Regional DMET—Efficient and Accurate Single-Fragment Embedding of Wave Functions in Kohn-Sham DFT

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Abstract:
We present Regional DMET, a simple wave function-in-wave function embedding technique, based on the density matrix embedding theory (DMET)[1]. Unlike the original DMET, Regional DMET is aimed at treating only a single fragment of interest of a larger system with a high-level correlated wave function, and retains the mean-field description of the rest of the system. This single-fragment focus allows large simplications of both the embedding theory and its implementation. Additionally, we show how the large computational basis sets required for accurate dynamical correlation treatments can be handled consistently and efficiently by defining the fragmentation in terms of intrinsic atomic orbitals (IAOs)[2], and local fragment virtual spaces. We also show how Kohn-Sham SCF wave functions can be used to define the full-system mean-field, instead of Hartree-Fock. Regional DMET retains DMET's ability to cut through covalent bonds (i.e., to form arbitrary fragmentations of molecules), and offers accurate embedding calculations at a cost of only one regular mean-field SCF wave function calculation on the full system, and a correlated fragment calculation with nearly the same computational cost as performing the calculation on only the fragment's atoms (in empty space), with the same basis set. The technique is shown to be highly accurate in various chemical reactions, and in the determination of properties of some transition metal complexes.

1. G. Knizia, G. K.-L. Chan, *"Density Matrix Embedding: A Strong-Coupling Quantum Embedding Theory"* J. Chem. Theory Comput. 9, pp 1428–1432 (2013), http://dx.doi.org/10.1021/ct301044e
2. G. Knizia, *"Intrinsic Atomic Orbitals: An Unbiased Bridge between Quantum Theory and Chemical Concepts"* J. Chem. Theory Comput. 9, pp 4834–4843 (2013), http://dx.doi.org/10.1021/ct400687b