TDCDFT: Basic formalism

Carsten A. Ullrich
University of Missouri

Benasque, January 2012
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2. Review of ground-state DFT

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Overview

Lecture I: Basic formalism of TDCDFT
► TDDFT and its limitations
► Existence theorems and properties of TDCDFT
► Memory and nonlocality in TDDFT
► The VK functional

Lecture II: Applications of TDCDFT in linear response

Lecture III: TDCDFT in the nonlinear regime
Consider an N-electron system with Hamiltonian

$$\hat{H}(t) = \sum_{j=1}^{N} \left[ -\frac{\nabla_j^2}{2} + V(r_j, t) \right] + \frac{1}{2} \sum_{j \neq k}^{N} \frac{1}{|r_j - r_k|}$$

\[V(r, t) \xrightarrow{i \frac{\partial \Psi}{\partial t} = \hat{H} \Psi} \Psi(t) \xrightarrow{\langle \Psi(t) | \hat{n} | \Psi(t) \rangle} n(r, t)\]

Therefore:

$$V(r, t) \leftrightarrow^{1:1} n(r, t)$$
Situations not covered by the RG theorem

1. TDDFT does not apply for time-dependent magnetic fields or for electromagnetic waves. These require vector potentials.

2. The original RG proof is for finite systems with potentials that vanish at infinity (step 2). Extended/periodic systems can be tricky:

- TDDFT works for periodic systems if the time-dependent potential is also periodic in space.
- The RG theorem does not apply when a homogeneous electric field (a linear potential) acts on a periodic system.

Reminder: longitudinal and transverse vector fields

\[ U = U_L + U_T \]

Any vector field can be decomposed into a longitudinal and a transverse field, which can be constructed as follows:

\[
U_L(\mathbf{r}) = -\frac{1}{4\pi} \nabla \int d^3 r' \frac{\nabla' \cdot U(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} 
\]

\[
U_T(\mathbf{r}) = \frac{1}{4\pi} \nabla \times \nabla \times \int d^3 r' \frac{U(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} 
\]
V-representability of current densities

Continuity equation only involves **longitudinal** part of the current density:

\[
\frac{\partial n(r,t)}{\partial t} = -\nabla \cdot j_L(r,t)
\]

If \( j(r,t) = j_L(r,t) + j_T(r,t) \) comes from a potential \( V(r,t) \)
then \( j'(r,t) = j_L(r,t) + j'_T(r,t) \) cannot come from \( V'(r,t) \).

[both have the same \( n(r,t) \), and this would violate the RG theorem]

In general, time-dependent currents are not \( V \)-representable.
This makes sense: \( j \) is vector (3 components), and \( V \) is scalar (1 component).

TDCDFT: basic existence theorems

The full current is uniquely determined by the pair of scalar and vector potentials \((V,A)\)

\[
\hat{H}(t) = \sum_{j=1}^{N} \left\{ \frac{1}{2} \left[ p_j + A(r_j,t) \right]^2 + V(r_j,t) \right\} + \frac{1}{2} \sum_{j \neq k}^{N} \frac{1}{|r_j - r_k|}
\]

\[
\hat{H}_{KS}(t) = \sum_{j=1}^{N} \left\{ \frac{1}{2} \left[ p_j + A_s(r_j,t) \right]^2 + V_s(r_j,t) \right\}
\]

V-representability of TDCDFT on lattices: I. Tokatly, PRB 83, 035127 (2011) (see workshop, Friday 9:30)
**TDKS equation in TDCDFT**

\[
i \frac{\partial}{\partial t} \varphi_j(\mathbf{r}, t) = \left( \frac{1}{2} \left[ \nabla + \mathbf{A}_s(\mathbf{r}, t) \right] \right)^2 + V_s(\mathbf{r}, t) \varphi_j(\mathbf{r}, t)
\]

Gauge-invariant physical current density:

\[
\mathbf{j}(\mathbf{r}, t) = n(\mathbf{r}, t) \mathbf{A}_s(\mathbf{r}, t) + \frac{1}{2i} \sum_{j=1}^{N} \left[ \varphi_j^*(\mathbf{r}, t) \nabla \varphi_j(\mathbf{r}, t) - \varphi_j(\mathbf{r}, t) \nabla \varphi_j^*(\mathbf{r}, t) \right]
\]

\[
= \mathbf{j}_{\text{dia}}(\mathbf{r}, t) + \mathbf{j}_{\text{para}}(\mathbf{r}, t)
\]

Scalar and vector potentials:

\[
V_s[\mathbf{j}](\mathbf{r}, t) = V(\mathbf{r}, t) + V_H(\mathbf{r}, t) + V_{xc}(\mathbf{r}, t)
\]

\[
A_s[\mathbf{j}](\mathbf{r}, t) = A(\mathbf{r}, t) + A_{xc}(\mathbf{r}, t)
\]

(ignore Hartree vector potential from induced currents)
Gauge transformations

The map

\[(V, A) \leftrightarrow j(r, t)\]

is unique up to within gauge transformations of the form

\[V(r, t) \rightarrow V(r, t) - \frac{\partial \Lambda(r, t)}{\partial t}\]

\[A(r, t) \rightarrow A(r, t) + \nabla \Lambda(r, t)\]

where \(\Lambda\) is an arbitrary well-behaved function which vanishes at the initial time.

**note:** can choose a particular gauge such that the scalar potential vanishes.
TDCDFT in the linear response regime

\[ j_1(r, \omega) = \int d^3r' \tilde{\chi}_s(r, r', \omega) \left\{ A_{\text{ext},1}(r, \omega) + A_{H,1}(r, \omega) + A_{xc,1}(r, \omega) \right\} \]

KS current-current response tensor: diamagnetic + paramagnetic part

\[ \chi_{s,\mu\nu}(r, r', \omega) = n_0(r)\delta(r-r')\delta_{\mu\nu} + \frac{1}{2} \sum_{j,k}^{\infty} \frac{f_k - f_j}{\varepsilon_k - \varepsilon_j + \omega + i\eta} P^{kj}_\mu(r)P^{jk}_\nu(r') \]

where \[ P^{kj}_\mu = \varphi^*_k(r)\nabla_\mu \varphi_j(r) - \varphi_j(r)\nabla_\mu \varphi^*_k(r) \]

Note:

\[ \chi_s(r, r', \omega) = \frac{1}{\omega^2} \sum_{\mu\nu} \nabla_\mu \nabla'_\nu \chi_{s,\mu\nu}(r, r', \omega) \]
TDCDFT: effective vector potential

\[ A_{ext,1}(r, \omega) : \text{external perturbation. Can be a true vector potential, or a gauge transformed scalar perturbation:} \]
\[ A_{ext,1} = \frac{1}{i \omega} \nabla V_{ext,1} \]

\[ A_{H,1}(r, \omega) = \frac{\nabla}{(i \omega)^2} \int d^3 r' \frac{\nabla' \cdot j_1(r', \omega)}{|r - r'|} \]
gauge transformed Hartree potential

\[ A_{xc,1}(r, \omega) = \int d^3 r' \hat{f}_{xc}(r, r', \omega) j_1(r', \omega) \]
the \( xc \) kernel is now a tensor!

\[ \text{ALDA: } A_{xc,1}^{ALDA}(r, \omega) = \frac{\nabla}{(i \omega)^2} \int d^3 r' f_{xc}^{ALDA}(r, r') \nabla \cdot j_1(r', \omega) \]
Why TDCDFT?

► TDCDFT overcomes several formal limitations of TDDFT:
  ● allows treatment of electromagnetic waves, vector potentials, uniform applied electric fields.
  ● works for all extended systems. One does not need the condition that the current density vanishes at infinity.

Example: Circular dichroism spectra require TDCDFT (formally)

\[ R_n = \text{Im} \left[ \mathbf{p}_1(\Omega_n) \cdot \mathbf{m}_1^*(\Omega_n) \right] \]

Rotatory strength

\[ \mathbf{m}_1(\omega) = \frac{1}{2} \int d^3r \, \mathbf{r} \times \mathbf{j}_1(\mathbf{r}, \omega) \]

Electric dipole response

Magnetic dipole response
But TDCDFT is also practically useful in situations that could, in principle, be fully described with TDDFT:

- Upgrading to the current density can be a more “natural” way to describe dynamical systems.
- Helps to deal with the **ultranonlocality** problem of TDDFT
- Provides ways to construct **nonadiabatic** approximations

Let’s talk about memory and spatial long-range in TD(C)DFT!
TDSE versus TDKS

\[
\sum_j \left( -\frac{\nabla_j^2}{2} + V(r_j, t) \right) + \sum_{j \neq k} \frac{1}{|r_j - r_k|} - i \frac{\partial}{\partial t} \right] \Psi(r_1, \ldots, r_N, t) = 0
\]

Full many-body TDSE: linear equation, instantaneous interactions.

\[
\left( -\frac{\nabla^2}{2} + V(r, t) + V_H(r, t) + V_{xc}(r, t) - i \frac{\partial}{\partial t} \right) \varphi_j(r, t) = 0
\]

TDKS equation: nonlinear (H+xc), memory-dependent (xc) Hamiltonian.

Via \( \partial / \partial t \), both TDSE and TDKS carry the memory of the initial states from where the time propagation starts, \( \Psi(0) \) and \( \varphi_j(0) \).
Two kinds of xc memory in TDDFT

dependence on initial states, except when starting from the ground state

\[ V_{xc} \left[ n, \Psi(0), \Phi_{KS}(0) \right](r, t) \]

dependence on densities:

\[ n(r', t'), \quad t' \leq t \]

(nonlocal in space and time)
The adiabatic approximation

\[ V_{xc}^A[n](\mathbf{r}, t) = V_{xc}^{\text{static}}[n(\mathbf{r}, t)](\mathbf{r}) \]

Take any approximate ground-state xc functional, and plug in a time-dependent density. Most widely used: ALDA

\[ V_{xc}^{\text{ALDA}}(\mathbf{r}, t) = \frac{d e_{xc}^{\text{unif}}(\bar{n})}{d \bar{n}} \bigg|_{\bar{n}=n(\mathbf{r}, t)} \]

ALDA depends only on the density at the same space-time point: \( n(\mathbf{r}, t) \)

“Adiabatic” means: no history dependence, no memory, no retardation.
Construction of the exact xc potential (2 electrons)

Step 1: solve full 2-electron Schrödinger equation

\[
\begin{bmatrix}
-\frac{\nabla_{1}^{2}}{2} - \frac{\nabla_{2}^{2}}{2} + V(r_{1}, t) + V(r_{2}, t) + \frac{1}{|r_{1} - r_{2}|} - i \frac{\partial}{\partial t}
\end{bmatrix} \Psi(r_{1}, r_{2}, t) = 0
\]

Step 2: calculate the exact time-dependent density

\[
\sum_{s_{1}, s_{2}} \int d\vec{r}_{2} |\Psi(r, r_{2}, t)|^{2} = n(r, t) = 2 |\varphi(r, t)|^{2}
\]

Step 3: find that TDKS system which reproduces the density

\[
\left[ -\frac{\nabla^{2}}{2} + V(r, t) + V_{H}(r, t) + V_{xc}(r, t) - i \frac{\partial}{\partial t} \right] \varphi(r, t) = 0
\]
Construction of the exact xc potential

Ansatz: \[ \varphi(r, t) = \sqrt{\frac{n(r, t)}{2}} \exp(i\alpha(r, t)) \]

\[ V_{xc}(r, t) = -V(r, t) - V_H(r, t) \]
\[ + \frac{1}{4} \nabla^2 \ln n(r, t) + \frac{1}{8} \left| \vec{\nabla} \ln n(r, t) \right|^2 \]
\[ - \dot{\alpha}(r, t) - \frac{1}{2} \left| \nabla \alpha(r, t) \right|^2 \]

\[ V^{A}_{xc} \]
\[ V^{dyn}_{xc} \]
Example

\[ n(x, t) = \frac{2}{a(t) \sqrt{\pi}} e^{-\frac{x^2}{a(t)^2}} \]

\[ a(t) = \overline{a}(2 - \cos(\omega t)) \]

is produced by this KS potential:

\[ V_s(x, t) = \frac{1}{2} k(t) x^2 \]

with TD curvature

\[ k(t) = \frac{1}{a(t)^4} - \frac{\ddot{a}(t)}{a(t)} \]

\[ \begin{align*}
A & \quad \text{dyn} \\
\text{large } V_{xc}^{\text{dyn}} & 
\end{align*} \]
The adiabatic approximation for excitation energies

- In general, the adiabatic approximation works well for excitations which have an analogue in the KS system (single excitations).

- Formally justified only for infinitely slow electron dynamics. But why is it that the frequency dependence seems less important?

The frequency scale of $f_{xc}$ is set by correlated multiple excitations, which are absent in the KS spectrum.

- Adiabatic approximation fails for more complicated excitations (multiple, charge-transfer). See lectures by Neepa Maitra.

- Misses dissipation of long-wavelength plasmon excitations.

Fundamental question: what is the proper extension of the LDA into the dynamical regime?
Nonlocality in space and time

Visualize electron dynamics as the motion (and deformation) of infinitesimal fluid elements:

\[ \mathbf{r}, t \quad \rightarrow \quad \mathbf{r}', t' \]

Nonlocality in time (memory) implies nonlocality in space!

I.V. Tokatly, PRB 71, 165104 and 165105 (2005), PRB 75, 125105 (2007)
Ultranonlocality in TDDFT

Zero-force theorem: \[ \int d^3r \, n(r, t) \nabla V_{xc}(r, t) = 0 \]

Linearized form: \[ \int d^3r' \nabla n_0(r') \, f_{xc}(r, r', \omega) = \nabla V_{xc,0}(r) \]

If the xc kernel has a **finite range**, we can write for slowly varying systems:

\[ \nabla n_0(r) \int d^3r' \, f_{xc}(r, r', \omega) = \nabla V_{xc,0}(r) \]

\[ \Rightarrow f_{xc}^{\text{hom}}(k = 0, \omega) \]

l.h.s. is frequency-dependent, r.h.s is not: **contradiction!**

\[ \rightarrow f_{xc}(r, r', \omega) \] has infinitely long spatial range!
An xc functional that depends only on the local density (or its gradients) cannot see the motion of the entire slab.

A density functional needs to have a long range to see the motion through the changes at the edges.
A parabolically confined, interacting N-electron system can carry out an undistorted, undamped, collective “sloshing” mode, where
\[ n(r, t) = n_0 (r - R(t)), \] with the CM position \( R(t) \).
Failure of nonadiabatic local density functionals

- undamped density oscillations
- xc potential rides along with density
- constant velocity field

► bulk plasmon: periodic compression and rarefaction of the density
► intrinsic damping due to decay of collective mode into single-particle excitations
► oscillating velocity field

xc functionals based on local **density** can’t distinguish the two cases! But one can capture the correct physics with **current** functionals.
“Upgrading” TDDFT: Current-TDDFT

\[ n(\mathbf{r}, t) \] \quad \text{nonlocal} \quad \rightarrow \quad \mathbf{V}_{xc}(\mathbf{r}, t) \\
\[ \mathbf{j}(\mathbf{r}, t) \] \quad \text{local} \quad \rightarrow \quad \mathbf{A}_{xc}(\mathbf{r}, t) \\

\[ \nabla \cdot \mathbf{j} = -\frac{\partial n}{\partial t} \]

\[ \mathbf{j}(\mathbf{r}, t) = \mathbf{j}_L(\mathbf{r}, t) + \mathbf{j}_T(\mathbf{r}, t), \quad \mathbf{j}_L(\mathbf{r}, t) = \frac{\nabla}{4\pi} \int \frac{n(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} \]

- Continuity equation only gives the longitudinal current
- TDDCDFT gives also the transverse current
- We can find a short-range current-dependent xc vector potential
End of the first lecture

Today’s summary:

► density-based nonadiabatic xc functionals in TDDFT are plagued by ultranonlocality

► a frequency-dependent LDA in TDDFT does not exist

► upgrading to TDCDFT makes a local approximation possible

Tomorrow:

● natural way of describing dynamical xc effects via viscoelastic stresses in the electron liquid: the VK functional

● Applications of TDCDFT in the linear regime: solids, nanostructures, polymers, molecules, atoms