Toward Doubly Local Double Hybrid Functionals Using Neural-Network Local Mixing Functions

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The first optimization and evaluation of "doubly local double hybrid" (DLDH) functionals is reported. DLDHs provide a position-dependent mixing not only of exact and semi-local exchange but at the same time also of second-order perturbational (PT2) and semi-local correlation. Both admixtures are governed by local mixing functions (LMFs) in coordinate space. The LMFs have been trained as neural networks, where the correlation LMF is either trained independently or fixed during training to the square of the exchange LMF (DL^2DH variant). Training and evaluation has been done for different combinations of W4-17 atomization-energy and BH76 barrier test sets with the Slim16 or Slim20 subset of the large GMTKN55 benchmark suite. Comparison is also made to local double hybrids exhibiting constant PT2 admixtures and to local hybrids, trained in the same way, and an application to the argon-benzene dissociation curve is provided. As training-set choices are currently limited by the availability of only an inefficient implementation of the PT2 energy density, this work serves as an initial evaluation of feasibility before implementing more efficient versions. Graphical comparisons of differently trained LMFs for both exchange and correlation provide appreciable insights into the function of DLDHs. Interestingly, we find that the best training runs make the addition of empirical dispersion corrections obsolete for optimum performance for either the Slim16 or Slim20 subsets. This can be traced to very large values of the correlation LMFs in spatial regions where noncovalent interactions originate. This observation indicates possible advantages of position-dependent PT2 admixtures in DLDHs, while the position-dependent exchange admixture offers the potential for subsequent inclusion of strong-correlation effects.

References

[1] Kovacs, Śmiga, Kaupp, Wodynski, J. Chem. Theory Comput. (2026) 22 (7): 3268–3281.