Challenges in orbital localization for orthonormal molecular orbitals

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Local orthonormal occupied and virtual Hartree–Fock (HF) orbitals are of interest in the area of local correlation methods, where the goal is to use a local description to express local physical effects. Until recently, local virtual HF orbitals could not be obtained due to inadequacies of the optimization algorithms used. It has been shown that by using a trust-region algorithm for the optimization of localization functions, both local occupied and local virtual HF orbitals may be obtained. Different localization schemes, e.g., Pipek–Mezey, Boys and powers of the second (PSM) and fourth (PFM) moments give orbitals with different characteristics in terms of the spatial locality of the bulk and tails of the orbitals. In particular, PSM minimization targets to reduce the bulk extent of the orbitals, while PFM minimization targets to reduce the thickness of the orbital tails. The effects of bulk and tail locality are explored from a local correlation method point of view. The orthogonality requirement for the molecular orbitals imposes a constraint on the locality through the orbital tails. The locality analysis is therefore extended to explore the non-orthogonal atomic orbitals and projected atomic orbitals, and orthogonalized atomic orbitals.