

A QUANTUM LEAP INTO THE FUTURE OF CHEMISTRY

Calculations of Excited States and Various Electronic Spectra with Q-Chem

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Excited states

- 1. Excited states: What are they?
- 2. Excited-state methods in Q-Chem: From basic to advanced methods.
- 3. EOM-CC family.
- 4. Excited state properties and wave-function analysis.
- 5. Examples:
 - Excited states of formaldehyde (TD-DFT);
 - Excited states of formaldehyde (EOM-EE);
 - 2PA of butadiene (EOM-EE);
 - Core-level states of formaldehyde (CVS-EOM-IP/EE);
 - Singlet-triplet gap in methylene (EOM-SF);
 - Open-shell states by EOM-EA and EOM-DEA.





 $H\Psi_L = E_L\Psi_L$ L=0: ground state, L>0: excited states.

For non-interacting electrons, excited states are just excited determinants and the excitation energies are orbital energy differences



For interacting electrons: Need to include configuration interaction

The simplest approach: configuration interaction singles (CIS) $\Psi_{ex} = \Sigma_{ia} C_i^a \Phi_i^a$



WFT

- 1. Perform SCF calculations: find Hartree-Fock orbitals.
- Φ_0 : zero-order w.f. for the ground state.
- 2. Include correlation (MP2,
- CCSD,...): improve zero-order wave function.
- 3. Excited states: diagonalize H/ effective H:
- Hartree-Fock-> single excitations only (CIS)
- Correlated methods (CC): larger

space.

DFT

- 1. Perform SCF calculations with V_{xc} : find Kohn-Sham orbitals. Φ_0 : correlated density for the ground state.
- 2. Excited states: diagonalize Kohn-Sham H in the space of singles.

In both schemes excited states are described as linear combinations of **excited determinants**



Excited states in Q-Chem

- CIS: Hartree-Fock ground state; Single excitations from HF wfn.
 TD-DFT: Kohn-Sham ground state; Excited states are single excitations from the KS determinant.
- 3. CIS(D) and SOS-CIS(D).
- 4. EOM-CCSD: CCSD for the ground state and single and double excitations for the excited states.
- 5. ADC methods.
- 6. Other methods: RASCI-SF, Delta-E, C-DFT, CASSCF, etc.
- 7. Properties and excited-state analysis; effect of the environment.
- 8. Special extensions:
- Methods for open-shell species: radicals, diradicals, etc (EOM-EA/ DEA/IP/SF);
- Core-level states by using core-level separation (CVS-EOM, CVS-ADC);
 - Metastable states (resonances) by using CAPs and CBFs.



CIS and TD-DFT

- Very inexpensive, give good quality zero-order wfns.
 CIS(D) and SOS-CIS(D): good accuracy in many cases, can be used for very large molecules (similar to CC2 and ADC(2)).
 TD-DFT: Remarkable improvement over CIS (for valence states, typical errors are 0.2 eV).
- 4. TD-DFT: Different meaning of amplitudes (we do not have w.f., we have change in density).
- 5. Failures of DFT: Rydberg states, charge-transfer states. Also, artificial states often appear (LRCs provide a solution).
- 6. CIS and TD-DFT: No doubly-excited states; problems with bond-breaking and conical intersections between ground and excited states (SF approach provides a solution).

$$\Psi_{CIS} = \sum_{ia} c_i^a \Phi_i^a$$





- Choose functional and basis.
- Specify of number of excited states to solve for.
- May request calculations of state and transition dipoles between excited states (CIS_MOM and STS_MOM).
- For wave-function analysis: (STATE_ANALYSIS).
- To perform optimization of frequency, need to specify which state to optimize (CIS_STATE_DERIV).

Excited states of formaldehyde (TD-DFT) example illustrates these points.



$\Psi = \operatorname{Re}^T \Phi_0$ T: satisfies CCSD equations for the reference

EOM-CC theory

$$R\Phi_{0} = (R_{0} + R_{1} + R_{2})\Phi_{0}$$

= $r_{0}\Phi_{0} + \sum_{ia} r_{i}^{a}\Phi_{i}^{a} + \frac{1}{4}\sum_{ijab} r_{ij}^{ab}\Phi_{ij}^{ab} + \frac{1}{4}\sum_{ijab} r_{ij}^{ab}\Phi_{ij}^{ab}$
$$\overline{H}R\Phi_{0} = ER\Phi_{0}$$

$$\overline{H} = \exp(-T)H\exp(T)$$

Specific EOM-CC model: -choice of excitation level in T & R; -choice of the reference and type of R.





CONTRACTOR How to set up EOM-CCSD CALLANTUM LEAP INTO THE FUTURE OF CHEMISTRY

- Decide which EOM model you need and set your <u>reference</u> state appropriately (charge and multiplicity in \$molecule).
- Specify type and number of <u>target</u> states:
- EE_STATES, IP_STATES, EA_STATES, SF_STATES
- Core-level states CVS_EE_STATES, (freeze the core appropriately!)
- Mind the symmetry!
- Mind the basis (diffuse functions, uncontracted bases)
- If properties/gradients required: specify which EOM state you need properties for (or between which EOM states you want to compute transition properties).
- Performance-related keywords: MEM_TOTAL, FNO, use RI (AUX_BASIS) or CD (CD_THRESH), CC_BACKEND (VM, XM).

HITO THE FUTURE OF CHEMISTRY Analysis of excited-state calculations

- 1. Determine spin-coupling (singlet or triplet), either from the amplitudes or from $\langle S^2 \rangle$.
- 2. Determine symmetry of the state (note symmetry of the state may not be the same as symmetry of the transition).
- 3. Look at dominant amplitudes. Which orbitals are involved? What is their character?
- 4. More rigorous methods: natural transition orbitals, Dyson orbitals.
- 5. Compute states' and interstate properties (need to specify in the input what you want).
- 6. Always look at the output and learn how to read it.
- Provided solutions to exercises illustrate these points.



- Valence, local excitations
- Rydberg states
- Charge-transfer states
- Mixed character
- Plasmons (collective excitations)
- Core-level states

Look at dominant amplitudes. Which orbitals are involved? What is their character?



Types of excited states



Core-level states



Various core-level spectra can be modeled using core-valence separation (CVS) extension of EOM-CC methods



Excited-state analysis

1. Can compute and visualize NTOs, densities, attachmentdetachment densities, spin densities, average particle-hole separation, and more.

2. Common set of tools for TD-DFT, CIS, EOM, ADC, and RAS-CI methods.



Invoke with 'state_analysis=true' Visualization: Jmol, Gabedit ...

Plasser, Krylov, Dreuw, libwfa: Wavefunction analysis tools for excited and open-shell electronic states, WIRES Comp. Mol. Sci. e1595 (2022); Krylov, From orbitals to observables and back, JCP **153** 080901 (2020).



• Gradients: CIS, TDDFT, EOM-CCSD

- Frequencies: CIS and TDDFT
- State dipole moments/transition dipole moments: All methods
- SOCs: EOM-CCSD and CVS-EOM-CCSD, (SF) TD-DFT/CIS, RAS-CI

Excited-state properties

- NACs: (SF) CIS, (SF) TD-DFT, EOM-CCSD
- 2PA: ADC, EOM-CCSD
- ECD and OR: ADC, EOM-CCSD
- XECD, X2PA: EOM-CCSD
- RIXS: ADC, EOM-CCSD
- Dyson orbitals: (CVS)-EOM-CC, ADC

See manual









- Excited-state calculations follow hierarchy of methods starting from CIS
- Excited states are described by some type of linear expansion of excited configurations from a ground-state wave-function
- EOM-CCSD methods are based on coupled-cluster ansatz
- Different types of states can be accessed by different EOM methods
- Core-level states are accessible by CVS-EOM-CC
- Methods for metastable states (resonances) are available
- Broad variety of state and interstate properties are available
- NTOs and Dyson orbitals provide rigorous MO picture of excited/ionized states

$$\Psi = \operatorname{Re}^{T} \Phi_{0}$$





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- 2. Dreuw, Head-Gordon, Single-reference ab initio methods for the calculation of excited states of large molecules, Chem. Rev. **105** 4009 (2005).
- 3. Krylov, Equation-of-motion coupled-cluster methods for electronically excited and open-shell species: The hitchhikers guide to Fock space, Ann. Rev. Phys. Chem. **59** 433 (2008).
- 4. Krylov, From orbitals to observables and back, J. Chem. Phys. **153** 080901 (2020).
- 5. Jagau, Bravaya, Krylov, Extending quantum chemistry of bound states to electronic resonances, Ann. Rev. Phys. Chem. **68** 525 (2017)
- 5. Webinars on Q-Chem website, Q-Chem manual.





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- 6. Open-shell states by EOM-EA and EOM-DEA.
- Download the structures from the provided link
- Lecture slides, inputs, outputs, and summaries are also available for download