Partially Internally Contracted Unitary Group Adapted State Specific Multi Reference Coupled Cluster Theory: Formulation and Pilot Numerical Implementations

Debalina Sinha, Rahul Maitra and Debashis Mukherjee
Raman Center for Atomic, Molecular and Optical Sciences,
Indian Association for the Cultivation of Science,
Jadavpur, Kolkata,
India

In this talk, I will discuss the development and the first numerical implementations of a partially Internally Contracted version of the Mukherjee Unitary Group Adapted State-Specific Multi-Reference Coupled Cluster Theory (UGA-SSMRCC). The UGA-SSMRCC uses the Ansatz: \[ \Psi = \sum_{\mu} \{\exp(T_{\mu}) \Phi_{\mu} \ c_{\mu} \} \], where \{..\} denotes the normal ordering with respect to the core, \( T_{\mu} \)s are the cluster operators written in terms of unitary generators, and \( C_{\mu} \)s are the coefficients accompanying \( \Phi_{\mu} \). Because of the large number of cluster amplitudes \( \{T_{\mu}\} \), it is always fruitful to look for suitable Ansatz which leads to reduction of cluster amplitudes. Of course, it is important not to sacrifice the accuracy very much. One way to attempt such a reduction is to treat the inactive double excitations \( T_{12} \) as \( \mu \)-independent for a CSF. We note that the \( T_{12} \) amplitudes are the most numerous and should logically be the first set that needs to be contracted. We call this theory as the Unitary Group Adapted SSMRCC with Internally Contracted treatment for the Inactive Doubles (UGA-ICID). The Ansatz for this theory is \[ \Psi = \exp(T_{12}) \sum_{\mu} \{\exp(T_{\mu}) \Phi_{\mu} \ c_{\mu} \} . \] It will be shown that this formalism is size-extensive and it captures the effect of coupling between different model functions in a more complete way for the inactive doubles cluster amplitudes. For its implementation, we have made use of an Automatic Program Generation (APG) strategy using a Generalized Tensor Contraction Engine (TCE) developed by us. APG involves generation of the expressions for the working equations followed by the generation of the program. The efficacy of spin-adaptation is shown by comparing our results with those of spinorbital based SSMRCC theory for non-singlet states. The pilot numerical results will be shown to illustrate the efficiency of our formulation. It will be demonstrated that the same numerical accuracy can be achieved at a lesser computational cost compared to UGA-SSMRCC.

References:
