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Atomic Hyperfine Structure. II. First-Order Wave Functions for the Ground States of B,C,N,O, and F

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Ab initio computations of hyperfine structure have been made for the ground states of B, C, N, O, and F using a first-order wave function designed to include the strongly structure-dependent part of the electron distribution. The magnetic hyperfine constants are in poorer agreement with experiment than for the previously studied and less extensive polarization wave functions, but the discrepancies are more uniform, particularly for the spin density at the nucleus.

I. INTRODUCTION

There has been much recent interest in the *ab initio* calculation of the hyperfine structure (hfs) of lighter atoms. A number of such studies have been made in the restricted Hartree-Fock (RHF) approximation, and in favorable cases RHF calculations have been in rather satisfactory agreement with experiment. However, the RHF wave function does not take account of the fact that the two electrons in a doubly occupied orbital may experience different environments, and this deficiency can cause the prediction of poor results for spin-dependent properties of open-shell systems.[1]

Although there are many possible ways to improve on the RHF method, it would be most desirable to proceed in ways which share with RHF the property that they form logical and relatively unarbitrary approximation schemes. In order to effect a real improvement over RHF, it is also important to introduce features which place open-shell systems, including those of nonzero spin, on an equal level of approximation with closed-shell systems.

Three main classes of approximations have received appreciable attention. First, there are schemes based on perturbation theory, in which the level of approximation can be the *order* to which calculations are taken or, if infinite-order theory is used, the *classes* of terms (diagrams) which are included. These methods have been applied to atomic systems by Kelly,[2] Das and coworkers,[3] Nesbet,[4] and others, and general features of perturbation formulations have recently been reviewed by Freed[5] and by Musher and Schulman.[6]

The second general class of approximations involves the use of variationally determined configuration interaction (CI) wave functions.[7,8] The level of approximation is defined by the number and types of configurations to be included. Under certain conditions CI methods can be identified with infinite-order perturbation approximations, and may in some cases define convenient ways of carrying out perturbation calculations.

A third approximation possibility is in the removal of the "restrictions" of RHF theory. Even for closed-shell atoms, these restrictions include the assumption of double-occupancy of spatial orbitals and the use of orbitals of definite angular momentum. Spin-extended[9] and spin-optimized[10] self-consistent-field (SCF) methods lift the first of these restrictions, and bring closed and open-shell atoms to a more nearly equivalent footing. However, no SCF method utilizing the one-electron approximation can completely describe electron correlation effects. Our recent experience has also indicated that it is easier to remove the angular momentum restrictions of SCF theory by limited CI methods than by further extensions of SCF methods.

To evaluate the relative effectiveness of perturbation and CI methods in hfs calculations, it is necessary to examine studies of both types for their accuracy and for the effort involved. This series of papers is designed to provide such information for the configuration interaction methods. The first paper[8] deals with calculations at a level of approximation defined by what we call the *polarization wave function.* This wave function includes the RHF configuration and all configurations whose orbital occupancies are singly excited relative thereto, projected to yield a state of definite L and S. The polarization wave function is therefore to first order a SCF function with no restrictions on angular momenta of individual orbitals, double orbital occupancy, or choice of spin function. An exact rendering of the polarization wave function would require the use of an infinite basis set; we actually extended the basis sets until the results were essentially basis-independent.

The present paper considers the further improvement of the polarization wave function by the addition of configurations whose importance is essentially derived from the shell structure of the atom involved. As the resulting CI wave function is believed to correct the most significant deficiencies of the RHF function, we call it the *first-order wave function.*

II. FIRST-ORDER WAVE FUNCTIONS

The first-order wave function is defined as the CI L-S eigenfunction based on all configurations whose orbital occupancies include at most one electron beyond the valence shell. This wave function therefore includes not only the RHF configuration, but also *all* excitations within the valence shell, together with arbitrary single excitations from all of these configurations. This choice of wave function is designed to include all configurations differing little in energy from the RHF configuration but excluded therefrom by its restricted form, and to permit for all these configurations the first-order correction of deficiencies associated with double orbital occupancy.

Specializing to first-row atoms, the first-order wave function includes the RHF configuration, any other configurations built from $1s$, $2s$, and $2p$ orbitals and capable of forming an appropriate L-S eigenfunction, plus single excitations to other orbitals. Thus the first-order wave function includes (when they exist) "degeneracy effect" configurations[11] such as $2s^2 \to 2p^2$ and the configurations describing polarization therefrom, while the previously considered polarization wave function included only the RHF function and its polarization. The types of configurations used in our calculations are enumerated in Table I.

The configurations of the first-order wave function include those which are most sensitive to the atomic structure and which the shell model suggests would be most important. It is therefore reasonable to argue that these configurations contain the portion of the electronic energy which is strongly structure-dependent. For this reason we refer to the difference between the RHF energy and the energy of the first-order wave function as the *orbital* correlation energy.[12]

Separation of the correlation energy into the structure-dependent and smoothly varying parts is not new to this work, since such a separation has been explicitly suggested by Silverstone and Sinanoğlu[13] some time ago. As they indicated, and as Sinanoğlu and Öksüz[14] have illustrated, the smoothly varying portion of the correlation energy might be expected to be susceptible to interpolative estimation. However, our specific identification of the orbital correlation energy with the first-order wave function differs in detail from the proposal of Silverstone and Sinanoğlu in that our classification of configurations is based on orbital occupancies rather than on Slater determinants. This difference causes us to include structure-sensitive determinants not previously considered.

TABLE I. Orbital occupancies, separated into three types, for first-order wave functions. X is an orbital occupied in the Hartree-Fock wave function, and Y is an orbital not occupied in the Hartree-Fock function. In general, there is more than one configuration of the proper symmetry corresponding to each orbital occupancy. The number n of $2p$ electrons goes from one for B to five for F. In these calculations, $s_i = \{s_1, s_2, s_3, s_4, s_5, s_6\}$: $p_i = \{p_1, p_2, p_3, p_4, p_5, p_6\}$; $d_i = \{d_1, d_2, d_3, d_4, d_5, d_6\}$; $f_i = \{f_1, f_2, f_3, f_4\}$.

1) $X_i \to Y_i$		
	$1s \to s_i$	$1s\ s_i\ 2s^2 2p^n$
	$1s \to d_i$	$1s\ d_i\ 2s^2 2p^n$
	$2s \to s_i$	$1s^2 2s\ s_i\ 2p^n$
	$2s \to d_i$	$1s^2 2s\ d_i\ 2p^n$
	$2p \to p_i$	$1s^2 2s^2 2p^{n-1} p_i$
	$2p \to f_i$	$1s^2 2s^2 2p^{n-1} f_i$
2) $X_i X_j \to X_k X_l$		
	$1s^2 \to 2p^2$	$2s^2 2p^{n+2}$
	$2s^2 \to 2p^2$	$1s^2 2p^{n+2}$
	$1s2s \to 2p^2$	$1s\ 2s 2p^{n+2}$
3) $X_i X_j \to X_k Y_i$		
	$1s^2 \to 2p p_i$	$2s^2 2p^{n+1} p_i$
	$1s^2 \to 2p f_i$	$2s^2 2p^{n+1} f_i$
	$2s^2 \to 2p p_i$	$1s^2 2p^{n+1} p_i$
	$2s^2 \to 2p f_i$	$1s^2 2p^{n+1} f_i$
	$1s2s \to 2p p_i$	$1s\ 2s 2p^{n+1} p_i$
	$1s2s \to 2p f_i$	$1s\ 2s 2p^{n+1} f_i$

First-order wave functions were determined in the present work for the ground states of B, C, N, O, and F, using basis sets large enough to produce convergence in energy believed to be within 0.0001 hartree. The basis sets were slightly larger than those which appeared necessary for the polarization wave functions, and consisted of the RHF orbitals plus 22 additional orbitals, six each of s, p, and d symmetry, and four of f symmetry. The basis sets and first-order wave functions of the states listed above and a number of other atomic states will be reported in detail elsewhere. The methods of calculation were as previously described. The first-order wave functions involve considerably larger CI's than do the polarization functions treated earlier. The ground states of

B, C, N, O, and F were described by 153, 181, 73, 113, and 95 configurations, respectively, as compared to polarization wave functions involving, respectively, 53, 65, 41, 77, and 65 configurations.

Before proceeding to an investigation of hyperfine structure, we note the energies given in Table II for first-order wave functions. The irregularity of the improvement over RHF and polarization-wave-function energies is a strong indication of the structure dependence of the configurations included. It may also be seen that a good fraction of the correlation energy remains to be accounted for by configurations not included in the present work. We shall shortly see the importance of these configurations in hfs calculations.

III. HYPERFINE STRUCTURE

The basic nonrelativistic theory of atomic hyperfine structure, which lead to the hfs formulas presented in detail in the preceding paper of this series, was developed by Goudsmit,[15] Fermi,[16] Casimer,[17] and Trees.[18] To summarize, the hyperfine energy levels W_F are given by

$$W_F = \tfrac{1}{2}AK + BK(K+1) \ , \qquad (1)$$

where $K = F(F+1) - I(I+1) - J(J+1)$. (2)

In Eq. (1), A arises from the magnetic dipole interaction and B from the electric quadrupole interaction between the nucleus and the electrons.

In the L-S coupling scheme

$$A = (2\mu_B \mu_I \mu_N / I)(\lambda_l \alpha_l + \lambda_d \alpha_d + \lambda_s \alpha_s) \ , \qquad (3)$$

$$B = [3e^2 Q / 2I(I-1)] \lambda_q \alpha_q \ , \qquad (4)$$

where μ_B is the Bohr magneton, μ_I is the nuclear magnetic dipole moment in nuclear magnetons, μ_N is the nuclear magneton, e is the electronic charge, and Q is the nuclear electric quadrupole moment. The quantities λ_l, λ_d, λ_s, and λ_q are rather complicated algebraic functions of L, S, and J, while α_l, α_d, α_s, and α_q are the reduced matrix elements[19]

$$\alpha_l = \langle LS \| \textstyle\sum_i (\vec{l}_i / r_i^3) \| LS \rangle \ , \qquad (5)$$

$$\alpha_d = \langle LS \| \sum_i \frac{3\vec{s}_i \cdot \vec{r}_i}{r_i^5} \vec{r}_i - \frac{\vec{s}_i}{r_i^3} \| LS \rangle \ , \qquad (6)$$

$$\alpha_s = \langle LS \| \textstyle\sum_i (8\pi/3) \delta(\vec{r}_i) \vec{s}_i \| LS \rangle \ , \qquad (7)$$

$$\alpha_q = \langle LS \| \textstyle\sum_i (\overleftrightarrow{C}_i^{(2)} / r_i^3) \| LS \rangle \ . \qquad (8)$$

Here $\overleftrightarrow{C}_i^{(2)}$ is the tensor of rank two introduced by Racah.[20] The preceding paper[8] gives explicit formulas for the λ's and relates the α's to expectation values calculated for wave functions with definite values of L, S, M_L, and M_S.

Using the first-order wave functions described in the preceding section, we have calculated the expectation values and reduced matrix elements relevant to the hyperfine structure of the ground states of first-row atoms, with the results listed in Table III. For comparison, we also list RHF values, computed from the "accurate" wave functions of Bagus and Gilbert.[21]

IV. RESULTS AND DISCUSSION

A. Magnetic Dipole Interaction

Using the reduced matrix elements in Table III and the nuclear magnetic dipole moments tabulated by Fuller and Cohen,[22] we may apply Eq. (3) to obtain the magnetic hyperfine constants A corresponding to the first-order wave functions. Table IV presents these A values, comparing them with values obtained from polarization and RHF functions and, where possible, comparing also with experiment. It is clear from Table IV that the first-order wave functions uniformly yield magnetic hyperfine constants in somewhat poorer agreement with experiment than do the previously considered polarization wave functions. In fact, for several atoms, the first-order function gives poorer results than the RHF function. In order to understand the performance of the first-order wave function, let us make a closer examination of the individual contributions to A corresponding to α_l, α_d, and α_s.

One of the main motivations for proceeding beyond the RHF approximation was the hope of improving the description of the spin densities of the nuclei of open-shell atoms, and therewith α_s. Several previous studies[7,23] of the spin densities of atoms larger than Li have given erratic results, sometimes even being incorrect as to sign. Nesbet has found that, in his Bethe-Goldstone perturbation approach,[4] the work must be carried through three-particle interactions before stable results are obtained. Schaefer and Kaldor[24] have also discussed this problem. However, unrestricted Hartree-Fock[25,26] (UHF) and polarization-function calculations have given spin densities of the correct order of magnitude.

Calculating the spin density for a state with $J = L + S$ from the formula[8]

$$|\psi(0)|^2 = (3J/4\pi)\lambda_s \alpha_s$$
$$= 2\langle J = L+S, M_J = J | \textstyle\sum_i \delta(\vec{r}_i) s_{zi} | J = L+S, M_J = J \rangle, \qquad (9)$$

we see in Table V that the first-order wave function provides spin densities whose deviations from the available experimental data are smaller than those of the UHF calculations, and compara-

TABLE II. Energies, in hartrees, of first-order wave functions. Basis sets will be described elsewhere, and were designed to guarantee convergence to within 0.0001 hartree of the exact first-order energy.

	^2P B	^3P C	^4S N	^3P O	^2P F
Restricted Hartree-Fock (Ref. 21)	−24.52906	−37.68862	−54.40093	−74.80938	−99.40933
Polarization wave function (Ref. 8)	−24.55129	−37.72814	−54.45176	−74.85571	−99.43811
First order wave function (this work)	−24.58742	−37.75068	−54.45663	−74.85898	−99.43976
Experiment[a]	−24.658	−37.856	−54.612	−75.110	−99.805

[a] P. E. Cade and W. M. Huo, J. Chem. Phys. 47, 614 (1967).

TABLE III. Calculated hyperfine-structure parameters in atomic units. First-order values are given above the Restricted-Hartree-Fock values. For polarization wave function values, see Ref. 8.

	^2P B	^3P C	^4S N	^3P O	^2P F
$\langle J=L+S, M_J=J \vert \sum_i (l_{zi}/r_i^3) \vert J=L+S, M_J=J \rangle$	0.757 217 1	1.663 347 8	0.0	4.570 200 7	7.233 549 6
	0.775 502 0	1.692 167 3	0.0	4.972 941 0	7.544 711 0
$\langle J=L+S, M_J=J \vert \sum_i [(3\cos^2\theta_i - 1) s_{zi}/r_i^3] \vert J=L+S, M_J=J \rangle$	−0.163 335 3	0.353 720 0	0.0	1.019 963 0	−1.590 012 1
	−0.155 100 4	0.338 433 5	0.0	0.994 588 2	−1.508 942 2
$\langle J=L+S, M_J=J \vert \sum_i (8\pi/3)\delta(\vec{r}_i) s_{zi} \vert J=L+S, M_J=J \rangle$	0.017 232 5	0.095 451 9	0.299 069 1	0.262 859 6	0.207 691 8
	0.0	0.0	0.0	0.0	0.0
$\langle J=L+S, M_J=J \vert \sum_i [(3\cos^2\theta_i - 1)/r_i^3] \vert J=L+S, M_J=J \rangle$	−0.273 313 1	0.614 845 0	0.0	−1.722 837 2	2.740 750 6
	−0.310 200 8	0.676 866 9	0.0	−1.989 176 4	3.017 884 4
$\alpha_l = \langle LS \Vert \sum_i (\vec{l}_i/r_i^3) \Vert LS \rangle$	1.854 795 5	4.074 353 3	0.0	11.194 659 6	17.718 505 5
	1.899 584 2	4.144 946 4	0.0	12.181 168 0	18.480 692 2
$\alpha_d = \langle LS \Vert \sum_i (3\vec{s}_i \cdot \vec{r}_i/r_i^5)\vec{r}_i - (\vec{s}_i/r_i^3) \Vert LS \rangle$	3.464 865 4	−7.503 533 6	0.0	−21.636 683 5	33.729 250 1
	3.290 176 3	−7.179 257 6	0.0	−21.098 402 0	32.009 497 9
$\alpha_s = \langle LS \Vert \sum_i (8\pi/3)\delta(\vec{r}_i)\vec{s}_i \Vert LS \rangle$	0.042 210 9	0.233 808 4	0.772 193 1	0.643 871 9	0.508 738 9
	0.0	0.0	0.0	0.0	0.0
$\alpha_q = \langle LS \Vert \sum_i (\overleftrightarrow{C}_i^{(2)}/r_i^3) \Vert LS \rangle$	−0.748 498 7	1.683 822 6	0.0	−4.718 184 1	7.505 854 6
	−0.849 519 9	1.853 676 4	0.0	−5.447 584 0	8.264 816 8

TABLE IV. Calculated magnetic hyperfine constants in MHz.[a]

^2P B	$A_{3/2}$ B^{10}	$A_{1/2}$ B^{10}	$A_{3/2}$ B^{11}	$A_{1/2}$ B^{11}
First order (this work)	23.331 55	119.5205	69.669 42	356.8955
Polarization (Ref. 8)	24.131 39	120.8027	72.057 81	360.7243
Hartree-Fock (Ref. 8)	23.686 12	118.4306	70.728 21	353.6411
Experiment	• • •	122.585[b]	73.347[c]	366.077[b]
^3P C	A_2 C^{13}	A_1 C^{13}		
First order (this work)	141.5720	−0.656 77		
Polarization (Ref. 8)	144.1604	0.818 56		
Hartree-Fock (Ref. 8)	136.0822	0.0		
Experiment	• • •	• • •		
^4S N	$A_{3/2}$ N^{13}	$A_{3/2}$ N^{14}	$A_{3/2}$ N^{15}	
First order (this work)	± 12.262 04	7.677 57	−10.770 66	
Polarization (Ref. 8)	± 12.535 07	7.848 52	−11.010 48	
Hartree-Fock (Ref. 8)	0.0	0.0	0.0	
Experiment	± 16.673[d]	10.450 93[e]	−14.645 44[e]	
^3P O	A_2 O^{15}	A_1 O^{15}	A_2 O^{17}	A_1 O^{17}
First order (this work)	401.4588	−18.296 72	−211.5016	9.639 31
Polarization (Ref. 8)	404.2390	−17.570 73	−212.9663	9.256 83
Hartree-Fock (Ref. 8)	409.313	0.0	−215.6393	0.0
Experiment	414.87[f]	• • •	−218.569[g]	4.738[g]
^2P F	$A_{3/2}$ F^{19}	$A_{1/2}$ F^{19}	$A_{3/2}$ F^{20}	$A_{1/2}$ F^{20}
First order (this work)	1956.677	10 085.48	389.6680	2008.502
Polarization (Ref. 8)	1966.328	10 126.42	391.5900	2016.656
Hartree-Fock (Ref. 8)	2018.388	10 091.94	401.9576	2009.788
Experiment	2009.99[h]	10 244.21[g]	• • •	• • •

[a] The nuclear magnetic dipole moments μ used are given in Ref. 8, and are from the tabulation of G. H. Fuller and V. W. Cohen (see Ref. 22).

[b] H. Lew and R. S. Title, Can. J. Phys. 38, 868 (1960).

[c] G. Wessel, Phys. Rev. 92, 1581 (1953).

[d] A. M. Bernstein, R. A. Haberstroh, D. R. Hamilton, M. Posner, and J. L. Snider, Phys. Rev. 136, B27 (1964).

[e] W. W. Holloway, E. Luscher, and R. Novick, Phys. Rev. 126, 2109 (1966).

[f] E. D. Commins and H. R. Feldman, Phys. Rev. 131, 700 (1963).

[g] J. S. M. Harvey, Proc. Roy. Soc. (London) A285, 581 (1965).

[h] H. E. Radford, V. W. Hughes, and V. Beltran-Lopez, Phys. Rev. 123, 153 (1961).

ble, but somewhat more uniform than the deviations generated by the less flexible polarization wave functions. (For all atoms tabulated, the limitations inherent in the RHF model cause it to predict a zero spin density). Presumably, the remaining deviations between calculation and experiment are now due to structure-insensitive correlation contributions. We note that the spin densities for B and C are decreased on going from polarization to first-order wave functions.

Looking next at the reduced matrix elements α_l and α_d, we find it convenient to carry on the discussion in terms of the parameters $\langle r_l^{-3}\rangle$ and $\langle r_s^{-3}\rangle$, corresponding to the radial integrations in α_l and α_d respectively. These quantities, and $\langle r_q^{-3}\rangle$, corresponding to α_q, differ from one another because the angular and radial parts of the reduced matrix elements cannot be exactly factored for CI wave functions. In Table VI we report the various $\langle r^{-3}\rangle$ values for first-order, polarization, and RHF wave functions. Experimental values are also given for O and F, for which the experimental data permit assignments of individual contributions α_l and α_d.

Table VI shows that the first-order wave functions give slightly lower values of $\langle r_l^{-3}\rangle$ and $\langle r_s^{-3}\rangle$ than do the polarization wavefunctions, thereby increasing the discrepancy with experiment in three of the four cases. The discrepancy is clearly of the right sense to be attributable to the neglect of correlation; inclusion of correlation would reduce electron repulsion, permitting some shrinkage of the entire electron distribution and concomitantly an increase in the $\langle r^{-3}\rangle$ averages.

TABLE V. Spin densities $|\psi(0)|^2$ for first-row atoms. Percentages shown are relative to experimental values.

	$B(^2P)$	$C(^3P)$	$N(^4S)$	$O(^3P)$	$F(^2P)$
Unrestricted Hartree-Fock[26]	0.0171	0.0772	0.1874 (193%)	0.1954 (172%)	0.1333 (186%)
Polarization wave function[8]	0.0073	0.0277	0.0730 (75%)	0.0610 (54%)	0.0470 (66%)
First order wave function (this work)	0.0041	0.0228	0.0714 (74%)	0.0628 (55%)	0.0496 (69%)
Experiment	• • •	• • •	0.0972[a]	0.1138[b]	0.0717[b]

[a] W. W. Holloway, E. Luscher, and R. Novick, Phys. Rev. 126, 2109 (1962).

[b] J. S. M. Harvey, Proc. Roy. Soc. (London) A285, 581 (1965).

TABLE VI. Values of $\langle r^{-3}\rangle$ in atomic units. First-order wave-function values are from the present work; polarization wave-function and RHF values are from Ref. 8; experimental values are from J. S. M. Harvey, Proc. Roy. Soc. (London) A285, 581 (1965).

		$B(^2P)$	$C(^3P)$	$O(^3P)$	$F(^2P)$
$\langle r_l^{-3}\rangle$	First order	0.7572	1.663	4.570	7.234
	Polarization	0.7674	1.679	4.613	7.276
	Experiment	• • •	• • •	4.58	7.35
$\langle r_s^{-3}\rangle$	First-order	0.8167	1.769	5.100	7.950
	Polarization	0.8301	1.782	5.125	7.963
	Experiment	• • •	• • •	5.19	8.14
$\langle r_q^{-3}\rangle$	First-order	0.6833	1.537	4.307	6.852
	Polarization	0.7436	1.637	4.334	6.880
$\langle r^{-3}\rangle$	RHF	0.7755	1.692	4.973	7.545

Summarizing, we conclude that passage to the first-order wave function tends to regularize the discrepancy from experiment, and that the increased deviation in A corresponds to a better assessment of the structure-sensitive correlation effects.

B. Magnetic Moment of C^{11}

The nuclear magnetic dipole moment of C^{11} has not been directly determined experimentally. However, an experimental value of A_2 for this nucleus is available,[27] and from the value $A_2 = \pm 68.203$ MHz we deduce the moment $\mu_I = \pm 1.015$ μ_N from the first-order wave function. This is to be compared with ± 0.997 for the polarization function[8] and ± 1.056 from the RHF function.[8] The previously accepted value was ± 1.027 μ_N, based on a value of $\langle r^{-3}\rangle$ calculated by Bessis *et al.*[7]

C. Nuclear Electric Quadrupole Moments

Nuclear electric quadrupole moments are determined by combining experimental determinations of hyperfine constants B with calculated values of α_q, or equivalently $\langle r_q^{-3}\rangle$, or also equivalently q, the electric field gradient[8] at the nucleus. It is therefore useful to have good estimates of the reliability of computed $\langle r_q^{-3}\rangle$ values. The data of Table VI show relatively large differences between $\langle r_q^{-3}\rangle$ computed from first-order and polarization wave functions for B and C atoms, and experimental results for $\langle r_l^{-3}\rangle$ and $\langle r_s^{-3}\rangle$ indicate that the polarization function values may be the more accurate. In Table VII we list the quadrupole moments predicted from first-order, polarization, and RHF wave functions.

We have made some investigations designed to provide indications of the relative reliability of the various quadrupole-moment calculations. First, we verified directly that the "degeneracy" configuration $2s^2 \to 2p^2$ was primarily responsible for the difference between polarization and first-order wave-function results by carrying out α_q calculations for B using a CI containing all configurations of the first-order function except the degeneracy configuration. This wave function gave quadrupole moments for B^{10} and B^{11} differing by only 2.2% from those for the polarization function. Next, we examined α_q values provided by a highly correlated wave function produced for the B atom in previous work.[28] This wave function, which yields about 90% of the correlation energy of boron, deduces quadrupole moments within 0.4% of the polarization-function values. Our con-

TABLE VII. Nuclear electric quadrupole moments (in barns) deduced from hfs experiments and *ab initio* wave functions. The experimental data used are listed in Ref. 8.

	B^{10}	B^{11}	C^{11}	O^{17}
First order (this work)	0.087 45	0.041 96	± 0.034 26	−0.025 78
Polarization[8]	0.080 35	0.038 56	± 0.032 17	−0.025 62
Restricted Hartree-Fock[8]	0.077 05	0.036 97	± 0.031 12	−0.022 33
Previously accepted value[a]	0.074	0.036	± 0.031	−0.030

[a] C. M. Lederer, J. M. Holland, and I. Perlman, Tables of Isotopes (John Wiley & Sons, Inc., New York, 1967).

clusion is that, in the absence of authoritative estimates of the effect of electron correlation on α_q, the polarization wave function appears likely to give far more accurate quadrupole moments than the first-order wave function.

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