Excited states methods: Review

Can be derived by considering linear response of time-dependent approximate ground-state w.f.:

HF→TD-HF → RR-TD-HF (RPA/CIS)
CCSD → LR-CCSD (same as EOM-CCSD)
CCSDT → LR-CCSDT (same as EOM-CCSDT)

Additional approximations:
EOM-CCSD > CIS(D) or CIS(2) or CC2
EOM-CCSDT > CC3 ....

Similar approach can be applied to DFT:
DFT→ (real-time) TDDFT → (linear-response) TDDFT (RPA or TDA)
Excited states methods: Review

In all approaches:
1. w.f. is described as linear combination of excited determinants;
2. Amplitudes are found from diagonalizing some matrix related to the Hamiltonain

Example: EOM-CCSD

\[ R\Phi_0 = (R_0 + R_1 + R_2)\Phi_0 \]

\[ = r_0\Phi_0 + \sum_{ia} r_i^a \Phi_i^a + \frac{1}{4} \sum_{ijab} r_{ij}^{ab} \Phi_{ij}^{ab} + \ldots \]

\[ \overline{HR\Phi_0} = ER\Phi_0 \]

\[ \overline{H} = \exp(-T)H \exp(T) \]
Excited states methods: Review

Methods applicable to large molecules:

W.F.
1. CIS (RPA): $N^5$, singles only. Diagonaize $H$ in the basis of singly excited det-s.
   $\Psi_{\text{CIS}} = \sum_{ia} c_i^a \Phi_i^a(r)$
   $AX = \omega X$
   $A_{ia,jb} = (\epsilon_a - \epsilon_i) \delta_{ij} \delta_{ab} + (ia||jb)$

2. CIS(D): $N^6$, CIS + perturbative account of doubles. SOS-CIS(D): $N^5$, very fast!

DFT:
1. TD-DFT: $N^5$. Just like CIS, only that Kohn-Sham Hamiltonian is used.

Recommended reading: Dreuw, Head-Gordon; Chem. Rev. 105 4009 (2005)
Excited states methods: Different flavors of LR

**Figure 1.** Schematic sketch of the relation between Hartree–Fock (HF) and density functional theory (DFT), time-dependent Hartree–Fock and time-dependent DFT (TDDFT), and configuration interaction singles (CIS) and the Tamm–Dancoff approximation to TDDFT (TDA).
TD-DFT: Success stories and limitations

1. Remarkable improvement over CIS (for valence states, typical errors are 0.2 eV).

2. Inexpensive!

3. Different meaning of amplitudes (we do not have w.f., we have change in density).


5. No doubly-excited states; problems with bond-breaking and conical intersections.
Different types of excited states: Valence, Rydberg, and charge-transfer

Figure 2. Schematic sketch of a typical valence-excited state, in which the transition occurs on one of the individual molecules, that is, the orbitals $i, j$ and $a, b$ are located on the same molecule in contrast to a charge-transfer excited state in which an electron is transferred from orbital $i$ on molecule A to orbital $a$ on molecule B. When the molecules A and B are spatially separated from each other the orbitals $i$ and $j$ do not overlap with $a$ and $b$. 
Figure 3. Comparison of the long-range behavior of the lowest CT excited state of an ethylene–tetrafluoroethylene dimer along the intermolecular separation coordinate computed with TDDFT employing the SVWN (black), LB94 (red), B3LYP (green), and “half-and-half” (blue) functionals with the curve obtained at the CIS (brown) level. The excitation energy of the lowest CT state at 4 Å is set to zero.
Origin of artifactual states in TD-DFT

Excitation energy, eV

\[ \Delta \varepsilon \]

\[ \Delta E \]

\[ \varepsilon \]

\[ \varepsilon \text{ HOMO} \]

\[ \varepsilon \text{ E } (f_L > 0.1) \]
KS orbital energies (Koopmans) versus deltaE

![Graph showing deviation from experiment for various methods, including BNL*, BNL Koop, HF, HF Koop, LSDA, LSDA Koop, B3LYP, B3LYP Koop, SAOP, and KS.]
KS orbital energies (Koopmans) vs. \( \delta E \)

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- IP-CISD
- \( \omega B97X-D/6-311+G(df,pd) \)
- \( M06-2X/6-311+G(df,pd) \)
- \( B3LYP/6-311+G(df,pd) \)

Tuesday, November 27, 2012
TD-DFT: Range-separated functionals

Range-separated (aka long-range corrected aka Coulomb-attenuated) functionals reduce SIE, improve Koopmans IEs, and, consequently, improve excited states.

\[
\frac{1}{r_{12}} = \frac{1 - \text{erf}(\mu r_{12})}{r_{12}} + \frac{\text{erf}(\mu r_{12})}{r_{12}}
\]