Unitary Group Adapted Approach to Spin-free Multi-Reference Coupled Cluster Theories: Formalisms and Applications

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In this talk, we will discuss the formulations and implementations of a suite of State-Specific (SS) and State-Universal (SU) Multi-reference Coupled Cluster (MRCC) theories, which are explicitly unitary group-adapted (UGA) and are spin-free. We will refer to all of them generically as UGA-SSMRCC and UGA-SUMRCC respectively. We will discuss briefly three distinct Ansatze for the wave operator: (a) a new multi-exponential cluster Ansatz, analogous to but different from, the one suggested by Jeziorski and Monkhorst (JM), (b) a partially contracted variant of (a), where the all-inactive double excitations are treated in an internally contracted manner, and (c) a completely internally contracted trategy (ic-MRCC). Unlike the JM Ansatz, our choice in (a) involves spin-free unitary generators for the cluster operators and we replace the traditional exponential structure for the wave-operator by a suitable normal ordered exponential. This Ansatz leads to fully spin-free finite power series structure of the 'direct term' of the MRCC equations. The UGA-SUMRCC and UGA-SSMRCC equations both follow from projection equations onto virtual functions reached from every model function. For the UGA-SUMRCC formalism, there are no redundancies for the cluster amplitudes, while the UGA-SSMRCC requires suitable sufficiency conditions to arrive at a well-defined set of equations for the cluster amplitudes. The UGA-SUMRCC and UGA-SSMRCC equations are manifestly connected and hence size-extensive. In the variant (b), the number of cluster amplitudes gets drastically reduced by internal contraction of the all-inactive cluster amplitudes for the doubles. The method (c) will be discussed to indicate the efficacy of using generalized normal ordered (GNO) representation of the cluster operators, and the manifest extensivity and orbital invariance following there from. The variants (a) and (b) will be exemplified by typical applications which will cover core ionization potentials and core-excited states. For the UGA-SSMRCC method, the effect of localization and size-consistency will also be demonstrated. Depending on the progress made, we will also present results for the method (c).