Quadratically-Convergent Orbital-Optimized Coupled-Cluster Doubles Method (QC-OD) and Orbital-Optimized Second-Order Möller-Plesset Perturbation Theory [QC-OMP2]

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We present an efficient, quadratically convergent algorithm for variational optimization of the molecular orbitals (MOs) for the coupled-cluster doubles (CCD) method and second-order Möller-Plesset perturbation (MP2) theory. Explicit equations for response density matrices, generalized-Fock matrix (thus the MO gradient), and the MO Hessian are reported both in spin-orbital and closed-shell spin-adapted forms. The Newton-Raphson algorithm is used for the optimization procedure using the MO gradient and Hessian. Further, orbital stability analyses are also carried out at correlated levels. Our quadratically-convergent orbital-optimized CCD (QC-OD) and MP2 [QC-OMP2] approaches are compared with the standard MP2, CCD, CCSD, and CCSD(T) methods. All these methods are applied to symmetry-breaking problem in O\textsubscript{4}$^+$ molecule. Application to O\textsubscript{4}$^+$ demonstrates the utility of orbital-optimized methods in symmetry breaking cases. Applications to H\textsubscript{2}O, C\textsubscript{2}, N\textsubscript{2}, and F\textsubscript{2} molecules demonstrate that the CCSD and QC-OD methods give nearly identical results in stable cases. However, orbital-optimized based methods (QC-OD and QC-OMP2) have certain advantages. They obey the Hellmann-Feynman theorem for orbital rotation parameters. Therefore, there is no need for orbital response terms in the evaluation of analytic gradients. The computation of one-electron properties are easier because there is no response contributions to the particle density matrices. Another advantage is that the variational optimized orbitals can be readily extended to allow inactive orbitals. Thus, frozen occupied and frozen virtual approximations can be incorporated to the CCD wave function [1-4]. Additionally, orbital-optimized coupled-cluster avoids spurious second-order poles in its response function, and its transition dipol moments are gauge invariant [5, 6].

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