Implications of systematic theoretical improvements in the formulation of spin-adapted state-specific multireference coupled cluster theories

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Abstract:

The Unitary Group Adaptation (UGA) offers a very compact and efficient spin adaptation strategy for any spin-free Hamiltonian in a many body framework. Our use of UGA in the context of state-specific Jeziorski-Monkhorst (JM) Ansatz based multireference coupled cluster (MRCC) theory obviates the non-commutativity between the spin-free cluster operators via a normal ordered exponential parametrization in the wave operator. The previous formulation of UGA-SSMRCC had employed sufficiency conditions to reach the final working equations, which cannot be improved systematically. In this talk I will present a more rigorous formulation which follows from an exact factorization of the unlinked terms of the Bloch equation, resulting in equations on which a hierarchy of approximations can be systematically performed on the emergent additional terms. A comparison between the earlier and current formulations will be shown via both a theoretical analysis of such additional terms and a numerical demonstration of the dramatic effect they have with an increase in the number of singly occupied active orbitals in the model space functions. We will illustrate this via example results for such spectroscopic energy differences as ionization potential (IP), electron affinity (EA) and excitation energy (EE) as well as potential energy curves (PECs) to indicate the effect of the additional terms brought in by the factorization.