Beyond the ground state

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Outline

1. Basics of electronic excitations
2. Time-dependent quantum mechanics
3. TDDFT: formalism
4. Linear response theory
5. Performance
6. Back to the ground state

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Types of excitations for interacting electronic systems

- Neutral excitations that conserve N
  - Often accessed in an optical experiment (either allowed or forbidden)
  - E.g., in He, excite one electron from 1s to 2p
  - The particle-particle response function $\chi(\mathbf{r}, \mathbf{r}, \omega)$ has poles at these excitations.

- Electron removal and addition events, $N \to N \pm 1$
  - Accessed in photoemission and photoabsorption experiments
  - The single-particle Green's function $G(\omega)$ has poles at differences between removal and addition energies.
  - Most infamous example is $I - A$, the fundamental gap.

- Excitations from ground-state DFT
  - Confusing: HK paper says excited-state energies are functionals of $n(\mathbf{r})$.
  - But knowledge of $E_{\mathrm{XC}}[n]$ does not yield them; need another functional.

Differences between molecules and solids

- In atoms and molecules, low-lying excitations are *discrete*
  - Naturally treated by ab inito quantum chemical methods using wavefunctions.
  - Often methods assume finite number of levels to be included.

- In solids, all states are in the continuum
  - Many methods for solids, like *GW*, work best with infinite numbers of excitations.

- Of course, very interesting to study transition between the two.

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Time-dependent Schrödinger equation

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

with kinetic energy operator:

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

electron interaction:

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

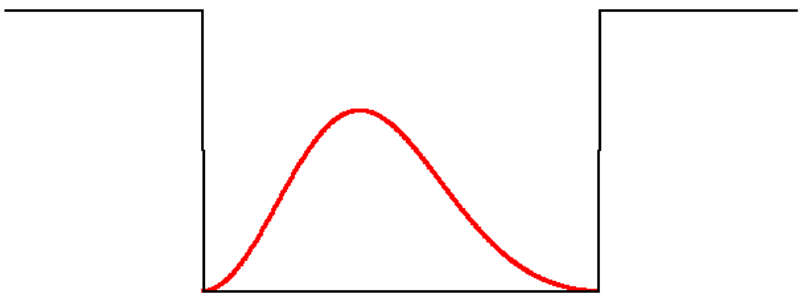
The TDSE describes the time evolution of a many-body state $\Psi(t)$ starting from an initial state $\Psi_0 = \Psi(t_0)$, under the influence of an external time-dependent potential:

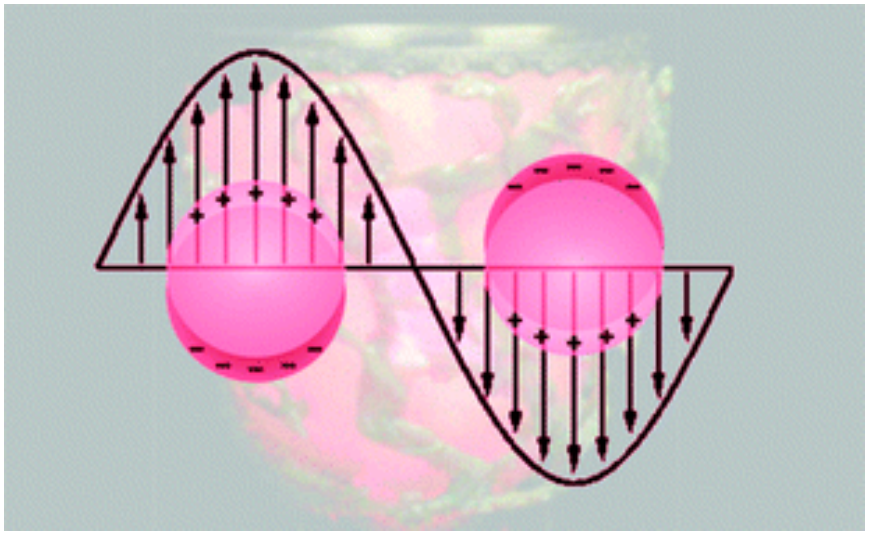
$$\hat{V}(t) = \sum_j v(\mathbf{r}_j,t).$$

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

Initial wavefunction is not an eigenstate: e.g.

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





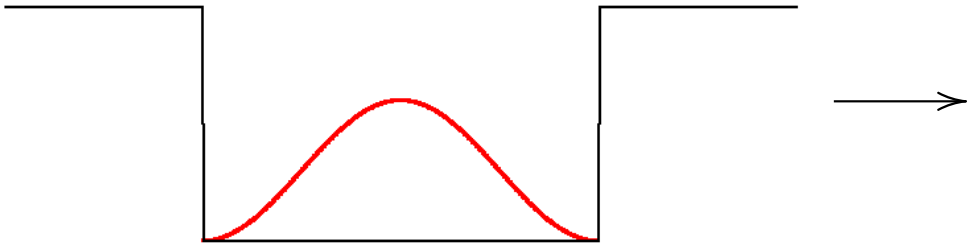
Plasmonics: oscillations of nanoparticles

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

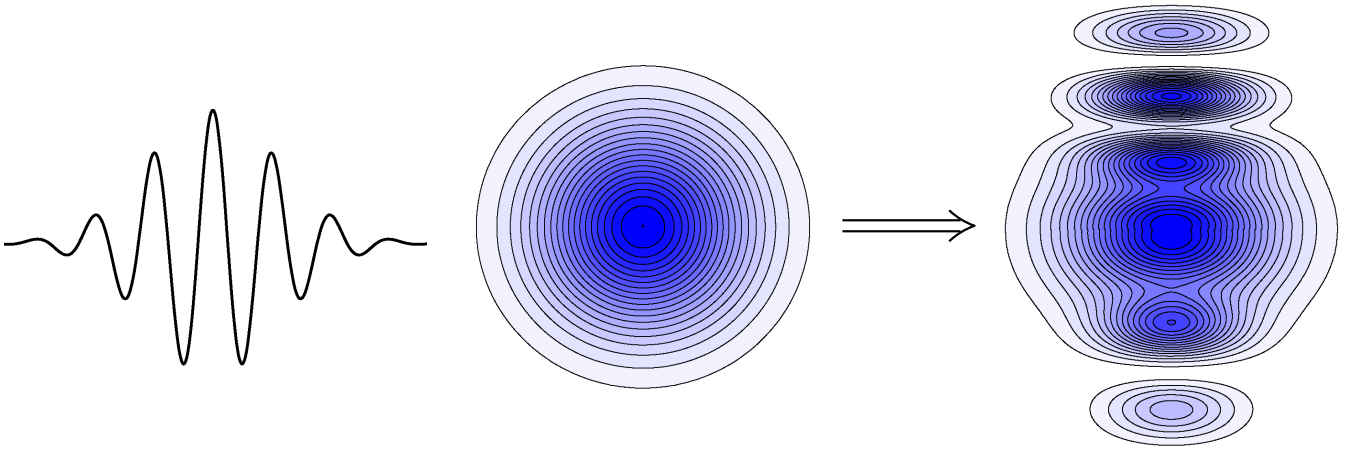
- Ullrich and Maitra's March 2010 APS TDDFT presentation

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:

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

- Continuity:

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

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Recent reviews on TDDFT

- *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* (2009). Also arXiv 0703590
- *TDDFT*, special issue of Phys. Chem. Chem. Phys., 2009 DOI: 10.1039/b908105b, eds. Miguel Marques and Angel Rubio.

Basic proof: Runge–Gross theorem (1984)

- For given Ψ_0, Taylor-expand two different $v(\mathbf{r}, t)$ around $t = 0$.
- From eqns of motion, find that if their j-th time-derivative differs, then the j-th time-derivative of the current densities must differ.
- So, given $\mathbf{j}(\mathbf{r}, t)$, Ψ_0, statistics, and e-e interaction, there's at most one $v(\mathbf{r}, t)$ that can produce it. This means $v(\mathbf{r}, t)$ (and all observables) are *functionals* of $\mathbf{j}(\mathbf{r}, t)$.
- Imposing a boundary condition and using continuity, find also true for $n(\mathbf{r}, t)$.
- Action in RG paper does not lead to TD KS equations in general.
- van Leeuwen gave a constructive proof to find the TD KS potential.
  - PRL **82**, 3863, (1999)

  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:

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

- Density:

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

- The KS potential is

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

  where $v_{\rm XC}$ 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 $v_{\rm XC}^{\rm GS}$ on time-dependent $n(\mathbf{r}, t)$:

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

- 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 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
  - Gaudoin and Burke, Phys. Rev. Lett. **93**, 173001, (2004)
- Would rather have variational approach (ensembles, constrained search, etc.)
  - For ensembles, see: Zenghui Yang, Aurora Pribram-Jones, et al, arXiv or my website
- 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:

$$\chi[n_0](\mathbf{r}, \mathbf{r}', t - t') = \left. \frac{\delta n(\mathbf{r} t)}{\delta v(\mathbf{r}' t')} \right|_{n_0}$$

(functional derivative)

Linear response in TDDFT

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

$$\begin{aligned}\delta n(\mathbf{r}\omega) &= \int d^3r' \; \chi[n_0](\mathbf{r}\mathbf{r}'\omega)\delta v(\mathbf{r}'\omega) \\ &= \int d^3r' \; \chi_{\rm S}[n_0](\mathbf{r}\mathbf{r}'\omega)\delta v_{\rm S}[n_0](\mathbf{r}'\omega)\end{aligned}$$

which implies

$$\delta v_{\rm S}[n_0](\mathbf{r}\omega) = \delta v(\mathbf{r}\omega) + \int d^3r' \; \left\{ \frac{1}{|\mathbf{r}-\mathbf{r}'|} + f_{\rm XC}[n_0](\mathbf{r}\mathbf{r}'\omega) \right\} \delta n(\mathbf{r}'\omega)$$

and the XC kernel is defined in time as

$$f_{\rm XC}[n_0](\mathbf{r}\mathbf{r}', t-t') = \left. \frac{\delta v_{\rm XC}(\mathbf{r}t)}{\delta n(\mathbf{r}'t')} \right|_{n_0}.$$

Dyson-like equation from equating density responses

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

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

with KS susceptibility

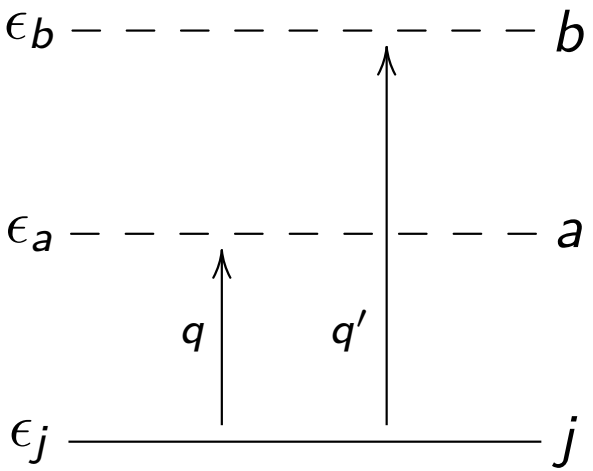
$$\chi_{\rm S}(\mathbf{r}\mathbf{r}'\omega) = \sum_{jk} f_{jk} \frac{\phi_j(\mathbf{r})\phi_k^*(\mathbf{r})\phi_j^*(\mathbf{r}')\phi_k(\mathbf{r}')}{\omega - (\epsilon_j - \epsilon_k) + i0_+}$$

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

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

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, $f_{\rm XC}[n](\mathbf{r}\mathbf{r}\omega)$
- 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

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

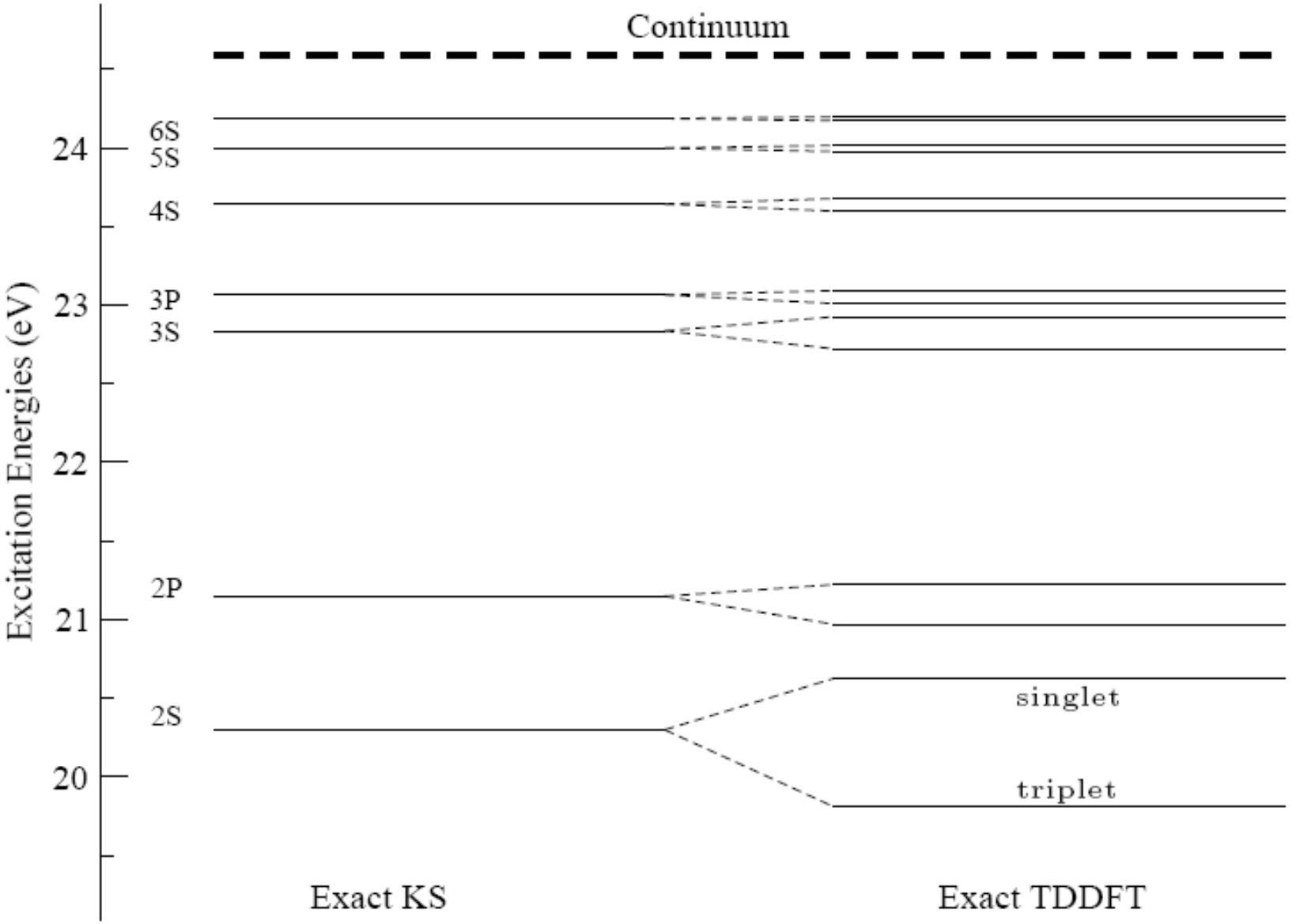
and

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

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


Continuum
6S
5S
4S
3P
3S
2P
2S
24
23
22
21
20
Excitation Energies (eV)
singlet
triplet
Exact KS
Exact TDDFT

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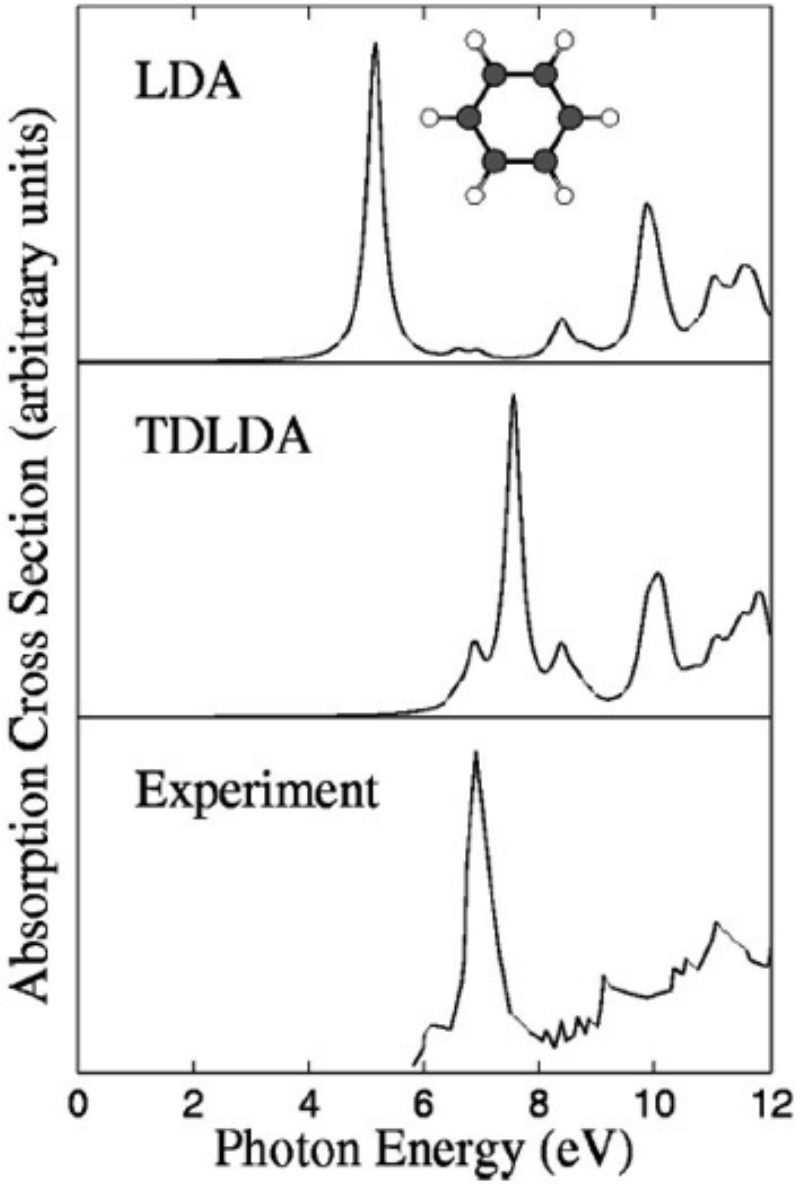
Benzene is the fruitfly of TDDFT



- *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
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

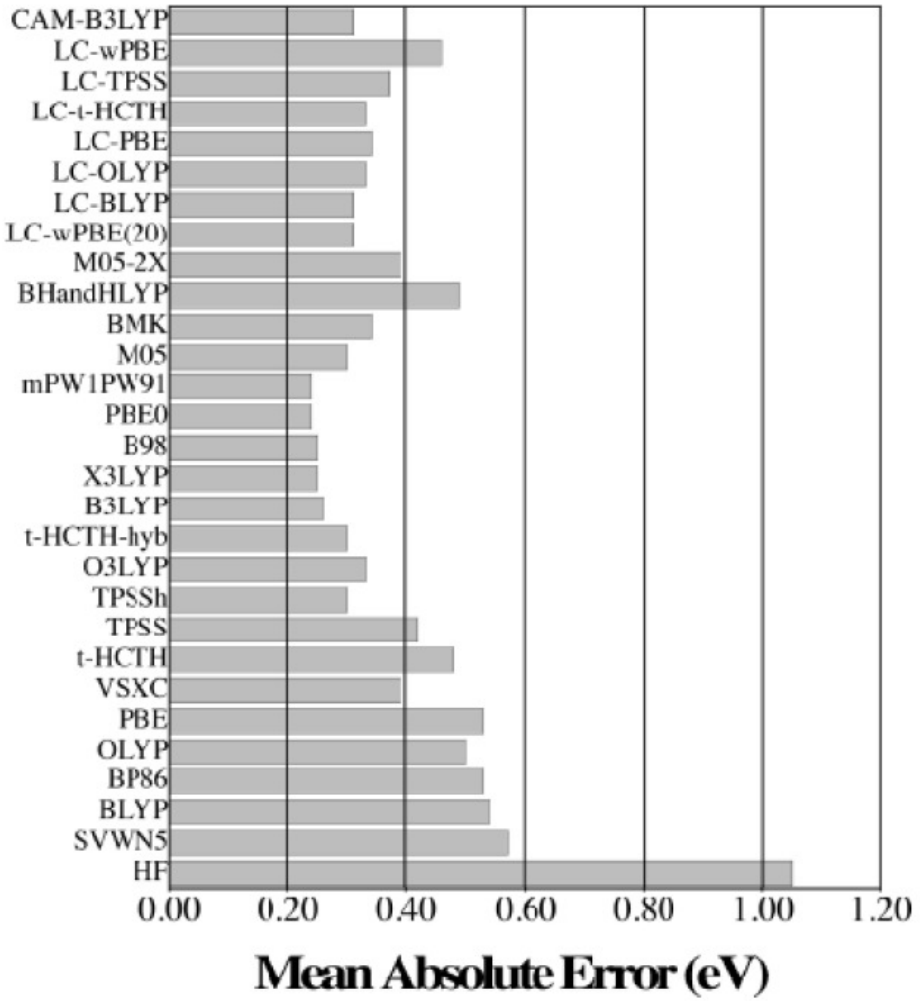
TABLE IV: Performance of various wavefunction methods for the excitations of Table I. The aug-TZVP basis set and the PBE/TZVP/RI ground state structure was used for all except the CASPT2 results, which were taken from Ref. [185]. Experimental results are also from Ref. [185].

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 $v_{\rm XC}(\mathbf{r})$ comparable to those in $f_{\rm XC}(\mathbf{r},\mathbf{r}')$.

- 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. Perpete, 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 linear response 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
  - Kronik, Stein, Refaely-Abramson, and Baer, JCTC 2012 8 (5), 1515-1531
- Polarizabilities of long-chain molecules
  - van Faassen *et al.*, J. Chem. Phys. 120, 5932, (2004)
- Conical intersections in molecular energy surfaces

Sins of TDDFT

- *The sin of the ground-state:* Errors in the underlying ground-state DFT calculation. If the KS orbital energies are wrong to begin with, TDDFT corrections cannot produce accurate results.
- *The sin of locality:* Errors due to semilocal approximations to an adiabatic XC kernel, i.e., properties that require nonlocality in $\mathbf{r} - \mathbf{r}'$.
- *The sin of forgetfulness:* Phenomena missing when the adiabatic approximation is made, i.e., properties that require nonlocality in time, i.e., memory.
- *The sin of the wave function:* Even if the exact functional is used, solution of the TDKS equations only yields the TDKS noninteracting wave function. The true wave function may differ so dramatically from the KS wave function that observables evaluated on the latter may be inaccurate.

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

From the fluctuation-dissipation theorem:

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

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

- 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.