

Löwdin Orthonormalized Fermi Orbitals for Self-Interaction-Corrected Density-Functional Approximations with Unitary Invariance

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An approach for implementing the self-interaction correction (SIC) to density-functional approximations and recovering an asymptotically exact effective potential is due to Perdew and Zunger and dates back to 1981. However the explicit orbital dependence, or alternatively unitary non-invariance, associated with this formulation leads to large increases in computational costs due to the need to solve the localization equations for SIC[1] and also leads to an energy expression that is not size extensive. In recent work[2] a size-extensive unitarily invariant reformulation of the self-interaction correction has been introduced which proceeds through the construction of energy-localized orthonormal orbitals that are referred to as Fermi-Löwdin Orbitals. Such orbitals depend on first constructing normalized “Fermi orbitals” which are explicitly dependent on a single-particle density matrix but depend parametrically on a set of quasi-classical electronic positions or descriptors. When orthogonalized via Löwdin’s method of symmetric orthonormalization, the formalism allows for the derivation of an $N \times N$ unitary matrix that depends explicitly on the density matrix and $3N$ classical electronic descriptors. Thus for any set of Kohn-Sham orbitals, the self-interaction energy is reduced to a function of $3N$ electronic positions that can be minimized using standard gradient methods[3]. An overview on applications to small molecules[2], medium sized molecules[4] and metal porphyrins[5] will be presented. These results suggest that binding energies may be improved[2] and that HOMO/LUMO gaps are increased relative to their Kohn-Sham counterparts[2-4]. Recent work on the description of metal centers in porphyrins will be discussed.

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