The hyperfine coupling constants of the $X\,^3\Sigma^-$ states of NH

Influence of polarization functions and configuration space on the description of spin polarization

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The hyperfine coupling constants for the $^3\Sigma^-$ ground state of the NH molecule are determined by configuration interaction calculations whereby the influence of polarization functions as well as of the configuration space on the spin polarization mechanism is analysed. The dipolar part $A_{zz}(\text{N})$ and $A_{zz}(\text{H})$ can be obtained very reliably without much computational effort ($A_{zz}(\text{N})$ = $-45\cdot3$ MHz and $A_{zz}(\text{H})$ = $-62\cdot3$ MHz). The value for the isotropic contribution a_{iso} in the best AO basis and MRD–CI treatment is $-64\cdot5$ MHz for H and $16\cdot6$ MHz for nitrogen compared to the corresponding experimental quantities of -66 MHz and 19 MHz respectively. Their determination depends on a subtle balance of the 1σ, 2σ and 3σ shell correlation description, whereby the dominant contribution to $a_{iso}(\text{H})$ results from the 2σ shell. It is shown that the often good agreement of a_{iso} values with experiment in a small basis single-double configuration interaction treatment results from a cancellation of two errors.

1. Introduction

The magnetic hyperfine interaction results from the interaction of the nuclear spin **I** with the angular momentum **L** and the spin **S** of the electrons. The interaction of **I** with **S** can be divided further into the dipole–dipole or anisotropic part and the isotropic (Fermi contact) term which possesses no classical analogue and arises from the interaction of **I** with the magnetic field produced at the nucleus by the spin of the unpaired electrons.

The present investigation will be concerned with first-order hyperfine parameters only. For an electronic state with angular momentum zero in a linear molecule at most two first-order magnetic hyperfine parameters for each nucleus with $\mathbf{I} \neq 0$ may be encountered [1]. The general definitions of these parameters using cartesian coordinates are as follows:

$$a_{iso}^{N} = (4\pi/3)g_e\,\beta_e\,g_N\,\beta_N 1/\Sigma\left\langle q\Lambda\Sigma\left|\sum_i \delta(r_{iN})2s_{zi}\right|q\Lambda\Sigma\right\rangle, \tag{1}$$

$$A_{zz}^{N} = g_e\,g_N\,\beta_e\,\beta_N\,1/\Sigma\left\langle q\Lambda\Sigma\left|\sum_i \frac{3z_i^2 - r_{Ni}^2}{r_{Ni}^5}s_{zi}\right|q\Lambda\Sigma\right\rangle. \tag{2}$$

Here the letters Λ and Σ denote in the standard manner the projection of the angular momentum **L** and the spin momentum **S** respectively onto the molecular axis. The term g_e is the g value for the electrons in the free radical. In the present work always a value of 2 was used. The quantities g_N and β_N are the nuclear g factor

and the value of the nuclear magneton respectively, while β_e is the value of the Bohr magneton. The electrons are denoted by the index i, s_{zi} is thus the z component of the spin operator with respect to the i-th electron.

The 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, while the anisotropic constants A_{zz} reflects the asymmetry of the spin density near each nucleus. For states with $L > 0$ two additional parameters arise [1] which are of no concern in the present work.

Despite tremendous progress made in computational capabilities during the last two decades, accurate predictions of a_{iso} by ab initio methods still remain an elusive problem. The reason for the difficulty lies in two facts: first a_{iso} is a local property for which only one point of the wave-function is considered and secondly, for molecules which involve first row elements all contributions from the doubly occupied shells are extremely important and must be evaluated with high accuracy since they tend to cancel each other to a large extent. At the same time the core contributions to A_{zz} are less important but it is known that in order to obtain a reliable result the use of polarization functions is essential [2].

In the late seventies the problems seemed to be solved [3, 4] for atomic systems. Also a large number of calculations dealing with small molecules gave results which were in good agreement with E.S.R. measurements [2] and only for some systems the differences between ab initio calculations and experimental results were unexpectedly high [5]. More recent calculations [6–10] reveal that the good agreement with experimental results happened by chance. In our last paper [10] we could show that for the ^4S state of the nitrogen atom the calculated value of a_{iso} increases from 3·4 MHz to 12·5 MHz if the $9s5p$ basis set of Huzinaga [11] is contracted to $[4s2p]$ as described by Dunning [12]. A similar effect was observed for the $X\,^3\Sigma^-$ state of the NH molecule. This basis set with double zeta quality was used very often for ab initio calculations of hyperfine coupling constants (hfcc) [2]. Similar effects are expected for the calculations of various atomic systems by Glass et al. [3, 4].

The goal of our present work on the hfcc of the $X^3\Sigma^-$ of the NH molecule is twofold. First we want to study the effects of several ingredients of ab initio calculations on the hfcc within a molecular system as it was performed for the atomic nitrogen [6–9], in particular the influence of polarization functions and the size of the configuration space employed will be considered. Secondly the spin polarization mechanism which is essential for the hfcc, especially for a_{iso}, will be discussed in detail.

2. Technical details

In NH both nuclei have a spin. Hence there will be two sets of constants, one set for the proton and the other for the ^{14}N nucleus. The hyperfine parameters of the $X\,^3\Sigma^-$ state in NH have recently been obtained experimentally by Ubachs et al. [13]. An older study was done by Wayne et al. [14]. To the knowledge of the authors there are only two theoretical studies which deal with the hyperfine coupling constants (hfcc) of the NH molecule [1, 15]. For comparison the results are summarized in table 1 together with the experimental values.

Table 1.　Hyperfine coupling constants A_{zz} and a_{iso} for the $X\,^3\Sigma^-$ of NH from the literature.

Reference	N		H	
	$a_{iso}/$ MHz	$A_{zz}/$ MHz	$a_{iso}/$ MHz	$A_{zz}/$ MHz
[13]	19·22	−45·28	−66·23	61·14
[14]	19·6 ± 0·4	−44·2 ± 0·6	−66·3 ± 1·2	60·4 ± 1·2
[15]	17·6		−53·6	
[1]	18·9	−44·24	−66·4	61·30

The NH molecule possesses $C_{\infty v}$ symmetry. The RHF configuration of the $X\,^3\Sigma^-$ is $1\sigma^2\,2\sigma^2\,3\sigma^2\,1\pi x^1\,1\pi y^1$. Because the singly occupied orbitals possess a nodal plane through the internuclear axis the value of a_{iso} is determined by correlation effects only, as is the case for the ^4S state of atomic nitrogen. In contrast to the ^4S state the dipolar constant A_{zz} in NH is not equal to zero. The value is dominated by the contributions of the singly occupied shells, but correlation effects cannot be neglected. Due to technical reasons the calculations were performed within the C_{2v} symmetry group which is the highest abelian subgroup of $C_{\infty v}$.

In the study of the polarization functions we always used the same (sp) basis set, which consist of a $13s8p$ basis set for the nitrogen centre and $8s$ for the hydrogen atom. Both were optimized by van Duijneveldt [16]. The nitrogen basis set was contracted to $[8s5p]$ with a contraction scheme $(5\,2\,1\,1\,1\,1\,1\,1/3\,2\,1\,1\,1)$ while for hydrogen a $[5s]$ basis with a $(4\,1\,1\,1)$ contraction was chosen. The results of this reference AO basis are given in table 2 together with the values of the uncontracted basis set. From there it can be seen that the contraction of the basis set gives a difference of about 5 per cent for the nitrogen centre and about 3 per cent for the hydrogen, although only a very modest contraction was used. The agreement with the experiment is improved, however. In order to test the influence of a p function which correlates the 1σ shell a function with $\zeta = 7\cdot8171$ was located at the nitrogen centre. It removes the effect of the contraction on the total energy and $a_{iso}(N)$ to some extent. The value of $a_{iso}(H)$ increases further, however. The overall influence is small compared to the effects arising from d polarization functions as will be discussed further in connection with the enlargement of the (sp) basis set.

All calculations for the study of the effects of polarization functions were performed at the equilibrium nuclear distance $r = 1\cdot9614$ a.u. [17]. For the calculations the MRD–CI program package [18, 19] was used. The z axis is taken to be the internuclear axis. Generally two types of CI calculations are performed. The widely

Table 2.　Calculations employing the uncontracted and contracted reference AO basis.

	SCF energy a.u.	SD–CI energy a.u.	N		H	
			$a_{iso}/$ MHz	$A_{zz}/$ MHz	$a_{iso}/$ MHz	$A_{zz}/$ MHz
$(13s8p/8s)$	−54·960600	−55·088646	13·0	−43·39	−68·5	66·75
$[8s5p/5s]$	−54·960515	−55·080860	13·8	−43·32	−66·4	66·86
$[8s5p1p/5s]$†	−54·960521	−55·086212	13·2	−43·33	−65·9	66·79

† $\zeta(p) = 7\cdot8171$.

used SD–CI, which uses all single and double excitation configurations relative to the dominant term in the wavefunction expansion. Furthermore the multi-reference CI, which generates all single and double excitations with respect to the most important terms (x main or reference configurations, generally contributing more than 0·2–0·05 per cent) in the final CI expansion; in this manner this procedure includes also the most important triple and quadruple excitation configurations (at least as far as the total energy is concerned) relative to the leading term or the SD–CI. Such treatment has been found to be necessary for obtaining energy surfaces over a large range of nuclear conformations or alternatively also for the description of many excited states. The procedure will be denoted by xM indicating that x main or reference configurations are employed in the MRD-CI procedure. If the number of generated configurations is large, a truncation of the CI expansion is undertaken in a manner, that all SAF which lower the energy of the set of reference configurations by more than an energy threshold T (individual SAF selection) are included directly in the secular equation and wavefunction expansion. The effect of the remaining less interacting SAF to the total energy is estimated via a perturbation-like treatment in the usual manner [18, 19]. In order to study their influence on other properties than the energy generally these properties are calculated at various thresholds T.

3. Effects of polarization functions and configuration space

In molecular calculations polarization functions are important not only to account for correlation effects as in atomic calculations but also to describe polarization which arise from the charge distortion in the molecular surrounding.

The first set of such polarization functions is a d function located at the nitrogen centre and a p function on hydrogen. Not surprisingly it is found that the influence of a d function, which has been studied in the nitrogen atom [7], is very analogous for the NH molecule. Details of the d function exponent variation has been investigated elsewhere [6]. Generally it can be said that the optimum d function exponent with respect to the total energy is not accompanied by any special behaviour of $a_{iso}(N)$, and that addition of a d function reduces the magnitude of this quantity. The dependence of $a_{iso}(H)$ on the d function exponent is very small, but the value is also lower in absolute value than if calculated without the polarization function. The use of a p function located at the hydrogen centre is essential for the description of $A_{zz}(H)$. Finally it is observed that the effect of the individual polarization function is preserved in the AO basis which combines both functions.

In order to see the influence of a larger number of polarization functions further calculations have been undertaken employing up to four d functions and two p functions. The optimized d function exponents are taken from the work on nitrogen [7], while the exponents of the p functions located at the hydrogen are constructed in the standard manner by decomposing one p function; this procedure is justified without further optimization because the hfcc are found to depend relatively little on the p function exponent.

Table 3 summarizes the results for the SD–CI calculations. In the calculations using more than a total of four polarization functions the number of symmetry-adapted configuration state functions (SAF) becomes quite large but the selected subset of SAFs seems high enough for a reliable calculation of a_{iso} in the $T = 0$ limit [7]. The SCF energy decreases with increasing size of the AO set; in the largest

Table 3. Summary of the SD–CI calculation by enlarging the basis set with polarization functions.

Exponents		$E(SCF)/$ h	$E(SCF)-E(MRD-CI)/$ eV	$E(MRD-CI)/$ h	Nitrogen		Hydrogen	
d functions	p functions				$a_{iso}/$ MHz	$A_{zz}/$ MHz	$a_{iso}/$ MHz	$A_{zz}/$ MHz
—	—	−54·960515	3·27	−55·08086	13·8	−43·32	−66·4	66·86
—	0·65	−54·971206	3·59	−55·10302	14·1	−43·59	−59·6	63·65
0·8	—	−54·973313	4·67	−55·14481	9·8	−43·76	−61·0	65·68
0·8	0·7	−54·975778	4·81	−55·15263	9·8	−43·72	−58·3	64·36
1·9, 0·5	1·4, 0·25	−54·977567	5·16	−55·16735	9·7	−44·11	−57·0	62·36
8·0, 1·9, 0·5†	1·4, 0·25	−54·977596	5·26	−55·17096	9·9	−45·12	−56·3	62·31
39.0, 8·0‡ 1·9, 0·5	1·4, 0·25	−54·977604	5·33	−55·17331	9·7	−45·26	−56·3	62·29

†$T = 1 \times 10^{-10}$ h, total number of SAFs $= 20308$, selected number of SAFs $= 17517$.
‡$T = 2.5 \times 10^{-9}$ h, total number of SAFs $= 25410$, selected number of SAFs $= 17898$.

basis the deviation from the Hartree Fock energy of Cade *et al.* [17] is 0·00046 a.u.
A further lowering would appear if functions with higher l quantum numbers, e.g. f
or g functions, would be used. Such functions were not tested, but their effect is
expected to be small [9].

Of the two type of hfcc the A_{zz} constants are the easiest to calculate. For the
smaller basis sets the value of the nitrogen centre $A_{zz}(N)$ is higher by roughly 2 MHz
than in the best calculation and the agreement with the experimental data is almost
perfect (table 1) if polarization functions are used. For the hydrogen centre the
agreement with the experiment improves also steadily upon increasing the basis set.
It is expected that A_{zz} decreases further if polarization functions with higher l
quantum number are used for the hydrogen centre [9, 21]. It is obvious that the
polarization functions of the respective centre are always more important than those
of the other centre. Generally the calculated results are very satisfactory.

The calculated values of a_{iso} behave similarly to those found in the study of
nitrogen atom. For both centres the SD–CI values decrease in absolute magnitude if
additional polarization functions are added. For the nitrogen centre the values
oscillate around 9·8 MHz if more than two polarization functions are used. The
value of $a_{iso}(H)$ decreases but seems to converge. The agreement with the experimen-
tal values in this SD–CI calculation is only about 49 per cent for the nitrogen centre
and 84 per cent for the hydrogen centre, however.

In order to study the effect of polarization functions in a multi-reference CI,
calculations are performed in the standard s and p [$8s5p/5s$] AO basis and in the
[$8s5p2d/5s2p$] basis including a moderate number of polarization functions. For the
latter a natural orbital transformation [20] is undertaken to obtain faster con-
vergence in the CI expansion. The results are given for various selection thresholds
T as discussed in §2. The results of a_{iso} for the hydrogen centre are plotted in
figure 1 (a) while those for the nitrogen centre are contained in figure 1 (b). Calcu-
lations are undertaken by employing different sizes of reference sets, namely 12 or 14
reference (main) configurations in the SCF–MO basis and 7 or 22 such reference
states in the natural orbital basis. For comparison the results of the SD–CI calcu-
lations (1 reference configuration) are also given.

The considerable effect of higher excitations on $a_{iso}(H)$ is quite obvious from
figure 1 (a). In the smaller basis (lower part, dotted lines) the multi-reference limit
seems well below −70 MHz, and it is seen that the good agreement of the SD–CI
value in the small AO basis with the experimental $a_{iso}(H)$ is accidental. In the larger
AO basis all values for hfcc are smaller in absolute magnitude. Unfortunately a
convergence is not visible yet in the a_{iso} value of the MRD–CI treatment; the best
treatment employing 22 reference configurations and natural orbitals, however, yield
already a value (−64·5 MHz) close to that determined from experiments (table 1) so
that it is quite conceivable that a larger MRD–CI vector than 18 000 SAFs corre-
sponding to a threshold of 10^{-7} hartree would give a quite reliable $a_{iso}(H)$ value not
too far distant from the actually converged number.

The results for the a_{iso} values on the nitrogen centre in figure 1 (b) show a similar
pattern. The SD–CI values in both basis sets seemed to have converged, whereby
again the small basis SD–CI results is fortuitously closest to the experimental
number. The influence of higher excitations is considerable and an extrapolation to
the full MRD–CI space or even to the full CI, which is generally possible for the
energy, is not feasible for the a_{iso} values yet based on the energy-selected configu-
rational subsets below 18 000 configurations or energy thresholds of 10^{-7} hartree.
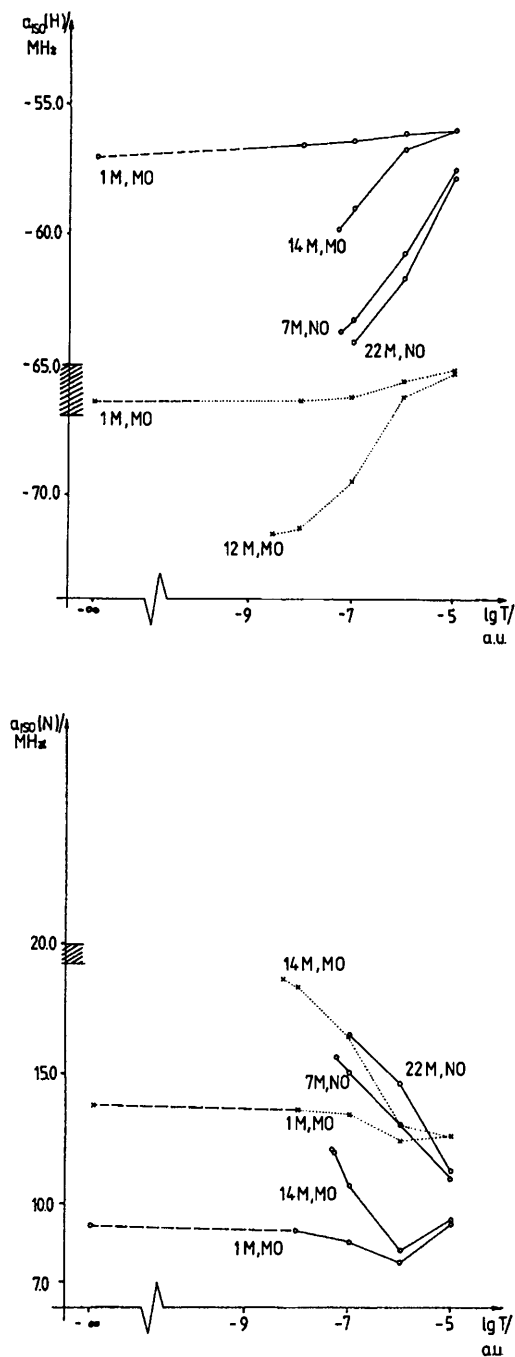
Figure 1. (a) Calculated values for $a_{iso}(H)$ in various treatments. The dotted lines refer to the small, the solid lines to the larger AO basis. The number of reference or main configurations (M) is always indicated, as well as the molecular orbital (MO) or natural orbital (NO) basis. The values are given as a function of the threshold T for configuration selection; ∞ refers to the entire MRD–CI space. (b) Calculated values for $a_{iso}(N)$ in various treatments. The notation is the same as in (a).

The best calculated value (22 M, Nos) for $a_{iso}(N)$ is 16·6 MHz. This finding is certainly different from what has been observed for simpler one-electron properties whose calculation seems to give reliable data in an energy-selected truncated MRD–CI.

The influence of the multi-reference CI on the value of the dipolar part A_{zz} has also been studied [6] but has been found to be very small as expected. The best calculated value within the present study obtained with the larger AO basis and the NO treatment are −45·26 MHz for nitrogen and 62·29 MHz at the hydrogen centre and compare very well with the corresponding measured values given in table 1.

4. Discussion of the spin polarization mechanism

In order to analyse the spin polarization mechanism, core calculations [10], i.e. calculations in which only the electrons of one of the doubly occupied shells are correlated, were performed. The results, obtained by employing various basis sets, are summarized in table 4. Such calculations are easier technically since they lead to a smaller CI space; hence a truncation of the MRD–CI wavefunction is not necessary.

It is obvious from the table that for an accurate calculation of $a_{iso}(N)$ the electrons of all shells must be correlated. The value of $a_{iso}(N)$ depends in a subtle way on the balance of the 1σ and 2σ, 3σ contribution which enter with opposite sign. Similar results have been observed for the nitrogen atom [7] in which the balance is between the $1s$ and $2s$ contribution. For $a_{iso}(H)$ the dominant contribution (more than 95 per cent) comes from the 2σ shell; the 3σ part is quite small but nevertheless sensitive to the AO basis set representation. The contribution to $a_{iso}(H)$ from the 1σ shell is zero; similar results have been obtained for the ground state $X\,^2\Pi$ of the CH molecule [21].

The charge densities of the three orbitals are plotted in figure 2. The 1σ MO is to a large extent a pure nitrogen $1s$ function and it is therefore understandable that this shell does not affect the a_{iso} value on the hydrogen centre. It is also obvious that the behaviour of this shell is analogous to that of the $1s$ shell in the corresponding atom [7]. The 2σ MO is predominantly a $2s$ nitrogen orbital with contributions from $2p_z$

Table 4. Core calculations for NH employing various polarization functions (SD–CI calculations).†

Functions		Nitrogen a_{iso} MHz correlated shell			Hydrogen a_{iso} MHz correlated shell		
d functions	p functions	1σ	2σ	3σ	1σ	2σ	3σ
—	—	−53·56	58·61	10·05	0·0	−52·01	−0·22
—	0·65	−53·38	58·30	10·15	0·0	−52·19	1·76
0·8	—	−53·20	57·71	7·62	0·0	−49·46	−1·20
1·9, 0·5	1·4, 0·25	−52·49	56·48	8·17	0·0	−47·00	−1·81
			57·50‡	8·40‡		−47·96‡	−1·74‡
39·0, 8·0, 1·9, 0·5	1·4, 0·25	−51·81	56·49	8·17	0·0	−46·96	−1·81

†Correlated shell means that only the shell given is correlated while all other shells are kept doubly-occupied.
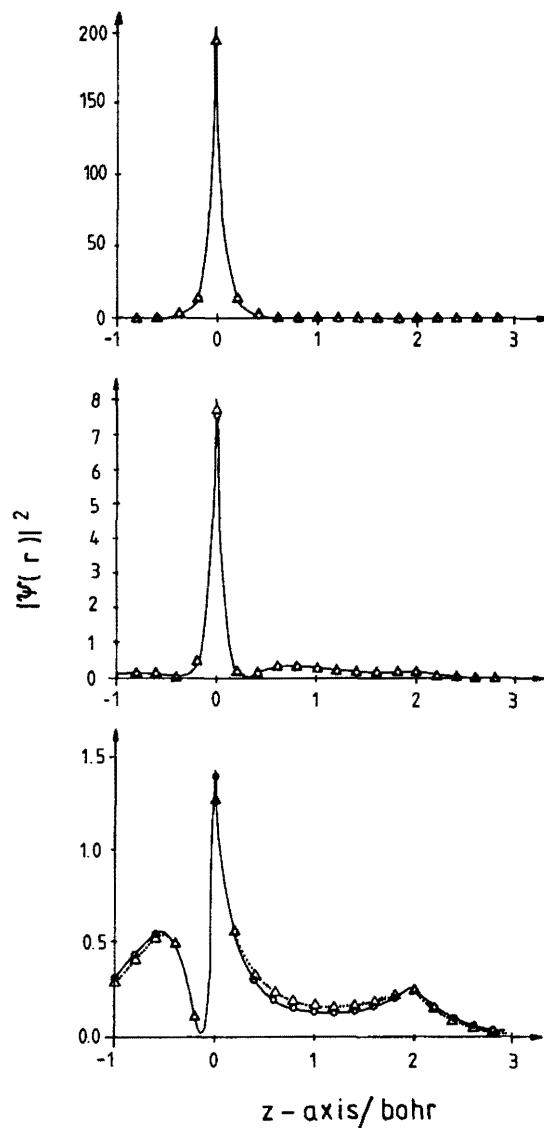‡ 8M1R calculations.

Figure 2. The density $|\Psi(r)|^2$ of the three doubly occupied SCF orbitals in the $X\ ^3\Sigma^-$ state. o basis $[8s5p/5s]$. △ basis $[8s5p2d/5s2p]$. The nitrogen is centred at $0\cdot0$ while the hydrogen centre lies at $r = 1\cdot96$ a.u.

and $(-1s)$ of nitrogen and $1s$ on hydrogen and possesses a node between the two atoms. It is surprising at first that nevertheless it is this orbital which dominates the value of $a_{iso}(\text{H})$ and not the 3σ orbital which represents the N–H bond in form of a $2pz(\text{N})$ and $1s(\text{H})$ linear combination.

These findings are contrary to the explanations for the mechanism of the spin polarization in the CH fragment of larger hydrocarbon radicals [22]. The situation in those compounds is similar to that in the NH molecule: the singly occupied shell of the CH fragment is a π orbital, so that a_{iso} is zero at both centres of the fragment within the RHF approach and qualitatively the same spin polarization mechanism

is expected as in the NH radical. In the model discussed in the literature [22] an indirect coupling between the odd electron and the $2pz$ (C)–$1s$ (H) bonding electrons through the CH bond is postulated resulting in a net spin density at the hydrogen centre. In other words the dominant contribution to a_{iso}(H) is assumed to originate from the bonding σ orbital which corresponds to the 3σ orbital in the NH or CH molecule. Our calculations show, however, that the dominant contribution arises from the 2σ orbital.

The cause for the dominance of the 2σ contribution can be seen from tables 5 and 6 which list the most important configurations in the CI calculations correlating all electrons simultaneously. For comparison the MRD–CI and SD–CI expansion coefficients are given; the standard trend is apparent, namely that the weight of the excited species increases in the multi-reference expansion relative to the SD–CI. From table 5 it can be seen that configurations possessing a singly-occupied 2σ orbital are more important than those with an open 3σ shell. (Note, that only configurations possessing singly-occupied orbitals contribute directly to the spin property a_{iso} or A_{zz}.) The configuration No. 1, for example, which describes by its $2\sigma \rightarrow 1\delta$ excitation a portion of the angular correlation of the 2σ shell possesses a weight in the total CI expansion (as measured by the square of the coefficient) of 0·2 per cent. The analogous configuration of the 3σ shell $3\sigma \rightarrow 1\delta$ (No. 14) contributes only 0·05 per cent. A similar trend is seen for the other most important configurations describing other types of correlation effects. It is furthermore seen that double-substitution configurations (such as No. 2 or No. 6), which give small contributions to a_{iso}, are obviously more important for the correlation description of the 3σ shell than for that of the 2σ.

Table 5. Summary of the configuration entering into the total MRD–CI wavefunction with a coefficient c whose square is larger than 0·0005. The larger [$8s5p2d/5s2p$] AO basis is employed; the 14 reference configurations are indicated by an asterisk.

NO	Doubly occupied†		Singly occupied				c² % MRD–CI	c² % SD–CI	Type of correlation
*0	2σ	3σ	$1\pi_x$	$1\pi_y$			94·897	95·237	
*1	3σ		2σ	$1\delta_{x^2-y^2}$	$1\pi_x$	$1\pi_y$	0·213	0·189	δ
2	2σ	6σ	$1\pi_x$	$1\pi_y$			0·192	0·149	σ
*3	3σ		2σ	6σ	$1\pi_x$	$1\pi_y$	0·146	0·119	σ
*4	3σ	$1\pi_x$	2σ	$1\delta_{xy}$			0·107	0·093	δ
*5	3σ	$1\pi_y$	2σ	$1\delta_{xy}$			0·107	0·093	δ
6	2σ		6σ	10σ	$1\pi_z$	$1\pi_y$	0·100	0·100	σ
*7	2σ		3σ	5σ	$1\pi_x$	$1\pi_y$	0·088	0·079	σ
*8	3σ		2σ	8σ	$1\pi_x$	$1\pi_y$	0·072	0·018	σ
9	2σ		6σ	9σ	$1\pi_x$	$1\pi_y$	0·070	0·058	σ
*10	$1\pi_x$		2σ	3σ	$3\pi_x$	$1\pi_y$	0·070	0·059	δ
*11	$1\pi_y$		2σ	3σ	$1\pi_x$	$3\pi_y$	0·070	0·059	δ
*12	3σ		2σ	9σ	$1\pi_x$	$1\pi_y$	0·067	0·114	σ
*13	3σ		2σ	4σ	$1\pi_x$	$1\pi_y$	0·062	0·050	δ
*14	2σ		3σ	$1\delta_{x^2-y^2}$	$1\pi_x$	$1\pi_y$	0·051	0·050	δ
*15	$1\pi_x$		2σ	3σ	$5\pi_x$	$1\pi_y$	0·051	0·046	δ
*16	$1\pi_y$		2σ	3σ	$1\pi_x$	$5\pi_y$	0·051	0·046	δ
17	2σ	10σ	$1\pi_x$	$1\pi_y$			0·050	0·053	σ

† The 1σ is always doubly occupied.

Table 6. Summary of the configuration entering into the total MRD–CI wavefunction with a coefficient c whose square is larger than 0·0005. The smaller $[8s5p5s]$ basis is employed in the MRD–CI treatment whereby the first 12 configurations (0–11) are chosen as the reference set.

No.	Doubly†	Singly	c² % MRD–CI	c² % SD–CI	Type of correlation
*0	2σ 3σ	$1\pi_x$ $1\pi_y$	96·092	96·389	
*1	2σ 6σ	$1\pi_x$ $1\pi_y$	0·311	0·265	σ
*2	3σ	2σ 6σ $1\pi_x$ $1\pi_y$	0·183	0·163	σ
*3	2σ	3σ 5σ $1\pi_x$ $1\pi_y$	0·146	0·118	σ
*4	3σ	2σ 8σ $1\pi_x$ $1\pi_y$	0·139	0·128	σ
*5	2σ	6σ 9σ $1\pi_x$ $1\pi_y$	0·120	0·108	σ
*6	2σ	6σ 8σ $1\pi_x$ $1\pi_y$	0·111	0·102	σ
*7	3σ	2σ 4σ $1\pi_x$ $1\pi_y$	0·100	0·085	σ
*8	2σ	3σ 6σ $1\pi_x$ $1\pi_y$	0·080	0·059	σ
*9	2σ	4σ 6σ $1\pi_x$ $1\pi_y$	0·078	0·067	σ
*10	3σ	2σ 7σ $1\pi_x$ $1\pi_y$	0·073	0·065	σ
*11	3σ	2σ 5σ $1\pi_x$ $1\pi_y$	0·070	0·061	σ
12	2σ 9σ	$1\pi_x$ $1\pi_y$	0·064	0·062	σ
13		2σ 3σ 6σ 7σ $1\pi_x$ $1\pi_y$	0·060	0·057	σ
14		2σ 3σ 7σ 9σ $1\pi_x$ $1\pi_y$	0·053	0·052	σ
15	2σ	3σ 6σ $1\pi_x$ $2\pi_y$	0·051	0·046	σ
16	2σ	3σ 6σ $2\pi_x$ $1\pi_y$	0·051	0·046	σ

† The 1σ orbital is always doubly occupied.

The different effects in the 2σ and 3σ shells can be explained by two factors. The π electrons which are responsible for the spin polarization are to a large extent localized at the nitrogen atom; their interactions with the 2σ electrons are stronger than with the 3σ electrons because the 3σ orbital is spanned over the entire molecule, while the 2σ orbital is localized more around the nitrogen atom (figure 2). Furthermore larger correlation effects are generally expected from the more contracted shape of the 2σ orbital.

From the fact that the nitrogen as the larger subsystem dominates the correlation effects of the entire molecule it is expected that the spin polarization mechanism in the NH molecule is similar to the mechanism found for the nitrogen atom [7], but modified due to the cylindrical NH geometry. From the core calculations it is seen that addition of d polarization functions in the SD–CI calculations decreases the magnitude of the contribution of each of the 1σ, 2σ and 3σ shells to a_{iso} of the nitrogen centre. Addition of the p functions on the hydrogen similarly decrease the magnitude of the 1σ and 2σ contribution but increases the 3σ part somewhat as a result of the modified 3σ MO which possess a non-zero value at the nitrogen in contrast to the simple pz nitrogen function. If higher excitations are taken into account, both 2σ and 3σ terms of $a_{iso}(N)$ become somewhat larger, but the values from the $[8s5p2d/5s2p]$ AO basis are still smaller than the SD–CI results in the simple sp basis (first row, table 4). For a_{iso} of the hydrogen centre the addition of the d functions affects also both the 2σ and 3σ shell but in opposite directions (reduces the 2σ in magnitude but enhances the size of the 3σ term about half as much) with a total result of a decrease in $a_{iso}(H)$. Addition of tight d functions affects only the 1σ contribution as has also been found for the nitrogen atom [7]. The hydrogen p

polarization function affects mostly the 3σ shell, in an opposite manner than the nitrogen d functions, i.e. makes the 3σ contribution more positive. Higher excitation configurations lower the 2σ contributions but this effect is smaller than that resulting from the addition of the extra polarization function.

The change in the spin polarization mechanism resulting from the addition of polarization functions to the NH basis set is thus somewhat more complicated than in the nitrogen atom [7]. In our previous analysis [10] we divided the 6 components of a d function into three different groups. The first consists of the $d_{x^2+y^2+z^2}$, which possesses s type character and therefore mixes with s functions in building the MOs. To the second group belong the two components $d_{x^2-y^2}$ and $d_{2z^2-x^2-y^2}$ which have the same symmetry as s functions only within the highest abelian subgroup D_{2h} but not in the correct atomic symmetry group O(3). They do not mix with s functions because the calculated integrals become numerically zero if the calculation is performed in the D_{2h} symmetry. The last group is given by the three remaining components d_{xy}, d_{xz} and d_{yz} which also belong to different irreducible representations than the other two groups in the D_{2h} symmetry, as is true for all p components. In the NH molecule with the correct symmetry group $C_{\infty v}$ the $d_{2z^2-x^2-y^2}$ function is transferred to the first group and the p_z components can also mix with s functions.

Therefore the influence of polarization functions on the spin polarization mechanism can be divided into three different effects:

(1) The influence of the components which do not transform as σ orbitals e.g. $d_{x^2-y^2}$, d_{xy}, d_{xz}, d_{yz}, p_x, p_y is the same as the effect of the five d components in the nitrogen atom. They are essential for the description of angular correlation effects which are to some extent also accounted for by the normal p functions of the nitrogen basis set. To distinguish between their effects and effects arising from σ orbitals these correlation effects will be referred to as δ type correlation.

(2) The influence of the other components which transform like σ orbitals. Together with the s functions they build the virtual space of σ symmetry. A distinction between angular and radial correlation effects (as measured relative to the N atom) arising from excitations into such species is hardly possible because orbitals including a pz function describe both type of correlation. Examples are the 6σ or 9σ orbital which are in the main p_z functions of the nitrogen atom distorted by contributions from the hydrogen basis set. Therefore the name σ type correlation is chosen to distinguish from effects arising from orbitals with a higher l quantum numbers. The influence on a_{iso} of the components which transform as σ orbitals is similar to the effect of enlarging the basis set by s function as it was found for the nitrogen atom [7].

(3) In addition to the effect on the virtual space the components of additional functions which are able to directly mix with the σ orbitals are able to influence the shape of occupied orbitals as can be seen from figure 2. If the polarization functions are added the value of the 3σ orbital increases between the two centres while it decreases in the outer region. In small molecules such as NH this effect is small, so that no further analysis was undertaken in the present work. In larger molecules this effect may become more important.

To study the different effects in more detail an analysis of the spin polarization is undertaken. In figure 3 the orbital energies of the σ orbitals for the two basis sets $[8s5p/5s]$ and $[8s5p2d/5s2p]$ are given. For the relation between the orbitals in the two basis sets their shape and their overlap integrals were used. A diagonalization of the one electron total spin density matrix (TSM) leads to eigenvalues and eigenvectors which give more insight into the spin polarization mechanism of the doubly occupied shells 1σ, 2σ and 3σ [7, 10]. The new basis in which the TSM is diagonal is called spin natural orbitals (SNO) basis. The eigenvalues of the SNOs give a quantitative measure for the spin polarization of the MOs, the structure of the eigenvectors exhibits which virtual orbitals are important to describe the spin polarization of the different doubly occupied shells. Because the off-diagonal elements are an order of magnitude larger than the diagonal elements a strong coupling of the MOs results.

In tables 7 and 8 the eigenvalues and eigenvectors of the most important SNOs using the two basis sets $[8s5p/5s]$ and $[8s5p2d/5s2p]$ are given. The enumeration of the SNOs is chosen such that SNO 1 and SNO 2 are connected in the main with the 1σ orbital, SNO 3 and SNO 4 with the 2σ and SNO 5 and SNO 6 with the 3σ function. The SNO 7 in table 8 is constructed from the $d_{x^2-y^2}$ components of the two d functions only. Clearly it is absent if no d polarization function is used.
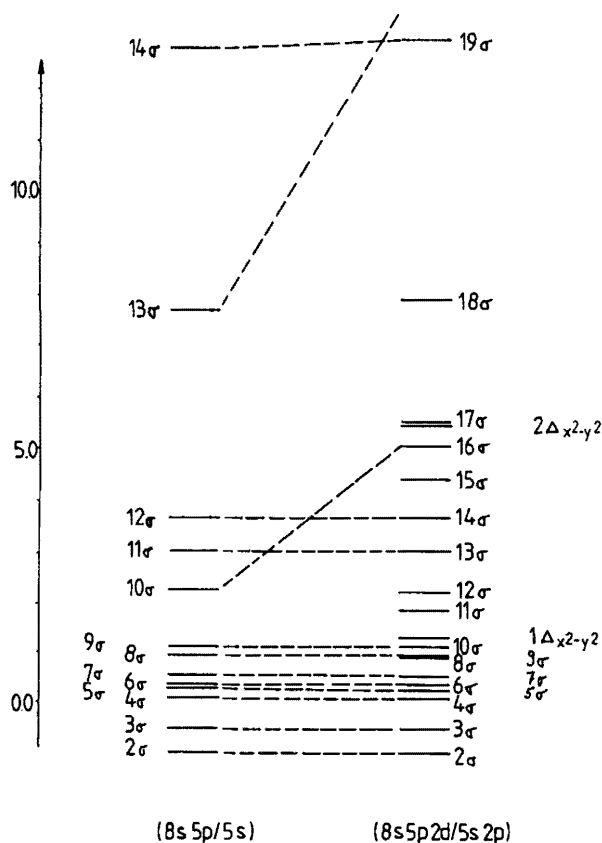

Figure 3.   Orbital energies of the NH molecule in two different gaussian basis sets.

Table 7. Eigenvectors and eigenvalues of the most important SNOs in the NH molecule.
Basis set: [8s5p/5s], 12 M CI treatment, based on MOs.

Eigenvalue/ eigenvector	SNO 1 −0·0021	SNO 2 0·0020	SNO 3 −0·0690	SNO 4 0·0754	SNO 5 −0·0470	SNO 6 0·0494
1σ	0·7041	0·7087	0·0140	0·0151	−0·0102	−0·0101
2σ	−0·0158	−0·0158	0·6909	0·7119	−0·0883	−0·0873
3σ	0·0114	0·0052	0·1007	0·0757	0·6857	0·7167
4σ	−0·0056	0·0298	0·3009	−0·2897	0·0254	−0·0383
5σ	0·1432	−0·1369	−0·1800	0·1802	0·5377	−0·5084
6σ	−0·0736	0·0742	0·4380	−0·4254	0·3058	−0·3035
7σ	−0·1658	0·1461	−0·2536	0·2456	0·1547	−0·1306
8σ	0·0337	−0·0018	−0·3541	0·3492	0·0741	−0·0606
9σ	−0·0054	0·0122	−0·0490	0·0478	−0·3160	0·3127
10σ	0·4889	−0·4798	0·0656	−0·0660	−0·0730	0·0630
11σ	0·0253	−0·0136	−0·0306	0·0288	−0·0609	0·0626
12σ	−0·0364	0·0184	−0·0163	0·0108	−0·0163	0·0124
13σ	0·4341	−0·4437	−0·0052	0·0041	0·0028	−0·0036
14σ	0·0048	−0·0064	0·0048	−0·0054	−0·0017	0·0011
15σ	0·0095	−0·0066	0·0015	−0·0011	0·0063	−0·0061
16σ	0·1397	−0·1512	−0·0033	0·0032	0·0029	−0·0028
17σ	−0·0148	0·0172	0·0001	0·0001	−0·0001	0·0001
18σ	−0·0001	0·0001	0·0000	0·0000	0·0000	−0·0000

For the polarization of the 1σ orbital in the smaller basis set the most important MOs are the 10σ and 13σ, while the 5σ, 7σ and 16σ contribute less. All other virtual MOs are of minor importance. This shows that the 1σ interacts mostly with the higher virtual orbitals, just as it has been found for the nitrogen atom. The energetically lower region (figure 3) of the virtual space 4σ to 9σ contains the most important MOs for the 2σ and 3σ spin polarization. The situation is also reflected by table 5 and table 6, which contain the most important configurations within the CI wavefunction.

Comparing with the [8s5p2d/5s2p] calculation (table 8) it is seen that the additional MOs, which are built from the σ type components of the added polarization functions, are localized in the higher energy region, so that for the 1σ polarization the second effect (a denser description of the σ or s space) should be stronger than the effect of δ correlation. Indeed it is seen that the contributions to SNO 1 and SNO 2 are distributed more over the higher virtual orbitals. This also takes place for the SNO 3, 4, 5 and 6 but to a much smaller extent because the region important for them is less influenced by the basis set extension. If the AO basis is enlarged differently, so that the lower-energy part is described by more functions, the SNO3 to SNO 6 description changes also markedly in that the expansion involves more terms of moderate size. This occurs, for example, if s functions with the proper (medium-size) exponents are added to the hydrogen basis [6].

The influence of the first effect δ type correlation can be seen either from the SNO 7 or by a comparison of tables 5 and 6, containing the most important configurations of the all-electron calculations of the basis sets [8s5p/5s] or [8s5p2d/5s2p], respectively. Without polarization functions (table 6) the σ type correlation is the most important effect. Configurations arising from excitation into π type orbitals are less important and therefore not included in the tables. If polarization functions are used (table 5) the picture changes because the σ type correlation becomes very

Table 8. Eigenvectors and eigenvalues of the most important SNOs in the NH molecule.† Basis set: [$8s5p2d/5s2p$], 14 M CI treatment based on MOs.

Eigenvalues/ Eigenvectors‡	SNO 1 −0·0022	SNO 2 0·0023	SNO 3 −0·0608	SNO 4 0·0743	SNO 5 −0·0423	SNO 6 0·0441	SNO 7 0·0040
1σ (1σ)	−0·7103	0·7023	0·0173	0·0210	−0·0095	−0·0078	0·0
2σ (2σ)	0·0190	−0·0186	0·6859	0·7220	0·0101	0·0851	0·0
3σ (3σ)	−0·0116	0·0084	0·0129	−0·1051	0·6950	0·7110	0·0
4σ (4σ)	0·0098	0·0148	0·2650	−0·2294	0·1022	−0·1402	0·0
5σ (5σ)	−0·1234	−0·1419	−0·1999	0·2258	0·4499	−0·4000	0·0
6σ (6σ)	0·0852	0·0953	0·3922	−0·3354	0·3261	−0·3702	0·0
7σ (7σ)	0·1275	0·1292	−0·2425	0·2179	0·0176	0·0255	0·0
8σ	−0·0206	−0·0186	−0·2841	0·2919	0·2437	−0·1902	0·0
9σ (8σ)	−0·0427	−0·0477	−0·2716	0·2471	−0·0865	0·1279	0·0
10σ (9σ)	0·0123	0·0340	−0·0685	0·0437	−0·2360	0·2408	0·0
$1\delta_{x^2-y^2}$	0·0	0·0	0·0	0·0	0·0	0·0	0·9541
11σ	0·3039	−0·2811	−0·0737	0·0912	0·1242	−0·1136	0·0
12σ	−0·2508	−0·2691	0·1762	−0·1910	−0·2134	0·1800	0·0
13σ (11σ)	0·0393	0·0415	−0·0364	0·0266	−0·0835	0·0910	0·0
14σ (12σ)	−0·0117	−0·0269	−0·0099	0·0023	−0·0334	0·0302	0·0
15σ	0·1379	0·1426	−0·0665	0·0634	−0·0210	0·0342	0·0
16 (10σ)	−0·3221	−0·3117	−0·0072	0·0069	−0·0024	0·0027	0·0
$2\delta_{x^2-y^2}$	0·0	0·0	0·0	0·0	0·0	0·0	0·2996
17σ	0·2627	0·2846	−0·0692	0·0761	0·0714	−0·0607	0·0
18σ	−0·2475	−0·2456	−0·0001	−0·0011	−0·0038	0·0034	0·0
19σ (14σ)	0·0411	0·0421	−0·0007	0·0009	0·0044	−0·0047	0·0
20σ (13σ)	−0·1878	−0·1867	−0·0056	0·0054	0·0034	−0·0024	0·0
21σ	−0·0036	−0·0022	0·0014	−0·0005	0·0048	−0·0044	0·0

† Only the first 23 MOs, which are the most important, are given.
‡ Corresponding orbitals from the [$8s5p/5s$] calculation in parentheses.

important as can be seen from the configurations 1, 4 and 5 of table 5. The higher 3π and 5π orbitals (configuration 10, 11, 15, 16 of table 5) are dominated in their composition by the added polarization functions. If no polarization functions are available the system is not able to describe the angular correlation in the proper manner.

To some extent a compensation of the missing δ type correlation takes place by taking into account a higher amount of σ type correlation. A comparison of both tables shows that the weight (c^2 values) of the configurations summarized in table 6 decreases if polarization functions are used (table 5). The best example is given by configuration 1 of table 6 which becomes configuration 2 in table 5 where its value decreases from 0·00311 to 0·00192.

This behaviour corresponds to a transfer of spin density from the σ orbitals to the δ orbitals. At the first glance an absolute decrease of a_{iso} is expected because δ orbitals possess a nodal plane in the nuclear axis. On the other hand a further polarization of the 2σ and 3σ shells due to δ type correlation effects occurs resulting in an absolute increase of both contributions. For the nitrogen atom the decreasing effect dominated if only SD–CI calculations were performed but if higher excitations are taken into account the increasing effect becomes the stronger [7]. In the NH molecule it seems that the first effect transferring spin-density from σ to δ is always the strongest as indicated by figure 1.

The spin polarization mechanism is also reflected in the eigenvalues of the SNOs. If polarization functions are added the absolute values of SNO 3–SNO 6 decrease with respect to the values obtained without polarization functions. The spin density is thereby transferred to the δ orbital as can be seen from the eigenvalues of SNO 7.

Effects arising from the polarization of the 1σ shell cannot be seen from tables 5, 6 because the c^2 values are smaller than 0·0005. The 1σ contribution is dominated by the large value of the 1σ orbital at the nitrogen centre.

5. Summary

In the present paper we have calculated the hfcc for the NH molecule in its ground state configuration. As known from previous studies it is found that the dipolar term $A_{zz}(\mathrm{N})$ and $A_{zz}(\mathrm{H})$ can be obtained relatively easily with high accuracy, i.e. is not very dependent on the size of the AO basis set (as long as a moderate number of polarization functions is present) or the type of CI expansion. The best value obtained in the present work is $A_{zz}(\mathrm{H}) = 62·29\,\mathrm{MHz}$ and $A_{zz}(\mathrm{N}) = -45·26\,\mathrm{MHz}$ compared to the most recent experimental inferences [13] of 61·14 MHz and $-45·28$ MHz respectively.

The calculation of the isotropic part a_{iso}, on the other hand, is quite troublesome. Simple SD–CI calculations in a moderate-sized AO basis of only s and p functions on nitrogen and s functions on hydrogen [$8s5p/5s$] yield values relatively close to experiment ($a_{\mathrm{iso}}(\mathrm{H}) = -66·4\,\mathrm{MHz}$, $a_{\mathrm{iso}}(\mathrm{N}) = 13·8\,\mathrm{MHz}$ compared to the experimental quantities around $-66\,\mathrm{MHz}$ and 19 MHz respectively). Further analysis shows that such agreement is accidental and that larger AO basis sets (using the same SD–CI treatment) give results which deviate considerably more from the measured data. A larger multi-reference CI expansion improves the situation but shows also that convergence in the CI expansion for a_{iso} does not go parallel to the convergence for the total energy; in other words a definite con-

vergence is not apparent after the first 18 000 (energy-wise most important) configurations in the MRD–CI treatment. The best calculated value employing a natural orbital transformation and a reference set of 22 configurations in a $[8s5p2d/5s2p]$ basis of contracted gaussians is $a_{iso}(H) = -64\cdot5$ MHz and $a_{iso}(N) = 16\cdot6$ MHz.

The results are analysed in detail, in particular the spin-polarization mechanism, by performing core calculations (i.e. such treatments, in which only one shell is correlated and all others are kept doubly occupied) and by a transformation to spin-natural orbitals as the eigenfunctions of the total one-electron spin density matrix.

The quantity a_{iso} at the nitrogen nucleus depends on the subtle balance of the 1σ on one hand (negative) and 2σ and 3σ contributions (positive) on the other; $a_{iso}(H)$ is dominated by the 2σ and not the 3σ shell contribution, whereby the 3σ MO represents the N–H σ bond. This is opposite to some previous interpretations.

As expected d polarization functions are most important for the 1σ and 2σ correlation description while hydrogen p functions affect the 3σ contribution most. Generally inclusion of d functions reduces the magnitude of the 1σ, 2σ and 3σ contributions to $a_{iso}(N)$ while inclusion of higher excitations reverses this trend (at least in the 2σ and 3σ MOs) somewhat. The d functions cause also a reduction in the size of the 2σ shell contribution to $a_{iso}(H)$, they make the 3σ contribution more negative while the hydrogen p functions act oppositely to make the 3σ contribution to $a_{iso}(H)$ more positive.

In the smaller basis without polarization functions the angular correlation (which is essential for the description of a_{iso}) cannot be described properly. To compensate for this shortcoming to some extent the amount of σ correlation is enhanced. The result is an overestimation of a_{iso} in the given basis. On the other hand, a SD–CI procedure *per se* is not adequate and shows a tendency to underestimate the a_{iso} value. As a consequence of the cancellation of the two errors a relatively good agreement of a_{iso} with experiment is observed in such SD–CI calculations in the absence of polarization functions. If polarization functions are added some spin density is transferred from the σ orbitals to those of δ character; this leads to the decrease in the absolute value of a_{iso} within the SD–CI calculation because δ orbitals possess a nodal plane in the nuclear axis. Inclusion of higher than double excitations removes this artefact and will finally lead to the reliable prediction of the hfcc if the proper (large) number of configurations is included in a calculation.

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