

THE EFFECT OF SYMMETRY RESTRICTIONS
UPON THE HYPERFINE PROPERTIES *

P. JEFFREY HAY[‡] and W. A. GODDARD III[‡]

*Arthur Amos Noyes Laboratory of Chemical Physics †,
California Institute of Technology, Pasadena, California 91109, USA*

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The effect of spatial symmetry restrictions upon the calculated values of the hyperfine splitting constants is examined and results are reported for B, C, O and F. It is found that, if no symmetry restrictions are placed upon the unrestricted Hartree-Fock orbitals, the resulting hyperfine constants (except spin densities) are in good agreement with experiment and with configuration interaction calculations. Nuclear magnetic moments and quadrupole moments are reported on the basis of these calculations and the observed hyperfine structure.

1. INTRODUCTION

The nuclear hyperfine interactions provide an important means of measuring the properties of nuclear and electronic charge distributions. The magnetic hyperfine interaction is proportional to the product of the nuclear dipole moment, μ_N , and the electronic magnetic field at the nucleus B_e while the electric hyperfine interaction is proportional to the product of the nuclear quadrupole moment Q_N , and the electric field gradient at the nucleus, q_e . Since the determination of μ_N and Q_N from the hyperfine structure depends very much on the accuracy of the theoretical calculation of B_e and q_e , a great deal of attention has been given to the theoretical treatment of these properties. Unfortunately even for the small atoms B, C, N, O and F the various theoretical treatments often disagree by 10% or more [1-6]. The most popular approach to these properties has been the unrestricted Hartree-Fock (UHF) method, although it sometimes does quite poorly for these properties [3, 4]. For smaller atoms, configuration interaction (CI) has led to a better description of these properties [1, 2] but such calculations may require a great deal more work than UHF.

In the usual treatment of UHF for an atom each orbital is allowed to be different but is still required to be a symmetry function. We show

here that by relaxing all symmetry restrictions on the orbitals in UHF one obtains hyperfine quantities often in as good agreement with experiment as the results from CI calculations. The occurrence of symmetry splitting in the orbitals of GF and SOGI wavefunctions was previously noted by Goddard [7] for Be, by Blint et al. [8, 9] for B and BH, and by Guberman and Goddard [10] for O and OH. Upon completion of the work reported here a paper by Larsson appeared reporting similar symmetry splittings for the UHF wavefunctions of Li and B [11].

2. THE PERTURBATION EQUATIONS

The hyperfine properties of interest here are determined by the first-order change in the energy, E^1 , due to some perturbation, \mathcal{H}^1 . Here E^1 is given by

$$E^1 = \langle \Psi^0 | \mathcal{H}^1 | \Psi^0 \rangle + 2\text{Re} \langle \Psi^1 | (\mathcal{H}^0 - E^0) | \Psi^0 \rangle, \quad (1)$$

where \mathcal{H}^0 is the zero-order many-electron hamiltonian and Ψ^0 and E^0 are the zero-order wavefunction and energy, respectively (we have taken Ψ^0 to be normalized). Since

$$(\mathcal{H}^0 - E^0) \Psi^0 = 0 \quad (2)$$

for the exact zero-order wavefunction, we obtain

$$E^1 = \langle \Psi^0 | \mathcal{H}^1 | \Psi^0 \rangle \quad (3)$$

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and hence only the zero-order wavefunction is required for evaluating first-order properties.

Unfortunately, except for the hydrogen atom, we do *not* have the exact solution Ψ^0 to (2) but rather some approximation, Ψ_{approx}^0 . Hence (3) is not really the correct equation for E^1 when Ψ_{approx}^0 is used. However, (1) requires Ψ^1 and hence a solution of the first-order equations

$$(H^0 - E^0)\Psi^1 + (H^1 - E^1)\Psi^0 = 0 \quad (3')$$

and thus is far more difficult to evaluate than is (3).

On the basis of several calculations, it appears that for some hyperfine quantities, (1) and (3) may differ by 10% when using restricted Hartree-Fock and other similarly restricted wavefunctions. *If no symmetry or equivalence restrictions are made upon the orbitals, however, such simple wavefunctions as UHF have the property that the second term of (1) is zero, even though Ψ_{approx}^0 is not a solution of (2).*

3. THE UNRESTRICTED HARTREE-FOCK METHOD

In the Hartree-Fock method we consider a Slater determinant of spin orbitals,

$$\mathcal{A}(\psi_1\psi_2\dots\psi_N) \equiv \mathcal{A}\Phi \quad (4)$$

(where \mathcal{A} is the antisymmetrizer ‡ or determinant operator) and require that the orbitals $\{\psi_i\}$ each be optimum. The resulting variational condition is that the first-order energy be zero under all variations of each orbital †,

$$\delta_i E = \langle \Phi_i \delta\psi_i | \mathcal{H} - E^0 | \mathcal{A}\Phi \rangle = 0, \quad (5)$$

where Φ_i indicates the orbital product Φ but with orbital ψ_i deleted.

Eq. (5) can be rewritten as

$$\langle \delta\psi_i | (H^{\text{UHF}} - \epsilon_i) | \psi_i \rangle = 0, \quad (6)$$

where

$$H^{\text{UHF}} = -\frac{1}{2}\nabla^2 - \frac{Z}{r} + \sum_j (J_j - K_j) \quad (7)$$

‡ The antisymmetrizer is defined here as

$$\mathcal{A} = \sum_P \xi_P \hat{P},$$

where the sum is over all $N!$ permutations, P , and ξ_P is the parity of P .

† For UHF all orthonormality constraints can be removed by using the form (5).

for an atom of charge Z ; here J_j and K_j are just the usual Coulomb and exchange operators. Since (6) must be true for all $\delta\psi_i$, the UHF equations are often written as

$$H^{\text{UHF}}\psi_i = \epsilon_i\psi_i. \quad (8)$$

If we now consider a one-electron perturbation \mathcal{H}^1 ,

$$\mathcal{H}^1 = \sum_{i=1}^N h^1(i), \quad (9)$$

such as the hyperfine interaction, and take Ψ^0 of (1) to be (4), we see that Ψ^1 can be expressed as a sum of single excitations from Ψ ,

$$\Psi^1 = \sum_{i=1}^N \mathcal{A}[\Phi_i\psi_i^1(i)]. \quad (10)$$

In this case the second term of (1) becomes

$$\langle \Psi^1 | (\mathcal{H}^0 - E^0) | \Psi^0 \rangle = \sum_i \langle \Phi_i\psi_i^1 | \mathcal{H}^0 - E^0 | \mathcal{A}\Phi^0 \rangle = 0 \quad (11)$$

since (5) must be zero for any $\delta\psi_i$ including $\delta\psi_i = \lambda\psi_i^1$. Thus for the UHF wavefunction E^1 is given by the usual simple form (3).

4. ORBITAL RESTRICTIONS

If one arbitrarily excludes certain variations $\delta\psi_i$ in determining the orbitals ψ_i of Ψ^0 eqs. (6) and (11) may not hold for all possible single excitations and hence one is not justified in using (3) to evaluate first-order properties. Such an example would be the restricted Hartree-Fock (RHF) method where one requires the spatial parts of the closed shell spin orbitals to be equal in pairs.

For a perturbation, \mathcal{H}^1 , which is not spherically symmetric the solution ψ^1 of the first order equation (3') will contain single excitations involving angular momentum changes. If the orbitals of Ψ^0 were restricted to be pure spatial symmetry functions (e.g., s or p functions) or if all p orbitals were restricted to have equivalent radial functions, once again the use of (3) would be invalid. [The former restriction above will be referred to as the L-restricted UHF method and denoted as UHF(LR); the latter restriction involving equivalence will be denoted as UHF(LR, EQ).]

‡ This result is often referred to as Brillouin's theorem.

Such effects become important in hyperfine interactions where one is dealing with the non-spherically symmetric nuclear quadrupole,

$$h_q^1 = Q_N P_{20} / r^3 \quad (12)$$

spin-dipole,

$$h_{sd}^1 = \mu_N P_{20} \hat{s}_z / r^3 \quad (13)$$

and orbital-dipole

$$h_{od}^1 = \mu_N \hat{l}_z / r^3 \quad (14)$$

operators. In the case of the nuclear quadrupole interaction, the well-known Sternheimer correction [13] † is a first-order correction to the second term of (1) for RHF wavefunctions. From the above discussion we see that the simplest wavefunction for which (3) may always be used to evaluate hyperfine constants is UHF with *no orbital restrictions on the spatial orbitals*.

The other common restriction on UHF spin orbitals is to take each spin orbital ψ_i to be the product of a spatial function times either an up-spin or down-spin spinfunction. However, in this case (11) holds even for a general ψ_i^1 and hence (1) reduces to (3). Therefore spin factorization restrictions should not cause poor values for properties from the use of (3). Indeed, we carried out UHF calculations on B starting with general trial functions and allowing each spin orbital to be a mixture of both spin components but found no improvement in energy over the spin-factorized solutions.

4.1. The form of the UHF orbitals

For the B and C atoms, the optimum UHF wavefunctions differs from the usual UHF(LR) description in that the s orbitals have some d character. For B, if the unpaired electron is in the $p_z\alpha$ orbital, the $s\alpha$ and $s\beta$ orbitals have the forms $s + d_0$ and $s - d_0$, respectively. The O and F atoms, in addition to having d admixtures into the s orbitals, have different radial dependencies for p orbitals of the same spin, a feature that this has previously been discussed by Bessis [15]. In each case the resulting wavefunction retains axial symmetry. The UHF(LR) wavefunction for N atom was found to be stable with respect both to admixture of d symmetry into the s orbitals and differences in radial dependence of the p orbitals. The optimum UHF configurations are characterized below (all orbitals are taken to be real) †.

‡ For a full discussion of this, see ref. [14].

† In (15) the character of each orbital is indicated by its angular components. These components are not normalized. Differing radial behavior for functions

$$\begin{aligned} \text{B}(^2\text{P}): & \mathcal{A} [(s + d_0)1a(s' + d'_0)2a(p_z)3a \\ & (s - d_0)1b(s' - d'_0)2b\alpha\alpha\alpha\beta\beta]; \\ \text{C}(^3\text{P}): & \mathcal{A} [(s - d_0)1a(s' - d'_0)2a(p_x)3a(p_y)4a \\ & (s + d_0)1b(s' + d'_0)2b\alpha\alpha\alpha\beta\beta]; \\ \text{N}(^4\text{S}): & \mathcal{A} [(s)1a(s')2a(p_x)3a(p_y)4a(p_z)5a \\ & (s)1b(s')2b\alpha\alpha\alpha\alpha\beta\beta]; \\ \text{O}(^3\text{P}): & \mathcal{A} [(s - d_0)1a(s' - d'_0)2a(p_x)3a(p_y)4a(p'_z)5a \\ & (s + d_0)1b(s' + d'_0)2b(p_z)3b\alpha\alpha\alpha\alpha\beta\beta\beta]; \\ \text{F}(^2\text{P}): & \mathcal{A} [(s + d_0)1a(s' + d'_0)2a(p_x)3a(p_y)4a(p'_z)5a \\ & (s - d_0)1b(s' - d'_0)2b(p_x)3b(p_y)4b \\ & \alpha\alpha\alpha\alpha\beta\beta\beta\beta]. \end{aligned} \quad (15)$$

We see that for B and C the $s\alpha$ orbitals polarize into the same region of space as the $p\alpha$ orbitals, whereas for O and F the $s\beta$ orbitals polarize such as to move into the same region of space as the $p\beta$ orbitals (in each case the other s orbitals polarize in the opposite direction). This is just what would be expected on the basis of the attractive exchange interactions between the p orbitals and s orbitals. Thus in B the spin-up orbitals become $s + \lambda(2z^2 - x^2 - y^2)$ (with $\lambda > 0$) to concentrate nearer the $p_z\alpha$ orbital while in C they become $s - \lambda(2z^2 - x^2 - y^2)$ so as to increase the amplitude in the plane of the $p_x\alpha$ and $p_y\alpha$ orbitals.

Note that in (15) there is in each case more than one choice for the angular character of the p orbitals. For example, for B we could have replaced $p_z\alpha$ by $p_x\alpha$ or by $(p_x + ip_y)\alpha$. However, given the restriction that the wavefunction be a single Slater determinant, these choices need not be equivalent when the s orbitals are allowed to have d character †. Our choice of $p_z\alpha$ in (15) gives an energy 0.0028 hartree lower than the choice of $(p_x + ip_y)\alpha$ in ref. [11].

Another manifestation of the effect of relaxing orbital symmetry requirements can be seen in the $\langle r^2 \rangle$ values of the p orbitals of O and F (see table 1). In O, $\langle r^2 \rangle$ decreases in the order $p_z\beta > p_z\alpha > p_x\alpha, p_y\alpha$ showing that the mutual Coulomb interaction of the z orbitals makes them more diffuse but that all the spin-up orbitals are nearer the nucleus than spin-down ones.

of the same spin are indicated by primes; no special notation is used to indicate that functions of differing spin do not have the same radial behavior.

‡ For example, \hat{L}^+ operating on the B wavefunction of (15) yields a dominant configuration in which $p_z\alpha$ is replaced by $(p_x + ip_y)\alpha$, but in addition there are other terms involving d_1 in place of one of the s orbitals. Conversely the optimum Slater determinant with $M_L = 1$ would yield a sum of Slater determinants after applying \hat{L}^- .

Table 1
 $\langle r^2 \rangle$ contributions - p orbitals

	O	F
$2p_z \alpha$	1.9795	1.4131
$2p_x \alpha$	1.8362	1.5306
$2p_y \alpha$	1.8362	1.5306
$2p_z \beta$	2.2360	
$2p_x \beta$		1.6258
$2p_y \beta$		1.6258

4.2. Computational details

The UHF orbitals were obtained in an analytic Slater basis set, where the exponents for the s and p functions were the same as those used in previous symmetry restricted UHF calculations †. Although we used a cusp-like s basis set to investigate spin density at the nucleus, the other hyperfine properties were not affected when more conventional basis sets were tried. For each atom the energy was lowered 0.0035 to 0.0039 hartree by the addition of d functions. Since the total energy was relatively insensitive to the nature of the d functions, the size of the d basis was increased until each orbital's contribution to the field gradient at the nucleus had converged. Usually at least nine different d functions were necessary to describe correctly the admixture of d character into the various orbitals ‡. Evaluation of all hyperfine properties is straightforward with the exception of $\langle r^{-3} \rangle_1$ which is discussed in the appendix.

4.3. Effect of hyperfine properties

Even though the many-electron wavefunction is neither an eigenfunction of \hat{L}^2 or \hat{S}^2 , the fact that there are no first-order changes in the orbitals makes the UHF wavefunction advantageous in that we may use (3) instead of (1) for first-order hyperfine properties. Relaxation of symmetry restrictions on the orbitals does little to affect spin densities $Q(0)$ obtained from UHF(LR) wavefunctions, which gave values about 75% greater than experiment.

† The s, p basis sets taken from ref. [3] were B20, C16, O6 and F6. The following exponents were used for the 3d Slater basis functions:

B: 6.9, 6.0, 5.2, 4.5, 3.9, 3.3, 2.7, 2.2, 1.8, 1.4, 0.8.
 C: 6.98, 5.9, 5.2, 4.6, 3.8, 3.0, 2.4, 2.0, 1.6, 1.3, 0.8.
 O: 9.0, 8.0, 6.9, 5.8, 4.9, 4.1, 3.5, 2.8, 2.1, 1.6, 1.0.
 F: 10.4, 8.0, 6.63, 5.0, 4.0, 3.1, 2.7, 2.3, 1.5.

‡ It is possible that the p orbitals would incorporate f character in O and F and that the wavefunction of N would symmetry split upon incorporation of f character into the p orbitals and g character into the s orbitals.

On the other hand, a drastic improvement is noted in the $\langle r^{-3} \rangle_1$ and $\langle r^{-3} \rangle_d$ magnetic and $\langle r^{-3} \rangle_q$ electric hyperfine parameters associated with the orbital dipole [$\sum_i \hat{l}_i / r_i^3$], spin dipolar [$\sum_i 2\hat{s}_z i P_{20}(i) / r_i^3$] and electric field gradient [$\sum_i P_{20}(i) / r_i^3$] one-electron properties, respectively. Whereas RHF and UHF(LR) give the same value for all three $\langle r^{-3} \rangle$ values, $\langle r^{-3} \rangle_d / \langle r^{-3} \rangle_1$ is known to be 1.13 and 1.11 for O and F, respectively. We obtain 1.10 and 1.09 for these values and in addition obtain an understanding of the ordering $\langle r^{-3} \rangle_d > \langle r^{-3} \rangle_1 > \langle r^{-3} \rangle_q$ observed in recent extensive CI calculations [1, 2]. As indicated in table 2, orbitals described by $s + d_0$ give a positive contribution to P_{20}/r^3 ; those by $s - d_0$, a negative one (with the exception of the $1(s, d) \alpha$ orbital of B where the contribution is small). Since

$$\langle \sum_i h(i) \rangle = \sum_{ia} \langle ia | h | ia \rangle + \sum_{ib} \langle ib | h | ib \rangle,$$

the contributions from the (s, d) orbitals tend to cancel for $\langle r^{-3} \rangle_q$, but because of the \hat{s}_z operator they will all contribute with the same sign to produce an increased value for $\langle r^{-3} \rangle_d$. The effect of the $1(s, d)$ and $2(s, d)$ orbitals on hyperfine properties becomes less pronounced in O and F where there are large anisotropic contributions from the p orbitals.

Despite the improvement in the effective $\langle r^{-3} \rangle$ values, the total hyperfine parameters a_J are not in good agreement with experiment in those cases where a_J is strongly dependent on $Q(0)$. Nonetheless $\langle r^{-3} \rangle_1$ and $\langle r^{-3} \rangle_d$ differ from experiment by little more than 4% at worst for O and F and by 3% from the polarization CI result for B and C. Furthermore, field gradients are in excellent agreement (within 0.6%) with the polarization CI values.

Table 2
 Orbital contributions to $\langle P_{20}/r^3 \rangle$ and $\langle 2\hat{s}_z P_{20}/r^3 \rangle$.
 All quantities are in atomic units

	B	C	O	F
$1(s, d) \alpha$	-0.0004	-0.0011	-0.0494	0.0703
$2(s, d) \alpha$	0.0068	-0.0086	-0.0172	0.0233
$2p_z \alpha$	0.3142		1.9948	3.1586
$2p_x \alpha$		-0.3421	-1.0385	-1.5192
$2p_y \alpha$		-0.3421	-1.0385	-1.5192
$1(s, d) \beta$	-0.0148	0.0255	0.0064	-0.0097
$2(s, d) \beta$	-0.0067	0.0106	0.0163	-0.0189
$2p_z \beta$			1.8318	
$2p_x \beta$				-1.4660
$2p_y \beta$				-1.4660
$\langle P_{20}/r^3 \rangle$	0.2992	-0.6577	1.7057	-2.7470
$\langle 2s_z P_{20}/r^3 \rangle$	0.3421	-0.7301	-2.0033	3.1742

Table 3
 Hyperfine constants as obtained from UHF and other methods. All quantities are in hartree atomic units

Method	Ref.	Energy E	Spin Density $Q(0)$	Orbital Dipole $\langle r^{-3} \rangle$	Spin Dipole $\langle r^{-3} \rangle d$	Quadru- pole $\langle r^{-3} \rangle q$	Ratio d/l	Hyperfine constants a)			
								a_{J+1}	a_J	$a_{J+1, J}$ $a_{J, J-1}$	
B (² P)	UHF	-24.53313	0.0218	0.7796	0.8551	0.7480	1.10	0.466	2.118	0.056	
	UHF	-24.53027	0.0178	0.7828	0.8522	0.7432	1.09	0.457	2.129		
	UHF(LR)	-24.52930	0.0192	0.7817	0.8517	0.7817	1.00	0.470	2.030	0.076	
	RHF	-24.52905	0.0000	0.7755	0.7755	0.7755	1.00	0.413	2.067	0.129	
	SOGI(LR)	-24.54605	0.0022	0.7900	0.7894	0.7894	0.99	0.427	2.098	0.125	
	SOGI	-24.56077				0.7175					
	CI-POL	-24.55129	0.0073	0.7674	0.8301	0.7436	1.08	0.421	2.107	0.097	
	CI-FO	-24.58742	0.0041	0.7572	0.8167	0.6833	1.08	0.407	2.085	0.105	
	CI	-24.6392	0.0045	0.7617	0.7725	0.740	1.01	0.417	2.031	0.112	
	BG	[7]		0.0038	0.7789	0.8367	0.7054	1.07	0.4177	2.142	0.109
UHF-ADJ	This paper		0.0083	0.7796	0.8551	0.7480	1.10	0.428	2.155	0.094	
EXPER	[18, 19]	-24.6579 [20]				-0.02867/q		0.4284	2.13824		
C (³ P)	UHF	-37.69371	0.0784	1.703	1.825	1.639	1.07	1.197	0.102	0.607	
	UHF(LR)	-37.68998	0.075	1.709	1.709	1.709	1.00	1.182	0.157	0.599	
	RHF	-37.68861	0.000	1.692	1.692	1.692	1.00	1.014	-0.001	0.683	
	SOGI(LR)	-37.70680	0.0423	1.7212	1.7195	1.72	1.00	1.120	-0.088	0.644	
	CI-POL	-37.72814	0.0277	1.679	1.782	1.637	1.06	1.074	0.0049	0.656	
	CI-FO	-37.75068	0.0228	1.663	1.769	1.537	1.07	1.055	-0.0061	0.644	
	UHF-ADJ	This paper		0.0391	1.703	1.825	1.639	1.07	1.115	-0.020	0.654
	EXPER	[21]	-37.8558 [20]				0.05265/q		1.071 / $ \mu $	0.0192 / $ \mu $	
	O (³ P)	UHF	-74.81738	0.194	4.565	5.007	4.265	1.10	3.187	0.183	1.660
		UHF(LR)	-74.81394	0.194	4.579 b)	4.746	4.370	1.04	3.168	0.321	1.633
UHF(LR, EQ)		-74.81353	0.197	4.544	4.544	4.544	1.00	3.137	0.410	1.596	
RHF		-74.80935	0.000	4.973	4.973	4.973	1.00	2.982	-0.003	2.009	
CI-POL		-74.85571	0.0610	4.613	5.125	4.344	1.11	2.943	-0.130	1.848	
CI-FO		-74.85398	0.0628	4.570	5.100	4.307	1.12	2.923	-0.133	1.831	
UHF-ADJ		This paper		0.1148	4.565	5.007	4.265	1.10	3.021	0.017	1.756
EXPER		[22]	-75.1099 [20]		4.541	5.144	0.11105/q	1.13	3.0208	-0.06548	1.750
F (² P)		UHF	-99.41478	0.122	7.310	7.935	6.867	1.09	4.150	19.975	0.771
		UHF(LR)	-99.41129	0.130	7.330 b)	7.611	7.033	1.04	4.229	19.547	0.810
	UHF(LR, EQ)	-99.41078	0.133	7.313	7.313	7.313	1.00	4.265	19.119	0.845	
	RHF	-99.40932	0.000	7.545	7.545	7.545	1.00	4.018	20.108	1.255	
	CI-POL	-99.43811	0.0470	7.276	7.963	6.880	1.09	3.916	20.166	0.964	
	CI-FO	-99.43976	0.0496	7.234	7.950	6.852	1.10	3.897	20.085	0.945	
	UHF-ADJ	This paper		0.0692	7.310	7.935	6.867	1.09	4.003	20.122	0.918
	EXPER	[22]	-99.8059 [20]		7.336	8.123	-	1.11	4.0028	20.4008	0.888

a) To convert the magnetic hyperfine constants from atomic units to MHz, multiply by 171.205 for ¹¹B, 184.183 for ¹³C, -72.3543 for ¹⁷O, and 502.147 for ¹⁹F.

b) These values have been corrected from ref. [3] using the method of calculation given here.

In light of the good agreement of $\langle r^{-3} \rangle_1$ and $\langle r^{-3} \rangle_Q$ with experiment, we have used our calculated values for these parameters along with the experimental hyperfine constants a_{J+1} to estimate the spin densities $Q(0)$ of B, O and F. These adjusted values (denoted as UHF-ADJ in table 3) agree quite well with the experimental spin densities of O and F and should provide a reasonable estimate for B where there is insufficient experimental data to determine $Q(0)$. For C we used the ratio a_{J+1}/a_J to estimate $Q(0)$, since the individual hyperfine constants are not known. From the experimental value of $a_2/|\mu|$ for ^{11}C and our calculated value of $a_2(\text{UHF-ADJ})$, we estimate the magnitude of μ_N to be 0.960 nuclear magnetons. Similarly from the measured quadrupole coupling constants and our calculated electric field gradients we obtain the following electric quadrupole moments (in barns); $Q = +0.038$ for ^{11}B , $Q = +0.032$ for ^{11}C (assuming μ_N for ^{11}C to be negative), and $Q = -0.026$ for ^{17}O .

5. CONCLUSIONS

For variationally based methods of calculating wavefunctions, such as Hartree-Fock, GF [3] or SOGI [9], the imposition of constraints on the variations in the orbitals can lead to significant errors in the properties calculated from such wavefunctions. In particular, we find that spatial symmetry restrictions upon the orbitals can lead to significant errors in the magnetic and electric hyperfine constants. Similar results can also be expected in some cases [e.g. $\text{CH}_2^{(2)\text{II}}$] for molecules of high symmetry.

APPENDIX

Since hyperfine constants are usually defined with respect to the matrix elements for maximum M_L , M_S and M_J , we shall consider how to evaluate these quantities for the optimum UHF wavefunction with $M_L = 0$. We denote the calculated UHF wavefunction as ψ_z (it is invariant under rotations about the z axis) and the equivalent functions defined with respect to the x and y axes as ψ_x and ψ_y . The resulting set of states $\{\psi_x, \psi_y, \psi_z\}$ forms a basis for the T_1 irreducible representation of O_h , with the combination $\psi_x + i\psi_y$ corresponding to the $M_L = 1$ state for

the full rotation group. In this case, $\langle r^{-3} \rangle_1$ becomes

$$\langle r^{-3} \rangle_1 = \langle p_x, 3b | r^{-3} | p_x, 3b \rangle \langle p_x, 5a | p_x, 4a \rangle \\ \times \langle p_y, 5a | p_y, 4a \rangle f_a f_b,$$

where

$$f_a = \langle (s - d_x)_{1a} | (s - d_y)_{1a} \rangle \langle (s - d_x)_{2a} | (s - d_y)_{2a} \rangle \\ - \langle (s - d_x)_{1a} | (s - d_y)_{2a} \rangle \langle (s - d_x)_{2a} | (s - d_y)_{1a} \rangle$$

and f_b is defined analogously. Numerically $\langle r^{-3} \rangle_1$ differs from $\langle p_x, 3b | r^{-3} | p_x, 3b \rangle$ by less than one percent.

Note that this function $\Psi_x + i\Psi_y$ does not describe exactly a P state of an atom, just as all of these UHF wavefunctions lead to some mixing in of incorrect spin components into the wavefunction. A proper procedure would be to symmetry project and optimize after projection.

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