Characterization and quantification of polyradical character

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The decomposition of $\langle \hat{S}^2 \rangle$ into atomic and diatomic contributions (local spin analysis) is used to detect and quantify the polyradical character of molecular systems. The behavior of several indices for diradical character is tested for a simple model diradical. The advantages of using descriptors derived from the local spin analysis is illustrated with more involved examples including complex dissociation profiles and prototypical diradical systems such as trimethylenethane. A model triradical system is also studied in detail and the local spin analysis is used to distinguish several patterns of spin distributions that can be found for different electronic states. How close a real molecular system is to an ideal system of k perfectly localized spin centers is utilized to define a measure of its k-radical character. The spin properties and triradical character of the lowest-lying electronic states of a number of all σ, all π and σ–π organic triradicals is discussed in detail. The local spin contributions exhibit good correlation with experimental triradical stabilization energies.

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