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S-State Matrix Elements for Muonic Molecules[1]

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ABSTRACT

Coordinates ξ, η, θ are introduced, one of which is the internuclear distance, and all of which are linear combinations of interparticle distances in a molecular three-body system. Each matrix element of the Hamiltonian or unity is shown to be the sum of a few products of reduced matrix elements, which are one- or two-dimensional integrals, provided that each basis function is the product of a function of ξ and η times a function of θ. For basis functions which are products of mononomials times exponentials in ξ, η, θ, the reduced matrix elements are represented as linear combinations of basic integrals, for which closed-form or recursive expressions are derived.

I. INTRODUCTION AND SUMMARY

The Hylleraas type of trial function for a three-body S-state [1] is an exponential times a polynomial in the interparticle distances (or linear combinations thereof). As the number of terms in the polynomial is increased, the convergence of the minimum Rayleigh quotient to the ground-state energy is quite rapid for helium-like systems, as was shown by Pekeris [2]. For muonic molecules the corresponding convergence rate has been found to be much slower ([3], [4]) than for helium.

Some improvement can be made by using a trial function which is the product of a Hylleraas function, or a sum of Hylleraas functions, times a Gaussian function of the internuclear distance. Fröman and Kinsey [5] have multiplied a Gaussian by a restricted form of Hylleraas function. Flügge and Schröder [6] have used sums of exponentials times a Gaussian. Wessel and Phillipson [7] have multiplied a Gaussian by a sum of products of polynomials times exponentials. The calculations show a marked improvement, compared to Hylleraas-type calculations, when the number of terms in the trial function is small. But it remains an open question whether the Gaussian dependence remains useful when the number of terms increases beyond about 100.

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In view of the situation outlined above, it seems to this writer that new methods are needed for the numerical treatment of muonic molecules. One approach is to use the Hylleraas basis (perhaps multiplied by a Gaussian) but search in a way which is not completely general for the polynomial coefficients. We have made a calculation of this sort, the results of which will be reported in a sequel to this paper. Here we point out that any such scheme must involve more basis functions than are needed in the straightforward Rayleigh–Ritz method, in order to achieve a given level of accuracy. The problem of computing and storing the matrix elements becomes acute when their number exceeds the tens of thousands of words of core memory in a typical large computer. We have solved this problem by using a basis in which each matrix element separates into a sum of a few products of quantities which we call reduced matrix elements. These quantities can be computed and stored quickly as a preliminary step. One can then compute the matrix elements more quickly (by using the reduced matrix elements) than by previous methods.

Section II of this paper contains expressions for matrix elements of arbitrary basis functions, in terms of the interparticle distances as coordinates. In Section III we transform to a new set of coordinates, ξ, η, θ, and restrict the basis functions to be products of functions of ξ and η times functions of θ. This restriction is necessary for the matrix elements to separate in the desired manner, but the trial function is still general enough to include the Hylleraas form as a special case. The Hylleraas-times-Gaussian trial function would be another special case.

In Section IV the matrix elements of the Hamiltonian and unity are represented as sums of products of reduced matrix elements. Each reduced matrix element is a definite integral over one or two variables. The latter part of Section IV is devoted to the evaluation of these integrals, in the case that the basis functions are mononomials times exponentials in ξ, η, θ. This case includes the Hylleraas type of trial function, but also allows for variation of the exponents. (In other words, the complete trial function could be a sum of functions of the Hylleraas type.) The reduced matrix elements are finally expressed in Section IV as linear combinations of certain basic integrals, the evaluation of which is discussed in Appendix A. Closed-form expressions are found for some of the basic integrals. For others, we find recursion relations, following Sack, Roothaan, and Kolos [8].

II. S-State Matrix Elements

Units and Notation

We use units such that $\hbar$ and the absolute electronic charge are unity. Our mass unit is $\mathscr{S}$ times the electron mass, where $\mathscr{S}$ is an arbitrary scale factor. A particular choice of $\mathscr{S}$ would fix the unit of energy to be $\mathscr{S}$ hartrees (one hartree $\approx$27.21 eV),

and would fix the unit of distance to be $1/\mathscr{S}$ Bohr radii. The various systems of units (atomic, muonic, reduced muonic) which have appeared in the literature on muonic molecules correspond to different values of $\mathscr{S}$.

Let m_i, q_i be the mass and charge of particle $i (i = 1, 2, 3)$. The distance from particle i to particle j is denoted by ρ_k, where i, j, k are any permutation of 1, 2, 3. The coordinates ρ_i are shown in Fig. 1. For muonic molecules we always choose particle 3 to be the muon, so that ρ_3 is the internuclear distance.

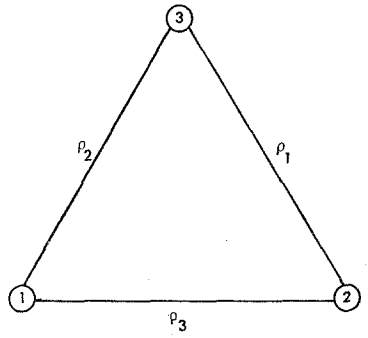

FIG. 1. Interparticle distances ρ_i as coordinates for S-states of three particles.

MATRIX ELEMENTS OF HAMILTONIAN AND UNITY

The spinless, nonrelativistic Hamiltonian for the three-particle system is

$$H = \sum_{i=1}^{3} [-w_i \nabla_i^2 + Q_i/\rho_i],$$

where ∇_i is the gradient with respect to the position of particle i, and where

$$w_i = 1/(2m_i), \tag{2.1}$$

$$Q_i = q_j q_k \qquad (i, j, k \text{ cyclic}). \tag{2.2}$$

Matrix elements of H and unity are of the form

$$\begin{aligned} \langle g \mid g' \rangle &= 8\pi^2 U, \\ \langle g \mid H \mid g' \rangle &= 8\pi^2 (T + V), \end{aligned} \tag{2.3}$$

which agrees with our previous form [9] except for trivial differences in notation.[2]

[2] The u, v of Ref. [9] correspond to g, g' here, and the r_1, r_2, r_{12} of Ref. [9] correspond to ρ_2, ρ_1, ρ_3, respectively. The factor $8\pi^2$ is not removed from U, V, T in Ref. [9] as it is in Eq. (2.3) above.

The terms T and V come from the kinetic and potential parts of H, respectively. From Reference [9] and taking into account the differences in notation, we obtain expressions for U, V and T. For U we obtain

$$U = \int gg'\rho_1\rho_2\rho_3 \, d\rho_1 \, d\rho_2 \, d\rho_3 \, . \tag{2.4}$$

For V we obtain

$$V = \sum_{i=1}^{3} Q_i V_i \, , \tag{2.5}$$

where Q_i is given by (2.2), and

$$V_i = \int gg'\rho_j\rho_k \, d\rho_1 \, d\rho_2 \, d\rho_3 \qquad (i, j, k \text{ cyclic}). \tag{2.6}$$

The expression for T involves derivatives of g, g' with respect to the coordinates. We denote logarithmic derivatives of g and g' by subscripts as follows:

$$g_i = \frac{1}{g}\frac{\partial g}{\partial \rho_i} \, , \qquad g_i' = \frac{1}{g'}\frac{\partial g'}{\partial \rho_i} \, . \tag{2.7}$$

We further define

$$\Omega_i = w_j + w_k \qquad (i, j, k \text{ cyclic}). \tag{2.8}$$

The expression for T is given by the following equations:

$$T = T^{(1)} + T^{(2)}, \tag{2.9}$$

$$T^{(1)} = \sum_{i=1}^{3} \Omega_i T_i^{(1)}, \tag{2.10}$$

$$T^{(2)} = \sum_{i=1}^{3} w_i T_i^{(2)}, \tag{2.11}$$

$$T_i^{(1)} = \int gg'g_ig_i'\rho_1\rho_2\rho_3 \, d\rho_1 \, d\rho_2 \, d\rho_3 \, , \tag{2.12}$$

$$T_i^{(2)} = \tfrac{1}{2} \int gg'(\rho_j^{\,2} + \rho_k^{\,2} - \rho_i^{\,2}) \, \rho_i(g_jg_k' + g_kg_j') \, d\rho_1 \, d\rho_2 \, d\rho_3 \, . \tag{2.13}$$

III. Coordinate Transformation

The formulas of the preceding section have a certain symmetry which is clear from Fig. (1). If two particles i, j are interchanged, then so are the coordinates

ρ_i , ρ_j and the various components of T and V. In this section we break the symmetry by introducing new coordinates ξ, η, θ defined as follows:

$$\begin{aligned} \xi &= \tfrac{1}{2}(x_1 + x_2) = \tfrac{1}{2}\rho_3 , \\ \eta &= \tfrac{1}{2}(x_1 - x_2) = \tfrac{1}{2}(\rho_2 - \rho_1), \\ \theta &= x_3 = \tfrac{1}{2}(\rho_1 + \rho_2 - \rho_3). \end{aligned} \tag{3.1}$$

Equations (3.1) also indicate the dependence of the new coordinates on a set of perimetric coordinates x_1 , x_2 , x_3 which run independently from 0 to ∞. All matrix elements are ultimately expressed as multiple integrals over x_1 , x_2 , x_3 .

At this point an explanation is in order as to why ξ, η, θ were chosen as indicated. First of all, the separability mentioned in Section I is a consequence of the fact that ξ and η depend only on x_1 and x_2 , while θ depends only on x_3 . Second, the reason why one of the new coordinates has been chosen proportional to ρ_3 is that ρ_3 (the internuclear distance) plays a special role in muonic molecules. The wave function varies more rapidly in ρ_3 than in ρ_1 and ρ_2 , and the trial function needs to be more flexible in ρ_3 than in the other coordinates. The greater flexibility can be accomplished by including higher powers of ρ_3 , than of ρ_1 or ρ_2 , in the polynomial part(s) of the trial function. To do this we need one of the new coordinates, in terms of which the polynomial is expanded, to be a multiple of ρ_3 .

The only nontrivial change we could make in Eqs. (3.1) without losing one of the desirable properties mentioned above, would be to add a multiple of ξ to η. But this would destroy what is left of the symmetry: ξ and θ are even, and η is odd, under interchange of 1 and 2. This is a third desirable property of the coordinates when the two nuclei are identical, since then one can delete odd terms in η from the trial function.

By solving (3.1) for the old coordinates ρ_i , we obtain the inverse relations:

$$\begin{aligned} \rho_1 &= x_2 + x_3 = \theta + \xi - \eta, \\ \rho_2 &= x_1 + x_3 = \theta + \xi + \eta, \\ \rho_3 &= x_1 + x_2 = 2\xi. \end{aligned} \tag{3.2}$$

The Jacobian of the transformation from ρ_i to x_i is 2:

$$d\rho_1\, d\rho_2\, d\rho_3 = 2\, dx_1\, dx_2\, dx_3 = 2\, d^3x. \tag{3.3}$$

Equations (2.4), (2.6), (2.12) and (2.13) can be written as

$$\begin{aligned} U &= \int gg' u\, d^3x, \\ V_i &= \int gg' v_i\, d^3x, \\ T_i^{(n)} &= \int gg' t_i^{(n)}\, d^3x, \end{aligned} \tag{3.4}$$

where the u, v_i, and $t_i^{(n)}$ are functions of the coordinates. In each case (3.3) brings in a factor of 2. Comparing (3.4) with the equations of Section II, we obtain

$$u = 2\rho_1\rho_2\rho_3, \tag{3.5}$$

$$v_i = 2\rho_j\rho_k, \tag{3.6}$$

$$t_i^{(1)} = 2g_ig_i'\rho_1\rho_2\rho_3, \tag{3.7}$$

$$t_i^{(2)} = (\rho_j^2 + \rho_k^2 - \rho_i^2)\,\rho_i(g_jg_k' + g_kg_j'). \tag{3.8}$$

Substituting (3.2) into (3.5), we obtain

$$u = (4\xi)\theta^2 + (8\xi^2)\theta + 4\xi(\xi^2 - \eta^2). \tag{3.9}$$

Substitution of (3.2) into (3.6) yields

$$\begin{aligned} v_1 &= (4\xi)\theta + 4\xi(\xi + \eta), \\ v_2 &= (4\xi)\theta + 4\xi(\xi - \eta), \\ v_3 &= 2\theta^2 + 4\xi\theta + 2(\xi^2 - \eta^2). \end{aligned} \tag{3.10}$$

Defining

$$v = \sum_{i=1}^{3} Q_iv_i, \tag{3.11}$$

and using (2.5) and (3.4), we obtain

$$V = \int gg'v\,d^3x. \tag{3.12}$$

Substitution of (3.10) into (3.11) yields

$$v = 2Q_3\theta^2 + 4(Q_1 + Q_2 + Q_3)\xi\theta + [4(Q_1 + Q_2) + 2Q_3]\xi^2 + 4(Q_1 - Q_2)\xi\eta - 2Q_3\eta^2. \tag{3.13}$$

Equation (3.13) is perfectly general, but most cases of physical interest have charges

$$q_1 = q_2 = \pm 1, \qquad q_3 = \mp z, \tag{3.14}$$

for some positive integer z. For instance H_2^+, H^-, $p\mu p$, $p\mu d$, etc., all correspond to $z = 1$, while He, Li^+,..., correspond to $z = 2, 3, \ldots$. Substituting (3.14) into (2.2), we obtain

$$Q_1 = Q_2 = -z, \qquad Q_3 = 1, \tag{3.15}$$

which simplifies (3.13):

$$v = 2\theta^2 + 4(1 - 2z)\xi\theta - 8z\xi^2 + 2(\xi^2 - \eta^2). \tag{3.16}$$

We use (3.16) for convenience in Section IV. Should anyone wish to solve a system not satisfying (3.14), the necessary modification of replacing (3.16) by (3.13) is straightforward.

To transform the logarithmic derivatives in (3.7) and (3.8) we restrict the basis functions to be products of the form

$$\begin{aligned} g &= d(\xi, \eta)\, e(\theta), \\ g' &= d'(\xi, \eta)\, e'(\theta), \end{aligned} \tag{3.17}$$

and denote logarithmic derivatives with respect to the new coordinates as follows:

$$d_\xi = \frac{1}{d}\frac{\partial d}{\partial \xi}, \qquad d_\eta = \frac{1}{d}\frac{\partial d}{\partial \eta}, \qquad e_\theta = \frac{1}{e}\frac{\partial e}{\partial \theta}, \tag{3.18}$$

and similarly for the primed quantities. (The partial differentiation symbol is used for the ordinary derivative of e above, to avoid confusion with the function d.) From (2.7), (3.1), and (3.17) we obtain the transformation of logarithmic derivatives:

$$\begin{aligned} g_1 &= \tfrac{1}{2}(e_\theta - d_\eta), \qquad g_2 = \tfrac{1}{2}(e_\theta + d_\eta), \qquad g_3 = \tfrac{1}{2}(d_\xi - e_\theta), \\ g'_1 &= \tfrac{1}{2}(e'_\theta - d'_\eta), \qquad g'_2 = \tfrac{1}{2}(e'_\theta + d'_\eta), \qquad g'_3 = \tfrac{1}{2}(d'_\xi - e'_\theta). \end{aligned} \tag{3.19}$$

The next steps are to substitute (3.19) into (3.7) and (3.8), and collect terms in the function

$$t = \sum_{i=1}^{3} (\Omega_i t_i^{(1)} + w_i t_i^{(2)}). \tag{3.20}$$

The algebra is lengthy but elementary. The result is in the form

$$t = (p_4\theta^2 + p_5\theta)\, e_\theta e'_\theta + (p_6\theta^2 + p_7\theta)\, e_\theta + (p_8\theta^2 + p_9\theta)\, e'_\theta + (a\theta^2 + b\theta + c), \tag{3.21}$$

where the coefficients p_i, a, b, c are functions of ξ and η. In terms of the constants

$$w = w_1 + w_2, \qquad h = w_1 - w_2, \tag{3.22}$$

the coefficients are as follows:

$$\begin{aligned} p_4 &= (2w + 4w_3)\,\xi - 2h\eta, \\ p_5 &= (2w + 8w_3)\,\xi^2 + 2w\eta^2 - 4h\xi\eta, \\ p_6 &= (h\xi - w\eta)\, d'_\eta + (h\eta - w\xi)\, d'_\xi, \\ p_7 &= [h(\xi^2 + \eta^2) - 2w\xi\eta]\, d'_\eta + [2h\xi\eta - w(\xi^2 + \eta^2)]\, d'_\xi, \\ p_8 &= (h\xi - w\eta)\, d_\eta + (h\eta - w\xi)\, d_\xi, \\ p_9 &= [h(\xi^2 + \eta^2) - 2w\xi\eta]\, d_\eta + [2h\xi\eta - w(\xi^2 + \eta^2)]\, d_\xi, \\ a &= w\xi(d_\xi d'_\xi + d_\eta d'_\eta) + w\eta(d_\xi d'_\eta + d_\eta d'_\xi), \\ b &= 2w\xi^2(d_\xi d'_\xi + d_\eta d'_\eta) + [2w\xi\eta + h(\xi^2 - \eta^2)](d_\xi d'_\eta + d_\eta d'_\xi), \\ c &= \xi(\xi^2 - \eta^2)[w d_\xi d'_\xi + (w + 4w_3)\, d_\eta d'_\eta + h(d_\xi d'_\eta + d_\eta d'_\xi)]. \end{aligned} \tag{3.23}$$

IV. Reduced Matrix Elements

In this section we derive reduced matrix elements R_i, P_i, S_i such that the matrix elements (2.3) separate into sums of products as follows:

$$U = \sum_{i=1}^{3} R_i S_i, \qquad T + V = \sum_{i=1}^{9} P_i S_i. \tag{4.1}$$

First we define nine functions $s_i(\theta)$ as follows:

$$\begin{aligned} s_1 &= \theta^2, & s_4 &= \theta^2 e_\theta e'_\theta, & s_7 &= \theta e_\theta, \\ s_2 &= \theta, & s_5 &= \theta e_\theta e'_\theta, & s_8 &= \theta^2 e'_\theta, \\ s_3 &= 1, & s_6 &= \theta^2 e_\theta, & s_9 &= \theta e'_\theta. \end{aligned} \tag{4.2}$$

Next we define some more functions $r_i(\xi, \eta)$ and $p_i(\xi, \eta)$ as follows:

$$r_1 = 4\xi, \qquad r_2 = 8\xi^2, \qquad r_3 = 4\xi(\xi^2 - \eta^2), \tag{4.3}$$

$$p_1 = 2 + a, \qquad p_2 = (1 - 2z)4\xi + b, \qquad p_3 = 2(\xi^2 - \eta^2) - 8z\xi^2 + c. \tag{4.4}$$

From (3.9), (4.2), and (4.3) we obtain

$$u = \sum_{i=1}^{3} r_i s_i. \tag{4.5}$$

From (3.16), (3.21), (4.2) and (4.4) we obtain

$$t + v = \sum_{i=1}^{9} p_i s_i. \tag{4.6}$$

Considering ξ and η as functions of x_1 and x_2, according to (3.1), we define

$$R_i = \int_0^\infty dx_1 \int_0^\infty dx_2 \, r_i(\xi, \eta) \, d(\xi, \eta) \, d'(\xi, \eta), \tag{4.7}$$

$$P_i = \int_0^\infty dx_1 \int_0^\infty dx_2 \, p_i(\xi, \eta) \, d(\xi, \eta) \, d'(\xi, \eta). \tag{4.8}$$

Similarly we define

$$S_i = \int_0^\infty dx_3 \, s_i(\theta) \, e(\theta) \, e'(\theta). \tag{4.9}$$

Substituting (3.17) and (4.5) into the first of Eqs. (3.4) we obtain

$$U = \sum_{i=1}^{3} \int de\, d'e' r_i s_i\, d^3x.$$

The first of Eqs. (4.1) follows directly from the above expression, (4.7), and (4.9). To prove the second of Eqs. (4.1) we need

$$T = \int gg't\, d^3x, \tag{4.10}$$

which follows from (2.9), (2.10), (2.11), (3.20), and the last of Eqs. (3.4). From (3.12), (3.17), (4.6), and (4.10), we obtain

$$T + V = \sum_{i=1}^{9} \int de\, d'e' p_i s_i\, d^3x.$$

The second of Eqs. (4.1) then follows from (4.8) and (4.9).

Hylleraas Basis

Now we specialize the basis functions as follows:

$$\begin{aligned} d &= \xi^l \eta^m e^{A\xi + B\eta}, & e &= \theta^n e^{C\theta}, \\ d' &= \xi^{l'} \eta^{m'} e^{A'\xi + B'\eta}, & e' &= \theta^{n'} e^{C'\theta}. \end{aligned} \tag{4.11}$$

These functions are slightly more general than those of References 2, 3, and 4, in that the exponents are not assumed to be the same for all elements of the basis. From (3.18) and (4.11) we have

$$\begin{aligned} d_\xi &= l\xi^{-1} + A, & d'_\xi &= l'\xi^{-1} + A', \\ d_\eta &= m\eta^{-1} + B, & d'_\eta &= m'\eta^{-1} + B', \\ e_\theta &= n\theta^{-1} + C, & e'_\theta &= n'\theta^{-1} + C'. \end{aligned} \tag{4.12}$$

The combinations of derivatives which appear in the expressions (3.23) for a, b, c are

$$\begin{aligned} d_\xi d'_\xi &= X_1\xi^{-2} + X_2\xi^{-1} + X_3, \\ d_\eta d'_\eta &= Y_1\eta^{-2} + Y_2\eta^{-1} + Y_3, \\ d_\xi d'_\eta + d_\eta d'_\xi &= D\xi^{-1}\eta^{-1} + E\xi^{-1} + F\eta^{-1} + G, \end{aligned} \tag{4.13}$$

where the coefficients, from (4.12), are

$$\begin{aligned} X_1 &= ll', \qquad X_2 = Al' + A'l, \qquad X_3 = AA', \\ Y_1 &= mm', \qquad Y_2 = Bm' + B'm, \qquad Y_3 = BB', \\ D &= lm' + l'm, \qquad E = lB' + l'B, \\ F &= Am' + A'm, \qquad G = AB' + A'B. \end{aligned}$$

From (3.23), (4.4), and (4.13) we obtain

$$\begin{aligned} p_1 &= 2 + w[(X_2 + F) + (X_1 + D)\xi^{-1} \\ &\quad + (X_3 + Y_3)\xi + E\eta\xi^{-1} + Y_2\xi\eta^{-1} + G\eta + Y_1\xi\eta^{-2}], \end{aligned} \tag{4.14}$$

$$\begin{aligned} p_2 &= (1 - 2z)4\xi + 2w(X_1 + X_2\xi + X_3\xi^2 + Y_1\xi^2\eta^{-2} + Y_2\xi^2\eta^{-1} + Y_3\xi^2) \\ &\quad + 2w(D + E\eta + F\xi + G\xi\eta) \\ &\quad + h(D\xi^{-1}\eta^{-1} + E\xi^{-1} + F\eta^{-1} + G)(\xi^2 - \eta^2), \end{aligned} \tag{4.15}$$

$$\begin{aligned} p_3 &= 2(\xi^2 - \eta^2) - 8z\xi^2 + [w(X_1\xi^{-1} + X_2 + X_3\xi) \\ &\quad + (w + 4w_3)(Y_1\xi\eta^{-2} + Y_2\xi\eta^{-1} + Y_3\xi) \\ &\quad + h(D\eta^{-1} + E + F\xi\eta^{-1} + G\xi)](\xi^2 - \eta^2). \end{aligned} \tag{4.16}$$

For p_6, p_7, p_8, and p_9, we rewrite (3.23) as

$$\begin{aligned} p_6 &= \tilde{\alpha}d_\eta' + \tilde{\beta}d_\xi', \\ p_7 &= \tilde{\gamma}d_\eta' + \tilde{\delta}d_\xi', \\ p_8 &= \tilde{\alpha}d_\eta + \tilde{\beta}d_\xi, \\ p_9 &= \tilde{\gamma}d_\eta + \tilde{\delta}d_\xi, \end{aligned} \tag{4.17}$$

where

$$\begin{aligned} \tilde{\alpha} &= h\xi - w\eta, \\ \tilde{\beta} &= h\eta - w\xi, \\ \tilde{\gamma} &= h(\xi^2 + \eta^2) - w(2\xi\eta), \\ \tilde{\delta} &= h(2\xi\eta) - w(\xi^2 + \eta^2). \end{aligned} \tag{4.18}$$

From (4.12) and (4.17) we obtain

$$\begin{aligned} p_6 &= (m'\eta^{-1} + B')\,\tilde{\alpha} + (l'\xi^{-1} + A')\,\tilde{\beta}, \\ p_7 &= (m'\eta^{-1} + B')\,\tilde{\gamma} + (l'\xi^{-1} + A')\,\tilde{\delta}, \\ p_8 &= (m\eta^{-1} + B)\,\tilde{\alpha} + (l\xi^{-1} + A)\,\tilde{\beta}, \\ p_9 &= (m\eta^{-1} + B)\,\tilde{\gamma} + (l\xi^{-1} + A)\,\tilde{\delta}. \end{aligned} \tag{4.19}$$

From (4.2) and (4.12) we obtain

$$\begin{aligned} s_4 &= nn' + (Cn' + C'n)\,\theta + CC'\theta^2, \\ s_5 &= nn'\theta^{-1} + (Cn' + C'n) + CC'\theta, \\ s_6 &= n\theta + C\theta^2, \qquad s_7 = n + C\theta, \\ s_8 &= n'\theta + C'\theta^2, \qquad s_9 = n' + C'\theta. \end{aligned} \tag{4.20}$$

The next step is to evaluate (4.7), (4.8), and (4.9). For this purpose it is convenient to define basic integrals as follows:

$$\begin{aligned} I(L, M) &= \iint \xi^L \eta^M \exp[(A + A')\,\xi + (B + B')\,\eta]\,dx_1\,dx_2\,, \\ J(L, M) &= \iint (\xi^2 - \eta^2)\,\xi^L \eta^M \exp[(A + A')\,\xi + (B + B')\,\eta]\,dx_1\,dx_2\,, \\ K(N) &= \int \theta^N \exp[(C + C')\,\theta]\,dx_3\,. \end{aligned} \tag{4.21}$$

The problem of evaluating these quantities is considered in Appendix A. In the remainder of this section, we reduce the quantities R_i, P_i, and S_i to linear combinations of the quantities I, J, K.

From (4.2), (4.9), (4.11), and (4.21), we obtain

$$S_1 = K(N + 2), \qquad S_2 = K(N + 1), \qquad S_3 = K(N),$$

where $N = n + n'$. Similarly from (4.9), (4.11), (4.20), and (4.21), we obtain

$$\begin{aligned} S_4 &= nn'K(N) + (Cn' + C'n)\,K(N + 1) + CC'K(N + 2), \\ S_5 &= nn'K(N - 1) + (Cn' + C'n)\,K(N) + CC'K(N + 1), \\ S_6 &= nK(N + 1) + CK(N + 2), \qquad S_7 = nK(N) + CK(N + 1), \\ S_8 &= n'K(N + 1) + C'K(N + 2), \qquad S_9 = n'K(N) + C'K(N + 1). \end{aligned}$$

From (4.3), (4.7), (4.11), and (4.21), we obtain

$$R_1 = 4I(L + 1, M), \qquad R_2 = 8I(L + 2, M), \qquad R_3 = 4J(L + 1, M),$$

where $L = l + l'$ and $M = m + m'$. Similarly from (4.14), (4.15), (4.16), (4.8), (4.11), and (4.21), we obtain

$$\begin{aligned} P_1 &= [2 + w(X_2 + F)]\,I(L, M) + w[(X_1 + D)\,I(L - 1, M) \\ &\quad + (X_3 + Y_3)\,I(L + 1, M) + EI(L - 1, M + 1) \\ &\quad + Y_2 I(L + 1, M - 1) + GI(L, M + 1) + Y_1 I(L + 1, M - 2)], \\ P_2 &= 2w(X_1 + D)\,I(L, M) + [4(1 - 2z) + 2w(X_2 + F)]\,I(L + 1, M) \\ &\quad + 2w[(X_3 + Y_3)\,I(L + 2, M) + Y_1 I(L + 2, M - 2) + Y_2 I(L + 2, M - 1) \\ &\quad + EI(L, M + 1) + GI(L + 1, M + 1)] + h[DJ(L - 1, M - 1) \\ &\quad + EJ(L - 1, M) + FJ(L, M - 1) + GJ(L, M)], \end{aligned}$$

$$P_3 = 2J(L, M) - 8zI(L+2, M) + (wX_2 + hE)\,J(L, M)$$
$$+ [wX_3 + (w + 4w_3)Y_3 + hG]\,J(L+1, M) + wX_1J(L-1, M)$$
$$+ (w + 4w_3)[Y_1J(L+1, M-2) + Y_2J(L+1, M-1)]$$
$$+ h[DJ(L, M-1) + FJ(L+1, M-1)].$$

From (3.23) etc., we obtain

$$P_4 = (2w + 4w_3)\,I(L+1, M) - 2hI(L, M+1),$$

$$P_5 = (2w + 8w_3)\,I(L+2, M) + 2wI(L, M+2) - 4hI(L+1, M+1).$$

For the remaining P_i we define

$$\alpha(L, M) = \iint \tilde{\alpha}\xi^L\eta^M \exp[(A + A')\,\xi + (B + B')\,\eta]\,dx_1\,dx_2,$$

and similarly for β, γ, and δ. From (4.18) we have

$$\alpha(L, M) = hI(L+1, M) - wI(L, M+1),$$
$$\beta(L, M) = hI(L, M+1) - wI(L+1, M),$$
$$\gamma(L, M) = h[I(L+2, M) + I(L, M+2)] - 2wI(L+1, M+1),$$
$$\delta(L, M) = 2hI(L+1, M+1) - w[I(L+2, M) + I(L, M+2)].$$

From (4.19) etc., we obtain

$$P_6 = m'\alpha(L, M-1) + B'\alpha(L, M) + l'\beta(L-1, M) + A'\beta(L, M),$$
$$P_7 = m'\gamma(L, M-1) + B'\gamma(L, M) + l'\delta(L-1, M) + A'\delta(L, M),$$
$$P_8 = m\alpha(L, M-1) + B\alpha(L, M) + l\beta(L-1, M) + A\beta(L, M),$$
$$P_9 = m\gamma(L, M-1) + B\gamma(L, M) + l\delta(L-1, M) + A\delta(L, M).$$

APPENDIX A

In this appendix we consider the problem of evaluating the basic integrals I, J, K of Section IV. From (4.21) we see that the K's are trivially related to the usual definition of the gamma function, and that the J's are simple differences between the I's. The only serious problem is to find an efficient method for calculating large numbers of integrals of the form

$$I(L, M) = \iint \xi^L\eta^M e^{-a\xi - b\eta}\,dx_1\,dx_2, \qquad \text{(A-1)}$$

where we have set $a = -A - A'$ and $b = +B - B'$ for brevity.

Of course one can use (3.1) to eliminate ξ and η, and then use the binomial theorem to represent (A-1) as a double sum of one-dimensional integrals. But the formal summations are needlessly time-consuming and can lead to excessive roundoff errors. A more satisfactory procedure is to evaluate (A-1) recursively. Using (3.1), we find that (A-1) reduces to

$$I(L, M) = (-\partial_a)^L (-\partial_b)^M [4/(a^2 - b^2)], \tag{A-2}$$

which is a special case of the problem considered by Sack, Roothaan, and Kolos [8]. One could apply their method directly to (A-2), but the resulting recursion relation would involve cancellations, with the danger of excussive roundoff errors. A safer way is to split (A-2) into two parts, as follows:

$$\begin{aligned} I(L, M) &= \Gamma_{LM}(a, b) + (-1)^M \Gamma_{LM}(a, -b), \\ \Gamma_{LM}(a, b) &= (-\partial_a)^L (-\partial_b)^M [2a^{-1}/(a + b)]. \end{aligned} \tag{A-3}$$

From Ref. [8] we obtain the following recursion relation, the terms of which are all of the same sign:

$$(a + b)\Gamma_{LM} = L\Gamma_{L-1,M} + M\Gamma_{L,M-1} + (-\partial_a)^L (-\partial_b)^M (2/a).$$

A further simplification is possible in the special case that $b = 0$. This case arises from a trial function of the Hylleraas type, when the exponential is symmetric in ρ_1 and ρ_2. In this case, the second of Eqs. (A-3) can be evaluated in closed form, as follows:

$$\Gamma_{LM}(a, 0) = [2(M + L + 1)!]/[(M + 1)\, a^{M+L+2}].$$

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