# Analysis of some integrals arising in the atomic four-electron problem

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An analysis is presented for the evaluation of the one-center integrals of the form $\int r_1^i\, r_2^j\, r_3^k\, r_4^l\, r_{12}^m\, r_{13}^n\, r_{14}^p\, r_{23}^q\, r_{24}^s\, r_{34}^t\, e^{-ar_1-br_2-cr_3-dr_4}\, d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{r}_3\, d\mathbf{r}_4$ which arise in the solution of the atomic four-electron problem when a Hylleraas expansion is employed. A majority of the cases that arise can be solved by a reduction of the four-electron integrals to integrals arising in the three-electron problem. A second general approach is developed which is able to handle almost all cases that arise in practical calculations.

## I. INTRODUCTION

The $^1S$ ground state of the Be atom has been the subject of recent interest.[1,2] Attention has focused on resolving a small discrepancy between the experimental and theoretical values of the ground state energy.[3] The most accurate theoretical determinations of the nonrelativistic ground state energy ($E_{\rm NR}$) have all involved CI calculations, and have required estimation of the truncation errors to arrive at the published values of $E_{\rm NR}$.[1,3]

For few-electron systems Hylleraas-type expansions lead to much more rapid convergence for the energy. A drawback, however, is the complexity of the basic integrals that arise. Relatively few investigations of the $^1S$ Be ground state have been carried out using a Hylleraas-type basis set.[4–8] All these calculations have placed major restrictions on the basis functions that were employed. This was done in order to avoid difficult integration problems. The purpose of this work is to carry out a general analysis of the integrals that arise in the evaluation of the Be ground state energy (or any other four-electron $S$-state species) when a Hylleraas-type basis set is employed.

Considerable attention has been devoted to the evaluation of the integrals

$$I(i,j,k,l,m,n,a,b,c)$$

$$= \int r_1^i r_2^j r_3^k r_{23}^l r_{31}^m r_{12}^n e^{-ar_1-br_2-cr_3}\, d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{r}_3 \qquad (1)$$

and the related auxiliary functions on which it depends.[9–24] In Eq. (1) $r_i$ represents an electron–nuclear separation and $r_{ij}$ denotes an interelectronic separation. These integrals arise in the atomic three-electron problem for $S$ states. In the conventional Hylleraas expansion only positive integer exponents are employed, which means only the cases $l \geqslant -1$, $m \geqslant -1$ and $n \geqslant -1$ are required for an energy evaluation. For other properties, such as certain relativistic corrections, cases arise in which $l$, $m$, or $n$ may equal $-2$. Such integrals are extremely difficult to evaluate.[23,24] Given that extensive efforts have been devoted to the evaluation of the $I$ integrals, the approach adopted in the first part of this investigation is to reduce where possible, the required four-electron integrals to the $I$ integrals. This reduction proves to be possible for a large number of integrals. For those integrals that cannot be so reduced, a general formula is worked out in the second part of this study. The next two sections cover each situation.

## II. REDUCTION OF THE FOUR-ELECTRON INTEGRALS TO *I*-INTEGRALS

For a four-electron $S$-state atom or ion, the Hylleraas expansion takes the form

$$\Psi = A \sum_{u=1}^{N} C_u r_1^{i_u} r_2^{j_u} r_3^{k_u} r_4^{l_u} r_{12}^{m_u} r_{13}^{n_u} r_{14}^{p_u} r_{23}^{q_u} r_{24}^{s_u} r_{34}^{t_u} \times e^{-a_u r_1 - b_u r_2 - c_u r_3 - d_u r_4} \chi_u, \qquad (2)$$

where $A$ is the antisymmetrizer, $C_u$ are the variationally determined expansion coefficients, $\chi_u$ is a spin function, and all powers in the set $\{i_u, j_u, k_u, l_u, m_u, n_u, p_u, q_u, s_u, t_u\}$ are each $\geqslant 0$. With this choice for $\Psi$ the basic integral that must be evaluated to determine the energy (and many other properties) is

$$I_4(i,j,k,l,m,n,p,q,s,t,a,b,c,d)$$

$$= \int r_1^i r_2^j r_3^k r_4^l r_{12}^m r_{13}^n r_{14}^p r_{23}^q r_{24}^s r_{34}^t e^{-ar_1-br_2-cr_3-dr_4} \times d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{r}_3\, d\mathbf{r}_4. \qquad (3)$$

Special cases of this integral have been considered previously. Gentner and Burke[5] evaluated the case where no more than three $r_{ij}$ terms appear, and that the power on the $r_{ij}$ factors did not exceed one. These authors allowed for additional factors of the form $\cos\theta_{ij}$ in the integrand. Perkins[25] also evaluated the case with three $r_{ij}$ factors, but allowed for general powers on each factor. The most extensive discussion is due to Sims and Hagstrom,[26] but these authors also restrict to the case of three $r_{ij}$ factors to a general power (taken to be $\geqslant -1$). They allow for additional angular dependence by including spherical harmonic factors for each electron. If a general term in Eq. (2) is selected with several different $r_{ij}$ factors, then it is necessary to go beyond these previous investigations and address the general integral in Eq. (3).

The cases that are considered in this work have $i \geqslant -2$, $j \geqslant -2$, $k \geqslant -2$, $l \geqslant -2$ and $m,n,p,q,s,t$ each $\geqslant -1$, with $a,b,c,d$ each $>0$. The first case considered is $p=0$ and $s$ and

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$t$ *not* both odd. The following development supposes $s$ is even. If $t$ is even and $s$ is odd, the obvious symmetry relation

$$I_4(i,j,k,l,m,n,p,q,s,t,a,b,c,d)$$
$$=I_4(i,k,j,l,n,m,p,q,t,s,a,c,b,d) \quad (4)$$

can be employed. This situation is a little restrictive, but it does, however, cover a very large number of possible cases. Although the final formulas may look a little involved, they can be programmed very efficiently.

The restriction imposed for the present case allows the $I_4$ integrals to be directly reduced to the $I$-integrals defined in Sec. I. Equation (3) for the case under consideration can be written as

$$I_4(i,j,k,l,m,n,0,q,s,t,a,b,c,d)$$
$$=\int r_1^i r_2^j r_3^k r_{23}^q r_{31}^n r_{12}^m e^{-ar_1-br_2-cr_3} d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{r}_3$$
$$\times \int r_4^l r_{24}^s r_{34}^t e^{-dr_4}\, d\mathbf{r}_4. \quad (5)$$

To handle the integral over $\mathbf{r}_4$ we proceed as follows. The Sack[27] expansions for $r_{24}^s$ and $r_{34}^t$ are inserted to yield

$$J(r_2,r_3,r_{23},l,s,t,d)=\int r_4^l r_{24}^s r_{34}^t e^{-dr_4}\, d\mathbf{r}_4$$
$$=\sum_{u=0}^{\infty}\sum_{v=0}^{\infty}\int r_4^l R_{su}(r_2,r_4)R_{tv}(r_3,r_4)$$
$$\times P_u(\cos\theta_{24})P_v(\cos\theta_{34})e^{-dr_4}\, d\mathbf{r}_4, \quad (6)$$

where $R_{su}(r_2,r_4)$ is a radial function and $P_u(\cos\theta_{24})$ a Legendre polynomial. Using the standard expansion of the Legendre polynomials in terms of spherical harmonics

$$P_u(\cos\theta_{24})=\frac{4\pi}{2u+1}\sum_{m_u=-u}^{u} Y_{um_u}^*(\theta_2,\phi_2)Y_{um_u}(\theta_4,\phi_4) \quad (7)$$

allows the angle integration in Eq. (6) to be evaluated as

$$J_\Omega=\int P_u(\cos\theta_{24})P_v(\cos\theta_{34})d\Omega_4$$
$$=\frac{4\pi}{2u+1}P_u(\cos\theta_{23})\delta_{uv}, \quad (8)$$

where

$$\int Y_{vm_v}^*(\theta_4,\phi_4)Y_{um_u}(\theta_4,\phi_4)d\Omega_4=\delta_{uv}\delta_{m_um_v} \quad (9)$$

has been employed. $\delta_{uv}$ denotes the Kronecker delta in Eqs. (8) and (9). Inserting Eq. (8) into Eq. (6) leads to

$$J(r_2,r_3,r_{23},l,s,t,d)=4\pi\sum_{u=0}^{\infty}\frac{P_u(\cos\theta_{23})}{2u+1}\int_0^\infty r_4^{l+2}$$
$$\times R_{su}(r_2,r_4)R_{tu}(r_3,r_4)e^{-dr_4}\, dr_4. \quad (10)$$

To evaluate the integral in Eq. (10) two different expansions of the Sack radial functions are employed

$$R_{tu}(r_3,r_4)=\frac{(-t/2)_u}{(1/2)_u}r_{34>}^{t-u}r_{34<}^u\sum_{z=0}^{\infty}a_{utz}\left(\frac{r_{34<}}{r_{34>}}\right)^{2z}, \quad (11)$$

$$R_{su}(r_2,r_4)=\frac{(-s/2)_u}{(1/2)_u}\frac{r_2^u r_4^u}{(r_2+r_4)^{2u-s}}\sum_{w=0}^{\infty}b_{usw}\left(\frac{r_2r_4}{(r_2+r_4)^2}\right)^w, \quad (12)$$

where

$$a_{utz}=\frac{(u-t/2)_z(-1/2-t/2)_z}{z!(u+3/2)_z} \quad (13)$$

and

$$b_{usw}=4^w\frac{(u-s/2)_w(1+u)_w}{w!(2+2u)_w}. \quad (14)$$

In Eq. (11) $r_{34>}$ denotes the greater of $(r_3,r_4)$ and $r_{34<}$ represents the lesser of $(r_3,r_4)$. In Eqs. (11)–(14) $(p)_q$ denotes a Pochhammer symbol. Inserting Eqs. (11) and (12) into the integral in Eq. (10) (denoted $J_R$) leads to

$$J_R(r_2,r_3,l,s,t,d,u)=\int r_4^{l+2}R_{su}(r_2,r_4)R_{tu}(r_3,r_4)e^{-dr_4}\, dr_4$$
$$=\frac{(-t/2)_u(-s/2)_u}{[(1/2)_u]^2}\sum_{z=0}^{\infty}a_{utz}\sum_{w=0}^{\infty}b_{usw}\sum_{v=0}^{s-2u-2w}\binom{s-2u-2w}{v}$$
$$\times d^{-(l+3+2u+v+w+2z)}r_2^{s-u-v-w}\{r_3^{t-u-2z}(l+2+2u+v+w+2z)![1-Z(l+2+2u+v+w+2z,d,r_3)]$$
$$+r_3^{u+2z}d^{2u+4z-t}(l+2+v+w+t-2z)!Z(l+2+v+w+t-2z,d,r_3)\} \quad (15)$$

with

$$Z(p,d,r_3)=e^{-dr_3}\sum_{z=0}^{p}\frac{(dr_3)^z}{z!}. \quad (16)$$

In Eq. (15) $\binom{a}{b}$ denotes a binominal coefficient.

To show the explicit dependence of $J$ [in Eq. (6)] on $r_{23}$, the following decomposition of the Legendre polynomial is required:

$$P_u(\cos\theta_{23})=\sum_{\nu=0}^{[u/2]}\sum_{\mu=0}^{u-2\nu}\sum_{\kappa=0}^{u-2\nu-\mu}\omega_{u\nu\mu\kappa}r_2{}^{u-2\nu-2\mu-2\kappa}r_3{}^{-u+2\nu+2\kappa}r_{23}{}^{2\mu} \tag{17}$$

with

$$\omega_{u\nu\mu\kappa}=\frac{(-1)^{\nu+\mu}\binom{u-2\nu}{\mu}\binom{u-2\nu-\mu}{\kappa}(2u-2\nu)!}{4^{u-\nu}\nu!(u-\nu)!(u-2\nu)!}, \tag{18}$$

and $[u/2]=u/2$ for $u$ even or $(u-1)/2$ for $u$ odd. Inserting Eqs. (6), (10), (15), and (17) into Eq. (5) leads to

$$\begin{aligned}I_4(i,j,k,l,m,n,0,q,s,t,a,b,c,d)=&4\pi\sum_{u=0}^{\infty}h_{ust}\sum_{\nu=0}^{[u/2]}\sum_{\mu=0}^{u-2\nu}\sum_{\kappa=0}^{u-2\nu-\mu}\sum_{z=0}^{\infty}\sum_{w=0}^{\infty}\sum_{v=0}^{s-2u-2w}\omega_{u\nu\mu\kappa}a_{utz}b_{usw}\binom{s-2u-2w}{v}\\&\times d^{-(l+3+2u+v+w+2z)}\int r_1^i r_2^{\jmath_3} r_3^{k-u+2\nu+2\kappa}r_{23}^{q+2\mu}r_{31}^n r_{12}^m e^{-ar_1-br_2-cr_3}\\&\times\{r_3^{t-u-2z}\jmath_1![1-Z(\jmath_1,d,r_3)]+r_3^{u+2z}d^{2u+4z-t}\jmath_2!Z(\jmath_2,d,r_3)\}d\mathbf{r}_1\,d\mathbf{r}_2\,d\mathbf{r}_3,\end{aligned} \tag{19}$$

where the notational simplifications

$$h_{ust}=\frac{(-s/2)_u(-t/2)_u}{(2u+1)[(1/2)_u]^2}, \tag{20}$$

$$\jmath_1=l+2+2u+v+w+2z, \tag{21}$$

$$\jmath_2=l+2+v+w+t-2z, \tag{22}$$

$$\jmath_3=j+s-v-w-2(\nu+\mu+\kappa) \tag{23}$$

have been employed. If the additional notational simplifications are utilized

$$\jmath_4=k+t+2(\nu+\kappa-u-z), \tag{24}$$

$$\jmath_5=k+2(\nu+\kappa+z), \tag{25}$$

$$\Omega_{u\nu\mu\kappa stzwv}=h_{ust}\omega_{u\nu\mu\kappa}a_{utz}b_{usw}\binom{s-2u-2w}{v} \tag{26}$$

then

$$\begin{aligned}&I_4(i,j,k,l,m,n,0,q,s,t,a,b,c,d)\\&=4\pi\sum_{u=0}^{\infty}\sum_{\nu=0}^{[u/2]}\sum_{\mu=0}^{u-2\nu}\sum_{\kappa=0}^{u-2\nu-\mu}\sum_{z=0}^{\infty}\sum_{w=0}^{\infty}\sum_{v=0}^{s-2u-2w}d^{-(\jmath_1+1)}\Omega_{u\nu\mu\kappa stzwv}\Bigg\{\jmath_1!\Bigg[I(i,\jmath_3,\jmath_4,q+2\mu,n,m,a,b,c)\\&\quad-\sum_{\lambda=0}^{\jmath_1}\frac{d^\lambda}{\lambda!}I(i,\jmath_3,\jmath_4+\lambda,q+2\mu,n,m,a,b,c+d)\Bigg]+\jmath_2!d^{2u+4z-t}\sum_{\lambda=0}^{\jmath_2}\frac{d^\lambda}{\lambda!}I(i,\jmath_3,\jmath_5+\lambda,q+2\mu,n,m,a,b,c+d)\Bigg\},\end{aligned} \tag{27}$$

where $I(i,j,k,l,m,n,a,b,c)$ is defined in Eq. (1). Equation (27) represents one of the principal results of this investigation. Two issues need to be addressed for this formula. The $u$, $z$, and $w$ summations all terminate at finite values. On noting the property (for integer $k$) of the Pochhammer symbol

$$(-k)_l=0 \quad l>k, \tag{28}$$

the $z$ summation terminates at $t/2-u$ if $t$ is even and $(t+1)/2$ if $t$ is odd [see Eq. (13)]. The $w$ summation terminates at $s/2-u$ [see Eq. (14)] and the $u$-summation terminates at min$[s/2,t/2]$ if $t$ is even, or $s/2$ if $t$ is odd. Both these conditions require $s$ to be even, which was a basic restriction mentioned towards the start of this section.

If $t$ is odd then $l$ must be $\geqslant -1$, otherwise $\jmath_2<0$ is possible and Eq. (27) does not hold. In its place a complicated integral having the exponential integral as part of the integrand arises. For the case of odd $t$ and $l=-2$ the method of the next section should be applied. An examination of Eq. (24) for the case of odd $t$ reveals the required condition

$$k\geqslant s-1 \tag{29}$$

otherwise the $I$ integrals in Eq. (27) depending on $\jmath_4$ will diverge when $\jmath_4+\lambda<-2$. A possible way to work around this constraint is to employ the following result in Eq. (19)

$$1-Z(\jmath_1,d,r_3)=e^{-dr_3}(dr_3)^{\jmath_1+1}\sum_{\lambda=0}^{\infty}\frac{(dr_3)^\lambda}{(\lambda+\jmath_1+1)!}. \tag{30}$$

The result is that the factor in square braces in Eq. (27) is replaced by

$$d^{\mathfrak{z}_1+1}\sum_{\lambda=0}^{\infty}\frac{d^{\lambda}}{(\lambda+\mathfrak{z}_1+1)!}I(i,\mathfrak{z}_3,\mathfrak{z}_1+\mathfrak{z}_4+\lambda+1,q$$

$$+2\mu,n,m,a,b,c+d).$$

This factor is well behaved for $k$, $l$, and $t$ values satisfying

$$k+l+t\geqslant -5, \tag{31}$$

though this is at the expense of a good deal of additional computational labor.

## III. THE GENERAL CASE

In this section the general case having $m,n,p,q,s,t$ each $\geqslant -1$ is considered. If the Sack expansion for each factor $r_{ij}^{k}$ is inserted into Eq. (3), the resulting integral is

$$I_4=\sum_{m_1=0}^{\infty}\sum_{n_1=0}^{\infty}\sum_{p_1=0}^{\infty}\sum_{q_1=0}^{\infty}\sum_{s_1=0}^{\infty}\sum_{t_1=0}^{\infty}$$

$$\times I_R(m_1,n_1,p_1,q_1,s_1,t_1)I_\Omega(m_1,n_1,p_1,q_1,s_1,t_1), \tag{32}$$

where $I_\Omega$ denotes the angular integral

$$I_\Omega\equiv I_\Omega(m_1,n_1,p_1,q_1,s_1,t_1)$$

$$=\int P_{m_1}(\cos\theta_{12})P_{n_1}(\cos\theta_{13})P_{p_1}(\cos\theta_{14})P_{q_1}$$

$$\times(\cos\theta_{23})P_{s_1}(\cos\theta_{24})P_{t_1}(\cos\theta_{34})d\Omega_1\,d\Omega_2\,d\Omega_3\,d\Omega_4 \tag{33}$$

and $I_R$ denotes the radial integral

$$I_R\equiv I_R(m_1,n_1,p_1,q_1,s_1,t_1)$$

$$=\int r_1^{i+2}r_2^{j+2}r_3^{k+2}r_4^{l+2}e^{-ar_1-br_2-cr_3-dr_4}$$

$$\times R_{mm_1}(r_1,r_2)R_{nn_1}(r_1,r_3)R_{pp_1}(r_1,r_4)$$

$$\times R_{qq_1}(r_2,r_3)R_{ss_1}(r_2,r_4)R_{tt_1}(r_3,r_4)dr_1\,dr_2\,dr_3\,dr_4. \tag{34}$$

Employing Eq. (7) and the result

$$\int Y_{l_1m_1}(\theta_1,\phi_1)Y_{l_2m_2}(\theta_1,\phi_1,)Y_{l_3m_3}(\theta_1,\phi_1)d\Omega_1$$

$$=\left[\frac{(2l_1+1)(2l_2+1)(2l_3+1)}{4\pi}\right]^{1/2}\begin{pmatrix}l_1 & l_2 & l_3\\ 0 & 0 & 0\end{pmatrix}$$

$$\times\begin{pmatrix}l_1 & l_2 & l_3\\ m_1 & m_2 & m_3\end{pmatrix} \tag{35}$$

allows Eq. (33) to be simplified to

$$I_\Omega=256\pi^4\begin{pmatrix}m_1 & n_1 & p_1\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}m_1 & q_1 & s_1\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}n_1 & q_1 & t_1\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}p_1 & s_1 & t_1\\ 0 & 0 & 0\end{pmatrix}\sum_{M=-m_1}^{m_1}\sum_{N=-n_1}^{n_1}\sum_{Q=-q_1}^{q_1}(-1)^{M+N+Q}$$

$$\times\begin{pmatrix}m_1 & n_1 & p_1\\ M & N & -M-N\end{pmatrix}\begin{pmatrix}m_1 & q_1 & s_1\\ -M & Q & M-Q\end{pmatrix}\begin{pmatrix}n_1 & q_1 & t_1\\ -N & -Q & N+Q\end{pmatrix}\begin{pmatrix}p_1 & s_1 & t_1\\ M+N & Q-M & -N-Q\end{pmatrix}. \tag{36}$$

In Eqs. (35) and (36) $\binom{abc}{def}$ denotes a $3j$ symbol. To evaluate the radial integral in Eq. (34), the Sack expansion for each of the radial functions [Eq. (11)] is inserted, leading to

$$I_R=f(m,n,p,q,s,t,m_1,n_1,p_1,q_1,s_1,t_1)\sum_{m_2=0}^{\infty}\sum_{n_2=0}^{\infty}\sum_{p_2=0}^{\infty}\sum_{q_2=0}^{\infty}\sum_{s_2=0}^{\infty}\sum_{t_2=0}^{\infty}g(m,n,p,q,s,t,m_1,n_1,p_1,q_1,s_1,t_1,m_2,n_2,p_2,q_2,s_2,t_2)$$

$$\times\int r_1^I r_2^J r_3^K r_4^L r_{12<}^{T1}r_{12>}^{T2}r_{13<}^{T3}r_{13>}^{T4}r_{14<}^{T5}r_{14>}^{T6}r_{23<}^{T7}r_{23>}^{T8}r_{24<}^{T9}r_{24>}^{T10}r_{34<}^{T11}r_{34>}^{T12}e^{-ar_1-br_2-cr_3-dr_4}dr_1\,dr_2\,dr_3\,dr_4, \tag{37}$$

where

$$f\equiv f(m,n,p,q,s,t,m_1,n_1,p_1,q_1,s_1,t_1)=\frac{\left(\frac{-m}{2}\right)_{m_1}\left(\frac{-n}{2}\right)_{n_1}\left(\frac{-p}{2}\right)_{p_1}\left(\frac{-q}{2}\right)_{q_1}\left(\frac{-s}{2}\right)_{s_1}\left(\frac{-t}{2}\right)_{t_1}}{\left(\frac{1}{2}\right)_{m_1}\left(\frac{1}{2}\right)_{n_1}\left(\frac{1}{2}\right)_{p_1}\left(\frac{1}{2}\right)_{q_1}\left(\frac{1}{2}\right)_{s_1}\left(\frac{1}{2}\right)_{t_1}} \tag{38}$$

and

$$g\equiv g(m,n,p,q,s,t,m_1,n_1,p_1,q_1,s_1,t_1,m_2,n_2,p_2,q_2,s_2,t_2)=a_{m_1mm_2}a_{n_1nn_2}a_{p_1pp_2}a_{q_1qq_2}a_{s_1ss_2}a_{t_1tt_2} \tag{39}$$

and the $a_{xyz}$ coefficient is defined in Eq. (13). The abbreviations

$$\begin{aligned}
&\tau_1=m_1+2m_2 \quad \tau_7=q_1+2q_2\\
&\tau_2=m-\tau_1 \quad \tau_8=q-\tau_7\\
&\tau_3=n_1+2n_2 \quad \tau_9=s_1+2s_2\\
&\tau_4=n-\tau_3 \quad \tau_{10}=s-\tau_9\\
&\tau_5=p_1+2p_2 \quad \tau_{11}=t_1+2t_2\\
&\tau_6=p-\tau_5 \quad \tau_{12}=t-\tau_{11}\\
&I=i+2, \quad J=j+2, \quad K=k+2, \quad L=l+2
\end{aligned} \tag{40}$$

have also been employed in Eq. (37). If the integral in Eq. (37) is broken up into different regions according to $0\leqslant r_i\leqslant r_j\leqslant r_k\leqslant r_l<\infty$, then $I_R$ simplifies using the additional abbreviations

$$\begin{aligned}
&\omega_1=I+\tau_1+\tau_3+\tau_5 \quad \omega_5=I+\tau_2+\tau_4+\tau_6\\
&\omega_2=J+\tau_1+\tau_7+\tau_9 \quad \omega_6=J+\tau_2+\tau_8+\tau_{10}\\
&\omega_3=K+\tau_3+\tau_7+\tau_{11} \quad \omega_7=K+\tau_4+\tau_8+\tau_{12}\\
&\omega_4=L+\tau_5+\tau_9+\tau_{11} \quad \omega_8=L+\tau_6+\tau_{10}+\tau_{12}
\end{aligned} \tag{41}$$

to yield

$$\begin{aligned}
I_R=f\sum_{m_2=0}^{\infty}\sum_{n_2=0}^{\infty}\sum_{p_2=0}^{\infty}\sum_{q_2=0}^{\infty}\sum_{s_2=0}^{\infty}\sum_{t_2=0}^{\infty} g\{&W_4(\omega_1,J+\tau_2+\tau_7+\tau_9,K+\tau_4+\tau_8+\tau_{11},\omega_8,a,b,c,d)\\
&+W_4(\omega_1,J+\tau_2+\tau_7+\tau_9,L+\tau_6+\tau_{10}+\tau_{11},\omega_7,a,b,d,c)+W_4(\omega_1,K+\tau_4+\tau_7+\tau_{11},J+\tau_2+\tau_8+\tau_9,\omega_8,a,c,b,d)\\
&+W_4(\omega_1,K+\tau_4+\tau_7+\tau_{11},L+\tau_6+\tau_9+\tau_{12},\omega_6,a,c,d,b)+W_4(\omega_1,L+\tau_6+\tau_9+\tau_{11},J+\tau_2+\tau_7+\tau_{10},\omega_7,a,d,b,c)\\
&+W_4(\omega_1,L+\tau_6+\tau_9+\tau_{11},K+\tau_4+\tau_7+\tau_{12},\omega_6,a,d,c,b)+W_4(\omega_2,I+\tau_2+\tau_3+\tau_5,K+\tau_4+\tau_7+\tau_{11},\omega_8,b,a,c,d)\\
&+W_4(\omega_2,I+\tau_2+\tau_3+\tau_5,L+\tau_6+\tau_{10}+\tau_{11},\omega_7,b,a,d,c)+W_4(\omega_2,K+\tau_3+\tau_8+\tau_{11},I+\tau_2+\tau_4+\tau_5,\omega_8,b,c,a,d)\\
&+W_4(\omega_2,K+\tau_3+\tau_8+\tau_{11},L+\tau_5+\tau_{10}+\tau_{12},\omega_5,b,c,d,a)+W_4(\omega_2,L+\tau_5+\tau_{10}+\tau_{11},I+\tau_2+\tau_3+\tau_6,\omega_7,b,d,a,c)\\
&+W_4(\omega_2,L+\tau_5+\tau_{10}+\tau_{11},K+\tau_3+\tau_8+\tau_{12},\omega_5,b,d,c,a)+W_4(\omega_3,I+\tau_1+\tau_4+\tau_5,J+\tau_2+\tau_8+\tau_9,\omega_8,c,a,b,d)\\
&+W_4(\omega_3,I+\tau_1+\tau_4+\tau_5,L+\tau_6+\tau_9+\tau_{12},\omega_6,c,a,d,b)+W_4(\omega_3,J+\tau_1+\tau_8+\tau_9,I+\tau_2+\tau_4+\tau_5,\omega_8,c,b,a,d)\\
&+W_4(\omega_3,J+\tau_1+\tau_8+\tau_9,L+\tau_5+\tau_{10}+\tau_{12},\omega_5,c,b,d,a)+W_4(\omega_3,L+\tau_5+\tau_9+\tau_{12},I+\tau_1+\tau_4+\tau_6,\omega_6,c,d,a,b)\\
&+W_4(\omega_3,L+\tau_5+\tau_9+\tau_{12},J+\tau_1+\tau_8+\tau_{10},\omega_5,c,d,b,a)+W_4(\omega_4,I+\tau_1+\tau_3+\tau_6,J+\tau_2+\tau_7+\tau_{10},\omega_7,d,a,b,c)\\
&+W_4(\omega_4,I+\tau_1+\tau_3+\tau_6,K+\tau_4+\tau_7+\tau_{12},\omega_6,d,a,c,b)+W_4(\omega_4,J+\tau_1+\tau_7+\tau_{10},I+\tau_2+\tau_3+\tau_4,\omega_7,d,b,a,c)\\
&+W_4(\omega_4,J+\tau_1+\tau_7+\tau_{10},K+\tau_3+\tau_8+\tau_{12},\omega_5,d,b,c,a)+W_4(\omega_4,K+\tau_3+\tau_7+\tau_{12},I+\tau_1+\tau_4+\tau_6,\omega_6,d,c,a,b)\\
&+W_4(\omega_4,K+\tau_3+\tau_7+\tau_{12},J+\tau_1+\tau_8+\tau_{10},\omega_5,d,c,b,a)\}.
\end{aligned} \tag{42}$$

In Eq. (42), $W_4$ denotes the integral

$$W_4(I,J,K,L,a,b,c,d)=\int_0^\infty x^Ie^{-ax}\,dx\int_x^\infty y^Je^{-by}\,dy\times\int_y^\infty z^Ke^{-cz}\,dz\int_z^\infty w^Le^{-dw}\,dw. \tag{43}$$

The $W_4$ integral has been discussed previously by Sims and Hagstrom.[26] These authors have given a recursion relation for the integral, as well as values for some special cases of the integral.

Since the integral

$$W(I,J,K,a,b,c)=\int_0^\infty x^Ie^{-ax}\,dx\int_x^\infty y^Je^{-by}\,dy\int_y^\infty z^Ke^{-cz}\,dz \tag{44}$$

arises in the context of the three-electron problem, and has been discussed extensively in the literature,[9,12,13,16] it is ad-

TABLE I. Values for some representative $I_4$ integrals evaluated using Eqs. (27) and (32). All entries have $a=3.6$, $b=3.8$, $c=0.8$, and $d=1.3$.

| $i$ | $j$ | $k$ | $l$ | $m$ | $n$ | $p$ | $q$ | $s$ | $t$ | $I_4$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 2 | 0 | 0 | 0 | 0 | 2 | $5.067\,939\,409\,842\,651\,008\,312\,359\,39\times10^{8}$ |
| 1 | 2 | 3 | 4 | 1 | 0 | 0 | 0 | 0 | 1 | $2.254\,207\,345\,236\,318\,617\,471\,135\,07\times10^{7}$ |
| 1 | 2 | 3 | 4 | 0 | 2 | 0 | 0 | 2 | 2 | $5.480\,393\,934\,991\,866\,264\,771\,878\,89\times10^{11}$ |
| 1 | 2 | 3 | 4 | 0 | 2 | 2 | 0 | 0 | 2 | $5.368\,252\,390\,484\,503\,824\,239\,842\,74\times10^{11}$ |
| 1 | 2 | 3 | 4 | 2 | 0 | 1 | 0 | 0 | 2 | $3.066\,337\,409\,317\,699\,286\,041\,877\,26\times10^{9}$ |
| 1 | 2 | 3 | 4 | 1 | 3 | 0 | 0 | 0 | 2 | $2.889\,914\,740\,840\,552\,356\,252\,969\,39\times10^{11}$ |
| 1 | 2 | 3 | 4 | 0 | 1 | 1 | 0 | 0 | 2 | $7.618\,678\,465\,825\,582\,751\,054\,564\,74\times10^{9}$ |
| −1 | −1 | −1 | −1 | 2 | 0 | 0 | −1 | 2 | −1 | $1.144\,435\,513\,036\,587\,426\,635\,712\,19\times10^{2}$ |
| 1 | 2 | 3 | 4 | 3 | 3 | 2 | 0 | 2 | 0 | $1.679\,228\,373\,678\,646\,793\,368\,058\,65\times10^{13}$ |
| 1 | 2 | 3 | 4 | 0 | 2 | 2 | 0 | 2 | 2 | $3.354\,413\,036\,967\,296\,133\,164\,196\,24\times10^{13}$ |
| 1 | 2 | 3 | 4 | 2 | 2 | 0 | 1 | 2 | 2 | $2.393\,675\,713\,692\,744\,849\,863\,600\,20\times10^{13}$ |
| 1 | 2 | 3 | 4 | 2 | 2 | 0 | 2 | 2 | 1 | $1.983\,354\,428\,418\,357\,876\,328\,875\,68\times10^{13}$ |
| 1 | 2 | −1 | −1 | −1 | 2 | 0 | −1 | 2 | 2 | $7.509\,027\,797\,562\,537\,372\,664\,899\,09\times10^{3}$ |
| −1 | −1 | −1 | −1 | 1 | 2 | 0 | −1 | 2 | −1 | $3.605\,710\,376\,746\,440\,557\,790\,661\,32\times10^{2}$ |
| −1 | 1 | 1 | −1 | 3 | −1 | 2 | 2 | 0 | 1 | $2.764\,452\,054\,064\,275\,956\,956\,217\,25\times10^{5}$ |
| 1 | 2 | 3 | −1 | 3 | 1 | 0 | 2 | 2 | 1 | $3.629\,849\,893\,779\,623\,694\,349\,389\,10\times10^{9}$ |
| 1 | 2 | 3 | 4 | 1 | 1 | 0 | 1 | 1 | 2 | $1.406\,388\,379\,915\,098\,238\,400\,955\,30\times10^{11}$ |
| 1 | 2 | 3 | −1 | 2 | 2 | 2 | 2 | 2 | 2 | $2.461\,716\,450\,527\,742\,587\,338\,204\,15\times10^{12}$ |
| 1 | 2 | 3 | −1 | 1 | 2 | 2 | 2 | 2 | 2 | $1.115\,320\,304\,884\,140\,744\,860\,690\,79\times10^{12}$ |
| 1 | 2 | 3 | −1 | 2 | 2 | 1 | 2 | 2 | 2 | $6.646\,114\,199\,531\,403\,444\,879\,760\,52\times10^{11}$ |
| 1 | 2 | 3 | −1 | 2 | 1 | 1 | 2 | 2 | 2 | $4.898\,202\,794\,184\,977\,140\,224\,588\,93\times10^{10}$ |

vantageous to exploit previous work and reduce the $W_4$ integral directly to the $W$ integrals. Two cases arise: $L\geqslant0$ and $L<0$. For $L\geqslant0$ the $W_4$ integral can be easily reduced to the form

$$W_4(I,J,K,L,a,b,c,d)=\frac{L!}{d^{L+1}}\sum_{v=0}^{L}\frac{d^v}{v!}W(I,J,K+v,a,b,c+d). \tag{45}$$

For the case when $L<0$, a rearrangement of the order of integration allows the following result to be obtained:

$$W_4(I,J,K,L,a,b,c,d)=\frac{I!}{a^{I+1}}\left\{W(J,K,L,b,c,d)-\sum_{m=0}^{I}\frac{a^m}{m!}\times W(J+m,K,L,a+b,c,d)\right\}. \tag{46}$$

Equation (46) applies when $J\geqslant0$, $J+K\geqslant-1$, and $J+K+L\geqslant-2$, and when the differencing does not result in the loss of too many digits of precision. Equation (46) is not expected to be numerically stable for general application. In its place the following result is employed

$$W_4(I,J,K,L,a,b,c,d)=I!\sum_{m=0}^{\infty}\frac{a^m}{(m+I+1)!}W(m+I+J+1,K,L,a+b,c,d). \tag{47}$$

Equation (32) represents the general solution of the integral given in Eq. (3), with $I_\Omega$ given by Eq. (36) and $I_R$ given by Eq. (42). All the summation limits in Eq. (42) terminate at finite values. This follows from the properties of the Pochhammer symbol [see Eq. (28)] and the definition of $g$ given in Eq. (39). For $m$ even in Eq. (37) the $m_2$ summation terminates at $m/2-m_1$ [see Eqs. (13) and (39)], and for $m$ odd the $m_2$ summation terminates at $(m+1)/2$. A similar argument applies for each of the summation limits in Eq. (37).

We now turn to the summation limits in Eq. (32). If any of $m$, $n$, $p$, $q$, $s$, and $t$ are even, the corresponding summation limit terminates at finite values [see Eq. (38)]. For example, if $t$ is even, then the $t_1$ summation limit is bounded above by $(t/2)$. The second condition that sets the summation limits is the triangle condition on the $3j$ symbols in Eq. (36). For example,

$$|n_1-q_1|\leqslant t_1\leqslant n_1+q_1, \tag{48}$$

$$|p_1-s_1|\leqslant t_1\leqslant p_1+s_1 \tag{49}$$

and all cyclic permutations for the sets $(m_1,n_1,p_1,)$, $(m_1,q_1,s_1)$, $(n_1,q_1,t_1)$, and $(p_1,s_1,t_1)$. From these considerations it is clear that the $t_1$ summation terminates at the value $\min\{t/2 \text{ if } t \text{ even}, n_{\max}+q_{\max}, p_{\max}+s_{\max}\}$ where $n_{\max}$ denotes the maximum summation index for the $n_1$ summation and similar definitions apply to $q_{\max}$, $p_{\max}$, and $s_{\max}$. So if $t$ is odd, then $n$ and $q$ both even, or $p$ and $s$ both even, would be sufficient to terminate the $t_1$ summation at finite values. If neither of these latter two conditions are satisfied then the $t_1$ summation may still terminate at finite values. This would follow if $m$, $n$, and $s$ are each even or if $m$, $p$, and $q$ were each even. These two conditions following from triangle inequalities on the $3j$ symbols in Eq. (36). A similar argument applies to each of the summation limits in Eq. (32). The most difficult case to deal with occurs when $m$, $n$, $p$, $q$, $s$, and $t$ are *all* odd. In this case an appropriate computational strategy would be to rearrange the summations in Eq. (32) according to the speed of convergence for representative test values of $a$, $b$, $c$, and $d$. From a practical point of view, it would be more appropriate to select the basis functions in Eq. (2) in such a way that integrals involving the all odd case do not arise. The triangle inequalities in Eqs. (48) and (49) and the others obtained by various cyclic permutation of the sets indicated after Eq. (49), lead to lower bounds on the summation limits in Eq. (32). For example, the $t_1$ summation starts at $\max\{|n_1-q_1|,|p_1-s_1|\}$.

## IV. RESULTS

In Table I a representative sample of $I_4$ integrals are tabulated. The first 17 entries were calculated using Eq. (27) and checked using Eq. (32). The last four entries can only be evaluated by the method of Sec. III. For the first 16 entries the number of digits of precision reported reflects the number of digits that agreed for the two computational methods. Entry 17 was calculated to 22 digits of precision using Eq. (32), and these agreed with the result obtained from Eq. (27). For the last four entries, the number of digits of precision is assumed to be similar. All the calculations were carried out on a Cray YMP in double precision.

## V. CONCLUDING REMARKS

A computationally viable scheme has been presented for the evaluation of atomic integrals for the four-electron problem involving up to six interelectronic separation factors $r_{ij}$. The methods of Secs. II and III can both be extended to integrals involving more than four electron coordinates, but the results will become increasingly involved. To apply the Hylleraas method to systems with more than four electrons, a judicious selection of basis functions with perhaps no more than two distinct $r_{ij}$ factors for each basis function may prove to be a viable strategy. In this case the methods of Sec. II might prove to be very useful.

To evaluate certain relativistic corrections or matrix elements of the square of the Hamiltonian (which are required for some lower bound formulas) for four-electron systems using a standard Hylleraas expansion, then $I_4$ integrals with $r_{ij}^{-2}$ factors arise. Such integrals can be attacked by an extension of the methods developed elsewhere.[23,24]

The solution of the four-electron integrals presented in this work should allow a general Hylleraas wave function to be constructed, leading to a much improved determination of $E_{\mathrm{NR}}$, without the need for extrapolation estimates. Work is in progress on this problem.

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