

Calculation of local spins for correlated wave functions

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The recent formula for decomposing the expectation value $\langle S^2 \rangle$ of the total spin operator for general (correlated) wave functions has been rewritten in terms of the cumulant and is realized numerically for the first time. The results confirm its conformity with the physical expectations.

1. Introduction

In many cases the spin properties of a molecular system can properly be characterized by the spin density. It vanishes identically for a singlet system in every point of the space.† This is in accord with the fact that the ground state of most (especially organic) molecules is a singlet and they do not exhibit any explicit spin (magnetic) properties. There are, however, systems for which description by using the spin density is not sufficient to characterize the physical situation: binuclear complexes, diradicals or antiferromagnets. In such systems one postulates the existence of some *local spins*, although the overall system is a singlet and there is no spin density.

In order to distinguish between a covalent molecule (crystal) and a system of the antiferromagnetic type in which the spins are coupled into a singlet, one should consider the decomposition of the expectation value of the total *spin-square operator*, $\langle S^2 \rangle$, into atomic and diatomic contributions, and the atomic ones will give the local spins (spin squares).

That problem was first approached by Clark and Davidson^{1–4} who decomposed the operator of total spin-square into a sum of atomic and diatomic contributions and computed the expectation value of each. Such a procedure permits one to spot every component of the wave function in which a given orbital appears singly occupied, and assign a contribution to the local spin given by the particular component. This approach is appropriate to identify the covalent (non-ionic) structures and may be used in constructing an effective Heisenberg Hamiltonian, but is not appropriate when the experimentally observable spin (*i.e.*, magnetic) properties are needed: it attributes the value of $\frac{3}{8}$ for the expectation value of the atomic spin-square for both hydrogen atoms in the H₂ molecule treated at the RHF level, in obvious contradiction with the non-magnetic character of this molecule. For other molecules, likewise, the scheme of Clark and Davidson attributes a local spin to each atom, equal to $\frac{3}{8}$ of its covalent valence. In such situation we have concluded, that instead of computing the expectation values of the atomic and diatomic components of the total S^2 operator, one has to decompose the resulting expectation value $\langle S^2 \rangle$ into a physically reasonable sum of atomic and diatomic contributions. As the partitioning of a single physical quantity into several components

is usually not unique, we have introduced the additional requirements, that (i) one should get *no spins whatever* for the covalent systems described by a *closed-shell RHF wave function* using doubly filled orbitals,^{5–7} and (ii) if the wave function is properly dissociating, then the *asymptotic values* of the atomic spins obtained for the atoms at large distances should coincide with the values pertinent to the respective *free atoms*.

That project has been fulfilled first for the single determinant (UHF wave) functions,⁷ the resulting formula of which has been used with success by Reiher *et al.* in ref. 8 and has also been realized in our free program.⁹ Most recently¹⁰ that approach has been extended to correlated wave functions, as well.

In the single determinant case we have presented the $\langle S^2 \rangle$ expectation value in terms of the spin density and overlap matrices \mathbf{P}^s and \mathbf{S} , respectively, as

$$\begin{aligned} \langle S^2 \rangle_{\text{SD}} = & \frac{1}{2} \sum_{\mu,\nu} (\mathbf{P}^s \mathbf{S})_{\mu\nu} (\mathbf{P}^s \mathbf{S})_{\nu\mu} \\ & + \frac{1}{4} \sum_{\mu,\nu} (\mathbf{P}^s \mathbf{S})_{\mu\mu} (\mathbf{P}^s \mathbf{S})_{\nu\nu}, \end{aligned} \quad (1)$$

thus requirement (i) above is fulfilled automatically. If an atom-centered basis is used, the different terms of eqn (1) can be naturally assigned to the individual atoms or pairs of atoms. In there exists a genuine UHF solution differing from RHF, then different parts of the molecule (*e.g.*, the dissociating atoms) are assigned spin densities of opposite sign, providing a qualitatively correct dissociation pattern and the overall $\langle S_z \rangle = 0$ simultaneously; the UHF scheme, however, suffers from the shortcoming that the overall wave function does not correspond to any pure spin state.

In order to describe situations in which the overall wave function is a singlet but there is a need to speak about local spins, one requires correlated (multideterminant) wave functions. The respective formula has been obtained¹⁰ by deriving the expectation value $\langle S^2 \rangle$ in a “mixed” second quantized framework and separating out the values which the different terms have in the single determinant case. Thus one obtains $\langle S^2 \rangle$ as the sum of the right-hand side of eqn (1) and two types of terms which vanish if the wave function is a single determinant. One group of these terms is connected with the deviation of the first-order density matrix from the idempotency characteristic for the single determinants, *i.e.*, with the differences $\mathbf{P}^\sigma \mathbf{S} - (\mathbf{P}^\sigma \mathbf{S})^2$ for the LCAO “density matrices” \mathbf{P}^σ ($\sigma = \alpha$ or β). Other terms are connected with the so-called “cumulant” describing the deviation of the second order density matrix from the expression which it would have in the single determinant case.

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† The same holds for the $S_z = 0$ component of a triplet, *etc.*

The authors of the recent papers^{11,12} performed a decomposition of $\langle \hat{S}^2 \rangle$ for correlated wave functions, which is applicable for open-shell systems only. In fact, in their scheme “zero value is obtained for all one-center and two-center contributions in singlet state systems”,¹¹ in accord with that, they expressed¹² the components of $\langle \hat{S}^2 \rangle$ in terms of the spin-density matrix—which identically vanishes for singlets. We consider that a physically inadequate approach: when, for instance, the H₂ molecule dissociates, then it dissociates into *free hydrogen atoms*, each being in doublet state, $\langle \hat{S}^2 \rangle_A = 3/4$, even if these doublets may be coupled into an overall singlet, leading to the absence of a definite value for the atomic S_z components and zero spin density. In contrast to that approach, we use the requirement that in the asymptotic regime the decomposition should recover the free atomic values.

In the present paper we are going to present the formula obtained in ref. 10 in a form more convenient for programming, describe briefly its numerical realization and discuss the results of the first exploratory calculations.

2. The working formula

The formula for the decomposition of $\langle \hat{S}^2 \rangle$ in the correlated case had been derived in ref. 10 in terms of the atomic basis orbitals. Owing to the fact that in the actual calculations the first and second order density matrices are available in terms of the molecular orbitals, we have rewritten that expression to the compact form

$$\begin{aligned} \langle \hat{S}^2 \rangle = & \frac{1}{2} \sum_{\mu, \nu} (\mathbf{P}^s \mathbf{S})_{\mu\nu} (\mathbf{P}^s \mathbf{S})_{\nu\mu} + \frac{1}{4} \sum_{\mu, \nu} (\mathbf{P}^s \mathbf{S})_{\mu\mu} (\mathbf{P}^s \mathbf{S})_{\nu\nu} \\ & + \frac{3}{4} \sum_{\mu} [(\mathbf{P}^z \mathbf{S})_{\mu\mu} - (\mathbf{P}^z \mathbf{S} \mathbf{P}^z \mathbf{S})_{\mu\mu} + (\mathbf{P}^\beta \mathbf{S})_{\mu\mu} - (\mathbf{P}^\beta \mathbf{S} \mathbf{P}^\beta \mathbf{S})_{\mu\mu}] \\ & + \frac{1}{4} \sum_{\mu, \nu} \sum_{i, j, k, l} [2(\mathbf{C}^{\beta\dagger} \mathbf{S})_{i\mu} (\mathbf{C}^{\alpha\dagger} \mathbf{S})_{j\nu} C_{\mu k}^\beta C_{\nu l}^\alpha \Delta_{i^z k^\beta j^\alpha l^\beta} \\ & - (\mathbf{C}^{\alpha\dagger} \mathbf{S})_{i\mu} (\mathbf{C}^{\beta\dagger} \mathbf{S})_{j\nu} C_{\mu k}^\alpha C_{\nu l}^\beta \Delta_{i^z k^\alpha j^\beta l^\alpha} \\ & - (\mathbf{C}^{\beta\dagger} \mathbf{S})_{i\mu} (\mathbf{C}^{\beta\dagger} \mathbf{S})_{j\nu} C_{\mu k}^\beta C_{\nu l}^\beta \Delta_{i^z k^\beta j^\beta l^\beta} \\ & - 4(\mathbf{C}^{\alpha\dagger} \mathbf{S})_{i\mu} (\mathbf{C}^{\beta\dagger} \mathbf{S})_{j\nu} C_{\mu k}^\beta C_{\nu l}^\alpha \Delta_{i^z k^\beta j^\alpha l^\beta}]. \end{aligned} \quad (2)$$

Here \mathbf{C}^σ is the coefficient matrix of the MO-s (natural orbitals) of spin σ , and the elements of the *cumulant* Δ of the second order density matrix Γ are defined as

$$\begin{aligned} \Delta_{i\sigma k\sigma' i'\sigma'' j\sigma'''} = & \Gamma_{i\sigma k\sigma' i'\sigma'' j\sigma'''} - \delta_{\sigma\sigma''} \delta_{\sigma'\sigma'''} (\rho_1^\sigma)_{ii'} (\rho_1^{\sigma'})_{kj} \\ & + \delta_{\sigma\sigma'''} \delta_{\sigma'\sigma''} (\rho_1^\sigma)_{ij} (\rho_1^{\sigma'})_{ki}. \end{aligned} \quad (3)$$

In practice one does not use natural spin-orbitals but applies a common set of one-electron MO-s (the spatial natural orbitals) to express the density matrices, so $\mathbf{C}^z = \mathbf{C}^\beta = \mathbf{C}$. The elements of the first- and second-order density matrices can be defined through the expectation values of the strings of creation and annihilation operators $\hat{\psi}_i^{\sigma+}$ and $\hat{\psi}_j^{\sigma-}$, respectively, as

$$(\rho_1^\sigma)_{ji} = \langle \hat{\psi}_i^{\sigma+} \hat{\psi}_j^{\sigma-} \rangle, \quad (4)$$

and

$$\Gamma_{i\sigma k\sigma' i'\sigma'' j\sigma'''} = \langle \hat{\psi}_i^{\sigma+} \hat{\psi}_j^{\sigma'''} \hat{\psi}_k^{\sigma''} \hat{\psi}_{i'}^{\sigma'} \rangle. \quad (5)$$

Their values should be extracted from the results of the actual quantum chemical calculations.

The different terms of expression (2) can be obviously assigned to the atoms on which basis orbitals χ_μ , χ_ν are centered, thus it can trivially be rewritten as a sum of atomic and diatomic contributions:

$$\langle \hat{S}^2 \rangle = \sum_A \langle \hat{S}^2 \rangle_A + \sum_{\substack{A, B \\ A \neq B}} \langle \hat{S}^2 \rangle_{AB}. \quad (6)$$

A quantity, closely related to the problems of local spins is the *free valence index* F_A of an atom;^{13,14} its advantage is that it can be calculated by using the first-order density matrix only. It gives the difference between the actual valence of the atom and the sum of the bond orders formed by it, so it can be considered as the effective number of the unpaired electrons on the atom. For correlated wave functions the free valence index can be written as

$$\begin{aligned} F_A = & \sum_{\mu, \nu \in A} (\mathbf{P}^s \mathbf{S})_{\mu\nu} (\mathbf{P}^s \mathbf{S})_{\nu\mu} + 2 \sum_{\mu \in A} [(\mathbf{P}^z \mathbf{S})_{\mu\mu} - (\mathbf{P}^z \mathbf{S} \mathbf{P}^z \mathbf{S})_{\mu\mu} \\ & + (\mathbf{P}^\beta \mathbf{S})_{\mu\mu} - (\mathbf{P}^\beta \mathbf{S} \mathbf{P}^\beta \mathbf{S})_{\mu\mu}]. \end{aligned} \quad (7)$$

In the previous papers^{7,10} we have presented the atomic contributions to $\langle \hat{S}^2 \rangle$ in the form explicitly containing the free valence F_A in order to discuss the similarities and differences with the results of Clark and Davidson.¹ Similarly to $\langle \hat{S}^2 \rangle$, the free valence index depends on the spin density (if any) and reflects the deviation of the first-order density matrix from the idempotency taking place if the wave function is not a single determinant; it, however, does not contain terms related to the cumulant. For a singlet system, in which $\mathbf{P}^s = \mathbf{0}$, the sum of the atomic free valence indices is equal to the “number of effectively unpaired electrons” as defined by Staroverov and Davidson.¹⁵

The analysis discussed in ref. 10 showed that our formula can describe that a dissociated H₂ molecule exhibits two local spins with $\langle \hat{S}^2 \rangle_A = 3/4$ on the individual atoms, while the overall system is singlet, $\langle \hat{S}^2 \rangle = 0$. Also, it was established that it describes correctly the dissociation of a singlet oxygen molecule into two triplet oxygen atoms—or that of a singlet ethylene into two triplet methylene moieties. Analytical considerations of more complex systems would be cumbersome and one would also be interested in following how exactly these spins emerge during the dissociation and how large spins can be detected in different interesting model systems, not necessarily undergoing dissociation.

3. Results of calculations

We have implemented the above equations and accomplished the calculation of first- and second-order density matrices for the wave functions obtained by the full CI (FCI) program of Knowles and Handy¹⁶ linked to an old HONDO version¹⁷ (the same suite that has already been used in ref. 18) as well as by a suitably modified CAS-SCF part of Gaussian-03.¹⁹

Standard basis sets have been used throughout, except that for the H₂ FCI calculations the cc-pVTZ basis set has been used with the 6 Cartesian d-orbitals, instead of the 5 pure ones, owing to the limitations of the HONDO version applied.

For H₂ we have performed CAS-SCF(2,2) calculations by using the standard cc-pVTZ basis set with 5 d-orbitals and FCI-ones with 6 d-orbitals. The additional s orbital which is effectively present in the latter case does not, however, cause any appreciable effects. Fig. 1 displays the atomic components $\langle \hat{S}^2 \rangle_A$ and free valences F_A for these two types of wave function. (Each interatomic component $\langle \hat{S}^2 \rangle_{AB}$ is simply equal to the atomic one but with sign minus, thus ensuring the overall $\langle \hat{S}^2 \rangle = 0$.) We can see that the CAS and FCI curves are very close to each other, although at the equilibrium distance the FCI method accounts for $\sim 91\%$ of the total energetic error remaining at the CAS-SCF level. (The lowest CAS-SCF energy is -1.151550 a.u., while the FCI one is -1.172456 a.u. and the exact Born–Oppenheimer minimum energy is -1.174476 .^{20,21}) That observation is important because it indicates that the “full valence CAS-SCF” calculations should be appropriate for our purposes.

Inspection of Fig. 1 indicates that the quantities $\langle \hat{S}^2 \rangle_A$ and F_A as functions of the internuclear distance behave as could be expected. Also, they basically change parallel to each other. However, the F_A curve is more smooth: the $\langle \hat{S}^2 \rangle_A$ curve exhibits an additional inflection point roughly at the same internuclear distance (*ca.* 1.22 Å) where the genuine UHF solution departs from the RHF one. At the present this is a curious detail only, because no analysis of the possible relations between the detailed behaviour of the $\langle \hat{S}^2 \rangle_A$ curve obtained at the FCI level and the existence of the distinct UHF solution has been performed as yet. The fact that the interrelations between these two quantities are not fully trivial is also illustrated by Fig. 2, indicating a change of behaviour at the values corresponding to the internuclear distance of *ca.* 1 Å.

Fig. 3 displays the $\langle \hat{S}^2 \rangle_A$ and F_A curves for the dissociation of the singlet N₂ molecule calculated by the 6 electrons in 6 orbitals CAS-SCF method and cc-pVTZ basis set. The free nitrogen atom (state $^4P_{3/2}$) has three electrons outside the closed shells, *i.e.*, for a free nitrogen atom $S = 3/2$ and $\langle \hat{S}^2 \rangle = 15/4 = 3.75$. One can see that the atomic spin-square curve approaches 3.75 upon the dissociation, and the free valence F_A tends to 3, indicating that our definitions permit to correctly recognize the two atomic quartet states within the global singlet wave function.

Fig. 4 displays the $\langle \hat{S}^2 \rangle_A$ and F_A curves for the dissociation of the triplet ground state and the lowest singlet state of the O₂ molecule calculated by the 8 electrons in 6 orbitals CAS-SCF method and cc-pVTZ basis set. In both cases the correct dissociation into the triplet oxygen atoms (state 3P_2) is observed. This is in accord with the theoretical discussion given in ref. 10. An interesting feature is that the free valence of the oxygen atom in the dissociated triplet state is 2.5, and not 2 as in the singlet case. This observation can be put in a direct correspondence with the result of Staroverov and Davidson¹⁵ who found and discussed in detail that the number of “effectively unpaired electrons” for the triplet O₂ is equal 5—in the dissociation limit the free valences of the atoms can be shown to sum to the number of “effectively unpaired

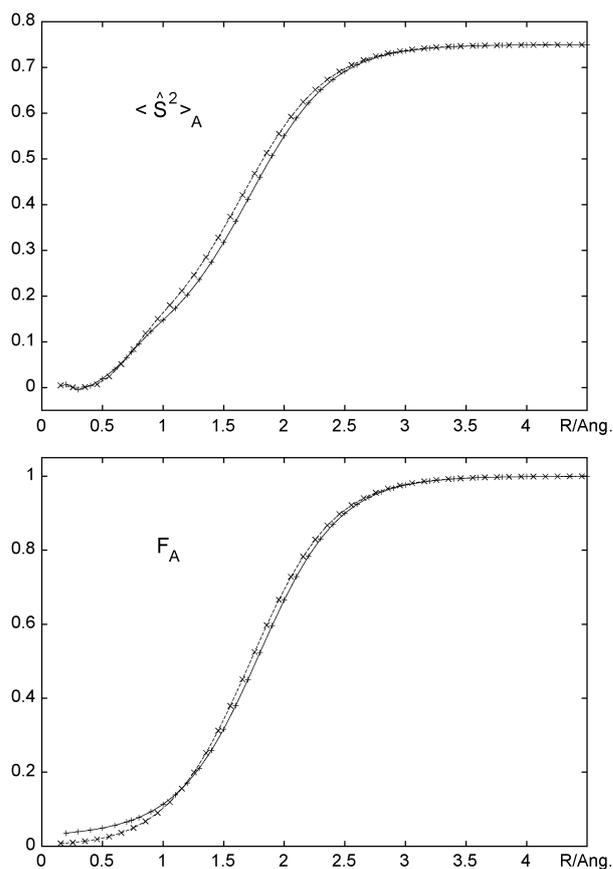


Fig. 1 Change of the atomic spin square $\langle \hat{S}^2 \rangle_A$ (upper part) and of the free valence index F_A (lower part) during the dissociation of the H₂ molecule calculated at the full CI (solid lines) and valence CAS-SCF levels (dashed lines) by using the cc-pVTZ basis set.

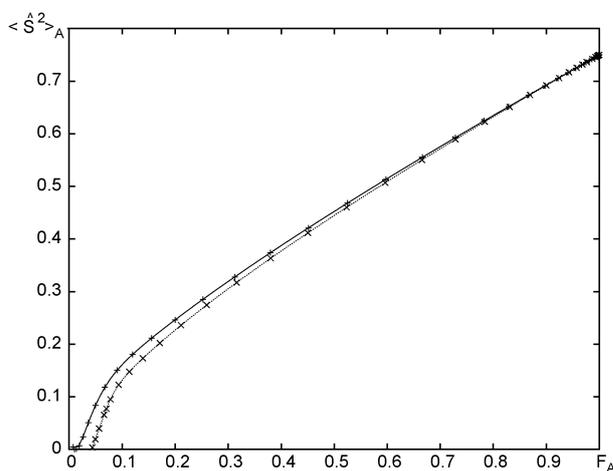


Fig. 2 Interrelation between the free valence index F_A and the atomic spin square $\langle \hat{S}^2 \rangle_A$ for the dissociation of the H₂ molecule calculated at the full CI (solid line) and valence CAS-SCF levels (dashed line) by using the cc-pVTZ basis set.

electrons”. (That counterintuitive result was attributed to a degeneracy of orbitals occupations present in the triplet case.¹⁵) It is also remarkable, that the $\langle \hat{S}^2 \rangle_A$ and F_A curves for the singlet state are nearly indistinguishable.

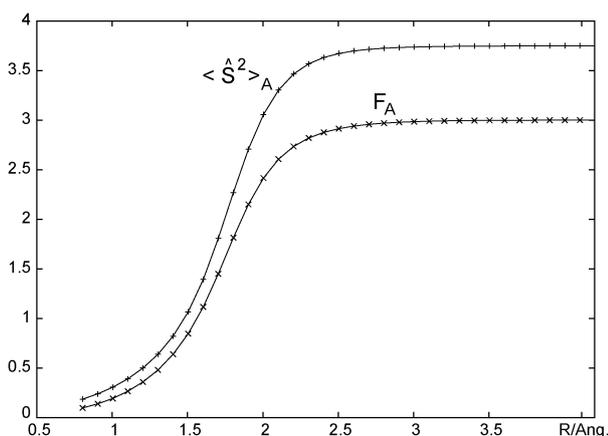


Fig. 3 Change of the atomic spin square $\langle S^2 \rangle_A$ and of the free valence index F_A during the dissociation of the N_2 molecule calculated at the (6,6) CAS-SCF level by using the cc-pVTZ basis set.

Fig. 5 displays the $\langle S^2 \rangle_A$ and F_A curves for the carbon atoms when the length of the C–C bond of the ethane molecule is increased, as obtained with the simplest 2 electrons in 2 orbitals CAS-SCF method and cc-pVTZ basis set. (The geometry of the CH_3 moieties is optimized for each C–C distance.) Both quantities behave as expected, *i.e.*, increase monotonically with the C–C distance. Similarly to the H_2 case discussed above, their interrelation becomes nearly linear over some C–C distance (~ 2 Å). It may be noted that both the free valences and the local spins are quite insignificant on the hydrogens in this system, as the small active space applied is sufficient to describe the dissociation of the C–C bond but not to take into account any correlation elsewhere.

Fig. 6 shows the local spin-square curves for the dissociation of ethylene C=C bond, by using 4 electrons in 4 orbitals CAS-SCF method and cc-pVTZ basis set. (The geometry of the CH_2 moieties was kept fixed.) Contrary to the ethane case, the contributions of the hydrogens are small but not negligible. Therefore, both the $\langle S^2 \rangle_A$ value for the carbon atoms and the sum of all atomic and diatomic components for a methylene moiety are shown—the latter tends exactly to the value of 2 characteristic for a pure triplet state. That curve is quite analogous to the singlet O_2 curve; also the free valence curve (not shown) goes very close to the local spin-square, although not so close as observed in the O_2 case.

It is known that conjugated (π -electron) systems usually have genuine UHF solutions with energies lower than the respective RHF ones even at the equilibrium geometries (see *e.g.*, ref. 22). These solutions break the spin-symmetry of the system, and for symmetric molecules they do not have strict spatial symmetry either. However, if the point group of a singlet molecule has a so called “halving subgroup” (subgroup in which the number of elements equals half of that in the whole group) then some symmetry operations only interchange the spins α and β in the wave function. For such systems the projection of the wave function on the singlet subspace restores the complete symmetry of the wave function^{23,24} and even at the unprojected UHF level a number of physical quantities have the proper symmetry. As the UHF method is the simplest one in which some correlation is accounted for

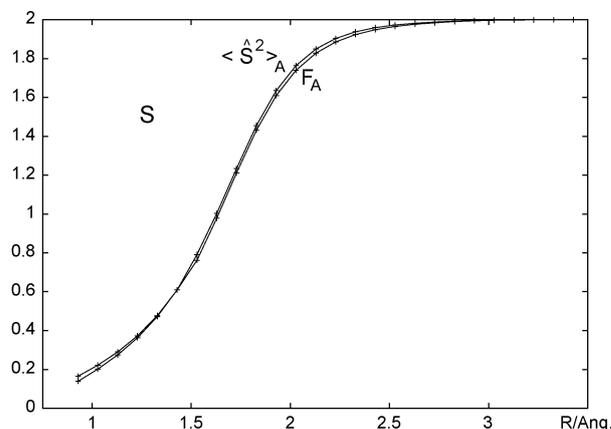
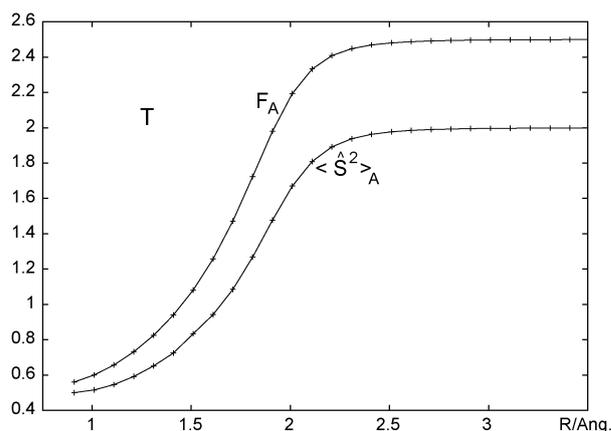


Fig. 4 Change of the atomic spin square $\langle S^2 \rangle_A$ and of the free valence index F_A during the dissociation of the triplet ground state (upper part) and of the lowest singlet state (lower part) of the O_2 molecule calculated at the (8,6) CAS-SCF level by using the cc-pVTZ basis set.

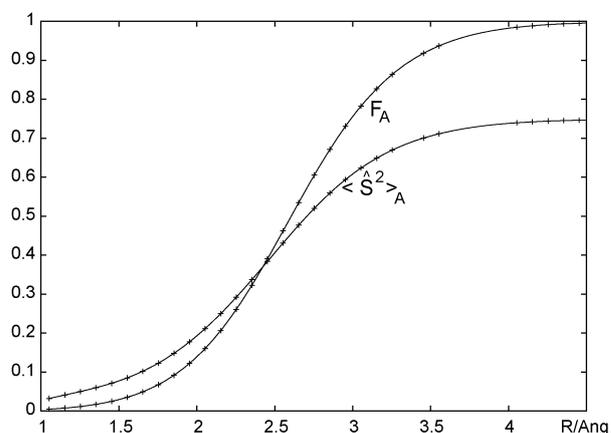


Fig. 5 Change of the atomic spin square $\langle S^2 \rangle_A$ and of the free valence index F_A of the carbon atoms with the increase of the C–C distance in the ethane molecule at the (2,2) CAS-SCF level by using the cc-pVTZ basis set.

and there appear local spins in the approximations to the singlet ground states, we present the UHF results for these molecules alongside with the CAS-SCF ones. (The UHF results were calculated by using the program ref. 9, realizing the formulae⁷ pertinent to the single determinant case.) As we

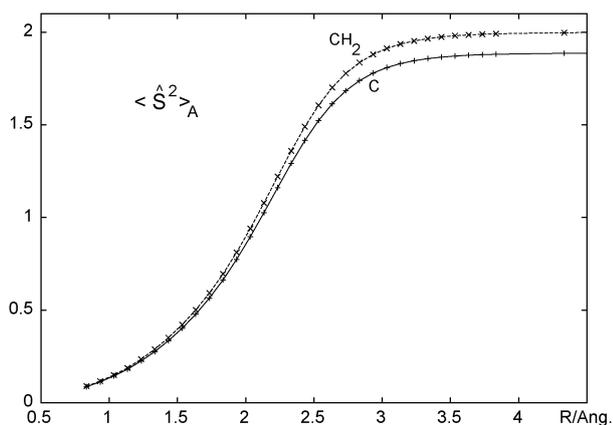


Fig. 6 Change of the atomic spin square $\langle S^2 \rangle_A$ of the carbon and of the sum of the $\langle S^2 \rangle$ components for a methylene moiety with the increase of the C-C distance in the ethylene molecule at the (4,4) CAS-SCF level by using the cc-pVTZ basis set.

shall see, the UHF results agree qualitatively with the (much more expensive) CAS-SCF ones, so the UHF method may be useful for a quick orientation.

Table 1 displays the free valence indices of carbon atoms and some of their $\langle S^2 \rangle$ components of *trans*-butadiene, cyclobutadiene and benzene, calculated by the “ π -electron full-valence”—*i.e.*, (4,4), (4,4) and (6,6)—CAS-SCF level of theory and by the UHF method, by using the cc-pVTZ basis set. All results are pertinent to the respective energy minima, except the cyclobutadiene UHF solution of the D_{2h} symmetry, which was calculated in the RHF minimum, because the only minimum at the UHF level has the symmetry of a square (D_{4h}).

The relatively large values of the free valences and local spins obtained for *trans*-butadiene indicate a significant importance of correlation for such a conjugated chain. At the CAS-SCF level, the largest off-diagonal $\langle S^2 \rangle$ element is within the formal “double bond”, which agrees with our qualitative picture on that molecule. (The negative sign of the $\langle S^2 \rangle_{12}$ component indicates that correlation does not basically destroy spin pairing in that bond.) The further off-diagonal elements are small and exhibit an antiferromagnetic type oscillation. The UHF results seem somewhat exaggerated, and the antiferromagnetic nature of the single UHF determinant is prominent.

Cyclobutadiene, this classical antiaromatic system, has a D_{2h} ground state, which means that the rectangular structure with two double and two single bonds, corresponding to only one of the two possible “Kekulé-structures”, has lower energy than a square permitting the resonance of the latter. This experimental finding is reproduced both at the RHF level and at the “ π -electron full-valence” CAS-SCF level, but not for UHF.

At the square geometry the RHF solution either corresponds to only one of the “Kekulé-structures”, and does not have the full symmetry of the system, or is symmetry-adapted but has a higher energy (Musher’s point-like discontinuity²⁵). Here the exact π -electron solution qualitatively differs from any closed-shell wave functions, because the π -electrons form a small “molecular antiferromagnet”.^{22,26} In that point (and practically only in that point) the π -electron wave function is almost exactly described by a spin-projected Slater determinant—the extended (or projected) Hartree-Fock (EHF) wave function.^{22,27} This EHF wave function can be best described by considering four *singly occupied* equivalent—but not strictly orthogonal—localized orbitals, each of which is basically (but not completely) localized on one corner of the square, putting on them alternatively α and β spins,²⁶ then first coupling the identical spins along the diagonals into two triplets (the two “antiferromagnetic sub-lattices”) and then coupling them into a resulting singlet.²⁸ In accord with that, each corner of the square cyclobutadiene carries a local spin with an $\langle S^2 \rangle_A$ value exceeding half of the value 3/4 characteristic for a free spin; the large value of the free valence index F_A is in accord with that. (The overlap of the four localized orbitals reduces the effectively unpaired character of the electron sitting at each corner.) The off-diagonal $\langle S^2 \rangle$ components also reflect well the antiferromagnetic character of the wave function.

In the D_{2h} conformation having the minimum energy, the local spins are much reduced, but still exceed the values of *trans*-butadiene. Similarly to the latter molecule, the off-diagonal $\langle S^2 \rangle$ elements again emphasize the spin-correlation within the bonds and exhibit an antiferromagnetic behaviour. The antiferromagnetic character of the wave function is significantly exaggerated by the UHF method, which can explain why there is no D_{2h} minimum on the UHF potential curve.

Fig. 7 displays some CAS-SCF results obtained for cyclobutadiene by changing the ratio between the sides of

Table 1 Free valence values and $\langle S^2 \rangle$ components for butadiene, cyclobutadiene and benzene treated at the “ π -electron full-valence” CAS-SCF and UHF levels of theory with the cc-pVTZ basis set

Molecule	F_1	F_2	$\langle S^2 \rangle_1$	$\langle S^2 \rangle_2$	$\langle S^2 \rangle_{12}$	$\langle S^2 \rangle_{23}$	$\langle S^2 \rangle_{13}$	$\langle S^2 \rangle_{14}$
CAS-SCF								
<i>trans</i> -Butadiene	0.1773	0.1519	0.2070	0.1814	−0.1851	−0.0299	0.0359	−0.0580
Cyclobutadiene D_{2h}	0.2415		0.2576		−0.2503	−0.0527	0.0465	−0.0527
Cyclobutadiene D_{4h}	0.5804		0.4363		−0.2947		0.1563	−0.2947
Benzene	0.1460		0.1568		−0.0978		0.0496	−0.0598
UHF								
<i>trans</i> -Butadiene	0.2577	0.1788	0.2324	0.1663	−0.0988	−0.0780	0.0944	−0.1049
Cyclobutadiene D_{4h}^a	0.4294		0.4081		−0.2055	−0.1957	0.2075	−0.1957
Cyclobutadiene D_{4h}	0.5947		0.5608		−0.2711		0.2830	−0.2711
Benzene	0.1432		0.1311		−0.0635		0.0609	−0.0604

^a At the RHF minimum.

the rectangle (the 6-31G** basis has been used). It can be seen that the energy minimum corresponds to a D_{2h} geometry, while at the square conformation the energy has a shoulder. Both the free valence and the local spin-square exhibit well-defined maxima at the square geometry.

Among the π -electron systems studied, benzene shows the smallest deviation from the closed-shell RHF structure characterized by zero values of all spin-components and of the free valences. The CAS-SCF and UHF values show an overall similarity; however, UHF can describe only the oscillating antiferromagnetic behaviour but not the finer details. For instance, at the CAS-SCF level the $\langle S^2 \rangle_{14}$ component has a larger absolute value than the $\langle S^2 \rangle_{13}$ one, which may be put into correspondence with the importance of spin-pairings in a “Dewar-benzene”, the latter being also of significance for aromaticity of benzene.²⁹

Finally we shall discuss very briefly a simple scheme imitating at the *ab initio* level of calculations the classical “three-center four-electron” model of superexchange, used to explain anti-ferromagnetism in systems like oxides or fluorides of transition metals. In this model one considers explicitly only two magnetic ions and one ligand atom, and each center is represented by only one orbital. These usually are the appropriate 3d orbitals

of the metals and a 2p orbital of the ligand. (For a detailed analysis of this model we refer to ref. 30 and references therein.) For that reason we selected the system Sc–OH₂–Sc with the linear arrangement of atoms Sc–O–Sc, in which the hydrogens were added to fix the otherwise “dangling” electrons of the oxygen atom. By performing (4,3) CAS-SCF calculations by using the cc-pVTZ basis set, we got the results which could be expected: the singlet is tangentially (by some 0.12 mH) lower in energy than the triplet, and in both cases there are sensible (exceeding 0.007) spin-square values only connected with the Sc atoms: the atomic spin-squares are in both cases close to that of a free spin (0.7248 for the singlet and 0.7205 for the triplet), and the interatomic off-diagonal ones (–0.7177 and 0.2411)—together with the minor components—provide the resulting $\langle S^2 \rangle$ to be exactly 0 and 2, respectively. The free valence indices are in full agreement with this picture: we got the values 0.976 and 0.960 on the Sc atoms in the singlet and triplet cases, respectively, and all the other ones are essentially negligible.

By extending the active space by 4 electrons and 4 orbitals, and doing (8,7) CAS-SCF calculations, we got a significantly lower energy but only slightly different qualitative results as far as the $\langle S^2 \rangle$ components are concerned. The increased flexibility resulted in a larger stabilization of the singlet with respect the triplet (*ca.* 2 mH) but the local spins remained essentially unchanged (0.7357 and 0.7365 in the singlet and triplet cases; the $\langle S^2 \rangle$ components not connected with the Sc atoms do not reach the value 0.02). There is, however, a significant difference in the free valences: the values 1.361 and 1.354 were obtained for the Sc atoms in the singlet and triplet cases, respectively, the other values again being very small. That difference indicates that in systems which are of interest from the point of view of magnetic properties, the information contained in the (much easier to calculate) free-valence index may be insufficient and one has to calculate explicitly the values of the respective local spins.

4. Conclusions

In this paper we have rewritten the formula proposed in ref. 10 for decomposing the expectation value $\langle S^2 \rangle$ of the total spin operator into atomic and diatomic components in the case of general (correlated) wave functions in terms of the cumulant and realized it numerically for the first time. The results confirm its conformity of this formula with the physical expectations; one may suppose that this is *the* proper decomposition which corresponds to the—physically rather obvious—requirements (i) and (ii), and perhaps no further freedom remained in choosing the scheme of that decomposition.‡ The atomic $\langle S^2 \rangle$ components in most cases change in parallel

‡ This is the case, even if for some exotic problems this decomposition may produce somewhat strange results. Thus, for the excited singlet state of H₂ one gets negative atomic $\langle S^2 \rangle$ components at shorter distances, while for the $S_2 = 0$ triplet state the atomic components can exceed the value 3/4 characteristic for a single electron. This phenomenon can perhaps be put in parallel with the negative spin densities which are observed for some atoms in many free radicals. However, we do not think that analogous results could be encountered for any ground state system. (We are grateful to a referee calling our attention to these excited states.)

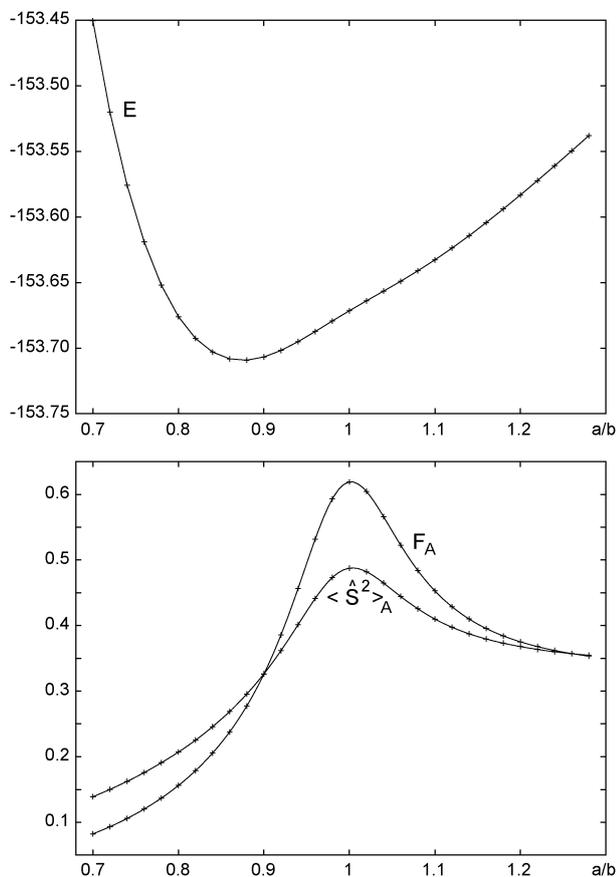


Fig. 7 Total energy of cyclobutadiene (a.u.), the atomic spin square $\langle S^2 \rangle_A$ and the free valence index F_A of the carbon atoms as functions of the ratio a/b of the sides of the rectangle, calculated at the (4,4) CAS-SCF level by using the 6-31G** basis set. (One of the sides of the rectangle has been kept fixed at the value optimized for the square conformation.)

with the free valence indices, but are not simple functions of the latter. That difference may be of high importance when magnetic properties are of interest.

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