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One-center Slater-type integrals with explicit correlation factors

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Abstract

The focus of this review is the treatment of one-center two-, three-, and four-electron integrals involving Slater-type functions with explicit dependence on inter-electronic factors. We illustrate the different approaches that have been employed to solve these correlated integrals. A concise summary of current problems and possible future directions is given.

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1. Introduction

In this review my intention is to discuss the treatment of integrals with explicit correlation factors using Slater-type functions as the basis. The focus is on few-electron systems: covering one-center integrals with as many as six factors of the inter-electronic separation distance, r_{ij} .

The idea to incorporate explicit factors of r_{ij} in the trial wave function, goes back to Slater [1-3], and to Hylleraas [4-8], who was the first to exploit the approach in practical calculations. The Hylleraas wave function for an S state of a two-electron atomic system can be written as:

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_{\mu=1}^N c_{\mu} r_1^{i_{\mu}} r_2^{j_{\mu}} r_{12}^{k_{\mu}} e^{-\alpha_{\mu} r_1 - \beta_{\mu} r_2} \pm \text{exchange term}, \quad (1.1)$$

where c_{μ} denotes the expansion coefficients, N represents the number of terms in the expansion, r_n designates the electron-nuclear separation distance for electron n , α_{μ} and β_{μ} are the non-linear parameters and satisfy $\alpha_{\mu} > 0$, $\beta_{\mu} > 0$, and the integer indices $\{i_{\mu}, j_{\mu}, k_{\mu}\}$ are each ≥ 0 . The electron-electron separation distance satisfies $r_{12} = r_{21} = |\mathbf{r}_1 - \mathbf{r}_2|$. The specific inclusion of non-zero values of k_{μ} in the summation yields the Hylleraas expansion. The terminology *correlation factor* is often used synonymously with the inclusion of explicit r_{12} factors in wave functions or in integrals. The inclusion of such factors in the wave function has led to very impressive results for few-electron systems. However, the complexities of the integration problems that emerge has led to limited success for larger electronic systems.

The layout of this review is as follows. The one-center two-electron integrals are covered in sections 2-8. Cases considered include those with linear terms like r_{ij}^m and with exponential terms like $e^{-\gamma r_{ij}}$, as well as the situation when logarithmic terms are also incorporated. Sections 2-4 include some material directed at the non-expert reader. Each of the common coordinate systems that have been employed: (i) spherical polar, (ii) the $\{r_1, r_2, r_{12}\}$ coordinates, (iii) the $\{s, t, u\}$ coordinates, and (iv) perimetric coordinates, are discussed. The use of Fourier transform techniques to deal with these integrals is also illustrated. One-center three-electron correlated integrals and the associated auxiliary functions, are discussed in sections 9-13. The different expansions that have been employed for r_{ij}^m are also treated. Sections 14-15 cover related ground for the one-center four-electron integrals. Section 16 provides a concise introduction to the treatment of few-electron

molecular systems. Finally, section 17 briefly outlines some of the challenges that remain.

2. Two-electron integrals involving explicit r_{12} factors

In this section we examine the simplest of the one-center correlated integrals, that is, integrals with explicit r_{ij} factors appearing. The problem is treated first in spherical polar coordinates. The non-relativistic Hamiltonian for a two-electron atomic S state in the infinite nuclear mass approximation can be written in the form:

$$H = -\frac{1}{2} \sum_{i=1}^2 \left(\frac{\partial^2}{\partial r_i^2} + \frac{2}{r_i} \frac{\partial}{\partial r_i} \right) - \frac{\partial^2}{\partial r_{12}^2} - \frac{2}{r_{12}} \frac{\partial}{\partial r_{12}} - \frac{1}{2} \left(\frac{r_1^2 + r_{12}^2 - r_2^2}{r_1 r_{12}} \frac{\partial^2}{\partial r_1 \partial r_{12}} \right) - \frac{1}{2} \left(\frac{r_2^2 + r_{12}^2 - r_1^2}{r_2 r_{12}} \frac{\partial^2}{\partial r_2 \partial r_{12}} \right) - \sum_{i=1}^2 \frac{Z}{r_i} + \frac{1}{r_{12}}, \quad (2.1)$$

where Z denotes the nuclear charge and atomic units have been employed. This form has been discussed in a number of sources [5, 8-12]. It is a straightforward calculation to show that using the choice of wave function given in Eq. (1.1), then the expectation value $\langle \psi(\mathbf{r}_1, \mathbf{r}_2) | H | \psi(\mathbf{r}_1, \mathbf{r}_2) \rangle$ reduces to a sum of integrals of the form:

$$I_2(i, j, k, \alpha, \beta) = \iint r_1^i r_2^j r_{12}^k e^{-\alpha r_1 - \beta r_2} d\mathbf{r}_1 d\mathbf{r}_2, \quad (2.2)$$

where the indices $\{i, j, k\}$ are integers. The constraints on the indices $\{i, j, k\}$ and the parameters α and β for the integral to be convergent, are: $\alpha > 0$, $\beta > 0$, and

$$i \geq -2, \quad j \geq -2, \quad k \geq -2, \quad \text{with } i + j + k \geq -5. \quad (2.3)$$

If the dummy integration variables are relabeled, then the symmetry property for this integral is

$$I_2(i, j, k, \alpha, \beta) = I_2(j, i, k, \beta, \alpha). \quad (2.4)$$

The simplest special case for this integral occurs when $k = 0$, so that

$$I_2(i, j, 0, \alpha, \beta) = I_1(i, \alpha) I_1(j, \beta), \quad (2.5)$$

where the one-electron integral I_1 is defined for $\alpha > 0$ and $i \geq -2$ by

$$I_1(i, \alpha) = \int r^i e^{-\alpha r} dr. \quad (2.6)$$

The I_1 integral can be evaluated in spherical polar coordinates on making use of the result:

$$\int_0^\infty r^m e^{-\alpha r} dr = \frac{m!}{\alpha^{m+1}}, \quad (2.7)$$

so that

$$I_1(i, \alpha) = \frac{4\pi(i+2)!}{\alpha^{i+3}}. \quad (2.8)$$

We will examine two simple cases, which will illustrate the important distinction between even and odd powers of the factor r_{12} . First, consider the case $k = 2$ in Eq. (2.2). From the cosine rule, we can write

$$r_{12}^2 = r_1^2 + r_2^2 - 2r_1r_2 \cos\theta_{12}, \quad (2.9)$$

so that

$$\begin{aligned} I_2(i, j, 2, \alpha, \beta) &= \iint r_1^i r_2^j (r_1^2 + r_2^2 - 2r_1r_2 \cos\theta_{12}) e^{-\alpha r_1 - \beta r_2} d\mathbf{r}_1 d\mathbf{r}_2 \\ &= I_1(i+2, \alpha) I_1(j, \beta) + I_1(i, \alpha) I_1(j+2, \beta) \\ &\quad - 2 \iint r_1^{i+1} r_2^{j+1} \cos\theta_{12} e^{-\alpha r_1 - \beta r_2} d\mathbf{r}_1 d\mathbf{r}_2. \end{aligned} \quad (2.10)$$

To deal with the last integral consider the angular integration first, which we denote by I_Ω . Then

$$I_\Omega = \iint \cos\theta_{12} d\Omega_1 d\Omega_2, \quad (2.11)$$

where $\int d\Omega$ is shorthand for $\int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi$. A simple way to carry out the integration is to express $\cos\theta_{12}$ in terms of the polar angles $\{\theta_1, \phi_1, \theta_2, \phi_2\}$ as

$$\cos\theta_{12} = \cos\theta_1 \cos\theta_2 + \sin\theta_1 \sin\theta_2 \cos(\phi_1 - \phi_2). \quad (2.12)$$

An alternative approach, and one that will prove to be useful for more complicated situations, is to write $\cos\theta_{12}$ in terms of a Legendre polynomial, and then take advantage of the addition theorem for spherical harmonics [p. 496, Vol. I, 13]:

$$P_l(\cos\theta_{12}) = \frac{4\pi}{2l+1} \sum_{m=-l}^l Y_{lm}^*(\theta_1, \phi_1) Y_{lm}(\theta_2, \phi_2), \quad (2.13)$$

where $Y_{lm}(\theta, \phi)$ denotes a spherical harmonic and * indicates a complex conjugate. The spherical harmonics form an orthonormal basis, so that

$$\int Y_{l_1 m_1}^*(\theta, \phi) Y_{l_2 m_2}(\theta, \phi) d\Omega = \delta_{l_1 l_2} \delta_{m_1 m_2}, \quad (2.14)$$

where the Kronecker delta δ_{jk} satisfies $\delta_{jk} = 1$, for $j = k$, and $\delta_{jk} = 0$, for $j \neq k$. Noting that $Y_{00}(\theta, \phi) = \frac{1}{\sqrt{4\pi}}$, then from Eq. (2.11),

$$\begin{aligned} I_\Omega &= \iint P_1(\cos\theta_{12}) d\Omega_1 d\Omega_2 \\ &= \frac{4\pi}{3} \sum_{m=-1}^1 \int Y_{1m}^*(\theta_1, \phi_1) d\Omega_1 \int Y_{1m}(\theta_2, \phi_2) d\Omega_2 \\ &= \frac{16\pi^2}{3} \sum_{m=-1}^1 \int Y_{1m}^*(\theta_1, \phi_1) Y_{00}(\theta_1, \phi_1) d\Omega_1 \int Y_{00}^*(\theta_1, \phi_1) Y_{1m}(\theta_2, \phi_2) d\Omega_2 \\ &= \frac{16\pi^2}{3} \sum_{m=-1}^1 \delta_{10}^2 \delta_{m0}^2 \\ &= 0. \end{aligned} \quad (2.15)$$

Hence,

$$I_2(i, j, 2, \alpha, \beta) = \frac{16\pi^2}{\alpha^{i+3}\beta^{j+3}} \left(\frac{(i+4)!(j+2)!}{\alpha^2} + \frac{(i+2)!(j+4)!}{\beta^2} \right). \quad (2.16)$$

This simple example illustrates a feature that is more general: positive even powers of r_{ij} do not lead to any particular complexity for the integral evaluation. For higher even powers of r_{ij} , a finite sum of terms is obtained.

We consider a second example which illustrates the increase in complexity, when the power on r_{ij} is odd. The case $k = -1$ is treated. To handle this situation, we introduce the first and best known of the expansions of r_{ij}^{-1} that will be dealt with in this review:

$$\frac{1}{r_{ij}} = \sum_{l=0}^{\infty} \frac{r_{<}^l}{r_{>}^{l+1}} P_l(\cos \theta_{ij}), \quad (2.17)$$

where $r_{<} = \min\{r_i, r_j\}$ and $r_{>} = \max\{r_i, r_j\}$. A general expansion for r_{ij}^n in terms of Legendre polynomials has been discussed by Chapman [14]. The derivation of the preceding result is straightforward on using the generating function expansion for the Legendre polynomials. For our second example, we have

$$\begin{aligned} I_2(i, j, -1, \alpha, \beta) &= \sum_{l=0}^{\infty} \iint r_1^i r_2^j \frac{r_{<}^l}{r_{>}^{l+1}} P_l(\cos \theta_{ij}) e^{-\alpha r_1 - \beta r_2} d\mathbf{r}_1 d\mathbf{r}_2 \\ &= \sum_{l=0}^{\infty} \int_0^{\infty} r_1^{i+2} e^{-\alpha r_1} dr_1 \int_0^{\infty} r_2^{j+2} e^{-\beta r_2} \frac{r_{<}^l}{r_{>}^{l+1}} dr_2 \iint P_l(\cos \theta_{ij}) d\Omega_1 d\Omega_2. \end{aligned} \quad (2.18)$$

The angular integration can be carried out in a similar fashion to Eq. (2.15), to yield:

$$\iint P_l(\cos \theta_{ij}) d\Omega_1 d\Omega_2 = 16\pi^2 \delta_{l0}, \quad (2.19)$$

so that Eq. (2.18) becomes

$$\begin{aligned} I_2(i, j, -1, \alpha, \beta) &= 16\pi^2 \int_0^{\infty} r_1^{i+2} e^{-\alpha r_1} dr_1 \int_0^{\infty} r_2^{j+2} e^{-\beta r_2} r_{>}^{-1} dr_2 \\ &= 16\pi^2 \int_0^{\infty} r_1^{i+2} e^{-\alpha r_1} dr_1 \left\{ \frac{1}{r_1} \int_0^{r_1} r_2^{j+2} e^{-\beta r_2} dr_2 + \int_{r_1}^{\infty} r_2^{j+1} e^{-\beta r_2} dr_2 \right\}. \end{aligned} \quad (2.20)$$

On making use of Eq. (2.7) and the result

$$\int_x^\infty r^i e^{-ar} dr = \frac{i! e^{-ax}}{a^{i+1}} \sum_{m=0}^i \frac{(ax)^m}{m!}, \quad (2.21)$$

leads to

$$\begin{aligned} I_2(i, j, -1, \alpha, \beta) &= 16\pi^2 \int_0^\infty r_1^{i+2} e^{-\alpha r_1} dr_1 \\ &\quad \left\{ \frac{1}{r_1} \int_0^\infty r_2^{j+2} e^{-\beta r_2} dr_2 - \frac{1}{r_1} \int_{r_1}^\infty r_2^{j+2} e^{-\beta r_2} dr_2 + \int_{r_1}^\infty r_2^{j+1} e^{-\beta r_2} dr_2 \right\} \\ &= 16\pi^2 \int_0^\infty r_1^{i+2} e^{-\alpha r_1} dr_1 \\ &\quad \left\{ \frac{(j+2)!}{r_1 \beta^{j+3}} - \frac{1}{r_1} \frac{(j+2)! e^{-\beta r_1}}{\beta^{j+3}} \sum_{m=0}^{j+2} \frac{(\beta r_1)^m}{m!} + \frac{(j+1)! e^{-\beta r_1}}{\beta^{j+2}} \sum_{m=0}^{j+1} \frac{(\beta r_1)^m}{m!} \right\} \\ &= \frac{16\pi^2}{\beta^{j+3}} \left\{ \frac{(i+1)!(j+2)!}{\alpha^{i+2}} - \frac{(j+2)!}{(\alpha+\beta)^{i+2}} \sum_{m=0}^{j+2} \frac{(i+1+m)!}{m!} \left(\frac{\beta}{\alpha+\beta} \right)^m \right. \\ &\quad \left. + \frac{(j+1)! \beta}{(\alpha+\beta)^{i+3}} \sum_{m=0}^{j+1} \frac{(i+1+m)!}{m!} \left(\frac{\beta}{\alpha+\beta} \right)^m \right\}. \quad (2.22) \end{aligned}$$

Particular cases are

$$I_2(-1, -1, -1, \alpha, \beta) = \frac{16\pi^2}{\alpha\beta(\alpha+\beta)}, \text{ and } I_2(0, 0, -1, \alpha, \beta) = \frac{32\pi^2(\alpha^2 + 3\alpha\beta + \beta^2)}{\alpha^2\beta^2(\alpha+\beta)^3} \quad (2.23)$$

The preceding analysis needs to be modified slightly to deal with the case $k = -2$, which arises in various applications. Discussion of this case can be found in [15-16].

There is one special point we want to emphasize in the preceding derivation. Since the goal of all the analytic developments is to eventually finish with a numerical result, it is always necessary to check derived formulas for the possibility of round-off errors becoming substantial, leading to a major loss of computational precision. For the formulas given in Eq. (2.23), all the terms are positive, so both these results would be stable for numerical evaluation. However, Eq. (2.22) may not be. Let us examine the evaluation of

Eq. (2.22) for the case $i = j = 0$ and consider the combination of the first two terms in the $\{.\}$, as might occur in a computer code. Let $\beta = \varepsilon\alpha$, then the first two terms in brackets lead to:

$$\text{first pair of terms} = \frac{2}{\alpha^2} \left\{ 1 - \frac{1}{(1+\varepsilon)^2} \left[1 + \frac{2\varepsilon}{1+\varepsilon} + \frac{3\varepsilon^2}{(1+\varepsilon)^2} \right] \right\}. \quad (2.24)$$

Now if ε turns out to be rather small, say, 10^{-3} , then the above calculation becomes:

$$\begin{aligned} \text{first pair of terms} &= 2\alpha^{-2} \{1 - 0.998002996\dots[1.002000996\dots]\} \\ &= 2\alpha^{-2} \{1 - 0.9999999960\dots\}, \end{aligned} \quad (2.25)$$

which represents a loss of eight digits of precision. While such a spread in the exponents just indicated is unlikely in a typical practical calculation, it is far better to produce algorithms that are robust towards changes in the parameters, and anticipate numerical instabilities of this type. A way to circumvent this particular numerical problem is to proceed as follows:

$$\begin{aligned} 16\pi^2 \int_0^\infty r_1^{i+2} e^{-\alpha r_1} &\left\{ \frac{(j+2)!}{r_1 \beta^{j+3}} - \frac{1}{r_1} \frac{(j+2)! e^{-\beta r_1}}{\beta^{j+3}} \sum_{m=0}^{j+2} \frac{(\beta r_1)^m}{m!} \right\} dr_1 \\ &= 16\pi^2 \frac{(j+2)!}{\beta^{j+3}} \int_0^\infty r_1^{i+1} e^{-\alpha r_1 - \beta r_1} \left\{ e^{\beta r_1} - \sum_{m=0}^{j+2} \frac{(\beta r_1)^m}{m!} \right\} dr_1 \\ &= 16\pi^2 \frac{(j+2)!}{\beta^{j+3}} \sum_{m=j+3}^\infty \frac{\beta^m}{m!} \int_0^\infty r_1^{i+1+m} e^{-\alpha r_1 - \beta r_1} dr_1 \\ &= \frac{16\pi^2 (j+2)!}{\beta^{j+3} (\alpha + \beta)^{i+2}} \sum_{m=j+3}^\infty \frac{(i+m+1)!}{m!} \left(\frac{\beta}{\alpha + \beta} \right)^m. \end{aligned} \quad (2.26)$$

This form is numerically stable when the value of β is small with respect to the value of α .

3. Two-electron integrals evaluated using r_1 , r_2 , and r_{12} variables

A straightforward approach to the evaluation of $I_2(i, j, k, \alpha, \beta)$ is to work directly in terms of the coordinates r_1 , r_2 , and r_{12} . The transformation from

spherical polar coordinates for an atomic system, to the coordinates r_1 , r_2 , and r_{12} , can be done as follows [17-19]. The triangle formed from the sides r_1 , r_2 , and r_{12} can rotate about the r_1 direction over the angle χ , which is $[0, 2\pi]$. The direction r_1 is allowed to rotate over the polar angles θ_1 , ϕ_1 . If we let the r_1 direction lie along the polar axis, and differentiate the cosine rule for r_{12} with respect to θ_{12} keeping the sides r_1 and r_2 fixed, so that $d\mathbf{r}_2 = r_2^2 dr_2 \left(\frac{r_{12}}{r_1 r_2} d\theta_{12} \right) d\chi$, and combine this with $d\mathbf{r}_1$ expressed in polar form, then

$$d\tau \equiv d\mathbf{r}_1 d\mathbf{r}_2 = r_1 r_2 r_{12} dr_1 dr_2 dr_{12} \sin\theta_1 d\theta_1 d\phi_1 d\chi. \quad (3.1)$$

From Eq. (3.1) it follows for S states that

$$\begin{aligned} \int d\tau &\equiv \int \int d\mathbf{r}_1 d\mathbf{r}_2 = \int_0^\infty r_1 dr_1 \int_0^\infty r_2 dr_2 \int_{|r_1-r_2|}^{r_1+r_2} r_{12} dr_{12} \int_0^\pi \sin\theta_1 d\theta_1 \int_0^{2\pi} d\phi_1 \int_0^{2\pi} d\chi \\ &= 8\pi^2 \int_0^\infty r_1 dr_1 \left\{ \int_0^{r_1} r_2 dr_2 \int_{r_1-r_2}^{r_1+r_2} r_{12} dr_{12} + \int_{r_1}^\infty r_2 dr_2 \int_{r_2-r_1}^{r_1+r_2} r_{12} dr_{12} \right\}. \end{aligned} \quad (3.2)$$

The $I_2(i, j, k, \alpha, \beta)$ integral can then be written for $k \geq -1$ as

$$\begin{aligned} I_2(i, j, k, \alpha, \beta) &= 8\pi^2 \int_0^\infty r_1^{i+1} e^{-\alpha r_1} dr_1 \left\{ \int_0^{r_1} r_2^{j+1} e^{-\beta r_2} dr_2 \int_{r_1-r_2}^{r_1+r_2} r_{12}^{k+1} dr_{12} \right. \\ &\quad \left. + \int_{r_1}^\infty r_2^{j+1} e^{-\beta r_2} dr_2 \int_{r_2-r_1}^{r_1+r_2} r_{12}^{k+1} dr_{12} \right\} \\ &= \frac{8\pi^2}{k+2} \int_0^\infty r_1^{i+1} e^{-\alpha r_1} dr_1 \left\{ \int_0^{r_1} r_2^{j+1} e^{-\beta r_2} dr_2 [(r_1+r_2)^{k+2} - (r_1-r_2)^{k+2}] \right. \\ &\quad \left. + \int_{r_1}^\infty r_2^{j+1} e^{-\beta r_2} dr_2 [(r_1+r_2)^{k+2} - (r_2-r_1)^{k+2}] \right\}. \end{aligned} \quad (3.3)$$

For the case of even k the preceding result simplifies to

$$I_2(i, j, k, \alpha, \beta) = \frac{8\pi^2}{k+2} \int_0^\infty r_1^{i+1} e^{-\alpha r_1} dr_1 \int_0^\infty r_2^{j+1} e^{-\beta r_2} [(r_1+r_2)^{k+2} - (r_1-r_2)^{k+2}] dr_2. \quad (3.4)$$

A binomial expansion can be carried out for the factor in square brackets in the preceding formula. However, to preserve invariance under the simultaneous interchange $i \leftrightarrow j$ and $\alpha \leftrightarrow \beta$ by visual inspection, a symmetric form for the binomial expansion is carried out, with the result that:

$$\begin{aligned}
 I_2(i, j, k, \alpha, \beta) = & \frac{8\pi^2}{(k+2)\alpha^{i+3}\beta^{j+3}} \left\{ \binom{k+2}{\frac{k}{2}+1} [1 + (-1)^{k/2}] (i+2 + \frac{k}{2})! (j+2 + \frac{k}{2})! (\alpha\beta)^{-k/2} \right. \\
 & + 2 \sum_{n=0}^{\lfloor \frac{k-2}{4} \rfloor} \binom{k+2}{2n+1} \{ (i+k+2-2n)! (j+2+2n)! \alpha^{2n-k} \beta^{-2n} \\
 & \left. + (i+2+2n)! (j+k+2-2n)! \beta^{2n-k} \alpha^{-2n} \right\}, \quad (3.5)
 \end{aligned}$$

where $\lfloor x \rfloor$ denotes the floor function, the greatest integer less than or equal to x . A related formula can be developed for the case k is odd, though attention needs to be paid to possible precision loss in the formula, as indicated in the discussion for Eqs. (2.24) – (2.26).

4. Two-electron integrals evaluated in the stu variables

In this section we consider the evaluation of the two-electron integral in the stu variables. The stu variables were introduced by Hylleraas [5, 8] and take the form:

$$s = r_1 + r_2, \quad t = r_2 - r_1, \quad u = r_{12}. \quad (4.1)$$

In the stu variables the Hylleraas wave function for S states of atomic two-electron systems can be written in the form

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = e^{-\zeta s} \sum_{i=1}^N c_i s^{l_i} t^{2m_i} u^{n_i}, \quad (4.2)$$

where the set $\{l_i, m_i, n_i\}$ are non-negative integers and the exponent ζ is > 0 . The non-relativistic Hamiltonian for a two-electron atomic S state in the infinite nuclear mass approximation in atomic units is given by [20]:

$$\begin{aligned}
H = & -\left(\frac{\partial^2}{\partial s^2} + \frac{\partial^2}{\partial u^2} + \frac{\partial^2}{\partial t^2}\right) - \frac{2s(u^2 - t^2)}{u(s^2 - t^2)} \frac{\partial^2}{\partial s \partial u} - \frac{2t(s^2 - u^2)}{u(s^2 - t^2)} \frac{\partial^2}{\partial u \partial t} \\
& - \frac{4s}{(s^2 - t^2)} \frac{\partial}{\partial s} - \frac{2}{u} \frac{\partial}{\partial u} + \frac{4t}{(s^2 - t^2)} \frac{\partial}{\partial t} - \frac{8s}{(s^2 - t^2)} + \frac{1}{u}. \quad (4.3)
\end{aligned}$$

The factor $(s^2 - t^2)$ that occurs in the denominator of several of the terms in the Hamiltonian might appear to be problematic, but this is not the case, since the volume element for the evaluation of expectation values involves a factor of $(s^2 - t^2)$.

A straightforward calculation shows that the evaluation of $\langle \psi(\mathbf{r}_1, \mathbf{r}_2) | H | \psi(\mathbf{r}_1, \mathbf{r}_2) \rangle$ using Eqs. (4.2) and (4.3) reduces to a sum of two-electron integrals that take the form:

$$I_2(i, j, k, \zeta) = \iiint s^i t^j u^k e^{-\zeta s} d\tau, \quad (4.4)$$

where $\zeta > 0$. The volume element $d\tau$ in Eq. (4.4) can be obtained directly from Eq. (3.1) by employing $dr_1 dr_2 = \frac{1}{2} ds dt$ and $r_1 r_2 = \frac{1}{4}(s^2 - t^2)$, so that

$$d\tau = \frac{1}{8} u(s^2 - t^2) ds dt du \sin \theta_1 d\theta_1 d\phi_1 d\chi. \quad (4.5)$$

On noting $-u \leq t \leq u \leq s < \infty$, then

$$\int d\tau = \pi^2 \int_0^\infty du \int_u^\infty ds \int_{-u}^u u(s^2 - t^2) dt. \quad (4.6)$$

Employing the change of integration order formula

$$\int_0^\infty dx \int_0^x f(x, y) dy = \int_0^\infty dy \int_y^\infty f(x, y) dx, \quad (4.7)$$

then Eq. (4.6) can be rewritten as

$$\int d\tau = \pi^2 \int_0^\infty ds \int_0^s du \int_{-u}^u u(s^2 - t^2) dt, \quad (4.8)$$

and when the wave function contains only even powers of the variable t , which is the required case for the two-electron ground state, to ensure the spatial part of the wave function is symmetric under interchange of the coordinates of the two electrons, then

$$\int d\tau = 2\pi^2 \int_0^\infty ds \int_0^s du \int_0^u u(s^2 - t^2) dt. \quad (4.9)$$

Since expectation values are computed as a ratio $\langle \psi | \mathcal{O} | \psi \rangle / \langle \psi | \psi \rangle$, prefactors such as the $2\pi^2$ are sometimes omitted from the integral expressions, anticipating their cancellation when an expectation value is computed.

As an example, the evaluation of $I_2(i, 2j, k, \zeta)$ is:

$$\begin{aligned} I_2(i, 2j, k, \zeta) &= 2\pi^2 \int_0^\infty e^{-\zeta s} ds \int_0^s u^{k+1} du \int_0^u \{s^{i+2} t^{2j} - s^i t^{2(j+1)}\} dt \\ &= 2\pi^2 \int_0^\infty e^{-\zeta s} ds \int_0^s \left\{ s^{i+2} \frac{u^{2j+k+2}}{2j+1} - s^i \frac{u^{2j+k+4}}{2j+3} \right\} du \\ &= 4\pi^2 \frac{(i+2j+k+5)!}{\zeta^{i+2j+k+6}} \frac{(4j+k+6)}{(2j+1)(2j+3)(2j+k+3)(2j+k+5)}. \end{aligned} \quad (4.10)$$

Kinoshita [20] generalized Eq. (4.2) to the form

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = e^{-\zeta s} \sum_{i=1}^N c_i s^{l_i - n_i} t^{2m_i} u^{n_i - 2m_i}, \quad (4.11)$$

thus allowing for the possibility of negative powers for the variables s and u to be employed. The result obtained for the ground state energy of the helium atom was impressive, considering the compact expansion employed. The Kinoshita approach does not lead to any additional complexity for the I_2 integrals evaluated in the stu variables. Thakkar and Koga [21] carried out high precision calculations on S states of two-electron systems using wave functions of the form:

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = e^{-\zeta s} \sum_{i=1}^N c_i s^{l_i/\lambda} t^{2m_i} u^{n_i/2}, \quad (4.12)$$

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = e^{-\zeta s} \sum_{i=1}^N c_i s^{(l_i - n_i)/\lambda} t^{2m_i} u^{(n_i - 2m_i)/\nu}, \quad (4.13)$$

for non-negative values of the parameters λ and ν . The only change necessary in the evaluation of the two-electron integrals that arise, is to replace Eq. (2.7) by the definition of the gamma function:

$$\int_0^\infty s^{\lambda-1} e^{-\alpha s} ds = \frac{\Gamma(\lambda)}{\alpha^\lambda}, \quad \text{for } \lambda > 0. \quad (4.14)$$

A slight modification of the standard stu variables has also been utilized. The following projective coordinates have been employed [22]:

$$s = r_1 + r_2, \quad v = \frac{r_{12}}{r_1 + r_2}, \quad w = \frac{r_1 - r_2}{r_{12}}. \quad (4.15)$$

Using this choice, the integrals appearing in Eq. (3.2) become uncoupled, so that

$$\iint d\mathbf{r}_1 d\mathbf{r}_2 = 2\pi^2 \int_0^\infty s^5 ds \int_0^1 v^2 dv \int_0^1 (1 - v^2 w^2) dw, \quad (4.16)$$

assuming that the wave function contains only even powers in the variable w . When the basis functions are selected as products of generalized Laguerre polynomials in the variable s , multiplied by Jacobi polynomials in the variables v and w , then the integral evaluations can be carried out in a straightforward manner [22].

5. Fourier transform approach to the evaluation of $I_2(i, j, k, \alpha, \beta)$

In this section, the evaluation of the two-electron correlated integral is considered, using a Fourier transform approach [23]. The particular case $i = j = 0$, and $k = -1$, is treated. Let $\varphi(\alpha, \mathbf{r}) = e^{-\alpha r}$, $h(\mathbf{r}_{12}) = \frac{1}{r_{12}}$, and

denote the Fourier transforms of $\varphi(\alpha, \mathbf{r}_1)$, $\varphi(\beta, \mathbf{r}_2)$, and $h(\mathbf{r}_{12})$ by $F(\mathbf{k}_1)$, $G(\mathbf{k}_2)$, and $H(\mathbf{k}_3)$, respectively.

The Fourier transform $F(\mathbf{k}_1)$ can be evaluated in spherical polar coordinates using the change of variables $r = \alpha^{-1} s$ and $\kappa_1 = \alpha^{-1} k_1$, and to simplify the calculation, the polar axis is placed along the vector \mathbf{k}_1 , so that:

$$\begin{aligned}
 F(\mathbf{k}_1) &= \int \varphi(\alpha, \mathbf{r}) e^{-i\mathbf{k}_1 \cdot \mathbf{r}} d\mathbf{r} \\
 &= \int_0^\infty r^2 e^{-\alpha r} dr \int_0^\pi \sin \theta e^{-ik_1 r \cos \theta} d\theta \int_0^{2\pi} d\phi \\
 &= 2\pi \alpha^{-3} \int_0^\infty s^2 e^{-s} ds \int_{-1}^1 e^{-i\kappa_1 s t} dt \\
 &= \frac{4\pi}{\alpha^3 \kappa_1} \int_0^\infty s \sin(\kappa_1 s) e^{-s} ds \\
 &= \frac{8\pi}{\alpha^3 (1 + \kappa_1^2)^2}. \tag{5.1}
 \end{aligned}$$

In a similar fashion, with $\kappa_2 = \beta^{-1} k_2$,

$$G(\mathbf{k}_2) = \frac{8\pi}{\beta^3 (1 + \kappa_2^2)^2}. \tag{5.2}$$

The Fourier transform of $h(\mathbf{r}_{12})$ does not exist in the conventional sense. This issue can be dealt with by modifying the definition of $h(\mathbf{r}_{12})$ by inserting in the numerator the factor $-\varepsilon |\mathbf{r}_{12}|$ for $\varepsilon > 0$, and taking the limit $\varepsilon \rightarrow 0+$ after evaluating the Fourier transform, but before performing the final integration. Spherical polar coordinates are employed with the polar axis placed along the vector $\mathbf{k} - \mathbf{k}_3$, and the substitutions $u = r_{12}$ and $k_3 = |\mathbf{k}_3|$ are used, so that

$$\begin{aligned}
 H(\mathbf{k}_3) &= \int h(\mathbf{r}_{12}) e^{-i\mathbf{k}_3 \cdot \mathbf{r}_{12}} d\mathbf{r}_{12} \\
 &= \int \frac{e^{-\varepsilon r_{12} - i\mathbf{k}_3 \cdot \mathbf{r}_{12}} d\mathbf{r}_{12}}{r_{12}}
 \end{aligned}$$

$$\begin{aligned}
&= 2\pi \int_0^\infty u e^{-\varepsilon u} du \int_0^\pi \sin \theta e^{-ik_3 u \cos \theta} d\theta \\
&= 2\pi \int_0^\infty u e^{-\varepsilon u} du \int_{-1}^1 e^{-ik_3 u t} dt \\
&= \frac{4\pi}{k_3} \int_0^\infty \sin(k_3 u) e^{-\varepsilon u} du \\
&= \frac{4\pi}{k_3^2 + \varepsilon^2}.
\end{aligned} \tag{5.3}$$

An alternative approach to evaluate $H(\mathbf{k}_3)$ which avoids the insertion of the convergence factor, is to take note of the distributional nature of the integral involved. To do this, we first introduce the Heisenberg delta functions, defined by:

$$\delta^+(x) = -\frac{1}{2\pi i} \lim_{\varepsilon \rightarrow 0^+} \frac{1}{(x+i\varepsilon)}, \quad \text{and} \quad \delta^-(x) = \frac{1}{2\pi i} \lim_{\varepsilon \rightarrow 0^+} \frac{1}{(x-i\varepsilon)}. \tag{5.4}$$

In the distributional sense we have

$$\begin{aligned}
\int_0^\infty \sin ku \, du &= \frac{1}{2i} \left\{ \int_0^\infty e^{iku} \, du - \int_0^\infty e^{-iku} \, du \right\} \\
&= \frac{1}{2i} \{2\pi \delta^+(k) - 2\pi \delta^-(k)\} \\
&= \frac{\pi}{i} \left\{ -\frac{1}{2\pi i} \lim_{\varepsilon \rightarrow 0^+} \frac{1}{k+i\varepsilon} - \frac{1}{2\pi i} \lim_{\varepsilon \rightarrow 0^+} \frac{1}{k-i\varepsilon} \right\} \\
&= \frac{1}{2} \lim_{\varepsilon \rightarrow 0^+} \left\{ \frac{1}{k+i\varepsilon} + \frac{1}{k-i\varepsilon} \right\} \\
&= \frac{k}{k^2 + 0_+}.
\end{aligned} \tag{5.5}$$

Inserting the inverse Fourier transforms for $\varphi(\alpha, \mathbf{r}_1)$, $\varphi(\beta, \mathbf{r}_2)$, and $h(\mathbf{r}_{12})$ leads to

$$\begin{aligned}
I(0,0,-1,\alpha,\beta) &= \iint \varphi(\alpha, \mathbf{r}_1) \varphi(\beta, \mathbf{r}_2) h(\mathbf{r}_{12}) d\mathbf{r}_1 d\mathbf{r}_2 \\
&= \frac{1}{(2\pi)^9} \iiint F(\mathbf{k}_1) e^{i\mathbf{k}_1 \cdot \mathbf{r}_1} d\mathbf{k}_1 \int G(\mathbf{k}_2) e^{i\mathbf{k}_2 \cdot \mathbf{r}_2} d\mathbf{k}_2 \int H(\mathbf{k}_3) e^{i\mathbf{k}_3 \cdot \mathbf{r}_{12}} d\mathbf{k}_3 d\mathbf{r}_1 d\mathbf{r}_2 \\
&= \frac{1}{(2\pi)^9} \iiint F(\mathbf{k}_1) G(\mathbf{k}_2) H(\mathbf{k}_3) d\mathbf{k}_1 d\mathbf{k}_2 d\mathbf{k}_3 \int \int e^{i\mathbf{k}_1 \cdot \mathbf{r}_1} e^{i\mathbf{k}_2 \cdot \mathbf{r}_2} e^{i\mathbf{k}_3 \cdot \mathbf{r}_{12}} d\mathbf{r}_1 d\mathbf{r}_2 \\
&= \frac{1}{(2\pi)^3} \iiint F(\mathbf{k}_1) F(\mathbf{k}_2) H(\mathbf{k}_3) \delta(\mathbf{k}_1 + \mathbf{k}_3) \delta(\mathbf{k}_2 - \mathbf{k}_3) d\mathbf{k}_1 d\mathbf{k}_2 d\mathbf{k}_3 \\
&= \frac{1}{(2\pi)^3} \int F(-\mathbf{k}_3) G(\mathbf{k}_3) H(\mathbf{k}_3) d\mathbf{k}_3 \\
&= \frac{32}{\alpha^3 \beta^3} \int \frac{1}{(1 + \alpha^{-2} k_3^2)^2 (1 + \beta^{-2} k_3^2)^2} \frac{1}{k_3^2} d\mathbf{k}_3 \\
&= \frac{128\pi}{\alpha^3 \beta^3} \int_0^\infty \frac{dk_3}{(1 + \alpha^{-2} k_3^2)^2 (1 + \beta^{-2} k_3^2)^2} \\
&= \frac{32\pi^2 (\alpha^2 + 3\alpha\beta + \beta^2)}{\alpha^2 \beta^2 (\alpha + \beta)^3}, \tag{5.6}
\end{aligned}$$

which is the required result.

6. The two-electron integral with exponential r_{12} factor

When the trial wave function of Eq. (1.1) is modified to include exponential correlation factors, so that

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_{\mu=1}^N c_\mu r_1^{i_\mu} r_2^{j_\mu} r_{12}^{k_\mu} e^{-\alpha_\mu r_1 - \beta_\mu r_2 - \gamma_\mu r_{12}} \pm \text{exchange term}, \tag{6.1}$$

then the quality of the results obtained for the energy and other properties, tends to be very good, even using rather compact wave functions [24]. Evaluation of the expectation value $\langle \psi(\mathbf{r}_1, \mathbf{r}_2) | H | \psi(\mathbf{r}_1, \mathbf{r}_2) \rangle$ using the preceding wave function and the Hamiltonian given in Eq. (2.1), reduces to a sum of one-center integrals of the form:

$$\mathcal{I}_2(i, j, k, \alpha, \beta, \gamma) = \iint r_1^i r_2^j r_{12}^k e^{-\alpha r_1 - \beta r_2 - \gamma r_{12}} d\mathbf{r}_1 d\mathbf{r}_2, \tag{6.2}$$

where $\alpha + \gamma > 0$, $\beta + \gamma > 0$, and $\alpha + \beta > 0$. The symmetry property for this integral is

$$\mathcal{I}_2(i, j, k, \alpha, \beta, \gamma) = \mathcal{I}_2(j, i, k, \beta, \alpha, \gamma). \quad (6.3)$$

One approach to the evaluation of $\mathcal{I}_2(i, j, k, \alpha, \beta, \gamma)$ makes use of perimetric coordinates. These coordinates are introduced with the definitions:

$$x = r_1 + r_2 - r_{12}, \quad y = r_2 + r_{12} - r_1, \quad \text{and} \quad z = r_{12} + r_1 - r_2. \quad (6.4)$$

These coordinates were introduced by Coolidge and James [25] and utilized and discussed by a number of authors [8, 18, 26-35]. Some of these authors use slightly different definitions of perimetric coordinates formed by inserting different multiplicative constants on the right hand side of each of the formulas in Eq. (6.4). The volume element $d\mathbf{r}_1 d\mathbf{r}_2$ can be evaluated from Eq. (3.1)

using Eq. (6.4) and $dr_1 dr_2 dr_{12} = \frac{1}{4} dx dy dz$, so that

$$d\mathbf{r}_1 d\mathbf{r}_2 = \frac{1}{32} (x+y)(x+z)(y+z) dx dy dz \sin \theta_1 d\theta_1 d\phi_1 d\chi. \quad (6.5)$$

The Hamiltonian in perimetric coordinates is discussed in [31, 34-35]. For an S state, we can write

$$\iint d\mathbf{r}_1 d\mathbf{r}_2 = \frac{\pi^2}{4} \int_0^\infty dx \int_0^\infty dy \int_0^\infty (x+y)(x+z)(y+z) dz. \quad (6.6)$$

We will consider the evaluation of $\mathcal{I}_2(-1, -1, -1, \alpha, \beta, \gamma)$, which will prove to be of use in the sequel. A straightforward calculation yields

$$\begin{aligned} \mathcal{I}_2(-1, -1, -1, \alpha, \beta, \gamma) &= 2\pi^2 \int_0^\infty dx \int_0^\infty dy \int_0^\infty e^{-\alpha(x+z)/2 - \beta(x+y)/2 - \gamma(y+z)/2} dz \\ &= \frac{16\pi^2}{(\alpha + \beta)(\beta + \gamma)(\alpha + \gamma)}. \end{aligned} \quad (6.7)$$

Now to evaluate the general integral $\mathcal{I}_2(i, j, k, \alpha, \beta, \gamma)$, we have

$$\mathcal{I}_2(i, j, k, \alpha, \beta, \gamma) = \frac{\pi^2}{2^{i+j+k+2}} \int_0^\infty dx \int_0^\infty dy \int_0^\infty (x+z)^{i+1} (x+y)^{j+1} (y+z)^{k+1} e^{-\alpha(x+z)/2 - \beta(x+y)/2 - \gamma(y+z)/2} dz. \quad (6.8)$$

We can proceed by making a binomial series expansion of $(x+z)^{i+1}$ and the two related terms. An alternative approach is to take advantage of the formula

$$(x+z)^{i+1} e^{-\alpha(x+z)/2} = (-2)^{i+1} \frac{\partial^{i+1} e^{-\alpha(x+z)/2}}{\partial \alpha^{i+1}}, \quad (6.9)$$

so that

$$\begin{aligned} \mathcal{I}_2(i, j, k, \alpha, \beta, \gamma) &= 2\pi^2 (-1)^{i+j+k+1} \int_0^\infty dx \int_0^\infty dy \int_0^\infty \frac{\partial^{i+j+k+3} e^{-\alpha(x+z)/2 - \beta(x+y)/2 - \gamma(y+z)/2}}{\partial \alpha^{i+1} \partial \beta^{j+1} \partial \gamma^{k+1}} dz \\ &= 2\pi^2 (-1)^{i+j+k+1} \frac{\partial^{i+j+k+3} \mathcal{I}_2(-1, -1, -1, \alpha, \beta, \gamma)}{\partial \alpha^{i+1} \partial \beta^{j+1} \partial \gamma^{k+1}}. \end{aligned} \quad (6.10)$$

The last formula can be readily evaluated using Eq. (6.7). The approach just outlined does not cover the situation when $k = -2$. This case can be conveniently treated in perimetric coordinates [24].

A recursive scheme for the evaluation of $\mathcal{I}_2(i, j, k, \alpha, \beta, \gamma)$ has been discussed by Sack *et al.* [36]. For additional discussion on the one-center two-electron integral with exponential r_{12} factor, see [24, 27, 36-38].

7. Two-electron correlated integrals with spherical harmonic factors

One-center two-electron correlated integrals with spherical harmonic terms take the form:

$$\mathcal{J}_2(i, j, k, l_1, m_1, l_2, m_2, \alpha, \beta) = \iint r_1^i r_2^j r_{12}^k e^{-\alpha r_1 - \beta r_2} Y_{l_1 m_1}(\theta_1, \phi_1) Y_{l_2 m_2}(\theta_2, \phi_2) d\mathbf{r}_1 d\mathbf{r}_2. \quad (7.1)$$

We illustrate how to deal with this type of integral involving spherical harmonic functions, by considering the case $k = -1$. On making use of Eq. (2.17) we have

$$\mathcal{J}_2(i, j, -1, l_1, m_1, l_2, m_2, \alpha, \beta) = \sum_{l=0}^{\infty} \int_0^{\infty} r_1^i e^{-\alpha r_1} dr_1 \int_0^{\infty} r_2^j e^{-\beta r_2} r_{<}^l r_{>}^{-l-1} dr_2 I_{\Omega}, \quad (7.2)$$

where the angular integral I_{Ω} can be evaluated by making use of Eqs. (2.13) and (2.14), so that

$$\begin{aligned} I_{\Omega} &= \iint P_l(\cos \theta_{12}) Y_{l_1 m_1}(\theta_1, \phi_1) Y_{l_2 m_2}(\theta_2, \phi_2) d\Omega_1 d\Omega_2 \\ &= \frac{4\pi}{2l+1} \sum_{m=-l}^l (-1)^m \int Y_{lm}^*(\theta_1, \phi_1) Y_{l_1 m_1}(\theta_1, \phi_1) d\Omega_1 \int Y_{l-m}^*(\theta_2, \phi_2) Y_{l_2 m_2}(\theta_2, \phi_2) d\Omega_2 \\ &= \frac{4\pi \delta_{ll_1} \delta_{ll_2}}{2l+1} \sum_{m=-l}^l (-1)^m \delta_{mm_1} \delta_{-mm_2} \\ &= \frac{4\pi \delta_{ll_1} \delta_{ll_2} (-1)^{m_1} \delta_{-m_1 m_2}}{2l+1}, \end{aligned} \quad (7.3)$$

and we have made use of the relationship [p. 495, Vol. I, 13]

$$Y_{lm}(\theta_2, \phi_2) = (-1)^m Y_{l-m}^*(\theta_2, \phi_2). \quad (7.4)$$

Equation (7.2) simplifies to give

$$\mathcal{J}_2(i, j, -1, l_1, m_1, l_2, m_2, \alpha, \beta) = \frac{4\pi (-1)^{m_1} \delta_{l_1 l_2} \delta_{-m_1 m_2}}{2l_1 + 1} \int_0^{\infty} r_1^i e^{-\alpha r_1} dr_1 \int_0^{\infty} \frac{r_2^j r_{<}^{l_1} e^{-\beta r_2}}{r_{>}^{l_1+1}} dr_2, \quad (7.5)$$

The preceding double integral evaluates as

$$\begin{aligned} &\int_0^{\infty} r_1^i e^{-\alpha r_1} dr_1 \int_0^{\infty} \frac{r_2^j r_{<}^{l_1} e^{-\beta r_2}}{r_{>}^{l_1+1}} dr_2 = \int_0^{\infty} r_1^i e^{-\alpha r_1} dr_1 \\ &\left\{ \frac{1}{r_1^{l_1+1}} \int_0^{r_1} r_2^{j+l_1} e^{-\beta r_2} dr_2 + r_1^{l_1} \int_{r_1}^{\infty} r_2^{j-l_1-1} e^{-\beta r_2} dr_2 \right\} \\ &= \int_0^{\infty} r_1^{i-l_1-1} e^{-\alpha r_1} dr_1 \int_0^{r_1} r_2^{j+l_1} e^{-\beta r_2} dr_2 \\ &+ \int_0^{\infty} r_1^{i+l_1} e^{-\alpha r_1} dr_1 \int_{r_1}^{\infty} r_2^{j-l_1-1} e^{-\beta r_2} dr_2 \end{aligned}$$

$$\begin{aligned}
&= \int_0^\infty r_2^{j+l_1} e^{-\beta r_2} dr_2 \int_{r_2}^\infty r_1^{i-l_1-1} e^{-\alpha r_1} dr_1 \\
&+ \int_0^\infty r_1^{i+l_1} e^{-\alpha r_1} dr_1 \int_{r_1}^\infty r_2^{j-l_1-1} e^{-\beta r_2} dr_2 \\
&= W_2(j+l_1, i-l_1-1, \beta, \alpha) + W_2(i+l_1, j-l_1-1, \alpha, \beta), \tag{7.6}
\end{aligned}$$

where a change of integration order (recall Eq. (4.7)) has been employed and the W_2 integral is defined by

$$W_2(i, j, a, b) = \int_0^\infty x^i e^{-ax} dx \int_x^\infty y^j e^{-by} dy. \tag{7.7}$$

The W_2 integral is convergent for $a > 0$, $b > 0$, $i \geq 0$, and $i + j \geq -1$. This auxiliary function has been extensively studied [39-50]. For the case that $j \geq 0$, W_2 can be evaluated using Eq. (2.21), so that

$$W_2(i, j, a, b) = \frac{j!}{b^{j+1}(a+b)^{i+1}} \sum_{m=0}^j \frac{(i+m)!}{m!} \left(\frac{b}{a+b} \right)^m. \tag{7.8}$$

Integration by parts using Eq. (7.7) for the case $j \geq 0$ leads to a simple recurrence relationship for $W_2(i, j, a, b)$. For the case $j < 0$, W_2 can be calculated using [44]

$$W_2(i, j, a, b) = \frac{i!}{a(a+b)^{i+j+1}} \sum_{m=1}^\infty \frac{(i+j+m)!}{(m+i)!} \left(\frac{a}{a+b} \right)^m, \tag{7.9}$$

provided b is not close to zero, in which case other computational strategies need to be employed [48].

The final result for the correlated integral is

$$\begin{aligned}
\mathcal{I}_2(i, j, -1, l_1, m_1, l_2, m_2, \alpha, \beta) &= \frac{4\pi(-1)^{m_1} \delta_{l_1 l_2} \delta_{-m_1 m_2}}{2l_1+1} \{W_2(j+l_1, i-l_1-1, \beta, \alpha) \\
&+ W_2(i+l_1, j-l_1-1, \alpha, \beta)\}. \tag{7.10}
\end{aligned}$$

Extensions and further reading on these types of integrals can be found in [45, 51-53].

8. Two-electron correlated integrals with logarithm factors

It has turned out to be effective to supplement the basis set for wave functions as given by Eq. (4.2), and the further extensions mentioned in section 4, by the inclusion of logarithmic factors [54-58], the simplest of which takes the form:

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = e^{-\zeta s} \sum_{i=1}^N c_i s^{l_i} t^{2m_i} u^{n_i} (\log_e s)^{p_i}. \quad (8.1)$$

Using the approach discussed in section 4, evaluation of the one-center correlated two-electron integrals in the stu variables reduces to the integral:

$$I_L(j, k, \zeta) = \int_0^\infty s^{j-1} (\log_e s)^k e^{-\zeta s} ds. \quad (8.2)$$

This integral can be evaluated [54, 57] by starting from the definition of the gamma function:

$$\Gamma(j) = \int_0^\infty x^{j-1} e^{-x} dx = \int_0^\infty e^{(j-1)\log_e x} e^{-x} dx, \quad \text{for } j > 0, \quad (8.3)$$

and then using the abbreviation $\Gamma^{(k)}(j) \equiv \frac{\partial^k \Gamma(j)}{\partial j^k}$, we have on employing the substitution $x = \zeta s$ and making a binomial expansion:

$$\begin{aligned} \Gamma^{(k)}(j) &= \int_0^\infty x^{j-1} (\log_e x)^k e^{-x} dx \\ &= \zeta^j \int_0^\infty s^{j-1} (\log_e \zeta s)^k e^{-\zeta s} ds \\ &= \zeta^j \sum_{l=0}^k \binom{k}{l} (\log_e \zeta)^{k-l} \int_0^\infty s^{j-1} (\log_e s)^l e^{-\zeta s} ds, \end{aligned} \quad (8.4)$$

where $\binom{k}{l}$ denotes a binomial coefficient, and hence

$$I_L(j, k, \varsigma) = \varsigma^{-j} \Gamma^{(k)}(j) - \sum_{l=0}^{k-1} \binom{k}{l} (\log_e \varsigma)^{k-l} I_L(j, l, \varsigma). \quad (8.5)$$

The derivative of the gamma function can be readily expressed in terms of derivatives of the digamma function.

An integration by parts directly on Eq. (8.2) yields the recursion formula,

$$I_L(j+1, k, \varsigma) = \varsigma^{-1} j I_L(j, k, \varsigma) + \varsigma^{-1} k I_L(j, k-1, \varsigma), \text{ for } j \geq 1 \text{ and } k \geq 1. \quad (8.6)$$

This formula can be evaluated using the starting values:

$$I_L(j, 0, \varsigma) = \varsigma^{-j} (j-1)!, \text{ for } j \geq 1, \quad (8.7)$$

and

$$I_L(j, 1, \varsigma) = \varsigma^{-j} (j-1)! \{\psi(j) - \log_e \varsigma\}, \text{ for } j \geq 1, \quad (8.8)$$

where $\psi(k)$ denotes the digamma function, which is defined by [59]

$$\psi(j) = -\gamma + \sum_{k=1}^{j-1} \frac{1}{k}, \quad (8.9)$$

and γ is Euler's constant. A generalization that includes an exponential r_{12} term is discussed in [60].

9. The one-center three-electron integral $I_3(i, j, k, l, m, n, \alpha, \beta, \gamma)$

In this section we examine the one-center three-electron correlated integrals that arise for the S states of atomic species. The trial Hylleraas wave function involves an expansion in terms of explicit factors of the electron-electron separation distance of the form:

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \mathcal{A} \sum_{\mu=1}^N C_{\mu} r_1^{i_{\mu}} r_2^{j_{\mu}} r_3^{k_{\mu}} r_{12}^{l_{\mu}} r_{13}^{m_{\mu}} r_{23}^{n_{\mu}} e^{-a_{\mu} r_1 - b_{\mu} r_2 - c_{\mu} r_3} \chi_{\mu}, \quad (9.1)$$

where \mathcal{A} is the three-electron antisymmetrizer, and χ_μ is a spin eigenfunction. The constants a_μ , b_μ , and c_μ are > 0 , and the integer indices $\{i_\mu, j_\mu, k_\mu, l_\mu, m_\mu, n_\mu\}$ are each ≥ 0 . The Hamiltonian for an atomic three-electron S state can be written as [9-11, 44]:

$$H_S = - \sum_{i=1}^3 \left(\frac{1}{2} \frac{\partial^2}{\partial r_i^2} + \frac{1}{r_i} \frac{\partial}{\partial r_i} + \frac{Z}{r_i} + \frac{\partial^2}{\partial u_i^2} + \frac{2}{u_i} \frac{\partial}{\partial u_i} - \frac{1}{u_i} \right) - \frac{1}{2} \sum_{\mathcal{P}_{ijk}} \left(\frac{r_i^2 + u_k^2 - r_j^2}{r_i u_k} \frac{\partial^2}{\partial r_i \partial u_k} + \frac{1}{2} \frac{u_i^2 + u_k^2 - u_j^2}{2u_i u_k} \frac{\partial^2}{\partial u_i \partial u_k} \right), \quad (9.2)$$

where \mathcal{P}_{ijk} indicates that the summation is over the six permutations $\begin{pmatrix} 1 & 2 & 3 \\ i & j & k \end{pmatrix}$ and the notational simplifications $u_1 = r_{23}$, $u_2 = r_{31}$, and $u_3 = r_{12}$ are employed. It can be shown that the expectation value $\langle \psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) | H | \psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \rangle$ for atomic S states is reducible to a sum of three-electron integrals of the form

$$I_3(i, j, k, l, m, n, \alpha, \beta, \gamma) = \iiint r_1^i r_2^j r_3^k r_{12}^l r_{13}^m r_{23}^n e^{-\alpha r_1 - \beta r_2 - \gamma r_3} d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3, \quad (9.3)$$

where $\alpha > 0$, $\beta > 0$, and $\gamma > 0$. The individual integer indices $\{i, j, k, l, m, n\}$ must be ≥ -2 for the integral to be convergent. The focus in this section will be on the cases for which the indices $\{l, m, n\}$ are each ≥ -1 , which applies for a calculation of the energy, and a number of other properties. Other cases will be discussed later in section 11. It should be noted that the integral is often defined with the order of the r_{ij} factors gives as $r_{23}^l r_{13}^m r_{12}^n$, so some care is needed when comparing numerical values from different sources. This integral has been discussed extensively in the literature [39-40, 43-44, 48, 61-71], with some effort directed towards the analytic evaluation of various cases [72-77].

The symmetry property for $I_3(i, j, k, l, m, n, \alpha, \beta, \gamma)$ is

$$\begin{aligned} I_3(i, j, k, l, m, n, \alpha, \beta, \gamma) &= I_3(i, k, j, m, l, n, \alpha, \gamma, \beta) \\ &= I_3(j, i, k, l, n, m, \beta, \alpha, \gamma) \\ &= I_3(j, k, i, n, l, m, \beta, \gamma, \alpha) \\ &= I_3(k, j, i, n, m, l, \gamma, \beta, \alpha) \\ &= I_3(k, i, j, m, n, l, \gamma, \alpha, \beta). \end{aligned} \quad (9.4)$$

Special cases of $I_3(i, j, k, l, m, n, \alpha, \beta, \gamma)$ are

$$I_3(i, j, k, 0, 0, 0, \alpha, \beta, \gamma) = I_1(i, \alpha) I_1(j, \beta) I_1(k, \gamma), \quad (9.5)$$

and

$$I_3(i, j, k, l, 0, 0, \alpha, \beta, \gamma) = I_2(i, j, l, \alpha, \beta) I_1(k, \gamma). \quad (9.6)$$

A useful test case for computational checking, is the result [72]

$$I_3(-1, -1, -1, -1, -1, -1, 1, 1, 1) = 48\pi^3 [2 \log_e 2 \log_e 3 - \{\log_e 2\}^2 - \frac{\pi^2}{6} - 2 \text{Li}_2(-1/2)], \quad (9.7)$$

where $\text{Li}_2(x)$ is the dilogarithm function, defined by [78-79]

$$\text{Li}_2(x) = - \int_0^x \frac{\log(1-t) dt}{t} = \sum_{n=1}^{\infty} \frac{x^n}{n^2}, \quad \text{for } |x| \leq 1. \quad (9.8)$$

We now consider the reduction of the three-electron integral to simpler auxiliary functions, focusing on the case where the indices $\{l, m, n\}$ are each ≥ -1 , which is the situation that has received the most attention. The Sack expansion [80] is given by

$$r_{12}^l = \sum_{l_1=0}^{\infty} R_{ll_1}(r_1, r_2) P_{l_1}(\cos \theta_{12}), \quad (9.9)$$

where $R_{ll_1}(r_1, r_2)$ is a Sack radial function. This represents a generalization of the expansion given in Eq. (2.17). Inserting the Sack expansion for each of the r_{ij} factors in Eq. (9.3), leads to

$$I_3(i, j, k, l, m, n, a, b, c) = \sum_{l_1=0}^{\infty} \sum_{m_1=0}^{\infty} \sum_{n_1=0}^{\infty} I_R(i, j, k, l, m, n, l_1, m_1, n_1, a, b, c) I_{\Omega}(l_1, m_1, n_1), \quad (9.10)$$

where the radial integrals are given by

$$I_R(i, j, k, l, m, n, l_1, m_1, n_1, a, b, c) = \iiint r_1^{i+2} r_2^{j+2} r_3^{k+2} R_{ll_1}(r_1, r_2) R_{mm_1}(r_1, r_3) R_{nn_1}(r_2, r_3) e^{-ar_1 - br_2 - cr_3} dr_1 dr_2 dr_3, \quad (9.11)$$

and the angular integrals are

$$I_{\Omega}(l_1, m_1, n_1) = \iiint P_{l_1}(\cos \theta_{12}) P_{m_1}(\cos \theta_{13}) P_{n_1}(\cos \theta_{23}) d\Omega_1 d\Omega_2 d\Omega_3. \quad (9.12)$$

The angular integral can be readily evaluated by employing the standard expansion of the Legendre polynomials in terms of spherical harmonics, so that

$$\begin{aligned} I_{\Omega}(l_1, m_1, n_1) &= \frac{64\pi^3}{(2l_1+1)(2m_1+1)(2n_1+1)} \sum_{s_1=-l_1}^{l_1} \sum_{t_1=-m_1}^{m_1} \sum_{u_1=-n_1}^{n_1} \iiint Y_{l_1 s_1}^*(\theta_1, \phi_1) Y_{l_1 s_1}(\theta_2, \phi_2) \\ &\quad Y_{n_1 u_1}^*(\theta_2, \phi_2) Y_{n_1 u_1}(\theta_3, \phi_3) Y_{m_1 t_1}^*(\theta_3, \phi_3) Y_{m_1 t_1}(\theta_1, \phi_1) d\Omega_1 d\Omega_2 d\Omega_3 \\ &= \frac{64\pi^3}{(2l_1+1)(2m_1+1)(2n_1+1)} \sum_{s_1=-l_1}^{l_1} \sum_{t_1=-m_1}^{m_1} \sum_{u_1=-n_1}^{n_1} \delta_{l_1 m_1} \delta_{s_1 t_1} \delta_{n_1 l_1} \delta_{u_1 s_1} \delta_{m_1 n_1} \delta_{t_1 u_1} \\ &= \frac{64\pi^3 \delta_{l_1 m_1} \delta_{l_1 n_1} \delta_{m_1 n_1}}{(2l_1+1)^3} \sum_{s_1=-l_1}^{l_1} \sum_{t_1=-m_1}^{m_1} \sum_{u_1=-n_1}^{n_1} \delta_{s_1 t_1} \delta_{u_1 s_1} \delta_{t_1 u_1} \\ &= \frac{64\pi^3 \delta_{l_1 m_1} \delta_{l_1 n_1} \delta_{m_1 n_1}}{(2l_1+1)^2}. \end{aligned} \quad (9.13)$$

Inserting this result into Eq. (9.10) leads to

$$I_3(i, j, k, l, m, n, a, b, c) = 64\pi^3 \sum_{w=0}^{\infty} \frac{1}{(2w+1)^2} I_R(i, j, k, l, m, n, w, w, w, a, b, c), \quad (9.14)$$

where

$$\begin{aligned} I_R(i, j, k, l, m, n, w, w, w, a, b, c) &= \\ &\iiint r_1^{i+2} r_2^{j+2} r_3^{k+2} R_{lw}(r_1, r_2) R_{mw}(r_1, r_3) R_{nw}(r_2, r_3) e^{-ar_1 - br_2 - cr_3} dr_1 dr_2 dr_3. \end{aligned} \quad (9.15)$$

The Sack radial function [80] can be written for $l \geq -1$ as

$$R_{lw}(r_1, r_2) = \frac{(-l/2)_w}{(1/2)_w} r_{12<}^w r_{12>}^{l-w} \sum_{u=0}^{\infty} a_{wlu} \left(\frac{r_{12<}}{r_{12>}} \right)^{2u}, \quad (9.16)$$

where $r_{12<} = \min(r_1, r_2)$ and $r_{12>} = \max(r_1, r_2)$, the coefficients a_{wlu} are given by

$$a_{wlu} = \frac{(w - \frac{l}{2})_u (-\frac{1}{2} - \frac{l}{2})_u}{u! (w + \frac{3}{2})_u}, \quad (9.17)$$

and $(\alpha)_n$ denotes a Pochhammer symbol, defined in terms of the gamma function $\Gamma(p)$ as [59]:

$$(p)_q = p(p+1)(p+2)\cdots(p+q-1) = \frac{\Gamma(p+q)}{\Gamma(p)}. \quad (9.18)$$

An alternative expansion for Eq. (9.9) has been given by Perkins [66]:

$$r_{12}^v = \sum_{q=0}^{\infty} P_q(\cos\theta_{12}) \sum_{k=0}^{\infty} C_{vqk} r_{12<}^{q+2k} r_{12>}^{v-q-2k}, \quad (9.19)$$

where C_{vqk} are coefficients. This expansion is a rewriting of Eqs. (9.9) and (9.16), since for $q = 0$ we have

$$C_{v0k} = \frac{(-\frac{v}{2})_k (-\frac{1}{2} - \frac{v}{2})_k}{k! (\frac{3}{2})_k} = \frac{(1+v)!}{2^{2k} (v+1-2k)!} = \frac{(1+v)!}{(2k+1)!(v+1-2k)!}, \quad (9.20)$$

and for $q \geq 1$

$$\begin{aligned} C_{vqk} &= \frac{(-v/2)_q (q - \frac{v}{2})_k (-\frac{1}{2} - \frac{v}{2})_k}{(1/2)_q (q + \frac{3}{2})_k k!} \\ &= \frac{(-v/2)_q [(k - \frac{v}{2})_q / (-v/2)_q] (-v/2)_k (-\frac{1}{2} - \frac{v}{2})_k}{(1/2)_q [(k + \frac{3}{2})_q / (3/2)_q] (3/2)_k k!} \end{aligned}$$

$$\begin{aligned}
&= \frac{(3/2)_q \left(k - \frac{\nu}{2}\right)_q}{(1/2)_q \left(k + \frac{3}{2}\right)_q} C_{\nu 0k} \\
&= (2q+1) C_{\nu 0k} \prod_{t=0}^{\min\{q-1, (\nu+1)/2\}} \frac{(2k - \nu + 2t)}{(2k + 1 + 2q - 2t)}. \tag{9.21}
\end{aligned}$$

The limit on the product takes advantage of term cancellation in the numerator and denominator in the expansion of the Pochhammer symbols. Equation (9.19) can be expressed as

$$r_{12}^{\nu} = \sum_{q=0}^{q_{\max}} P_q(\cos\theta_{12}) \sum_{k=0}^{k_{\max}} C_{\nu qk} r_{12<}^{q+2k} r_{12>}^{\nu-q-2k}, \tag{9.22}$$

where $q_{\max} = \nu/2$ for ν even, $q_{\max} = \infty$ for ν odd, $k_{\max} = (\nu/2) - q$ for ν even, and $k_{\max} = (\nu+1)/2$ for ν odd. These summation constraints follow from the property of the Pochhammer symbol: $(-p)_q = 0$ for integer p and $q > p$.

Inserting the expansions for the Sack radial functions into Eqs. (9.14) – (9.15) leads to:

$$\begin{aligned}
I_3(i, j, k, l, m, n, a, b, c) &= 64\pi^3 \sum_{w=0}^{\infty} \frac{(-l/2)_w (-m/2)_w (-n/2)_w}{(2w+1)^2 \{(1/2)_w\}^3} \sum_{u=0}^{\infty} a_{wlr} \sum_{v=0}^{\infty} a_{wmv} \sum_{s=0}^{\infty} a_{wvs} \\
&\{W_3(I+\omega_1, J+l-\omega_5, K+m+n-\omega_3, a, b, c) + W_3(J+\omega_2, I+l-\omega_4, K+m+n-\omega_3, b, a, c) \\
&+ W_3(K+\omega_3, J+\omega_5+n, I+l+m-\omega_1, c, b, a) + W_3(I+\omega_1, K+m-\omega_6, J+l+n-\omega_2, a, c, b) \\
&+ W_3(J+\omega_2, K+n+\omega_6, I+l+m-\omega_1, b, c, a) + W_3(K+\omega_3, I+m+\omega_4, J+l+n-\omega_2, c, a, b)\}, \tag{9.23}
\end{aligned}$$

where the W_3 -integral is defined for integer i, j , and k by

$$W_3(i, j, k, a, b, c) = \int_0^{\infty} x^i e^{-ax} dx \int_x^{\infty} y^j e^{-by} dy \int_y^{\infty} z^k e^{-cz} dz, \tag{9.24}$$

and the notational simplifications,

$$I = i + 2, \quad J = j + 2, \quad K = k + 2, \tag{9.25}$$

$$\omega_1 = 2u + 2v + 2w, \quad \omega_2 = 2u + 2s + 2w, \quad \omega_3 = 2v + 2s + 2w, \quad (9.26)$$

$$\omega_4 = 2u - 2v, \quad \omega_5 = 2u - 2s, \quad \omega_6 = 2v - 2s, \quad (9.27)$$

have been employed. The W_3 -integrals have received extensive study, and there are well-developed algorithms for the high precision evaluation of these auxiliary functions [39-48, 61-69].

Recalling $(-p)_q = 0$ for integer p and $q > p$, then each of the summations over u , v , and s , in Eq. (9.23) terminate at finite values. For example, the u summation terminates at $(l+1)/2$ if l is odd, and at $(l-2w)/2$ if l is even. The w summation terminates at $\min\{l/2, m/2, n/2\}$ for l , m , and n each even; at $\min\{l/2, m/2\}$, l and m even, and n odd; at $\min\{l/2, n/2\}$, l and n even, and m odd; at $\min\{m/2, n/2\}$, m and n even, and l odd; at $\min\{l/2\}$, l even, m and n odd; at $\min\{m/2\}$, m even, l and n odd; and at $\min\{n/2\}$, n even, l and m odd. The only case leading to an infinite summation is the case l , m , and n each odd.

When the w summation is infinite, it can be shown that the asymptotic behavior of the series is of the form [44, 69]

$$I_3(i, j, k, l, m, n, a, b, c) \sim \sum_{s=1}^{\infty} \frac{\alpha_s}{s^{(l+m+n+1)/2}}. \quad (9.28)$$

For the evaluation of the energy, only one of the indices l , m , and n takes the value -1, the other two values are ≥ 0 . Hence, the slowest case scenario for the convergence in Eq. (9.28) arises for the three-odd case with $l + m + n = 1$, so the series takes the asymptotic form

$$I_3 \sim \sum_{s=1}^{\infty} \frac{\alpha_s}{s^6}. \quad (9.29)$$

Methods to sum slowly converging series are called convergence acceleration techniques. These methods utilize knowledge of the asymptotic behavior of the series, and thus restrict the number of series terms that require evaluation. In some cases, the results can be extremely impressive. There are however well-known numerical stability issues that may arise. Some references that the reader might pursue on this vast topic are [81-95].

The result given in Eq. (9.23) might be regarded as the classical approach to the I_3 integral evaluation. Two other schemes deserve mention. The first has focused on the analytic evaluation of the I_3 in terms of standard functions. Remiddi [72] succeeded in deriving closed form expressions for selected I_3 integrals, of which Eq. (9.7) is an example. He treated one of the important cases required for the evaluation of the energy. However, the final result is rather lengthy. Further work on the Remiddi approach has appeared [73-77].

An alternative approach to this integration problem involves setting up a fairly long recursive scheme [76]. This recursive scheme has been implemented in practical calculations, and the current best available results for the ground state energy of the lithium atom have been determined with this approach by Puchalski and Pachucki [96].

The reader might wonder if there is an extension of the scheme discussed in section 3 to the case of the three-electron integrals. It is possible to write the radial part of $d\tau$ in the form $d\tau_{radial} = J dr_1 dr_2 dr_3 dr_{12} dr_{13} dr_{23}$, unfortunately, the Jacobian of the transformation involves a denominator term involving the square root of a sixth-order polynomial in the variables $\{r_1, r_2, r_3, r_{12}, r_{13}, r_{23}\}$ [97-98]. Therefore, this coordinate system does not look promising for the evaluation of the I_3 integrals.

10. The auxiliary function $W_3(i, j, k, a, b, c)$

The W_3 auxiliary function defined in Eq. (9.24) is convergent for $a > 0$, $b > 0$, $c > 0$, and

$$i \geq 0, \quad i + j \geq -1, \quad i + j + k \geq -2. \quad (10.1)$$

The numerical evaluation of W_3 is best considered as two separate cases: (1) j and k are both positive, and (2) one or both of j and k are negative. For the first case, Eq. (2.21) can be employed to give

$$W_3(i, j, k, a, b, c) = \frac{k!}{(a+b+c)^{i+1} (b+c)^{j+1} c^{k+1}} \sum_{m=0}^k \frac{(j+m)!}{m!} \left(\frac{c}{b+c}\right)^m \sum_{n=0}^{j+m} \frac{(i+n)!}{n!} \left(\frac{b+c}{a+b+c}\right)^n. \quad (10.2)$$

A simple recurrence relationship can also be set up for this case of the W_3 auxiliary function [39-40]. For the second case, the following formula [40, 44] can be used

$$W_3(i, j, k, a, b, c) = \frac{i!}{a} \sum_{m=1}^{\infty} \frac{a^m W_2(i + j + m, k, a + b, c)}{(m + i)!}. \quad (10.3)$$

Further discussion on the numerical evaluation of this auxiliary function, including recurrence schemes, can be found in [39-49, 61-69].

11. $I_3(i, j, k, l, m, n, \alpha, \beta, \gamma)$ with arguments $\{l, m, n\}$ equal to -2

The cases where one or two of the indices $\{l, m, n\}$ are allowed to be -2 , lead to significant additional complications, and some of these problems have been addressed in the literature [99-107]. These integral cases are required for the evaluation of lower bounds to the energy of three-electron atomic systems [108-109], as well as relativistic effects [96, 110-111].

There are two different expansions of r_{ij}^{-2} that have been employed to handle these more recalcitrant integrals. The first expansion takes the form

$$\begin{aligned} r_{ij}^{-2} = & \sum_{l=0}^{\infty} \frac{2l+1}{2^{2l+1}} \left\{ \log_e \left| \frac{r_i + r_j}{r_i - r_j} \right| \sum_{\kappa=0}^l r_i^{2\kappa-l-1} r_j^{l-2\kappa-1} \sum_{\nu=0}^{\min[\kappa, l-\kappa]} (-4)^\nu \binom{l}{\nu} \binom{2l-2\nu}{l} \binom{l-2\nu}{\kappa-\nu} \right. \\ & \left. - 2 \sum_{\kappa=0}^{l-1} r_i^{2\kappa-l} r_j^{l-2\kappa-2} \sum_{j=0}^{\min[\kappa, l-\kappa-1]} 4^j \binom{l-2j-1}{\kappa-j} \sum_{\nu=0}^j \frac{(-1)^\nu}{2j-2\nu+1} \binom{l}{\nu} \binom{2l-2\nu}{l} \right\} P_l(\cos \theta_{ij}). \end{aligned} \quad (11.1)$$

This expansion can be derived by starting with the Sack expansion [80]

$$r_{ij}^{-2} = \sum_{l=0}^{\infty} R_{-2l}(r_i, r_j) P_l(\cos \theta_{ij}), \quad (11.2)$$

where the Sack radial function $R_{-2l}(r_i, r_j)$ is given in terms of a hypergeometric function as

$$R_{-2l}(r_i, r_j) = \frac{(1)_l r_i^l r_j^l}{(1/2)_l (r_i^2 + r_j^2)^{l+1}} {}_2F_1\left(1 + \frac{l}{2}, \frac{1}{2} + \frac{l}{2}; \frac{3}{2} + l; \rho^2\right), \quad (11.3)$$

and $\rho = 2r_i r_j (r_i^2 + r_j^2)^{-2}$. The preceding result can be written in terms of the Legendre functions of the second kind, Q_l , so that

$$R_{-2l}(r_i, r_j) = \frac{2l+1}{2r_i r_j} Q_l(\rho^{-1}). \quad (11.4)$$

Expressing Q_l in terms of the Legendre polynomial P_l , and after some algebraic manipulation (see [99] for details), then Eq. (11.1) is obtained. The expansion in Eq. (11.1) was given first by Pauli and Kleindienst [112] in a slightly different but mathematically equivalent form [100]. For other additional discussion on the expansion of r_{ij}^{-2} , see [113-114].

The key factor that should catch the reader's attention in Eq. (11.1) is the appearance of the logarithmic term. This contribution significantly complicates the evaluation of the radial integrals that arise. Three different auxiliary functions occur for the evaluation of the radial integrals; these are extensions of the W_3 integrals defined in Eq. (9.24):

$$W_{L_1}(i, j, k, a, b, c) = \int_0^\infty x^i e^{-ax} dx \int_x^\infty y^j e^{-by} dy \int_y^\infty z^k \log_e \left| \frac{z+y}{z-y} \right| e^{-cz} dz, \quad (11.5)$$

$$W_{L_2}(i, j, k, a, b, c) = \int_0^\infty x^i e^{-ax} dx \int_x^\infty y^j \log_e \left| \frac{y+x}{y-x} \right| e^{-by} dy \int_y^\infty z^k e^{-cz} dz, \quad (11.6)$$

$$W_{L_3}(i, j, k, a, b, c) = \int_0^\infty x^i e^{-ax} dx \int_x^\infty y^j e^{-by} dy \int_y^\infty z^k \log_e \left| \frac{z+x}{z-x} \right| e^{-cz} dz. \quad (11.7)$$

Numerical approaches to treat these auxiliary functions have been discussed in [99-100, 102, 105-106]. Specialized Gaussian quadrature procedures and convergence acceleration methods have proved to be useful numerical methods to obtain reasonably accurate values for these auxiliary functions. There is no increase in complexity for the angular integration.

An alternative expansion of r_{ij}^{-2} , and one having a closer structure to the expansion of r_{ij}^{-1} given in Eq. (2.17), is [99, 103, 114-115]:

$$r_{ij}^{-2} = \sum_{l=0}^{\infty} \frac{r_{ij<}^l}{r_{ij>}^{l+2}} C_l^1(\cos \theta_{ij}), \quad (11.8)$$

where $C_l^1(\cos \theta_{ij})$ denotes a Gegenbauer polynomial. Using this expansion means that the radial integrals that arise from the evaluation of $I_3(i, j, k, l, m, n, \alpha, \beta, \gamma)$ reduce to the W_3 auxiliary functions defined in Eq. (9.24). The increased complexity of the integral evaluation now occurs in the angular integration. A straightforward approach that has been implemented, is to expand $C_l^1(\cos \theta_{ij})$ as a series of Legendre polynomials $P_l(\cos \theta_{ij})$, and then proceed as indicated in Eqs. (9.12) – (9.13). If $l = -2$, then it can be shown [103] that the convergence of the resulting series for the I_3 integral for the case $m = -1$ and $n = -1$, behaves as

$$I_3 \sim \sum_s \frac{\alpha_s}{s^{3.5}}. \quad (11.9)$$

This series converges too slowly for a brute force numerical evaluation of the sum. Various techniques have been discussed to treat this evaluation problem [103-104, 106]. Judicious application of convergence acceleration techniques have proved to be fairly effective to deal with this problem [103, 106].

Some extensions of the I_3 integral to include kernels that contain terms like $(r_i^2 - r_j^2)r_{ij}^{-3}$ and $(r_{ki}^2 - r_{jk}^2)r_{ij}^{-3}$ have been treated [116]. In these cases, the factors cannot be broken apart into two integrals, since each of the separate integrals would diverge.

12. Three-electron integrals with exponential r_{ij} factors

As remarked at the start of section 6, the introduction of exponential terms with explicit r_{ij} factors into the wave function, leads to quality results for two-electron systems. It would be expected that a generalization of the wave function given in Eq. (9.1) to the form:

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \sum_{\mu=1}^N C_{\mu} \eta_1^{i_{\mu}} r_2^{j_{\mu}} r_3^{k_{\mu}} \eta_2^{l_{\mu}} \eta_3^{m_{\mu}} r_{23}^{n_{\mu}} e^{-\alpha_{\mu} r_1 - \beta_{\mu} r_2 - \gamma_{\mu} r_3 - \alpha_{12\mu} r_{12} - \alpha_{13\mu} r_{13} - \alpha_{23\mu} r_{23}} \chi_{\mu}, \quad (12.1)$$

would also lead to improved results for the properties of the S states of members of the lithium isoelectronic series. Evaluation of $\langle \psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) | H | \psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \rangle$ using the Hamiltonian given in Eq. (9.2) requires the following one-center integrals:

$$\mathcal{I}_3(i, j, k, l, m, n, \alpha, \beta, \gamma) = \iiint r_1^i r_2^j r_3^k r_{12}^l r_{13}^m r_{23}^n e^{-\alpha r_1 - \beta r_2 - \gamma r_3 - \alpha_{12} r_{12} - \alpha_{13} r_{13} - \alpha_{23} r_{23}} d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3. \quad (12.2)$$

A detailed study of these integrals was undertaken by Fromm and Hill [37]. The analysis depends heavily on tracking the branch structure for the multi-valued functions involved. Harris [117] has presented a simplification of the results and further discussion is given in [97]. No computational program employing this approach for atomic systems is known to the author.

13. Three-electron integrals with spherical harmonic factors

To treat states of non S symmetry for three-electron atomic systems, the wave function of Eq. (9.1) is modified so that the basis functions are of the form [53, 104]:

$$\phi_\mu(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = r_1^{i_\mu} r_2^{j_\mu} r_3^{k_\mu} r_{12}^{l_\mu} r_{13}^{m_\mu} r_{23}^{n_\mu} e^{-a_\mu r_1 - b_\mu r_2 - c_\mu r_3} \mathcal{Y}_{(l_1 l_2) l_{12}, l_3}^{LM}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \chi_\mu. \quad (13.1)$$

The additional term $\mathcal{Y}_{(l_1 l_2) l_{12}, l_3}^{LM}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ that appears is an angular momentum eigenfunction involving an expansion in terms of the spherical harmonics $Y_{l_1 m_1}(\hat{\mathbf{r}}_1)$, $Y_{l_2 m_2}(\hat{\mathbf{r}}_2)$, and $Y_{l_3 m_3}(\hat{\mathbf{r}}_3)$, where $\hat{\mathbf{r}}_1 = \mathbf{r}_1 / r_1$, with appropriate coupling coefficients, so that a state of total angular momentum L is obtained. The Hamiltonian for a general symmetry state of a three-electron atom takes the form [10, 118-119]:

$$H_L = H_S - \frac{1}{2} \sum_{i=1}^3 \left(\frac{1}{r_i^2} \frac{\partial^2}{\partial \theta_i^2} + \frac{\cot \theta_i}{r_i^2} \frac{\partial}{\partial \theta_i} + \frac{1}{r_i^2 \sin^2 \theta_i} \frac{\partial^2}{\partial \phi_i^2} \right) - \sum_{i=1}^3 \sum_{\substack{j=1 \\ (j \neq i)}}^3 \frac{r_j \{ \sin \theta_i \cos \theta_j - \cos \theta_i \sin \theta_j \cos(\phi_i - \phi_j) \}}{r_i r_{ij}} \frac{\partial^2}{\partial \theta_i \partial r_{ij}}$$

$$-\sum_{i=1}^3 \sum_{\substack{j=1 \\ (j \neq i)}}^3 \frac{r_j \sin \theta_j \sin(\phi_i - \phi_j)}{r_i r_{ij} \sin \theta_i} \frac{\partial^2}{\partial \phi_i \partial r_{ij}}, \quad (13.2)$$

where H_S is the S state contribution given in Eq. (9.2). The generalization of Eq. (13.2) to include multiple nuclear centers is given in [120]. Using the basis functions given in Eq. (13.1), then evaluation of $\langle \psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) | H | \psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \rangle$ using the Hamiltonian H_L leads to one class of one-center integrals that take the form:

$$\begin{aligned} \mathcal{I}_3(i, j, k, l, m, n, l_1, m_1, l_2, m_2, l_3, m_3, l'_1, m'_1, l'_2, m'_2, l'_3, m'_3, \alpha, \beta, \gamma) = \\ \iiint r_1^i r_2^j r_3^k r_{12}^l r_{13}^m r_{23}^n e^{-\alpha r_1 - \beta r_2 - \gamma r_3} Y_{l_1 m_1}(\theta_1, \phi_1) Y_{l_2 m_2}(\theta_2, \phi_2) \\ Y_{l_3 m_3}(\theta_3, \phi_3) Y_{l'_1 m'_1}(\theta_1, \phi_1) Y_{l'_2 m'_2}(\theta_2, \phi_2) Y_{l'_3 m'_3}(\theta_3, \phi_3) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3. \end{aligned} \quad (13.3)$$

Each of the r_{ij} factors will generate a pair of spherical harmonics, so that the angular integration leads to integrals involving a product of four spherical harmonics of the form $Y_{l_1 m_1}(\theta, \phi) Y_{l_2 m_2}(\theta, \phi) Y_{l_3 m_3}(\theta, \phi) Y_{l_4 m_4}(\theta, \phi)$. These products can be simplified by taking advantage of the result [Vol. II, p. 1057, 13]:

$$\begin{aligned} Y_{l_1 m_1}(\theta, \phi) Y_{l_2 m_2}(\theta, \phi) = \sum_{L=|l_1-l_2|}^{l_1+l_2} \sum_{M=-L}^L (-1)^M \left[\frac{(2l_1+1)(2l_2+1)(2L+1)}{4\pi} \right]^{1/2} \\ \begin{pmatrix} l_1 & l_2 & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & L \\ m_1 & m_2 & M \end{pmatrix} Y_{L-M}(\theta, \phi), \end{aligned} \quad (13.4)$$

where $\begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$ denotes a $3j$ symbol [Vol. II, 13; 121-123]. This leaves

an integral over a product of three spherical harmonics. The approach to solve this is discussed in the following section. Other integrals obtained using the basis set of Eq. (13.1) are discussed in [98, 104].

14. The one-center four-electron integral $I_4(i, j, k, l, m, n, p, q, s, t, \alpha, \beta, \gamma, \delta)$

Extension of Eqs. (9.1) and (9.2) to treat four-electron atomic S states leads to integrals that are the obvious extension of Eq. (9.3):

$$I_4(i, j, k, l, m, n, p, q, s, t, \alpha, \beta, \gamma, \delta) = \iiint\int r_1^i r_2^j r_3^k r_4^l r_{12}^m r_{13}^n r_{14}^p r_{23}^q r_{24}^s r_{34}^t e^{-\alpha r_1 - \beta r_2 - \gamma r_3 - \delta r_4} d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4, \quad (14.1)$$

where $\alpha > 0$, $\beta > 0$, $\gamma > 0$, and $\delta > 0$. The individual indices i through t must be ≥ -2 for the integral to be convergent. The focus in this section will be on the case for which these indices are each ≥ -1 , which is the situation required for an energy evaluation. Various cases of this integral have been discussed in the literature [124-132]. One particular result I indicate is that for a number of special cases, the I_4 integrals can be reduced to a sum of I_3 integrals [127].

The symmetry property for I_4 is

$$\begin{aligned} I_4(i, j, k, l, m, n, p, q, s, t, \alpha, \beta, \gamma, \delta) &= I_4(j, i, k, l, m, q, s, n, p, t, \beta, \alpha, \gamma, \delta) \\ &= I_4(k, j, i, l, q, n, t, m, s, p, \gamma, \beta, \alpha, \delta) \\ &= I_4(l, j, k, i, s, t, p, q, m, n, \delta, \beta, \gamma, \alpha), \text{ etcetera.} \end{aligned} \quad (14.2)$$

Particular special cases are:

$$I_4(i, j, k, l, m, 0, 0, 0, 0, t, \alpha, \beta, \gamma, \delta) = I_2(i, j, m, \alpha, \beta) I_2(k, l, t, \gamma, \delta), \quad (14.3)$$

$$I_4(i, j, k, l, m, n, 0, q, 0, 0, \alpha, \beta, \gamma, \delta) = I_3(i, j, k, m, n, q, \alpha, \beta, \gamma) I_1(l, \delta), \quad (14.4)$$

and some symmetry related results for each of these formulas.

To evaluate the I_4 integral insert the Sack expansion given in Eq. (9.9) for each of the r_{ij} factors, the result is

$$\begin{aligned} I_4(i, j, k, l, m, n, p, q, s, t, \alpha, \beta, \gamma, \delta) &= \sum_{m_1=0}^{\infty} \sum_{n_1=0}^{\infty} \sum_{p_1=0}^{\infty} \sum_{q_1=0}^{\infty} \sum_{s_1=0}^{\infty} \sum_{t_1=0}^{\infty} I_{\Omega}(m_1, n_1, p_1, q_1, s_1, t_1) \\ &I_R(m, n, p, q, s, t, m_1, n_1, p_1, q_1, s_1, t), \end{aligned} \quad (14.5)$$

where the angular integral $I_{\Omega}(m_1, n_1, p_1, q_1, s_1, t_1)$ is given by

$$I_{\Omega}(m_1, n_1, p_1, q_1, s_1, t_1) = \iiint P_{m_1}(\cos \theta_{12}) P_{n_1}(\cos \theta_{13}) P_{p_1}(\cos \theta_{14}) \\ P_{q_1}(\cos \theta_{23}) P_{s_1}(\cos \theta_{24}) P_{t_1}(\cos \theta_{34}) d\Omega_1 d\Omega_2 d\Omega_3 d\Omega_4, \quad (14.6)$$

and I_R denotes the radial integral

$$I_R(m, n, p, q, s, t, m_1, n_1, p_1, q_1, s_1, t, \alpha, \beta, \gamma, \delta) = \\ \iiint r_1^{i+2} r_2^{j+2} r_3^{k+2} r_4^{l+2} e^{-\alpha r_1 - \beta r_2 - \gamma r_3 - \delta r_4} \\ R_{mm_1}(r_1, r_2) R_{nn_1}(r_1, r_3) R_{pp_1}(r_1, r_4) R_{qq_1}(r_2, r_3) \\ R_{ss_1}(r_2, r_4) R_{tt_1}(r_3, r_4) dr_1 dr_2 dr_3 dr_4. \quad (14.7)$$

To handle the angular integral, we make use of the result [Vol. II, p. 1057, 13]:

$$\int Y_{l_1 m_1}(\theta, \phi) Y_{l_2 m_2}(\theta, \phi) Y_{l_3 m_3}(\theta, \phi) d\Omega = \left[\frac{(2l_1+1)(2l_2+1)(2l_3+1)}{4\pi} \right]^{1/2} \begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \quad (14.8)$$

Then Eq. (14.6) can be expressed as

$$I_{\Omega}(m_1, n_1, p_1, q_1, s_1, t_1) = 256\pi^4 \begin{pmatrix} m_1 & n_1 & p_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} m_1 & q_1 & s_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} n_1 & q_1 & t_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} p_1 & s_1 & t_1 \\ 0 & 0 & 0 \end{pmatrix} \\ \sum_{M=-m_1}^{m_1} \sum_{N=-n_1}^{n_1} \sum_{Q=-q_1}^{q_1} (-1)^{M+N+Q} \begin{pmatrix} m_1 & n_1 & p_1 \\ M & N & -M-N \end{pmatrix} \begin{pmatrix} m_1 & q_1 & s_1 \\ -M & Q & M-Q \end{pmatrix} \\ \begin{pmatrix} n_1 & q_1 & t_1 \\ -N & -Q & N+Q \end{pmatrix} \begin{pmatrix} p_1 & s_1 & t_1 \\ M+N & Q-M & -N-Q \end{pmatrix}. \quad (14.9)$$

The triple summation simplifies using a contraction formula for the sum of four $3j$ symbols [p. 146, 123] so that [129]:

$$I_{\Omega}(m_1, n_1, p_1, q_1, s_1, t_1) = 256\pi^4 (-1)^{n_1+s_1} \begin{pmatrix} m_1 & n_1 & p_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} m_1 & q_1 & s_1 \\ 0 & 0 & 0 \end{pmatrix} \\ \begin{pmatrix} n_1 & q_1 & t_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} p_1 & s_1 & t_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} m_1 & n_1 & p_1 \\ t_1 & s_1 & q_1 \end{pmatrix}, \quad (14.10)$$

where $\left\{ \begin{matrix} m & n & p \\ t & s & q \end{matrix} \right\}$ denotes a 6j symbol [121-123].

The radial integral in Eq. (14.7) reduces to a six-fold infinite summation of a set of 24 W_4 auxiliary functions [127-128]. The W_4 auxiliary function is treated in the following section. As indicated in section 2, there is a substantial difference between odd and even powers of r_{ij} as far as finding efficient numerical schemes to evaluate the resulting radial integrals. Currently, as many as four odd powers of r_{ij} and two nonzero even powers can be effectively dealt with [127]. This leaves the two cases of five and six odd powers of r_{ij} in Eq. (14.1) to be evaluated accurately and quickly. Both these cases are important if accurate calculations are to be made for the S states of atomic four-electron systems using the Hylleraas approach.

The general four-electron correlated integral with additional spherical harmonic factors can be treated by an extension of the approach indicated in section 13. Some special cases of the four-electron integral with additional angular factors have been considered in [133].

15. The auxiliary function $W_4(i, j, k, l, a, b, c, d)$

The auxiliary function required for a treatment of the four-electron problem takes the form:

$$W_4(i, j, k, l, a, b, c, d) = \int_0^\infty x^i e^{-ax} dx \int_x^\infty y^j e^{-by} dy \int_y^\infty z^k e^{-cz} dz \int_z^\infty w^l e^{-dw} dw. \quad (15.1)$$

The conditions required for a convergent W_4 integral are: $a > 0$, $b > 0$, $c > 0$, $d > 0$, and

$$i \geq 0, i + j \geq -1, i + j + k \geq -2, i + j + k + l \geq -3. \quad (15.2)$$

This integral has received considerable attention in the literature [124, 127, 131, 134-138]. When $l \geq 0$ the W_4 integrals can be reduced to a sum of W_3 integrals using the formula

$$W_4(i, j, k, l, a, b, c, d) = \frac{l!}{d^{l+1}} \sum_{v=0}^l \frac{d^v W_3(i, j, k + v, a, b, c + d)}{v!}. \quad (15.3)$$

When $l < 0$ an integral rearrangement leads to

$$W_4(i, j, k, l, a, b, c, d) = \frac{i!}{a^{i+1}} \left\{ W_3(j, k, l, b, c, d) - \sum_{v=0}^i \frac{a^v W_3(j+v, k, l, a+b, c, d)}{v!} \right\}, \quad (15.4)$$

which is valid when $j \geq 0$, $j+k \geq -1$, $j+k+l \geq -2$, and when the differencing does not lead to the loss of too many digits of precision. A general result that has increased numerical stability is

$$W_4(i, j, k, l, a, b, c, d) = i! \sum_{v=0}^{\infty} \frac{a^v W_3(i+j+v+1, k, l, a+b, c, d)}{(v+i+1)!}. \quad (15.5)$$

16. Few-electron molecular systems

Space considerations prevent a detailed discussion of the correlated integrals that arise in the treatment of few-electron molecular systems. The recent book [139] and review [140] provide general discussion of this topic. I want to draw attention to some explicitly correlated calculations on few-electron diatomic systems, which instead of working with the standard Neumann expansion in elliptical coordinates, transform the Hamiltonian in a different manner. A focus of the discussion will be the positive ion, HeH^+ . A conventional chemical view of HeH^+ is that the molecule has two natural centers, located at the two nuclei. This viewpoint leads to the use of elliptical coordinates to treat the integrals that arise.

An alternative description is to start with the total Hamiltonian H_T written in terms of the coordinates of the laboratory frame, \mathbf{R}_i , where one particle is identified as the reference particle, and the other n particles are treated on an equal footing:

$$H_T = -\frac{1}{2m_0} \nabla_{R_0}^2 - \sum_{i=1}^n \frac{1}{2m_i} \nabla_{R_i}^2 + \sum_{i=0}^n \sum_{j>i}^n \frac{q_i q_j}{|\mathbf{R}_i - \mathbf{R}_j|}, \quad (16.1)$$

where q_i is the charge of particle i , m_i is the corresponding mass of the particle, and atomic units are employed. For $i=1, 2, \dots, n$ employ the following coordinate transformations:

$$\mathbf{r}_i = \mathbf{R}_i - \mathbf{R}_0, \quad \text{and} \quad \mathbf{X} = \frac{1}{M_T} \sum_{i=0}^n m_i \mathbf{R}_i, \quad (16.2)$$

where \mathbf{X} denotes the center-of-mass coordinate and M_T is the total mass of the system. This converts Eq. (16.1) into a separable Hamiltonian: $H_T = H + H_X$, where H_X accounts for the translation of the entire system, and a term H , which covers the internal system dynamics. The former is not of interest for the particular application at hand, and is dropped from further consideration. The Hamiltonian H takes the form

$$H = -\sum_{i=1}^n \frac{1}{2\mu_i} \nabla_i^2 - \frac{1}{m_0} \sum_{i=1}^n \sum_{j>i}^n \nabla_i \cdot \nabla_j + q_0 \sum_{i=1}^n \frac{q_i}{r_i} + \sum_{i=1}^n \sum_{j>i}^n \frac{q_i q_j}{r_{ij}}, \quad (16.3)$$

where the reduced mass relative to the reference particle is $\mu_i = m_i m_0 / (m_i + m_0)$ and $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$. For the particular case of HeH^+ , with the helium nucleus taken as the reference particle, the Hamiltonian takes the form

$$H = -\frac{1+m_{\text{He}}}{2m_{\text{He}}} (\nabla_1^2 + \nabla_2^2) - \frac{m_{\text{p}} + m_{\text{He}}}{2m_{\text{p}}m_{\text{He}}} \nabla_3^2 - \frac{1}{m_{\text{He}}} (\nabla_1 \cdot \nabla_2 + \nabla_1 \cdot \nabla_3 + \nabla_2 \cdot \nabla_3) - \frac{2}{r_1} - \frac{2}{r_2} + \frac{2}{r_3} + \frac{1}{r_{12}} - \frac{1}{r_{23}} - \frac{1}{r_{13}}, \quad (16.4)$$

where the position vectors of the two electrons and the proton are \mathbf{r}_1 , \mathbf{r}_2 , and \mathbf{r}_3 , respectively, and m_{p} and m_{He} denote the mass of the proton and the helium nucleus, respectively. Using this Hamiltonian, and assuming basis functions of the form:

$$\phi_{\nu}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = r_1^{i_{\nu}} r_2^{j_{\nu}} r_3^{k_{\nu}} r_{12}^{l_{\nu}} r_{13}^{m_{\nu}} r_{23}^{n_{\nu}} e^{-a_{\nu} r_1 - b_{\nu} r_2 - c_{\nu} r_3}, \quad (16.5)$$

leads to integrals that take the form of the I_3 integrals given in Eq. (9.3). Employing this approach, Zhou, Zhu, and Yan [141] obtained a ground-state energy converged to a few parts in 10^{10} . The interested reader can pursue further discussion on this species [142] and a similar approach for other few-electron diatomic molecules in [143-145].

17. Progress, problems, and some future directions

Progress on the accurate evaluation of the properties of few-electron systems has been tied to advances in computer technology, the development of

new integral formula evaluations, and improvements in numerical strategies for various types of calculation.

Over the past forty years, considerable progress has been made on the evaluation of properties using explicit r_{ij} factors in the wave function for two-electron [21-22, 26, 54-58, 146-160], three-electron [44, 161-190], and four-electron atomic systems [191-195]. The results for the two- and three-electron systems indicate the significant progress that has been made using correlated STO basis functions with explicit r_{ij} factors. It is noteworthy that similar progress on the calculation of the properties of the beryllium atom and members of its isoelectronic series using correlated STO basis functions, has been somewhat limited. The best results for the energy of atomic Be have been obtained with a basis set of exponentially correlated Gaussian functions [196]. In order to match calculated results with experimental transition energies or ionization potentials, several contributions to the total energy of each state are needed, including the non-relativistic energy, finite mass corrections, relativistic contributions, and quantum electrodynamic corrections. For two- and three-electron atomic systems, the non-relativistic energy contribution is now known with an accuracy well beyond what is required to make a match with the currently best available experimental results.

The focus of most of this review has been on few-electron atomic systems, where the natural center for the coordinates is the nucleus. In the infinite nuclear mass approximation, the center of mass is at the nucleus. For more exotic atomic species, containing a collection of elementary particles, there is no longer a natural center at a particular particle. In a general three-body problem, it makes more sense to replace the set of coordinates $\{r_1, r_2, r_{12}\}$ by the set $\{r_{12}, r_{13}, r_{23}\}$, thereby giving no special place to any one particle. The analogue of Eq. (6.2) then becomes the general correlated three-body integral

$$\mathcal{I}(i, j, k, \alpha, \beta, \gamma) = \int r_{12}^i r_{13}^j r_{23}^k e^{-\alpha r_{12} - \beta r_{13} - \gamma r_{23}} d\tau, \quad (17.1)$$

with $d\tau \rightarrow r_{12} r_{13} r_{23} dr_{12} dr_{13} dr_{23}$ after dealing with the angular integration. A considerable number of papers have appeared on the discussion of general correlated three-body and four-body integrals [33, 47, 60, 97-98, 197-198].

To treat electronic systems beyond the four-electron level using Hylleraas basis sets, several mathematical problems will need to be addressed. Employing the expansion for the Sack radial function given in Eq. (9.16) generates for an N -electron atomic system, an $N!$ problem – that is, there are $N!$ W_N auxiliary functions that arise. Judicious selection of basis sets can considerably reduce this problem. It would be useful to have an effective

computational strategy that avoids this issue, which means looking for alternative expansions of the Sack radial functions, avoiding the $r_<$ and $r_>$ variables. A second issue that arises in integral evaluations is the requirement to deal with the numerical evaluation of *multiple* nested infinite summations. There is a clear need to have available, convergence acceleration techniques for multiply nested sums that do not scale as \mathcal{N}^n , where \mathcal{N} is the typical number of term evaluations that are required to accelerate a single infinite summation, and n is the number of nested infinite summations. Such procedures would have the potential to improve substantially, various integral evaluation algorithms.

Progress beyond four-electron systems has been very limited using explicitly correlated STOs. Examples such as the CI-Hylleraas calculation on the ground state of the neon atom have been forced to use a restricted basis expansion, with only terms linear in r_{ij} being employed [199]. It appears that it would be useful to resolve some of the more recalcitrant integral issues associated with the four-electron problem. That will probably provide a guide for the solution of the correlated integration problem for more complicated electronic systems.

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