

## Study of the 1s and 2s shell contributions to the isotropic hyperfine coupling constant in nitrogen

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**Abstract.** The isotropic part of the hyperfine coupling constant is investigated by means of multireference configuration interaction calculations employing Gaussian basis sets. A detailed study of the 1s and 2s spin polarisation in the nitrogen atom and the NH molecule shows that the structure of the lower-energy space of the unoccupied orbitals is essential for the results. A contraction of the Gaussian basis is possible without loss of accuracy if enough flexibility is retained to describe the main features of the original space of unoccupied functions. Higher than double excitations are found to be non-negligible for the description of  $a_{\text{iso}}$ .

### 1. Introduction

The hyperfine structure in the spectra of atoms or diatomic molecules results from several factors. First from an interaction of the nuclear spin  $I$  with the angular momentum  $L$  and the spin  $S$  of the electrons and secondly from the interaction of the quadrupole moment of the nucleus (for  $I > \frac{1}{2}$ ) with the gradient of the electric field at the location of the nucleus. The interaction of  $I$  with  $S$  can be divided further into the dipole-dipole or *anisotropic* interaction and the *isotropic* interaction 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 isotropic part of the hyperfine coupling constant (HFCC),  $a_{\text{iso}}$ , which is also referred to as the Fermi contact term, is thus directly related to the spin density of the electrons  $\langle \delta(r_N) \rangle$  of the nucleus N.

The present work will deal with the theoretical determination of the *isotropic hyperfine constant* which is given in first order by the expression:

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

where the term in angular brackets is the total spin density  $\langle \delta(r_N) \rangle$  of the electrons at the location of the nucleus N in the electronic state  $q$  and  $\Lambda$  and  $\Sigma$  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. Throughout the present work a value of 2 was used for  $g$ . The quantities  $g_N$  and  $\beta_N$  are the nuclear  $g$  factor and the value for the nuclear magneton respectively.

The isotropic part of the hyperfine interaction is the most difficult to obtain from molecular structure calculations. Numerous attempts to calculate the spin density  $\langle\delta(r_N)\rangle$  in atoms and diatomic molecules are found in the literature. Most such calculations employ the UHF method or a modified procedure thereof to remedy the spin contamination problem (Karna and Grein 1988, Goddard 1969, McDonald and Golding 1978, Ohta *et al* 1980). Configuration interaction methods of various levels of sophistication have also been employed (Chipman 1983, Schaefer *et al* 1968, 1969, Glass and Hibbert 1976, 1978, Hibbert 1975, Engels *et al* 1987, Knight *et al* 1987, Feller and Davidson 1984, 1985).

Generally Slater-type orbitals (STO) are to be preferred for the description of atoms and diatomic molecules. Glass and Hibbert (1976, 1978) employed STOs in SDCI calculations on atoms and obtained agreement within a few per cent with experimental measurements. Likewise Kristiansen and Veseth (1986) used STO basis sets in combination with perturbation theory for the HFCC calculation in the first-row hydrides.

Since molecular structure calculations for polyatomic molecules are generally performed in a Gaussian (GTO) rather than in an STO basis for computational reasons, the question arises as to whether the GTOs are adequate to describe the spin density at the nucleus. A study employing SOSCF wavefunctions (Kaldor and Harris 1969, Kaldor 1970a, b) showed that STO basis sets which satisfy the cusp condition (Roothaan and Kelly 1963, Hurley 1976, Klopper and Kutzelnigg 1987) are superior to STO sets which do not. GTO orbitals on the other hand are not able to satisfy the cusp condition by definition.

Our own *ab initio* configuration interaction (CI) study (Engels *et al* 1987) to obtain  $a_{\text{iso}}$  for the nitrogen atom in a Gaussian basis investigated in considerable detail its dependence on various parameters of the calculations, such as size and type of the GTO basis, inclusion of polarisation and correlation functions, type and lengths of the CI expansion and choice of the molecular basis set. This study shows clearly the difficulties in determining the spin density  $\delta(r_N)$  at the nuclear position. Similar results have also been found in a calculation (Knight *et al* 1987) of the HFCC of  $\text{N}_4^+$  in which part of the work has also been dedicated to the nitrogen atom. In contrast to the STO-CI studies of Glass and Hibbert (1978) our calculations on nitrogen (Engels *et al* 1987) and carbon (Engels *et al* in preparation) show a marked dependence of  $\langle\delta(r_N)\rangle$  on triple and higher excitations which becomes even stronger upon inclusion of d polarisation functions. Knight *et al* (1979, 1980) find agreement within a few per cent with experimental values of the isotropic HFCC of the non-hydrogen nuclei in selected systems employing standard GTO plus polarisation basis sets while the agreement at the hydrogen nucleus in the same system is only in the 50-90% range. The standard Huzinaga-Dunning 9s5p GTO basis (Huzinaga 1971, Dunning 1970) gives a large error (50%) for the HFCC of the nitrogen atom (Engels *et al* 1987), and smaller basis sets predict even the incorrect sign for  $a_{\text{iso}}$ . The analysis shows (Engels *et al* 1987) that the balanced description of the 1s and 2s spin polarisation in first-row atoms is essential for a reliable computation of  $a_{\text{iso}}$  since both are approximately of the same magnitude but opposite in sign. Technically this means that the low-lying virtual orbitals are very important for the description of the spin polarisation of both shells.

Computationally the spin density  $\langle\delta(r_N)\rangle$  is determined by the total one-electron spin density matrix (TSM) and the matrix of integrals (IM) which will be introduced in the next section. Variations in the calculated value of  $\langle\delta(r_N)\rangle$  which arise from different parameters of the calculation procedure occur in the TSM; we will therefore study the behaviour of this matrix with respect to variations in the treatment. The

structure of the TSM which will be obtained from MRD-CI calculations will then be compared with the TSM resulting from the single-excitation SEC1 calculations of Chipman (1983).

## 2. Theory

The spin density at the nucleus  $\langle \delta(r_N) \rangle$  in first-order perturbation theory can be expressed (Chipman 1983, Hurley 1976, McWeeny and Sutcliffe 1969) as

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

where  $\Psi(r, R_0)$  is the electronic CI wavefunction of electronic state  $q$  with the quantum numbers  $\Lambda$  and  $\Sigma$  (see equation (1)) within the Born-Oppenheimer approximation. In most of the calculations presented here it includes all single and double excitations with respect to a set of reference configurations (Buenker and Peyerimhoff 1968, 1975), i.e. it contains higher than double excitations with respect to the Hartree-Fock determinant  $|\Phi_0\rangle$ . The CI wavefunction is often written in terms of Slater determinants (Slater 1960, Szabo and Ostlund 1982):

$$\Psi(r, R_0) = c_0 |\Phi_0\rangle + \sum_{a,r} c_a^r |\Phi_a^r\rangle + \sum_{\substack{a<b \\ r<s}} c_{ab}^{rs} |\Phi_{ab}^{rs}\rangle + \sum_{\substack{a<b<c \\ r<s<t}} c_{abc}^{rst} |\Phi_{abc}^{rst}\rangle + \dots \quad (3)$$

where  $|\Phi_a^r\rangle$  represents a single excited determinant with respect to  $|\Phi_0\rangle$ ,  $|\Phi_{ab}^{rs}\rangle$  a double replacement with respect to  $|\Phi_0\rangle$  and so on. The  $c_a^r$ ,  $c_{ab}^{rs}$ , ... are the CI coefficients belonging to the excitation under consideration. Normalisation of  $\Psi(r, R_0)$  requires that the sum of the squares of the coefficients be unity, whereby orthogonal one-electron functions are assumed.

By insertion of equation (3) into equation (2) it follows that  $\langle \delta(r_N) \rangle$  can be expressed in a sum over matrix elements between determinants:

$$\langle \delta(r_N) \rangle = \sum c_{kl} \left\langle \Phi_k \left| \sum_{i=1}^n \delta(r_i - r_N) 2s_{zi} \right| \Phi_l \right\rangle. \quad (4)$$

In this expression  $\Phi_k$  cannot be more than a single excitation with respect to  $\Phi_l$  because  $\langle \delta(r_N) \rangle$  is a one-electron property;  $c_{kl}$  is the product of corresponding expansion coefficients. Using the rules for the evaluation of the matrix elements of a one-electron property between Slater determinants (Slater 1960),  $\langle \delta(r_N) \rangle$  can be expanded in terms of the one-electron functions (molecular orbitals)  $\varphi_p$ :

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

The term  $\gamma_{pq}$  is the TSM which contains the product of CI coefficients and the factors resulting from applying the spin operator  $S_z$ . Because  $\langle \delta(r_N) \rangle$  is a one-electron property  $\gamma_{pq}$  is blocked according to irreducible representations. The diagonalisation of the TSM produces the spin natural orbitals (SNO) (Engels *et al* 1987, in preparation, Chipman 1983, Engels 1987) which will be discussed in the study of differences in the TSM. The second term  $\langle \varphi_p | \delta(r - r_N) | \varphi_q \rangle$  is the matrix of integrals (IM) over the molecular orbitals, which is also blocked according to irreducible representations, if the nucleus studied is left invariant by all symmetry elements, e.g. for atoms or heteronuclear diatomic molecules.

In this decomposition the contribution of a single molecular orbital to  $\langle \delta(r_N) \rangle$  can be written as

$$\langle \delta(r_N) \rangle_p = \sum_q \gamma_{pq} \langle \varphi_p | \delta(r - r_N) | \varphi_q \rangle. \quad (6)$$

The situation is different if core calculations (Engels *et al* 1987) are carried out, i.e. calculations in which only one of the doubly occupied shells is correlated. In the nitrogen atom, for example, two different calculations are undertaken; a 1s core calculation in which the 1s shell is frozen and all other electrons are allowed to participate in the CI expansion and a 2s core calculation in which the 2s shell is doubly occupied and all other electrons, including those of the 1s, are allowed to populate the various molecular orbitals. In this case the 1s contribution to the spin polarisation (referred to as  $\langle \delta(r_N) \rangle(1s)$ ) is obtained by the 2s core calculation according to equation (5), where the doubly occupied 2s obviously does not appear in the sum. The 2s contribution is obtained in analogy. In comparison with the other CI calculations carried out in this work, which correlate all electrons, the intershell correlation contribution is not accounted for in such core calculations.

### 3. Influence of s-type basis functions

Basis functions of the s type influence the TSM as well as the IM. In an atomic calculation they represent the occupied s shells, and the virtual orbitals describe the radial correlation of the s electrons (Slater 1960). In our previous study (Engels *et al* 1987) we discussed the dependence of  $a_{\text{iso}}$  on the size of the basis set. It was found that small basis sets are not appropriate for an  $a_{\text{iso}}$  calculation because their virtual space is not able to describe the polarisation of the 1s and 2s shells appropriately. Furthermore the analysis showed that the energetically low-lying virtual molecular orbitals are especially important. In contrast a contraction of the (13s8p) basis set of van Duijneveldt (1971) to a [8s4p] was found to have only a minor effect on  $a_{\text{iso}}$ .

In order to explain this behaviour the various characteristics of the orbitals are calculated. Table 1 contains the total energies, the total value of  $a_{\text{iso}}$  and the 1s and 2s contributions to  $a_{\text{iso}}$  for various basis sets, namely the uncontracted (13s8p) set and its contraction to [8s4p], the uncontracted (5s2p) and (9s5p) sets all taken from the work of van Duijneveldt (1971) and the [4s2p] contraction of the (9s5p) Huzinaga set (Huzinaga 1971, Dunning 1970). Since the differences between the van Duijneveldt (9s5p) and Huzinaga (9s5p) basis sets are quite small as discussed earlier (Engels *et al* 1987), the results of the present [4s2p] set can be realistically attributed to the contraction procedure when compared with the (9s5p) basis. Table 2 gives the orbital energies of the lower atomic orbitals of s symmetry for the basis sets under consideration together with their spatial extension as measured by  $\langle r \rangle$ , while table 3 contains the composition of the most important SNOS for the five different basis sets. Since all calculations are carried out technically in the Abelian subgroup  $D_{2h}$ , the s orbitals are formally found in the  $A_{1g}$  irreducible representation.

As discussed before (Engels *et al* 1987) the absolute value of  $a_{\text{iso}}$  decreases steadily when the basis set is reduced from (13s8p) in various steps (13s7p, 12s7p, 11s6p, 10s6p) to (9s5p). Use of the very small basis (5s2p) results in a negative sign for  $a_{\text{iso}}$ . The reason for this behaviour lies in the inadequate description of the 1s and 2s spin

**Table 1.** Total energy and calculated  $a_{\text{iso}}$  values<sup>a</sup> for the nitrogen atom obtained from the various basis sets (2M1R calculation,  $T=0.0$  Hartree)<sup>b</sup>.

AO basis	5s2p	9s5p	4s2p contracted	13s8p	8s4p contracted	Expt <sup>c</sup>
Total energy (Hartree)	-54.1050	-54.4788	-54.4418	-54.4929	-54.4709	
$a_{\text{iso}}$ (MHz)	-31.5	3.4	12.5	6.9	7.2	10.45
$a_{\text{iso}}$ (1s)(MHz) <sup>d</sup>	-32.9	-52.9	-56.0	-54.6	-54.9	
$a_{\text{iso}}$ (2s)(MHz) <sup>d</sup>	1.7	53.0	62.2	58.5	58.8	

<sup>a</sup> Unfortunately we detected an error in the computer code with which the results of Engels *et al* (1987) were obtained. This error does not affect the general conclusions of Engels *et al* (1987) since all trends discussed therein remain; the correct absolute numbers, however, are smaller by about 0.6 MHz than values given originally.

<sup>b</sup> xMYR refers to an MRD-CI calculation with  $x$  main or reference configurations in which configuration selection is undertaken with respect to  $y$  roots;  $T$  refers to the selection threshold employed.

<sup>c</sup> The experimental value is taken from Hirsch *et al* (1977), Holloway *et al* (1962) and Anderson *et al* (1959).

<sup>d</sup> The contributions of the 1s and 2s shells respectively are calculated by always maintaining the complementary shell doubly occupied in the CI procedure.

polarisations (table 1), in particular that of the 2s. It is seen that both contributions decrease in magnitude, but while the 1s term decreases from -54.6 to -32.9 MHz, the 2s contribution almost vanishes in the small basis.

In contrast, the change from the (13s8p) uncontracted to the [8s5p] contracted basis is quite small (table 1). Both the 1s and 2s contributions remain nearly constant so that the total value of  $a_{\text{iso}}$  remains essentially the same upon contraction of the atomic orbital basis. If the (9s5p) set is contracted to [4s2p], on the other hand, an entirely different behaviour is seen. The calculated value of  $a_{\text{iso}}$  increases to 12.5 MHz in a 1M1R treatment and to 13.4 MHz if six reference configurations are employed (6M1R calculations).

This behaviour can be rationalised by inspection of the structure of the virtual  $A_{1g}$  space (table 2) which makes polarisation possible, as discussed earlier (Engels *et al* 1987). The lower energy  $A_{1g}$  virtual space in the (5s2p) basis is spanned by only one orbital with an energy of 16.18 au while the two other orbitals are energetically too high to be effective in describing excitations. Hence this space is not flexible enough to describe the spin polarisation properly.

This argument is supported by an analysis of the composition of the sNOS in which the structure of the virtual space is reflected (table 3). The (9s5p) basis exhibits a relatively compact expansion, in which sNO1 and sNO2 are primarily composed from orbitals  $1a_{1g}(1s)$  and  $4a_{1g}$  while the other two sNOS are made up in the main from the  $2a_{1g}(2s)$  and  $3a_{1g}$  functions. The two contributors to the 2s shell have orbital energies of -0.94 and +0.95 (table 2) and are apparently matched quite nicely as is also seen from the corresponding spatial extension of 1.33 and 1.95 au for  $2a_{1g}$  and  $3a_{1g}$ . The optimal orbital in this basis to match the 1s SCF molecular orbital is  $4a_{1g}$  with an orbital energy of +8.9 au and an average radius of 0.78 au compared with the 0.23 au of the 1s orbital; a closer matching in radii would occur by the  $7a_{1g}$  and  $8a_{1g}$  orbitals which have too high an energy to play a role. The greater flexibility of the (13s8p) relative to the (9s5p) set is also obvious and has been discussed earlier (Engels *et al* 1987). In going from (9s5p) to the smaller (5s2p) basis the virtual space corresponding to orbital energy between zero and 2.0, which is apparently the important region for the

**Table 2.** SCF orbital energies,  $\epsilon$ , of the various  $a_{1g}$  orbitals in the N atom using different basis sets (energies in Hartree) and their spatial extension,  $\langle r \rangle$  (in au).

	5s2p		9s5p		[4s2p]		13s8p		[8s4p]	
	$\epsilon$	$\langle r \rangle$	$\epsilon$	$\langle r \rangle$	$\epsilon$	$\langle r \rangle$	$\epsilon$	$\langle r \rangle$	$\epsilon$	$\langle r \rangle$
1a <sub>1g</sub>	-15.6402	0.227	-15.6254	0.228	-15.6288	0.2283	15.6291	0.228	-15.6290	0.228
2a <sub>1g</sub>	-0.9005	1.280	-0.9435	1.330	-0.9441	1.3318	-0.9453	1.332	-0.9453	1.332
3a <sub>1g</sub>	16.1801	0.422	0.9568	1.951	0.9191	1.9585	0.3777	2.997	0.3782	2.995
4a <sub>1g</sub>	138.000	0.161	8.9318	0.781	32.8122	0.2986	2.0563	1.899	2.0618	1.894
5a <sub>1g</sub>	1035.76	0.053	44.4033	0.376			7.4237	1.122	7.5111	1.108
6a <sub>1g</sub>			167.872	0.194			23.2307	0.656	24.0359	0.626
7a <sub>1g</sub>			615.630	0.096			67.748	0.376	81.9872	0.302
8a <sub>1g</sub>			2 620.47	0.041			194.873	0.211	535.113	0.096
9a <sub>1g</sub>			15 711.20	0.014			575.251	0.116		
10a <sub>1g</sub>							1801.44	0.061		
11a <sub>1g</sub>							6235.15	0.030		

**Table 3.** Eigenvectors of the lowest SNOs obtained from diagonalising the total spin density matrix (TSM) for various basis sets.

	Eigenvectors					
	$1a_{1g}$	$2a_{1g}$	$3a_{1g}$	$4a_{1g}$	$5a_{1g}$	$6a_{1g}$
<b>Basis 5s2p</b>						
SNO1	-0.6788	0.1957	-0.7065	0.0419	0.0	
SNO2	0.6747	0.2141	0.7051	-0.0424	-0.0	
SNO3	-0.1348	0.4465	-0.0466	-0.8834	0.0	
SNO4	0.2565	-0.8465	0.0395	0.4649	0.0	
<b>Basis 9s5p</b>						
SNO1	-0.7058	0.0370	-0.0139	0.7028	-0.0803	0.0
SNO2	0.7064	-0.0385	-0.0102	0.7021	0.0805	0.0
SNO3	0.0387	0.6881	0.7245	0.0120	0.0029	0.0
SNO4	-0.0368	-0.7236	-0.6891	0.0129	0.0029	0.0
<b>Basis [4s2p]</b>						
SNO1	0.7055	-0.0360	0.0016	-0.7078		
SNO2	0.7068	-0.0359	-0.0054	0.7064		
SNO3	0.0370	0.6873	0.7254	0.0035		
SNO4	0.0350	0.7246	-0.6883	-0.0035		
<b>Basis 13s8p</b>						
SNO1	-0.7021	0.0235	0.1270	-0.4850	-0.4767	-0.1655
SNO2	0.7111	-0.0246	0.1214	-0.4652	-0.4818	-0.1728
SNO3	0.0228	0.6844	0.7018	0.1961	-0.0104	-0.0054
SNO4	0.0243	0.7284	-0.6593	-0.1845	0.0106	0.0053
<b>Basis [8s4p]</b>						
SNO1	-0.7030	0.0236	0.1268	-0.4838	-0.4769	-0.1662
SNO2	0.7104	-0.0231	0.1211	-0.4676	-0.4814	-0.1719
SNO3	0.0231	0.6836	0.7027	-0.1956	-0.0099	-0.0054
SNO4	0.0236	0.7291	-0.6586	-0.1840	0.0110	0.0053

proper description of SNO3 and SNO4, is empty and hence the 2s spin polarisation cannot be described in the smaller atomic orbital basis (1.7 instead of 53 MHz). The space corresponding to an orbital energy between 2 and 25 au is represented by one function ( $3a_{1g}$ ) with an orbital energy of 16 au and an  $\langle r \rangle$  value of 0.44 au in the smaller basis; hence the situation is somewhat better for the 1s shell in this basis and reduces the calculated value for  $a_{iso}(1s)$  from -52.9 MHz in the (9s5p) to only -32.9 MHz in the (5s2p) basis.

In contrast to this situation a balanced reduction of the atomic orbital basis set size due to contraction does not affect the important portion of the virtual orbital space. Only the two highest  $a_{1g}$  orbitals in the [8s4p] basis differ from their corresponding virtual orbitals in the uncontracted (13s8p) basis. The highest two,  $10a_{1g}$  and  $11a_{1g}$ , are not dominant in any of the contracted orbitals and the  $9a_{1g}$  seems to become the main contributor to the  $8a_{1g}$  in the contracted set, based on inspection of orbital energy and radial expansion. The calculated values for the total value of  $a_{iso}$  as well as for the different contributions from the 1s and 2s shell are almost identical in the contracted and uncontracted basis (table 1) and underline again the importance of the lower-energy

virtual orbital space. The considerable reduction in atomic orbital basis set size by the contraction (9s5p) to [4s2p] again affects the lowest three s orbitals relatively little if the corresponding orbital energies and mean radii (table 2) are compared. There is only a single orbital available to describe the correlation in each doubly occupied shell, i.e. the 3s ( $3a_{1g}$ ) correlates with the 2s shell and the  $4a_{1g}$  accounts for the 1s correlation (table 3). Due to this inflexibility both the 1s and 2s contributions to  $a_{iso}$  increase in magnitude (table 1), the 2s contribution more than that of the 1s.

The influence of higher orbitals has been studied in calculations in which a d function with an exponent of 0.8 was also present in addition to the [8s4p] contracted basis. In these calculations one of the four highest orbitals of the  $A_{1g}$  space has always been deleted from the CI to investigate how it affects the results. From table 4 it is seen that the highest molecular orbital  $11a_{1g}$  has almost no effect. The lower orbitals  $10a_{1g}$ ,  $9a_{1g}$  and  $8a_{1g}$  change the 2s contributions very little while the magnitude of the 1s contribution decreases considerably from 54 to 39 MHz. As a result the total value of  $a_{iso}$  increases upon neglect of the higher virtual molecular orbitals. The 2s contribution increases if the  $8a_{1g}$  or  $9a_{1g}$  are deleted. This is similar to the behaviour which occurs if the basis set is contracted too much.

Table 4. Influence of the highest virtual orbitals. Basis set [8s4p] augmented by a d function.

Molecular orbital	Orbital energy (Hartree)	$\langle r \rangle$ (au)	MRD-CI energy (Hartree)	$a_{iso}$ (total) (MHz)	$a_{iso}(1s)$ (MHz)	$a_{iso}(2s)$ (MHz)
$1a_{1g}$	-15.6290	0.228				
$2a_{1g}$	-0.9450	1.332				
All orbitals			-54.52533	6.3	-54.4	57.3
Discarded						
$8a_{1g}$	10.3707	1.137	-54.51765	22.5	-39.3	59.5
$9a_{1g}$	26.9945	0.656	-54.51750	17.9	-42.9	58.8
$10a_{1g}$	84.9706	0.312	-54.51945	8.1	-51.3	57.4
$11a_{1g}$	539.1432	0.098	-54.52489	5.9	-54.2	57.3

In summary it can be stated that contraction of a basis set is possible in calculation of the hyperfine interaction as long as the low-energy virtual space possesses a structure which is similar to that of the uncontracted basis set. If the contraction changes this space the description of the 1s and 2s spin polarisation must be critically evaluated, whereby it may happen that the errors which occur in both contributions to  $a_{iso}$  may cancel each other. A study of the various effects will appear elsewhere (Engels *et al* in preparation).

#### 4. Influence of basis functions with $l > 1$

Basis functions with  $l > 1$  are important in atomic calculations of the first row because they describe the angular correlation of the electrons (Slater 1960). They make no direct contribution to  $a_{iso}$  because they possess a node at the nucleus. Therefore their influence is restricted to the TSM. In the CI procedure their effect is included by taking



into account double and higher excitations with respect to the RHF determinant, because single excitations are allowed only within the irreducible representation.

Functions of the p type describe the distribution of the p electrons and are furthermore important for the description of angular correlation of the s electrons. Their influence on  $a_{\text{iso}}$  is solely due to this latter property. Hence their effect, as far as their number and contraction scheme is concerned, is expected as already discussed earlier (Engels *et al* 1987). A more detailed study of these effects using the carbon atom as a model system will be given elsewhere (Engels *et al* in preparation).

Using Cartesian d-type orbitals the  $d_{(x^2+y^2+z^2)}$  component is an s-type function which effects  $a_{\text{iso}}$  like a normal s function. In order to differentiate between the effect of this function and the other d components we added an s function with the exponent of the d function under consideration to the [8s4p] basis. Table 5 contains the results of the calculations. For comparison the  $a_{\text{iso}}$  values which we calculated using the full d function are added.

**Table 5.** Effect of the  $d_{(x^2+y^2+z^2)}$  component (represented by an s function) on  $a_{\text{iso}}$  in comparison with a six-component d function. Basis set: 13s8p of van Duijneveldt contracted to a [8s4p] basis set (1M1R calculation with  $T=0.0$  Hartree).

Exponent of the extra function	s contribution of the d function $a_{\text{iso}}$ (MHz)	Full set of Cartesian d functions $a_{\text{iso}}$ (MHz)
$\zeta = 1.0$	5.6	0.4
$\zeta = 0.8$	5.7	3.3
$\zeta = 0.6$	5.7	7.3
Without	5.7	

It is seen that the effect of this component is small when the s-type space is nearly saturated in this region of exponents, as is the case for the [8s4p] set. At the same time it is seen that d functions in the atomic orbital basis are essential for the calculation of  $a_{\text{iso}}$ . This result stands in contrast to the effect of the d function in UHF calculations (Karna and Grein 1988) on  $F_2^-$  and  $Cl_2^-$  employing basis sets of only double-zeta quality.

As described in Engels *et al* (1987) the other d components must be divided into two groups, because the calculation was not performed in the symmetry group  $O(3)$ , but in the largest Abelian subgroup  $D_{2h}$ . The first group consists of the two components  $d_{(2z^2-x^2-y^2)}$  and  $d_{(x^2-y^2)}$  which belongs in the  $D_{2h}$  symmetry to the  $A_{1g}$  irreducible representation while the other three components  $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$  belong to the irreducible representation  $B_{1g}$ ,  $B_{2g}$  and  $B_{3g}$ . The influence of the second group on  $a_{\text{iso}}$  is equal to that of the p functions, but because their  $l$  value is higher a smaller effect is expected. The components of the first group contribute to  $a_{\text{iso}}$  also but by higher than single excitations, which can be seen from the blocked structure of the TSM, but electronic configurations which appear formally as single excitations from the 2s orbital to the d components  $d_{2z^2-x^2-z^2}$  and  $d_{z^2-y^2}$  are necessary to incorporate important higher excitations into the wavefunction. In Engels *et al* (1987) we found that triple excitations with respect to the ground state are important to give a correct description of  $a_{\text{iso}}$ . This seems to stand in contrast to the studies of Glass and Hibbert (1978), which state that excitations higher than double excitations give a negligible contribution to  $a_{\text{iso}}$ .

In the present MRD-CI procedure triple and higher excitations are considered by adding important configurations to the reference space from which all single and

double excitations are generated. In our previous study (Engels *et al* 1987) the most important higher excitations resulted from three reference configurations, which in turn are single replacements from the 2s orbital into the 3s and the  $d_{x^2-y^2}$  or the  $d_{2z^2-x^2-y^2}$  component of the d polarisation function. Consideration of these excitations improves the result by about 20–30%. Glass and Hibbert (1978) have found in their study of the boron atom that three-electron excitations are unimportant for the determination of the Fermi contact term  $a_{\text{iso}}$ , from which result they assumed that higher excitations are unimportant for the first-row atoms. The argument was supported by the very good agreement of their result, e.g. 9.92 MHz for the nitrogen atom. Hence the question arises about the differences in the two treatments which seem to lead to opposite conclusions. First, in contrast to our basis set, Glass and Hibbert used an STO basis. The occupied functions 1s, 2s and 2p were taken from the tables of Clementi. Their unoccupied orbitals consist of optimised 3s, 3d correlation functions for the 1s and the 2s, respectively.

Finally, these functions were supplemented up to  $n=4$  optimising 3p and 4p exponents with respect to the two-electron correlation replacements  $1s^2 \rightarrow 3p^2$  and  $2s^2 \rightarrow (3p^2 + 3p4p + 4p^2)$ , respectively. Hence the question is whether the STO functions by themselves or possibly the optimisation procedure of orbitals is the reason for the excellent agreement with experiment without considering triple excitations.

From the description of Glass and Hibbert and our own experience it is to be expected that most of the 1s and 2s polarisation is described by the orbitals optimised to correlate these shells and that the  $n=4$  orbitals play a minor role. Hence the situation is similar to that of the contracted [4s2p] basis set discussed in the present work. Considering the fact that d polarisation functions decrease the 2s contribution more than the 1s contribution a cancellation of several errors seems to occur and may lead to perfect results.

## 5. Differences between molecular and atomic calculations

In calculations of  $a_{\text{iso}}$  in molecular systems the effects of the various ingredients of an *ab initio* calculation seem to be similar to those in atomic calculations.

Table 6 contains a comparison between the calculations using the 9s5p Huzinaga basis set contracted to [4s2p] as suggested by Dunning (1970) and the [8s5p] basis set which was obtained by contracting the (13s8p) basis set of van Duijneveldt (1971); the p contraction is kept somewhat more flexible to 5p in the molecule while it was 4p in the atom. The basis set for the H atom is the (4s) of Huzinaga contracted to [2s] by Dunning and the (8s) of van Duijneveldt contracted to [5s], respectively.

It is seen that the calculated values using the smaller basis sets are higher in absolute magnitude. This is based on a higher contribution of the  $2a_1$  shell. In the case of the hydrogen centre the effect in the  $2a_1$  shell is weakened by an increase of the  $3a_1$  contribution.

Figure 1 contains the orbital energies of the orbitals with  $A_1$  symmetry of both basis sets. It is seen that both virtual spaces are similar in the lower region (0–1.5 au) while the higher region is empty when the smaller basis set is employed (orbitals with an energy of more than 12 au are not given). This situation is quite similar to that for the atoms (tables 1 and 2), in which the [4s2p] basis leads to higher values for  $a_{\text{iso}}$  than the larger [8s4p] basis set. It seems that the polarisation of a doubly occupied

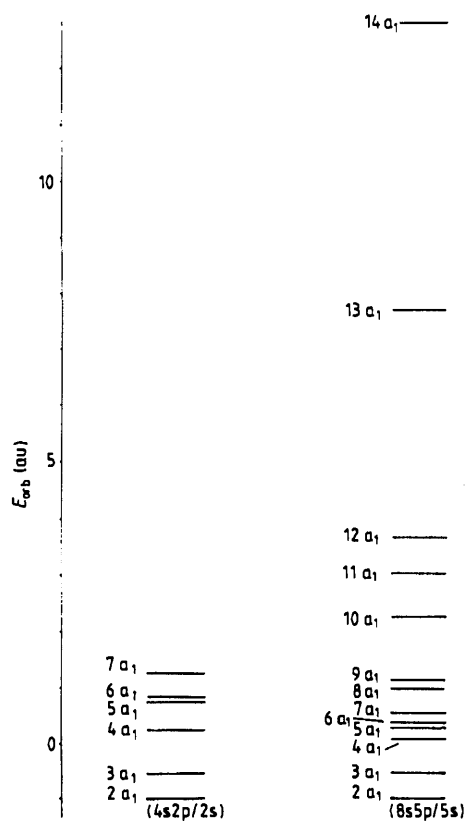
**Table 6.** Comparison between the  $a_{\text{iso}}$  values of the NH ground state  $^3\Sigma^-$  using different basis sets.<sup>a</sup>

	$a_{\text{iso}}$ (total) (MHz)	$a_{\text{iso}}(1a_1)$ (MHz)	$a_{\text{iso}}(2a_1)$ (MHz)	$a_{\text{iso}}(3a_1)$ (MHz)
$a_{\text{iso}}$ of the N centre				
8s5p/5s <sup>b</sup>	14.3	-53.6	58.6	10.1
4s2p/2s <sup>c</sup>	22.2	-55.7	63.4	9.9
$a_{\text{iso}}$ of the H centre				
8s5p/5s <sup>b</sup>	-66.4	0.0	-52.0	-0.2
4s2p/2s <sup>c</sup>	-69.9	0.0	-57.4	3.7

<sup>a</sup> Explanations of the basis sets are given in the text.

<sup>b</sup> Treatment: 4M1R,  $T=0.0$  Hartree.

<sup>c</sup> Treatment: 3M1R,  $T=0.0$  Hartree, chosen for a standard MRD-CI calculation.


**Figure 1.** Orbital energies for the NH molecule in two different contracted Gaussian basis sets.

shell due to different regions of the  $A_1$  virtual space contains contributions of different sign. It may be possible to study these effects by the  $a_{\text{iso}}$  values of the single orbital.

## 6. Comparison of the TSM using different CI methods

Chipman (1983) discussed the structure of the SNOS in a single-excitation type SECI study of the  $\text{CH}_3$  molecule employing the double-zeta basis sets of Dunning. In this SECI wavefunction only certain single excitations are included. Because of the properties of this CI wavefunction the TSM can be transformed to a form that contains  $2 \times 2$  blocks. The final result is that the different SNOS are given by a linear combination of one doubly occupied orbital and one appropriate virtual orbital. This form of the SNOS is very similar to that of UHF SNOS (Harriman 1964).

This structure resembles the SNOS which result from our nitrogen calculations using smaller basis sets (table 3) although the MRD-CI instead of the SECI is used. If we go to larger basis sets each SNO contains more virtual orbitals in its expansion. This scheme is maintained if the basis set is contracted to [8s4p] (table 3). In the calculations on NH the differences between the SNOS using the [4s2p/2s] or the [8s5p/4s] basis set are smaller. This is expected, because the difference in the lower virtual space of both basis sets is small and the pairing structure of the (9s5p) or (5s2p) calculations of the N atom is based on the low density of this part of the virtual space.

## 7. Summary

The calculation of the isotropic part of the HFCC depends critically on the balanced description of the 1s and 2s shells, which give contributions to  $a_{\text{iso}}$  which are comparable in magnitude but opposite in sign; the case study is made for the nitrogen atom. Small basis sets such as (5s2p) give entirely unrealistic results while sets of the size (13s8p) give around 70% of  $a_{\text{iso}}$ . An analysis in terms of SNOS shows that for each occupied s shell at least one unoccupied partner is required whose energy and spatial character must match the occupied shell in a certain manner in order to give an appropriate description of the spin polarisation. Larger basis sets have more flexibility in the SNO expansion and are therefore able to give a more balanced description of the 1s-2s spin polarisation. If a contraction, such as (13s8p)  $\rightarrow$  [8s4p] maintains the critical structure of the low-energy unoccupied space it can be employed with very little loss in accuracy in place of the original larger basis. A contraction to [4s2p] gives only the minimum freedom for an s-shell SNO expansion and the results will thus depend critically on the individual functions (or on fortunate error cancelling).

Functions of higher quantum number than s make no direct contribution to  $a_{\text{iso}}$  but describe correlation effects; it is found that double excitations (into d functions) are not negligible. All results obtained for the case study nitrogen atom seem to be carried over to the molecules as well.

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## References

- Anderson L W, Pipkin F M and Baird J C 1959 *Phys. Rev.* **116** 87  
Buenker R J and Peyerimhoff S D 1968 *Theor. Chim. Acta* **12** 183  
— 1975 *Theor. Chim. Acta* **39** 217  
Chipman D M 1983 *J. Chem. Phys.* **78** 3112  
Dunning T H 1970 *J. Chem. Phys.* **53** 2823  
Engels B 1987 *Dissertation* Bonn University  
Engels B, Peyerimhoff S D and Davidson E R 1987 *Mol. Phys.* **62** 109  
Engels B, Peyerimhoff S D, Grein F and Karna S in preparation  
Feller D and Davidson E R 1984 *J. Chem. Phys.* **80** 1006  
— 1985 *Theor. Chim. Acta* **68** 57  
Glass R and Hibbert A 1976 *J. Phys. B: At. Mol. Phys.* **9** 875  
— 1978 *J. Phys. B: At. Mol. Phys.* **11** 2257  
Goddard W A III 1969 *Phys. Rev.* **182** 48  
Harriman J E 1964 *J. Chem. Phys.* **40** 2827  
Hibbert A 1975 *Rep. Prog. Phys.* **38** 1217  
Hirsch J M, Zimmermann G H III, Larson D J and Ramsay N F 1977 *Phys. Rev. A* **16** 484  
Holloway W W, Luescher E and Novick R 1962 *Phys. Rev.* **126** 2109  
Hurley A C 1976 *Electronic Correlation in Small Molecules* (New York: Academic)  
Huzinaga S 1971 *Approximate Arithmetic Wavefunctions I, II* (Department of Chemistry Report, University of Alberta, Edmonton, Canada)  
Kaldor U 1970a *Phys. Rev. A* **1** 1586  
— 1970b *Phys. Rev. A* **2** 1267  
Kaldor U and Harris F E 1969 *Phys. Rev.* **183** 1  
Karna S and Grein F 1988 *Chem. Phys.* submitted for publication  
Klopper W and Kutzelnigg W 1987 *Chem. Phys. Lett.* **134** 17  
Knight L B Jr, Johannessen K D, Cobranchi D C, Earl E A, Feller D and Davidson E R 1987 *J. Chem. Phys.* **87** 885  
Knight L B Jr, Martin R L and Davidson E R 1979 *J. Chem. Phys.* **71** 3991  
Knight L B Jr, Wise M B, Childers A G, Davidson E R and Daasch W R 1980 *J. Chem. Phys.* **73** 4198  
Kristiansen P and Veseth L 1986 *J. Chem. Phys.* **84** 2711, 6336  
McDonald J R and Golding R M 1978 *Theor. Chim. Acta* **47** 1  
McWeeny R and Sutcliffe B T 1969 *Methods of Molecular Quantum Mechanics* (New York: Academic)  
Ohta K, Nakatsuji H, Hirao K and Yonezawa T 1980 *J. Chem. Phys.* **73** 1770  
Roothaan C C and Kelly P S 1963 *Phys. Rev.* **131** 1177  
Schaefer H F III, Klemm R A and Harris F E 1968 *Phys. Rev.* **176** 49  
— 1969 *Phys. Rev.* **181** 137  
Slater J C 1960 *Quantum Theory of Atomic Structure* (New York: McGraw Hill)  
Szabo A and Ostlund N S 1982 *Modern Quantum Chemistry* (New York: Macmillan)  
van Duijneveldt F B 1971 *Technical Report* RJ945 (IBM Research Laboratory, San Jose, CA)