

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*



meaning semi-local in space and local in time

Poor Performance of the Usual Functionals

Within Linear Response:

- Rydberg states
- Polarizabilities of long-chain molecules
- Optical response (gap, excitons..) of solids

Spatially local/semilocal approx inadequate.

Solids: Need $\sim 1/q^2$ and
Im part of fxc to open gap

Development of **orbital-dependent fnals** (exact-exchange/sic), or **TD current-DFT**, or **Nanoquanta kernel**

Haunted by static correlation in the gs

Lectures 2 and 3

- Molecular dissociation
- Long-range charge transfer
- Conical Intersections
- Double excitations

Adiabatic approximation fails

Development of **frequency-dependent kernels**

Poor Performance of the Usual Functionals

or, questionable...

This lecture

Beyond Linear Response

- Some strong-field dynamics calculations

Adiabatic approx fails --
memory-dependence crucial

- Certain electronic quantum control problems

- Momentum distributions (eg in ion-recoil experiments)

TD Static
correlation

- Non-sequential double ionization

Cannot extract
observable
simply from KS
system

- Coupled correlated electron-ion dynamics

- Electronic transport

-- Need essential derivative discontinuity lacking in approx

Plan

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

- **II. Frequency-Dependent kernels: Double Excitations**

- **III. Static Correlation, Molecular Dissociation and Long-Range Charge-Transfer**

Memory

RG:
$$n(\mathbf{r}, t) \xleftrightarrow[\Psi_0]{1-1} v_{\text{ext}}(\mathbf{r}, t)$$

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

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

Actually, $v_{\text{ext}}[n, \Psi_0](\mathbf{r}, t)$
 but as v_{ext} is usually given,
 functional dependence not
 considered.

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

Ψ_0 : the true initial state

Φ_0 : the initial state to start the KS calculation in -- essentially any (SSD) that has
 same $n(\mathbf{r}, 0)$ and $\dot{n}(\mathbf{r}, 0)$ as Ψ_0 -- *R. van Leeuwen PRL* **82**, 3863 (1999)

Memory

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

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

- Also, for general observable $A[n, \Psi_0, \Phi_0]$
- Why do we have memory?

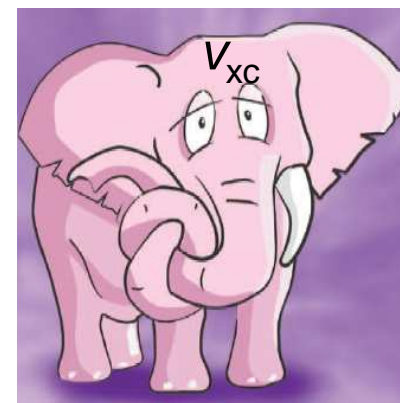
Due to having a *reduced* variable, $n(\mathbf{r}, t)$, which traces over $N-1$ spatial variables \rightarrow memory-dependence.

- But almost all calculations ignore this, and use an **adiabatic approximation**:

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

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

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



Now, will play with some examples, clarify what is meant by memory, and uncover some exact properties of memory-dependence.

Let's start with initial-state dependence.

Initial-state dependence (ISD)

RG: $n(\mathbf{r}, t) \leftarrow \frac{\Psi_0}{1-1} \rightarrow v_{\text{ext}}(\mathbf{r}, t)$

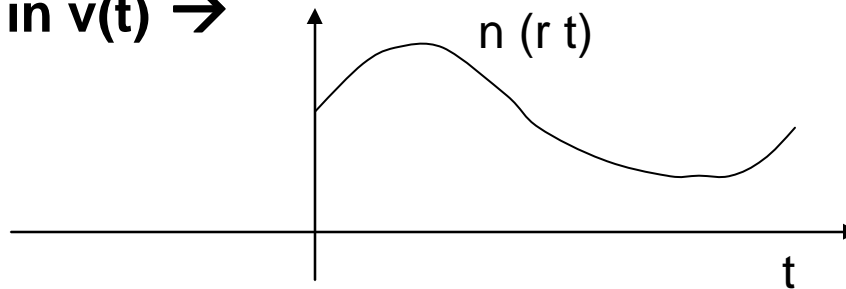
$$v_{\text{xc}}[n; \Psi_0, \Phi_0](\mathbf{r}, t)$$

$$v_{\text{ext}}[n, \Psi_0](\mathbf{r}, t)$$

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

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? i.e.

Evolve Ψ_0 in $v(t) \rightarrow$



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

? Evolve $\tilde{\Psi}_0$ in $\tilde{v}(t) \rightarrow$ same n ?

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

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

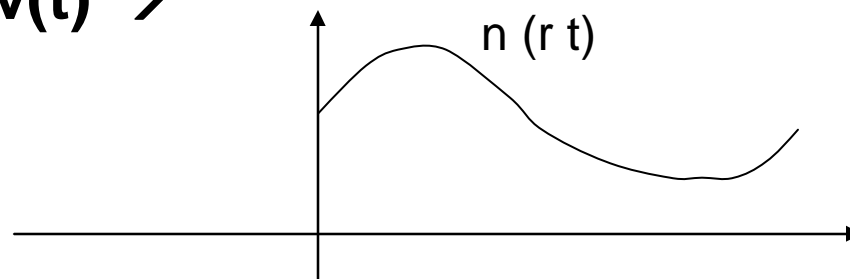
with $\mathbf{j}(\mathbf{r}, t) = \frac{i}{2}[\varphi(\mathbf{r}, t)\nabla\varphi^*(\mathbf{r}, t) - \varphi^*(\mathbf{r}, t)\nabla\varphi(\mathbf{r}, t)]$

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

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

So, for one electron:

Evolve Ψ_0 in $v(t) \rightarrow$



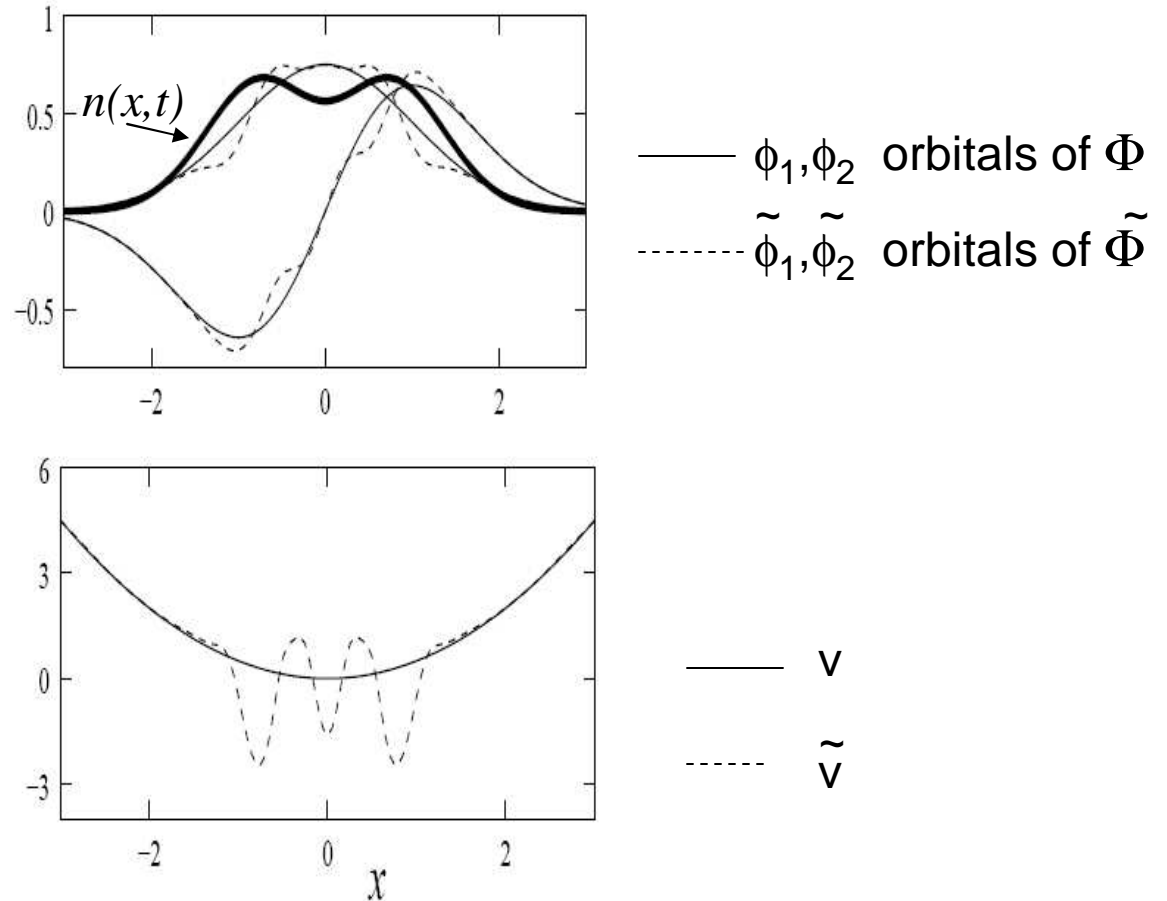
Evolve $\tilde{\Psi}_0$ in $\tilde{v}(t) \rightarrow$ ~~same n~~

No ISD needed in functionals since the time-evolving density itself contains the information about the initial state.

More than one electron:

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

More than one electron: 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:

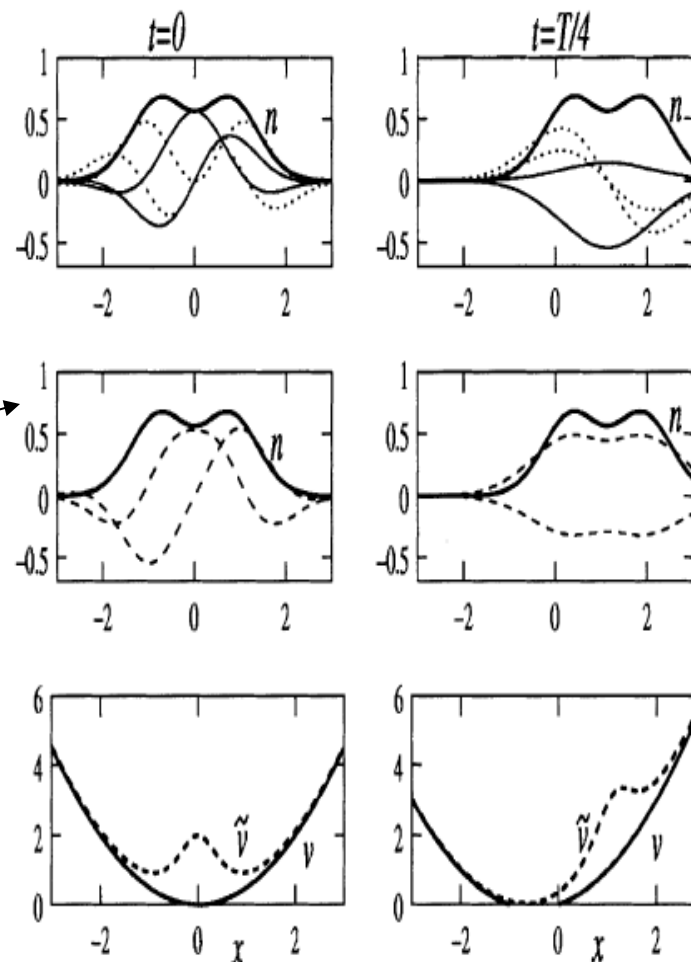
Same n , but with a doubly-occupied Floquet orbital (middle panel), living in \tilde{v}

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

$$V_S - \tilde{V}_S = V_{xc} - \tilde{V}_{xc}$$

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

Another 2-e non-interacting example:



Floquet DFT: No 1-1 mapping between densities and time-periodic potentials – need ISD
 N.T. Maitra & K. Burke, *Chem. Phys. Lett.* **359**, 237 (2002); *ibid.* **441**, 167 (2007)

- 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:

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

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

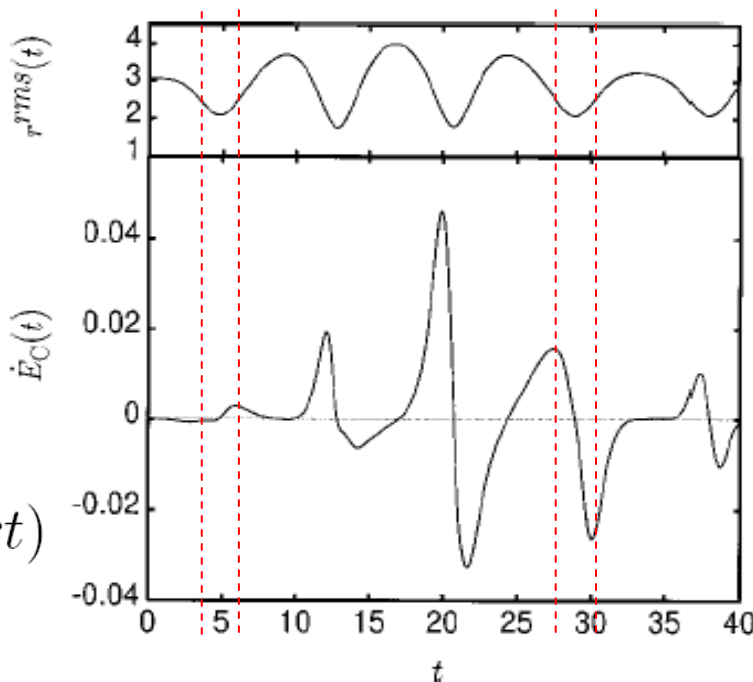
2 electrons in parabolic well, time-varying force constant

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

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

parametrizes density

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



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

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 Carsten's talk!

P. Hessler, N.T. Maitra, K. Burke, J. Chem. Phys, 117, 72 (2002)

Other Explorations of Memory-Dependence in Real-Time

- First exploration of memory-dependence in real-time, using 2e in 2D parabolic well, *I. d'Amico & G. Vignale, PRB 59, 7876 (1999)*.
- Demonstrating memory in VUC for charge-density oscillations in quantum wells, *H.O. Wijewardane and C.A. Ullrich, Phys. Rev. Lett. 95, 086401 (2005)*
- Comparing exact, ALDA, and VK approximations for 2e in a 2D quantum strip, *C.A. Ullrich, JCP 125, 234108, (2006)*.
- Demonstrating memory-dependence using an orbital-dependent functional – exact-exchange via TDOEP in quantum wells, *H. Wijewardane & C.A. Ullrich, PRL 100, 056404 (2008)*
- Strong-field double-ionization of atoms, at intensities/frequencies usually used, memory effects are minimal, *M. Thiele, E.K.U. Gross, S. Kuemmel, Phys. Rev. Lett. 100, 153004 (2008)*.
- Analytical demonstration that ATDDFT exact for atoms in infinitely-slowly ramped up high-frequency, intense fields, *R. Baer, J. Mol. Structure: THEOCHEM 914, 19 (2009)*.

Development of Memory-Dependent Functionals...

➤ **Gross-Kohn (1985)**

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

$$v_{XC,1}^{GK}(\mathbf{r}, t) = \int_{-\infty}^{\infty} f_{XCL}^{\text{hom}}(n_0(\mathbf{r}), t - t') n_1(\mathbf{r}, t') dt'$$

Spatially local but time-non-local

from t-dep linear-response of the homogeneous electron gas

Violates harmonic potential theorem

Dobson (*PRL* **73**, 2244, 1994) showed that non-adiabaticity → spatial non-local n-dependence

➤ **Dobson-Bünner-Gross (1997)**

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

Apply Gross-Kohn in frame that moves along with local velocity of electron fluid.

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

➤ **Vignale-Kohn (VK) (1996)** – TD-current-density-FT

Phys. Rev. Lett. **77**, 2037 (1996)

--- see Carsten's lectures!

Spatially local in current \mathbf{j} → spatially ultra-nonlocal in density n

... Development of Memory-Dependent Functionals

- Vignale-Ullrich-Conti (1997) – extend VK to non-linear regime.
G. Vignale, C.A. Ullrich, and S. Conti, PRL **79**, 4878 (1997)
- Kurzweil & Baer (2004, 2005, 2006) – memory-dependent xc based on Galilean- invariant action, *J. Chem. Phys.* **121**, 8731 (2004).
- Tokatly (2005, 2007) –TD-deformation-FT
I.V. Tokatly, PRB **71**, 165104 and 165105 (2005); *PRB* **75**, 125105 (2007)

General formulation in a Lagrangian frame. Since going with the flow, spatially local xc possible & all complications including memory are contained in Green's deformation tensor g_{ij}

➤ 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..

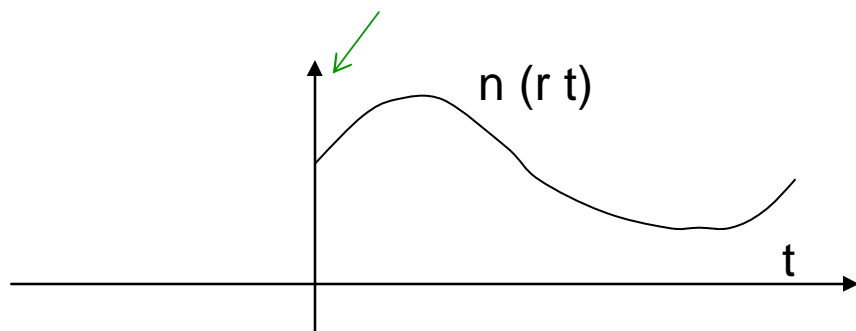
Trading ISD for more history

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”

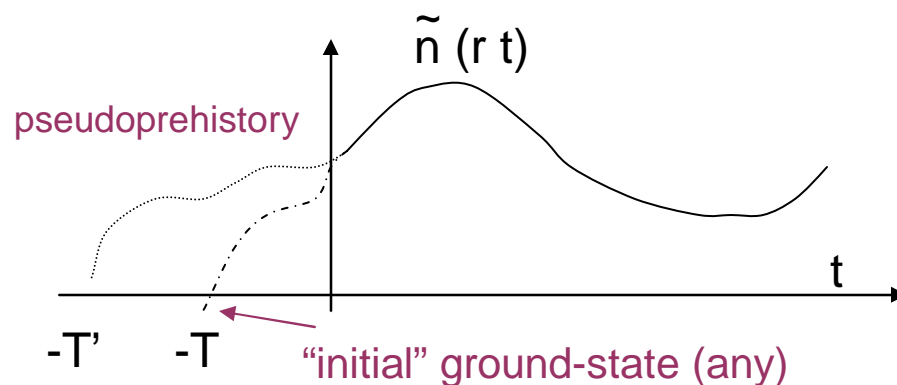
“memory condition”

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

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 v 's.
- Eqn applies to all – and gives a strict exact test for approximate history-dependent functionals.

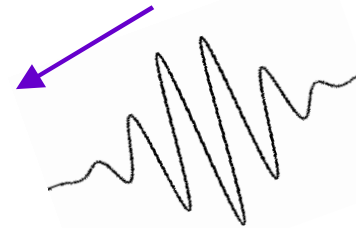
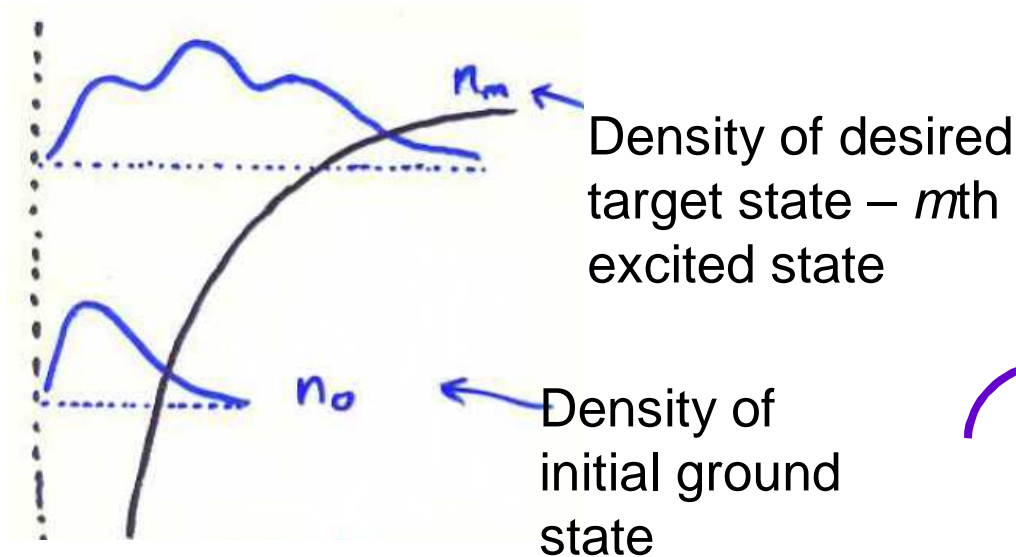
A couple of small exercises!

- 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”?

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 ?

Maitra, Burke, & Woodward *PRL*, **89**, 023002 (2002); Maitra in “TDDFT” ed. Marques et al.(2006)

“Gedanken” Quantum Control...

? 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.

How important is this in practise?

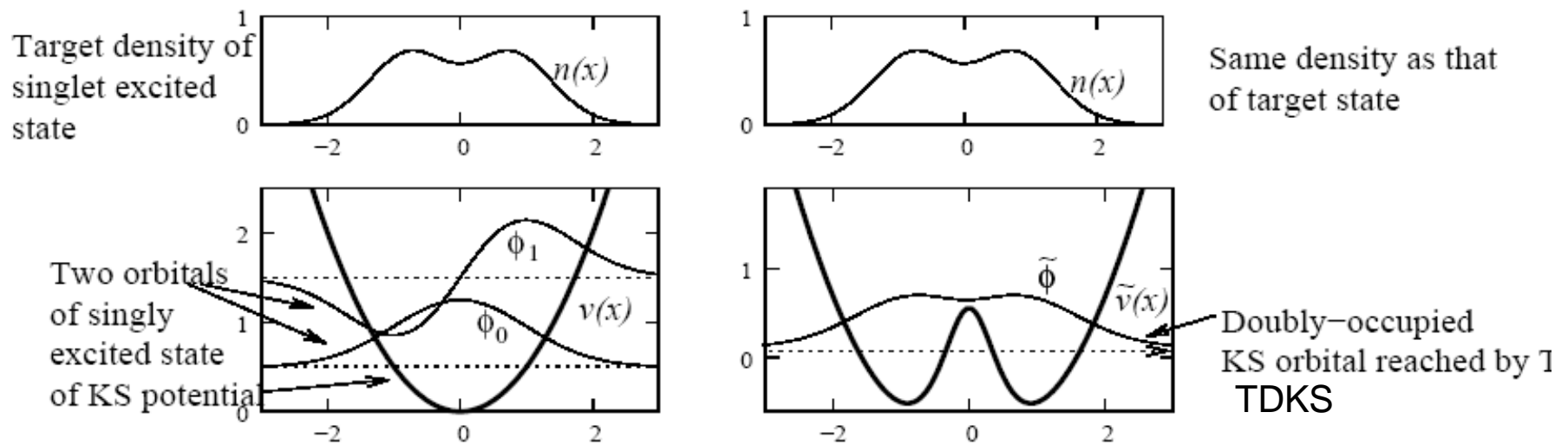
Outside of Gedanken Expt, into Realität \rightarrow Quantum Control in practise...see **Alberto's** talk next !!

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, as are observable-functionals of the final state...

... Quantum Control Difficulty ...

Different control targets? Instead of targetting the density, what about trying to optimize $\langle \Phi(T) | 1s2p \rangle$?

- max would be $\frac{1}{2}$

(c.f. close to 100% in the interacting He problem – *Werschnik & Gross (2005)*)

i.e. the interacting system is controllable in this sense, but the non-interacting is not

Maitra, Burke, & Woodward PRL, 89, 023002 (2002); Maitra in “TDDFT” ed. Marques et al.(2006);

K. Burke, J. Werschnik, and E.K.U. Gross, JCP, 123, 062206 (2005)

Another Exercise!

Consider exciting a two electron non-interacting ground-state into its first excited state. Pretend that you have found a laser field that gets the target density exactly. Find an expression for the overlap of the state that is reached and the desired state. Evaluate this for a simple potential (eg. Harmonic oscillator, or hydrogen atom).

Summary

- Exact xc functionals in TDDFT are generally memory-dependent – but adiabatic approximations are not.
- Functionals for more than one electron depend on the initial-state.
- Several recent attempts to develop history-dependent functionals, none commonly used.
- 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 a good approach – but more study needed.
- *Next time*: memory in linear response – frequency-dependent kernels in double-excitations.

To illustrate how the adiabatic approx can go wrong, can even just consider a *stationary excited state*:

A Final Exercise!

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?

(Hint: Inserting its density into the eqn above, you should find a singularity in the adiabatic potential at the origin of the form $\delta(x)/|x|$ -- unphysical and not allowed!)

(Note that we wouldn't usually use a density-fnal for v_s – we only use a fnal 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 fnal as above)