The Electronic Structure of the NF$_2$ Radical

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Ab initio unrestricted Hartree-Fock (UHF) calculations (with and without single annihilation) have been performed on the radical NF$_2$ using four different basis sets; namely, a minimal basis Slater set, two minimal basis Gaussian sets and a Gaussian set of approximately double zeta accuracy.

Several one-electron charge dependent properties have been calculated with each basis set and it is most apparent that near double zeta accuracy 2p functions are necessary to produce reliable values.

Single annihilation of the UHF wavefunctions calculated with the two basis sets containing near double zeta 2p functions, was found to give an accurate representation of the anisotropic coupling constants at both the nitrogen and fluorine atoms. Less satisfactory agreement with the experimental isotropic coupling constants was found with all calculations.

This investigation of the NF$_2$ radical indicates that, providing a good quality basis set is used, the single annihilated UHF method can provide accurate values for most charge and spin dependent observable properties of open shell molecules.

Ab initio-Rechnungen nach der uneingeschränkten Hartree-Fock-Methode (UHF-Methode) (mit und ohne einfache Auslöschung) wurden für das Radikal NF$_2$ mit verschiedenen Basissätzen durchgeführt. Die vier Basissätze sind: ein minimaler Basissatz von Slaterfunktionen, zwei minimale Basissätze von Gaußfunktionen und ein größerer Satz von Gaußfunktionen von angenäherter Genauigkeit einer Doppelzeta-Basis. Der Vergleich der Basissätze bei der Berechnung von ladungsabhängigen Einelektron-Eigenschaften zeigt, daß der angenäherte Doppelzeta-Basissatz zur Berechnung geeigneter Werte notwendig ist. Eine einfache Auslöschung in den UHF-Wellenfunktionen, die mit den beiden Basissätzen mit genäherten Doppelzeta-2p-Funktionen berechnet wurden, führte auf eine genaue Darstellung der anisotropen Kopplungskonstanten am Stickstoff und an Fluor. Die Übereinstimmung der berechneten isotropen Kopplungskonstanten war bei allen Rechnungen weniger gut. Diese Ergebnisse für das NF$_2$-Radikal zeigen, daß bei Verwendung einer geeigneten Basis mit Hilfe der UHF-Methode mit einfacher Auslöschung genaue Werte für die meisten von der Ladung oder vom Spin abhängigen Eigenschaften von Molekülen mit offenen Schalen gewonnen werden können.

Introduction

Only a very small number of molecules which contain an odd number of electrons are sufficiently unreactive under normal conditions of temperature and pressure to permit investigations by physical methods. Two members of this select group which have been extensively studied, both experimentally and theoretically, are NO and NO$_2$ [1]. Another member of the group which has been given some experimental, but little theoretical [2], attention is the molecule NF$_2$. An electron diffraction study of its geometry [3] and some infra-red [4], ultraviolet [5], e.s.r. [6] and photoelectron [7] studies have been made. However, no definitive study of the microwave spectrum has been reported [8].

In collaboration with our microwave group, who are currently engaged in the analysis of a complex spectrum which has been observed in K-, R- and F-bands [8], we have investigated the electronic structure of NF_2 using *ab initio* SCF procedures based on both Slater-type orbitals (STO's) and Gaussian functions. A particular aim of the work has been to compute the various spin-coupling parameters involved in the Hamiltonian of the freely rotating molecule in order to aid the spectral analysis. We report here the results of this study.

Method

We have investigated the charge and spin properties of NF_2 using the unrestricted Hartree-Fock method (UHF) [9]. The spin-dependent properties were all calculated from the modified UHFAA (unrestricted Hartree-Fock after single annihilation) wavefunction in which the contaminating quartet spin state of the UHF wavefunction had been annihilated [10]. It is reassuring to note that recent work by Claxton and Weiner [11] on hydrocarbon radicals has shown that spin densities calculated using the UHFAA method are of comparable accuracy to those obtained using the much more time consuming SCF configuration interaction (SCFCI) and multi-configuration SCF (MSCF) methods.

The calculations reported here have employed both STO's and Gaussian functions. For the calculations based on STO's the Multicentre Gaussian Expansion (MGE) method [12, 28] has been employed. In this method, all one-electron integrals are computed exactly (in the Slater basis) by the use of analytical or C-function techniques. Two electron integrals involving the overlaps of two monocentric charge distributions are also calculated by the use of analytical of C-function techniques. The remaining repulsion integrals are computed via the Gaussian expansion method [15] employing an expansion of 3 GTO/STO. Trial calculations on a number of small molecules have shown that the use of this expansion technique to evaluate repulsion integrals leads to the following levels of error in the resultant mean values of one electrons operators: r^2 : <0.1%; r : 0.2%; r^{-1} : 0.1%; r^{-3} : 1%. The level of error in the calculated total energy is even lower – about 1 in 5000. These errors are significantly lower than those resulting from the limited size of the basis (and of course lower than those arising from the inadequate treatment of correlation in the Hartree Fock formulation).

The exponents [29] used for the STO's were:

$$\text{Nitrogen:} \quad \xi_{1s} = 6.6652, \quad \xi_{2s} = 1.9236, \quad \xi_{2p} = 1.9170.$$

$$\text{Fluorine:} \quad \xi_{1s} = 8.6501, \quad \xi_{2s} = 2.5639, \quad \xi_{2p} = 2.5485.$$

Hereafter, this STO set is referred to as the S basis set.

Three Gaussian lobe basis sets were used, two which have been shown [13] to be of minimal basis Slater accuracy and one of double zeta accuracy. A summary of these basis sets is as follows:

(a) The LG basis set consists of a five component $1s$ function, a three component $2s$ function and a three component $2p$ function. The exponents and coefficients were obtained from Stewart's work [14], the final exponents being obtained after the usual scaling procedure [15] (multiply Stewart's exponent

Table 1. LW basis set $2p$ functions

Nitrogen			Fluorine		
Coefficients	Exponents	Distances[a]	Coefficients	Exponents	Distances[a]
11.4992	0.3271	0.0525	11.1035	0.5174	0.0417
7.3312	1.6332	0.0235	7.8209	2.7128	0.0182
1.2518	9.9557	0.0095	1.4534	16.5056	0.0074

[a] All distances in atomic units.

by ξ^2 where ξ is the relevant STO exponent). The distances of the lobe centres from the orbital centre were obtained using the relation $R = 0.03\,\alpha^{-\frac{1}{2}}$ [16] where R is the required distance and α is the Gaussian exponent. We have shown that this basis set may be regarded as identical to the corresponding cartesian Gaussian set for molecular calculations [17].

(b) The LW basis set employs the same s functions as the LG set but the three component $2p$ function was obtained by a least squares fit to a five component lobe function of double zeta accuracy [18]. The values of the exponents, coefficients and lobe distances for the p functions are given in Table 1. This basis set has been shown in calculations on small polyatomic molecules [13] to produce one-electron expectation values which are generally closer to the experimental values than those produced by the LG set.

(c) The W basis set consists of the large Gaussian lobe basis set produced by Whitten [18] and is of double zeta STO accuracy [19].

For the geometrical model of NF_2 we have chosen, from the small amount of experimental work available [3], an NF bond length of 1.37 Å (137 pm) and an angle of 103°.

Results and Discussion

The ground state of NF_2 is ${}^2B_1$ [20]. If electrons of opposite spin are paired in spatial orbitals of the same symmetry we obtain, for all calculations, the following ground state configuration:

$$(1a_1)^2\,(1b_2)^2\,(2a_1)^2\,(3a_1)^2\,(2b_2)^2\,(4a_1)^2\,(1b)_1)^2\,(5a_1)^2\,(3b_2)^2\,(1a_2)^2\,(4b_2)^2\,(6a_1)^2\,(2b_1)^1\,.$$

This pairing of electrons has merit in providing a conceptually simple picture, however, it negates the major advantage of the UHF method in allowing the use of different orbitals for different spins.

Fig. 1 is a diagram of the spatial orbital energies for the two spin sets, calculated with the W basis set. It is significant that molecular orbitals (MO) of the same symmetry often have quite different energies and may be concentrated in different regions of space. This is best shown by the π-type $1b_1$ MO, which is noticeably more stable (by 0.0994 a.u.) for the α-electron spin set than for the β-electron spin set. The $1b_1$ MO coefficients for each spin set are recorded in Table 2 and show that the α-electron distribution is very different to the β-electron distribution with the latter closer to the fluorine nucleus. Thus although the overall charge
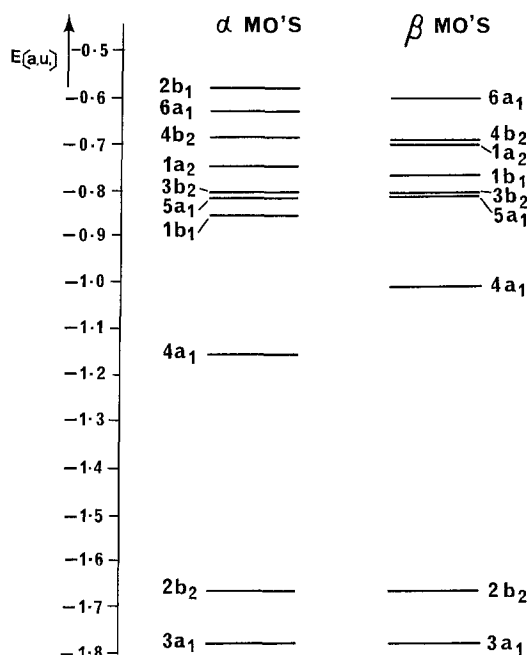
Fig. 1. UHF energy levels of NF_2 calculated with the W basis set

Table 2. The $1b_1$ MO coefficients in NF_2 with the W basis set

Spin set	Coefficients	
	C_1 [a]	C_2^a
α set	0.5637	0.4937
β set	0.2338	0.6435

[a] $\chi(1b_1) = C_1 p_x(N) + C_2(p_x(F_1) + p_x(F_2))$.

Table 3. Total energy of the NF_2 molecule (in a.u.)

Energy	Basis set			
	S	LG	LW	W
E	−252.1476	−251.7269	−252.4081	−253.0485
ΔE[a]	−0.4207	—	−0.6812	−1.3216

[a] ΔE is the amount by which the energy from each set is lower than that from the LG set.

distribution may not be significantly altered by allowing extra MO freedom (as in the UHF method), the spin distribution may be quite radically changed.

Total energies are reported in Table 3 for each basis set and, as expected, the large double zeta W basis set gives the lowest energy. However, care must be exercised in using the total energy to judge the accuracy of a wavefunction; we prefer to use the calculated one-electron properties as the criteria.

Table 4. One-electron charge properties for NF$_2$

Property[a]	Basis set			
	S	LG	LW	W
$\langle z_N \rangle^e$ [a.u.]	28.7505	28.8092	29.0646	29.0627
$\langle z_N \rangle^n$	29.0084	29.0084	29.0084	29.0084
$\langle z_N \rangle^t$	0.2579	0.1992	$-$ 0.0562	$-$ 0.0543
μ [Debye]	0.656	0.506	$-$ 0.143	$-$ 0.138
$\langle x^2 \rangle^b$ [a.u.]	9.2655	9.2878	10.4691	11.0562
$\langle y^2 \rangle$	83.7116	83.7732	85.6371	86.3073
$\langle z^2 \rangle$	23.6076	23.4904	24.5267	25.1170
$\langle r^2 \rangle$	116.5847	116.5514	120.6329	122.4806
χ_{av}^d [10^{-6} emu mole^{-1}]	$-$ 92.3337	$-$ 92.3073	$-$ 95.5398	$-$ 97.0032
$\theta_{xx} e$ [a] [10^{-26} esu cm^2]	59.7064	59.6391	60.8471	60.0586
$\theta_{xx} n$	$-$ 58.5006	$-$ 58.5006	$-$ 58.5006	$-$ 58.5006
$\theta_{xx} t$	1.2058	1.1385	2.3465	1.5580
$\theta_{yy} e$	$-$ 90.4796	$-$ 90.6264	$-$ 92.6916	$-$ 91.7514
$\theta_{yy} n$	90.5795	90.5795	90.5795	90.5795
$\theta_{yy} t$	0.0999	$-$ 0.0469	$-$ 2.1122	$-$ 1.1720
$\theta_{zz} e$	30.7730	30.9872	31.8443	31.6927
$\theta_{zz} n$	$-$ 32.0787	$-$ 32.0787	$-$ 32.0787	$-$ 32.0787
$\theta_{zz} t$	$-$ 1.3057	$-$ 1.0915	$-$ 0.2346	$-$ 0.3860
$\langle r_N^{-1} \rangle$ [a.u.]	25.0876	25.0460	24.9339	24.9342
$\sigma_{av}^d(N)$ [ppm]	445.3	444.6	442.6	442.6
$\langle r_F^{-1} \rangle$	31.3524	31.2767	31.3884	31.4379
$\sigma_{av}^d(F)$	556.5	555.2	557.1	558.6
Q_N [c]	0.08	0.08	0.32	0.36
Q_F	$-$ 0.04	$-$ 0.04	$-$ 0.16	$-$ 0.18

[a] $e =$ electronic contribution, $n =$ nuclear contribution, $t =$ total contribution.
[b] Refered to the centre of mass.
[c] Mulliken net charges.

Table 5. Molecular quadrupole moments for molecules related to NF$_2$ [a]

	θ_{xx} [b]	θ_{yy}	θ_{zz}
OF$_2$ [c]	$-(0.5 \pm 1.9)$	$-(1.6 \pm 1.4)$	(2.1 ± 1.0)
O$_3$ [c]	(7.9 ± 7.9)	$-(17.1 \pm 5.2)$	(9.2 ± 4.7)
NO$_2$ [d]	2.17	$-$ 3.65	1.48

[a] In units of 10^{-26} esu $\cdot$ cm^2.
[b] Axis system is same as for NF$_2$ (see Fig. 6).
[c] Experimental values.
[d] Ref. [1a].

To simplify the discussion of the electronic structure of NF$_2$, the calculated one-electron properties have been divided into two sections, namely, those dependent on the total charge density matrix and those dependent on the spin density matrix. The former properties are recorded in Tables 4–6 and the latter properties in Tables 7–9. All charge properties have been calculated using both

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Table 6. Field gradients and quadrupole coupling constants for NF$_2$

Property	Basis set			
	S	LG	LW	W
$q_{xx}(N)$[a]	−0.3905	−0.4257	−0.8633	−0.8554
$q_{yy}(N)$	0.8228	0.7729	1.2809	1.3067
$q_{zz}(N)$	−0.4323	−0.3472	−0.4176	−0.4514
$\chi_{xx}^{Q}(N)$[b]	−1.3488	−1.4703	−2.9819	−2.9545
$\chi_{yy}^{Q}(N)$	2.8420	2.6696	4.4242	4.5136
$\chi_{zz}^{Q}(N)$	−1.4932	−1.1993	−1.4424	−1.5591
$q_{xx}(F)$[a]	−1.9944	−1.7672	−2.2118	−2.2458
$q_{yy}(F)$	1.7424	1.6200	2.0558	2.0405
$q_{zz}(F)$	0.2518	0.1472	0.1560	0.2053
$q_{yz}(F)$	3.2104	2.8099	3.5209	3.6132

[a] Total field gradient in a.u.
[b] In MHz with nuclear quadrupole moment

$Q(N) = 1.47 \times 10^{-26}$ esu · cm^2.

Table 7. Isotropic spin properties for NF$_2$

Property	Basis set								Expt.
	S		LG		LW		W		
	UHF	UHFAA	UHF	UHFAA	UHF	UHFAA	UHF	UHFAA	
$\langle S^2 \rangle$	0.7690	0.7502	0.7631	0.7501	0.7596	0.7501	0.7613	0.7501	0.7500
$\varrho(O)$ N [a.u.$^{-3}$]	0.2362	0.0816	0.1432	0.0492	0.1555	0.0532	0.1366	0.0472	
$\varrho(O)$ F [a.u.$^{-3}$]	0.0926	0.0321	0.0683	0.0235	0.0627	0.0215	0.0903	0.0311	
A_N [MHz]	76.2889	26.3616	46.2624	15.8924	50.2110	17.1890	44.1212	15.2382	45.1[a]
A_F [MHz]	389.4319	135.1151	287.2509	99.0039	263.8497	90.4839	379.6799	130.6276	168.8

[a] Ref. [6].

Table 8. Spin polarization and spin delocalization contributions to the total spin density in NF$_2$ for the W basis set calculations

	ϱ_{Total}	ϱ_{SP}	ϱ_{SD}
ϱ^N_{UHF}	0.1366	0.1341 (98 %)[a]	0.0025 (2 %)
$\varrho^{N\;b}_{aa}$	0.0472	0.0447 (95 %)	0.0025 (5 %)
ϱ^F_{UHF}	0.0903	0.0888 (98 %)	0.0015 (2 %)
ϱ^F_{aa}	0.0311	0.0296 (95 %)	0.0015 (5 %)

[a] % contribution to total spin density i.e. $\dfrac{\varrho_{SP}}{\varrho_{Total}} \times 100$.

[b] aa = after annihilation; Ref. [10].

Table 9. Anisotropic spin properties for NF$_2$

Component	Basic set								Expt. [b]
	S		LG		LW		W		
	UHF	UHFAA	UHF	UHFAA	UHF	UHFAA	UHF	UHFAA	
$T_{xx}(N)$[a]	62.0502	65.2756	56.7861	59.1935	84.1903	86.8772	86.3527	89.4633	90.3
$T_{yy}(N)$	− 29.5530	− 32.1280	− 27.4107	− 29.2580	− 40.5467	− 42.9304	− 41.7926	− 44.2667	− 45.1
$T_{zz}(N)$	− 32.4972	− 33.1476	− 29.3754	− 29.9355	− 43.6436	− 43.9467	− 44.5600	− 45.1966	− 45.1
$T_{xx}(F)$	274.1254	200.1356	241.1852	186.1943	353.8130	299.3238	389.1121	310.6073	425.6
$T_{yy}(F)$	−162.8328	−104.3112	−139.9636	− 95.3584	−206.4200	−155.5809	−224.2910	−161.1502	−212.8
$T_{zz}(F)$	−111.2927	− 95.8244	−101.2216	− 90.8359	−147.3939	−143.7429	−164.821	−149.4571	−212.8
$T_{yz}(F)$	−141.8653	− 29.1633	− 98.3980	− 15.4896	−131.2122	− 27.6945	−152.0354	− 33.4644	

[a] Units MHz.

[b] Experimental values, from Ref. [6], are within ±0.5 %.

the UHF and UHFAA wavefunctions but only the UHF results are tabulated since annihilation is found to cause insignificant changes. The properties were calculated using computer programs which were written by us and thoroughly tested [28, 31, 32].

Simple Picture of the Electronic Distribution of NF_2

In an attempt to obtain a simple orbital picture of NF_2 we have localized the α- and β-electron sets of MO's obtained from the UHF calculation. The localization method used was that proposed by Foster and Boys [21] and involves maximizing the squares of the distances of the orbital centroids from each other.

The most interesting result obtained by using the local orbitals is the arrangement of the electrons around the nitrogen atom. In terms of simple valence theory the structure would be written as depicted in Fig. 2, were only the valence electrons are considered. The localized orbital picture gives a very similar structure and shows the arrangement of the three non-bonding electrons around nitrogen very clearly. The electrons are arranged as shown in Fig. 3. The two electrons with α spin occupy orbitals that are directed out of the molecular plane while the electron with β spin is in an orbital lying between those of the two α-electrons and concentrated in the molecular plane. This simple picture is appealing in that it allows for spin polarization in spreading the two α-electrons further apart than suggested by the simple valence structure.
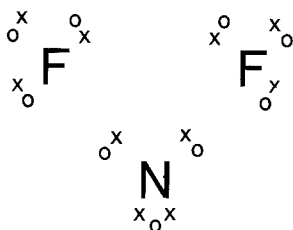

Fig. 2. Simple valence bond electron distribution for NF_2
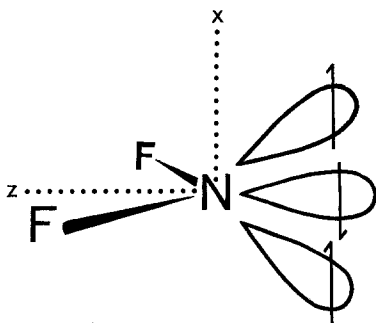

Fig. 3. Schematic diagram of the localized orbitals in NF_2 showing the three non-bonding electrons on nitrogen

Dipole Moment

Table 4 records the electronic contribution to mean z at nitrogen ($\langle z_N \rangle$) and the dipole moment (μ) for each basis set; note that the dipole moment is very sensitive to changes in basis set. Values calculated with the S and LG basis sets are in close agreement with one another, which might have been expected from our previous work [17] where we demonstrated that results obtained with LG basis sets are of comparable accuracy to calculations with equivalent cartesian Gaussian basis sets known to be of minimal basis Slater accuracy.

Note also that the S and LG basis set calculations give the dipole moment with the positive end towards the fluorine as in Fig. 4 (a), while the LW and W basis sets predict a small dipole in the opposite direction as in Fig. 4 (b).

Fig. 4 a and b. Dipole moment directions for NF$_2$ (arrow points towards the positive end of the dipole). a Direction calculated with the S and LG basis sets. b Direction calculated with the LW and W basis sets

Pople has performed both CNDO/2 and INDO calculations on NF$_2$ [2b] and obtains dipole moments of magnitude $0.12 D$ and $0.38 D$ respectively, both in the same direction as the LW and W predictions, while Del Bene [2a], using an expansion set of three Gaussian functions per STO, calculates a dipole moment of $0.49 D$ in the opposite direction.

From these calculations we see that the overall value of the electronic contribution $\langle r \rangle^e$ (which in turn decides the magnitude and direction of μ after combination with the nuclear contribution $\langle r \rangle^n$) is dependent on quite small and subtle changes in the electron distribution due to the bonding between the atoms.

$\langle r^2 \rangle$, average diamagnetic susceptibility, molecular quadrupole moment

The second moments of the electronic charge distribution $\langle x^2 \rangle$, $\langle y^2 \rangle$, $\langle z^2 \rangle$ and $\langle r^2 \rangle$, referred to the centre of mass, give a measure of how diffuse or compact the charge distribution is in each direction. From the results in Table 4 the W basis set gives a charge distribution which is more diffuse than that given by the smaller basis sets. The S and LG basis sets again give quite comparable results while the LW basis set predicts values which are between those given by W and S basis sets.

On the basis of previous work in which the LW basis set has been shown to give quite accurate values for the average diamagnetic susceptibility, χ_{av}^d [13], we predict the value of -95.5×10^{-6} emu mole^{-1} as the most probable experimental result.

Molecular quadrupole moments, denoted θ_{xx}, θ_{yy}, θ_{zz}, measure the deviation of the change distribution from spherical symmetry by calculating the difference between an electronic and a nuclear contribution. They have been shown to be extremely sensitive to the accuracy of the wavefunction and hence the choice of basis set [19, 22]. This sensitivity to the basis set is noted in the results for θ_{xx}, θ_{yy} and θ_{zz} recorded in Table 4. Thus, while all basis sets give an approximately

prolate spheroidal shape (elongated in the y direction) for the electronic distribution of NF_2, the more contracted electronic charge given by the S and LG basis sets when combined with the nuclear contribution gives a quite different result for the molecular quadrupole moments than is given by the LW and W basis sets.

To assist in determining the most likely experimental values of θ_{xx}, θ_{yy} and θ_{zz} we have recorded in Table 5 the relevant experimental values for OF_2 and O_3 together with the results from a near Hartree-Fock calculation on NO_2 [1a]. In each of these related molecules θ_{yy} is negative, indicating an excess of negative charge in the y direction. If this trend is maintained in NF_2 we expect the LW and W basis set values to be the best predictions of the experimental results.

$\langle r^{-1} \rangle$, Diamagnetic Nuclear Shielding

The potential at the nuclei are given in Table 4, together with the corresponding values of the average diamagnetic shielding constant (σ_{av}^{d}).

Since this property is closely coupled to the energy one would expect the larger basis calculation, which gives the lowest energy 1.3216 a.u. or 0.5%, to produce the most reliable values of $\langle r^{-1} \rangle$ and σ_{av}^{d} at each nucleus.

$\langle r^{-1} \rangle$ may be interpreted as the electronic contribution to the potential at a particular nucleus. The total potential $\Phi(n)$ at nucleus n is given by:

$$\Phi(n) = -\langle r_n^{-1} \rangle + \sum_{k \neq n} \frac{Z_k}{R_{kn}}$$

where
$$Z_k = \text{charge of nucleus } k,$$

$$R_{kn} = \text{distance of nucleus } k \text{ from } n$$

and may be used as a measure of the atomic environment of atom n [23]. For example, the less negative the potential, the more positive the average atomic environment. In using the calculated $\langle r^{-1} \rangle$ data note that the nuclear contribution will be the *same* for each calculation and thus the *larger* the magnitude of $\langle r^{-1} \rangle$ the more *negative* is the atomic environment.

The $\langle r^{-1} \rangle$ values at the nitrogen nucleus indicate that the environment is calculated most negative by the S basis set and more positive by the LW and W basis sets. This trend is also given by the net charge on nitrogen (Q_N) calculated from the Mulliken population analysis (see Table 4).

At the fluorine atoms the average atomic environment predicted by each basis set is in qualitative agreement with that given by the net changes (Q_F). Thus fluorine is predicted to be most negative by the W basis set.

$\langle r^{-3} \rangle$, the Electric Field Gradient and Quadrupole Coupling Constant

The components of the field gradient tensor ($q_{\alpha\beta}$) at both nitrogen and fluorine are reported in Table 6 together with the quadrupole coupling constants at nitrogen ($\chi_{\alpha\beta}^{Q}$). For nitrogen all basis sets predict the same trends for $q(N)$ and $\chi^Q(N)$. These quantities are negative in the out-of-plane x direction and in the z direction, and positive in the y direction.

The magnitude of $\chi_{xx}^{Q}(N)$ and $\chi_{yy}^{Q}(N)$, calculated using the LW and W basis sets, are approximately twice those obtained with the S basis set, while the value

of $\chi_{zz}^Q(N)$ is almost the same for all three basis sets. The difference between the S basis set and the LW and W basis sets is probably in the description of the α-electron distribution around the nitrogen atom.

From Table 6 the agreement between the calculated field gradient tensor elements at fluorine is closer than is the case at nitrogen. This presumably indicates that the charge asymmetry around the fluorine atoms is less influenced by the basis set.

Importance of the Representation of the 2p Function

A wide variation in the calculated one-electron properties is noted for the LG and LW basis sets. Since these two basis sets only differ in their representation of the 2p function, we see the importance of this function in accounting for the asymmetry of the charge distribution. Fig. 5 is a plot of the nitrogen 2p functions from each basis set. A Hartree-Fock (HF) 2p function [24] is also plotted for comparison. The curves for fluorine produced the same trends. Similar curves are noted for the LW and W basis set 2p functions but the curves differ from those representing the S and LG 2p functions both close to the nucleus and at distances far from it.

The greater reliability of the one-electron property values calculated with the double zeta accuracy W basis set, coupled with the very close resemblance between the 2p function from this basis set and the HF 2p function, suggests the desirability of using double zeta accuracy 2p functions for molecular calculations.
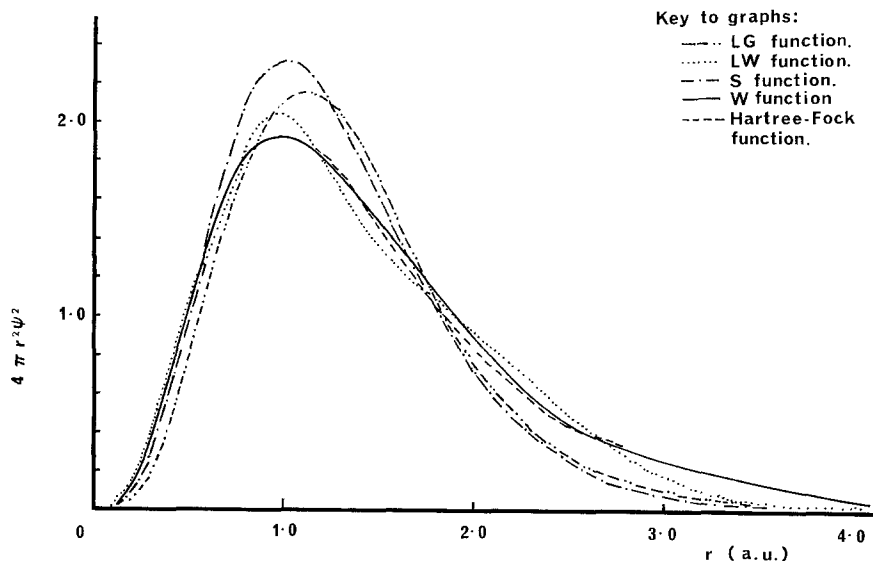

Key to graphs:
—··· LG function.
······· LW function.
—·— S function.
——— W function
- - - - Hartree-Fock function.

Fig. 5. Graphical comparison of the 2p-functions from the different basis sets used in calculations on NF$_2$

Spin Dependent Properties

The microwave spectrum of NF$_2$ shows hyperfine structure from the interaction of the electron spin with both the nitrogen and the fluorine nuclear spins.

To assist in the interpretation of the hyperfine structure we have calculated the isotropic coupling constants at each nucleus, $(A_N, A_F,$ or Fermi contact term) and the anisotropic coupling constant tensor $(T_{xx}, T_{yy}, T_{zz},$ etc. or dipole-dipole term). The coupling constants derived from both the UHF and UHFAA wavefunctions are reported for each basis set to indicate the sensitivity of these terms to spin contamination in the wavefunction.

The results reported in Table 7 show that annihilation of the contaminating quartet spin state reduces the spin density $\varrho(O)$, and hence the isotropic coupling constant at each nucleus, by around one third. This change occurs with all four basis sets.

To explain this observation we make use of a recent analysis of the UHF wavefunction [25–27] which allows the computed spin density to be separated into components arising from the spin polarization and spin delocalization mechanisms. Spin polarization is the production of spin density due to correlation between electrons while spin delocalization is the spin density which would be due to the singly occupied orbital in a restricted HF wavefunction.

The spin polarization (SP) contributions to the spin density for the UHF and UHFAA (denoted here aa) wavefunctions, are given by:

$$(\varrho_{UHF}^A)_{SP} = \tfrac{3}{2}(\varrho_{UHF}^A - \varrho_{aa}^A),$$
$$(\varrho_{aa}^A)_{SP} = \tfrac{1}{2}(\varrho_{UHF}^A - \varrho_{aa}^A).$$

The corresponding spin delocalization (SD) contributions are obtained from the general expression:

$$(\varrho^A)_{SD} = \varrho^A - (\varrho^A)_{SP}.$$

Note that when only the SP mechanism is important we have

$$\varrho_{UHF}^A = 3\,\varrho_{aa}^A.$$

The W basis set UHF and UHFAA wavefunctions have been analysed for the SP and SD contributions to the spin density and the results are given in Table 8. It is evident that the majority of the spin density at both the nitrogen and fluorine atoms arises from the SP mechanism giving the expected reduction of spin density on single annihilation of the UHF wavefunction. The dominance of the SP mechanism in π-radicals has been shown previously [28].

Note also from Table 7 that the isotropic coupling constants calculated with the S basis set (UHFAA results) are in closest agreement with the experimental values. This result is not unexpected since the isotropic constants are dependent upon the square of the wavefunction at the nucleus (predominantly the $1s$ functions) and it is well known that Gaussian functions give a less accurate representation in this region.

The higher spin density on the nitrogen atom is consistent with the simple pictures of the unpaired electron being essentially centred on this atom.

The anisotropic coupling constants, recorded in Table 9, are not as significantly affected by the application of a single annihilator to the UHF wavefunction as are the isotropic coupling constants; however the absolute magnitudes of the anisotropic coupling constants at nitrogen are increased slightly while at fluorine they are decreased substantially after annihilation of the UHF wavefunction.

As the T values are dependent on the asymmetry of the spin density around the nucleus and therefore most influenced by the $2p$ orbital populations, these results are possibly due to annihilation of the quartet spin state allowing spin density to be transferred from the fluorine $2p$ orbitals to the nitrogen $2p$ orbitals.

The theoretical values obtained for the anisotropic tensor at nitrogen, with all four basis sets, correctly predict the relative signs and magnitudes of the diagonal elements. The double zeta accuracy W basis set gives excellent agreement with the experimental values while the values from the S basis set are in error by about 30%. Note that the largest anisotropic coupling constant in NF$_2$ is the out-of-plane T_{xx} element and that the tensor is almost axially symmetric (i.e. $|T_{yy}| \simeq T_{zz}| \simeq \frac{1}{2} T_{xx}$). These results are due to the unpaired electron mainly residing in the $2p_x$ orbital on nitrogen.

e.s.r. data are available for the anisotropic coupling at the fluorine atom in NF$_2$ and are tabulated, together with the theoretically calculated values, in Table 9. Note that the tensor elements are quoted in terms of the molecular axis system and not the principal axis system of the tensor. The "experimental" values for T_{yy} and T_{zz} are quoted as being equal because there is insufficient information available from the e.s.r. experiment (the magnitude of the T_{yz} component is needed) to enable explicit values to be assigned to these elements.

It is evident that the anisotropic coupling constants calculated with the LW and W basis sets are in much better agreement with experiment than those values calculated with the S and LG basis sets. This indicates the sensitivity of the anisotropic coupling tensor to the $2p$ function chosen in the basis; for fluorine it appears that single exponent STO's are inadequate and one needs to use at least double zeta accuracy $2p$ functions to correctly describe the anisotropy of the charge distribution around the fluorine atom.

An interesting aspect of single annihilation on UHF wave-functions is the effect on the principal axis directions for the anisotropic coupling constant tensor at fluorine. From Fig. 6 we see that one principal axis is almost along the N–F bond and that this axis is rotated by around 3.5° (for the W basis set results) after annihilation. Thus we have another indication of the sensitivity of the electron spin distribution to single annihilation.
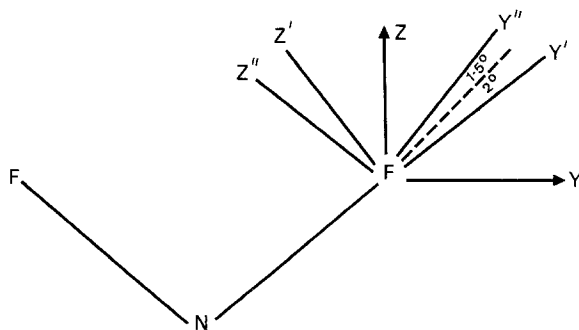

Fig. 6. Axis systems for NF$_2$. (X, Y, Z) coordinate axis system. (X', Y', Z') principal axis system for UHF calculated anisotropic coupling tensor. (X'', Y'', Z'') principal axis system for UHFAA calculated anisotropic coupling tensor. $X = X' = X''$ out of plane axis

Conclusion

The calculations we have performed on the NF_2 radical, using four different basis sets, underline the importance of a flexible $2p$ function for describing the asymmetry of the electronic distribution. The LW and W Gaussian function basis sets, which have near double zeta accuracy $2p$ functions, are found to give more reliable values for most one-electron properties than does a single STO basis set.

The accuracy of the predicted properties derived from any gaussian basis set depends upon the reliability of that basis set in the appropriate region of space. For instance, predictions of the isotropic spin parameters, A, are less reliable since they depend on the value of the wavefunction at the various nuclei and only large, carefully chosen representations of the $1s$ functions will achieve consistent accuracy. Presumably this inaccuracy in the representation of the $1s$ functions near the nuclei is also the cause of the large variation in the A values upon annihilation.

Thus we recommend the following one-electron properties as being the best theoretical predictions to date:

$$\chi_{av}^d = -95.5 \times 10^{-6} \text{ emu mole}^{-1}; \quad \theta_{xx} = 1.6, \theta_{yy} = -1.2,$$

$$\theta_{zz} = -0.4 \text{ in units of } 10^{-26} \text{ esu cm}^{-2}; \quad \sigma_{av}^d(N) = 442.6 \text{ ppm},$$

$$\sigma_{av}^d(F) = 558.6 \text{ ppm}; \quad \chi_{xx}^Q(N) = -2.95 \text{ MHz}, \chi_{yy}^Q = 4.51 \text{ MHz},$$

$$\chi_{zz}^Q = -1.56 \text{ MHz}.$$

The dipole moment is uncertain since it is predicted to be $-0.14D$ by the LW and W Gaussian basis sets and $+0.66D$ by the STO basis set (see Fig. 2). In view of the generally poor representation of the fluorine atom by STO's, the value given by the Gaussian basis sets is possibly more reliable. It seems there may be a near cancellation of oppositely directed lone "pair" and bond moments.

Single annihilated UHF wavefunctions, from the LW or W basis sets, give an accurate representation of the anisotropic coupling constants at both the nitrogen and fluorine atoms. However, rather poor agreement with the experimental isotropic coupling constants was found with all basis sets.

Thus this investigation of the NF_2 radical indicates that, providing a good quality basis set is used, the single annihilated UHF method can provide values for most charge and spin dependent observable properties of open shell molecules.

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