

Measuring the Myopia of Molecules

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It has long been known the electronic correlation is an inherently short-range phenomenon. This effect has enabled the rousing success of localized electronic structure methods of many different flavors. As an alternative to localization, one can attempt a global factorization of electronic interactions via the electron repulsion integrals and/or the wavefunction itself. One example is the tensor hypercontraction approximation of Hohenstein et al., in particular the least-squares variant (LS-THC) which achieves great simplicity by adopting a molecular “integration” grid. In our work, we have found that the LS-THC method has a particular blind spot for the doubles amplitudes, and neglects important electron correlation effects. We have developed an extension of standard LS-THC which augments the grid with new basis functions which explicitly address such pairwise correlations. Interestingly, we find that we can also use these basis functions to directly measure the spatial properties of electron correlation, including inter-electron distance and angular dependence.