Overview

Lecture I: Basic formalism of TDCDFT

Lecture II: Applications of TDCDFT in linear response

Lecture III: TDCDFT in the nonlinear regime

- Time-dependent Kohn-Sham with memory
- Energy dissipation
- TDDFT in the Lagrangian frame
- Another way to treat memory in TDDFT: time-dependent OEP (TDOEP)
TDKS equation in TDCDFT

\[
\left[ \frac{1}{2} \left( \frac{\nabla}{i} + \frac{1}{c} A_{\text{ext}}(\mathbf{r},t) + \frac{1}{c} A_{xc}(\mathbf{r},t) \right)^2 + V_{\text{ext}}(\mathbf{r},t) + V_H(\mathbf{r},t) - i \frac{\partial}{\partial t} \right] \varphi_j(\mathbf{r},t) = 0
\]

- A rigorous extension of the LDA into the nonlinear dynamical regime has recently been formulated (Lagrangian TDDFT, see later)
- However, the viscoelastic expression of linear-response TDCDFT can be easily (but somewhat ad hoc) extended into the dynamical regime:

\[
\frac{1}{c} \frac{\partial A_{xc}}{\partial t} = -\nabla V^{ALDA}_{xc} + \frac{\nabla \cdot \bar{\sigma}_{xc}}{n(\mathbf{r},t)}
\]


- Valid up to second order in the spatial derivatives
- The gradients need to be small, but the velocities themselves can be large
Nonlinear VK-TDCDFT: xc stress tensor

time-dependent velocity field: \( \mathbf{v}(\mathbf{r}, t) = \mathbf{j}(\mathbf{r}, t) / n(\mathbf{r}, t) \)

\[
\sigma_{xc,ij}(\mathbf{r}, t) = \int_{-\infty}^{t} dt' \eta_{xc}(\mathbf{r}, t, t') \left[ \nabla_i v_j(\mathbf{r}, t') + \nabla_j v_i(\mathbf{r}, t') - \frac{2}{3} \nabla \cdot \mathbf{v}(\mathbf{r}, t') \delta_{ij} \right] \\
+ \int_{-\infty}^{t} dt' \zeta_{xc}(\mathbf{r}, t, t') \nabla \cdot \mathbf{v}(\mathbf{r}, t') \delta_{ij}
\]

where the viscosity coefficients are defined as Fourier transforms:

\[
\eta_{xc}(\mathbf{r}, t, t') = \int \frac{d\omega}{2\pi} \tilde{\eta}(\bar{n}, \omega) e^{-i\omega(t-t')} \bigg|_{\bar{n}=n(\mathbf{r}, t)}
\]
Nonlinear TDCDFT: “1D” systems

Consider a 3D system which is uniform along two directions. We can transform xc vector potential into scalar potential:

\[
V_{xc}(z, t) = V_{xc}^{ALDA}(z, t) + V_{xc}^M(z, t)
\]

with the memory-dependent xc potential

\[
V_{xc}^M(z, t) = -\int_{-\infty}^{z} dz' \frac{\nabla_{z'} \sigma_{xc,zz}(z', t)}{n(z', t)}
\]
The xc memory kernel

Assuming that the system has been in the ground state (with zero velocity) for $t<0$, the zz component of the xc stress tensor is

$$\sigma_{xc,zz}(z', t) = \int_0^t dt' Y(n(z', t), t-t') \nabla_z v_{z'}(z', t')$$

where the memory kernel is given by

$$Y(n, t-t') = \frac{4}{3} \eta(n, t-t') + \zeta(n, t-t')$$

Using the definition of the viscosity coefficients, one finds explicitly

$$Y(n, t-t') = \frac{4}{3} S_{xc}^{L}(0) - \frac{n^2}{\pi} \int \frac{d\omega}{\omega} \text{Im} f_{xc}^{L}(\omega) \cos[\omega(t-t')]$$
The xc memory kernel

H.O. Wijewardane and C.A. Ullrich, PRL 95, 086401 (2005)

\[ \frac{4}{3} S_{xc}(\infty) \]

\( Y(0) \) has zero slope → purely elastic in high-frequency limit

\( 4 S_{xc}(0) \)

\(~ 0.25 T_{\text{plasma}}\)
\[ n(z,t) = \frac{2N_s}{L} \cos^2\left(\frac{z\pi}{L}\right) \left[ 1 + A \sin \omega t \sin\left(\frac{z\pi}{L}\right) \right] \]
xc potential with memory: full TDKS calculation

Weak excitation (initial field 0.01)

Strong excitation (initial field 0.5)

40 nm GaAs/AlGaAs

H.O. Wijewardane and C.A. Ullrich, PRL 95, 086401 (2005)
...but where does the energy go?

- The system is not driven by external fields, so the energy should be conserved.
- In linear response calculations of atomic excitation energies, the VK functional gives a finite linewidth, which is unphysical.


- collective motion along z is coupled to the in-plane degrees of freedom
- the x-y degrees of freedom act like a reservoir
- decay into multiple particle-hole excitations

This is the situation for infinite systems. But what about finite systems?
Example: two electrons on a 2D quantum strip

- hard walls
- periodic boundaries (traveling waves)
- standing waves

Charge-density oscillations

C.A. Ullrich, JCP 125, 234108 (2006)
Example: two electrons on a 2D quantum strip

- Compare exact calculation (time-dependent CI) with TDKS
- Initial state: constant electric field, which is suddenly switched off
- After switch-off, free propagation of the charge-density oscillations
2D quantum strip: time-dependent dipole moment

\[ \Delta=10, L=50, F=0.02 \]

\[ \Delta=10, L=100, F=0.02 \]

- Exact calculations give a beating pattern of \( d(t) \), due to a superposition of dipole oscillations involving single and double excitations.
- Recurrence time increases with length of the strip.
- To modulate \( d(t) \), the exact \( V_{xc}(t) \) alternately damps and drives the system.
- ALDA misses the beating pattern since it has no multiple excitations.
2D quantum strip: ALDA+M

- $d(t)$ is exponentially damped
- Unlike the exact $V_{xc}(t)$, the $VK$ functional only damps, but does not drive back (only accounts for retardation)
- The $VK$ functional cannot tell that the system is finite. It treats the system locally like a homogeneous electron gas.
- Infinite recurrence time emerges in the thermodynamic limit of the system
- Damping of $d(t)$ is due to decoherence, involving many excitations with a continuous spectrum
In the nonlinear, real-time domain, the frequency-dependence of the XC stress tensor translates into memory dependence.

We solved TDKS equations with memory for charge-density oscillations in quantum well.

The VK functional causes dissipation, where energy gets transferred into incoherent multiple particle-hole excitations.

Model calculations for 2D quantum strip show how the exact TDKS xc potential causes multiple excitations by its nonadiabatic behavior (driving and damping).

The VK functional misses this behavior, but becomes correct in the thermodynamic limit (infinite system size and particle number).
TDDFT in the Lagrangian frame (L-TDDFT)

I.V. Tokatly, PRB 71, 165104 and 165105 (2005), and TDDFT book (Ch. 8)
C.A.U. and I.V. Tokatly, PRB 73, 235102 (2006); I.V. Tokatly, PRB 75, 125105 (2007)

- use a reference frame that moves with the fluid.
- basic variables: positions of fluid elements and their deformations
- nonlinear coordinate transformation \( r = r(\xi, t) \)

\[
\begin{align*}
\frac{\partial r(\xi, t)}{\partial t} &= v(r(\xi, t), t), \quad r(\xi, 0) = \xi \\
\bar{g}_{ij}(r, t) &= \frac{\partial \xi_k(r, t)}{\partial r_i} \frac{\partial \xi_k(r, t)}{\partial r_j}
\end{align*}
\]

Cauchy’s deformation tensor in the laboratory frame (a functional of the velocity)

\[
n(r, t) = \sqrt{\bar{g}(r, t)} n_0(\xi(r, t))
\]
TDDFT in the Lagrangian frame: stress tensor

\[- \frac{\partial A_{xc,i}}{\partial t} + \mathbf{v}_j \left( \nabla_i A_{xc,j} - \nabla_j A_{xc,i} \right) = \frac{c}{n} \nabla_j P_{xc,ij} [\bar{g}_{ij}] \]

where \( P_{xc,ij} = P_{ij} - T_{ij}^{KS} \) (stress tensor of interacting minus kinetic stress tensor of KS system)

► This is a **formally exact** time-dependent many-body theory. The interacting stress tensor is of course only approximately known.

► For **small gradients** of \( \bar{g}_{ij} \), the xc stress tensor is a **spatially local** functional of \( \bar{g}_{ij} \) (but a nonlocal functional in time).

This is the exact extension of LDA into the dynamical regime. In general, it contains both elastic and dissipative effects.
The small deformation approximation

\[
P_{xc,ij}(t) = P_{xc}^{ALDA}(t)\delta_{ij}
\]

\[
+ \int_0^t dt' \left[ \frac{\delta_{ij}}{2} K_{xc}(t-t') \bar{\delta g}_{kk}(t') + \mu_{xc}(t-t') \left( 1 - \frac{\delta_{ij}}{3} \right) \bar{\delta g}_{kk}(t') \right]
\]

\[
\bar{\delta g}_{ij}(r,t) = -\left( \frac{\partial u_i}{\partial r_j} + \frac{\partial u_j}{\partial r_i} \right) \quad \text{and} \quad \partial_t u = v
\]

in the regime of small deformations, we recover the nonlinear form of VK-TDCDFT (i.e., ALDA+M), where

\[
\mu_{xc} = -i\omega \widetilde{\eta}_{xc} \quad K_{xc} = -i\omega \zeta
\]

- **This puts nonlinear VK-TDCDFT on firm grounds.**
- **Remember, the deformations are small, but the velocities can be large.**
Nonlinear elastic approximation

If we neglect dissipation, a nonlinear local approximation for the stress tensor can be rigorously derived:

\[
P_{xc,ij} = \frac{2}{3} \bar{g}_{ij} \sqrt{\bar{g}} E_{xc}^{kin} \left( \frac{n}{\sqrt{\bar{g}}} \right) + L_{ij} (\bar{g}_{kl}) E_{xc}^{pot} \left( \frac{n}{\sqrt{\bar{g}}} \right)
\]

where

\[E_{xc}^{kin} (n) = 3n^{7/3} \left( \frac{e_{xc}^{\text{unif}}}{n^{4/3}} \right) \quad \text{and} \quad E_{xc}^{pot} (n) = -3n^{8/3} \left( \frac{e_{xc}^{\text{unif}}}{n^{5/3}} \right)\]

and \(L_{ij}\) is a known function.

► **Exact dynamical LDA** in the high-frequency limit, for any deformation

► For small deformations, this reduces to the purely elastic high-frequency limit of VK-TDCDFT.

► deviations of the deformation tensor \(g\) from \(\delta_{ij}\) can be viewed as a measure of nonadiabaticity.
L-TDDFT versus VK-TDCDFT: simple “1D” models

C.A. Ullrich and I.V. Tokatly, PRB 73, 235102 (2006)

\[ n(x,t) = \sqrt{g(x,t)} \ n_0(\xi(x,t)) \quad \text{and} \quad g(x,t) = \left(\frac{\partial \xi}{\partial t}\right)^2 \]

let \[ n_0(\xi) = \frac{2N}{L} \cos^2\left(\frac{\pi \xi}{L}\right) \]

and choose analytical expressions for \( v(\xi,t) \) and \( x(\xi,t) \) which can easily be inverted.

sloshing mode

breathing mode
L-TDDFT versus TDCDFT: simple “1D” models

sloshing mode: not too strongly deformed (cousin of Kohn’s mode)

breathing mode: strongly deformed everywhere (very un-hydrodynamic)
L-TDDFT versus TDCDFT: high-frequency limit

- in the high-frequency limit, the elastic approximation for L-TDDFT becomes the exact dynamical extension of the LDA (for all deformations)

- for small deformations, TDCDFT becomes exact (for all frequencies)

- for largest amplitudes, TDCDFT deviates:
  <2.5% for sloshing mode
  ~100% for breathing mode

The nonlinear TDCDFT remains good for moderate deformations!
L-TDDFT in the high-frequency, purely elastic limit ($\omega \gg \omega_p$)

- $V^{ALDA}_{xc}$
- $V^{L-TDDFT}_{xc}$ (exact)

**Sloshing mode:** small deformation, minor corrections to ALDA

**Breathing mode:** large deformation, ALDA breaks down
A rigorous formulation of local time-dependent xc effects is established by TDDFT in the Lagrangian frame.

VK-TDCDFT emerges as small-deformation approximation.

Nonadiabatic effects are both elastic and dissipative. It depends on the frequency which effect is more important.

The ALDA breaks down when the electronic density rapidly undergoes large deformations.

A more general formulation of Lagrangian TDDFT has recently become available: TDDefFT (TD deformation functional theory), including vector potentials (Tokatly 2007).
Time-dependent optimized effective potential


\[
0 = i \sum_{j=1}^{N_{\sigma}} \int_{-\infty}^{t} dt' \int d^3 r' \left[ V_{xc\sigma}(\mathbf{r}', t') - u_{xcj\sigma}(\mathbf{r}', t') \right] \\
\times \sum_{k=1}^{\infty} \varphi_{k\sigma}(\mathbf{r}', t') \varphi^*_{k\sigma}(\mathbf{r}, t) \varphi_{j\sigma}(\mathbf{r}, t) \varphi^*_{j\sigma}(\mathbf{r}', t') + c.c.
\]

where

\[
u_{xcj\sigma}(\mathbf{r}, t) = \frac{1}{\varphi^*_{j\sigma}(\mathbf{r}, t)} \frac{\delta A_{xc}}{\delta \varphi_{j\sigma}(\mathbf{r}, t)} \{ \varphi_{i\sigma} \}
\]

exact exchange:

\[
u_{xj\sigma}(\mathbf{r}, t) = -\frac{1}{\varphi^*_{j\sigma}(\mathbf{r}, t)} \sum_{k=1}^{N_{\sigma}} \int d^3 r' \frac{\varphi^*_{j\sigma}(\mathbf{r}', t) \varphi_{k\sigma}(\mathbf{r}', t) \varphi^*_{k\sigma}(\mathbf{r}, t)}{|\mathbf{r} - \mathbf{r}'|}
\]
Applications of TDOEP in the linear regime

- Optical spectra of solids
  Kim and Goerling, PRL 89, 096402 (2002)

- Molecular excitation energies and dynamic polarizabilities
  Hirata et al., PRA 71, 032507 (2005)
  Shigeta, Hirao, Hirata, PRA 73, 010502 (2006)

\[ \omega \text{-dependent kernel} \]

\[ \text{static (} \omega=0 \text{)} \]

Shigeta et al. (Neon)
Kim and Goerling (Silicon)
Applications of TDKLI in the nonlinear regime:

- **Atoms in strong fields**
  
  M. Mundt and S. Kuemmel, PRL 95, 203004 (2005)

- **Metallic clusters**
  

- **No zero-force theorem for TDKLI**
  
  Mundt, Kuemmel, van Leeuwen, Reinhard, PRA 75, 050501 (2007)
Adiabatic approximation to TDOEP

AOEP: static OEP which produces $n(t)$ as selfconsistent ground-state density

$$V_{KS}^t[n(t)] = V_{ext}^t + V_H[n(t)] + V_{AOEP}^{AOEP}$$

Step 1: invert static KS equation: $n(t) \rightarrow V_{KS}^t, \left\{ \phi_{j\sigma}^t(\vec{r}), \epsilon_{j\sigma}^t \right\}$

Step 2: construct $V_{xc}^{AOEP}$ from $\left\{ \phi_{j\sigma}^t(\vec{r}), \epsilon_{j\sigma}^t \right\}$

Numerical solution of TDOEP: step-by-step?

\[ 0 = i \sum_{j=1}^{N_\sigma} \int_{-\infty}^{t} dt' \int d^3r' \left[ V_{xc\sigma}(r',t') - u_{xcj\sigma}(r',t') \right] \]
\[ \times \sum_{k=1}^{\infty} \varphi_{k\sigma}(r',t') \varphi_{k\sigma}^*(r,t) \varphi_{j\sigma}(r,t) \varphi_{j\sigma}^*(r',t') + c.c. \]

- Integrand vanishes at upper limit \((t' = t)\)
- \(V_{xc\sigma}(t')\) only determined for \(t' < t\)
- Step-by-step time propagation fails

Mundt and Kümmel, PRA 74, 022511 (2006): numerical instabilities??
Numerical solution of TDOEP: global iteration

\[ \varphi_j(0) \quad \text{global selfconsistency} \quad \varphi_j(T) \]

\[
t = 0 \quad t = T
\]

\[ n^{\text{th}} \text{ iteration:} \quad i \frac{\partial \varphi_j^{(n)}}{\partial t} = \left( -\frac{\nabla^2}{2} + V^{(n-1)}(t) \right) \varphi_j^{(n)}, \quad t = [0, T] \]

\[ \{ \varphi_j^{(n)}(t) \} \xrightarrow{\text{TDOEP}} V^{(n)}(t), \quad t = [0, T] \]

\[ (n+1)^{\text{st}} \text{ iteration:} \quad i \frac{\partial \varphi_j^{(n+1)}}{\partial t} = \left( -\frac{\nabla^2}{2} + V^{(n)}(t) \right) \varphi_j^{(n+1)} \]

\[ : \]

Convergence index:

\[ G = \int_0^T \left| d_{\text{old}}(t) - d_{\text{new}}(t) \right| dt \]

\[ \int_0^T |d_{\text{new}}(t)| dt \]
Free charge-density oscillations

Initially $\varepsilon$, suddenly switching to $\varepsilon=0$

- TDOEP slightly blueshifted: memory gives rise to elastic contribution (x-only)

![Graph showing oscillations over time for different parameters](image)

- TDOEP
- AOEP
- TDKLI
Driven oscillations

\[ \omega = 11 \text{ meV} \]

close to \( \omega_{12} \) resonance

\[ \omega = 20 \text{ meV} \]

close to \( \omega_{23} \) resonance

XC power: \[ P(t) = \int dz \, j(z, t) \nabla_z \left[ V_x(z, t) - V_x^0(z) \right] \]
Driven oscillations

\( \omega = 40 \text{ meV} \)

close to \( \omega_{14} \) resonance

\( \omega = 50 \text{ meV} \)

between \( \omega_{14} \) and \( \omega_{25} \)

(away from resonances)
Summary third part

- Stable algorithm for full TDOEP in quantum wells
- AOEP is very similar to TDKLI
- No problems with zero-force theorem in TDKLI
- Memory effects in TDOEP become significant for high frequencies and close to resonances
- Intrinsically nonadiabatic phenomena (multiple excitations, dissipation): need to go beyond exact-exchange

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Postdoc opening
(TDDFT for excitonic effects in materials)