Resolution of some mathematical problems arising in the relativistic treatment of the *S* states of three-electron systems

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Some of the mathematical difficulties that arise in the evaluation of the Breit–Pauli relativistic energy corrections for the *S* states of three-electron systems are resolved. Evaluation of the expectation value of the Breit–Pauli Hamiltonian using explicitly correlated wave functions leads to sets of integrals that diverge individually. By appropriately combining these integrals, and using some judicious series expansions, all the integration problems are resolved in terms of well-known auxiliary functions. © *1998 American Institute of Physics.* [S0022-2488(98)02512-2]

I. INTRODUCTION

There has been considerable progress over the past ten years on the calculation of high-precision properties of the lithium atom and other members of the Li isoelectronic series (for a recent summary of this progress see Refs. 1 and 2). A large part of this effort has been achieved using Hylleraas (or configuration interaction (CI)-Hylleraas) type wave functions.

One important property that has received limited theoretical attention is the high-precision calculation of the relativistic correction to the energy, ΔE_{REL}. This is a key contribution in determining a precise theoretical estimate of the first ionization potential. At present, the only calculations of the relativistic correction to the ground state energy for the lithium atom are due to Chung,[3] who used the CI technique, the very recent paper of Yan and Drake using the Hylleraas technique,[4] and the work of King *et al.*,[5] who also employed the Hylleraas method. Chung's calculation required a significant core correction, determined by first computing the relativistic correction for Li^+, and then comparing with precise calculations for Li^+ using Hylleraas-type wave functions.[6,7] This core correction was then applied directly to the Li calculation. A very effective approach to obtaining high-precision estimates of ΔE_{REL} is to make use of large-scale Hylleraas-type expansions. Progress in this area has been hampered by the mathematical difficulties which arise for the operators

$$H_{\mathrm{mass}} = -\frac{\alpha^2}{8}\sum_{i=1}^{3}\nabla_i^4, \tag{1a}$$

$$H_{\mathrm{oo}} = \frac{\alpha^2}{2}\sum_{i=1}^{3}\sum_{j>i}^{3}\frac{1}{r_{ij}}\left(\nabla_i\cdot\nabla_j + \frac{\mathbf{r}_{ij}\cdot(\mathbf{r}_{ij}\cdot\nabla_i)\nabla_j}{r_{ij}^2}\right), \tag{1b}$$

where α is the fine structure constant and r_{ij} is the interelectronic separation. For the three-electron problem, evaluation of the matrix elements of H_{mass} or H_{oo} [in the form displayed in Eqs. (1a) and (1b)] using a general Hylleraas expansion can be shown to involve the following integrals:

$$I(i,j,k,l,m,n,\alpha,\beta,\gamma) \equiv \int r_1^i r_2^j r_3^k r_{23}^l r_{31}^m r_{12}^n e^{-\alpha r_1 - \beta r_2 - \gamma r_3}\, d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{r}_3, \tag{2}$$

where $i,j,k \geqslant -2$, $l \geqslant -2$, $m \geqslant -2$, and $n \geqslant -1$;

$$I_1(i,j,k,l,m,\alpha,\beta,\gamma)\equiv\int r_1^i r_2^j r_3^k\left(\frac{r_1^2-r_2^2}{r_{12}^3}\right)r_{23}^l r_{31}^m e^{-\alpha r_1-\beta r_2-\gamma r_3}\,d\mathbf{r}_1\,d\mathbf{r}_2\,d\mathbf{r}_3, \tag{3}$$

$$I_2(i,j,k,l,m,\alpha,\beta,\gamma)\equiv\int r_1^i r_2^j r_3^k\left(\frac{r_{31}^2-r_{23}^2}{r_{12}^3}\right)r_{23}^l r_{31}^m e^{-\alpha r_1-\beta r_2-\gamma r_3}\,d\mathbf{r}_1\,d\mathbf{r}_2\,d\mathbf{r}_3, \tag{4}$$

and

$$I_3(i,j,k,l,m,\alpha,\beta,\gamma)\equiv\int r_1^i r_2^j r_3^k\left(\frac{r_1^2-r_2^2}{r_{12}^2}\right)r_{23}^l r_{31}^m e^{-\alpha r_1-\beta r_2-\gamma r_3}\,d\mathbf{r}_1\,d\mathbf{r}_2\,d\mathbf{r}_3, \tag{5}$$

where $i,j,k\geqslant -2$, $l\geqslant -1$, and $m\geqslant 1$. The combination of terms displayed in Eqs. (3) and (4) is essential, if a finite value of the expectation value of the Breit–Pauli Hamiltonian is to be obtained using a first-order perturbation theory approach. For Eq. (2) and some related generalizations, several evaluation approaches exist in the literature for the case where l, m, and n are $\geqslant -1$,[8–18] and for the more difficult cases involving $l=-2$ (and $m=-2$).[19–24] Some of the published techniques could be applied to evaluate I_3.

The purpose of this paper is to present an efficient method for the evaluation of the integrals I_1, I_2, and I_3. The integrals are evaluated for the cases $i,j,k\geqslant -2$, $l\geqslant -1$, and $m\geqslant -1$. The obvious reduction of the I_1 and I_2 integrals into a difference of I integrals is not possible, because the separate I integrals both diverge. This is discussed further in Appendix A. While I_3 could be calculated by taking a difference of I integrals, a computationally superior approach is discussed in Sec. IV. The solution method is to reduce each of the integrals to a series of well-known auxiliary functions.

II. EVALUATION OF I_1

To evaluate I_1, the following expansions are employed:[25–27]

$$r_{23}^l=\sum_{w_2=0}^{\infty} R_{lw_2}(r_2,r_3)P_{w_2}(\cos\,\theta_{23}), \tag{6}$$

$$r_{31}^m=\sum_{w_3=0}^{\infty} R_{mw_3}(r_1,r_3)P_{w_3}(\cos\,\theta_{31}), \tag{7}$$

and

$$\frac{1}{r_{12}^3}=\frac{1}{r_{12>}^2-r_{12<}^2}\sum_{w_1=0}^{\infty}(2w_1+1)\,\frac{r_{12<}^{w_1}}{r_{12>}^{w_1+1}}\,P_{w_1}(\cos\,\theta_{12}). \tag{8}$$

Equations (6) and (7) are the Sack expansions for the interelectron coordinates.[25] Equation (8) is discussed in Appendix B. Here $r_{12<}$ denotes the lesser of (r_1,r_2), $r_{12>}$ represents the greater of (r_1,r_2), and $P_n(x)$ designates a Legendre polynomial throughout this work.

Substituting Eqs. (6), (7), and (8) into Eq. (3) gives

$$I_1=\sum_{w_1=0}^{\infty}\sum_{w_2=0}^{\infty}\sum_{w_3=0}^{\infty}(2w_1+1)I_R(w_1,w_2,w_3)I_\Omega(w_1,w_2,w_3), \tag{9}$$

where I_R is the integral over the radial coordinates,

$$I_R(w_1,w_2,w_3)=\int r_1^{i+2}r_2^{j+2}r_3^{k+2}r_{12<}^{w_1}r_{12>}^{-w_1-1}\left(\frac{r_1^2-r_2^2}{r_{12>}^2-r_{12<}^2}\right)R_{lw_2}(r_2,r_3)$$
$$\times R_{mw_3}(r_1,r_3)e^{-\alpha r_1-\beta r_2-\gamma r_3}\,dr_1\,dr_2\,dr_3, \tag{10}$$

and I_Ω is the integral over the angular variables,

$$I_\Omega(w_1,w_2,w_3)=\int P_{w_1}(\cos\,\theta_{12})P_{w_2}(\cos\,\theta_{23})P_{w_3}(\cos\,\theta_{31})d\Omega_1\;d\Omega_2\;d\Omega_3. \tag{11}$$

The functional dependence of I_R on $\{i,j,k,l,m,\alpha,\beta,\gamma\}$ is suppressed to simplify the notation. Expanding the Legendre polynomials in terms of spherical harmonics, the angular integral simplifies to

$$I_\Omega(w_1,w_2,w_3)=\frac{64\pi^3}{(2w_1+1)^2}\;\delta_{w_1w_2}\delta_{w_2w_3}, \tag{12}$$

where δ_{ij} denotes a Kronecker delta. Equation (9) now becomes

$$I_1=64\pi^3\sum_{w_1=0}^{\infty}\;\frac{I_R(w_1)}{(2w_1+1)}, \tag{13}$$

where $I_R(w_1)\equiv I_R(w_1,w_1,w_1)$.

To evaluate the radial integral the formulas for the Sack radial functions are employed:[25]

$$R_{lw_1}(r_2,r_3)=\sum_{p=0}^{\infty}\;a_{w_1lp}r_{23<}^{w_1+2p}r_{23>}^{l-w_1-2p} \tag{14}$$

and

$$R_{mw_1}(r_1,r_3)=\sum_{q=0}^{\infty}\;a_{w_1mq}r_{31<}^{w_1+2q}r_{31>}^{m-w_1-2q}, \tag{15}$$

where

$$a_{tuv}=\frac{(-u/2)_t(t-u/2)_v(-1/2-u/2)_v}{(1/2)_t v!(t+3/2)_v} \tag{16}$$

and $(z)_n$ denotes a Pochhammer symbol. Inserting Eqs. (14) and (15) into Eq. (10) gives

$$\begin{aligned}I_R(w_1)=\sum_{p=0}^{\infty}\sum_{q=0}^{\infty}\;a_{w_1lp}a_{w_1mq}\int\;&r_1^{i+2}r_2^{j+2}r_3^{k+2}r_{12<}^{w_1}r_{12>}^{-w_1-1}\left(\frac{r_1^2-r_2^2}{r_{12>}^2-r_{12<}^2}\right)\\&\times r_{23<}^{w_1+2p}r_{23>}^{l-w_1-2p}r_{31<}^{w_1+2q}r_{31>}^{m-w_1-2q}e^{-\alpha r_1-\beta r_2-\gamma r_3}\;dr_1\;dr_2\;dr_3.\end{aligned} \tag{17}$$

If the integration in Eq. (17) is broken up into the six regions $r_i\leq r_j\leq r_k$, then I_1 can be written as

$$\begin{aligned}I_1(i,j,k,l,m,\alpha,\beta,\gamma)=64\pi^3\sum_{w=0}^{\infty}\;&\frac{1}{(2w+1)}\sum_{p=0}^{\infty}\sum_{q=0}^{\infty}\;a_{wlp}a_{wmq}\\&\times\{W(k+2+2p+2q+2w,j+2+l-2p,i+m+1-2q-2w,\gamma,\beta,\alpha)\\&+W(j+2+2w+2p,k+2+2q+l-2p,i+m+1-2q-2w,\beta,\gamma,\alpha)\\&+W(j+2+2w+2p,i+1+2q,k+m+l+2-2w-2p-2q,\beta,\alpha,\gamma)\\&-W(i+2+2w+2q,j+1+2p,k+m+l+2-2w-2p-2q,\alpha,\beta,\gamma)\\&-W(i+2+2w+2q,k+2+m-2q+2p,j+1+l-2w-2p,\alpha,\gamma,\beta)\\&-W(k+2+2p+2q+2w,i+2+m-2q,j+1+l-2w-2p,\gamma,\alpha,\beta)\},\end{aligned} \tag{18}$$

where

$$W(L,M,N,a,b,c)=\int_0^\infty x^L e^{-ax}\,dx\int_x^\infty y^M e^{-by}\,dy\int_y^\infty z^N e^{-cz}\,dz. \tag{19}$$

The W integrals have been well studied in the literature,[8,9,13,16,28–30] and efficient algorithms exist for the evaluation of these auxiliary functions.

We now examine the summation limits of the w, p, and q sums of Eq. (18). Because of the following property of the Pochhammer symbol,

$$(-k)_l=0, \quad l>k \text{ for positive integer } k, \tag{20}$$

the p summation terminates at $(l+1)/2$ for odd l, and $(l/2)-w$ for even l. Similarly, the q summation terminates at $(m+1)/2$ for odd m, and $(m/2)-w$ for even m. These conditions follow from the definition of a_{tuv} given in Eq. (16). This leads to the following termination conditions for the w sum:

$$\begin{aligned} &\frac{m}{2}, \quad m \text{ even and } n \text{ odd},\\ &\frac{n}{2}, \quad n \text{ even and } m \text{ odd},\\ \min&\left\{\frac{m}{2},\frac{n}{2}\right\}, \quad m \text{ and } n \text{ both even}. \end{aligned}$$

For m and n both odd, the w sum is nonterminating.

In addition to the individual constraints on i, j, k, l, and m mentioned in the Introduction, it is also necessary that

$$i+j+k+l+m\geqslant -7. \tag{21}$$

This follows directly from a known constraint on the arguments of the W integrals, namely

$$L+M+N\geqslant -2. \tag{22}$$

Yan and Drake[23] give a reduction formula [see their Eq. (128)] for a radial integral which is related to I_1. This radial integral is part of a nested sum, which for the general case would involve a double infinite sum.

III. EVALUATION OF I_2

For this integral, the coordinate system of choice is a three-dimensional analog of the one used by Hylleraas,[31] where the directions of the vectors $\mathbf{r}_1$ and $\mathbf{r}_2$ are given relative to $\mathbf{r}_3$. This method has been previously employed to consider other three-electron integration problems.[10] In this coordinate system the volume element becomes

$$d\mathbf{r}_1\,d\mathbf{r}_2\,d\mathbf{r}_3=r_1^2r_2^2r_3^2\,dr_1\,dr_2\,dr_3\,\sin\theta_3\,d\theta_3\,d\phi_3\,\sin\theta_{23}\,d\theta_{23}\,d\phi_{23}\,\sin\theta_{31}\,d\theta_{31}\,d\phi_{31}. \tag{23}$$

If $r_{31}^2-r_{23}^2$ is written as

$$r_{31}^2-r_{23}^2=r_1^2-r_2^2-2r_1r_3\cos\theta_{31}+2r_2r_3\cos\theta_{23}, \tag{24}$$

then I_2 may be expressed as

$$I_2(i,j,k,l,m,\alpha,\beta,\gamma)=I_1(i,j,k,l,m,\alpha,\beta,\gamma)-2J_1(i,j,k,l,m,\alpha,\beta,\gamma), \tag{25}$$

where

$$J_1(i,j,k,l,m,\alpha,\beta,\gamma)=\int r_1^i r_2^j r_3^{k+1}\left(\frac{r_1\cos\theta_{31}-r_2\cos\theta_{23}}{r_{12}^3}\right) r_{23}^l r_{31}^m e^{-\alpha r_1-\beta r_2-\gamma r_3}\, d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{r}_3. \tag{26}$$

J_1 is simplified by substituting Eqs. (6), (7), (8), (14), and (15) into Eq. (26) and integrating over θ_3 and ϕ_3 to obtain

$$J_1=4\pi\sum_{w_1=0}^{\infty}(2w_1+1)\sum_{w_2=0}^{\infty}\sum_{w_3=0}^{\infty}\sum_{p=0}^{\infty}\sum_{q=0}^{\infty} a_{w_2lp}a_{w_3mq}\int r_1^{i+2}r_2^{j+2}r_3^{k+3}r_{23<}^{w_2+2p}r_{23>}^{l-w_2-2p}$$
$$\times r_{31<}^{w_3+2q}r_{31>}^{m-w_3-2q}r_{12<}^{w_1}r_{12>}^{-w_1-1}\left(\frac{r_1\Phi_1-r_2\Phi_2}{r_{12>}^2-r_{12<}^2}\right)e^{-\alpha r_1-\beta r_2-\gamma r_3}\, dr_1\, dr_2\, dr_3, \tag{27}$$

where

$$\Phi_1=\int_0^{2\pi}d\phi_{23}\int_0^{2\pi}d\phi_{31}\int_0^{\pi}d\theta_{31}\sin\theta_{31}\int_0^{\pi}d\theta_{23}\sin\theta_{23}\cos\theta_{31}$$
$$\times P_{w_1}(\cos\theta_{12})P_{w_2}(\cos\theta_{23})P_{w_3}(\cos\theta_{31}) \tag{28}$$

and

$$\Phi_2=\int_0^{2\pi}d\phi_{23}\int_0^{2\pi}d\phi_{31}\int_0^{\pi}d\theta_{31}\sin\theta_{31}\int_0^{\pi}d\theta_{23}\sin\theta_{23}\cos\theta_{23}$$
$$\times P_{w_1}(\cos\theta_{12})P_{w_2}(\cos\theta_{23})P_{w_3}(\cos\theta_{31}). \tag{29}$$

Evaluation of the integrals Φ_1 and Φ_2 leads to

$$\Phi_1=\frac{16\pi^2\delta_{w_1w_2}}{2w_1+1}\left\{\frac{w_2}{4w_2^2-1}\,\delta_{w_2,w_3+1}+\frac{w_3}{4w_3^2-1}\,\delta_{w_3,w_2+1}\right\} \tag{30}$$

and

$$\Phi_2=\frac{16\pi^2\delta_{w_1w_3}}{2w_1+1}\left\{\frac{w_2}{4w_2^2-1}\,\delta_{w_2,w_3+1}+\frac{w_3}{4w_3^2-1}\,\delta_{w_3,w_2+1}\right\}. \tag{31}$$

The solution of these integrals is discussed in Appendix C. Substituting Eqs. (30) and (31) into Eq. (27) leads to

$$J_1=64\pi^3\sum_{w_2=0}^{\infty}\sum_{w_3=0}^{\infty}\sum_{p=0}^{\infty}\sum_{q=0}^{\infty} a_{w_2lp}a_{w_3mq}\int r_1^{i+2}r_2^{j+2}r_3^{k+3}r_{23<}^{w_2+2p}r_{23>}^{l-w_2-2p}r_{31<}^{w_3+2q}$$
$$\times r_{31>}^{m-w_3-2q}e^{-\alpha r_1-\beta r_2-\gamma r_3}\left(\frac{r_1 r_{12<}^{w_2}r_{12>}^{-w_2-1}-r_2 r_{12<}^{w_3}r_{12>}^{-w_3-1}}{r_{12>}^2-r_{12<}^2}\right)$$
$$\times\left[\frac{w_2}{4w_2^2-1}\,\delta_{w_2,w_3+1}+\frac{w_3}{4w_3^2-1}\,\delta_{w_3,w_2+1}\right]dr_1\, dr_2\, dr_3. \tag{32}$$

Using the fact that

$$a_{(t+1)uv}=\left(\frac{2t+3}{2t+1}\right)\left(\frac{2t+2v-u}{2t+2v+3}\right)a_{tuv} \tag{33}$$

allows I_2 to be simplified to

$$I_2(i,j,k,l,m,\alpha,\beta,\gamma)=I_1(i,j,k,l,m,\alpha,\beta,\gamma)$$
$$+128\pi^3\sum_{w=0}^{\infty}\frac{(w+1)}{(2w+1)^2}\sum_{q=0}^{\infty}\sum_{p=0}^{\infty}a_{wmq}a_{wlp}\Bigg[\left(\frac{2w+2p-l}{2w+2p+3}\right)$$
$$\times\{W(i+2+2w+2q,j+1+2p,k+m+l+2-2w-2p-2q,\alpha,\beta,\gamma)$$
$$+W(i+2+2w+2q,k+m+4+2p-2q,j+l-1-2w-2p,\alpha,\gamma,\beta)$$
$$+W(k+4+2w+2p+2q,i+m+2-2q,j+l-1-2w-2p,\gamma,\alpha,\beta)\}$$
$$-\left(\frac{2w+2q-m}{2w+2q+3}\right)\{W(j+2+2w+2p,i+1+2q,k+m$$
$$+l+2-2w-2p-2q,\beta,\alpha,\gamma)$$
$$+W(j+2+2w+2p,k+4+l-2p+2q,i+m-1-2w-2q,\beta,\gamma,\alpha)$$
$$+W(k+4+2w+2p+2q,j+2+l-2p,i+m-1-2w-2q,\gamma,\beta,\alpha)\}\Bigg].\tag{34}$$

Equation (34) represents the solution to I_2. The summation limits of the w, p, and q sums are the same as those for the I_1 integral. The constraint given in Eq. (21) also applies for Eq. (34).

VI. EVALUATION OF I_3

The generating function for the Chebyshev polynomials of the first kind is

$$\frac{1-r^2}{1-2rx+r^2}=1+2\sum_{w_1=1}^{\infty}r^{w_1}T_{w_1}(x).\tag{35}$$

Letting $r=r_{12<}/r_{12>}$ and $x=\cos\,\theta_{12}$ in Eq. (35) yields

$$\frac{1}{r_{12}^2}=\frac{1}{r_{12>}^2-r_{12<}^2}\left[1+2\sum_{w_1=1}^{\infty}\left(\frac{r_{12<}}{r_{12>}}\right)^{w_1}T_{w_1}(\cos\,\theta_{12})\right].\tag{36}$$

Substituting Eqs. (6), (7), and (36) into Eq. (5) leads to the result

$$I_3=F(i,j,k,l,m,\alpha,\beta,\gamma)+2\sum_{w_1=1}^{\infty}\sum_{w_2=0}^{\infty}\sum_{w_3=0}^{\infty}I_\Omega(w_1,w_2,w_3)I_R(w_1,w_2,w_3),\tag{37}$$

where

$$F(i,j,k,l,m,\alpha,\beta,\gamma)=\sum_{w_2=0}^{\infty}\sum_{w_3=0}^{\infty}\int r_1^ir_2^jr_3^k\left(\frac{r_1^2-r_2^2}{r_{12>}^2-r_{12<}^2}\right)R_{lw_2}(r_2,r_3)R_{mw_3}(r_3,r_1)$$
$$\times P_{w_2}(\cos\,\theta_{23})P_{w_3}(\cos\,\theta_{31})d\mathbf{r}_1\,d\mathbf{r}_2\,d\mathbf{r}_3,\tag{38}$$

$$I_\Omega=\int T_{w_1}(\cos\,\theta_{12})P_{w_2}(\cos\,\theta_{23})P_{w_3}(\cos\,\theta_{31})d\Omega_1\,d\Omega_2\,d\Omega_3\tag{39}$$

and

$$I_R=\int r_1^{i+2}r_2^{j+2}r_3^{k+2}r_{12<}^{w_1}r_{12>}^{-w_1}\left(\frac{r_1^2-r_2^2}{r_{12>}^2-r_{12<}^2}\right)R_{lw_2}(r_2,r_3)R_{mw_3}(r_3,r_1)dr_1\,dr_2\,dr_3.\tag{40}$$

Employing Eqs. (14) and (15), and expanding the Legendre polynomials in terms of spherical harmonics, Eq. (38) may be easily evaluated to yield

$$F(i,j,k,l,m,\alpha,\beta,\gamma)=64\pi^3\sum_{p=0}^{\infty}\sum_{q=0}^{\infty}a_{0lp}a_{0mq}$$
$$\times\{W(k+2+2p+2q,j+2+l-2p,i+m+2-2q,\gamma,\beta,\alpha)$$
$$+W(j+2+2p,k+2+l-2p+2q,i+m+2-2q,\beta,\gamma,\alpha)$$
$$+W(j+2+2p,i+2+2q,k+m+l+2-2p-2q,\beta,\alpha,\gamma)$$
$$-W(i+2+2q,j+2+2p,k+m+l+2-2p-2q,\alpha,\beta,\gamma)$$
$$-W(i+2+2q,k+m+2+2p-2q,j+l+2-2p,\alpha,\gamma,\beta)$$
$$-W(k+2+2p+2q,i+m+2-2q,j+l+2-2p,\gamma,\alpha,\beta)\}. \quad (41)$$

Due to the property of the Pochhammer symbol given in Eq. (20), the p summation in Eq. (41) will terminate at $l/2$ for even l, and $(l+1)/2$ for odd l. Similarly, the q summation will terminate at $m/2$ for even m, and $(m+1)/2$ for odd m.

The integral I_Ω can be evaluated to give

$$I_\Omega=\frac{32\pi^3}{2w_2+1}\,\delta_{w_2w_3}\times\begin{cases}\dfrac{\sqrt{\pi}\Gamma(w_1+1)}{2\Gamma(w_1+\frac{3}{2})}, & w_1=w_2,\\[2ex] \dfrac{-w_1}{(w_1-w_2)(w_1+w_2+1)}\,\dfrac{\Gamma\left(\dfrac{w_1-w_2-1}{2}\right)\Gamma\left(\dfrac{w_1+w_2}{2}\right)}{\Gamma\left(\dfrac{w_1-w_2}{2}\right)\Gamma\left(\dfrac{w_1+w_2+1}{2}\right)}, & w_1\geqslant w_2+2,\quad w_1+w_2\ \text{even},\\[2ex] 0, & \text{elsewhere},\end{cases} \quad (42)$$

where $\Gamma(n)$ denotes the Gamma function. The evaluation of this integral is discussed in Appendix D. Since I_Ω is independent of $\{i,j,k,l,m,\alpha,\beta,\gamma\}$, it can be stored in table form to increase the computational speed of the integral evaluation. Equation (37) may now be written

$$I_3=F(i,j,k,l,m,\alpha,\beta,\gamma)+2\sum_{w_1=1}^{\infty}\sum_{w_2=0}^{w_1}I_\Omega(w_1,w_2)I_R(w_1,w_2), \quad (43)$$

where

$$I_\Omega(w_1,w_2)\equiv I_\Omega(w_1,w_2,w_2) \quad (44)$$

and

$$I_R(w_1,w_2)\equiv I_R(w_1,w_2,w_2). \quad (45)$$

Inserting Eqs. (14) and (15) into Eq. (43), then breaking up the region of integration as $r_i\leqslant r_j\leqslant r_k$, allows us to write Eq. (43) as

$$I_3(i,j,k,l,m,\alpha,\beta,\gamma)$$
$$=F(i,j,k,l,m,\alpha,\beta,\gamma)+2\sum_{\substack{w_1=1\\(w_1+w_2\ \text{even})}}^{\infty}\sum_{w_2=0}^{w_1} I_\Omega(w_1,w_2)\sum_{p=0}^{\infty}\sum_{q=0}^{\infty} a_{w_2lp}a_{w_2mq}$$
$$\times\{W(j+2+w_1+w_2+2p,i+2-w_1+w_2+2q,k+2+l+m-2w_2-2p-2q,\beta,\alpha,\gamma)$$
$$+W(j+2+w_1+w_2+2p,k+2+l-2p+2q,i+2-w_1+m-w_2-2q,\beta,\gamma,\alpha)$$
$$+W(k+2+2w_2+2p+2q,j+2+l+w_1-2p-w_2,i+2+m-w_1-w_2-2q,\gamma,\beta,\alpha)$$
$$-W(k+2+2w_2+2p+2q,i+2+w_1+m-w_2-2q,j+2-w_1+l-w_2-2p,\gamma,\alpha,\beta)$$
$$-W(i+2+w_1+w_2+2q,j+2-w_1+w_2+2p,k+2+l+m-2w_2-2p-2q,\alpha,\beta,\gamma)$$
$$-W(i+2+w_1+w_2+2q,k+2+m-2q+2p,j+2-w_1-w_2+l-2p,\alpha,\gamma,\beta)\}. \quad (46)$$

Due to properties of the Pochhammer symbol, the p summation in Eq. (46) will terminate at $l/2$ for even l, and $(l+1)/2$ for odd l. Similarly, the q summation will terminate at $m/2$ for even m, and $(m+1)/2$ for odd m. Also, due to the Pochhammer symbols in Eq. (46) and the restriction on w_2 given in Eq. (42), the w_2 sum has the following termination conditions:

$$\min\left\{w_1,\frac{l}{2}\right\},\quad l\ \text{even and}\ m\ \text{odd},$$

$$\min\left\{w_1,\frac{m}{2}\right\},\quad m\ \text{even and}\ l\ \text{odd},$$

$$\min\left\{w_1,\frac{l}{2},\frac{m}{2}\right\},\quad l\ \text{and}\ m\ \text{both even},$$

$$w_1,\quad l\ \text{and}\ m\ \text{both odd}.$$

The w_1 sum is always nonterminating.

In addition to the individual constraints on i, j, k, l, and m mentioned in the Introduction, Eq. (46) requires that

$$i+j+k+l+m\geqslant -8, \quad (47)$$

which follows from Eq. (22).

V. NUMERICAL EVALUATION

For even l or m, the evaluation of I_1 and I_2 reduces to a finite sum of terms. For l and m both odd, it is useful to examine the asymptotic behavior of the series. I_1 is considered first.

The asymptotic behavior of a single W integral appearing in Eq. (18) is[32]

$$W\sim\frac{1}{w^2}. \quad (48)$$

However, if the W integrals are taken in the appropriate pairs, it can be shown that the set of six W integrals in Eq. (18) behaves like

$$\text{set of six}\ W\sim\frac{1}{w^3}, \quad (49)$$

due to the difference in signs. The product of the a_{tuv} coefficients in Eq. (17) exhibits the asymptotic behavior[32]

TABLE I. Values of $I_1(i,j,k,l,m,n,\alpha,\beta,\gamma)$.

i	j	k	l	m	α	β	γ	$I_1(i,j,k,l,m,n,\alpha,\beta,\gamma)$
0	0	0	−1	1	2.7	2.9	0.65	8.947 959 925 047 512 835 052 492
2	−1	1	3	−1	2.7	2.9	0.65	$3.066\,249\,710\,874\,801\,140\,638\,611\times10^4$
1	2	3	1	3	2.7	2.9	0.65	$-7.127\,529\,951\,937\,274\,842\,240\,935\times10^7$
0	2	0	2	1	2.7	2.9	0.65	$-1.155\,955\,548\,991\,711\,453\,287\,647\times10^4$
−1	3	2	0	4	2.7	2.9	0.65	$-4.898\,965\,561\,162\,249\,945\,560\,093\times10^7$
1	2	−1	3	4	2.7	2.9	0.65	$-5.595\,918\,656\,196\,395\,007\,062\,751\times10^6$

$$\frac{(-m/2)_w(-l/2)_w}{[(\frac{1}{2})_w]^2}\sim\frac{1}{w^{(l+m+2)/2}}. \tag{50}$$

Combining Eqs. (49) and (50) with the factor $1/(2w+1)$ from Eq. (18) leads to

$$I_1\sim\sum_w \frac{1}{w^{(l+m+10)/2}}. \tag{51}$$

The worst case that arises in the evaluation of the matrix elements of H_{oo} is $l=-1$ and $m=1$, where

$$I_1\sim\sum_w \frac{1}{w^5}, \tag{52}$$

which is suitable for direct numerical evaluation.

The asymptotic form for I_2 can be determined in a similar manner to that described for I_1. The result is

$$I_2\sim\sum_w \frac{1}{w^{(l+m+10)/2}}. \tag{53}$$

The worst case asymptotic behavior for I_2 is the same as that of I_1.

While the series representations of I_1 and I_2 are suitable for direct summation, such a process is rather time consuming for the most slowly converging cases. An improved approach is to apply the techniques discussed in Ref. 18. By first converting these monotonic series into equivalent alternating series, then applying convergence accelerators to the transformed series, a high-precision evaluation scheme is produced which is far more rapid for the most slowly converging integrals.

The sign differences on the coefficients of the W integrals in Eqs. (18) and (34) might be suggestive of possible numerical precision problems. However, both equations have been tested and found to be numerically stable. Tables I and II present some representative values for the I_1 and I_2 integrals, respectively.

A useful check for I_1 and I_2 can be derived by considering the integral

TABLE II. Values of $I_2(i,j,k,l,m,n,\alpha,\beta,\gamma)$.

i	j	k	l	m	α	β	γ	$I_2(i,j,k,l,m,n,\alpha,\beta,\gamma)$
0	2	0	−1	−1	2.7	2.9	0.65	−2.943 608 978 543 536 288 422 283
1	4	3	−1	3	2.7	2.9	0.65	$2.755\,380\,752\,419\,424\,787\,112\,100\times10^6$
2	1	1	1	−1	2.7	2.9	0.65	$-1.874\,264\,201\,450\,095\,466\,617\,095\times10^2$
1	3	2	0	2	2.7	2.9	0.65	$6.929\,145\,321\,870\,892\,125\,904\,854\times10^3$
0	4	0	2	−1	2.7	2.9	0.65	$-2.953\,164\,176\,902\,131\,531\,016\,592\times10^3$
3	2	−1	3	2	2.7	2.9	0.65	$2.411\,321\,913\,805\,718\,749\,043\,867\times10^5$

$$I_4(i,j,k,l,m,\alpha,\beta,\gamma)=\int r_1^i r_2^j r_3^k \frac{(r_1^2-r_2^2)(r_{31}^2-r_{23}^2)}{r_{12}^3} r_{23}^l r_{31}^m e^{-\alpha r_1-\beta r_2-\gamma r_3}\, d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{r}_3. \tag{54}$$

Equation (54) can be evaluated using either I_1 or I_2, resulting in the following relationship:

$$I_1(i,j,k,l,m+2,\alpha,\beta,\gamma)-I_1(i,j,k,l+2,m,\alpha,\beta,\gamma)$$
$$=I_2(i+2,j,k,l,m,\alpha,\beta,\gamma)-I_2(i,j+2,k,l,m,\alpha,\beta,\gamma). \tag{55}$$

Hence, Eqs. (18) and (34) may checked against each other. Also, if $l=m=0$ in Eq. (26), $J_1=0$, and therefore

$$I_1(i,j,k,0,0,\alpha,\beta,\gamma)=I_2(i,j,k,0,0,\alpha,\beta,\gamma). \tag{56}$$

The asymptotic behavior of I_3 is the most difficult to estimate, due to the nested w_2 sum in Eq. (46). Let us define K to be the infinite series portion of the I_3 integral. The technique used to analyze the asymptotic behavior of K will be to divide the w_1, w_2 plane into three regions:

$$w_2=0,$$

$$0<w_2<w_1,$$

$$w_2=w_1.$$

Making these simplifications, it is possible to arrive at upper and lower bound estimates on the convergence rate for the w_1 summation.

First we examine the region where $w_2=0$. From Eq. (42), it can easily be shown that

$$I_\Omega \sim \frac{1}{w_1^2}. \tag{57}$$

If taken in the appropriate pairs, the sum of the W integrals in Eq. (46) behaves like

$$\text{set of six } W\sim \frac{1}{w_1^2}. \tag{58}$$

For the case $w_2=0$, the a_{tuv} coefficients in Eq. (46) lead to

$$\frac{(-m/2)_0(-l/2)_0}{[(\frac{1}{2})_0]^2}\sim 1. \tag{59}$$

Combining Eqs. (57), (58), and (59) gives the result

$$K\sim \sum_{w_1} \frac{1}{w_1^4}. \tag{60}$$

The asymptotic behavior of K in the other two regions may be obtained by similar methods. The results are

$$K\sim \sum_{w_1} \frac{1}{w_1^4} \quad \text{to} \quad \sum_{w_1} \frac{1}{w_1^{(l+m+14)/2}} \tag{61}$$

and

$$K\sim \sum_{w_1} \frac{1}{w_1^{(l+m+11)/2}}, \tag{62}$$

TABLE III. Values of $I_3(i,j,k,l,m,\alpha,\beta,\gamma)$.

i	j	k	l	m	α	β	γ	$I_3(i,j,k,l,m,\alpha,\beta,\gamma)$
1	−1	0	−1	1	2.7	2.9	0.65	$1.356\,087\,352\,189\,092\,17\times10^{2}$
1	2	2	1	1	2.7	2.9	0.65	$-6.371\,117\,492\,583\,756\times10^{4}$
3	1	2	3	1	2.7	2.9	0.65	$4.870\,134\,178\,451\,231\,6\times10^{7}$
2	2	3	−1	3	2.7	2.9	0.65	$6.471\,807\,181\,649\,945\times10^{5}$
4	1	2	3	3	2.7	2.9	0.65	$3.203\,917\,521\,846\,703\,1\times10^{10}$
3	1	−1	1	5	2.7	2.9	0.65	$5.849\,805\,492\,834\,822\,33\times10^{6}$

respectively. The second of the two results given in Eq. (61) was obtained using $w_2=w_1/2$. If instead we employ $w_2\approx w_1$ (with $w_2<w_1$), the same asymptotic behavior given in Eq. (62) would be obtained.

The convergence of the entire sum will be determined by the most slowly converging portion of that sum, which was found at $w_2=0$. So the entire sum behaves asymptotically like

$$K\sim\sum_{w_1}\frac{1}{w_1^4}. \tag{63}$$

It should be clear from this result that a large number of terms are needed to obtain an accurate result for K. Rather than directly summing the series, a convergence acceleration technique was applied to the infinite series portion of Eq. (46). The acceleration method employed was the Richardson extrapolation,[33] which has been used previously in the evaluation of other three-electron integration problems.[22] The Richardson extrapolation is given by

$$S_0=\sum_{k=0}^{N}\frac{S_{n+k}(n+k)^N(-1)^{k+N}}{k!(N-k)!}, \tag{64}$$

where S_0 is an approximation to the total sum in Eq. (46). A well-known difficulty associated with the application of Eq. (64) is that it is subject to numerical precision loss for higher values of N.

Careful examination of Eq. (46) shows it to be composed of two monotonically decreasing series, one for w_1 even and one for w_1 odd. Because the individual terms of the two series differ significantly in magnitude, a direct application of the Richardson extrapolation produces quite poor results. However, if Eq. (64) is applied individually to these two series, then a significant improvement in convergence is obtained. For both of these series, choosing $n=1$, the optimal value of N appears to be at about $N=23$. At this value, approximately 17 digits of precision may be obtained using 30 digit arithmetic. As was found for I_1 and I_2, the sign differences on the coefficients of the W integrals in Eq. (46) do not appear to be problematic. Some representative values of I_3 are presented in Table III.

For the case l and m both odd, evaluation of Eq. (5) via the approach developed in Sec. IV requires about half the computational time of previously published methods. For a number of test cases investigated, several more significant digits were obtained using the present approach. The increased speed of evaluation is directly tied to the much simpler formula that results in the present work, in comparison with what is obtained by breaking the integral into two separate parts. For l and m not both odd, evaluation methods may be employed which are both computationally faster and produce higher-precision results.[19]

VI. DISCUSSION

In this work, some key integrals are solved which are needed for the evaluation of ΔE_{REL} (the non-fine-structure contributions) for the ^2S states of three-electron systems. The basic approach employed in this work is to treat each of the integrand factors $(r_1^2-r_2^2)r_{12}^{-3}$, $(r_{31}^2-r_{23}^2)r_{12}^{-3}$, and $(r_1^2-r_2^2)r_{12}^{-2}$ as single expansions. For the I_1 and I_2 integrals investigated, the option of splitting these factors into separate parts does not exist, as each of the separate integrals diverge. A recursive scheme for an integral related to I_1 is developed by Yan and Drake.[23]

With the evaluation of I_1, I_2, and I_3, the difficulties associated with the evaluation of the matrix elements of the Breit–Pauli relativistic operators now lie elsewhere. Integrals of the form shown in Eq. (2) with $l=-2$ also arise in the evaluation of H_{oo} and H_{mass}, and these have known computational difficulties.[19] While several methods exist for their evaluation,[19–24] they are relatively slow for some choices of the arguments and are subject to precision loss. Development of better methods for handling integrals of this form would be useful.

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APPENDIX A: DIVERGENCE OF *I* INTEGRAL WHEN $n=-3$

This appendix illustrates that Eq. (2) diverges for at least one of *l*, *m* and $n=-3$. Consequently, Eqs. (3) and (4) cannot be broken into separate integrals of the form of Eq. (2).

Let

$$I(i,j,k,l,m,-3,\alpha,\beta,\gamma)\equiv\int r_1^i r_2^j r_3^k r_{23}^l r_{31}^m r_{12}^{-3} e^{-\alpha r_1-\beta r_2-\gamma r_3}\, d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{r}_3. \tag{A1}$$

Because the integrand is everywhere positive,

$$I\geqslant\int_{(r_3-\varepsilon)\geqslant r_p} r_1^i r_2^j r_3^k r_{23}^l r_{31}^m r_{12}^{-3} e^{-\alpha r_1-\beta r_2-\gamma r_3}\, d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{r}_3, \tag{A2}$$

where $(r_3-\varepsilon)>0$ and $p=1,2$.

Furthermore,

$$I\geqslant \min_{\substack{\mathbb{R}^9\\(r_3-\varepsilon)\geqslant r_p}}\{r_{23}^l\} \min_{\substack{\mathbb{R}^9\\(r_3-\varepsilon)\geqslant r_p}}\{r_{31}^m\}\int_{(r_3-\varepsilon)\geqslant r_p} r_1^i r_2^j r_3^k r_{12}^{-3} e^{-\alpha r_1-\beta r_2-\gamma r_3}\, d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{r}_3. \tag{A3}$$

Due to the restrictions placed on the region of integration,

$$\min_{\substack{\mathbb{R}^9\\(r_3-\varepsilon)\geqslant r_p}}\{r_{23}^l\} \min_{\substack{\mathbb{R}^9\\(r_3-\varepsilon)\geqslant r_l}}\{r_{31}^m\}=\varepsilon^{l+m}. \tag{A4}$$

Substituting Eq. (A4) into Eq. (A3) yields,

$$I\geqslant\varepsilon^{l+m}\times\int_{(r_3-\varepsilon)\geqslant r_p} r_1^i r_2^j r_3^k r_{12}^{-3} e^{-\alpha r_1-\beta r_2-\gamma r_3}\, d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{r}_3. \tag{A5}$$

Integration over $\mathbf{r}_3$ produces a finite sum of positive terms involving integrals of the form

$$\int r_1^s r_2^t r_{12}^{-3} e^{-ar_1-br_2}\, d\mathbf{r}_1\, d\mathbf{r}_2. \tag{A6}$$

Choosing perimetric coordinates[6] it can easily be shown that Eq. (A6) diverges irrespective of the values of *s*, *t*, *a*, and *b*. Therefore Eq. (A5) must be divergent, and so Eq. (A1) must also diverge.

The extension to *N*-electron systems is obvious.

APPENDIX B: EXPANSION FOR r_{12}^{-3}

The generating function for the Legendre polynomials is[34]

$$\frac{1}{\sqrt{1-2rx+r^2}}=\sum_{n=0}^{\infty} r^n P_n(x). \tag{B1}$$

If the operator $\hat{O}\equiv 1+2r\ \partial/\partial r$ is applied to both sides of Eq. (B1)[26] one obtains

$$\frac{1-r^2}{(1-2rx+r^2)^{3/2}}=\sum_{n=0}^{\infty}(2n+1)r^n P_n(x). \tag{B2}$$

Making the substitutions $r=r_{12<}/r_{12>}$, $x=\cos\ \theta_{12}$, and $n=w_1$ in Eq. (B2) results in Eq. (8).

APPENDIX C: SOLUTION OF ANGULAR INTEGRALS FOR I_2

This appendix discusses the evaluation of the angular integrals Φ_1 and Φ_2 which arise in Eq. (27). If the addition theorem for Legendre polynomials,[26]

$$P_{w_1}(\cos\ \theta_{12})=P_{w_1}(\cos\ \theta_{23})P_{w_1}(\cos\ \theta_{31}) +2\sum_{n=1}^{w_1}\frac{(w_1-n)!}{(w_1+n)!}P_{w_1}^n(\cos\ \theta_{23})P_{w_1}^n(\cos\ \theta_{31})\cos(n(\phi_{23}-\phi_{31})), \tag{C1}$$

is applied to $P_{w_1}(\cos\ \theta_{12})$ in Eq. (28), and the integration over ϕ_{23} and ϕ_{31} is performed, then the finite sum in Eq. (C1) vanishes. Thus Φ_1 simplifies to

$$\Phi_1=4\pi^2\int_{-1}^{1}xP_{w_1}(x)P_{w_3}(x)dx\int_{-1}^{1}P_{w_1}(x)P_{w_2}(x)dx. \tag{C2}$$

Using the standard recurrence relationship

$$(2v+1)xP_v(x)=(v+1)P_{v+1}(x)+vP_{v-1}(x), \tag{C3}$$

and the orthogonality property of the Legendre polynomials, allows Eq. (C2) to be simplified to Eq. (30). The result for Φ_2 can be obtained by symmetry [switch $1\leftrightarrow 2$ and $w_2\leftrightarrow w_3$ in Eq. (28), thereby obtaining Eq. (31)].

APPENDIX D: SOLUTION OF ANGULAR INTEGRAL FOR I_3

This appendix discusses the evaluation of the angular integral I_Ω, Eq. (39), which occurs in I_3. We choose our coordinate system such that

$$d\Omega_1\ d\Omega_2\ d\Omega_3=\sin\ \theta_{12}\ d\theta_{12}\ d\phi_{12}\ \sin\ \theta_{31}\ d\theta_{31}\ d\phi_{31}\ \sin\ \theta_1\ d\theta_1\ d\phi_1. \tag{D1}$$

Expanding $P_{w_2}(\cos\ \theta_{23})$ by the addition theorem for Legendre polynomials, then integrating over θ_1, ϕ_1, ϕ_{12}, ϕ_{31}, and θ_{31}, yields

$$I_\Omega(w_1,w_2,w_3)=\frac{32\pi^3}{2w_2+1}\ \delta_{w_2w_3}\int_0^{\pi}T_{w_1}(\cos\ \theta_{12})P_{w_2}(\cos\ \theta_{12})\sin\ \theta_{12}\ d\theta_{12}. \tag{D2}$$

Expanding $P_{w_2}(\cos\ \theta_{12})$ in a Fourier sine series,[34] and using the identity

$$T_{w_1}(\cos\ \theta_{12})=\cos(w_1\theta_{12}), \tag{D3}$$

produces

$$I_\Omega = \frac{64\pi^{5/2}}{2w_2+1}\,\delta_{w_2w_3}\sum_{k=0}^{\infty}\frac{(\frac{1}{2})_k\Gamma(w_2+k+1)}{k!\,\Gamma(w_2+k+\frac{3}{2})}\int_0^{\pi}\cos(w_1\theta_{12})\sin[(w_2+2k+1)\theta_{12}]\sin\,\theta_{12}\,d\theta_{12}. \tag{D4}$$

Evaluation of this integral, followed by some straightforward simplification, leads to Eq. (42).

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