

Lecture 1

TDCDFT: Basic formalism

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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

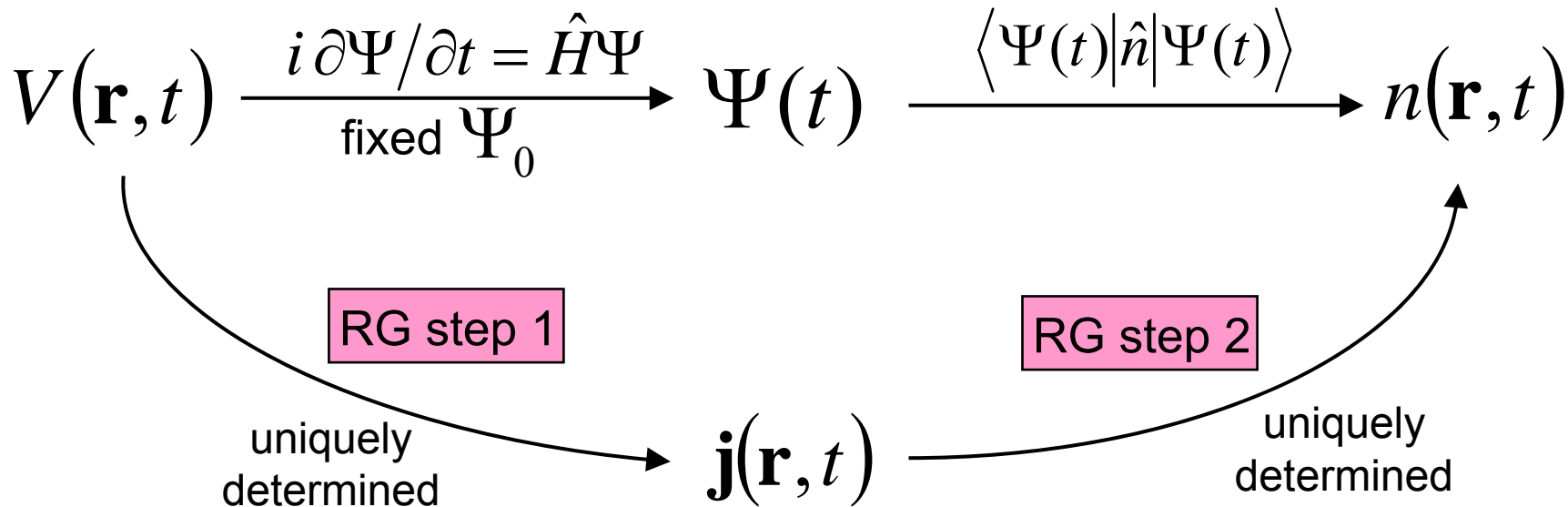
Lecture III: TDCDFT in the nonlinear regime



The Runge-Gross theorem of TDDFT

Consider an N-electron system with Hamiltonian

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



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

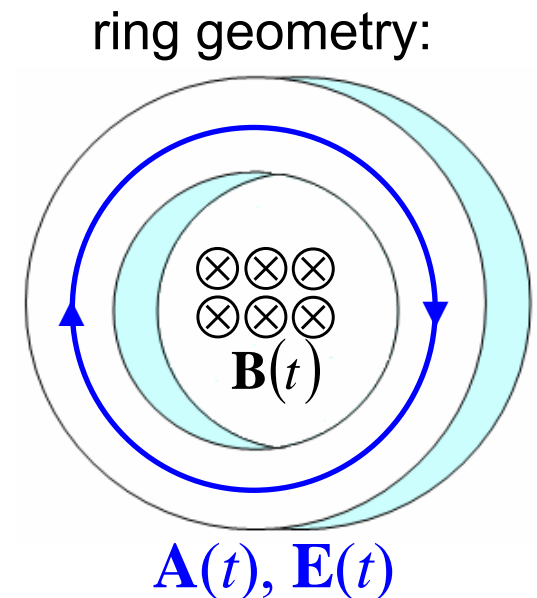


Situations not covered by the RG theorem

- 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)





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:

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

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



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, since \mathbf{j} is vector (3 components), and V is scalar (1 component).

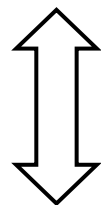
R. D'Agosta and G. Vignale, PRB 71, 245103 (2005)



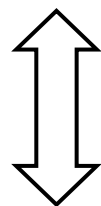
TDCDFT

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

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



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



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

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



Gauge transformations

The map

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

is unique up to within gauge transformations of the form

$$V(\mathbf{r}, t) \rightarrow V(\mathbf{r}, t) - \frac{\partial \Lambda(\mathbf{r}, t)}{\partial t}$$
$$\mathbf{A}(\mathbf{r}, t) \rightarrow \mathbf{A}(\mathbf{r}, t) + \nabla \Lambda(\mathbf{r}, t)$$

where Λ is an arbitrary well-behaved function which vanishes at the initial time.



TDCDFT in the linear response regime

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

KS current-current response tensor: diamagnetic + paramagnetic part

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

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

Exercise: show that

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



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: $\mathbf{A}_{ext,1} = \frac{1}{i\omega} \nabla V_{ext,1}$

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

gauge transformed Hartree potential

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

the xc kernel is now a tensor!

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



TDCDFT: discussion

- ▶ **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.
- ▶ **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

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

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 (N. Maitra, TDDFT book, Ch.4)

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



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

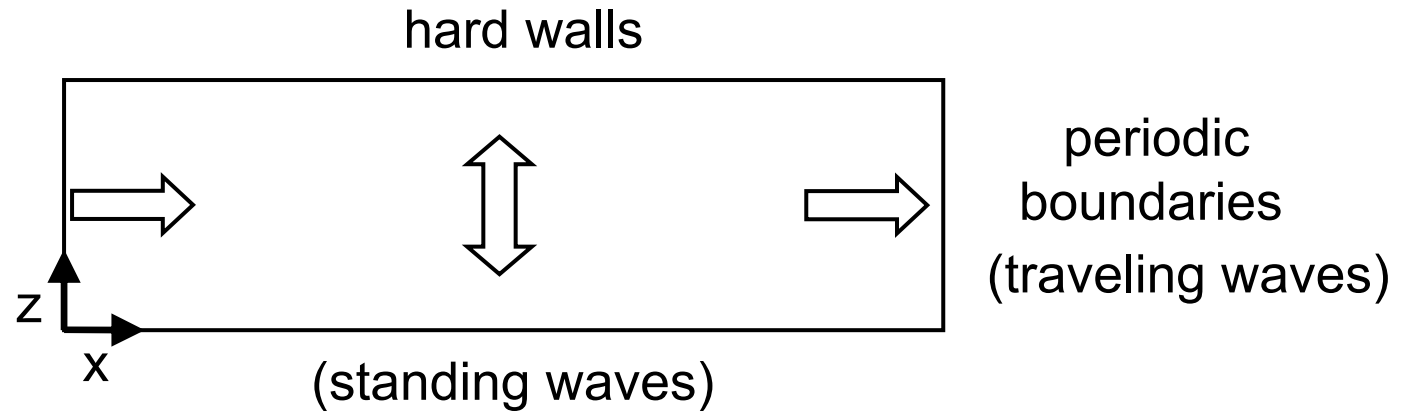
$$V_{xc}^{ALDA}(\mathbf{r}, t) = \left. \frac{de_{xc}^{unif}(\bar{n})}{d\bar{n}} \right|_{\bar{n}=n(\mathbf{r}, t)}$$

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

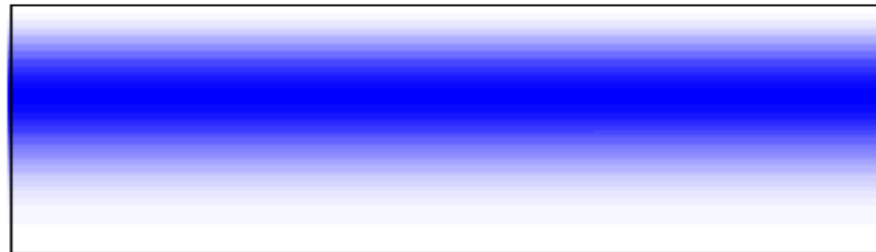
“Adiabatic” means: no history dependence, no memory, no retardation.



Example: two electrons on a 2D quantum strip



Charge-density oscillations





Construction of the exact xc potential

Step 1: solve full 2-electron Schrödinger equation

$$\left[-\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} + V(z_1, t) + V(z_2, t) + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} - i \frac{\partial}{\partial t} \right] \Psi(\mathbf{r}_1, \mathbf{r}_2, t) = 0$$

Step 2: calculate the exact time-dependent density

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

Step 3: find that TDKS system which reproduces the density

$$\left[-\frac{1}{2} \frac{d^2}{dz^2} + V(z, t) + V_H(z, t) + V_{xc}(z, t) - i \frac{\partial}{\partial t} \right] \varphi(z, t) = 0$$



Construction of the exact xc potential

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

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

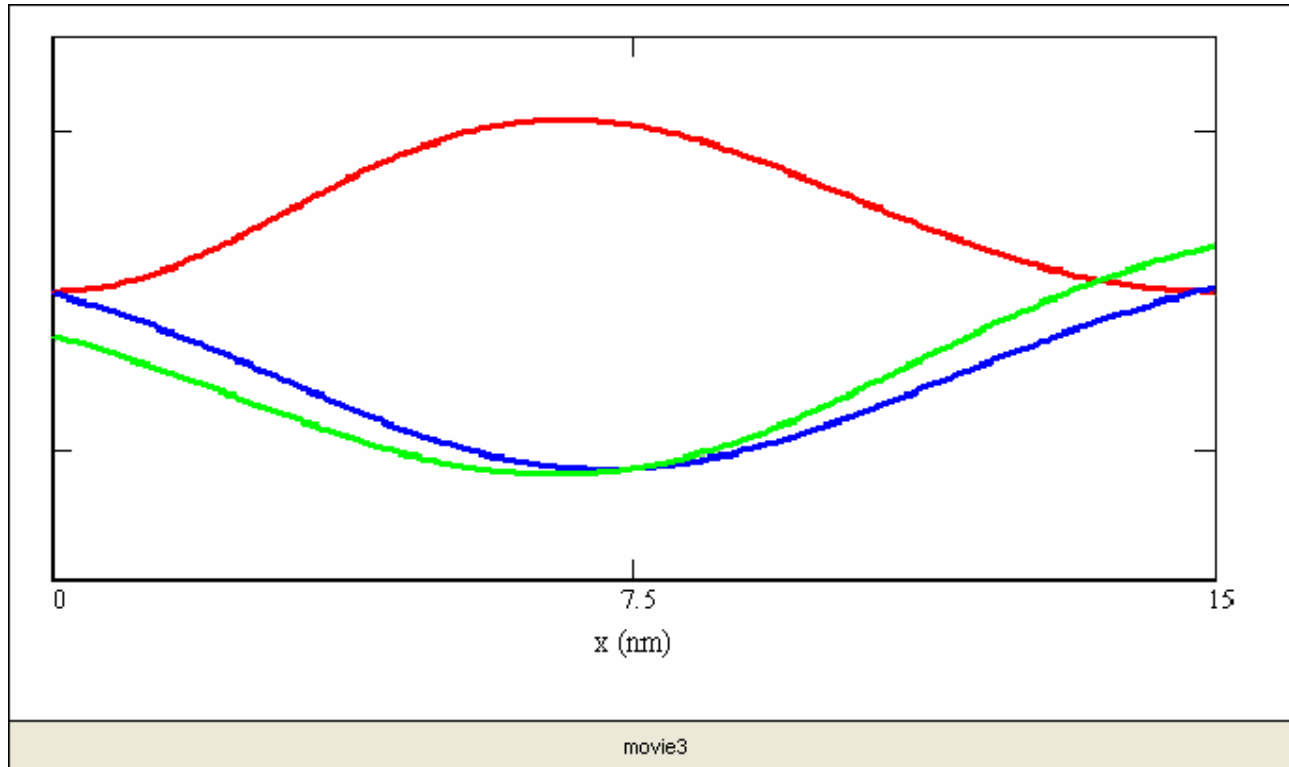
V_{xc}^A

V_{xc}^{dyn}

Exercise: verify this result!



2D quantum strip: charge-density oscillations



- density
- exact V_{xc}
- adiabatic V_{xc}



The adiabatic approximation

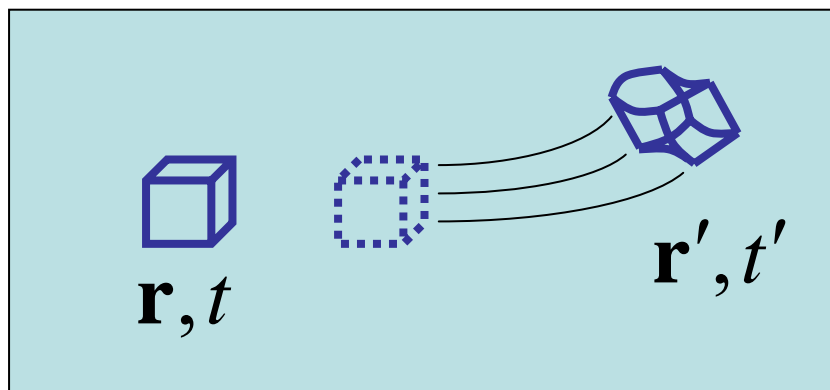
- In general, the adiabatic approximation works well for excitations which have an analogue in the KS system (single excitations)
- formally justified only for infinitely slow electron dynamics. But why is it that the frequency dependence seems less important?

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)
- misses dissipation of long-wavelength plasmon excitations

Fundamental question: what is the proper extension of the LDA into the dynamical regime?

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

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

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

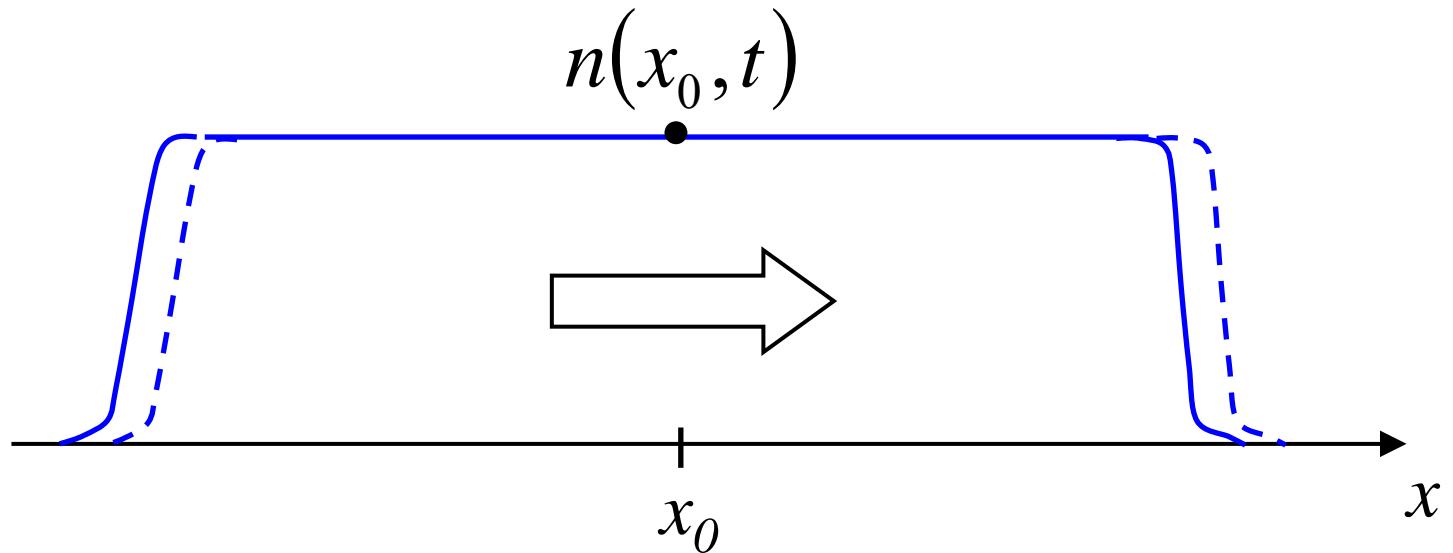
$$\nabla n_0(\mathbf{r}) \underbrace{\int d^3 r' f_{xc}(\mathbf{r}, \mathbf{r}', \omega)}_{\Rightarrow f_{xc}^{\text{hom}}(\mathbf{k} = 0, \omega)} = \nabla V_{xc,0}(\mathbf{r})$$

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

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



Ultranonlocality and the density



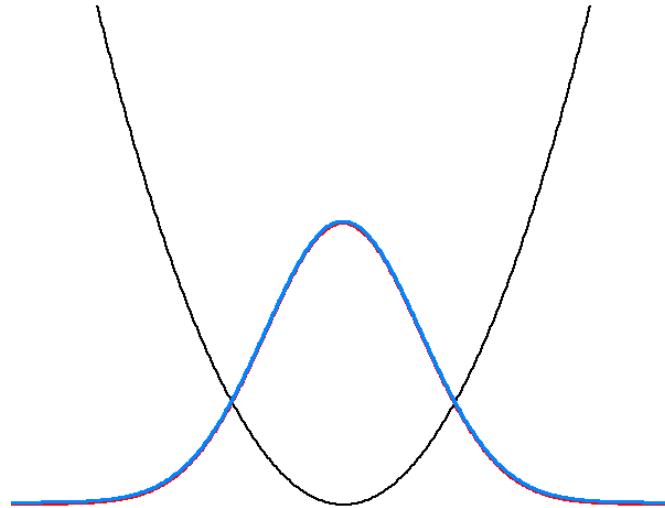
An xc functional that depends only on the local density (or its gradients) cannot see the motion of the entire slab.

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)

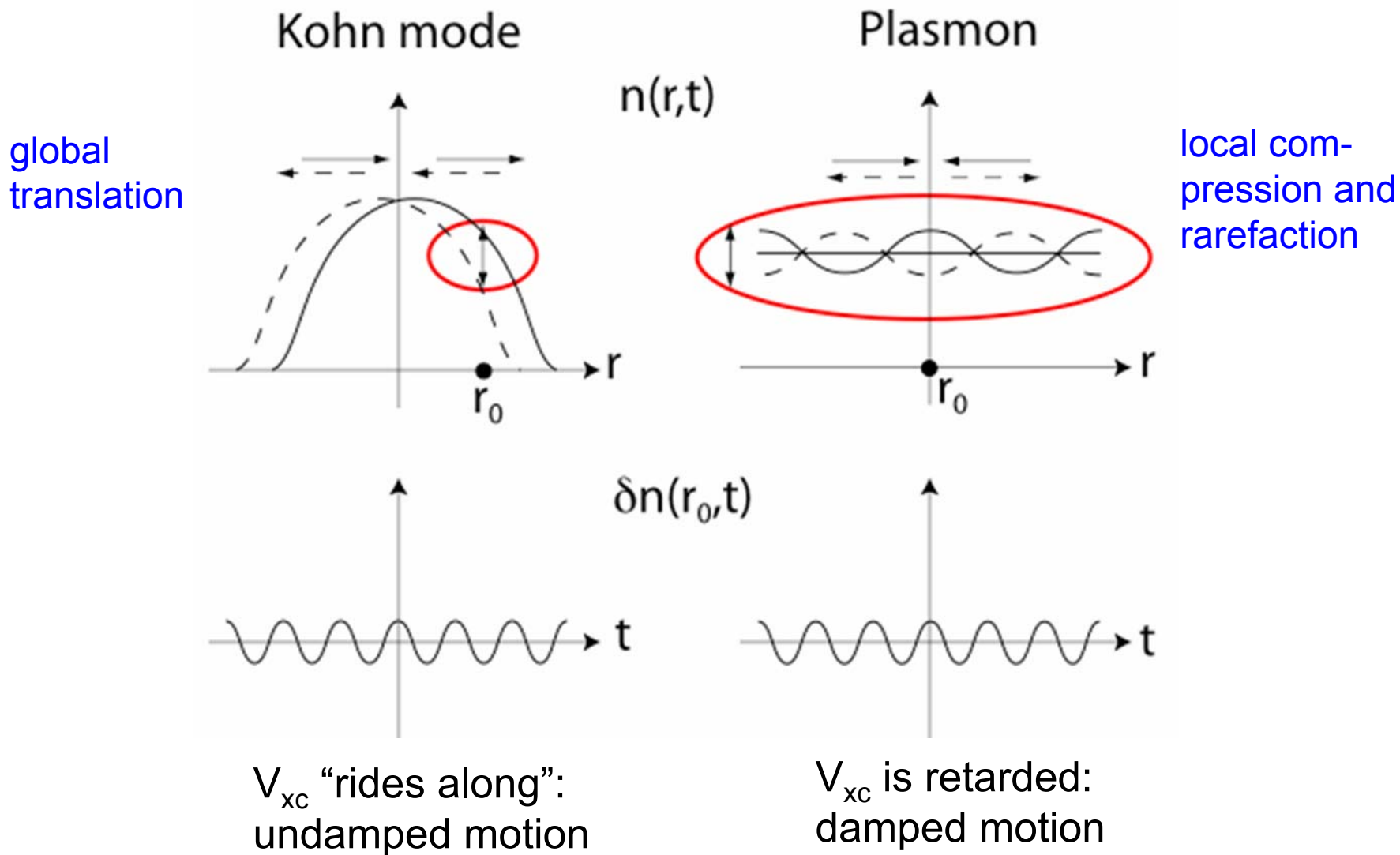


A parabolically confined, interacting N-electron system can carry out an undistorted, undamped, collective “sloshing” mode, where $n(\mathbf{r}, t) = n_0(\mathbf{r} - \mathbf{R}(t))$, with the CM position $\mathbf{R}(t)$.

Exercise: Verify that the ALDA satisfies the HPT!

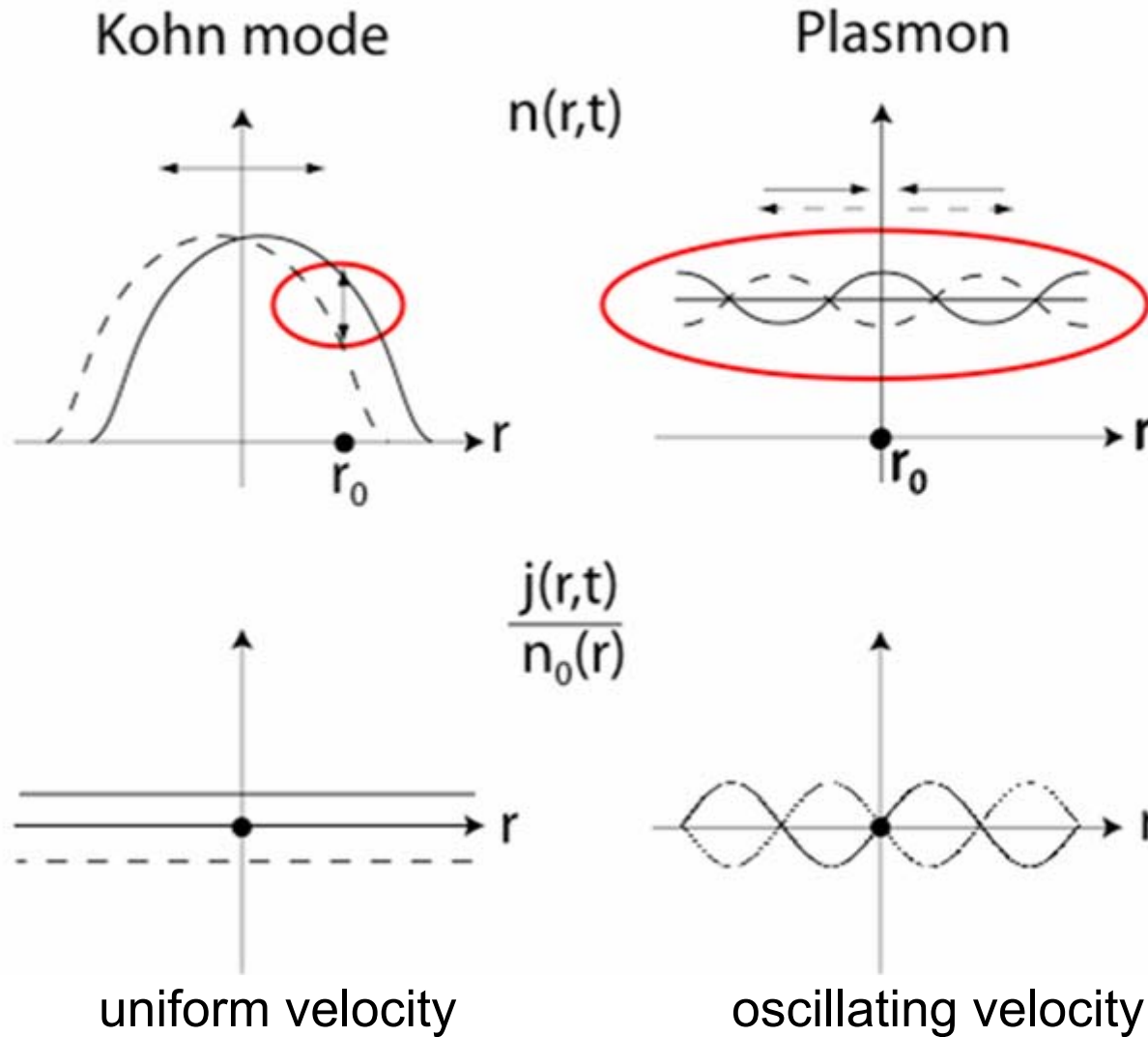


Point of view of the local density



➔ xc functionals based on local density can't distinguish the two cases!

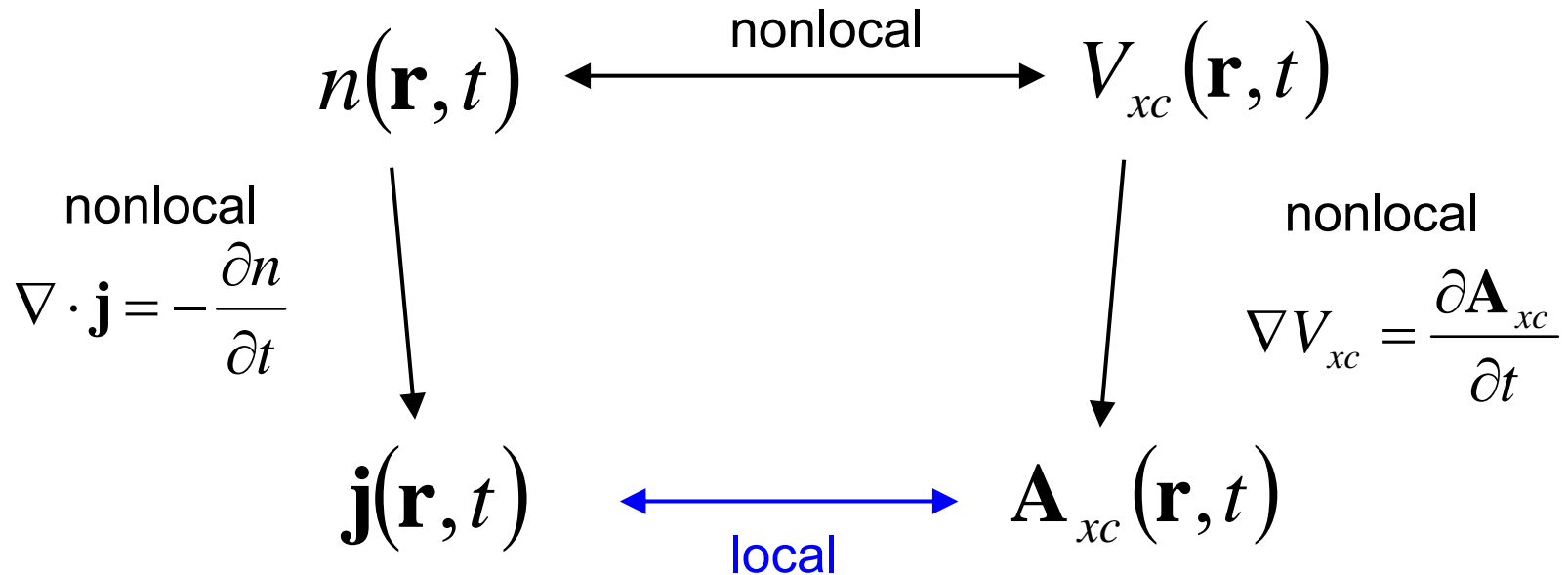
Point of view of the local current



➔ much better chance to capture the physics correctly!



“Upgrading” TDDFT: Current-TDDFT



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

- Continuity equation only gives the longitudinal current
- TDCDFT gives also the transverse current
- We can find a short-range current-dependent xc vector potential



TDCDFT beyond the ALDA: the VK functional

$$\mathbf{A}_{xc,1}(\mathbf{r}, \omega) = \mathbf{A}_{xc,1}^{ALDA}(\mathbf{r}, \omega) - \frac{c}{i\omega n_0(\mathbf{r})} \nabla \cdot \vec{\sigma}_{xc}(\mathbf{r}, \omega)$$

xc viscoelastic stress tensor:

$$\sigma_{xc,jk} = \tilde{\eta}_{xc} \left(\nabla_j v_{1,k} + \nabla_k v_{1,j} - \frac{2}{3} \nabla \cdot \mathbf{v}_1 \delta_{jk} \right) + \tilde{\zeta}_{xc} \nabla \cdot \mathbf{v}_1 \delta_{jk}$$

$$\mathbf{v}(\mathbf{r}, \omega) = \mathbf{j}(\mathbf{r}, \omega) / n_0(\mathbf{r}) \quad \text{velocity field}$$

- automatically satisfies zero-force theorem/Newton's 3rd law
- automatically satisfies the Harmonic Potential theorem
- is local in the current, but nonlocal in the density
- introduces dissipation/retardation effects

...but how on earth did they come up with this expression??



TDCDFT beyond the ALDA

- 1 Derivation by “brute force” [G. Vignale and W. Kohn, PRL **77**, 2037 (1996)]
 - ▶ Consider weakly inhomogeneous electron liquid, modulated by a charge-density wave of small amplitude and wavevector.
 - ▶ Calculate xc kernel $f_{xc}(k+q, k, \omega)$ where $k, q \ll k_F, \omega / v_F$
 - ▶ It turned out later that the resulting expression can be cast into hydrodynamic form

- 2 Physical insight [G. Vignale, C.A.U., and S. Conti, PRL **79**, 4878 (1997), G. Vignale, TDDFT-book, chapter 5]
 - ▶ Classical theories of the dynamics of continuous media (elasticity and hydrodynamics) express many-body forces as divergences of stress tensors
 - ▶ want local functionals of the displacement or velocity field
 - ▶ use general symmetries and sum rules



xc viscosity coefficients

$$\tilde{\eta}_{xc}(n, \omega) = -\frac{n^2}{i\omega} f_{xc}^T(n, \omega)$$

$$\tilde{\zeta}_{xc}(n, \omega) = -\frac{n^2}{i\omega} \left(f_{xc}^L(n, \omega) - \frac{4}{3} f_{xc}^T(n, \omega) - \frac{d^2 e_{xc}^{unif}}{dn^2} \right)$$

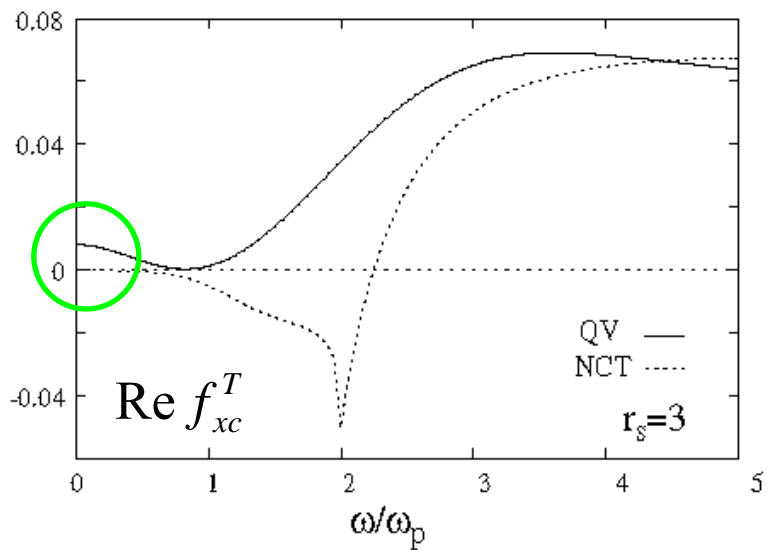
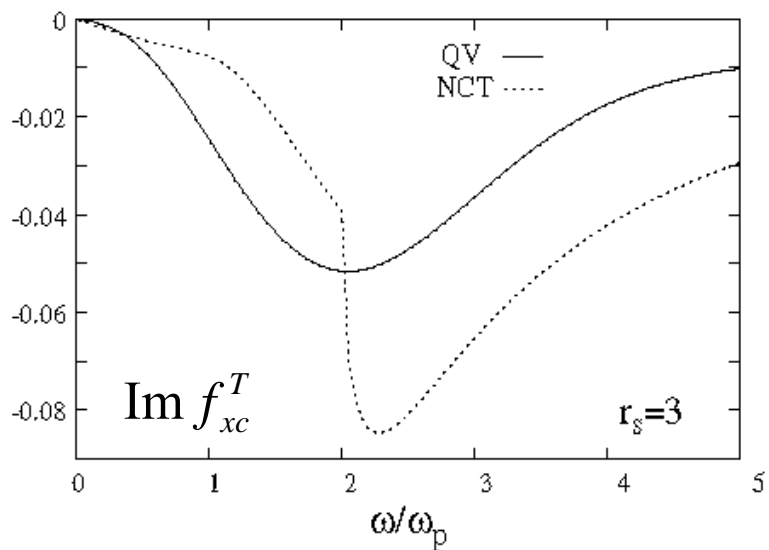
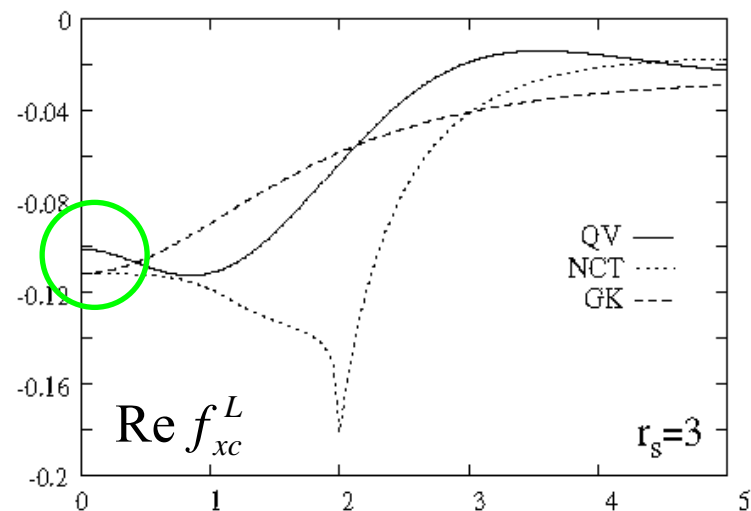
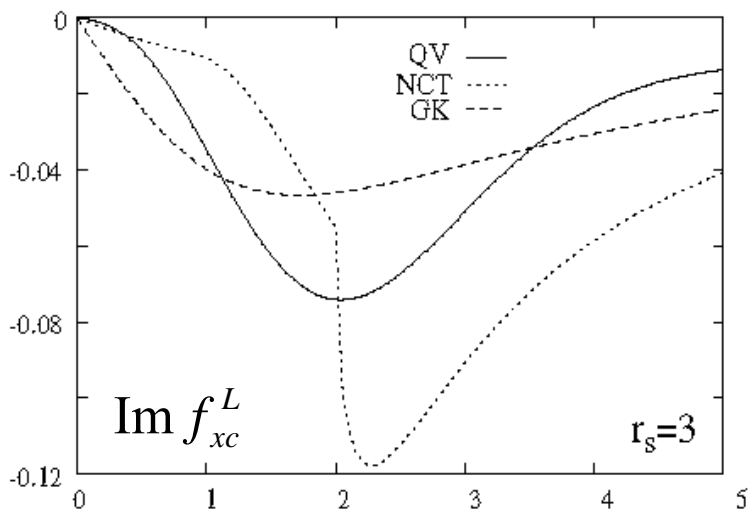
The xc viscosities have both real and imaginary parts, describing **dissipative** and **elastic** behavior:

$$\tilde{\eta}(\omega) = \eta(\omega) - \frac{S_{xc}(\omega)}{i\omega} \quad \text{shear modulus}$$
$$\tilde{\zeta}(\omega) = \zeta(\omega) - \frac{B_{xc}^{dyn}(\omega)}{i\omega} \quad \text{dynamical bulk modulus}$$

reflect the stiffness of Fermi surface against deformations



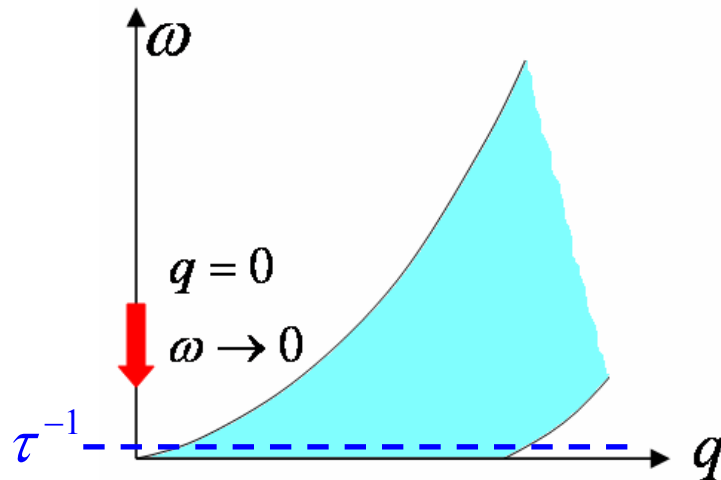
xc kernels of the homogeneous electron gas



GK: E.K.U. Gross and W. Kohn, PRL **55**, 2850 (1985)

NCT: R. Nifosi, S. Conti, and M.P. Tosi, PRB **58**, 12758 (1998)

QV: X. Qian and G. Vignale, PRB **65**, 235121 (2002)



$$f_{xc}^L(0) = \frac{d^2 e_{xc}^{unif}(n)}{dn^2} + \frac{4}{3} \frac{S_{xc}(0)}{n^2}$$

$$f_{xc}^T(0) = \frac{S_{xc}(0)}{n^2}$$

The shear modulus of the electron liquid does **not** disappear for $\omega \rightarrow 0$. (as long as the limit $q \rightarrow 0$ is taken first). Physical reason:

- Even very small frequencies $\ll E_F$ are large compared to relaxation rates τ^{-1} from electron-electron collisions.
- The zero-frequency limit is taken such that local equilibrium is not reached.
- The Fermi surface remains stiff against deformations since we're above the electron-hole continuum.



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
- ▶ natural way of describing dynamical xc effects via viscoelastic stresses in the electron liquid

Tomorrow:

- Applications of TDCDFT in the linear regime: solids, nanostructures, polymers, molecules, atoms
- TDCDFT for spin-dependent systems: spin Coulomb drag