

Aspects of Non-Adiabaticity in TDDFT

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Memory in TDDFT

Never forget...

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

(i) entire history of the density, $n(\mathbf{r}, t' < t)$ and (ii) initial states Ψ_0, Φ_0

Hessler, NTM, & Burke, *JCP* **117**, 72 (2002);
NTM & Burke, *PRA* **63** 042501 (2001); **64** 039901 (E)
(2001); *CPL* **359**, 237 (2002);
NTM, Burke, & Woodward, *PRL* **89**, 023002 (2002).
NTM, *sub. to IJQC* (2004).

- Linear response: only need to worry about (i)
- Almost all calculations are "Adiabatic" - input only the instantaneous density into a ground-state functional: e.g. in ALDA, $v_{xc}^{unif}[n(rt)](rt)$
Neglect all memory-dependence.
- Functionals that include some non-adiabaticity:
 - Gross-Kohn (1990)
 - Vignale-Kohn (1996)
 - Dobson-Bünner-Gross (1997)
 - Tokatly-Pankratov (2003)
 - Kurzweil-Baer (2004)
- My talk today: focus on 3 situations where strong memory-dependence (non-adiabaticity) is essential.

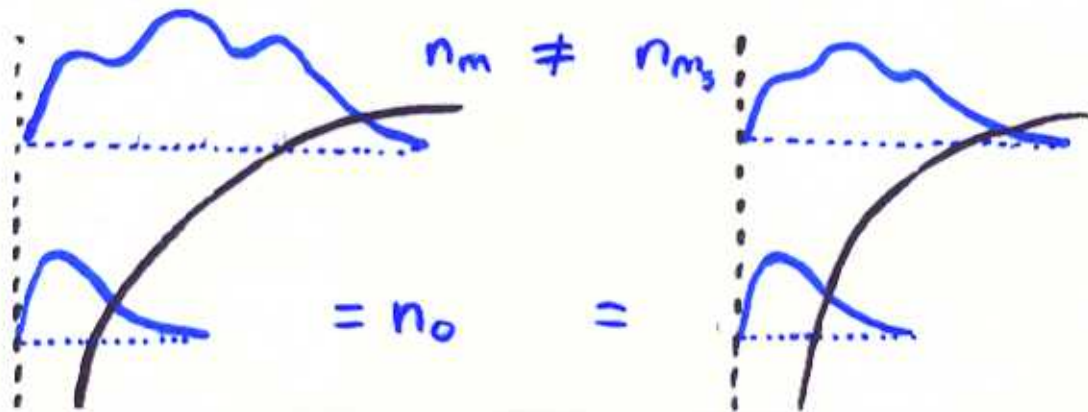
Outline

- Memory in Quantum Control Problems
- Memory in Linear Response:
 - ★ Double excitations
 - ★ Long Range Charge Transfer between Open Shells

- How does the KS system describe this?

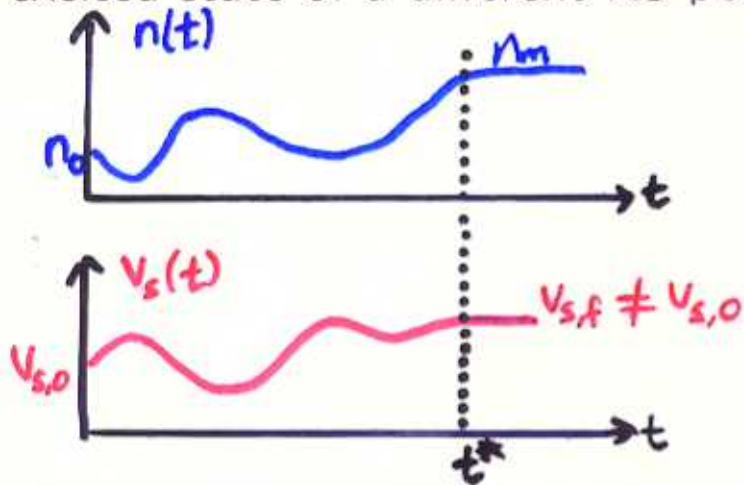
Consider the final KS state.

Immediate observation: Excited KS states of a fixed v_s do not have the same density as the excited states of the corresponding $v_{\text{ext}} \rightarrow v_{s,1} \neq v_{s,0}$



Scenario (i): Ground state $\Phi_0 \rightarrow \Phi_{m_s}$

Φ_{m_s} is a SSD with constant density $n_m(\mathbf{r})$, the m_s th excited state of a *different* KS potential, $v_{s,f} \neq v_{s,0}$.



$v_{s,f} = v_s[n](r, t > t^*)$

$v_{s,f}(\mathbf{r}) = v_s[n](\mathbf{r}, t > t^*)$, a functional of the *entire* history of the density, *necessarily* including the early history $< t^*$.

(If it didn't, $v_{s,f}(\mathbf{r})$ would be e.g. the potential in which $n_m(\mathbf{r})$ is the ground-state density, rather than that of the m_s th excited state).

$\rightarrow v_s$ has 'infinite' memory!

Alternatively, think of $v_{s,f}(\mathbf{r}) = v_s[n_{m_s}; \Phi_{m_s}](\mathbf{r}, t > t^*)$ (a special case of the exact condition in MBW02, with initial time t^*)

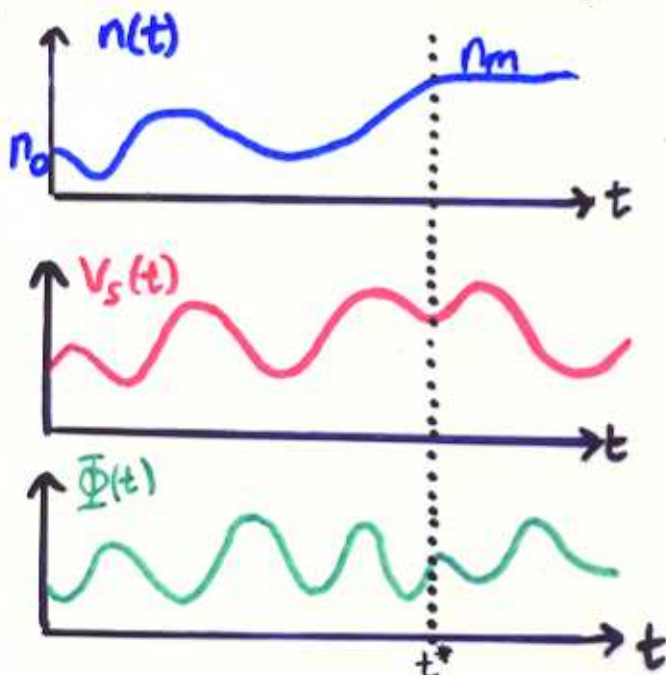
What would an adiabatic approximation give?

Const $n = n_m \rightarrow v_{s,f}$ const, *but* it will be the potential where the *ground-state has density* n_m , $v_s[n_m]$, rather than the m th excited state of the corresponding v_{ext} having density n_m .

Need infinite history-dependence to get it right.

Scenario (ii): Ground state $\Phi_0 \rightarrow \Phi(t)$

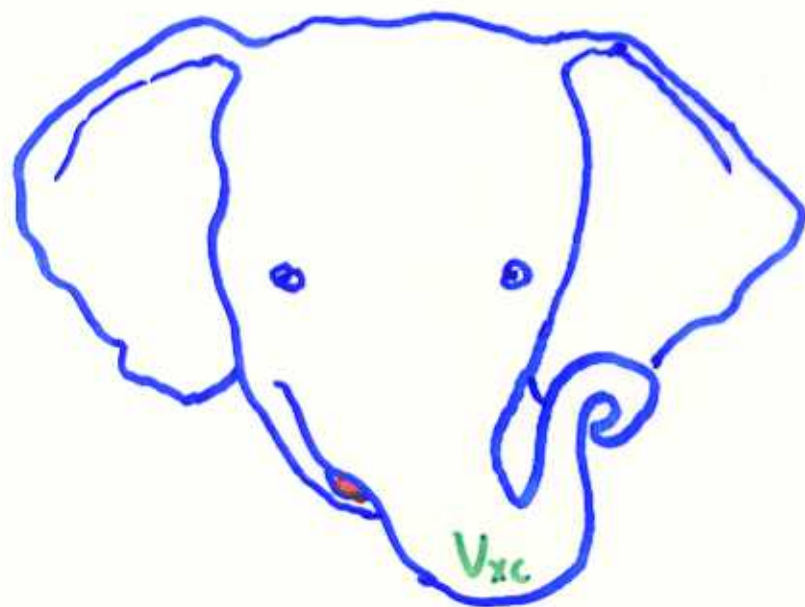
where $\Phi(t)$ and $v_s(t)$ continue to evolve forever in time, $t > t^*$, but with a constant density $\rightarrow v_s$ has 'infinite' memory



- The Kohn-Sham state is of a fundamentally different nature than the true state \rightarrow challenging for TDDFT. An adiabatic approx. , or anything not entirely non-local in time, can never get this as it would be constant in time, as the density is.

- Orbital functionals Incorporate "infinite KS memory", so most likely the best approach for these problems.

Hunt for the elephant....



(..Elephants never
forget...)

Linear response: Memory-dependence in excitation energy calculations

$$\begin{aligned}\delta n(\mathbf{r}\omega) &= \int d^3r' \chi[n_0](\mathbf{r}\mathbf{r}'\omega) \delta v_{\text{ext}}(\mathbf{r}'\omega) \\ &= \int d^3r' \chi_s[n_0](\mathbf{r}\mathbf{r}'\omega) \delta v_s(\mathbf{r}'\omega)\end{aligned}$$

f_{HXC} ↪ Poles of $\chi_s(\mathbf{r}, \mathbf{r}'; \omega) \rightarrow$ KS single excitation energies
 Poles of $\chi(\mathbf{r}, \mathbf{r}'; \omega) \rightarrow$ physical excitation energies

$$\chi[n_0](\omega) = \chi_s[n_0](\omega) + \chi_s[n_0](\omega) * f_{\text{HXC}}(\omega) * \chi[n_0](\omega)$$

where

$$f_{\text{HXC}}[n_0](\mathbf{r}, \mathbf{r}', \omega) = 1/|\mathbf{r} - \mathbf{r}'| + f_{\text{xc}}[n_0](\mathbf{r}, \mathbf{r}', \omega)$$

f_{xc} is the exchange-correlation kernel:

$$f_{\text{xc}}[n_0](\mathbf{r}, \mathbf{r}', t - t') = \delta v_{\text{xc}}(\mathbf{r}t) / \delta n(\mathbf{r}t')|_{n_0}$$

• We note the single-pole approximation (SPA):

$$\begin{aligned}\omega &= \omega_q + 2[q|f_{\text{HXC}}(\omega_q)|q], \\ &\quad \text{KS transition freq. } \epsilon_a - \epsilon_i \quad \uparrow \\ [q|f_{\text{HXC}}(\omega)|q'] &= \int d\mathbf{r}d\mathbf{r}' \phi_i^*(\mathbf{r}) \phi_a(\mathbf{r}) f_{\text{HXC}}(\mathbf{r}, \mathbf{r}', \omega) \phi_i(\mathbf{r}') \phi_a^*(\mathbf{r}'),\end{aligned}$$

valid when the excitation is "well-separated" from all others.

• Formally, memory shows up as frequency-dependence in f_{xc} .

In the ubiquitous **adiabatic approximations**, f_{xc} is proportional to $\delta(t-t')$, and its Fourier transform is **frequency-independent** – has *no* memory.

Yet often, but not always, this yields very good approximations for the interacting energies.

• When and why does the adiabatic approx work well? Well, I don't know exactly, but I will instead show you two cases where it will fail - where strong ω -dependence is essential.