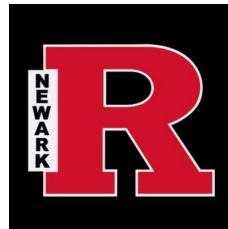


Time-Dependent Density Functional Theory: An Introduction

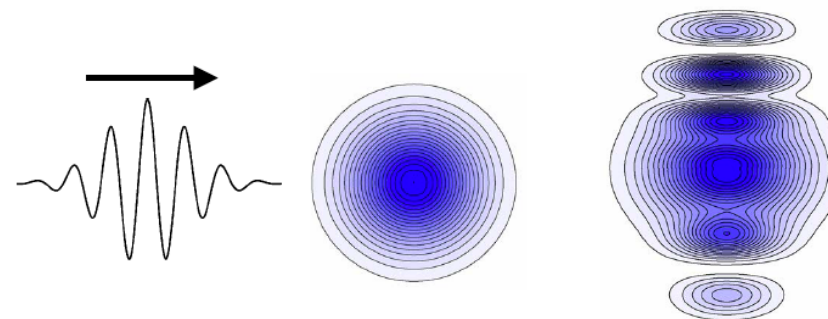
Neepa T. Maitra

Rutgers University at Newark



We want to describe phenomena beyond the ground-state

- excited states and response
- laser-driven systems
- non-stationary states



Outline

- ❖ The many-electron problem and TDDFT
- ❖ A few sample applications
- ❖ Linear response formalism
- ❖ What works and what doesn't...

What is the Problem?

Wish to describe a system of N electrons in atom, molecule, solid, possibly non-stationary state, possibly subject to an applied field:

$$\hat{H}(t)\Psi(t) = i\frac{\partial\Psi(t)}{\partial t}$$

$$\Psi = \Psi(r_1\sigma_1, r_2\sigma_2 \dots r_N\sigma_N, t)$$

$$\hat{H}(t) = \hat{T} + \hat{V}_{ee} + \hat{V}_{\text{ext}}(t)$$

$$\hat{T} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2$$

$$\hat{V}_{ee} = \frac{1}{2} \sum_{i \neq j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$\hat{V}_{\text{ext}}(t) = \sum_{i=1}^N v_{\text{ext}}(\mathbf{r}_i, t)$$

same for all systems of electrons

“external” to the electronic system

e.g. electron-nuclear attraction

$$v_{\text{ext}}(\mathbf{r}, t) = - \sum_{\nu=1}^{N_n} \frac{Z_\nu}{|\mathbf{r} - \mathbf{R}_\nu(t)|}$$

e.g. laser field

$$v_{\text{ext}}(\mathbf{r}, t) = E f(t) \sin(\omega t) \mathbf{r} \cdot \boldsymbol{\alpha} - \sum_{\nu=1}^{N_n} \frac{Z_\nu}{|\mathbf{r} - \mathbf{R}_\nu|}$$

What is the Problem?

Solving for Ψ scales exponentially with the size of the system...

Even just storing the wavefunction:

For N electrons $\rightarrow 3N$ spatial coordinates $\rightarrow M^{3N}$ grid points if use M points for each coordinate \rightarrow exponentially large as N grows



... And besides, Ψ contains far more information than we could possibly want.

Usually interested in e.g.

energies

equilibrium geometries, lattice constants

potential energy surfaces

polarizabilities

photo-absorption cross-sections

ionization probabilities

I/V characteristics



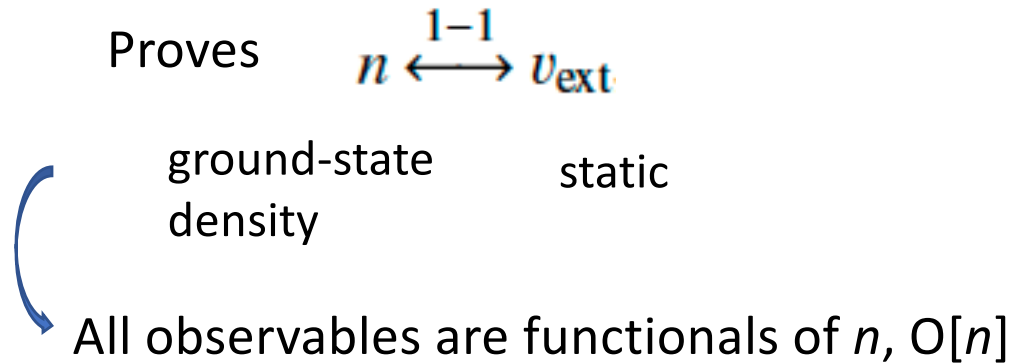
These involve “reduced” quantities:
e.g. densities, current-densities, two-
body-densities...

(TD)DFT provides a way to get observables without computing Ψ , in principle exactly.

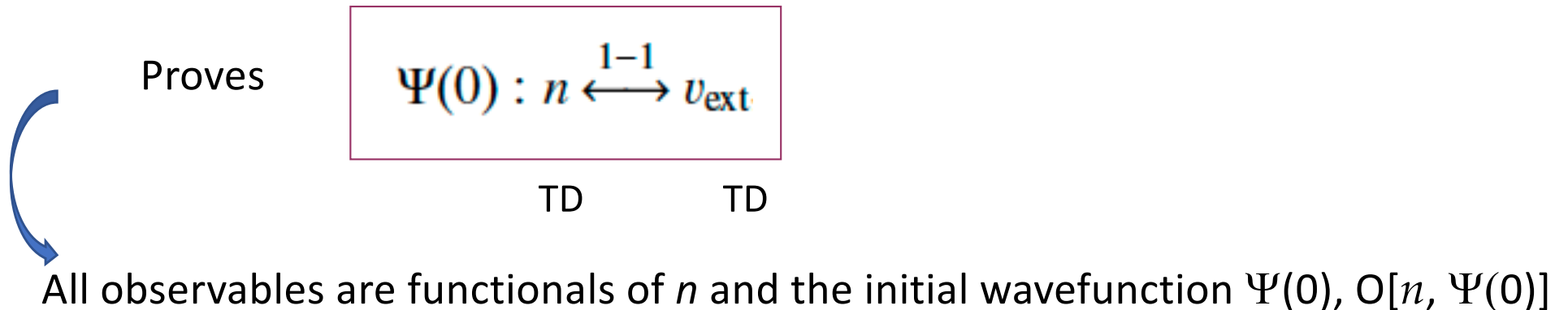
Just need the density:
$$n(\mathbf{r}, t) = N \sum_{\sigma, \sigma_2 \dots \sigma_N} \int d^3 r_2 \cdots \int d^3 r_N |\Psi(\mathbf{r}\sigma, \mathbf{r}_2\sigma_2 \cdots \mathbf{r}_N\sigma_N, t)|^2$$

For a given particle-particle interaction and statistics:

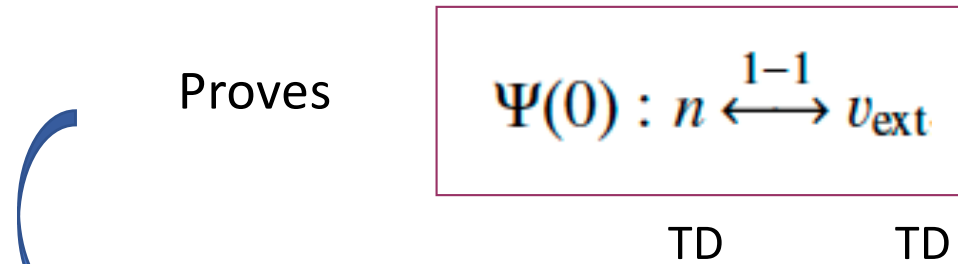
❖ **Ground-state DFT for static V_{ext} : Hohenberg-Kohn (1965)**



❖ **Time-Dependent (TD) DFT for $V_{\text{ext}}(t)$: Runge-Gross (PRL 52, 997 (1984))**

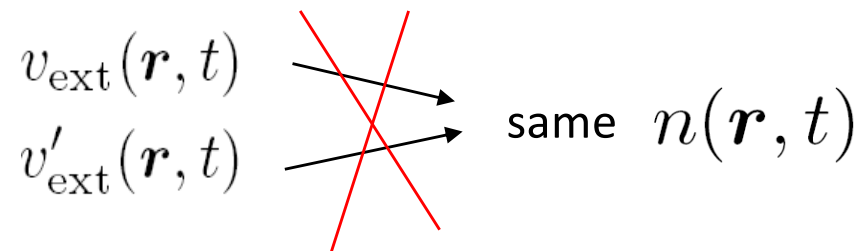
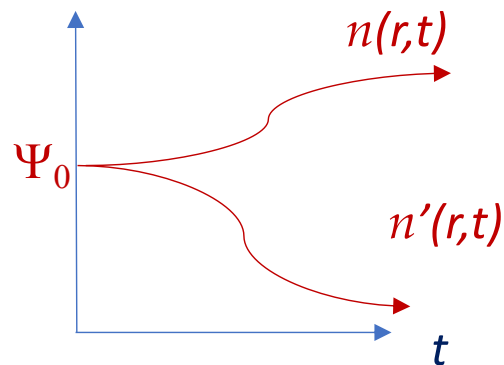


❖ Time-Dependent (TD) DFT for $V_{\text{ext}}(\mathbf{r}, t)$: Runge-Gross (PRL 52, 997 (1984))



All observables are functionals of n and the initial wavefunction $\Psi(0)$, $O[n, \Psi(0)]$

Proof based on Heisenberg equation of motion for the current-density.



But, given a density, how to get the observables?

Consider kinetic energy.

$$\langle \hat{T} \rangle = \int \Psi^*(\mathbf{r}_1 \dots \mathbf{r}_N) \sum_{i=1}^N -\frac{\nabla_i^2}{2} \Psi(\mathbf{r}_1 \dots \mathbf{r}_N) d^3 r_1 \dots d^3 r_N = ??[n]$$

$\langle T \rangle$ is unknown as a functional of n . Yet T is a large part of the total energy

- ❖ The **Kohn-Sham system** makes our lives a bit easier.
= A *non-interacting* system that has the same density as the interacting system.

Kohn-Sham wavefunction involves products of single-particle orbitals, antisymmetrized to take care of Pauli, i.e. Slater determinant (*usually*)

→ Treat *non-interacting kinetic energy* exactly, in terms of the orbitals

$$\text{GS KS: } \epsilon_j \phi_j(\mathbf{r}) = \left(-\frac{\nabla^2}{2} + v_s[n_{\text{GS}}](\mathbf{r}) \right) \phi_j(\mathbf{r}) \quad n_{\text{GS}}(\mathbf{r}) = \sum_{j=1}^N |\phi_j(\mathbf{r})|^2$$

$$\text{TD KS: } i \frac{\partial}{\partial t} \phi_j(\mathbf{r}, t) = \left(-\frac{\nabla^2}{2} + v_s[n, \Phi_0](\mathbf{r}, t) \right) \phi_j(\mathbf{r}, t) \quad n(\mathbf{r}, t) = \sum_{j=1}^N |\phi_j(\mathbf{r}, t)|^2$$

The Time-Dependent Kohn-Sham (KS) System

$$i\frac{\partial}{\partial t}\phi_j(\mathbf{r}, t) = \left(-\frac{\nabla^2}{2} + v_s[n, \Phi_0](\mathbf{r}, t) \right) \phi_j(\mathbf{r}, t) \quad n(\mathbf{r}, t) = \sum_{j=1}^N |\phi_j(\mathbf{r}, t)|^2$$

defined such that the density of interacting system reproduced

❖ Φ_0 , the initial KS wavefunction, must have the same initial $n(\mathbf{r}, 0)$ and $\partial_t n(\mathbf{r}, t)|_{t=0}$ as Ψ_0 , the true initial wavefunction (*this gives a large choice! See example later*)

❖ Decompose V_s into 3 terms:

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

Hartree, $v_H[n](\mathbf{r}, t)$:
classical electrostatic potential

exchange-correlation potential:
approx. in practise

❖ Note that the structure is set up similar to the (older) **ground-state DFT** :

$$\left\{ -\frac{1}{2}\nabla^2 + v_s(\mathbf{r}) \right\} \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}), \quad n(\mathbf{r}) = \sum^N |\phi_i(\mathbf{r})|^2$$

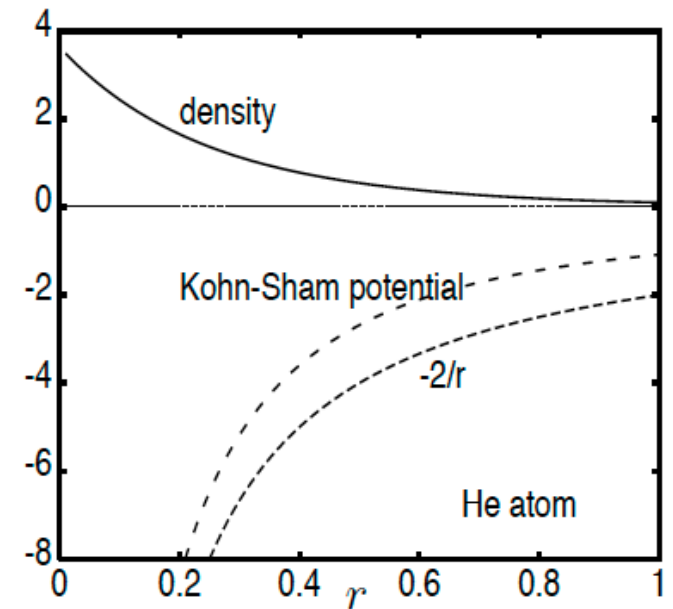
$$v_s(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{\text{xc}}[n](\mathbf{r})$$

where $v_{\text{xc}}(\mathbf{r}) = \delta E_{\text{xc}}/\delta n(\mathbf{r})$.

Differences: simpler functional dependence, and an energy variational principle

- But in either case, $v_s(r)$, by definition, reproduces the N -e interacting density with non-interacting electrons, e.g. He atom ground-state, exact v_s :

*What about TDDFT potentials, how do they look?
See an example soon!*



Back to the Time-Dependent Kohn-Sham System

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

- ❖ Functional dependences: Since, by RG, $v_s = v_s[n; \Phi_0]$ and $v_{\text{ext}} = v_{\text{ext}}[n; \Psi_0] \rightarrow$ this means $v_{\text{xc}}[n; \Psi_0, \Phi_0]$.

Note: functional dep of v_{ext} is never directly used! v_{ext} is input as the physical potential applied to the system

- ❖ If begin in ground-state, then no initial-state dependence, since by HK, $\Psi_0 = \Psi_0[n(0)]$ (e.g. in linear response). Then $v_{\text{xc}} = v_{\text{xc}}[n](\mathbf{r}t)$
- ❖ In general, $v_{\text{xc}}[n; \Psi_0, \Phi_0](\mathbf{r}, t)$ depends on $n(\mathbf{r}', t')$ everywhere in space and at all earlier times, as well as initial interacting state and KS state \rightarrow **Memory dependence**
- ❖ In practice $v_{\text{xc}}[n; \Psi_0, \Phi_0](\mathbf{r}, t)$ must be approximated – almost all approximations neglect memory!!

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

Almost all approximations simply select an approximation from ground-state DFT, and plug in the instantaneous density.

-- Called “adiabatic” due to implicit assumption that system is in some ground-state at each time.

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

Simplest: adiabatic local density approximation (ALDA)

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

where $\mathcal{E}_{xc}^{unif}(n)$ is the exchange-correlation energy per particle of a uniform electron gas of density n

-- completely local dependence on the density in both space and time.

How a TDDFT calculation works in practise.

1. Choose an approximation for $v_{xc}[n, \Psi_0, \Phi_0](\mathbf{r}, t)$

e.g. ALDA-x, where
 $v_{xc}[n](\mathbf{r}, t) = -a n^{1/3}(\mathbf{r}, t)$

2. Select initial KS state Φ_0 with same $n(\mathbf{r}, 0)$ and $\partial_t n(\mathbf{r}, t)|_{t=0}$ as the physical problem you're trying to model.

E.g. N orbitals (in a determinant), $\{\phi_i(\mathbf{r})\}$

If system starts in a ground state, then use the initial ground-state KS orbitals, as calculated from N lowest energy orbitals of

$$\left(-\frac{\nabla^2}{2} + v_{\text{ext}}(\mathbf{r}) + v_{\text{H}}[n](\mathbf{r}) + v_{\text{XC}}[n](\mathbf{r}) \right) \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}) \quad n(\mathbf{r}) = \sum_{i=1}^N |\phi_i(\mathbf{r})|^2$$

using chosen approximation for $v_{xc}[n]$.

3. Propagate the time-dependent Kohn-Sham equation

$$i \frac{\partial}{\partial t} \phi_j(\mathbf{r}, t) = \left(-\frac{\nabla^2}{2} + v_{\text{ext}}(\mathbf{r}, t) + v_{\text{H}}[n](\mathbf{r}, t) + v_{\text{XC}}[n, \Psi_0, \Phi_0](\mathbf{r}, t) \right) \phi_j(\mathbf{r}, t)$$
$$n(\mathbf{r}, t) = \sum_{j=1}^N |\phi_j(\mathbf{r}, t)|^2$$

using the applied v_{ext} from the physical problem (e.g. laser field and electron-nuclear potential) and your chosen approximation for $v_{xc}[n; \Psi_0, \Phi_0]$

Outline

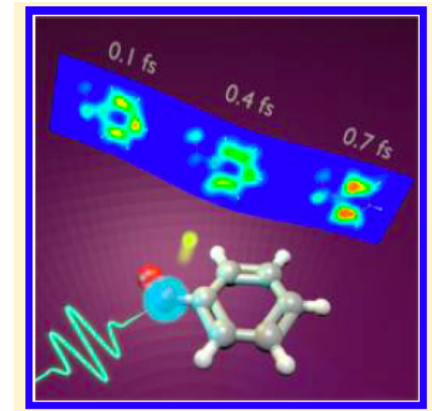
- ❖ The many-electron problem and TDDFT
- ❖ *A few sample applications*
- ❖ Linear response formalism
- ❖ What works and what doesn't...

Brief sampling of applications

- Strong fields applied to molecules:

High-harmonic generation, enhanced ionization, Coulomb explosion imaging, laser control of electronic motion...

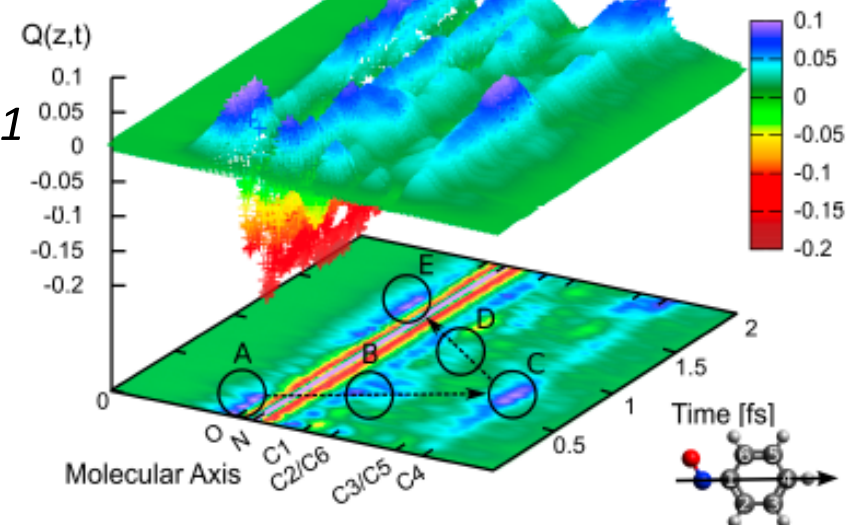
e.g. watching attosecond charge migration after nitrogen K-edge ionization in nitrosobenzene



Time-Dependent Hole Density

Bruner, Hernandez, Mauger, Abanador, LaMaster, Gaarde, Schafer, Lopata, J. Phys. Chem. Lett. 8, 3991 (2017)

$$Q(z,t) = \rho^+ - \rho_0$$



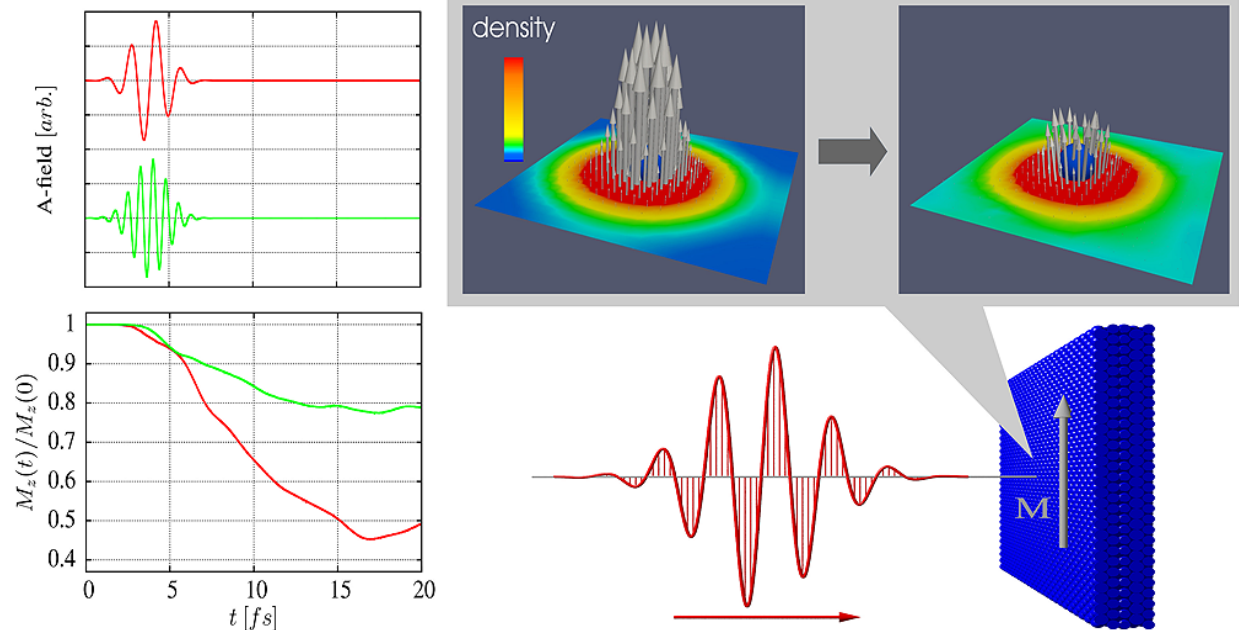
Brief sampling of applications

- Strong-fields applied to solids:

e.g. stopping power of projectiles, dielectric breakdown in semiconductors, high harmonic generation, plasmonics, Maxwell eqns + TDDFT...

e.g. ultrafast laser-induced demagnetization, and control of magnetization

*Krieger, Dewhurst, Elliott, Sharma,
Gross, J. Chem. Theory Comput. **11**,
4870 (2015)*



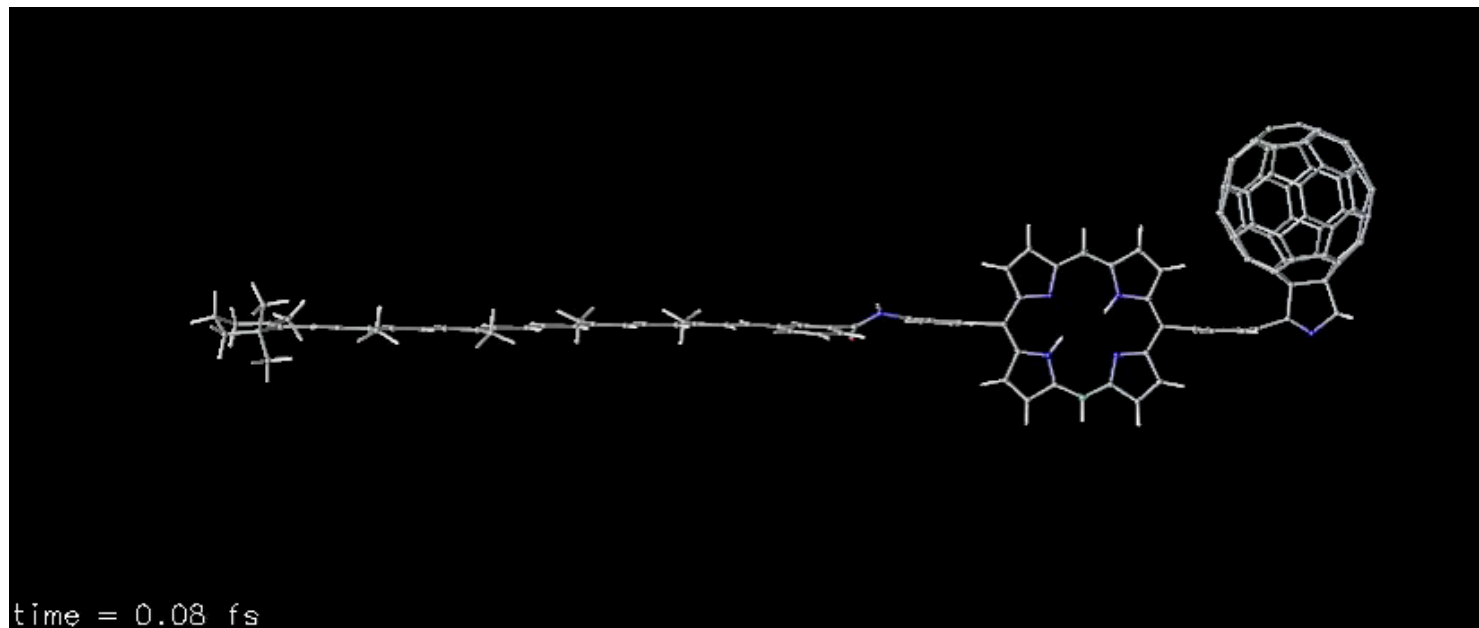
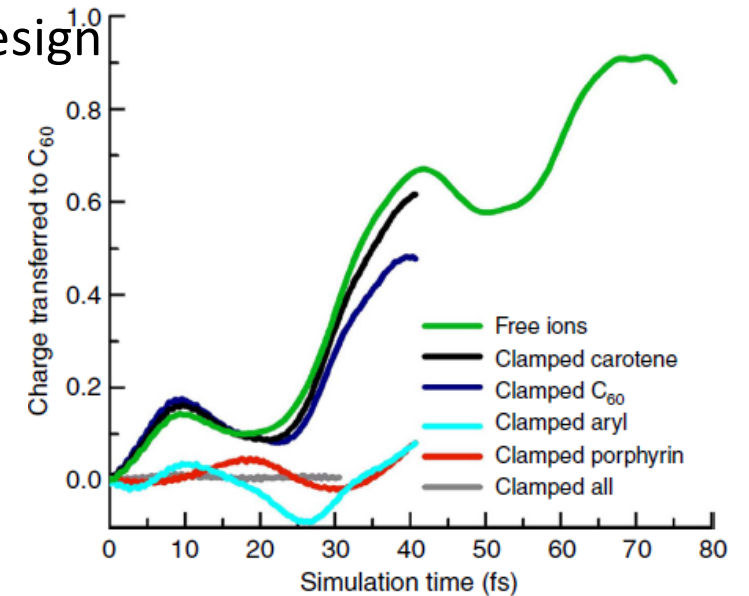
Brief sampling of applications

- Dynamics after photo-excitation: e.g. Photovoltaic design

Rozzi et al. Nature. Comm. 4, 1602 (2013)

Light-harvesting molecular triad:

Electron-ion dynamics in charge-transport needed.

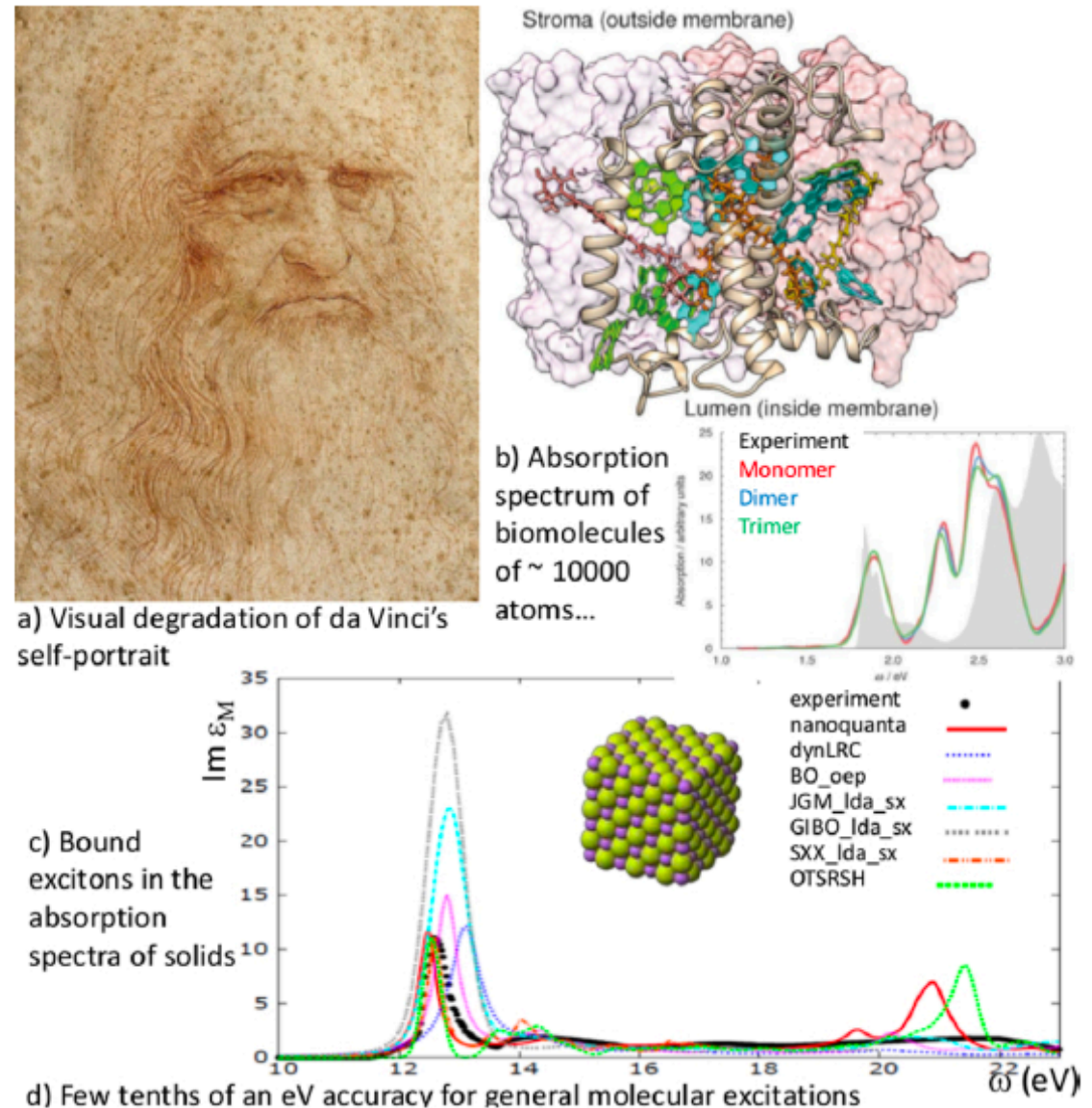


$\delta n(r,t)$

TDDFT in Linear Response → Spectra

Vast majority of applications of TDDFT are to get excitation energies and optical spectra

- a) Mosca Conta et al, *App. Phys. Lett.* **104**, 224101 (2014);
 b) Jornet-Somoza et al. *Phys.Chem.Chem.Phys.*, **17**, 26599 (2015)
 c) Marini et al. , *Phys. Rev. Lett.* **91**, 256402 (2003); Botti et al. *Phys. Rev. B* **72**, 125203 (2005); Sharma et al. *Phys. Rev. Lett.* **107**, 186401 (2011); Trevisanutto et al., *Phys. Rev. B* **87**, 205143 (2013); Rigamonti et al., *Phys. Rev. Lett.* **114**, 146402 (2015); Z.-h. Yang et al. *Phys. Rev. B* **92**, 035202 (2015); Refaely-Abramson et al. *Phys. Rev. B* **92**, 081204 (2015);
 d) Rappoport and J. Hutter, in *Fundamentals of Time-Dependent Density Functional Theory*, edited by M. A. Marques et al. (Springer Berlin Heidelberg, Berlin, Heidelberg, 2012), pp. 317–336.



	TDHF	LDA	BP86	PBE	TPSS	B3LYP
Mean	0.99	-0.48	-0.44	-0.45	-0.29	-0.08
Mean uns.	1.05	0.57	0.52	0.53	0.42	0.26
RMS dev.	1.23	0.68	0.62	0.64	0.51	0.32

	PBE0	BHLYP	LC-ωPBE	CAM-B3LYP	B2PLYP
Mean	0.05	0.42	0.41	0.22	0.01
Mean uns.	0.24	0.49	0.46	0.31	0.19
RMS dev.	0.32	0.60	0.61	0.42	0.25

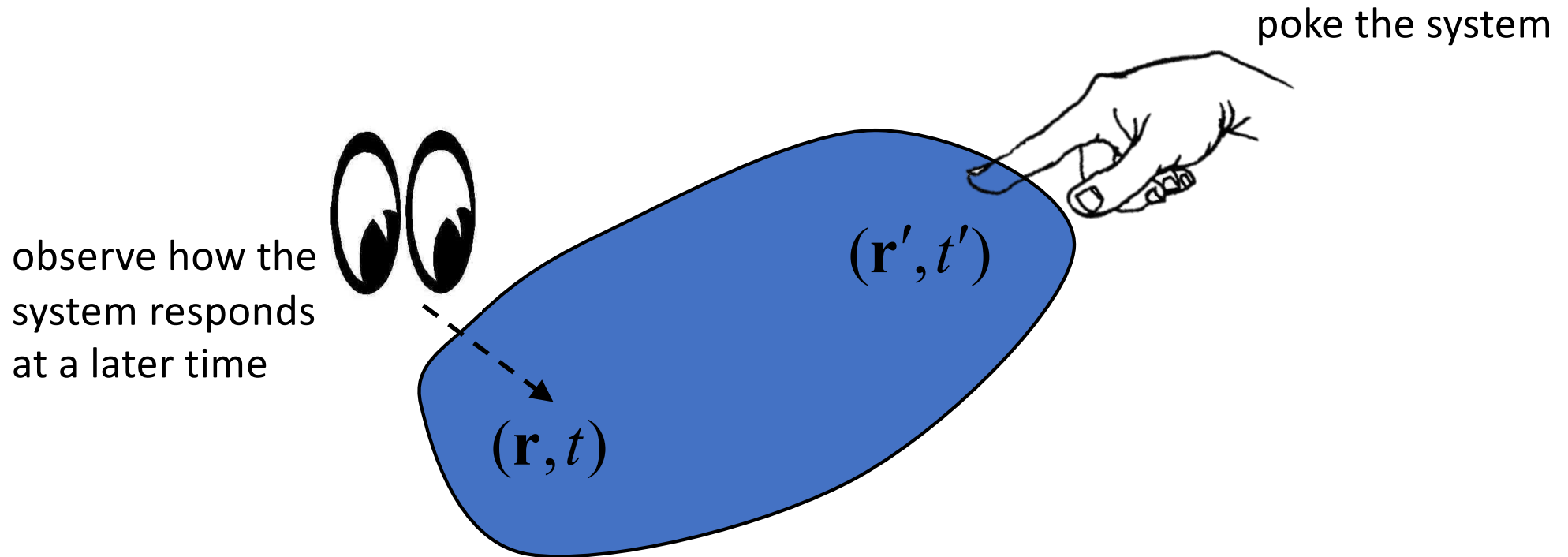
Outline

- ❖ The many-electron problem and TDDFT
- ❖ A few sample applications
- ❖ **Linear response formalism**
- ❖ What works and what doesn't...

In fact, the vast majority of calculations are in the linear response regime, to calculate spectra, and these usually operate directly in the frequency-domain.

So we'll now discuss how that works.

What do we actually mean by linear response?



density response

perturbation

$$n_1(\mathbf{r}, t) = \int d\mathbf{r}' \int dt' \chi(\mathbf{r}, t, \mathbf{r}', t') V_1(\mathbf{r}', t')$$

density-density
response function,
a.k.a. susceptibility

Fourier transform $\chi^{[n]}(\mathbf{r}, \mathbf{r}', \omega) \rightarrow$ poles at the excitation energies
& residues give oscillator strength

Extracting spectra (excitation energies/oscillator strengths) from TDDFT

A brief sketch (1/2)

$$\chi[n_{\text{GS}}](\mathbf{r}t; \mathbf{r}'t') = \left. \frac{\delta n(\mathbf{r}, t)}{\delta v_{\text{ext}}(\mathbf{r}', t')} \right|_{v_{\text{ext}}[n_{\text{GS}}(\mathbf{r})]} \quad \chi \text{ is a functional of } n_{\text{GS}}, \text{ the unperturbed ground-state density}$$

Use TD QM perturbation theory

And take the Fourier transform w.r.t. $(t-t')$ \rightarrow Frequency-domain response function:

$$\chi(\mathbf{r}, \mathbf{r}'; \omega) = \sum_I \left\{ \frac{F_I(\mathbf{r})F_I^*(\mathbf{r}')}{\omega - \omega_I + i0^+} - \frac{F_I^*(\mathbf{r})F_I(\mathbf{r}')}{\omega + \omega_I + i0^+} \right\} \quad F_I(\mathbf{r}) = \langle \Psi_0 | \hat{n}(\mathbf{r}) | \Psi_I \rangle$$

Poles at excitation frequencies, $\omega_I = E_I - E_0$

And residues are transition densities, giving oscillator strengths (transition dipoles)

$$\omega_I = E_I - E_0$$

But we don't have wavefunctions in TDDFT! So how to get χ from TDDFT?

Extracting spectra (excitation energies/oscillator strengths) from TDDFT

A brief sketch (2/2)

$$n^{(1)}(\mathbf{r}t) = \int_0^\infty dt' \int d^3r' \chi_S(\mathbf{r}t, \mathbf{r}'t') \delta v_S(\mathbf{r}'t')$$

$$\chi_S(\mathbf{r}t, \mathbf{r}'t') = \left. \frac{\delta n(\mathbf{r}t)}{\delta v_S(\mathbf{r}'t')} \right|_{v_S^{(0)}[n_{GS}]}$$

same as that of the physical system... ...but $\chi \neq \chi_S$

Evaluate previous expression for the case of non-interacting system \rightarrow

$$\chi_S(\mathbf{r}, \mathbf{r}', \omega) = \sum_{j,k} (f_j - f_k) \delta_{\sigma_j, \sigma_k} \frac{\phi_k^*(\mathbf{r}) \phi_j(\mathbf{r}) \phi_j^*(\mathbf{r}') \phi_k(\mathbf{r}')}{\omega - (\epsilon_k - \epsilon_j) + i0^+}$$

Poles at KS frequencies, NOT the true excitation energies

Now use functional chain rule to relate the two functional derivatives, and obtain:

\rightarrow Central Equation of TDDFT Linear Response

$$\chi[n_{GS}](\mathbf{r}, \mathbf{r}', \omega) = \chi_S[n_{GS}](\mathbf{r}, \mathbf{r}', \omega) + \int d^3r_1 d^3r_2 \chi_S[n_{GS}](\mathbf{r}, \mathbf{r}_1, \omega) \left(\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + f_{XC}[n_{GS}](\mathbf{r}_1, \mathbf{r}_2, \omega) \right) \chi[n_{GS}](\mathbf{r}_2, \mathbf{r}', \omega)$$

$$f_{XC}[n_{GS}](\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) = \left. \frac{\delta v_{XC}(\mathbf{r}_1 t_1)}{\delta n(\mathbf{r}_2 t_2)} \right|_{n_{GS}} \text{ exchange-correlation kernel}$$

Spectra from TDDFT

Poles at true
excitations

Poles at KS
excitations

$$\chi[n_{GS}](\mathbf{r}, \mathbf{r}', \omega) = \chi_s[n_{GS}](\mathbf{r}, \mathbf{r}', \omega) + \int d^3r_1 d^3r_2 \chi_s[n_{GS}](\mathbf{r}, \mathbf{r}_1, \omega) \left(\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + f_{xc}[n_{GS}](\mathbf{r}_1, \mathbf{r}_2, \omega) \right) \chi[n_{GS}](\mathbf{r}_2, \mathbf{r}', \omega)$$

Yields exact spectra in principle.

In practice, approxs needed in (1) and (2).



Need (1) ground-state $v_{S,0}[n_0](r)$, and its bare excitations

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

- Cast into matrix equations coded in quantum chemistry codes
- For extended systems, tend to work directly with the Dyson-like equation
- Linear response can also be formulated as a “TD density-functional perturbation theory”, a.k.a Sternheimer approach, a.k.a coupled-perturbed KS
- And can also be obtained by Fourier transform under a weak perturbation/delta-kick

Casida, in Recent Advances in Density Functional Methods, ed. D.E. Chong pp. 155–192 (World Scientific, Singapore, 1995); Petersilka, Gossmann, Gross, *PRL* **76**, 1212 (1996); Andrade et al. JCP 126,184106 (2007); Yabana et al. Phys. Status Solidi B 243, 1121 (2006).

Approximate Functionals in Linear Response

- Almost all calculations today use an **adiabatic approximation**:
input instantaneous density into a ground-state approximation

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

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

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

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

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

Outline

- ❖ The many-electron problem and TDDFT
- ❖ A few sample applications
- ❖ Linear response formalism
- ❖ What works and what doesn't...

How well does adiabatic TDDFT do in linear response?

- Energies typically to within a few tenths of an eV, bond lengths to within about 1%, dipoles and vibrational frequencies to about 5%
- Cost scales as N^3 or less
- Available now in many electronic structure codes



- Unprecedented balance between accuracy and efficiency

TDDFT Sales Tag



But, there are cases where the usual functional approximations do quite badly...

Where the *usual* approxs give poor excitations

i.e. the usual xc approxs that are semi-local in space and local in time (GGAs). Hybrids can partially ameliorate *some* of these problems.

- Rydberg states
- Polarizabilities of long-chain molecules

} problem primarily is gs v_{xc}

- Optical response of solids
- Double excitations
- Conical intersections with the ground-state
- Derivative couplings between excited states
- Long-range charge-transfer excitations

} problem primarily is f_{xc}

But recent and ongoing functional development has helped with many of these!

Perspective on TDDFT, N. T. Maitra, in J. Chem. Phys. **144**, 220901 (2016) is a semi-recent review with many references...

Returning to fully non-perturbative TDDFT: How well does adiabatic TDDFT do?

- Often gives results accurate enough to be useful, but not always...
 - fails for certain phenomena
 - e.g. charge-transfer dynamics
 - e.g. resonant Rabi oscillations
 - e.g. some pump-probe situations
- We still need better predictions of what the errors will be in a given situation
- A useful tool for analysis is to disentangle errors in the adiabatic approx.:

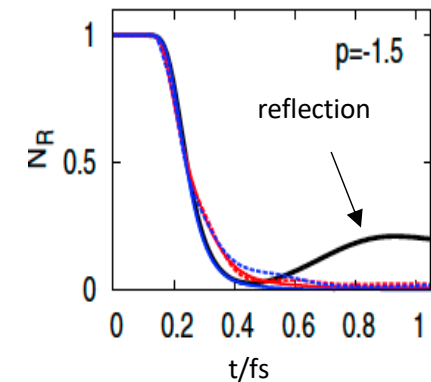
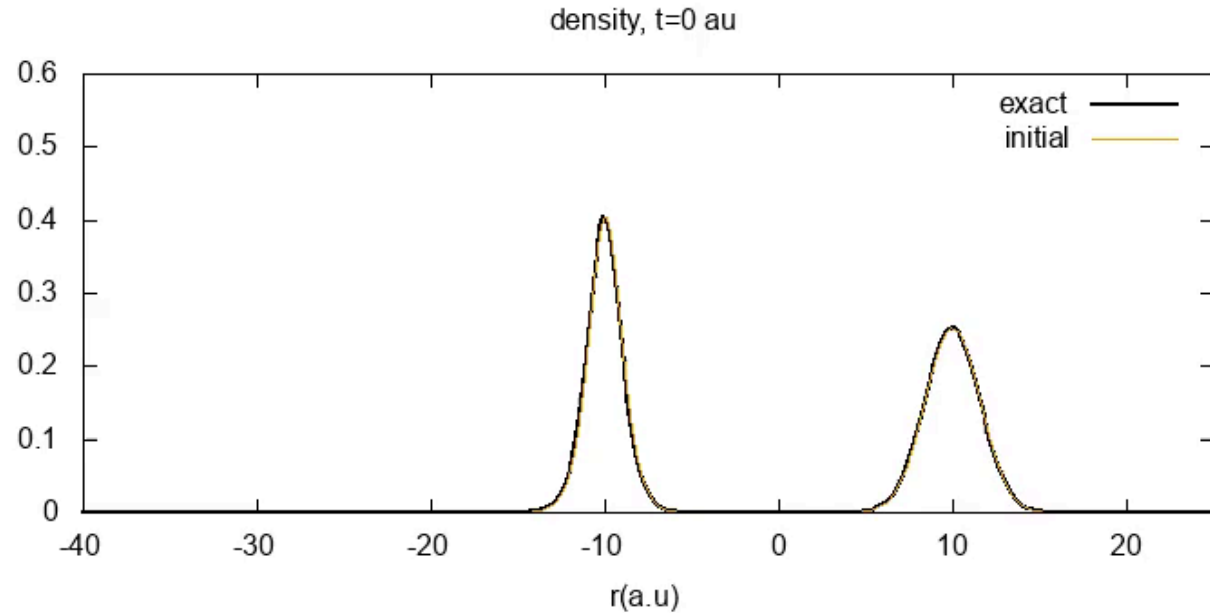
$$v_{\text{XC}}^{\text{A}}[n; \Psi_0, \Phi_0](\mathbf{r}, t) = v_{\text{XC}}^{\text{g.s.}}[n(t)](\mathbf{r}) = \left. \frac{\delta E_{\text{XC}}[n]}{\delta n(\mathbf{r})} \right|_{n=n(\mathbf{r}, t)}$$

- Two sources of error:
 - (i) Adiabatic approximation itself
 - (ii) Ground-state functional approximation

To disentangle, can study “adiabatically-exact” potential:

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

An example: The *exact* TD xc potential and Time-Resolved e-H scattering



How do the TDDFT approximations do?

Choice of initial spin-singlet KS wavefunction:

- (1) Slater determinant (one orbital, doubly-occupied)
- (2) Two-orbital state: one for the electron in the atom, one for the incoming

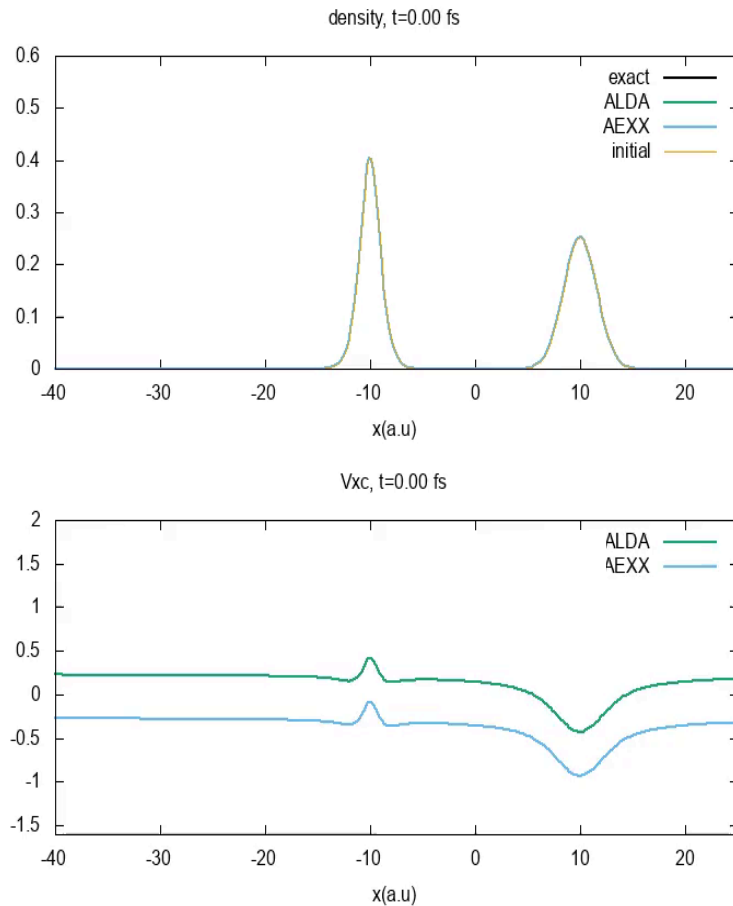
Y. Suzuki, L. Lacombe, K. Watanabe, N. T. Maitra, PRL **119**, 263401 (2017)

L. Lacombe, Y. Suzuki, K. Watanabe, N. T. Maitra, Eur. Phys. J. B. **91**, 96 (2018)

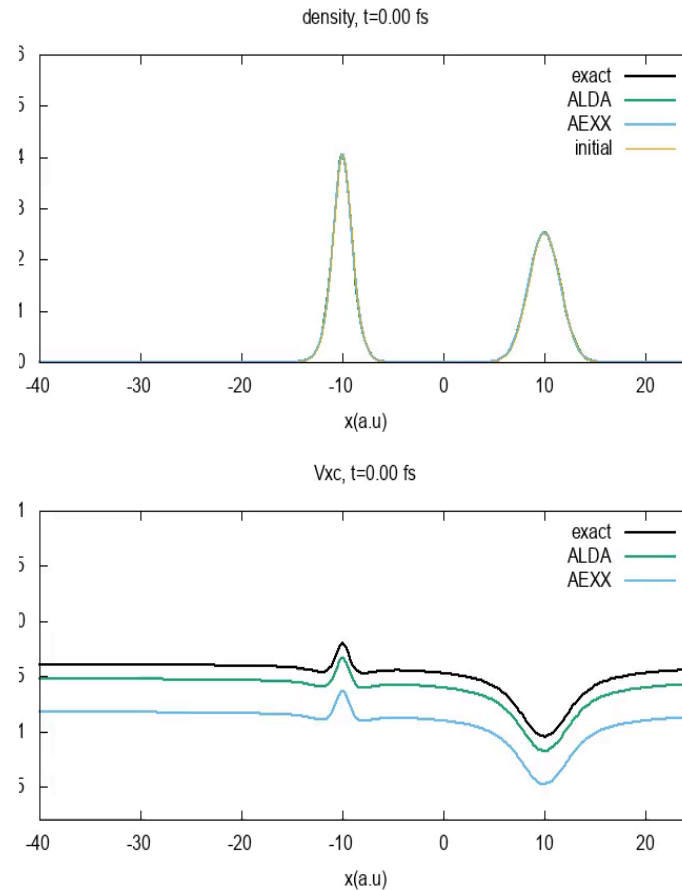
Time-Resolved e-H scattering



Choice (1) Slater determinant



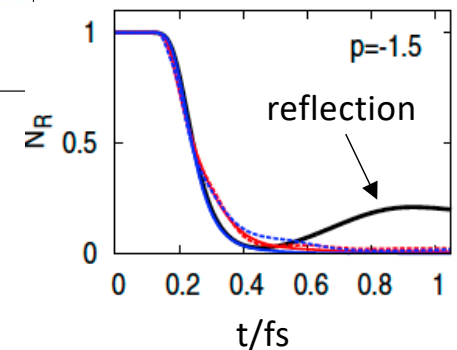
Choice (2) Two-orbital state



- ❖ Although ALDA and AEXX densities don't show unphysical oscillations for choice (2), they overspread and ultimately fail to scatter – v_{xc} lacks crucial peak and valley structures.

Adiabatically-exact lacks these features too.

Need memory!!



Y. Suzuki, L. Lacombe, K. Watanabe, N. T. Maitra, PRL **119**, 263401 (2017)

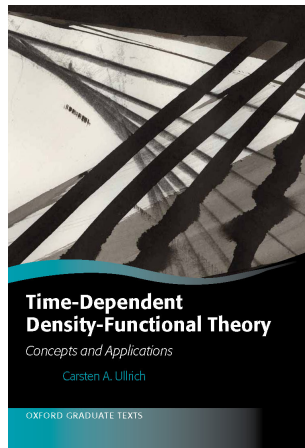
L. Lacombe, Y. Suzuki, K. Watanabe, N. T. Maitra, Eur. Phys. J. B. **91**, 96 (2018)

Summary and Outlook

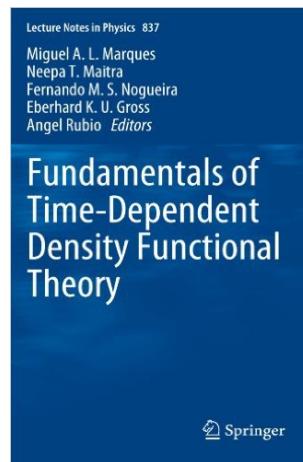
- ❖ There are so many different interesting things to do with TDDFT!
 - time-dependence opens up a wealth of interesting applications
 - optical absorption spectra
 - attosecond laser control of electronic motion
 - photovoltaic design
 - time-resolved spectroscopy
 - functional development (memory...implementing exact conditions...)
 - frequency-dependence in linear-response
 - full memory-dependence for non-perturbative dynamics
 - extensions
 - Coupling of TDDFT to ionic motion (phonons)
 - QED-DFT for polaritonic systems
 - Finite temperature for warm dense matter

Thanks for your attention!

Some Literature on TDDFT



- TDDFT: Concepts and Applications, by Carsten Ullrich (Oxford University Press 2012)



- Fundamentals of TDDFT, ed. Marques et al. (Springer, 2012)

- A semi-recent review on theory of TDDFT, by N. T. Maitra, *Perspective* in J. Chem. Phys. **144**, 220901 (2016).

- Graduate Student Seminar Series on theory developments in DFT and TDDFT

<https://sites.rutgers.edu/dft-student-seminar/>

