Capturing static correlation using a new DFT+U-type functional

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Current state of the art Density Functional Theory plus Hubbard U (DFT+U) type functionals [1] offer an imperfect correction to the notorious Many-Electron Self-Interaction Error (MSIE) that affects standard DFT calculations. Traditional DFT+U type functionals are derived from the Hubbard model and it is merely fortuitous that the method offers a partial correction to MSIE. DFT+U also fails to account for Static Correlation Error, and can even increase it. We present a new DFT+U type functional [2] which is explicitly derived to enforce the flat plane condition [3], on localised subspaces. The new functional yields near exact quantum mechanical total energies for the dissociated molecular dimers: H_2, He_2^+, Li_2 and Be_2^+. This shows that a semi-local exchange-correlation functional equipped with a flat-plane correction, with first-principles parameters only, can capture strong static correlation effects in the total energy under certain conditions. We also report the existence of another systematic error, termed Asymmetric-MSIE. The new functional successfully ameliorates Asymmetric-MSIE in the triplet H_5^+ ring, the smallest stringent test system for this error.

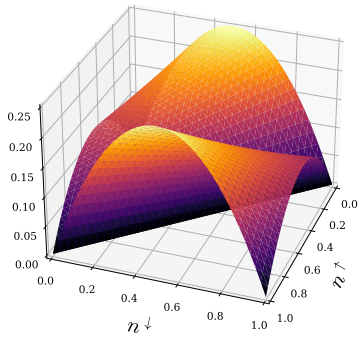

Figure 1: Sum of the Symmetric-MSIE & Asymmetric-MSIE corrections for an s-orbital subspace.

[1] S. L. Dudarev et al. "Electron-Energy-Loss Spectra and the Structural Stability of Nickel Oxide: An LSDA+U Study". In: *Phys. Rev. B* 57.3 (Jan. 1998), pp. 1505–1509. DOI: 10.1103/PhysRevB.57.1505.

[2] Andrew C. Burgess, Edward Linscott, and David D. O'Regan. "DFT+U-Type Functional Derived to Explicitly Address the Flat Plane Condition". In: *Phys. Rev. B* 107.12 (Mar. 2023), p. L121115. DOI: 10.1103/PhysRevB.107.L121115.

[3] Paula Mori-Sánchez, Aron J. Cohen, and Weitao Yang. "Discontinuous Nature of the Exchange-Correlation Functional in Strongly Correlated Systems". In: *Phys. Rev. Lett.* 102.6 (Feb. 2009), p. 066403. DOI: 10.1103/PhysRevLett.102.066403.