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Self-Interaction Corrected Density Functional Approximations with Unitary Invariance: Applications to Molecules

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For a system of 2N electrons, the Fermi-hole may be interpreted as the square of a normalized "Fermi orbital", $F(\mathbf{a}) \equiv \rho_\sigma(\mathbf{a},\mathbf{r})/\sqrt{\rho_\sigma(\mathbf{a})}$. This normalized orbital captures all of the spin density at its position of definition, or descriptor, $(\mathbf{a})$. Given a set of N quasi-classical electronic positions $(\mathbf{a_i})$ and a spin density-matrix composed of N Kohn-Sham orbitals, the resulting set of Fermi orbitals may then be used to construct a set of localized Loewdin-orthonormalized orbitals[1]. These orbitals are explicitly a functional of the spin density and are related to the Kohn-Sham orbitals by a unitary transformation that is parametrically dependent on the set quasi-classical electronic descriptors. The construction of such localized orbitals allows for the restoration of unitary invariance into the original Perdew-Zunger self-interaction correction[2,3] and provides a possible simplification compared to the localization-equation based solution of self-interaction corrected functionals[4]. This talk will discuss the construction of this Fermi-orbital-based self-interaction corrected method and the minimization algorithm that relies upon analytical derivatives[3] of the self-interaction energy with respect to the Fermi-orbital descriptors. Recent applications to a large set of molecules including aromatic molecules, molecules with open transition-metal centers, and molecules with frustrated Kekule' structures will be discussed. Initial applications indicate improvements in atomization energies of pi-bonded systems and demonstrate the desired downward shift of orbital energies relative to their Kohn-Sham counterparts. [1]W.L.Luken and D.N. Beratan, Theo. Chim. Acta **61**, 265-281 (1982). [2]M.R. Pederson, A. Ruzsinszky and J. P. Perdew, J. Chem. Phys. **140**, 121103 (2014). [3]M.R. Pederson and T. Baruah, Advance in Atomic, Molecular and Optical Physics **64**, 153-180 (2015). [4]M. R. Pederson, R. A. Heaton, and C. C. Lin, J. Chem. Phys. **80**, 1972 (1984).