Gauge-problem free local hybrid functionals without calibration function

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ABSTRACT

In local hybrid functionals (local hybrids), the exact-exchange (EXX) admixture is position-dependent and is governed by a so-called local mixing function (LMF). [1] Despite an overall success of local hybrids, a mismatch between EXX and (semi)local (SL) energy *densities* (gauge problem) gives rise to a number of artifacts, such as (i) non-physical (too high) Pauli repulsions that affect non-covalent interactions; (ii) not enough negative (or even positive) energy contributions from the term which is loosely associated with the non-dynamical correlation (NDC); etc. In practice, these problems can be reduced significantly by adding calibration functions (whose integral over three-dimensional space vanishes) to the difference of SL and EXX energy densities, $e_{\mathrm{x}}^{\mathrm{sl}}(\mathbf{r}) - e_{\mathrm{x}}^{\mathrm{exact}}(\mathbf{r})$.

In this work we introduce a very simple and physically intuitive LMF ("x-LMF") which is an analytical function of the ratio $e_{\mathrm{x}}^{\mathrm{exact}}(\mathbf{r}) / e_{\mathrm{x}}^{\mathrm{sl}}(\mathbf{r})$. By construction, our x-LMF efficiently suppresses spurious positive energy-density contributions associated with the NDC. Indeed, the resulting functional does not appear to require addition of a calibration function, as monitored by the potential-energy curves of noble-gas dimers.

The performance of new local hybrids based on such LMFs for ground-state properties (evaluated over the full GMTKN55 database [2]) are comparable to that of the recent efficient LH20t functional [3] that *does* include a calibration function.

References

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