

# A Proposed Coupled-Cluster Wavefunction Diagnostic Based Upon Density Matrices

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There exist several techniques in the electronic structure community to address the degree of nondynamical correlation for a chosen molecule within a particular correlation method. Popular choices include the  $T_1$  [1] and  $T_2$  diagnostics whereby the Euclidean norm of the  $T_1$  vector of the coupled-cluster wavefunction or the largest  $T_2$  amplitude in a CCSD calculation are examined, respectively. Monitoring both will detect several problematic cases [2], however, a certain degree of ambiguity persists in these diagnostics. Here, we present the results of a new potential diagnostic – specifically the degree of asymmetry in the single-particle density matrix – which will vanish in the full CI limit but persists in standard coupled-cluster calculations (due to the fact that the coupled-cluster method is an intrinsically non-hermitian theory). Results are given for several small molecules and the potential of using this to assess the quality of coupled-cluster calculations is discussed.

## References

- [1] T.J. Lee and P.R. Taylor, *Int. J. Quantum Chem. Symp.* S23, 199 (1989).
- [2] U.R. Fogueri, S. Kozuch, A. Karton, and J.M.L. Martin, *Theor. Chem. Acc.* 132, 1291 (2013).