Compact expressions for the radial electronic density functions for the ^2S states of three-electron systems

Frederick W. King[a] and Paul R. Dressel
Department of Chemistry, University of Wisconsin-Eau Claire, Eau Claire, Wisconsin 54702

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The radial electronic density function $D_0(r)$ has been evaluated in closed form for the ^2S states of three-electron systems that are described by Hylleraas-type wave functions. The density function $D_0(r)$ can be reduced to the form:

$$D_0(r) = \sum_{I=1}^{7} \sum_{K=0}^{g_I} \mathscr{A}_{IK} r^K e^{-\alpha_I r}.$$

Numerical values of the expansion coefficients $\mathscr{A}_{IK}$, summation limits g_I and exponents α_I are determined for the ground states of the following members of the Li I isoelectronic series: Li, Be^+, B^{2+}, C^{3+}, N^{4+}, O^{5+}, F^{6+}, and Ne^{7+}. A discussion is given on the constraints that must be imposed on the choice of the basis set for the Hylleraas wave function, in order that $D_0(r)$ be reducible to the aforementioned compact analytic form. Expectation values for several moments $\langle r^n \rangle$ are calculated using $D_0(r)$. The electron–nuclear cusp condition is evaluated for the wave functions used to determine $D_0(r)$ for each member of the Li I sequence examined in this investigation.

I. INTRODUCTION

There is a dearth of results in the literature that allows the determination of relatively accurate electron densities from fairly simple and compact analytic expressions. While reasonable quality electronic densities can be obtained from the extensive Hartree–Fock tabulations of atomic wave functions by Clementi and Roetti[1] (with a small investment of labor), the situation for the rapid determination of electronic densities giving a good account of electron correlation is considerably more limited.

The principal efforts that have taken place so far have been restricted to two-electron systems. A key paper in this area is that of Benesch,[2] where a formula manipulation program is used to derive expressions for the electron–nucleus and electron–electron distribution functions in closed form, starting with Hylleraas-type wave functions. Benesch analyzed the ^2S ground state wave functions of Hart and Herzberg[3] for several members of the helium isoelectronic series. Some earlier work by Coulson and Neilson[4] gave compact closed-form expressions for the electron–electron distribution function, however, this work was based on a small basis set. Later efforts for two-electron systems[5–7] have focused attention on analyzing wave functions of higher quality than those employed in the Benesch study.

For atoms with more than two electrons, two approaches are commonly taken for presenting correlated densities. The first involves numerical tabulation of the density at various values of the radial coordinate.[8] The second approach involves expressing the electronic density in terms of the natural radial orbitals, and tabulating orbital expansion coefficients and occupation numbers, which allow the density to be evaluated as a function of the radial coordinate.[9]

II. THEORY

A. Reduction of $D_0(r)$ to basic integrals

The radial electronic density function $D_0(r)$is evaluated from

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

where

$$\rho(\mathbf{r}) = N \int \psi^*(x_1,x_2,x_3,\ldots x_N)\psi(x_1,x_2,x_3,\ldots x_N) \times ds_1\, dx_2\, dx_3 \cdots dx_N. \tag{2}$$

The following standard notation has been employed in Eqs. (1) and (2). $d\Omega = \sin\theta\, d\theta\, d\phi$, x_i denotes a combined spatial and spin coordinate, $\psi(x_1,x_2,x_3\cdots x_N)$ is a normalized wave function and in the present work $N = 3$. The wave functions employed in this study are of Hylleraas type,

$$\psi(x_1,x_2,x_3) = \mathscr{A}\Phi(x_1,x_2,x_3) \tag{3a}$$

$$= \mathscr{A} \sum_{\mu}^{\mathscr{N}} C_\mu \phi_\mu \chi_\mu, \tag{3b}$$

where $\mathscr{A}$ is the antisymmetrizer, C_μ are the variationally determined expansion coefficients, $\mathscr{N}$ is the number of basis functions, and χ_μ denotes the doublet spin eigenfunction. The wave functions utilized in this work have employed a single doublet spin eigenfunction:

$$\chi_\mu = \alpha(1)\beta(2)\alpha(3) - \beta(1)\alpha(2)\alpha(3) \quad (\text{all } \mu). \tag{4}$$

The basis functions ϕ_μ appearing in Eq. (3b) take the form

$$\phi_\mu \equiv \phi_\mu(r_1,r_2,r_3,r_{23},r_{31},r_{12}) = r_1^{i_\mu} r_2^{j_\mu} r_3^{k_\mu} r_{23}^{l_\mu} r_{31}^{m_\mu} r_{12}^{n_\mu} \exp(-\alpha_\mu r_1 - \beta_\mu r_2 - \gamma_\mu r_3), \tag{5}$$

where the exponents $i_\mu, j_\mu, k_\mu, l_\mu, m_\mu$, and n_μ are each $\geqslant 0$. Additional constraints on these exponents will be imposed

[a] Camille and Henry Dreyfus Teacher–Scholar.

below. Inserting Eq. (3a) into Eq. (2) leads to

$$\rho(\mathbf{r}) = N\int\{\tfrac{1}{3}(1-P_{12}-P_{13})\Phi(x_1,x_2,x_3)\}$$
$$\times\Big\{\sum_P(-1)^P\mathscr{P}\Phi(x_1,x_2,x_3)\Big\}ds_1\,dx_2\,dx_3, \quad (6)$$

where $\Sigma_P(-1)^P\mathscr{P} = 1 - P_{23} - P_{12} + P_{123} - P_{13} + P_{321}$. Equation (6) can be contracted for the problem of interest from the 18 separate integrals in Eq. (6) to a total of 12 integrals. The 18 permutations have been efficiently handled by a computer. If Eq. (6) is inserted into Eq. (1), then

$$D_0(r) = \int\Big\{\sum_{P'}(-1)^{P'}\mathscr{P}'\Phi(x_1,x_2,x_3)\Big\}$$
$$\times\Big\{\sum_P(-1)^P\mathscr{P}\Phi(x_1,x_2,x_3)\Big\}ds_1\,dx_2\,dx_3\,r^2\,d\Omega$$
$$=\sum_u^{\mathscr{N}}\sum_v^{\mathscr{N}}C_uC_v\int\Big\{\sum_{P'}(-1)^{P'}\mathscr{P}'\phi_u\chi_u\Big\}$$
$$\times\Big\{\sum_P(-1)^P\mathscr{P}\phi_v\chi_v\Big\}ds_1\,dx_2\,dx_3\,r^2\,d\Omega, \quad (7)$$

where $\Sigma_{P'}(-1)^{P'}\mathscr{P}'$ denotes the restricted sum of permutations $(1 - P_{12} - P_{13})$. Equation (7) is a sum of integrals that take the form

$$I(r_1) \equiv I(i,j,k,l,m,n,\alpha,\beta,\gamma,r_1)$$
$$= \int r_1^{i+2}r_2^jr_3^ku_1^lu_2^mu_3^ne^{-\alpha r_1-\beta r_2-\gamma r_3}\,d\Omega_1\,d\mathbf{r}_2\,d\mathbf{r}_3, \quad (8)$$

where $u_1 = r_{23}$, $u_2 = r_{31}$, and $u_3 = r_{12}$.
Integrals related to those in Eq. (8) have been discussed in the context of matrix element evaluations for the atomic three-electron problem.[10-15] The integral in Eq. (8) can be evaluated as follows. The Sack expansion[16] for each u_i is employed:

$$u_1^l \equiv r_{23}^l = \sum_{l_1=0}^{\infty}R_{ll_1}(r_2,r_3)P_{l_1}(\cos\theta_{23}), \quad (9)$$

where P_l are the Legendre polynomials, θ_{23} is the angle between $\mathbf{r}_2$ and $\mathbf{r}_3$, and Sack has derived the following result[16]:

$$R_{ll_1}(r_2,r_3) = \frac{(-l/2)_{l_1}}{(1/2)_{l_1}}r_>^{l-l_1}r_<^{l_1}$$
$$\times F\Big(l_1-\frac{l}{2},-\frac{1}{2}-\frac{l}{2},l_1+3/2;\frac{r_<^2}{r_>^2}\Big). \quad (10)$$

In Eq. (10) $(a)_b$ denotes the Pochhammer symbol, $r_< \equiv r_{23<} = \min(r_2,r_3)$, $r_> \equiv r_{23>} = \max(r_2,r_3)$ and $F(a,b,c;y)$ denotes a hypergeometric function. Inserting Eq. (9) and analogous results for u_2 and u_3 into Eq. (8), and employing the standard expansion of the Legendre polynomials in terms of spherical harmonics leads to

$$I(r_1) = 64\pi^3\sum_{w=0}^{\infty}\frac{1}{(2w+1)^2}$$
$$\times\int r_1^{i+2}r_2^{j+2}r_3^{k+2}e^{-\alpha r_1-\beta r_2-\gamma r_3}$$
$$\times R_{lw}(r_2,r_3)R_{mw}(r_3,r_1)R_{nw}(r_1,r_2)dr_2\,dr_3. \quad (11)$$

If the Sack functions $R_{lw}(r_2,r_3)$, $R_{mw}(r_3,r_1)$, and $R_{nw}(r_1,r_2)$ are now inserted into Eq. (11) and the following integral notation introduced:

$$A(k,\alpha) = \int_0^\infty z^ke^{-\alpha z}\,dz, \quad (12)$$

$$B(k,\alpha,x) = \int_x^\infty z^ke^{-\alpha z}\,dz, \quad (13)$$

$$C(k,l,\alpha,\beta) = \int_0^\infty y^ke^{-\alpha y}\,dy\int_y^\infty z^le^{-\beta z}\,dz, \quad (14)$$

$$D(k,l,\alpha,\beta,x) = \int_x^\infty y^ke^{-\alpha y}\,dy\int_y^\infty z^le^{-\beta z}\,dz, \quad (15)$$

then Eq. (11) can be evaluated to yield (see Appendix A for details and notational simplifications):

$$I(x) = 64\pi^3e^{-\alpha x}\sum_{w=0}^{\infty}a_{wlmn}\sum_{r=0}^{\infty}a_{wnr}\sum_{s=0}^{\infty}a_{wms}\sum_{t=0}^{\infty}a_{wlt}\{x^{\omega_9}B(\omega_1,\beta,x)[A(\omega_2,\gamma)-B(\omega_2,\gamma,x)]$$
$$+x^{\omega_{10}}B(\omega_3,\gamma,x)[A(\omega_4,\beta)-B(\omega_4,\beta,x)]+x^{\omega_{11}}\{D(\omega_5,\omega_2,\beta,\gamma,x)+D(\omega_6,\omega_4,\gamma,\beta,x)-C(\omega_5,\omega_2,\beta,\gamma)-C(\omega_6,\omega_4,\gamma,\beta)$$
$$+A(\omega_2,\gamma)[A(\omega_5,\beta)-B(\omega_5,\beta,x)]+A(\omega_4,\beta)[A(\omega_6,\gamma)-B(\omega_6,\gamma,x)]\}$$
$$+x^{\omega_{12}}[D(\omega_7,\omega_3,\beta,\gamma,x)+D(\omega_8,\omega_1,\gamma,\beta,x)]\}. \quad (16)$$

B. Constraints on the set {ijklmn}

The basis functions appearing in Eq. (5) were defined with each exponent being $\geqslant 0$. With only this set of constraints a simple compact closed form for the I integral, and hence $D_0(r)$ does not appear possible. In order to obtain a functional form for $D_0(r)$ suitable for numerical evaluation, additional constraints on the basis set $\{i_\mu\,j_\mu\,k_\mu\,l_\mu\,m_\mu\,n_\mu\}$ are imposed. The constraints to be employed are obtained directly from a consideration of the A, B, C, and D integrals defined in Eqs. (12)–(15). These integrals can be evaluated as

$$A(k,\alpha) = \frac{k!}{\alpha^{k+1}} \quad k \geqslant 0, \quad \alpha > 0, \tag{17}$$

$$B(k,\alpha,x) = \frac{k! e^{-\alpha x}}{\alpha^{k+1}} \sum_{j=0}^{k} \frac{(\alpha x)^j}{j!} \quad k \geqslant 0, \quad \alpha > 0, \tag{18}$$

$$C(k,l,\alpha,\beta) = \frac{l!}{\beta^{l+1}} \sum_{j=0}^{l} \frac{\beta^j (k+j)!}{j!(\alpha+\beta)^{k+j+1}} \quad k \geqslant 0, \ \alpha > 0 \quad l \geqslant 0, \ \beta > 0, \tag{19}$$

$$D(k,l,\alpha,\beta,x) = \frac{e^{-(\alpha+\beta)x} l!}{\beta^{l+1}(\alpha+\beta)^{k+1}} \sum_{j=0}^{l} \left(\frac{\beta}{\alpha+\beta}\right)^j \frac{(k+j)!}{j!} \times \sum_{m=0}^{k+j} \frac{(\alpha+\beta)^m x^m}{m!} \quad k,l \geqslant 0, \ \alpha > 0, \ \beta > 0. \tag{20}$$

The B, C, and D integrals are defined for ranges other than those given in Eqs. (18)–(20). $B(k, \alpha, x)$ is directly related to the exponential integral $E_{-k}(\alpha x)$ for negative values of k. $C(k,l,\alpha,\beta)$ actually converges for $k \geqslant 0$, $k + l \geqslant -1$. The general C integral has been discussed in several places in the literature.[11,12,17]

The necessary constraints that must be imposed on the set $\{ijklmn\}$ to ensure the conditions stated in Eqs. (17)–(20) are satisfied can be found by examining Eq. (16). The arguments of A are ω_2, ω_4, ω_5, and ω_6 and are required to be $\geqslant 0$. ω_2 and ω_4 are both positive by inspection of Eqs. (A7) and (A9). To prove that ω_5 and ω_6 are $\geqslant 0$, we need to determine the maximum value of t in Eqs. (A10) and (A11); this can be done by an examination of Eqs. (A3a) and (A3b). If l is odd (and $\geqslant -1$) then the maximum value of t is $(l+1)/2$ because of the Pockhammer result:

$$(-a)_b = 0 \quad \text{for } b > a \text{ and integer } a. \tag{21}$$

For l even the maximum value of w is bounded above by $\frac{1}{2}l$; the actual maximum for w is $\frac{1}{2}$ (smallest even value of the set l, m, n), which follows from an inspection of Eqs. (A3a) and (21). Hence for l even (and $\geqslant 0$) we have $w - \frac{1}{2}l \leqslant 0$, and therefore t has a maximum value of $\frac{1}{2}l - w$ using Eqs. (A3b) and (21). Therefore for odd and even values of l (and $l \geqslant -1$) ω_5 and ω_6 are both positive values.

We next turn our attention to the B integrals in Eq. (16). If Eq. (18) is utilized for the B integrals, this avoids Eq. (16) having a complicated dependence on the exponential integrals $E_n(x)$, which requires that the constraints $\omega_i \geqslant 0$ for $i = 1$ to 6 be satisfied. The cases ω_2, ω_4, ω_5, and ω_6 have already been discussed above. The conditions that must be imposed on the set $\{ijklmn\}$ in order that $\omega_1 \geqslant 0$ and $\omega_3 \geqslant 0$ are now examined. If the set $\{lmn\}$ contains no even entry, the w summation in Eq. (16) does not terminate for any finite value, since there is no longer a termination condition on the coefficient a_{wlmn} defined in Eq. (A3a). In order to arrive at a functional form for $D_0(r)$ suitable for simple numerical evaluation, an obvious requirement is to avoid any possible infinite expansion for the I integral. Therefore, the constraint

$$l,m,n \quad \text{not all odd} \tag{22}$$

is imposed. Without the above constraint, ω_1 and ω_3 both take on negative values. Now consider the situation that one member of the set $\{lmn\}$ is even. If that member is m, then ω_1 and ω_3 satisfy

$$\omega_1 = j + 2 + l + n - m - (n+1) - (l+1) = j - m \tag{23}$$

and

$$\omega_3 = k + 2 + l + m - 2w - (m - 2w) - (l+1) = k + 1. \tag{24}$$

From Eq. (23), it is necessary to impose the following condition:

$$j \geqslant m \quad \text{if } l,n \text{ odd; } m \text{ even} \tag{25}$$

in order to ensure that $\omega_1 \geqslant 0$. From Eq. (24), ω_3 satisfies $\omega_3 \geqslant 0$. A similar analysis for the cases l even, m and n odd, and n even, l and m odd yields the single constraint

$$k \geqslant n \quad \text{if } l,m \text{ odd; } n \text{ even.} \tag{26}$$

When only one member of the set $\{lmn\}$ is odd, no additional constraints emerge. With the imposition of the constraints given in Eqs. (22), (25), and (26), the B integrals appearing in Eq. (16) involve only finite sums.

Attention is now turned to the C and D integrals appearing in Eq. (16). The constraints given in Eq. (19) require that $\omega_i \geqslant 0$ for $i = 2$, 4, 5, and 6. As discussed above, these conditions are satisfied. In order that Eq. (20) can be employed for the D integrals in Eq. (16), it is necessary that $\omega_i \geqslant 0$ for $i = 1$ to 8. The first six values of ω_i have been considered above. ω_7 and ω_8 are also both $\geqslant 0$ on employing Eqs. (A12), (A13), (A3b), and (21).

Since $D_0(r)$ is a sum of integrals of the form represented by Eq. (16), it is necessary to ensure $\omega_i \geqslant 0$ for $i = 9$ to 12. $\omega_{12} \geqslant 0$ by inspection of Eq. (A17). ω_9 and ω_{10} are both observed to be positive on using Eqs. (A14), (A15), (A3b), and (21). Since we have previously imposed the restriction (22), the only other situation requiring discussion occurs for l even, m and n odd. This latter case requires

$$i \geqslant l \quad \text{if } m,n \text{ odd; } l \text{ even} \tag{27}$$

in order that $\omega_{11} \geqslant 0$. All other possibilities for the set $\{lmn\}$ yield $\omega_{11} \geqslant 0$.

Once the constraints necessary for the A, B, C, and D integrals to be expressed by Eqs. (17)–(20) are determined, it is straightforward to decide what individual basis functions are allowed. An examination of the product of a basis function with itself and every other selected basis function is made, to ensure the appropriate constraints listed above are satisfied. Simple inspection of the odd–even character of the basis functions has been employed to minimize the selection effort.

C. Simplification of the I integrals [Eq. (16)]

The first step in the simplification of Eq. (16) is to rearrange products of sums (from the multiplication of two B integrals) of the form

$$\sum_{j=0}^{k} a_j x^j \sum_{m=0}^{l} b_m x^m$$

and double sums (from the D integrals) of the form

$$\sum_{j=0}^{l} c_j \sum_{m=0}^{k+j} d_m x^m$$

into the format

$$\sum_j a_j x^j \sum_m b_m,$$

where the upper and lower limits on the latter sums are determined from the previous summation limits. A product of B integrals can be written as

$$B(k,\beta,x)B(l,\gamma,x) = \frac{k!l!e^{-(\beta+\gamma)x}}{\beta^{k+1}\gamma^{l+1}}\left\{\sum_{j=0}^{k+l} x^j \sum_{m=0}^{j} \frac{\beta^m\gamma^{j-m}}{m!(j-m)!} - \sum_{j=k+1}^{k+l} x^j \sum_{m=k+1}^{j} \frac{\beta^m\gamma^{j-m}}{m!(j-m)!} - \sum_{j=l+1}^{k+l} x^j \sum_{m=l+1}^{j} \frac{\beta^{j-m}\gamma^m}{(j-m)!m!}\right\}. \quad (28)$$

For the D integral double summation, the following rearrangement can be written:

$$D(k,l,\beta,\gamma,x) = \frac{e^{-(\beta+\gamma)x}l!}{\gamma^{l+1}(\beta+\gamma)^{k+1}}\left\{\sum_{j=0}^{k+l} \frac{(\beta+\gamma)^j x^j}{j!} \sum_{m=0}^{l} \left(\frac{\gamma}{\beta+\gamma}\right)^m \frac{(k+m)!}{m!} - \sum_{j=k+1}^{k+l} \frac{(\gamma+\beta)^j x^j}{j!} \sum_{m=0}^{j-k-1} \left(\frac{\gamma}{\beta+\gamma}\right)^m \frac{(k+m)!}{m!}\right\}. \quad (29)$$

In order to collect the summations together in Eq. (16), it is advantageous to introduce the notational device

$$\Delta_{j,k} = \begin{cases} 0 & j<k \\ 1 & j\geqslant k \end{cases} \quad (30a)$$

and

$$\nabla_{j,k} = \begin{cases} 0 & j>k \\ 1 & j\leqslant k \end{cases}. \quad (30b)$$

If Eqs. (17) to (20) are substituted into Eq. (16) and the summation rearrangements given in Eqs. (28) and (29) are employed, Eq. (16) simplifies with the aid of the definitions

$$a = \frac{\omega_1!\omega_2!}{\beta^{\omega_1+1}\gamma^{\omega_2+1}}; \quad d = \frac{\omega_3!\omega_4!}{\gamma^{\omega_3+1}\beta^{\omega_4+1}}, \quad (31)$$

$$b_j = \frac{\beta^j}{j!}; \quad c_j = \frac{\gamma^j}{j!}, \quad (32)$$

$$f_j = \frac{(\beta+\gamma)^j}{j!}; \quad g_j = \left(\frac{\gamma}{\beta+\gamma}\right)^j \frac{1}{j!}; \quad h_j = \left(\frac{\beta}{\gamma+\beta}\right)^j \frac{1}{j!}, \quad (33)$$

to yield

$$I(x) = 64\pi^3 e^{-\alpha x} \sum_{w=0}^{\infty}\sum_{r=0}^{\infty}\sum_{s=0}^{\infty}\sum_{t=0}^{\infty}\left\{x^{\omega_{11}}\mathscr{K}_{ijklmnwrst} + \sum_{J=0}^{\Omega} x^J\left[\mathscr{L}_{ijklmnwrstJ}e^{-(\beta+\gamma)x} + \mathscr{M}_{ijklmnwrstJ}e^{-\beta x} + \mathscr{N}_{ijklmnwrstJ}e^{-\gamma x}\right]\right\}, \quad (34)$$

where

$$\mathscr{K}_{ijklmnwrst} = a_{wrstlmn}\left\{\frac{\omega_2!\omega_5!}{\gamma^{\omega_2+1}\beta^{\omega_5+1}} + \frac{\omega_4!\omega_6!}{\beta^{\omega_4+1}\gamma^{\omega_6+1}} - \frac{\omega_2!}{\gamma^{\omega_2+1}(\beta+\gamma)^{\omega_5+1}}\sum_{p=0}^{\omega_2} g_p(\omega_5+p)! - \frac{\omega_4!}{\beta^{\omega_4+1}(\gamma+\beta)^{\omega_6+1}}\sum_{p=0}^{\omega_4} h_p(\omega_6+p)!\right\}, \quad (35)$$

$$\mathscr{L}_{ijklmnwrstJ} = a_{wrstlmn}\left\{\Delta_{J,\omega_1+\omega_9+1}a\sum_{p=\omega_1+1}^{J-\omega_9} b_p c_{J-\omega_9-p} - \Delta_{J,\omega_9}a\sum_{p=0}^{J-\omega_9} b_p c_{J-\omega_9-p} + \Delta_{J,\omega_2+\omega_9+1}a\sum_{p=\omega_2+1}^{J-\omega_9} b_{J-\omega_9-p}c_p - \Delta_{J,\omega_{10}}d\sum_{p=0}^{J-\omega_{10}} c_p b_{J-\omega_{10}-p} + \Delta_{J,\omega_3+\omega_{10}+1}d\sum_{p=\omega_3+1}^{J-\omega_{10}} c_p b_{J-\omega_{10}-p} + \Delta_{J,\omega_4+\omega_{10}+1}d\sum_{p=\omega_4+1}^{J-\omega_{10}} c_{J-\omega_{10}-p}b_p + \frac{\omega_2! f_{J-\omega_{11}}}{\gamma^{\omega_2+1}(\beta+\gamma)^{\omega_5+1}} \times\left[\Delta_{J,\omega_{11}}\sum_{p=0}^{\omega_2} g_p(\omega_5+p)! - \Delta_{J,\omega_5+\omega_{11}+1}\sum_{p=0}^{J-\omega_5-\omega_{11}-1} g_p(\omega_5+p)!\right] + \frac{\omega_4! f_{J-\omega_{11}}}{\beta^{\omega_4+1}(\beta+\gamma)^{\omega_6+1}} \times\left[\Delta_{J,\omega_{11}}\sum_{p=0}^{\omega_4} h_p(\omega_6+p)! - \Delta_{J,\omega_6+\omega_{11}+1}\sum_{p=0}^{J-\omega_6-\omega_{11}-1} h_p(\omega_6+p)!\right]$$

$$+\frac{\omega_3!f_{J-\omega_{12}}}{\gamma^{\omega_3+1}(\beta+\gamma)^{\omega_7+1}}\left[\Delta_{J,\omega_{12}}\sum_{p=0}^{\omega_3}g_p(\omega_7+p)!-\Delta_{J,\omega_7+\omega_{12}+1}\sum_{p=0}^{J-\omega_7-\omega_{12}-1}g_p(\omega_7+p)!\right]$$

$$+\frac{\omega_1!f_{J-\omega_{12}}}{\beta^{\omega_1+1}(\beta+\gamma)^{\omega_8+1}}\left[\Delta_{J,\omega_{12}}\sum_{p=0}^{\omega_1}h_p(\omega_8+p)!-\Delta_{J,\omega_8+\omega_{12}+1}\sum_{p=0}^{J-\omega_8-\omega_{12}-1}h_p(\omega_8+p)!\right]\Bigg\}, \quad (36)$$

$$\mathcal{M}_{ijklmnwrstJ}=a_{wrstlmn}\left\{\Delta_{J,\omega_9}\nabla_{J,\omega_1+\omega_9}a\,b_{J-\omega_9}-\frac{\Delta_{J,\omega_{11}}\nabla_{J,\omega_5+\omega_{11}}\omega_2!\omega_5!b_{J-\omega_{11}}}{\gamma^{\omega_2+1}\beta^{\omega_5+1}}\right\}, \quad (37)$$

$$\mathcal{N}_{ijklmnwrstJ}=a_{wrstlmn}\left\{\Delta_{J,\omega_{10}}\nabla_{J,\omega_3+\omega_{10}}d\,c_{J-\omega_{10}}-\frac{\Delta_{J,\omega_{11}}\nabla_{J,\omega_6+\omega_{11}}\omega_4!\omega_6!c_{J-\omega_{11}}}{\beta^{\omega_4+1}\gamma^{\omega_6+1}}\right\}, \quad (38)$$

and

$$a_{wrstlmn}=a_{wlmn}a_{wnr}a_{wms}a_{wlt}. \quad (39$$

D. Compact formula for $D_0(r)$

The following restrictions are employed for the exponents in the Hylleraas expansion [Eq. (5)]:

$$\alpha_\mu=\beta_\mu=\alpha \quad (40a)$$

$$\gamma_\mu=\gamma. \quad (40b)$$

Without a restriction to a modest number of fixed exponents, the possibility for constructing a simple compact formula for $D_0(r)$ is lost. The basic strategy is now to expand both permutation summations in Eq. (7) and collect together terms for each distinct exponential term that arises. When this is done the following form for the radial electronic density is obtained:

$$D_0(r)=64\pi^3\sum_{P'}\sum_{P}\chi_{P'P}\sum_u\sum_v C_uC_v\sum_w\sum_r\sum_s\sum_t a_{wrstlmn}\times\Bigg\{\mathcal{A}_{P'P\omega_{11}}r^{\omega_{11}}e^{-\alpha_{P'P}r}+\sum_{J=0}^{\Omega}r^J\big(\mathcal{B}_{P'PJ}e^{-\beta_{P'P}r}+\mathcal{D}_{P'PJ}e^{-\gamma_{P'P}r}+\mathcal{E}_{P'PJ}e^{-\epsilon_{P'P}r}\big)\Bigg\}, \quad (41)$$

where the values of the exponents $\alpha_{P'P}$, $\beta_{P'P}$, $\gamma_{P'P}$, and $\epsilon_{P'P}$ for the different permutations are collected in Table I. $\chi_{P'P}$ is the spin factor from Eq. (7). The structure of the functions $\mathcal{A}_{P'P\omega_{11}}$, $\mathcal{B}_{P'PJ}$, $\mathcal{D}_{P'PJ}$, and $\mathcal{E}_{P'PJ}$ can be written down by examination of Eqs. (34)–(38). By noting, for example, the first entry of Table I and that the exponents appearing in Eq. (8) and hence Eq. (34) are $\alpha\equiv\alpha_u+\alpha_v\Rightarrow 2\alpha$ (in Table I); $\beta\equiv\beta_u+\beta_v\Rightarrow 2\beta=2\alpha$ and $\gamma\equiv\gamma_u+\gamma_v\Rightarrow 2\gamma$ [recall Eqs. (40a), (40b)], the functional forms of $\mathcal{A}_{P'P\omega_{11}}$, $\mathcal{B}_{P'PJ}$, $\mathcal{D}_{P'PJ}$, and $\mathcal{E}_{P'PJ}$ are given in Eqs. (35)–(38) exclusive of the $a_{wrstlmn}$ factor.

Examination of Table I indicates that seven distinct exponential terms arise. Therefore, Eq. (41) can be simplified to:

$$D_0(r)=\sum_{K=0}^{g_1}\mathcal{A}_{1K}r^Ke^{-(\alpha+\gamma)r}+\sum_{K=0}^{g_2}\mathcal{A}_{2K}r^Ke^{-2\alpha r}+\sum_{K=0}^{g_3}\mathcal{A}_{3K}r^Ke^{-2\gamma r}+\sum_{K=0}^{g_4}\mathcal{A}_{4K}r^Ke^{-(4\alpha+2\gamma)r}+\sum_{K=0}^{g_5}\mathcal{A}_{5K}r^Ke^{-4\alpha r}+\sum_{K=0}^{g_6}\mathcal{A}_{6K}r^Ke^{-(3\alpha+\gamma)r}+\sum_{K=0}^{g_7}\mathcal{A}_{7K}r^Ke^{-(2\alpha+2\gamma)r}. \quad (42)$$

The explicit form for the coefficients $\mathcal{A}_{iK}$ can be found by collecting terms with the same exponential factor that appear in Eq. (41). Utilizing Table I, we have, for example:

$$\mathcal{A}_{3K}=64\pi^3\sum_u\sum_v C_uC_v\Bigg\{\chi_{35}\sum_w\sum_r\sum_s\sum_t a_{wrstlmn}\mathcal{A}_{35\omega_{11}}+\chi_{36}\sum_w\sum_r\sum_s\sum_t a_{wrstlmn}\mathcal{A}_{36\omega_{11}}\Bigg\} \quad (43)$$

$$\mathcal{A}_{5K}=64\pi^3\sum_u\sum_v C_uC_v\Bigg\{\chi_{11}\sum_w\sum_r\sum_s\sum_t a_{wrstlmn}\times\sum_{J=0}^{\Omega}\mathcal{D}_{11J}+\chi_{13}\sum_w\sum_r\sum_s\sum_t a_{wrstlmn}\sum_{J=0}^{\Omega}\mathcal{D}_{13J}$$

TABLE I. Exponential factors that arise for the different permutations in Eq. (41).

Permutation	Exponents			
$(P'P)$	$\alpha_{P'P}$	$\beta_{P'P}$	$\gamma_{P'P}$	$\epsilon_{P'P}$
(1,1)	2α	$4\alpha+2\gamma$	4α	$2\alpha+2\gamma$
(1,2)	2α	$4\alpha+2\gamma$	$3\alpha+\gamma$	$3\alpha+\gamma$
(1,3)	2α	$4\alpha+2\gamma$	4α	$2\alpha+2\gamma$
(1,4)	2α	$4\alpha+2\gamma$	$3\alpha+\gamma$	$3\alpha+\gamma$
(1,5)	$\alpha+\gamma$	$4\alpha+2\gamma$	$3\alpha+\gamma$	$2\alpha+2\gamma$
(1,6)	$\alpha+\gamma$	$4\alpha+2\gamma$	$3\alpha+\gamma$	$2\alpha+2\gamma$
(2,1)	2α	$4\alpha+2\gamma$	4α	$2\alpha+2\gamma$
(2,2)	2α	$4\alpha+2\gamma$	$3\alpha+\gamma$	$3\alpha+\gamma$
(2,3)	2α	$4\alpha+2\gamma$	4α	$2\alpha+2\gamma$
(2,4)	2α	$4\alpha+2\gamma$	$3\alpha+\gamma$	$3\alpha+\gamma$
(2,5)	$\alpha+\gamma$	$4\alpha+2\gamma$	$3\alpha+\gamma$	$2\alpha+2\gamma$
(2,6)	$\alpha+\gamma$	$4\alpha+2\gamma$	$3\alpha+\gamma$	$2\alpha+2\gamma$
(3,1)	$\alpha+\gamma$	$4\alpha+2\gamma$	$3\alpha+\gamma$	$2\alpha+2\gamma$
(3,2)	$\alpha+\gamma$	$4\alpha+2\gamma$	$2\alpha+2\gamma$	$3\alpha+\gamma$
(3,3)	$\alpha+\gamma$	$4\alpha+2\gamma$	$3\alpha+\gamma$	$2\alpha+2\gamma$
(3,4)	$\alpha+\gamma$	$4\alpha+2\gamma$	$2\alpha+2\gamma$	$3\alpha+\gamma$
(3,5)	2γ	$4\alpha+2\gamma$	$2\alpha+2\gamma$	$2\alpha+2\gamma$
(3,6)	2γ	$4\alpha+2\gamma$	$2\alpha+2\gamma$	$2\alpha+2\gamma$

$$+\chi_{21}\sum_w\sum_r\sum_s\sum_t a_{wrstlmn}\sum_{J=0}^{\Omega}\mathscr{D}_{21J}$$
$$\left.+\chi_{23}\sum_w\sum_r\sum_s\sum_t a_{wrstlmn}\sum_{J=0}^{\Omega}\mathscr{D}_{23J}\right\}. \quad (44)$$

It should be kept in mind the multiple sums $\Sigma_w\ \Sigma_r\ \Sigma_s\ \Sigma_t$ depend *explicitly* on the particular combination of permutations made, and hence these four nested summations cannot be simply factored in Eqs. (43) and (44).

The summation limits g_i appearing in Eq. (42) are determined by examination of the entire basis set to be employed. g_i, $i = 4$ to 7, each have Ω_m as the upper limit where

$$\Omega_m = 6 + 2\max\{i_u + j_u + k_u + l_u + m_u + n_u\} \quad (45)$$

and the index u spans the entire basis set employed. The maximum values of g_i, $i = 1$ to 3 are determined by the maximum value of ω_{11} [see Eq. (A16)] for the appropriate permutations listed in Table I. For example, g_1 is given as the maximum value of $(i_u + m_u + n_u) + (i_v + m_v + n_v) + 2$ or of any of the possible permutations of the bracketed factors.

Equation (42) can be written in the compact form

$$D_0(r) = \sum_{I=1}^{7}\sum_{K=0}^{g_I}\mathscr{A}_{IK}r^K e^{-\alpha_I r}, \quad (46)$$

where the values of $\mathscr{A}_{IK}$ and α_I can be obtained by examination of Eq. (42). Equation (46) is the principal result of this study.

III. COMPUTATIONAL DETAILS

Evaluation of the coefficients $\mathscr{A}_{IK}$ appearing in Eq. (46) has been carried out for several members of the Li I isoelectronic series. The wave functions that have been employed in the present work are derived from more elaborate wave functions reported elsewhere.[18,19] Four different size basis sets were employed in this work. Table II shows the basis functions used in the construction of $D_0(r)$. The calculations for Be II employed the first 164 functions, for B III the first 201 functions were used, for each of C IV through Ne VIII all entries except those with a value of seven or greater for any member of the set $\{i, j, k, l, m, n\}$ were used (leading to 213 terms) and for Li I, all 233 entries in the table were employed. The selection of basis functions was made in accordance with the constraints listed in Eqs. (22), (25), (26), and (27). The fixed exponents that have been employed can be found in Refs. 18 and 19. In order to get some idea of the quality of the wave functions employed in this work, the nonrelativistic ground state energy E_{NR} for each wave function is reported in Table III. These energy values are compared with the best literature values available for E_{NR}, and an estimate of the correlation energy is also reported in Table III. Although Eqs. (22), (25), (26), and (27) do put restrictions on the basis set, and prevent in principle a complete set of Hylleraas functions from being employed, this is not really a practical restriction at all, as the high quality of the wave functions is clearly evident from the results in Table III. Further justification for this statement is the quality of the moments of $\langle r_i^n\rangle$ given below.

The calculations were carried out on a Honeywell DPS8/49 at the University of Wisconsin-Eau Claire, on a Cray 1S at Cray Research, Inc., and on a Cray XMP/48 at the National Center for Supercomputer Applications at the University of Illinois at Urbana-Champaign. All calculations were performed in double precision.

IV. RESULTS

Values of the exponential factors α_I, summation limits g_I and $\mathscr{A}_{IK}$ coefficients for each member of the Li I isoelectronic series studied are available from the Physics Auxiliary Publication Service (PAPS).[25] Using the tabulated α_I and g_I factors and the $\mathscr{A}_{IK}$ coefficients, Eq. (46) has been employed to evaluate the moments of $\langle r_i^n\rangle$ defined via

$$\langle r_i^n\rangle \equiv \sum_{i=1}^{3}\langle\psi|r_i^n|\psi\rangle. \quad (47)$$

The required formula is

$$\langle r_i^n\rangle = \int_0^\infty D_0(r)r^n\,dr, \quad (48)$$

which has been evaluated using a Gauss–Laguerre quadrature. Because of the simple analytic form obtained for $D_0(r)$, the integral in Eq. (48) is trivial to evaluate. The electron density at the nucleus

$$\rho(0) = \langle\delta(\mathbf{r}_i)\rangle \quad (49)$$

has also been evaluated.

A check was made to ensure that the results obtained using Eqs. (46) and (48) were in agreement with the values obtained directly from the use of the wave function [Eq. (47)]. Complete agreement was found for all moments calculated. Tables IV to XI list some calculated moments and the electron density evaluated at the nucleus. Also listed are some values taken from the literature[18,19] which have been obtained using wave functions employing somewhat larger basis sets. All results are given in atomic units and have not been corrected for the finite mass of the nucleus.

The results reported in Tables IV–XI were computed using the coefficients $\mathscr{A}_{IK}$ evaluated in double precision. The $\mathscr{A}_{IK}$ coefficients available from PAPS, which report 12 decimal digits, were employed to reevaluate the moments $\langle r_i^n\rangle$. In just a few cases, a small change was noted in the eight significant figure, which led to a change on roundoff of one in the seventh significant figure for some values of the moments reported in Tables IV–XI.

V. DISCUSSION

A. Calculation of ρ(0)

From Eq. (1), the electron density at the nucleus can be evaluated using

$$\rho(0) = \left\{\frac{D_0(r)}{4\pi r^2}\right\}_{r\to 0}. \quad (50)$$

It is not immediately clear from the form of $D_0(r)$ given in Eq. (46) that the right-hand side of Eq. (50) is in fact well defined. Substitution of Eq. (46) into Eq. (50) leads to

TABLE II. Basis functions employed to evaluate $D_0(r)$.

No.	i	j	k	l	m	n	No.	i	j	k	l	m	n	No.	i	j	k	l	m	n	No.	i	j	k	l	m	n	No.	i	j	k	l	m	n
1	0	0	0	0	0	0	48	0	0	3	0	0	1	95	0	0	4	0	0	1	142	0	1	1	0	0	5	188	0	0	1	0	9	0
2	0	0	0	0	0	1	49	0	0	3	0	1	0	96	0	0	4	0	1	0	143	0	2	1	0	0	4	189	1	7	1	0	0	0
3	0	0	0	0	1	0	50	0	0	4	0	0	0	97	0	0	5	0	0	0	144	0	6	1	0	0	0	190	1	8	1	0	0	0
4	0	0	1	0	0	0	51	0	1	0	0	0	3	98	0	1	0	0	0	4	145	0	5	1	0	0	1	191	1	9	1	0	0	0
5	0	1	0	0	0	0	52	0	1	0	0	3	0	99	0	1	0	0	2	2	146	0	4	1	0	0	2	192	0	2	1	0	0	6
6	0	0	0	0	0	2	53	0	1	0	3	0	0	100	0	1	0	0	4	0	147	0	6	1	0	0	1	193	0	2	1	0	0	7
7	0	0	0	0	2	0	54	0	1	1	0	0	2	101	0	4	1	0	0	0	148	0	0	1	0	0	7	194	0	3	1	0	0	6
8	0	0	1	0	0	1	55	0	1	1	0	2	0	102	1	3	1	0	0	0	149	0	2	1	0	0	5	195	0	4	1	0	0	3
9	0	0	1	0	1	0	56	0	1	1	2	0	0	103	2	2	1	0	0	0	150	0	1	1	0	0	6	196	0	4	1	0	0	4
10	0	0	2	0	0	0	57	0	1	2	0	0	1	104	0	1	4	0	0	0	151	0	3	1	0	0	5	197	0	1	0	2	0	2
11	0	1	0	0	0	1	58	0	1	2	0	1	0	105	0	2	3	0	0	0	152	0	0	1	0	0	8	198	0	1	0	2	2	0
12	0	1	0	0	1	0	59	0	1	2	1	0	0	106	0	3	2	0	0	0	153	0	1	1	0	0	7	199	0	1	0	4	0	0
13	0	1	0	1	0	0	60	0	1	3	0	0	0	107	0	5	0	0	0	0	154	1	2	1	0	0	3	200	0	1	2	0	0	2
14	0	1	1	0	0	0	61	0	2	0	0	0	2	108	1	1	3	0	0	0	155	1	2	1	0	0	4	201	0	1	2	0	2	0
15	0	2	0	0	0	0	62	0	2	0	0	2	0	109	1	2	2	0	0	0	156	1	5	1	0	0	0	202	0	1	2	2	0	0
16	1	1	0	0	0	0	63	0	2	0	2	0	0	110	0	3	1	0	0	1	157	0	5	1	0	0	2	203	0	1	3	0	0	1
17	0	0	0	0	0	3	64	0	2	1	0	0	1	111	1	2	1	0	0	1	158	0	7	1	0	0	0	204	0	1	3	0	1	0
18	0	0	0	0	3	0	65	0	2	1	0	1	0	112	0	2	1	0	0	2	159	1	6	1	0	0	0	205	0	1	3	1	0	0
19	0	0	1	0	0	2	66	0	2	1	1	0	0	113	1	1	1	0	0	2	160	1	3	1	0	0	2	206	0	2	0	0	0	3
20	0	0	1	0	2	0	67	0	2	2	0	0	0	114	0	3	1	0	1	0	161	0	0	1	0	7	0	207	0	2	0	0	2	1
21	0	0	2	0	0	1	68	0	3	0	0	0	1	115	1	2	1	0	1	0	162	0	2	1	0	2	2	208	0	2	0	0	3	0
22	0	0	2	0	1	0	69	0	3	0	0	1	0	116	0	2	1	0	2	0	163	0	1	1	0	5	0	209	0	2	0	1	2	0
23	0	0	3	0	0	0	70	0	3	0	1	0	0	117	1	1	1	0	2	0	164	0	1	1	0	6	0	210	0	2	0	3	0	0
24	0	1	0	0	0	2	71	0	3	1	0	0	0	118	0	1	1	0	3	0	165	0	0	7	0	0	0	211	0	2	2	0	0	1
25	0	1	0	0	2	0	72	0	4	0	0	0	0	119	0	3	1	1	0	0	166	7	0	1	0	0	1	212	0	2	2	0	1	0
26	0	1	0	2	0	0	73	1	1	0	0	0	2	120	1	2	1	1	0	0	167	0	1	2	3	0	0	213	0	2	2	1	0	0
27	0	1	1	0	0	1	74	1	1	0	0	2	0	121	0	2	1	2	0	0	168	0	1	1	5	0	0	214	0	3	0	0	0	2
28	0	1	1	0	1	0	75	1	1	1	0	0	1	122	0	1	1	3	0	0	169	0	5	1	0	1	0	215	0	3	0	0	2	0
29	0	1	1	1	0	0	76	1	1	1	0	1	0	123	0	1	1	0	0	3	170	0	0	1	0	0	9	216	0	3	0	2	0	0
30	0	1	2	0	0	0	77	1	1	2	0	0	0	124	1	4	1	0	0	0	171	8	0	1	0	0	1	217	0	4	0	0	0	1
31	0	2	0	0	0	1	78	1	2	0	0	0	1	125	0	5	1	0	0	0	172	0	0	2	0	0	4	218	0	4	0	0	1	0
32	0	2	0	0	1	0	79	1	2	0	0	1	0	126	0	4	1	0	0	1	173	0	0	2	0	0	5	219	0	4	0	1	0	0
33	0	2	0	1	0	0	80	1	2	0	1	0	0	127	2	3	1	0	0	0	174	8	0	1	0	0	0	220	1	1	0	0	0	3
34	0	2	1	0	0	0	81	1	2	1	0	0	0	128	1	3	1	0	0	1	175	9	0	1	0	0	0	221	1	1	0	0	3	0
35	0	3	0	0	0	0	82	1	3	0	0	0	0	129	0	3	1	0	0	2	176	4	1	1	0	0	1	222	1	1	2	0	0	1
36	1	1	0	0	0	1	83	2	2	0	0	0	0	130	0	1	5	0	0	0	177	5	1	1	0	0	1	223	1	1	2	0	1	0
37	1	1	0	0	1	0	84	0	0	0	0	0	5	131	0	0	1	0	0	5	178	3	2	1	0	0	1	224	1	2	0	0	0	2
38	1	1	1	0	0	0	85	0	0	0	0	5	0	132	2	2	1	0	0	1	179	3	3	1	0	0	0	225	1	2	0	0	2	0
39	1	2	0	0	0	0	86	0	0	1	0	0	4	133	0	2	1	0	0	3	180	2	2	2	0	0	0	226	1	2	0	2	0	0
40	0	0	0	0	0	4	87	0	0	1	0	2	2	134	0	1	1	0	0	4	181	0	3	1	0	0	3	227	1	3	0	0	0	1
41	0	0	0	0	2	2	88	0	0	1	0	4	0	135	0	0	1	0	5	0	182	0	3	1	0	0	4	228	1	3	0	0	1	0
42	0	0	0	0	4	0	89	0	0	1	2	2	0	136	1	2	1	0	0	2	183	1	0	1	0	0	8	229	1	3	0	1	0	0
43	0	0	0	2	2	0	90	0	0	2	0	0	3	137	0	1	1	4	0	0	184	1	0	1	0	0	9	230	1	4	0	0	0	0
44	0	0	1	0	0	3	91	0	0	2	0	1	2	138	0	0	6	0	0	0	185	6	1	1	0	0	1	231	2	2	0	0	0	1
45	0	0	1	0	3	0	92	0	0	2	0	3	0	139	0	2	1	3	0	0	186	7	1	1	0	0	1	232	2	2	0	0	1	0
46	0	0	2	0	0	2	93	0	0	3	0	0	2	140	0	0	1	0	0	6	187	0	0	1	0	8	0	233	2	3	0	0	0	0
47	0	0	2	0	2	0	94	0	0	3	0	2	0	141	0	0	1	0	6	0														

TABLE III. Nonrelativistic ground state energy and percentage of the correlation energy 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]	Percentage of correlation energy obtained with wave functions of the present work[d]
Li	233	− 7.478 051	− 7.478 059 (602)[b]	99.95
Be^{+}	164	− 14.324 751	− 14.324 760 (401)[c]	99.88
B^{2+}	201	− 23.424 597	− 23.424 604 (503)[b]	99.71
C^{3+}	213	− 34.775 505	− 34.775 509 (561)[b]	99.52
N^{4+}	213	− 48.376 892	− 48.376 896 (561)[b]	99.23
O^{5+}	213	− 64.228 536	− 64.228 540 (561)[b]	99.19
F^{6+}	213	− 82.330 333	− 82.330 336 (561)[b]	99.13
Ne^{7+}	213	− 102.682 226	− 102.682 229 (561)[b]	99.06

[a] Size of the wave function is shown in brackets.
[b] Values taken from Ref. 19.
[c] Value taken from Ref. 18.
[d] Data from Refs. 1 and 20 to 24 has been employed to estimate the correlation energies.

TABLE IV. Expectation values for the ^2S ground state of Li.

Expectation value	Evaluated from $D_0(r)$	Literature values
$\langle r_i^{-2}\rangle$	3.024 071 (1)[a]	3.024 6 (1)[b]
$\langle r_i^{-1}\rangle$	5.718 087	5.718 110[c]
$\langle r_i\rangle$	4.989 765	4.989 538[c]
$\langle r_i^2\rangle$	1.835 707 (1)	1.835 474 (1)[c]
$\langle r_i^3\rangle$	9.262 792 (1)	9.260 364 (1)[c]
$\langle r_i^4\rangle$	5.504 163 (2)	5.4580 (2)[b]
$\langle r_i^5\rangle$	3.706 018 (3)	
$\langle r_i^6\rangle$	2.788 971 (4)	
$\langle r_i^7\rangle$	2.340 648 (5)	
$\langle r_i^8\rangle$	2.232 172 (6)	
$\langle r_i^9\rangle$	2.582 619 (7)	
$\langle r_i^{10}\rangle$	4.074 779 (8)	
$\langle\delta(\mathbf{r}_i)\rangle$	1.384 170 (1)	1.384 182 (1)[b]

[a] The notation (n) signifies $\times 10^n$.
[b] Literature values taken from Ref. 26 and are derived from the 45 term CI wave function of Weiss, Ref. 23.
[c] Literature values taken from Ref. 19 and are derived from a wave function employing 602 expansion terms.

TABLE V. Expectation values for the ^2S ground state of Be^+.

Expectation value	Evaluated using $D_0(r)$	Literature values
$\langle r_i^{-2}\rangle$	5.699 557 (1)	5.700 4 (1)[a]
$\langle r_i^{-1}\rangle$	7.973 875	7.973 888[b]
$\langle r_i\rangle$	3.101 439	3.101 401[b]
$\langle r_i^2\rangle$	6.508 210	6.507 998[b]
$\langle r_i^3\rangle$	1.868 829 (1)	1.868 715 (1)[b]
$\langle r_i^4\rangle$	6.323 114 (1)	6.371 1 (1)[a]
$\langle r_i^5\rangle$	2.414 227 (2)	
$\langle r_i^6\rangle$	1.023 073 (3)	
$\langle r_i^7\rangle$	4.767 613 (3)	
$\langle r_i^8\rangle$	2.430 401 (4)	
$\langle r_i^9\rangle$	1.355 799 (5)	
$\langle r_i^{10}\rangle$	8.372 421 (5)	
$\langle\delta(\mathbf{r}_i)\rangle$	3.510 330 (1)	3.510 357 (1)[b]

[a] Literature values taken from Ref. 26 and are derived from the 45 term CI wave function of Weiss, Ref. 23.
[b] Literature values are taken from Ref. 18, and based on a wave function with 401 terms.

TABLE VI. Expectation values for the ^2S ground state of B III.

Expectation value	Evaluated from $D_0(r)$	Literature values
$\langle r_i^{-2}\rangle$	9.226 189 (1)	9.227 1 (1)[a]
$\langle r_i^{-1}\rangle$	1.022 552 (1)	1.022 553 (1)[b]
$\langle r_i\rangle$	2.282 859	2.282 848[b]
$\langle r_i^2\rangle$	3.398 147	3.398 093[b]
$\langle r_i^3\rangle$	6.902 840	6.902 609[b]
$\langle r_i^4\rangle$	1.652 841 (1)	1.663 6 (1)[a]
$\langle r_i^5\rangle$	4.460 256 (1)	
$\langle r_i^6\rangle$	1.333 398 (2)	
$\langle r_i^7\rangle$	4.376 609 (2)	
$\langle r_i^8\rangle$	1.571 403 (3)	
$\langle r_i^9\rangle$	6.210 715 (3)	
$\langle r_i^{10}\rangle$	2.787 850 (4)	
$\langle\delta(\mathbf{r}_i)\rangle$	7.145 810 (1)	7.145 863 (1)[b]

[a] Literature values taken from Ref. 26 and are derived from the 45 term CI wave function of Weiss, Ref. 23.
[b] Literature values are taken from Ref. 19 and are derived from a wave function employing 503 expansion terms.

TABLE VII. Expectation values for the ^2S ground state of C IV.

Expectation value	Evaluated from $D_0(r)$	Literature values
$\langle r_i^{-2}\rangle$	1.360 328 (2)	1.356 57 (2)[a]
$\langle r_i^{-1}\rangle$	1.247 620 (1)	1.247 620 (1)[b]
$\langle r_i\rangle$	1.812 800	1.812 796[b]
$\langle r_i^2\rangle$	2.098 812	2.098 797[b]
$\langle r_i^3\rangle$	3.309 300	3.309 249[b]
$\langle r_i^4\rangle$	6.151 805	6.208 5[a]
$\langle r_i^5\rangle$	1.287 913 (1)	
$\langle r_i^6\rangle$	2.983 012 (1)	
$\langle r_i^7\rangle$	7.567 432 (1)	
$\langle r_i^8\rangle$	2.087 147 (2)	
$\langle r_i^9\rangle$	6.220 152 (2)	
$\langle r_i^{10}\rangle$	1.992 588 (3)	
$\langle\delta(\mathbf{r}_i)\rangle$	1.269 645 (2)	1.269 640 (2)[b]

[a] Literature values taken from Ref. 26 and are derived from the 45 term CI wave function of Weiss, Ref. 23.
[b] Literature values are taken from Ref. 19 and are derived from a wave function employing 561 expansion terms.

TABLE VIII. Expectation values for the ^2S ground state of N V.

Expectation value	Evaluated from $D_0(r)$	Literature values
$\langle r_i^{-2}\rangle$	1.883 062 (2)	1.883 20 (2)[a]
$\langle r_i^{-1}\rangle$	1.472 654 (1)	1.472 654 (1)[b]
$\langle r_i\rangle$	1.505 322	1.505 320[b]
$\langle r_i^2\rangle$	1.428 073	1.428 065[b]
$\langle r_i^3\rangle$	1.842 296	1.842 276[b]
$\langle r_i^4\rangle$	2.802 382	2.813 9[a]
$\langle r_i^5\rangle$	4.798 954	
$\langle r_i^6\rangle$	9.085 959	
$\langle r_i^7\rangle$	1.882 907 (1)	
$\langle r_i^8\rangle$	4.239 639 (1)	
$\langle r_i^9\rangle$	1.030 909 (2)	
$\langle r_i^{10}\rangle$	2.692 792 (2)	
$\langle\delta(\mathbf{r}_i)\rangle$	2.056 795 (2)	2.056 786 (2)[b]

[a] Literature values taken from Ref. 26 and are derived from the 45 term CI wave function of Weiss, Ref. 23.
[b] Literature values are taken from Ref. 19 and are derived from a wave function employing 400 expansion terms for the expectation values $\langle r_i\rangle$, $\langle r_i^2\rangle$, and $\langle r_i^3\rangle$ and 561 terms for $\langle r_i^{-1}\rangle$ and $\langle\delta(\mathbf{r}_i)\rangle$.

TABLE IX. Expectation values for the ^2S ground state of O VI.

Expectation value	Evaluated from $D_0(r)$	Literature values
$\langle r_i^{-2}\rangle$	2.490 810 (2)	2.490 98 (2)[a]
$\langle r_i^{-1}\rangle$	1.697 673 (1)	1.697 673 (1)[b]
$\langle r_i\rangle$	1.287 827	1.287 826[b]
$\langle r_i^2\rangle$	1.035 562	1.035 560[b]
$\langle r_i^3\rangle$	1.131 070	1.131 063[b]
$\langle r_i^4\rangle$	1.456 792	
$\langle r_i^5\rangle$	2.111 773	
$\langle r_i^6\rangle$	3.383 070	
$\langle r_i^7\rangle$	5.929 356	
$\langle r_i^8\rangle$	1.128 655 (1)	
$\langle r_i^9\rangle$	2.319 209 (1)	
$\langle r_i^{10}\rangle$	5.117 315 (1)	
$\langle\delta(\mathbf{r}_i)\rangle$	3.116 619 (2)	3.116 604 (2)[b]

[a] Literature value taken from Ref. 27 and is derived from the 45 term CI wave function of Weiss, Ref. 23.
[b] Literature values are taken from Ref. 19 and are derived from a wave function employing 561 expansion terms.

TABLE X. Expectation values for the ^2S ground state of F VII.

Expectation value	Evaluated from $D_0(r)$	Literature values[a]
$\langle r_i^{-2}\rangle$	3.183 568 (2)	
$\langle r_i^{-1}\rangle$	1.922 685 (1)	1.922 685 (1)
$\langle r_i\rangle$	1.125 614	1.125 614
$\langle r_i^2\rangle$	7.857 211 (− 1)	7.857 196 (− 1)
$\langle r_i^3\rangle$	7.443 151 (− 1)	7.443 120 (− 1)
$\langle r_i^4\rangle$	8.315 050 (− 1)	
$\langle r_i^5\rangle$	1.045 291	
$\langle r_i^6\rangle$	1.451 732	
$\langle r_i^7\rangle$	2.205 077	
$\langle r_i^8\rangle$	3.636 541	
$\langle r_i^9\rangle$	6.472 472	
$\langle r_i^{10}\rangle$	1.236 763 (1)	
$\langle\delta(\mathbf{r}_i)\rangle$	4.489 703 (2)	4.489 681 (2)

[a] Literature values are taken from Ref. 19 and are derived from a wave function employing 561 expansion terms.

$$\rho(0)=\frac{1}{4\pi}\left\{\frac{1}{r^2}\sum_{I=1}^{7}\mathscr{A}_{I0}+\frac{1}{r}\sum_{I=1}^{7}(\mathscr{A}_{I1}-\alpha_I\mathscr{A}_{I0})\right\}_{r\to 0}+\frac{1}{4\pi}\sum_{I=1}^{7}(\mathscr{A}_{I2}-\alpha_I\mathscr{A}_{I1}+\tfrac{1}{2}\alpha_I^2\mathscr{A}_{I0}). \quad (51)$$

The requirements for a well behaved electron density at the nucleus is that the following two conditions hold:

$$\sum_{I=1}^{7}\mathscr{A}_{I0}=0 \quad (52)$$

$$\sum_{I=1}^{7}(\mathscr{A}_{I1}-\alpha_I\mathscr{A}_{I0})=0. \quad (53)$$

See Appendix B for a discussion of these two equations. Equations (52) and (53) have been evaluated numerically for each atom studied, and have been found to be satisfied to an accuracy expected on the basis of some accumulation of roundoff errors. The values of $\rho(0)$ reported in Tables IV to XI have been evaluated using the result

$$\rho(0)=\frac{1}{4\pi}\sum_{I=1}^{7}(\mathscr{A}_{I2}-\alpha_I\mathscr{A}_{I1}+\tfrac{1}{2}\alpha_I^2\mathscr{A}_{I0}). \quad (54)$$

TABLE XI. Expectation values for the ^2S ground state of Ne VIII.

Expectation value	Evaluated from $D_0(r)$	Literature values[a]
$\langle r_i^{-2}\rangle$	3.961 332 (2)	
$\langle r_i^{-1}\rangle$	2.147 693 (1)	2.147 693 (1)
$\langle r_i\rangle$	9.998 807 (− 1)	9.998 803 (− 1)
$\langle r_i^2\rangle$	6.167 417 (− 1)	6.167 409 (− 1)
$\langle r_i^3\rangle$	5.158 932 (− 1)	5.158 917 (− 1)
$\langle r_i^4\rangle$	5.089 250 (− 1)	
$\langle r_i^5\rangle$	5.648 780 (− 1)	
$\langle r_i^6\rangle$	6.925 128 (− 1)	
$\langle r_i^7\rangle$	9.282 768 (− 1)	
$\langle r_i^8\rangle$	1.350 685	
$\langle r_i^9\rangle$	2.120 623	
$\langle r_i^{10}\rangle$	3.573 861	
$\langle\delta(\mathbf{r}_i)\rangle$	6.216 629 (2)	6.216 599 (2)

[a] Literature values are taken from Ref. 19 and are derived from a wave function employing 561 expansion terms.

The values of $\rho(0)$ tabulated are in excellent agreement with the results determined from much larger wave functions.

B. Evaluation of the moments $\langle r_i^{-1}\rangle$ and $\langle r_i^{-2}\rangle$

To evaluate $\langle r_i^{-1}\rangle$, the following approach was taken:

$$\langle r_i^{-1}\rangle=\int_0^\infty r^{-1}D_0(r)dr=\int_0^\infty r^{-1}\sum_{I=1}^{7}\mathscr{A}_{I0}e^{-\alpha_I r}dr+\sum_{I=1}^{7}\sum_{K=1}^{g_I}\mathscr{A}_{IK}\int_0^\infty r^{K-1}e^{-\alpha_I r}dr. \quad (55)$$

The second integral in Eq. (55) is trivial and the first can be evaluated using Eq. (52) to yield

$$\int_0^\infty r^{-1}\sum_{I=1}^{7}\mathscr{A}_{I0}e^{-\alpha_I r}dr=\sum_{I=1}^{6}\mathscr{A}_{I0}\int_0^\infty\left(\frac{e^{-\alpha_I r}-e^{-\alpha_7 r}}{r}\right)dr=\sum_{I=1}^{6}\mathscr{A}_{I0}\ln(\alpha_7/\alpha_I). \quad (56)$$

In a similar fashion, the moment $\langle r_i^{-2}\rangle$ was evaluated as

$$\langle r_i^{-2}\rangle=\int_0^\infty r^{-2}D_0(r)dr=\int_0^\infty\sum_{I=1}^{7}e^{-\alpha_I r}(r^{-2}\mathscr{A}_{I0}+r^{-1}\mathscr{A}_{I1})dr+\sum_{I=1}^{7}\sum_{K=2}^{g_I}\mathscr{A}_{IK}\int_0^\infty r^{K-2}e^{-\alpha_I r}dr. \quad (57)$$

The second integral in Eq. (57) is trivial. The first integral can be written as

$$\int_0^\infty\sum_{I=1}^{7}e^{-\alpha_I r}(\mathscr{A}_{I0}r^{-2}+r^{-1}\mathscr{A}_{I1})dr=\left\{\frac{1}{r}\sum_{I=1}^{7}\mathscr{A}_{I0}\right\}_{r\to 0}-\sum_{I=1}^{7}\alpha_I\mathscr{A}_{I0}+\int_0^\infty r^{-1}\sum_{I=1}^{7}(\mathscr{A}_{I1}-\alpha_I\mathscr{A}_{I0})e^{-\alpha_I r}dr=-\sum_{I=1}^{7}\alpha_I\mathscr{A}_{I0}+\sum_{I=1}^{6}(\mathscr{A}_{I1}-\alpha_I\mathscr{A}_{I0})\ln(\alpha_7/\alpha_I) \quad (58)$$

on employing Eqs. (52) and (53). It has been established numerically that

$$\sum_{I=1}^{7}\alpha_I\mathscr{A}_{I0}=0, \quad (59)$$

which allows the integral in Eq. (58) to be simplified.

C. Electron–nuclear cusp condition

The electron–nuclear cusp condition takes the form[28]

$$\left.\frac{\partial\rho(r)}{\partial r}\right|_{r=0}=-2Z\rho(0), \quad (60)$$

TABLE XII. Cusp condition check.

Species	$\left.\frac{\partial\rho(r)}{\partial r}\right\|_{r=0}$	$-2Z\rho(0)$
Li	− 8.303 171 (1)	− 8.305 019 (1)
Be^{+}	− 2.808 100 (2)	− 2.808 264 (2)
B^{2+}	− 7.144 828 (2)	− 7.145 810 (2)
C^{3+}	− 1.523 448 (3)	− 1.523 574 (3)
N^{4+}	− 2.879 305 (3)	− 2.879 512 (3)
O^{5+}	− 4.986 279 (3)	− 4.986 591 (3)
F^{6+}	− 8.081 016 (3)	− 8.081 465 (3)
Ne^{7+}	− 1.243 264 (4)	− 1.243 326 (4)

where Z is the nuclear charge. The right-hand side of Eq. (60) has been evaluated using Eq. (54) and the left-hand side is, on employing Eqs. (52) and (53):

$$\left.\frac{\partial\rho(r)}{\partial r}\right|_{r=0} = \frac{1}{4\pi}\sum_{I=1}^{7}(\mathscr{A}_{I3} - \alpha_I\mathscr{A}_{I2} + \tfrac{1}{2}\alpha_I^2\mathscr{A}_{I1} - \tfrac{1}{6}\alpha_I^3\mathscr{A}_{I0}). \tag{61}$$

The results checking the extent to which Eq. (60) is satisfied are presented in Table XII. As can be observed the values for both sides of Eq. (60) are in fairly reasonable agreement, which improves with increasing nuclear charge.

D. Quality of calculated moments

It is clear from an inspection of Tables IV to XI that the computed moments $\langle r_i^n\rangle$, $n = -1, 1, 2, 3$ and of $\rho(0)$, are in very close agreement with the values computed from much larger wave functions.[18,19] The CPU costs required to evaluate $\langle r_i^n\rangle$ directly from the wave function are significant. This cost increases considerably for larger values of n, because the size of the integral look-up tables required in the computation become very large, adding greatly to the cost of the calculation. It should therefore be clear, just how cost effective working directly with the analytic form for the radial electronic density given in this work proves to be.

E. Quality of calculated density

There is a scarcity of numerical data available for the density $\rho(r)$ derived from wave functions of high quality for members of the Li I series. There is, however, one test of the quality of the numerical results for $\rho(r)$ that can be made. It has been proved[29–31] that $\rho(\mathbf{r})^{1/2}$ is subharmonic for $|\mathbf{r}| > Z/\epsilon$, where ϵ is the first ionization potential of the atom or ion. Therefore, $\rho(r)$ should exhibit no local maximum for $|\mathbf{r}| > Z/\epsilon$. Several failures of this restriction on $\rho(r)$ were noted, but these were all observed when the density dropped below $\sim 1\times 10^{-12}$ (or smaller). Such departures from the rigorous behavior expected are attributed to round off errors, which have an increasing impact when $\rho(r)$ becomes very small.

VI. CONCLUSION

Expressions are reported in this work for the radial electronic density for the ^2S ground states of the Li I series with $Z \leqslant 10$. Since the wave functions from which the radial densities are derived contain a large fraction of the correlation energy, the results of this work should represent useful benchmarks for other density calculations. The simple and compact nature of the final results should make these formulas very useful in practical applications.

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APPENDIX A: DERIVATION OF EQ. (16)

Inserting the Sack formula [Eq. (10)] for each radial function $R_{ab}(r_i, r_j)$ into Eq. (11) yields

$$\begin{aligned}I(r_1) &= 64\pi^3 r_1^{i+2} e^{-\alpha r_1} \\ &\times \sum_{w=0}^{\infty} a_{wlmn} \sum_{r=0}^{\infty} a_{wnr} \sum_{s=0}^{\infty} a_{wms} \sum_{t=0}^{\infty} a_{wlt} \\ &\times \int_0^{\infty}\int_0^{\infty} dr_2\, dr_3\, r_2^{j+2} r_3^{k+2} e^{-\beta r_2 - \gamma r_3} r_{23>}^{l-w-2t} r_{23<}^{2t+w} \\ &\times r_{13>}^{m-w-2s} r_{13<}^{w+2s} r_{12>}^{n-w-2r} r_{12<}^{w+2r},\end{aligned} \tag{A1}$$

where the expansion formula for the hypergeometric functions,

$$F(a,b,c;y) = \sum_{p=0}^{\infty} \frac{(a)_p (b)_p y^p}{(c)_p p!} \tag{A2}$$

has been employed and the notational simplifications

$$a_{wlmn} = \frac{(-l/2)_w(-m/2)_w(-n/2)_w}{(2w+1)^2[(1/2)_w]^3} \tag{A3a}$$

$$a_{wlt} = \frac{(w-(l/2))_t(-(1/2)-(l/2))_t}{(w+(3/2))_t t!} \tag{A3b}$$

have been introduced. If we employ the abbreviation

$$f \equiv f(r_2,r_3) = r_2^{j+2} r_3^{k+2} e^{-\beta r_2 - \gamma r_3}$$

the double integral in Eq. (A1) can be reduced to the form

$$
\begin{aligned}
&\int_0^\infty \int_0^\infty dr_2\, dr_3\, f r_{23>}^{l-w-2t} r_{23<}^{2t+w} r_{13>}^{m-w-2s} r_{13<}^{w+2s} r_{12>}^{n-w-2r} r_{12<}^{w+2r} \\
&\quad = \int_{r_1}^\infty dr_2 \int_0^{r_1} dr_3\, f r_2^{l-w-2t} r_3^{2t+w} r_1^{m-w-2s} r_3^{w+2s} r_2^{n-w-2r} r_1^{w+2r} \\
&\qquad + \int_0^{r_1} dr_2 \int_{r_1}^\infty dr_3\, f r_3^{l-w-2t} r_2^{2t+w} r_3^{m-w-2s} r_1^{w+2s} r_1^{n-w-2r} r_2^{w+2r} \\
&\qquad + \int_0^{r_1} dr_2 \int_0^{r_2} dr_3\, f r_2^{l-w-2t} r_3^{2t+w} r_1^{m-w-2s} r_3^{w+2s} r_1^{n-w-2r} r_2^{w+2r} \\
&\qquad + \int_{r_1}^\infty dr_2 \int_{r_2}^\infty dr_3\, f r_3^{l-w-2t} r_2^{2t+w} r_3^{m-w-2s} r_1^{w+2s} r_2^{n-w-2r} r_1^{w+2r} \\
&\qquad + \int_{r_1}^\infty dr_3 \int_{r_3}^\infty dr_2\, f r_2^{l-w-2t} r_3^{2t+w} r_3^{m-w-2s} r_1^{w+2s} r_2^{n-w-2r} r_1^{w+2r} \\
&\qquad + \int_0^{r_1} dr_3 \int_0^{r_3} dr_2\, f r_3^{l-w-2t} r_2^{2t+w} r_1^{m-w-2s} r_3^{w+2s} r_1^{n-w-2r} r_2^{w+2r}.
\end{aligned}
\tag{A4}
$$

The double integral in Eq. (A4) can be simplified by using the functions defined in Eqs. (12)–(15) to yield

$$
\begin{aligned}
&\int_0^\infty \int_0^\infty dr_2\, dr_3\, f r_{23>}^{l-w-2t} r_{23<}^{2t+w} r_{13>}^{m-w-2s} r_{13<}^{w+2s} r_{12>}^{n-w-2r} r_{12<}^{w+2r} \\
&\quad = r_1^{m+2r-2s} B(j+2+l+n-2w-2t-2r,\beta,r_1)\,[A(k+2+2t+2w+2s,\gamma) - B(k+2+2t+2w+2s,\gamma,r_1)] \\
&\qquad + r_1^{n+2s-2r} B(k+2+l+m-2w-2t-2s,\gamma,r_1)\,[A(j+2+2t+2w+2r,\beta) - B(j+2+2t+2w+2r,\beta,r_1)] \\
&\qquad + r_1^{m+n-2w-2s-2r}\{A(k+2+2t+2w+2s,\gamma)\,[A(j+2+l-2t+2r,\beta) - B(j+2+l-2t+2r,\beta,r_1)] \\
&\qquad + A(j+2+2t+2w+2r,\beta)\,[A(k+2+l-2t+2s,\gamma) - B(k+2+l-2t+2s,\gamma,r_1)] \\
&\qquad - C(j+2+l-2t+2r,k+2+2t+2w+2s,\beta,\gamma) - C(k+2+l-2t+2s,j+2+2t+2w+2r,\gamma,\beta) \\
&\qquad + D(j+2+l-2t+2r,k+2+2t+2w+2s,\beta,\gamma,r_1) + D(k+2+l-2t+2s,j+2+2t+2w+2r,\gamma,\beta,r_1)\} \\
&\qquad + r_1^{2w+2s+2r}\{D(j+2+2t+n-2r,k+2+l+m-2w-2t-2s,\beta,\gamma,r_1) \\
&\qquad + D(k+2+2t+m-2s,j+2+l+n-2w-2t-2r,\gamma,\beta,r_1)\}.
\end{aligned}
\tag{A5}
$$

Since certain combinations of the exponents and summation indices reoccur, the following notational simplifications are introduced:

$$\omega_1 = j+2+l+n-2w-2r-2t, \tag{A6}$$

$$\omega_2 = k+2+2w+2s+2t, \tag{A7}$$

$$\omega_3 = k+2+l+m-2w-2s-2t, \tag{A8}$$

$$\omega_4 = j+2+2w+2r+2t, \tag{A9}$$

$$\omega_5 = j+2+l+2r-2t, \tag{A10}$$

$$\omega_6 = k+2+l+2s-2t, \tag{A11}$$

$$\omega_7 = j+2+n-2r+2t, \tag{A12}$$

$$\omega_8 = k+2+m-2s+2t, \tag{A13}$$

$$\omega_9 = i+2+m+2r-2s, \tag{A14}$$

$$\omega_{10} = i+2+n-2r+2s, \tag{A15}$$

$$\omega_{11} = i+2+m+n-2w-2r-2s, \tag{A16}$$

$$\omega_{12} = i+2+2w+2r+2s, \tag{A17}$$

$$\Omega = i+j+k+l+m+n+6. \tag{A18}$$

If Eq. (A5) is inserted into Eq. (A1) and some of the notational abbreviations just given are employed, then Eq. (16) in Sec. II results.

APPENDIX B: PROOF OF EQS. (52) and (53)

In this appendix a proof is presented for Eqs. (52) and (53), which are of central importance for discussing $\rho(0)$, the moments $\langle r_i^{-1}\rangle$ and $\langle r_i^{-2}\rangle$ and the cusp condition. Expansion of Eq. (46) and Eq. (41) according to powers of r yields

$$
D_0(r) = \sum_{I=1}^{7} \mathscr{A}_{I0} + r\left\{\sum_{I=1}^{7} \mathscr{A}_{I1} - \alpha_I \mathscr{A}_{I0}\right\}
+ \text{terms in higher powers of } r, \tag{B1}
$$

and

$$D_0(r) = 64\pi^3 \sum_{P'} \sum_{P} \chi_{P'P} \sum_u \sum_v C_u C_v \sum_w \sum_r \sum_s \sum_t a_{wrstlmn}$$
$$\times\{(\mathscr{A}_{P'P0}\delta_{\omega_{11},0} + \mathscr{B}_{P'P0} + \mathscr{D}_{P'P0} + \mathscr{E}_{P'P0}) + r(\mathscr{A}_{P'P1}\delta_{\omega_{11},1} + \mathscr{B}_{P'P1} + \mathscr{D}_{P'P1} + \mathscr{E}_{P'P1}$$
$$- \alpha_{P'P}\mathscr{A}_{P'P0}\delta_{\omega_{11},0} - \beta_{P'P}\mathscr{B}_{P'P0} - \gamma_{P'P}\mathscr{D}_{P'P0} - \epsilon_{P'P0}\mathscr{E}_{P'P0})$$
$$+ \text{terms in higher powers of } r\}. \tag{B2}$$

In Eq. (B2) $\delta_{i,j}$ is the Kronecker delta. By equating corresponding powers of r for Eqs. (B1) and (B2), the following results emerge:

$$\sum_{I=1}^{7} \mathscr{A}_{I0} = 64\pi^3 \sum_{P'} \sum_{P} \chi_{P'P} \sum_u \sum_v C_u C_v \sum_w \sum_r \sum_s \sum_t a_{wrstlmn}$$
$$\times\{\mathscr{A}_{P'P1}\delta_{\omega_{11},0} + \mathscr{B}_{P'P0} + \mathscr{D}_{P'P0} + \mathscr{E}_{P'P0}\} \tag{B3}$$

and

$$\sum_{I=1}^{7} (\mathscr{A}_{I1} - \alpha_I\mathscr{A}_{I0}) = 64\pi^3 \sum_{P'} \sum_{P} \chi_{P'P} \sum_u \sum_v C_u C_v \sum_w \sum_r \sum_s \sum_t a_{wrstlmn}$$
$$\times\{\mathscr{A}_{P'P1}\delta_{\omega_{11},1} + \mathscr{B}_{P'P1} + \mathscr{D}_{P'P1} + \mathscr{E}_{P'P1}$$
$$- \alpha_{P'P}\mathscr{A}_{P'P0}\delta_{\omega_{11},0} - \beta_{P'P}\mathscr{B}_{P'P0} - \gamma_{P'P}\mathscr{D}_{P'P0} - \epsilon_{P'P}\mathscr{E}_{P'P0}\}. \tag{B4}$$

Equations (52) and (53) can be established if the terms in braces in Eqs. (B3) and (B4) can be proved to be zero. Five separate cases must be proved. They are

$$\mathscr{A}_{P'P0} + \mathscr{B}_{P'P0} + \mathscr{D}_{P'P0} + \mathscr{E}_{P'P0} = 0 \text{ for } \omega_{11} = 0, \tag{B5}$$
$$\mathscr{B}_{P'P0} + \mathscr{D}_{P'P0} + \mathscr{E}_{P'P0} = 0 \text{ for } \omega_{11} \neq 0, \tag{B6}$$
$$\mathscr{A}_{P'P1} + \mathscr{B}_{P'P1} + \mathscr{D}_{P'P1} + \mathscr{E}_{P'P1}$$
$$- \beta_{P'P}\mathscr{B}_{P'P0} - \gamma_{P'P}\mathscr{D}_{P'P0} - \epsilon_{P'P}\mathscr{E}_{P'P0} = 0 \text{ for } \omega_{11} = 1, \tag{B7}$$
$$\mathscr{B}_{P'P1} + \mathscr{D}_{P'P1} + \mathscr{E}_{P'P1} - \beta_{P'P}\mathscr{B}_{P'P0} - \gamma_{P'P}\mathscr{D}_{P'P0} - \epsilon_{P'P}\mathscr{E}_{P'P0} = 0, \quad \text{for } \omega_{11} > 1 \tag{B8}$$
$$\mathscr{B}_{P'P1} + \mathscr{D}_{P'P1} + \mathscr{E}_{P'P1} - \alpha_{P'P}\mathscr{A}_{P'P0} - \beta_{P'P}\mathscr{B}_{P'P0}$$
$$- \gamma_{P'P}\mathscr{D}_{P'P0} - \epsilon_{P'P}\mathscr{E}_{P'P0} = 0 \text{ for } \omega_{11} = 0. \tag{B9}$$

For proofs given below, it will be useful to keep in mind the minimum values of the ω_i factors. These minimum values are 0, 2, 0, 2, 1, 1, 1, 1, 1, 1, 0, 2 for $i = 1$ to 12, respectively. The results for $\mathscr{A}_{P'P0}$, etc., given below are obtained from Eqs. (34) to (38) and the abbreviations presented in Eqs. (31) and (33) are employed.

To prove Eq. (B5), the following results are required for $\omega_{11} = 0$:

$$\mathscr{A}_{P'P0} = \frac{-\omega_2!}{\gamma^{\omega_2+1}(\beta+\gamma)^{\omega_5+1}} \sum_{p=0}^{\omega_2} g_p(\omega_5+p)! + \frac{\omega_2!\omega_5!}{\gamma^{\omega_2+1}\beta^{\omega_5+1}} - \frac{\omega_4!}{\beta^{\omega_4+1}(\beta+\gamma)^{\omega_6+1}} \sum_{p=0}^{\omega_4} h_p(\omega_6+p)! + \frac{\omega_4!\omega_6!}{\beta^{\omega_4+1}\gamma^{\omega_6+1}}, \tag{B10}$$

$$\mathscr{B}_{P'P0} = \frac{\omega_2!}{\gamma^{\omega_2+1}(\beta+\gamma)^{\omega_5+1}} \sum_{p=0}^{\omega_2} g_p(\omega_5+p)! + \frac{\omega_4!}{\beta^{\omega_4+1}(\beta+\gamma)^{\omega_6+1}} \sum_{p=0}^{\omega_4} h_p(\omega_6+p)!, \tag{B11}$$

$$\mathscr{D}_{P'P0} = \frac{-\omega_2!\omega_5!}{\gamma^{\omega_2+1}\beta^{\omega_5+1}}, \tag{B12}$$

$$\mathscr{E}_{P'P0} = \frac{-\omega_4!\omega_6!}{\beta^{\omega_4+1}\gamma^{\omega_6+1}}. \tag{B13}$$

Adding Eqs. (B10) through (B13) thus proves Eq. (B5). The proof of Eq. (B6) is straightforward. For $\omega_{11} \neq 0$,

$$\mathscr{B}_{P'P0} = 0, \tag{B14}$$
$$\mathscr{D}_{P'P0} = 0, \tag{B15}$$
$$\mathscr{E}_{P'P0} = 0, \tag{B16}$$

and hence Eq. (B6) is proved. The proof of Eqs. (B5) and (B6) establishes Eq. (52).

To prove Eq. (B7), first note that with the results

$$\left.\begin{aligned}\mathscr{B}_{P'P0} &= 0\\ \mathscr{D}_{P'P0} &= 0\\ \mathscr{E}_{P'P0} &= 0\end{aligned}\right\} \text{for } \omega_{11} = 1, \tag{B17}$$

Eq. (B7) simplifies to

$$\mathscr{A}_{P'P1} + \mathscr{B}_{P'P1} + \mathscr{D}_{P'P1} + \mathscr{E}_{P'P1} = 0. \tag{B18}$$

To prove Eq. (B18), the following results are needed for

$\omega_{11}=1,$

$$\mathscr{A}_{P'P1}=\frac{-\omega_2!}{\gamma^{\omega_2+1}(\beta+\gamma)^{\omega_5+1}}\sum_{p=0}^{\omega_2}g_p(\omega_5+p)! -\frac{\omega_4!}{\beta^{\omega_4+1}(\beta+\gamma)^{\omega_6+1}}\sum_{p=0}^{\omega_4}h_p(\omega_6+p)! \quad \text{(B19)}$$

$$+\frac{\omega_2!\omega_5!}{\gamma^{\omega_2+1}\beta^{\omega_5+1}}+\frac{\omega_4!\omega_6!}{\beta^{\omega_4+1}\gamma^{\omega_6+1}},$$

$$\mathscr{B}_{P'P1}=\frac{\omega_2!}{\gamma^{\omega_2+1}(\beta+\gamma)^{\omega_5+1}}\sum_{p=0}^{\omega_2}g_p(\omega_5+p)! +\frac{\omega_4!}{\beta^{\omega_4+1}(\beta+\gamma)^{\omega_6+1}}\sum_{p=0}^{\omega_4}h_p(\omega_6+p)! \quad \text{(B20)}$$

$$-a\delta_{\omega_9,1}-d\delta_{\omega_{10},1}$$

$$\mathscr{D}_{P'P1}=a\delta_{\omega_9,1}-\frac{\omega_2!\omega_5!}{\gamma^{\omega_2+1}\beta^{\omega_5+1}}, \quad \text{(B21)}$$

$$\mathscr{E}_{P'P1}=d\delta_{\omega_{10},1}-\frac{\omega_4!\omega_6!}{\beta^{\omega_4+1}\gamma^{\omega_6+1}}. \quad \text{(B22)}$$

Addition of Eqs. (B19) to (B22) proves Eq. (B18) and hence proves Eq. (B7).

To prove Eq. (B8) we note that Eq. (B17) also holds for $\omega_{11}>1$, which requires that we prove (for $\omega_{11}>1$)

$$\mathscr{B}_{P'P1}+\mathscr{D}_{P'P1}+\mathscr{E}_{P'P1}=0. \quad \text{(B23)}$$

For $\omega_{11}>1$

$$\mathscr{B}_{P'P1}=-a\delta_{\omega_9,1}-d\delta_{\omega_{10},1}, \quad \text{(B24)}$$

$$\mathscr{D}_{P'P1}=a\delta_{\omega_9,1}, \quad \text{(B25)}$$

$$\mathscr{E}_{P'P1}=d\delta_{\omega_{10},1}. \quad \text{(B26)}$$

Addition of Eqs. (B24) to (B26) proves (B23) and hence Eq. (B8).

The last case to be proved, Eq. (B9), is the most difficult, as it is necessary to prove this result for each of the 18 separate permutations. For $\omega_{11}=0$, the following results are needed:

$$\mathscr{B}_{P'P1}=-a\delta_{\omega_9,1}-d\delta_{\omega_{10},1}+\frac{\omega_2!}{\gamma^{\omega_2+1}(\beta+\gamma)^{\omega_5}}\sum_{p=0}^{\omega_2}g_p(\omega_5+p)! +\frac{\omega_4!}{\beta^{\omega_4}(\beta+\gamma)^{\omega_6}}\sum_{p=0}^{\omega_4}h_p(\omega_6+p)!, \quad \text{(B27)}$$

$$\mathscr{D}_{P'P1}=a\delta_{\omega_9,1}-\frac{\omega_2!\omega_5!}{\gamma^{\omega_2+1}\beta^{\omega_5}}, \quad \text{(B28)}$$

$$\mathscr{E}_{P'P1}=d\delta_{\omega_{10},1}-\frac{\omega_4!\omega_6!}{\beta^{\omega_4+1}\gamma^{\omega_6}}. \quad \text{(B29)}$$

Now adding Eqs. (B27) through (B29) and using Eqs. (B10) to (B13) leads to

$$\mathscr{B}_{P'P1}+\mathscr{D}_{P'P1}+\mathscr{E}_{P'P1}-\alpha_{P'P}\mathscr{A}_{P'P0}-\beta_{P'P}\mathscr{B}_{P'P0}-\gamma_{P'P}\mathscr{D}_{P'P0}-\epsilon_{P'P}\mathscr{E}_{P'P0}$$
$$=(\alpha_{P'P}-\beta_{P'P}+\beta+\gamma)\left\{\frac{\omega_2!}{\gamma^{\omega_2+1}(\beta+\gamma)^{\omega_5+1}}\sum_{p=0}^{\omega_2}g_p(\omega_5+p)! +\frac{\omega_4!}{\beta^{\omega_4+1}(\beta+\gamma)^{\omega_6+1}}\sum_{p=0}^{\omega_4}h_p(\omega_6+p)!\right\}$$
$$+\frac{\omega_2!\omega_5!}{\gamma^{\omega_2+1}\beta^{\omega_5+1}}(\gamma_{P'P}-\alpha_{P'P}-\beta)+\frac{\omega_4!\omega_6!}{\beta^{\omega_4+1}\gamma^{\omega_6+1}}(\epsilon_{P'P}-\alpha_{P'P}-\gamma). \quad \text{(B30)}$$

Now to prove that the right-hand side of Eq. (B30) = 0, it is necessary to prove for each permutation that:

$$\beta=\gamma_{P'P}-\alpha_{P'P}, \quad \text{(B31)}$$

$$\gamma=\epsilon_{P'P}-\alpha_{P'P}, \quad \text{(B32)}$$

$$\beta+\gamma=\beta_{P'P}-\alpha_{P'P}. \quad \text{(B33)}$$

By inspection of Table I, it can be shown that:

$$\beta_{P'P}-\alpha_{P'P}=\gamma_{P'P}+\epsilon_{P'P}-2\alpha_{P'P} \quad \text{(B34)}$$

and hence a proof of Eqs. (B31) and (B32) also proves Eq. (B33). By recalling the remarks made just above Eq. (42), that is, $\beta\equiv\beta_u+\beta_v$ and $\gamma\equiv\gamma_u+\gamma_v$ and noting Eqs. (40a) and (40b), Eqs. (B31) and (B32) can be verified for each row of Table I. With these two results, Eq. (B9) is proved. This completes the proof of Eq. (53).

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