

On the definition of local spin in relativistic and nonrelativistic quantum chemistry

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In this work, a survey is given on the definition of electron spin as a local property in nonrelativistic and relativistic quantum chemistry and in wavefunction- and density-based theories. In particular, the transition from four-component theory to the two- and one-component Douglas–Kroll–Hess framework with respect to the electronic density is considered. Local spin is an important concept in chemistry comparable to the partial charge concept. It is often applied in transition metal chemistry and especially needed for the description and understanding of the electronic structure of spin–spin interactions in polynuclear clusters. The relevance of spin contamination and the effect of the approximate nature of contemporary density functionals is discussed in the light of results obtained for dinuclear manganese and rhenium model clusters.

1. Introduction

Paramagnetic, ferromagnetic and antiferromagnetic substances—either built up by isolated molecules or by extended solids exhibiting magnetic properties—are of interest in chemistry because of their special magnetic properties.¹ The rational design of the properties of these substances is desirable but requires a well-defined theoretical framework. An important concept for this endeavour is *local spin*, which needs to be defined for individual atoms or groups of atoms and which plays an equally important role as the local charge, *i.e.* the partial charge concept. For example, understanding the chemistry of open-shell transition metal complexes and clusters requires a reliable description of the (local) spin interactions within these systems. *But* what is *local spin* and how can it be defined? In principle, the calculation of the spin distribution depends on two major choices: the Hamiltonian and the approximation of the wave function, from which the (spin) density is calculated. This work is therefore concerned with the discussion of three questions: (i) How can local spin be defined in a strongly interacting system like a many-electron molecule or cluster, (ii) how does this definition depend on the quantum mechanical framework, which may be of nonrelativistic Schrödinger type, of relativistic Dirac type or which may take a ‘quasi-relativistic’ view and (iii) how does the definition depend on the electronic structure method which can be based on a wavefunction or on an electronic density formulation.

Before we begin the discussion of the theoretical foundations of local spin and spin distributions in molecules we should make some comments on how these quantities

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can be measured. An important experimental method is polarized neutron diffraction (PND).^{2,3} In general, calculated (Mulliken) spin populations obtained within density functional theory (DFT) tend to agree well with experimentally measured spin populations (see, *e.g.*, ref. 3–6). Compared to magnetization measurements, electron spin resonance, or Mössbauer spectroscopy PND is able to provide not only information on the spin density at certain positions in space (*e.g.*, at the positions of the nuclei) but complete spin density maps are obtained and the relation between the spin density and the measured quantities is a direct one.

In this context, it is particularly interesting to note that the experimental determination of spin densities is difficult for molecules containing heavy atoms like those with the rare earth atom gadolinium⁷ because refinement procedures require reliable starting approximations for the (spin) density that are difficult to obtain because of relativistic as well as electron correlation effects. Nevertheless, it was found for an yttrium complex that already quasi-relativistic DFT calculations (using the local density approximation and the generalized gradient approximation) within the zeroth order regular approximation (ZORA without spin–orbit coupling in this case; *cf.* also the next section) are in quantitative agreement with respect to a comparison of the total density, whereas the calculated spin density underestimates spin delocalization.⁸ The question arises whether such discrepancies are due to the approximate one-component relativistic description or due to the approximate density functional used in Kohn–Sham(KS)-DFT calculations.⁹ In general, this will be difficult to answer as we shall see in the course of this work. However, one should try to understand the various ingredients in sufficient depth in order to understand possible sources of inaccuracies and this account intends to serve this aim.

Many research papers have been devoted to the role of local spin, for example, in the context of the phenomenological Heisenberg Hamiltonian. However, the fact that spin must then not be delocalized (*e.g.*, on adjacent ligand atoms like μ -oxo bridges in binuclear clusters) is neglected. Also, the fact that today almost all quantum chemical calculations are carried out within KS-DFT—mainly for feasibility reasons—needs to be considered. The results obtained are usually discussed in the light of a *wavefunction-based* method as if the KS wavefunction was the true wavefunction of the electronic system (*i.e.*, of the molecule) under consideration. Accordingly, the basic Kohn–Sham idea of calculating a surrogate system of noninteracting fermions possessing the same density as the fully interacting electronic system is then forgotten.

This discussion will be of increasing importance in view of ongoing efforts to understand chemical reactivity on the basis of the electronic density only.^{10,11} An extension of these efforts to spin density will certainly follow and it is thus decisive to elaborate on the theoretical foundations on which such studies would be based. The local analysis of spin densities in static quantum chemical studies will certainly be also extended to the molecular dynamics regime (see the study in ref. 12 by Kirchner *et al.* for an example of the dynamics of an open-shell condensed-phase system).

In this work, we shall try to present a unified discussion of local spin in quantum chemistry. The main purpose is to obtain results from different areas of theoretical chemistry and to draw conclusions from these different perspectives. For this it is necessary to assess the significance of numerical results obtained with approximate DFT methods. We begin this presentation with a general and fundamental relativistic point of view on the calculation of electronic total and spin densities and then turn to the definition of local spin in nonrelativistic quantum mechanics. Relativistic and nonrelativistic approaches are joined in the framework of Douglas–Kroll–Hess (DKH) theory, which implements in its scalar-relativistic variant kinematic relativistic effects within a nonrelativistic framework. Special emphasis is on the KS-DFT framework, which is currently most important for quantum chemical calculations. The discussion is supplemented by extensive calculations on spin–spin interacting dinuclear clusters.

2. Spin in relativistic quantum chemistry

It is well known that nonrelativistic quantum chemistry based on Schrödinger quantum mechanics does not provide a universal theoretical framework for chemistry—apart from the fact that a fundamental physical theory must fulfil the principles of special relativity. For molecules containing heavy elements, *i.e.*, those with a large nuclear charge Z , there are significant deviations of molecular properties (*e.g.*, bond lengths) from nonrelativistic results leading even to noncontinuous trends of properties within a homogeneous series of elements (*e.g.*, within a group of the periodic table).^{13,14}

In relativistic quantum chemistry, the first-quantized Dirac–Coulomb operator turned out to be a sufficiently accurate approximation for almost any chemical system.¹⁵ We shall not enter into the discussion of fundamental problems on whether it is possible at all to avoid the mathematical difficulties of the many-electron Dirac–Coulomb operator,¹⁶ which is neither Lorentz covariant nor bounded from below such that projection operators onto electronic positive-energy states are required in practical applications. Also, we may avoid a discussion of relativistic corrections, namely the Breit interaction, to the (instantaneous) Coulombic electron–electron interaction, which would introduce additional two-electron spin operators into the four-component Hamiltonian, since these corrections turned out to be of little importance for ordinary chemical problems.

In the absence of external magnetic fields, the Dirac one-electron Hamiltonian \hat{h}_D ,

$$\hat{h}_D = c\boldsymbol{\alpha} \cdot \mathbf{p} + \beta mc^2 + V \quad (1)$$

contains the rest energy βmc^2 of an electron (m is the electron's rest mass and $\beta = \text{diag}(1, 1, -1, -1)$ is a diagonal 4×4 matrix and c denotes the speed of light) and scalar potential energy operators V for the description of instantaneous Coulombic interactions of the electrons with the atomic nuclei as in the nonrelativistic case. But the relativistic 4×4 kinetic energy operators \hat{t}_r are totally different in form if compared with the Schrödinger kinetic energy operators,

$$\hat{t}_r = c\boldsymbol{\alpha} \cdot \mathbf{p} = \begin{pmatrix} \mathbf{0}_2 & c\boldsymbol{\sigma} \cdot \mathbf{p} \\ c\boldsymbol{\sigma} \cdot \mathbf{p} & \mathbf{0}_2 \end{pmatrix}, \quad (2)$$

where each $\boldsymbol{\sigma}$ is a 3-vector of 2×2 Pauli spin matrices, \mathbf{p} is the well-known linear momentum operator and $\mathbf{0}_2$ is a 2×2 zero matrix [external magnetic fields (in terms of the corresponding vector potentials \mathbf{A}) have been excluded]. In contrast to the nonrelativistic Hamiltonian the spin is now implemented in the relativistic Hamiltonian through these one-electron terms and the corresponding relativistic orbitals featuring four components are called 4-spinors. A study of the Dirac hydrogen atom highlights that angular momentum and spin are no longer good quantum numbers—only the square of the total angular momentum operator commutes with this relativistic Hamiltonian. The fact that spin is no longer well defined in a relativistic framework raises doubts on the definition of local spins for strongly relativistic systems. However, the phrase “strongly relativistic” already indicates that one would like to recover a “spin-independent” description whenever this is possible. Relativistic effects, which are nonphysical effects but merely denote the difference between results obtained from a relativistic and a nonrelativistic calculation, increase with some power of the nuclear charge Z . Hence, it is obvious to assume that the “spin-operator-free” picture can be adopted as long as the nuclear charge of all atoms in a molecule is sufficiently small.

In order to derive a meaningful “spin-independent” picture from a generally valid four-component theory it is advisable to find a scheme, which allows us to separate all spin operators from the remaining scalar operators. A nonrelativistic “spin-operator-free” analogue is then obtained by simply neglecting all spin-dependent terms. Whether such an approximation is justified or not can then be assessed, for

instance, through an evaluation of the magnitude of the expectation value over the neglected spin-dependent contributions to the total energy. If the expectation value is large, it contributes significantly to the total energy and must not be neglected from the Hamiltonian—especially if one can expect that this contribution becomes important for relative energies of chemical processes. Remember that the elimination of spin-dependent terms in the Dirac–Coulomb Hamiltonian affects only the *one-electron* terms since the first spin-dependent two-electron terms, which arise when the Gaunt terms $-(\boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j)/r_{12}$ of the full Breit operator would be included, are neglected in a description of the electronic structure based on the Dirac–Coulomb Hamiltonian.

But is it possible to unambiguously separate spin-dependent terms? Here, Dirac's relation,

$$(\boldsymbol{\sigma} \cdot \mathbf{p}) \omega (\boldsymbol{\sigma} \cdot \mathbf{p}) = \mathbf{p} \cdot \omega \mathbf{p} + i \boldsymbol{\sigma} (\mathbf{p} \times \omega \mathbf{p}), \quad (3)$$

is usually applied for this purpose (ω denotes a scalar operator like the scalar electron–nucleus interaction potential). However, this does not guarantee a unique separation of spin terms as has been emphasized by Visscher and van Lenthe.¹⁷

2.1. Current density, magnetization, electronic density and spin density

As in nonrelativistic quantum mechanics, a wavefunction-based four-component *ab initio* theory can be opposed to a relativistic generalization of density functional theory. The latter is, however, rather involved and results in the fact that the standard so-called collinear representation has to be substituted by a noncollinear approach (see, for example, ref. 18 and 19 for a discussion of this issue in the context of molecular quantum chemistry). *Collinear* denotes the existence of an external quantization axis for the spin and can only be justified if spin is a good quantum number. This is not the case in the four-component spin-dependent theory.

In 1973, Rajagopal and Callaway²⁰ derived most general relativistic KS-DFT equations,

$$\left[c \boldsymbol{\alpha} \cdot \left(\mathbf{p} + \frac{1}{c} \mathbf{A}_{\text{eff}} \right) + \beta m c^2 + V_{\text{eff}} \right] \psi_i = \varepsilon_i \psi_i \quad (4)$$

that can be used for the determination of the four-component KS orbitals ψ_i . Note that the rest energy $\beta m c^2$ has not been shifted by $-m c^2$ to match the nonrelativistic energy scale in this case. The effective potential energy terms depend on the electronic four-current J^μ (for this and the following see the discussion in ref. 21 and 22),

$$V_{\text{eff}} = - \left[V + \frac{1}{c} \text{d}^3 r' \frac{J^0(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + c \frac{\delta E_{\text{XC}}[J^\mu]}{\delta J^0(\mathbf{r})} \right] \quad (5)$$

$$\mathbf{A}_{\text{eff}} = - \left[\mathbf{A} + \frac{1}{c} \text{d}^3 r' \frac{\mathbf{J}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + c \frac{\delta E_{\text{XC}}[J^\mu]}{\delta \mathbf{J}(\mathbf{r})} \right], \quad (6)$$

where $E_{\text{XC}}[J^\mu]$ denotes the exchange–correlation current density functional and V the external scalar potential. The four-current is easily related to the electronic density ρ (from which the *charge* density is obtained by multiplication with $(-e)$ [or (-1) in hartree atomic units]) and to the electronic (particle) current density \mathbf{j} :

$$\rho = \sum_i \psi_i^\dagger \cdot \psi_i = -J^0/c \quad (7)$$

$$\mathbf{j}^l = c \sum_i \psi_i^\dagger \cdot \boldsymbol{\alpha}^l \cdot \psi_i = -J^l \quad (8)$$

The general derivation of the electronic density is to define the density as the solution function of a continuity equation,²³

$$\frac{\partial}{\partial t}\rho + \text{div}\mathbf{j} = 0. \quad (9)$$

A Gordon decomposition of the spatial current density provides orbital and spin parts (see ref. 21 and 22 for more details, which are not important for the purposes of this work), of which the neglect of the former and the introduction of the magnetization \mathbf{m} ,

$$\mathbf{m} = \sum_i \psi_i^\dagger \cdot \boldsymbol{\sigma} \cdot \psi_i, \quad (10)$$

for the latter yields four-component KS-DFT equations,²⁴ which are analogous to their counterparts in nonrelativistic spin-KS-DFT. This definition of the (particle) magnetization \mathbf{m} may differ from other presentations by a multiplicative constant $-\mu_B$ with μ_B being the Bohr magneton which is neglected here for the sake of a direct comparison with the nonrelativistic spin density in a later section. Hence, the magnetization emerges naturally in the framework of relativistic DFT and it is important to note that the magnetization couples to the vector potential terms. For the discussion of electronic structures in chemistry, however, we may assume that external vector potentials need not to be considered (of course, external vector potentials play a role in certain kinds of spectroscopy but we may leave this aside for the moment). In the case of the absence of external magnetic fields Saue and Helgaker²⁵ nicely demonstrated for four-component quantum chemical calculations that the current density would only occur if the Gaunt term of the Breit interaction would be considered—apart from the fact that the current density would couple to the vector potential, which we assumed to be absent for our purposes. If, however, the description is restricted to the Dirac–Coulomb Hamiltonian (projection onto the positive-energy states to produce a suitable no-pair operator is to be introduced at a convenient stage), it will be sufficient to calculate the KS spinors and total energies from the electronic density alone.²⁵ This even holds for open-shell systems, but Saue and Helgaker argue that it may be advantageous in view of the approximate nature of present-day functionals to introduce spin-dependent functionals as proposed by MacDonald and Vosko²⁴ and as applied for a long time in nonrelativistic spin-DFT.

The next question that arises is whether it is possible to restrict such a relativistic spin-DFT framework to the z -component of the magnetization, which would have to employ a fixed external quantization axis for the spin (usually the z -axis) and is thus called the collinear approach. The z -component of the magnetization is then essentially the same as the spin density in the collinear approach. However, a spin-operator-dependent Hamiltonian like any of the above mentioned four-component KS Hamiltonians or like the Dirac–Coulomb Hamiltonian does in general not commute with spin operators so that the collinear approach, which requires spin to be a good quantum number, cannot be applied. In the noncollinear approach one may define a spin density which is equal to the length of the magnetization vector and thus always positive. Also, this spin density is invariant under rotations in spin space as the length of the magnetization vector would be invariant. This is a convenient feature regarding the invariance properties of the exchange–correlation contribution to the total DFT energy as discussed in detail by van Wüllen in ref. 18.

3. Relativistic DKH transformation theory

Actual four-component Dirac–Coulomb calculations are (currently) extremely computer resource demanding. Therefore, methods with approximate quasi-relativistic Hamiltonians have been devised. These approximate methods realize a decoupling of the negative-energy (positronic) and electronic degrees of freedom present in the four-component formulation by unitary transformation (*i.e.*, block-

diagonalization) of the four-component Hamiltonian or by elimination of the lower two components (see ref. 26–32 for reviews of these methods). The resulting 2-component Hamiltonians define an electrons-only quasi-relativistic framework, which still includes spin–orbit interactions. The most important and widely used methods are the Zeroth-Order-Regular-Approximation (ZORA) and its variants^{33–36} and the Douglas–Kroll–Hess (DKH) approach.^{37–42} Though the development of quasi-relativistic Hamiltonians is still ongoing and new operators are proposed from time to time, the aforementioned efficient relativistic methods yield a sufficiently accurate description of relativistic effects in chemistry.¹⁶ In this sense, the development of relativistic Hamiltonians has certainly come to an end.

The standard DKH protocol does only consider the block-diagonalization of the individual one-electron terms in the many-electron Hamiltonian *via* a unitary transformation U . The generalization to many-electron systems is straightforward but computationally much more demanding. The DKH n Hamiltonian $\hat{h}_{\text{DKH}n}$ of given order n in the external scalar electron–nucleus potential V represents an expansion of the Dirac Hamiltonian \hat{h}_D in terms of block-diagonal (so-called even) operators \mathcal{E}_i of well-defined order i in the external potential V ,

$$U \hat{h}_D U^\dagger = \hat{h}_{\text{block-diag.}} \Rightarrow \hat{h}_{\text{block-diag.}} \approx \hat{h}_{\text{DKH}n} = \sum_{i=0}^n \mathcal{E}_i, \quad (11)$$

obtained through a sequence of unitary transformations (for a discussion of the DKH transformation in the case of additional external vector potentials \mathbf{A} see ref. 43). The explicit expressions of the individual terms are usually given in commutator form⁴⁰—and get the more complicated the higher the order is—but they are always evaluated *via* matrix multiplications performed in a transformed basis set which diagonalizes p^2 .^{38,44}

A very nice feature of the DKH scheme is that it can be driven to infinite-order,⁴² *i.e.*, to the four-component reference—if really needed. This holds for the DKH Hamiltonian⁴⁴ as well as for the calculation of DKH molecular properties.^{43,45} Needless to say, the resulting electrons-only theory can be subjected to variational approaches without extra precautions like the projection on positive-energy states required in the four-component case. Moreover, Dirac's relation given in eqn (3) can be extensively utilized to derive a one-component spin-independent scalar-relativistic Hamiltonian of any order with respect to the external potential. Then, discussion of spin in the nonrelativistic framework as presented in the following sections can be directly applied to the scalar-relativistic DKH scheme in which the Schrödinger-type one-electron operators are substituted by the spin-free DKH Hamiltonian so that spin remains a good quantum number. However, the spin-free scalar-relativistic DKH Hamiltonian may become inappropriate for molecules containing heavy and super-heavy elements. Then, the spin-dependent terms cannot be neglected.

3.1. The electronic density in DKH theory

From the discussion in Section 1 we understand that it is most desirable to have a relativistic DFT method at hand, which resembles the standard nonrelativistic approach as closely as possible. The standard, *i.e.* scalar-relativistic DKH protocol would provide such a framework, in which all kinematic relativistic effects would be perfectly described. The one-electron spin-dependent terms may be incorporated in a straightforward manner within this approach if necessary, while the two-electron spin-dependent terms arising from the Breit interaction are completely neglected as the four-component reference Hamiltonian of sufficient accuracy in molecular calculations is the Dirac–Coulomb Hamiltonian. (Another peculiarity, namely the so-called picture change effect, which is briefly explained below, arises if the electron–electron terms are simply added to the one-electron DKH operators,

but this deficiency should be of minor importance in numerical applications to molecules.)

If the unique unitary transformation DKH scheme is employed in calculations on open-shell systems and subsequent local spin analysis are carried out, it will be important to correctly calculate density and spin density from DKH orbitals. Therefore, we address in this section the definition of the electronic density within DKH theory, whose generalization for spin densities defined as the difference between α - and β -densities is straightforward.

Consider a single Dirac electron with density distribution $\psi^\dagger\psi$. After unitary transformation we may still calculate the electronic density of this single electron from the square of the DKH 2-spinor ϕ_L according to

$$\psi(\mathbf{r})^\dagger \psi(\mathbf{r}) = \psi^\dagger(\mathbf{r})\mathbf{1}\psi(\mathbf{r}) = \psi^\dagger(\mathbf{r})U^\dagger U\psi(\mathbf{r}) = (U\psi(\mathbf{r}))^\dagger U\psi(\mathbf{r}) = \phi_L^\dagger(\mathbf{r})\phi_L(\mathbf{r}) \quad (12)$$

(following the lines of reasoning in ref. 16). The two-component *infinite-order* DKH density should therefore match the four-component reference density exactly. Thus, the electronic density may be directly computed from the DKH-transformed orbitals as is also the case for other unitary-transformed sets of orbitals such as molecular orbital transformations, for instance, from canonical orbitals to some sort of localized orbitals. One might worry about the validity of equality $\psi^\dagger(\mathbf{r})U^\dagger = (U\psi(\mathbf{r}))^\dagger$ used in the equation above since U is parametrized by an anti-hermitian operator W as, for instance, in $U = \exp(W)$. The operator W may depend on the linear momentum $W = W(\mathbf{p})$, which is a differential operator in position space. But note that \mathbf{p} is multiplicative in momentum space, where the DKH transformation is carried out. Also, the DKH transformation is performed in practice in matrix representation, which encounters only multiplicative matrix operators (and thus linear transformations).

But we should consider this matter for scalar-relativistic DKH calculations on a highly-charged one-electron system, which would be very sensible to effects of relativity. Therefore, *scalar-relativistic* DKH calculations on the one-electron heavy ion Hg^{79+} (with nuclear charge $Z = 80$) and the lighter one-electron ion Ca^{19+} ($Z = 20$) employing primitive Gaussian basis functions were carried out with an atomic structure program based on the work by Roothaan and Bagus.⁴⁶ All operators were represented in a basis of 29 primitive Gaussian-type functions with exponential parameters ζ_i ranging from 154323772.909130 to 0.021248. These parameters are all related through a ratio of 2.25. Test calculations with eleven additional steep Gaussian functions with exponential parameters up to six orders of magnitude larger than the original largest exponent as well as calculations with only two additional steep exponents and nine additional exponents distributed between the primitives with maximum atomic orbital coefficients confirmed the results obtained with the original basis set comprising only 29 primitive Gaussians.

For comparison, the Dirac $1s_{1/2}$ ground state of Hg^{79+} is calculated with a fully numerical atomic structure program,⁴⁷ which yields the upper radial component $G(r) = P(r)/r$ and the lower radial component $F(r) = Q(r)/r$ of the 4-spinor from which the radial density $\rho(r) = r^2[G^2(r) + F^2(r)] = [P^2(r) + Q^2(r)]$ is obtained. These radial functions of the 4-spinor are obtained on a logarithmic grid consisting of 3500 inner grid points distributed over an r -interval of $[0,10]$ bohr using a grid parameter of $b = 0.000004$.⁴⁸ Regarding the accuracy achieved in the numerical Dirac calculations we note that the ground state energies agree very well with the analytically known eigenvalue. In both atomic structure programs, a point-like nucleus with singular Coulombic nuclear attraction potential $-Z/r$ was employed. In all calculations the same value for the speed of light $c = 137.03598950 \text{ au}$ ⁴⁹ was used.

The calculated radial four- and one-component-based densities of Ca^{19+} and Hg^{79+} are depicted in Fig. 1. For the low-order DKH2, DKH3, DKH4 and DKH5 radial densities we note that they can hardly be distinguished on the given scale, *i.e.*, they are practically identical and only a blow-up around the maximum (see inset in

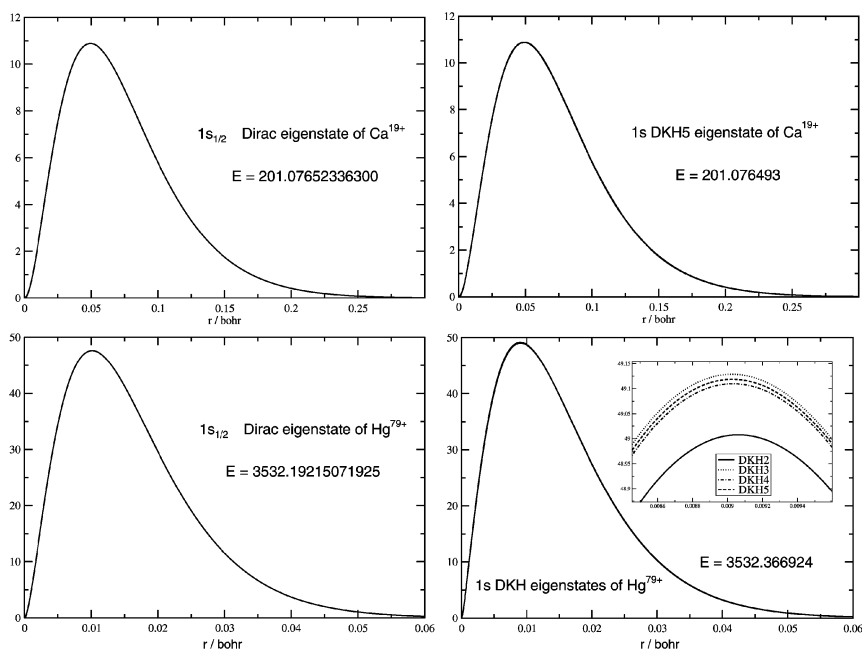


Fig. 1 Radial four-component-based densities [$P^2(r) + Q^2(r)$] (left) compared to scalar-relativistic radial DKH n densities $P_{\text{DKH}n}^2(r)$ (right) for the H-like ions Ca^{19+} ($n = 5$) and Hg^{79+} ($n = 2, 3, 4, 5$) in hartree atomic units. Note that the four-component and DKH densities are different in the case of the heavy ion Hg^{79+} (as witnessed, for instance, by the different heights of the maximum). The different low-order DKH orders yield densities which lie on top of one another. Only the blow-up around the maximum as depicted in the inset shows the slightly different densities stemming from different DKH orders; DKH2: bottom; DKH3: top; DKH4: 2nd from below; DKH5: 3rd from below. The ordering of the DKH densities follows the oscillating order observed for the corresponding electronic energy (see ref. 40 and 42). For comparison, total energies are given for DKH5 in comparison to the numerical Dirac results in hartree atomic units. Note that the form of the radial density is also determined by the normalization condition so that the radial density changes if only the height and/or position of the maximum change slightly. (For comparison: the nonrelativistic total energies in atomic units are $-Z^2/2$, i.e., -200 hartree for Ca^{19+} and -3200 hartree for Hg^{79+}).

the graph on the right hand side of Fig. 1) highlights the difference resulting from different DKH orders. Nevertheless, for Hg^{79+} we detect a notable deviation of the one-component DKH densities $P_{\text{DKH}n}^2(r) = r^2 R_{\text{DKH}n}^2(r)$ from the four-component-based density. This deviation is most prominent in the position and height of the maximum.

In order to ensure that the basis set of primitive Gaussian functions is not a source of errors, we demonstrate in Fig. 2 that the basis functions are nicely distributed over the relevant radial distance range. The reliability of the chosen basis set is also evident by a comparison of Dirac and DKH total energies for the Ca^{19+} ion given in Fig. 1. It is thus highly unlikely that the discrepancies are due to basis set deficiencies. To better understand the origin of the differences in the four- and one-component radial densities they are plotted after division by r^2 in Fig. 3.

Hence, the graphs in Fig. 3 correspond to the squared radial functions $[G(r)^2 + F(r)^2]$ and $R_{\text{DKH}5}^2$. It is immediately clear that the difference in radial density stems from the different short-range behaviour of the radial functions: the slope close to the origin is much larger in the DKH case than it is in the four-component reference. This different short-range behaviour has also been observed in independent calculations.⁵⁰ We shall discuss this aspect in greater detail in the following in order to shed light on the possible sources of the discrepancy.

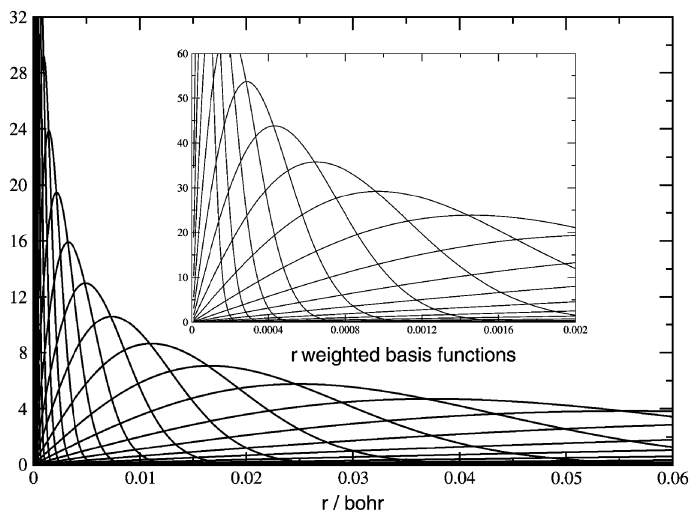


Fig. 2 Distribution of primitive Gaussian basis functions (weighted with r in order to match the representation of the radial densities in Fig. 1).

At first sight one may assume a picture-change effect,⁵¹ which denotes the numerical difference that is observed when an untransformed, *i.e.* inappropriate operator is used in DKH expectation values, to be present, although this is not obvious in view of eqn (12). In order to understand the origin of this suspicion one may write the electronic density as $\langle \psi | \delta(\mathbf{r} - \mathbf{r}') | \psi \rangle$,

$$\rho(\mathbf{r}) = \int [d^3r' \delta(\mathbf{r} - \mathbf{r}') |\psi(\mathbf{r}')|^2] = \int [d^3r' \delta(\mathbf{r} - \mathbf{r}') \psi^\dagger(\mathbf{r}') \cdot \psi(\mathbf{r}') \rightarrow \int [d^3r' \psi^\dagger(\mathbf{r}') \delta(\mathbf{r} - \mathbf{r}') \psi(\mathbf{r}')], \quad (13)$$

though it is not obvious why there should be a necessity for the ground state of the one-electron systems under consideration here to introduce a δ -distribution as a somewhat artificial operator. Note that the restriction of our discussion to the most simple case of a one-electron system like the one under consideration here is without loss of generality. It is also interesting in this context to study the general case of a local multiplicative operator $\hat{A}_4(\mathbf{r}) = \mathbf{1}_4 \hat{A}(\mathbf{r})$ in position space (like the electric field gradient or the external potential), for which one might be tempted to formulate

$$\langle \psi | \hat{A}_4 | \psi \rangle = \int d^3r \psi^\dagger \mathbf{1}_4 \hat{A} \psi \rightarrow \int d^3r' \psi^\dagger \mathbf{1}_4 \psi \hat{A} = \int d^3r \rho \hat{A} = \int d^3r \rho_{LL} \hat{A}. \quad (14)$$

If this was true, no multiplicative operator would show a picture-change effect owing to the last equality in the above equation, where the four-component-based density ρ is substituted by the equivalent DKH density ρ_{LL} . But eqn (14) does not hold because the step is not allowed to commute the 4-spinor ψ and the multiplicative form in position space of \hat{A} . One may understand this if the expression is formulated in momentum space, in which the DKH transformation can be conveniently formulated and where \hat{A} does no longer remain to be local and may not commute with the DKH unitary transformation.

Note that the DKH density may well be derived from the DKH transformation of the continuity equation (eqn (9)).¹⁶ However, not the one-component-based scalar-relativistic DKH density but the two-component-based DKH density is directly compared to the full four-component-based density.

In this context, an interesting qualitative feature of the one-component-based DKH radial density should be mentioned. This is the fact that the one-component-based DKH radial density shows radial nodes for, *e.g.*, $n > 1$, $l = 0$, whilst this is not the case for the four-component-based radial density. This issue has been raised

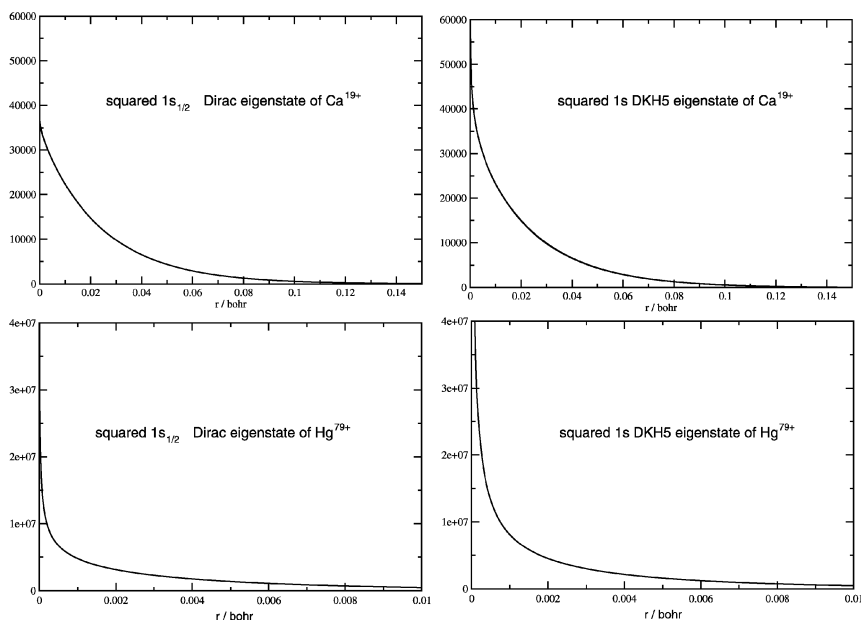


Fig. 3 Comparison of squared radial functions $[G(r)^2 + F(r)^2] = [P^2(r) + Q^2(r)]/r^2 = [P^2(r) + Q^2(r)]/r^2$ (four-component-based, left) and $P_{\text{DKH}n}^2(r)/r^2$ (one-component-based with $n = 5$, right) for Ca^{19+} and Hg^{79+} in hartree atomic units. This figure clearly demonstrates that the difference in radial densities of four- and one-component methods stems from the different origin behaviour of the four-component and DKH radial functions (for a discussion see text). However, in any expectation value the plotted functions are weighted by r^2 , which diminishes the effect largely as witnessed in the case of Ca^{19+} when we compare with the true radial density depicted in Fig. 1. Note that the weakly singular short-range behaviour $G(r \rightarrow 0), F(r \rightarrow 0) \propto r\sqrt{1-Z^2/c^2-1}$ of the Dirac spinor is not visible at this scale.

recently in ref. 16, where it was pointed out that the DKH transformed radial functions in the product $\phi_L^\dagger \phi_L$ are, in general, complex-valued so that $\phi_L^\dagger \phi_L = |\phi_L|^2 = \phi_{L,\text{Re}}^2 + \phi_{L,\text{Im}}^2$, which is also non-zero if real and imaginary parts possess nodes at different radial distances. If ϕ_L was a real-valued function, we would have to have two different radial parts for the two components of the 2-spinor ϕ_L in order to obtain a nodeless radial density distribution as in the four-component case. In the one-component *scalar*-relativistic approximation, which neglects all spin-dependent terms, we lose this feature and observe radial nodes for the real one-component DKH orbitals.

The result obtained in this section is that the electronic density of *highly charged* heavy ions obtained in a standard *scalar*-relativistic DKH framework, which simply neglects all spin-dependent terms in the DKH Hamiltonian, deviates noticeably from the four-component reference density. However, the magnitude of the effect is determined by the nuclear charge and total charge of the system under consideration. *i.e.*, the magnitude will be larger the larger the nuclear charge of an individual atomic nucleus is, but it will be decreased significantly for neutral systems, which do not feature heavily contracted total densities like those discussed here for highly-charged heavy systems. Hence, the effect may be neglected for neutral species (only the innermost one-electron core shells of heavy and super-heavy atoms in neutral molecules might require some attention). In addition, when total α - and β -populations are calculated (see below), residual effects from the steep behaviour of the DKH orbitals and density will cancel upon subtraction of these populations to yield the excess spin population.

4. Definition of total and local spin

Up to this point, we addressed the emergence of spin depending on the form of the Hamiltonian. Only one-electron atoms have been considered so far and we shall now turn to the many-electron case.

In nonrelativistic Schrödinger quantum mechanics, the many-electron Hamiltonian \hat{H}_{nr} is exactly known and does not depend on the electronic spin.⁵² Since spin was observed experimentally, a spin variable was added to the set of three spatial coordinates per electron in such a way that the Pauli antisymmetry principle must be applied to sets of four such coordinates per electron. Since \hat{H}_{nr} does not depend on spin variables it can be shown to commute with the (scalar) square S^2 of the (vectorial) total spin operator $\hat{S} = \sum_{i=1}^N \hat{s}(i)$ (where N is the total number of electrons in the system and i denotes the i -th electron). Accordingly, the electronic wave function Ψ_{el} is simultaneous eigenfunction of \hat{H}_{nr} and S^2 and can be classified with respect to the spin eigenvalues S and M_S .⁵²

In the following, we may restrict the discussion to single-determinant approximations of Ψ_{el} in order to keep the presentation simple. The discussion can, however, be generalized to multi-determinant *ab initio* methods. This single-determinant approximation Φ to Ψ_{el} ,⁵³

$$\psi_{el} \approx \Phi = \hat{A}\psi_1(\mathbf{x}_1)\psi_2(\mathbf{x}_2)\cdots\psi_N(\mathbf{x}_N), \quad (15)$$

is a Slater determinant and serves as a basis of Hartree–Fock and Kohn–Sham theory. The composite variable \mathbf{x}_i comprises the usual spatial coordinates \mathbf{r}_i and a spin label σ_i . The antisymmetrizer \hat{A} ensures that the Pauli principle is fulfilled.⁵² The auxiliary functions $\psi_i(\mathbf{x})$ are the well-known (one-component) molecular orbitals, which are not uniquely defined due to the possibility of an arbitrary unitary transformation often used in localization procedures.⁵⁴ For a closed-shell system we are free to choose these orbitals as a product of spatial orbitals $\psi_i(\mathbf{r})$ and α - or β -spin functions, which are eigenfunctions of the square of the one-electron spin operator \hat{s}_i^2 . We then work in a (spin-) *restricted* framework.

A single Slater determinant is an eigenfunction of S^2 and of its z -component S_z ,

$$S^2\Phi = S(S+1)\Phi, \quad (16)$$

$$S_z\Phi = M_S\Phi, \quad (17)$$

in case of a closed-shell $S = 0$ or a high-spin $S = S_{\max}$ state. Note that high-spin here does not refer to $S_{\max} = N/2$ but is usually perceived as the maximum spin within a given open sub-shell, *e.g.* the d shell in an isolated transition metal atom. As introduced above, we again employ hartree atomic units, where the numerical values of the rest mass of an electron m , the elementary charge e and \hbar are equal to one.

A general open-shell system can, however, not be represented by a single Slater determinant if the approximate wavefunction shall still be an eigenfunction of S^2 . Already the triplet components of a two-electron system contain two single high-spin determinants with $S = |M_S|$, while the third is necessarily a linear combination of two Slater determinants. If a single *unrestricted* Slater determinant shall be constructed for an open-shell system by occupying α and β molecular orbitals, the number of excess α spin orbitals N^α is chosen such that $M_S = (N^\alpha - N^\beta)/2$. This *unrestricted* determinant is in general no longer a spin eigenfunction but one relies in practice on the fact that often the $M_S = S$ state is approximated. The deviation of the expectation value $\langle S^2 \rangle$ from the eigenvalue $S(S+1)$ is a descriptor for the amount of spin contamination. It is important to emphasize that the actual $\langle S^2 \rangle$ expectation value of a Slater determinant depends on the overlap integrals $O_{ij}^{\beta\alpha} = \langle \psi_i^\beta | \psi_j^\alpha \rangle$ of the *spatial* parts $|\psi_j^\alpha\rangle$ and $|\psi_i^\beta\rangle$ of the α and β

spin orbitals,

$$\langle \hat{S}^2 \rangle = S(S+1) + N^\beta - \sum_{i,j}^{N^\alpha, N^\beta} (O_{ij}^{\beta\alpha})^2, \quad (18)$$

as can be easily shown.⁵³ Thus, a single unrestricted Slater determinant is only an eigenfunction of \hat{S}^2 if all $\langle \psi_i^\beta | \psi_j^\alpha \rangle = \delta_{ij}$ and $N^\alpha = N^\beta$, which is usually not the case. However, an unrestricted Slater determinant is *always* an eigenfunction of \hat{S}_z ,

$$\hat{S}_z \Phi = \frac{1}{2}(N^\alpha - N^\beta)\Phi \Rightarrow \langle \Phi | \hat{S}_z | \Phi \rangle = \frac{1}{2}(N^\alpha - N^\beta), \quad (19)$$

as can be easily verified by virtue of Slater–Condon rules for one-electron operators.⁵³

4.1 Differential versus integral picture

In a paramagnetic substance an excess of α over β electrons exists in certain spatial regions (note that the denominations α and β are arbitrary so that the β excess does not need to be considered explicitly). The excess of α electrons ΔN can always be computed as an expectation value from a single Slater determinant containing one-electron spin orbitals, which are eigenfunctions of the squared one-electron spin operator, using eqn (19),

$$\Delta N = N^\alpha - N^\beta = 2\langle \Phi | \hat{S}_z | \Phi \rangle. \quad (20)$$

The connection between the wavefunction-based picture and a density-based description can be made if the nonrelativistic definition of the density,

$$\rho(\mathbf{r}_1) = N \int \sigma_1 \int d^3\mathbf{x}_2 \cdots \int d^3\mathbf{x}_N |\psi(\mathbf{x}_1, \mathbf{x}_2, \cdots, \mathbf{x}_N)|^2 \quad (21)$$

is employed. From this definition the electronic density of a single Slater determinant, which is simply the sum of the squared spin orbitals (see also the discussion of KS theory below), can be easily derived.

It is intuitively clear that the same result for $N^\alpha - N^\beta$ can also be obtained in a density-based scheme,

$$N^\alpha - N^\beta = \int [\rho^\alpha(\mathbf{r}) - \rho^\beta(\mathbf{r})] d^3r, \quad (22)$$

if the density is decomposed into two separate contributions from α and β electrons, i.e. $\rho = \rho^\alpha + \rho^\beta$, such that the spin polarization is then given by $m_z = \rho^\alpha - \rho^\beta$. Note that from a formal point of view, the use of the variables ρ and m_z is equivalent to the use of the individual variables ρ^α and ρ^β (in a nonrelativistic theory where spin is a good quantum number).

It is interesting to note that the spin polarization m_z facilitates a switch from the integral picture described so far to a differential, local picture, which allows us to assign a spin excess $m_z(\mathbf{r})$ to each point \mathbf{r} in space. Thus, once atomic or local basins are defined in coordinate space (for instance, through the quantum theory of atoms in molecules (AIM) developed by Bader⁵⁵) one may integrate $m_z(\mathbf{r})$ over such a basin A to obtain the local spin excess ΔN_A in this basin,

$$\Delta N_A = N_A^\alpha - N_A^\beta = \int_A [\rho^\alpha(\mathbf{r}) - \rho^\beta(\mathbf{r})] d^3r. \quad (23)$$

In general, we may define a couple of density functions from which any kind of expectation value can be calculated. Concerning spin the relevant density functions have been discussed in detail by McWeeny (see, for instance, his textbook⁵⁶). The density functions account for the fact that operators in quantum chemistry depend on one or two coordinates only so that integrations over all other coordinates can be carried out readily. An important finding regarding spin is the observation that one may define^{56,57} an invariant spin density so that the spin polarisation needs to be

considered only for one component of a multiplet, *e.g.* for $M_S = S$. All other components of the multiplet can then be calculated from this.

4.2. Local spin

As the spin state of any system is characterized in nonrelativistic quantum mechanics by the two quantum numbers S and M_S , the local values of these two quantum numbers are needed in order to characterize the subsystem A with respect to its local spin. The scalar total spin operators \hat{S}^2 and \hat{S}_z may be partitioned by local projection operators \hat{p}_A introduced by Clark and Davidson⁵⁸ in order to define corresponding local spin operators $\hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B$ and \hat{S}_{zA} ,^{58,59}

$$\hat{S}^2 = \sum_A \sum_B \hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B \quad \text{with} \quad \hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B = \sum_{ij}^{NN} \hat{p}_A(i) \hat{s}(i) \hat{p}_B(j) \hat{s}(j), \quad (24)$$

$$\hat{S}_z = \sum_A \hat{S}_{zA} \quad \text{with} \quad \hat{S}_{zA} = \sum_i^N \hat{p}_A(i) \hat{s}_z(i). \quad (25)$$

Note that the problem to define local or atomic basins is then moved to the definition of these projectors. However, they cannot be uniquely defined from a physical point of view; for instance, they depend on the choice of the atom-centered basis functions used for their construction. Nevertheless, the projection operators \hat{p}_A need to fulfil certain boundary conditions (see, *e.g.*, ref. 59 for a presentation) and their value depends significantly on the choice of proper atom-centered basis functions, which then define the atomic basin.

For a single-determinant wave function we obtain^{58,59} for the expectation values

$$\begin{aligned} \langle \hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B \rangle &= \frac{3}{4} \delta_{AB} \left[\sum_i^{N^\alpha} \langle i | \hat{p}_A | i \rangle + \sum_{\bar{i}}^{N^\beta} \langle \bar{i} | \hat{p}_A | \bar{i} \rangle \right] \\ &\quad + \frac{1}{4} \sum_{ij}^{N^\alpha N^\alpha} \langle i | \hat{p}_A | i \rangle \langle j | \hat{p}_B | j \rangle + \frac{1}{4} \sum_{\bar{i}\bar{j}}^{N^\beta N^\beta} \langle \bar{i} | \hat{p}_A | \bar{i} \rangle \langle \bar{j} | \hat{p}_B | \bar{j} \rangle \\ &\quad - \frac{1}{4} \sum_{ij}^{N^\alpha N^\alpha} \langle i | \hat{p}_A | j \rangle \langle j | \hat{p}_B | i \rangle - \frac{1}{4} \sum_{\bar{i}\bar{j}}^{N^\beta N^\beta} \langle \bar{i} | \hat{p}_A | \bar{j} \rangle \langle \bar{j} | \hat{p}_B | \bar{i} \rangle \\ &\quad - \frac{1}{4} \sum_{ij}^{N^\alpha N^\beta} \langle i | \hat{p}_A | i \rangle \langle \bar{j} | \hat{p}_B | \bar{j} \rangle - \frac{1}{4} \sum_{\bar{i}\bar{j}}^{N^\alpha N^\beta} \langle i | \hat{p}_B | i \rangle \langle \bar{j} | \hat{p}_A | \bar{j} \rangle \\ &\quad - \sum_{\bar{i}\bar{j}}^{N^\alpha N^\beta} \langle i | \hat{p}_A | \bar{j} \rangle \langle \bar{j} | \hat{p}_B | i \rangle \end{aligned} \quad (26)$$

and

$$\begin{aligned} \langle \hat{S}_{zA} \rangle &= \sum_i^{N^\alpha} \langle i | \hat{p}_A \hat{s}_z | i \rangle + \sum_{\bar{i}}^{N^\beta} \langle \bar{i} | \hat{p}_A \hat{s}_z | \bar{i} \rangle \\ &= \frac{1}{2} \sum_i^{N^\alpha} \langle i | \hat{p}_A | i \rangle - \frac{1}{2} \sum_{\bar{i}}^{N^\beta} \langle \bar{i} | \hat{p}_A | \bar{i} \rangle \\ &= \frac{1}{2} (N_A^\alpha - N_A^\beta), \end{aligned} \quad (27)$$

where the shorthand notation $\psi_i^\alpha = i$ and $\psi_{\bar{i}}^\beta = \bar{i}$ was used.

These last two equations provide two measures of local spin. Owing to the simple expression in eqn (27) obtained for a decomposed \hat{S}_z operator, its direct and intuitive interpretation and the fact, that it can be easily related to the definition of local spin in a density-based scheme as defined by eqn (23), we may propose $\langle \hat{S}_{zA} \rangle$ as the ultimate integral measure for local spin. Moreover, we should emphasize that conceptual problems arise because of nonzero $\langle \hat{S}_A \cdot \hat{S}_B \rangle$ expectation values for closed-shell molecules.⁵⁹

Since $\langle \hat{S}_{zA} \rangle$ is equal to $\frac{1}{2}(N_A^\alpha - N_A^\beta)$, where N_A^α and N_A^β are the α - and β -population of A, respectively, local spin can be calculated from standard basis-set-based population analysis (see also ref. 60) as well as from Bader's AIM-approach according to eqn (23). It is interesting to note that a Clark–Davidson analysis provides results for $\langle \hat{S}_{zA} \rangle$ very similar to those obtained according to Bader's AIM theory.⁵⁹ This is surprising because AIM relies on a real-space partitioning of the density, while a basis-set-based approach allows a decomposition with respect to the space of one-particle functions which are not confined to a given spatial region but produce a local, spatially not strictly bounded basin through the exponentially decaying tails of the atom-centered basis functions.

The most important population-analysis-based approach for the analysis of local spins, *i.e.*, for the calculation of N_A^α and N_A^β is likely to be a Mulliken population analysis of an unrestricted Slater determinant,⁵² which has been used for a long time for the determination of α - and β -spin excesses (see, for instance, the references given in McWeeny's book on 'Spins in Chemistry' first published in 1970⁵⁷). Apart from the fact that the Mulliken analysis is strongly basis set dependent, Mulliken "projectors" to represent \hat{p}_A are not rigorously defined, *i.e.*, they are not true projection operators as discussed in ref. 59. Nevertheless, calculations on open-shell clusters are routinely carried out based on this special type of population analysis and turned out to yield results comparable to those from the Clark–Davidson scheme (see also ref. 61). This is likely to be due to the fact that the resulting spin excess ΔN_A on atom A is calculated from a difference such that errors may cancel out. For an illustration of this point we refer to the data presented for the NO molecule in Table 1.

To conclude, local spin is for several reasons best captured *via* a decomposition of the \hat{S}_z operator allowing us to calculate $\langle \hat{S}_{zA} \rangle$ expectation values. In qualitative discussions, one is then led to say that a negative ΔN_A for basin A is due to an excess of *spin-down* electrons in that basin, while a positive value documents a *spin-up* excess. But note that this is only possible because M_S is a good quantum number for any kind of Slater determinant (while S is usually not for unrestricted Slater determinants).

Finally, it is important to note that the analysis of local spin expectation values or spin densities integrated over atomic basins is only valid if the reference wavefunction used for the decomposition is meaningful. This crucial prerequisite is difficult to confirm within the framework of Kohn–Sham DFT as we shall discuss now.

4.3. Kohn–Sham (KS) and broken-(spin)-symmetry in Density Functional Theory (DFT)

The discussion of spin in the context of single (unrestricted) Slater determinants is of tremendous importance to computational chemistry because most quantum chemical calculations carried out these days are performed within the theoretical framework of KS-DFT. The most important obstacle in these calculations is the problem of spin contamination in open-shell cases. If spin contamination is detected as a deviation of $\langle \hat{S}^2 \rangle$ from $S(S + 1)$ it is either neglected if the deviation is small or it is discussed that a spin projection technique⁶² should be applied. Results from such a DFT calculation are treated as if they need to be discussed like those from a wavefunction-based method with respect to spin.

Table 1 Comparison of partial spins \hat{S}_{zA} (in hartree atomic units) calculated according to eqn (27) employing Mulliken, Löwdin and Löwdin* projectors for the doublet state of NO with different basis sets (the B3LYP functional as implemented in TURBOMOLE was used^{104,105}). For Löwdin* projectors the standard Löwdin protocol was modified in such a way that the basis set was first orthonormalized within the basis functions centered on one atom and it was afterwards subjected to the usual Löwdin orthonormalization procedure. The local spin expectation values were calculated with our implementation in the MOLOCH module of TURBOMOLE⁵⁹

		N (NO)			
		N_A	N_A^α	N_A^β	$2\langle\hat{S}_{zA}\rangle$
3-21G	Mulliken	6.78	3.56	3.22	0.34
	Löwdin	6.99	3.66	3.33	0.33
	Löwdin*	6.98	3.65	3.33	0.33
6-31G*	Mulliken	6.89	3.62	3.27	0.35
	Löwdin	7.00	3.66	3.34	0.33
	Löwdin*	7.01	3.66	3.35	0.32
SV(P)	Mulliken	6.96	3.65	3.31	0.35
	Löwdin	7.02	3.67	3.35	0.33
	Löwdin*	7.05	3.69	3.36	0.33
TZVP	Mulliken	7.01	3.68	3.33	0.35
	Löwdin	6.99	3.67	3.33	0.34
	Löwdin*	6.95	3.64	3.31	0.33
TZVPP	Mulliken	7.54	3.94	3.60	0.35
	Löwdin	7.15	3.74	3.41	0.33
	Löwdin*	7.15	3.74	3.41	0.33

The important point of Kohn and Sham is that their scheme calculates a surrogate density ρ^{KS} to be exactly identical with the sought-for density ρ of the N -electron molecule. The surrogate density shall be the density of a noninteracting Fermionic system. Noninteracting means that the corresponding Hamiltonian \hat{H}^{KS} does not contribute two-electron terms like Coulombic interaction operators $1/r_{ij}$ but only local potential energy operators $\hat{v}(\mathbf{r})$. It can thus be exactly decomposed into a sum of one-electron operators \hat{h}_i ,

$$\hat{H}^{\text{KS}} = \sum_{i=1}^N \hat{h}_i = \sum_{i=1}^N [\hat{t}_i + \hat{v}_i], \quad (28)$$

where all local potential energy terms are collected in \hat{v}_i while the kinetic energy operator \hat{t}_i is chosen to be identical to the one used in Hartree–Fock theory and in the exact nonrelativistic many-electron Hamiltonian, respectively. As usual, all errors arising from this particular choice of the kinetic energy are also absorbed in the only unknown though existing quantity of this procedure, namely the exchange–correlation potential which is included in the potential term \hat{v}_i . Thus, the KS Hamiltonian does not contain any two-electron coupling terms and the *exact* eigenfunction is an antisymmetrized Hartree product, *i.e.*, a Slater determinant. In the KS approach, the problem of treating exactly electron correlation is thus shifted from the problem to construct the exact wavefunction, which is in a complete one-particle basis an infinite sum of Slater determinants in wavefunction-based theories (full configuration interaction), to the problem of finding the correct local potential $v(r)$, which guarantees that $\rho^{\text{KS}} = \rho$. The exact local potential $v(\mathbf{r})$ is (currently) not known and only approximate exchange–correlation functionals are at hand.

It is most important to understand the decisive point of the Kohn–Sham scheme which is the fact that $\rho^{\text{KS}} = \rho$ can indeed be fulfilled by a single Kohn–Sham Slater determinant Φ^{KS} .⁶³ It exists a Slater determinant Φ^{KS} , which is the exact eigenfunction of \hat{H}^{KS} , whose corresponding density,

$$\rho^{\text{KS}} = \sum_{i=1}^N |\psi_i^{\text{KS}}(\mathbf{r})|^2 \quad (29)$$

equals exactly the density ρ of the fully interacting N -electron system.^{9,63}

If a single Slater determinant for an open-shell system is calculated within the Kohn–Sham scheme with present-day functionals, the spin symmetry with respect to S^2 should not be forced to be conserved (see also ref. 64), as the variational condition from which the orbitals are calculated would be lifted and the energy would rise. Also, if spin symmetry is enforced, results for dissociation energies as witnessed in the simple but prototypical case of H_2 come out wrong.⁶⁵ The spin constraint can, however, be always introduced if the corresponding Hamiltonian does not depend on spin variables.

An antiferromagnetically coupled (open-shell) singlet state represents a severe problem for KS-DFT since it is, qualitatively speaking, a generic *degenerate* two-determinant case and thus difficult to describe by a single-determinant method. A problem of a broken-symmetry Slater determinant is, as has been discussed recently by Neese⁶⁶ in the context of a proper definition of ‘magnetic’ orbitals, that the spin density of an antiferromagnetically coupled, open-shell singlet state should vanish at any point in space, because any singlet wavefunction should not produce a spin excess anywhere in space. To derive this result for a general many-electron system it is necessary to demonstrate that matrix elements over (symmetry-adapted) singlet configuration state functions needed for the calculation of the spin density in the exact full configuration interaction case are all zero. (This can be accomplished, for instance, from the derivation of Slater–Condon-type rules most conveniently treated in the language of second quantization as revisited by Ganyushin and Neese in a recent work⁶⁷).

Nonetheless, the broken-symmetry KS determinant is often treated as a true wavefunction and then decomposed into contributions from pure-spin configuration state functions (see, *e.g.*, ref. 66), *i.e.*, expanded in a basis set of such configuration state functions. Practical experience with approximate density functionals shows that the spin is broken in such cases due to the approximate nature of current density functionals. The situation is most easily explained with the example of dihydrogen dissociation, which can be understood as a generic model system of any transition metal cluster. Therefore, the KS symmetry problem has been discussed for the H_2 example and the consequences for the density functionals and the resulting exchange and correlation energy contributions^{65,68,69} (see also the recent account on the unrestricted Hartree–Fock model by Nesbet⁷⁰ and his very early papers on the H_2 dissociation problem cited therein).

The H_2 molecule undoubtedly features a closed-shell singlet ground state at its equilibrium bond distance. Once the two hydrogen atoms are moved away from one another to the limit of isolated but spin-coupled atoms, the true singlet wavefunction would still not show any spin polarization. The triplet state would be degenerate with this singlet state in the asymptotic limit at very large distances. From an experimental point of view, one would be able to determine the spin state of the isolated hydrogen atom no matter how this hydrogen atom was produced. Although this is not relevant for the line of reasoning in theory as the KS approach should match the exact solution from the wavefunction-based formulation, it may give a hint why the calculation and interpretation of broken-symmetry states is so popular and perhaps also why it is so successful if one considers antiferromagnetically coupled systems in the weak coupling limit. The question is, how the total electronic

energy behaves upon breaking the spin symmetry, which shall be considered at the end of this section.

Thus, problems arise if one considers symmetries like spatial point group symmetries or spin symmetries. Since the density enters the electron–electron interaction functional from which the potential of the KS Hamiltonian is derived, the KS Hamiltonian may be of different symmetry than the exact many-electron Hamiltonian. For instance, the exact Hamiltonian does not depend on spin operators and is thus invariant under rotations in spin space, which does not apply to a KS Hamiltonian used within a spin-unrestricted formulation that may allow for different broken-symmetry α - and β -spin densities, which in turn affect the symmetry of the KS Hamiltonian through the functional (see the account by Görling⁷¹ for an extensive discussion of this symmetry dilemma and its possible solution).

Contemporary approximate density functionals tend to break spatial and spin symmetry of the single-determinant wavefunction. One can easily observe this if the self-consistent field procedure is started with an Extended-Hückel guess for the molecular orbitals of a binuclear cluster. The EHT guess avoids spin-symmetry breaking but this is then introduced upon optimization of the orbitals within a Kohn–Sham DFT computer program (see ref. 72 for examples).

After these remarks we recall the Broken-Symmetry (BS) approach proposed by Noodleman.^{73–75} This method is based on the construction of two states. One of these states is the high-spin state, where all active orbitals are singly occupied and have spin up. Such a state can always be represented by a single determinant (see above). The molecular orbitals in this determinant are assumed to be essentially localized on the two centers i and j having $M_i = S_i$ and $M_j = S_j$ so that $S = S_i + S_j$. The second state is the broken-symmetry state with $M_i = S_i$ and $M_j = S_j$ so that $M_S = S_i - S_j$ but with undefined total spin S . The construction of the broken-symmetry state, which may either be converged accidentally⁷² or by a suitably chosen starting approximation for the orbitals or through a constrained DFT approach,^{62,76} is the crucial part in this approach. In Noodleman's description, the broken-symmetry ansatz relies on spin projection procedures and on *local* (or localizable) orbitals. From the point of view of basic KS-DFT with approximate functionals we stress that the correct state is the one with lowest energy with respect to the variational procedure for a given (approximate) functional.

In the recent literature, there have been extensive discussions on whether spin projection should be enforced or not for broken-symmetry solutions (see, *e.g.*, ref. 77–80). The main argument in favor of spin projection is that the broken-symmetry state may be expanded in terms of pure spin states with corresponding total energies in one way or another. This projection should be carried out since the exact nonrelativistic many-electron Hamiltonian commutes with the total spin operators and the wavefunction should thus be classified according to a definite total spin quantum number (see also the most recent work by Illas *et al.*⁸¹).

If spin projection is carried out to obtain a pure spin state, this raises, in general, the total KS energy (obtained with some standard approximate functional) because an additional constraint is applied. In principle, this is not wanted since the KS energy is determined in a variational procedure and the variational degrees of freedom are solely defined through the theorems of spin-DFT^{82,83} and should not be restricted through requirements which limit the variational space as in the case of spin projection. However, if the Hamiltonian in the exact Kohn–Sham approach or in one of its approximate variants does not explicitly depend on spin, the Kohn–Sham Slater determinant may well be classified according to spin and spin symmetry breaking should not occur. This dilemma is most pronounced in the case of bond breaking, where a non-degenerate true singlet wavefunction possesses multireference character and requires at least two Slater determinants for its qualitatively correct approximation.

It must be stressed that if numerical results obtained in contemporary Kohn–Sham calculations do not agree with any chosen reference or with fundamental facts,

this is usually due to the approximate nature of present-day density functionals and is the main problem for all numerical comparisons. Some general types of error occurring for the approximate density functionals have been identified. The one which is most important in our context is the self interaction error introduced through the approximate exchange functional not capable of compensating the self-interaction terms in the Coulomb contribution—a second one, which is the dispersion error, is of less importance here. However, it is very difficult to draw conclusions and obtain results of general validity from numerical studies of these errors as these would also depend on the particular system (see, for instance, the strong system dependence of spin state energy splittings with respect to the admixture of (self-interaction correcting) exact exchange in ref. 84 and 85).

There has also been some discussion about the possibility and usefulness of interpreting Kohn–Sham molecular orbitals^{86–88} (occasionally such discussions are even based on purely numerical and pictorial comparisons of KS orbitals and orbitals obtained with other wavefunction-based methods like Hartree–Fock theory). A straightforward interpretation of Kohn–Sham orbitals is at hand owing to the simple relation between the KS density and the KS orbitals given in eqn (29). The square of each KS orbital adds up to the density and the spatial extent of a KS orbital is thus of direct significance. Even a theorem similar to Koopmans' theorem in Hartree–Fock theory, which provides an interpretive basis for the Hartree–Fock model, holds.^{89–91}

The next question that arises is whether the local spin concept discussed above can be directly transferred to the KS Slater determinant and its KS orbitals, which refer to a noninteracting surrogate system of fermions. We may adopt the pragmatic point of view that the KS orbitals directly determine the spin densities $\rho^\alpha = \sum_i |\psi_i^\alpha|^2$ and $\rho^\beta = \sum_i |\psi_i^\beta|^2$. Therefore, we may decompose $\langle \Phi^{\text{KS}} | \hat{S}_z | \Phi^{\text{KS}} \rangle$ in order to obtain the difference of α and β electrons at a given center according to the principles described in the preceding two sections, which relate a density-based scheme to a single-determinant wavefunction picture (*i.e.*, the KS determinant of the surrogate system). An interpretation of KS orbitals is thus allowed, meaningful and useful if this interpretation rests on the fact that the squared KS orbitals add up to yield the total electronic density. The relation between the spin densities and the (surrogate) KS orbitals can be established through eqn (27) (or through the corresponding equation for the total spin operator \hat{S}_z):

$$N_A^\alpha - N_A^\beta = \sum_i^{N^\alpha} \langle \hat{p}_A | i \rangle - \sum_i^{N^\beta} \langle \hat{p}_A | \bar{i} \rangle \rightarrow \langle \rho_A^\alpha \rangle - \langle \rho_A^\beta \rangle = N_A^\alpha - N_A^\beta, \quad (30)$$

(the arrow sign, \rightarrow , has been chosen instead of the equality sign in order to emphasize that the projection operator to decompose the total spin densities need not be a projector defined through atom-centered basis functions.)

To conclude this section, we note that due to the surprising success of broken-symmetry methods—even when employed directly, *i.e.*, without the detour to spin project *via*, *e.g.*, a Heisenberg Hamiltonian as commented on in the next section—one may wonder whether this is because of the fact that the total electronic density obtained in a broken-symmetry calculation approximates the exact total density well so that the energy values are meaningful. One would like to assume in this case that the two broken-symmetry solutions of an antiferromagnetically coupled system, $(\rho_{\text{left}}^\uparrow, \rho_{\text{right}}^\downarrow)$ and $(\rho_{\text{left}}^\downarrow, \rho_{\text{right}}^\uparrow)$, respectively, with identical total densities represent an ensemble of densities for which the total electronic energies $E^{\text{BS1}}[\rho_{\text{left}}^\uparrow, \rho_{\text{right}}^\downarrow] = E^{\text{BS2}}[\rho_{\text{left}}^\downarrow, \rho_{\text{right}}^\uparrow]$ approximate $E_{\text{exact}}^{\text{KS}}[\rho]$ well. However, a detailed study of the problem would be hampered by the fact that we have only approximate exchange and correlation functionals at hand, which are subject to mutual error compensations. The difficulty here is that the broken-symmetry solution does produce results in good agreement with experimental data (or even with calculated reference data) but only in combination with the approximate, symmetry-breaking density functionals, which

would have to be compared with the exact density to enter the exact KS density functional. Not surprisingly, a cross combination would not provide such ‘good’ results (if the exact density would be used in combination with the approximate density functional). This issue has been elaborated by Perdew, Savin and Burke⁶⁵ who define an on-top pair density to be interpreted in broken-symmetry cases instead of the doubtful spin density in order to deal with the excellent results obtained directly from the broken-symmetry state without altering the broken-symmetry calculations.

If, on the other hand, one is not satisfied with the situation that the Kohn–Sham description in the broken-symmetry case does not feature the correct symmetry properties of the true states and Hamiltonian, a solution might be brought about by sophisticated new functionals as advanced by Della Sala and Görling.⁶⁹

4.4. A comment on the Heisenberg Hamiltonian

The energy difference of the ferromagnetic and the antiferromagnetic state of a system with two coupled magnetic centers A and B is usually described by the exchange contribution of the unpaired electrons in the Hartree–Fock picture. Dirac, Heisenberg and van Vleck have pointed out that such a system can be described phenomenologically by a vector coupling model,^{92–95} in which the Heisenberg Hamiltonian is represented by⁹⁶

$$\hat{H} = -2J_{AB}\hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B. \quad (31)$$

This model does not describe electrons but two interacting local spin vectors fixed at some point in space. The orientation of the two vectors is allowed to be either parallel (ferromagnetic coupling) or antiparallel (antiferromagnetic coupling). The local spins, S_A and S_B , are traditionally assigned by chemical intuition. Naturally, in view of our discussion so far it is not surprising that $\hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B$ has been taken literally as a quantum chemical operator which acts on electronic wavefunctions. The expectation value of $\langle \hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B \rangle$ may then be calculated in a rigorous way using the local projector technique by Clark and Davidson.^{58,97}

The structure of the BS wavefunction lends itself to an interpretation in terms of the interacting Heisenberg spins although this is not even advised by the re-interpretation of broken-symmetry results in terms of the on-top pair density.⁶⁵ Noodleman’s scheme allows the calculation of J_{AB} based on the energy difference between a BS determinant which describes the antiferromagnetically coupled state (usually with $S = 0$ if the two local spins on A and B are equal) and a determinant which describes the ferromagnetically coupled state (usually the high-spin state if no intermediate local spins are energetically low lying)⁷³. Broken-symmetry and high-spin states are related by an inversion of the *local* spins of all unpaired electrons on one center and thus have the same local S_A and S_B quantum numbers, but M_{S_A} or M_{S_B} with inverted sign. Noodleman’s original expression has been used and extended by various authors (as Clark and Davidson⁵⁸ note, too many papers have appeared such that a comprehensive review would not be possible within the framework of a single paper like this one). A comparison of different ways of calculating Heisenberg coupling constants with BS approaches for systems containing two magnetic centers was given by Soda and Yamaguchi *et al.*,⁹⁸ who also addressed the strong dependence of the coupling constant on the parameters which enter the approximate exchange–correlation potentials in present-day density functionals (see also the extensive study in ref. 72).

It should be emphasized that the calculated Heisenberg coupling constants are in general small. The typical range covers 10 to 500 cm^{−1} in absolute value, *i.e.*, 0.1 to 6 kJ mol^{−1}, which is in the range of the thermal energy RT and thus below the accuracy of present-day DFT methods. To achieve the required accuracy of DFT results one needs therefore to trust in a systematic error cancellation to take place when energies of two different spin states are compared. This error compensation

may be invoked because of the fact that the same or at least very similar molecular structures are used for the optimization of the KS energy.

5. The problem of approximate density functionals: a typical example

As discussed so far, actual calculations on open-shell systems are hampered by the accuracy of currently available density functionals. While contemporary density functionals are already of questionable reliability for paramagnetic and ferromagnetic states, the situation is even more critical for antiferromagnetic (broken-symmetry) states. Nonetheless, the latter type of states is often the energy minimum (ground) state (as will also be shown for the examples discussed in this section). Due to the lack of accurate *ab initio* results most studies usually compare directly with experiment, which may easily lead to the wrong conclusions about the reliability of a given DFT approach (remember also that not only the energy but also the corresponding molecular structure needs to be determined within the computational approach).

In order to investigate the range of results one may obtain from DFT calculations on a typical system— $\text{Mn}_2\text{O}_2^{2+}$ in this case—we present data relevant for our discussion of local spin expectation values as well as of energy splittings, which would be relevant for a derivation of Heisenberg coupling constants. Results on $\text{Mn}_2\text{O}_2^{2+}$ are complemented by a study of the heavier homologue $\text{Re}_2\text{O}_2^{2+}$ so that the role of relativity in such calculations can be highlighted.

All one-component results presented in this section were obtained with the TURBOMOLE suite of DFT programs,⁹⁹ into which we have implemented our arbitrary-order one-component DKH algorithm,⁴⁴ which replaces the one-electron Schrödinger operator in matrix form by the *n*th order DKH*n* operator. The calculations on $\text{Mn}_2\text{O}_2^{2+}$ were performed as all-electron calculations employing the TZVP basis set by Schäfer *et al.*¹⁰⁰ (in addition, for the BP86 functional we utilized the resolution-of-the-identity (RI) density fitting method with auxiliary bases produced by the Karlsruhe group¹⁰¹). For Re we employed a Stuttgart effective core potential (ECP).¹⁰² But we also carried out scalar-relativistic DKH*n* all-electron calculations for $\text{Re}_2\text{O}_2^{2+}$ with a decontracted basis set by Dyall¹⁰³ comprising 29 s-type, 24 p-type, 15 d-type, 10 f-type and one g-type primitive Gaussian basis functions. For the open-shell singlet state and the triplet state separate optimizations were carried out with equal and different (*i.e.*, two electron excess for the α -orbital series compared to the β occupation) occupation numbers, respectively. The open-shell singlet state turned out to be always the minimum energy state when compared to the triplet state. Thus, the triplet state is an excited state, which is treated here with ground-state DFT methods due to the fact that it is the lowest energy state within triplet spin symmetry. A closed-shell singlet state is difficult to optimize and always much higher in energy than the open-shell singlet. For the following discussion we note that no irregularities like orbitals with positive orbital energies or unoccupied orbitals with energies below those of the occupied ones were observed in the calculations.

In order to probe the effect of approximate density functionals on molecular structure, spin state energy splittings and local spin, we use the B3LYP functional^{104,105} as implemented in TURBOMOLE and modify the admixture of Hartree–Fock-type exact exchange from 0% to 25% in steps of 5% monitored by the coefficient c_3 (according to the notation of ref. 106). The role of Hartree–Fock-type exchange in density functionals for spin-symmetry breaking for small molecules such as NO_3 , O_4^+ and O_2^+ has been emphasized by Sherrill, Lee and Head-Gordon¹⁰⁷ who observed this for unusually large fractions of Hartree–Fock-type exchange but not for pure density functionals and small fractions of exact exchange. In the case of transition metal systems the situation is different and a small modification of the exact exchange admixture *via* parameter $c_3 \in \{0.00, \dots, 0.25\}$ affects spin breaking and spin state energetics significantly. However, incorporation

of exact exchange into the functional produces nonlocal functionals, which partially also correct for the notorious self interaction error with increasing admixture. It is thus not easy (if desired at all) to understand and decompose total energy differences into various effects. Nevertheless, many hybrid functionals are in use and it is therefore illustrative and important for computational chemistry to show the magnitude of effects—especially in combination with effects concerning the molecular structure.

In the case of the Mn cluster, spin delocalization onto the μ -oxo bridges is found to be negligible: for all exact exchange admixture values it is below 0.00022 au in the single point calculations and only slightly (but not systematically) larger if the optimized structures are considered. A similar picture emerges for the Re cluster.

It is important to understand that the seemingly erratic behaviour of energies and local spin values as witnessed in Fig. 4 and 5 is solely determined by changes in the optimized molecular structures with changing functional. For fixed molecular structures, the spin state energy difference and the local spin change monotonously with varying exact exchange admixture. However, abrupt changes in the molecular structure with smoothly varying amounts of exact exchange in the density functional result in nonmonotonous changes of energy splittings and local spin. Fig. 6 shows for which exact exchange admixture structural changes occur. The change of structure of $\text{Re}_2\text{O}_2^{2+}$ at $c_3 = 0.15$ for the open-shell singlet and at $c_3 = 0.20$ for the triplet state is the reason for the peak in energy difference witnessed in Fig. 4, which is not present if a fixed structure is used throughout the energy calculation. We should mention that calculations with exchanged structures confirm this picture, *i.e.*, the structural changes do not appear to be artifacts of simultaneous existence of distinguishable but similar local minima for a given density functional in the unrestricted framework.

The problem of different local minimum structures obtained in structure optimizations within *unrestricted* schemes is well-known even for small and light molecules like the diatomic CN diradical as discussed in some detail in ref. 108. In the case of

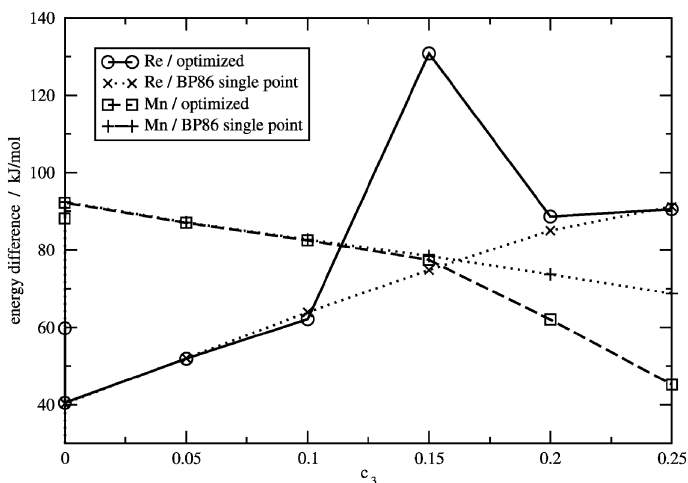


Fig. 4 Singlet–triplet energy differences of $\text{Re}_2\text{O}_2^{2+}$ and $\text{Mn}_2\text{O}_2^{2+}$ model clusters in kJ mol^{-1} . Note that the singlet is the open-shell, antiferromagnetically coupled singlet state. The closed-shell singlet lies either higher in energy (Re case) or cannot be converged in the SCF procedure (Mn case; convergence cannot even be achieved if strong damping is applied). The open-shell singlet is in all cases lower in energy than the triplet. Note that the seemingly irregular behavior is due to the different optimized structures as discussed in the text. The additional symbol at $c_3 = 0$ for the optimized curves denotes the value calculated for BP86/R1/TZVP. The dinuclear Mn cluster was considered in nonrelativistic all-electron calculations, while for the corresponding Re system a Stuttgart ECP¹⁰² was used.

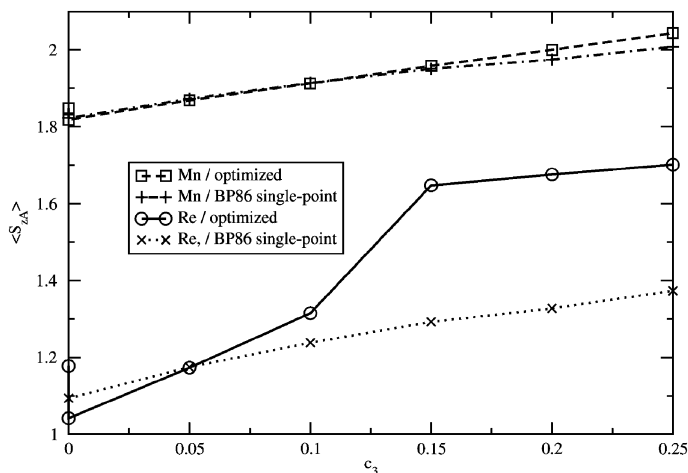


Fig. 5 Local spin values $\langle \hat{S}_{zA} \rangle$ (in hartree atomic units) for one Mn and one Re center in the open-shell singlet complexes $\text{Mn}_2\text{O}_2^{2+}$ and $\text{Re}_2\text{O}_2^{2+}$, respectively, are plotted against the admixture c_3 of exact Hartree-Fock-type exchange. The 'optimized' data was obtained with the corresponding modified B3LYP density functional, while the single-point calculations were carried out for the BP86/RI/TZVP-optimized structures. Note that the corresponding second metal center in each complex features a comparable absolute local spin but with opposite sign as one would expect. The dinuclear Mn cluster was considered in nonrelativistic all-electron calculations, while for the corresponding Re system a Stuttgart ECP¹⁰² was used.

transition metal complexes and clusters this situation appears to get more severe. Slight changes of the density functional have a substantial effect on the structure. One might argue that this could be pronounced in the case under study because of the possible existence of a more symmetric quadratic structure for the metal clusters whose *spatial* symmetry is broken by the density functionals employed. Even if this

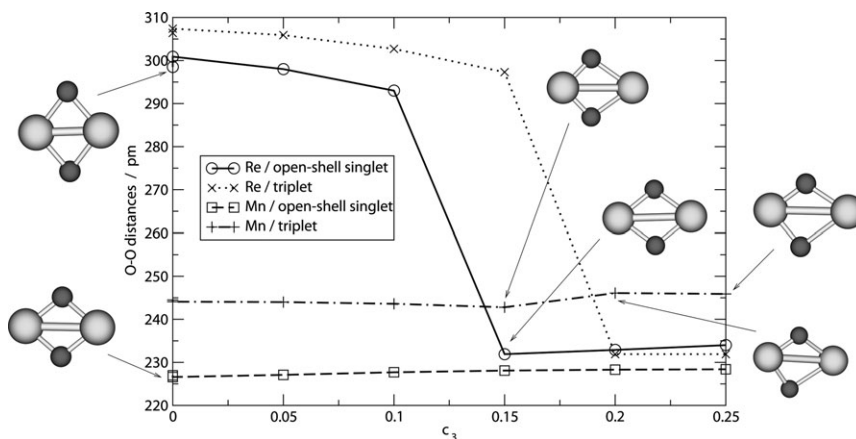


Fig. 6 O–O distances in pm of optimized molecular structures obtained for $\text{Re}_2\text{O}_2^{2+}$ and $\text{Mn}_2\text{O}_2^{2+}$ in the open-shell singlet (= broken-symmetry) and in the triplet states. All structures are planar. For the broken-symmetry $\text{Re}_2\text{O}_2^{2+}$ structure a change from obtuse OReO angle to acute OReO angle with long Re–Re distance occurs at $c_3 = 0.15$, while this structural change is found at $c_3 = 0.20$ for the corresponding triplet state. In the case of the Mn cluster, no such abrupt change only a slight change takes place. The structure is then in general not symmetric and becomes more skew if more exact exchange is admixed to the functional. The dinuclear Mn cluster was considered in nonrelativistic all-electron calculations, while for the corresponding Re system a Stuttgart ECP¹⁰² was used.

Table 2 Comparison of nonrelativistic and scalar-relativistic *all-electron* single-point calculations for the two model clusters $\text{Mn}_2\text{O}_2^{2+}$ and $\text{Re}_2\text{O}_2^{2+}$ for the BP86/RI/TZVP optimized open-shell singlet structures. The open-shell singlet (oss) KS energies $E_{\text{KS}}^{\text{oss}}$ and triplet energies E_t^{KS} (n hartree atomic units) and their difference $\Delta E_{\text{KS}} = E_t^{\text{KS}} - E_{\text{oss}}^{\text{KS}}$ (in kJ mol^{-1}) are given. The local spin values $\langle \hat{S}_{zA} \rangle$ for one of the Mn and Re metal centers, respectively, in the open shell singlet are given in the last column. The \hat{S}_{zA} expectation values correspond to those depicted in Fig. 5. Note that the energy differences ΔE^{KS} are to be understood as vertical excitation energies

Cluster	Method	$E_{\text{oss}}^{\text{KS}}$	E_t^{KS}	ΔE^{KS}	$\langle \hat{S}_{zA} \rangle$
$\text{Mn}_2\text{O}_2^{2+}$	BP86/TZVP,nr	−2452.2045055	−2452.1480230	148.3	1.851
	BP86/TZVP,DKH10	−2464.3157051	−2464.2589791	148.9	1.857
$\text{Re}_2\text{O}_2^{2+}$	BP86/Dyall,nr	−31 730.253 2211	−31 730.230 6166	59.3	1.077
	BP86/Dyall,DKH2	−33 518.476 0800	−33 518.450 6667	66.7	1.121
	BP86/Dyall,DKH4	−33 544.815 2990	−33 544.789 8571	66.8	1.121
	BP86/Dyall,DKH6	−33 545.910 7275	−33 545.885 3255	66.7	1.121
	BP86/Dyall,DKH8	−33 546.069 1386	−33 546.043 7874	66.6	1.121

would be the case the significant dependence of the structures on slight changes of the parameters in the functional is crucial for many areas of computational chemistry if, for example, questions in catalysis or bioinorganic chemistry with polynuclear clusters are addressed.

In order to investigate the effect of relativity on the local spin values and energy splittings we carried out scalar-relativistic DKH calculations to high order (see Table 2). The relativistic ECP of the Stuttgart group used so far does also include scalar-relativistic effects but in an effective manner introduced in the fitting procedure of the ECP. The DKH protocol allows us to study scalar-relativistic effects in detail in a rigorous *all-electron* theory.

As expected, for the manganese cluster $\text{Mn}_2\text{O}_2^{2+}$ data hardly changes if the nonrelativistic and DKH results are compared since manganese is considered to be a light element. The situation changes for the higher homologue $\text{Re}_2\text{O}_2^{2+}$, where the scalar-relativistic description has a noticeable effect on the energy splitting, which is increased by 7.4 kJ mol^{-1} (*i.e.*, the singlet state is more stable when relativistic effects are included). The local spin values are affected in a similar manner and increase from 1.077 to 1.121 (*i.e.*, by 4.1%), which may be traced back to the general contraction of the electronic density at heavy nuclei due to relativity (and must not be confused with the steep radial density increase in the case of highly charged ions described above). Note that the energy splittings and the local spin values do not change when different DKH orders are considered. It is well known that valence-shell properties are already converged at the second order, *i.e.*, within the DKH2 framework.^{109,110} Of course, in the case of both model clusters, the total energy is decreased, but this effect usually cancels when valence shell properties are considered since the main effect on the total energy stems from energetic core shell stabilization effects.

We should stress that the problem of qualitatively different cluster structures optimized with density functionals, which vary only little in their contribution of exact exchange, is a severe one since cluster structures optimized with unrestricted methods are afflicted with a unignorable uncertainty.

Note that numerical values of local spin and of energy differences of different total spin states (correspondingly, also of Heisenberg coupling constants) may depend significantly on the approximate exchange–correlation functional chosen because of the exact role Hartree–Fock-type exchange plays in the calculation of states of different spin multiplicity.^{84,85,106} For a detailed discussion and comparison of numerical results see ref. 72. One must also keep in mind that the effects discussed for exact exchange admixture are different in magnitude depending on the transition

metal complexes under consideration (see, *e.g.*, the classification scheme for mono-nuclear complexes in ref. 84).

After having discussed all parameters that affect results for different clusters in different ways, we may emphasize that a direct comparison of calculated and experimental results should be performed with great caution. The phenomenological Heisenberg Hamiltonian is often used to compare calculated and experimentally devised coupling constants J_{AB} between two local spin–spin-interacting centers A and B. However, if the BS solution is accepted to produce a density, which yields reliable energetics in combination with an approximate functional, we do not need to refer to such a Hamiltonian model. Also, coupling constants are often derived from the measured temperature dependence of the magnetic susceptibility and theory advises directly calculating this dependence within a response theory framework¹¹¹ instead comparing derivative quantities like J_{AB} , which also are not directly obtained from experiment. Nevertheless, we should stress that this view would not be generally shared because of the symmetry dilemma discussed above (see, for instance, the recent discussion by Moreira and Illas¹¹²).

5.1. Conclusions

In the preceding sections we have discussed the concept of local spin in wavefunction-based theory as well as in the framework of Kohn–Sham DFT. Special attention has been paid to spin emerging in the transition of a generally valid relativistic theory to a scalar-relativistic theory like Douglas–Kroll–Hess transformation theory.

In this context, the foundations of Kohn–Sham DFT are of special importance since this is the framework in which most of the quantum chemical calculations are carried out. However, in the chemical community KS-DFT is usually perceived as a Hartree–Fock variant with additional model potentials to account for electron correlation rather than as an independent approach to the electron correlation problem.

The direct interpretation of the KS wavefunction of a surrogate system of fermionic particles in this context might be possible owing to the direct contribution of the squared KS orbitals to the total electronic density and to the spin density in the context of approximate functionals. We also argued under which circumstances the broken-symmetry state may be interpreted and thus follow the lines of reasoning by Perdew, Savin and Burke⁶⁵ in order to account for the good results obtained from broken-symmetry calculations.

Even in the relativistic regime, the decomposition of \hat{S}_z into local contributions \hat{S}_{zA} is possible if spin-free scalar-relativistic one-electron Hamiltonians can be used so that an external quantization axis can be chosen (standard collinear approach). Whether the explicit use of spin in a relativistic framework can be justified may be quantitatively assessed in terms of the energy contribution of the neglected spin-dependent terms in the Hamiltonian. If these terms cannot be neglected (as a result of the calculation of their contribution to the energy or as a result of experience gained for certain molecular systems), the noncollinear approach in a two- or four-component framework will be unavoidable.

In this context it was necessary to discuss the electronic density computed within the standard scalar-relativistic DKH framework. It turned out that this density does not compare sufficiently well with the corresponding four-component-based density for $1s_{1/2}$ eigenstates of heavy ions like Hg^{79+} . For standard (*i.e.*, scalar-relativistic) DKH calculations one should keep in mind that the discrepancy was found for a highly-charged one-electron heavy ion. The effect is negligible in the case of Ca^{19+} . Moreover, for neutral molecules, the effect would be much less visible (if at all) so that one may safely conclude that the analysis of a scalar-relativistic DKH density in terms of local spin expectation values or within the AIM theory is reliable (if spin–orbit coupling can be neglected for this purpose). Then the DKH density may be

studied instead of an analysis of the corresponding four-component-based density, which is often cumbersome to obtain.

From the discussion of local spin in this work we summarize the following results: Local spin, which can be conveniently defined through the projection operator technique introduced by Clark and Davidson, should be defined based on the decomposition of the z -component of the total spin operator \hat{S}_z instead of to \hat{S}^2 because of the direct link to the local excess ΔN_A of α or β electrons, which can also be obtained in a density-based scheme. Accordingly, the decomposition of \hat{S}_z may also be applied in Kohn–Sham DFT to supplement the computationally involved “real-space projection” of Bader’s AIM theory.

From the study of the NO radical we understand that despite the different quantitative predictions of spin populations obtained with basis sets, the qualitative picture of local spins always remained essentially the same. For this reason, the standard Mulliken approach to assign a local spin state to a given atomic basin within a cluster works fine. Note that the local spin values are comparatively stable with respect to an exchange of the projection operator used to produce the atomic basin and with respect to the basis set chosen. This is due to a cancellation of errors upon subtracting absolute populations of α - and β -electrons as we have demonstrated for the NO example.

We included case studies on the $\text{Mn}_2\text{O}_2^{2+}$ cluster and its heavy homologue $\text{Re}_2\text{O}_2^{2+}$ in order to highlight the many difficulties, which one faces when spin state energetics need to be reliably calculated.

We have pointed out that the contribution of Hartree–Fock-type exact exchange dominates the absolute values of spin state energy splittings and local spin. This may be traced to particular deficiencies in the functional (*e.g.*, partial compensation of the self interaction error), but the main point to make is that hybrid functionals with varying Hartree–Fock-type exchange admixture are heavily used in computational chemistry and may thus provide significantly deviating results. This makes a direct comparison with experiment very difficult. To use such a comparison for a calibration of density functionals requires great caution. Also, a comparison to highly accurate *ab initio* reference data is difficult because of the large computational requirements. Nevertheless, initial attempts have been made (see the systematic studies by Casida and collaborators^{113–116}). As a consequence, assessing the reliability for spin state energetics is highly important but extraordinarily difficult.¹¹⁷

The at first sight erratic behaviour of energy splittings and local spin with varying exact exchange admixture has been traced back to abrupt structural changes with modified exact exchange. Note that the change in molecular structure described here is pronounced. This observation poses a very severe problem for calculations on any kind of spin–spin-interacting transition metal cluster since the structure of any cluster would have been optimized with a density functional whose selection cannot be carried out on the basis of empirical knowledge about the accuracy of the given functional because its accuracy depends on the system to be studied: there are no generally valid rules available that favor one functional over another for structure optimizations of polynuclear transition metal complexes. All highly correlated *ab initio* calculations on such systems would require a molecular structure, which is usually not obtained from structure optimization within the *ab initio* method chosen (owing to the size of such clusters) but which often stems from a DFT optimization and is thus affected by the difficulty to optimize a reliable molecular structure.

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References

- O. Kahn, *Molecular Magnetism*, Wiley VCH, New York, 1993.
- B. Gillon, *Mol. Cryst. Liq. Cryst.*, 1999, **334**, 765–784.
- E. Ressouche and J. Schweizer, *Monatsh. Chem.*, 2003, **134**, 235–253.
- S. Pillet, M. Souhassou and C. Lecomte, *Acta Crystallogr., Sect. A*, 2004, **A60**, 455–464.
- V. Baron, B. Gillon, O. Plantevin, A. Cousson, C. Mathonière, O. Kahn, A. Grand, L. Öhrström and B. Delley, *J. Am. Chem. Soc.*, 1996, **118**, 11822–11830.
- P. Javorský, M. Divis, F. Givord, J.-X. Boucherle, J. Ruzs, E. Lelièvre-Berna, V. Sechovský, A. V. Andreev and F. Bourdarot, *Phys. Rev. B*, 2003, **67**, 224429.
- N. Clauser, M. Souhassou and C. Lecomte, *J. Phys. Chem. Solids*, 2004, **65**, 1927–1933.
- N. Clauser, M. Souhassou, C. Lecomte, B. Gillon, C. Carbonera, A. Caneschi, A. Dei, D. Gatteschi, A. Bencini, Y. Pontillon and E. Lelièvre-Berna, *J. Phys. Chem. B*, 2005, **109**, 2723–2732.
- W. Kohn and L. J. Sham, *Phys. Rev. Sect. A*, 1965, **140**(4A), A1133–A1138.
- W. Scherer and G. S. McGrady, *Angew. Chem., Int. Ed.*, 2004, **43**, 1782–1806.
- G. S. McGrady, A. Haaland, H. P. Verne, H. V. Volden, A. J. Downs, D. Shorokhov, G. Eickerling and W. Scherer, *Chem.–Eur. J.*, 2005, **11**, 4921–4934.
- B. Kirchner, J. Stubbs and D. Marx, *Phys. Rev. Lett.*, 2002, **89**, 215901.
- P. Pykkö, *Chem. Rev.*, 1988, **88**, 563–594.
- P. Pykkö, *Chem. Rev.*, 1997, **97**, 597–636.
- M. Reiher and J. Hinze, in *Relativistic Effects in Heavy-Element Chemistry and Physics*, ed. B. A. Hess, Wiley, Chichester, 2003, pp. 61–88.
- M. Reiher, *Theor. Chem. Acc.*, 2006, **116**, 241–252.
- L. Visscher and E. van Lenthe, *Chem. Phys. Lett.*, 1999, **306**, 357–365.
- C. van Wüllen, *J. Comput. Chem.*, 2002, **23**, 779–785.
- J. Anton, B. Fricke and E. Engel, *Phys. Rev. A*, 2004, **69**, 012505.
- A. K. Rajagopal and J. Callaway, *Phys. Rev. B*, 1973, **7**, 1912–1919.
- E. Engel, R. M. Dreizler, S. Varga and B. Fricke, in *Relativistic Effects in Heavy-Element Chemistry and Physics*, ed. B. A. Hess, Wiley, Chichester, 2003, pp. 123–161.
- H. Ebert and E. K. U. Gross, in *Relativistic Effects in Heavy-Element Chemistry and Physics*, ed. B. A. Hess, Wiley, Chichester, 2003, pp. 163–217.
- F. Schwabl, *Quantenmechanik für Fortgeschrittene*, Springer-Verlag, Berlin, 3rd edn, 2004.
- A. H. MacDonald and S. H. Vosko, *J. Phys. C: Solid State Phys.*, 1979, **12**, 2977–2990.
- T. Saue and T. Helgaker, *J. Comput. Chem.*, 2002, **23**, 814–823.
- B. A. Hess, C. M. Marian and S. D. Peyerimhoff, in *Modern Electronic Structure Theory*, ed. D. R. Yarkony, World Scientific, 1995, pp. 152–278.
- B. A. Heß, *Ber. Bunsen-Ges. Phys. Chem.*, 1997, **101**(1), 1–10.
- B. A. Hess and C. M. Marian, in *Computational Molecular Spectroscopy*, ed. P. Jensen and P. Bunker, Wiley, Chichester, W. Sussex, 2000, pp. 169–219.
- M. Reiher and B. A. Hess, in *Modern Methods and Algorithms of Quantum Chemistry*, ed. J. Grotendorst, NIC Proceedings, Jülich, 2000, vol. **3**, pp. 479–505.
- Relativistic Effects in Heavy-Element Chemistry and Physics*, ed. B. A. Hess, Wiley, 2003.
- A. Wolf, M. Reiher and B. A. Hess, *Relativistic Quantum Chemistry—Theory of Theoretical and Computational Chemistry*, Elsevier, 2002, vol. **1**, pp. 622–663.
- A. Wolf, M. Reiher and B. A. Hess, in *Recent Advances in Relativistic Molecular Theory*, ed. K. Hirao and Y. Ishikawa, World Scientific Publishing, Singapore, 2004, pp. 137–190.
- E. van Lenthe, E. J. Baerends and J. G. Snijders, *J. Chem. Phys.*, 1993, **99**, 4597–4610.
- E. van Lenthe, E. J. Baerends and J. G. Snijders, *J. Chem. Phys.*, 1994, **101**, 9783–9792.
- R. van Leeuwen, E. van Lenthe, E. J. Baerends and J. G. Snijders, *J. Chem. Phys.*, 1994, **101**, 1271–1281.
- C. van Wüllen, *J. Chem. Phys.*, 1998, **109**, 392–400.
- M. Douglas and N. M. Kroll, *Ann. Phys.*, 1974, **82**, 89–155.
- B. A. Hess, *Phys. Rev. A*, 1986, **33**, 3742–3748.
- G. Jansen and B. A. Hess, *Phys. Rev. A*, 1989, **39**, 6016–6017.
- A. Wolf, M. Reiher and B. A. Hess, *J. Chem. Phys.*, 2002, **117**, 9215–9226.
- C. van Wüllen, *J. Chem. Phys.*, 2004, **120**, 7307–7313.
- M. Reiher and A. Wolf, *J. Chem. Phys.*, 2004, **121**, 2037–2047.
- A. Wolf and M. Reiher, *J. Chem. Phys.*, 2006, **124**, 064102.

- 44 M. Reiher and A. Wolf, *J. Chem. Phys.*, 2004, **121**, 10945–10956.
- 45 A. Wolf and M. Reiher, *J. Chem. Phys.*, 2006, **124**, 064103.
- 46 C. C. J. Roothaan and P. S. Bagus, in *Methods in Computational Physics. Quantum Mechanics*, eds. B. Alder, S. Fernbach and M. Rotenberg, Academic Press, London, 1963, vol. 2, pp. 47–94.
- 47 M. Reiher, PhD Thesis, Fakultät für Chemie, Universität Bielefeld, 1998.
- 48 D. Andrae, M. Reiher and J. Hinze, *Int. J. Quantum Chem.*, 2000, **76**, 473–499.
- 49 P. J. Mohr and B. N. Taylor, *Rev. Mod. Phys.*, 2000, **72**, 351–495.
- 50 C. van Wüllen, private communication, 2006.
- 51 V. Kellö and A. J. Sadlej, *Int. J. Quantum Chem.*, 1998, **68**, 159–174.
- 52 F. L. Pilar, *Elementary Quantum Chemistry*, McGraw-Hill, 2nd edn., 1990.
- 53 A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry*, Dover, New York, USA, 1996.
- 54 H. Primas and U. Müller-Herold, *Elementare Quantenchemie*, B. G. Teubner, Stuttgart, 2nd edn, 1990.
- 55 R. F. W. Bader, *Atoms in Molecules—A Quantum Theory*, Vol. 22 of International Series of Monographs on Chemistry, Oxford Science Publications, Oxford, 1990.
- 56 R. McWeeny, *Methods of Molecular Quantum Mechanics*, Academic Press, San Diego, 2nd edn, 2001.
- 57 R. McWeeny, *Spins in Chemistry*, Dover, New York, 1988.
- 58 A. E. Clark and E. R. Davidson, *J. Chem. Phys.*, 2001, **115**(16), 7382–7392.
- 59 C. Herrmann, M. Reiher and B. A. Hess, *J. Chem. Phys.*, 2005, **122**, 034102.
- 60 A. E. Clark and E. R. Davidson, *Int. J. Quantum Chem.*, 2003, **93**, 384–394.
- 61 C. Herrmann, J. Neugebauer, J. A. Gladysz and M. Reiher, *Inorg. Chem.*, 2005, **44**, 6174–6182.
- 62 J. S. Andrews, D. Jayatilaka, R. G. A. Bone, N. C. Handy and R. D. Amos, *Chem. Phys. Lett.*, 1991, **183**(5), 423–431.
- 63 J. E. Harriman, *Phys. Rev. A*, 1981, **24**, 680–682.
- 64 U. von Barth, *Phys. Rev. A*, 1979, **20**, 1693–1703.
- 65 J. Perdew, A. Savin and K. Burke, *Phys. Rev. A*, 1995, **51**, 4531–4541.
- 66 F. Neese, *J. Phys. Chem. Solids*, 2004, **65**, 781–785.
- 67 D. Ganyushin and F. Neese, *J. Chem. Phys.*, 2006, **125**, 024103.
- 68 A. Savin, in *Recent Developments and Applications of Modern Density Functional Theory*, ed. J. M. Seminario, Elsevier, 1996, p. 327.
- 69 F. Della Sala and A. Görling, *J. Chem. Phys.*, 2003, **118**, 10439–10454.
- 70 R. K. Nesbet, *Int. J. Quantum Chem.*, 2004, **102**, 602–605.
- 71 A. Görling, *Phys. Rev. A*, 1993, **47**, 2783–2799.
- 72 C. Herrmann, L. Yu and M. Reiher, *J. Comput. Chem.*, 2006, **27**, 1223–1239.
- 73 L. Noodleman, *J. Chem. Phys.*, 1981, **74**, 5737–5743.
- 74 L. Noodleman and D. A. Case, *Adv. Inorg. Chem.*, 1992, **38**, 423.
- 75 L. Noodleman, C. Y. Peng, D. A. Case and J. M. Mouesca, *Coord. Chem. Rev.*, 1995, **144**, 199.
- 76 I. Rudra, Q. Wu and T. V. Voorhis, *J. Chem. Phys.*, 2006, **124**, 024103.
- 77 F. Illas, I. de P. R. Moreira, J. M. Bofill and M. Filatov, *Phys. Rev. B*, 2004, **70**, 132414.
- 78 E. Ruiz, S. Alvarez, J. Cano and V. Polo, *J. Chem. Phys.*, 2005, **123**, 164110.
- 79 C. Adamo, V. Barone, A. Bencini, R. Broer, M. Filatov, N. M. Harrison, F. Illas, J. P. Malrieu and I. de P. R. Moreira, *J. Chem. Phys.*, 2006, **124**, 107101.
- 80 E. Ruiz, J. Cano, S. Alvarez and V. Polo, *J. Chem. Phys.*, 2006, **124**, 107102.
- 81 F. Illas, I. de P. R. Moreira, J. M. Bofill and M. Filatov, *Theor. Chem. Acc.*, 2006, **116**, 587–597.
- 82 U. von Barth and L. Hedin, *J. Phys. C: Solid State Phys.*, 1972, **5**, 1629–1642.
- 83 O. Gunnarsson and B. I. Lundqvist, *Phys. Rev. B*, 1976, **13**, 4274–4298.
- 84 M. Reiher, *Inorg. Chem.*, 2002, **41**, 6928–6935.
- 85 O. Salomon, M. Reiher and B. A. Hess, *J. Chem. Phys.*, 2002, **117**, 4729–4737.
- 86 R. Stowasser and R. Hoffmann, *J. Am. Chem. Soc.*, 1999, **121**, 3414–3420.
- 87 F. M. Bickelhaupt and E. J. Baerends, *Kohn-Sham Density Functional Theory: Predicting and Understanding Chemistry*, Wiley-VCH, New York, 2000, vol. 15, pp. 1–86.
- 88 D. P. Chong, O. V. Gritsenko and E. J. Baerends, *J. Chem. Phys.*, 2002, **116**, 1760–1772.
- 89 O. V. Gritsenko and E. J. Baerends, *J. Chem. Phys.*, 2002, **117**, 9154.
- 90 O. V. Gritsenko, B. Braida and E. J. Baerends, *J. Chem. Phys.*, 2003, **119**, 1937.
- 91 O. V. Gritsenko and E. J. Baerends, *J. Chem. Phys.*, 2004, **120**, 8364.
- 92 P. A. M. Dirac, *Proc. R. Soc. London, Ser. A*, 1926, **112**, 661–677.
- 93 P. A. M. Dirac, *Proc. R. Soc. London, Ser. A*, 1929, **123**, 714–733.
- 94 W. Heisenberg, *Z. Phys.*, 1926, **38**, 411.
- 95 W. Heisenberg, *Z. Phys.*, 1928, **49**, 619.

- 96 J. H. V. Vleck, *The Theory of Electric and Magnetic Susceptibilities*, Oxford University Press, Oxford, 1932.
- 97 E. R. Davidson and A. E. Clark, *J. Phys. Chem. A*, 2002, **106**, 7456–7461.
- 98 T. Soda, Y. Kitagawa, T. Onishi, Y. Takano, Y. Shigeta, H. Nagao, Y. Yoshioka and K. Yamaguchi, *Chem. Phys. Lett.*, 2000, **319**, 223–230.
- 99 R. Ahlrichs *et al.*, TURBOMOLE, <http://www.cosmologic.de/turbomole.html>.
- 100 <ftp://ftp.chemie.uni-karlsruhe.de/pub/basen>.
- 101 <ftp://ftp.chemie.uni-karlsruhe.de/pub/jbasen>.
- 102 D. Andrae, U. Häussermann, M. Dolg, H. Stoll and H. Preuss, *Theor. Chim. Acta*, 1990, **77**, 123–141.
- 103 K. G. Dyall, *Theor. Chem. Acc.*, 2002, **108**, 335.
- 104 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648–5652.
- 105 P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623–11627.
- 106 M. Reiher, O. Salomon and B. A. Hess, *Theor. Chem. Acc.*, 2001, **107**, 48–55.
- 107 C. D. Sherrill, M. S. Lee and M. Head-Gordon, *Chem. Phys. Lett.*, 1999, **302**, 425–430.
- 108 J. F. Stanton and J. Gauss, *Adv. Chem. Phys.*, 2003, **125**, 101–145.
- 109 A. Wolf, M. Reiher and B. A. Hess, *J. Chem. Phys.*, 2004, **120**, 8624–8631.
- 110 F. Neese, A. Wolf, T. Fleig, M. Reiher and B. A. Hess, *J. Chem. Phys.*, 2005, **122**, 204107.
- 111 J. Autschbach and T. Ziegler, *Coord. Chem. Rev.*, 2003, **238–239**, 83–126.
- 112 I. de P. R. Moreira and F. Illas, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1645–1659.
- 113 A. Fouqueau, S. Mer, M. E. Casida, L. M. Lawson Daku, A. Hauser, T. Mineva and F. Neese, *J. Chem. Phys.*, 2004, **120**, 9473.
- 114 A. Fouqueau, M. E. Casida, L. M. Lawson Daku, A. Hauser and F. Neese, *J. Chem. Phys.*, 2005, **122**, 044110.
- 115 L. M. Lawson Daku, A. Vargas, A. Hauser, A. Fouqueau and M. E. Casida, *Chem-PhysChem*, 2005, **6**, 1393–1410.
- 116 G. Ganzenmüller, N. Berkaine, A. Fouqueau, M. E. Casida and M. Reiher, *J. Chem. Phys.*, 2005, **122**, 234321.
- 117 J. N. Harvey, *Struct. Bonding*, 2004, **112**, 151–184.