

Tackling the Static Correlation Challenge with the Δ NO Method

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The static correlation challenge, which results due to the degeneracy of molecular orbitals in a system, is still a significant obstacle to electronic structure methods. This work investigates hydrogen clusters in arrangements with particularly significant amounts of static correlation using a cumulant functional theory, Δ NO. Analysis of the performance of Δ NO in conjunction with the on-top dynamic correlation functionals: Colle--Salvetti (CS) and opposite-spin exponential-cusp and Fermi-hole correction (OF), shows that it performs better than functionals that describe systems with a multi-reference and also single-reference wave function. The potential energy surfaces (PESs) of H3 and H4 clusters are analyzed and compared to B3LYP, CCSD(T), and full CI. The H3 dissociation curve computed using Δ NO is near exact. Among the challenging systems, is the H4 cluster and its rectangle (D2h) to square (D4h) geometry transition, which appears as a cusp in energy at $\theta = 90^\circ$ on the PES for methods with an inadequate description of static correlation. The vicinity of the cusp region is the challenging part of the system, not only quantitatively but also qualitatively. The dissociation curve of square H4 (D4h) is also computed where Δ NO calculated energies are comparable to full CI energies. The Δ NO method effectively describes not only the linear hydrogen systems but also the H4 D2h/D4h transition, and produces a cusp-free PES with adequate description of occupancies.