In situ correction of self-interaction & static correlation errors

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ABSTRACT

Approximate exchange-correlation (XC) functionals are known to break the piecewise linearity condition with respect to electron count [1] and the constancy condition with respect to magnetisation [2] causing many-electron self interaction error (MSIE) and static correlation error (SCE), respectively. We derive a DFT+U type functional directly from the flat-condition [3], and prove its uniqueness. For selected subspaces, this can mitigate both MSIE and SCE using corrective parameters evaluated in situ using the spin-indexed minimum-tracking linear response method [4].

The corrective functional 'BLOR' yields near exact total energies for dissociated s-block dimers, systems which prototypically suffer from significant MSIE and SCE, with relative errors in the total energy below 0.6%. Uncorrected PBE and PBE+U (using the widely-used Dudarev 1998 Hubbard functional) yield relative energetic errors as high as 8.0% and 20.5%, respectively. The new corrective functional also yields near exact total energies for the triplet H_5^+ ring, a stringent non KS-degenerate test system where MSIE, SIE and a newly-classified error, termed asymmetric-MSIE, are active.

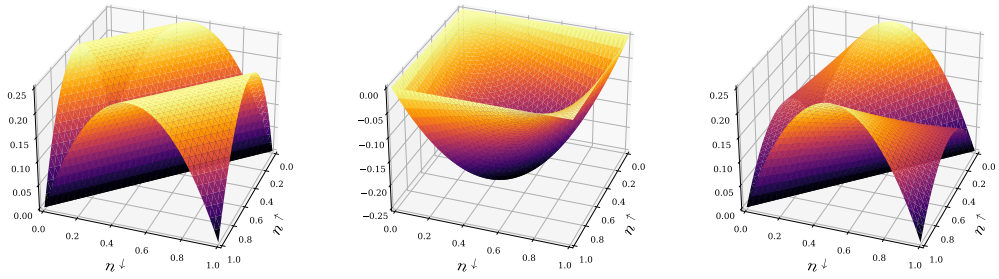

Fig.1: Spin-occupancy dependent terms in the flat-plane derived DFT+U like energy functional BLOR for (left) symmetric-only MSIE, (middle) SCE, and (right) all MSIE.

References

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