

Spin density and density moments for the lithium ground state

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(Received 12 September 1990)

Accurate analytical charge and spin-electron densities for the lithium atom are obtained by using a systematic and reliable method recently developed and applied to closed-shell atoms. The convergence of the densities is analyzed in terms of well-defined improvements in the corresponding configuration-interaction wave functions, and mathematical criteria are used to test the stability of the densities and their derivatives. Fully converged results for one-electron properties and, in particular, for the Fermi-contact interaction are reported.

I. INTRODUCTION

We have developed^{1,2} a systematic and reliable way of obtaining accurate analytical electron densities. In this method, which is based on configuration-interaction (CI) calculations, successive wave functions are optimized by expanding the significant electron-correlation regions. The optimization of the orbital basis is guided both by an energy criterion and by a best density criterion. The charge densities for Ne (Ref. 1) and Be (Ref. 2) converge monotonically to definite values as the basis and, hence, the size of the CI expansion, is increased. They obey the theoretical conditions at the nucleus and at large distances, they reproduce densities obtained from almost "exact" CI wave functions, and accurate one-electron properties are obtained from them.

In previous calculations, the method was applied to closed-shell atoms. The purpose of the present study is to calculate the charge density, the spin density, and the density moments of the lithium atom. Because of the well-known difficulties³ in theoretically obtaining the Fermi-contact term, this property is a particularly sensitive test for trying our method.

II. CALCULATION OF THE DENSITY

The nonrelativistic CI wave functions are expressed as

$$\Psi = \sum_{K,p} \Phi_{K,p} a_{K,p} \tag{1}$$

where the $\Phi_{K,p}$'s are successively orthonormalized L^2 - and S^2 -symmetric projections of Slater determinants which are built of orthonormal spin-orbitals:

$$\Phi_{K,p} = O(L^2, S^2) \sum_{\alpha=p}^{n_K} D_{K\alpha} b_{K\alpha}^{(p)} \tag{2}$$

The spin-orbitals are linear combinations of Slater-type orbitals (STO's) times a spherical harmonic, times a spin function:

$$\psi_{ilm_l m_s} = R_{il}(r) Y_{lm_l}(\phi, \theta) \xi_{m_s}(\sigma_s) \tag{3a}$$

$$R_{il}(r) = \sum_j S_{jl}(r) a_{ijl} \tag{3b}$$

$$S_{jl}(r) = N_{jl} r^{(n_j-1)} \exp(-Z_{jl}r) \tag{3c}$$

The charge and spin densities are obtained through the one-electron density matrix:

$$\gamma(x|x') = N \int \Psi^*(x_1, x_2, \dots, x_N) \times \Psi(x'_1, x_2, \dots, x_N) dx_2 \dots dx_N \tag{4}$$

by means of its diagonal spin-free representation.

Since the first-order density matrix commutes with L_Z , it is m_S -block diagonal, so that charge and spin densities can be written in terms of α and β contributions:

$$\rho_C(r) = \rho_\alpha(r) + \rho_\beta(r) \tag{5}$$

$$\rho_S(r) = (\rho_\alpha - \rho_\beta) / (N_\alpha - N_\beta) \tag{6}$$

Upon spatial integration, one gets

$$\int \rho_C(r) dr = N_\alpha + N_\beta = N \tag{7}$$

$$\int \rho_S(x) dx = 1 \tag{8}$$

The reduced first-order density matrix may be expanded in a spin-orbital basis and, by using a suitable unitary transformation, it may be diagonalized to obtain the natural expansion. Then, the densities are given in terms of STO's as

$$\rho_\gamma(r) = \sum_i f_{ils} n_{il}^\gamma \left[\sum_{j,k} N_{jl} N_{kl} c_{ji}^\gamma c_{ki}^\gamma r^{(n_j+n_k-2)} \times \exp[-(Z_{jl} + Z_{kl})r] \right] \tag{9}$$

where γ stands for the α - or β -type density contribution.

The n_{ji}^{χ} and the c_{ji}^{χ} are the natural expansion parameters. The f_{ils} are symmetry factors which take advantage of the parity-, of the m_s -, and m_l -block diagonal structure of the density matrix, and of the LS symmetry of each atom. An atomic CI program is available⁴ for the calculation of the wave function and the one-electron density matrix.

The main idea is to obtain a wave function Ψ such that the electron density calculated from it does not vary appreciably upon further improvements in Ψ . The CI method is especially appropriate for this endeavor since one can always extend the basis set and check the stability of the density upon each addition of a new basis orbital.

It has been shown⁵ that, for a given orbital symmetry and electron-correlation region (K , L , and intershell), successively energy-optimized STO's participate with decreasing energy contributions. In previous work,^{1,2} we have found that, besides an energy pattern of convergence, there exists a pattern of convergence for the electron density which follows analogous steps, although the structure of the resulting STO sets is very different.

According to the method, one starts from the self-consistent-field (SCF) orbitals of Clementi and Roetti,⁶ supplemented by orbitals that are obtained by successive orthogonalization of the functions in the SCF basis. An energy criterion is then used to optimize additional STO's. At each stage, the nonlinear exponents are optimized cyclically until the energy becomes stable within 10^{-9} a.u. Bunge has pointed out the importance of the numerical accuracy of the eigenvector components⁷ in the calculation of very sensitive properties such as the Fermi-contact interaction. In this work, it has been set at 10^{-7} . The STO's are included in the final basis according to a convergence in norm criterion for the spin density (Sec. III).

The Coulombic singularities of the wave function have been studied by Kato,⁸ who introduced the cusp condition. Steiner⁹ extended this condition in the case of the charge density and obtained the relationship

$$\left. \frac{d\rho(r)}{dr} \right|_{r=0} = -2Z\rho(0), \quad (10)$$

which conditions the slope of the density at $r=0$. Also, for the correct behavior of the electron density at large values of r , Hoffman-Ostenhof and Hoffman-Ostenhof¹⁰ have shown that the density should obey the following inequality:

$$|\rho(r)|^{1/2} \leq kr^{\gamma-1} \exp(-\sqrt{2\epsilon}r) \quad (11)$$

for $r \geq r_0$, where

$$\gamma = \frac{Z}{\sqrt{2\epsilon}}, \quad r_0 \geq \frac{Z}{\epsilon},$$

ϵ is the ionization potential, and Z is an effective charge.¹¹ The densities obtained should obey conditions (10) and (11).

III. CONVERGENCE CRITERIA

In order to assess the quality of the results, we have analyzed the convergence of the charge and spin density, and their first and second derivatives, by using a sequence of increasingly improved densities converging towards the full stabilized density. For this purpose, it is possible to apply the criteria of the metric spaces theory.¹²

The strongest of all is the point-by-point convergence, which requires that, at each point in space, the absolute value of the difference between two consecutive functions f_m and f_n vanishes at the limit

$$\lim_{m,n \rightarrow \infty} |f_n(r) - f_m(r)| = 0, \quad n > m \text{ for all } r. \quad (12)$$

A somewhat less demanding criterion is the convergence in norm. A metric induced by the norm is represented by the distance

$$d(f_m, f_n) = \|f_m - f_n\| = \int_0^\infty |f_m(r) - f_n(r)| dr \quad (13)$$

such that (i) d is finite and non-negative, (ii) $d=0$ if and only if $f_m = f_n$, and (iii) d is symmetric and the triangle inequality is obeyed. Now, since a normed space is a metric space, the basic concepts of the convergence of sequences are applicable.

(1) A sequence (f_n) in a normed space is convergent if it contains f such that

$$\lim_{n \rightarrow \infty} d(f, f_n) = \lim_{n \rightarrow \infty} \|f - f_n\| = 0, \quad (14)$$

i.e., f_n converges to f . A sequence obeying Eq. (14) is said to be strongly convergent, or convergent in norm.

(2) In addition, sequence (f_n) in a normed space satisfies the Cauchy convergence criterion if, for each $\epsilon > 0$, there exists an $N(\epsilon)$ such that

$$\|f_m - f_n\| < \epsilon \text{ for all } m, n > N(\epsilon). \quad (15)$$

The sequence (f_n) is then called a Cauchy sequence. Then the distances between successive functions in the sequence decrease monotonically.

Since the densities (and their derivatives) are continuous, real-valued functions in the interval $[0, \infty]$, they belong to the normed spaces L^p . In previous calculations of the densities of neon¹ and beryllium,² we used the criterion of point-by-point convergence [Eq. (12)]. In this study, we have employed the metric of the L^1 space as a convergence criterion, because it is more practical to consider the densities themselves as elements of the metric space, instead of individual points. The convergence in norm for the first and second derivatives has also been imposed.

IV. CHARGE AND SPIN-DENSITY RESULTS

In order to achieve the stability of the electron and spin density, eight s -, six p -, six d -, four f -, four g -, two h -, and two i -type STO's were required, distributed among the K shell and intershell regions.

The distances, as calculated from Eq. (13) for a sequence of spin densities and their first and second derivatives, are shown in Table I. As expected, the charge den-

TABLE I. Distances of the convergent sequence of the spin density and its first and second derivatives.

Sequence		$\ \rho_m - \rho_m\ $	$\ \rho'_m - \rho'_n\ $	$\ \rho''_m - \rho''_n\ $
SCF	[8] ^a	105.112	709.791	4081.337
[8]	[86]	17.016	100.028	598.153
[86]	[866]	1.650	9.613	57.204
[866]	[8664]	0.262	1.507	8.923
[8664]	[86644]	0.074	0.420	2.529
[86644]	[866442]	0.029	0.170	1.039
[866442]	[8664422]	0.013	0.076	0.466

^aWave functions are denoted $[abc \dots]$, where a, b, c, \dots are equal to the number of s, p, d, \dots STO's.

sity converges fast, in a manner similar to the one observed for neon and beryllium. When the STO's from both shells are mixed to form the complete basis set, it is found that the charge densities change little upon a cyclic reoptimization of the total basis, and, in fact, this reoptimization was not carried out for neon and beryllium. Here, a total density-restricted cyclic reoptimization has been performed automatically, to obtain the best possible variational CI of this size, energywise. In the case of the spin density, convergence is slower, and, in this work, special attention was devoted to the convergence of its value at the nucleus. Significant changes are observed upon cyclic reoptimization.

The final STO basis is given in Table II. All single, double, and triple excited configurations obtained by promoting K and L electrons in the Hartree-Fock configuration are included in the final wave function. The result is a compact wave function, which represents the final stage of a convergent series, both in the charge and spin densities, and in their first and second derivatives.¹³ It contains 1760 terms and yields a total nonrelativistic energy of $-7.477\,699\,96$ a.u. (Li), which represents 99.18% of the correlation energy.

The analytical charge and spin electron densities may be reproduced from the expression for the density [Eq. (9)] using the parameters of the orbital set (Table II) and the coefficients of the natural expansion given in Table III.

The cusp ratio

$$\frac{[d\rho(r)/dr]_{r=0}}{-2\rho(0)} = Z', \quad (16)$$

for our density is 3.008.

With respect to the asymptotic behavior, for lithium the ionization potential $\epsilon = 0.1963$ a.u. and then $r_0 \geq 5.09$. We have calculated the ratio

$$\frac{\rho(r)}{[r^{\gamma-1} \exp(-\sqrt{2\epsilon}r)]^2} \quad (17)$$

for values of r from 1 to 30 bohrs. This ratio is plotted against the radial coordinate in Fig. 1. It is seen to be approximately constant ($0.5 \leq k^2 \leq 0.54$) and to present a maximum of 0.574 at $r = 11.9$ bohrs. If we use this maximum value for k^2 our density strictly obeys the inequali-

ty in Eq. (12). It is interesting to note that for the SCF density there is no constant zone. Also shown for comparison in Fig. 1 is the value of the asymptotic ratio for the density calculated by King *et al.*¹⁴ with a 233-term Hylleraas-type wave function which accounts for 99.95% of the correlation energy: the authors have pointed out departures from the rigorous behavior when $\rho(r)$ becomes very small.

The definite integral

$$N_{\alpha(\beta)}(r_{\max}) = \int_0^{r_{\max}} r^2 \rho_{\alpha(\beta)} dr \quad (18)$$

is a suitable criterion to determine the size of the region of interest for the charge and spin density. It is found that the β density contribution is almost totally included

TABLE II. The STO orbital set.

j	Type	Z_{ji}	Shell ^a
1	1s	2.476 73	K (SCF) ^b
2	1s	4.698 73	K (SCF)
3	2s	0.383 50	L (SCF)
4	2s	0.660 55	L (SCF)
5	2s	1.070 00	L (SCF)
6	2s	1.632 00	L (SCF)
7	3s	3.961 19	K
8	4s	8.006 31	KL
1	2p	4.156 18	K
2	2p	2.513 09	KL
3	3p	4.850 36	K
4	3p	1.466 17	KL
5	4p	13.414 80	K
6	4p	5.712 19	KL
1	3d	5.004 33	K
2	3d	2.841 14	KL
3	4d	11.500 00	K
4	4d	2.239 05	KL
5	5d	11.230 40	K
6	5d	11.230 00	KL
1	4f	7.465 93	K
2	4f	5.575 71	KL
3	5f	12.970 00	K
4	5f	11.150 00	KL
1	5g	9.410 00	K
2	5g	4.440 00	KL
3	6g	14.660 00	K
4	6g	13.780 00	KL
1	6h	11.240 0	K
2	6h	3.850 00	KL
1	7i	13.150 00	K
2	7i	4.480 00	KL

^aLocalized mainly in the shell as indicated.

^bSTO's of analytical SCF orbital basis (Ref. 6).

TABLE III. Orbital expansion coefficients and occupation numbers for the natural orbitals. Square brackets denote powers of 10.

Density-matrix Block with α spin				
	s_1	s_2	s_3	s_4
n_i	0.999 499 443 0	0.996 635 603 0	0.133 619 987 4[−2]	0.287 869 023 2[−4]
	−0.635 227 513 1[−1]	0.912 327 734 5	−0.165 221 522 4[1]	0.272 949 620 3
	−0.384 879 260 8[−2]	0.111 915 803 3	−0.480 169 973 8[−1]	0.937 862 869 9
	−0.105 205 767 5[−2]	0.247 882 175 0[−3]	−0.329 805 982 3[−1]	−0.124 103 130 1
	0.965 684 339 0	−0.933 078 637 9[−1]	−0.129 842 503 8	0.192 211 910 9
	0.127 576 552 4	−0.127 783 618 2[−1]	−0.437 910 270 3	−0.129 630 084 2[1]
	−0.110 195 267 2	0.173 740 078 0[−1]	0.751 992 995 0	0.195 212 620 8[1]
	0.421 535 326 2[−4]	−0.280 142 599 0[−2]	0.160 923 730 3[1]	−0.333 389 409 3
	0.475 652 520 7[−3]	−0.739 346 537 1[−3]	0.493 983 469 0[−1]	−0.169 349 095 7[1]
	s_5	s_6	s_7	s_8
n_i	0.299 204 164 9[−5]	0.269 072 445 7[−6]	0.117 960 785 7[−6]	0.709 502 076 3[−9]
	0.565 909 549 9[1]	0.406 953 387 1[2]	−0.292 198 799 5[2]	0.327 843 631 0
	−0.350 913 672 6[1]	−0.198 512 101 3[2]	0.139 318 260 7[2]	−0.133 244 179 9
	−0.346 008 198 5	−0.400 554 762 4	−0.161 499 512 8[1]	0.304 588 153 8[1]
	0.918 636 422 9	0.199 105 976 7[1]	0.722 582 293 5[1]	−0.557 840 655 0[1]
	−0.335 166 010 7[1]	−0.194 984 735 8[1]	−0.138 698 296 8[2]	0.511 276 147 2[1]
	0.495 031 320 2[1]	−0.242 656 632 4[1]	0.134 994 907 5[2]	−0.246 973 328 1[1]
	−0.693 893 231 3[1]	−0.175 941 179 4[2]	0.848 693 269 8[1]	0.294 540 448 6
	0.161 211 522 6[1]	−0.661 931 680 6[1]	0.578 800 031 4[1]	−0.739 894 943 2[−1]
	p_1	p_2	p_3	p_4
n_i	0.613 979 433 5[−3]	0.140 271 723 4[−3]	0.278 150 585 7[−4]	0.426 266 472 4[−5]
	0.420 262 997 8	−0.374 915 258 4	−0.155 290 560 1[1]	0.123 582 098 0[1]
	0.211 001 799 9	0.425 153 320 6	0.183 979 718 7[1]	0.374 920 044 2[1]
	0.686 221 869 8	−0.177 165 533 3	−0.195 224 348 5[1]	−0.374 163 081 4[1]
	−0.113 132 438 7[−1]	0.885 332 807 2	−0.883 802 656 9	−0.102 186 599 5[1]
	−0.116 337 827 8[−1]	−0.232 331 593 8[−1]	−0.629 991 001 3[−2]	0.474 376 165 5
	−0.288 963 344 3	−0.123 045 143 3	0.214 300 150 7[1]	−0.976 375 796 7
	p_5	p_6		
n_i	0.600 683 073 7[−6]	0.466 545 248 7[−7]		
	0.828 015 167 4[1]	−0.213 225 951 8[2]		
	−0.218 456 589 6[1]	−0.193 210 467 1[1]		
	−0.343 291 709 8[2]	0.172 420 945 5[2]		
	0.631 414 952 3	0.372 083 388 7		
	0.223 262 626 4[1]	0.650 435 251 8[1]		
	0.271 594 993 5[2]	0.135 714 588 0[1]		
	d_1	d_2	d_3	d_4
n_i	0.173 098 426 5[−4]	0.400 226 001 5[−5]	0.164 958 097 8[−5]	0.400 824 975 8[−6]
	0.806 243 447 1	−0.273 801 090 0	−0.106 026 972 5[1]	−0.223 529 985 9[1]
	0.114 418 368 4	0.396 485 453 9	−0.830 375 305 6	0.300 920 051 9[1]
	−0.403 503 198 5[−1]	−0.138 485 235 9	0.951 461 356 0	0.162 243 635 8[1]
	−0.185 234 916 2[−1]	0.720 248 852 4	0.107 422 301 9[1]	−0.164 607 682 1[1]
	−0.340 702 058 3[3]	0.657 568 563 7[3]	−0.319 873 877 8[4]	0.362 255 501 3[4]
	0.340 856 017 0[3]	−0.657 773 651 8[3]	0.319 938 694 7[4]	−0.362 322 355 6[4]
	d_5	d_6		
n_i	0.108 335 717 1[−6]	0.286 269 907 2[−7]		
	−0.724 742 366 8[1]	−0.100 818 593 6[2]		
	0.443 804 442 1[1]	0.425 897 814 1[1]		
	−0.851 680 828 5	0.114 901 298 7[2]		
	−0.181 615 822 7[1]	−0.146 496 086 2[1]		
	−0.150 823 927 4[5]	−0.924 811 934 8[5]		
	0.150 878 302 5[5]	0.924 774 438 2[5]		

TABLE III. (Continued).

Density-matrix Block with α spin				
	f_1	f_2	f_3	f_4
n_i	0.158 456 604 2[-5]	0.305 229 305 1[-6]	0.824 148 748 1[-7]	0.205 289 364 2[-7]
	0.442 783 590 4	-0.873 459 587 4	-0.598 707 411 9[1]	-0.160 410 048 6[2]
	0.489 855 581 1	0.172 075 968 5[1]	0.345 349 890 9[1]	0.537 600 886 0[1]
	-0.254 988 939 8	0.128 435 245 8	0.315 123 465 8[1]	-0.737 128 945 2[1]
	0.322 212 734 7	-0.107 393 553 4[1]	0.170 406 045 9	0.183 793 289 0[2]
	g_1	g_2	g_3	g_4
n_i	0.260 386 704 2[-6]	0.695 438 940 2[-7]	0.286 098 809 8[-7]	0.835 905 271 0[-8]
	0.129 715 059 2[1]	0.993 846 939 5	-0.307 479 993 5[1]	-0.657 264 583 9[1]
	0.179 989 194 7	0.697 484 187 8	0.105 635 491 1[1]	0.754 137 946 9
	-0.191 503 797 4	0.174 683 566 2[1]	0.510 190 049 5	-0.202 160 597 2[2]
	-0.274 710 797 6	-0.339 946 395 2[1]	0.233 553 669 0[1]	0.259 681 087 2[2]
	h_1	h_2	i_1	i_2
n_i	0.468 965 934 9[-7]	0.148 800 581 1[-7]	n_i 0.133 765 146 0[-7]	0.436 607 326 4[-8]
	0.980 723 278 8	-0.259 437 417 7	0.997 749 865 7	-0.143 051 816 5
	0.907 519 266 1[-1]	0.101 039 101 9[1]	0.168 352 814 4[-1]	0.100 781 208 1[1]
Density-matrix block with β spin				
	s_1	s_2	s_3	s_4
n_i	0.996 447 143 2	0.133 026 866 4[-2]	0.299 591 307 2[-4]	0.395 700 312 2[-5]
	0.896 729 915 6	-0.164 613 940 6[1]	0.274 478 705 1	0.414 554 914 8[1]
	0.111 114 180 7	-0.509 826 594 3[-1]	0.909 564 148 5	-0.278 694 783 6[1]
	-0.198 231 708 0[-3]	-0.293 973 899 1[-1]	-0.940 291 075 8[-1]	-0.188 664 840 4
	0.109 038 587 4[-2]	0.132 995 434 7	0.402 421 534 0	0.791 166 190 9
	-0.411 511 138 3[-2]	-0.365 775 043 7	-0.101 326 945 3[1]	-0.194 544 513 3[1]
	0.136 264 834 6[-1]	0.678 295 824 8	0.170 967 974 7[1]	0.345 442 579 0[1]
	0.858 685 975 5[-4]	0.154 966 561 3[1]	-0.464 354 976 3	-0.567 939 710 8[1]
	-0.106 824 718 2[-2]	0.622 179 799 3[-1]	-0.154 777 681 8[1]	0.181 815 651 3[1]
	s_5	s_6	s_7	s_8
n_i	0.344 786 978 6[-6]	0.141 066 084 3[-6]	0.754 962 021 3[-9]	0.399 974 346 9[-12]
	-0.322 492 854 1[2]	0.385 171 911 2[2]	-0.114 762 446 5[1]	0.568 764 042 0[-1]
	0.158 881 270 7[2]	-0.184 417 933 3[2]	0.500 465 382 0	-0.207 150 435 7[-1]
	0.651 696 784 0[2]	0.127 856 743 7[1]	-0.204 072 036 0[1]	0.243 166 131 6[1]
	-0.249 068 341 2[1]	-0.525 121 380 0[1]	0.668 802 451 7[1]	-0.313 375 294 6[1]
	0.465 996 956 3[1]	0.118 851 147 2[2]	-0.793 510 956 7[1]	0.213 403 927 2[1]
	-0.149 809 679 8[1]	-0.135 908 478 7[2]	0.449 277 263 5[1]	-0.813 396 499 3
	0.156 588 434 4[2]	0.123 381 337 2[2]	-0.457 607 265 6	0.798 944 375 9[-1]
	0.465 307 713 1[1]	-0.744 014 855 5[1]	0.280 845 816 8	-0.742 088 917 5[-2]
	p_1	p_2	p_3	p_4
n_i	0.632 424 913 4[-3]	0.474 249 545 5[-4]	0.685 612 301 5[-5]	0.797 487 946 2[-6]
	0.403 183 709 4	-0.129 192 580 0[1]	-0.136 182 400 6[1]	-0.663 771 927 3[1]
	0.239 566 596 4	0.171 576 961 0[1]	-0.193 240 600 2[1]	-0.202 663 557 2
	0.668 654 977 5	-0.146 754 121 9[1]	0.771 424 525 5	0.297 569 606 6[2]
	0.200 518 980 1[-2]	0.249 322 717 0[-1]	-0.118 621 342 3	0.417 853 170 1
	-0.115 930 930 7[-1]	-0.116 585 422 6[-1]	-0.260 708 290 9	-0.209 837 101 5[1]
	-0.285 516 996 9	0.117 056 251 6[1]	0.267 233 635 2[1]	-0.223 121 820 9[2]

TABLE III. (Continued).

Density-matrix Block with β spin				
	p_5	p_6		
n_i	0.108 038 635 9[-6]	0.390 298 276 6[-7]		
	0.110 984 920 3[2]	-0.188 824 757 9[2]		
	-0.315 652 599 8[1]	-0.307 112 552 7[1]		
	-0.218 263 340 1[2]	0.113 593 006 9[2]		
	0.147 576 871 1[1]	0.882 722 540 6		
	-0.104 431 829 3[1]	0.647 726 551 3[1]		
	0.143 040 565 5[2]	0.583 883 832 8[1]		
	d_1	d_2	d_3	d_4
n_i	0.177 581 287 1[-4]	0.274 838 166 1[-5]	0.718 158 802 6[-6]	0.161 971 303 4[-6]
	0.789 841 334 3	0.827 433 016 6[-1]	-0.261 641 944 5[1]	-0.424 560 962 4[1]
	0.132 810 295 6	0.948 479 754 1	0.149 825 035 6[1]	0.106 277 423 4[1]
	-0.418 284 984 3[-1]	-0.502 021 919 1	0.157 795 653 5[1]	-0.881 632 524 0
	0.387 589 697 9[-2]	-0.127 549 884 8[-1]	0.381 699 852 0[-1]	0.258 703 108 2
	-0.315 093 427 6[3]	0.210 876 144 4[4]	-0.155 568 589 6[4]	-0.168 970 678 6[5]
	0.315 241 849 2[3]	-0.210 926 123 3[4]	0.155 598 643 0[4]	0.169 011 601 1[5]
	d_5	d_6		
n_i	0.381 653 878 3[-7]	0.156 993 093 5[-7]		
	-0.264 406 730 0[1]	0.113 367 601 8[2]		
	-0.633 057 332 9	-0.656 185 789 7[1]		
	0.815 726 401 8[1]	-0.813 909 545 7[1]		
	0.912 627 737 0	0.298 759 354 9[1]		
	-0.588 950 688 7[5]	0.710 144 117 1[5]		
	0.588 898 393 8[5]	-0.710 140 905 9[5]		
	f_1	f_2	f_3	f_4
n_i	0.159 890 246 2[-5]	0.292 275 705 8[-6]	0.686 784 471 2[-7]	0.175 800 433 6[-7]
	0.405 286 454 7	-0.268 068 220 0	-0.422 514 671 4[1]	-0.166 141 475 9[2]
	0.517 443 776 6	0.142 806 994 4[1]	0.292 828 525 3[1]	0.575 735 286 5[1]
	-0.249 234 474 7	0.713 996 985 4[-1]	0.394 674 560 8[1]	-0.697 880 264 7[1]
	0.328 428 930 5	-0.138 718 335 4[1]	-0.191 451 604 3[1]	0.182 589 269 3[2]
	g_1	g_2	g_3	g_4
n_i	0.263 442 703 1[-6]	0.683 656 975 2[-7]	0.247 738 615 4[-7]	0.780 911 729 1[-8]
	0.128 594 605 3[1]	0.123 453 383 7[1]	-0.251 315 368 3[1]	-0.676 983 950 2[1]
	0.198 219 770 7	0.623 474 145 6	0.103 149 297 6[1]	0.843 505 303 8
	-0.177 166 699 7	0.198 226 058 8[1]	0.215 131 612 0[1]	-0.200 860 291 5[2]
	-0.290 043 982 0	-0.386 269 901 4[1]	0.153 483 067 4	0.260 077 122 6[2]
	h_1	h_2	i_1	i_2
n_i	0.470 946 878 3[-7]	0.146 394 911 2[-7]	n_i 0.133 955 918 7[-7]	0.434 188 926 7[-8]
	0.976 891 515 9	-0.273 512 137 6	0.996 214 703 8	-0.153 378 227 1
	0.105 270 669 1	0.100 898 167 0[1]	0.272 726 804 7[-1]	0.100 758 365 3[1]

at a distance of 2.0 bohrs, whereas the α density contribution extends to about 8.0 bohrs. These contributions are shown in Fig. 2 where the values of the definite integral for α , β and total densities are plotted for different values of r_{\max} . Figure 3 shows the radial density functions $D(r) = 4\pi r^2 \rho(r)$ for the α and β densities.

A comparison between our best density and the one ob-

tained from an SCF wave function⁶ is shown in Fig. 4, which represents plots of the differences in the charge and spin-density distributions $D_C(r)$ and $D_S(r)$:

$$\Delta D_C(r) = D_{CI}(r) - D_{SCF}(r), \quad (19a)$$

$$\Delta D_S(r) = D_{CI}(r) - D_{SCF}(r). \quad (19b)$$

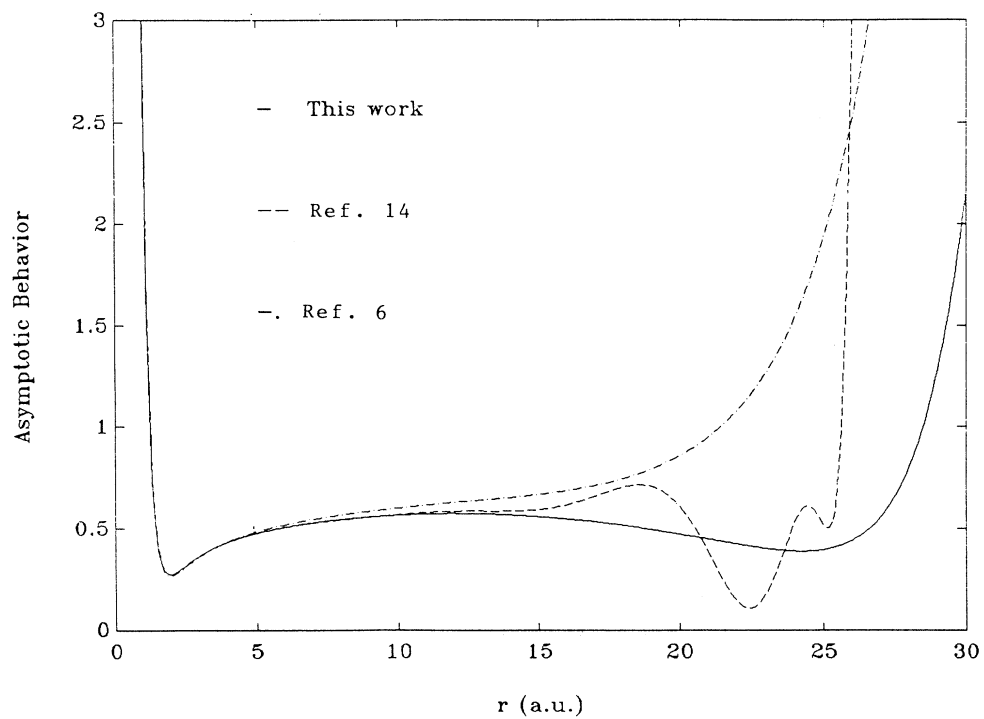


FIG. 1. Comparison of the asymptotic behavior of different calculated densities: King's (Ref. 14) and SCF (Ref. 6).

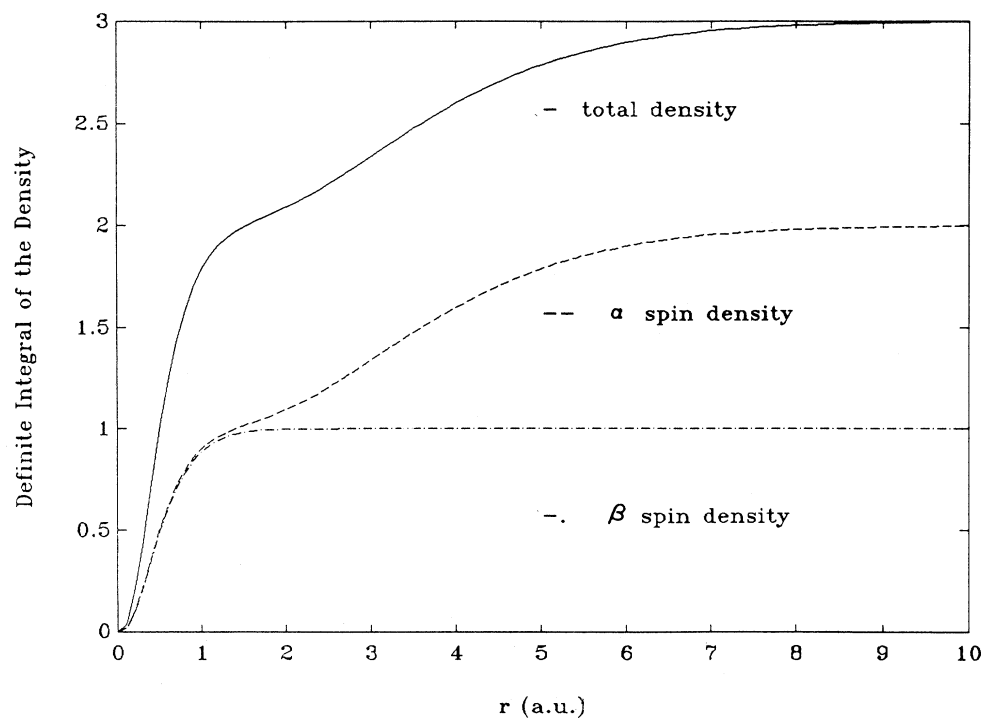


FIG. 2. Definite integral of the charge and spin densities.

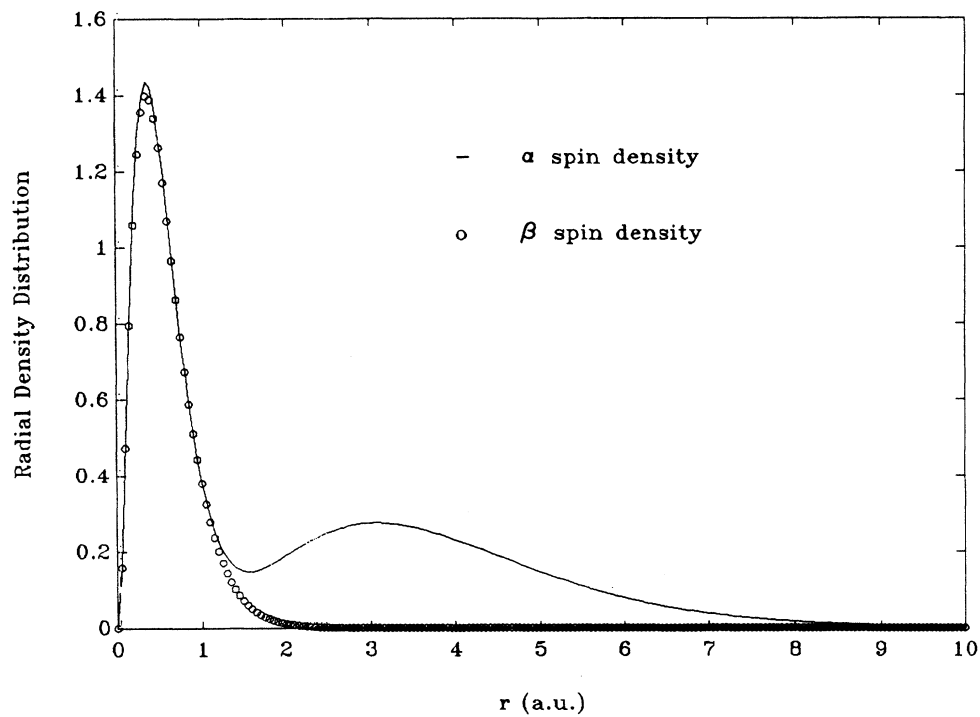


FIG. 3. Radial distribution functions for the spin densities.

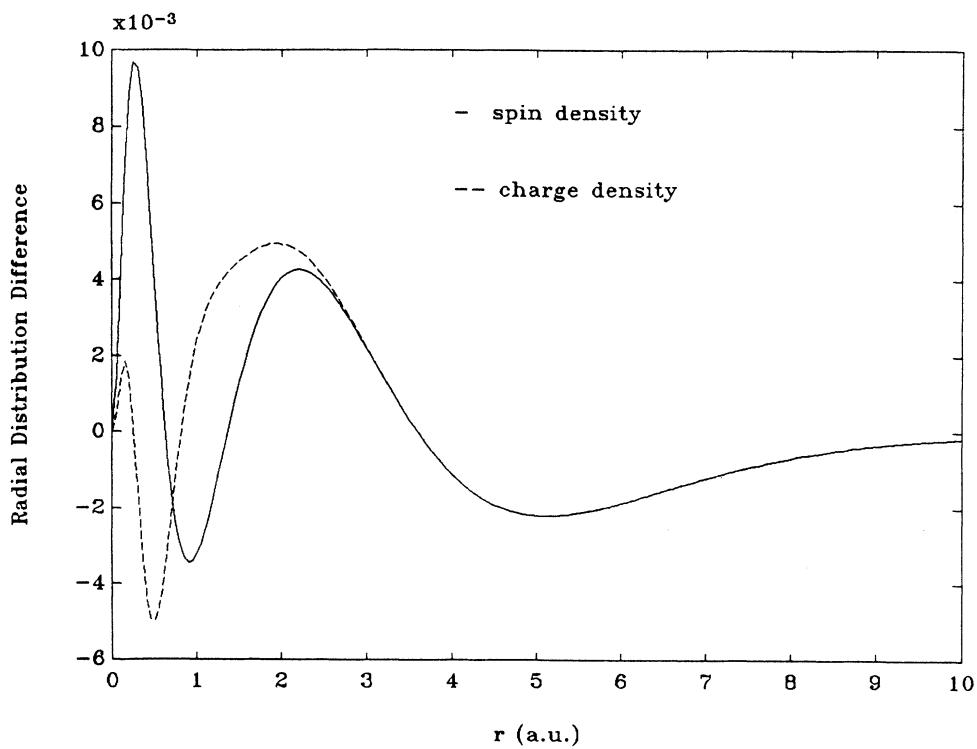


FIG. 4. Radial distribution difference between the SCF density (Ref. 6) and this work.

TABLE IV. Comparison of the density moments results.

$\langle r^n \rangle$	This work	Literature values	
$\langle r^{-2} \rangle$	30.242 52	30.240 71 ^a	30.246 ^b
$\langle r^{-1} \rangle$	5.717 929	5.718 087	5.718 110 ^c
$\langle r^1 \rangle$	4.990 184	4.989 765	4.989 538
$\langle r^2 \rangle$	18.359 90	18.357 07	18.354 74
$\langle r^3 \rangle$	92.629 12	92.627 92	92.603 64
$\langle r^4 \rangle$	550.040 2	550.416 3	545.80 ^b
$\langle r^5 \rangle$	3 695.848	3 706.018	
$\langle r^6 \rangle$	27 648.79	27 889.71	
$\langle r^7 \rangle$	227 842.1	234 064.8	
$\langle r^8 \rangle$	2 050 515.1	2 232 172.0	
$\langle r^9 \rangle$	20 008 387.7	25 826 190.0	
$\langle r^{10} \rangle$	210 364 940.2	407 477 900.0	

^aFrom the 233-term Hylleraas wave function of King (Ref. 14).

^bFrom the 45-term CI wave function of Weiss (Ref. 15).

^cFrom the 602-term Hylleraas wave function of King (Ref. 16).

It can be seen that the effect of correlation is to increase both the charge and spin densities within the *K* and *L* shells, and that the spin density is much more sensitive to correlation than the charge density, especially in the vicinity of the nucleus.

V. ONE-ELECTRON PROPERTIES FOR LITHIUM

The density moments $\langle r^n \rangle$ for powers *n* from -2 to 10 have been calculated from the final charge densities and are given in Table IV, together with results obtained by other authors. The values for these properties as the basis is improved converge quite fast: in fact, an $[8s, 4p, 4d, 2f]$ basis is sufficient to obtain the final results.¹³ As an example, the convergence of r^{-1} , r^2 , and r^{10} is shown in Table V. An analysis of the convergence of $\langle r^n \rangle$ for positive values of *n* shows that it follows a pattern similar to that of the spin density, i.e., it is more dependent on a good representation of the density close to the nucleus. On the contrary, for negative *n*, $\langle r^n \rangle$ converges in the same way as the charge density. The good convergence of r^{10} is another proof of the goodness of the density at large distances.

Of special importance, in this study is the accurate calculation of the Fermi-contact term *f* for lithium, which is

obtained from the hyperfine structure constant $A_{1/2}$:

$$A_{1/2} = \left[\frac{\mu_0 \mu_B \mu_N g_e \mu_I}{6\pi \hbar a_0^3 I} \right] f, \quad (20)$$

where μ_0 is the vacuum permeability, g_e is the electronic gyromagnetic factor, μ_B and μ_N are the Bohr and nuclear magneton, respectively, *I* is the nuclear spin angular momentum, and μ_I is the magnetic moment of the nucleus. *f* can be theoretically calculated as the spin density at the nucleus, $\rho_S(0)$.^{3,17}

It is well known that the Fermi-contact term represents a very sensitive test of the accuracy of the wave function, and, in the case of the lithium atom, it has received considerable attention for almost 20 years.³ The main difficulties which arise in the calculation of an accurate value for this interaction are that (i) it is very sensitive to the electronic correlation, (ii) it is strongly dependent on the choice of the orbital basis parameters used to represent the wave function, and (iii) since it is a property that represents a single point in the spin-density function, it is imperative that the latter be well represented everywhere.

Harriman³ has discussed the results of more than 40 calculations of various types [Hartree-Fock (HF), multiconfiguration Hartree-Fock (MCHF), CI, and Hylleraas], and he has noted the lack of a direct relationship between the precision of the energies and that of *f*. The best result in Harriman's review is that of Larsson,¹⁸ obtained with a Hylleraas-type wave function containing 100 terms, $f=2.9060$, which agrees with one of the theoretical-experimental values accepted in the literature and reported for the first time by Larsson himself. However, Bunge⁷ has shown that Larsson's result has not converged, and still oscillates markedly when the number of basis functions is increased. Also, King *et al.*'s¹⁶ Hylleraas-type function of 602 terms, which accounts for 99.96% of the correlation energy, yields an *f* value which still has not quite converged. Some representative results are presented in Table VI.

The converged value obtained for the Fermi-contact term *f* in this work is $f=2.908\,56+0.000\,08$ a.u. When multiplied by the correction factor for the effect of the

TABLE V. Convergence of some density moments.

Function	$\langle r^{-2} \rangle$	$\langle r^{-1} \rangle$	$\langle r^2 \rangle$	$\langle r^{10} \rangle$
$[8s]^a$	30.264 068	5.714 589	18.6596	23 366[4] ^b
$[8s, 6p]$	30.242 285	5.717 170	18.3892	21 234[4]
$[8s, 6p, 6d]$	30.242 411	5.717 659	18.3640	21 060[4]
$[8s, 6p, 6d, 4f]$	30.242 646	5.717 784	18.3602	21 034[4]
$[8s, 6p, 6d, 4f, 4g]$	30.242 740	5.717 829	18.3590	21 025[4]
$[8s, 6p, 6d, 4f, 4g, 2h]$	30.242 723	5.717 837	18.3587	21 023[4]
$[8s, 6p, 6d, 4f, 4g, 2h, 2i]$	30.242 718	5.717 841	18.3585	21 022[4]

^aWave functions are denoted $[a, b, c, \dots]$, where *a, b, c, \dots* are equal to the number of *s, p, d, \dots* STO's.

^bThe notation $[n]$ means 1×10^n .

TABLE VI. Comparison of Fermi-contact interaction values obtained by various methods.

Method	Reference	$f = 4\pi\rho_s(0)$
Hylleraas (100 terms)	Larsson (Ref. 18)	2.907 0 ^a
Hylleraas (352 terms)	King and Shoup (Ref. 19)	2.905 1(20)
Hylleraas (602 terms)	King (Ref. 16)	2.906 7(4) ^a
MCHF	Sundholm and Olsen (Ref. 20)	2.904 9(20)
Bruckner-Goldstone	Garpman <i>et al.</i> (Ref. 21)	2.909 5 ^a
MBPT-coupled-cluster	Lindgren (Ref. 22)	2.917 2
MBPT-relativistic	Blundell <i>et al.</i> (Ref. 23)	2.911 2
CI-spin-density convergence	This work	2.909 53(8)
Experimental ^b	Beckmann, Böklen, and Elke (Ref. 24)	2.909 40(10)
Experimental ^c	Beckmann, Böklen, and Elke (Ref. 24)	2.906 06(10)

^aRecalculated in this work to include the reduced mass effect and the relativistic and nuclear-size corrections (Ref. 22).

^bTheoretical-experimental value without QED effects, as computed by Lindgren (Ref. 22).

^cTheoretical-experimental value including QED effects, as computed by King (Ref. 16).

finite nuclear mass,

$$[m_e/(m_e + M_{\text{nuc}})]^3 \cong 0.999\,765\,4$$

it becomes $f = 2.907\,88$ a.u. In addition, the f value has to be corrected for relativistic and finite-nuclear size effects. These corrections are not negligible. Lindgren²² has used a model of homogeneous nuclear charge density and pointlike nuclear moments to estimate them to be $\Delta f_{\text{rel}} = 0.001\,65$ a.u. The uncertainty of these corrections is not known. Finally, the Fermi-contact term is found to be

$$f = f_{\text{NR}} + \Delta f_{\text{rel}} = 2.909\,53 + 0.000\,08 \text{ a.u.},$$

which agrees with the experimental result obtained by Lindgren.²²

VI. CONCLUSION

Precise charge and spin densities and one-electron properties have been obtained for the lithium atom. The procedure used to optimize the basis functions ensures that the sequence of calculations is a Cauchy sequence, where densities, their derivatives, and properties converge monotonically to their final values.

We note that other manners of enlarging the basis set do not, in general, lead to converging results.¹³ In particular, we have verified that, when only an energy criterion is used, neither the SCF orbitals nor the additional orbitals obtained by adding STO's to the basis are adequately distributed among the K and L shells of the atom. The minimizing sequence, in this case, neither converges in the Cauchy sense, nor does it produce accurate densities and properties. For lithium, in order to obtain a very good energy eigenvalue it is necessary to crowd most STO orbitals within the K shell, thus unbalancing the

basis set and, consequently, the wave function. These facts support the notion mentioned by Pilar²⁵ that "the best wave function can be chosen from several alternatives by using the criterion of lowest energy, but the energy turns out to be an insensitive criterion with respect to a best wave function for other physical properties."

Accurate converged density moments have been obtained for all powers of r from -2 to 10 , this being one more check on the goodness of the density in all regions of space.

The result obtained for the Fermi-contact term represents the best calculation of this property to date, in the sense that it is the only one which has clearly converged to a definite value, and for which an error margin can be indicated. Two conflicting theoretical-experimental values are usually reported in the literature,¹⁶⁻²² but a careful analysis^{26,27} of their origin shows that the difference between them resides in the use of different values for the electronic gyromagnetic factor in the expression relating the experimental hyperfine splitting²⁴ and the spin density at the nucleus. Calculated nonrelativistic spin densities do not, in general, include quantum-electrodynamics (QED) corrections, and hence they should be compared with Lindgren's result, $f = 2.9096$. (Actually, when the latest values for the fundamental constants are used, f becomes 2.9094.) If the first-order QED correction were estimated and taken into account, then the calculated f values could be compared to King's theoretical-experimental Fermi-contact term,¹⁶ i.e., $f = 2.9060$ a.u. However, this is not straightforward, since the magnetic Hamiltonian contains additional higher-order relativistic and magnetic interaction terms where radiative effects are included. To our knowledge, no estimates of these effects have been reported to date. A more detailed study of the Fermi-contact interaction in the isoelectronic series of lithium will be published elsewhere.

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