

## Core Polarization and Hyperfine Structure of the B, C, N, O, and F Atoms\*

William A. Goddard III<sup>†</sup>

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

(Received 9 September 1968)

Calculations on the hyperfine-splitting constants for the atoms B, C, N, O, and F have been carried out by both the unrestricted Hartree-Fock (UHF) method and a method corresponding to optimizing the orbitals of a Slater determinant *after* spin projection (the GF method). This is equivalent to one form of Löwdin's extended Hartree-Fock method. These calculations account for core-polarization contributions to the spin density but not for any significant part of the electron correlation. It is found that the core-polarization term is significantly larger (for N about 65% larger) than the experimental value, indicating that the remaining correlation effects significantly *decrease* the magnitude of the spin density at the nucleus.

Since these calculations used analytic expansions, an extensive set of basis sets was examined in order to determine what type of basis set is required in order to obtain accurate values for various properties.

On the basis of these calculations and the observed hyperfine structure, we obtain a magnetic moment (in nuclear magnetons) of  $\mu_N = \pm 0.97$  for  $^{11}\text{C}$  and electric quadrupole moments (in barns) of  $Q = 0.037$  for  $^{11}\text{B}$ ,  $Q = 0.031$  for  $^{11}\text{C}$  (assuming  $\mu_N$  for  $^{11}\text{C}$  to be negative), and  $Q = -0.025$  for  $^{17}\text{O}$ .

### INTRODUCTION

Of the interactions responsible for the hyperfine structure in atoms, the Fermi contact term<sup>1-5</sup> has been the most difficult to predict accurately. The reason is that this term is proportional to the spin density at the nucleus,  $Q(0)$ , and thus depends solely on the accuracy of the wave function at a single point, the nucleus, which does not even contribute significantly to the energy. It was recognized early that the Hartree-Fock (HF) wave function does not lead to reliable values for  $Q(0)$ .<sup>6</sup> The reason is that only  $s$  orbitals can contribute to  $Q(0)$  yet in most atoms, such as C, N, O, P, and Mn, the  $s$  orbitals are all spin paired, leading to a predicted  $Q(0)$  of zero. One solution<sup>7-16</sup> to this problem has been to retain a Slater determinant wave function, but relax the restriction that the  $s$  orbitals be doubly occupied. This method, called the unrestricted Hartree-Fock (UHF) method, leads to nonzero  $Q(0)$  which are generally within a factor of 2 of the experimental value. However the UHF wave function does not have the correct spin symmetry.<sup>1,10,17,18</sup> This led to the use of wave functions which were spin projected in order to have the correct spin symmetry (PUHF).<sup>10,12-16,19</sup> For some systems PUHF led to worse results<sup>10,20</sup> than UHF and for others it was better.<sup>12-16</sup> It was generally felt<sup>1-5,12,20</sup> that the problem is that the orbitals should be optimized after spin projection rather than before.<sup>21,22</sup> This approach is called the spin-polarized extended Hartree-Fock (SPEHF) method and was originally suggested by Löwdin.<sup>21,22</sup> However, the complexity of such procedures prevented<sup>1-5</sup> such

calculations until the recent development of the GF method,<sup>23,24</sup> which leads to wave functions equivalent to those obtained by optimizing the orbitals of a Slater determinant after spin projection. This method has been used to calculate the  $Q(0)$  for the ground<sup>25</sup> and excited<sup>26</sup> states of Li, and as expected the results are in good agreement with experiment. However, we expect more trouble for larger atoms since the contributions to  $Q(0)$  from different closed shells often tend to cancel one another. In this paper we present the results of GF calculations on the ground states of B, C, N, O, and F. We find that the calculated  $Q(0)$  depends very sensitively upon the basis set for both GF and UHF wave functions. For these atoms the  $Q(0)$  from GF and UHF calculations are 60% to 250% higher than the experimental values while the PUHF results are rather close to experiment. This is in contrast to the results for the Li atom.

### THE CALCULATIONS

The GF method has been described in detail elsewhere.<sup>23,24,27</sup> The equations which must be solved for the GF orbitals are similar to the HF equations and are solved in the same way. We expand each orbital in terms of a finite set of basis functions,  $\{\chi_\mu\}$ , and solve for the coefficients of the expansion.<sup>28</sup> Slater orbitals<sup>29</sup> are used, and in order to minimize bias in the basis set, the orbital exponents are optimized. We found that the spin density at the nucleus,<sup>30</sup>

$$Q(0) = \langle \Psi | \sum_i \delta(r_i) (2s_z) | \Psi \rangle, \quad (1)$$

is quite sensitive to the specific basis set used. Consequently, we considered a number of different kinds of basis sets in order to determine if certain types of basis sets might lead to faster convergence in  $Q(0)$  (as the size of the basis set is increased). We were also interested in determining if any small basis sets (i. e., about double zeta size) would consistently yield reliable values for  $Q(0)$ , the reason being that calculations in polyatomic molecules cannot presently use basis sets as large as those we can consider for atoms, yet it would be of great interest to calculate spin densities for polyatomic molecules and radicals for comparison to the experimental information available.

Extensive calculations<sup>31, 32</sup> were carried out on B, C, and N and are reported in Tables I, II, and III (the basis sets are listed in Tables IV, V, and VI). In addition to the energies and  $Q(0)$  for the UHF and GF calculations, we report the values for several properties,  $\langle \sum l_z / r^3 \rangle$ ,  $\rho(0) = \langle \sum \delta(r_i) \rangle$  (the density of electrons at the nucleus), and  $\langle \sum r^2 \rangle$ , in order to give an idea of how well these quantities converge for large atomic basis sets. We found that the trends for  $Q(0)$  and other properties were the same for both UHF and GF, so many basis sets were rejected before carrying out GF calculations.

We separately optimized the orbital exponents for several basis sets for the HF, UHF, and GF wave functions and found the orbital exponents to be the same within the estimated error in determining the orbital exponents. Consequently, all orbital exponents were optimized for the HF wave functions since the efficient LMSS atomic program<sup>33</sup> was available. For the larger basis sets we found that reoptimization of the orbital exponents was often not necessary (e. g., compare the  $p$  orbitals of the C5 and C14 basis sets).

We considered two different types of basis sets. The first is the usual type with several  $1s$ ,  $2s$ , and  $3s$  orbitals and several  $2p$  orbitals. These are listed first in each of the tables. The second type has one  $1s$ , no  $2s$ , and several  $3s$  orbitals (and maybe a  $4s$ ). As pointed out by Roothaan and Kelly<sup>34</sup> such a basis set would automatically lead to each self-consistent field (SCF)  $s$  orbital satisfying the cusp condition if  $\zeta_{1s} = Z$ , the nuclear charge. We will call such a basis set an  $s$ -cusp set. We thought that the cusp condition would be quite important for a good  $Q(0)$ , so we considered an extensive series of  $s$ -cusp sets. As expected the  $Q(0)$  converged far more rapidly (as a function of the number of basis functions) for the  $s$ -cusp sets than for the regular-type basis sets. It was not clear that the cusp condition for the  $p$  orbitals

TABLE I. Energies and properties from UHF and GF calculations on B. All quantities are in Hartree atomic units.<sup>a</sup>

Basis set <sup>b</sup>	Energy	$Q(0)^c$	UHF			GF	
			$\langle \sum l_z / r^3 \rangle$	$\rho(0)^d$	$\langle \sum r^2 \rangle$	Energy	$Q(0)^c$
1 2/1	-24.49837	0.0000	0.5916	68.193	14.752	-24.49837	0.0000
2 3/1	-24.50546	-0.0492	0.5891	69.453	14.395		
3 3/2	-24.52676	-0.0856	0.7506	71.692	15.401		
4 3/2	-24.52694	-0.0932	0.7485	71.858	15.364		
5 4/2	-24.52812	0.0032	0.7572	71.569	15.752		
6 4/3	-24.52918	0.0057	0.7787	71.937	15.832	-24.52952	0.0256
7 5/4	-24.52925	0.0110	0.7806	71.979	15.825	-24.52966	0.0483
8 6/4	-24.52909	-0.0121	0.7825	71.931	15.879		
9 6/4	-24.52889	0.0205	0.7828	71.538	15.762	-24.52938	0.0385
10 6/4	-24.52930	0.0258	0.7814	71.927	15.837	-24.52980	0.0439
11 3/1	-24.49644	-0.0690	0.5808	72.918	13.786		
12 3/1	-24.50899	0.0235	0.5872	68.917	14.612		
13 3/2	-24.51972	0.0135	0.7486	68.882	15.486		
14 4/2	-24.52873	-0.0153	0.7540	71.874	15.705		
15 5/2	-24.52885	0.0115	0.7544	71.957	15.701		
16 5/3	-24.52920	0.0145	0.7789	71.973	15.767	-24.52959	0.0285
17 6/3	-24.52928	0.0192	0.7797	71.959	15.846	-24.52975	0.0350
18 6/4	-24.52928	0.0195	0.7816	71.958	15.842		
19 7/3	-24.52929	0.0189	0.7798	71.965	15.844		
20 7/4	-24.52930	0.0192	0.7817	71.964	15.840	-24.52980	0.0361
Numerical <sup>e</sup>		0.0172	0.7819				

<sup>a</sup>In Hartree atomic units,  $m_e = 1$ ,  $\hbar = 1$ ,  $e = 1$ , the unit of energy is the Hartree (27.2107 eV),<sup>63</sup> and the unit of length is the bohr (0.529167 Å).<sup>63</sup>

<sup>b</sup>See Table IV for the basis functions.

<sup>c</sup>The spin density at the nucleus, see Eq. (1).

<sup>d</sup>The electronic density at the nucleus.

<sup>e</sup>Reference 11.

TABLE II. Energies and properties from UHF and GF calculations on C. All quantities are in Hartree atomic units.<sup>a</sup>

Basis set <sup>b</sup>	Energy	$Q(0)^c$	UHF			GF	
			$\langle \Sigma \hat{l}_z / r^3 \rangle$	$\rho(0)^d$	$\langle \Sigma r^2 \rangle$	Energy	$Q(0)^c$
1 2/1	-37.622 39	0.0000	1.2848	122.039	12.312	-37.622 39	0.0000
2 3/2	-37.683 96	-0.2856	1.6404	127.192	13.377		
3 4/2	-37.687 88	0.0057	1.6601	126.822	13.661		
4 4/3	-37.689 42	0.0194	1.6996	127.454	13.747	-37.690 21	0.0244
5 5/4	-37.689 70	0.1334	1.7060	127.548	13.751	-37.690 68	0.1302
6 6/4	-37.689 48	0.0887	1.7079	126.873	13.733		
7 6/4	-37.689 98	0.1011	1.7080	127.472	13.780		
8 3/1	-37.637 49	0.1493	1.2789	123.017	12.317		
9 4/2	-37.688 24	-0.0219	1.6547	127.261	13.636		
10 5/2	-37.688 64	0.0650	1.6565	127.453	13.649		
11 5/3	-37.689 67	0.0709	1.7012	127.460	13.740	-37.690 66	0.0675
12 6/3	-37.689 90	0.0819	1.7036	127.452	13.796	-37.691 01	0.0786
13 6/5	-37.689 95	0.0811	1.7094	127.484	13.787		
14 6/4	-37.689 94	0.0824	1.7088	127.492	13.783		
15 7/3	-37.689 95	0.0743	1.7039	127.517	13.791		
16 7/4	-37.689 98	0.0753	1.7091	127.515	13.778	-37.691 14	0.0733

<sup>a</sup>See footnote a, Table I.<sup>b</sup>See Table V for the basis functions.<sup>c</sup>The spin density at the nucleus, see Eq. (1).<sup>d</sup>The electronic density at the nucleus.TABLE III. Energies and properties from UHF and GF calculations on N. All quantities are in Hartree atomic units.<sup>a</sup>

Basis set <sup>b</sup>	Energy	UHF			GF	
		$Q(0)^c$	$\rho(0)^d$	$\langle \Sigma r^2 \rangle$	Energy	$Q(0)^c$
1 2/1	-54.268 90	0.0000	198.536	10.476	-54.268 90	0.0000
2 3/2	-54.392 88	-0.5447	205.283	11.719		
3 4/2	-54.410 05	0.0033	204.930	11.926		
4 4/2	-54.401 03	-0.0262	204.686	11.949		
5 4/3	-54.403 08	0.0263	205.933	12.032	-54.404 39	0.0118
6 5/4	-54.403 85	0.3187	206.014	12.038		
7 6/4	-54.403 37	0.2237	204.979	12.058		
8 6/4	-54.404 51	0.2127	205.867	12.054		
9 3/1	-54.290 40	0.4198	199.817			
10 4/2	-54.400 84	-0.0313	205.529	11.918		
11 5/2	-54.401 74	0.1611	205.883	11.942		
12 5/3	-54.403 92	0.1751	205.892	12.042	-54.405 62	0.1461
13 6/3	-54.404 32	0.1934	205.569	12.092		
14 6/3	-54.404 37	0.1922	205.941	12.092	-54.406 21	0.1629
15 6/4	-54.404 44	0.1940	205.939	12.078		
16 7/3	-54.404 46	0.1835	206.029	12.088		
17 7/4	-54.404 53	0.1853	206.026	12.073	-54.406 42	0.1579
Numerical <sup>e</sup>		0.1883				

<sup>a</sup>See footnote a, Table I.<sup>b</sup>See Table VI for the basis functions.<sup>c</sup>The spin density at the nucleus, see Eq. (1).<sup>d</sup>The electronic density at the nucleus.<sup>e</sup>Reference 11.

would be important for  $Q(0)$ , and this was verified for C where the 6/5  $sp$ -cusp set<sup>32</sup> led to essentially the same  $Q(0)$  as the 6/4 and 6/3  $s$ -cusp sets. In addition the  $sp$ -cusp set required at least one additional  $p$  basis function for an energy comparable to that for an  $s$ -cusp set (using  $2p$  orbitals). For this reason only  $s$ -cusp sets were con-

sidered in the other atoms. It is possible that an  $sp$ -cusp set would attain greater importance for F or O because of the greater numbers of  $p$  electrons.

For a given  $s$ -cusp set the optimum  $\zeta_{1s}$  is not usually  $Z$ ; consequently the cusp condition is not exactly satisfied although typically it is within

TABLE IV. Basis sets (Ref. 32) for boron. An asterisk indicates that the orbital exponent was not reoptimized.

1. CR:	1s 4.6795, 2s 1.2881, 2p 1.2107
2.	1s 4.7841, 2s 1.3319, 3s 1.7110, 2p 1.2090
3. BGCR:	1s 4.353, 1s 7.177, 2s 1.317, 2p 2.218, 2p 1.004
4.	1s 6.2495, 2s 5.0445, 2s 1.3221, 2p 2.2121, 2p 1.0025
5. CDZ:	1s 4.30481, 1s 6.84691, 2s 0.88143, 2s 1.40704, 2p 1.00366, 2p 2.20855
6. BGCR:	1s 7.732, 1s 4.413, 3s 2.431, 2s 1.152, 2p 4.558, 2p 1.753, 2p 0.931
7. BGCR:	1s 7.338, 1s 3.996, 3s 4.796, 2s 1.724, 2s 1.110, 2p 5.509, 2p 2.155, 2p 1.243, 2p 0.845
8. BLM:	1s 3.9469, 1s 4.3308, 1s 7.605, 2s 1.1571, 2s 2.0887, 2s 8.682, 2p 0.8662, 2p 1.3946, 2p 2.7692, 2p 7.3539
9. BLM:	1s 5.0, 2s 5.0, 3s 5.0, 1s 1.14, 2s 1.14, 3s 1.14, 2p's as in set 8
10. CRY:	1s 4.4661, 1s 7.8500, 2s 0.8320, 2s 1.1565, 2s 1.9120, 2s 3.5213, 2p 0.8783, 2p 1.3543, 2p 2.2296, 2p 5.3665
11.	1s 5.0*, 3s 4.9485, 3s 1.8123, 2p 1.2033
12.	1s 4.7411, 3s 2.931, 3s 1.5352, 2p 1.2077
13.	1s 4.7403, 3s 2.931, 3s 1.538, 2p 1.003, 2p 2.210
14.	1s 4.9986, 3s 5.431, 3s 2.537, 3s 1.398, 2p 1.0029, 2p 2.210
15.	1s 5.0145, 3s 5.794, 3s 4.08, 3s 2.4173, 3s 1.3776, 2p 1.003, 2p 2.2082
16.	1s 5.016, 3s 5.79*, 3s 4.08*, 3s 2.405, 3s 1.374, 2p 0.934, 2p 1.754, 2p 4.54*
17.	1s 5.015, 3s 5.79, 3s 4.06, 3s 2.424, 3s 1.393, 3s 0.69, 2p 0.931, 2p 1.752, 2p 4.54*
18.	s orbitals as in set 18, p orbitals as in set 7
19.	1s 5.0172, 3s 5.83, 3s 3.98, 3s 2.392, 3s 1.403, 3s 0.65, 4s 0.88, p orbitals as in set 17
20.	s orbitals as in set 19, p orbitals as in set 7.

TABLE V. Basis sets (Ref. 32) for carbon. An asterisk indicates that the orbital exponent was not reoptimized.

1. CR:	1s 5.6727, 2s 1.6083, 2p 1.5679
2. BGCR:	1s 5.332, 1s 8.696, 2s 1.647, 2p 2.73, 2p 1.255
3. CDZ:	1s 5.2309, 1s 7.96897, 2s 1.16782, 2s 1.82031, 2p 1.25572, 2p 2.72625
4. BGCR:	1s 9.153, 1s 5.382, 3s 3.076, 2s 1.428, 2p 5.152, 2p 2.177, 2p 1.150
5. BGCR:	1s 9.055, 1s 5.025, 3s 6.081, 2s 2.141, 2s 1.354, 2p 6.827, 2p 2.779, 2p 1.625, 2p 1.054
6. BLM:	1s 6.0, 2s 6.0, 3s 6.0, 1s 1.42, 2s 1.42, 3s 1.42, orbitals as in set 5
7. CRY:	1s 5.4125, 1s 9.2863, 2s 1.011, 2s 1.502, 2s 2.5897, 2s 4.2595, 2p 0.9554, 2p 1.4209, 2p 2.5873, 2p 6.3438
8.	1s 5.7386, 3s 3.535, 3s 1.859, 2p 1.5655
9.	1s 5.989, 3s 6.464, 3s 3.08, 3s 1.691, 2p 1.2547, 2p 2.725
10.	1s 6.012, 3s 6.93, 3s 4.84, 3s 2.872, 3s 1.648, 2p 1.255, 2p 2.725
11.	1s 6.0129, 3s 6.93, 3s 4.77, 3s 2.877, 3s 1.6553, 2p 1.1502, 2p 2.178, 2p 5.159
12.	1s 6.013, 3s 6.93, 3s 4.75, 3s 2.877, 3s 1.673, 3s 0.85, p orbitals as in set 10
13.	s orbitals as in set 14, 2p 3.088, 4p 1.163, 4p 1.847, 4p 2.998, 4p 4.85
14.	1s 6.016, 3s 6.95, 3s 4.74, 3s 2.859, 3s 1.675, 3s 0.89, 2p 1.054, 2p 1.625, 2p 2.781, 2p 6.824
15.	1s 6.018, 3s 6.98, 3s 4.58, 3s 2.894, 3s 1.667, 3s 0.87, 4s 0.996, 2p 1.1505, 2p 2.179, 2p 5.17
16.	s orbitals as in set 15, p orbitals as in set 14

0.02 of  $Z$  for the larger basis sets. For larger basis sets forcing  $\zeta_{1s} = Z$  typically changed  $Q(0)$  only slightly (e.g., compare basis sets 13 and 14 for N in Table III) and led to a significantly larger error in the virial ratio.<sup>35</sup> For this reason the  $\zeta_{1s}$  was optimized for most  $s$ -cusp sets.

The BGCR (5/4) and CRY (6/4) basis sets<sup>31,32</sup> are essentially at the Hartree-Fock limit; however, we see that they lead to rather different  $Q(0)$  and that both are probably still somewhat from the limiting value. The slightly smaller BGCR (4/3) sets although yielding nearly as good as energy as the BGCR (5/4) lead to quite poor  $Q(0)$  for all these atoms, as do the double-zeta (4/2) sets.<sup>36</sup> In contrast the  $Q(0)$  for  $s$ -cusp sets

seems to have converged for (7/3) and is fair even for (6/3), (5/3), and (5/2) sets. It may be that the use of an  $s$ -cusp (5/2) set for polyatomic molecules would lead to fairly accurate<sup>37</sup>  $Q(0)$  if they were corrected for the error in  $Q(0)$  for the atom.

In Tables VII and VIII we report some calculations for O and F (the basis sets are listed in Tables IX and X). In the UHF and GF calculations for O and F, we solved for all  $p$  orbitals independently as for B, C, and N. However, for O and F this led to different radial dependencies for different  $m_l$  and the same spin. Thus in these calculations the many-electron wave function does not have the correct spatial symmetry. For com-

TABLE VI. Basis sets (Ref. 32) for nitrogen. An asterisk indicates that the orbital exponent was not reoptimized.

1. CR:	1s 6.6651, 2s 1.9237, 2p 1.917
2. BGCR:	1s 6.395, 2s 8.28, 2s 1.967, 2p 3.247, 2p 1.497
3. CDZ:	1s 6.118 63, 1s 8.938 43, 2s 1.393 27, 2s 2.221 57, 2p 1.505 85, 2p 3.267 41
4.	1s 5.969, 1s 8.445, 2s 1.438, 2s 2.272, 2p 1.4959, 2p 3.2386
5. BGCR:	1s 10.507, 1s 6.346, 3s 3.715, 2s 1.697, 2p 5.573, 2p 2.555, 2p 1.352
6. BGCR:	1s 10.586, 1s 6.037, 2s 7.334, 2s 2.539, 2s 1.588, 2p 7.677, 2p 3.270, 2p 1.890, 2p 1.222
7. BLM:	1s 6.9, 2s 6.9, 3s 6.9, 1s 1.6, 2s 1.6, 3s 1.6, 2p 0.952, 2p 1.2264, 2p 1.9087, 2p 3.8675, (see Ref. 13)
8. CRY:	1s 6.4595, 1s 10.8389, 2s 1.4699, 2s 1.9161, 2s 3.156, 2s 5.0338, 2p 1.1937, 2p 1.7124, 2p 3.0012, 2p 7.1018
9.	1p 6.7366, 3s 4.147, 3s 2.174, 2p 1.9155
10.	1s 6.9800, 3s 7.45, 3s 3.690, 3s 2.012, 2p 1.4948, 2p 3.236
11.	1s 7.010, 3s 8.06, 3s 5.58, 3s 3.34, 3s 1.921, 2p 1.495, 2p 3.236
12.	1s 7.011, 3s 8.07, 3s 5.53, 3s 3.326, 3s 1.920, 2p 1.3527, 2p 2.560, 2p 5.6
13.	1s 7.0*, 3s 8.1, 3s 5.48, 3s 3.327, 3s 1.935, 3s 0.93, 2p 1.353, 2p 2.56, 2p 5.6*
14.	1s 7.015, 3s 8.1, 3s 5.48, 3s 3.302, 3s 1.938, 3s 1.0, 2p 1.353, sp 2.56, 2p 5.6*
15.	s orbitals as in set 13, p orbitals as in set 6
16.	1s 7.020, 3s 8.20, 3s 5.49, 3s 3.438, 3s 2.054, 3s 1.03, 4s 1.13, 2p 1.353, 2p 2.56, 2p 5.60*
17.	s orbitals as in set 16, p orbitals as in set 6

TABLE VII. Energies and properties from UHF and GF calculations on O. All quantities are in Hartree atomic units.<sup>a</sup>

Basis set <sup>b</sup>	Energy	Q(0) <sup>c</sup>	UHF			GF	
			$\langle \Sigma \hat{l}_z / r^3 \rangle$	$\rho(0)$ <sup>d</sup>	$\langle \Sigma r^2 \rangle$	Energy	Q(0)
1 6/4	-74.813 96	0.1939	4.3698	311.775	11.205		
2 5/2	-74.807 00	0.1113	4.4278	311.734	10.979		
3 5/3	-74.812 52	0.1746	4.5186	311.716	11.130		
4 6/3	-74.812 66	0.1741	4.5177	311.727	11.140	-74.814 95	0.1889
5 7/3	-74.812 68	0.1781	4.5178	311.692	11.140		
6 7/4	-74.813 94	0.1944	4.3701	311.701	11.211	-74.816 84	0.2137
7 7/4	-74.813 87	0.1979	4.3753	311.697	11.189		

<sup>a</sup>See footnote a, Table I.<sup>c</sup>The spin density of the nucleus, see Eq. (1).<sup>b</sup>See Table IX for the basis functions.<sup>d</sup>The electronic density at the nucleus.TABLE VIII. Energies and properties from UHF and GF calculations on F. All quantities are in Hartree atomic units.<sup>a</sup>

Basis set <sup>b</sup>	Energy	Q(0) <sup>c</sup>	UHF			GF	
			$\langle \Sigma \hat{l}_z / r^3 \rangle$	$\rho(0)$ <sup>d</sup>	$\langle \Sigma r^2 \rangle$	Energy	Q(0) <sup>c</sup>
1 6/4	-99.411 29	0.1432	7.0337	448.505	10.250		
2 5/2	-99.402 77	0.0604	6.9583	448.510	10.017		
3 5/3	-99.410 60	0.1215	7.1025	448.495	10.208		
4 6/3	-99.410 64	0.1229	7.1009	448.491	10.217	-99.412 99	0.2303
5 7/3	-99.410 67	0.1216	7.1007	448.457	10.216		
6 7/4	-99.411 27	0.1267	7.0379	448.465	10.251		
7 7/4	-99.411 29	0.1298	7.0332	448.462	10.240	-99.414 15	0.2455
Numerical <sup>e</sup>		0.1335	7.309				

<sup>a</sup>See footnote a, Table I.<sup>b</sup>See Table X for the basis functions.<sup>c</sup>The spin density at the nucleus, see Eq. (1).<sup>d</sup>The electronic density at the nucleus.<sup>e</sup>Reference 11. This is an LRUHF calculation and should be compared with the analytic LRUHF calculation in Table XI, i.e., Q(0)=0.1327,  $\langle r^{-3} \rangle = 7.3128$ .

TABLE IX. Basis sets (Ref. 32) for oxygen. An asterisk indicates that the orbital exponent was not reoptimized.

1. CRY:	1s 7.6160, 1s 13.3243, 2s 1.7582, 2s 2.5627, 2s 4.2832, 2s 5.9445, 2p 1.1536, 2p 1.7960, 2p 3.4379, 2p 7.9070
2.	s orbitals as in set 3, 2p 3.692*, 2p 1.656* (from BGCR)
3.	1s 8.015, 3s 9.23, 3s 6.22, 3s 3.757, 3s 2.182, 2p 1.4788, 2p 2.897, 2p 5.87
4.	1s 8.016, 3s 9.21, 3s 6.03, 3s 3.69, 3s 2.196, 3s 1.04, 2p 1.4777, 2p 2.895, 2p 5.88
5.	1s 8.0138, 3s 9.18, 3s 6.00, 3s 3.796, 3s 2.249, 3s 1.03, 4s 1.28, p orbitals as in set 4
6.	s orbitals as in set 5, p orbitals as in set 1
7.	s orbitals as in set 5, 2p 1.318*, 2p 2.121*, 2p 3.744*, 2p 8.45* (from BGCR)

TABLE X. Basis sets (Ref. 32) for fluorine. An asterisk indicates that the orbital exponent was not reoptimized.

1. CRY:	1s 8.5126, 1s 14.4130, 2s 1.8599, 2s 2.7056, 2s 4.9019, 2s 6.4440, 2p 1.2655, 2p 2.0301, 2p 3.9106, 2p 8.6363
2.	s orbitals as in set 3, 2p 4.180, 2p 1.848 (from BGCR)
3.	1s 9.017, 3s 10.37, 3s 6.79, 3s 4.169, 3s 2.452, 2p 1.603, 2p 3.125, 2p 6.00
4.	1s 9.016, 3s 10.32, 3s 6.80, 3s 4.136, 3s 2.433, 3s 1.11, 2p 1.601, 2p 3.124, 2p 6.00*
5.	1s 9.0167, 3s 10.40, 3s 6.63, 3s 4.209, 3s 3.513, 3s 1.11*, 4s 1.44*, p orbitals as in set 4
6.	s orbitals as in set 5, p orbitals as in set 1
7.	s orbitals as in set 5, 2p 1.434*, 2p 2.356*, 2p 4.249*, 2p 9.435* (from BGCR)

parison we also carried out UHF and GF type calculations where the orbitals of different  $m_l$  and same spin were restricted to have the same radial dependence. We will refer to these as LRUHF and LRGF calculations (LR stands for  $L$  restricted).

The hyperfine constants and some other properties for HF, UHF, PUHF, and GF calculations using the  $s$ -cusp (7/4) sets are collected together in Tables XI, XII, and XIII<sup>36</sup> (see Appendix B for definitions of terms). The equations used to calculate  $Q(0)$  for GF and PUHF wave functions are derived in Appendix A.

## DISCUSSION

### Spin Densities

The spin density,  $Q(0)$ , has not been unambiguously determined experimentally for B and C; thus there is some difficulty in assessing the accuracy of  $Q(0)$  for these atoms. However, for N, O, and F the GF results are 63, 87, and 242% too high and the UHF results 91, 71, and 81% too high. On the other hand PUHF leads to a  $Q(0)$  21% too high for N and 11 and 38% too low for O and F. Similarly it appears that GF and UHF lead to too high a value of  $Q(0)$  for B and C and that PUHF leads to more nearly correct values for these systems. This better agreement for PUHF is probably just due to a peculiar canceling

of errors in the contribution to  $Q(0)$  from the 1s and 2s shells and may not occur for atoms in other rows of the periodic table.

The difference between the experimental and Hartree-Fock values of  $Q(0)$  is said to be due to core polarization since the primary change from the Hartree-Fock wave function is an incorporation of spin density into the atomic core. We see here that for B, C, N, O, and F, correlation effects not included in the GF and UHF wave functions must have an effect on  $Q(0)$  comparable with the effect which are included. This is in contrast with the case of the Li atom where the correlation effects were small.

Even poorer results have been reported<sup>16</sup> for  $Q(0)$  of the P atom using UHF wave functions; in this case the calculated  $Q(0)$  had the wrong sign. On the other hand, for some transition metal ions<sup>9, 39</sup> rather good agreement had been obtained between the UHF-calculated and experimental values of  $Q(0)$ . This may indicate that the GF and UHF methods will treat core polarization for  $d$  electrons more accurately than for  $p$  electrons. On the other hand, this agreement may be just a coincidence and of no general significance.

We should point out that because of the extreme sensitivity of  $Q(0)$  to basis set, one must be careful to use large appropriate basis sets to ensure that  $Q(0)$  has converged with respect to further increase in the basis set. Because of the large basis sets required for only fair convergence of

$Q(0)$  it would seem appropriate to solve the SCF<sup>40</sup> equations numerically if a reliable value for the SCF value of  $Q(0)$  is desired. However, the numerical approach would be far more difficult for molecules. Because of the apparent importance

of the cusp condition for spin densities, it would be sheer folly to expect the  $Q(0)$  from calculations using Gaussian orbitals<sup>41</sup> to be even remotely related to the correct  $Q(0)$  without extensive calculations and comparisons to atomic results.

TABLE XI. Properties for B and F. All quantities are in Hartree atomic units.

Energy	$\rho(0)$	$\langle \sum r^{-2} \rangle$	$Q(0)$	$\langle r^{-3} \rangle_I$	$\langle r^{-3} \rangle_d$	$\langle r^{-3} \rangle_d / \langle r^{-3} \rangle_I$	$a_{3/2}$	$a_{1/2}$	$a_{3/2, 1/2}$	$q_{3/2}$
B <sup>a</sup> HF	-24.529 05	71.972	0.0000	0.7755	0.7755	1.000	0.413	2.067	0.129	-0.310
UHF	-24.529 30	71.964	0.0192	0.7817	0.7817	1.000	0.470	2.030	0.076	-0.313
PUHF	-24.529 47	71.964	0.0067	0.7817	0.7817	1.000	0.435	2.065	0.111	-0.313
GF	-24.529 80	71.949	0.0362	0.7943	0.7924	0.998	0.524	2.013	0.031	-0.318
EXPER	-24.657 9b	...	(0.0003) <sup>c</sup>	(0.8027) <sup>c</sup>	(0.8027) <sup>c</sup>	...	0.428 42 <sup>c</sup>	2.138 24 <sup>c</sup>	...	-0.011 47 <sup>c</sup>
F <sup>d</sup> HF	-99.409 32	448.477	0.0000	7.5447	7.5447	1.000	4.018	20.108	1.255	3.018
LRUHF	-99.410 78	448.462	0.1327	7.3128	7.3128	1.000	4.265	19.119	0.845	2.925
UHF	-99.411 29	448.462	0.1298	7.0332	7.6106	1.082	4.031	19.152	0.711	2.813
PLRUHF	-99.411 79	448.462	0.0454	7.3142	7.5673	1.035	3.988	19.704	1.047	2.926
PUHF	-99.411 95	448.462	0.0444	7.0339	7.7940	1.108	3.769	19.636	0.919	2.814
LRGF	-99.414 08	448.424	0.2396	6.7778	7.5643	1.116	4.174	18.443	0.327	2.711
GF	-99.414 15	448.424	0.2454	6.8987	7.4065	1.074	4.292	18.378	0.377	2.760
EXPER	-99.805 9b	...	0.0718 <sub>85</sub>	7.33 <sub>84</sub>	8.12 <sub>84</sub>	1.107	4.002 79 <sup>e</sup>	20.400 82 <sup>e</sup>	0.888 <sup>e</sup>	...

<sup>a</sup>Using basis set B20.

<sup>b</sup>From C. W. Scherr, J. N. Silverman, and F. A. Matsen, Phys. Rev. 127, 830 (1962).

<sup>c</sup>From G. Wessel, Ref. 47, and H. Lew and R. S. Title, Can. J. Phys. 38, 868 (1960).

<sup>d</sup>B. See Ref. 38.

<sup>e</sup>Using basis set F7.

<sup>f</sup>From J. S. M. Harvey, Ref. 43, see Ref. 38: <sup>13</sup>F.

TABLE XII. Properties for C and O. All quantities are in Hartree atomic units.

Energy	$\rho(0)$	$\langle \sum r^{-2} \rangle$	$Q(0)$	$\langle r^{-3} \rangle_I$	$\langle r^{-3} \rangle_d$	$\langle r^{-3} \rangle_d / \langle r^{-3} \rangle_I$	$a_2$	$a_1$	$a_{2,1}$	$a_{1,0}$	$q_2$
C <sup>a</sup> HF	-37.688 61	127.553	0.000 0	1.6920	1.6920	1.000	1.014	-0.001	0.683	0.689	0.677
UHF	-37.689 98	127.515	0.075 3	1.7091	1.7091	1.000	1.182	0.157	0.599	0.439	0.684
PUHF	-37.690 61	127.516	0.039 8	1.7091	1.7091	1.000	1.108	0.082	0.642	0.560	0.684
GF	-37.691 14	127.484	0.073 3	1.7233	1.7202	0.998	1.186	0.154	0.607	0.453	0.689
EXPER	-37.855 8b	...	0.008 89	1.753 <sub>02</sub>	1.753 <sub>02</sub>	...	1.0710 <sup>c</sup>	0.019 19 <sup>c</sup>	...	...	0.021 06 <sup>c</sup>
O <sup>d</sup> HF	-74.809 35	311.749	0.000 0	4.9744	4.9744	1.000	2.982	-0.003	2.009	2.026	-1.199
LRUHF	-74.813 53	311.701	0.1972	4.5437	4.5437	1.000	3.137	0.410	1.596	1.176	-1.817
UHF	-74.813 94	311.701	0.1944	4.3701	4.7456	1.086	3.064	0.217	1.573	0.962	-1.748
PLRUHF	-74.815 36	311.701	0.1027	4.5480	4.8248	1.061	2.969	0.074	1.744	1.388	-1.819
PUHF	-74.815 31	311.702	0.1013	4.3722	4.604	1.135	2.892	-0.085	1.711	1.194	-1.749
LRGF	-74.816 83	311.653	0.2131	4.2369	4.6967	1.109	3.032	0.214	1.506	0.809	-1.695
GF	-74.816 84	311.652	0.2137	4.2788	4.6467	1.086	3.049	0.261	1.512	0.862	-1.712
EXPER	-75.105 9b	...	0.113 <sub>86</sub> <sup>f</sup>	4.54 <sub>01</sub> <sup>f</sup>	5.1438 <sub>3</sub> <sup>f</sup>	1.133	3.020 82 <sup>e</sup>	-0.065 48 <sup>e</sup>	1.750 <sup>e</sup>	1.27 <sup>e</sup>	0.044 42

<sup>a</sup>Using basis set C16.

<sup>b</sup>See footnote b, Table VI.

<sup>c</sup>From Haberstroh *et al.*, Ref. 46. See Ref. 38.

<sup>d</sup>Q is positive if  $\mu_N$  is negative: <sup>11</sup>C.

<sup>e</sup>Using basis set O6.

<sup>f</sup>From Harvey, Ref. 43: <sup>17</sup>O.

<sup>g</sup>These values of  $Q(0)$ ,  $\langle r^{-3} \rangle_I$ , and  $\langle r^{-3} \rangle_d$  lead to  $a_2 = 3.020 83$ ,

$a_1 = -0.065 47$ ,  $a_{2,1} = 1.765$ , and  $a_{1,0} = 1.21$ .

TABLE XIII. Properties for N. All quantities are in Hartree atomic units.

	Energy	$\rho(0)$	$\langle \Sigma r^2 \rangle$	$Q(0)$	$a_{3/2}$
N <sup>a</sup> HF	-54.400 92	206.126	12.080	0.0000	0.000
UHF	-54.404 53	206.026	12.073	0.1853	0.517
PUHF	-54.405 77	206.027	12.064	0.1179	0.329
GF	-54.406 42	205.975	12.067	0.1579	0.441
EXPER	-54.612 2 <sup>b</sup>	...	...	0.097 0505	0.271 015 <sup>c</sup>

<sup>a</sup>Using basis set N17.<sup>b</sup>See Ref. b, Table VI.,<sup>c</sup>From L. W. Anderson, F. M. Pipkin, and J. C. Baird, Jr., Phys. Rev. 116, 87 (1959), <sup>14</sup>N.

For C, N, and O we obtain rather similar values of  $Q(0)$  from the UHF and GF calculation. This is in agreement with the proofs by Marshall<sup>20</sup> and Bessis *et al.*<sup>12</sup> that  $Q(0)^{\text{UHF}} = Q(0)^{\text{GF}}$  through first order in the splitting of the orbitals. On the other hand we find that  $Q(0)^{\text{PUHF}}$  is quite different from  $Q(0)$ . This should settle speculations<sup>3,13-16</sup> that for the first-row atoms  $Q(0)^{\text{PUHF}}$  rather than  $Q(0)^{\text{UHF}}$  would be closer to the  $Q(0)$  obtained by orbital optimization after spin projection [i. e.,  $Q(0)^{\text{GF}}$ ].

In summary we have the following results for  $Q(0)$ . If for the atoms B through F we consider the HF wave function, we calculate that the spin density is zero. Allowing the exchange terms to split the core electrons (to obtain the GF wave function) induces a net positive spin density at the nucleus, referred to as core polarization. This core polarization is accompanied by only a small decrease in energy. Accounting for the remaining instantaneous correlations of the electrons decreases the energy sharply down to the experimental energy and also must lead to a significant reduction of the spin density at the nucleus.

More pictorially one can consider the change from HF to GF as primarily that of allowing triplet character in the 1s and 2s shells (coupled together to yield a singlet). As expected this leads to significant changes in  $Q(0)$  but not in the energy. Enormously more significant changes in the energy are obtained by correlation within the 1s shell and the 2s shell and between these shells, where each is taken to be singlet coupled. Such effects would not lead to any change in  $Q(0)$  except that they reduce the importance of the core-polarization terms (since there are now other avenues for effecting correlation) and thus lead to a decrease (in magnitude) in  $Q(0)$  from the GF value. On the basis of this physical argument we would expect the magnitude of the GF value of  $Q(0)$  to always be larger than the experimental value; this has been observed for all calculations carried out to date.<sup>24, 25</sup>

#### Magnetic Hyperfine Radial Constants

The orbital and spin-dipole magnetic hyperfine interactions are characterized by the parameters<sup>42</sup>  $\langle r^{-3} \rangle_l$  and  $\langle r^{-3} \rangle_d$ , respectively (see Appendix B). The accuracy of these parameters depends on the quality of the wave function over the whole atom; hence all of the wave functions lead to somewhat similar values for these parameters.

The HF wave functions for these atoms lead to  $\langle r^{-3} \rangle_l = \langle r^{-3} \rangle_d$ , as do the UHF and PUHF wave functions for B, C, and N and the LRUHF wave functions for O and F. However the experimental<sup>43</sup> value for this ratio  $\langle r^{-3} \rangle_d / \langle r^{-3} \rangle_l$  is 1.133 for O and 1.074 for F, which are close to the ratios obtained from the UHF, PUHF, LRGF, and GF calculations.<sup>44</sup> Since the UHF, PUHF, and GF wave functions allow  $p$  orbitals of the same spin but different  $m_l$  to split, the above agreement would seem to indicate that the 10% splitting in  $\langle r^{-3} \rangle$  is due to an orbital exchange effect quite analogous to the spin exchange effect leading to nonzero spin densities for these atoms. However the LRGF calculations also lead to good values for  $\langle r^{-3} \rangle_d / \langle r^{-3} \rangle_l$  despite the fact that such splitting is not allowed. In this case the  $\langle r^{-3} \rangle_d$  differs from  $\langle r^{-3} \rangle_l$  because in an expanded LRGF wave function each orbital is sometimes associated with an up spin and sometimes with a down spin. Thus since the spin-dipole operator involves the product  $[(3z^2 - r^2)/r^5] \hat{s}_z$ , we obtain a different weighting of various terms than is the case for the orbital operator  $\hat{l}_z/r^3$ . From this analysis it appears that the correct  $\langle r^{-3} \rangle$  splitting is a natural result of considering general SCF wave functions which have the correct spin symmetry. However recent limited configuration interaction (CI) calculations<sup>45</sup> indicate similar  $\langle r^{-3} \rangle$  splitting for B and C, whereas the GF wave function leads only to a very small splitting here (the splitting has not been determined experimentally for either atom).

Since the magnetic moment of <sup>11</sup>C is not known experimentally,<sup>46</sup> we could not compare our calculated hyperfine constants directly with the ex-



perimental values.<sup>46</sup> However, we may use the calculated and experimental  $a_J$ , to deduce the magnitude of  $\mu_N$  for <sup>11</sup>C. From the HF, UHF, PUHF, and GF calculations of  $a_2$ , we obtain 1.056, 0.906, 0.967, and 0.903 for  $|\mu_N|$ , respectively. Comparing the errors in the calculated  $a_J$ , for other atoms, we estimate  $\mu_N = 0.97 \pm 0.06$  for <sup>11</sup>C. This is similar to a value of  $|\mu_N| = 0.997$  obtained by Schaefer *et al.*<sup>45</sup> from the limited CI calculations. Previously Bessis *et al.*<sup>15</sup> obtained  $|\mu_N| = 1.0563$ , 0.8856, and 0.9591 for HF, UHF, and approximate PUHF calculations, respectively, and Haberstroh *et al.*<sup>46</sup> obtained  $|\mu_N| = 1.027$  using a privately communicated wave function from Moser.

#### Electric Hyperfine Interactions

The effective  $\langle r^{-3} \rangle$  labeled as  $\langle r^{-3} \rangle_I$  and  $\langle r^{-3} \rangle_d$  in Tables XI and XII are related to the orbital and spin-dipole hyperfine constants,  $a_I$  and  $a_d$  in exactly the same way as would be the case for the HF wave functions. For all the wave functions (HF, UHF, PUHF, and GF) discussed here, the  $\langle r^{-3} \rangle_I$  is similarly related to the electric field gradient at the nucleus and  $\langle r^{-3} \rangle_d$  is similarly related to the expectation values of  $\sum_e (\vec{l} \cdot \vec{s})/r^3$ , which would be required in evaluating the electron-nuclear part of the fine-structure splitting.

Using the  $\langle r^{-3} \rangle_I$  from the calculations best fitting the observed magnetic hyperfine structure and the measured<sup>43,46,47</sup> quadrupole coupling constants (see Tables XI and XII), we calculate the following nuclear quadrupole moments (in barns) <sup>11</sup>B:  $Q = 0.037$ , <sup>11</sup>C:  $Q = 0.031$  (assuming  $\mu_N$  for <sup>11</sup>C to be negative), and <sup>17</sup>O:  $Q = -0.025$ . These values should be good to about 10% and are similar to the values predicted by Schaefer *et al.*<sup>45</sup> See Appendix B for definitions relating to the electric hyperfine constants.

We have restricted the SCF<sup>40</sup> orbitals to be eigenfunctions of  $\hat{l}_z$ ; we will call this the  $m_l$  restriction. If upon relaxation of the  $m_l$  restriction the SCF are still eigenfunctions of  $\hat{l}_z$ , then because of Brillouin's theorem<sup>27</sup> for HF, UHF, and GF wave functions, the first-order perturbation energy is given by the diagonal matrix element, as has been assumed in discussing the hyperfine interactions. However, if upon dropping the  $m_l$  restriction, the SCF orbitals should change, then the other part of the first-order energy,<sup>27</sup>  $2R_e \times \langle \psi^0 | H^0 | \psi^1 \rangle$ , may be nonzero (here  $H^0$  and  $\psi^0$  are the zero-order many-electron Hamiltonian and wave function and  $\psi^1$  is the first-order many-electron wave function; bear in mind that  $\psi^0$  is an approximate wave function and thus *not* an eigenstate of  $H^0$ ). Such corrections are usually referred to as Sternheimer<sup>48</sup> corrections and have *not* been applied in this paper since no reliable values for these corrections are available.

#### Comparison with Previous Calculations

Blinder<sup>49</sup> and Das and Mukherjee<sup>50</sup> carried out early calculations for the UHF value of  $Q(0)$  of N. Blinder's result has the wrong sign while Das and Mukherjee used a perturbation approach to obtain the correct sign but only 1/3 of  $Q(0)^{\text{UHF}}$ . Goodings<sup>11</sup> carried out numerical UHF calculations on B, N, and F obtaining values in good agreement with those reported here. As discussed earlier the numerical approach is probably superior to the analytic approach since it avoids problems with optimizing basis sets and leads to accurate values for the wave function at the nucleus. Bessis *et al.*<sup>12-16</sup> carried out calculations for B, C, N, O, and F using non *s*-cusp 6/4 basis sets. Since their basis sets were neither optimized nor of *s*-cusp type, their values of  $Q(0)^{\text{UHF}}$  were not always close to the correct value. Bessis *et al.*<sup>12-16</sup> found that in all cases the PUHF led to better values of  $Q(0)$  than did UHF. However, they did not actually calculate the PUHF wave function. Instead they used

$$Q(0)^{\text{PUHF}} = [S/(S+1)] Q(0)^{\text{UHF}} \quad (2)$$

This approximation (see Ref. 12, also see Appendix A) holds if the splitting of each pair of orbitals  $\phi_{ia}$  and  $\phi_{ib}$  (corresponding to the doubly occupied orbital  $\phi_i$  in the HF wave function) is so small that  $\langle \phi_{ia} | \phi_{ib} \rangle = 1$ . The exact expression for  $Q(0)$  for a spin-projected Slater determinant is derived in Appendix A<sup>51</sup> (the expectation values for spin-independent properties are found with the expressions given in Ref. 24). We have correctly projected many of the wave functions in Tables I, II, III, VII, and VIII and found that (2) is a fairly good approximation for large basis set calculations (see Tables XI, XII, and XIII). Note that for approximate PUHF it was not at all clear how the spin dipole term

$$\langle \sum_e [(3z^2 - r^2)/r^5] s_z | \rangle$$

was to be obtained for the projected wave function. The expression in Appendix A obtains the exact value for this property also, and values for B, C, O, and F are given in Tables XI and XII.

Nesbet<sup>52</sup> has recently carried out calculations on N using generalized Bethe-Goldstone equations. The calculations for  $Q(0)$  were only through third order and it could be that higher-order terms are important; however, the calculated  $Q(0)$  was 0.1008 which is in excellent agreement with experiment. In addition Schaeffer, Klemm, and Harris<sup>45</sup> have recently carried out single-excitation configuration interaction calculations which account for a large fraction of the correlation energy but lead to  $Q(0)$  somewhat less than the experimental values. After submission of this

manuscript, a calculation on B by Kaldor appeared<sup>53</sup> which used the spin-polarized extended Hartree-Fock (SPEHF) method (which obtains wave functions equivalent to the GF wave functions). This calculation used a restricted basis set, B7, and thus obtained a  $Q(0)$  about 33% too large (see Table I). Other approaches have recently been applied to Li by Larsson<sup>54</sup> and Lunell.<sup>55</sup>

A recently developed method<sup>56</sup> combining various  $G_i^\gamma$  operators has given even better results for Li than GF and promises to do well on larger systems also since this method generally leads to smaller  $Q(0)$  than GF. Work is now in progress in applying this method to larger systems.

### CONCLUSIONS

The GF and UHF methods do not lead to particularly good values of spin density for B, C, N, O, and F, not even when very large basis sets are used. This means that correlation effects are important here and that they decrease the magnitude of  $Q(0)$ . In addition the usual type of basis set leads to slowly converging  $Q(0)$ . For these reasons most published calculations of the Fermi contact contributions to the hyperfine splitting in atoms and molecules are not expected to be very reliable.

### APPENDIX A. SPIN-DEPENDENT PROPERTIES

Expectation values and matrix elements for spin-independent operators are quite simple and have been treated before.<sup>23-25</sup> If  $F = \sum_i f(i)$  is a one-electron spinless operator, then<sup>57</sup>

$$\langle F \rangle = \langle G_f \Phi \chi | \sum_i f(i) | G_f \Phi \chi \rangle / \langle G_f \Phi \chi | G_f \Phi \chi \rangle. \quad (\text{A-1})$$

But

$$\begin{aligned} & \langle G_f \Phi \chi | \sum_i f(i) | G_f \Phi \chi \rangle \\ &= \sum_{rs} \xi_{\sigma_{rs}} \langle O_{rf} \Phi \omega_{rf}^- \chi | \sum_i f(i) | O_{sf} \Phi \omega_{sf}^- \chi \rangle \quad (\text{A-2}) \end{aligned}$$

and, since  $\sum_i f(i)$  commutes with  $\omega$  and  $O$  we obtain

$$\langle \Phi \chi | \sum_i f(i) | O_{fr} O_{sf} \Phi \omega_{fr}^- \omega_{sf}^- \chi \rangle. \quad (\text{A-3})$$

Thus

$$\begin{aligned} & \langle G_f \Phi \chi | \sum_i f(i) | G_f \Phi \chi \rangle \\ &= f^\gamma \langle \Phi | \sum_i f(i) | O_{ff} \Phi \rangle \langle \chi | \omega_{ff}^- \chi \rangle, \end{aligned}$$

where  $f^\gamma$  is the number of terms in the sum over  $r$ . Hence<sup>23</sup>

$$\langle F \rangle = \langle \Phi | \sum_i f(i) | O_{ff} \Phi \rangle / \langle \Phi | O_{ff} \Phi \rangle, \quad (\text{A-4})$$

which can be evaluated from the density matrices given in III.<sup>24</sup> Now consider the operator

$$M = \sum_i m(i) \xi_z(i), \quad (\text{A-5})$$

where  $m(i)$  is independent of spin. Here we cannot carry out the steps taking (A-2) to (A-3) since  $\omega$  and  $O$  do not commute with  $M$ . Thus we will use a different approach. From Appendix C of I (Ref. 57) we have<sup>58</sup>

$$G_f \Phi \chi = (N!/\theta^\gamma) \alpha(\Phi \omega_{11} \chi), \quad (\text{A-6})$$

where  $\alpha$  is the antisymmetrizer,

$$\alpha = (1/N!) \sum_{\tau} \xi_{\tau} \tau.$$

Thus  $\langle M \rangle = A/2B$ , (A-7)

where  $A \equiv 2 \frac{\theta N!}{n!m!} \left( \frac{\theta}{N!} \right)^2 \langle G_f \Phi \chi | M | G_f \Phi \chi \rangle$

$$= \frac{2\theta N!}{n!m!} \langle \alpha \Phi \omega_{11} \chi | M | \alpha \Phi \omega_{11} \chi \rangle$$

$$= \frac{\theta N!}{n!m!} \langle \Phi \omega_{11} \chi | 2M | \alpha \Phi \omega_{11} \chi \rangle, \quad (\text{A-8})$$

since  $\alpha \alpha = \alpha$ . Similarly

$$B \equiv \frac{\theta N!}{n!m!} \left( \frac{\theta}{N!} \right)^2 \langle G_f \Phi \chi | G_f \Phi \chi \rangle \quad (\text{A-9})$$

$$= \frac{\theta N!}{n!m!} \langle \Phi \omega_{11} \chi | \alpha \Phi \omega_{11} \chi \rangle.$$

The numerical factors introduced in  $A$  and  $B$  are for later convenience. Expanding  $\alpha$  and separating the integrals over spatial and spin coordinates, we obtain

$$B = \sum_{\tau} \langle \Phi | \tau \Phi \rangle \xi_{\tau} \frac{\theta}{n!m!} \langle \omega_{11} \chi | \tau \omega_{11} \chi \rangle. \quad (\text{A-10})$$

Now  $\Phi = \phi_{1a} \phi_{2a} \cdots \phi_{na} \phi_{1b} \phi_{2b} \cdots \phi_{mb}$ , (A-11)

where<sup>59</sup>  $\langle \phi_{ia} | \phi_{ja} \rangle = \delta_{ij}$ ,

$$\langle \phi_{ib} | \phi_{jb} \rangle = \delta_{ij}, \quad (\text{A-12})$$

$$\langle \phi_{ia} | \phi_{jb} \rangle = \lambda_i \delta_{ij}.$$

Thus the sum over  $\tau$  in (A-10) may be restricted to permutations which do *not* interchange elements of different columns of the tableau in Fig. 1. The group of such permutations is called<sup>60</sup>  $\mathfrak{P}_1$ , the group on the columns. Now consider

$$\langle \omega_{11}\chi | \tau \omega_{11}\chi \rangle = \langle \chi | \omega_{11}\tau \omega_{11}\chi \rangle$$

and expand  $\tau$ ,

$$\tau = \sum_{\beta, r, s} U_{rs\tau} \omega_{rs}^\beta. \quad (\text{A-13})$$

Using A-13 we obtain

$$\omega_{11}^\alpha \tau \omega_{11}^\alpha = U_{11\tau} \omega_{11}^\alpha \omega_{11}^\alpha = U_{11\tau} \omega_{11}^\alpha.$$

$$\text{But}^{61} \quad \theta \langle \chi | \omega_{11}\chi \rangle = \sum_{\sigma} U_{11\sigma} \langle \chi | \sigma \chi \rangle$$

$$= \sum_{\sigma \in \mathcal{O}_1} U_{11\sigma} = n!m!,$$

where<sup>60</sup>  $\mathcal{O}_1$  is the group on the rows of  $S_1$  in Fig. 1. Thus

$$B = \sum_{\tau \in \mathfrak{P}_1} \langle \Phi | \tau \Phi \rangle \xi_\tau U_{11\tau}. \quad (\text{A-14})$$

Now we rewrite A as

$$A = \sum_i \sum_{\tau \in \mathfrak{P}_1} \langle \Phi | m(i) | \tau \Phi \rangle V_\tau^i, \quad (\text{A-15})$$

where

$$\begin{aligned} V_\tau^i &= \frac{\theta}{n!m!} \xi_\tau \langle \omega_{11}\chi | 2s_z(i) | \tau \omega_{11}\chi \rangle \\ &= \frac{1}{n!m!} \xi_\tau \sum_{\sigma \in \mathfrak{S}_N} U_{11\sigma} \\ &\quad \times \langle \chi | \sigma^{-1} [2s_z(i)] \sigma | \sigma^{-1} \tau \omega_{11}\chi \rangle. \quad (\text{A-16}) \end{aligned}$$

$$\text{But} \quad \sum_{\sigma \in \mathfrak{S}_N} \sum_{j=1}^N \sum_{\sigma_{N-1,i}} \sigma_{N-1,i}(j,i), \quad (\text{A-17})$$

$$S_1^{[n,m]} = \begin{array}{|c|c|c|c|} \hline 1 & 2 & \cdots & m \\ \hline n+1 & n+2 & \cdots & N \\ \hline \end{array}$$

FIG. 1. The first Young's tableau for the shape  $[n, m]$ . This is the tableau used for  $\omega$ .

where  $\sigma_{N-1,i}$  is a permutation over the  $N-1$  elements *not including*  $i$ , and since

$$\sigma^{-1} [2s_z(i)] \sigma = 2s_z(j),$$

we have

$$\begin{aligned} V_\tau^i &= \frac{1}{n!m!} \xi_\tau \sum_{j=1}^N \sum_{\sigma_{N-1,i}} U_{11\sigma_{N-1,i}} \sigma_{N-1,i}(j,i) \\ &\quad \times \langle \chi | 2s_z(j) | (j,i) \sigma_{N-1,i}^{-1} \tau \omega_{11}\chi \rangle. \end{aligned}$$

However because of the form of  $\chi$ ,

$$\chi = \alpha(1)\alpha(2)\cdots\alpha(n)\beta(n+1)\cdots\beta(N), \quad (\text{A-18})$$

we have

$$\langle \chi | 2s_z(j) | \sigma \omega_{11}\chi \rangle = \frac{1}{\theta} \sum_{\pi \in \mathcal{O}_1} U_{11\sigma^{-1}\pi} \langle \chi | 2s_z(j) | \pi \chi \rangle.$$

Thus

$$\begin{aligned} V_\tau^i &= \frac{1}{\theta} \xi_\tau \sum_{j=1}^N \sum_{\sigma_{N-1,i}} U_{11\sigma_{N-1,i}} \sigma_{N-1,i}(j,i) \\ &\quad \times U_{11\tau \sigma_{N-1,i}} \langle \chi | 2s_z(j) | \chi \rangle \\ &= \frac{1}{\theta} \xi_\tau \left( \sum_{j=1}^n A_j - \sum_{j=n+1}^N A_j \right) \\ &= \frac{1}{\theta} \xi_\tau \left( \sum_{j=1}^N A_j - 2 \sum_{j=n+1}^N A_j \right), \quad (\text{A-19}) \end{aligned}$$

where

$$A_j = \sum_{\sigma_{N-1,i}} U_{11\sigma_{N-1,i}} \sigma_{N-1,i}(j,i) U_{11\tau \sigma_{N-1,i}} \sigma_{N-1,i}(j,i).$$

$$\text{But} \quad \sum_{j=1}^N A_j = \sum_{\sigma} U_{11\sigma} U_{11\tau \sigma} = \theta U_{11\tau}$$

(from the orthogonality theorem on group representations),

thus

$$V_\tau^i = \xi_\tau \left( U_{11\tau} - \frac{2}{\theta} \sum_{j=n+1}^N A_j \right).$$

Now consider  $i=N$ , in this case

$$U_{11\sigma_{N-1,N}}(j,N) = U_{11\sigma_{N-1,N}}, \quad \text{for } j > n,$$

thus

$$V_{\tau}^N = \xi_{\tau} \left( U_{11\tau} - \frac{2m}{\theta} \sum_{\sigma_{N-1,N}} U_{11\sigma_{N-1,N}} U_{11\tau\sigma_{N-1,N}} \right).$$

Since  $i=N$  we have

$$U_{11\sigma_{N-1,N}}^{\alpha} = U_{11\sigma_{N-1}}^{\alpha*},$$

where  $\alpha^*$  is the shape obtained from  $\alpha$  by deleting  $N$ , thus

$$\sum_{\sigma_{N-1,N}} U_{11\sigma_{N-1,N}} U_{11\tau\sigma_{N-1,N}} = \theta^* U_{11\tau}$$

(by the orthogonality theorem for  $s_{N-1}$ ), where  $\theta^*$  is the  $\theta$  for  $\alpha^*$ . Hence

$$V_{\tau}^N = \xi_{\tau} U_{11\tau} (1 - 2m\theta^*/\theta). \quad (\text{A-20})$$

But  $m\theta^*/\theta = (n+1-m)/(n+2-m)$ ,

and if  $\tau$  involves  $r$  disjoint transpositions, then<sup>57</sup>  $U_{11\tau r} = 1/\binom{n}{r}$ .

$$\text{Thus } V_{\tau r}^N = -\frac{(n-m)}{(n+2-m)\binom{n}{r}}. \quad (\text{A-21})$$

A related analysis yields

$$V_{\tau r}^n = -\frac{(n+2+r)}{(n-r)} V_{\tau r}^N. \quad (\text{A-22})$$

From (A-16) we see that for  $i > n$ , we have  $V_{\tau r}^i = V_{\tau r}^N$ ; and for  $i < n$ , we have  $V_{\tau r}^i = V_{\tau r}^n$ , if  $i$  is not included in  $\tau r$ . However if  $i$  is included in  $\tau r$ , the derivation proceeds just as for  $i=N$ , and we obtain  $V_{\tau r}^i = V_{\tau r}^N$ .

If in (A-5) we take  $m(i) = \delta(r_i)$ , we call the expectation value of  $2M$  the spin density,  $Q(0)$ . Thus (A-21) and (A-22) are sufficient to exactly evaluate the spin density.

In the past the spin density has been obtained<sup>12-16</sup> by approximating  $\langle \phi_{ia} | \phi_{jb} \rangle$  as

$$\langle \phi_{ia} | \phi_{jb} \rangle = \delta_{ij}, \quad (\text{A-23})$$

that is,  $\lambda_i = 1$ . In this case  $\langle \Phi | \tau \Phi \rangle = 1$  for all  $\tau \in \mathfrak{S}_1$  (see A-14) and

$$B = \frac{m!}{n!} \sum_{r=0}^m \frac{(n-r)!}{(m-r)!} = \frac{(n+1)}{(n-m+1)}.$$

Similarly if  $\tau$  does not include  $i$ , then

$$\langle \Phi | m(i) | \tau \Phi \rangle = |\phi_i(0)|^2$$

(see A-15), and if  $\tau$  includes  $i$ ,

$$\langle \Phi | m(i) | \tau \Phi \rangle = \phi_i(0) \phi_{i'}(0),$$

where  $i' = i+n$  if  $i \leq n$ , and  $i' = i-n$  if  $i > n$ . Using these values and (A-21) and (A-22) we obtain

$$Q(0) = [(n-m)/(n+2-m)(n+2-m)] \\ \times \left\{ \sum_{i=1}^m \left[ (n+3-m)[\phi_{ia}(0)]^2 - 2\phi_{ia}(0)\phi_{ib}(0) \right. \right. \\ \left. \left. - (n-m+1)[\phi_{ib}(0)]^2 \right] + \sum_{i=m+1}^n [\phi_{ia}(0)]^2 \right\}.$$

We will refer to the part of  $Q(0)$  involving  $\phi_{ia}$  and  $\phi_{ib}$  with  $i$  up to  $m$  as  $Q(0)_{\text{core}}$ . Thus within the approximation (A-23) we obtain

$$Q(0)_{\text{PUHF}}^{\text{core}} = \frac{(n-m)}{(n+2-m)} Q(0)_{\text{UHF}}^{\text{core}} \\ + \frac{(n-m)}{(n+2-m)(n+2-m)} \sum_{i=1}^m [\phi_{ia}(0) - \phi_{ib}(0)]^2,$$

where

$$Q(0)_{\text{UHF}}^{\text{core}} = \sum_{i=1}^m \{ [\phi_{ia}(0)]^2 - [\phi_{ib}(0)]^2 \}$$

is the core part of the spin density for UHF wave functions. Since

$$(n-m)/(n+2-m) = 2S/(2S+2) = S/(S+1),$$

this leads to

$$Q(0)_{\text{PUHF}}^{\text{core}} \approx \frac{S}{S+1} Q(0)_{\text{UHF}}^{\text{core}},$$

which has usually been used<sup>12-16</sup> to obtain approximate values for  $Q(0)_{\text{PUHF}}^{\text{core}}$

## APPENDIX B. THE HYPERFINE SPLITTING CONSTANTS

## (1) The Magnetic Hyperfine-Splitting Constants.

We take the magnetic hyperfine interaction operator as<sup>26</sup>

$$H_{\text{hfi}} = g_S \mu_B g_N \mu_N \left[ \left( \frac{2}{g_S} \right) \sum_e \frac{(\hat{l} \cdot \hat{I})}{r^3} + \sum_e \frac{3(\hat{s} \cdot \hat{r})(\hat{r} \cdot \hat{I}) - r^2(\hat{s} \cdot \hat{I})}{r^5} + \frac{8\pi}{3} \sum_e \delta(r)(\hat{r} \cdot \hat{I}) \right] \quad (\text{B-1})$$

and we take the matrix elements to be<sup>43</sup>

$$\langle JM_J IM_I | H_{\text{hfi}} | JM_J IM_I \rangle = A_{J, J, J} M_J M_I, \quad \langle JM_J IM_I | H_{\text{hfi}} | J-1, M_J IM_J \rangle = A_{J, J-1} (J^2 - M_J^2)^{1/2} M_I. \quad (\text{B-2})$$

In addition we define the reduced hyperfine constants,  $a_J$  and  $a_{J, J-1}$ ,

$$A_{J, J, J} = g_S \mu_B g_N \mu_N a_J, \quad A_{J, J-1} = g_S \mu_B g_N \mu_N a_{J, J-1} \quad (\text{B-3})$$

and define

$$a_l = (1/L) \langle LSLS | \sum_e (\hat{l}_z / r^3) | LSLS \rangle, \quad (\text{B-4})$$

$$a_c = S^{-1} \langle LSLS | \sum_e \delta(r) \hat{s}_z | LSLS \rangle = (2S)^{-1} Q(0), \quad (\text{B-5})$$

$$a_d = [SL(2L-1)]^{-1} \langle LSLS | \sum_e [(3z^2 - r^2)/r^5] \hat{s}_z | LSLS \rangle, \quad (\text{B-6})$$

where  $Q(0)$  is called the spin density at the nucleus. Then for  ${}^2P$  states we have

$$a_{3/2} = \frac{1}{3} [2(2/g_S) a_l + a_d + a_c] = \frac{2}{3} [(2/g_S) \langle r^{-3} \rangle_l - \frac{1}{3} \langle r^{-3} \rangle_d] + (8\pi/9) Q(0),$$

$$a_{1/2} = \frac{1}{3} [4(2/g_S) a_l - 10a_d - a_c] = \frac{4}{3} [(2/g_S) \langle r^{-3} \rangle_l + \langle r^{-3} \rangle_d] - (8\pi/9) Q(0),$$

$$a_{3/2, 1/2} = \frac{1}{3} [(2/g_S) a_l + \frac{5}{3} a_d - a_c] = \frac{1}{3} [(2/g_S) \langle r^{-3} \rangle_l - \frac{1}{2} \langle r^{-3} \rangle_d] - (8\pi/9) Q(0),$$

where the  $\langle r^{-3} \rangle_l$  and  $\langle r^{-3} \rangle_d$  parameters have been introduced for convenient comparison of terms. For  ${}^3P$  states we have

$$a_2 = \frac{1}{2} [(2/g_S) a_l + a_d + a_c] = \frac{1}{2} [(2/g_S) \langle r^{-3} \rangle_l + \frac{1}{3} \langle r^{-3} \rangle_d] + (2\pi/3) Q(0),$$

$$a_1 = \frac{1}{2} [(2/g_S) a_l - 5a_d + a_c] = \frac{1}{2} [(2/g_S) \langle r^{-3} \rangle_l - \langle r^{-3} \rangle_d] + (2\pi/3) Q(0),$$

$$a_{2, 1} = (1/2\sqrt{3}) [(2/g_S) a_l + 2a_d - a_c] = (1/2\sqrt{3}) [(2/g_S) \langle r^{-3} \rangle_l + \frac{2}{3} \langle r^{-3} \rangle_d - (4\pi/3) Q(0)],$$

$$a_{1, 0} = (2/3)^{1/2} [(2/g_S) a_l - \frac{5}{2} a_d - a_c] = (2/3)^{1/2} [(2/g_S) \langle r^{-3} \rangle_l - \frac{1}{2} \langle r^{-3} \rangle_d - (4\pi/3) Q(0)],$$

$$a_{2, 0} = 0.$$

For  ${}^4S$  states we have  $a_{3/2} = a_c = (8\pi/9) Q(0)$ .

To convert  $a_J$  from atomic units to Mc/sec, we multiply by  $C = 95,519 g_N$ .<sup>26</sup> For comparison to experimental results we have used the following values of  $I g_N^{62}$  and  $C$ :

<sup>11</sup>B: 2.688 52, 171.205; <sup>13</sup>C: 0.702 381, 134.183; <sup>14</sup>N: 0.403 71, 38.562;  
<sup>17</sup>O: -1.893 70, -72.3543; <sup>19</sup>F: 2.628 50, 502.147.

## (2) The Electric Hyperfine Constants

We take the perturbation to be

$$H_q = -\frac{1}{6} \sum_{ij} \bar{Q}_{ij} \bar{q}_{ij}, \quad (\text{B-7})$$

where  $\bar{Q}_{ij} = \sum_n (3R_i R_j - R^2 \delta_{ij})$ ,  $\bar{q}_{ij} = \sum_e (3r_i r_j - r^2 \delta_{ij})/r^5$ ,

and  $R$  and  $r$  represent nuclear and electronic coordinates, respectively. Then for an atom

$$\langle JIFM_F | H_q | JIFM_F \rangle = [b_J/2I(2I-1)J(2J-1)] [3\langle I \cdot J \rangle^2 + \frac{3}{2} \langle I \cdot J \rangle - I(I+1)J(J+1)] \quad (\text{B-8})$$

where  $\langle I \cdot J \rangle \equiv \frac{1}{2} [F(F+1) - I(I+1) - J(J+1)]$ .

The quadrupole coupling constant,  $b_J$ , can be written as

$$b_J = -q_J Q, \quad (\text{B-9})$$

where the nuclear quadrupole moment,  $Q$ , is

$$Q = \langle II | \sum_n 3Z^2 - R^2 | II \rangle \quad (\text{B-10})$$

and the electric field gradient,  $q_J$ , is

$$q_J = \langle JJ | \sum_e (3z^2 - r^2)/r^5 | JJ \rangle. \quad (\text{B-11})$$

We will evaluate electric field gradients for  $|LM_L SM_S\rangle$  type wave functions, for which we define

$$q_L \equiv \langle LLSM_S | \sum_e (3z^2 - r^2)/r^5 | LLSM_S \rangle. \quad (\text{B-12})$$

In this case  $q_J = C_{Jq}^{LS} q_L$ , (B-13)

where (see Appendix C)

$$C_{Jq}^{LS} = [6\langle L \cdot J \rangle^2 - 3\langle L \cdot J \rangle - 2L(L+1)J(J+1)]/L(2L-1)(J+1)(2J+3) \quad (\text{B-14})$$

and  $\langle L \cdot J \rangle = \frac{1}{2} [J(J+1) + L(L+1) - S(S+1)]$ . (B-15)

For maximum  $J$ , we obtain  $C_{Jq}^{LS} = 1$ , and for <sup>3</sup>P we obtain  $C_{1q}^{11} = -\frac{1}{2}$ . For the states and wave functions considered in this paper we have

$$q_J = -\frac{2}{5} \langle r^{-3} \rangle_l \text{ for } B^2P_{3/2} \text{ and } O^3P_2; \quad \text{and } q_J = +\frac{2}{5} \langle r^{-3} \rangle_l \text{ for } F^2P_{3/2} \text{ and } C^3P_2.$$

If in Eq. (B-9)  $b_J$  is in  $M_C$ ,  $q_J$  is in a.u., and  $Q$  is in barns, then

$$b_J(M_C) = 234.974 \times q_J(\text{a.u.}) Q(\text{barn}), \quad (\text{B-16})$$

where the conversion factor is based upon  $1 \text{ cm}^{-1} = 4.556 336 \times 10^{-6} \text{ hartree} = 2.997 925 \times 10^{10} \text{ Hz}$  and  $1 a_0 = 0.529 167 \text{ \AA}$ .

## APPENDIX C

The relationship between  $q_J$  and  $q_L$  is derived as follows. Using the Wigner-Eckart theorem<sup>64</sup> we have

$$\langle LM_L SM_S | \tilde{q}_{ij} | LM_L SM_S \rangle = [q_L/L(2L-1)] \langle LM_L SM_S | \tilde{T}_{ij}^L | LM_L SM_S \rangle, \quad (C-1)$$

where 
$$\tilde{T}_{ij}^L \equiv \frac{3}{2} (\tilde{L}_i \tilde{L}_j + \tilde{L}_j \tilde{L}_i) - \tilde{L}^2 \delta_{ij},$$

and 
$$\langle JM_J | \tilde{q}_{ij} | JM_J \rangle = [q_J/J(2J-1)] \langle JM_J | \tilde{T}_{ij}^J | JM_J \rangle, \quad (C-2)$$

where 
$$\tilde{T}_{ij}^J \equiv \frac{3}{2} (\tilde{J}_i \tilde{J}_j + \tilde{J}_j \tilde{J}_i) - \tilde{J}^2 \delta_{ij}.$$

But for  $LS$  coupling we can expand  $|LSJM_J\rangle$  in terms of  $|LM_L SM_S\rangle$  to obtain

$$\langle LSJM_J | \tilde{q}_{ij} | LSJM_J \rangle = [q_L/L(2L-1)] \langle LSJM_J | \tilde{T}_{ij}^L | LSJM_J \rangle. \quad (C-3)$$

In order to evaluate the right side of (C-3), we use the Wigner-Eckart theorem to write

$$\langle LSJM_J | \tilde{T}_{ij}^L | LSJM_J \rangle = C \langle LSJM_J | \tilde{T}_{ij}^J | LSJM_J \rangle. \quad (C-4)$$

Next we note that

$$\langle LSJM_J | \sum_{ij} \tilde{T}_{ij}^L \tilde{T}_{ij}^J | LSJM_J \rangle = C \langle LSJM_J | \sum_{ij} \tilde{T}_{ij}^J \tilde{T}_{ij}^J | LSJM_J \rangle \quad (C-5)$$

with the same constant  $C$  as in (C-4).

But 
$$\frac{1}{3} \sum_{ij} \tilde{T}_{ij}^L \tilde{T}_{ij}^J = 3(\tilde{L} \cdot \tilde{J})(\tilde{L} \cdot \tilde{J}) - \frac{3}{2} (\tilde{L} \cdot \tilde{J}) - \tilde{L}^2 \tilde{J}^2, \text{ and } \frac{1}{3} \sum_{ij} \tilde{T}_{ij}^J \tilde{T}_{ij}^J = 2\hat{J}^2 \tilde{J}^2 - \frac{3}{2} \hat{J}^2,$$

and  $|LSJM_J\rangle$  is one eigenstate of both of these operators. Thus

$$C = [6\langle L \cdot J \rangle^2 - 3\langle L \cdot J \rangle - 2L(C+1)J(J+1)]/J(J+1)(2J-1)(2J+3),$$

where the number  $\langle L \cdot J \rangle$  is given in (B-15). Hence we obtain  $q_J = C_{Jq}^{LS} q_L$  with  $C_{Jq}^{LS}$  as given in Eq. (B-14). A similar approach is used to relate  $a_J$  and  $a_l$ ,  $a_d$ , and  $a_c$  as given in Ref. 26.

\* Partially supported by a Grant (GP-6965) from the National Science Foundation.

† Alfred P. Sloan Research Fellow.

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<sup>13</sup>N. Bessis, H. Lefebvre-Brion, and C. M. Moser,

Phys. Rev. 128, 213 (1962): B and O atoms.

<sup>14</sup>N. Bessis, H. Lefebvre-Brion, and C. M. Moser, Phys. Rev. 130, 1441 (1963): F atom.

<sup>15</sup>N. Bessis, H. Lefebvre-Brion, and C. M. Moser, Phys. Rev. Mod. Phys. 35, 548 (1963): C atom.

<sup>16</sup>N. Bessis *et al.* Phys. Rev. 135, A588 (1964): P atom.

<sup>17</sup>For example, the UHF wave function for N is a mixture of <sup>4</sup>S, <sup>6</sup>S, and <sup>8</sup>S states rather than just <sup>4</sup>S.

<sup>18</sup>P. O. Löwdin, Advan. Chem. Phys. 2, 207 (1959).

<sup>19</sup>Actually except for Li<sup>10</sup> these calculations (Refs. 12–16) just approximated the PUHF wave function.

<sup>20</sup>W. Marshall, Proc. Phys. Soc. (London) 78, 113 (1961).

<sup>21</sup>P. O. Löwdin, Phys. Rev. 97, 1509 (1955).

<sup>22</sup>This method is sometimes referred to as spin-polarized extended Hartree-Fock, or else just extended Hartree-Fock, or else projected Hartree-Fock. For a recent review see P. O. Löwdin, in Quantum Theory of Atoms, Molecules and Solid-State (Academic Press, Inc., New York, 1966) p. 601.

<sup>23</sup>W. A. Goddard III, Phys. Rev. 157, 81 (1967), referred to as II.

<sup>24</sup>W. A. Goddard III, J. Chem. Phys. 48, 450 (1968), referred to as III.

<sup>25</sup>W. A. Goddard III, Phys. Rev. 157, 93 (1967).

<sup>26</sup>W. A. Goddard III, Phys. Rev. 176, 106 (1968).

<sup>27</sup>W. A. Goddard III, J. Chem. Phys. 48, 5337 (1968), referred to as IV.

<sup>28</sup>C. C. J. Roothaan, Rev. Mod. Phys. 23, 69 (1951).

<sup>29</sup>A Slater orbital is a function of the form  $\chi_{nlm} = N_n r^{-\zeta} e^{-\zeta r} Y_{lm}$ , where  $\zeta$  is a variable parameter called the orbital exponent and  $N_n$  is a normalization factor.

<sup>30</sup>Using this definition of the spin density, the  $Q(0)$  for an UHF wave function is just the density at the nucleus for up-spin electrons minus that for down-spin electrons.

<sup>31</sup>The following notation is used to refer to published basis sets: CR: E. Clementi and D. L. Raimonde, J. Chem. Phys. 38, 2686 (1963), minimum basis set; CDZ: E. Clementi, J. Chem. Phys. 40, 1944 (1964) [see also IBM Technical Report No. RJ-256, 1963 (unpublished)] double zeta; BGCR: P. S. Bagus, T. L. Gilbert, H. D. Cohen, and C. C. J. Roothaan, to be published; CRY: E. Clementi, C. C. J. Roothaan, and M. Yoshimine, Phys. Rev. 127, 1618 (1962); BLM: N. Bessis, H. Lefebvre-Brion, and C. M. Moser, Ref. 11–15.

<sup>32</sup>When referring to a basis set we use the notation ( $n_1/n_2$ ) to indicate a basis set with  $n_1$  different  $s$  basis functions and  $n_2$  different sets of  $p$  basis functions. An asterisk next to an orbital exponent means that the orbital exponent was not reoptimized for this basis set. Note that the orbital exponents are not generally optimized to the last place quoted.

<sup>33</sup>LMSS atomic program No. 3. Laboratory of Molecular Structure and Spectra, University of Chicago.

<sup>34</sup>C. C. J. Roothaan and P. S. Kelly, Phys. Rev. 131, 1177 (1963).

<sup>35</sup>The virial ratio is  $V/2E$ , the total potential energy divided by twice the total energy.  $V/2E$  is 1.0 for the exact wave function and should be within 0.00001 of 1 for a fairly well optimized basis set. Scaling of the wave

function could have been used to assure  $V/2E=1$ ; however we felt that this would hide flaws of the basis sets and would not necessarily lead to properties closer to the theoretical limit.

<sup>36</sup>The  $N$  double zeta set has been reoptimized starting with the CDZ orbital exponents. The orbital exponents change a great deal but the HF energy drops only 0.00005. However  $Q(0)$  changes sign; this indicates just how sensitive  $Q(0)$  is to this type of basis set.

<sup>37</sup>By accurate here, we of course mean a good approximation to the value we would obtain with a complete basis set.

<sup>38</sup>The experimental hyperfine constants were recalculated from the experimental data using the relations in Appendix B. For <sup>11</sup>B and <sup>11</sup>C we had to assume  $\langle r^{-3} \rangle_I = \langle r^{-3} \rangle_d$  since the  $a_J, J$  have not been measured.

<sup>39</sup>P. S. Bagus and B. Liu, Phys. Rev. 148, 79 (1966).

<sup>40</sup>We used the term SCF meaning self-consistent field to collectively refer to any or all of the HF, UHF, or GF methods.

<sup>41</sup>Gaussian functions [S. Huzinaga, J. Chem. Phys. 42, 1293 (1965)] have the form  $Ne^{-\zeta r^2} Y_{lm}(\theta, \phi)$ , and thus a finite number of them cannot lead to a cusp. Such functions are being used in polyatomic calculations because the many-center electron repulsion integrals are far simpler than for Slater orbitals.

<sup>42</sup>We let  $\langle r^{-3} \rangle_I$  represent the effective  $\langle r^{-3} \rangle$  for the orbital operator,  $\Sigma \hat{l}_z / r^3$ , and  $\langle r^{-3} \rangle_d$  represent the effective  $\langle r^{-3} \rangle$  for the spin-dipole operator,  $\Sigma [3(s \cdot r)z - r^2 s_z] / r^5$ ; see Appendix B.

<sup>43</sup>J. S. M. Harvey, Proc. Roy. Soc. (London) A285, 581 (1965).

<sup>44</sup>Note that for O and F the GF and UHF wave functions are not eigenfunctions of  $\hat{J}^2$  and  $\hat{L}^2$ . As is the usual practice for UHF (where the wave function is also not an eigenfunction of  $\hat{S}^2$ ) we calculate the wave function for  $M_L=L$  and  $M_S=S$  to obtain  $a_I, a_d$ , and  $Q(0)$  and use the usual relations connecting these to  $a_J$ .

<sup>45</sup>H. F. Schaefer III, R. A. Klemm, and F. E. Harris, Phys. Rev., 176, 49 (1968).

<sup>46</sup>R. A. Haberstroh, W. J. Kossler, O. Ames, and D. R. Hamilton, Phys. Rev. 136, B932 (1964).

<sup>47</sup>G. Wessel, Phys. Rev. 92, 1581 (1953).

<sup>48</sup>R. M. Sternheimer, Phys. Rev. 164, 10 (1967), and references given therein.

<sup>49</sup>S. M. Blinder, Bull. Am. Phys. Soc. 5, 14 (1960).

<sup>50</sup>T. P. Das and A. Mukherjee, J. Chem. Phys. 33, 1808 (1960).

<sup>51</sup>The program which evaluates  $Q(0)$ , the energy, and other properties for PUHF wave functions is rather simple and could be made available for distribution if there is any demand for such a program.

<sup>52</sup>R. K. Nesbet, in La Structure Hyperfine Magnétique des Atomes et des Molécules (Centre National de la Recherche Scientifique, Paris, 1967), p. 87.

<sup>53</sup>U. Kaldor, J. Chem. Phys. 49, 6 (1968).

<sup>54</sup>S. Larsson, Phys. Rev. 169, 49 (1968).

<sup>55</sup>S. Lunell, Phys. Rev. 173, 85 (1968).

<sup>56</sup>R. C. Ladner and W. A. Goddard, J. Chem. Phys. (to be published).



<sup>57</sup>W. A. Goddard III, *Phys. Rev.* **157**, 73 (1967), referred to as I.

<sup>58</sup>The  $\omega_{11}\chi$  here should be  $\omega_{\bar{f}\bar{f}}\chi$ , but the tableau associated with the  $f$  tableau of a two-columned shape is the 1 tableau of the associated two-rowed shape. This is shown in Fig. 1.

<sup>59</sup>As was shown in III (Ref. 24) we may take a unitary transformation on the GF orbitals such that all expectation values are invariant but such that  $\langle \phi_{ia} | \phi_{jb} \rangle = \lambda_j \delta_{ij}$  for the new orbitals.

<sup>60</sup>D. E. Rutherford, *Substitutional Analysis* (Edinburgh

University Press, London, 1948).

<sup>61</sup>We will generally delete the shape symbol  $\alpha$  on  $O_n^\alpha$ ,  $\omega_{11}^\alpha$ , and  $U_{11\tau}^\alpha$ .

<sup>62</sup>N. F. Ramsey, *Molecular Beams* (Oxford University Press, London, 1956), p. 172.

<sup>63</sup>E. R. Cohen and J. W. M. Dumond, *Rev. Mod. Phys.* **37**, 537 (1965).

<sup>64</sup>B. R. Judd, *Operator Techniques in Atomic Spectroscopy* (McGraw-Hill Book Co., Inc., New York, 1963); V. Heine, *Group Theory in Quantum Mechanics* (Pergamon Press, Ltd., New York, 1960).

## Dispersion Calculation of Resonant Photo-Ionization Line Shapes: Application to Helium

William P. Reinhardt\*

*Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138*

(Received 16 January 1969)

For resonant photo-ionization of spherical atoms, unitarity and simple assumptions about the analytic properties of inelastic scattering amplitudes allow calculation of the photo-ionization line shape from the elastic final-state phase shift. Explicitly, the Fano shape factor,  $q$ , is given by  $\cot \delta^{\text{nr}}$ , where  $\delta^{\text{nr}}$  is the nonresonant elastic phase shift for the final state. This result predicts that if  $\delta^{\text{nr}}$  is constant for a series of resonances below an inelastic threshold, the values of  $q$  will be constant for the series and independent of the type of resonance. For photo-ionization of helium, values of  $q$  calculated from the elastic phase shifts are seen to be in fair agreement with those calculated from wave functions.

### I. INTRODUCTION

In atomic and molecular physics it is usual to assume that the Hamiltonian is known. This means that, in principle, one can determine wave functions appropriate to processes of interest and, using these wave functions, calculate or predict experimental results. However, in many cases of interest the wave function is not immediately available or would be difficult to calculate to the necessary accuracy. It is thus of interest to investigate the use of mathematical techniques which do not depend directly on the use of wave functions, but rather on the symmetries of the Hamiltonian and on simple conjectures as to the analytic structure of certain amplitudes which describe processes of interest. These techniques<sup>1</sup> have been developed for use in high-energy particle physics where even the existence of potentials (in the ordinary sense) is in doubt and thus theories must be based on unitarity (conservation of probability) and con-

jectures as to symmetries of the unknown equations of motion.

In atomic and molecular scattering processes, as in particle physics, it will prove useful to consider determining the scattering amplitude directly, rather than calculating it through the intermediary of the wave function. Rather than directly making use of the Mandelstam double dispersion<sup>2</sup> relation which provides a dynamical framework for direct calculation of the scattering amplitudes, and, thus, is equivalent to the familiar Schrödinger dynamics,<sup>3</sup> we will concentrate on those aspects of the theory which point to relationships between the results of different experiments. For example, in the case where an inelastic process is dominated by a single final-state interaction we shall see that the phase of the inelastic amplitude is determined by the phase shift for elastic scattering in the dominant final channel. This result is known as Watson's theorem<sup>4</sup> and is often useful because the phase of the inelastic amplitude determines the discontinu-