Ring Coupled Cluster Doubles at the Multireference Level

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Ring approximation within the internally contracted multireference (MR) coupled cluster (CC) framework of Mukherjee et al.[1] is worked out and tested. Derivation of the equations is based on generalized normal ordering and applies the corresponding generalized Wick-theorem. Contractions among cluster operators is avoided by adopting a normal ordered exponential Ansatz.
The MR ring CCD (MR rCCD) amplitude equations[2] show kinship, but are not equivalent with the extended random phase approximation (ERPA) based energy correction scheme, put forward by Pernal[3]. Original version of MR rCCD equations are presently amended with proper treatment of redundancy among double excitations. In the original formulation, huge number of cumulant contractions has been cut back by (i) the ring approximation and by (ii) restricting maximal cumulant rank at two. We find the latter approximation inappropriate. Equations are presently expanded with terms involving cumulants up to rank four.
Application of a generalized valence bond type reference function ensures a fragment structure of cumulants: nonzero elements appear with all indices assigned to the same bond. As a consequence, cumulant involving terms remain less expensive than their solely pair-contracted counterpart.
As compared with ERPA based energy correction, the advantage of MR rCCD lies with the availability of the wavefunction and its potential to abandon the need of filtering excitations allowed to enter the Ansatz.
Pilot applications are presented for torsional potentials and on examples of covalent bond breaking.

References

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