Lecture 1

TDCDFT: Basic formalism

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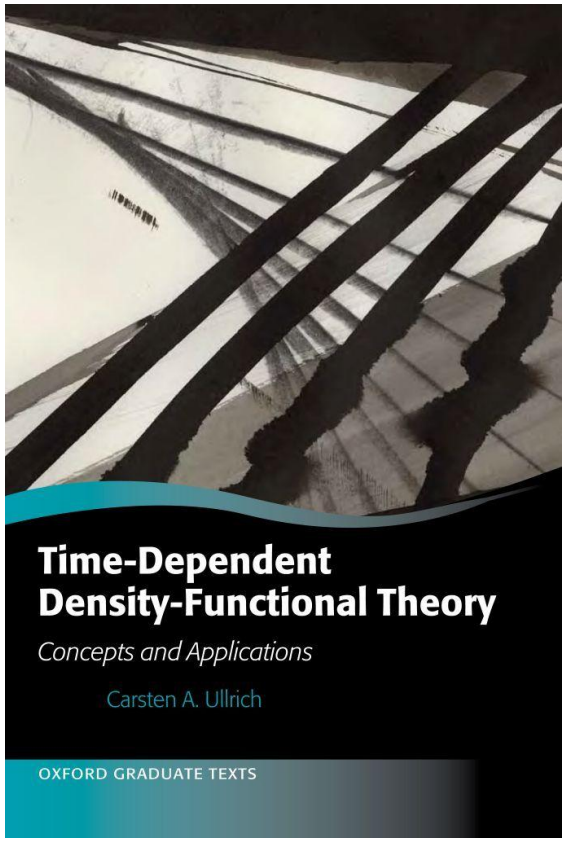
Overview



1. Introduction
2. Review of ground-state DFT

PART I: BASIC FORMALISM OF TDDFT

3. Fundamental existence theorems
4. Time-dependent Kohn-Sham scheme
5. Time-dependent observables
6. Properties of the time-dependent xc potential

PART II: LINEAR RESPONSE AND EXCITATIONS

7. Formal framework of linear-response TDDFT
8. The frequency-dependent xc kernel
9. Application to atomic and molecular systems

PART III: FURTHER DEVELOPMENTS

10. Time-dependent current-DFT
11. Time-dependent OEP
12. Extended systems
13. TDDFT and Many-body theory

PART IV: SPECIAL TOPICS

14. Long-range correlations and dispersion interactions
15. Nanoscale transport and molecular junctions
16. Strong-field phenomena and optimal control
17. Nuclear motion

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

The Runge-Gross theorem of TDDFT

Consider an N-electron system with Hamiltonian

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

$$V(\mathbf{r},t) \xrightarrow[\text{fixed } \Psi_0]{i\partial\Psi/\partial t = \hat{H}\Psi} \Psi(t) \xrightarrow{\langle\Psi(t)|\hat{n}|\Psi(t)\rangle} n(\mathbf{r},t)$$

RG step 1

uniquely determined

$$\mathbf{j}(\mathbf{r},t)$$

RG step 2

uniquely determined

Therefore: $V(\mathbf{r},t) \xleftrightarrow{1:1} n(\mathbf{r},t)$

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**.

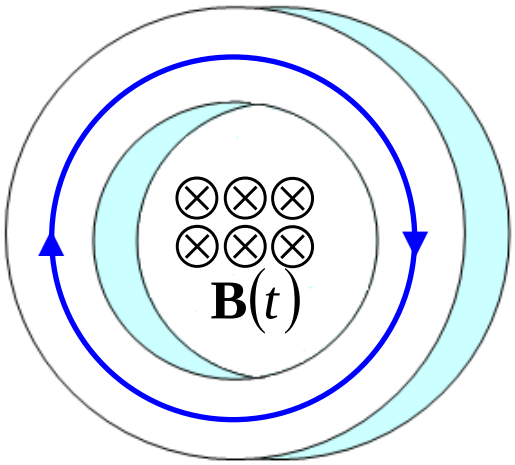
2. The original RG proof is for **finite** systems with potentials that vanish at infinity (step 2). **Extended/periodic** systems can be tricky:

- 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.

N.T. Maitra, I. Souza, and K. Burke,
PRB **68**, 045109 (2003)

ring geometry:



Reminder: longitudinal and transverse vector fields

$$\mathbf{U} = \mathbf{U}_L + \mathbf{U}_T$$

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

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

$$\mathbf{U}_T(\mathbf{r}) = \frac{1}{4\pi}\nabla\times\nabla\times\int d^3r' \frac{\mathbf{U}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

V-representability of current densities

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

$$\frac{\partial n(\mathbf{r},t)}{\partial t} = -\nabla \cdot \mathbf{j}_L(\mathbf{r},t)$$

If $\mathbf{j}(\mathbf{r},t) = \mathbf{j}_L(\mathbf{r},t) + \mathbf{j}_T(\mathbf{r},t)$ **comes from a potential** $V(\mathbf{r},t)$

then $\mathbf{j}'(\mathbf{r},t) = \mathbf{j}_L(\mathbf{r},t) + \mathbf{j}'_T(\mathbf{r},t)$ **cannot come from** $V'(\mathbf{r},t)$.

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

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

R. D'Agosta and G. Vignale, PRB **71**, 245103 (2005)

TDCDFT: basic existence theorems

generalization of RG theorem: Ghosh and Dhara, PRA **38**, 1149 (1988)
G. Vignale, PRB **70**, 201102 (2004)

$$\hat{H}(t) = \sum_{j=1}^{N} \left\{ \frac{1}{2} \left[\mathbf{p}_j + \mathbf{A}\left(\mathbf{r}_j, t\right) \right]^2 + V\left(\mathbf{r}_j, t\right) \right\} + \frac{1}{2} \sum_{j \neq k}^{N} \frac{1}{\left| \mathbf{r}_j - \mathbf{r}_k \right|}$$

$$\Updownarrow$$

$$\mathbf{j}\left(\mathbf{r}, t\right) = \mathbf{j}_L\left(\mathbf{r}, t\right) + \mathbf{j}_T\left(\mathbf{r}, t\right)$$

$$\Updownarrow$$

$$\hat{H}_{KS}\left(t\right) = \sum_{j=1}^{N} \left\{ \frac{1}{2} \left[\mathbf{p}_j + \mathbf{A}_s\left(\mathbf{r}_j, t\right) \right]^2 + V_s\left(\mathbf{r}_j, t\right) \right\}$$

The full current is uniquely determined by the pair of scalar and vector potentials $\left(V, \mathbf{A}\right)$

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

TDKS equation in TDCDFT

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

Gauge-invariant physical current density:

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

$$=\mathbf{j_{dia}}(\mathbf{r},t)+\mathbf{j_{para}}(\mathbf{r},t)$$

Scalar and vector potentials:

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

$$\mathbf{A}_s[\mathbf{j}](\mathbf{r},t)=\mathbf{A}(\mathbf{r},t)+\mathbf{A}_{xc}(\mathbf{r},t)$$

(ignore Hartree vector potential from induced currents)

Gauge transformations

The map

$$\left(V,\mathbf{A}\right) \longleftrightarrow \mathbf{j}\left(\mathbf{r},t\right)$$

is unique up to within gauge transformations of the form

$$V\left(\mathbf{r},t\right) \rightarrow V\left(\mathbf{r},t\right) - \frac{\partial \Lambda\left(\mathbf{r},t\right)}{\partial t}$$

$$\mathbf{A}\left(\mathbf{r},t\right) \rightarrow \mathbf{A}\left(\mathbf{r},t\right) + \nabla \Lambda\left(\mathbf{r},t\right)$$

where Λ 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

$$\mathbf{j}_1(\mathbf{r},\omega) = \int d^3r' \, \vec{\vec{\chi}}_s(\mathbf{r},\mathbf{r}',\omega)\left\{\mathbf{A}_{ext,1}(\mathbf{r},\omega) + \mathbf{A}_{H,1}(\mathbf{r},\omega) + \mathbf{A}_{xc,1}(\mathbf{r},\omega)\right\}$$

KS current-current response tensor: diamagnetic + paramagnetic part

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

where $$P_\mu^{kj} = \varphi_k^*(\mathbf{r})\nabla_\mu\varphi_j(\mathbf{r}) - \varphi_j(\mathbf{r})\nabla_\mu\varphi_k^*(\mathbf{r})$$

Note:

$$\chi_s(\mathbf{r},\mathbf{r}',\omega) = \frac{1}{\omega^2}\sum_{\mu\nu}\nabla_\mu\nabla'_\nu\chi_{s,\mu\nu}(\mathbf{r},\mathbf{r}',\omega)$$

TDCDFT: effective vector potential

$\mathbf{A}_{ext,1}(\mathbf{r},\omega)$: external perturbation. Can be a true vector potential, or a gauge transformed scalar perturbation: $\mathbf{A}_{ext,1} = \frac{1}{i\omega}\nabla V_{ext,1}$

$$\mathbf{A}_{H,1}(\mathbf{r},\omega) = \frac{\nabla}{(i\omega)^2}\int d^3r' \frac{\nabla'\cdot\mathbf{j}_1(\mathbf{r}',\omega)}{|\mathbf{r}-\mathbf{r}'|}$$

gauge transformed Hartree potential

$$\mathbf{A}_{xc,1}(\mathbf{r},\omega) = \int d^3r' \; \overleftrightarrow{f}_{xc}(\mathbf{r},\mathbf{r}',\omega)\mathbf{j}_1(\mathbf{r}',\omega)$$

the xc kernel is now a tensor!

ALDA: $$\mathbf{A}^{ALDA}_{xc,1}(\mathbf{r},\omega) = \frac{\nabla}{(i\omega)^2}\int d^3r' \; f^{ALDA}_{xc}(\mathbf{r},\mathbf{r}')\nabla\cdot\mathbf{j}_1(\mathbf{r}',\omega)$$

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)

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

Rotatory strength

Electric dipole response

Magnetic dipole response

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

Why TDCDFT?

- **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

$$\left[\sum_j\left(-\frac{\nabla_j^2}{2}+V(\mathbf{r}_j,t)\right)+\sum_{j\neq k}\frac{1}{|\mathbf{r}_j-\mathbf{r}_k|}-i\frac{\partial}{\partial t}\right]\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N,t)=0$$

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

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

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

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

dependence on densities:

$$n(\mathbf{r}', t'), \quad t' \leq t$$

(nonlocal in space and time)

The adiabatic approximation

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

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

$$V_{xc}^{ALDA}(\mathbf{r},t) = \left.\frac{de_{xc}^{unif}(\bar{n})}{d\bar{n}}\right|_{\bar{n}=n(\mathbf{r},t)}$$

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

$$\left[-\frac{\nabla_1^2}{2}-\frac{\nabla_2^2}{2}+V(\mathbf{r}_1,t)+V(\mathbf{r}_2,t)+\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}-i\frac{\partial}{\partial t}\right]\Psi(\mathbf{r}_1,\mathbf{r}_2,t)=0$$

Step 2: calculate the exact time-dependent density

$$\sum_{s_1,s_2}\int d\vec{r}_2\left|\Psi(\mathbf{r},\mathbf{r}_2,t)\right|^2=n(\mathbf{r},t)=2\left|\varphi(\mathbf{r},t)\right|^2$$

Step 3: find that TDKS system which reproduces the density

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

Construction of the exact xc potential

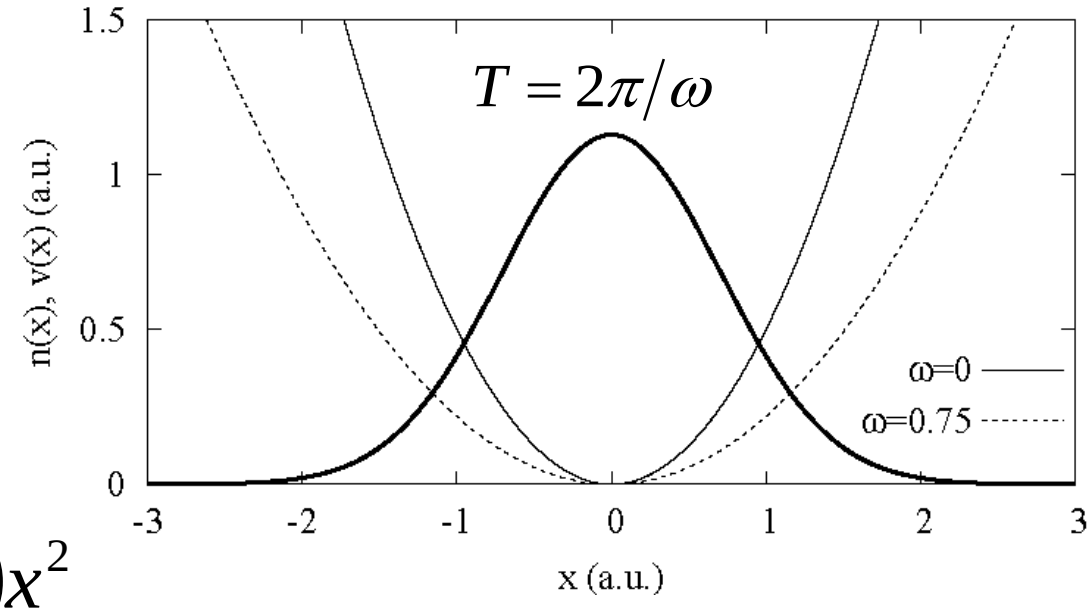
Ansatz: $$\varphi(\mathbf{r},t)=\sqrt{\frac{n(\mathbf{r},t)}{2}}\exp\left(i\alpha(\mathbf{r},t)\right)$$

$$\Longrightarrow V_{xc}(\mathbf{r},t) = \underbrace{\begin{aligned}&-V(\mathbf{r},t)-V_H(\mathbf{r},t)\\&+\frac{1}{4}\nabla^2\ln n(\mathbf{r},t)+\frac{1}{8}\left|\vec{\nabla}\ln n(\mathbf{r},t)\right|^2\end{aligned}}_{V_{xc}^{A}} \underbrace{\begin{aligned}&-\dot{\alpha}(\mathbf{r},t)-\frac{1}{2}\left|\nabla\alpha(\mathbf{r},t)\right|^2\end{aligned}}_{V_{xc}^{dyn}}$$

Example

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

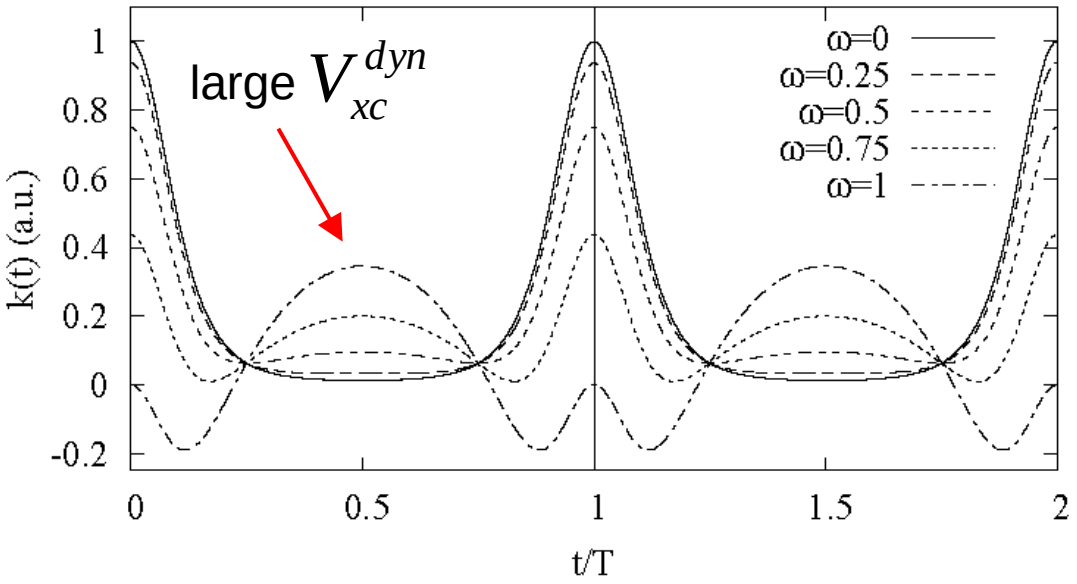
$$a(t) = \bar{a}(2 - \cos(\omega t))$$



is produced by this KS potential: $V_s(x,t) = \frac{1}{2}k(t)x^2$

with TD curvature

$$k(t) = \underbrace{\frac{1}{a(t)^4}}_{A} \underbrace{- \frac{\ddot{a}(t)}{a(t)}}_{dyn}$$



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.

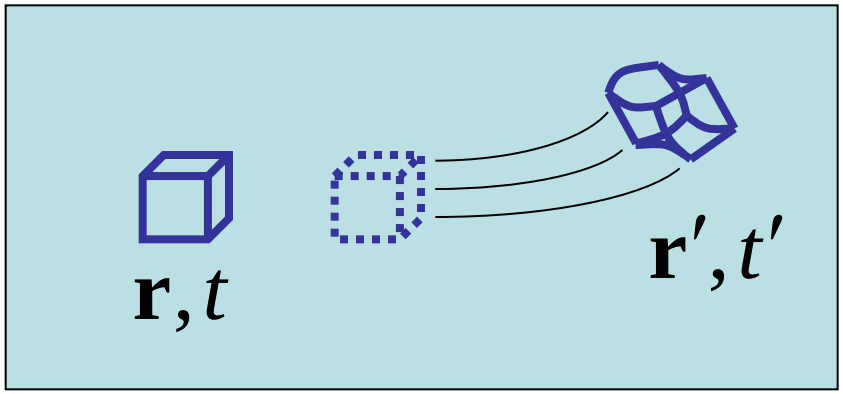
- Adiabatic approximation fails for more complicated excitations (multiple, charge-transfer). See lectures by Neepa Maitra.

- 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:



Nonlocality in time (memory) implies nonlocality in space!

Dobson, Bünner, and Gross, PRL **79**, 1905 (1997)
I.V. Tokatly, PRB **71**, 165104 and 165105 (2005), PRB **75**, 125105 (2007)

Ultranonlocality in TDDFT

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

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

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

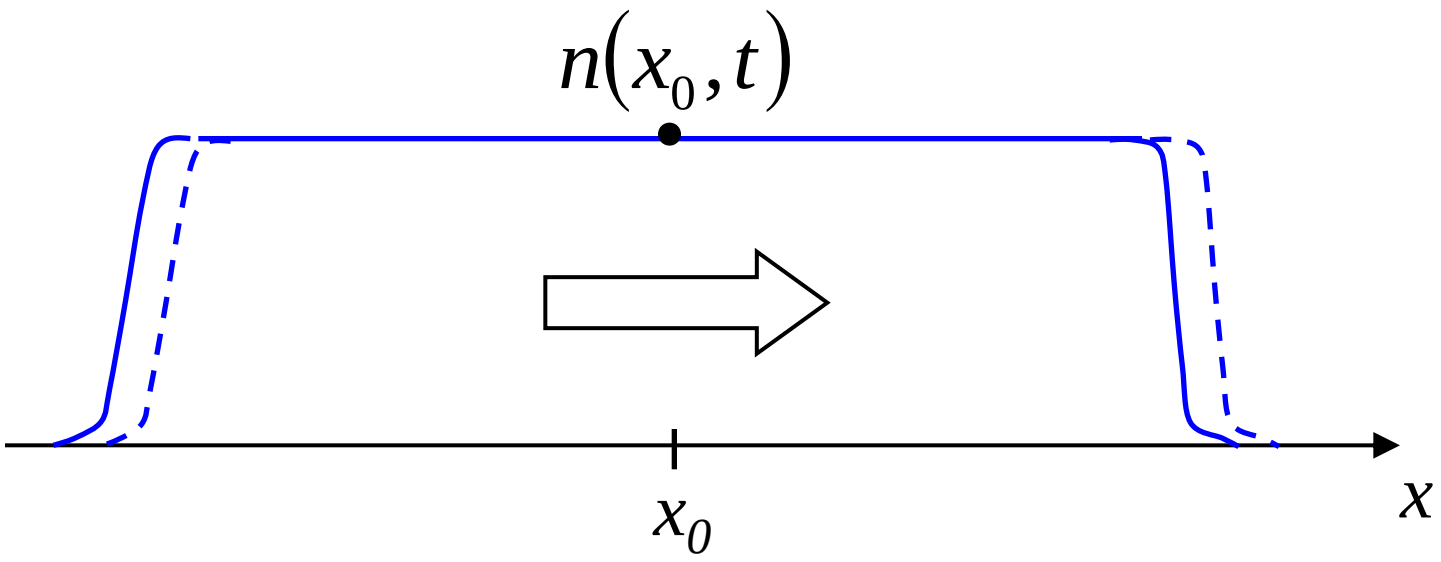
$$\nabla n_0(\mathbf{r})\underbrace{\int d^3r'\; f_{xc}(\mathbf{r},\mathbf{r}',\omega)}=\nabla V_{xc,0}(\mathbf{r})$$

$$\Rightarrow f_{xc}^{\mathrm{hom}}(\mathbf{k}=0,\omega)$$

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

$\Longrightarrow$ $f_{xc}(\mathbf{r},\mathbf{r}',\omega)$ has infinitely long spatial range!

Ultranonlocality and the density

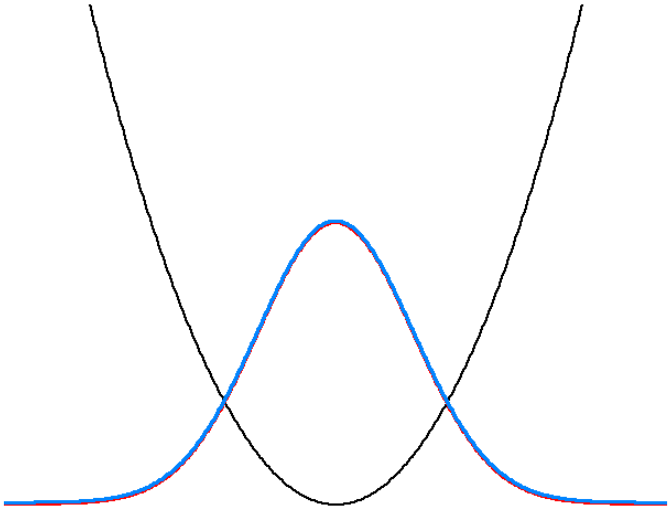


An xc functional that depends only on the local density (or its gradients) cannot see the motion of the entire slab.

A density functional needs to have a long range to see the motion through the changes at the edges.

Harmonic Potential Theorem – Kohn's mode

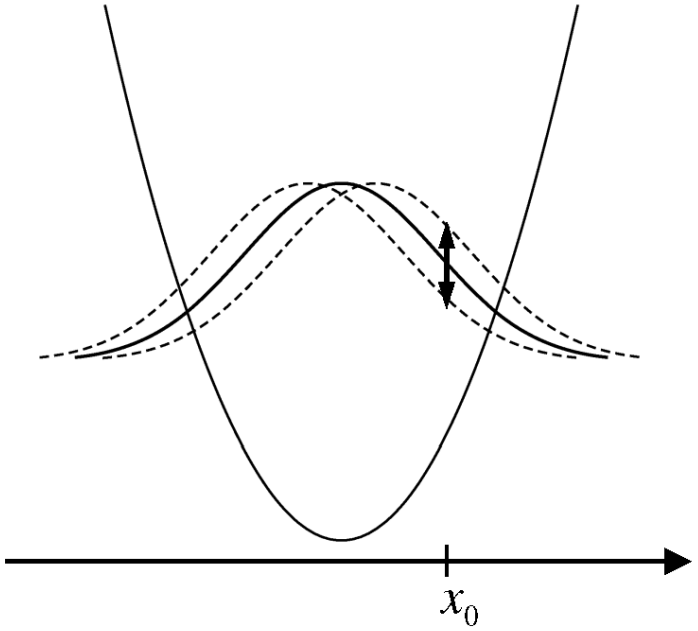
J.F. Dobson, PRL **73**, 2244 (1994)

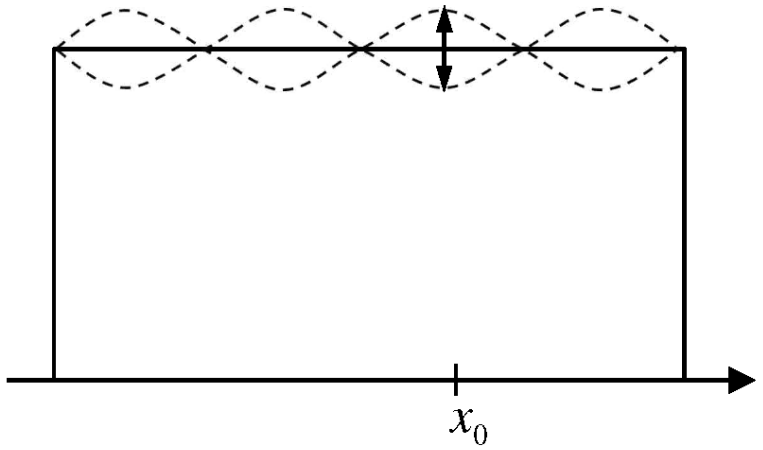


A parabolically confined, interacting N-electron system can carry out an undistorted, undamped, collective "sloshing" mode, where

$n(\mathbf{r},t) = n_0(\mathbf{r} - \mathbf{R}(t))$, with the CM position $\mathbf{R}(t)$.

Failure of nonadiabatic local density functionals



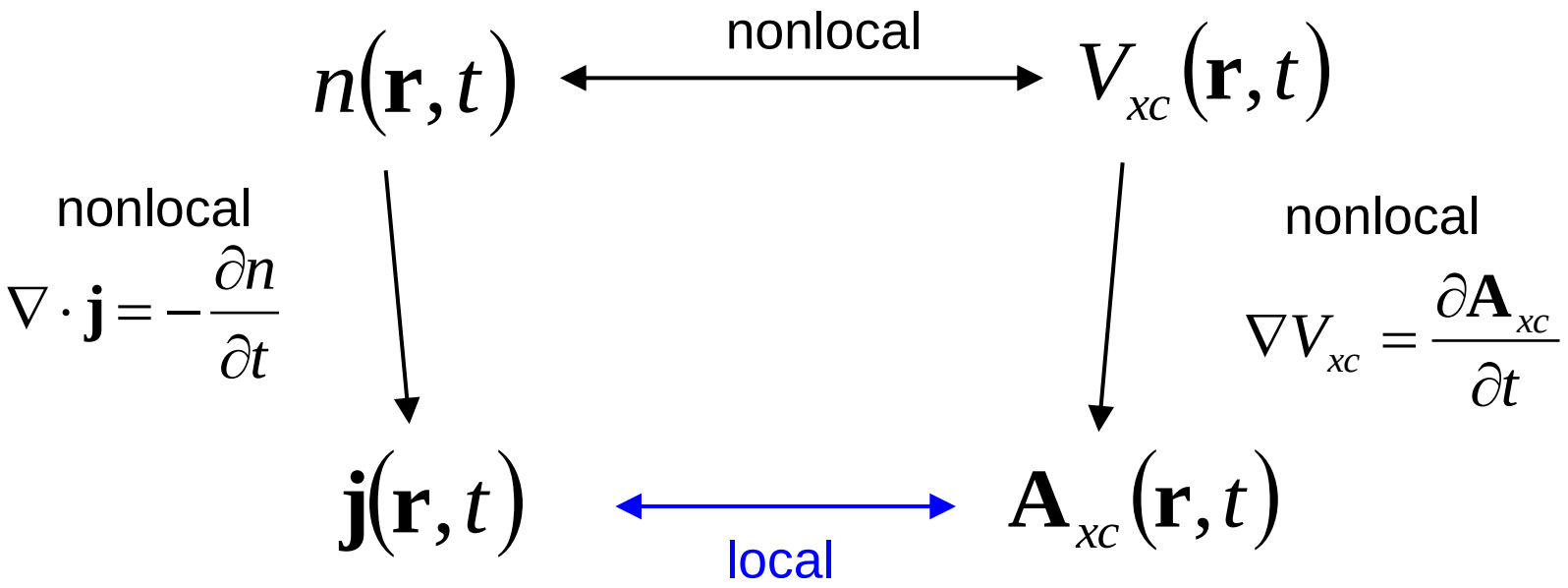


- ►undamped density oscillations
- ►xc potential rides along with density
- ►constant velocity field

- ►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



$$\mathbf{j}(\mathbf{r},t)=\mathbf{j}_L(\mathbf{r},t)+\mathbf{j}_T(\mathbf{r},t), \qquad \mathbf{j}_L(\vec{r},t)=\frac{\nabla}{4\pi}\int\frac{\dot{n}(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}$$

- Continuity equation only gives the longitudinal current
- TDCDFT 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