Time-Dependent Electron Localization Function (TD-ELF)

**GOAL**
Time-resolved visualization of the breaking and formation of chemical bonds.
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)
\[ D_{\sigma} (\vec{r}, \vec{r}') = \sum_{\sigma_3\sigma_4 \ldots \sigma_N} \int d^3 r_3 \ldots \int d^3 r_N \left| \Psi (\vec{r}\sigma, \vec{r}'\sigma, \vec{r}_3\sigma_3, \ldots, \vec{r}_N\sigma_N) \right|^2 \]

= diagonal of two-body density matrix

= probability of finding an electron with spin \( \sigma \) 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 \( \sigma \) 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 $\sigma$ at $\vec{r}$, then $P_\sigma (\vec{r}, \vec{r} + \vec{s})$ is the (conditional) probability of finding another electron at $\vec{s}$, where $\vec{s}$ is measured from the reference point $\vec{r}$.

Spherical average

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

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

Expand in a Taylor series:

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

The first two terms vanish.
$C_\sigma(\vec{r})$ is a measure of electron localization.

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

$C_\sigma(\vec{r})$ small means strong localization at $\vec{r}$
\( C_\sigma \) is always \( \geq 0 \) (because \( p_\sigma \) 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))

\[
\text{ELF} = \frac{1}{1 + \left( \frac{C_\sigma(\vec{r})}{C^\text{uni}_\sigma(\vec{r})} \right)^2}
\]

where
\[
C^\text{uni}_\sigma(\vec{r}) = \frac{3}{5} (6\pi^2)^{2/3} \rho^{5/3}_\sigma(\vec{r}) = \tau^\text{uni}_\sigma(\vec{r})
\]
is the kinetic energy density of the uniform gas.

**Advantage:** ELF is dimensionless and \( 0 \leq \text{ELF} \leq 1 \)
12-electron 2D quantum dot with four minima

Density

ELF

For a determinantal wave function one obtains

in the static case:

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

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

in the time-dependent case:

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

(T. Burnus, M. Marques, E.K.U.G., PRA (Rapid Comm) 71, 010501 (2005))
TDELF for acetylene in strong laser field

($\hbar \omega = 17.15$ eV, $I = 1.2 \times 10^{14}$ W/cm$^2$)
TDELF for scattering process

2 keV proton colliding with ethylene
How long does it take to break a bond in a laser field?

Which bond breaks first, which second, etc, in a collision process?

Are there intermediary (short-lived) bonds formed during a collision, which are not present any more in the collision products?
Use TD Kohn-Sham equations

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

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

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

\texttt{www.tddft.org}

- more TDELF movies
- download \textit{octopus}

**Molecular Electronics**

**Dream:** Use single molecules as basic units (transistors, diodes, …) of electronic devices

Bias between L and R is turned on: $U(t) \rightarrow V$ for large $t$

A steady current, $I$, may develop as a result.

**Goal 1:** Calculate current-voltage characteristics $I(V)$

**Goal 2:** Analyze how steady state evolves, if it evolves at all

**Goal 3:** Control path of current through molecule by laser
Molecular Electronics

Control the path of the current with laser
Molecular Electronics

Control the path of the current with laser

left lead  right lead
Standard approach: Landauer-Büttiker formalism

\[ I(V) = \frac{e}{h} \int dE \ T(E,V) \left[ f(E - \mu_1) - f(E - \mu_2) \right] \]

Transmission function
T(E,V) calculated from static, i.e. ground-state DFT

\[ \mu_{1,2} = E_F \mp \frac{eV}{2} \]
Chrysazine

Relative Total Energies and HOMO-LUMO Gaps

Chrysazine (a)
0.0 eV 3.35 eV

Chrysazine (b)
0.54 eV 3.41 eV

Chrysazine (c)
1.19 eV 3.77 eV
Possible use: Optical switch

Motivation to develop a time-dependent approach:

Two conceptual issues:
🌟 Assumption that upon switching-on the bias a steady state is reached
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🌟 Steady state is treated with ground-state DFT
Motivation to develop a time-dependent approach:

Two conceptual issues:
👩 Assumption that upon switching-on the bias a steady state is reached
👩 Steady state is treated with ground-state DFT

One practical issue:
👩 TD external fields, AC bias, laser control, etc, cannot be treated within the static approach
**TDKS equation** (E. Runge, EKUG, PRL 52, 997 (1984))

\[
\begin{align*}
\text{i}\hbar \frac{\partial}{\partial t} \varphi_j(r,t) &= \left( -\frac{\hbar^2 \nabla^2}{2m} + v_{\text{KS}}[\rho](r,t) \right) \varphi_j(r,t) \\
v_{\text{KS}}[\rho(r',t')](r,t) &= v(r,t) + \int d^3r' \frac{\rho(r',t)}{|r-r'|} + v_{\text{xc}}[\rho(r',t')](r,t)
\end{align*}
\]
**Molecular Electronics with TDDFT**

**TDKS equation**

\[
\begin{align*}
    i \frac{\partial}{\partial t} \begin{pmatrix}
        \phi_L(t) \\
        \phi_C(t) \\
        \phi_R(t)
    \end{pmatrix} &= \begin{pmatrix}
        H_{LL}(t) & H_{LC}(t) & H_{LR}(t) \\
        H_{CL}(t) & H_{CC}(t) & H_{CR}(t) \\
        H_{RL}(t) & H_{RC}(t) & H_{RR}(t)
    \end{pmatrix} \begin{pmatrix}
        \phi_L(t) \\
        \phi_C(t) \\
        \phi_R(t)
    \end{pmatrix}
\end{align*}
\]
Propagate TDKS equation on spatial grid

- \( \varphi_A(t) = \text{vector}(\varphi(r_1,t), \varphi(r_2,t), \ldots) \) with grid points \( r_1, r_2, \ldots \) in region \( A \) (\( A = L, C, R \))

- \( H_{AB}(t) = \) corresponding grid - blocks of TDKS Hamiltonian

\[
H_{AB}(t) \text{ for } A \neq B \quad \text{is purely kinetic, because KS potential is local}
\]

\[
H_{CL}, H_{LC}, H_{CR}, H_{RC} \quad \text{are time-independent}
\]

\[
H_{LR} = H_{RL} = 0
\]
\[ i \frac{\partial}{\partial t} \begin{pmatrix} \varphi_L(t) \\ \varphi_C(t) \\ \varphi_R(t) \end{pmatrix} = \begin{pmatrix} H_{LL}(t) & H_{LC}(t) & H_{XR}(t) \\ H_{CL}(t) & H_{CC}(t) & H_{CR}(t) \\ H_{RL}(t) & H_{RC}(t) & H_{RR}(t) \end{pmatrix} \begin{pmatrix} \varphi_L(t) \\ \varphi_C(t) \\ \varphi_R(t) \end{pmatrix} \]

Hence:

\[ \left( i \frac{\partial}{\partial t} - H_{\text{LL}}(t) \right) \varphi_L(t) = H_{\text{LC}} \varphi_C(t) \]

\[ i \frac{\partial}{\partial t} \varphi_C(t) = H_{\text{CL}} \varphi_L(t) + H_{\text{CC}}(t) \varphi_C(t) + H_{\text{CR}} \varphi_R(t) \]

\[ \left( i \frac{\partial}{\partial t} - H_{\text{RR}}(t) \right) \varphi_R(t) = H_{\text{RC}} \varphi_C(t) \]

Next step: Solve inhomogeneous Schrödinger equations \( L \), \( R \) for \( \varphi_L, \varphi_R \) using Green’s functions of \( L, R \), leads
Define Green’s Functions of left and right leads:

\[
\left( i \frac{\partial}{\partial t} - H_{LL} (t) \right) G_L (t, t') = \delta (t - t') \quad \left( i \frac{\partial}{\partial t} - H_{RR} (t) \right) G_R (t, t') = \delta (t - t')
\]

\[\Rightarrow \quad \varphi_L = \hat{G}_L \left[ \text{r.h.s. of } \text{(L)} \right] + \left[ \text{solution of hom. SE } \left( i \frac{\partial}{\partial t} - H_{LL} (t) \right) \psi = 0 \right] \]

\[\varphi_R = \hat{G}_R \left[ \text{r.h.s. of } \text{(R)} \right] + \left[ \text{solution of hom. SE } \left( i \frac{\partial}{\partial t} - H_{RR} (t) \right) \psi = 0 \right] \]

Explicitly:

\[\varphi_L (t) = \int_0^t dt' G_L (t, t') H_{LC} \varphi_C (t') + i G_L (t, 0) \varphi_L (0) \]

\[\varphi_R (t) = \int_0^t dt' G_R (t, t') H_{RC} \varphi_C (t') + i G_R (t, 0) \varphi_R (0) \]

insert this in equation \( \text{(C)} \)
Effective TDKS Equation for the central (molecular) region

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

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

\[ + i H_{CL} G_L(t,0) \varphi_L(0) + i H_{CR} G_R(t,0) \varphi_R(0) \]

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
Test 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 $\epsilon_F = 0.3$ a.u.
Steady state coincides with Landauer formula and is reached after a few femtoseconds
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.

Recent 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 $U(x,t) = U_o \sin(kx-\omega t)$  
($k = 1.6$ a.u., $\omega = 0.2$ a.u. 
Fermi energy = 0.3 a.u.)
Experimental result:

Current flows in direction opposite to sound wave
Current goes in direction opposite to the external field!!

Bound state oscillations and memory effects

Numerical: E. Khosravi, S. Kurth, G. Stefanucci, E.K.U.G.,

If Hamiltonian of a (non-interacting) biased system in the long-time limit supports two or more bound states then current has steady, $I^{(S)}$, and dynamical, $I^{(D)}$, parts:

$$I(t \to \infty) = I^{(S)} + I^{(D)}(t)$$

$$I^{(D)}(t) = \sum_{b,b'} \Lambda_{bb'} \sin[(\varepsilon_b - \varepsilon_{b'})t]$$

Note: $\Lambda_{bb'}$ depends on history of TD Hamiltonian (memory!)

Questions: -- How large is $I^{(D)}$ vs $I^{(S)}$?
-- How pronounced is history dependence?
History dependence of undamped oscillations

1-D model:
start with flat potential, switch on constant bias, wait until transients die out, switch on gate potential with different switching times to create two bound states

note: amplitude of bound-state oscillations may not be small compared to steady-state current
So far: systems without e-e interaction

**Next step:** TDKS, i.e. inclusion of e-e interaction via approximate xc potential

→ time-dependent picture of Coulomb blockade
Model system
\[ \hat{H}(t) = \hat{H}_{\text{QD}} + \sum_{\alpha=L,R} \hat{H}_\alpha + \hat{H}_T + \hat{H}_{\text{bias}}(t) \]

\[ \hat{H}_{\text{QD}} = v_{\text{ext}} \sum_{\sigma} \hat{n}_{0\sigma} + U\hat{n}_{0\uparrow}\hat{n}_{0\downarrow} \]

\[ \hat{H}_\alpha(t) = -\sum_{\sigma} \sum_{i=1}^\infty (V\hat{c}_{i+1\alpha,\sigma}\hat{c}_{i\alpha,\sigma} + \text{h.c.}) \]

\[ \hat{H}_T = -\sum_{\alpha,\sigma} \sum_{i=1}^\infty (V_{\text{link}}\hat{c}_{i\alpha,\sigma}^\dagger\hat{c}_{0\sigma} + \text{h.c.}) \]

\[ \hat{H}_{\text{bias}}(t) = -\sum_{\alpha,\sigma} \sum_{i=1}^\infty W_\alpha(t)\hat{n}_{i\alpha,\sigma} \]
Solve TDKS equations (instead of fully interacting problem):

\[
\hat{H}_{KS}(t) = \hat{H}_{QD,KS}(t) + \sum_{\alpha=L,R} \hat{H}_{\alpha} + \hat{H}_{T} + \hat{H}_{\text{bias}}(t)
\]

\[
\hat{H}_{QD,KS}(t) = \sum_{\sigma} v_{KS} \left[ n_0(t) \right] \hat{n}_{0\sigma}
\]

\[
n_0(t) = \sum_{\sigma} n_{0\sigma}(t)
\]

\[
v_{KS} \left[ n_0(t) \right] = v_{\text{ext}} + \frac{1}{2} U n_0(t) + v_{xc} \left[ n_0(t) \right]
\]

LDA functional for \(v_{xc}\) is available from exact Bethe-ansatz solution of the 1D Hubbard model.

\[ v_{xc}^{LDA}[n] = \theta(1-n)v_{xc}^{(1)}[n] - \theta(n-1)v_{xc}^{(1)}[2-n] \]

\[ v_{xc}^{(1)}[n] = -\frac{1}{2} Un - 2V_{\text{link}} \left[ \cos\left(\frac{\pi n}{2}\right) - \cos\left(\frac{\pi n}{\beta}\right) \right] \]

We use this functional as Adiabatic LDA (ALDA) in the TD simulations.

**Note:** \[ v_{xc}^{LDA}[n] \] has a discontinuity at \( n = 1 \)
Is this Coulomb blockade??
Is this Coulomb blockade??

Steady-state equation has no solution in this parameter regime (if $v_{KS}$ has sharp discontinuity)!!
Steady-state density as function of applied bias for KS potential with smoothened discontinuity

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**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?

possible goals:  

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:

$$J_1 = \left| \langle \Psi(T) | \Phi_f \rangle \right|^2 = \langle \Psi(T) | \Phi_f \rangle \langle \Phi_f | \Psi(T) \rangle = \langle \Psi(T) | \hat{O} | \Psi(T) \rangle$$
Optimal control of static goals
(standard formulation)

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with the constraints:

$$J_2 = -\alpha \left[ \int_0^T dt \varepsilon^2(t) - E_0 \right] \quad \text{with} \quad E_0 = \text{given fluence}$$
Optimal control of static targets  
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For given target state $\Phi_f$, maximize the functional:

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with the constraints:

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

$E_0 = \text{given fluence}$

$$J_3[\varepsilon, \Psi, \chi] = -2 \text{Im} \int_0^T dt \langle \chi(t) | -i \partial_t - [\hat{T} + \hat{V} - \mu \varepsilon(t)] | \Psi(t) \rangle$$
Optimal control of static targets
(standard formulation)

For given target state $\Phi_f$, maximize the functional:

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TDSE
Optimal control of static targets
(standard formulation)

For **given** target state $\Phi_f$, maximize the functional:

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

with the constraints:

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

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

**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:

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

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:

   $$\delta \varepsilon J = 0 \rightarrow \varepsilon(t) = \frac{1}{\alpha} \text{Im}\langle \chi(t) | \hat{\mu} | \psi(t) \rangle$$

**Algorithm**

- Forward propagation
- Backward propagation
- New laser field

Quantum ring: Control of circular current

TD-SE:

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

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

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

30 nm

\[ V_{\text{ext}}(r) \]

\[ \mathcal{E}(t) \]

\[ E_i \]

\[ l \]

Levels:
1. 1.04
2. 1.12
3. 1.24
Control of currents

$|\psi(t)|^2$ and $j(t)$

Control of charge transfer along selected pathways

Trajectory 1

Trajectory 2
Time-evolution of wavepacket with the optimal laser pulse for trajectory 1
Optimal pulse
Optimal pulse
Thanks!