Understanding Adiabatic Connection Models performance in the context of density variations.

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ABSTRACT

We have analyzed[1] the performance of a few Adiabatic Connection Integrand Interpolation (ACII) methods (e.g., ISI, SPL, genISI2[2]) using several choices of orbitals and eigenvalues to feed their energy expression. These quantities have been obtained from self-consistent field calculations, i.e., HF, KS-DFT, and Wu-Yang[3] inversion method, taking the HF, MP2, and CCSD density matrixes as a starting point. Our data are analyzed by means of density- and functional-driven errors decomposition, taking as a reference the nearly exact set of Kohn-Sham orbitals and eigenvalues obtained from the CCSD(T) relaxed density matrix. In our analysis we consider the total, reaction, and binding energies as well as strongly correlated systems such as Hook's atom and stretched H_2.

The error decomposition demonstrates that the performance of ACII functionals is greatly hindered by significant functional-driven error which can be controlled by a proper choice of reference orbitals and eigenvalues that feed their energy expression. The analysis also reveals a clear path to improve this type of approximation.

References

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[3] Wu, Yang, *J.Chem.Phys.*118, 2498-2509 (2003)