

Title: Affordable and Accurate Transition Metal Spin State Energetics via MC-PDFT Using tPBE with High Local Exchange

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Abstract: The spin energetics of transition metal complexes are important for a variety of applications, but most available methods require compromising between accuracy and affordability. In this work, spin splittings of several iron complexes were studied with multiconfigurational pair-density functional theory (MC-PDFT), a method that inexpensively includes full correlation without distinguishing between core and valence, and compared to previously published complete active space second-order perturbation theory (CASPT2) and CASPT2 with coupled-cluster semi-core correlation (CASPT2/CC) results. In contrast to the high-spin bias of CASPT2 with respect to the CASPT2/CC reference, MC-PDFT with the tPBE on-top functional in its original form exhibits a low-spin bias which can be largely corrected by modifying the exchange and correlation contributions to the on-top density functional using high local exchange (tPBE-HLE). This first application of tPBE-HLE to transition metal excitation energies has a mean unsigned deviation (MUD) from CASPT2/CC of only 5.07 kcal/mol, which is competitive with the CASPT2 MUD of 3.33 kcal/mol. Moreover, tPBE-HLE accurately predicts most experimental ground states, while CASPT2 incorrectly predicts high-spin ground states in all cases. MC-PDFT also demonstrates a performance advantage over CASPT2-based methods, with tPBE being faster than CASPT2 by a factor of 50 in a moderately-sized example.