Multireference Equation of Motion Coupled Cluster: a Transform & Diagonalize approach to Electronic Structure

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The novel Multireference Equation-of-Motion Coupled-Cluster approaches provide versatile and accurate access to a large number of electronic states. The methods proceed by a sequence of many-body similarity transformations and a subsequent diagonalization of the transformed Hamiltonian over a compact subspace. The transformed Hamiltonian is a connected entity and preserves spin- and spatial symmetry properties of the original Hamiltonian, but is no longer Hermitean. The final diagonalization spaces are defined in terms of a complete active space (CAS) and limited excitations (1h, 1p, 2h …) out of the CAS. The methods are invariant to rotations of orbitals within their respective subspaces (inactive, active, external). Applications to first row transition metal atoms (Cr, Mn and Fe) yield results for up to 524 electronic states (for Cr) with an RMS error compared to experiment of about 0.05 eV. The accuracy of the MREOM family of methods is closely related to its favorable extensivity properties. Further examples and prospects of MREOM-CC will be discussed.