

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

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:

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

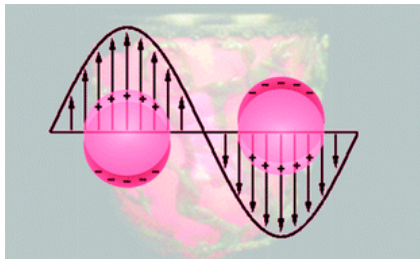
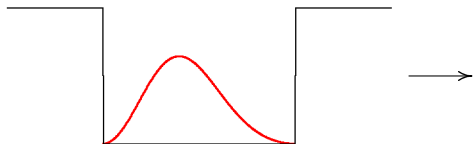
The TDSE describes the time evolution of a many-body state $\Psi(t)$ starting from an initial state $\Psi_0 = \Psi(t_0)$, under the influence of an external time-dependent potential:

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

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

Initial wavefunction is not an eigenstate: e.g.

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



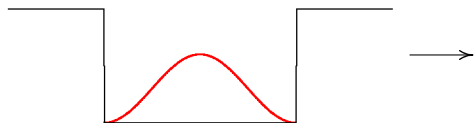
Plasmonics: oscillations of nanoparticles

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

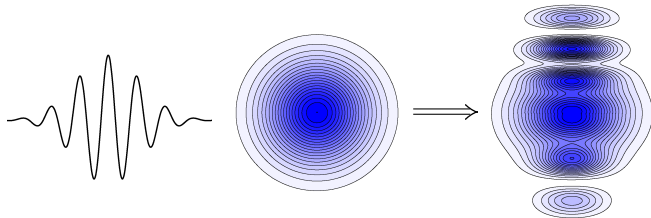
- Ullrich and Maitra's March 2010 APS TDDFT presentation

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:



- Ullrich and Maitra's March 2010 APS TDDFT presentation

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:

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

Recent reviews on TDDFT

- *Fundamentals of Time-Dependent Density Functional Theory* (Lecture Notes in Physics) by Miguel A.L. Marques, Neepa T. Maitra, Fernando M.S. Nogueira and E.K.U. Gross (Springer, 2012).
- *Time-dependent density functional theory*, Carsten Ullrich (Oxford, 2012).
- *Time-dependent density functional theory: Past, present, and future* K. Burke, Jan Werschnik, and E.K.U. Gross, J. Chem. Phys. **123**, 062206 (2005)
- *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 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
 - ▶ PRL **80**, 1280, (1998)but see
 - ▶ Yang, Maitra, and Burke, Phys. Rev. Lett. **108**, 063003, (2012)

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 trickier
- yields a new expensive way to get ground-state E_{XC} , but see
 - ▶ H. Eshuis, J. E. Bates, and F. Furche, *Theor. Chem. Acc.* **131** 1084 (2012)

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

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

where v_{XC} depends on memory:

- ▶ entire history of $n(\mathbf{r}, t)$
- ▶ initial state Ψ_0 and Φ_0 .

Adiabatic approximation

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

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

- Often, error is due to ground-state approximation, *not* missing frequency dependence.
 - ▶ Thiele and Kümmel, Phys. Chem. Chem. Phys., **11**, 4631 (2009)

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)

- Many approaches to excitations in DFT
- There is no HK theorem from excited-state density
 - ▶ Gaudoin and Burke, Phys. Rev. Lett. **93**, 173001, (2004)
- 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
- χ 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:

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

with KS susceptibility

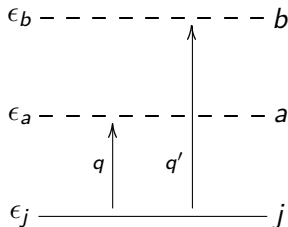
$$\chi_s(\mathbf{r}\mathbf{r}'\omega) = \sum_{jk} f_{jk} \frac{\phi_j(\mathbf{r})\phi_k^*(\mathbf{r})\phi_j^*(\mathbf{r}')\phi_k(\mathbf{r}')}{\omega - (\epsilon_j - \epsilon_k) + i0_+}$$

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

- Gross and Kohn, Phys. Rev. Lett. **55**, 2850 (1985)

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 ω
- See at what ω 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 ω -dependence (called adiabatic approximation)
- Can view as corrections to KS response
 - ▶ Appel, Gross, and Burke, Phys. Rev. Lett. **90**, 043005, (2003)

Casida's matrix formulation (1996)

Get true transition frequencies ω as eigenvalues of

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

where

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

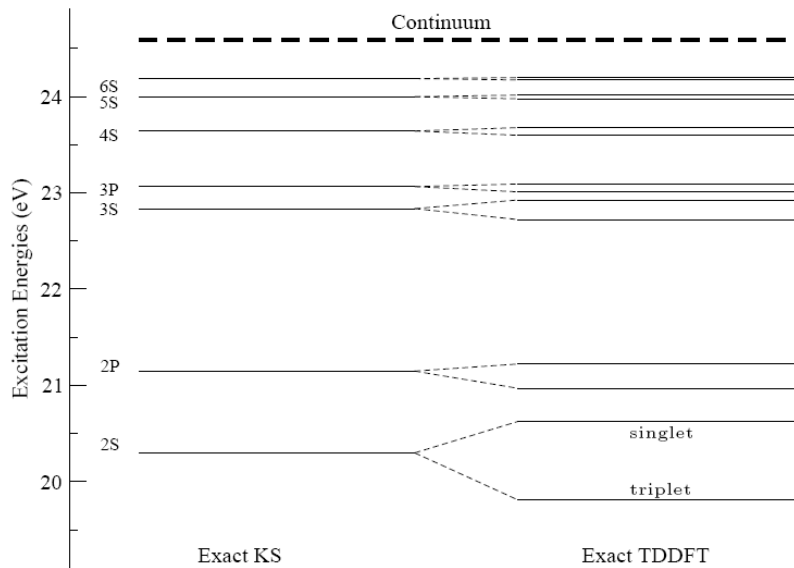
and

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

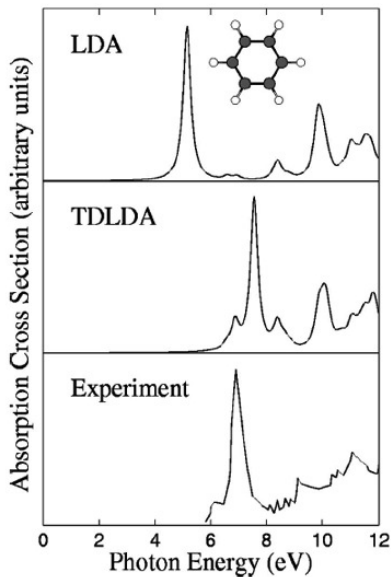
and the eigenvectors ν_q determine the optical strength.

- *Time-dependent density functional response theory of molecular systems*, M.E. Casida, in *Recent developments and applications in DFT*, ed. J.M. Seminario (Elsevier, Amsterdam, 1996).

KS response



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
BP86	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

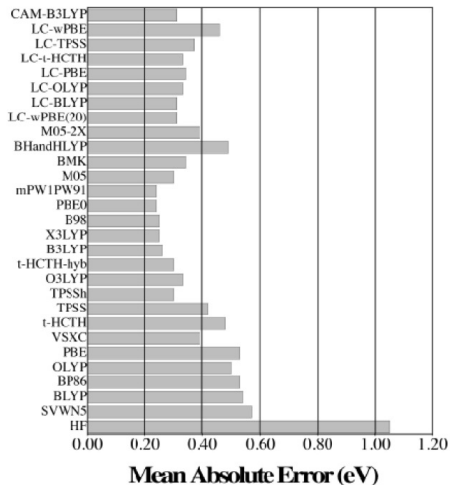
TABLE IV: Performance of various wavefunction methods for the excitations of Table I. The aug-TZVP basis set and the PBE/TZVP/RI ground state structure was used for all except the CASPT2 results, which were taken from Ref. [185]. Experimental results are also from Ref. [185].

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 (Turbomole)

Current challenges in TDDFT

- Rydberg states
 - ▶ Wasserman and Burke, PRL **95**, 163006, (2005)
 - ▶ Wasserman, Maitra, and Burke, PRL **91**, 263001, (2003)
- Double excitations
 - ▶ Maitra *et al.*, J. Chem. Phys. **120**, 5932-5937, (2004)
- Optical response of solids
 - ▶ Sharma *et al.*, PRL **107**, 186401 (2011)
- Long-range charge transfer
 - ▶ Stein, Kronik, and Baer, J. Am. Chem. Soc. **131**, 2818 (2009)
- Polarizabilities of long-chain molecules
 - ▶ van Faassen *et al.*, J. Chem. Phys. **120**, 5932, (2004)

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_{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.