

Multireference Coupled-Cluster Benchmark for Transition Metal Molecules: Comparison with Experimental Data and Assessment of Standard Coupled-Cluster and Kohn–Sham DFT

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Abstract: We present Coupled-Cluster (CC) and Kohn–Sham Density Functional Theory (DFT) calculations of dissociation energies (D_e), equilibrium bond distances (R_e), and harmonic vibrational constants (ω_e) for 60 diatomic molecules containing 3d, 4d, and 5d transition metals and compare to experimental data. To arrive at accurate benchmark values, we employ a CC based composite approach with basis set extrapolation, inclusion of core-valence correlation, and corrections for relativistic and multireference effects. The latter correction was obtained from internally contracted multireference Coupled-Cluster (icMRCC) theory. In accordance with previous studies on a subset of molecules[1-3], we find that multireference corrections are rather small in many cases and CCSD(T) can provide accurate reference values, if the complete basis set limit is explored. In addition, the multireference correction improves the results in cases where CCSD(T) is not a good approximation. For a few cases, however, strong deviations from experiment persist, which cannot be explained by the remaining error in the computational approach. We suggest that these experimentally derived values require careful revision. We also tested ten DFT functionals for the molecules in the present data set against experimental and calculated reference values.

Key-words: CCSD(T), MRCC, ab initio, transition metals, DFT

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