Use of Edmiston-Ruedenberg and Fermi-Löwdin Orbitals in Orbital-Based Quantum Theories

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The goal of deriving localized-orbitals as a means for describing transferable bonding orbitals or for more efficiently describing electronic correlation has a long history. Much of the inspiration in this area arose from a seminal paper by Edmiston and Ruedenberg[1] that derived localized orbitals based upon minimization of the mutual exchange energy, and which were observed to exhibit features that match ideas about chemical bonding. Until recently such energy-localized orbitals have been determined in both self-interaction-corrected density functional (methods and multi-configurational self-consistent (MCSDF) methods, using the Jacobi-based determination of unitary matrices, originally suggested in Ref. [1]. For example, many authors, including Ref [2-3], have used such techniques to rigorously minimize density-functional energies based upon the so-call localization equation[2] and complex extensions[3] that have been corrected for self-interaction error through the use of orbital-dependent corrections. In contrast to the use of such methods for qualitatively understanding chemical bonding, an issue that arises in both self-interaction-corrected formulations and in MCSCF methods is that the resulting unitary transformation between localized and canonical orbitals that leads to a variational expression for the total energy also leads to energy expressions that violate size extensivity. To address this issue, a new way to construct energy-localized orbitals based on Fermi-Löwdin Orbitals was introduced[4]. These localized orbitals depend on a quasi-classical electronic geometry, the Fermi exchange hole, and Löwdin’s method of symmetric orthogonalization. In applications to date, the orbitals are explicitly real and unsurprisingly bear a strikingly similar resemblance to the energy localized-orbitals due to Edmiston and Ruedenberg. Recent discussions about such orbitals have questioned (1) whether the constraint of real rather than complex[3] orbitals associated with the original FL formulation is a limiting factor for their use in density functional theory and (2) whether the original methods based upon the localization equations[2] are in fact equivalent to the Fermi-Löwdin orbitals[4].

In this talk I will introduce a new formulation for complex Fermi-Löwdin orbitals and provide initial applications to simple molecules, address recent commentary[5] about the possibility of equivalence to earlier localization schemes, and discuss the possible use of the Fermi-Löwdin construction as a means for attaining size-extensivity in multi-configurational formulations.

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