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Study of the Contact-Term Contribution to the Hyperfine Structure Obtained from Spin-Unrestricted Hartree-Fock Wave Functions

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Numerical spin-unrestricted Hartree-Fock (SUHF) wave functions have been computed for the neutral open-shell atoms Li to Br and the transition-metal ions Sc^{2+} to Cu^{2+}. These wave functions have been used to obtain accurate values of the SUHF spin densities. These calculations are used to make a critical review of the numerical accuracy of previously reported SUHF spin densities and to compare our accurate values of the SUHF spin densities with those extracted from experimental data. A large majority of previous SUHF calculations have been performed using the analytic-expansion method. The spin density at the origin computed from analytic-expansion calculations is sensitive to the choice of basis functions, and it is very difficult to obtain a precise measure of its accuracy. Our numerical SUHF calculations yield the SUHF value of the spin density χ to an accuracy conservatively estimated to be ± 0.01 a.u. Comparison with analytic-expansion calculations indicates that the use of large, carefully selected basis sets usually yields spin densities within 20% of the numerical SUHF values reported here. The calculated SUHF spin densities are compared with available experimental values and it is found that (a) for the alkali atoms Li, Na, and K, the SUHF spin densities are 97, 86, and 77% of experiment; (b) for the first-row atoms N, O, and F, the SUHF spin densities are 193, 172, and 186% of experiment; (c) the SUHF spin density for P is opposite in sign and 153% of the absolute value of the experimental spin density; (d) the SUHF spin densities of the $4s^2 3d^n$ transition-metal atoms Ti, V, Mn, and Co are 82, 75, 72, and 67% of experiment; and (e) the SUHF spin density of As is 231% of experiment. It is concluded that, although some correlations are possible between SUHF and experimental values, the SUHF method should be used with extreme caution for the prediction of spin densities at the origin. This work provides a guide to the reliability of the SUHF predictions.

I. INTRODUCTION

A large number of atomic calculations have been made using the spin-unrestricted Hartree-Fock (SUHF) method, also referred to as the unrestricted spin-polarized or exchange-polarized Hartree-Fock method. As the term is commonly used, the SUHF method is "unrestricted" in that orbitals with the same n and l but different m_s are allowed to have different radial functions; orbitals with different m_l but the same n and l are still constrained to have the same radial functions. For a description of the SUHF formalism see, for example, Pople and Nesbet[1] and Pratt[2]; the method has also been discussed in detail in several review articles.[3-5]

The SUHF method has been used primarily for the purpose of calculating atomic hyperfine structure (hfs) parameters. The parameter of particular interest is the spin density at the nucleus which appears in the Fermi contact interaction.[6] A convenient measure of the spin density is the quantity

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χ defined by Abragam and Pryce[7] as

$$\chi = (4\pi/S)\langle J = L + S,\ M_J = J \,| \times \textstyle\sum_i \delta(\vec{r}_i) S_{zi} \,| J = L + S,\ M_J = J\rangle . \quad (1)$$

For a SUHF wave function, the spin density is given by

$$\chi = (2\pi/S) \sum_{s\,\mathrm{orb}\,i} [\,|\,\phi_{i\alpha}(0)|^2 - |\,\phi_{i\beta}(0)|^2], \quad (2)$$

where the $\phi_{i\alpha}$ are the occupied orbitals with $l = 0$ and $m_s = +\frac{1}{2}$ and $\phi_{i\beta}$ are the occupied orbitals with $l = 0$ and $m_s = -\frac{1}{2}$. Another frequently used[8-10] measure of the spin density is $|\psi(0)|^2$, where

$$|\psi(0)|^2 = 2\langle J = L + S,\ M_J = J| \times \textstyle\sum_i (\vec{r}_i) S_{zi} \,| J = L + S,\ M_J = J\rangle = (S/2\pi)\chi . \quad (3)$$

Until recently, it has been difficult to assess fully the usefulness of the SUHF method owing, in part, to a lack of experimental information about spin densities. In 1960 the only known spin densities were those of the alkali atoms[11] Li, Na, and K and those[12] of N and Mn.[13] The extraction of spin densities from experimental hfs constants has been impeded because, despite the earlier theoretical work of Trees,[14] it has only recently been accepted[9,15,16] that there are three, rather than two, independent magnetic hfs parameters. For our comparisons with experiment, we have only used experimental data which do have sufficient information for the calculation of these three parameters. Recent experiments have now been analyzed to give reliable values of the spin densities of O,[15] F,[16] P,[17,18] Ti,[19] V,[20] Co,[19,21] and As.[18]

A further hindrance to the evaluation of the SUHF method has been the uncertainty associated with SUHF spin densities calculated using the analytic-expansion method.[22] This property is very sensitive to the choice of the parameters of functions used in the basis set. For example, Bessis, Lefebvre-Brion, and Moser[23] obtained SUHF spin densities χ of $+0.13$ and -0.16 a.u. for B ^2P using different large basis sets which yielded identical energies. Almost all of the SUHF calculations in the literature[10,23-31] are analytic-expansion calculations. Only five papers,[8,32-35] besides the present work, report numerical solutions of the SUHF equations. Two of these[32,33] use Slater's[36] approximation to the exchange potential; one[33] uses several other approximations as well.

In the present paper we present numerical solutions of the SUHF equations[1] for the open-shell atoms from Li to Br and for the transition-metal ions Sc^{2+} to Cu^{2+}. The purpose of this work is twofold – first, to compare the accurate SUHF spin densities obtained here with previous analytic-expansion calculations,[10,23-29] second, to critically evaluate the SUHF method by comparing our SUHF spin densities to the most accurate experimental values now available.[11,15-21,37,38]

II. CALCULATIONS

The calculations were performed using an SUHF program written by one of us (P.S.B.) based on the numerical restricted Hartree-Fock (RHF) program of Froese-Fischer.[39,40] The SUHF total electronic energies reported here are in most cases accurate to better than one or two units in the seventh significant figure. The error is always less than one unit in the sixth significant figure. This assessment of accuracy is based, in part, on a comparison of numerical RHF calculations, using the same integration parameters as the SUHF calculations, with highly accurate analytic RHF calculations for first-row atoms.[41] It is also based on extensive comparisons between numerical RHF calculations for heavier atoms using different numerical-integration parameters.

Of particular importance in the present work is the accuracy of the calculated spin densities. The numerical accuracy of the spin densities is suspect because they are obtained by taking differences of very large numbers. In the bromine atom, where this problem is most serious, the total calculated spin density χ is only -0.6626 a.u., but the contribution from the $1s\alpha$ and $1s\beta$ orbitals are, respectively, 166 582.4790 and $-166\,584.3344$. One way to test the accuracy of the total spin density is to observe its development during the SCF iteration procedure. For bromine, the last three iterations yielded χ values of -0.6587, -0.6627, and -0.6626 a.u. Similar patterns were observed in other cases. We conservatively conclude that the calculated SUHF spin densities for the heaviest atoms and ions studied here are accurate to at least 0.01 a.u. For the lightest system studied, the lithium atom, our calculated UHF spin density should be accurate to at least 0.0001 a.u.

The calculations were done on the IBM 360/91 computer and total computation time for all SUHF wave functions was 5 min and 57 sec.

III. RESULTS

Table I summarizes the work reported here; for each system considered, we present the SUHF total electronic energy and the spin densities. [The spin density is given both as χ and as $|\psi(0)|^2$; cf. Eqs. (2) and (3).] We have also included in Table I the RHF total energies, values of χ obtained from experimental data and previously calculated SUHF values of χ. We have recalculated the RHF energies by numerical integration of the Fock equations,[39] using the same integration parameters as for the SUHF calculations. When

TABLE I. Total energies and spin densities for the open-shell atoms and ions Li to Br and Sc^{2+} to Cu^{2+}. (All quantities are in a.u.)

Atom	Open-shell occupation	E_{SUHF}	E_{RHF}	$\lvert\psi(0)\rvert^2$	χ	χ(expt)[a]	χ(numerical SUHF)[b]	χ(analytic SUHF calc)
Li(^2S)	$2s$	−7.432 751	−7.432 728	0.225	2.823	2.9062	2.823	2.8251,[c] 2.923[d]
B(^2P)	$2p$	−24.529 32	−24.529 07	0.017	0.215	⋯	0.216	0.241,[e] 0.134,[f] −0.16[f]
C(^3P)	$2p^2$	−37.690 00	−37.688 63	0.077	0.485	⋯	⋯	0.473,[e] 0.28[f]
N(^4S)	$2p^3$	−54.404 56	−54.400 94	0.187	0.785	0.4071	0.7888	1.251,[d] 0.7762,[e] 0.64,[f] 0.9366[f]
O(^3P)	$2p^4$	−74.813 64	−74.809 41	0.195	1.228	0.715	⋯	1.239,[e] 1.4[f]
F(^2P)	$2p^5$	−99.410 85	−99.409 36	0.133	1.675	0.901	1.678	1.668,[e] 1.979[f]
Na(^2S)	$3s$	−161.859 0	−161.859 0	0.647	8.136	9.42	8.129	8.136[d]
Al(^2P)	$3p$	−241.876 8	−241.876 7	−0.109	−1.370	⋯	⋯	⋯
Si(^3P)	$3p^2$	−288.854 6	−288.854 3	−0.155	−0.972	⋯	⋯	⋯
P(^4S)	$3p^3$	−340.719 3	−340.718 7	−0.139	−0.584	0.3824	⋯	−0.747,[d] −0.49 to −0.74[g]
S(^3P)	$3p^4$	−397.506 3	−397.505 0	−0.009	−0.055	⋯	⋯	⋯
Cl(^2P)	$3p^5$	−459.482 6	−459.482 2	0.034	0.425	⋯	0.43	⋯
K(^2S)	$4s$	−599.165 1	−599.164 9	0.854	10.727	13.91	10.734	⋯
Sc(^2D)	$3d$	−759.736 0	−759.736 2	−0.024	−0.301	⋯	⋯	−0.17[h]
Ti(^3F)	$3d^2$	−848.406 7	−848.406 5	−0.067	−0.423	−0.508	⋯	⋯
V(^4F)	$3d^3$	−942.885 9	−942.884 6	−0.116	−0.487	−0.646	⋯	−0.45[h]
Cr(^5D)	$3d^4$	−1043.312	−1043.310	−0.171	−0.537	⋯	⋯	⋯
Mn(^6S)	$3d^5$	−1149.870	−1149.867	−0.238	−0.598	−0.826	⋯	−0.54[h]
Fe(^5D)	$3d^6$	−1262.450	−1262.444	−0.206	−0.648	⋯	−0.63	−0.59,[h] −0.768[i]
Co(^4F)	$3d^7$	−1381.419	−1381.415	−0.163	−0.682	−1.02	⋯	−0.61[h]
Ni(^3F)	$3d^8$	−1506.873	−1506.871	−0.116	−0.726	⋯	⋯	⋯
Cu(^2D)	$3d^9$	−1638.951	−1638.950	−0.063	−0.794	⋯	⋯	−0.69[h]
Ga(^2P)	$4p$	−1923.262	−1923.260	−0.346	−4.353	⋯	⋯	⋯
Ge(^3P)	$4p^2$	−2075.361	−2075.361	−0.529	−3.324	⋯	⋯	⋯
As(^4S)	$4p^3$	−2234.241	−2234.241	−0.597	−2.501	−1.085	⋯	⋯
Se(^3P)	$4p^4$	−2399.870	−2399.869	−0.238	−1.495	⋯	⋯	⋯
Br(^2P)	$4p^5$	−2572.443	−2572.441	−0.053	−0.663	⋯	⋯	⋯
Sc^{2+}(^2D)	$3d$	−759.092 6	−759.092 2	−0.275	−3.451	⋯	⋯	⋯
Ti^{2+}(^3F)	$3d^2$	−847.731 2	−847.731 3	−0.556	−3.494	⋯	⋯	⋯
V^{2+}(^4F)	$3d^3$	−942.180 5	−942.180 0	−0.857	−3.591	⋯	⋯	⋯
Cr^{2+}(^5D)	$3d^4$	−1042.579	−1042.578	−1.182	−3.714	⋯	⋯	⋯
Mn^{2+}(^6S)	$3d^5$	−1149.111	−1149.110	−1.522	−3.826	⋯	⋯	−3.34[h]
Fe^{2+}(^5D)	$3d^6$	−1261.662	−1261.658	−1.233	−3.872	⋯	⋯	−3.29[h]
Co^{2+}(^4F)	$3d^7$	−1380.604	−1380.601	−0.950	−3.979	⋯	⋯	⋯
Ni^{2+}(^3F)	$3d^8$	−1506.033	−1506.031	−0.648	−4.074	⋯	⋯	−3.94[h]
Cu^{2+}(^2D)	$3d^9$	−1638.086	−1638.085	−0.325	−4.081	⋯	⋯	⋯

[a] See Sec. III for references to experimental data.

[b] Goodings, Ref. 8; for Fe atom see Goodings and Heine, Ref. 34.

[c] Reference 25.

[d] Reference 29.

[e] Reference 10.

[f] Reference 23.

[g] Reference 26.

[h] Reference 27.

[i] Reference 28.

values of the spin density were not given in other papers in terms of χ, we have converted these values to χ.

Additional results of these calculations, including orbital energies, contributions to χ from individual spin orbitals, and values of $\langle r^{-3} \rangle$, have been presented elsewhere.[40]

IV. DISCUSSION

The SUHF total energies are not significantly lower than RHF energies. For example, the SUHF energy for $O\,{}^3P$ is 0.004 hartrees lower than the RHF energy; the SUHF energy for Mn ${}^6S$ is 0.003 hartrees lower. Thus, only an insignificant fraction of the correlation energy is obtained with the SUHF method.

A comparison between the SUHF spin densities reported here and those obtained from analytic-expansion SUHF calculations shows that the analytic-expansion results are often considerably different than the true SUHF results. The following points should be noted.

(a) The analytic expansion SUHF results of Goddard[10] are in good agreement with our results. For B his spin density is 12% larger than our value; for C, N, O, and F his values are within 2% of ours. Goddard carefully examined the convergence properties of the spin densities; the importance of this will be discussed below.

(b) The spin densities obtained by Sachs[25] and Nesbet[29] for Li and by Nesbet[29] for Na are quite close to our results. However, Nesbet's[29] spin densities for N and P differ from ours by 59 and 28%, respectively. Both Nesbet and Sachs used basis sets for these calculations which had been carefully optimized for very accurate RHF calculations.[42] Thus, basis sets suitable for accurate analytic expansion RHF calculations may not always be suitable for SUHF calculations.

(c) The analytic expansion results of Watson and Freeman[27] are in fairly good agreement with our results. With one exception the differences between our values of χ and theirs range between 8% for V and 18% for Fe; the absolute magnitude of their value for Sc is almost half (57%) of our value. The analytic expansion result of Bagus and Liu[28] for Fe differs by 18% from our numerical SUHF spin density. Although the wave function of Bagus and Liu[28] yields a better energy than the function of Watson and Freeman,[27] the spin density obtained from the former function is in poorer agreement with the numerical SUHF spin density.

(d) Agreement between the calculations of Bessis *et al.*[23,26] and the present work is not good. Bessis, Lefebvre-Brion, and Moser[23] were probably the first to point out and demonstrate that analytic-expansion SUHF spin densities are extremely sensitive to the basis sets used. For boron,[23] they report two calculations with the same energy (to five significant figures) which give spin densities with almost the same magnitude but *opposite* signs. For P,[26] they report spin densities which range from 16% smaller than our numerical result to 27% larger. This range is obtained for calculations which differ in energy by only four units in the seventh significant figure.

The only criterion for judging the accuracy of spin densities obtained from SUHF calculations (besides comparison with numerical SUHF results) is an examination of the convergence of the spin densities obtained from calculations, using successively larger, carefully optimized basis sets. This is the procedure followed by Goddard and appears to be the reason that he obtained accurate SUHF spin densities for B through F. This is a difficult and tedious process since, as discussed above, the spin density is quite sensitive to changes in the basis set which hardly change the energy. The minimization of the total energy is the criterion normally used for the optimization of basis set parameters for analytic-expansion calculations. Note that even though he took great pains in determining optimum basis set parameters, Goddard's[10] result for the SUHF spin density of B is still 12% larger than the true SUHF value. The difficulties of basis set optimization increase substantially as the number of shells in the system increases. We conclude that the utmost care should be used when analytic-expansion SUHF wave functions are used to predict spin densities.

The spin densities obtained from numerical solutions of the SUHF equations by Goodings[8] for Li, B, N, F, Na, Cl, and K and by Goodings and Heine[34] for Fe are essentially identical to our results. The largest difference between our results and theirs is 3% for Fe.

The first SUHF calculations reported in the literature are the numerical integration calculations of Wood and Pratt[32] on Fe and Heine[33] on Mn. Wood and Pratt[32] approximated the nonlocal exchange potential with the local Slater $\rho^{1/3}$ potential.[36] They report only the contributions to χ from the $1s$, $2s$, and $3s$ shells; this contribution is -2.4 a.u., the same contribution from our calculation is -3.55 a.u. (cf. also our result for Fe^{2+}, $\chi = -3.87$ a.u.). In addition to using the Slater $\rho^{1/3}$ exchange potential, Heine[33] also used a central field for Cu and only solved for the $2s$, $3s$, and $4s$ orbitals. From this calculation, he estimated values of χ of $+0.9$ and -3.3 a.u. for Mn and Mn^{2+}, respectively; our values for these systems are -0.60 and -3.83 a.u. Because of the approximations used in these calculations, they are not directly comparable to our work. They have not been included in Table I.

Inspection of Table I shows that the relationship between the SUHF and experimental spin densities varies. In order to better understand the results we divide the systems studied into six groups.

(a) Alkali atoms: The SUHF spin densities for Li, Na, and K, as has been pointed out by Goodings,[8] are in rather good agreement with experiment, being 97, 86, and 77% of the values determined by Kusch and Taub.[11] The largest contribution to the spin density in these cases comes from the unpaired 2*s*, 3*s*, or 4*s* electron.

(b) First-row atoms: The spin densities of $N^{12,37}$, O^{15}, and F^{16} are known from experiment. The SUHF spin densities are, respectively, 193, 172, and 186% of the experimental values. Several recent studies have been done on these simple atoms using more advanced theoretical approaches such as configuration interaction[9] variational solution of the Bethe-Goldstone equations,[29,43] and the Brueckner-Goldstone many-body perturbation theory.[44,45] All of these calculations indicate that a very accurate treatment of the wave function is required in order to obtain spin densities in good agreement with experiment. In fact, an accurate treatment of the correlation energy is not sufficient to guarantee accurate spin densities.[46]

(c) Second-row atoms: The only experimentally determined spin density in this group is that of phosphorous.[17,18] Calculations by Bessis *et al.*[26] in 1964 gave the result, qualitatively verified by the present work, that the sign of the SUHF spin density is opposite to that of the experimental value. This result remains the most dramatic failure of the SUHF method. We note that a recent many-body calculation[47] including correlation effects, yielded a spin density of the correct sign and within 10% of the correct magnitude. It is of interest to note the trend in the values of the SUHF spin density χ in going from aluminum (− 1.370 a.u.) to chlorine (+ 0.425 a.u.) The rapidly changing spin densities are not in keeping with the idea, suggested by Abragam *et al.*[48] and discussed by Watson and Freeman,[4] that χ values remain approximately constant across a row in the Periodic Table.

(d) Third-row transition-metal atoms: Experimental χ values are now available for Ti,[19] V,[20] Mn,[13,38] and Co[11,21] in the $4s^2 3d$ states. The SUHF spin densities are 82, 75, 72, and 67% of the experimental values. This represents the best agreement obtained between SUHF and experiment for any group of atoms. As has been discussed by Freeman and Watson,[3,4,27] the SUHF spin densities for Sc through Cu are all negative and monotonically increasing in magnitude. This trend has been discussed from an experimental point of view by Winkler[49] and by Childs.[16]

(e) Third-row $4p^n$ atoms: The experimental spin density of arsenic has been determined by Pendlebury and Smith[18] and the SUHF value is of the correct sign but 231% of the experimental value. The SUHF spin densities χ of the third-row atoms gallium through bromine are all negative but vary greatly between gallium (− 4.353 a.u.) and bromine (− 0.663 a.u.). The magnitudes of the spin densities decrease monotonically across the row.

(f) Transition-metal ions Sc^{2+} to Cu^{2+}: In 1955, Abragam, Horowitz, and Pryce[48] noted a crude experimental constancy of about − 3 a.u. for χ for these ions. Calculations by Watson and Freeman[27] on Mn^{2+}, Fe^{2+}, and Ni^{2+} reproduced this trend. Later experimental analysis by Locher and Geschwind[50] verified the work of Abragam *et al.* and noted a slight decrease in χ values in going from V^{2+} to Ni^{2+}. However, we have not included any experimental values for the spin densities of these ions in Table I since the experiments[48,50] were done on solids rather than the free ions. The numerical SUHF results are in agreement with Freeman and Watson's qualitative conclusions[3,4,27]; the χ values decrease monotonically from Sc^{2+} (− 3.451 a.u.) to Cu^{2+} (− 4.081 a.u.).

V. CONCLUSIONS

The SUHF spin densities for the systems reported here may differ from experiment by as much as 200%. In this sense the SUHF method is inappropriate as a tool for predicting spin densities. However, this paper shows that in quite a number of circumstances (for example, the third-row transition-metal atoms) there are roughly constant relationships between the SUHF spin densities and the true spin densities.

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