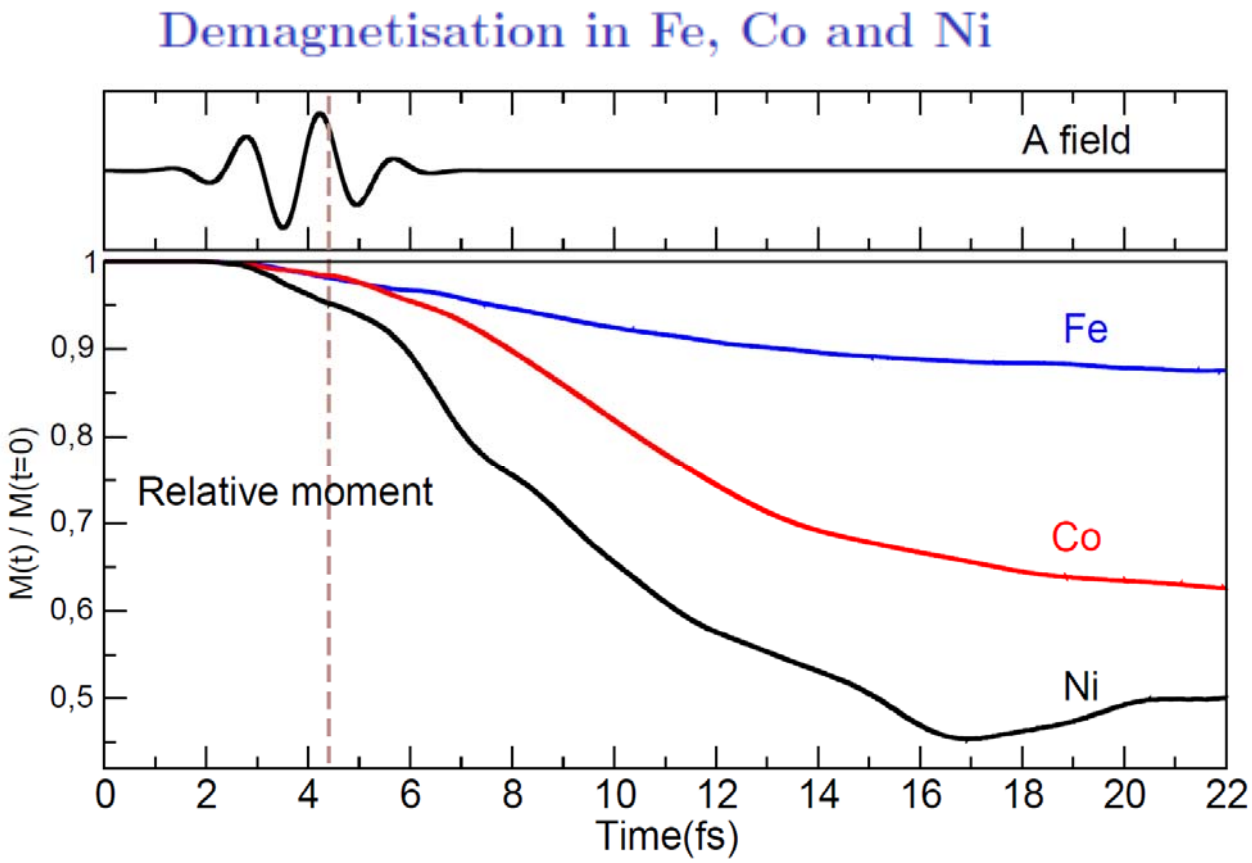
$$v_S[\rho,\boldsymbol{m}](r,t) = v_{lattice}(r) + \int\frac{\rho(r',t)}{|r-r'|}d^3r' + v_{xc}[\rho,\boldsymbol{m}](r,t)$$

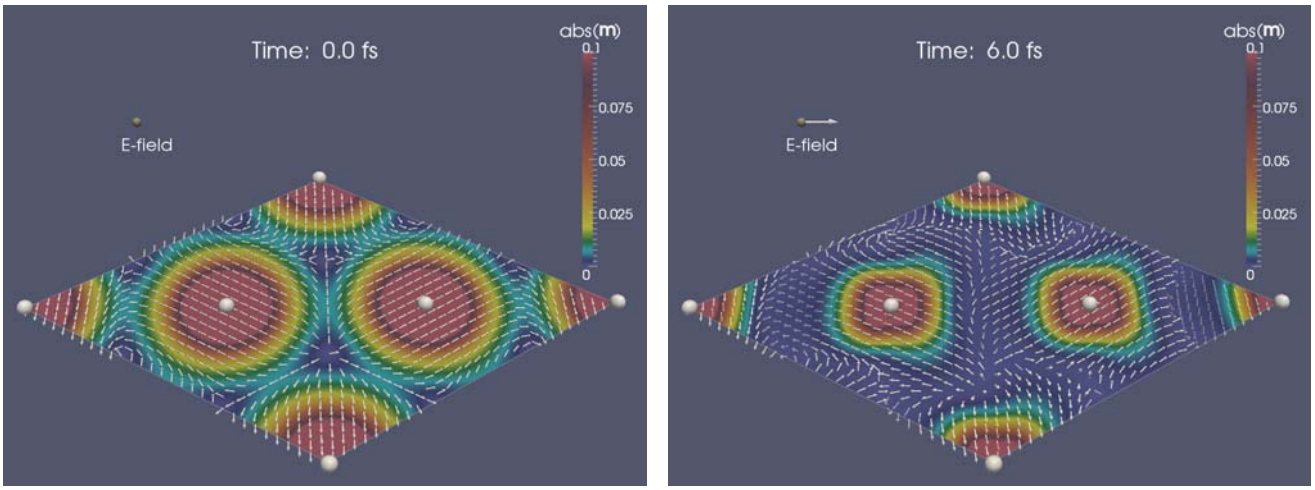
$$B_S[\rho,\boldsymbol{m}](r,t) = B_{external}(r,t) + B_{xc}[\rho,\boldsymbol{m}](r,t)$$

where $\varphi_k(r,t)$ are Pauli spinors

Aspects of the implementation

- Wave length of laser in the visible regime
  (very large compared to unit cell)
- Dipole approximation is made
  (i.e. electric field of laser is assumed to be spatially constant)
- Laser can be described by a purely time-dependent vector potential
- **Periodicity of the TDKS Hamiltonian is preserved!**
- **Implementation in ELK code (FLAPW)**
  (http://elk.sourceforge.net)



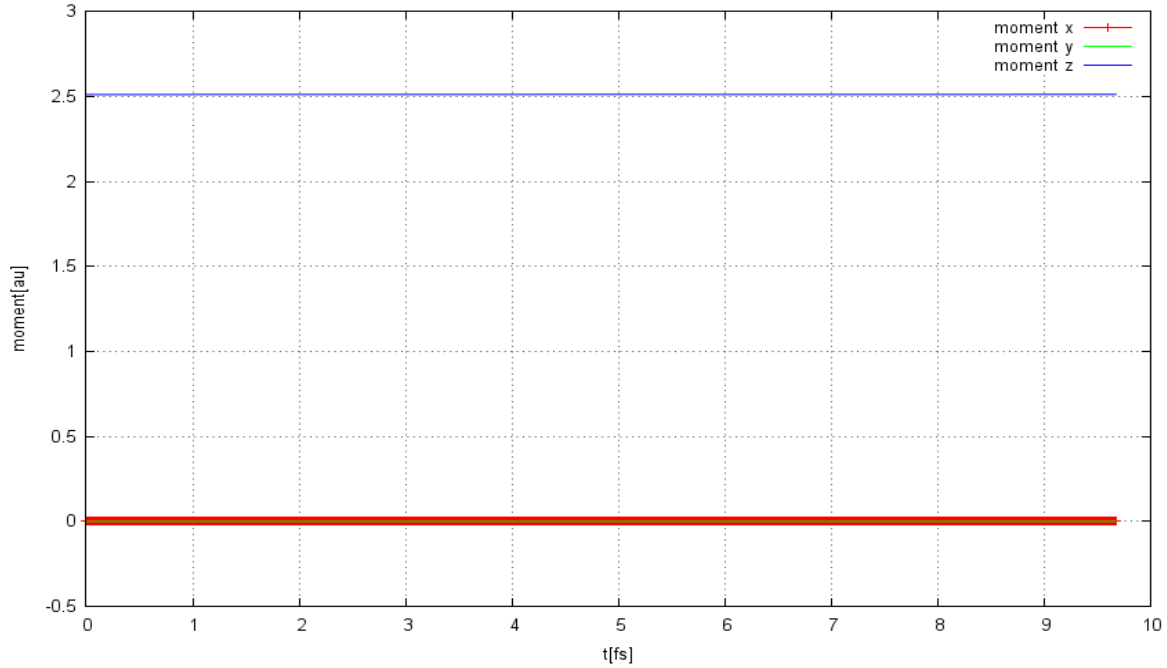


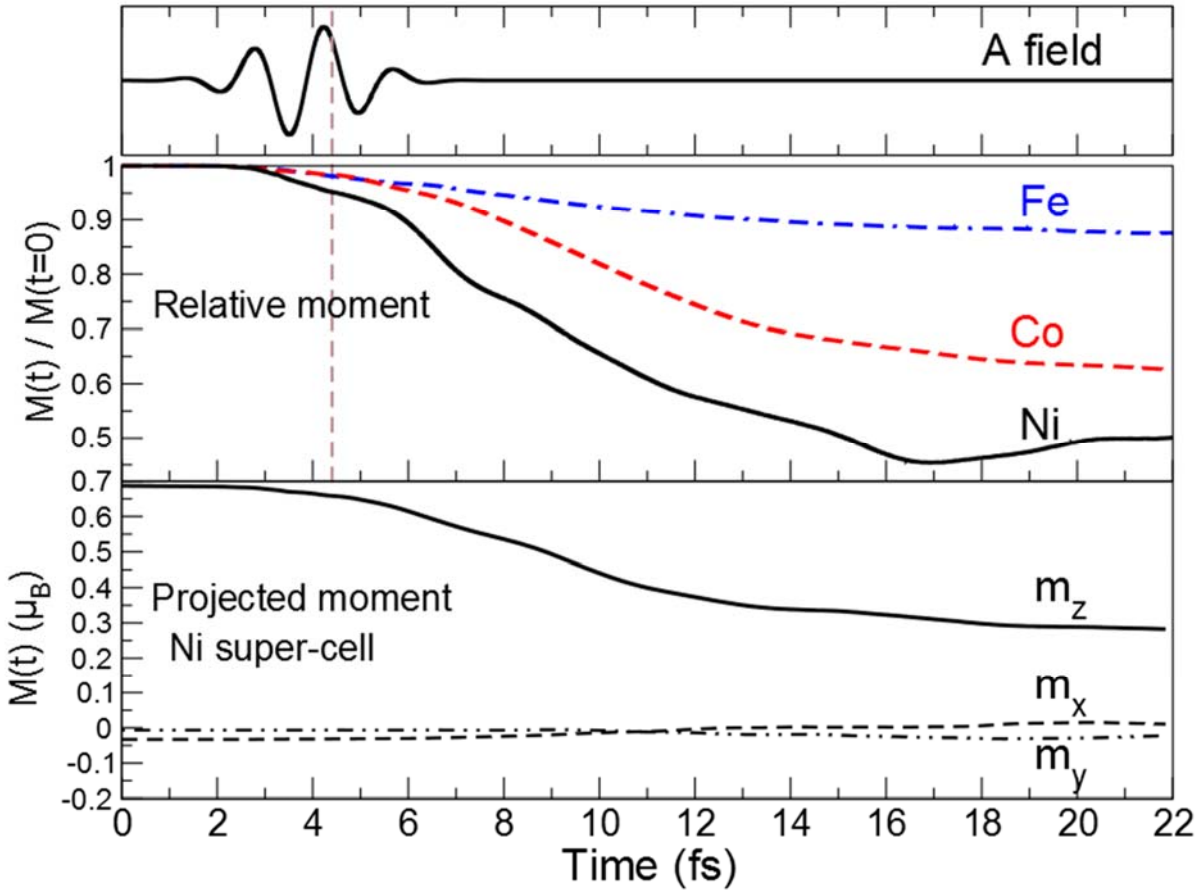
Cr monolayer

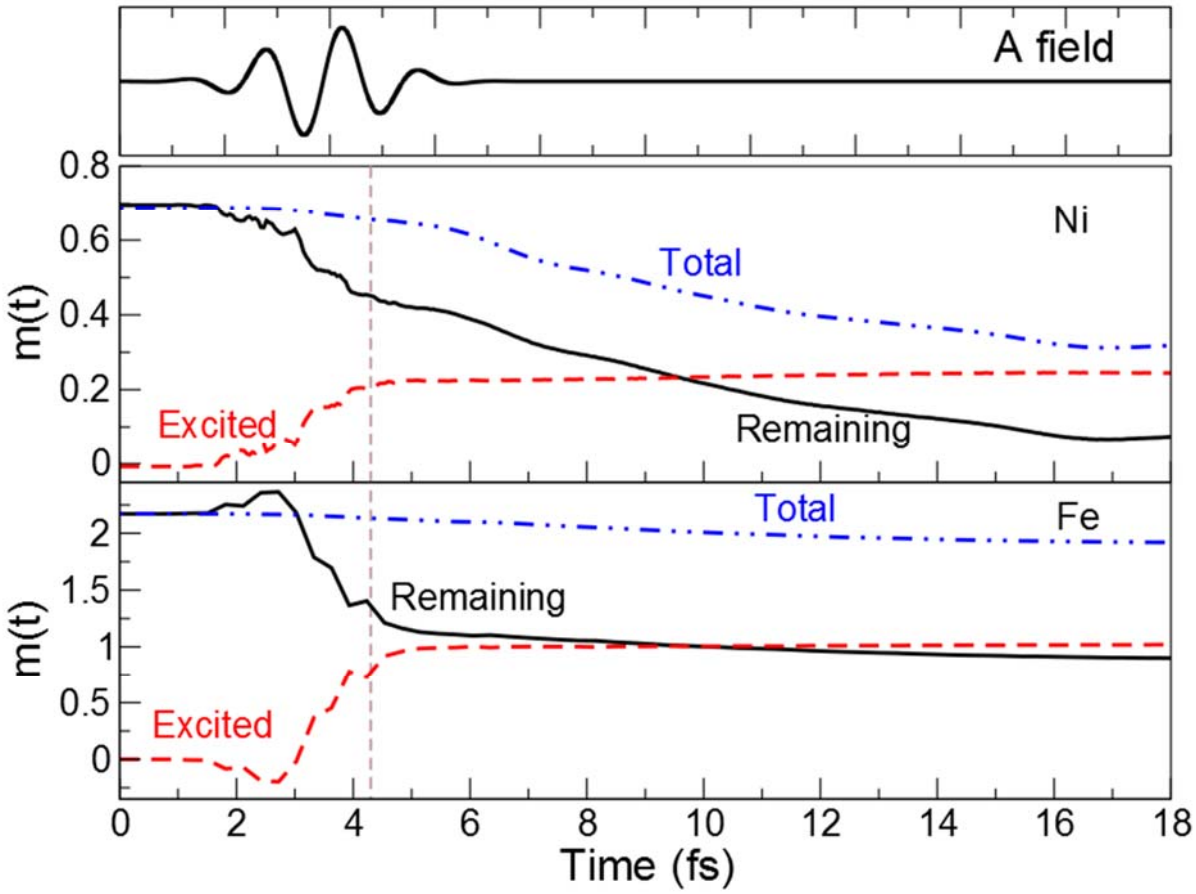
Analysis of the results

Calculation without spin-orbit coupling

components of spin moment







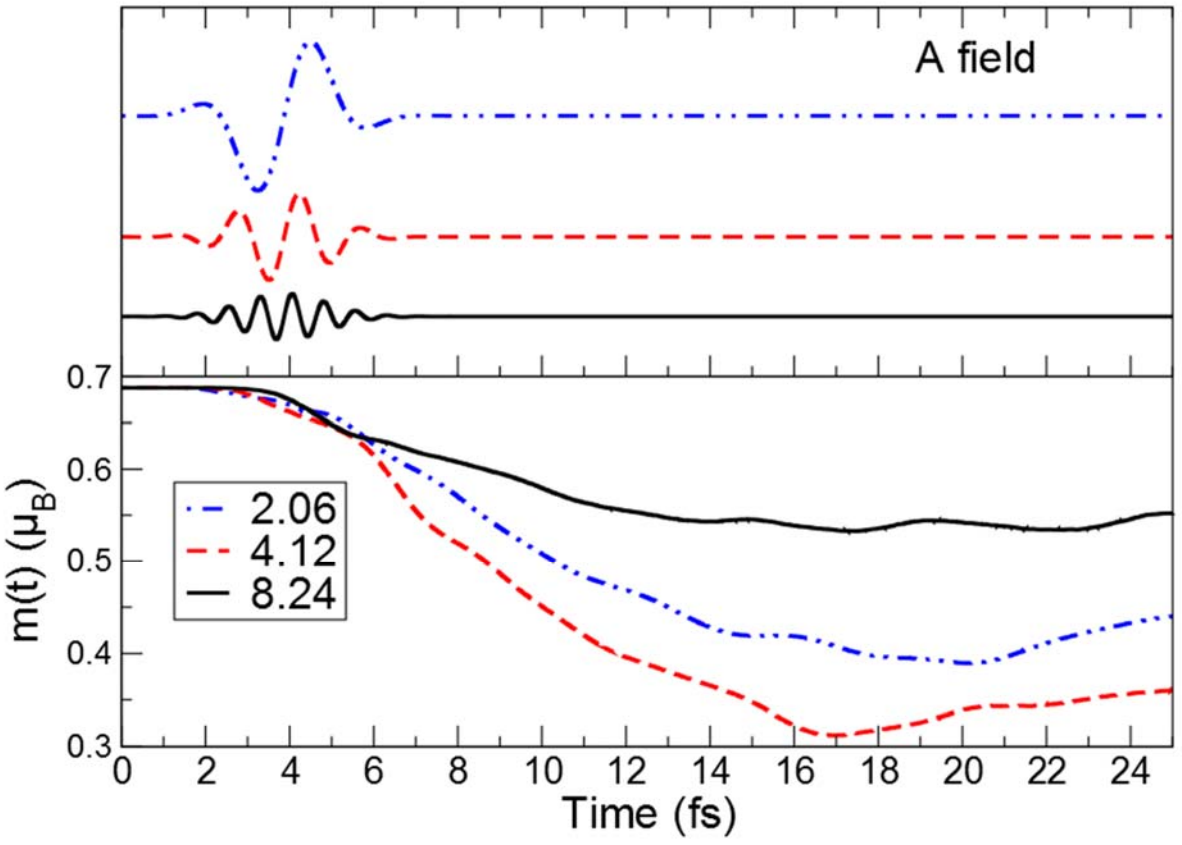
Demagnetization occurs in two steps:

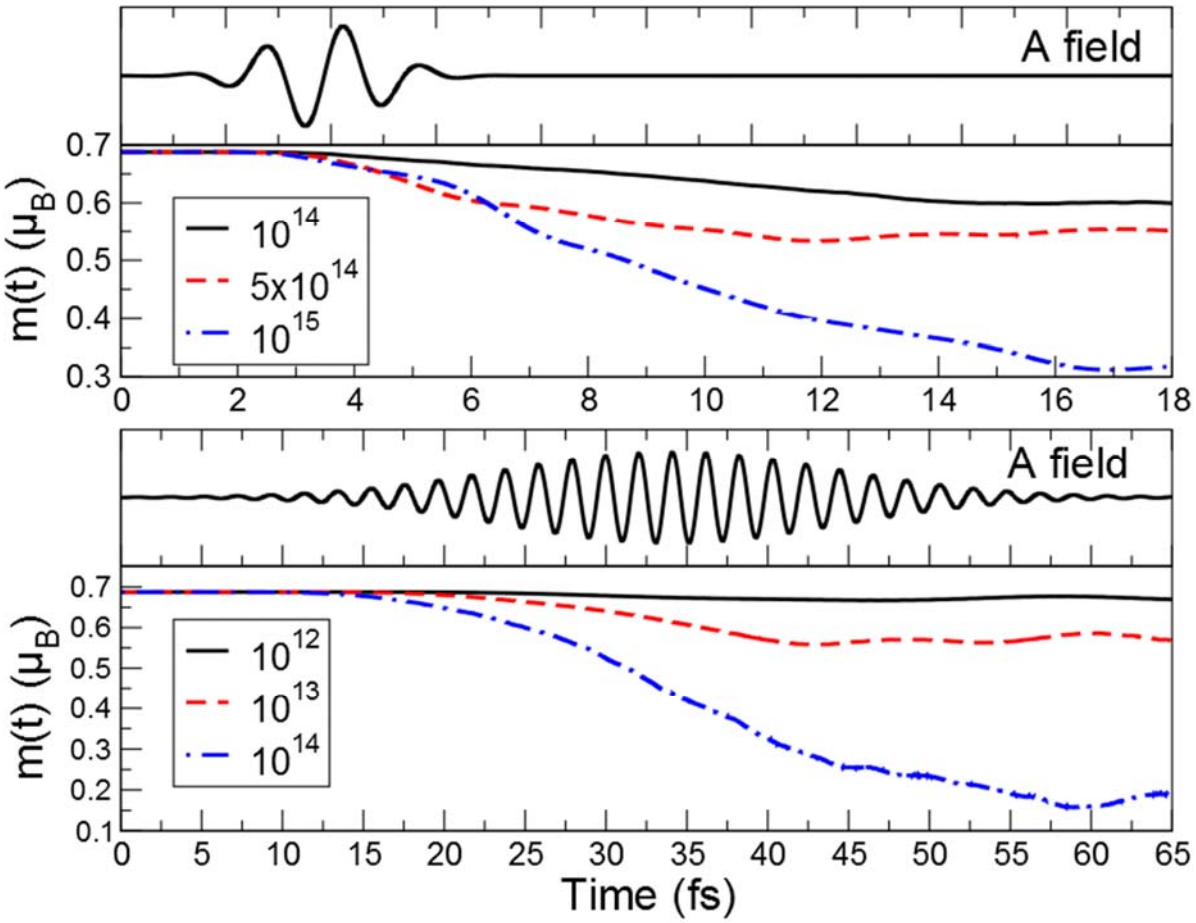
- Initial excitation by laser *moves* magnetization from MT region into interstitial region. Total Moment is basically conserved during this phase.

- Spin-Orbit term drives demagnetization of localized electrons until stabilization at much lower moment is achieved

K. Krieger, J.K. Dewhurst, P. Elliott, S. Sharma, E.K.U. Gross, arXiv:1406.6607 (2014)

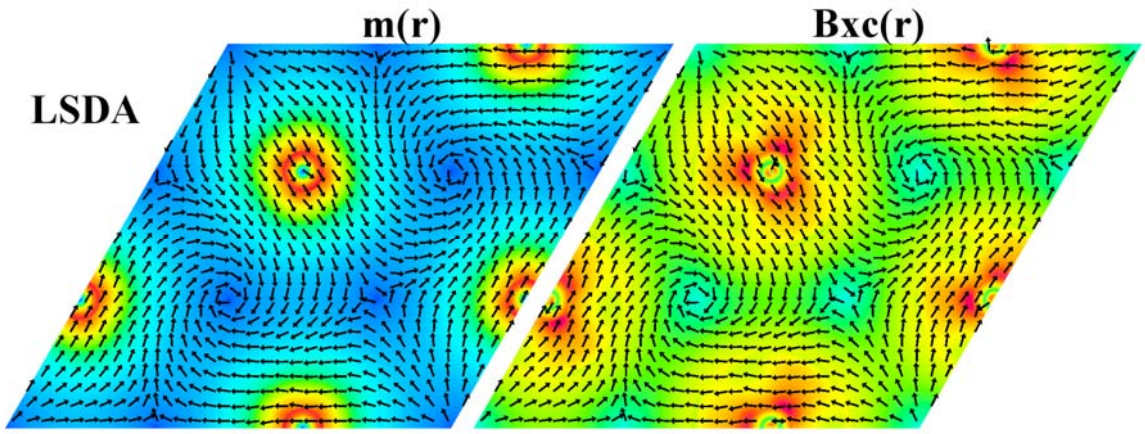
Playing with laser parameters





Influence of approximation for xc functional

Problem: In all standard approximations of E_{xc} (LSDA, GGAs) m(r) and $B_{xc}(r)$ are locally collinear



S. Sharma, J.K. Dewhurst, C. Ambrosch-Draxl, S. Kurth, N. Helbig, S. Pittalis, S. Shallcross, L. Nordstroem E.K.U.G., Phys. Rev. Lett. 98, 196405 (2007)

Why is that important?

Ab-initio description of spin dynamics:

microscopic equation of motion (following from TDSDFT)

$$\dot{\vec{m}}(\vec{r},t) = \vec{m}(\vec{r},t)\times\vec{B}_{XC}(\vec{r},t) - \vec{\nabla}\cdot\vec{\vec{J}}_S(\vec{r},t)$$

in absence of external magnetic field

Consequence of local collinearity: $m\times B_{xc} = 0$:
→ wrong spin dynamics
→ how important is this term in real-time dynamics?

Construction of a novel GGA-type functional

Traditional LSDA: Start from uniform electron gas in collinear magnetic state. Determine $e_{XC}[n,m]$ from QMC or MBPT and parametrize $e_{XC}[n,m]$ to use in LSDA.

New non-collinear functional: Start from spin-spiral phase of e-gas. Determine $e_{XC}[n,\vec{m}]$ from MBPT and parametrize $e_{XC}[n,\vec{m}]$ to use as non-collinear GGA.

F.G. Eich and E.K.U. Gross, Phys. Rev. Lett. 111, 156401 (2013)

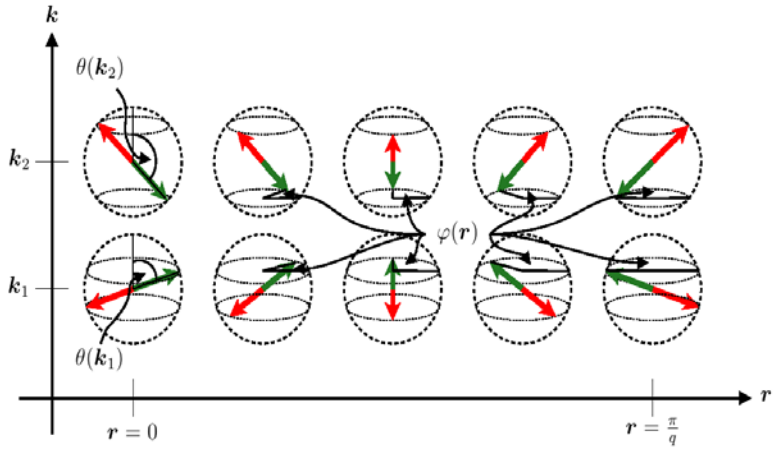


Illustration of spin spiral waves along one spatial coordinate for two different choices of wavevector $q=k_{1/2}$.

Magnetisation of a spin-spiral state in the uniform electron gas

$$\mathbf{m}(\mathbf{r}) = m\begin{pmatrix} s\cos(\mathbf{q}\cdot\mathbf{r}) \\ s\sin(\mathbf{q}\cdot\mathbf{r}) \\ \sqrt{1-s^2} \end{pmatrix}$$

$$\varepsilon_{xc}^{SSW} = \varepsilon_{xc}^{SSW}(n,m,q,s)$$

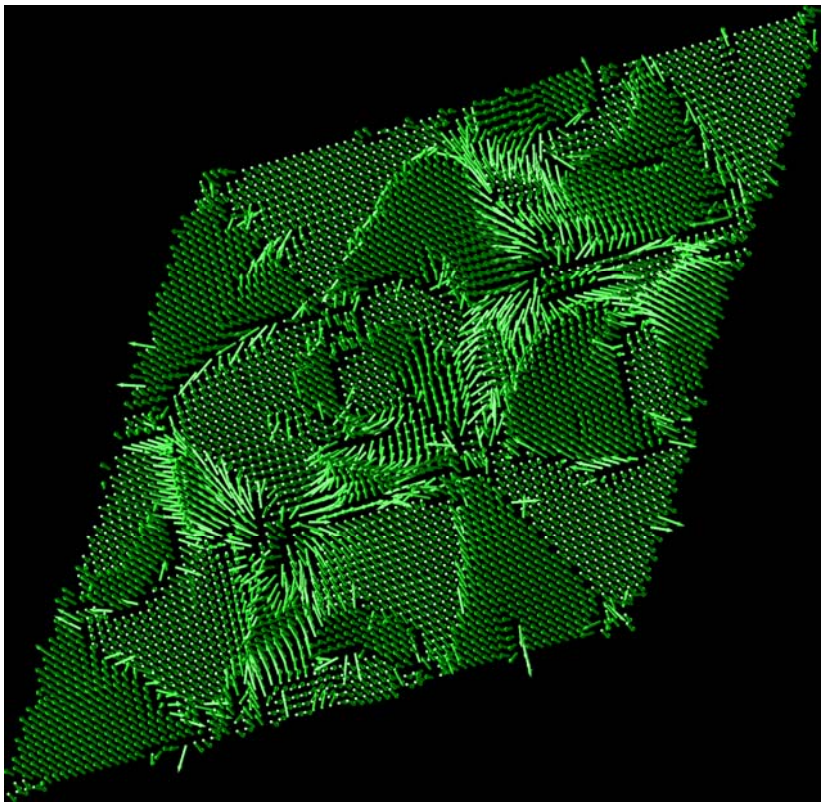
$$E_{xc}^{GGA}[n,\vec{m}] = \int d^3r\, n(\mathbf{r})\,\varepsilon_{xc}^{SSW}\left(n(\mathbf{r}), m(\mathbf{r}), q(\mathbf{r}), s(\mathbf{r})\right)$$

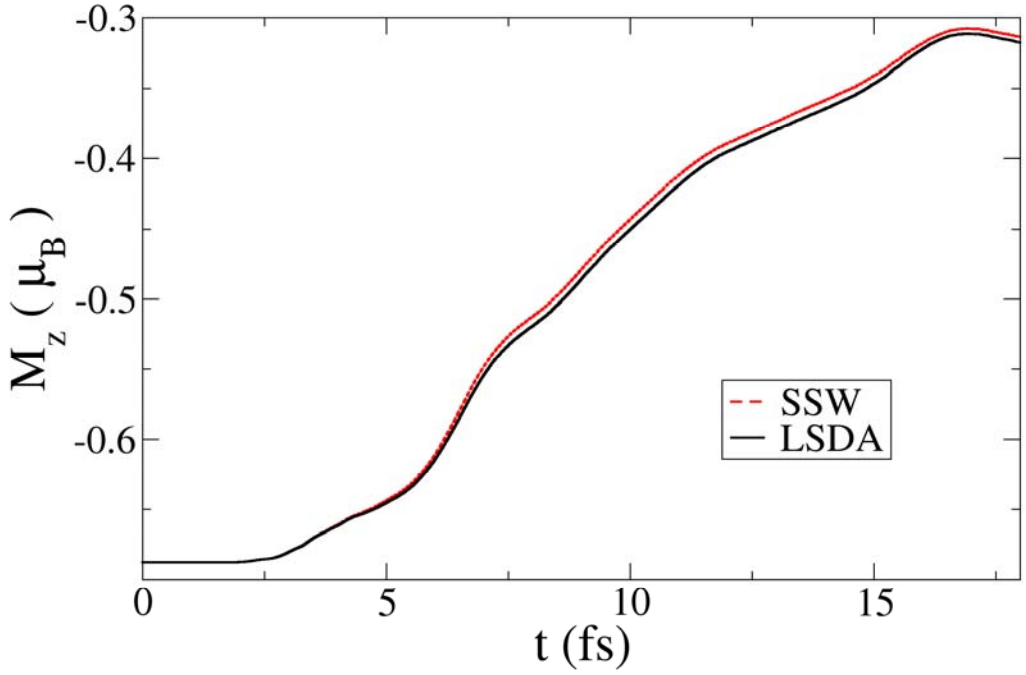
$$s^2(\mathbf{r}) = \frac{D_T^2(\mathbf{r})}{D_T^2(\mathbf{r}) + m^4(\mathbf{r})\,d_T(\mathbf{r})} \qquad q^2(\mathbf{r}) = \frac{D_T^2(\mathbf{r}) + m^4(\mathbf{r})\,d_T(\mathbf{r})}{m^4(\mathbf{r})\,D_T(\mathbf{r})}$$

$$D_T(\mathbf{r}) = \left|\vec{m}(\mathbf{r}) \times \left(\nabla \otimes \vec{m}(\mathbf{r})\right)\right|^2 \qquad d_T(\mathbf{r}) = \left|\vec{m}(\mathbf{r}) \times \left(\nabla^2 \vec{m}(\mathbf{r})\right)\right|^2$$

F.G. Eich and E.K.U. Gross, Phys. Rev. Lett. 111, 156401 (2013)

$m \times B_{xc}$





Summary

- No demagnetization without Spin-Orbit coupling
- Demagnetization in first 100 fs is a two-step process:
  1. Initial excitation of electrons into highly excited states (without much of a change in the total magnetization)
  2. Spin-orbit coupling drives demagnetization of localized electrons (mainly d electrons)
- Similar demagnetization behavior for Fe, Co, Ni
- No significant change in M_x and M_y
- New xc functional derived from spin-spiral phase of uniform e-gas
- Very little difference in demagnetization dynamics comparing the new xc functional with the traditional non-collinear LSDA

Optimal control of ultra-short processes

Review Article on Quantum Optimal Control Theory:
J. Werschnik, E.K.U. Gross, J. Phys. B 40, R175-R211 (2007)

Optimal Control Theory (OCT) of static targets

Normal question:

What happens if a system is exposed to a given laser pulse?

Inverse question (solved by OCT):

Which is the laser pulse that achieves a prescribed goal (target)?

possible targets:

a) system should end up in a given final state ϕ_f at the end of the pulse
b) wave function should follow a given trajectory in Hilbert space
c) density should follow a given classical trajectory r(t)

Optimal control of static targets (standard formulation)

For <u>given</u> target state Φ_f , maximize the functional:

$$J_1 = \left| \langle \Psi(T) | \Phi_f \rangle \right|^2 = \langle \Psi(T) | \Phi_f \rangle \langle \Phi_f | \Psi(T) \rangle = \langle \Psi(T) | \hat{O} | \Psi(T) \rangle$$

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$\hat{O}$

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$\hat{O}$

with the constraints:

$$J_2 = -\alpha \left[\int_0^T dt \varepsilon^2(t) - E_0 \right]$$

E_0 = <u>given</u> fluence

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$$J_3[\varepsilon, \Psi, \chi] = -2 \, \mathrm{Im} \int_0^T dt \left\langle \chi(t) \left| -i\partial_t - \left[\hat{T} + \hat{V} - \mu\varepsilon(t) \right] \right| \Psi(t) \right\rangle$$

Optimal control of static targets (standard formulation)

For <u>given</u> target state Φ_f , maximize the functional:

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TDSE

GOAL: Maximize $J = J_1 + J_2 + J_3$

Set the total variation of $J = J_1 + J_2 + J_3$ equal to zero:

Control equations

1. Schrödinger equation with initial condition:

$$\delta_\chi J = 0 \rightarrow \boxed{i\partial_t \psi(t) = \hat{H}(t)\psi(t), \quad \psi(0) = \phi}$$

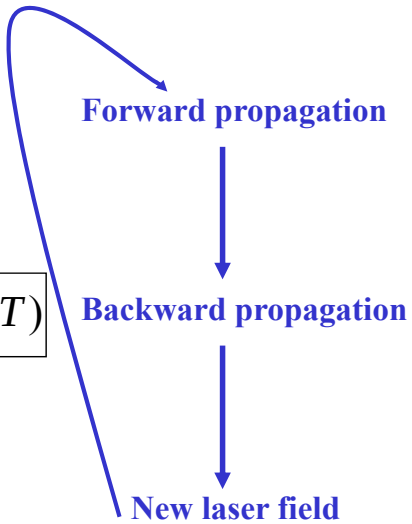
2. Schrödinger equation with final condition:

$$\delta_\psi J = 0 \rightarrow \boxed{i\partial_t \chi(t) = \hat{H}(t)\chi(t), \quad \chi(T) = \hat{O}\psi(T)}$$

3. Field equation:

$$\delta_\varepsilon J = 0 \rightarrow \boxed{\varepsilon(t) = \frac{1}{\alpha}\,\mathrm{Im}\langle \chi(t)|\hat{\mu}|\psi(t)\rangle}$$

Algorithm

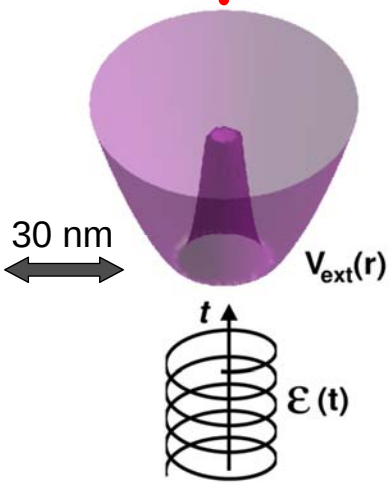


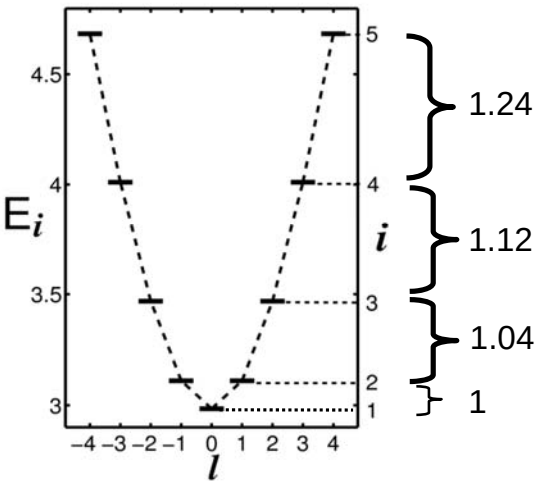
Algorithm monotonically convergent: W. Zhu, J. Botina, H. Rabitz, J. Chem. Phys. 108, 1953 (1998))

Quantum ring: Control of circular current

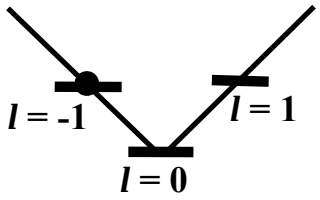
TDSE: $$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},t) = \left[\hat{H}_0 + e\,\mathbf{r}\,\epsilon(t)\right]\Psi(\mathbf{r},t)$$

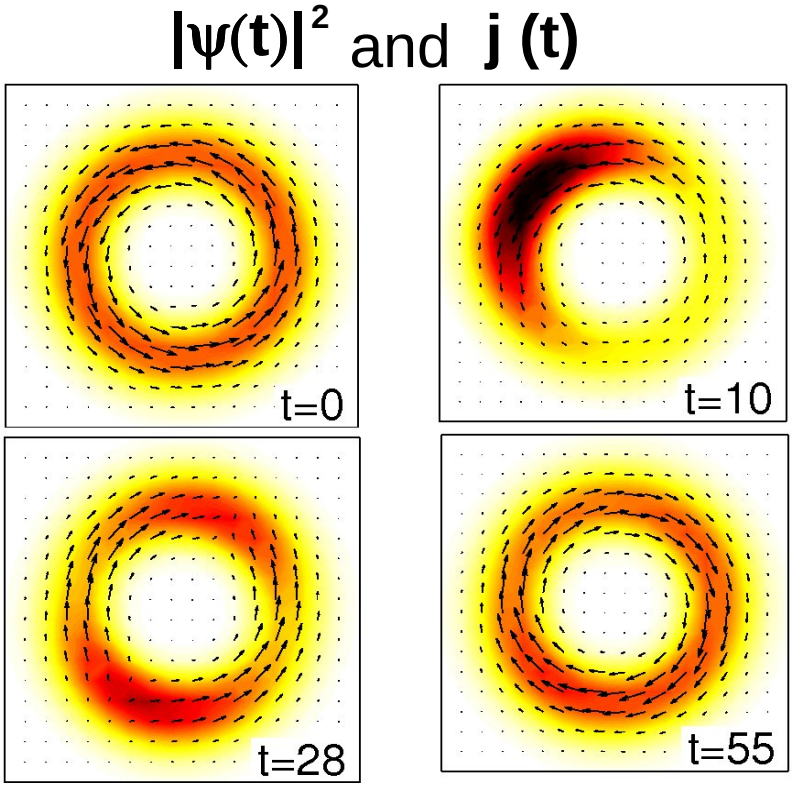
$$\hat{H}_0 = -\frac{\hbar^2}{2m^*}\nabla^2 + \frac{1}{2}m^*\omega_0^2 r^2 + V_0 e^{-r^2/d^2} \qquad \epsilon(t) = (\epsilon_x(t), \epsilon_y(t))$$



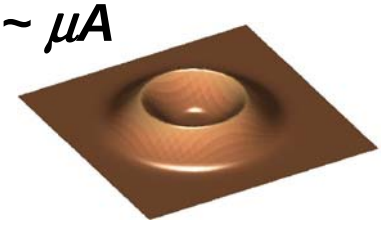


Control of currents





I ~ μA



E. Räsänen, A. Castro, J. Werschnik, A. Rubio, E.K.U.G., PRL 98, 157404 (2007)

OCT of ionization

- Calculations for 1-electron system H_2^+ in 3D
- Restriction to ultrashort pulses (T<5fs)
  - ➢ nuclear motion can be neglected
- Only linear polarization of laser (parallel or perpendicular to molecular axis)
- Look for enhancement of ionization by pulse-shaping only, keeping the time-integrated intensity (fluence) fixed

Control target to be maximized:

$$J_1 = \left\langle \Psi(T) \middle| \hat{O} \middle| \Psi(T) \right\rangle$$

with $$\hat{O} = \hat{1} - \sum_{i}^{\text{bound}} \left| \varphi_i \right\rangle \left\langle \varphi_i \right|$$

Standard OCT algorithm (forward-backward propagation) does not converge:

Acting with $\hat{O}$ before the backward-propagation eliminates the smooth (numerically friendly) part of the wave function.

Instead of forward-backward propagation, parameterize the laser pulse to be optimized in the form

$$\epsilon(t) = f(t)\cos(\omega_0 t) \quad , \qquad \text{with } \omega_0 = 0.114 \text{ a.u. } (\lambda = 400 \text{ nm})$$

$$f(t) = \sum_{n=1}^{N} \left[f_n \sqrt{\frac{2}{T}} \cos(\omega_n t) + g_n \sqrt{\frac{2}{T}} \sin(\omega_n t) \right] , \qquad \text{with } \omega_n = 2\pi n/T$$

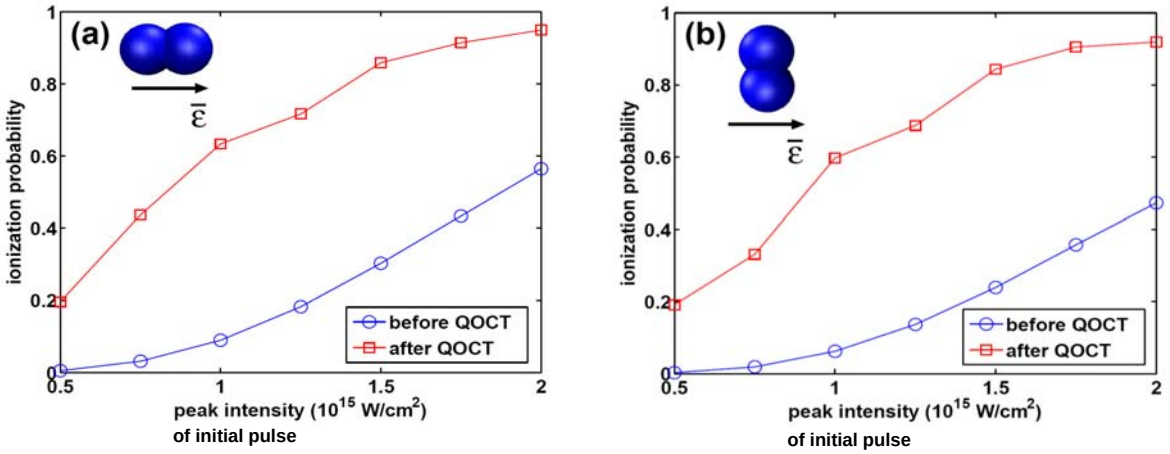
Choose N such that maximum frequency is $2\omega_0$ or $4\omega_0$. T is fixed to 5 fs.

Maximize J_1 ($f_1 \ldots f_N$, $g_1 \ldots g_N$) directly with constraints:

$$\text{(i)} \quad f(0) = f(T) = 0 \quad \Rightarrow \quad \sum_{n=1}^{N} f_n = 0$$

$$\text{(ii)} \quad \int_0^T dt \varepsilon^2(t) = E_0 .$$

using algorithm NEWUOA (M.J.D. Powell, *IMA J. Numer. Analysis* 28, 649 (2008))



Ionization probability for the initial (circles) and the optimized (squares) pulse as function of the peak intensity of the initial pulse.
Pulse length and fluence is kept fixed during the optimization.

Control of many-body systems

- Formally the same OCT equations
- Problem: For 3 or more degrees of freedom, the full solution of the TDSE becomes computationally very hard

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Important: Control target must be formulated in terms of the density!

Enhancement of a single harmonic peak

Harmonic Spectrum:

$$H(\omega) = \left| \int dt e^{i\omega t} \frac{d^2}{dt^t} \left\{ \int d^3 r z \rho(\vec{r}, t) \right\} \right|^2$$

Maximize: $$F = \sum_k \alpha_k \max_{\omega \in [k\omega_0 - \beta, k\omega_0 + \beta]} H(\omega)$$

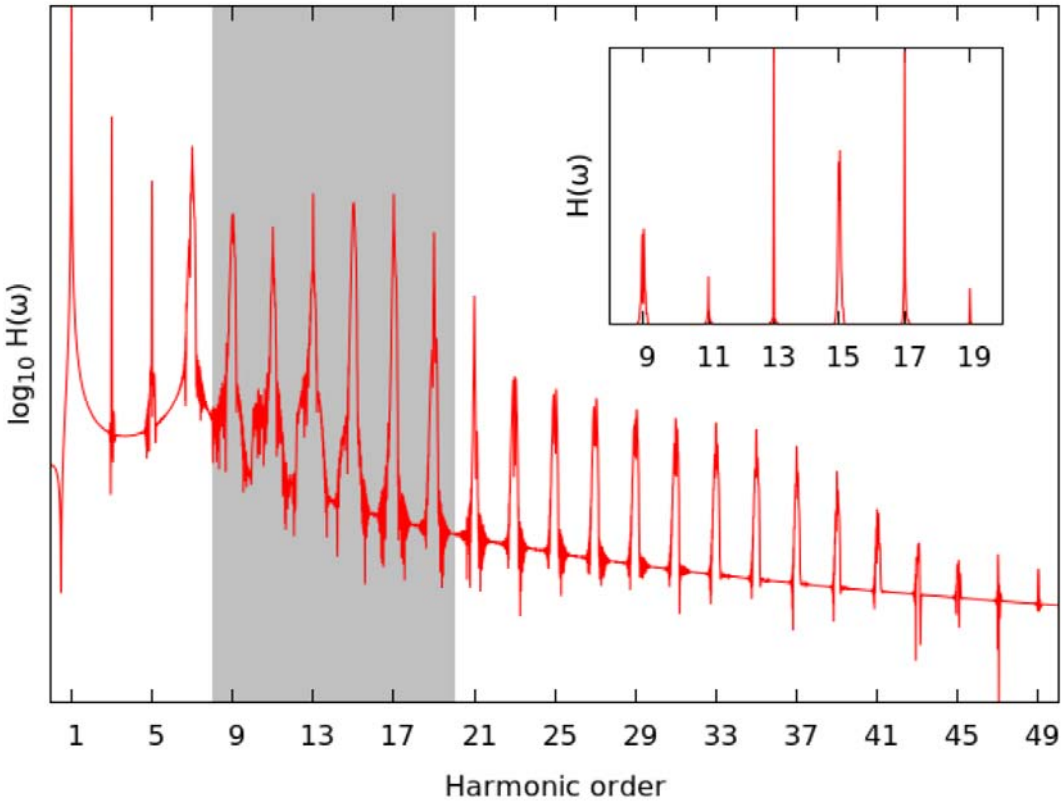
To maximize, e.g., the 7th harmonic of ω_0 , choose coefficients as
$\alpha_7 = 4$, $\alpha_3 = \alpha_5 = \alpha_9 = \alpha_{11} = -1$

Measure of enhancement: Compare with reference pulse:

$$\varepsilon_{ref}(t) = \varepsilon_0 \cos\left(\frac{\pi}{2}\frac{2t - T}{T}\right)\cos(\omega t)$$

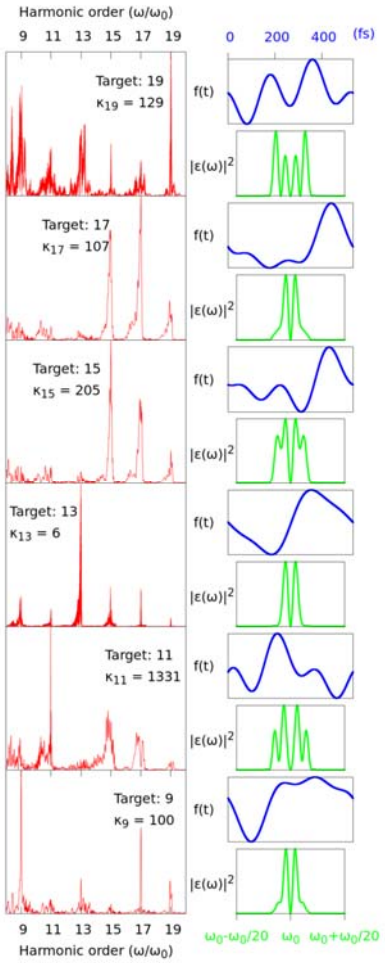
$$\kappa_j = \frac{\max_{\omega \in [j\omega_0 - \beta, j\omega_0 + \beta]} H(\omega)}{H_{ref}(j\omega_0)}$$

Harmonic spectrum of reference pulse for hydrogen atom



Results for Hydrogen

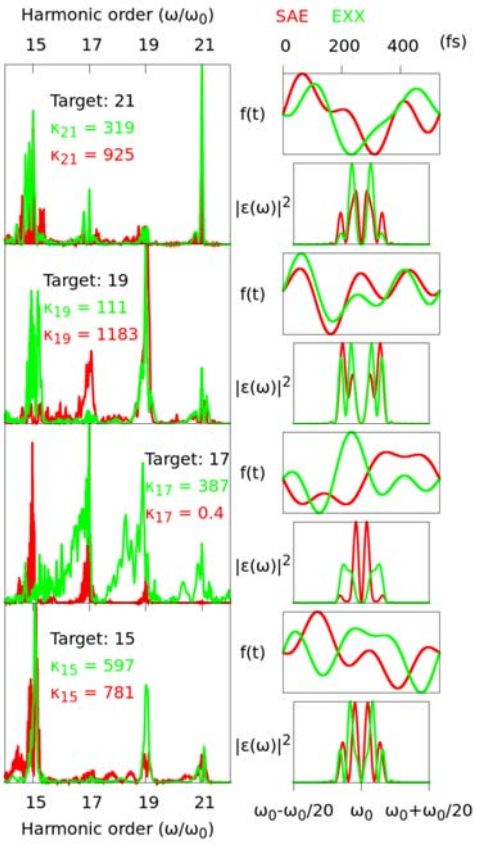
A. Castro, A. Rubio, E.K.U.Gross,
arXiv:1409.4070,
to appear in EPJ B (2015).

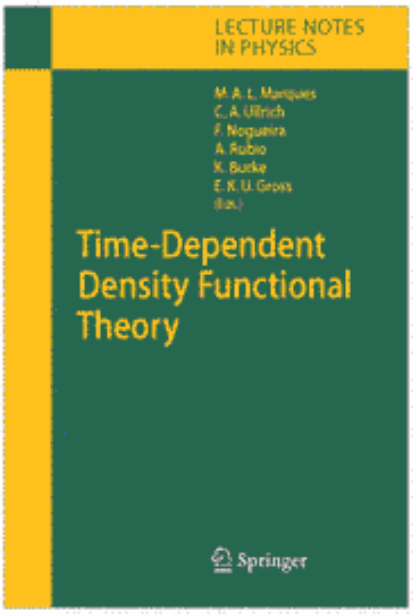


Results for Helium

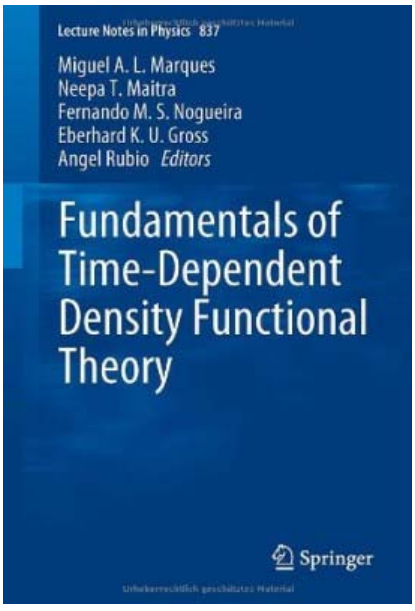
(Using TDDFT with EXX functional)

A. Castro, A. Rubio, E.K.U.Gross,
arXiv:1409.4070,
to appear in EPJ B (2015).





Lecture Notes in Physics 706
(Springer, 2006)



Lecture Notes in Physics 837
(Springer, 2012)