State-specific Multi-reference Coupled Cluster Formalisms: An Overview of a Suite of Recent Developments

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In this talk, I will present an overview of some of the recent developments in State-specific Multi-reference (SS-MR) many-body formalisms. The overarching theoretical framework is the use of the Jeziorski-Monkhorst (JM) cluster ansatz for the state-specific (SS) wave operator acting on a linear combination of model functions spanning a complete active space (CAS). The JM ansatz, when used in the context of the SS formalism, induces the "redundancy problem" of the number of cluster amplitudes which exceeds the number of combining coefficients of the virtual functions present in the target state. By imposing two desirable features, from the formalism, viz. the avoidance of intruders and the maintenance of size-extensivity, essentially unique sufficiency conditions resolving the redundancy can be found. I will give a survey of not only the parent formalism (the State-specific MRCC) but also will discuss an approximant where an **I**nternally **C**ontracted treatment of the **I**nactive (**ICI)** is done to reduce the number of the most numerous amplitudes. Numerical performance of the various methods will be illustrated by example applications to challenging prototypical systems, with pronounced and varied multi-reference character. In particular, I will highlight the following insights gained from the applications (1) the parent SS-MRCC theory in the usual CCSD truncation undermines the importance of coupling of virtual functions which are doubly excited with respect to another, thereby posing both slowness of convergence of the solutions and of somewhat poor performance; (2) an extended hierarchy of truncation schemes, viz. the SS-MRCCSDt/CCSDtq, with the t/q having the same meaning as in the Adamowicz SR-MR Ansatz allows the leading missing virtual couplings and it performs very well; (3) the SS-MRCCSD scheme, with localized orbitals obtained from individual transformations on the core, active and virtual orbitals, performs spectacularly well, presumably because the vastly reduced importance of the doubles-quadruples virtual couplings; (4) the ICID-MRCCSD, with the internally contracted treatment of the inactive double excitations perform nearly as well as the parent SS-MRCCSD. The finding (3) indicates the potential importance of the SS-MRCCSD method to treat large systems in a 'local correlation' framework. The finding (4) implies that essentially the same accuracy as the parent theory can be attained if the inactive doubles are treated in a contracted manner.