

Radial electronic density functions for selected low-lying excited 2S states of the Li I isoelectronic series

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The radial electronic density function $D_0(r)$, has been evaluated in closed form for some low-lying excited 2S states of the Li I isoelectronic series that are described by Hylleraas-type wave functions. The radial density for each state considered is determined by a set of expansion coefficients, exponent values, and a set of summation limits. Numerical values for each of these are reported for the species Li I, Be II ($3{}^2S$ and $4{}^2S$ states) and B III, C IV, N V, O VI, F VII, and Ne VIII for the $3{}^2S$ states. The nuclear-magnetic shielding constant, the diamagnetic susceptibility and the expectation values $\langle r_i^n \rangle$ (for $n = -2$ to 8) and $\langle \delta(\mathbf{r}_i) \rangle$ are evaluated using $D_0(r)$. The electron-nuclear cusp condition is also examined for each state investigated.

I. INTRODUCTION

The electronic density function can be regarded as the central quantity for the evaluation of nondifferential one-electron properties. This function is a major by-product and an important quantity in atomic and molecular quantum structure calculations. The electronic density is also an important component in density-functional theory. Despite the aforementioned reasons why access to the electronic density is of importance, exceedingly few studies have appeared where theoretical procedures are developed to obtain relatively accurately densities from simple analytical formulas. The extensive tabulation of wave functions by Clementi and Rosetti [1] allows Hartree-Fock quality electronic densities to be obtained with minimal labor. Beyond the Hartree-Fock level few studies have produced formulas for correlated electronic densities.

Benesch [2] developed explicit formulas for the radial electronic density functions for the 1S ground states of members of the He isoelectronic series described by Hylleraas-type wave functions. The radial electronic density $D_0(r)$ is evaluated for an N -electron system using

$$D_0(r) = \int_0^\pi \int_0^{2\pi} r^2 \rho(\mathbf{r}) d\Omega, \quad (1)$$

where

$$\rho(\mathbf{r}) = N \int \Psi^*(x_1, x_2, \dots, x_N) \times \Psi(x_1, x_2, \dots, x_N) ds_1 dx_2 dx_3 \cdots dx_N \quad (2)$$

and the standard notation $d\Omega = (\sin\theta)d\theta d\phi$ is employed. x_i denotes a combined spatial and spin coordinate and $\Psi(x_1, x_2, \dots, x_N)$ is normalized.

A few additional studies have appeared [3–5] on the two-electron systems, using wave functions of a much higher quality than those employed by Benesch. Beyond the two-electron systems little work has been published leading to simple analytic formulas [6]. For these systems other approaches have been utilized [7–9], but they are somewhat less convenient to employ, in comparison

with results such as those obtained by Benesch.

For excited states very little published information is available. Tabulated Hartree-Fock wave functions have been reported for a number of excited states and electronic densities can be obtained from these. The author is unaware of any published work providing compact formulas for access to a highly correlated electronic density for excited states.

The objective of the present investigation is to calculate the radial electronic density functions for the low-lying 2S states of some members of the Li I isoelectronic series for $Z \leq 10$, where Z is the nuclear charge. From these functions, several one-electron properties are evaluated. These include the nuclear-magnetic susceptibility, the electronic density at the nucleus, and several moments $\langle r_i^n \rangle$.

II. THEORY

A general analysis of the 2S states of the Li I isoelectronic series in the same spirit as Benesch has recently been carried out [6]. Only a brief sketch of the theory is presented below; the interested reader can consult Ref. [6] for the details. The wave function employed is

$$\Psi(x_1, x_2, x_3) = \mathcal{A} \Phi(x_1, x_2, x_3) = \mathcal{A} \sum_{\mu=1}^{\mathcal{N}} C_{\mu} \phi_{\mu} \chi_{\mu}, \quad (3)$$

where the basis functions ϕ_{μ} are

$$\phi_{\mu} \equiv \phi_{\mu}(r_1, r_2, r_3, r_{23}, r_{31}, r_{12}) \\ = r_1^{i_{\mu}} r_2^{j_{\mu}} r_3^{k_{\mu}} r_{23}^{l_{\mu}} r_{31}^{m_{\mu}} r_{12}^{n_{\mu}} \exp(-\alpha_{\mu} r_1 - \beta_{\mu} r_2 - \gamma_{\mu} r_3). \quad (4)$$

χ_{μ} is the doublet spin eigenfunction and the functional form employed is

TABLE I. Nonrelativistic energies calculated employing the wave functions of the present study.

Species	Number of terms in wave function	Nonrelativistic ground-state energy	Lowest E_{NR} reported in literature ^a
3^2S Li I	162	-7.353 993	-7.354 076
4^2S Li I	185	-7.317 862	-7.318 491
3^2S Be II	162	-13.922 699	-13.922 764
4^2S Be II	185	-13.798 554	-13.798 662
3^2S B III	159	-22.603 667	-22.603 724
3^2S C IV	159	-33.396 143	-33.396 188
3^2S N V	159	-46.299 898	-46.299 936
3^2S O VI	159	-61.314 852	-61.314 886
3^2S F VII	159	-78.440 966	-78.440 999
3^2S Ne VIII	159	-97.678 223	-97.678 256

^aValues taken from Ref. [10].

$$\chi_\mu = \alpha(1)\beta(2)\alpha(3) - \beta(1)\alpha(2)\alpha(3). \quad (5)$$

\mathcal{A} is the antisymmetrizer, C_μ are the variationally determined expansion coefficients, and \mathcal{N} is the number of basis functions. On evaluation of Eqs. (1) and (2), the resulting expression for the radial electronic density is

$$D_0(r) = \sum_{I=1}^7 \sum_{K=0}^{g_I} A_{IK} r^K e^{-\alpha_I r}. \quad (6)$$

The summation limits g_I are governed by the number of basis functions and the particular choice of basis terms ($i_\mu, j_\mu, k_\mu, l_\mu, m_\mu, n_\mu$).

The particularly simple form given by Eq. (6) can only be obtained with some mathematically based restrictions on the basis set. The first restriction is on the exponents in Eq. (4):

$$\begin{aligned} \alpha_\mu &= \beta_\mu = \alpha, \\ \gamma_\mu &= \gamma \end{aligned} \quad (7)$$

for all μ . The second restriction is on the basis-set indices ($i_\mu, j_\mu, k_\mu, l_\mu, m_\mu, n_\mu$). Functions with l, m, n each odd are excluded, as well as some related sets. The exclusion of such terms has a very minor impact on the energy and a range of properties, and in any case, their omission can be compensated for by increasing the size of the basis set.

III. COMPUTATIONAL DETAILS

The wave functions employed in the present study were obtained as a subset of previously constructed wave functions for the low lying excited 2S states [10]. Three basis sets of different sizes were employed. These are available from the Physics Auxiliary Publication Service (PAPS) [11]. For the 3^2S excited states of Li I and Be II, the radial density was evaluated using 162 terms. For the 3^2S excited states of B III, C IV, N V, O VI, F VII, and Ne VIII 159

terms were employed. For the 4^2S excited states of Li I and Be II a total of 185 terms were employed. The orbital exponents employed can be found in Ref. [10]. All calculations were performed in double precision.

In order to get some idea of the quality of the wave functions employed, at least in the energetic sense, a comparison of the calculated energies with results obtained using larger basis sets is presented in Table I. For the 3^2S states the energies obtained from the wave functions employed in this study range from 33 to 83 μ hartrees above the results from more elaborate wave functions. It is therefore expected that the present wave functions for the 3^2S states should lead to reasonably accurate radial densities, at least in the energy important region of configuration space. The results for the 4^2S states are not as accurate (see Table I for the energy comparisons).

IV. RESULTS AND DISCUSSION

Values for the exponential factors α_I , summation limits g_I , and coefficients A_{IK} for each state are available

TABLE II. Diamagnetic susceptibilities and nuclear-magnetic shielding constants for some low-lying excited 2S states for selected members of the Li I isoelectronic series.

Species	Nuclear-magnetic shielding constant (a.u.)	Diamagnetic susceptibility ($\text{cm}^3 \text{mol}^{-1}$)
3^2S Li I	9.782×10^{-5}	-9.3979×10^{-5}
4^2S Li I	9.665×10^{-5}	-3.582×10^{-4}
3^2S Be II	1.3534×10^{-4}	-2.8955×10^{-5}
4^2S Be II	1.3332×10^{-4}	-9.881×10^{-5}
3^2S B III	1.7283×10^{-4}	-1.4195×10^{-5}
3^2S C IV	2.1031×10^{-4}	-8.4551×10^{-6}
3^2S N V	2.47783×10^{-4}	-5.6189×10^{-6}
3^2S O VI	2.85258×10^{-4}	-4.0074×10^{-6}
3^2S F VII	3.22732×10^{-4}	-3.0033×10^{-6}
3^2S Ne VIII	3.60206×10^{-4}	-2.3351×10^{-6}

from the PAPS [11]. Using the tabulated α_I , g_I , and A_{IK} coefficients, the nuclear-magnetic shielding constant (diamagnetic shielding factor) and the molar diamagnetic susceptibility have been determined and tabulated in Table II. The moments $\langle r_i^n \rangle$ and the electron density at the nucleus $\rho(0)$, have been evaluated and are tabulated in Table III.

In order to assess the quality of the wave functions in the near-nuclear region, the electron-nuclear cusp condition [12] was evaluated and the results are tabulated in Table IV. The differences apparent in Table IV range from about $\sim 0.15\%$ down to $\sim 0.025\%$ improving as the nuclear charge increases. This is consistent with the expectation that the wave functions are of higher quality for increasing Z (cf. Table I). Based on observations of the convergence patterns for $\rho(0)$ reported elsewhere [10], it is the derivative term which is mostly responsible for the failure of the cusp condition to be satisfied.

The CPU costs to evaluate the moments $\langle r_i^n \rangle$ directly from the wave function are rather high for highly correlated Hylleraas-type basis sets. The CPU costs to employ Eq. (6) to calculate a particular moment $\langle r_i^n \rangle$ are almost negligible in comparison with the direct wave-function evaluation approach. This constitutes one of the enormous advantages of extracting the radial electronic densities.

Unfortunately, for the systems studied herein, there are few accurate values for $\langle r_i^n \rangle$ with which to compare the present results. Our previous work [10] provides a point of comparison for at least the nuclear-magnetic shielding constants. The results in Table II are in rather good agreement with the results evaluated with more elaborate wave functions. The difference is 1–2 in the last quoted digit for the entries in Table II, except for the 4^2S state of Li I, where the difference is 6 in the least significant digit reported.

Since the variation method emphasizes the energy important contributions, the moment $\langle r_i^{-1} \rangle$ is expected to be somewhat more accurate than the higher moments. The lack of a large number of diffuse functions in the basis set and the less than optimal values for the exponents of the diffuse functions would be expected to lead to a deterioration of the quality of the calculated $\langle r_i^n \rangle$ with increasing n . The moments reported in Table III are expected to increase in accuracy with increasing Z . The moments for smaller values of n are probably accurate to 4–5 significant figures, and the moments for larger n to 3–4 significant figures. The exceptions expected are the 4^2S states where probably one less significant figure has been obtained. The latter is a reflection of the overall quality of the wave functions for the 4^2S states.

The value of $\langle \delta(r_i) \rangle$ reported in Table IV can be compared with the results from more elaborate wave functions. The differences amount to approximately 2–5 in the last reported digit for the entries in Table III.

A better handle on the quality of the expectation values could be obtained by examining $D_0(r)$ for a series of correlated wave functions of progressive increasing size. The convergence patterns for the expectation values could then be monitored. The drawback is that the CPU

TABLE III. Expectation values for some low-lying excited 2^2S states for the Li I series for $Z \leq 10$. Numbers in square brackets are powers of 10.

Species	$\langle r_i^{-2} \rangle$	$\langle r_i^{-1} \rangle$	$\langle r_i^1 \rangle$	$\langle r_i^2 \rangle$	$\langle r_i^3 \rangle$	$\langle r_i^4 \rangle$	$\langle r_i^5 \rangle$	$\langle r_i^6 \rangle$	$\langle r_i^7 \rangle$	$\langle r_i^8 \rangle$	$\langle \delta(r_i) \rangle$
3^2S Li I	2.9942[1]	5.5110	1.1316[1]	1.1866[2]	1.4924[3]	2.0458[4]	3.0362[5]	4.9181[6]	8.9429[7]	1.9415[9]	1.3730[1]
4^2S Li I	2.988[1]	5.445	2.118[1]	4.523[2]	1.104[4]	2.971[5]	9.445[6]	4.021[8]	2.456[10]	1.961[12]	1.3701[1]
3^2S Be II	5.6014[1]	7.6247	6.4641	3.6559[1]	2.5241[2]	1.8983[3]	1.5341[4]	1.3271[5]	1.2261[6]	1.2088[7]	3.4564[1]
4^2S Be II	5.5805[1]	7.5110	1.1343[1]	1.2475[2]	1.5745[3]	2.1068[4]	2.9661[5]	4.3914[6]	6.8571[7]	1.1396[9]	3.4447[1]
3^2S B III	9.0238[1]	9.7365	4.5897	1.7923[1]	8.6134[1]	4.5130[2]	2.5384[3]	1.5265[4]	9.7888[4]	6.6774[5]	7.0013[1]
3^2S C IV	1.3261[2]	3.5719	2.9281	1.0675[1]	3.9450[1]	1.5903[2]	6.8791[2]	3.1797[3]	1.5663[4]	8.1999[4]	1.2397[2]
3^2S N V	1.8314[2]	1.1848[1]	2.2827	7.0944	2.1317[1]	6.9905[1]	2.4589[2]	9.2386[2]	3.6980[3]	1.5727[4]	2.0031[2]
3^2S O VI	2.4181[2]	1.6070[1]	2.4827	5.0598	1.2815[1]	3.5435[1]	1.0507[2]	3.3266[2]	1.1217[3]	4.0181[3]	3.0295[2]
3^2S F VII	3.0863[2]	1.8182[1]	2.1557	3.7920	8.3025	1.9850[1]	5.0878[1]	1.3922[2]	4.0561[2]	1.2551[3]	4.3576[2]
3^2S Ne VIII	2.8360[2]	2.0293[1]	1.9052	2.9483	5.6854	1.1974[1]	2.7032[1]	6.5132[1]	1.6707[2]	4.5507[2]	6.0264[2]

TABLE IV. Cusp condition check.

Species	$\left. \frac{\partial \rho(r)}{\partial r} \right _{r=0}$	$-2Z\rho(0)$
3^2S Li I	-8.2303×10^1	-8.2377×10^1
4^2S Li I	-8.2077×10^1	-8.2204×10^1
3^2S Be II	-2.7632×10^2	-2.7652×10^2
4^2S Be II	-2.7536×10^2	-2.7558×10^2
3^2S B III	-6.9974×10^2	-7.0013×10^2
3^2S C IV	-1.4869×10^3	-1.4876×10^3
3^2S N V	-2.8033×10^3	-2.8044×10^3
3^2S O VI	-4.8455×10^3	-4.8472×10^3
3^2S F VII	-7.8414×10^3	-7.8437×10^3
3^2S Ne VIII	-1.2050×10^4	-1.2053×10^4

overhead for the calculations would markedly increase. This problem does not exist when determining expectation values directly from the wave function, since eigenvector determinations are a relatively minor component of the total CPU cost.

Expressions are reported in this work for the radial electronic density for several low-lying excited 2S states for selected members of the Li I isoelectronic series. The simplicity and compact nature of the formula for $D_0(r)$ allows expectation values of one-electron nondifferential spin-independent properties to be evaluated with ease.

Since the radial densities are obtained from highly correlated wave functions, they should serve as very good benchmarks for more approximate density determinations.

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 [11] See AIP document No. PAPS PLRAA-44-3350-12 for 12 pages of tables reporting α_J , g_I , and A_{JK} values and the basis sets employed in the density determinations. Order by PAPS number and journal reference from American Institute of Physics, Physics Auxiliary Publication Service, 335 East 45th Street, New York, NY 10017. The price is \$1.50 for each microfiche or \$5.00 for photocopies up to 30 pages, and \$0.15 for each additional page over 30 pages. Airmail additional.
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