

Quasi-Variational Coupled Cluster Theory

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A modification is presented of the variational configuration interaction functional in the first-order interacting space for molecular electronic structure. The modified functional is a fully-linked expression, that by construction is extensive and invariant to transformations of the underlying orbital basis, and is exact for an ensemble of separated 2-electron subsystems. The method is then extended by including additional terms in the functional that can be computed with $O(N^6)$ work, and which make it agree at low order with variational coupled-cluster with double excitations (VCCD). The effect of single excitations is then introduced through variational optimization of orbitals, and this Quasi-Variational Coupled Cluster Doubles (OQVCCD) method demonstrates accuracy that exceeds that of the standard coupled-cluster (CCSD) method, in particular in situations where the reference Slater determinant is not a good approximation.

We then enhance OQVCCD by augmenting it with the standard perturbative (T) correction for the effects of connected triple excitations, and apply this method to several systems in order to benchmark its performance. When there is no qualitative difference between CCSD and OQVCCD, the corresponding methods including the triples corrections also perform similarly. However, the OQVCCD(T) ansatz is demonstrated to be outstandingly robust and accurate in the description of the breaking of multiple chemical bonds, where traditional CCSD and CCSD(T) completely fail, yet with a computational cost that is nearly the same as that of CCSD(T). The results presented provide insight into the failure of CCSD(T) and related methods for such systems, and establish the validity of the new method that can replace it.

A further extension generalises the use of the functional to a multiconfigurational reference wavefunction.

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