

Comparative analysis of local spin definitions

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This work provides a survey of the definition of electron spin as a local property and its dependence on several parameters in actual calculations. We analyze one-determinant wave functions constructed from Hartree-Fock and, in particular, from Kohn-Sham orbitals within the collinear approach to electron spin. The scalar total spin operators \hat{S}^2 and \hat{S}_z are partitioned by projection operators, as introduced by Clark and Davidson, in order to obtain local spin operators $\hat{S}_A \cdot \hat{S}_B$ and \hat{S}_{zA} , respectively. To complement the work of Davidson and co-workers, we analyze some features of local spins which have not yet been discussed in sufficient depth. The dependence of local spin on the choice of basis set, density functional, and projector is studied. We also discuss the results of \hat{S}_z partitioning and show that $\langle \hat{S}_{zA} \rangle$ values depend less on these parameters than $\langle \hat{S}_A \cdot \hat{S}_B \rangle$ values. Furthermore, we demonstrate that for small organic test molecules, a partitioning of \hat{S}_z with preorthogonalized Löwdin projectors yields nearly the same results as one obtains using atoms-in-molecules projectors. In addition, the physical significance of nonzero $\langle \hat{S}_A \cdot \hat{S}_B \rangle$ values for closed-shell molecules is investigated. It is shown that due to this problem, $\langle \hat{S}_A \cdot \hat{S}_B \rangle$ values are useful for calculations of relative spin values, but not for absolute local spins, where $\langle \hat{S}_{zA} \rangle$ values appear to be better suited. © 2005 American Institute of Physics. [DOI: 10.1063/1.1829050]

I. INTRODUCTION

Local properties, that is properties of atoms or functional groups in molecules, have always been an important concept to chemists, since it makes an abstract molecular wave function interpretable in terms of intuitive building blocks. The best-known example of local properties are partial charges (see the comparative review by Meister and Schwarz¹ and also Ref. 2), but in principle, any molecular property may be distributed among any set of subsystems of a molecule in order to gain information which guides qualitative understanding of chemical processes.^{3,4} Assigning portions of the total molecular electron spin to individual atoms (or groups of atoms), for example, is necessary for predicting electronic spin-spin coupling constants within the Heisenberg spin-ladder model. Such local decomposition schemes have a long history and range from Bader's atoms-in-molecules theory⁵ to most recent developments in Car-Parrinello molecular dynamics based on local orbitals.⁶ Recently, Clark and Davidson have proposed a rigorous definition of local electron spins using projection operators onto local basins,⁷⁻⁹ which might also be called partial spins in analogy to partial charges based on population analyses. For local spin, as for all local properties, a proper definition of an atom in a molecule is required. It is common knowledge that the definition and the properties of atoms in molecules cannot be deduced from first principles of quantum mechanics, but require additional postulates and are thus defined somewhat arbitrarily. A vast amount of literature has been written on this subject, mostly in the context of population analyses.^{5,10-15} In this work, we shift the definition of atoms in molecules to the

definition of local projection operators as, for instance, proposed by Davidson,¹² and as applied to local electron spin by Clark and Davidson.¹⁶ The aim of this work is to study those aspects of local spin which have not yet been addressed in the work of Davidson and collaborators. These aspects range from purely formal points such as local spin in closed-shell molecules to purely practical points like the dependence on the size of the atom-centered basis set.

We will work within the collinear approach to electron spin, which means that the same quantization axis is used for all spin operators, so that information on *spin* can be extracted from *spatial* orbitals. From a puristic point of view, the underlying physics would be reflected better by a description of electron spin within a noncollinear framework. What makes the collinear approach interesting is that most quantum chemistry programs work within this (nonrelativistic) framework for the sake of lower computational cost. Furthermore, we restrict this study to single-determinant wave functions, constructed from Hartree-Fock (HF) or Kohn-Sham (KS) orbitals. However, the results may be easily transferred to multideterminant wave functions.

This paper is organized as follows: In Sec. II, the definition of local basins by projection operators is outlined and the explicit form of Mulliken, Löwdin, preorthogonalized Löwdin and Bader's atoms-in-molecules projectors is given. In Sec. III, partitioning of the total spin expectation values $\langle \hat{S}^2 \rangle$ and $\langle \hat{S}_z \rangle$ is discussed, and the dependence of local spins on the choice of the projector, the basis set, and the orbitals from which the wave function is constructed is investigated for some small test molecules. The results are summarized in Sec. IV. The computational methodology is outlined in the Appendix.

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II. DEFINITION OF THE LOCAL BASINS

Local basins A in a molecule can be defined by local one-electron projection operators \hat{p}_A , which have to fulfill two conditions:

(1). The sum of all projectors must be equal to the identity operator,

$$\sum_A \hat{p}_A = \hat{1}. \quad (1)$$

This makes it possible to multiply $\sum_A \hat{p}_A$ with any operator without changing its expectation value, thus partitioning the operator into local operators.

(2). The p_A should be idempotent and orthogonal,

$$\hat{p}_B \hat{p}_A = \delta_{AB} \hat{p}_A, \quad (2)$$

which reflects the natural requirements that operation of \hat{p}_A on basin A does not change any quantity at A and operation of \hat{p}_B on basin A , which is chosen to have no overlap with basin B , cannot yield contributions to quantities at A .

There is a multitude of ways to define local basins which have been developed for the partitioning of the electron density, i.e., for performing population analyses (see, e.g., Refs. 5 and 10–15), which are in general not formulated in terms of projection operators for historical reasons. The connection between classical population analysis and the projection operator formulation is as follows: The one-electron projectors \hat{p}_A can be summed up to an all-electron projector \hat{P}_A ,

$$\hat{P}_A = \sum_i \hat{p}_A(i). \quad (3)$$

If the one-electron projection operators fulfill condition (1), the sum over the expectation values of all \hat{P}_A will be equal to the total electron number N due to the normalization of the molecular orbitals,

$$\begin{aligned} \sum_A \langle \hat{P}_A \rangle &= \sum_A \sum_i^N \langle i | \hat{p}_A | i \rangle \\ &= \sum_i^N \langle i | \sum_A \hat{p}_A | i \rangle = \sum_i^N \langle i | \hat{1} | i \rangle = N, \end{aligned} \quad (4)$$

where the sum is running over all occupied molecular orbitals (MOs) denoted by i . Then, the partial population N_A of center A can be defined as the expectation value of \hat{P}_A ,

$$N_A = \langle \hat{P}_A \rangle = \sum_i^N \langle i | \hat{p}_A | i \rangle, \quad (5)$$

since the $\langle \hat{P}_A \rangle$ sum up correctly to the total electron number N . In principle, for each population analysis scheme, a projector \hat{p}_A can be defined that yields the corresponding partial population according to Eq. (5). The sum over all all-electron projectors \hat{P}_A is equal to the number operator \hat{N} ,

$$\sum_A \hat{P}_A = \hat{N}. \quad (6)$$

Among others, we employ Mulliken “projectors”¹⁰ in this work, which do not fulfill condition (2). Still, Mulliken

partial populations sum up correctly to the total electron number N . Strictly speaking, Mulliken’s scheme therefore does not define true projection operators, which is the reason why we will use the phrase “Mulliken pseudoprojector” in the following. For several (among other historical) reasons, the Mulliken partitioning scheme is in spite of its formal deficiencies by far the most popular way of performing population analyses. This is why we also use the Mulliken pseudoprojectors, which can be defined in the following way:

$$\hat{p}_A^M = \sum_{\mu \in A, \nu} |\nu\rangle S_{\nu\mu}^{-1} \langle \mu|. \quad (7)$$

Although Eq. (7) looks somewhat unusual because the sum is running over $\mu \in A, \nu$ instead of $\mu \in A, \nu \in A$, this definition ensures that $\langle \hat{p}_A^M \rangle = \sum_i^N \langle i | \hat{p}_A^M | i \rangle$ is equal to the Mulliken population of center A , N_A^M ,

$$\begin{aligned} \langle \hat{p}_A^M \rangle &= \sum_i \langle i | \hat{p}_A^M | i \rangle \\ &= \sum_i \langle i | \sum_{\mu \in A, \nu} |\nu\rangle S_{\nu\mu}^{-1} \langle \mu | i \rangle \\ &= \sum_{i, k, \lambda} \sum_{\mu \in A, \nu} C_{ki}^* C_{\lambda i} S_{\nu\mu}^{-1} S_{k\nu} S_{\mu\lambda} \\ &= \sum_{\mu \in A, \nu} P_{\nu\mu} S_{\nu\mu} = \sum_{\mu \in A} (\mathbf{P}\mathbf{S})_{\mu\mu} = N_A^M. \end{aligned} \quad (8)$$

\mathbf{P} is the (symmetric) density matrix for an unrestricted Slater determinant. The $|\mu\rangle$ are elements of an arbitrary atom-centered basis set with $S_{\mu\nu}$ being the corresponding overlap matrix element. These Mulliken pseudoprojectors are real and not symmetric and thus not Hermitian,

$$\hat{p}_A^{M\dagger} = \sum_{\mu \in A, \nu} \langle \mu |^\dagger S_{\nu\mu}^{-1\dagger} | \nu \rangle^\dagger = \sum_{\mu \in A, \nu} |\mu\rangle S_{\mu\nu}^{-1} \langle \nu| \neq \hat{p}_A^M \quad (9)$$

and will yield non-Hermitean local spin operators. Nonetheless, it is interesting to investigate the performance of such ill-conditioned pseudoprojectors in local spin analyses, and results of the Mulliken partitioning scheme obtained for local spins in this work are compared to two different types of Löwdin projector-based partitioning schemes.¹¹ Since the Löwdin basis is orthonormal, the idempotent Löwdin projectors are given by

$$\hat{p}_A^L = \sum_{\mu' \in A} |\mu'\rangle \langle \mu'|. \quad (10)$$

The $|\mu'\rangle$ are elements of a Löwdin-orthonormalized basis, defined as a linear combination of basis functions $|\nu\rangle$, which are centered at any atom in the molecule,

$$|\mu'\rangle = \sum_{\nu} |\nu\rangle S_{\nu\mu}^{-1/2}. \quad (11)$$

Although a Löwdin basis is in general not atom centered, $\mu' \in A$ denotes the Löwdin-basis functions that appear at the same place in the overlap matrix as the original, atom-centered basis functions located on atom A . According to Clark and Davidson,⁷ before performing the Löwdin orthonormalization, the original basis set has to be orthonormalized within the centers A in order to obtain sensible results. We will denote this approach as Löwdin* and compare its results to those of the “standard” Löwdin analysis. By comparison with the Mulliken results, local spins obtained with Löwdin projectors illustrate the influence of the basis set orthonormalization on local expectation values. For \hat{S}_z partitioning, we will also use projectors \hat{p}_A^{AIM} that project onto atomic basins according to Bader’s atoms-in-molecules (AIM) theory.⁵ These projectors are a conceptually different and thus interesting complement to Mulliken and Löwdin projectors, since they partition the three-dimensional space of Cartesian coordinates instead of the high-dimensional space of one-electron basis functions. Such projectors can formally be written as

$$\hat{p}_A^{\text{AIM}} = \begin{cases} \hat{1} & \text{at all points in space within the AIM basin } A \\ 0 & \text{else} \end{cases}. \quad (12)$$

III. LOCAL SPINS

Apart from the difficulties in defining local basins, “local spin” is not a well-defined concept in quantum chemistry. What we are looking for is a quantity that gives information on the portion of total molecular electron spin located at a certain part of this molecule. In order to characterize this local spin fully, we need local values for the two spin quantum numbers M_S and S . The elegant general idea by Clark and Davidson is now to apply the local projectors as defined above to the two scalar total spin operators \hat{S}^2 and \hat{S}_z ,⁷ since the former gives information on S and the latter on M_S . Both are briefly revisited in the following sections.

A. Partitioning of $\langle \hat{S}^2 \rangle$

Clark and Davidson have used Hermitean one-electron projection operators to partition the \hat{S}^2 operator.⁷ When $\Sigma_A \hat{p}_A = \hat{1}$ is inserted twice into the decomposition of $\hat{S}^2 = \sum_{ij} \hat{s}(i)\hat{s}(j)$, one can define local spin operators that sum up to the total \hat{S}^2 operator,

$$\sum_A \sum_B \hat{S}_A \cdot \hat{S}_B = \hat{S}^2, \quad (13)$$

with

$$\hat{S}_A \cdot \hat{S}_B = \sum_{ij}^{NN} \hat{p}_A(i) \hat{s}(i) \hat{p}_B(j) \hat{s}(j). \quad (14)$$

These projectors can be separated into a one- and a two-electron part, which are then evaluated separately, using $\hat{p}_A \hat{p}_B = \delta_{AB} \hat{p}_A$. For wave functions which consist of a single Slater determinant, the expectation value $\langle \hat{S}_A \cdot \hat{S}_B \rangle$ is given by sums of products of projector matrix elements in a basis of molecular orbitals,

$$\begin{aligned} \langle \hat{S}_A \cdot \hat{S}_B \rangle &= \frac{3}{4} \delta_{AB} \left[\sum_i^{N^\alpha} \langle i | \hat{p}_A | i \rangle + \sum_{\bar{i}}^{N^\beta} \langle \bar{i} | \hat{p}_A | \bar{i} \rangle \right] \\ &+ \frac{1}{4} \sum_{ij}^{N^\alpha N^\alpha} \langle i | \hat{p}_A | i \rangle \langle j | \hat{p}_B | j \rangle + \frac{1}{4} \sum_{\bar{i}\bar{j}}^{N^\beta N^\beta} \langle \bar{i} | \hat{p}_A | \bar{i} \rangle \langle \bar{j} | \hat{p}_B | \bar{j} \rangle \\ &- \frac{1}{4} \sum_{ij}^{N^\alpha N^\alpha} \langle i | \hat{p}_A | j \rangle \langle j | \hat{p}_B | i \rangle - \frac{1}{4} \sum_{\bar{i}\bar{j}}^{N^\beta N^\beta} \langle \bar{i} | \hat{p}_A | \bar{j} \rangle \langle \bar{j} | \hat{p}_B | \bar{i} \rangle \\ &- \frac{1}{4} \sum_{ij}^{N^\alpha N^\beta} \langle i | \hat{p}_A | i \rangle \langle \bar{j} | \hat{p}_B | \bar{j} \rangle - \frac{1}{4} \sum_{\bar{i}\bar{j}}^{N^\alpha N^\beta} \langle \bar{i} | \hat{p}_B | \bar{i} \rangle \langle j | \hat{p}_A | j \rangle \\ &- \sum_{i\bar{j}}^{N^\alpha N^\beta} \langle i | \hat{p}_A | \bar{j} \rangle \langle \bar{j} | \hat{p}_B | i \rangle. \end{aligned} \quad (15)$$

The first derivation of this equation was given in Ref. 7. The differences between Eq. (15) in this paper and the analogous Eq. (27) in Ref. 7 are obviously due to typing errors in Ref. 7, since our validation calculations based on Eq. (15) on the diatomic test molecules given in Ref. 7 have yielded exactly identical results. A more detailed derivation of Eq. (15) can be found in Ref. 17, although typing errors also affect this equation. In Eq. (22) in Ref. 17, which is the equivalent of Eq. (15) here, the term $-\frac{1}{4} \sum_{i\bar{j}}^{N^\alpha N^\beta} \langle i | \hat{p}_A | i \rangle \langle \bar{j} | \hat{p}_B | \bar{j} \rangle$ is misprinted as $-\frac{1}{4} \sum_{i\bar{j}}^{N^\alpha N^\beta} \langle i | \hat{p}_B | i \rangle \langle \bar{j} | \hat{p}_A | \bar{j} \rangle$. When Löwdin projectors are employed for the \hat{p}_A , one obtains an expression for $\langle \hat{S}_A \cdot \hat{S}_B \rangle$ which is a function of elements of the overlap and the α - and β -density matrix analogous to Eq. (27) in Ref. 17,

$$\begin{aligned} \langle \hat{S}_A \cdot \hat{S}_B \rangle^L &= \frac{3}{4} \delta_{AB} \left[\sum_{\mu \in A} \mathbf{P}_{\mu\mu}^{\alpha'} + \sum_{\mu \in A} \mathbf{P}_{\mu\mu}^{\beta'} \right] \\ &+ \frac{1}{4} \sum_{\mu \in A, \nu \in B} \mathbf{P}_{\mu\mu}^{\alpha'} \mathbf{P}_{\nu\nu}^{\alpha'} + \frac{1}{4} \sum_{\mu \in A, \nu \in B} \mathbf{P}_{\mu\mu}^{\beta'} \mathbf{P}_{\nu\nu}^{\beta'} \\ &- \frac{1}{4} \sum_{\mu \in A, \nu \in B} \mathbf{P}_{\mu\nu}^{\alpha'} \mathbf{P}_{\nu\mu}^{\alpha'} - \frac{1}{4} \sum_{\mu \in A, \nu \in B} \mathbf{P}_{\mu\nu}^{\beta'} \mathbf{P}_{\nu\mu}^{\beta'} \\ &- \frac{1}{4} \sum_{\mu \in A, \nu \in B} \mathbf{P}_{\mu\mu}^{\alpha'} \mathbf{P}_{\nu\nu}^{\beta'} - \frac{1}{4} \sum_{\mu \in A, \nu \in B} \mathbf{P}_{\mu\mu}^{\beta'} \mathbf{P}_{\nu\nu}^{\alpha'} \\ &- \sum_{\mu \in A, \nu \in B} \mathbf{P}_{\mu\nu}^{\alpha'} \mathbf{P}_{\nu\mu}^{\beta'}, \end{aligned} \quad (16)$$

where matrix elements in a Löwdin basis are primed. Constructing $\langle \hat{S}_A \cdot \hat{S}_B \rangle$ according to Eq. (15) with Mulliken “projectors” is, of course, not rigorously correct, since Mulliken pseudoprojectors do not fulfill the projection operator condi-

tions (cf. preceding section) which are used in the derivation of Eq. (15). We recall that Mulliken pseudoprojectors are not Hermitean and yield non-Hermitean local spin operators \hat{S}_A , which do thus not fulfill all conditions necessary for angular

momentum operators. However, since the Mulliken $\langle \hat{S}_A \cdot \hat{S}_B \rangle$ values sum up in good approximation to the total $\langle \hat{S}^2 \rangle$, they are interpreted as local spins and compared to results obtained with Löwdin projectors in this work. One obtains

$$\begin{aligned} \langle \hat{S}_A \cdot \hat{S}_B \rangle^M = & \frac{3}{4} \delta_{AB} \left[\sum_{\mu \in A, \nu \in A} (\mathbf{P}^\alpha \mathbf{S})_{\mu\nu} + \sum_{\mu \in A, \nu \in A} (\mathbf{P}^\beta \mathbf{S})_{\mu\nu} \right] + \frac{1}{4} \sum_{\mu \in A, \nu \in B} (\mathbf{P}^\alpha \mathbf{S})_{\mu\mu} (\mathbf{P}^\alpha \mathbf{S})_{\nu\nu} + \frac{1}{4} \sum_{\mu \in A, \nu \in B} (\mathbf{P}^\beta \mathbf{S})_{\mu\mu} (\mathbf{P}^\beta \mathbf{S})_{\nu\nu} \\ & - \frac{1}{4} \sum_{\mu \in A, \nu \in B} (\mathbf{P}^\alpha \mathbf{S})_{\mu\nu} (\mathbf{P}^\alpha \mathbf{S})_{\nu\mu} - \frac{1}{4} \sum_{\mu \in A, \nu \in B} (\mathbf{P}^\beta \mathbf{S})_{\mu\nu} (\mathbf{P}^\beta \mathbf{S})_{\nu\mu} - \frac{1}{4} \sum_{\mu \in A, \nu \in B} (\mathbf{P}^\alpha \mathbf{S})_{\mu\mu} (\mathbf{P}^\beta \mathbf{S})_{\nu\nu} \\ & - \frac{1}{4} \sum_{\mu \in A, \nu \in B} (\mathbf{P}^\beta \mathbf{S})_{\mu\mu} (\mathbf{P}^\alpha \mathbf{S})_{\nu\nu} - \sum_{\mu \in A, \nu \in B} (\mathbf{P}^\alpha \mathbf{S})_{\mu\nu} (\mathbf{P}^\beta \mathbf{S})_{\nu\mu}, \end{aligned} \quad (17)$$

where $|\mu\rangle, |\nu\rangle, \dots$ is an atom-centered basis.

There are some requirements which $\langle \hat{S}_A \cdot \hat{S}_B \rangle$ should satisfy in order to be physically meaningful. The diagonal terms $\langle \hat{S}_A^2 \rangle$ should give information on the electron spin that is located on a subsystem A , and the cross terms $\langle \hat{S}_A \cdot \hat{S}_B \rangle_{A \neq B}$ should give information on how strongly the electron spin attributed to subsystem A is coupled with the electron spin on subsystem B . Clearly, from this point of view, one expects subsystems (atoms or functional groups) of closed-shell molecules whose wave function is constructed within a restricted MO framework to have local spins $\langle \hat{S}_A^2 \rangle$ and hence $\langle \hat{S}_A \cdot \hat{S}_B \rangle_{A \neq B}$ equal to zero. But in fact, when Eq. (15) is applied to a closed-shell MO wave function, one obtains local spins that are different from zero regardless of the projector chosen. This fact has been mentioned, but not yet been discussed in depth with respect to its physical interpretation in previous work.⁷ A closed-shell Slater determinant is built from pairs of α and β orbitals which share the same spatial one-electron function. Applying this to Eq. (15), we have

$$\begin{aligned} \langle \hat{S}_A \cdot \hat{S}_B \rangle_{\text{closedshell}} &= \frac{3}{2} \delta_{AB} \sum_i^{N/2} \langle i | \hat{p}_A | i \rangle - \frac{3}{2} \sum_{ij}^{N/2} \langle i | \hat{p}_A | j \rangle \langle j | \hat{p}_B | i \rangle. \end{aligned} \quad (18)$$

If the sum were running over a complete set of functions i and j , the completeness relation could be used, and since $\hat{p}_A \hat{p}_B = \delta_{AB} \hat{p}_A$, $\langle \hat{S}_A \cdot \hat{S}_B \rangle_{\text{closedshell}}$ would indeed be equal to zero. However, since occupied MOs do not form a complete basis, Clark and Davidson's closed-shell local spin values can be equal to zero only by accident. Surely, one could argue that in molecules with a closed-shell ground state, one does not necessarily have zero spin on each atom, which would be consistent with a valence bond (VB) description of these molecules. For the sake of clarity, it should be noted that the term "closed-shell" in this work does not refer to molecules with a closed-shell ground state, but rather to their description by a closed-shell restricted one-determinant wave function within a MO framework, without any implications concerning a VB description of these molecules. Surely, a local spin analysis of a VB wave function may give a better

description of the true electronic structure, but from our point of view, a local spin analysis of a closed-shell MO wave function should reflect all the deficiencies/features this MO wave function has in describing a given system. According to Clark and Davidson, $\sum_{ij} \langle i | \hat{p}_A | j \rangle \langle j | \hat{p}_B | i \rangle$ can be regarded as a bond-order contribution that affects the *absolute* energy of several spin states, but not their *relative* energies within a family of spin states.¹⁸ It is therefore possible that this closed-shell inconsistency does not affect the use of $\langle \hat{S}_A \cdot \hat{S}_B \rangle$ values for the description of spin ladders within the Heisenberg spin model, whereas care should be taken when interpreting $\langle \hat{S}_A^2 \rangle$ as an absolute measure for the local spin of a certain subsystem A . In particular, as discussed by Clark and Davidson in Ref. 7, $\langle \hat{S}_A^2 \rangle$ cannot be interpreted as $S_A(S_A + 1)$.

Apart from this conceptual difficulty, the dependence of $\langle \hat{S}_A \cdot \hat{S}_B \rangle$ values on the construction of the wave function and the local projector has not yet been evaluated. This shall be done in the following for one-determinant wave functions, using manganocene as an example. We picked out this particular transition metal complex because it is known that a description of different spin states based on density functional theory (DFT) yields unreliable energetics. Consequently, the wave function (or electron density, respectively) of transition metal complexes can be very sensitive to the choice of the density functional.^{19–21} This is, in particular, the case for the class of complicated cases²⁰ to which thermal crossover complexes such as manganocene belong.

1. Dependence of $\langle \hat{S}_A \cdot \hat{S}_B \rangle$ on the basis set

We optimized high-spin manganocene (staggered conformation) using the B3LYP density functional and analyzed local spins with Löwdin* projectors acting on wave functions constructed with five different basis sets of increasing size, SV(P), TZV, TZVP, and TZVPP (see methodology section in the Appendix). The local spins were calculated for a fixed geometry optimized with B3LYP/TZVP (see also methodology section) in order to exclude the influence of the molecular geometry on local spins for this comparison of basis sets. As test calculations have shown, the local $\langle \hat{S}^2 \rangle$

TABLE I. Local Löwdin* $\langle \hat{S}^2 \rangle$ values and selected atomic populations for high-spin (sextet) manganocene (wave function, B3LYP; geometry optimization, B3LYP/TZVP) for several basis sets. To illustrate a reverse trend of the local spin values with increasing size of the basis set, we include SVP and TZVP results for three diatomics in this table [wave function: B3LYP, geometry: experimental interatomic distances (Ref. 22)]. Local spin results for these diatomics have been previously published by Clark and Davidson for HF/6-31G* in Ref. 7. Local spin values for symmetrically equivalent atoms are virtually identical within the given accuracy. $\langle \hat{S}_{\text{O}}^2 \rangle_{\text{CO}}$ and $-\langle \hat{\mathbf{S}}_{\text{C}} \cdot \hat{\mathbf{S}}_{\text{O}} \rangle_{\text{CO}}$ are equal to $\langle \hat{S}_{\text{C}}^2 \rangle_{\text{CO}}$. Note that CO is an example for nonzero local spins within a closed-shell electronic structure.

Basis set	Manganocene							N_{Mn}	N_{C}	N_{H}
	$\langle \hat{S}_{\text{Mn}}^2 \rangle$	$\langle \hat{S}_{\text{C}}^2 \rangle$	$\langle \hat{S}_{\text{H}}^2 \rangle$	$\langle \hat{\mathbf{S}}_{\text{Mn}} \cdot \hat{\mathbf{S}}_{\text{C}} \rangle$	$\langle \hat{\mathbf{S}}_{\text{C}} \cdot \hat{\mathbf{S}}_{\text{C}} \rangle$	$\langle \hat{\mathbf{S}}_{\text{C}} \cdot \hat{\mathbf{S}}_{\text{H}} \rangle$				
SV(P)	8.91	1.75	0.40	-0.08	-0.52	-0.31		24.69	6.15	0.88
TZV	8.45	1.83	0.40	-0.04	-0.55	-0.28		23.90	6.26	0.85
TZVP	9.03	1.85	0.44	-0.10	-0.53	-0.30		24.75	6.08	0.94
TZVPP	8.66	2.16	0.56	-0.08	-0.56	-0.31		24.20	6.03	1.05
	Carbon monoxide	Dioxygen		Nitric oxide				N_{N}	N_{O}	
	$\langle \hat{S}_{\text{C}}^2 \rangle$	$\langle \hat{S}_{\text{O}}^2 \rangle$	$\langle \hat{\mathbf{S}}_{\text{O1}} \cdot \hat{\mathbf{S}}_{\text{O1}} \rangle$	$\langle \hat{S}_{\text{N}}^2 \rangle$	$\langle \hat{S}_{\text{O}}^2 \rangle$	$\langle \hat{\mathbf{S}}_{\text{N}} \cdot \hat{\mathbf{S}}_{\text{O}} \rangle$				
SVP	1.35	1.60	-0.60	1.60	1.36	-1.10		7.05	7.95	
TZVP	1.44	1.76	-0.74	1.85	1.41	-1.22		6.89	8.11	

values are identical within a range of ± 0.01 a.u. to those in Table I when the geometry is optimized for each basis set. We expect the local $\langle \hat{S}^2 \rangle$ values to converge to a certain limit when the quality of the basis set is increased.

As can be seen from Table I, the local $\langle \hat{S}^2 \rangle$ values do not converge as the basis set is extended. For example, $\langle \hat{S}_{\text{Mn}}^2 \rangle$, $\langle \hat{S}_{\text{C}}^2 \rangle$, and $\langle \hat{S}_{\text{H}}^2 \rangle$ vary within a range of 0.58, 0.41, and 0.16, respectively, which corresponds to 7%, 22%, and 36% of the respective mean $\langle \hat{S}_{\text{A}}^2 \rangle$ value over all basis sets. Whereas no systematic trend can be observed for the central atom and for the cross terms $\langle \hat{\mathbf{S}}_{\text{Mn}} \cdot \hat{\mathbf{S}}_{\text{C}} \rangle$, $\langle \hat{\mathbf{S}}_{\text{C}} \cdot \hat{\mathbf{S}}_{\text{C}} \rangle$, and $\langle \hat{\mathbf{S}}_{\text{C}} \cdot \hat{\mathbf{S}}_{\text{H}} \rangle$, the local spins on the ligand atoms increase systematically when the basis set is extended. On the other hand, we observe that for several diatomic molecules $|\langle \hat{\mathbf{S}}_{\text{A}} \cdot \hat{\mathbf{S}}_{\text{B}} \rangle|$ values are smaller in a TZVP basis than in a SV(P) basis set (see also Table I). Consequently, we conclude that local $\langle \hat{S}^2 \rangle$ values do not depend on the size of the basis set in a systematic way. However, the deviation of local expectation values calculated with various basis sets is often not much larger than about 0.30 a.u., so that the same qualitative results are obtained for all basis sets. For comparison, some partial populations are given in Table I, and it can be observed that their dependence on the basis set is also small, although changes in sign may occur when the reference point is shifted as it is the case when partial charges are calculated from partial populations.

2. Dependence of $\langle \hat{\mathbf{S}}_{\text{A}} \cdot \hat{\mathbf{S}}_{\text{B}} \rangle$ on the density functional

In order to investigate the influence of the type of orbitals from which a single-determinant wave function is constructed, we compare the Löwdin* local $\langle \hat{S}^2 \rangle$ values for a Hartree-Fock wave function and wave functions constructed from Kohn-Sham orbitals using two pure and three hybrid density functionals (see methodology section in the Appendix). For this purpose, we analyze manganocene in three different total spin states ($S = \frac{1}{2}$ (doublet, low spin), $\frac{3}{2}$ (quartet,

intermediate spin), and $\frac{5}{2}$ (sextet, high spin), respectively; note that spin contamination is in most cases negligible (compare also Table II).

In Ref. 7, a similar set of data for unrestricted HF wave functions of the manganese complex $\text{MnCl}_2 (\text{H}_2\text{O})_2$ is given, where the occupation of d orbitals in the initial guess had been modified in such a way that the three degenerate M_S states of the $S = \frac{5}{2}$ state were obtained.²³ We also tested modified initial guesses, but in the case of manganocene, the total energies for $M_S = \frac{1}{2}$ and $M_S = \frac{3}{2}$ did not converge to the energy of the $M_S = \frac{5}{2}$ state. In other words, we could not converge the $(S = \frac{5}{2}, M_S = \{\frac{1}{2}, \frac{3}{2}\})$ states but only the $(S = \frac{1}{2}, M_S = \frac{1}{2})$ and $(S = \frac{3}{2}, M_S = \frac{3}{2})$ states. Since we are mainly interested in the performance of different density functionals for a given state, the nature of this state should not matter as long as it is the same for all functionals. The results in Table II (with the exception of the spin contaminated PBE0 and B3LYP values for $M_S = \frac{1}{2}$) should therefore be significant for our analysis of different method-inherent approximations.

When comparing the results for the three different total spin states in Table II, it can be seen that the $\langle \hat{\mathbf{S}}_{\text{A}} \cdot \hat{\mathbf{S}}_{\text{B}} \rangle$ values for the ligand atoms are unaffected by changes of both the total spin and the density functional. The ligand-to-metal coupling terms $\langle \hat{\mathbf{S}}_{\text{Mn}} \cdot \hat{\mathbf{S}}_{\text{C}} \rangle$ are only slightly affected, while virtually all changes in total spin and density functional are reflected in the local spin at the manganese center $\langle \hat{S}_{\text{Mn}}^2 \rangle$. For example, $\langle \hat{S}_{\text{Mn}}^2 \rangle$ in high-spin manganocene ranges from 9.75 a.u. (HF) to 8.67 a.u. (BLYP), which corresponds to an absolute difference of 1.08 a.u. and a relative difference of 12.5% (with respect to the lower value). As one would expect, no systematic trend can be observed for the dependence of $\langle \hat{\mathbf{S}}_{\text{A}} \cdot \hat{\mathbf{S}}_{\text{B}} \rangle$ values on the density functional, as there is no systematic connection between the different density functionals. The local spin property therefore reflects the general incapability of standard density functionals to describe the energetics and thus the wave function (or electron density,

TABLE II. Löwdin* local $\langle \hat{S}^2 \rangle$ values for manganocene in three different total M_S states for a one-determinant wave function constructed from Hartree-Fock and Kohn-Sham orbitals, respectively, in a TZVP basis with several density functionals (geometry optimization: B3LYP/TZVP, high-spin). Local spin values for symmetrically equivalent atoms are virtually identical within the given accuracy.

M_S	Functional	$\langle \hat{S}_{Mn}^2 \rangle$	$\langle \hat{S}_C^2 \rangle$	$\langle \hat{S}_H^2 \rangle$	$\langle \hat{S}_{Mn} \cdot \hat{S}_C \rangle$	$\langle \hat{S}_C \cdot \hat{S}_C \rangle$	$\langle \hat{S}_C \cdot \hat{S}_H \rangle$	$\langle \hat{S}^2 \rangle$
5/2	HF	9.75	1.85	0.44	-0.13	-0.53	-0.30	8.76
	PBE0	9.20	1.85	0.44	-0.10	-0.53	-0.29	8.76
	B3LYP	9.03	1.85	0.44	-0.10	-0.53	-0.30	8.76
	B3LYP*	8.96	1.85	0.44	-0.10	-0.53	-0.29	8.76
	BP86	8.79	1.86	0.44	-0.09	-0.52	-0.29	8.76
	BLYP	8.67	1.85	0.44	-0.08	-0.52	-0.29	8.76
3/2	HF	5.32	1.85	0.44	-0.15	-0.53	-0.30	3.77
	PBE0	5.50	1.85	0.44	-0.16	-0.52	-0.29	3.84
	B3LYP	5.43	1.85	0.44	-0.16	-0.52	-0.30	3.83
	B3LYP*	5.42	1.85	0.44	-0.16	-0.52	-0.29	3.83
	BP86	5.43	1.86	0.44	-0.16	-0.52	-0.29	3.84
	BLYP	5.33	1.86	0.44	-0.15	-0.52	-0.29	3.83
1/2	HF	2.49	1.84	0.44	-0.17	-0.53	-0.30	0.76
	PBE0	3.35	1.86	0.44	-0.18	-0.52	-0.29	1.66
	B3LYP	2.98	1.85	0.44	-0.19	-0.52	-0.30	1.10
	B3LYP*	2.89	1.86	0.44	-0.20	-0.52	-0.29	0.94
	BP86	2.89	1.86	0.44	-0.21	-0.52	-0.29	0.78
	BLYP	2.86	1.86	0.44	-0.20	-0.52	-0.29	0.77

respectively) of transition metal complexes with sufficient accuracy.^{19–21} This fact has also been observed by other groups for the calculation of exchange coupling constants in Heisenberg spin ladders.^{24,25} As the best relative energies for the different total spin states of manganocene are obtained with B3LYP*,^{19–21} this functional will be used in further investigations on the projector dependence of local $\langle \hat{S}^2 \rangle$ values.

3. Dependence of $\langle \hat{S}_A \cdot \hat{S}_B \rangle$ on the local projector

Having analyzed the dependence of $\langle \hat{S}_A \cdot \hat{S}_B \rangle$ on the basis set and the density functional, we now investigate its dependence on the choice of local projectors. The question is whether an optimum projector can be identified or whether $\langle \hat{S}_A \cdot \hat{S}_B \rangle$ depends on the basis set and density functional more strongly than on the particular projector chosen.

From Table III, it can be understood that local $\langle \hat{S}^2 \rangle$ values depend less on the choice of the projector than on the

basis set and functional. Still, the dependence on the projector is not negligible. The $\langle \hat{S}_{Mn}^2 \rangle$ values for Mulliken and Löwdin* projectors, for example, differ by 0.54 a.u. which corresponds to a relative difference of 6% (with respect to the lower value). In contrast to what has been observed for the dependence of $\langle \hat{S}_A \cdot \hat{S}_B \rangle$ on basis set and density functional, this projector dependence is not only present in the local spin on the metal atom $\langle \hat{S}_{Mn}^2 \rangle$ but also in the local spins on the ligand atoms, $\langle \hat{S}_C^2 \rangle$ and $\langle \hat{S}_H^2 \rangle$, and for the coupling terms $\langle \hat{S}_{Mn} \cdot \hat{S}_C \rangle$, $\langle \hat{S}_C \cdot \hat{S}_C \rangle$, and $\langle \hat{S}_C \cdot \hat{S}_H \rangle$. The values of these quantities increase systematically in the order Mulliken < Löwdin < Löwdin*, except one, $\langle \hat{S}_C \cdot \hat{S}_C \rangle$, whose values decrease in this order. This projector dependence can be expected from what is known about population analyses. Compared to population analyses, the dependence of $\langle \hat{S}^2 \rangle$ partitioning on the type of projection operator is small, since all projectors yield qualitatively equivalent results, whereas partial charges obtained from different population analyses may even differ in sign.^{1,2} As there is no practical criterion for an ideal projector that is valuable for all molecular systems, we choose for subsequent analyses the projection operator which is best from a formal point of view. This is the Löwdin* projector, since it is based on an orthonormal basis and, compared to the standard Löwdin projector, it has the extra feature of preorthonormalization within the atomic centers.

4. Local spin of different total spin states

We have shown that the absolute local $\langle \hat{S}^2 \rangle$ values can depend strongly on various parameters in actual calculations. Since for the calculation of Heisenberg coupling constants only the local spin *differences* between two different total spin states and not the absolute values are relevant, we should now investigate whether this dependence is still

TABLE III. Local $\langle \hat{S}^2 \rangle$ values obtained with several local projectors for high-spin and low-spin manganocene for a one-determinant wave function constructed from Kohn-Sham orbitals in a TZVP basis using B3LYP* (geometry optimization: B3LYP/TZVP, high spin). Local spin values for symmetrically equivalent atoms are virtually identical within the given accuracy.

	High spin			Low spin		
	Mulliken	Löwdin	Löwdin*	Mulliken	Löwdin	Löwdin*
$\langle \hat{S}_{Mn}^2 \rangle$	8.42	8.51	8.96	2.16	2.29	2.89
$\langle \hat{S}_C^2 \rangle$	1.40	1.60	1.85	1.43	1.60	1.86
$\langle \hat{S}_H^2 \rangle$	0.37	0.39	0.44	0.36	0.39	0.44
$\langle \hat{S}_{Mn} \cdot \hat{S}_C \rangle$	-0.03	-0.04	-0.10	-0.13	-0.14	-0.20
$\langle \hat{S}_C \cdot \hat{S}_C \rangle$	-0.46	-0.51	-0.53	-0.47	-0.50	-0.52
$\langle \hat{S}_C \cdot \hat{S}_H \rangle$	-0.37	-0.33	-0.29	-0.36	-0.33	-0.29

TABLE IV. Absolute and relative $\langle \hat{S}_{\text{Mn}}^2 \rangle$ values obtained with several density functionals and local projectors in a TZVP basis for high-spin (HS) and low-spin (LS) manganocene (geometry optimization: B3LYP/TZVP, high spin).

		$\langle \hat{S}_{\text{Mn}}^2 \rangle_{\text{HS}}$	$\langle \hat{S}_{\text{Mn}}^2 \rangle_{\text{LS}}$	$\langle \hat{S}_{\text{Mn}}^2 \rangle_{\text{HS}} - \langle \hat{S}_{\text{Mn}}^2 \rangle_{\text{LS}}$
HF	Löwdin*	9.75	2.49	7.26
BP86	Löwdin*	8.79	2.89	5.90
BLYP	Löwdin*	8.67	2.86	5.81
PBE0	Löwdin*	9.20	3.35	5.85
B3LYP	Löwdin*	9.03	2.98	6.05
B3LYP*	Löwdin*	8.96	2.89	6.07
B3LYP*	Löwdin	8.51	2.29	6.22
B3LYP*	Mulliken	8.42	2.16	6.26

present when differences in local $\langle \hat{S}^2 \rangle$ values between different total spin states of a molecule are compared. In order to keep absolute and relative data comparable to one another, we again investigated the manganocene molecule. Of course, as a mononuclear complex, it exhibits no spin coupling and therefore the results given in Table IV permit no direct conclusions concerning the Heisenberg model. Still, the observations made in this simple molecule can provide an indication of the trends one might observe in a systematic investigation of polynuclear complexes.

Whereas the absolute local $\langle \hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B \rangle$ values depend strongly on the choice of the density functional, this is not the case for the corresponding *relative* values between the different total spin states of manganocene given in Table IV. The large difference between the absolute PBE0 and BLYP results has almost vanished when relative local spins are considered, while in most other cases, this effect is less pronounced or not present at all. The dependence of relative local spins on the projector and the choice of HF versus KS orbitals, however, is not reduced in comparison to the absolute values. Interestingly, compared to the DFT data, the HF value is much closer to what one would expect for a system where the electron spin is completely located at the central atom.

B. Partitioning of $\langle S_z \rangle$

Having discussed the considerable parameter dependence of local $\langle \hat{S}^2 \rangle$ values, we now investigate this issue for local $\langle \hat{S}_z \rangle$ values, which contain information on the distribution of the total M_S onto molecular subunits. Within the collinear approach, the axis of spin-quantization is chosen to be the z axis. While not every single determinant wave function is an eigenfunction of the \hat{S}^2 operator, restricted as well as unrestricted wave functions in the collinear approach are always eigenfunctions of the \hat{S}_z operator. Applying the same local projection operator technique as above, one obtains local operators \hat{S}_{zA} that sum up to the total \hat{S}_z operator,

$$\sum_A \hat{S}_{zA} = \hat{S}_z, \quad (19)$$

with \hat{S}_{zA} defined as the sum over all N one-electron operators $\hat{S}_{zA} = \hat{p}_A \hat{S}_z$,

$$\hat{S}_{zA} = \sum_i \hat{S}_{zA}(i) = \sum_i \hat{p}_A(i) \hat{S}_z(i). \quad (20)$$

By applying the standard rules for calculating expectation values of one-electron operators for Slater determinants, one obtains the local expectation value $\langle \hat{S}_{zA} \rangle$,

$$\begin{aligned} \langle \hat{S}_{zA} \rangle &= \sum_i^{N^\alpha} \langle i | \hat{p}_A \hat{S}_z | i \rangle + \sum_{\bar{i}}^{N^\beta} \langle \bar{i} | \hat{p}_A \hat{S}_z | \bar{i} \rangle \\ &= \frac{1}{2} \sum_i^{N^\alpha} \langle i | \hat{p}_A | i \rangle - \frac{1}{2} \sum_{\bar{i}}^{N^\beta} \langle \bar{i} | \hat{p}_A | \bar{i} \rangle = \frac{1}{2} (N_A^\alpha - N_A^\beta). \end{aligned} \quad (21)$$

In the second line of equation (21), it can be nicely seen that local $\langle S_z \rangle$ values for closed-shell singlet MO Slater determinants will be equal to zero, which is in agreement with what one intuitively expects.

For open-shell singlets, on the other hand, things are more complicated. Describing an open-shell singlet with a single Slater determinant is obviously not rigorous, but an extension into the multiconfigurational regime is straightforward. In the most simple model case, an open-shell singlet consists of two symmetric spin centers A and B with one α electron on center A and one β electron on center B . A one-determinant wave function for this system—abbreviated as $|\uparrow\downarrow\rangle$ —is not an eigenfunction of the \hat{S}^2 operator. On the other hand, the most simple multiconfiguration singlet wave function $|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle$ is an eigenfunction of the \hat{S}^2 operator. When a local spin analysis based on $\langle S_z \rangle$ is performed for such a wave function describing an open-shell singlet state formed by antiferromagnetic coupling of two separated spin centers as a superposition of Slater determinants, one will obtain zero local $\langle S_{zA} \rangle$ values as can be easily shown by operating with $S_{zA} = \sum_i S_{zA}(i)$ on the superimposed Slater determinants. The question now is, whether zero local spins $\langle S_{zA} \rangle$ are reasonable for such systems. At first sight, a negative answer to this question would restrict the applicability of a local spin analysis based on \hat{S}_z partitioning to single-determinant wave functions. However, the zero S_{zA} values obtained for a multiconfigurational wave function result from a superposition of two homologous determinants with same weight, which in the qualitative picture thus purely reflects the “Schrödinger cat behavior” of the superposition in this simple model of two interacting spins.

We should note that partitioning of \hat{S}_z has already been introduced by Clark and Davidson in the context of local \hat{S}^2 (Ref. 7) and shall here be compared to \hat{S}^2 partitioning as an alternative tool for local spin analysis. For Mulliken and Löwdin projectors, $\langle S_{zA} \rangle$ is

$$\langle \hat{S}_{zA} \rangle^M = \sum_{\mu \in A} (\mathbf{P}^\alpha \mathbf{S})_{\mu\mu} - \sum_{\mu \in A} (\mathbf{P}^\beta \mathbf{S})_{\mu\mu} \quad (22)$$

and

$$\langle \hat{S}_{zA} \rangle^L = \sum_{\mu \in A} \mathbf{P}_{\mu\mu}^{\alpha'} - \sum_{\mu \in A} \mathbf{P}_{\mu\mu}^{\beta'}, \quad (23)$$

TABLE V. Local spins and partial populations for HF/TZVP wave functions for NO at the experimental interatomic equilibrium distance 115.1 pm (Ref. 22) and two carbenes, CH₂ and C(NH₂)₂ (abbreviated as “ard”) in the triplet state (geometry optimization: HF/TZVP). Local spin values for symmetrically equivalent atoms are virtually identical within the given accuracy.

		N(NO)	O(NO)	C(CH ₂)	H(CH ₂)	C(ard)	N(ard)	H(ard)
N_A	Mulliken	6.91	8.09	6.21	0.90	6.05	7.40	0.79
	Löwdin	6.92	8.08	6.31	0.85	6.07	7.35	0.81
	Löwdin*	6.89	8.11	5.89	1.06	6.07	7.35	0.81
	AIM	6.57	8.29	6.12	0.90	5.29	7.93	0.63
$\langle \hat{S}_{zA} \rangle$	Mulliken	0.52	−0.02	1.11	−0.06	0.99	−0.02	0.02
	Löwdin	0.48	0.02	1.01	0.00	0.83	0.06	0.02
	Löwdin*	0.46	0.04	0.98	0.01	0.76	0.08	0.02
	AIM	0.46	0.02	0.98	0.01	0.78	0.08	0.02
$\langle \hat{S}_A^2 \rangle$	Mulliken	1.34	0.80	2.93	0.37	2.62	1.08	0.36
	Löwdin	1.52	1.07	2.70	0.40	2.46	1.29	0.40
	Löwdin*	1.85	1.41	2.68	0.47	2.62	1.51	0.49

respectively. Partitioning of \hat{S}_z is straightforward to implement into any program that performs population analyses, because no knowledge of the action of the projection operators on a single molecular orbital is required. It is sufficient to carry out separate population analyses with only α - or β -molecular orbitals as input. Especially if one wants to perform spin analyses with numerical local projectors like Bader's AIM projectors, this simple calculation of local $\langle S_{zA} \rangle$ based on population analyses has an advantage with respect to the computational costs compared to the partitioning of $\langle \hat{S}^2 \rangle$. An AIM projector \hat{p}_A^{AIM} projects onto the atomic basin Ω_A within the three-dimensional space of Cartesian coordinates. AIM local $\langle S_{zA} \rangle$ values can be understood as integrals over the spin density $\rho^\alpha(\mathbf{r}) - \rho^\beta(\mathbf{r})$ within an atomic basin, defined by the AIM theory,

$$\langle S_{zA} \rangle^{\text{AIM}} = \frac{1}{2} \int_{\Omega_A} d\mathbf{r} [\rho^\alpha(\mathbf{r}) - \rho^\beta(\mathbf{r})] = \frac{1}{2} [N_A^{\alpha, \text{AIM}} - N_A^{\beta, \text{AIM}}], \quad (24)$$

which is a more intuitive (and, of course, less basis set dependent) concept than projections on subspaces of an atom-centered basis set. We have computed $\langle S_{zA} \rangle^{\text{AIM}}$ values for small molecules for comparison with basis-set-based partitioning schemes (see below). However, the AIM evaluation is very time consuming so that it is difficult to routinely obtain $\langle S_{zA} \rangle$ values for large molecules like transition metal complexes. The basis-set-based calculation of $\langle S_{zA} \rangle$ would thus be a viable alternative in such cases.

As can be seen from Eq. (21), partitioning the \hat{S}_z operator is essentially the same as computing atomic spin densities, with the exception of a factor 1/2 that stems from the spin properties of electrons as fermions. Atomic spin densities for interesting molecules have been reported in many different contexts in the literature, so that it is hardly possible to give a survey on these results here. Just to mention one recent example, we refer the reader to the interesting study of a nitrogenase FeMo-cofactor model by Huniar, Ahlrichs, and Coucouvanis,²⁶ where the calculation of atomic spin densities based on Mulliken pseudoprojectors was employed. A systematic study on the dependence of these quantities on

projector, basis set, and density functional has not been reported so far. In the following, we will investigate the projector dependence for some small test molecules—beginning with NO, which is one of the most simple diatomic radicals and therefore an ideal test case, and continuing with two radicaloid systems which are conceptually interesting organic molecules [the triplet carbenes CH₂ and the Arduengo-carbene model C(NH₂)₂]. Furthermore, due to its sensitivity to the choice of the density functional, high-spin manganese is used as a test case for the dependence on density functional and basis set as before.

1. Comparison between different projectors for $\langle \hat{S}_{zA} \rangle$

In this section, the projector dependence of $\langle \hat{S}_{zA} \rangle$ is studied.

Two observations can be made for the examples given in Table V: First, local $\langle \hat{S}_z \rangle$ values are much less sensitive to the choice of the projector than local $\langle \hat{S}^2 \rangle$ values. The largest difference is the one between the $\langle \hat{S}_{zN} \rangle_{\text{NO}}$ values calculated with a Mulliken and a Löwdin* projector, respectively, which differ by only 0.04 a.u. or 8% (with respect to the lower value), whereas the corresponding values for $\langle \hat{S}^2 \rangle$ partitioning differ by 0.51 a.u. or 38%. From all partitioning schemes it follows that the total $\langle \hat{S}_z \rangle$ of the NO molecule is completely located at the nitrogen atom, which is in agreement with qualitative MO-theory: the singly occupied molecular orbital should have a larger coefficient on the less electronegative atom, which is nitrogen. Local $\langle \hat{S}^2 \rangle$ values, on the other hand, suggest that a rather large portion of local spin (about 41% for the Löwdin projector) is located on the oxygen atom, which is due to the “closed-shell contamination” of $\langle \hat{S}^2 \rangle$ partitioning. This demonstrates that in order to calculate absolute local spin values, local $\langle \hat{S}_z \rangle$ values should be used instead of local $\langle \hat{S}^2 \rangle$ values. Second, although the Löwdin* partial populations differ from AIM partial populations at least as much as from those obtained with the other two projectors, the Löwdin*-local $\langle \hat{S}_z \rangle$ values are virtually identical to the corresponding AIM values for the whole

TABLE VI. Local Löwdin* $\langle S_z \rangle$ values for the manganese center in high-spin (sextet) manganocene, calculated with different density functionals basis sets. Geometry optimization: B3LYP/TZVP, high spin.

	SV(P)	TZV	TZVP	TZVPP
B3LYP	2.31	2.29	2.28	2.22
B3LYP*	2.30	2.27	2.27	2.21
PBE0	2.34	2.31	2.31	2.24
BP86	2.28	2.23	2.24	2.18
BLYP	2.26	2.22	2.22	2.16
HF	2.44	2.41	2.41	2.35

range of atoms of the three molecules in Table V. This is an important result, since it makes the calculation of AIM-like local $\langle \hat{S}_z \rangle$ values feasible in a much more efficient way and thus at very low computational costs.

2. Comparison of different basis sets and density functionals for the calculation of $\langle \hat{S}_{zA} \rangle$

The dependence of local $\langle \hat{S}_z \rangle$ values on the basis set and on the density functional is now discussed for manganocene as a test case. For the reasons mentioned above, all values were calculated with Löwdin* projectors. Since the (absolute) local $|\langle \hat{S}_z \rangle|$ values are around 0.02 or even lower regardless which density functional and basis set has been used, only the local $\langle \hat{S}_z \rangle$ for the manganese center is considered.

The relative dependence on basis set and density functional in Table VI is less pronounced than in the case of local $\langle \hat{S}^2 \rangle$ values: For example, in the worst case the $\langle S_{zMn} \rangle$ values differ by only 0.18 a.u. or 8% when comparing BLYP and HF for SV(P), and by only 0.09 or 4% when comparing SV(P) and TZVPP for B3LYP. In addition, the dependence appears to be systematic: $\langle \hat{S}_{zMn} \rangle_{\text{sextet}}$ decreases when the number of polarization functions in the basis set is augmented. The values obtained with the two pure functionals are similar, as well as those obtained with the three hybrid functionals. This also documents that $\langle S_{zA} \rangle$ values are better suited for investigations on absolute local spins than local $\langle \hat{S}^2 \rangle$ values not only because the former are not affected by the closed-shell inconsistencies the latter suffer from, but also because they do not depend that strongly on basis set, density functional and projector as the latter.

IV. CONCLUSION

Since the spin state of any system is characterized by the two quantum numbers S and M_S , the local values of these two quantum numbers, S_A and M_{SA} , are needed to characterize the electron spin of a subsystem A completely. $\langle \hat{S}_{zA} \rangle$ gives information on M_{SA} , but due to the nonzero closed-shell $\langle \hat{S}_A^2 \rangle$ values, $\langle \hat{S}_A^2 \rangle$ cannot be interpreted as an absolute measure for S_A (or $S_A(S_A + 1)$, respectively).⁷ Local $\langle \hat{S}_z \rangle$ values, on the other hand, do not suffer from closed-shell contamination. Apart from this formal aspect, local $\langle \hat{S}_z \rangle$ values have the practical advantage that they depend considerably less on the basis set, density functional and projection

operator than local $\langle \hat{S}^2 \rangle$ values. Therefore, in order to investigate the absolute local spin distribution in a given Slater determinant, $\langle \hat{S}_z \rangle$ partitioning appears to be a much better choice than $\langle \hat{S}^2 \rangle$ partitioning.

As far as the dependence of local spin values on the density functional is concerned, no systematic trends can be expected, as there is no systematic connection between the different density functionals. In agreement with this expectation, we observe no systematic dependence on the density functional for local $\langle \hat{S}^2 \rangle$ values. However, in the case of manganocene, local $\langle \hat{S}_z \rangle$ values depend in a systematic way on whether a pure or a hybrid density functional is chosen as the results fall into the two groups (BLYP, BP86) and (B3LYP, B3LYP*, PBE0).

Furthermore, $\langle \hat{S}_{zA} \rangle$ values for manganocene decrease systematically with an increasing number of polarization functions in the basis set, as can be observed in the series TZV, TZVP, and TZVPP. In other words, the spin polarization is somewhat reduced when the number of polarization functions in the basis is enlarged. $\langle \hat{S}_A^2 \rangle$ values, on the other hand, do not depend on the basis set in a systematic way.

When Mulliken, Löwdin, and Löwdin* local projectors are applied, most (absolute) $|\langle \hat{S}_A \cdot \hat{S}_B \rangle|$ values increase and (absolute) $|\langle \hat{S}_{zA} \rangle|$ values decrease in this order. Although $\langle \hat{S}_A \cdot \hat{S}_B \rangle$ values depend less on the projector than on the basis set and density functional, they appear to be still much more sensitive to the choice of the projector than $\langle \hat{S}_{zA} \rangle$ values. An important result concerning the projector dependence of local spins is the observation that the local $\langle \hat{S}_z \rangle$ values obtained with preorthogonalized Löwdin* projectors for our three test molecules NO, CH₂, and C(NH₂)₂ are virtually identical to those obtained with Bader's AIM approach. Assuming that this also holds for other molecules, we have a method at hand to calculate AIM-like local $\langle \hat{S}_z \rangle$ values with much less computational effort.

Since the partitioning of $\langle \hat{S}^2 \rangle$ as introduced by Clark and Davidson has been designed for the calculation of spin-spin coupling constants within the Heisenberg model,⁷ where differences between local spins for different total spin states are important, the effect of the parameter dependence of local $\langle \hat{S}^2 \rangle$ values on the calculation of the coupling constants needed to be investigated. We have found that the parameter dependence of local spin differences may be reduced in comparison to the corresponding absolute values in a mononuclear test case, so it is likely that the relevant $\langle \hat{S}_A \cdot \hat{S}_B \rangle$ differences in polynuclear complexes and thus the spin-spin coupling constants calculated from Clark and Davidson's local spins are in general less sensitive to the choice of these parameters than the absolute values. For future work, it might be fruitful to study new projectors which have not yet been investigated like the one introduced by Heinzmann and Ahlrichs in combination with the so-called shared-electron-numbers approach,^{12,13,27} as this approach is characterized by a small basis set dependence.

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APPENDIX: COMPUTATIONAL METHODOLOGY

All calculations were performed with the TURBOMOLE (Ref. 28) suite of programs. If not mentioned otherwise, wave functions were constructed within an unrestricted framework. Convergence criteria were set to 10^{-6} Hartree in all calculations. We employed Ahlrichs' basis sets SV(P) (split-valence with polarization functions on all atoms except hydrogen), TZV, TZVP, and TZVPP (triple-zeta valence basis sets with an increasing number of polarization functions).^{29,30} In the TZVPP basis set, Ahlrichs' TZV kernel is increased by two polarization functions taken from Dunning cc-pVTZ basis.^{31–33} In the all-electron DFT calculations, two pure and three hybrid density functionals were employed as implemented in TURBOMOLE, BP86,^{34,35} BLYP,^{34,36} PBE0,^{37–39} B3LYP,^{40,41} and B3LYP*.^{19–21} BP86 was always combined with the resolution-of-the-identity approach.^{42,43} Local spins were calculated with our own implementation of \hat{S}^2 and \hat{S}_z partitioning in the TURBOMOLE module MOLOCH. This implementation was validated by comparing our results for some test molecules to those published by Davidson.⁷ In the MOLOCH module, Löwdin analyses can be performed in a cartesian or a spherical atomic orbital basis. The results of both do not differ much. In this work, we employed a cartesian basis throughout. In the DFT calculations Slater determinants were constructed from Kohn-Sham orbitals and treated as molecular wave functions.

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