

Local spin in the 3D analysis: single determinant and correlated case

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The concept of local spin is routinely used in transition metal chemistry and needed for the description of the nature of the spin-spin interactions in polynuclear clusters. In recent years, there has been an increasing interest in recovering local spins from ab initio wavefunctions. In 2001 Clark and Davidson¹ proposed a general framework for a proper definition of local spin operators. For closed-shell in the single determinant case the expected value of the squared atomic spin operator is 3/8 of Mayer's atomic valence and the diatomic spin terms are -3/8 of the respective Mayer bond order. Hence, within this framework significant local spin contributions are obtained for genuine closed-shell diamagnetic molecular systems.

Later, Mayer² proposed an alternative partitioning of the of the expectation value of the total spin-squared operator in terms of atomic and diatomic contributions in the framework of the so-called Hilbert-space analysis. This alternative definition of local spins differentiates between a covalent molecule and an antiferromagnetic system in which the spins are coupled as a singlet.

We present here the generalization of the formulation proposed by Mayer for single-determinant and correlated wavefunctions in the framework of the 3D-space analysis. We have implemented different atomic partitions within the 3D analysis, namely Bader's 'Atoms in Molecules' disjoint domains and several fuzzy atom definitions including the latest Hirshfeld-Iterative scheme.

We report results for local spin components of several systems of particular interest such as polyradical organic molecules and transition complexes with multiple metal centers. The local spin states determined conform with physical expectations.

1. Clark, A. E.; Davison, E. R. *J. Chem.Phys.* **115**, 7382 (2001)

2. Mayer, I. *Chem. Phys. Lett.* **440**, 357 (2007)