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**

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

**Electronic transport:**

**Generic situation**

- left lead L
- central region C
- right lead R

Bias between L and R is turned on: \( U(t) \) → \( V \)
\[ \hat{H}(t) = \hat{T} + \hat{W} + \sum_{j, \alpha} - \frac{Z_\alpha e^2}{|\mathbf{r}_j - \mathbf{R}_\alpha|} + \mathbf{r}_j \cdot \mathbf{E}(t) \cdot \sin \omega t \]

**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 \( \rho_1(\mathbf{r}, t) \)  
2. Dynamical polarizability \( \alpha(\omega) = -\frac{e}{E} \int z \rho_1(\mathbf{r}, \omega) d^3r \)  
3. Photo-absorption cross section \( \sigma(\omega) = -\frac{4\pi\omega}{c} \text{Im} \alpha \)

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**Photo-absorption in weak lasers**

Diagram showing the energy levels and photo-absorption cross section as a function of laser frequency. The diagram illustrates the transitions between occupied and unoccupied bound states, as well as the continuum states, with peaks corresponding to photo-absorption cross section values.
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
  \[ = 10^9 \text{ t DVDs} \]

**Essence of density-functional 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
Basic 1-1 correspondence:

\[ v(rt) \xleftarrow{\text{1-1}} \rho(rt) \]

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

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

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

Curse or blessing?
The functional $v_{xc}[\rho]$ is universal:

Curse or blessing?

Only ONE functional needs to be approximated

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):

\[ \mathbf{v}(\vec{r}, t) \neq \mathbf{v}'(\vec{r}, t) + \mathbf{c}(t) \Rightarrow \rho(\vec{r}, t) \neq \rho'(\vec{r}, t) \]

\[ \begin{array}{ccc}
\mathbf{v}(\vec{r}, t) & \rightarrow & \mathbf{j}(\vec{r}, t) \\
\mathbf{v}'(\vec{r}, t) & \rightarrow & \mathbf{j}'(\vec{r}, t)
\end{array} \]

\[ \rho(\vec{r}, t) \rightarrow \rho'(\vec{r}, t) \]

\[ \textbf{use} \quad i \partial_t \mathbf{j}(\vec{r}) = \langle \phi(t) \mid [\hat{\mathbf{j}}(\vec{r}), \hat{H}(t)] \mid \phi(t) \rangle \]

\[ \text{equation of motion for } \mathbf{j} \]

\[ \frac{\partial \mathbf{j}}{\partial t} \bigg|_{t=t_0} \neq \frac{\partial \mathbf{j}'}{\partial t} \bigg|_{t=t_0} \]

\[ \frac{\partial^2 \rho}{\partial t^2} \bigg|_{t_0} \neq \frac{\partial^2 \rho'}{\partial t^2} \bigg|_{t_0} \]

\[ \Rightarrow \rho \text{ and } \rho' \text{ will become different from each other infinitesimally later than } t_0 \]
Simplest possible approximation for $v_{xc}[\rho](\vec{r}t)$

Adiabatic Local Density Approximation (ALDA)

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

$V_{xc,\text{stat}}^{\text{hom}}$ = xc potential of static homogeneous e-gas

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


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 $v_0$:

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

$$= \rho[v_0](r \ t) \quad \rightarrow \quad \rho_0(r)$$

$$+ \int \frac{\delta \rho[v]}{\delta v}(r \ t') v_1(r' t') d^3 r' dt' \quad \rightarrow \quad \rho_1(r \ t)$$

$$+ \frac{1}{2} \int \int \frac{\delta^2 \rho[v]}{\delta v(r', t') \delta v(r'' t'')}(r \ t') v_1(r' t') v_1(r'' t'') d^3 r' d^3 r'' dt' dt'' \quad \rightarrow \quad \rho_2(r \ t)$$

...
\[ \rho_1(r,t) = \text{linear density response of interacting system} \]

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

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

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

\[ \chi_s(r,t,r',t') := \left. \frac{\delta \rho_s[v_s](r,t)}{\delta v_s(r',t')} \right|_{v_{s,0}} = \text{density-density response function of non-interacting system} \]

**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

\[ v_{xc}[\rho](r,t) := v_s[\rho](r,t) - v_{\text{ext}}[\rho](r,t) - v_{\text{H}}[\rho](r,t) \]

\( v_{xc} \) is well-defined through non-interacting/interacting 1-1 mapping.
\[
\frac{\delta v_{xc}[\rho](r \, t)}{\delta \rho(r' \, t')} \bigg|_{\rho_0} = \frac{\delta v_S[\rho](r \, t)}{\delta \rho(r' \, t')} \bigg|_{\rho_0} - \frac{\delta v_{\text{ext}}[\rho](r \, t)}{\delta \rho(r' \, t')} \bigg|_{\rho_0} - \frac{\delta(t - t')}{|r - r'|}
\]
\[
\frac{\delta v_{xc}[\rho](r\ t)}{\delta \rho(r't')} \bigg|_{\rho_0} = \frac{\delta v_s[\rho](r\ t)}{\delta \rho(r't')} \bigg|_{\rho_0} - \frac{\delta v_{ext}[\rho](r\ t)}{\delta \rho(r't')} \bigg|_{\rho_0} - \frac{\delta(t-t')}{|r-r'|} \\
\quad \uparrow \quad \uparrow \quad \uparrow \quad \uparrow \\
\quad f_{xc}(r\ t, r't') \quad \chi_s^{-1}(r\ t, r't') \quad \chi^{-1}(r\ t, r't') \quad W_C(r\ t, r't')
\]

\[
f_{xc} + W_C = \chi_s^{-1} - \chi^{-1}
\]
\[
\frac{\delta v_{xc}[\rho](r,t)}{\delta \rho(r',t')}\bigg|_{\rho_o} = \frac{\delta v_S[\rho](r,t)}{\delta \rho(r',t')}\bigg|_{\rho_o} - \frac{\delta v_{ext}[\rho](r,t)}{\delta \rho(r',t')}\bigg|_{\rho_o} - \frac{\delta(t-t')}{|r-r'|}
\]

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

\[\chi_S \cdot \left[ f_{xc} + W_C \right] = \chi_S^{-1} - \chi^{-1} \cdot \chi \]

\[\chi_S \left( f_{xc} + W_C \right) \chi = \chi - \chi_S \]

\[\chi = \chi_S + \chi_S \left( W_{ee} + f_{xc} \right) \chi \]

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

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

- Exact integral equation for \(\rho_1(r,t)\), to be solved iteratively
- Need approximation for \(f_{xc}(r',t'',t''')\) (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.

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

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

where

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

$q = (j, a)$ double index  \hspace{2cm} \alpha_q = f_a - f_j

\[
\Phi_q(r) = \varphi_a^*(r) \varphi_j(r)
\]

\[
\omega_q = \varepsilon_a - \varepsilon_j
\]

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

### Excitation energies of CO molecule

<table>
<thead>
<tr>
<th>State</th>
<th>$\Omega_{\text{expt}}$</th>
<th>KS-transition</th>
<th>$\Delta \epsilon_{\text{KS}}$</th>
<th>TDDFT</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1$\Pi$</td>
<td>5$\Sigma \rightarrow 2\Pi$</td>
<td>0.2523</td>
<td>0.3267</td>
</tr>
<tr>
<td>a</td>
<td>3$\Pi$</td>
<td></td>
<td>0.2323</td>
<td>0.2238</td>
</tr>
<tr>
<td>I</td>
<td>1$\Sigma^-$</td>
<td>1$\Pi \rightarrow 2\Pi$</td>
<td>0.3626</td>
<td>0.3626</td>
</tr>
<tr>
<td>D</td>
<td>1$\Delta$</td>
<td></td>
<td>0.3759</td>
<td>0.3812</td>
</tr>
<tr>
<td>a'</td>
<td>3$\Sigma^+$</td>
<td></td>
<td>0.3127</td>
<td>0.3181</td>
</tr>
<tr>
<td>e</td>
<td>3$\Sigma^-$</td>
<td></td>
<td>0.3631</td>
<td>0.3626</td>
</tr>
<tr>
<td>d</td>
<td>3$\Delta$</td>
<td></td>
<td>0.3440</td>
<td>0.3404</td>
</tr>
</tbody>
</table>


**approximations made:** $v_{\text{xc}}^{\text{LDA}}$ and $f_{\text{xc}}^{\text{ALDA}}$

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**Failures of ALDA in the linear response regime**

- **H$_2$ dissociation is incorrect:**
  
  $$E\left(1\Sigma_u^+\right) - E\left(1\Sigma_g^+\right) \xrightarrow{R \rightarrow \infty} 0 \text{ (in ALDA)}$$


- **response of long chains strongly overestimated**


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

  for insulators, $f_{\text{xc}}^{\text{exact}}(q \rightarrow 0) \xrightarrow{q \rightarrow 0} 1/q^2$ divergent.

- **charge-transfer excitations not properly described**

(see: Dreuw et al., J. Chem. Phys. 119, 2943 (2003))
Failures of ALDA in the linear response regime

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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)

$$D_\sigma (\mathbf{r}, \mathbf{r'}) = \sum_{\sigma_1, \sigma_2, \ldots, \sigma_N} \int d^3r_1 \ldots \int d^3r_N |\Psi (\mathbf{r}\sigma_1, \mathbf{r'}\sigma_2, \mathbf{r}_3\sigma_3, \ldots, \mathbf{r}_N\sigma_N)|^2$$

- diagonal of two-body density matrix
- probability of finding an electron with spin $\sigma$ at $\mathbf{r}$ and another electron with the same spin at $\mathbf{r}'$.

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

- conditional probability of finding an electron with spin $\sigma$ at $\mathbf{r}'$ if we know with certainty that there is an electron with the same spin at $\mathbf{r}$. 
Coordinate transformation

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

**Spherical average**

$$p_\sigma(\mathbf{r},|\mathbf{s}|) = \frac{1}{4\pi} \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi P_\sigma(\mathbf{r},|\mathbf{s}|,\theta,\phi)$$

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

**Expand in a Taylor series:**

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

The first two terms vanish.

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

Why? $C_\sigma(\mathbf{r})$, 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.

$C_\sigma(\mathbf{r})$ small means strong localization at $\mathbf{r}$.
$C_\sigma$ is always $\geq 0$ (because $p_\sigma$ is a probability) and $C_\sigma(\mathbf{r})$ is not bounded from above.

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

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

where

$$C_{\sigma}^{\text{uni}}(\mathbf{r}) = \frac{3}{5} \left( 6\pi^2 \right)^{1/3} \rho_\sigma^{5/3}(\mathbf{r}) = \tau_\sigma^{\text{uni}}(\mathbf{r})$$

is the kinetic energy density of the uniform gas.

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

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**ELF**

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For a determinantal wave function one obtains

in the static case:

\[ C_{\sigma}^{\text{det}}(\vec{r}) = \sum_{i=1}^{N_{\sigma}} \left| \nabla \phi_{\sigma_i}(\vec{r}) \right|^2 - \frac{1}{4} \frac{\left( \nabla \rho_{\sigma}(\vec{r}) \right)^2}{\rho_{\sigma}(\vec{r})} \]

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

in the time-dependent case:

\[ C_{\sigma}^{\text{det}}(\vec{r}, t) = \sum_{i=1}^{N_{\sigma}} \left| \nabla \phi_{\sigma_i}(\vec{r}, t) \right|^2 - \frac{1}{4} \frac{\left( \nabla \rho_{\sigma}(\vec{r}, t) \right)^2}{\rho_{\sigma}(\vec{r}, t)} - j_{\sigma}(\vec{r}, t)^2 / \rho_{\sigma}(\vec{r}, t) \]

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

Acetylene in laser field
(h\omega = 17.15 eV, I = 1.2\times10^{14} \text{ W/cm}^2)
Scattering of a proton from ethylene
(E_{\text{kin(proton)}} = 2 \text{ keV})
TDEL for acetylene in strong laser field
\( (\hbar \omega = 17.15 \text{ eV}, I = 1.2 \times 10^{14} \text{ W/cm}^2) \)

TDEL for scattering process
2 keV proton colliding with ethylene
TDELF movies produced from TD Kohn-Sham equations

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

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

propagated numerically on real-space grid using \textit{octopus} code


Electronic transport with TDDFT

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

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

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

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.,

\[ i \frac{\partial}{\partial t} \phi_C(t) = H_{CC}(t)\phi_C(t) \]

\[ + \int_0^t dt' [H_{CL} G_L(t,t')H_{LC} + H_{CR} G_R(t,t')H_{RC}]\phi_C(t') \]

\[ + iH_{CL} G_L(t,0)\phi_L(0) + iH_{CR} G_R(t,0)\phi_R(0) \]

source term: \( L \rightarrow C \) and \( R \rightarrow C \) charge injection
memory term: \( C \rightarrow L \rightarrow C \) and \( C \rightarrow R \rightarrow C \) 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

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

\[ U(x,t) = U_0 \sin(kx - wt) \]

\( k = 1.6 \ \text{a.u., } w = 0.2 \ \text{a.u.} \)

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!!


Laser-induced ultrafast demagnetization of solids: The first 100 femto-seconds
First experiment on ultrafast laser induced demagnetisation

More recent experiments show demagnetization in less than 100 fs

Beaurepaire et al, PRL 76, 4250 (1996)
Possible mechanisms for demagnetisation

- Direct interaction of spins with the magnetic component of the laser
  Zhang, Huebner, PRL 85, 3025 (2000)
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  (ultimately leading to transfer of spin angular momentum to the lattice)
  Koopmans et al, PRL 95, 267207 (2005)

• Super-diffusive spin transport
  Battiatto, Carva, Oppeneer, PRL 105, 027203 (2010)
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• Ab-initio (TDDFT) result for the first 50 fs:
  Laser-driven charge excitation followed by spin-orbit-driven
  demagnetization of the localized d-electrons

Theoretical approach: TDDFT with SOC

\[
\frac{i}{\partial t} \varphi_k (r,t) = \left[ \frac{1}{2} (-i\nabla - A_{laser}(t))^2 + v_S [\rho, m](r,t) - \mu_B \sigma \cdot B_S [\rho, m](r,t) \right]

+ \frac{\mu_B}{2c} \sigma \cdot (\nabla v_S [\rho, m](r,t)) \times (-i\nabla) \varphi_k (r,t)
\]

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

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

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)

![Demagnetisation in Fe, Co and Ni](image)
Cr monolayer

Analysis of the results
Calculation without spin-orbit coupling

components of spin moment

![Graph showing components of spin moment](image1)

![Graph showing relative and projected moments](image2)
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.

Playing with laser parameters

![Graph showing magnetic moment over time for different field strengths.](image)
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.


Why is that important?

Ab-initio description of spin dynamics:

microscopic equation of motion (following from TDSDFT)

$$\dot{m}(\vec{r}, t) = m(\vec{r}, t) \times B_{xc}(\vec{r}, t) - \nabla \cdot J_s(\vec{r}, t)$$

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 $e_{XC}[n,m]$ from MBPT and parametrize $e_{XC}[n,m]$ to use as non-collinear GGA.


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

$$m(r) = m \begin{pmatrix} \frac{s \cos(q \cdot r)}{\sqrt{1-s^2}} \\ \frac{s \sin(q \cdot r)}{\sqrt{1-s^2}} \end{pmatrix}$$
\[ E_{xc}^{GGA}[n, \tilde{m}] = \int d^3r \, n(r) \, e_{xc}^{SSW}(n(r), m(r), q(r), s(r)) \]

\[
S^2(r) = \frac{D_T^2(r)}{D_T^2(r) + m^4(r) d_T(r)} \quad q^2(r) = \frac{D_T^2(r) + m^4(r) d_T(r)}{m^4(r) D_T(r)}
\]

\[
D_T(r) = |\tilde{m}(r) \times (\nabla \otimes \tilde{m}(r))|^2 \quad d_T(r) = |\tilde{m}(r) \times (\nabla^2 \tilde{m}(r))|^2
\]

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:**

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**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 $\phi_f$ 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 given target state $\Phi_f$, 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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with $\hat{T}$ and $\hat{V}$ the Hamiltonians, $\mu$ the nonlinear susceptibility, and $\epsilon$ the control parameter.

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:
   \[ \delta_x J = 0 \rightarrow i \partial_t \psi(t) = \hat{H}(t)\psi(t), \quad \psi(0) = \phi \]

2. Schrödinger equation with final condition:
   \[ \delta_\psi J = 0 \rightarrow i \partial_t \chi(t) = \hat{H}(t)\chi(t), \quad \chi(T) = \hat{O}\psi(T) \]

3. Field equation:
   \[ \delta_\varepsilon J = 0 \rightarrow \varepsilon(t) = \frac{1}{\alpha} \text{Im} \left\langle \chi(t) | \hat{\mu} | \psi(t) \right\rangle \]

**Algorithm**

- Forward propagation
- Backward propagation
- New laser field


**Quantum ring: Control of circular current**

TDSE:

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

\[ \hat{H}_0 = -\frac{\hbar^2}{2m^*} \nabla^2 + \frac{1}{2} m^* \Omega^2 r^2 + V_0 e^{-r^2/d^2} \]

\[ \epsilon(t) = (\epsilon_x(t), \epsilon_y(t)) \]

$30 \text{ nm}$

$V_{\text{ext}}(r)$

$\varepsilon(t)$

$E_i$

$i$

$L$
Control of currents

\[ |\psi(t)|^2 \text{ and } j(t) \]

\[ l = -1 \]
\[ l = 0 \]
\[ l = 1 \]

\[ I \sim \mu A \]


OCT of ionization

- Calculations for 1-electron system \( \text{H}_2^+ \) 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:

\[ J_1 = \langle \Psi (T) \hat{O} \Psi (T) \rangle \]

with \( \hat{O} = \hat{1} - \sum_{i}^\text{bound} |\varphi_i\rangle \langle \varphi_i| \)

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

\[ \varepsilon (t) = f (t) \cos (\omega_0 t) \quad \text{with} \quad \omega_0 = 0.114 \text{ a.u.} \quad (\lambda = 400 \text{ nm}) \]

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

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:

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

(ii) \( \int_{0}^{T} dt \varepsilon^2 (t) = E_0 \).

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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\[\text{Instead of solving the many-body TDSE, combine OCT with TDDFT}\]

**Important**: Control target must be formulated in terms of the density!
Enhancement of a single harmonic peak

Harmonic Spectrum:

\[ H(\omega) = \left| \int dt e^{i\omega t} \frac{d^2}{dt^2} \left\{ \int d^3 r z p(\bar{r}, t) \right\} \right|^2 \]

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 \( \omega_0 \), choose coefficients as \( \alpha_7 = 4, \alpha_3 = \alpha_5 = \alpha_9 = \alpha_{11} = -1 \)

Measure of enhancement: Compare with reference pulse:

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

\[ \kappa_j = \max_{\omega \in [j\omega_0 - \beta, j\omega_0 + \beta]} \frac{H(\omega)}{H_{\text{ref}}(j\omega_0)} \]
Harmonic spectrum of reference pulse for hydrogen atom

Results for Hydrogen

A. Castro, A. Rubio, E.K.U. Gross,
arXiv:1409.4070,
Results for Helium

(Using TDDFT with EXX functional)


Lecture Notes in Physics 706
(Springer, 2006)

Lecture Notes in Physics 837
(Springer, 2012)