

Study of orbital transformation in configuration interaction calculations of hyperfine coupling in nitrogen and the CH molecule

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Multi-reference configuration interaction calculations employing various orbital transformations are undertaken to obtain the isotropic hyperfine coupling constant a_{iso} in nitrogen and $a_{\text{iso}}(\text{H})$ in the CH molecule. The natural orbital (NO) basis is found to be more effective than the simple RHF-MO basis; the most obvious is a basis of spin natural orbitals (SNO). It is found that a_{iso} is approached from opposite sides in the NO and $2s$ shell SNO basis if the CI expansion is increased. Both results are within a few percent of the full CI limit for the nitrogen atom (in the given AO basis) and the experimental value for H in the CH radical. Various features of the SNO are discussed.

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1. Introduction

The magnetic hyperfine splitting arises from the interaction of the nuclear spin I with the angular momentum L and the electron spin S . The analysis is generally undertaken in terms of an isotropic and anisotropic contribution [1]. For an electronic state with angular momentum zero in a linear molecule at most two first-order magnetic hyperfine coupling constants (hfcc) for each nucleus with $I \neq 0$ may be encountered [2]. The general definition of the parameters using cartesian coordinates are

$$a_{\text{iso}} = \frac{4\pi}{3} g_e g_N \beta_e \beta_N \frac{1}{\Sigma} \langle \Psi(r, R_0) | \sum_i \delta(r_{iN}) 2s_{zi} | \Psi(r, R_0) \rangle \quad (1)$$

and

$$A_{zz} = g_e g_N \beta_e \beta_N \frac{1}{\Sigma} \left\langle \Psi(r, R_0) \left| \sum_i \frac{3z_i^2 - r_{Ni}^2}{r_{Ni}^5} s_{zi} \right| \Psi(r, R_0) \right\rangle \quad (2)$$

whereby $\Psi(r, R_0)$ is the electronic wavefunction within the Born-Oppenheimer approximation for the nuclear position R_0 ; the letter Σ denotes in the standard manner the projection of the spin momentum S onto the molecular axis. All electronic variables are denoted by small letters. The term g_e is the g value for the electrons in the free radical. In the present work always a value of two was used. The quantities g_N and β_N are the nuclear g factors and the value for the nuclear magneton respectively, while β_e is the value of the bohr magneton.

Both parameters, a_{iso} and A_{zz} , are defined in terms of the electronic orbitals and spin states, with redundant quantum numbers related to nuclear spin and total angular momentum omitted. The constant a_{iso} is called isotropic hyperfine coupling constant or Fermi contact term and provides a measure of the unpaired spin density at the nucleus N in the molecule.

The present paper will deal with the calculation of a_{iso} whose reliable prediction is a very troublesome problem in ab initio calculations. The study of A_{zz} is comparatively quite easy and will therefore not be discussed any further in the present work.

One of the difficulties in determining a_{iso} is the fact that it requires the wavefunction at one point only, so that error cancellation is not effective. Furthermore the description of spin polarization effects in $\Psi(r, R_0)$ are very important. In the restricted Hartree-Fock (RHF) approximation the contribution of the closed shells to a_{iso} is zero; it becomes large, however, if spin polarization is taken into account by the proper description of the electron correlation. In such approach the contributions of all closed shells must be calculated very carefully because they are similar in magnitude but possess opposite signs.

From both points a strong dependence on the AO basis set employed results, which was the subject of recent work [3–7]. Meanwhile it is clear that the use of large (sp) basis sets as well as the use of polarization functions are essential. For the ground state 4S of the nitrogen atom, which became a standard system for ab initio calculations of the Fermi contact term, an extension of the standard basis set from $9s\ 5p$ to $13s\ 8p$, both given by van Duijneveldt [8] results in an increase of a_{iso} from 0.9 MHz to 4.5 MHz, both calculated within a SD-CI procedure. This behavior can be explained by the improved description of the $2s$ polarization. Because the energetical lower virtual space is essential for $2s$ polarization effects, similar effects result if one diffuse s function is added to the $9s\ 5p$ basis [5]. The contraction of the sp basis is also a very sensitive ingredient; for the 4S state of the nitrogen atom it was found, for example, that in the $9s\ 5p$ basis of Huzinaga, contracted to $[4s\ 2p]$ [9], the calculated value for a_{iso} increases from 3.4 MHz to 12.5 MHz [6].

The effect of polarization functions was estimated in large-scale CI calculations for the 4S state of the nitrogen atom [3, 5]. They estimated the influence of d functions to about 2 MHz, while f functions increase a_{iso} by about 0.4 MHz. Nearly no effect was found if g functions were introduced.

In addition to the AO basis the quality of the CI treatment accounting for correlation possesses a strong influence on a_{iso} . The effect of higher than double excitations can be seen by the fact that a multi-reference (MR) CI calculation employing the $13s\ 8p$ AO basis yields a value for a_{iso} of 6.9 MHz if the reference set consists of the RHF determinant ($c^2 \approx 0.95$) and one additional configuration ($c^2 \approx 0.003$). The corresponding SD-CI calculation yields only 4.5 MHz. The importance of higher excitations is furthermore enhanced if polarization functions are present in the AO basis. Very often it is not possible to consider all single and double excitations from a set of reference configurations. In such cases only those configurations are added to the wavefunctions which lower the total energy by more than a given threshold

T . As expected a strong dependence of a_{iso} on T is found, which disappears only at very small thresholds ($T < 10^{-9}$ a.u.).

A further dependence arises from the one-particle basis in which the MR-CI calculation is performed (in what follows referred to as CI basis to differentiate from the AO basis). Clearly this dependence is not present in the full CI (FCI) limit but FCI calculations are only possible for very small systems. Bauschlicher et al. [5] studied these effects by employing various orbital transformations, namely molecular orbitals (MO) obtained from a RHF calculation, modified coupled pair functions (MCPF) and CASSCF orbitals, whereby all calculations were performed for $T=0.0$. They found not surprisingly that there is an influence of the active space and of the reference set involved in the MR-CI calculation upon the result of a_{iso} . They found that the results of the CASSCF/MR-CI calculations are closer to the FCI limit than those of the SCF/MR-CI procedure. The main differences between both lie in the fact that the SCF/MR-CI treatment seems to underestimate a_{iso} , approaching the FCI limit from below if more and more configurations are added to the reference set. The CASSCF calculations overestimate a_{iso} for smaller reference sets, but the value is lowered if the reference set is enlarged. It is seen that the effects of very high excitations are small indicating that a more economical MR-CI calculation should yield values near the FCI limit [3].

Similar studies were performed by Engels [10] involving MO's and natural orbitals (NO). The NO basis was obtained in the usual way by diagonalizing the total MRD-CI density matrix (CIDM). Both one-particle bases, CASSCF orbitals and NO, are superior to the MO basis because they introduce correlation effects into the charge density of the system. On the other hand a_{iso} depends on the spin density rather than on the charge density. Correlation effects of the spin density are included into spin natural orbitals (SNO) [6, 11] which are obtained by diagonalizing the total one electron spin density matrix (TM) [6]. Hence SNO should be an optimal starting point for calculations of spin density dependent properties such as a_{iso} .

In the present paper we will study the effects of three different one-particle CI basis sets, namely MO, NO and SNO on sensitive parameters of an a_{iso} calculation, i.e. variations of the configuration selection threshold T , and on different configuration sets. After a brief introduction of theoretical aspects in Sect. 2 our results for the 4S ground state of the nitrogen atom and the $X^2\Pi$ state of the CH molecule are discussed. A summary of previous theoretical determinations of a_{iso} together with the experimental values is

Table 1. Summary of previous calculations for the isotropic hyperfine coupling constant a_{iso} of the nitrogen atom in its $^4S_{3/2}$ state

Treatment	a_{iso} (MHz)
Approximate Extended HF	10.6 [16]
Numerical UHF	60.4 [17]
Numerical MCSCF	10.0 [18]
10s 5p 1d, CASSCF/MR-CI (4 ref.)	7.22 [5]
SCF/full CI	6.91 [5]
10s 5p 2d, CASSCF/MR-CI (4 ref.)	7.97 [5]
CASSCF/MR-CI (15 ref.)	7.64 [5]
23s 12p 10d 4f 2g, k-orbitals/MR-CI	10.1 [3]
Experiment	10.45092912 [19]

Table 2. Basis sets employed in the present work

Nitrogen atom		
Nitrogen	AO: (13s 8p) → [8s 4p] MO: MO from a RHF calculation for the 4S state of N	according to [8, 10]
CH molecule		
Carbon	AO: (13s 8p) → [8s 5p] plus 2 × d (1.5, 0.4) plus 1 × f (0.7)	according to [8, 21]
Hydrogen	AO: (8s) → [5s] plus 2p (1.4, 0.25) MO: MO from a RHF calculation for the $a^4\Sigma^-$ state of CH	according to [8, 21]

given in Table 1. In order to differentiate between the various effects the AO basis used in the present study was fixed. They are summarized in Table 2. For all calculations the MRD-CI program package of Buenker and Peyerimhoff [12] is used.

2. Theory

The difficult term in the calculation of a_{iso} is the total spin density at the nucleus N . It is a one-electron property and defined (see 1) as

$$\langle \delta(r_N) \rangle_s = \left\langle \Psi(r, R_0) \left| \sum_{i=1}^n \delta(r_i - R_N) 2s_{zi} \right| \Psi(r, R_0) \right\rangle, \quad (3)$$

The subscript s indicates averaging over the unpaired spin density.

If the electronic wavefunction $\Psi(r, R_0)$ is written as a linear combination of Slater determinants, the

term $\langle \delta(r_N) \rangle_s$ can be expressed in a sum over matrix elements between determinants [13]:

$$\langle \delta(r_N) \rangle_s = \sum_k \sum_l (c_k c_l) \left\langle \Phi_k \left| \sum_{i=1}^n \delta(r_i - R_N) 2s_{zi} \right| \Phi_l \right\rangle. \quad (4)$$

Using the Slater-Condon rules [13] for the evaluation of one-electron matrix elements the term $\langle \delta(r_N) \rangle_s$ can also be expanded in terms of the one-electron CI basis functions φ_p employing to construct the various Slater determinants:

$$\langle \delta(r_N) \rangle_s = \sum_{p,q} \gamma_{pq} \langle \varphi_p | \delta(r - r_N) | \varphi_q \rangle. \quad (5)$$

The two terms in (5) will be referred to as the integral matrix (IM) $\langle \varphi_p | \delta(r - r_N) | \varphi_q \rangle$ and the one-electron total spin density matrix φ_{pq} (TSM). This matrix contains the product of the coefficients belonging to the orbitals φ_p and φ_q together with the factors resulting from the s_z operator. Just as the total charge density matrix it is a symmetric matrix. In RHF calculations all matrix elements of the TSM are zero with the exception of the diagonal elements corresponding to singly occupied orbitals. They are $+1/2$ if the spin quantum number m_s is chosen to be maximal. In CI calculations other matrix elements will become different from zero because a net contribution can also arise from doubly-occupied orbitals.

The quality of the one-particle CI basis for calculating a_{iso} can also be inferred from the structure of the TSM. If off-diagonal elements are dominant, the basis is not properly optimized to describe the spin density since these functions are far from being eigenfunctions of the TSM. Among the basis sets for the CI configurations the RHF-MO's and the natural orbitals (NO) are widely known. The first results directly from an SCF calculation in the RHF scheme while the second result as eigenfunctions from diagonalizing the total CI density matrix (TCM) of a particular CI calculation. They differ to some extent depending on the CI treatment: single-excitation CI, single-double (SD) CI or multi-reference (MR) CI. The third basis, spin natural orbitals (SNO) have first been discussed by Harriman [14] using UHF calculations. They were also used by Meyer [16] using an approximate extended Hartree Fock approach (AEHF). Chipman [11] defined SNO in a single excitation CI (SECI). In the present work the SNO are constructed similar to NO from a multi-reference CI configuration, whereby the TSM matrix instead of the TCM is diagonalized. Details are given in the next section.

Table 3. Expansion of the NO and SNO in terms of the SCF-MO basis for the $4S$ ground state of the nitrogen atom. AO basis [$8s\ 4p\ 2d$]

	NO ^a		SNO ^b			
	1s	2s	1s SNO (SNO 13)	1s' SNO ^d (SNO 4)	2s SNO (SNO 1)	2s' SNO (SNO 14)
Eigenvalue						
Eigenvector ^c	-1.99923	1.96693	-0.00294	0.00292	0.07673	-0.05515
1s	0.9999	0.0095	0.7058	0.7074	0.0272	0.0258
2s	-0.0094	0.9998	-0.0272	-0.0267	0.7665	0.6410
3s	0.0000	0.0066	-0.1408	0.1347	-0.6075	0.7262
4s	0.0003	-0.0016	0.4090	-0.4020	-0.2059	0.2464
5s	-0.0001	0.0009	-0.2567	0.2559	0.0073	-0.0097
6s	-0.0003	-0.0011	-0.4010	0.4010	-0.0013	0.0032
7s	0.0000	0.0000	-0.2848	0.2766	0.0089	-0.0100
SCF-MO						

^a The NO result from a CI treatment based on 4 reference configurations and a configuration selection threshold of $T=0.1$ mh

^b The SNO result from a CI treatment based on 4 reference configurations and a configuration threshold of $T=0.0$

^c The MO 3s to 7s are virtual orbitals; only the most important MO are listed

^d The SNO are labelled according to their physical description; the actual eigenvalue number is also given in parentheses

3. Results for the $4S$ state of the nitrogen atom

A. Orbital characteristics

As the first step in our study the three different CI basis sets used in the present paper for the $4S$ ground state of the nitrogen atom will be characterized. In Table 3 the eigenvectors of the most important natural orbitals (NO) and spin natural orbitals (SNO), expanded in the MO basis, are given. Only orbitals of s symmetry are contained, because orbitals possessing other symmetry make no direct contribution to a_{1s0} . In addition to the eigenvectors the eigenvalues (occupation numbers) of the orbitals within the diagonalized TCM or TSM are also summarized. The natural orbitals are the result of diagonalizing the MR-CI density matrix obtained for the $4S$ state by performing a CI calculation with four reference ($4M$) configurations in the MO basis, whereby excitations from the 1s core were also allowed. The configuration selection threshold was $T=10^{-7}$ h. The SNO are obtained from the same MR-CI calculation and for comparison also from a SD-CI (1 reference configuration). The shape of the orbitals can be seen from Figs. 1 and 2 which contain the plots of $|\Psi(r)|^2$ versus R_z for the different orbitals. While Fig. 1 contains the orbitals which can be connected with the 1s MO, those connected with the 2s MO are given in Fig. 2. It is found that the NO are nearly identical to the doubly occupied MO. Their occupation numbers in the TCM are also nearly 2.0 which would be the eigenvalues of the MO. The near identity between NO and MO is expected because the weight of the RHF determi-

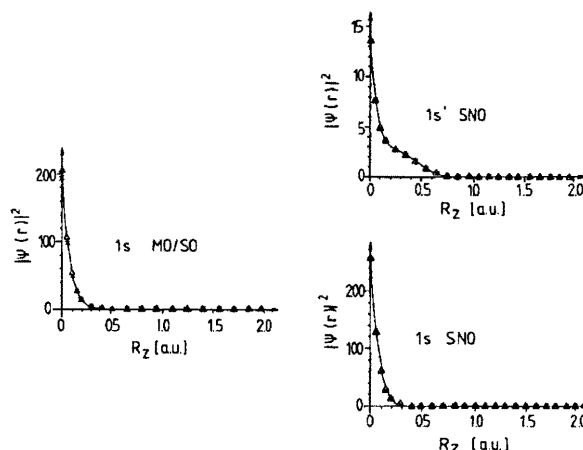


Fig. 1. Plot of the 1s nitrogen shell in the SCF-MO, the NO and the SNO representation. Left side: \times MO obtained by SCF ($4S$ state); Δ NO obtained by $4MT=10^{-4}$ h CI calculation. Right side: \times SNO obtained by $1MT=10^{-4}$ h CI calculation; Δ SNO obtained by $4MT=10^{-4}$ h CI calculation. (\times M denotes \times reference configurations)

nant in the CI expansion (measured by the square of the expansion coefficient c) is greater than 0.95.

As described in a recent paper [4, 6] the situation changes entirely if the SNO are considered. Table 3 shows a strong mixing between the occupied MO (1s and 2s) and the virtual MO in the SNO expansion. The 1s strongly interacts with the 4s and 6s, resulting in two SNO with nearly identical portion of the 1s MO. The eigenvalues of these 1s and 1s' NO are of the same magnitude but possess different signs (0.00292 vs. -0.00294). The eigenvalues of both SNO connected with the 2s MO (denoted by 2s and 2s'

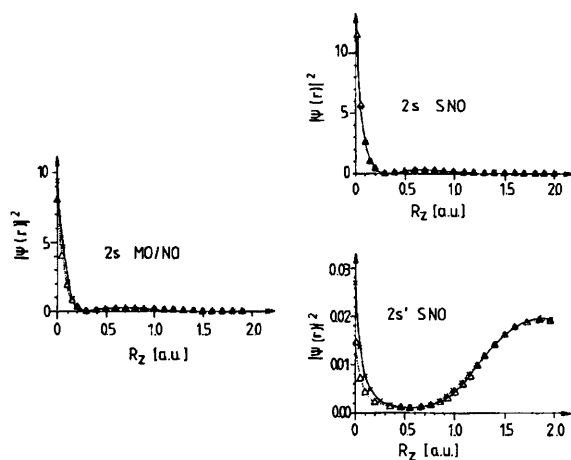


Fig. 2. Plot of the 2s nitrogen shell in the SCF-MO, the NO and the SNO representation. Notation as in Fig. 1

SNO) are also different in sign, but the positive eigenvalue is somewhat greater in absolute value than the negative (0.07673 vs. -0.05515). The mixing occurs in the main between the 2s and 3s MO, the latter being the first virtual orbital. The influence of orbitals higher than 5s is very small.

The shape of the two SNO connected with a single MO are also given in Figs. 1 and 2. It is seen that one of them has the form of the original MO, normally somewhat more contracted while the second SNO is much more diffuse. The SNO obtained in the present work as eigenfunctions of the CI spin density matrix behave similar to spin natural orbitals defined by Chipman [11], to UHF natural orbitals given by Harriman [14], and the AEHF orbitals derived by Meyer [16]. For example, the eigenvalue of the 1s and 1s' SNO given by Meyer (-0.00293 , 0.00294) are similar to ours (-0.00294 , 0.00292). Small differences arise for 2s and 2s' (-0.07062 , 0.07411 vs. -0.05515 , 0.07673). The present value of the various SNO at the position of the nucleus is higher by approximately a factor of two compared to the corresponding quantities given by Meyer. The well known fact [1] that for atoms of the first row the contribution to a_{iso} of the 1s shell and the 2s shell possess different signs but are of similar magnitude can be understood by combining eigenvalues and eigenvectors of the SNO. Although the absolute eigenvalues of the 1s and 1s' SNO are nearly identical the net contribution of the 1s shell is negative because the 1s is much more compact than the 1s'. The same arguments hold for the 2s shell in which the more compact 2s NO possesses the positive eigenvalue (dominating the 2s contribution) while the 2s' SNO with the negative eigenvalue is quite diffuse. The fact that the 1s and 2s shell contributions to a_{iso} are almost of the same

Table 4a. Technical details of the various MRD-CI calculations in the MO or NO basis ($\Sigma c_i^2 = 0.9753$) for the ground state of the nitrogen atom

Reference set		Square of CI (NO) expansion coefficient c^2
$1s^2 2s^2$	$2px 2py 2pz$	0.9674
$1s^2 2s 3s$	$2px 2py 2pz$	0.0027
$1s^2 2s d_{2x^2-x^2-y^2}$	$2px 2py 2pz$	0.0026
$1s^2 2s d_{x^2-y^2}$	$2px 2py 2pz$	0.0026

Table 4b. Technical details of the MRD-CI calculations employing the MO/SNO basis ($\Sigma c_i^2 = 0.9705$) for the ground state of the nitrogen atom

Reference set		Square of CI coefficient c^2
$1s^2 2s 2s'$	$2px 2py 2pz$	0.4964
$1s^2 2s^2$	$2px 2py 2pz$	0.3153
$1s^2 2s'^2$	$2px 2py 2pz$	0.1546
$1s^2 2s d_{2x^2-x^2-y^2}$	$2px 2py 2pz$	0.0021
$1s^2 2s d_{x^2-y^2}$	$2px 2py 2pz$	0.0021

magnitude are not predictable solely from the size of the eigenvalue, but the more compact 1s density has also to be taken into consideration.

B. CI calculations

The use of MO or NO in CI calculations can be made in the standard manner. The reference set for the MRD-CI treatment is listed in Table 4. Because the natural orbitals of the 4S ground state are so similar to the corresponding SCF-MO orbitals the same reference configurations can be employed in the CI (MO) and CI (NO) calculation. It should be noted that the reference configuration including *d* orbitals can mix in the 4S state by a recoupling within the *p* shell occupation.

The difficulty arises if SNO are employed. Since each MO is represented by two SNO, the nitrogen ground state configuration must be written as $1s 1s' 2s 2s' 2px 2py 2pz$ with 7 open shells. Preliminary calculations show that this configuration enters into the CI expansion with a weight of about $c^2 = 0.5$ while further dominant terms are $1s'^2 2s^2 2px 2py 2pz$ ($c^2 \approx 0.3$ or $1s'^2 2s'^2 2px 2py 2pz$ ($c^2 \approx 0.2$). Since a reference set of configurations with seven open shells is beyond the present scope of the computer program, an alternative route was taken for subsequent calculations.

In analogy to the construction of natural orbitals, for which the inner shell is oftentimes not included in the orbital transformation, the spin natural orbital transformation is undertaken for an MRD-CI calcu-

Table 5. Dominant part of the TSM in an MRD-CI calculation for the ground state of the nitrogen atom employing the NO (Table 3a) and MO/SNO (see text) basis. The lower triangular part is given only. The MRD-CI calculations employ the reference sets of Tables 4a, b at a configuration selection threshold of $T=0.0$ h

MRD-CI (NO) [†]									
1s	0.0000								
2s	0.0003	0.0220							
3s	-0.0020	0.0629	-0.0004						
$d_{x^2-y^2}$	0.0	0.0	0.0	0.0046					
$d_{2z^2-x^2-y^2}$	0.0	0.0	0.0	0.0000	0.0046				
4s	-0.0025	0.0156	-0.0002	0.0	0.0	0.0001			
5s	0.0000	0.0062	0.0001	0.0	0.0	0.0000	0.0000		
6s	0.0005	0.0013	0.000	0.0	0.0	0.0000	0.0000	0.0000	
MRD-CI (MO/SNO)									
1s	0.0000								
2s	0.0021	0.0756							
2s'	-0.0014	-0.0003	-0.0560						
$d_{x^2-y^2}$	0.0	0.0	0.0	0.0045					
$d_{2z^2-x^2-y^2}$	0.0	0.0	0.0	0.0000	0.0045				
3s	-0.0028	0.0001	0.0001	0.0	0.0	0.0000			
4s	-0.0007	0.0001	0.0001	0.0	0.0	0.0000	0.0000		
5s	-0.0004	0.0000	0.0000	0.0	0.0	0.0000	0.0000	0.0000	

lation in which the 1s core is kept doubly occupied. In other words the 1s shell is described by the 1s MO while the 2s shell (and the virtual space) is represented by spin natural orbitals; this basis will be referred to as MO/SNO basis. In the ensuing MRD-CI calculation CI (MO/SNO) all shells (1s and 2s) are correlated (reference set in Table 4b). From this construction it is expected that the 2s correlation is accounted for to a large extent in a small CI expansion while the 1s contribution to a_{iso} will need an extended CI wavefunction. This approach, describing the 2s shell by SNO's and leaving the 1s shell unaltered is assumed to be more adequate than the opposite procedure (representing the 1s by SNO's and the 2s shell by MO's) because the 1s shell polarization is easier to account for [4]. For a more detailed examination of this point the boron atom with the $1s^2 2s^2 2p$ configuration would be the more appropriate system. Such a MO/SNO basis might be required for technical reasons also if many shells are present in a molecule, or if not all shells are equally important for the calculation of a_{iso} , as for example in a hydride such as CH, in which the 1s shell does not contribute anything to the isotropic hfcc at the hydrogen center.

The most important elements of the spin density matrix TSM (γ_{pq}) for the MRD-CI (NO) and MRD-CI (MO/SNO) calculations are listed in Table 5a, b. The typical mixing of the 1s and 2s NO with higher s orbitals seen in the off-diagonal elements of the MRD-CI (NO) matrix is still present in the interaction of the 1s MO with the higher s SNO (MRD-CI (MO/SNO) TSM) while the TSM of this MRD-CI calculation is almost diagonal for the 2s and 2s' SNO.

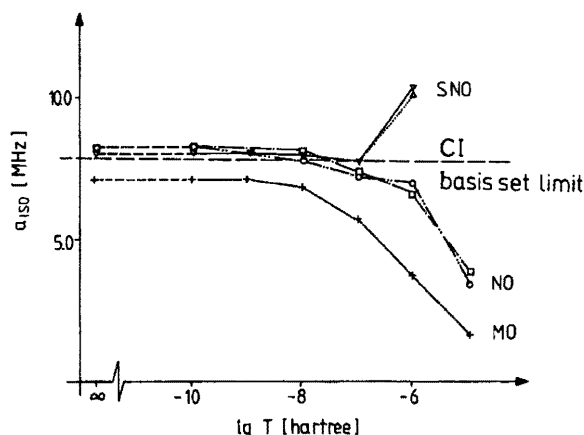


Fig. 3. Calculated a_{iso} for the nitrogen molecule obtained from various treatments as a function of the configuration selection threshold T + MRD-CI (MO), 4 M treatment (see notation Fig. 1), \square MRD-CI (NO), NO result from SD-CI, $T=2 \cdot 10^{-5}$ h, \circ MRD-CI (NO), NO result from 4 M treatment, $T=10^{-7}$ h, Δ MRD-CI (MO/SNO), SNO result from SD-CI, $T=10^{-5}$ h, ∇ MRD-CI (MO/SNO), SNO result from 4 M treatment, $T=0.0$ h, 1s shell in SNO constructions always doubly occupied. The dashed line represents the full CI basis set limit [5]

The corresponding MRD-CI (MO) matrix is similar to the MRD-CI (NO) matrix whereby the 1s–ns and 2s–ns interaction is spread over a slightly larger range of orbitals. Mixing between s and d type orbitals does not occur, of course.

The results of a_{iso} obtained by employing the MO, NO or MO/SNO basis sets are contained in Fig. 3. The reference sets are those of Table 4; they should

be fairly equivalent since their contribution to the total CI expansion, measured by the square of the expansion coefficients, is very similar ($\Sigma c^2 = 0.9716$ MO, 0.9753 NO and 0.9705 SNO). The calculations are carried out in the standard manner whereby the MRD-CI truncation is made on the basis of the energy selection threshold T . The AO set limit corresponding to the full CI limit is taken from the work of Bauschlicher et al. [5].

It is seen that the CI (MO) treatment possesses the slowest convergence with respect to a_{iso} . The CI (NO) calculation improves the situation and the CI (MO/SNO) is practically converged for $T=10^{-7}$ h. There is one important difference, however: the MO and NO basis set calculations approach the limit from below while the MO/SNO basis shows the opposite behavior and overestimates a_{iso} for large threshold values or smaller CI spaces. This is of course to be expected, since the optimal SNO are only employed for the $2s$ shell while the primary contribution of the $1s$ shell must be brought in by the CI expansion; note that the total value is the sum of the $2s$ (positive) and $1s$ (negative) contribution. Modifications in constructing the natural orbitals or the spin natural orbitals (from a SD-CI calculation at larger threshold T) show little effect on the total result as expected from earlier NO studies [20].

The influence of higher excitations not included in the MRD-CI calculations can be evaluated from a comparison with the AO basis set limit; the latter has been obtained by Bauschlicher et al. [5] with considerable computational expenditure, and this will not be feasible for larger systems, for which CI truncation will be necessary, at least in the near future. Increasing the reference set in the MRD-CI (MO) calculation to include higher excitations should add eventually a value of about 0.8 MHz to the presently calculated result. The deviation (overestimation) in the NO and MO/SNO basis set calculation is only 0.4–0.2 MHz. Similar behavior has been observed by employing CASSCF orbitals [5].

In summary it is seen that the choice of the CI orbital basis is a quite helpful means to estimate the error in the calculated a_{iso} result in a truncated CI calculation. The natural orbital basis is expected to lead to faster convergence in accounting for electron correlation than the SCF-MO basis, a behavior which is carried over to the calculation of a_{iso} which is dominated by the balance of the electron correlation in the $1s$ and $2s$ shells. The MO/SNO basis which accounts for an optimal $2s$ shell spin distribution underestimates the $1s$ shell contribution to a_{iso} in short CI expansions so that the direction (decrease) in the change of the a_{iso} value along the convergence path is predictable.

4. Results for the $X^2\Pi$ state of the CH molecule

In the nitrogen atom the hfcc refers only to one center. Hence it is interesting to see how the procedures tested affect the spin density distribution if more than one center is of interest. The simplest isoelectronic molecule is CH. Hence in this section we study how CI basis sets affect the Fermi contact term on the hydrogen center. The electronic configuration of the $X^2\Pi$ ground state is $1\sigma^2 2\sigma^2 3\sigma^2 1\pi$, so that again a_{iso} (H) is determined by correlation effects alone.

Similar to the nitrogen atom three different CI basis sets, namely $^4\Sigma^-$ SCF-MO, NO and MO/SNO are employed. The latter are constructed in analogy to the previous calculations for nitrogen, i.e. by retaining the 1σ MO in the otherwise SNO basis.

Various MRD-CI calculations are undertaken: for the MO basis three different reference sets employing six, eleven and seventeen configurations respectively are chosen. The MRD-CI treatments employing the NO basis are somewhat more compact and use four, eleven and sixteen configurations (which correspond to a smaller number of configuration state or symmetry-adapted functions SAF than the configurations based on the SCF orbitals) while only one MRD-CI calculation is undertaken in the MO/SNO basis using 12 configurations (or 21 SAF). The calculated values a_{iso} (H) are plotted in Fig. 4 for the various treatments as a function of the CI expansion length (selection threshold T). In this case full CI limit for the AO basis employed is not known but test

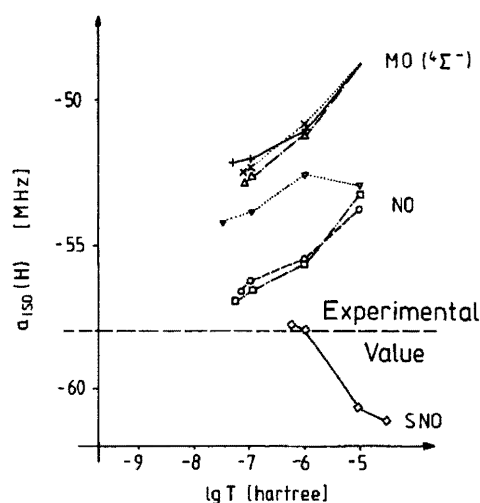


Fig. 4. Calculated a_{iso} (H) for the $X^2\Pi$ state of CH obtained from various treatments as a function of the configuration selection threshold T . MO basis: + 6 M (9 SAF), \times 11 M (22 SAF), Δ 17 M (37 SAF). NO basis: ∇ 4 M (5 SAF), \square 11 M (19 SAF), \circ 16 M (25 SAF). MO/SNO: \diamond 12 M (21 SAF). The dashed line represents the experimental value [21].

calculations indicate that the experimental value should be approached if d and f functions are included for the heavier atom as well as p polarization functions on the hydrogen, as is done in the present work (Table 2). This evaluation agrees with studies on the nitrogen atom [3, 5] in which the effect of f and g AO basis functions of an a_{iso} (N) have been tested. For this reason comparison will be made with the experimental value of a_{iso} (H) given by [21].

It is seen, that both, the CI (MO) and the CI (NO) calculations approach the experimental value of a_{iso} from above, if the CI space is increased, which is accomplished by lowering the threshold T and/or enlarging the set of reference configurations. In both variations for increasing the CI space the description of correlation effects is improved. In this connection it should be realized, that the RHF value for a_{iso} (H) as the starting for the correlation treatment is zero. The actual value of a_{iso} (H) stems from a dominant negative 2σ and a minor positive 3σ contribution [21] so that the improved correlation description should indeed lower the total value of a_{iso} (H), i.e. approach it from above. The CI (NO) results are superior to those from the CI (MO) calculation. This pattern is similar to that found for the nitrogen atom: an acceleration of the CI expansion is expected in the NO relative to the MO basis. A second factor might be added in this case: the MO set is not optimized for the $X^2\Pi$ but for the $^4\Sigma^-$ state of the CH molecule (those MO are more convenient for various reasons) and this also affects the a_{iso} (H) description in the truncated CI to some extent.

The CI (MO/SNO) calculation approaches the experimental a_{iso} (H) value from the opposite side as the CI (MO) or CI (NO) calculations, in analogy to what has been found for the a_{iso} calculation in nitrogen; the absolute deviations (at $T=10^{-6}$ h) are much smaller, however. The dependence on T is not entirely obvious since both, the 2σ and 3σ shell are represented by SNO and the 1σ shell (represented by the $1s$ MO) is not found [22] to contribute to a_{iso} (H) directly. An indirect effect of the 1σ shell might be operative. The present SNO are similar to the UHF natural orbitals discussed by Harriman [14] or Phillips and Schug [15], which are known to overestimate the absolute value of a_{iso} . This finding would be in accord with the present observations for the CI (MO/SNO) treatment at large thresholds.

On an absolute scale, however, it is seen that the CI (MO/SNO) values give already excellent results at a configuration threshold of $T=10^{-6}$ h. Similarly, the CI (NO) results are relatively close to the experimental a_{iso} (H). Hence on a percentage scale the errors

– regardless of what CI basis is employed – are smaller than for nitrogen, whose a_{iso} value seems to be one of the very difficult quantities to obtain with high accuracy.

5. Summary and conclusion

While the dipolar or anisotropic part of the hyperfine coupling constant is obtained relatively easily within a few percent error from ab initio calculations, the isotropic part or Fermi contact term is difficult to obtain with sufficient accuracy from such calculations. It requires a good description of the electron correlation. For this reason a large AO basis set including d and f functions on the heavier atoms and p functions on hydrogen are necessary for a proper evaluation of the spin polarization. Configuration interaction calculations which are necessary to account for electron correlation must normally be truncated for practical reasons if large AO basis sets are employed. Hence the CI orbital transformation for constructing the determinants becomes a critical factor.

The present paper has compared three different orbital transformations, RHF-MO, natural orbitals NO and spin natural orbitals SNO in multi-reference CI calculations for obtaining a_{iso} . While the SNO basis is the most appropriate from pedagogical considerations, its use may be restricted for practical reasons. Nevertheless, even a partial SNO transformation can be employed very efficiently as shown for the a_{iso} value of the nitrogen atom and the a_{iso} (H) in the CH molecule. It is found that the MRD-CI (NO) and MRD-CI (MO/SNO) values for a_{iso} approach the correct a_{iso} value from opposite sides with increasing length of the CI expansion, so that inherent error estimates are conceivable if a small number of truncated CI calculations are undertaken. In both examples nitrogen atom and CH molecule treated the final a_{iso} results obtained from an NO and SNO basis were in error by only a few percent, while errors in the RHF-MO basis were considerably larger (convergence much slower). For the CH molecule the best calculated value for a_{iso} (H) is -57.8 MHz using SNO's whereas the measured value lies at -58.0 MHz (Fig. 4). In the nitrogen molecule the calculation employing SNO's also converges quite rapidly to the corresponding full CI limit (7.7 MHz compared to the experimental 10.45 MHz). It is expected that calculations on further systems will show similar trends, so that it is hoped to obtain reliable prediction of the isotropic hfcc with an appropriate gaussian AO basis without the necessity of going to the full CI limit.

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References

1. Weltner Jr., W.: *Magnetic atoms and molecules*. New York: van Nostrand Reinhold 1983
2. Kristiansen, P., Veseth, E.: *J. Chem. Phys.* **84**, 6336 (1986)
3. Feller, D., Davidson, E.R.: *J. Chem. Phys.* **88**, 7580 (1988)
4. Engels, B., Peyerimhoff, S.D., Davidson, E.R.: *Mol. Phys.* **62**, 109 (1987)
5. Bauschlicher Jr., C.W., Langhoff, S.R., Partridge, H., Chong, D.P.: *J. Chem. Phys.* **89**, 2985 (1988)
6. Engels, B., Peyerimhoff, S.D.: *J. Phys. B: At. Mol. Opt. Phys.* **21**, 3459 (1988)
7. Engels, B., Peyerimhoff, S.D.: *Mol. Phys.* (in press)
8. van Duijneveldt, F.B.: Tech. Report RJ945 (IBM Research Laboratory, San Jose, CA) (1971)
9. Dunning, T.H.: *J. Chem. Phys.* **53**, 2823 (1970)
10. Engels, B.: PhD thesis, Bonn (1987)
11. Chipman, D.M.: *J. Chem. Phys.* **78**, 3112 (1983)
12. a Buenker, R.J., Peyerimhoff, S.D.: *Theor. Chim. Acta* **12**, 183 (1968)
b Buenker, R.J., Peyerimhoff, S.D.: *Theor. Chim. Acta* **39**, 217 (1975)
13. Szabo, A., Ostlund, N.S.: *Modern quantum chemistry*. New York: Macmillan 1982
14. Harriman, J.E.: *J. Chem. Phys.* **40**, 2827 (1964)
15. Phillips, D.H., Schug, J.C.: *J. Chem. Phys.* **61**, 1031 (1974)
16. Meyer, W.: *J. Chem. Phys.* **51**, 5149 (1969)
17. Bagus, P.S., Liu, B., Schaefer III, H.F.: *Phys. Rev. A* **2**, 555 (1970)
18. Chipman, D.: Presented at the American Conference on Theoretical Chemistry, Gull Lake, Minnesota (1987)
19. Hirsch, J.M., Zimmermann III, G.H., Lasson, D.J., Ramsay, N.F.: *Phys. Rev. A* **16**, 484 (1977)
20. Thunemann, K.H., Römelt, J., Peyerimhoff, S.D., Buenker, R.J.: *Int. J. Quantum Chem.* **11**, 743 (1977)
21. Brazier, C.R., Brown, J.M.: *Can. J. Phys.* **62**, 1563 (1984)
22. Engels, B., Peyerimhoff, S.D., Karna, S.P., Grein, F.: *Chem. Phys. Letters* **152**, 397 (1988)