Compact expressions for the electron–electron distribution function for the ^2S states of three-electron systems

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The electron–electron distribution function $P(r_{ij})$ has been evaluated in closed form for the ^2S states of three-electron systems that are described by Hylleraas-type wave functions. The function $P(r_{ij})$ can be reduced to the form $P(r_{ij}) = \Sigma_{I=1}^{3} \Sigma_{K=1}^{g_I} \mathscr{A}_{IK} r_{ij}^{K} e^{-\alpha_I r_{ij}}$. Numerical values of the expansion coefficients $\mathscr{A}_{IK}$, summation limits g_I, and exponents α_I are determined for the ground states of selected members of the lithium isoelectronic series. A discussion is given on the necessary conditions that must be imposed on the basis set in order that $P(r_{ij})$ be given by the analytical formula presented above. Expectation values for several moments $\langle r_{ij}^n \rangle$ and $\langle \delta(\mathbf{r}_{ij}) \rangle$ are evaluated.

I. INTRODUCTION

The electron–electron distribution function $P(r_{ij})$ plays a central role in the discussion of correlation holes in many-electron systems.[1–21] Despite this fact, there are relatively few compact and convenient to use formulas available to calculate this quantity. A notable exception is the work of Benesch[22] who derived the following result:

$$P(r_{12}) = \sum_{n=2}^{16} c_n r_{12}^n e^{-k r_{12}} \tag{1}$$

for two-electron ^1S ground states of the helium isoelectronic series that have been described by Hylleraas-type wave functions. Benesch analyzed the Hart–Herzberg[23] wave functions and determined values of the c_n coefficients. The summation limit in Eq. (1) is determined by the particular basis functions that make up the wave function. Coulson and Neilson[1] had earlier given analytic expressions for $P(r_{12})$ for the ground state of the helium atom using some fairly simple wave functions. Thakkar and Smith[24] developed formulas for the calculation of $P(r_{12})$ for two-electron atoms which were based on more accurate wave functions than those considered by Benesch.

There has been some recent interest in finding theoretical bounds on $P(r_{ij})$ and a related function, the intracule density.[25–27] The bounds obtained involve the moments $\langle r_{ij}^n \rangle$. Also, it can be shown that a lower bound for the electronic density at the nucleus can be obtained in terms of the moment $\langle r_{ij}^{-2} \rangle$.[28]

The purpose of the present work is to obtain relatively compact formulas for $P(r_{ij})$ for the ground states of selected members of the lithium isoelectronic series. Our effort has focused on obtaining formulas that are convenient to use rather than necessarily obtaining results of the highest possible precision.

II. THEORY

If $\Psi(x_1,x_2,\ldots,x_n)$ denotes an N-electron wave function, where x_i denotes a combined space and spin coordinate $x_i=(\mathbf{r}_i,s_i)$, the radial electron–electron distribution function is defined by[3]

$$P(r_{ij}) = \int \Gamma^{(2)}(\mathbf{r}_i,\mathbf{r}_j|\mathbf{r}_i,\mathbf{r}_j) \frac{d\mathbf{r}_i\, d\mathbf{r}_j}{dr_{ij}}, \tag{2}$$

where $\Gamma^{(2)}$ is the spin-free 2 matrix defined by

$$\Gamma^{(2)}(\mathbf{r}_i,\mathbf{r}_j|\mathbf{r}_i',\mathbf{r}_j') = \binom{N}{2} \int \Psi(x_1,x_2,\ldots,x_i,\ldots,x_j,\ldots,x_n) \times \Psi^*(x_1,x_2,\ldots,x_i',\ldots,x_j',\ldots,x_n)\, ds_i\, ds_j\, dx_k, \tag{3}$$

where dx_k denotes combined integration over all coordinates except those with $k=i$ and j. The normalization for $P(r_{ij})$ employed is thus

$$\int_0^\infty P(r_{ij})\, dr_{ij} = \frac{1}{2} N(N-1). \tag{4}$$

The case of specific interest in this work are the ^2S states of three-electron systems described by Hylleraas-type wave functions. The wave function employed is given by

$$\Psi(1,2,3) = \mathscr{A} \sum_{\mu=1}^{N} C_\mu \phi_\mu \chi_\mu \tag{5}$$

with

$$\phi_\mu \equiv \phi_\mu(r_1,r_2,r_3,r_{23},r_{31},r_{12}) = r_1^{i_\mu} r_2^{j_\mu} r_3^{k_\mu} r_{23}^{l_\mu} r_{31}^{m_\mu} r_{12}^{n_\mu} \exp(-\alpha_\mu r_1 - \beta_\mu r_2 - \gamma_\mu r_3) \tag{6}$$

and $\mathscr{A}$ is the three-electron antisymmetrizer, C_μ's are the variationally determined expansion coefficients, and χ_μ is the spin function

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$$\chi_\mu \equiv \chi_\mu(1,2,3) = \alpha(1)\beta(2)\alpha(3) - \beta(1)\alpha(2)\alpha(3). \tag{7}$$

The basis set exponent indices $\{i_\mu, j_\mu, k_\mu, l_\mu, m_\mu, n_\mu\}$ are each $\geqslant 0$.

Inserting Eqs. (5) and (3) into Eq. (2) leads to the result

$$P(r_{23}) = \sqrt{6} \sum_u \sum_v C_u C_v \int [(1 - P_{12} - P_{13}) \times \phi_u(1,2,3)\chi_u(1,2,3)] \times \{\mathscr{A}\phi_v(1,2,3)\chi_v(1,2,3)\} dx_1\, ds_2\, ds_3 \frac{d\mathbf{r}_2\, d\mathbf{r}_3}{dr_{23}}. \tag{8}$$

It is straightforward to show that Eq. (8) simplifies to a sum of integrals of the form

$$I(r_{23}) = \int r_1^i r_2^j r_3^k r_{23}^l r_{31}^m r_{12}^n \exp(-\alpha r_1 - \beta r_2 - \gamma r_3) \times \frac{d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{r}_3}{dr_{23}}. \tag{9}$$

A convenient way to deal with the above integral is to rotate the coordinate system, so that $\mathbf{r}_3$ is along the polar axis (the z axis).[29] When this is done, the set $\{(r_1,\theta_1,\phi_1), (r_2,\theta_2,\phi_2),(r_3,\theta_3,\phi_3)\}$ becomes $\{(r_1,\theta_{13},\phi_{13}), (r_2,\theta_{23},\phi_{23}),(r_3,\theta_3,\phi_3)\}$ and so Eq. (9) simplifies to

$$I(r_{23}) = \int r_1^{i+2} r_2^{j+1} r_3^{k+1} r_{23}^{l+1} r_{31}^m r_{12}^n \exp(-\alpha r_1 - \beta r_2 - \gamma r_3) \times \sin\theta_{13} \sin\theta_3\, d\theta_{13}\, d\phi_{13}\, d\phi_{23} \times d\theta_3\, d\phi_3\, dr_1\, dr_2\, dr_3. \tag{10}$$

To get Eq. (10), the result

$$\sin\theta_{23}\, d\theta_{23} = \frac{r_{23}\, dr_{23}}{r_2 r_3} \tag{11}$$

has been employed. Equation (11) follows directly from the cosine rule.

To further simplify Eq. (10), the Sack expansion[30] for the factor r_{12}^n is employed. This expansion takes the form

$$r_{12}^n = \sum_{v=0}^{\infty} R_{nv}(r_1, r_2) P_v(\cos\theta_{12}), \tag{12}$$

where $P_v(\cos\theta_{12})$ is a Legendre polynomial and $R_{nv}(r_1,r_2)$ are the Sack radial functions. Inserting Eq. (12) and the analogous expansion for r_{31}^m into Eq. (10) leads to

$$I(r_{23}) = \sum_{w=0}^{\infty} \sum_{v=0}^{\infty} \int r_1^{i+2} r_2^{j+1} r_3^{k+1} r_{23}^{l+1} R_{nv}(r_1,r_2) R_{mw}(r_1,r_3) \times \exp(-\alpha r_1 - \beta r_2 - \gamma r_3) I_\Omega\, dr_1\, dr_2\, dr_3, \tag{13}$$

where the angle integration is

$$I_\Omega = \int P_v(\cos\theta_{12}) P_w(\cos\theta_{13}) \sin\theta_{13} \times \sin\theta_3\, d\theta_{13}\, d\phi_{13}\, d\phi_{23}\, d\theta_3\, d\phi_3. \tag{14}$$

In the rotated coordinate system, r_{23} and r_{13} do not depend on ϕ_{23} and ϕ_{13}, respectively, so the integration over $d\phi_{13}$ and $d\phi_{23}$ can be carried out to yield

$$\begin{aligned} I_\phi &= \int P_v(\cos\theta_{12}) d\phi_{13}\, d\phi_{23} \\ &= \frac{4\pi}{2v+1} \sum_{m_v=-v}^{v} \int Y_{vm_v}^*(\theta_{23},\phi_{23}) Y_{vm_v} \times (\theta_{13},\phi_{13}) \phi_{13}\, d\phi_{23} \\ &= 4\pi^2 P_v(\cos\theta_{13}) P_v(\cos\theta_{23}). \end{aligned} \tag{15}$$

On inserting Eq. (15) into Eq. (14), the following result is obtained:

$$I_\Omega = \frac{32\pi^3 \delta_{wv}}{2w+1} P_w(\cos\theta_{23}). \tag{16}$$

The following expansion for $P_w(\cos\theta_{23})$ is employed:

$$P_w(\cos\theta_{23}) = \left(\frac{r_2}{4r_3}\right)^w \sum_{J=0}^{w} r_2^{-2J} r_{23}^{2J} \sum_{L=0}^{w-J} A(w,J,L) \left(\frac{r_3}{r_2}\right)^{2L}, \tag{17}$$

where

$$\begin{aligned} A(w,J,L) = (-1)^J \Bigg[& \nabla_{L,[(w-J)/2]-1} \sum_{s=0}^{L} Q(s)P(s,L-s) \\ & + \Delta_{L,[(w-J)/2]} \nabla_{L,\lceil (w-J)/2 \rceil} \times \sum_{s=0}^{[(w-J)/2]} Q(s)P(s,L-s) + \Delta_{L,\lceil (w-J)/2\rceil+1} \\ & \times \sum_{s=0}^{w-J-L} Q(s)P(s,L-s) \Bigg] \end{aligned} \tag{18}$$

and

$$Q(s) \equiv Q_{wJ}(s) = \binom{w-2s}{J} \frac{(-4)^s (2w-2s)!}{s!(w-s)!(w-2s)!}, \tag{19}$$

$$P(L,s) \equiv P_{wJ}(L,s) = \binom{w-2L-J}{s}, \tag{20}$$

and the notational device

$$\Delta_{J,K} = \begin{cases} 0, & J < K \\ 1, & J \geqslant K \end{cases} \tag{21}$$

$$\nabla_{J,K} = \begin{cases} 0, & J > K \\ 1, & J \leqslant K \end{cases} \tag{22}$$

has been employed. The standard notation $[x/2] = x/2$ if x is even and $[x/2] = (x-1)/2$ if x is odd, and $\lceil x \rceil = x/2$ if x even and $\lceil x \rceil = (x+1)/2$ if x is odd have been employed in Eq. (18). $\binom{b}{a}$ denotes a binomial coefficient in Eq. (19). The particular form of the expansion given in Eq. (17) is most useful because it allows much of the complexity to be submerged in a single coefficient (the A coefficient). Equation (17) was obtained by employing the cosine rule, followed by a binomial expansion of the resulting numerator and then a summation rearrangement was carried out. If Eqs. (16) and (17) are inserted into Eq. (13), then

$$I(r_{23})=32\pi^3\sum_{w=0}^{\infty}\frac{1}{4^w(2w+1)}\sum_{J=0}^{w}r_{23}^{l+1+2J}\sum_{L=0}^{w-J}A(w,J,L)$$
$$\times\int r_1^{i+2}r_2^{j+1+w-2J-2L}r_3^{k+1-w+2L}$$
$$\times R_{mw}(r_1,r_3)R_{nw}(r_1,r_2)\exp(-\alpha r_1-\beta r_2-\gamma r_3)$$
$$\times dr_1\,dr_2\,dr_3. \quad (23)$$

To handle the radial integral in Eq. (23), the Sack expansions for $R_{mw}(r_1,r_3)$ and $R_{nw}(r_1,r_2)$ are utilized. The Sack expansion employed is[30]

$$R_{mw}(r_1,r_3)=\sum_{s=0}^{(m/2)-w}b_{mws}(r_1r_3)^{w+s}(r_1+r_3)^{m-2w-2s}, \quad (24)$$

where

$$b_{mws}=4^s\frac{(-m/2)_w(w-(m/2))_s(1+w)_s}{(1/2)_w s!(2+2w)_s}. \quad (25)$$

In Eq. (25) $(a)_b$ denotes a Pochhammer symbol. The particular choice made in Eq. (24) forces the restriction that m be even. Employing the analogous expansion for $R_{nw}(r_1,r_2)$ also forces the restriction that n be even. An alternative Sack expansion for $R_{mw}(r_1,r_3)$ is possible, which is terminating for m even or odd, but involves the variables $r_{13<}$ and $r_{13>}$, where $r_{13<}$ denotes $\min(r_1,r_3)$ and $r_{13>}$ designates max (r_1,r_3). Unfortunately, the alternative Sack expansion leads to a radial integral that is difficult to deal with.

Inserting Eq. (24) and the analogous expansion for $R_{nw}(r_1,r_2)$ into Eq. (23), and employing a binomial expansion for each of the factors $(r_1+r_3)^{m-2w-2s}$ and $(r_1+r_2)^{n-2w-2r}$, leads to the result

$$I(r_{23})=32\pi^3\sum_{w=0}^{w_{\max}}\frac{1}{4^w(2w+1)}\sum_{J=0}^{w}r_{23}^{l+1+2J}\sum_{L=0}^{w-J}A(w,J,L)$$
$$\times\sum_{s=0}^{(m/2)-w}b_{mws}\sum_{r=0}^{(n/2)-w}b_{nwr}\sum_{p=0}^{m-2w-2s}\binom{m-2w-2s}{p}$$
$$\times\sum_{t=0}^{n-2w-2r}\binom{n-2w-2r}{t}$$
$$\times\frac{\mathscr{Z}_1!}{\alpha^{\mathscr{Z}_1+1}}\mathscr{H}(\mathscr{Z}_2,\mathscr{Z}_3,\beta,\gamma,r_{23}), \quad (26)$$

where

$$\mathscr{H}(\mathscr{Z}_2,\mathscr{Z}_3,\beta,\gamma,r_{23})=\int r_2^{\mathscr{Z}_2}r_3^{\mathscr{Z}_3}\exp(-\beta r_2-\gamma r_3)dr_2\,dr_3, \quad (27)$$

and the notational simplifications

$$\mathscr{Z}_1=i+2+2w+r+s+t+p\geqslant 2, \quad (28)$$

$$\mathscr{Z}_2=j+1-2J-2L+n-r-t\geqslant 1, \quad (29)$$

$$\mathscr{Z}_3=k+1-2w+2L+m-s-p\geqslant 1 \quad (30)$$

have been employed. The w summation terminates at $w_{\max}=\min(m/2,n/2)$, which follows from the definition of b_{xyz} given in Eq. (25) and the result

$$(-k)_l=0,\quad \text{for integer } k \text{ and } l>k. \quad (31)$$

The radial integral over r_1 in Eq. (23) can be carried out simply because it is independent (in the transformed coordinate system) of r_{13} and r_{12}. The integral in Eq. (27) can be evaluated as

$$\mathscr{H}(i,j,\beta,\gamma,r_{23})=\int_0^{r_{23}}r_2^ie^{-\beta r_2}dr_2\int_{r_{23}-r_2}^{r_{23}+r_2}r_3^je^{-\gamma r_3}dr_3$$
$$+\int_{r_{23}}^{\infty}r_2^ie^{-\beta r_2}dr_2\int_{r_2-r_{23}}^{r_2+r_{23}}r_3^je^{-\gamma r_3}dr_3. \quad (32)$$

For the case $\beta\neq\gamma$, Eq. (32) evaluates to

$$\mathscr{H}(i,j,\beta,\gamma,r_{23})$$
$$=j!\left\{e^{-\beta r_{23}}\sum_{m=0}^{i+j}r_{23}^m\sum_{l=0}^{\min(j,i+j-m)}C_{ij}(l,m,\beta,\gamma)\gamma^{-l-1}\right.$$
$$\left.+e^{-\gamma r_{23}}\sum_{m=0}^{j}r_{23}^m\sum_{l=0}^{j-m}D_{ij}(l,m,\beta,\gamma)\gamma^{-l-1}\right\} \quad (33a)$$
$$=e^{-\beta r_{23}}i!\sum_{m=0}^{i}r_{23}^m\sum_{l=0}^{i-m}D_{ji}(l,m,\gamma,\beta)\beta^{-l-1}$$
$$+e^{-\gamma r_{23}}j!\sum_{m=0}^{j}r_{23}^m\sum_{l=0}^{j-m}D_{ij}(l,m,\beta,\gamma)\gamma^{-l-1}, \quad (33b)$$

with

$$C_{ij}(l,m,\beta,\gamma)=[(\beta+\gamma)^{l+m-i-j-1}-(-1)^{j-l}(\beta-\gamma)^{l+m-i-j-1}]$$
$$\times\sum_{n=0}^{\min(m,j-l)}\frac{(-1)^n(i+j-l-n)!}{n!(j-l-n)!(m-n)!} \quad (34)$$

and

$$D_{ij}(l,m,\beta,\gamma)=\frac{(i+j-l-m)!}{m!(j-l-m)!}[(-1)^{j-l+m}$$
$$\times(\beta-\gamma)^{l+m-i-j-1}-(\beta+\gamma)^{l+m-i-j-1}]. \quad (35)$$

Some summation rearrangement is necessary to obtain Eq. (33a) in the form given above. Equation (33a) can be converted to Eq. (33b) on noting the relationships

$$\sum_{l=0}^{i+j-m} C_{ij}(l,m,\beta,\gamma)\gamma^{-l-1}=0, \quad \text{for } m=i+1,\ldots,i+j \tag{36}$$

and

$$\sum_{l=0}^{i} C_{ji}(l,m,\gamma,\beta)\beta^{-l-1} =(j!/i!)\sum_{l=0}^{j-m} D_{ij}(l,m,\beta,\gamma)\gamma^{-l-1}. \tag{37}$$

When $\beta=\gamma$, Eq. (32) evaluates to

$$\mathscr{H}(i,j,\beta,\beta,r_{23}) =j!e^{-\beta r_{23}}\left[\sum_{m=1}^{i+j} r_{23}^m \sum_{l=0}^{\min(j,i+j-m)} E_{ij}(l,m,\beta)\beta^{-l-1} + \sum_{m=0}^{j} r_{23}^{i+j+1-m}F_{ij}(m)\beta^{-m-1} - \sum_{m=1}^{j} r_{23}^m \sum_{l=0}^{j-m} G_{ij}(l,m,\beta)\beta^{-l-1}\right], \tag{38}$$

where

$$E_{ij}(l,m,\beta)=(2\beta)^{l+m-1-i-j} \times \sum_{n=0}^{\min(m,j-l)} \frac{(-1)^n(i+j-l-n)!}{n!(j-l-n)!(m-n)!}, \tag{39}$$

$$F_{ij}(l)=(-1)^{j-l}\sum_{n=0}^{j-l} \frac{(-1)^n}{n!(j-l-n)!(i+j+1-l-n)!}, \tag{40}$$

and

$$G_{ij}(l,m,\beta)=\frac{(2\beta)^{l+m-1-i-j}(i+j-l-m)!}{m!(j-l-m)!}. \tag{41}$$

The following restrictions are employed for the orbital exponents in the Hylleraas expansion [Eq. (6)]

$$\left.\begin{array}{l}\alpha_\mu=\beta_\mu=\alpha\\ \gamma_\mu=\gamma\end{array}\right\} \quad \text{all } \mu. \tag{42}$$

Without the restrictions indicated in Eq. (42), the possibility of constructing a simple compact formula for $P(r_{23})$ is lost. There are two permutation sums in Eq. (8). Table I shows the effects of the different permutations on the orbital exponent factors. The net effect is that three distinct exponential factors will occur in Eq. (26). The permutation combinations where Eq. (38) must be employed are indicated by an asterisk, otherwise Eq. (33b) is employed in Eq. (26).

If Eq. (26) is now inserted into Eq. (8), then

TABLE I. Exponential factors that arise from the different permutations in Eq. (43).

Permutations ($\mathscr{P}'\mathscr{P}$)	Exponents		
	$\alpha\equiv\alpha_u+\alpha_v$	$\beta\equiv\beta_u+\beta_v$	$\gamma\equiv\gamma_u+\gamma_v$
(123)(123)	2α	2α	2γ
(123)(132)*	2α	$\alpha+\gamma$	$\alpha+\gamma$
(123)(213)	2α	2α	2γ
(123)(312)*	2α	$\alpha+\gamma$	$\alpha+\gamma$
(123)(321)	$\alpha+\gamma$	2α	$\alpha+\gamma$
(123)(231)	$\alpha+\gamma$	2α	$\alpha+\gamma$
(213)(123)	2α	2α	2γ
(213)(132)*	2α	$\alpha+\gamma$	$\alpha+\gamma$
(213)(213)	2α	2α	2γ
(213)(312)*	2α	$\alpha+\gamma$	$\alpha+\gamma$
(213)(321)	$\alpha+\gamma$	2α	$\alpha+\gamma$
(213)(231)	$\alpha+\gamma$	2α	$\alpha+\gamma$
(321)(123)	$\alpha+\gamma$	2α	$\alpha+\gamma$
(321)(132)	$\alpha+\gamma$	$\alpha+\gamma$	2α
(321)(213)	$\alpha+\gamma$	2α	$\alpha+\gamma$
(321)(312)	$\alpha+\gamma$	$\alpha+\gamma$	2α
(321)(321)*	2γ	2α	2α
(321)(231)*	2γ	2α	2α

$$P(r_{23})=32\pi^3\sum_{\mathscr{P}'}\sum_{\mathscr{P}}\chi_{\mathscr{P}'\mathscr{P}}\sum_u\sum_v C_uC_v \times\sum_w\sum_J\sum_L\sum_s\sum_r\sum_p\sum_t a_{wJLsrpt} \times\mathscr{H}(\mathscr{Z}_2,\mathscr{Z}_3,\beta,\gamma,r_{23})r_{23}^{l+1+2J} \tag{43}$$

with

$$a_{wJLsrpt}\equiv\frac{A(w,J,L)b_{mws}b_{nwr}}{4^w(2w+1)\alpha^{\mathscr{Z}_1+1}}\binom{m-2w-2s}{p} \times\binom{n-2w-2r}{t}\mathscr{Z}_1!. \tag{44}$$

The a coefficient defined in Eq. (44) and the $\mathscr{Z}_2$, $\mathscr{Z}_3$ arguments in Eq. (43) depend on the particular permutations carried out. In Eq. (43), $\Sigma_{\mathscr{P}'}$ denotes $(1-P_{12}-P_{23})$, $\Sigma_{\mathscr{P}}\equiv\sqrt{6}\mathscr{A}$, and $\chi_{\mathscr{P}'\mathscr{P}}$ denotes the appropriate spin matrix element. From Eqs. (33b) and (38),

$$\mathscr{H}(\mathscr{Z}_2,\mathscr{Z}_3,\beta,\gamma,r_{23})=e^{-\beta r_{23}}\sum_{m=0}^{\mathscr{Z}_2} a_1(\mathscr{Z}_2,\mathscr{Z}_3)r_{23}^m +e^{-\gamma r_{23}}\sum_{m=0}^{\mathscr{Z}_3} a_2(\mathscr{Z}_2,\mathscr{Z}_3)r_{23}^m, \tag{45}$$

$$\mathscr{H}(\mathscr{Z}_2,\mathscr{Z}_3,\beta,\beta,r_{23}) =e^{-\beta r_{23}}\sum_{m=0}^{\mathscr{Z}_2+\mathscr{Z}_3+1} a_3(\mathscr{Z}_2,\mathscr{Z}_3)r_{23}^m, \tag{46}$$

where the coefficients a_i can be identified from Eqs. (33b) and (38). The coefficient $a_3(\mathscr{Z}_2,\mathscr{Z}_3)$ will have a dependence on the delta factors introduced in Eqs. (21) and (22). With the information in Table I, Eq. (43) can be reduced to the form

$$P(r_{23})=\sum_{K=1}^{g_1} \mathscr{A}_{1K}r_{23}^K e^{-(\alpha+\gamma)r_{23}}+\sum_{K=1}^{g_2} \mathscr{A}_{2K}r_{23}^K e^{-2\alpha r_{23}} +\sum_{K=1}^{g_3} \mathscr{A}_{3K}r_{23}^K e^{-2\gamma r_{23}}, \tag{47}$$

i.e.,

$$P(r_{23})=\sum_{I=1}^{3}\sum_{K=1}^{g_I} \mathscr{A}_{IK}r_{23}^K e^{-\alpha_I r_{23}}. \tag{48}$$

The reduction procedure is similar to what the authors have done previously for the electronic density function.[31] The $\mathscr{A}_{IK}$ coefficients can be obtained from Eq. (43) using the information of Table I. For example,

$$\mathscr{A}_{1K}=32\pi^3\sum_u\sum_v C_uC_v\left(\sum_{\mathscr{P}=1}^{4} S_{\mathscr{P}}\sum_w\sum_J\sum_L\sum_s\sum_r\sum_p\sum_t\sum_m a_{wJLsrpt}a_3 +\sum_{\mathscr{P}=1}^{6} S_{\mathscr{P}}\sum_w\sum_J\sum_L\sum_s\sum_r\sum_p\sum_t\sum_m a_{wJLsrpt}a_2+\sum_{\mathscr{P}=1}^{2} S_{\mathscr{P}}\cdots a_{wJLsrpt}a_1\right). \tag{49}$$

In Eq. (49), each sum over $\mathscr{P}$ designates the set of permutations giving rise to $\beta=\gamma$ with $\gamma\Rightarrow\alpha+\gamma$, or $\beta\neq\gamma$ and $\gamma\Rightarrow\alpha+\gamma$, or $\beta\neq\gamma$ and $\beta\Rightarrow\alpha+\gamma$. $S_{\mathscr{P}}$ denotes the appropriate spin matrix element for each combination of permutations with the parity factors from the permutations incorporated with this factor. Similar expressions can be written for $\mathscr{A}_{2K}$ and $\mathscr{A}_{3K}$. It should be kept in mind that the multiple sum combinations over w, J,... depends explicitly on the particular combination of permutations made, and hence these eight nested summations cannot be simply factored in Eq. (49). The summation limits g_I that appear in Eq. (48) are determined by the exact choice of basis functions employed in the Hylleraas expansion.

III. EXPECTATION VALUES $\langle r_{ij}^n\rangle$

The moments $\langle r_{ij}^n\rangle$ are defined by

$$\langle r_{ij}^n\rangle\equiv\left\langle \Psi\left|\sum_{i=1}^{3}\sum_{j>i}^{3} r_{ij}^n\right|\Psi\right\rangle. \tag{50}$$

Given the formula for $P(r_{ij})$ in Eq. (48), then

$$\langle r_{ij}^n\rangle=\int_0^\infty P(r_{ij})r_{ij}^n dr_{ij} =\sum_{I=1}^{3}\sum_{K=1}^{g_I} \mathscr{A}_{IK}(n+K)!\,\alpha_I^{-(n+K+1)}, \quad \text{for } n\geqslant -1. \tag{51}$$

For the special case $n=-2$,

$$\langle r_{ij}^n\rangle=\sum_{I=1}^{3}\sum_{K=1}^{g_I} \mathscr{A}_{IK}\int_0^\infty r_{ij}^{K-2}e^{-\alpha_I r_{ij}}dr_{ij} =\sum_{I=1}^{3} \mathscr{A}_{I1}\int_0^\infty r_{ij}^{-1}e^{-\alpha_I r_{ij}}dr_{ij} +\sum_{I=1}^{3}\sum_{K=2}^{g_I} \mathscr{A}_{IK}(n+K)!\,\alpha_I^{-(n+K+1)}. \tag{52}$$

The first term in Eq. (52) can be simplified by noting

$$\sum_{I=1}^{3} \mathscr{A}_{I1}=0, \tag{53}$$

which is proved in the Appendix. Then

$$\sum_{I=1}^{3} \mathscr{A}_{I1}\int_0^\infty r_{ij}^{-1}e^{-\alpha_I r_{ij}}dr_{ij} =\sum_{I=1}^{2} \mathscr{A}_{I1}\int_0^\infty\left(\frac{e^{-\alpha_I r_{ij}}-e^{-\alpha_3 r_{ij}}}{r_{ij}}\right)dr_{ij} =\sum_{I=1}^{2} \mathscr{A}_{I1}\ln(\alpha_3/\alpha_I). \tag{54}$$

IV. CALCULATION OF $h(0)$ AND THE CUSP CONDITION

The spherical average of the intracule function is given by[32]

$$h(r_{ij})=\frac{1}{4\pi}r_{ij}^{-2}P(r_{ij}), \tag{55}$$

and hence

TABLE II. Exponents and nonrelativistic energies for the wave functions employed in the present study.

Species	Number of terms	Orbital exponents		Energy (a.u.)	
		α	γ	Present work	Literature
Li	120	2.76	0.65	−7.474 060	−7.478 060[a]
Be^+	91	3.80	1.15	−14.319 997	−14.324 760[b]
B^{2+}	111	4.65	1.60	−23.419 437	−23.424 604[c]
F^{6+}	110	8.97	3.77	−82.324 900	−82.330 336[c]
Ne^{7+}	110	9.97	4.28	−102.676 684	−102.682 229[c]

[a]Value from Ref. 36.
[b]Value from Ref. 37.
[c]Values from Ref. 38.

$$h(0)=\frac{1}{4\pi}\lim_{r_{ij}\to 0}\left[\frac{P(r_{ij})}{r_{ij}^2}\right]=\frac{1}{4\pi}\sum_{I=1}^{3}(\mathscr{A}_{I2}-\alpha_I\mathscr{A}_{I1}) \tag{56}$$

and the use of Eq. (53) has been employed to obtain Eq. (56). The expectation value $\langle\delta(\mathbf{r}_{ij})\rangle$ is given by

$$\langle\delta(\mathbf{r}_{ij})\rangle=\left[\frac{P(r_{ij})}{4\pi r_{ij}^2}\right]_{r_{ij}\to 0}=h(0). \tag{57}$$

The cusp condition for h can be written as[33,34]

$$\left.\frac{\partial h(r_{ij})}{\partial r_{ij}}\right|_{r_{ij}\to 0}=h(r_{ij})|_{r_{ij}\to 0}. \tag{58}$$

Evaluation of the derivative leads to

$$\left.\frac{\partial h(r_{ij})}{\partial r_{ij}}\right|_{r_{ij}\to 0}=\frac{1}{4\pi}\sum_{I=1}^{3}\left(\frac{\alpha_I^2}{2}\mathscr{A}_{I1}-\alpha_I\mathscr{A}_{I2}+\mathscr{A}_{I3}\right). \tag{59}$$

If the cusp condition is satisfied, then the following result should hold:

$$\sum_{I=1}^{3}\left[\mathscr{A}_{I3}-(1+\alpha_I)\mathscr{A}_{I2}+\left(\alpha_I+\frac{\alpha_I^2}{2}\right)\mathscr{A}_{I1}\right]=0. \tag{60}$$

For the basis set selected in the present study, the cusp condition does not hold. In fact

$$\left.\frac{\partial h(r_{ij})}{\partial r_{ij}}\right|_{r_{ij}\to 0}=0 \tag{61}$$

for the wave functions employed. This result can be demonstrated rigorously in the following manner. From Eq. (33), it can be shown that

$$\mathscr{H}(i,j,\beta,\gamma,r_{23})=a_1r_{23}+a_2r_{23}^2+a_3r_{23}^3+\cdots \tag{62}$$

and an analogous result also holds for the case $\beta=\gamma$ in Eq. (38). In Appendix B, it is demonstrated that the coefficient of r_{23}^2 is zero. Now an examination of Eq. (26) leads to the result

$$\left.\frac{\partial h(r_{23})}{\partial r_{23}}\right|_{r_{23}\to 0}\sim\lim_{r_{23}\to 0}\frac{\partial}{\partial r_{23}}[r_{23}^{-2}(r_{23}^{l+1+2J})\times(a_1r_{23}+a_2r_{23}^2+\cdots)]. \tag{63}$$

For $J>0$, the right-hand side of Eq. (63) equals zero, so the only case of interest is $J=0$, and hence

$$\left.\frac{\partial h(r_{23})}{\partial r_{23}}\right|_{r_{23}\to 0}\sim\lim_{r_{23}\to 0}[a_1lr_{23}^{l-1}+a_2(l+1)r_{23}^l+\cdots]. \tag{64}$$

The right-hand side of Eq. (64) vanishes for $l\geqslant 2$; that leaves the cases $l=0$ and $l=1$ to consider. The case $l=1$ is excluded by the restriction imposed on the basis functions so that Eq. (24) could be employed. For the case $l=0$, Eq. (61) holds because $a_2=0$ (see Appendix B), which means the cusp condition cannot be satisfied. That is, a wave function with all even powers of the interelectronic coordinates cannot satisfy the cusp condition given in Eq. (58).

V. COMPUTATIONAL DETAILS

The method set out in Sec. II was applied to the ground state of the Li atom and some members of its isoelectronic series that included Be^+, B^{2+}, F^{6+}, and Ne^{7+}. The size of the wave functions and a rough idea of their quality (in the energetic sense) is given in Table II. The fixed set of exponents employed for the wave functions are also indicated in Table II. The sets of coefficients $\mathscr{A}_{IK}$ and exponents α_I for each system can be obtained from the Physics Auxiliary Publication Service.[35]

The particular basis sets employed can be obtained by writing the authors. All the calculations were carried out in double precision.

VI. RESULTS AND DISCUSSION

Table III reports a selection of moments $\langle r_{ij}^n\rangle$ for n in the range −2 to 4. Also reported in Table III are values for the expectation value $\langle\delta(\mathbf{r}_{ij})\rangle$. For the moments $\langle r_{ij}^n\rangle$ for $n=-1$, 1, and 2, it was possible to compare values determined from Eq. (50) with those computed from $P(r_{ij})$ using Eq. (51). This provided a valuable check on both the algebraic formulation and the computer code.

In Table III, a comparison is made for the moments $\langle r_{ij}^n\rangle$ for $n=-1$, 1, and 2 computed using Eq. (51) with values obtained from large scale Hylleraas-type wave functions. The comparisons are generally fairly satisfactory and improve with increasing nuclear charge. The quality of the moments $\langle r_{ij}^{-2}\rangle$ is less certain. The only point of comparison

TABLE III. Expectation values determined from Eqs. (51), (52), and (57).

	Expectation values									
Species	$\langle r_{ij}^{-2}\rangle$	$\langle r_{ij}^{-1}\rangle$	$\langle r_{ij}^{-1}\rangle_{\mathrm{lit}}$ [a]	$\langle r_{ij}\rangle$	$\langle r_{ij}\rangle_{\mathrm{lit}}$ [a]	$\langle r_{ij}^{2}\rangle$	$\langle r_{ij}^{2}\rangle_{\mathrm{lit}}$ [a]	$\langle r_{ij}^{3}\rangle$	$\langle r_{ij}^{4}\rangle$	$\langle \delta(\mathbf{r}_{ij})\rangle$
Li	4.50	2.204	2.198	8.680	8.668	36.95	36.84	192.8	1161	0.6354
Be^+	9.09	3.254	3.246	5.270	5.267	13.09	13.07	39.49	136.7	1.776
B^{2+}	15.3	4.287	4.278	3.837	3.836	6.829	6.825	14.70	36.21	3.815
F^{6+}	56.0	8.391	8.380	1.863	1.863	1.576	1.576	1.603	1.860	26.18
Ne^{7+}	70.2	9.415	9.405	1.652	1.652	1.237	1.237	1.113	1.141	36.65

[a]Literature values taken from Refs. 37 and 38.

available is an unpublished value for the ground state of Li, $\langle r_{ij}^{-2}\rangle=4.38$, obtained from a fairly compact Hylleraas-type wave function. The value reported in Table III is approximately 2.7% higher. Values of $\langle r_{ij}^{-2}\rangle$ for the Li I series are rather difficult to compute when a Hylleraas-type expansion is employed because of the tough integration problems that emerge. A number of these problems have recently been resolved.[39–42] It is probably wise to treat the reported values of $\langle r_{ij}^{-2}\rangle$ with some caution because the basis sets employed may not give a totally satisfactory description of the near-nuclear region of configuration space.

The general central processing unit (CPU) cost of determining moments $\langle r_{ij}^{n}\rangle$ directly from the wave function [Eq. (50)] is significant and this is particularly so for the case of $\langle r_{ij}^{-2}\rangle$. The approach outlined in this work allows all the moments $\langle r_{ij}^{n}\rangle$ (excluding $\langle r_{ij}^{-1}\rangle$ which is needed to obtain the variational expansion coefficients) and $\langle \delta(\mathbf{r}_{ij})\rangle$ to be determined at minimal CPU costs.

A check was made that Eq. (61) holds for the basis sets employed in this study. Equation (61) was verified for each species, allowing for minor round-off errors.

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APPENDIX A

This appendix proves the result

$$\sum_{l=1}^{3} \mathscr{A}_{l1}=0, \tag{A1}$$

which is used in the evaluation of the moment $\langle r_{ij}^{-2}\rangle$ and the cusp condition. Consider first the case of Eq. (26) when $\beta=\gamma$. Examining Eq. (38) and keeping in mind the minimum values of the arguments i and j [see Eqs. (29) and (30)] indicates the series behaves like r_{23}+higher powers of r_{23}. If this is combined with the result from Eq. (26), then $P(r_{23})\sim r_{23}^2$+higher order terms. This implies Eq. (A1). For the case $\beta\neq\gamma$, Eq. (26) indicates that the first term behaves like r_{23}, so it is necessary to demonstrate that the coefficient $a_0=0$ for the expansion

$$\mathscr{H}(\mathscr{Z}_2,\mathscr{Z}_3,\beta,\gamma,r_{23})=a_0+a_1 r_{23}+\text{higher order terms.} \tag{A2}$$

By inspection of Eqs. (34) and (35), it follows that

$$C_{ij}(l,0,\beta,\gamma)=-D_{ij}(l,0,\beta,\gamma). \tag{A3}$$

Now if the factors $e^{-\beta r_{23}}$ and $e^{-\gamma r_{23}}$ in Eq. (33) are expanded as a power series, then

$$\mathscr{H}(i,j,\beta,\gamma,r_{23}) \sim j!\left\{\sum_{l=0}^{j}[C_{ij}(l,0,\beta,\gamma)+D_{ij}(l,0,\beta,\gamma)]\gamma^{-l-1}\right\} + \text{higher order terms in } r_{23}. \tag{A4}$$

Using Eq. (A3) in Eq. (A4) leads to the result that

$$\mathscr{H}(i,j,\beta,\gamma,r_{23})=a_1 r_{23}+\text{higher order terms,}$$

i.e., $a_0=0$, and hence Eq. (A1) follows.

APPENDIX B

This appendix demonstrates that the coefficients a_2 and a_2' in each of the following equations:

$$\mathscr{H}(i,j,\alpha,\beta,r_{23})=a_1 r_{23}+a_2 r_{23}^2+a_3 r_{23}^3+\cdots, \tag{B1}$$

$$\mathscr{H}(i,j,\alpha,\alpha,r_{23})=a_1' r_{23}+a_2' r_{23}^2+a_3' r_{23}^3+\cdots \tag{B2}$$

is equal to zero. We consider Eq. (B1) first. Expanding the exponential term in Eq. (33) leads to Eq. (B1) and allows a_2 to be identified as

$$a_2=\sum_{l=0}^{\min(j,i+j-2)} C(l,2)\beta^{-l-1}+\sum_{l=0}^{j-2} D(l,2)\beta^{-l-1} -\alpha\sum_{l=0}^{\min(j,i+j-1)} C(l,1)\beta^{-l-1}-\beta\sum_{l=0}^{j-1} D(l,1)\beta^{-l-1} +\frac{\alpha^2}{2}\sum_{l=0}^{\min(j,i+j)} C(l,0)\beta^{-l-1}+\frac{\beta^2}{2}\sum_{l=0}^{j} D(l,0)\beta^{-l-1}. \tag{B3}$$

In Eq. (B3) and the remaining equations in Appendix B, the additional ij label on the C, D, E, F, and G functions will be dropped, as well as the functional dependence on β and α. Keeping in mind that i and j take a minimum value of 1 [see Eqs. (29) and (30)], then Eq. (B3) can be written as

$$a_2=\sum_{l=0}^{j-2}\beta^{-l-1}\left[C(l,2)+D(l,2)-\alpha C(l,1)-\beta D(l,1)+\frac{1}{2}(\alpha^2-\beta^2)C(l,0)\right]+\beta^{-j-1}[\Delta_{i,2}C(j,2)-\alpha C(j,1)+\tfrac{1}{2}(\alpha^2-\beta^2)C(j,0)]+\beta^{-j}[C(j-1,2)-\alpha C(j-1,1)-\beta D(j-1,1)+\tfrac{1}{2}(\alpha^2-\beta^2)C(j-1,0)]. \tag{B4}$$

Using the definitions of the C and D functions given in Eqs. (34) and (35), it is possible to prove that

$$C(l,2)+D(l,2)-\alpha C(l,1)-\beta D(l,1)+\tfrac{1}{2}(\alpha^2-\beta^2)C(l,0)=0,\quad \text{for}\quad l\leqslant j-2, \tag{B5}$$

$$\Delta_{i,2}C(j,2)-\alpha C(j,1)+\tfrac{1}{2}(\alpha^2-\beta^2)C(j,0)=0, \tag{B6}$$

and

$$C(j-1,2)-\alpha C(j-1,1)-\beta D(j-1,1)+\tfrac{1}{2}(\alpha^2-\beta^2)\times C(j-1,0)=0, \tag{B7}$$

which for the case $\alpha\neq\beta$ proves

$$a_2=0. \tag{B8}$$

Expanding the exponential term in Eq. (38) allows us to establish a_2' in Eq. (B2) as

$$a_2'=\sum_{l=0}^{\min(j,i+j-2)}E(l,2)\alpha^{-l-1}+\delta_{i,1}F(j)\alpha^{-j-1}-\sum_{l=0}^{j-2}G(l,2)\alpha^{-l-1}-\sum_{l=0}^{\min(j,i+j-1)}E(l,i)\alpha^{-l}+\sum_{l=0}^{j-1}G(l,1)\alpha^{-l} \tag{B9}$$

$$=\sum_{l=0}^{j-2}\alpha^{-l-1}[E(l,2)-G(l,2)+\alpha G(l,1)-\alpha E(l,1)]+\alpha^{-j-1}\{\Delta_{i,2}E(j,2)+\alpha E(j-1,2)+\delta_{i,1}F(j)-\alpha E(j,1)+\alpha^2[G(j-1,1)-E(j-1,1)]\}. \tag{B10}$$

Utilizing the definitions given in Eqs. (39), (40), and (41), it can be shown that

$$E(l,2)-G(l,2)+\alpha G(l,1)-\alpha E(l,1)=0,\quad \text{for}\quad l\leqslant j-2 \tag{B11}$$

and

$$\Delta_{i,2}E(j,2)+\delta_{i,1}F(j)+\alpha[E(j-1,2)-E(j,1)]+\alpha^2[G(j-1,1)-E(j-1,1)]=0. \tag{B12}$$

Hence from Eq. (B10),

$$a_2'=0. \tag{B13}$$

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