

Hierarchies of local coupled-cluster truncations

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We present a hierarchy of local approximations to complete active space self-consistent field model (CASSCF) in an active space of one active orbital per active electron, based on the valence orbital-optimized coupled-cluster (VOO-CC) formalism. Following the perfect pairing (PP) model, which is exact for a single electron pair and extensive, and the perfect quadruples (PQ) model, which is exact for two pairs, we introduce the perfect hexuples (PH) model, which is exact for three pairs. PH is an approximation to the VOO-CC method truncated at hexuples containing all correlations between three electron pairs. While VOO-CCDTQ56 requires computational effort scaling with the 14th power of molecular size, PH requires only 6th power effort. Our implementation also introduces some techniques which reduce the scaling to fifth order, and has been applied to active spaces roughly twice the size of the CASSCF limit without any symmetry. Because PH explicitly correlates up to six electrons at a time, it can faithfully model the static correlations of molecules with up to triple bonds in a size-consistent fashion and for organic reactions usually reproduces CASSCF with chemical accuracy. The convergence of the PP, PQ, PH hierarchy is demonstrated on a variety of examples including symmetry breaking in benzene, the Cope rearrangement, the Bergman reaction and the dissociation of fluorine.

Paired, active-space treatments of static correlation are used to produce a hierarchy of parsimonious and efficient cluster truncations which are shown to accurately provide the total energy of several strongly correlated problems. The number of parameters introduced in these models grow with system size in a tractable way; between cubic for the models built on PP and fifth-order for the models built on PH. An implementation of the methods is compared to benchmark results for F_2 and H_2O dissociation problems, the H_4 and H_8 model systems, and the insertion of beryllium into hydrogen. In the cases examined even the quartic number of parameters introduced by PQSD are able to provide results which meaningfully improve on CCSD and compete with similar alternatives. These models demonstrate the simplicity, accuracy and compactness offered by orbital-optimized coupled cluster models (OO-CC).