Contributions from the Krylov group for a new Q-Chem release

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I am not sure the EOM methods were properly advertised in the last release, so I will go over these important features again.

1 EOM-XX-CCSD suit of methods

Q-Chem features the most complete set of EOM-CCSD models that enables accurate, robust, and efficient calculations of electronically excited states (EOM-EE-CCSD); ground and excited states of diradicals and triradicals (EOM-SF-CCSD, available only in Q-Chem); ionization potentials and electron attachment energies as well as problematic doublet radicals, cation- or anion- radicals, (EOM-IP/EA-CCSD). Conceptually, EOM is very similar to configuration interaction (CI): target EOM states are found by diagonalizing the so-called similarity transformed Hamiltonian $\bar{H} = e^{-T} H e^{T}$:

$$\bar{H} R = E R, \tag{1}$$

where T and R are general excitation operators with respect to the reference determinant $|\Phi_0>$. In the EOM-CCSD models, T and R are truncated at single and double excitations, and the amplitudes T satisfy the CC equations for the reference state $|\Phi_0>$:

$$\begin{aligned} &< \Phi_i^a | \bar{H} | \Phi_0 > \\ &< \Phi_{ij}^{ab} | \bar{H} | \Phi_0 > \end{aligned} \tag{2}$$

The computational scaling of EOM-CCSD and CISD methods is identical, i.e., N^6, however EOM-CCSD is numerically superior to CISD because correlation effects are "folded in" in the transformed Hamiltonian, and because EOM-CCSD is rigorously size-extensive.

By combining different types of excitation operators and references $|\Phi_0>$, different groups of target states can be accessed as explained in Fig. 1. For example, electronically excited states can be described when the reference $|\Phi_0>$ corresponds to the ground state wave function, and operators R conserve the number of electrons and a total spin[1]. In the ionized/electron attached EOM models[2, 3], operators R are not electron conserving (i.e., include different number of creation and annihilation operators) — these models can accurately treat ground and excited states of doublet radicals and some other other open-shell systems. For example, singly ionized EOM methods, i.e., EOM-IP-CCSD and EOM-EA-CCSD, have proven very useful for doublet radicals whose theoretical treatment is often plagued by symmetry breaking. Finally, the EOM-SF method[4, 5] in which the excitation operators include spin-flip allows one to access diradicals, triradicals, and bond-breaking.

Q-Chem featuers EOM-EE/SF/IP/EA-CCSD methods for both closed and open-shell references (RHF/UHF/ROHF), including frozen core/virtual options. All EOM models take the full advantage of molecular point group symmetry. Analytic gradients are available for RHF and UHF references.0 Properties calculations (permanent and transition dipole moments, $< S^2 >$, etc) are also available. The current implementation of the EOM-XX-CCSD methods enables calculations of medium-size molecules, e.g., up to 10-14 heavy atoms.

2 Analytic gradients for the CCSD and EOM-XX-CCSD methods

Analytic gradients are available for the CCSD and all EOM-CCSD methods for both closed- and open-shell referneces (UHF and RHF only), including frozen core/virtuals functionality[6].

Practical computational studies of spectroscopic and dynamical properties usually focus on stationary points of PESs and thus require energy derivatives. For example, first derivatives allow one to characterize molecular equilibrium geometries, transition structures, and to calculate minimum energy paths and intrinsic reaction coordinates. In principle, derivatives of any

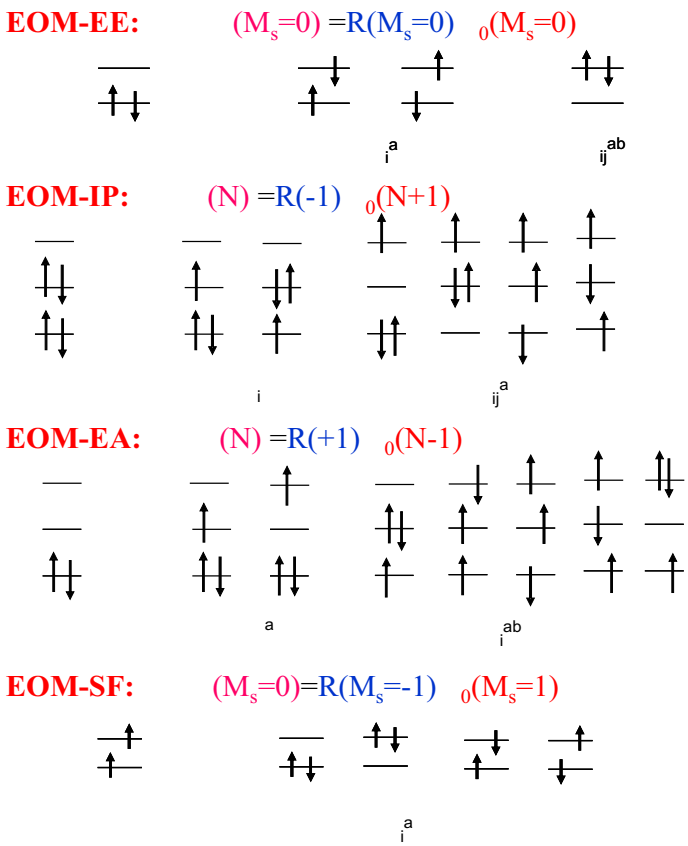

Figure 1: In the EOM formalism, target states Ψ are described as excitations from a reference state Ψ_0: $\Psi = R\Psi_0$, where R is a general excitation operator. Different EOM models are defined by choosing the reference and the form of the operator R. In the EOM models for electronically excitated states (EOM-EE, upper panel), the reference is the closed-shell ground state Hartree-Fock determinant, and the operator R conserves the number of α and β electrons. Note that two-configurational open-shell singlets can be correctly described by EOM-EE since both leading determinants appear as single electron excitations. The second and third panels present the EOM-IP/EA models. The reference states for EOM-IP/EA are determinants for $N+1/N-1$ electron states, and the excitation operator R is ionizing or electron-attaching, respectively. Note that both the EOM-IP and EOM-EA sets of determinants are spin-complete and balanced w.r.t. the target multi-configurational ground and excited states of doublet radicals. Finally, the EOM-SF method (the lowest panel) employs the hight-spin triplet state as a reference, and the operator R includes spin-flip, i.e., does not conserve the number of α and β electrons. All the determinants present in the target low-spin states appear as single excitations which ensures their balanced treatment both in the limit of large and small HOMO-LUMO gaps.

order can be computed numerically from total energies by a finite difference procedure. Since such calculations require only total energies, they can be performed for any electronic structure method. However, this universality of the numerical derivatives is their only advantage. The numerical evaluation of energy gradient for a system with N degrees of freedom requires

at least $2N$ single point energy calculations. Moreover, the finite difference procedure often encounters numerical problems, such as poor convergence, numerical noise, etc. Calculation of analytic gradients is free of numerical instabilities, and can be performed approximately at a cost of a single point energy calculation, which results in significant time savings for polyatomic molecules.

Application limit: same as for the single-point CCSD or EOM-CCSD calculations.

Limitations: ROHF-CCSD and ROHF-EOM-CCSD gradients are not yet available.

3 Properties

For direct comparisons with experiments, calculation of molecular properties is extremely important. For the CCSD and EOM-CCSD wave functions, Q-Chem currently can calculate permanent and transiotion dipole moments, oscillator strengths, and $< S^2 >$ values. Interface of the CCSD and EOM-CCSD codes with the NBO package is also availablee.

4 Recent success stories

The following recent works demonstrate the power of the EOM-SF-CCSD method and efectivness of the Q-Chem implementatrion: series of triradical papers from Krylov group (check out the Angewandte Chemie cover!) [7, 8, 9], and state-of-the art studies of diradicals[10, 11, 12].

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