

Advanced TDDFT

TDDFT

"~~Humanity~~ has advanced, when it has advanced, not because it has been sober, responsible, and cautious, but because it has been playful, rebellious, and immature"

Tom Robbins
US novelist (1936 -)

These lectures:

some cases where the usual approximations in TDDFT break down and something more “rebellious/playful/immature” must be done...



Neepa T. Maitra

*Hunter College and the Graduate Center of the
City University of New York*



Plan

- **Memory in TDDFT** – introduction to what is memory and some of its general properties
 - initial-state dependence
 - history-dependence
 - “gedanken” electronic quantum control

Next, two practical cases where memory is vital, and we'll derive frequency-dependent kernels using simple models:

- **Double-excitations** (and autoionizing resonances)
- **Long-range charge-transfer** (between open-shell fragments)

Memory

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

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

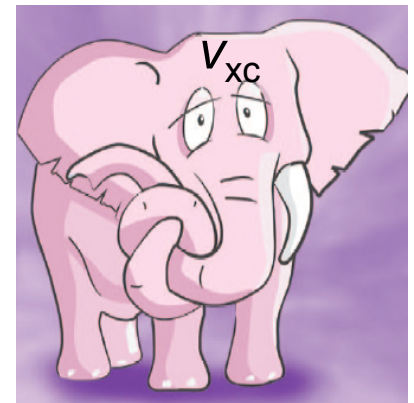
functional dependence on history, $n(\mathbf{r} t' < t)$, and on initial states of true and KS systems

Almost all calculations today ignore this, and use an “**adiabatic approximation**” :

$$v_{\text{xc}}^{\text{A}}[n; \Psi_0, \Phi_0](\mathbf{r}t) = v_{\text{xc}}^{\text{GS}}[n(\mathbf{r}t)]$$

$$\text{e.g. } v_{\text{xc}}^{\text{ALDA}}(\mathbf{r}t) = v_{\text{xc}}^{\text{LDA}}[n(\mathbf{r}t)] = \frac{de_{\text{xc}}^{\text{unif}}(n(\mathbf{r}t))}{dn}$$

$$f_{\text{xc}}^{\text{ALDA}}(\mathbf{r}, \mathbf{r}', t - t') = \frac{d^2e_{\text{xc}}^{\text{unif}}(n(\mathbf{r}t))}{dn^2} \delta(\mathbf{r} - \mathbf{r}') \delta(t - t')$$



Memory-dependence

? How valid is the adiabatic approximation (ATDDFT) – can we really ignore memory?

● **Linear response** – excitations and response properties:

-- AA seems to work well – not entirely understood why.

ATDDFT achieves unprecedented balance between accuracy and efficiency

-- For some excitations, ATDDFT fails badly

eg. double excitations

eg. certain long-range charge-transfer excitations

eg. Auto-ionizing resonances arising from double-excitations

See soon!
(Lecs 2 & 3)

• **Strong- field dynamics?** Examples where exact solutions are available indicate memory often plays a significant role and ATDDFT fails.

Now, will play with some such examples, clarifying what is meant by memory, and uncovering some exact properties of memory-dependence.

Initial-state dependence (ISD)

$$v_{xc}[n; \Psi_0, \Phi_0](\mathbf{r}t) \quad v_{\text{ext}}[n_0, \Psi_0](\mathbf{r}t) \quad v_s[n; \Phi_0](\mathbf{r}t)$$

But is there ISD? That is, if we start in different Ψ_0 's, *can* we get the same $n(\mathbf{r}t)$, for all t , by evolving in different potentials?

(If no, then ISD redundant, i.e. the functional dependence on the density is enough)

The answer is: No! for one electron, but,
Yes! for 2 or more electrons

ISD? One electron case:

Can $\varphi(\mathbf{r}, t)$ and $\tilde{\varphi}(\mathbf{r}, t)$ be found, that evolve with the same density for all t ?

means $\tilde{\varphi}(\mathbf{r}, t) = \varphi(\mathbf{r}, t)e^{i\alpha(\mathbf{r}, t)}$

where α is a real phase

Also, must have

$$0 = \dot{n}_\varphi(\mathbf{r}, t) - \dot{n}_{\tilde{\varphi}}(\mathbf{r}, t) = \nabla \cdot [n(\mathbf{r}, t)\nabla\alpha(\mathbf{r}, t)]$$

using eqn of continuity, $\dot{n}(\mathbf{r}, t) = -\nabla \cdot \mathbf{j}(\mathbf{r}, t)$

with $\mathbf{j}(\mathbf{r}, t) = \frac{i}{2}[\varphi(\mathbf{r}, t)\nabla\varphi^*(\mathbf{r}, t) - \varphi^*(\mathbf{r}, t)\nabla\varphi(\mathbf{r}, t)]$

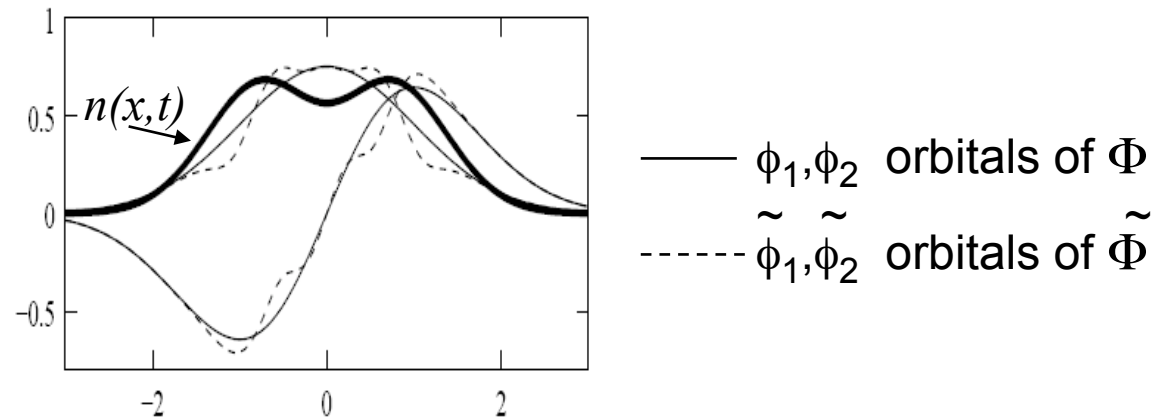
$$0 = \int d^3r \alpha(\mathbf{r}, t)\nabla \cdot [n(\mathbf{r}, t)\nabla\alpha(\mathbf{r}, t)] = - \int d^3r \underbrace{n(\mathbf{r}, t)|\nabla\alpha(\mathbf{r}, t)|^2}_{\text{everywhere non-negative}} + \text{surface term}$$

$\Rightarrow \nabla\alpha(\mathbf{r}, t) = 0 \quad \Rightarrow \varphi$ and $\tilde{\varphi}$ differ only by irrelevant t-dep phase

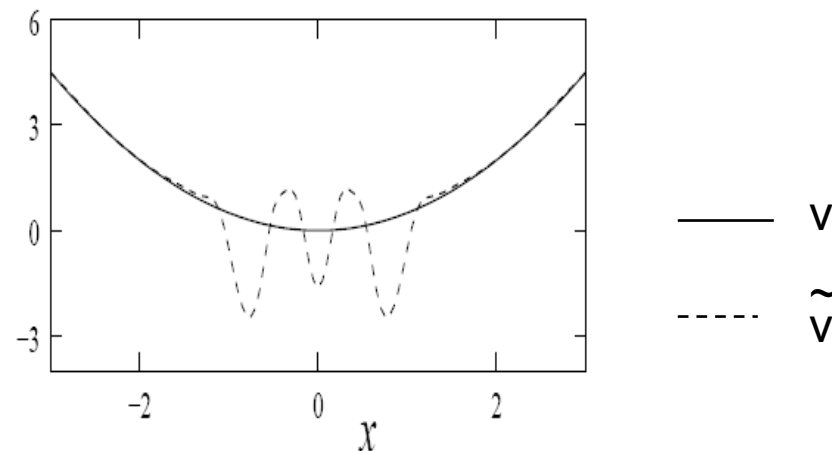
More than two electrons:

The time-evolving density does *not* uniquely define the potential

Two non-interacting electron example in 1d:



The initial KS potentials in which these two different initial-states evolve with the same n



• Say this is the density of an interacting system. Both are possible KS systems.

➤ v_{xc} different for each. Cannot be captured by any adiabatic approximation

Maitra & Burke, (PRA 2001)(2001, E)

ISD in Floquet states

Reference system:

$$v = \frac{1}{2} \omega_0^2 x^2 + \lambda x \sin(\omega t)$$

ϕ_1, ϕ_2 are lowest Floquet orbitals (top panel);
 n their density

Alternate system:

Same n , but with a doubly-occupied Floquet orbital (middle panel), living in \tilde{v}

- Say this is the density of an interacting system. Both are possible KS systems, and

$$v - \tilde{v} = v_{xc} - \tilde{v}_{xc}$$

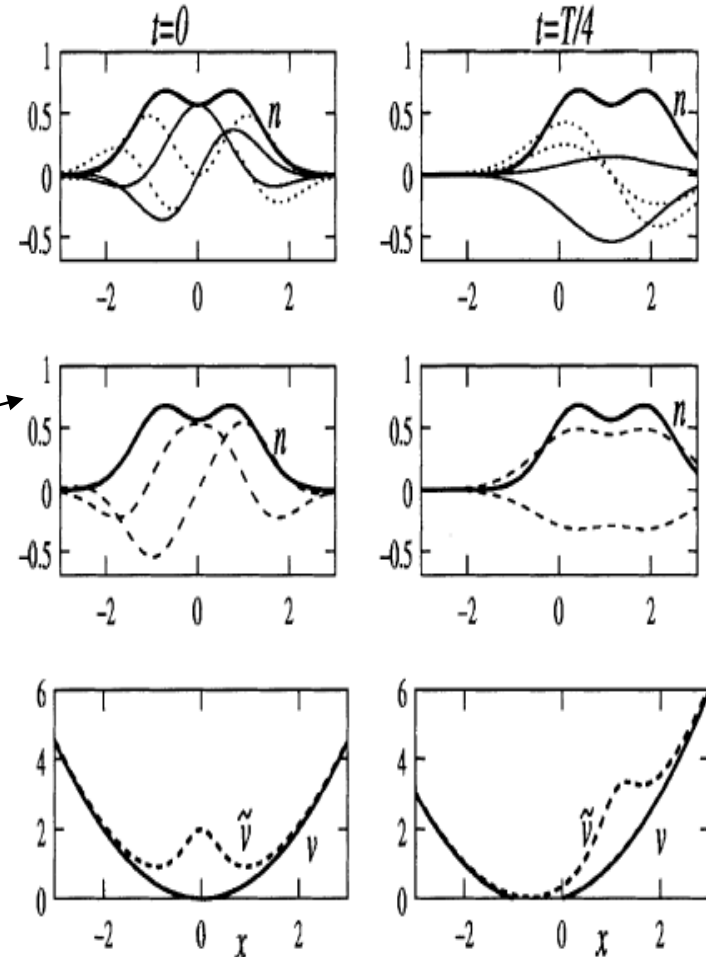
➤ v_{xc} different for each. Cannot be captured by any adiabatic approximation

Floquet DFT: No 1-1 mapping between densities and time-periodic potentials – need ISD

Another 2-e non-interacting example:

Re and Im parts

Re and Im parts



- So initial-state-dependence is important for 2 or more electrons
- Special case of much practical interest: start in a ground-state.

Then, by the Hohenberg-Kohn thm, $\Psi_0 = \Psi_0[n(0)]$ and $\Phi_0 = \Phi_0[n(0)]$ – no explicit ISD needed!

- But there's still history-dependence, and we'll look at this now for the two electron case, starting in ground-state:

KS gs is doubly-occupied spatial orbital, $\phi_0(r)$

History-dependence: studying it via numerically solvable 2-electron systems

If somehow we can solve the many-electron problem exactly, can we find the exact xc potential, and study its features?

Two electrons in spin-singlet

Assume $n(r,t)$ known. What is v_s ?

The KS orbital is doubly-occupied, & of form: $\varphi(\vec{r},t) = \sqrt{\frac{n(\vec{r},t)}{2}} \exp(i\alpha(\vec{r},t))$

Substitute into TDKS eqn and invert to get:

$$v_s = \frac{1}{4} \frac{\nabla^2 n}{n} - \frac{1}{8} \frac{|\nabla n|^2}{n^2} - \frac{1}{2} \frac{|\nabla \alpha|^2}{n} - \frac{\partial \alpha}{\partial t} \left[v_{\text{ext}}(\mathbf{r}t) + \int d^3r' \frac{n(\mathbf{r}'t)}{|\mathbf{r} - \mathbf{r}'|} + v_{\text{xc}}(\mathbf{r}t) \right]$$

non-adiabatic (memory)

where α is determined by eqn of continuity,

$$\nabla \cdot \nabla \alpha + \frac{1}{n} \nabla \alpha \cdot \nabla n + \frac{1}{n} \frac{\partial n}{\partial t} = 0$$

$$v_x = -v_H/2$$

$$v_c = v_{\text{xc}} - v_x$$

Two-electron example of history-dependence

Eg. Time-dependent Hooke's atom –exactly numerically solvable

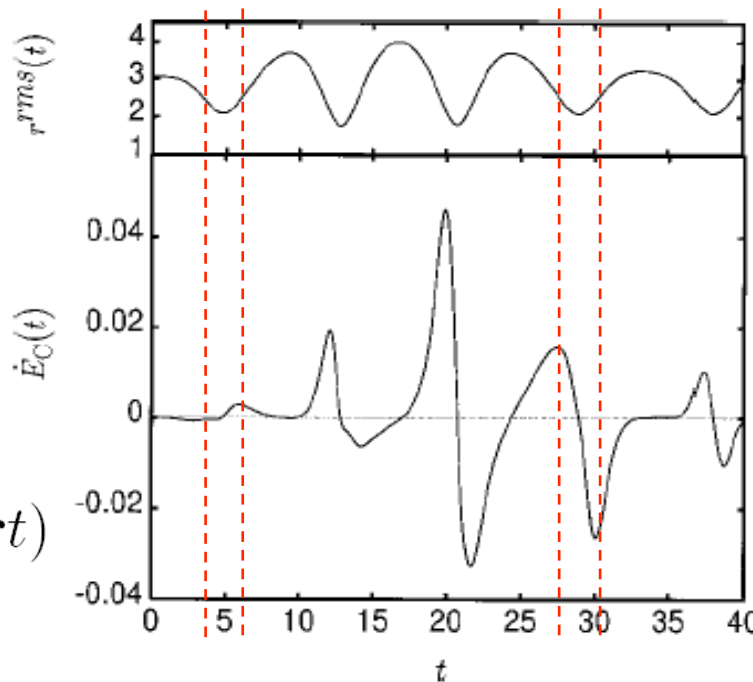
$$v_{xc}[n; \Psi_0, \Phi_0](\mathbf{r}t)$$

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

2 electrons in parabolic well,
time-varying force constant

parametrizes
density

$$\int d^3r \dot{n}(\mathbf{r}t) v_C(\mathbf{r}t)$$



$$k(t) = 0.25 - 0.1 * \cos(0.75 t)$$

Any adiabatic (or even semi-local-in-time) approximation would incorrectly predict the same v_C at both times.

Time-slices where $n(t)$ is locally and semi-locally identical but v_C is quite distinct \rightarrow v_C is generally a very non-local functional in time of the density

- See also examples in: *d'Amico & Vignale (1999)*; *Ullrich (JCP, 2006)* – 2e in 2d qm strip; *Wijewardane & Ullrich, (PRL 2008)* – TDOEP (EXX) in qm wells

- Development of History-Dependent Functionals:

Gross & Kohn (1985), *Dobson, Bunner & Gross (1997)*, *Vignale & Kohn (1996)*, *Vignale, Ullrich, & Conti (1997)*, *Kurzweil & Baer (2004)*, *Tokatly (2005)* ...

- Orbital functionals – as orbitals incorporate “infinite KS memory”, so may be most promising approach in many situations

- Development of true ISD-Functionals: none yet!

Nevertheless, ISD and history-dependence are intimately entangled....next slide..

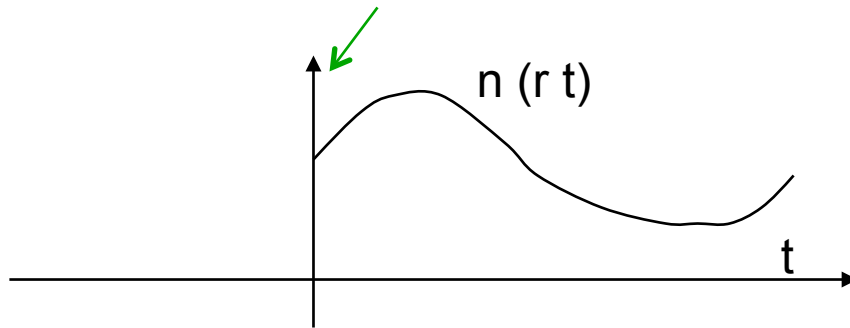
Trading ISD for more history

Evolve initial states backward in time, in some potential, to a *ground-state* → no ISD due to Hohenberg-Kohn DFT → instead, must tack on extra piece of “pseudo pre-history”

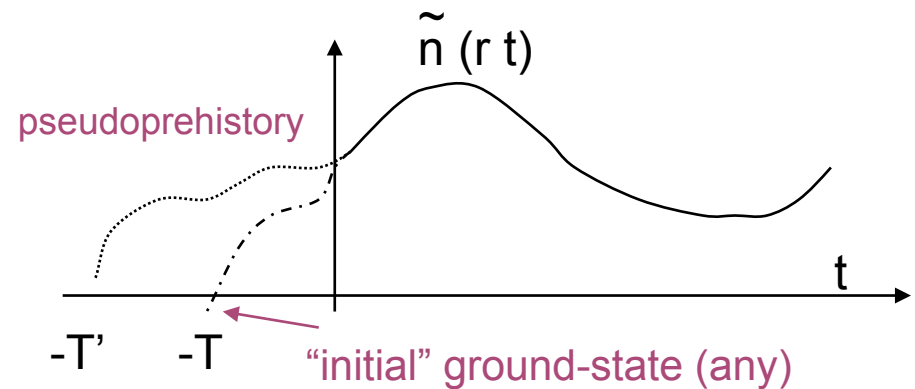
“memory condition”

$$V_{xc}[n; \psi_0, \Phi_0](\mathbf{r}, t) = V_{xc}[\tilde{n}](\mathbf{r}, t)$$

Starts at $t=0$ in initial true state Ψ_0 and KS evolves from initial state Φ_0



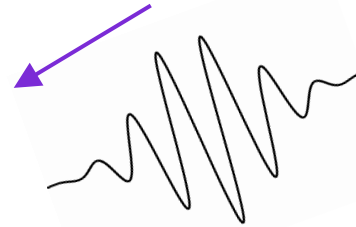
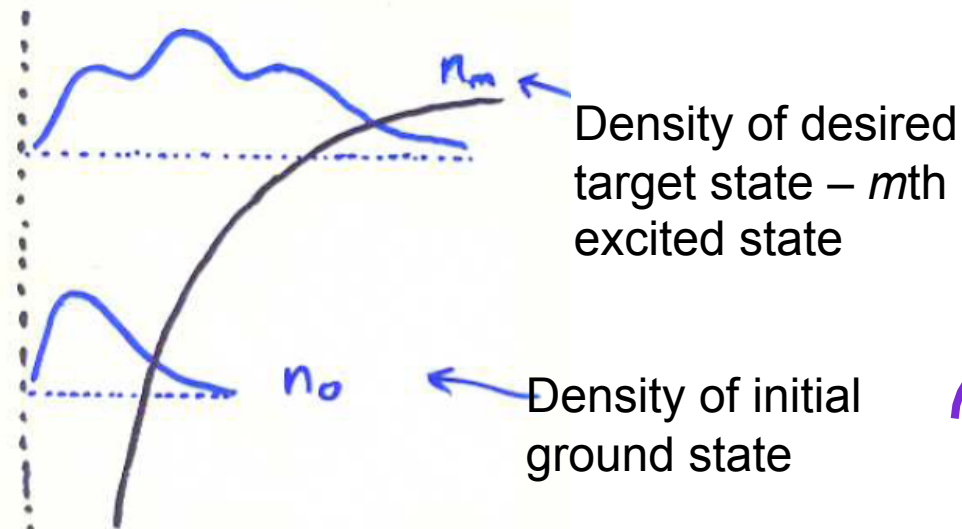
Starts at some time $-T$ from some ground state:



- The pseudoprehistory is not unique – may find many ground-states that evolve to the same state at $t=0$, in different amounts of time, in different potentials.
- Eqn applies to all – and gives a strict exact test for approximate history-dependent functionals.

Importance of Memory in Electronic Quantum Control

Interacting (true) system:



Achieve this by turning on some laser field for some time until m th state reached, at time t^* , say,

i.e. evolve in a given $v_{\text{ext}}(t)$, s.t.

$$v_{\text{ext}}(t^*) = v_{\text{ext}}(0)$$

Kohn-Sham description of dynamics:

? Does v_s also return to its initial value ?

? Is an adiabatic approx adequate ?

? Does v_s also return to its initial value ?

No, it cannot!

First note that the KS $n(t > t^*) = n_m$

IF $v_s(t > t^*) = v_s(0)$, then n_m would have to be an excited-state density of $v_s(0)$.

But $v_s(0)$ is the KS potential whose *ground-state* has the same density as interacting ground-state of $v_{\text{ext}}(0)$.

Excited KS states do *not* have the same density as the excited states of the corresponding v_{ext}

$$\rightarrow v_s(0) \neq v_s(t^*)$$

? Is an adiabatic approx adequate ?

No!

2 possibilities:

- (i) exact KS potential becomes static, with $\Phi(t>t^*) = \Phi_m$, -- an excited state of $v_s(t^*)$. But ATDDFT instead finds KS potential which has n_m as *ground-state* density.

The excited state info is encoded in the memory-dependence of the exact KS potential, lacking in ATDDFT.

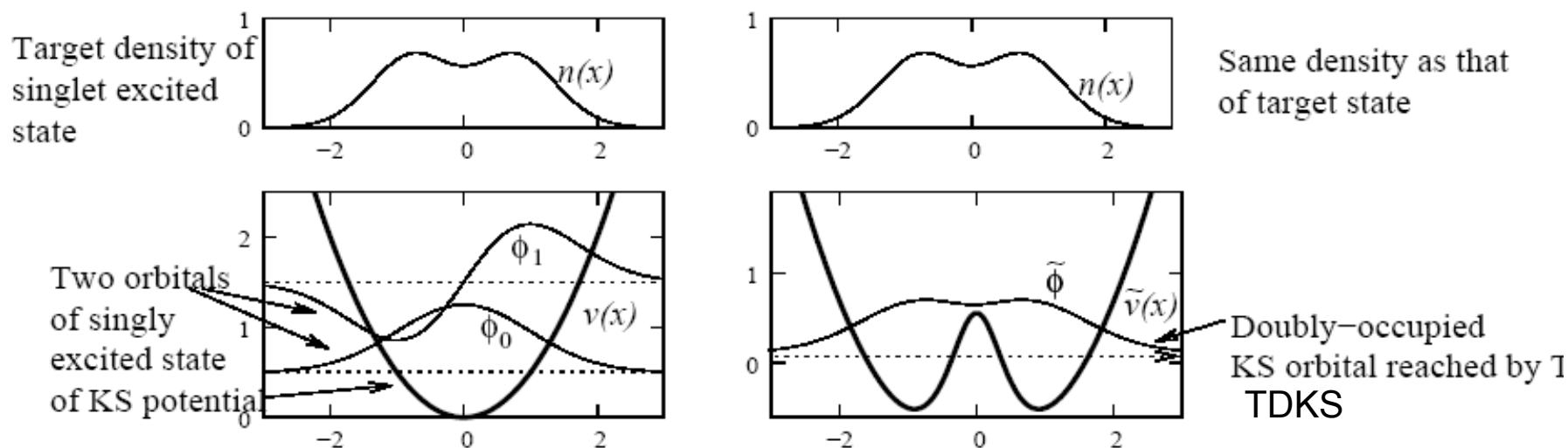
- (ii) exact KS (and xc potential) continue to change in time after t^* , with densities of KS orbitals evolving such that their sum remains static, and equal to n_m . ATDDFT clearly fails, as static $n \rightarrow$ ATDDFT v_{xc} static too.

A particularly challenging control problem for TDDFT:

Consider pumping He from ground ($1s^2$) to first accessible excited state ($1s2p$).

Problem!! The KS state remains doubly-occupied throughout – *cannot* evolve into a singly-excited KS state.

Simple model: evolve two electrons in a harmonic potential from ground-state (KS doubly-occupied ϕ_0) to the first excited state (ϕ_0, ϕ_1):



-- KS achieves target excited density, but with a doubly-occupied *ground-state* orbital !

-- Yet this is how *exact TDDFT* describes the dynamics – the exact v_{xc} is unnatural and difficult to approximate.

Summary

- Exact xc functionals in TDDFT are generally memory-dependent – but adiabatic approximations are not.
- There is no initial-state dependence for one electron, but there is for more than one.
- History-dependence and initial-state dependence are entangled with each other.
- Memory appears to be an important feature to capture in many applications, like electronic quantum control processes – orbital functionals may be the best way to go – but more needs to be done to study this.
- Next time: memory in linear response – frequency-dependent kernels in double-excitations.

An exercise or two, for you!

- (1) For a one-electron ground-state, the KS potential-functional is easily determined by inversion of the TDKS eqn as:

$$v_S(x) = \frac{d^2 \sqrt{n(x)} / dx^2}{2 \sqrt{n(x)}} + \epsilon$$

Now consider beginning an adiabatic calculation in the first excited state of the 1-d harmonic oscillator. What would the initial exact *adiabatic* KS potential be at this time be? Comment.

(Note that we wouldn't usually use a density-fnl for v_S – we only use a fnl for v_{xc} , as v_{ext} is given by problem at hand. But for the purposes of this exercise, treat v_S as a density fnl as above)

(2) a) Does ALDA satisfy the “memory condition”?

b) Will a functional with history-dependence but no initial-state dependence (such as Vignale-Kohn, or VUC – see Carsten's lectures), satisfy the “memory condition”?

References

- “Initial-state dependence and memory”, N.T. Maitra, in “*Time-dependent density functional theory*, edited by M.A.L. Marques, C.A. Ullrich, F. Nogueira, A. Rubio, K. Burke, and E.K.U. Gross, Springer Lecture Notes in Physics Vol. 706 (2006)
- “*Mapping from densities to potentials in time-dependent density functional theory*”, R. van Leeuwen, Phys. Rev. Lett. **72**, 3863 (1999)
- “*Correlation in time-dependent density functional theory*”, P. Hessler, N.T. Maitra, and K. Burke, J. Chem. Phys. **117**, 72 (2002)
- “*Memory in time-dependent density functional theory*”, N. T. Maitra, K. Burke, and C. Woodward, Phys. Rev. Lett. **89**, 023002 (2002)
- “*On the Floquet formulation of time-dependent density functional theory*”, N.T. Maitra, and K. Burke, Chem. Phys. Lett. **359**, 237 (2002); *Comment on ‘‘Analysis of Floquet formulation of time-dependent density functional theory [Chem. Phys. Lett. 433 (2006) 204]’’*, Chem. Phys. Lett. **441**, 167 (2007)
- “*Demonstration of initial-state dependence in density functional theory*”, N.T. Maitra and K. Burke, Phys. Rev. A. **63** 042501 (2001); *ibid.* **64** 039901 (E) (2001)
- “*Local density-functional theory of frequency-dependent linear response*”, E.K.U. Gross and W. Kohn, Phys. Rev. Lett. **55**, 2850 (1985)
- “*Time-dependent exchange-correlation current density functionals with memory*”, Y. Kurzweil and R. Baer J. Chem. Phys. **121**, 8731 (2004)
- “*Time-dependent density functional theory beyond linear response: An exchange-correlation potential with memory*”, J.F. Dobson, M.J. Büchner, and E.K.U. Gross, Phys. Rev. Lett. **79**, 1905 (1997)
- “*Current-dependent exchange-correlation potential for dynamical linear response theory*”, G. Vignale and W. Kohn, Phys. Rev. Lett. **77**, 2037 (1996)
- “*Time-dependent density-functional theory beyond the adiabatic approximation*”, G. Vignale, C.A. Ullrich, and S. Conti, Phys. Rev. Lett. **79**, 4878 (1997)
- “*Quantum many-body dynamics in a Lagrangian frame I and II*”, I.V. Tokatly, Phys. Rev. B **71**, 165104 and 165105 (2005)
- “*Time-dependent density-functional theory beyond the adiabatic approximation: insights from a two-electron model system*”, C.A. Ullrich, J. Chem. Phys. **125**, 234108 (2006)
- “*Time-dependent Kohn-Sham theory with memory*”, H.O. Wijewardane and C.A. Ullrich, Phys. Rev. Lett. **95**, 086401 (2005)
- “*Real-time electron dynamics with exact-exchange time-dependent density-functional theory*”, H.O. Wijewardane and C.A. Ullrich, Phys. Rev. Lett. **100**, 056404 (2008)