

Approximate 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). This method demonstrates accuracy that exceeds that of the standard Slater coupled-cluster (CCD) method, in particular in situations where the reference Slater determinant is not a good approximation.

We also discuss the inclusion of the effect of single orbital excitations, either through minimisation of the approximate VCCD functional with respect to the orbitals, or through an explicit generalisation of the functional to approximate VCCSD.

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

[1] P. J. Knowles and B. Cooper, *J. Chem. Phys.*, 133 (2010) 224106