

Atomic Hyperfine Structure. IV Positive and Negative First-Row Ions

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(Received 19 November 1969)

Using restricted Hartree-Fock (RHF) wave functions and two previously defined types of configuration interaction (CI) wave functions, the polarization wave function and the first-order wave function, we have made *ab initio* calculations of the hyperfine structure (hfs) of: ${}^2P\ C^+$; 3P and ${}^1D\ N^+$; 4S , 2D , and ${}^2P\ O^+$; 3P and ${}^1D\ F^+$; ${}^2P\ Ne^+$; 3P and ${}^1D\ B^-$; 4S , 2D , and ${}^2P\ C^-$; 3P and ${}^1D\ N^-$; ${}^2P\ O^-$. For the polarization wave functions, the calculated parameters $\langle r_l^{-3} \rangle$, $\langle r_s^{-3} \rangle$, and $\langle r_q^{-3} \rangle$ are expected to be within 2% of the exact values, and the calculated spin densities are expected to be between 55% and 80% of the exact values. All calculated spin densities except that for ${}^3P\ B^-$ are positive, and the polarization spin density is usually slightly larger than the first-order value. For all positive ions and neutral atoms, the relationship $\langle r_q^{-3} \rangle < \langle r_l^{-3} \rangle < \langle r_s^{-3} \rangle_{RHF} < \langle r_s^{-3} \rangle$ holds. Calculated diamagnetic susceptibilities and nuclear magnetic shielding constants are reported for both the ions and the corresponding neutral atoms, using the present CI wave functions. Finally, we tabulate the angular integration coefficients needed to compute $\langle r_s^{-3} \rangle$ and $\langle r_q^{-3} \rangle$, and discuss a procedure used in this work to compact the form of a CI wave function.

INTRODUCTION

This is the last of a series of papers,^{1,2} the purpose of which is to predict atomic hyperfine structure (hfs) from *ab initio* configuration interaction (CI) wave functions, the polarization wave function (Ref. 1a), and the first-order wave function (Ref. 1b). The polarization wave function includes the restricted Hartree-Fock (RHF) configuration plus all singly-excited configurations $X_i - Y_i$, where X_i is a RHF occupied orbital and Y_i is an orbital not occupied in the RHF approximation. The first-order wave function includes all the configurations in the polarization function plus double excitations of the type $X_i X_j - X_k X_l$ and $X_i X_j - X_k Y_l$.

In the previous papers in this series, it was shown that, in general, the polarization wave function yields hfs parameters in better agreement with experiment than does the more accurate (in an energy sense) first-order wave function. To be specific, it was found (Ref. 1a) that polarization function values of the hfs parameters $\langle r_l^{-3} \rangle$ and $\langle r_s^{-3} \rangle$ were within 2% of experiment³ for both ${}^3P\ O$ and ${}^2P\ F$. Spin densities $|\Psi(0)|^2$ calculated from polarization wave functions were between 54 and 75% of experiment.

Since the publication of the first two¹ papers in this series, measurements of the hfs constants A_2 and A_1 have been made⁴ for ${}^3P\ C^{13}$. Although a rigorous determination of the three magnetic hfs parameters awaits the determination of a third con-

stant, a preliminary analysis⁵ indicates that $\langle r_l^{-3} \rangle$ and $\langle r_s^{-3} \rangle$ differ by 2% from the polarization function values (Ref. 1a), and that the experimental spin density is 120% of the polarization function spin density. These measurements⁴ give further evidence that polarization wave functions provide a powerful theoretical tool for the analysis of atomic hfs.

Since the previous papers^{1,2} contain detailed comparisons of the different theoretical approaches used in the study of hfs, we only note here that the only other method which yields hfs parameters as accurately as the polarization wave function is the Brueckner-Goldstone many-body perturbation theory⁶ (MBPT). Kelly's results⁵ indicate that effective values of $\langle r^{-3} \rangle$ from MBPT are in about the same agreement with experiment as are polarization function values, but that spin densities can be more accurately predicted using MBPT. However, computation of a polarization wave function and hfs parameters requires about 1 h of card punching time and less than 10 min of IBM 360/65 computer time. An MBPT hfs study⁷ of the same atom, however, can require 2 years of work by a competent graduate student.

Although no experiments have yet been carried out to determine the hfs parameters of positive and negative first-row atomic ions, it now appears likely⁸ that for at least one system, O^+ , paramagnetic-resonance experiments can soon be undertaken. It is hoped that the present calculations

will stimulate further experimental studies. The field of hfs is one that provides considerable opportunity for interaction between theory and experiment, in order both to understand the applicability of certain models of electronic structure and to predict nuclear moments.

In addition to the hfs parameters reported here, diamagnetic susceptibilities and nuclear magnetic shielding constants were also calculated. These quantities are reported for both the ions and the neutral atoms of the first row.

During this study, a procedure was developed to substantially simplify the form of a CI wave function after said wave function has been determined. This procedure is discussed, and also reported are the angular integration coefficients required to compute $\langle r_s^{-3} \rangle$ and $\langle r_q^{-3} \rangle$.

COMPACTING OF CONFIGURATION INTERACTION WAVE FUNCTIONS

The problem of obtaining as accurate as possible a wave function using as few configurations as possible has long been of interest in atomic and molecular physics. In particular, considerable advances⁹ have been made using Löwdin's idea of natural orbitals.¹⁰ However, there is a further simple concept which can be used to greatly simplify the form of a complicated CI wave function. When one makes a serious effort to obtain a large percentage of the correlation energy of an atom,

there are many orbital occupancies which give rise to more than one L - S eigenfunction of the proper symmetry.¹¹ Here we point out that the wave function can be expressed in a form in which the total number of configurations is just the number of orbital occupancies. This can be a drastic simplification, since for as simple an atom as oxygen, the important $1s^2 2s 2p^3 d_{f_1}$ orbital occupancy gives rise to 18 linearly independent 3P configurations.

A CI wave function can be written

$$\Psi = \sum_{\alpha, i} C_{\alpha i} \Phi_{\alpha i}, \quad (1)$$

where $\Phi_{\alpha i}$ is the i th configuration corresponding to orbital occupancy α . $\Phi_{\alpha i}$ has the form

$$\Phi_{\alpha i} = \sum_j^{n_\alpha} b_{\alpha i j} D_{\alpha j}, \quad (2)$$

where $D_{\alpha j}$ is the j th determinant arising from the α th orbital occupancy. So if there are m_α configurations $\Phi_{\alpha 1}, \Phi_{\alpha 2}, \dots, \Phi_{\alpha m_\alpha}$ corresponding to orbital occupancy α , then all m_α of these configurations are expressed in terms of the same Slater determinants $D_{\alpha 1}, D_{\alpha 2}, \dots, D_{\alpha m_\alpha}$. Given the coefficients $C_{\alpha i}$ in Eq. (1), it is possible to compact these m_α configurations $\Phi_{\alpha i}$ into a single configuration Φ_α .

The contribution of these m_α configurations to the final wave function is, from Eqs. (1) and (2),

$$C_{\alpha 1} \sum_{j=1}^{n_\alpha} b_{\alpha 1 j} D_{\alpha 1 j} + C_{\alpha 2} \sum_{j=1}^{n_\alpha} b_{\alpha 2 j} D_{\alpha 2 j} + \dots + C_{\alpha m_\alpha} \sum_{j=1}^{n_\alpha} b_{\alpha m_\alpha j} D_{\alpha j} = \sum_{j=1}^{n_\alpha} \sum_{k=1}^{m_\alpha} C_{\alpha k} b_{\alpha k j} D_{\alpha j}. \quad (3)$$

If we let

$$S_\alpha = \left(\sum_{j=1}^{n_\alpha} \sum_{k=1}^{m_\alpha} C_{\alpha k} b_{\alpha k j} \right)^2,$$

the final wave function can be written in the simplified form

$$\Psi = \sum_{\alpha} S_{\alpha}^{1/2} \Phi_{\alpha}, \quad (4)$$

where

$$\Phi_{\alpha} = \sum_{j=1}^{n_\alpha} t_{\alpha j} D_{\alpha j}, \quad (5)$$

in which

$$t_{\alpha j} = S_{\alpha}^{-1/2} \sum_{k=1}^{m_\alpha} C_{\alpha k} b_{\alpha k j}. \quad (6)$$

The compacted wave function of Eq. (4) is identical to that of Eq. (1), but the compact wave function has only one configuration for each orbital occupancy. In our computer programs,¹² the compact wave function is used to compute expectation values. For the 2D state of C^- , for example, the 195-configuration wave function of Eq. (1) becomes a 65-configuration wave function in Eq. (4).

ANGULAR INTEGRALS FOR HYPERFINE STRUCTURE

In order to evaluate the orbital and spin-dipolar terms of the hfs Hamiltonian, it is necessary to compute the integrals

$$E(l_i m_i; l_j m_j) = \int_0^{2\pi} \int_0^\pi Y_{l_i m_i}(\theta, \phi) (3 \cos^2 \theta - 1)$$

$$\times Y_{l_j m_j}(\theta, \phi) \sin \theta d\theta d\phi. \quad (7)$$

Since the values of these angular integration coefficients do not appear in the literature, it should be useful to tabulate them here. Using

$$(3 \cos^2 \theta - 1) = \left(\frac{4\pi}{5}\right)^{1/2} Y_{20}(\theta, \phi)$$

and the standard formula¹³ for the integral of the product of three spherical harmonics, we find

$$E(l_i m_i; l_j m_j) = 2[(2l_j + 1)/(2l_i + 1)]^{1/2} \times C(l_j 2l_i; m_j 0 m_i) C(l_j 2l_i; 000), \quad (8)$$

where the $C(l_1 l_2 l_3; m_1 m_2 m_3)$ are the Clebsch-Gordan coefficients as defined by Rose.¹³ Using tabulated values¹⁴ of the Clebsch-Gordan coefficients, we have evaluated all possible E coefficients for s , p , d , and f electrons. The nonvanishing angular integrals are given in Table I.

WAVE FUNCTIONS AND ENERGIES

The first-order wave functions used here were reported previously in a study¹⁵ of the electron affinities of first-row atoms. Polarization functions were calculated in the present work from the previously reported basis sets.¹⁵ Energies of

RHF,¹⁶ polarization, and first-order wave functions are given in Table II.

TABLE II. Calculated energies in hartrees, for RHF, polarization, and first-order wave functions. RHF energies are those of Clementi (Ref. 16).

| State | RHF | Polarization | First-order |
|--------------------------------|-------------|--------------|-------------|
| ² P C ⁺ | -37.292 21 | -37.318 34 | -37.363 87 |
| ³ P N ⁺ | -53.887 97 | -53.933 77 | -53.959 27 |
| ¹ D N ⁺ | -53.807 35 | -53.854 78 | -53.881 07 |
| ¹ S N ⁺ | -53.690 08 | -53.690 92 | -53.776 22 |
| ⁴ S O ⁺ | -74.372 55 | -74.428 90 | -74.433 67 |
| ² D O ⁺ | -74.233 29 | -74.293 25 | -74.298 11 |
| ² P O ⁺ | -74.142 04 | -74.171 61 | -74.218 22 |
| ³ P F ⁺ | -98.831 61 | -98.881 75 | -98.884 82 |
| ¹ D F ⁺ | -98.728 46 | -98.778 43 | -98.781 67 |
| ¹ S F ⁺ | -98.575 57 | -98.576 44 | -98.645 33 |
| ² P Ne ⁺ | -127.817 65 | -127.848 43 | -127.849 98 |
| ³ P B ⁻ | -24.519 19 | -24.545 40 | -24.564 93 |
| ¹ D B ⁻ | -24.490 48 | -24.515 79 | -24.535 48 |
| ¹ S B ⁻ | -24.439 50 | -24.453 36 | -24.494 87 |
| ⁴ S C ⁻ | -37.708 78 | -37.748 44 | -37.754 82 |
| ² D C ⁻ | -37.642 52 | -37.684 26 | -37.691 75 |
| ² P C ⁻ | -37.600 84 | -37.624 74 | -37.653 55 |
| ³ P N ⁻ | -54.321 89 | -54.362 87 | -54.366 50 |
| ¹ D N ⁻ | -54.266 87 | -54.304 89 | -54.309 22 |
| ¹ S N ⁻ | -54.186 82 | -54.187 74 | -54.233 90 |
| ² P O ⁻ | -74.789 48 | -74.816 05 | -74.817 78 |

TABLE I. Nonvanishing values of the coefficients $E(l_i m_i; l_j m_j) = \int_0^{2\pi} \int_0^\pi Y_{l_i m_i}(\theta, \phi) (3 \cos^2 \theta - 1) Y_{l_j m_j}(\theta, \phi) \sin \theta d\theta d\phi$.

| Type | l_i | m_i | l_j | m_j | $E(i m_i; j m_j)$ |
|-----------------|-------|-------|-------|-------|-------------------------|
| $p_{-1} p_{-1}$ | 1 | -1 | 1 | -1 | $-\frac{2}{5}$ |
| $p_0 p_0$ | 1 | 0 | 1 | 0 | $\frac{4}{5}$ |
| $p_{+1} p_{+1}$ | 1 | +1 | 1 | +1 | $-\frac{2}{5}$ |
| $d_{-2} d_{-2}$ | 2 | -2 | 2 | -2 | $-\frac{4}{7}$ |
| $d_{-1} d_{-1}$ | 2 | -1 | 2 | -1 | $\frac{2}{7}$ |
| $d_0 d_0$ | 2 | 0 | 2 | 0 | $\frac{4}{7}$ |
| $d_{+1} d_{+1}$ | 2 | +1 | 2 | +1 | $\frac{2}{7}$ |
| $d_{+2} d_{+2}$ | 2 | +2 | 2 | +2 | $-\frac{4}{7}$ |
| $f_{-3} f_{-3}$ | 3 | -3 | 3 | -3 | $-\frac{2}{5}$ |
| $f_{-2} f_{-2}$ | 3 | -2 | 3 | -2 | 0 |
| $f_{-1} f_{-1}$ | 3 | -1 | 3 | -1 | $\frac{1}{5} \sqrt{2}$ |
| $f_0 f_0$ | 3 | 0 | 3 | 0 | $\frac{4}{15} \sqrt{2}$ |
| $f_{+1} f_{+1}$ | 3 | +1 | 3 | +1 | $\frac{1}{5} \sqrt{2}$ |
| $f_{+2} f_{+2}$ | 3 | +2 | 3 | +2 | 0 |
| $f_{+3} f_{+3}$ | 3 | +3 | 3 | +3 | $-\frac{2}{5}$ |
| $s_0 d_0$ | 0 | 0 | 2 | 0 | $2/\sqrt{5}$ |
| $p_{-1} f_{-1}$ | 1 | -1 | 3 | -1 | $2\sqrt{6}/5\sqrt{7}$ |
| $p_{+1} f_{+1}$ | 1 | +1 | 3 | +1 | $2\sqrt{6}/5\sqrt{7}$ |
| $p_0 f_0$ | 1 | 0 | 3 | 0 | $6/5\sqrt{7}$ |

TABLE III. Calculated hfs parameters for positive and negative first-row ions. Three values of each parameter are given — the top entry is the RHF value, the middle entry is the polarization wave-function value, and the bottom entry the first-order wave-function value.

| State | $\langle r_l^{-3} \rangle$ | $\langle r_s^{-3} \rangle$ | $\langle r_q^{-3} \rangle$ | $ \Psi(0) ^2$ |
|-------------|----------------------------|----------------------------|----------------------------|---------------|
| $^2P\ C^+$ | 2.220 92 | 2.220 92 | 2.220 92 | 0.0 |
| | 2.196 28 | 2.331 63 | 2.137 79 | 0.017 31 |
| | 2.181 60 | 2.311 65 | 2.018 00 | 0.011 68 |
| $^3P\ N^+$ | 3.831 67 | 3.831 67 | 3.831 67 | 0.0 |
| | 3.804 95 | 3.998 35 | 3.613 53 | 0.047 30 |
| | 3.786 87 | 3.981 92 | 3.545 74 | 0.040 03 |
| $^1D\ N^+$ | 3.743 38 | NA | 3.743 38 | 0.0 |
| | 3.698 25 | NA | 3.460 66 | 0.0 |
| | 3.685 79 | NA | 3.296 78 | 0.0 |
| $^4S\ O^+$ | NA | NA | NA | 0.0 |
| | NA | NA | NA | 0.080 57 |
| | NA | NA | NA | 0.073 21 |
| $^2D\ O^+$ | 5.959 65 | 5.959 65 | NA ^a | 0.0 |
| | 5.856 16 | 6.245 79 | NA ^a | 0.034 75 |
| | 5.842 98 | 6.231 96 | NA ^a | 0.033 62 |
| $^2P\ O^+$ | 5.883 83 | 5.883 83 | NA ^a | 0.0 |
| | 5.864 73 | 6.274 35 | NA ^a | 0.033 94 |
| | 5.846 43 | 6.245 59 | NA ^a | 0.028 42 |
| $^3P\ F^+$ | 8.860 53 | 8.860 53 | 8.860 53 | 0.0 |
| | 8.408 82 | 9.117 77 | 8.005 11 | 0.093 56 |
| | 8.397 34 | 9.103 60 | 8.014 65 | 0.093 35 |
| $^1D\ F^+$ | 8.790 28 | NA | 8.790 28 | 0.0 |
| | 8.758 07 | NA | 8.363 33 | 0.0 |
| | 8.774 32 | NA | 8.352 32 | 0.0 |
| $^2P\ Ne^+$ | 12.493 23 | 12.493 23 | 12.493 23 | 0.0 |
| | 12.172 16 | 13.109 34 | 11.609 07 | 0.063 02 |
| | 12.156 22 | 13.090 71 | 11.618 29 | 0.063 78 |
| $^3P\ B^-$ | 0.466 08 | 0.466 08 | 0.466 08 | 0.0 |
| | 0.475 84 | 0.514 68 | 0.463 59 | -0.011 94 |
| | 0.458 73 | 0.497 31 | 0.404 99 | -0.013 51 |
| $^1D\ B^-$ | 0.420 34 | NA | 0.420 34 | 0.0 |
| | 0.432 61 | NA | 0.421 99 | 0.0 |
| | 0.415 16 | NA | 0.364 43 | 0.0 |
| $^4S\ C^-$ | NA | NA | NA | 0.0 |
| | NA | NA | NA | 0.011 49 |
| | NA | NA | NA | 0.009 04 |
| $^2D\ C^-$ | 1.178 57 | 1.178 57 | NA ^a | 0.0 |
| | 1.136 47 | 1.294 51 | NA ^a | 0.005 56 |
| | 1.114 16 | 1.272 72 | NA ^a | 0.004 48 |
| $^2P\ C^-$ | 1.142 63 | 1.142 63 | NA ^a | 0.0 |
| | 1.114 39 | 1.318 74 | NA ^a | 0.009 67 |
| | 1.114 73 | 1.298 99 | NA ^a | 0.008 42 |
| $^3P\ N^-$ | 2.367 46 | 2.367 46 | 2.367 46 | 0.0 |
| | 1.942 90 | 2.357 60 | 1.744 16 | 0.041 19 |
| | 1.933 04 | 2.340 97 | 1.782 23 | 0.042 00 |

TABLE III. (continued).

| State | $\langle r_l^{-3} \rangle$ | $\langle r_s^{-3} \rangle$ | $\langle r_q^{-3} \rangle$ | $ \Psi(0) ^2$ |
|--------------|----------------------------|----------------------------|----------------------------|---------------|
| $^1D\ N^-$ | 2.331 85 | NA | 2.331 85 | 0.0 |
| | 2.358 46 | NA | 2.077 85 | 0.0 |
| | 2.413 49 | NA | 2.151 52 | 0.0 |
| $^2P\ O^-$ | 4.055 08 | 4.055 08 | 4.055 08 | 0.0 |
| | 3.735 35 | 4.330 58 | 3.420 04 | 0.045 33 |
| | 3.711 93 | 4.302 35 | 3.453 05 | 0.047 19 |
| | $^2D\ O^+$ | $^2P\ O^+$ | $^2D\ C^-$ | $^2P\ C^-$ |
| RHF | 0.0 | 0.0 | 0.0 | 0.0 |
| Polarization | 0.123 39 | -0.144 08 | 0.091 73 | -0.131 64 |
| First-order | 0.124 06 | -0.050 63 | 0.093 88 | -0.069 52 |

^aFor 2D and 2P seven electron systems, an $\langle r_q^{-3} \rangle$ analysis is not applicable, but there is a small electric-quadrupole hyperfine interaction. For these states we give the calculated values of the expectation value $\langle J=L+S, M_J=J | \sum_i (3 \cos^2 \theta_i - 1)/r_i^3 | J=L+S, M_J=J \rangle$.

hfs Results

Reference 1(a) contains a complete discussion of the formulas needed to predict atomic hyperfine structure. The previous papers^{1,2} of this series presented calculated expectation values, reduced matrix elements, hfs parameters, and hfs constants A and B . For the sake of brevity, we report here only the hfs parameters $\langle r_l^{-3} \rangle$, $\langle r_s^{-3} \rangle$, $\langle r_q^{-3} \rangle$, and $|\Psi(0)|^2$. Using previously discussed relationships,^{1,2} all other hfs information can be derived from these four hfs parameters.

Table III contains values of $\langle r_l^{-3} \rangle$, $\langle r_s^{-3} \rangle$, $\langle r_q^{-3} \rangle$, and $|\Psi(0)|^2$ obtained from RHF, polarization and first-order wave functions.

It is interesting to note that all the calculated spin densities are positive except for $^3P\ B^-$, where both polarization and first-order spin densities are negative. The polarization-wave-function spin density $|\Psi(0)|^2$ is usually slightly larger than the first-order spin density.

Several interesting relationships can be seen in Table III between the calculated parameters $\langle r_l^{-3} \rangle$, $\langle r_s^{-3} \rangle$, and $\langle r_q^{-3} \rangle$. For both polarization and first-order wave functions, the calculated positive ion parameters obey

$$\langle r_q^{-3} \rangle < \langle r_l^{-3} \rangle < \langle r_s^{-3} \rangle_{\text{RHF}} < \langle r_s^{-3} \rangle. \quad (9)$$

It was pointed out in Paper I that this relationship also holds for the ground states of the neutral first-row atoms. The only states for which Eq. (9) does not hold are some of the negative ions, which can have very irregular electron distributions. In paper III it was pointed out that the hfs parameters are not, in general, transferable between different

states of the same atom (e.g., 4S , 2D , and $^2P\ N$). This is confirmed for ions in Table III. However, there do seem to be certain consistencies in hfs parameters computed for isoelectronic systems of the same symmetry. For example, for $^2D\ O^+$, $^2D\ N$, and $^2D\ C^-$, polarization and first-order wave functions yield nearly identical calculated electric field gradients. However, for $^2P\ O^+$, $^2P\ N$, and $^2P\ C^-$, the polarization and first-order values of $\langle (3 \cos^2 \theta - 1)/r^3 \rangle$ differ by more than a factor of 2.

DIAMAGNETIC SUSCEPTIBILITIES AND NUCLEAR MAGNETIC SHIELDING CONSTANTS

In the course of this work we routinely computed two additional properties. The molar diamagnetic susceptibility $\chi^{(d)}$ in cm^3/mole is given by¹⁷

$$\chi^{(d)} = -\frac{1}{6} N \alpha^2 a_0^3 \langle \Psi | \sum_i r_i^2 | \Psi \rangle, \quad (10)$$

where N is Avogadro's number, α is the fine-structure constant, and a_0 is the Bohr radius. The diamagnetic contribution $\sigma^{(d)}$ to the nuclear magnetic shielding is given by¹⁸

$$\sigma^{(d)} = \frac{1}{3} \alpha^2 \langle \Psi | \sum_i (1/r_i) | \Psi \rangle. \quad (11)$$

In Table IV, we tabulate calculated values of $\chi^{(d)}$ and $\sigma^{(d)}$ for positive ions, neutral atoms, and negative ions of the first row. The RHF values of Malli and Fraga¹⁹ are included for comparison in Table IV.

Although the theorem of Møller and Plesset²⁰ does not apply to open-shell RHF wave functions,

TABLE IV. Calculated diamagnetic susceptibilities $\chi^{(d)}$ and diamagnetic contributions $\sigma^{(d)}$ to the nuclear-magnetic shielding. As in Table II, values are given for RHF, polarization, and first-order wave functions. $\chi^{(d)}$ is given in 10^{-6} cm³/mole and $\sigma^{(d)}$ in 10^{-5} a.u. RHF values are those of Malli and Fraga (Ref. 19).

| | $\chi^{(d)}$ | $\sigma^{(d)}$ |
|--------------------------------|--------------|----------------|
| ² P C ⁺ | 6.388 | 25.107 |
| | 6.361 | 25.106 |
| | 6.282 | 25.120 |
| ³ P N ⁺ | 6.138 | 31.430 |
| | 6.124 | 31.428 |
| | 6.108 | 31.433 |
| ¹ D N ⁺ | 6.267 | 31.391 |
| | 6.239 | 31.391 |
| | 6.228 | 31.395 |
| ¹ S N ⁺ | 6.490 | 31.328 |
| | 6.492 | 31.328 |
| | 6.356 | 31.364 |
| ⁴ S O ⁺ | 5.802 | 38.350 |
| | 5.799 | 38.346 |
| | 5.967 | 38.318 |
| ² D O ⁺ | 5.932 | 38.290 |
| | 5.915 | 38.289 |
| | 5.928 | 38.285 |
| ² P O ⁺ | 6.026 | 38.249 |
| | 6.029 | 38.246 |
| | 5.988 | 38.261 |
| ³ P F ⁺ | 5.604 | 45.766 |
| | 5.612 | 45.759 |
| | 5.616 | 45.757 |
| ¹ D F ⁺ | 5.666 | 45.726 |
| | 5.662 | 45.724 |
| | 5.668 | 45.721 |
| ¹ S F ⁺ | 5.767 | 45.667 |
| | 5.776 | 45.663 |
| | 5.730 | 45.687 |
| ² P Ne ⁺ | 5.352 | 53.775 |
| | 5.354 | 53.772 |
| | 5.356 | 53.771 |
| ² P B | 12.556 | 20.199 |
| | 12.429 | 20.198 |
| | 12.276 | 20.213 |
| ³ P C | 10.930 | 26.074 |
| | 10.847 | 26.073 |
| | 10.843 | 26.076 |
| ¹ D C | 11.354 | 26.031 |
| | 11.215 | 26.033 |
| | 11.248 | 26.035 |

TABLE IV. (continued).

| | $\chi^{(d)}$ | $\sigma^{(d)}$ |
|-------------------------------|--------------|----------------|
| ¹ S C | 12.153 | 25.965 |
| | 12.200 | 25.962 |
| | 11.729 | 26.009 |
| ⁴ S N | 9.565 | 32.547 |
| | 9.533 | 32.543 |
| | 9.573 | 32.537 |
| ² D N | 9.918 | 32.484 |
| | 9.852 | 32.483 |
| | 9.914 | 32.476 |
| ² P N | 10.175 | 32.441 |
| | 10.204 | 32.435 |
| | 10.093 | 32.455 |
| ³ P O | 8.846 | 39.511 |
| | 8.852 | 39.504 |
| | 8.874 | 39.500 |
| ¹ D O | 9.008 | 39.468 |
| | 8.979 | 39.468 |
| | 9.000 | 39.464 |
| ¹ S O | 9.264 | 39.405 |
| | 9.271 | 39.403 |
| | 9.155 | 39.435 |
| ² P F | 8.110 | 47.071 |
| | 8.107 | 47.067 |
| | 8.117 | 47.065 |
| ³ P B ⁻ | 31.529 | 20.651 |
| | 29.487 | 20.663 |
| | 30.991 | 20.650 |
| ¹ D B ⁻ | 40.898 | 20.578 |
| | 35.928 | 20.607 |
| | 38.888 | 20.584 |
| ¹ S B ⁻ | 29.126 | 20.622 |
| | 44.508 | 20.424 |
| | 37.087 | 20.548 |
| ⁴ S C ⁻ | 20.830 | 26.696 |
| | 20.353 | 26.700 |
| | 20.833 | 26.683 |
| ² D C ⁻ | 23.315 | 26.617 |
| | 22.700 | 26.625 |
| | 23.469 | 26.602 |
| ² P C ⁻ | 25.481 | 26.562 |
| | 26.539 | 26.501 |
| | 25.320 | 26.579 |
| ³ P N ⁻ | 17.665 | 33.205 |
| | 17.978 | 33.184 |
| | 18.044 | 33.179 |

TABLE IV. (continued).

| | $\chi^{(d)}$ | $\sigma^{(d)}$ |
|--------------|--------------|----------------|
| ${}^1D\ N^-$ | 18.511 | 33.155 |
| | 18.313 | 33.158 |
| | 18.414 | 33.396 |
| ${}^1S\ N^-$ | 19.992 | 33.080 |
| | 20.032 | 33.076 |
| | 19.422 | 33.126 |
| ${}^2P\ O^-$ | 14.845 | 40.317 |
| | 14.992 | 40.301 |
| | 15.006 | 40.299 |

rigorously expect polarization wave functions to give expectation values of one-electron operators to "first-order" accuracy. We have seen that for the one-electron operators that give rise to hfs, polarization wave functions yield results very different from the RHF results. However, Table IV indicates that for the less complicated expectation values $\langle 1/r \rangle$ and $\langle r^2 \rangle$, RHF, polarization, and first-order wave functions usually yield very similar results (typically the three values agree within 1%). We conclude that even for open-shell systems expectation values such as $\langle 1/r \rangle$ and $\langle r^2 \rangle$ are quite adequately predicted by the RHF method.

ACKNOWLEDGMENT

We would like to thank Professor Frank E. Harris for helpful discussions.

a similar theorem does apply to polarization wave functions for open-shell systems. Thus, we can

*Supported in part by the Petroleum Research Fund, administered by the American Chemical Society.

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¹H. F. Schaefer, R. A. Klemm, and F. E. Harris, (a) Phys. Rev. 176, 49 (1968); (b) 181, 137 (1968).

²H. F. Schaefer and R. A. Klemm, Phys. Rev. 188, 152 (1969).

³J. S. M. Harvey, Proc. Roy. Soc. (London) A285, 581 (1965).

⁴G. Wolber, H. Finner, R. A. Haberstroh, and S. Penselin, Phys. Letters 29A, 461 (1969).

⁵G. Wolber (private communication).

⁶H. P. Kelly, Phys. Rev. 173, 142 (1968); 180, 55 (1969).

⁷N. C. Dutta, C. Matsubara, R. T. Pu, and T. P. Das, Phys. Rev. 177, 33 (1969).

⁸J. S. M. Harvey (private communication).

⁹C. F. Bunge, Phys. Rev. 168, 92 (1968); A. Bunge and C. F. Bunge, Bull. Am. Phys. Soc. 14, 939 (1969).

¹⁰P. O. Löwdin, Phys. Rev. 97, 1509 (1955).

¹¹H. F. Schaefer and F. E. Harris, J. Comput. Phys. 3, 217 (1968).

¹²H. F. Schaefer, Ph.D. thesis, Stanford University, 1969 (unpublished).

¹³M. E. Rose, Elementary Theory of Angular Momentum (John Wiley & Sons, Inc., New York, 1957).

¹⁴Tables of the Clebsch-Gordan Coefficients, (Science Press, Peking, 1965).

¹⁵H. F. Schaefer and F. E. Harris, Phys. Rev. Letters 21, 1561 (1968); H. F. Schaefer, R. A. Klemm, and F. E. Harris, J. Chem. Phys. (to be published).

¹⁶E. Clementi, IBM J. Res. Develop. 9, 2 (1965).

¹⁷J. H. Van Vleck, The Theory of Electric and Magnetic Susceptibilities (Oxford University Press, New York, 1932).

¹⁸N. F. Ramsay, Phys. Rev. 78, 699 (1950).

¹⁹G. Malli and S. Fraga, Theoret. Chim. Acta, 5, 275, 284 (1966).

²⁰C. Møller and M. S. Plesset, Phys. Rev. 46, 618 (1934).