

# TDDFT

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# Outline

- 1 Time-dependent quantum mechanics
- 2 TDDFT: formalism
- 3 Linear response theory
- 4 Performance
- 5 Back to the ground state

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# Time-dependent Schrödinger equation

$$i\frac{\partial}{\partial t}\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N; t) = (\hat{T} + \hat{V}(t) + \hat{V}_{ee})\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N; t)$$

with kinetic energy operator:

$$\hat{T} = -\frac{1}{2} \sum_{j=1}^N \nabla_j^2$$

electron interaction:

$$\hat{V}_{ee} = \frac{1}{2} \sum_{j \neq k} \frac{1}{|\mathbf{r}_j - \mathbf{r}_k|}$$

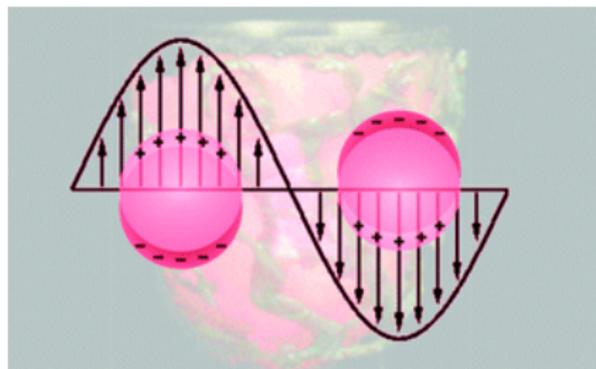
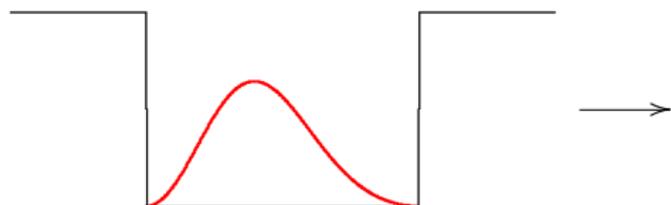
The TDSE describes the time evolution of a many-body state  $\Psi(t)$  starting from an initial state  $\Psi_0 = \Psi(t_0)$ , under the influence of an external time-dependent potential:

$$\hat{V}(t) = \sum_j v(\mathbf{r}_j, t).$$

# Two types of time-dependence: 1. Due to initial state

Initial wavefunction is not an eigenstate: e.g.

$$\psi(x, t = 0) = \frac{1}{\sqrt{5}} \{2\phi_1(x) + \phi_2(x)\}.$$



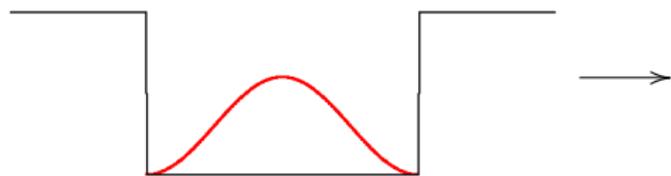
Plasmonics: oscillations of nanoparticles

- New J. Chem. **30**, 1121 (2006)
- Nature Mat. Vol. 2 No. 4 (2003)

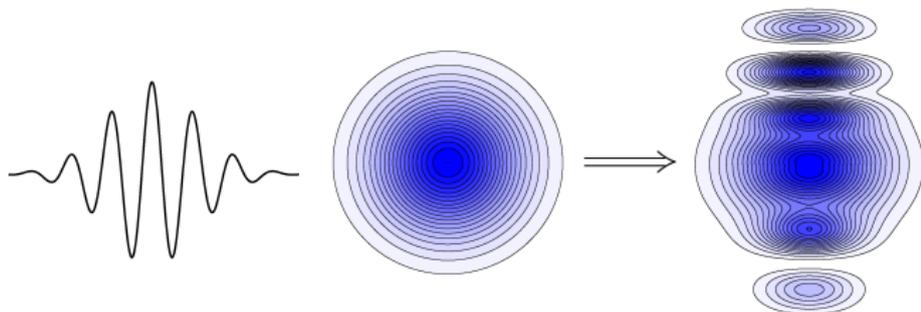
- Ullrich and Maitra's March 2010 APS TDDFT presentation

## 2nd type: Potential starts changing

Start in ground state, evolve in time-dependent potential  $v(x, t)$ :



Nonlinear response of molecules in strong laser fields:



# Conservation of density in time-dependent problems

- Current operator:

$$\hat{\mathbf{j}}(\mathbf{r}) = \frac{1}{2} \sum_j (\hat{\mathbf{p}}_j \delta(\mathbf{r} - \mathbf{r}_j) + \delta(\mathbf{r} - \mathbf{r}_j) \hat{\mathbf{p}}_j)$$

- Acting on wavefunction:

$$\mathbf{j}(\mathbf{r}, t) = N \int d^3 r_2 \cdots \int d^3 r_N \Im \{ \Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N; t) \nabla \Psi^*(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N; t) \}$$

- Continuity:

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

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# Recent reviews on TDDFT

- *Excited states from time-dependent density functional theory*, P. Elliott, F. Furche, and K. Burke, in *Reviews in Computational Chemistry*, eds. K. B. Lipkowitz and T. R. Cundari, (Wiley, Hoboken, NJ, 2009), pp 91-165. Also arXiv:cond-mat/0703590
- *Time-dependent density functional theory*, edited by M. Marques, C.A. Ullrich, F. Noguiera, A. Rubio, K. Burke, and E.K.U. Gross (Springer, Heidelberg, 2006).
- *Time-dependent density functional theory: Past, present, and future* K. Burke, Jan Werschnik, and E.K.U. Gross, *J. Chem. Phys.* 123, 062206 (2005)
- Time-dependent density-functional theory *Phys. Chem. Chem. Phys.*, 2009 DOI: 10.1039/b908105b, eds. Miguel Marques and Angel Rubio.

# Basic proof: Runge–Gross theorem (1984)

- Any given current density,  $\mathbf{j}(\mathbf{r}, t)$ , initial wavefunction, statistics, and interaction, there's only one external potential,  $v(\mathbf{r}, t)$ , that can produce it.
- Imposing a boundary condition and using continuity, find also true for  $n(\mathbf{r}, t)$ .
- Action in RG paper is **WRONG**.
- van Leeuwen gave a constructive proof (PRL98).

# Basic points

## TDDFT:

- is an addition to DFT, using a different theorem
- allows you to convert your KS orbitals into optical excitations of the system
- for excitations usually uses ground-state approximations that usually work OK
- has not been very useful for strong laser fields
- is in its expansion phase: Being extended to whole new areas, not much known about functionals
- with present approximations has problems for solids
- with currents is more powerful, but harder to follow
- yields a new expensive way to get ground-state  $E_{XC}$ .

# TD Kohn–Sham equations

- Time-dependent KS equations:

$$i \frac{\partial}{\partial t} \phi_j(\mathbf{r}, t) = \left\{ -\frac{1}{2} \nabla^2 + v_S(\mathbf{r}, t) \right\} \phi_j(\mathbf{r}, t)$$

- Density:

$$n(\mathbf{r}, t) = \sum_{j=1}^N |\phi_j(\mathbf{r}, t)|^2$$

- The KS potential is

$$v_S(\mathbf{r}, t) = v(\mathbf{r}, t) + \int d^3 r' \frac{n(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} + v_{XC}[n; \Psi_0, \Phi_0](\mathbf{r}, t),$$

where  $v_{XC}$  depends on memory:

- ▶ entire history of  $n(\mathbf{r}, t)$
- ▶ initial state  $\Psi_0$  and  $\Phi_0$ .

# Adiabatic approximation

- Almost all calculations use adiabatic approximation
- No standard improvement over this
- Use ground state functional  $v_{XC}^{GS}$  on time-dependent  $n(\mathbf{r}, t)$ :

$$v_{XC}^{adia}[n](\mathbf{r}, t) = v_{XC}^{GS}[n(t)](\mathbf{r}).$$

# Overview of ALL TDDFT

TDDFT is applied in 3 distinct regimes:

- **Strong fields**, where time-dependence is not perturbative.
  - ▶ Properties: double ionization probabilities, momentum distributions, high-harmonic generation
  - ▶ Methodology: Must be real time, usually on a grid in real space.
  - ▶ Performance: Several problems, including that  $n(\mathbf{r}, t)$  is not enough info to get the desired property, and that no good approximations when  $n(\mathbf{r}, t)$  is not close to ground state.
- **Excitations**: To extract excitations and optical absorption, only need linear response theory
  - ▶ Methodology: Either real time, fourier transform dipole moment, or response equations in frequency space.
  - ▶ Performance: Usually quite good (good properties of excited molecules) but growing list of deficiencies, e.g.:
    - ★ Extended systems and non-locality
    - ★ Charge transfer
- **Ground-state approximations**: Via fluctuation-dissipation theorem, can calculate the XC energy from TDDFT (very expensive - RPA cost) ↻

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# Excitations from DFT

- Many approaches to excitations in DFT
- There is no HK theorem from excited-state density (PRL with Rene Gaudoin)
- Would rather have variational approach (ensembles, constrained search, etc.)
- TDDFT yields a response approach, i.e, looks at TD perturbations around ground-state

# Linear response theory

We will need the density-density response function:

$$\delta n(\mathbf{r}, t) = \int d^3 r' \int dt' \chi(\mathbf{r}\mathbf{r}', t - t') \delta v(\mathbf{r}', t')$$

where

- $\delta v(\mathbf{r}, t)$  is a perturbation to the potential,
- $\delta n(\mathbf{r}, t)$  is the density response to this perturbation, and
- $\chi$  is the density-density response (susceptibility) function:

$$\chi(\mathbf{r}, \mathbf{r}', t - t') = \frac{\delta n(\mathbf{r}t)}{\delta v(\mathbf{r}'t')}$$

(functional derivative)

# Linear response in TDDFT

Equate density change in reality with that of KS system (and Fourier transform):

$$\begin{aligned}\delta n(\mathbf{r}\omega) &= \int d^3r' \chi[n](\mathbf{r}\mathbf{r}'\omega) \delta v(\mathbf{r}'\omega) \\ &= \int d^3r' \chi_S[n](\mathbf{r}\mathbf{r}'\omega) \delta v_S[n](\mathbf{r}'\omega)\end{aligned}$$

which implies

$$\delta v_S[n](\mathbf{r}\omega) = \delta v(\mathbf{r}\omega) + \int d^3r' \left\{ \frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{XC}[n](\mathbf{r}\mathbf{r}'\omega) \right\} \delta n(\mathbf{r}'\omega)$$

and the XC kernel is defined in time as

$$f_{XC}(\mathbf{r}\mathbf{r}', t - t') = \frac{\delta v_{XC}(\mathbf{r}t)}{\delta n(\mathbf{r}'t')}.$$

# Dyson-like equation from equating density responses

Get the real response function from the *ground-state* KS response function plus kernel:

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

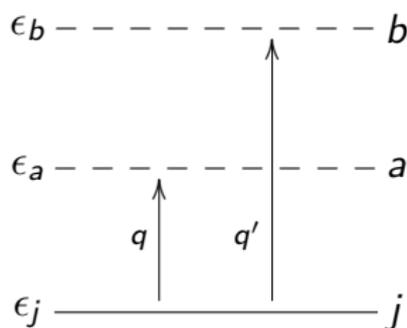
with KS susceptibility

$$\chi_S(\mathbf{r}\mathbf{r}'\omega) = \sum_{jk} f_{jk} \frac{\phi_j(\mathbf{r})\phi_k^*(\mathbf{r})\phi_j^*(\mathbf{r}')\phi_k(\mathbf{r}')}{\omega - (\epsilon_j - \epsilon_k) + i0_+}$$

where  $f_{jk} = f_j - f_k$ ,  $\epsilon_j$  is the KS orbital energy and  $\phi_j(\mathbf{r})$  is the orbital. If adiabatic approximation, the ground-state functional determines all.

# Transitions

Look at KS transition frequencies  $\omega_q = \epsilon_a - \epsilon_j$ , where  $j$  is an occupied and  $a$  an unoccupied orbital. Thus  $q$  is a double index  $(j, a)$ .



If we consider

$$\Phi_q(\mathbf{r}) = \phi_j^*(\mathbf{r})\phi_a(\mathbf{r}),$$

we can rewrite

$$\chi_s(\mathbf{r}\mathbf{r}'\omega) = 2 \sum_q \left\{ \frac{\Phi_q(\mathbf{r})\Phi_q^*(\mathbf{r}')}{\omega - \omega_q + i0_+} - \frac{\Phi_q^*(\mathbf{r})\Phi_q(\mathbf{r}')}{\omega + \omega_q - i0_+} \right\}.$$

# TDDFT linear response

- Probe system with AC field of frequency  $\omega$
- See at what  $\omega$  you find a self-sustaining response
- That's a transition frequency!
- Need a new functional, the XC kernel,  $f_{\text{XC}}[n](\mathbf{r}\mathbf{r}\omega)$
- Almost always ignore  $\omega$ -dependence (called adiabatic approximation)
- Can view as corrections to KS response

# Casida's matrix formulation (1996)

Get true transition frequencies  $\omega$  as eigenvalues of

$$\sum_{q'} \Omega_{qq'}(\omega) \nu_{q'} = \omega^2 \nu_q,$$

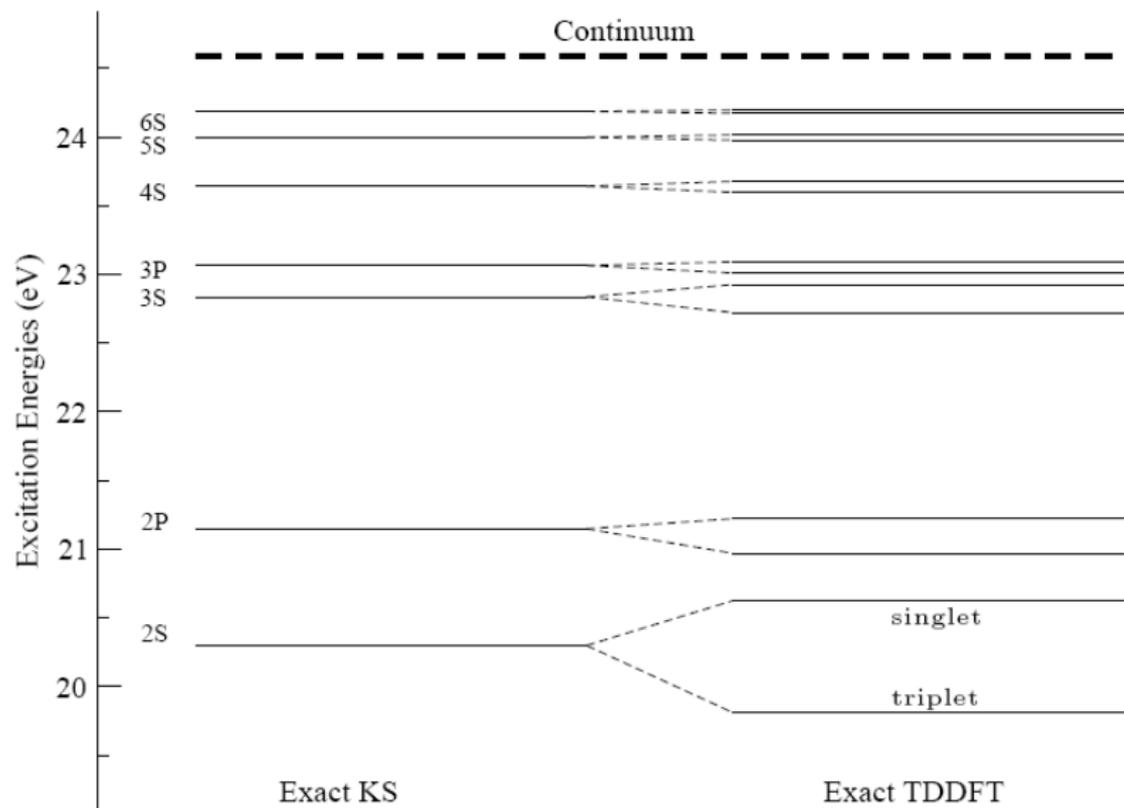
where  $\nu_q = ?$ ,

$$\Omega_{qq'} = \delta_{qq'} \omega_q^2 + 4 \sqrt{\omega_q \omega_{q'}} [q | f_{\text{HXC}}(\omega) | q']$$

and

$$[q | f_{\text{HXC}}(\omega) | q'] = \iint d^3r d^3r' \Phi_q^*(\mathbf{r}') f_{\text{HXC}}(\mathbf{r}\mathbf{r}'\omega) \Phi_{q'}(\mathbf{r})$$

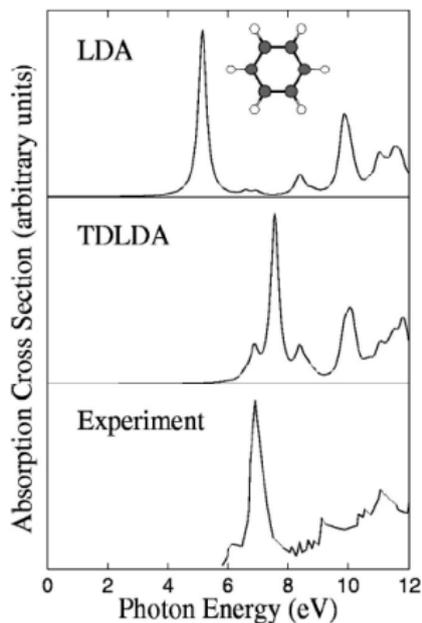
# KS response



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# Benzene is the fruitfly of TDDFT



- *First-principles density-functional calculations for optical spectra of clusters and nanocrystals*, I. Vasiliev, S. Ogut, and J.R. Chelikowsky, Phys. Rev. B 65, 1 15416 (2002).

# Case study: Naphthalene

TABLE III: Performance of various density functionals for the first six singlet excitation energies (in eV) of naphthalene. An aug-TZVP basis set and the PBE/TZVP/RI ground state structure was used. The “best” estimates of the true excitations were from experiment and calculations, as described in text.

Method	$1^1B_{3u}$	$1^1B_{2u}$	$2^1A_g$	$1^1B_{1g}$	$2^1B_{3u}$	$1^1A_u$
Pure density functionals						
LSDA	4.191	4.026	5.751	4.940	5.623	5.332
BPs6	4.193	4.027	5.770	4.974	5.627	5.337
PBE	4.193	4.031	5.753	4.957	5.622	5.141
Hybrids						
B3LYP	4.393	4.282	6.062	5.422	5.794	5.311
PBE0	4.474	4.379	6.205	5.611	5.889	5.603
“best”	4.0	4.5	5.5	5.5	5.5	5.7

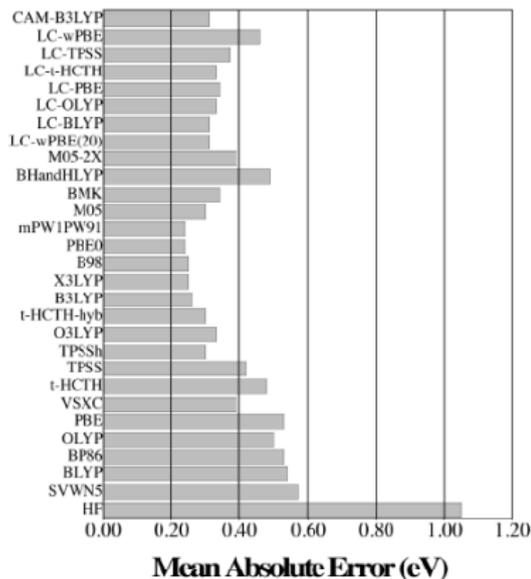
TABLE IV: Performance of various wavefunction methods for the excitations of Table I. The aug-TZVP basis set and the PBE/TZVP/RI ground state structure was used for all except the CASPT2 results, which were taken from Ref. [185]. Experimental results are also from Ref. [185].

Method	$1^1B_{3u}$	$1^1B_{2u}$	$2^1A_g$	$1^1B_{1g}$	$2^1B_{3u}$	$1^1A_u$
CIS	5.139	4.984	7.038	6.251	6.770	5.862
CC2	4.376	4.758	6.068	5.838	6.018	5.736
CASPT2	4.03	4.56	5.39	5.53	5.54	5.54
expt.	3.97, 4.0	4.45, 4.7	5.50, 5.52	5.28, 5.22	5.63, 5.55	5.89
“best”	4.0	4.5	5.5	5.5	5.5	5.7

Study of various functionals for Naphthalene. Variations in  $v_{XC}(\mathbf{r})$  comparable to those in  $f_{XC}(\mathbf{r}, \mathbf{r}')$ .

- P. Elliott, F.Furche, KB, Reviews Comp Chem, 2008.

# Performance of functionals in TDDFT



Study of various functionals over a set of 500 organic compounds, 700 excited singlet states

- D. Jacquemin, V. Wathelet, E. A. Perpète, C. Adamo, *J. Chem. Theory Comput.* (2009).

# Typical success of TDDFT for excited states

- Energies to within about 0.4 eV
- Bonds to within about 1%
- Dipoles good to about 5
- Vibrational frequencies good to 5
- Cost scales as  $N^2$ , vs  $N^5$  for CCSD
- Available now in your favorite quantum chemical code

# Current challenges in TDDFT

- Rydberg states - know what to do
- Polarizabilities of long-chain molecules
- Optical response of solids
- Double excitations
- Long-range charge transfer
-

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# Extracting $E_{\text{XC}}[n]$ from TDDFT

From the fluctuation-dissipation theorem:

$$E_{\text{XC}}[n] = -\frac{1}{2} \int_0^1 d\lambda \int d^3r \int d^3r' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \times \int_0^\infty \frac{d\omega}{\pi} \left\{ \chi_\lambda[n](\mathbf{r}\mathbf{r}'\omega) + n(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}') \right\}$$

Plug in ground-state  $n(\mathbf{r})$  to obtain  $E_{\text{XC}}$ .

- Combine with TDDFT Dyson-like equation to get new approximations from old functionals, but demanding response calculation.
- For separated systems, gives van der Waals coefficients.
- Approximate frequency integration and factorization of response functions yields Langreth-Lunqvist van der Waals function—a non-local ground-state density functional.

► M Dion et al, PRL **92**, 24601 (2004).

# Lessons about TDDFT

- A way to extract electronic excitations using new theorem, from ground-state DFT calculation.
- Only real game in town for excitations in chemistry for decent-sized molecules.
- Cost comparable to single-point ground-state calculation.
- Uses adiabatic approximation.
- Problems for large systems due to locality of approximate functionals.