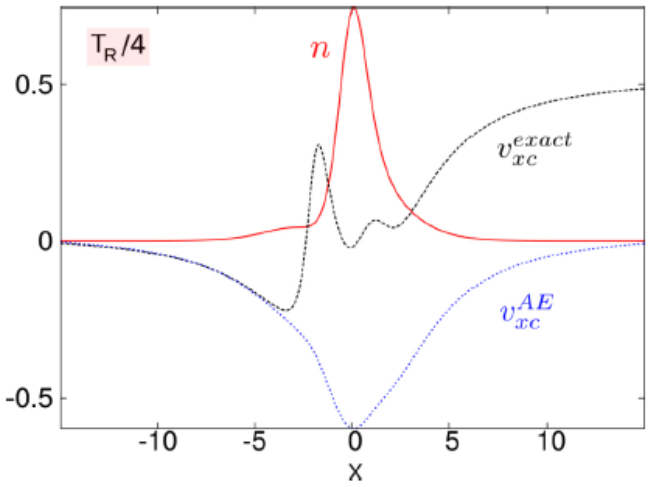
Memory in TDDFT



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Plan

- Introduction to what is memory in TDDFT
- Approximations including memory, and some exact conditions
- Some examples (including charge-transfer dynamics)
- Memory in linear response: double-excitations

Whence Memory?

Runge-Gross: $n \xleftrightarrow[1\text{-}1]{\Psi_0} v_{ext}$ true system

$n \xleftrightarrow[1\text{-}1]{\Phi_0} v_s$ KS system

Hartree is naturally *adiabatic* – depends only on instantaneous density

$$v_s[n;\Phi_0](\mathbf{r}t) = v_{ext}(\mathbf{r}t) + \int d^3r' \frac{n(\mathbf{r}'t)}{|\mathbf{r}-\mathbf{r}'|} + v_{xc}[n;\Psi_0,\Phi_0](\mathbf{r}t)$$

Actually, $v_{ext}\,[n,\Psi_0]\,(rt)$

but v_{ext} is prescribed by problem at hand, so functional dependence not so important.

History: *n(r t'<t)*, and, initial states Ψ_0, and Φ_0 of true and KS systems

Ψ_0: the true initial state

Φ_0: the initial state to start the KS calculation in -- any state with same *n(r,0)* and *n(r,0)* as Ψ_0

usually choose Slater determinant but not necessary

Memory

$v_{xc}[n; \Psi_0, \Phi_0](rt)$

functional depends on history, *n(r t'<t)*, and on initial states of true and KS systems

- Also, for a general observable: A[*n*; Φ_0]

- Memory can be thought to arise from using a *reduced* variable, *n*(r,t): tracing over N-1 spatial variables → memory-dependence.

- Special, and common, case:

$\Psi_0 = \Psi_{GS}$

$\Phi_0 = \Phi_{GS}$

Then, by the Hohenberg-Kohn theorem, $\Psi_0 = \Psi_0[n(0)]$ and $\Phi_0 = \Phi_0[n(0)]$

-- no explicit initial-state-dependence → $v_{xc}[n](r,t)$

e.g. linear response regime.

The Adiabatic Approximation

- Almost all calculations today ignore memory, and use an

adiabatic approximation:

input instantaneous density into a ground-state approximation

$$v_{\rm XC}^{\rm A}[n;\Psi_0,\Phi_0](\mathbf{r},t) = v_{\rm XC}^{\rm g.s.}[n(t)](\mathbf{r}) = \left.\frac{\delta E_{\rm XC}[n]}{\delta n(\mathbf{r})}\right|_{n=n(\mathbf{r},t)}$$

$$f_{\rm XC}^{\rm A}[n_0](\mathbf{r},\mathbf{r}',t-t') = \left.\frac{\delta^2 E_{\rm XC}[n]}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}\right|_{n=n_0(\mathbf{r})} \delta(t-t')$$

$$f_{\rm XC}^{\rm A}[n_0](\mathbf{r},\mathbf{r}',\omega) = \left.\frac{\delta^2 E_{\rm XC}[n]}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}\right|_{n=n_0(\mathbf{r})}$$

Example: $$v_{\rm XC}^{\rm ALDA}(\mathbf{r},t) = v_{\rm XC}^{\rm LDA}[n(\mathbf{r},t)] = \left.\frac{d\left(n\mathcal{E}_{\rm XC}^{unif}(n)\right)}{dn}\right|_{n=n(\mathbf{r},t)}$$

$$f_{\rm XC}^{\rm ALDA}[n_0](\mathbf{r},\mathbf{r}',t-t') = \left.\frac{d^2\left(n\mathcal{E}_{\rm XC}^{unif}(n)\right)}{dn^2}\right|_{n=n_0(\mathbf{r})} \delta(\mathbf{r}-\mathbf{r}')\delta(t-t')$$

The Adiabatic Approximation

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$$f_{\rm XC}^{\rm A}[n_0](\mathbf{r},\mathbf{r}',\omega) = \left.\frac{\delta^2 E_{\rm XC}[n]}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}\right|_{n=n_0(\mathbf{r})}$$

- Two sources of error:

(i) Adiabatic approximation itself

(ii) Ground-state functional approximation

- To disentangle, study "adiabatically-exact" potential:

$$v_{xc}^{\text{A-ex}}(r,t) = v_{xc}^{\text{exact-gs}}[n(t)](r)$$

Development of Memory-Dependent Functionals…

- Gross-Kohn (1985)

Phys. Rev. Lett. ***55,*** *2850 (1985)*

linear-response kernel of the uniform electron gas at finite frequency

$$f_{\rm XC}^{\rm GK}[n_0](\mathbf{r},\mathbf{r}',\omega) = \delta(\mathbf{r}-\mathbf{r}')f_{\rm XC}^{unif}[n_0(\mathbf{r})](q=0,\omega)$$

$$v_{\rm XC}^{(1)\rm GK}[n](\mathbf{r},t) = \int f_{\rm XC}^{unif}[n_0(\mathbf{r})](t-t')\delta n(\mathbf{r},t')dt'$$

✓ Non-adiabatic -- time-non-local although spatially local; “finite-frequency LDA”

Violates exact conditions: harmonic potential theorem, zero-force theorem

A couple of exact conditions in TDDFT:

(i) Harmonic Potential Theorem (Dobson (*PRL* ***73****, 2244, (1994*); Vignale *PRL* ***74****, 3233, (1995*))

N electrons in a harmonic well subject to a TD uniform electric field, E(t)
→ density rigidly sloshes back and forth following classical center of mass oscillations

$$n(\mathbf{r},t) = n_{GS}(\mathbf{r} - \mathbf{r}_{CM}(t))$$

$$\rightarrow Vxc(\mathbf{r},t) = Vxc^{GS}(\mathbf{r} - \mathbf{r}_{CM}(t))$$

- Instead, GK finds an n-dependent shift in the frequency of the CM motion, and a damping of the oscillations.

  One way to think about why is that when you only look locally at the density at r, you can't tell difference between sloshing motion and local compression/rarefaction ….

A couple of exact conditions in TDDFT:

(ii) Zero Force Theorem (Vignale *PRL* ***74****, 3233, (1995)*; *Phys. Lett. A,* ***209****, 206 (1995)*)

xc field cannot exert a net force on itself $\int n(\mathbf{r},t)\nabla v_{\mathrm{XC}}(\mathbf{r},t)d^3r = 0$

Can prove by: evaluate $\frac{d^2}{dt^2}$<r> using Ψ(t) and then Φ(t); then subtract…)

(exercise! Prove this !)

Linear response regime: $\int d^3r'\, f_{\mathrm{XC}}[n^{\mathrm{GS}}](\mathbf{r},\mathbf{r}',\omega)\nabla n^{\mathrm{GS}}(\mathbf{r}') = \nabla v_{\mathrm{XC}}^{\mathrm{GS}}[n^{\mathrm{GS}}](\mathbf{r})$

- Using GK:

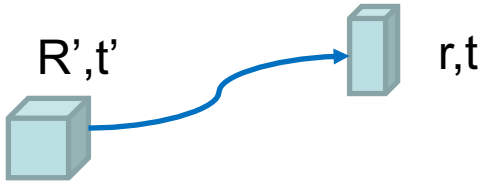
$f_{\mathrm{xc}}^{unif}[n_0(r)](q=0,\omega)$ ω-dependent

ω-independent

❖ The exact conditions imply *time-non-locality → spatially non-local n-dependence*, i.e. a local density approximation with memory does not exist.

even in limit of slowly-varying densities → "ultra-non-locality"

… Development of Memory-Dependent Functionals



➢ Dobson-Bünner-Gross (1997)

Phys. Rev. Lett. ***79****, 1905 (1997)*

Apply Gross-Kohn in frame that moves along with local velocity of electron fluid: memory resides with the fluid element.

Spatially-local relative to where a fluid element at *(r,t)* was at earlier times *t', R'(t'|r,t)*

✓ Non-adiabatic, and satisfies harmonic potential theorem, zero-force theorem

➢ Vignale-Kohn (VK) (1996) – spatially local approx in terms of the *current-density,* ***j****(****r****,t)* → TD-current-density-FT

Phys. Rev. Lett. ***77****, 2037 (1996); Vignale, Ullrich, Conti, , PRL* ***79****, 4878 (1997)*

Based on map: $\boldsymbol{j} \xleftrightarrow[1\text{-}1]{\Psi_0} \boldsymbol{A}_{\text{ext}}$

VK constructed from dynamical longitudinal and transverse responses to slowly-varying perturbations of uniform electron liquid; involves Navier-Stokes-like eqn with complex viscosity coefficients.

✓ Non-adiabatic, and satisfies harmonic potential theorem, zero-force theorems…

… A little more about Vignale-Kohn and TDCDFT…

- Note that RG's 1st step was j ←→ v_{ext}

Using **A** instead of v makes it easier to satisfy *non-interacting representability*: many currents of interacting systems in *scalar* potentials can only be reproduced by a non-interacting systems in *vector* potentials

- Note that spatially local current ***j*** dependence → spatially ultra-nonlocal dependence on density *n*

E.g. $$\boldsymbol{j}_{\mathrm{L}}(\boldsymbol{r},t)=\int \mathrm{d}^3r'\frac{\partial n(\boldsymbol{r}',t)}{\partial t}\nabla_r\frac{1}{4\pi|\boldsymbol{r}-\boldsymbol{r}'|}$$

So even for static response (no memory), VK can help when spatial-non-locality important.

- Some success for: correcting overestimate of LDA polarizabilities in long-chain polymers, dissipation in extended systems, spin-Coulomb drag, stopping power in metals….BUT problems for finite systems due to spurious damping

… Other Memory-Dependent Functionals

- Kurzweil & Baer (2004, 2005, 2006), Tokatly (2005, 2007)

- Orbital functionals $v_{xc}[\{\phi_i(t)\}]$

– instantaneous KS orbitals incorporate “infinite KS memory”

Computationally more involved: TDOEP

- Approximations based on an exact decomposition of the xc potential

Fuks, Lacombe, Nielsen, Maitra, Phys. Chem. Chem. Phys. **20**, 26145 (2018).
L. Lacombe and N. T. Maitra, J. Chem. Theory and Comput. **15**, 1672 (2019).

What about initial state dependence?

The 1-1 *n-v* mapping formally depends on the initial-state.

$$v_{\mathrm{xc}}[n;\Psi_0,\Phi_0](\mathbf{r}t) \qquad v_{\mathrm{ext}}[n;\Psi_0](\mathbf{r}t) \qquad v_{\mathrm{s}}[n;\Phi_0](\mathbf{r}t)$$

n(r,t) does *not* uniquely define the xc potential…

Which raises the question: if stuck with an adiabatic approximation, is there a "best" Φ_0 to start evolving in for a given Ψ_0 ?

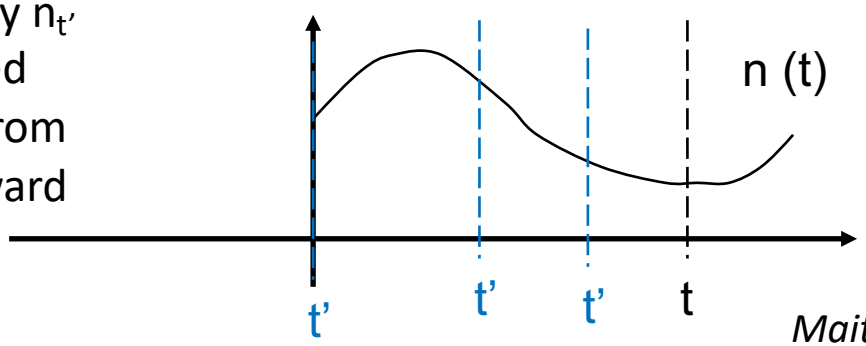
See shortly, but first, note that initial-state-dependence and history-dependence are intimately entangled…

Another exact condition: **"Memory" condition**

❖ History and initial-state dependence are entangled

$V_{xc}[n_{t'}; \Psi_0 = \Psi(t'), \Phi_0 = \Phi(t')](r,t)$ independent of t' (for $t>t'$)

density $n_{t'}$ defined only from t' onward



*Maitra, Burke, Woodward, PRL **89**, 023002 (2002*

❖ This is a very hard condition to satisfy for non-adiabatic functionals.

Question for you! Does ALDA satisfy this? Do you think VK satisfies this?