

DFT Functionals Simultaneously Targeting Fractional Charge and Spin Challenges

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ABSTRACT

This presentation highlights the development of novel exchange-correlation functionals, specifically ω LH23tdE and ω LH23tdP, which are range-separated local hybrids.¹ These functionals escape to a significant extent the usual zero-sum-game between small fractional charge errors (related to self-interaction or delocalization errors) and small fractional spin errors (related to static correlation errors). Their unique design and incorporation of both strong-correlation and delocalization error corrections make them particularly effective in calculations of problematic transition metal open-shell systems, at the computational cost of the underlying ω LH22t functional. A key aspect of the work is the meticulous tailoring of the exact-exchange admixture by the modulation of local mixing functions (LMF), which enhances the versatility of KS-DFT calculations across a wide spectrum of systems. The application of these functionals to the hyperfine couplings and spin-symmetry breaking of a set of open-shell mononuclear manganese complexes demonstrates the effectiveness of these approaches, and we anticipate functionals like ω LH23tdE and ω LH23tdP to become important tools in transition-metal chemistry, as well as for composite systems where fractional charge and fractional spin errors may be particularly important in different parts.

References

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- [2] Wodyński, A.; Lauw, B.; Reimann, M.; Kaupp, M. Spin-symmetry breaking and hyperfine couplings in transition-metal complexes revisited using density functionals based on the exact-exchange energy density. *J. Chem. Theory Comput.* **2024**. DOI: 10.1021/acs.jctc.3c01422.