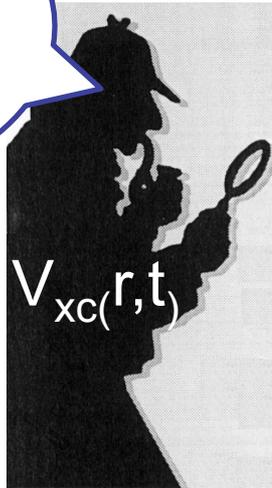


Advanced TDDFT I:

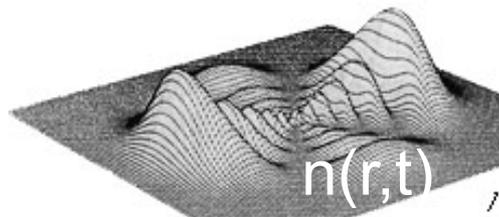
Memory and Initial-State Dependence

... when the adiabatic approximation commits a crime ...

Where were you at the time the photon was annihilated?



I..um...I just can't remember!



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Hunter College and the Graduate Center of the
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Plan

- introduction to what is memory and some general properties
- initial-state dependence
- history-dependence
- “gedanken” calculation of electronic quantum control

See also Ch. 8 in your “Fundamentals of TDDFT” book

Memory

Runge-Gross:

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

$v_{\text{ext}}(\mathbf{r}, t)$ system

$$n(\mathbf{r}, t) \xleftrightarrow[\text{1-1}]{\Phi_0}$$

$v_s(\mathbf{r}, t)$ system

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 prescribed,
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 $A[n; \Phi_0]$
- Memory can be thought to arise from using 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)

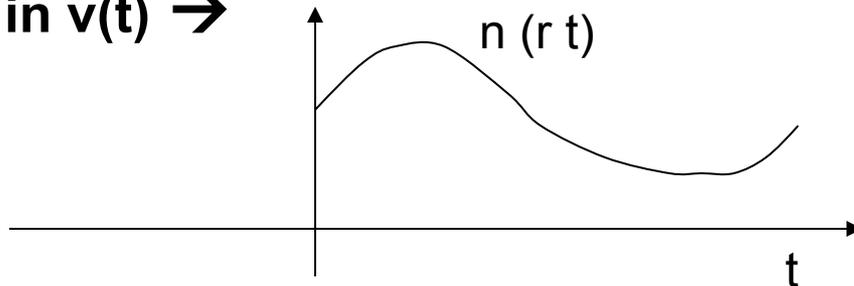
The 1-1 n-v mapping formally depends on the initial-state.

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

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

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

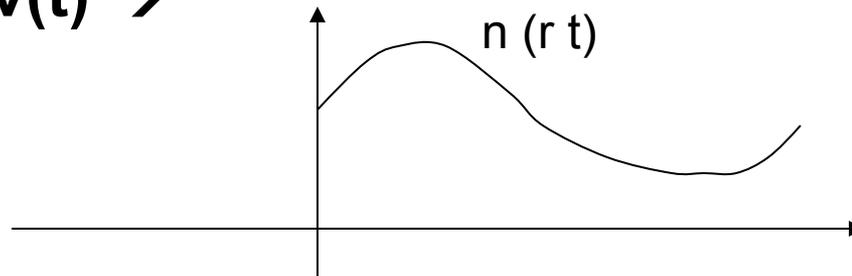
with $\mathbf{j}(\mathbf{r}, t) = \frac{i}{2}[\varphi(\mathbf{r}, t)\nabla\varphi^*(\mathbf{r}, t) - \varphi^*(\mathbf{r}, t)\nabla\varphi(\mathbf{r}, t)]$

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

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

So, for one electron:

Evolve Ψ_0 in $v(t) \rightarrow$



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

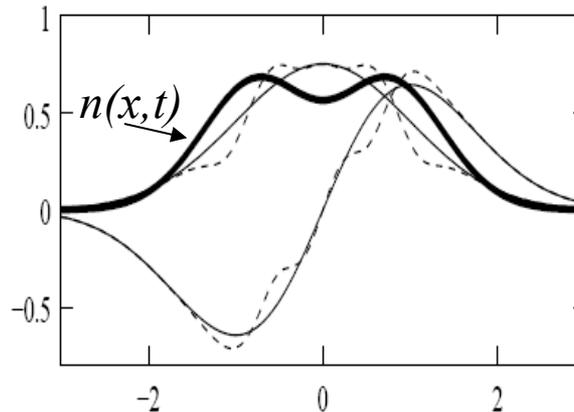
No ISD needed in functionals since the time-evolving density itself contains the information about the initial state.

More than one electron:

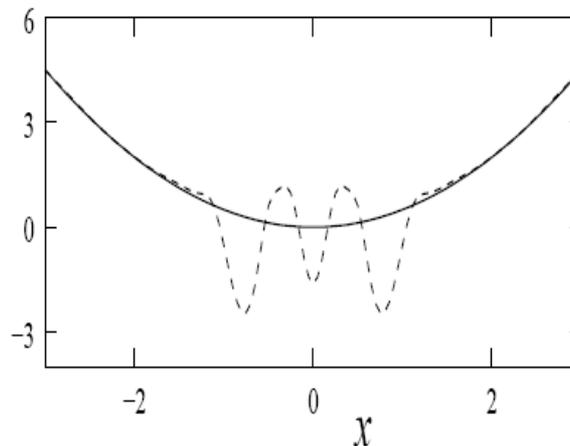
The time-evolving density does *not* uniquely define the potential

Example:

two non-interacting
electrons 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

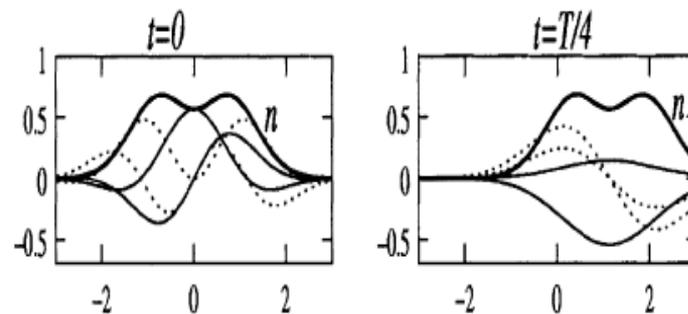
Reference system:

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

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

Re and Im parts

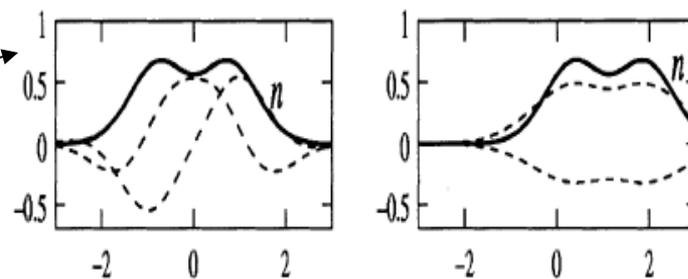
Another 2-e non-interacting example:



Alternate system:

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

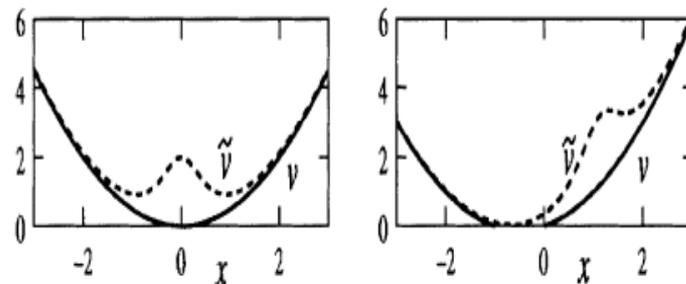
Re and Im parts



• 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



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 $n(\mathbf{r}, t)$ 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 $i\partial_t \phi_i(\mathbf{r}, t) = (-\nabla^2/2 + v_s(\mathbf{r}, t))\phi_i(\mathbf{r}, t)$

and invert to get:

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

where α is determined by eqn of continuity,

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

$$v_x = -v_H/2$$

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

History-dependence in 2 e systems

We found for two electrons in spin-singlet:

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

non-adiabatic (memory)

where α is determined by eqn of continuity,

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

$$v_x = -v_H/2$$

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

V_s appears not very non-local in time then – depends only on $n, \partial n / \partial t, \partial^2 n / \partial t^2$

But it is not V_s that we need approximate – it is V_{xc} , because V_{ext} is given in practise by the problem at hand.

In fact V_{xc} *does* depend very non-locally in time on the density, in general, and this is what we will now look at...

Two-electron example of history-dependence

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

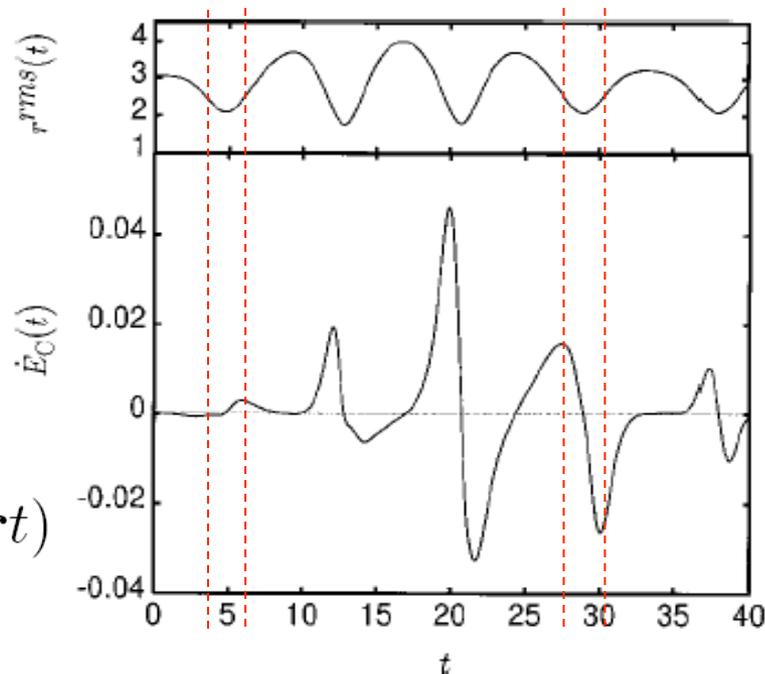
$$v_{xc}[n; \Psi_0, \Phi_0](\mathbf{r}t)$$

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

2 electrons in parabolic well,
time-varying force constant

parametrizes
density

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



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

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!

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. Kümmel, 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)*.
- Rabi oscillations get dynamically detuned in ATDDFT, *J. I Fuks, N. Helbig, I. Tokatly, A. Rubio, Phys. Rev. B. 84, 075107 (2011)*

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 zero-force, harmonic potential theorems

In fact, Dobson (*PRL* **73**, 2244, 1994) showed that *time-non-locality* \rightarrow *spatial non-local n-dependence* (...more in Carsten's lectures)

➤ 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 (\mathbf{r}, t) was at earlier times t' , $R'(t'|\mathbf{r}, t)$

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

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

\rightarrow Carsten's lectures!

Spatially local in current \mathbf{j} \rightarrow 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) – Galilean- invariant “memory action functional”, *J. Chem. Phys. 121, 8731 (2004)*.
- Tokatly (2005, 2007) –TD-deformation-FT
Ch. 25 in “Fundamentals of TDDFT” book, I.V. Tokatly, PRB 71, 165104 and 165105 (2005); PRB 75, 125105 (2007)

Formulate density & current dynamics in a Lagrangian frame. Since going with the flow, spatially local xc is sensible & 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..

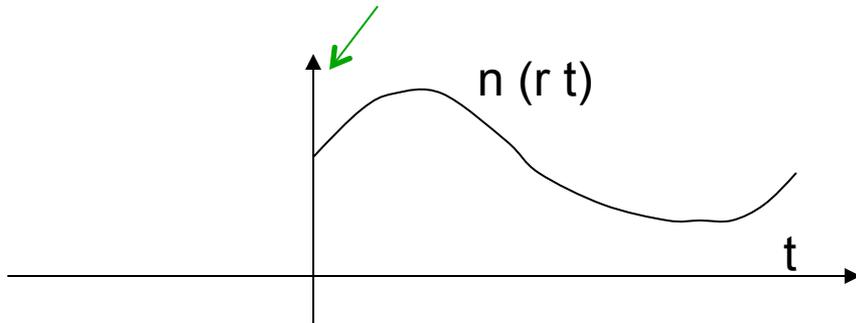
Trading ISD for more history

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”

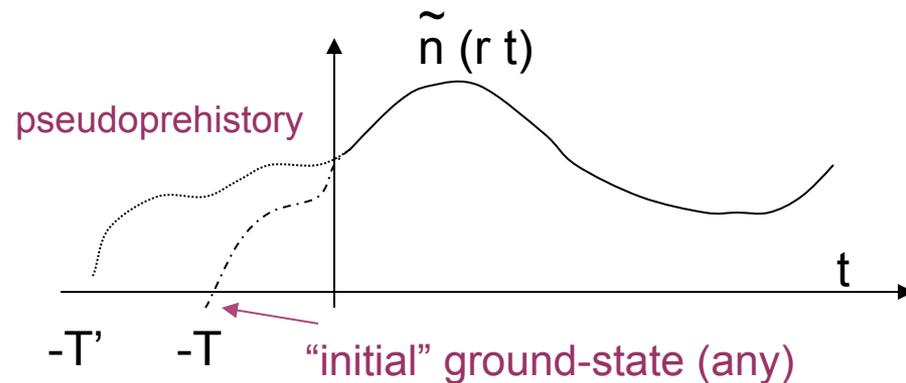
“memory condition”

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

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.

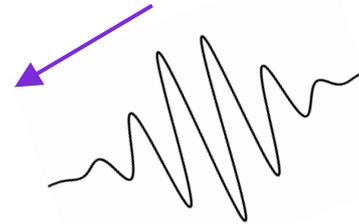
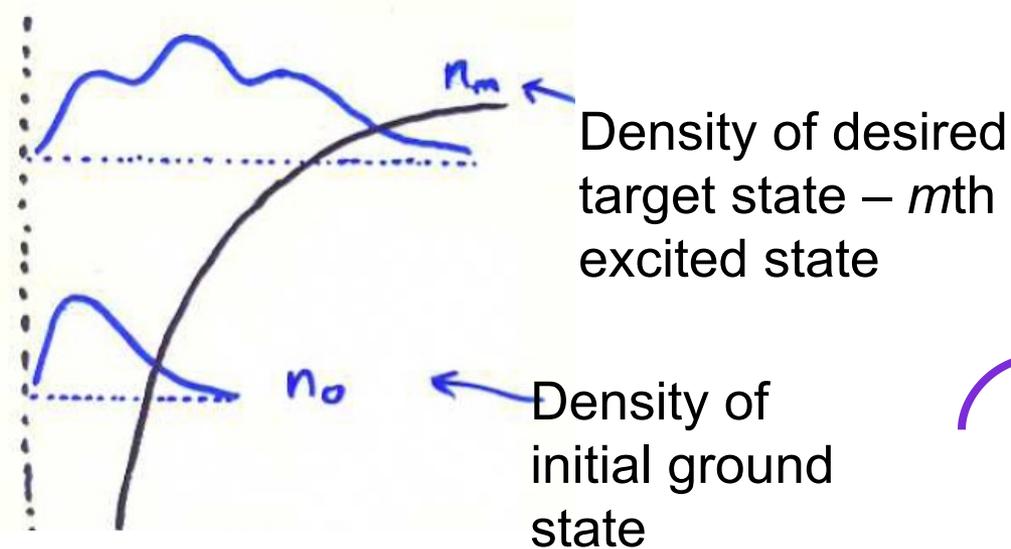
A couple of small exercises!

- 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”?

Memory in Electronic Quantum Control

Interacting (true) system: state-to-state control



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 the exact v_s also return to its initial value ?

? Is an adiabatic approx adequate ?

“Gedanken” Calculation of Quantum Control...

? Does the exact v_s also return to its initial value ?

No, it cannot!

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

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 problem in practise?

Should we give up on doing electronic control until we have good non-adiabatic functionals?

No!

➤ Choose a target functional other than the true excited-state density: e.g. optimize instead the corresponding KS excited state density, or an overlap with it. The optimal field found for the KS system may also achieve a good outcome for the true system

➤ State-control is perhaps the hardest: control of other observables, directly related to the density, is less problematic and also interesting

e.g. transfer of density between quantum wells, bond-cleavage...

Ch. 13 in "Fundamentals of TDDFT" book;

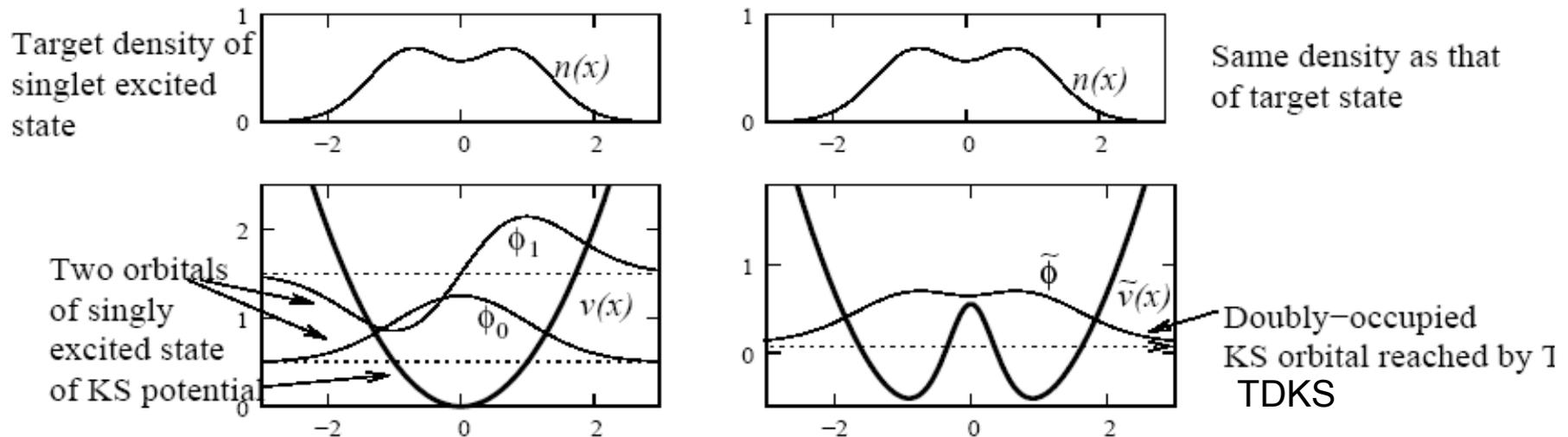
*A. Castro, J. Werschnik, E.K.U. Gross arXiv:1009.2241v1; K. Krieger, A. Castro, E. K. U. Gross, Chem. Phys. **391**, 50 (2011)*

A particularly challenging problem for *exact* 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 targeting 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

-- **But again, the optimist speaks!** A clever choice of target functional may yet be found, for which the optimal field found from KS evolution yields a large overlap with the target in the interacting system.

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, determined by inversion of the TDKS eqn, defines an exact adiabatic KS potential, which could be written as:

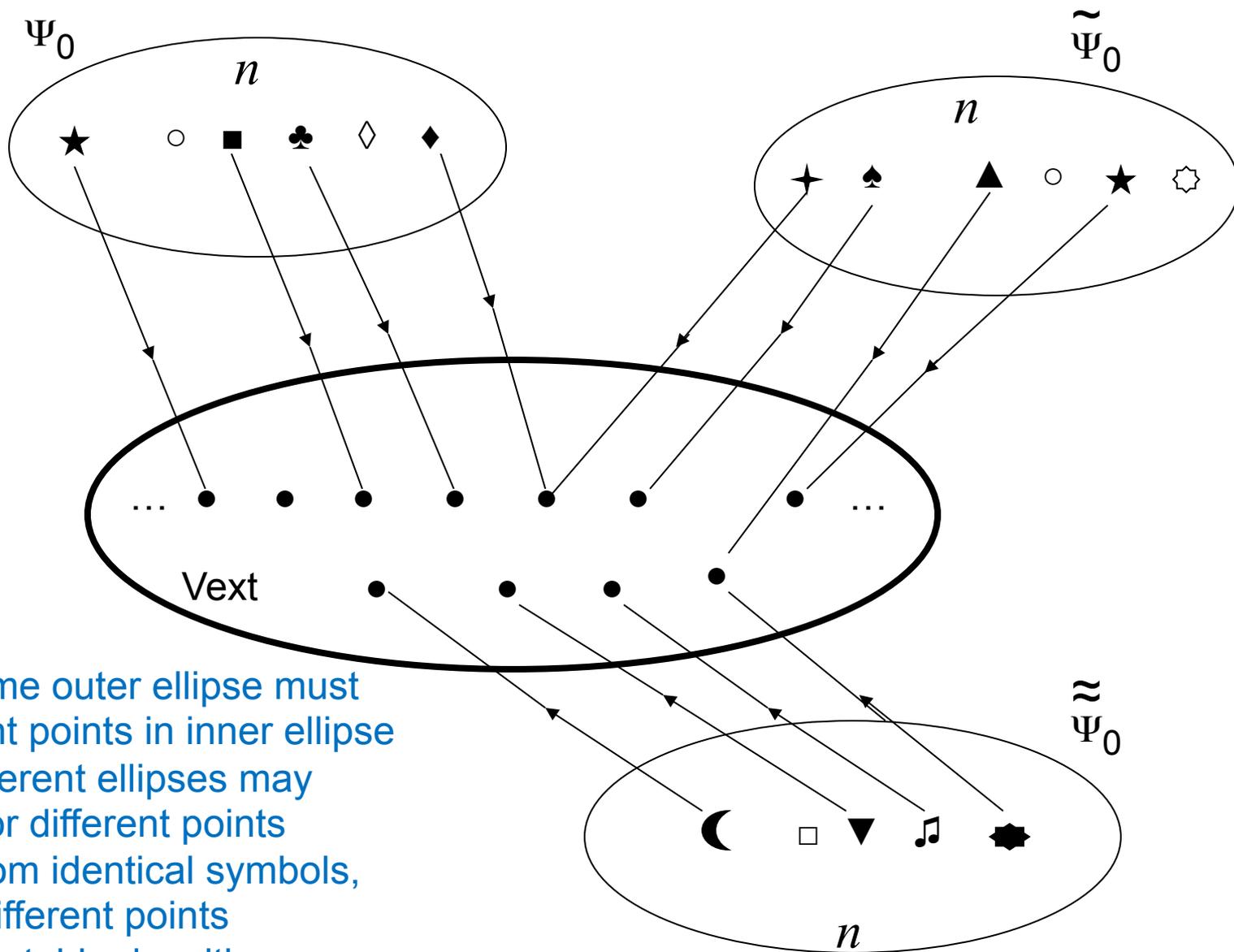
$$v_s(x) = \frac{d^2 \sqrt{n(x)} / dx^2}{2 \sqrt{n(x)}} + \epsilon$$

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)

Runge-Gross Theorem



- Lines from same outer ellipse must point to different points in inner ellipse
- Lines from different ellipses may point to same or different points
 - if from identical symbols, must point to different points
- Non-v-representable densities are open symbols – no lines emanate