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Violation of Hund's Rule by Spin Polarization in Molecules

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It is shown that spin polarization effects can lead to violations of Hund's multiplicity rule, particularly for singlet-triplet pairs. In systems with more than one unpaired electron we observe a dynamic spin polarization which depends on the relative spin orientation of the unpaired electrons and is different in open-shell singlet and triplet states. These effects are described by including singly substituted configurations in CI-type wavefunctions for the two states. In analyzing the contributions of the various singly substituted configurations a quantitative understanding of violations of Hund's rule is obtained; at the same time it is possible to calculate quantitatively spin polarization contributions to the correlation energies of open-shell singlet and triplet states.

A series of model calculations is performed on systems like square planar H_4 and C_4H_4, $n\pi^*$ states of formaldehyde, rotated cumulenes, NH and O_2, in order to investigate how strongly spin polarization influences singlet-triplet energy splittings and what are the properties of a molecule that lead to a violation of Hund's multiplicity rule.

Key words: Spin polarization – Hund's multiplicity rule – Singlet-triplet energy splitting

1. Introduction

Hund's rules are a valuable tool for determining the energetic order of the different electronic states arising from a given electronic configuration in atoms and molecules without performing extensive numerical calculations. They have been derived empirically from atomic spectra [1] and hold generally for the lower states of atomic systems. For higher states they do not apply strictly, one famous counterexample is the 3*snd*, $n=3,\ldots,13$ series of magnesium where the ^1D states are lower than the ^3D states, whereas for the $3snp$ and $3sns$ series the triplets are well below the singlets [2]. For molecules only Hund's multiplicity rule is generally applied since the lower point symmetry removes orbital degeneracies such that most configurations give rise to only one electronic state. For molecules with two singly occupied orbitals (e.g. biradicals) Hund's rule predicts the triplet to be lower in energy than the corresponding singlet. (If the two singly occupied orbitals are not degenerate or nearly degenerate one of the closed-shell singlets can lie well below the singlet-triplet pair, but Hund's rule does not apply to them [3].) To our knowledge, no molecular singlet-triplet pair is known where experiment unambiguously proves the singlet to be lower than the triplet.

However, one can find some examples in the literature where the results of *ab initio* calculations indicate violations of Hund's rule. These are

1) Planar square cyclobutadiene: A minimal basis CI calculation with all $\pi\pi^*$ configurations performed by Buenker and Peyerimhoff [4] yielded the $^1B_{1g}$ state by as much as 13.6 kcal/mole lower than the $^3A_{2g}$ state, both of them belonging to the same $\cdots a_{2u}^2 e_g^2$ configuration.

2) Planar square H_4: There are rather extensive CI calculations on the H_4 potential surface by different authors [5–7]. All of them agree that planar square H_4 has a triplet ground state at small R, but a singlet at large R.

3) Rotated ethylene: In a recent large scale CI calculation on the UV spectrum of ethylene Buenker and Peyerimhoff [8] found the $^1B_1(N)$ state of rotated ethylene to lie approximately 2 kcal/mole below the $^3A_2(T)$ state (both for $R = 1.48$ Å), while SCF and small CI calculations found the triplet being 1–2 kcal/mole below the singlet. Validity of Hund's rule is also assumed by Merer and Mulliken in their review article [9] on the UV spectrum of ethylene.

4) Planar methane (D_{4h}): In a CI study of distorted geometries of the methane molecule Shavitt found that the $^1B_{2u}$ state is lower than the corresponding $^3B_{2u}$ state [10]. In SCF approximation or if only small basis sets are used for the CI Hund's rule is still valid.

None of these authors made a comment on the possible origin of these apparent violations of Hund's rule. On the other hand, Borden qualitatively proposed a mechanism which accounts for a stabilization of the singlet state by electron correlation in order to support some speculations about a square singlet ground state of cyclobutadiene [11]. A related, but formally rather different approach has been proposed by Yamaguchi [12, 13] by applying the theory of Hartree–Fock instabilities to antiaromatic molecules.

It is shown in this paper that these violations of Hund's rule are due to spin polarization effects. We present a quantitative numerical description of the spin polarization in triplet and open-shell singlet states and perform some model calculations on a number of examples in which a violation of Hund's rule can be expected.

2. Spin Polarization in Open-Shell Singlet and Triplet States

2.1. CI-Formulation

Let us consider a four-electron system with two unpaired electrons. The SCF wavefunctions for the singlet and triplet ($M_S = 0$) states consist of two determinants and can be written as

$$\phi_S = \frac{1}{\sqrt{2}}\{|i\bar{i}x\bar{y}| - |i\bar{i}\bar{x}y|\} \tag{1}$$

$$\phi_T = \frac{1}{\sqrt{2}}\{|i\bar{i}x\bar{y}| + |i\bar{i}\bar{x}y|\} \tag{2}$$

(i denotes doubly occupied, x, y singly occupied, and k, l virtual molecular orbitals, respectively).

We will limit our treatment to singlet states of the form (1), i.e. we will assume that the singly occupied orbitals are chosen in a way that the open-shell singlet state is well represented by an SCF wavefunction (1).

If the orbitals occupied in ϕ_S and ϕ_T are identical, the energy difference between the two states is simply given by an exchange integral

$$\Delta E_{\mathrm{SCF}} = E(\phi_S) - E(\phi_T) = 2(xy \mid yx) = 2(x|K_y|x) \tag{3}$$

If the orbitals are determined by independent SCF calculations we only have the inequality

$$2(xy \mid yx)^S \leqslant \Delta E_{\mathrm{SCF}} \leqslant 2(xy|yx)^T \tag{4}$$

[14] where the superscript S or T distinguishes between singlet and triplet SCF orbitals, or

$$\Delta E_{\mathrm{SCF}} \approx (xy|yx)^S + (xy|yx)^T \tag{5}$$

Since all of these exchange integrals are positive, in SCF approximation the singlet state always is higher in energy than the triplet (Hund's rule valid!) [15, 16].

Let us assume in the following that the orbitals in ϕ_S and ϕ_T have been determined by separate SCF-calculations. Then Brillouin's theorem holds for almost all singly excited configurations, the only ones having nonvanishing matrix elements with ϕ_S and ϕ_T, respectively, are [17]

$$\phi_S^1 = \frac{1}{\sqrt{12}}\{2|\bar{i}\bar{k}xy| + 2|ik\bar{x}\bar{y}| - |\bar{i}k\bar{x}y| - |\bar{i}kx\bar{y}| - |i\bar{k}\bar{x}y| - |i\bar{k}x\bar{y}|\} \tag{6}$$

$$\phi_T^1 = \tfrac{1}{2}\{|\bar{i}k\bar{x}y| - |\bar{i}kx\bar{y}| + |i\bar{k}\bar{x}y| - |i\bar{k}x\bar{y}|\} \tag{7}$$

$$\phi_T^2 = \frac{1}{\sqrt{2}}\{|\bar{i}\bar{k}xy| - |ik\bar{x}\bar{y}|\} \tag{8}$$

and the matrix elements with ϕ_S and ϕ_T are

$$(\phi_S|H|\phi_S^1) = \sqrt{\tfrac{3}{2}}(i|K_x - K_y|k) \tag{9}$$

$$(\phi_T|H|\phi_T^1) = \frac{1}{\sqrt{2}}(i|K_x - K_y|k) \tag{10}$$

$$(\phi_T|H|\phi_T^2) = (i|K_x + K_y|k) \tag{11}$$

(To avoid too many indices we did not denote explicitly that singlet and triplet SCF orbitals might be different.) Borden [11] recognized the importance of the configuration (6) for the stabilization of the singlet state of square cyclobutadiene.

Since the matrix element between ϕ_S^1 and ϕ_S is $\sqrt{3}$ times as large as the one between ϕ_T^1 and ϕ_T we expect the singlet to be stabilized about 3 times as much by ϕ_S^1 as is ϕ_T by ϕ_T^1, provided that the exchange integrals in (9) and (10) and the energy denominators are similar. Additionally, there is a further stabilization for ϕ_T due to ϕ_T^2 such that we can write the contributions of the singly excited configurations to the singlet-triplet energy difference perturbationally as

$$\Delta E^{(1)} = -\sum_i \sum_k^{\text{virt}} \frac{1}{2} \left\{ \frac{3(i|K_x - K_y|k)^2}{E(\phi_S^1) - E(\phi_S)} - \frac{(i|K_x - K_y|k)^2}{E(\phi_T^1) - E(\phi_T)} - \frac{2(i|K_x + K_y|k)^2}{E(\phi_T^2) - E(\phi_T)} \right\} \tag{12}$$

The condition that the singlet state is below the triplet then simply reads

$$|\Delta E^{(1)}| > |\Delta E_{\text{SCF}}| \approx 2(xy|yx) \tag{13}$$

This can be accomplished by a low-lying virtual orbital k giving rise to a large value of $(i|K_x - K_y|k)$ and a small one for $(i|K_x + K_y|k)$, provided that $(xy\,|\,yx)$ is small as well.

There are of course many doubly excited configurations which also give first order contributions to the correlation energies of the two states and can influence the singlet-triplet energy difference. Excitations of the type $ii \rightarrow kl$ do not affect the singlet-triplet energy difference since both the matrix element $(ik\,|\,li)$ with the Hartree–Fock function and the energy denominator are the same for ϕ_S and ϕ_T. The same conclusion, however, is not valid for other classes of double substitutions:

a) The direct correlation between the two single electrons is described by double substitutions of the type $xy \rightarrow kl$ (singly occupied to virtual). The matrix elements connecting the corresponding singlet and triplet functions with ϕ_S and ϕ_T, respectively, are

$$(xk\,|\,ly) \pm (xl\,|\,ky)$$

(–sign for triplet) and the energy denominators also differ in the sign of the exchange integrals $(xy\,|\,yx)$ and $(kl\,|\,lk)$.

The contribution of the direct correlation of the single electrons to the energy is large where the SCF exchange integral $(xy\,|\,xy)$ is large. (The violation of Hund's rule in the $3snd$ series of magnesium is caused by this effect.)

b) The internal double substitutions of the type $ij \to xy$. Their matrix elements with ϕ_S and ϕ_T, respectively, are

$$(ix \mid yj) \pm (iy \mid xj)$$

In most of the cases considered in this paper all of these matrix elements vanish because of symmetry or are at least very small. The only exception is the oxygen molecule.

In the following we discuss mainly the spin polarization terms. The double substitutions outlined above are considered only in those cases where their contributions to the total energy cannot be neglected.

2.2. Physical Interpretation

The physical meaning of the singly substituted configurations can be most easily understood in comparison with the well-known phenomenon of spin-polarization in systems with a single unpaired electron [18, 19]. Let us consider a three-electron doublet state with an SCF wave-function ($M_S = \frac{1}{2}$)

$$\phi_D^{\mathrm{SCF}} = |i\bar{i}x| \tag{14}$$

The odd electron in φ_x polarizes the core $|i\bar{i}|$ since its interaction with φ_i is different from that with $\bar{\varphi}_i$: The repulsion between the two electrons with the same spin is $J_{ix} - K_{ix}$; this is smaller than the repulsion J_{ix} between the electrons with different spins. Therefore electrons with the same spin are found closer together than electrons with different spins. One possibility to take care of this "spin polarization" is by allowing different orbitals for different spins, i.e. by replacing the core orbitals φ_i and $\bar{\varphi}_i$ in (14) by $\varphi_i + \lambda\varphi_a$ and $\overline{\varphi_i - \lambda\varphi_a}$, respectively, φ_a being normalized and orthogonal to φ_i and φ_x (unrestricted Hartree–Fock, UHF). Neglecting the term in λ^2 we obtain

$$\phi_D^z = |i + \lambda a, \overline{i - \lambda a}, x| \approx \phi_D^{\mathrm{SCF}} + \sqrt{2}\,\lambda D^z$$

$$D^z = \frac{1}{\sqrt{2}}\{|a\bar{i}x| - |i\bar{a}x|\}$$

Obviously, D^z is singly excited with respect to ϕ_D^{SCF}, its interaction matrix element with ϕ_D^{SCF} is given by

$$(D^z|H|\phi_D^{\mathrm{SCF}}) = \frac{1}{\sqrt{2}}\,(ix \mid xa) = \frac{1}{\sqrt{2}}\,(i|K_x|a)$$

It is well known that D^z is not a spin-adapted function, i.e. not an eigenfunction of S^2. The reason is that we have included the spin-polarization only along one quantization axis in spin space (z-axis, therefore a superscript z). Inclusion of the corresponding spin-polarization contributions D^x and D^y leads to the spin-adapted wavefunction

$$\phi_D^{\mathrm{SP}} = \phi_D^{\mathrm{SCF}} + \sqrt{2}\,\lambda D$$

$$D = \frac{1}{\sqrt{6}}\{|a\bar{i}x| - |i\bar{a}x| + 2|ia\bar{x}|\} \tag{15}$$

with

$$(D|H|\phi_D^{\mathrm{SCF}})=\sqrt{\tfrac{3}{2}}(ix \mid xa)=\sqrt{\tfrac{3}{2}}(i|K_x|a) \tag{16}$$

(The contributions D^x and D^y are most easily calculated in representations in which S_x and S_y, respectively, are diagonal and then transformed to the representation in which S_z is diagonal.)

The result (15) shows that spin polarization is described in first order by adding singly substituted configurations to the restricted SCF determinant (14).

Now let us try to use the same scheme in the case of two unpaired electrons. According to the relative spin orientation of these two single electrons we have to distinguish between two cases:

a) Parallel spins:
The triplet SCF function for $M_S=1$ is given by the determinant

$$\phi_T^{\mathrm{SCF}}=|i\bar{i}xy|$$

Spin polarization leads to

$$\phi_T^z=|i+\lambda a, \overline{i-\lambda a}, x, y|=\phi_T^{\mathrm{SCF}}+\sqrt{2}\,\lambda D_T^z$$

$$D_T^z=\frac{1}{\sqrt{2}}\{|a\bar{i}xy|-|i\bar{a}xy|\}$$

Again, D_T^z is not a spin-adapted configuration since the spin-polarization is accounted for only in the z spin direction; inclusion of the other spin directions in which the spins are parallel in a triplet state leads to

$$D_T=\tfrac{1}{2}\{|a\bar{i}xy|-|i\bar{a}xy|+|ia\bar{x}y|-|ia\bar{y}x|\}$$

with the matrix element

$$(D_T|H|\phi_T^{\mathrm{SCF}})=(ix \mid xa)+(iy \mid ya)=(i|K_x+K_y|a) \tag{17}$$

The $M_S=0$ partner of D_T is obtained simply by applying the step-down operator S_- to D_T and reads

$$\frac{1}{\sqrt{2}}\{|\bar{a}\bar{i}xy|-|ai\bar{x}\bar{y}|\} \tag{18}$$

b) Opposite spins:
Starting from the singlet and triplet SCF functions for $M_S=0$

$$\phi_S^{\mathrm{SCF}}=\frac{1}{\sqrt{2}}\{|i\bar{i}x\bar{y}|-|i\bar{i}\bar{x}y|\}$$

$$\phi_T^{\mathrm{SCF}}=\frac{1}{\sqrt{2}}\{|i\bar{i}x\bar{y}|+|i\bar{i}\bar{x}y|\}$$

spin polarization leads to

$$\phi_S^{\mathrm{SCF}} \rightarrow \phi_S^{\mathrm{SCF}} + \sqrt{2}\,\lambda A_S^z$$
$$\phi_T^{\mathrm{SCF}} \rightarrow \phi_T^{\mathrm{SCF}} + \sqrt{2}\,\lambda A_T^z$$

with

$$\begin{aligned} A_S^z &= \tfrac{1}{2}\{|a\bar{i}x\bar{y}| - |i\bar{a}x\bar{y}| - |a\bar{i}\bar{x}y| + |i\bar{a}\bar{x}y|\} \\ A_T^z &= \tfrac{1}{2}\{|a\bar{i}x\bar{y}| - |i\bar{a}x\bar{y}| + |a\bar{i}\bar{x}y| - |i\bar{a}\bar{x}y|\} \end{aligned} \tag{19}$$

Again, these functions describe the spin polarization only along the z spin axis. For the triplet state this is sufficient since the spins are parallel in the other two spin directions ($\langle S^2 \rangle = 2$) and this type of spin polarization is taken care of by case a). Thus A_T^z is already a spin eigenfunction. On the other hand A_S^z is not a spin eigenfunction. Since the spin polarization in all three spin directions must be identical in a singlet state

$$\begin{aligned} A_S &= \frac{1}{\sqrt{3}}(A_S^x + A_S^y + A_S^z) \\ &= \frac{1}{\sqrt{12}}\{2|\bar{a}\bar{i}xy| + 2|ai\bar{x}\bar{y}| + |a\bar{i}x\bar{y}| - |i\bar{a}x\bar{y}| - |a\bar{i}\bar{x}y| + |i\bar{a}\bar{x}y|\} \end{aligned} \tag{20}$$

is the pure spin function corresponding to A_S^z.

The matrix elements for the singlet and triplet states with $M_S = 0$ are

$$(A_T|H|\phi_T^{\mathrm{SCF}}) = \frac{1}{\sqrt{2}}(i|K_x - K_y|a) \tag{21a}$$

$$(A_S|H|\phi_S^{\mathrm{SCF}}) = \sqrt{\tfrac{3}{2}}(i|K_x - K_y|a) \tag{21b}$$

Therefore, the spin polarization in triplet and open shell singlet states can be described by singly substituted configurations, in close analogy to the case of one single unpaired electron. The energy contribution of a configuration corresponding to an $i \rightarrow a$ single substitution depends on the relative spin orientation of the two odd electrons: in the singlet case in which the spins must be antiparallel along all three directions in spin-space we get three times the contribution with the exchange integral $(i|K_x - K_y|a)$ for opposite spins; in the triplet case the spins are antiparallel in one and parallel in two spin-directions, the energy contribution therefore contains three parts, one with $(i|K_x - K_y|a)$ and two with $(i|K_x + K_y|a)$.

McConnell's theory of spin polarization [18, 19] is often understood in the sense that the non-zero spin-density due to the odd electron polarizes the core. In a singlet state there is no non-zero spin-density ($M_S = 0$); nevertheless we got some amount of spin-polarization also for open-shell singlet states. We like to call this "dynamic" spin polarization in order to indicate that it does not originate from a static non-zero spin-density.

Of course, static and dynamic spin-polarization generally are different from each other, their respective magnitudes crucially depend on exchange integrals of the type $(i|K_x \pm K_y|a)$.

3. Numerical Calculations

In order to obtain a more quantitative understanding of spin polarization effects in singlet and triplet states we have performed a series of calculations for different molecular systems using a perturbation theory (PT) approach on two different levels:

a) The individual PT contributions (compare Eq. (12)) are simply added up for all virtual orbitals k and all doubly occupied orbitals i;

b) For each occupied orbital one single optimal virtual orbital is determined by maximizing the exchange integrals $(i|K_x + K_y|k)$ and $(i|K_x - K_y|k)$, respectively. Thus, the sum over k is reduced to just one term.

In most cases the results of these two procedures are almost identical, particularly if only one term in (12) is predominant or if all large terms have similar energy denominators. In the following tables generally the results of the latter procedure will be given.

3.1. Basis Sets

Since we found that the choice of an adequate basis set is crucial in order to obtain reliable values for the spin-polarization contributions to the singlet-triplet splitting all our calculations have been performed with three different basis sets. They are described as follows:

a) MB: Minimal basis, contracted from a $5s$, $2p/2s$ Gaussian lobe basis for hydrocarbons and a Huzinaga $3s$ basis [21] in the case of H_4. The contraction coefficients were taken from molecular calculations [22].

b) DZ: Double zeta basis, contracted from a Huzinaga $7s$, $3p/3s$ basis [21]. In some cases this basis was augmented by a set of d-functions at the C, N, or O-atoms with an exponent of 1.0 (DZ+d) or by a set of p-functions at the H-atoms with an exponent of 0.65 (DZ+p). For N and O a further set of diffuse s- and p-functions (exponents 0.055 and 0.07, respectively) was added. In the case of the larger hydrocarbons the s-functions at the hydrogens were contracted to just one group (DZ*).

c) LB: Large basis: This is essentially a triple zeta basis contracted from a Huzinaga $9s$, $5p/5s$ basis, augmented by three sets of d-functions on N (3.6, 1.2, 0.4) and two sets of d-functions on O (2.0, 0.5) and two sets of p-functions at the hydrogens (1.2, 0.3).

3.2. Molecular Systems

If we are interested in open-shell systems *violating* Hund's rule we have to look for molecules in which the SCF exchange integral $(xy \mid yx)$ is small. That means, the differential overlap between the two singly occupied orbitals must be small, or the two unpaired electrons must be localized in almost non-penetrating regions of space. On the other hand, there should be at least one large exchange integral of the type $(i|K_x \pm K_y|k)$, otherwise the spin-polarization effects themselves are negligible.

3.2.1. Square Planar $H_4(D_{4h}$ Symmetry)

In a minimal basis set square planar H_4 has four molecular orbitals: a doubly occupied a_{1g} orbital (φ_1), two singly occupied e_g orbitals (φ_2, φ_3) which can be chosen as to have no H-atom in common, and the non-occupied antibonding b_{2g} orbital (φ_4). The two lowest states originating from the $a_{1g}{}^2e_g^2$ configuration are separated in SCF approximation by the small exchange integral $(23 \mid 32)$. It is easily seen that $(1|K_2-K_3|4)$ must be large while $(1|K_2+K_3|4)$ vanishes by symmetry. Therefore we expect a rather spectacular violation of Hund's rule, in close analogy to the case of square planar cyclobutadiene which has been discussed in a previous paper [20]. The results of our model calculations on H_4 for two different distances ($R_{\text{HH}}=2.0a_0$, $2.4a_0$) and different basis sets are given in Table 1.

Table 1. Spin polarization effects in square planar H_4 [a]

		MB	DZ	DZ+p	LB
$R=2.4a_0$	$(xy \mid yx)^T$	0.0064	0.0094	0.0129	0.0132
	$(xy \mid yx)^S$	0.0064	0.0093	0.0109	0.0106
	$E_{\text{SCF}}(T)$	−1.9163	−1.9969	−2.0134	−2.0248
	ΔE_{SCF}	0.0127	0.0187	0.0237	0.0236
	SP T^1	−0.0553	−0.0334	−0.0296	−0.0282
	T^2	0.0	−0.0033	−0.0053	−0.0053
	S	−0.0903	−0.0632	−0.0593	−0.0576
	ΔE_{SP}	−0.0350	−0.0265	−0.0243	−0.0241
	$\Delta E_{\text{SCF+SP}}$	−0.0223	−0.0078	−0.0006	−0.0004
	$\Delta E_{\text{CI}}{}^{\text{b}}$	−0.0186	−0.0105	−0.0075	
$R=2.0a_0$	$(xy \mid yx)^T$	0.0102	0.0123	0.0165	0.0167
	$(xy \mid yx)^S$	0.0102	0.0122	0.0141	0.0136
	$E_{\text{SCF}}(T)$	−1.9089	−1.9948	−2.0156	−2.0283
	ΔE_{SCF}	0.0204	0.0246	0.0304	0.0301
	SP T^1	−0.0367	−0.0233	−0.0200	−0.0192
	T^2	0.0	−0.0013	−0.0049	−0.0046
	S	−0.0707	−0.0497	−0.0453	−0.0441
	ΔE_{SP}	−0.0340	−0.0252	−0.0204	−0.0203
	$\Delta E_{\text{SCF+SP}}$	−0.0136	−0.0007	+0.0100	+0.0098
	$\Delta E_{\text{CI}}{}^{\text{b}}$	−0.0107	−0.0012	+0.0053	

[a] All energies in atomic units; a positive value for ΔE means that the triplet state is lower than the singlet.

[b] CI-calculation, Ref. [7].

One first observes a rather pronounced basis effect: The minimal basis predicts the singlet to be considerably lower than the triplet at both geometries; increase of the basis size (MB → DZ → DZ+p → LB) stabilizes the triplet more than the singlet such that finally at smaller distances the triplet will be the ground state. At large distances Hund's rule remains violated even with LB. This basis effect is a combination of two factors: By going from the minimal basis to the double zeta basis the flexibility of the orbitals is increased and the spin polarization reduced (the singly occupied orbitals become more diffuse than the doubly occupied orbital); addition of *p*-functions allows the singly occupied orbitals to spread over all centers, thus increasing the SCF exchange integral.

As noted earlier there cannot be a contribution from antiparallel spins (i.e. type T^2) to the spin polarization in the case of the minimal basis. However, increasing the basis size one has virtual orbitals giving non-zero T^2 contributions, but all of them are still rather small.

H_4 is the best case to compare our results with rather extensive previous CI calculations [5–7]. The results of Silver and Stevens [7] obtained with STO basis sets of the same quality as our Gaussian basis sets, namely MB, DZ, and DZ+p, have been included in Table 1. They clearly show that the spin polarization is the main source for the stabilization of the singlet state. Qualitatively, we get the same basis set and *R*-dependence as did Silver and Stevens with full CI, quantitatively, the stability of the triplet seems to be still overestimated in our treatment, at least for the larger basis sets.

3.2.2. Square Planar Cyclobutadiene (D_{4h})

Our results for C_4H_4 in its planar square geometry are given in Table 2. All calculations are performed for $R_{CC} = 1.44$ Å, $R_{CH} = 1.10$ Å, $\sphericalangle CCH = 135°$.

Table 2. Spin polarization effects in square planar cyclobutadiene (C_4H_4)[a]

	Polarization of all doubly occ. orb.			Polarization of the π-orbital only		
	MB	DZ*	DZ*+d	MB	DZ*	DZ*+d
$(xy \mid yx)^T$	0.0033	0.0038	0.0053			
$(xy \mid yx)^S$	0.0033	0.0037	0.0049			
$E_{SCF}(T)$	−152.0162	−153.4248	−153.4982			
ΔE_{SCF}	0.0066	0.0076	0.0102			
SP T^1	−0.0455	−0.0354	−0.0329	−0.0426	−0.0324	−0.0300
T^2	−0.0028	−0.0069	−0.0079	0.0	−0.0032	−0.0033
S	−0.0769	−0.0655	−0.0628	−0.0687	−0.0569	−0.0543
ΔE_{SP}	−0.0287	−0.0232	−0.0219	−0.0261	−0.0213	−0.0210
ΔE_{SCF+SP}	−0.0221	−0.0156	−0.0118	−0.0195	−0.0137	−0.0108
ΔE_{CI}[b]				−0.0217		

[a] All energies in atomic units; a positive ΔE means that the triplet state is lower than the singlet.

[b] Ref. [4], full CI with all excitations within the π-system (minimal basis).

If we limit our discussion to the four π-electrons, everything is analogous to the case of planar square H_4. But C_4H_4 possesses a σ-frame which can be polarized too. Our results however show that 90% of the SP contribution to both states are due to the polarization of the doubly occupied π-orbital.

Our MB result for $\Delta E_{\mathrm{SCF+SP}}$ of -0.0221 a.u. $= 13.9$ kcal/mole is very close to the one obtained by Buenker and Peyerimhoff [4]: -0.0217 a.u. $= 13.6$ kcal/mole. By increase of the basis size this value is very strongly reduced to 7.4 kcal/mole, but Hund's rule remains violated, probably also if we go to even larger basis sets. In the case of the antiaromatic homologues $C_3H_3{}^-$, $C_5H_5{}^+$, $C_6H_6{}^{++}$ we expect a completely different behaviour: Since the two singly occupied π-orbitals cannot be localized such that they have no carbon center in common the SCF exchange integral $(xy \mid yx)$ is very large and spin polarization much less important. Therefore, Hund's rule will certainly be valid in these systems [20].

3.2.3. Twisted Ethylene and Cumulenes

Ethylene in D_{2d} symmetry, i.e. with one CH_2 group rotated by 90° versus the other, is another candidate for the violation of Hund's rule. As mentioned earlier, a recent CI calculation by Buenker and Peyerimhoff [8] predicted the singlet to be about 1.5 kcal/mole lower than the triplet.

The results of our calculations are collected in Table 3. Since the SCF exchange integral between the two singly occupied orbitals which are localized on different C atoms is very small (~ 0.001 a.u.), rather small polarization effects can easily give rise to a violation of Hund's rule. On the other hand, in ethylene there is only the σ-frame which can be polarized. In our best calculation the singlet is about 1 kcal/mole below the triplet, in good agreement with Buenker's CI value [8].

The situation is somewhat different in cumulenes, the homologues of ethylene with cumulated double bonds. In their twisted form (which is planar for an odd number of carbon atoms) each of the two π systems contains one unpaired electron, which will polarize the underlying doubly occupied π-orbitals of its own π-system, while the spin relation between the two electrons is of less importance. Thus, the spin polarization effects should be rather large, but not very different for the singlet and triplet states. The results of our calculations in Table 3 confirm this expectation.

For butatriene we did calculations for different C–C bond lengths and found an interesting dependence of SCF- and SP-terms on the geometry: SCF favours a structure with a central triple bond and the two unpaired electrons located on the terminal C-atoms. Contrary to that, SP favours a structure with a longer central and shorter terminal C–C bonds since this allows the unpaired electron of each of the two perpendicular π-systems to spread over three C atoms (allyl resonance) and to polarize the underlying π-orbital more effectively.

3.2.4. $n\pi^*$ Excitations in Formaldehyde

Our calculations on the $n\pi^*$ excited states of formaldehyde ($\tilde{A}\,{}^1A_2$ and $\tilde{a}\,{}^3A_2$) were performed for three different geometries (Table 4). The results show that the SP

Table 3. Spin polarization effects in cumulenes[a]

Molecule	Basis	$(xy\mid yx)$[b]	$E_{SCF}(T)$	ΔE_{SCF}	T^1	T^2	S	ΔE_{SP}	ΔE_{SCF+SP}
Twisted	MB	0.0009	−77.1252	0.0018	−0.0063	−0.0045	−0.0166	−0.0058	−0.0040
ethylene	DZ	0.0010	−77.8600	0.0019	−0.0061	−0.0055	−0.0161	−0.0045	−0.0027
$R_{CC}=1.47$ Å	DZ+d	0.0011	−77.8823	0.0022	−0.0065	−0.0076	−0.0176	−0.0035	−0.0012
Allene	MB	0.0010	−114.5568	0.0021	−0.0271	−0.0217	−0.0507	−0.0020	+0.0002
planar	DZ	0.0011	−115.6474	0.0022	−0.0197	−0.0176	−0.0417	−0.0044	−0.0022
$R_{CC}=1.35$ Å	DZ+d	0.0014	−115.6844	0.0028	−0.0190	−0.0177	−0.0415	−0.0048	−0.0020
Butatriene[c]	MB	0.0002	−152.0553	0.0005	−0.0097	−0.0144	−0.0235	+0.0006	+0.0010
1.21/1.43 Å	DZ*	0.0002	−153.4644	0.0005	−0.0082	−0.0130	−0.0210	+0.0003	+0.0009
1.24/1.40 Å	DZ*	0.0003	−153.4623	0.0006	−0.0103	−0.0158	−0.0251	+0.0010	+0.0016
1.27/1.37 Å	DZ*	0.0005	−153.4556	0.0009	−0.0136	−0.0196	−0.0316	+0.0016	+0.0025
Pentatetraene planar	MB	0.0008	−189.4723	0.0017	−0.0331	−0.0360	−0.0679	+0.0011	+0.0028

[a] All energies in atomic units; ΔE positive, if triplet state lower than singlet.

[b] $(xy\mid yx)^T=(xy\mid yx)^S$ within the given accuracy.

[c] Twisted, i.e. terminal CH_2 groups at 90°; the lengths of the central and terminal C–C bonds are indicated.

Table 4. Spin polarization effects in CH_2O, NH, O_2[a]

Molecule	Basis	$(xy \mid yx)^T$	$(xy \mid yx)^S$	$E_{SCF}(T)$	ΔE_{SCF}	T^1	T^2	S	ΔE_{SP}	ΔE_{SCF+SP}
Formaldehyde[b]										
1.21 Å/*pl.*	DZ	0.0080	0.0057	−113.6131	0.0134	−0.0048	−0.0072	−0.0130	−0.0010	0.0124
1.21 Å/*pl.*	DZ+*d*	0.0077	0.0056	−113.6587	0.0131	−0.0075	−0.0113	−0.0197	−0.0010	0.0121
1.31 Å/*pl.*	DZ+*p*(O)[c]	0.0063	0.0044	−113.6327	0.0105	−0.0042	−0.0065	−0.0113	−0.0006	0.0098
1.31 Å/*pl.*	DZ+*p*+*d*	0.0061	0.0043	−113.6715	0.0102	−0.0069	−0.0109	−0.0184	−0.0006	0.0097
1.31 Å/*pyr.*	DZ+*p*(O)[c]	0.0064	0.0045	−113.6362	0.0107	−0.0034	−0.0057	−0.0090	+0.0001	0.0108
1.31 Å/*pyr.*	DZ+*p*+*d*	0.0063	0.0045	−113.6770	0.0105	−0.0063	−0.0103	−0.0164	+0.0002	0.0108
NH	DZ+2*d*	0.0339	0.0329	−54.9067	0.0668	−0.0065	−0.0074	−0.0174	−0.0035	0.0633
$R = 1.04$ Å	LB	0.0341	0.0329	−54.9704	0.0670	−0.0065	−0.0075	−0.0174	−0.0034	0.0636
O_2	DZ+*d*	0.0238	0.0237	−149.4311	0.0475	−0.0123	−0.0248	−0.0329	0.0042	0.0517
$R = 1.21$ Å	LB	0.0236	0.0233	−149.6372	0.0469	−0.0118	−0.0249	−0.0314	0.0053	0.0522

[a] All energies in atomic units. A positive value for ΔE means that the triplet state is lower than the singlet.

[b] $n\pi^*$ excited states; C–O distance and planarity (*pl.*) or non-planarity (*pyr.*) indicated [23].

[c] DZ + one diffuse *p*-function at the O atom.

effects are almost identical in the two states, irrespective of the geometry or basis set used. The largest contribution to SP is a polarization of the π^2 lone pair of O by the singly occupied σ orbital at the same nucleus, this contribution of course is the same in the two states. One should note that the *d*-functions contribute almost 50% to the SP energy lowerings. The SCF excitation energy of the triplet with respect to the ground state is 2.21 eV which is well below the experimental figure of 3.12 eV [24]. It is a common experience that SCF overestimates the stability of open shell states relative to closed shell states which have more paired electrons and therefore a higher correlation energy. Our SP value of 0.45 eV accounts for about 50% of this difference.

3.2.5. NH and O_2

The lowest electronic configuration of both NH and O_2 is π^2 ($1\pi^2$ for NH, $1\pi_g^2$ for O_2). From these three electronic states arise: $^3\Sigma^-$($^3\Sigma_g^-$ for O_2), $^1\Delta$($^1\Delta_g$), and $^1\Sigma^+$($^1\Sigma_g^+$). In Table 4 we include some results of calculations for the $^3\Sigma^- \rightarrow {}^1\Delta$ splitting in the two molecules. In both cases we used an internuclear distance R which is approximately the arithmetic mean of the experimental equilibrium distances in the two states. In NH the π-orbital is essentially an atomic $2p$-orbital which can polarize the NH σ-bond and the N lone pair. Our SCF splitting of 1.82 eV (in fairly good agreement with the HF-limit of 1.83 eV [25]) is reduced by SP to 1.73 eV. But this is still considerably higher than the experimental value of 1.56 eV [26, 27]. This discrepancy is due to the "direct correlation" of the two unpaired electrons, which is expected to be fairly important in NH since the SCF exchange integral is large. In order to evaluate this correlation contribution we used the Ahlrichs–Driessler scheme [34] to calculate correlation energies of two-electron systems. Within the large basis set the direct correlation lowers the triplet energy by 0.010 a.u., the singlet by 0.016 a.u., thus favouring the singlet by another 0.006 a.u. = 0.16 eV. Taking into account both spin polarization and direct correlation the singlet-triplet splitting is 1.57 eV, in close agreement with experiment. (Because of symmetry the internal double substitutions give vanishing contributions to both states and do not affect the singlet-triplet splitting.)

In O_2, again, the calculated SCF splitting of 1.27 eV is considerably larger than the experimental value of 0.98 eV [28]. O_2 is a still more complicated case since all of the first order contributions to the $^3\Sigma_g^- \rightarrow {}^1\Delta_g$ splitting are of the same order of magnitude, as it can be seen in Table 5. The spin polarization contribution even consists of two terms with opposite signs: Polarization of the σ-orbitals favours the singlet, polarization of the doubly occupied π-orbital the triplet. Considering only the SP one would get a singlet-triplet splitting which is even larger than the SCF value of 1.27 eV. Furthermore, in O_2 we find a remarkable difference between our two perturbation schemes. This, too, indicates that there is not one single effect responsible for the splitting and that the PT treatment has to be applied carefully. Using the conventional PT scheme with summation of the individual PT contributions according to Eq. (12) we obtain a value of $\Delta E = 0.99$ eV which is surprisingly close to the experimental value.

Table 5. Energy contributions to the $^3\Sigma_g^- - {}^1\Delta_g$ splitting in O_2 (large basis set; in atomic units)

	$^1\Delta_g$	$^3\Sigma_g^-$	ΔE	ΔE (eV)
SCF	−149.5917	−149.6384	0.0468	1.27
spin polarization[a]				
σ-core	−0.0133	−0.0116	−0.0017	−0.05
π-core	−0.0260	−0.0393	0.0133	0.36
spin polarization[b]				
σ-core	−0.0107	−0.0080	−0.0028	−0.08
π-core	−0.0206	−0.0288	0.0082	0.22
direct correlation	−0.0100	−0.0064	−0.0036	−0.10
internal doubles	−0.0563	−0.0377	−0.0186	−0.51
total[a]			0.0362	0.99
[b]			0.0300	0.82
exp. [28]				0.98

[a] Double sum used in perturbation theory (compare Eq. (12)).
[b] One optimized virtual orbital used in perturbation theory.

3.3. *Limiting Cases*

3.3.1. Two Independent Doublets

If in a molecule the two unpaired electrons become more and more separated in space we approach the case of two independent doublets which can be coupled either to a singlet or to a triplet state. Their SCF energies must be the same as well as the SP energies; furthermore, in the case of the triplet the two types of SP should contribute $\frac{1}{3}$ and $\frac{2}{3}$ to the overall SP energy.

As an example for such a case we did a calculation for ethane with a C–C distance of 5.0 Å, i.e. for two almost independent pyramidal methyl radicals. The SCF exchange integral between the two singly occupied radical orbitals is already so small that the SCF splitting between singlet and triplet is slightly less than 10^{-6} a.u. The SP energies were obtained to be 0.0043 a.u. in the case of the singlet and 0.0045 a.u. for the triplet, the two types of SP contributing 0.0015 a.u. and 0.0030 a.u., respectively, to the latter (DZ basis set). Thus, also the SP contribution to the total energy of the two states is nearly the same. The remaining small difference of 0.0002 a.u. is due to our PT treatment.

3.3.2. Transition from a Closed-Shell to an Open-Shell Singlet

In cyclobutadiene we observe a continuous transition from an open-shell singlet state at the square geometry to a closed-shell singlet at the rectangular equilibrium geometry. Part of the electronic correlation of the open-shell state can be interpreted as SP as discussed before, but the question remains what happens to the spin polarization during this transition? Which contributions to the overall correlation energy of a closed-shell system do correspond to the SP term for the open-shell singlet? In order to answer this question we first transform the singly occupied SCF orbitals of Eq. (1) into symmetry adapted orbitals corresponding to the symmetry of the rectangular C_4H_4:

$$\varphi_x, \varphi_y = \frac{1}{\sqrt{2}}(\varphi_a \pm \varphi_b) \tag{22}$$

ϕ_S and ϕ_S^1 now read

$$\phi_S = \frac{1}{\sqrt{2}}\{|i\bar{i}a\bar{a}| - |i\bar{i}b\bar{b}|\} \tag{23}$$

$$\phi_S^1 = \frac{1}{\sqrt{12}}\{2|\bar{i}\bar{k}ab| + 2|ik\bar{a}\bar{b}| - |i\bar{k}a\bar{b}| - |i\bar{k}\bar{a}b| - |\bar{i}ka\bar{b}| - |\bar{i}k\bar{a}b|\} \tag{24}$$

This means that the form of ϕ_S^1 is invariant under the transformation (22) which can be easily derived from the spin-coupling scheme involved in ϕ_S^1.

The transition to a rectangular structure means that the weights of the two determinants in (23) become different, at the rectangular equilibrium geometry the weight of the first one is already 0.98. Using the terminology of electron pair theories [29–33] we interpret the first determinant in (23) as HF determinant, the second one as an intra-pair correlation configuration where the pair $|a\bar{a}|$ is replaced by $|b\bar{b}|$. Further inspection of the explicit formulas for singlet- and triplet interpair-functions ${}^{1,3}\phi(ia \to kb)$ [33] shows that ϕ_S^1 can be expressed as:

$$\phi_S^1 \equiv \frac{\sqrt{3}}{2}{}^1\phi(ia \to kb) - \frac{1}{2}{}^3\phi(ia \to kb) \tag{25}$$

Our result can be formulated as follows: The SCF wavefunction for the open-shell singlet goes over into SCF-determinant + one intra-pair function, ϕ_S^1 mainly into the singlet-interpair excitation $ia \to kb$.

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