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Muonic-Molecule Calculations by Variation of Functions[1]

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ABSTRACT

The adiabatic method is generalized by a trial function ψ containing products of arbitrary functions, each of which depends on the internuclear distance and on one ellipsoidal coordinate. The arbitrary functions are varied to optimize ψ. Numerical examples include several S- and P-states of muonic molecules.

I. INTRODUCTION

The adiabatic method, including dynamic correction terms for the motion of the nuclei, has been applied to muonic molecules by several authors. The most recent and extensive calculations are those by Patterson and Becker [1], who also review the previous calculations by Cohen, Judd, and Riddell [2], Belyaev *et al.* [3], and others. Patterson and Becker use linear combinations of up to $N = 6$ eigenstates of a clamped-nuclei problem, but their computed values of dissociation energies are generally a few eV less than the best values available from variational calculations of the Rayleigh–Ritz type [4–11].

In this paper we will show that the high accuracy characteristic of Rayleigh–Ritz calculations can be attained, in practice, with a trial function of a form similar to that of an adiabatic wavefunction. The method to be introduced here is a special case of the method of variation of functions, i.e., the use of a trial function ψ containing arbitrary *functions* instead of arbitrary constants. The trial function for S states is a generalization of the form of an N-term adiabatic wavefunction. This generalization is discussed in Sec. II for arbitrary N, but subsequent sections are restricted to the case $N = 1$, in which case ψ reduces to the product of an arbitrary function $F(\xi, \theta)$ times another arbitrary function $G(\xi, \eta)$, where ξ, η, θ are coordinates introduced previously [12]. In Sec. III we expand F and G in terms of complete

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sets of basis functions, and describe an iterative method for optimizing the coefficients of the expansions. In Sec. IV we simplify the iteration equations by using the reduced matrix elements of Ref. [12]. In Sec. V we show, by means of numerical examples, that the iterative method competes favorably with the other methods which have been used to calculate energy levels and wavefunctions of muonic molecules.

A generalization to states of arbitrary orbital angular momentum L is presented in Appendix A, and applied to P states of homonuclear muonic molecules in the last subsection of Sec. V. The method for $L \neq 0$ makes use of a simplifying approximation, which is the restriction to "sigma" orbitals of the muon, as described in Appendix A.

II. GENERALIZATION OF THE ADIABATIC METHOD

The adiabatic method, the method of this paper, and the Rayleigh–Ritz method are all special cases of variational methods based on the minimization of the expectation value of the nonrelativistic Hamiltonian operator H. We discuss first the general methods, and then the relationships between special cases.

Variational Methods

The energy expectation value of a trial wavefunction ψ is given by the Rayleigh quotient:

$$R[\psi] = \langle \psi H \psi \rangle / \langle \psi \psi \rangle. \tag{1}$$

Two general classes of approximations to Schrödinger's equation are the methods of *variation-of-constants* and *variation-of-functions*. These methods consist of minimizing $R[\psi]$ with respect to trial functions of two different kinds. The former method corresponds to a trial function which depends on a finite set of arbitrary parameters (constants) as well as on the coordinates of the problem. The latter method corresponds to a trial function ψ which contains arbitrary functions. Of course arbitrary functions may be approximated by finite linear combinations of fixed "basis" functions; in this way the latter method is reduced (approximately) to the former, which is usually more tractable in a practical calculation.

A special case of variation of constants is the Rayleigh–Ritz method, in which ψ is linear in the constants. In this case the simultaneous variation of all the constants reduces immediately to a matrix eigenvalue problem.

Special cases of variation-of-functions include the Hartree and Hartree–Fock methods, correlated-shell methods which have been applied to the Coulombic three-body problem [13, 14], and the methods described in the remainder of this section. Except for the adiabatic method, each of these special cases involves a trial function which is *multi-linear* in the arbitrary functions. In other words, ψ is linear in each of several sets of arbitrary functions. When the latter are expanded in terms of basis functions, one obtains several interdependent matrix-eigenvalue problems, which are exemplified by the discussions in [14] and in Sec. III of this paper.

Adiabatic Method

Let r_1 and r_2 be muon-nucleus distances, and r_3 be the internuclear distance, in a muonic molecule. For S states, the adiabatic method consists of approximating the three-body wavefunction by a finite linear combination

$$\psi = \sum_{n=1}^{N} C_n(r_3)\, \phi_n(r_1, r_2, r_3), \tag{2}$$

where ϕ_n is a bound-state solution of a "clamped-nuclei" problem. That is to say, ϕ_n satisfies a Schrödinger equation for the motion of the muon in the electrostatic field of the nuclei, which are at fixed positions in space. In this two-center problem r_3 is not a coordinate, but merely a parameter. The electrostatic potential (and hence, the solution) depends on r_3. The index n symbolizes the quantum numbers of the bound state.

The two-center problem separates in ellipsoidal coordinates, and the solutions which appear in (2) have the functional form

$$\phi_n(r_1, r_2, r_3) = f_n(x, r_3)\, g_n(y, r_3), \tag{3}$$

where $x = (r_1 + r_2)/r_3$ and $y = (r_1 - r_2)/r_3$ are two of the three ellipsoidal coordinates. (The third coordinate is an angle about the internuclear axis, and the expansion for S states does not include terms which depend on this angle.)

The accuracy of an adiabatic approximation is limited by the number of terms N. In practice one picks a few states ϕ_n with low quantum numbers. The trial function ψ is then a linear combination of the form (2), with arbitrary coefficients C_n which are functions of r_3. A set of coupled, ordinary differential equations for the coefficients C_n can be obtained by setting the functional derivative of (1) with respect to C_n equal to zero. The differential equations for the C's will involve dynamic potentials (which take account of the recoil of the nuclei) as well as the Born-Oppenheimer potential.

Sum-of-Products Trial Function

Every function of the form (2) can also be written in the following form:

$$\psi = \sum_{n=1}^{N} F_n(r_1 + r_2, r_3)\, G_n(r_1 - r_2, r_3). \tag{4}$$

For example, we may set $F_n = C_n f_n$ and $G_n = g_n$, according to (3). We now consider (4) as a trial function, where F_n and G_n are perfectly general functions to be varied. Since (4) is a generalization of (2), an optimized trial function of the form (4) will have at least as low an energy expectation value as that of any N-term adiabatic wavefunction. It is also clear that (4) can be made arbitrarily accurate if N becomes arbitrarily large, whereas (2) is limited by the restriction to bound states (as opposed to continuum states) of the two-center problem.

One way to optimize a trial function of the form (4) is to vary the F's and G's alternately. Each such variation is equivalent to a linear eigenvalue problem, since (4) is linear in the F's, and also in the G's. Each variation reduces the energy expectation value; so the process must eventually converge. However, we have no theoretical estimate of the *rate* of convergence. Numerical examples are therefore required in order to test the practicality of the method.

In the following sections we treat only the case $N = 1$. The extension of this treatment to arbitrary N would be straightforward, but would complicate the notation by the addition of extra indices and summations.

III. SINGLE-PRODUCT TRIAL FUNCTION

For the case $N = 1$, a function of the form (4) can also be represented as follows:

$$\psi = F(\xi, \theta)\, G(\xi, \eta), \tag{5}$$

where the coordinates ξ, η, θ are related to the interparticle distances as follows: $r_1 = \xi - \eta + \theta$, $r_2 = \xi + \eta + \theta$, $r_3 = 2\xi$. The reasons for introducing ξ, η, θ were given in a previous paper [12]. One of those reasons is that the region of integration in the (ξ, η) plane is independent of θ. This independence implies the separability of integrals involving products of functions of θ times functions of ξ and η. To take advantage of this separability, we expand F in terms of such products:

$$F(\xi, \theta) = \sum_{jn} X_{jn} a_j(\xi)\, e_n(\theta). \tag{6}$$

Here $\{a_j\}$ and $\{e_n\}$ are complete basis sets of real functions, and the summation is over a finite set of pairs of indices j, n. The quantities X_{jn} are undetermined real coefficients to be optimized.

The function G can be expanded more generally, since it has no θ-dependence. We expand G in terms of a complete set $\{c_l\}$ of real functions of two variables:

$$G(\xi, \eta) = \sum_{l} Y_l c_l(\xi, \eta). \tag{7}$$

Again, the summation is over a finite but arbitrary set of indices l, and the quantities Y_l are undetermined real coefficients.

The expansions (6), (7) approximate the variation of functions by variation of constants.

Expansion of Matrix Elements in Terms of Supermatrices

The numerator and denominator of (1) are matrix elements of H and unity, respectively. We expand them, using (5)–(7):

$$\begin{aligned} \langle\psi\psi\rangle &= \sum_{jn}\sum_{j'n'}\sum_{l}\sum_{l'} U_{jnlj'n'l'}X_{jn}X_{j'n'}Y_lY_{l'}\,, \\ \langle\psi H\psi\rangle &= \sum_{jn}\sum_{j'n'}\sum_{l}\sum_{l'} H_{jnlj'n'l'}X_{jn}X_{j'n'}Y_lY_{l'}\,. \end{aligned} \tag{8}$$

The primed indices of course run over the same values as the corresponding unprimed indices in (8). The six-index quantities which appear on the right-hand side of (8) are the following:

$$\begin{aligned} U_{jnlj'n'l'} &= \langle a_j(\xi)\, c_l(\xi, \eta)\, e_n(\theta) \mid a_{j'}(\xi)\, c_{l'}(\xi, \eta)\, e_{n'}(\theta)\rangle, \\ H_{jnlj'n'l'} &= \langle a_j(\xi)\, c_l(\xi, \eta)\, e_n(\theta)|\, H \mid a_{j'}(\xi)\, c_{l'}(\xi, \eta)\, e_{n'}(\theta)\rangle. \end{aligned} \tag{9}$$

Quantities similar to (9) have been called *supermatrices* by Roothaan and Weiss, in connection with a correlated-shell approximation for atoms [14]. In this paper we use the terminology of [14], even though the quantities (9) are matrix elements in the sense of Ref. [12].

Expansion of Matrices in Terms of Supermatrices

The matrix elements (8) are quadratic forms in the Y's (for fixed X's). The coefficients of the quadratic forms are real, symmetric matrices:

$$\begin{aligned} U_{ll'} &= \sum_{jn}\sum_{j'n'} U_{jnlj'n'l'}X_{jn}X_{j'n'}\,, \\ H_{ll'} &= \sum_{jn}\sum_{j'n'} H_{jnlj'n'l'}X_{jn}X_{j'n'}\,, \end{aligned} \tag{10}$$

of which the first is positive definite (unless $X_{jn} \equiv 0$). The variation of the Y's is equivalent to the eigenvalue problem $H\mathbf{Y} = EU\mathbf{Y}$ involving the matrices (10), where $\mathbf{Y}$ is the vector with components Y_l.

Similarly, the variation of the X's (for fixed Y's) is equivalent to an eigenvalue problem involving the following matrices:

$$\begin{aligned} U_{jn,j'n'} &= \sum_{l} \sum_{l'} U_{jnlj'n'l'} Y_l Y_{l'} , \\ H_{jn,j'n'} &= \sum_{l} \sum_{l'} H_{jnlj'n'l'} Y_l Y_{l'} . \end{aligned} \tag{11}$$

In calling these quantities matrices, we think of the pair j, n as one index, and j', n' as another index. Again H and U are real and symmetric, and U is positive definite if $Y \neq 0$. (These properties insure the existence of real eigenvalues and eigenvectors.)

Each iteration requires the evaluation of the matrices H and U, and the solution of a matrix eigenvalue problem. Simple estimates show that the eigenvalue problem takes a trivial amount of computing time, compared to the time needed to evaluate (10) or (11). For example, if (6) and (7) each have $\mathcal{N}$ terms, then (10) or (11) requires $\mathcal{N}^4$ multiplications and $\mathcal{N}^4$ additions, whereas the number of arithmetic operations needed to find the lowest eigenvalue (and corresponding eigenvector) is proportional to $\mathcal{N}^3$.

In the following section we will ignore the eigenvalue problem (which can be solved by standard techniques) and concentrate on the more difficult problems of evaluating (10) and (11) efficiently.

IV. EXPANSIONS INVOLVING REDUCED MATRIX ELEMENTS

In this section we make use of the separability of integrals over θ from integrals over ξ and η. Let d, d' be functions of ξ and η. Let e, e' be functions of θ. We assume that the products de, $d'e'$ are well-behaved basis functions. This means that they fall off rapidly at large distances, and that they have the properties of differentiability and integrability which are necessary in order to define matrix elements of the Hamiltonian and unity. From Ref. [12] we then have the following decompositions:

$$\begin{aligned} \langle de \mid d'e' \rangle &= 8\pi^2 \sum_{i=1}^{3} R_i(d, d')\, S_i(e, e'), \\ \langle de \mid H \mid d'e' \rangle &= 8\pi^2 \sum_{i=1}^{9} P_i(d, d')\, S_i(e, e'). \end{aligned} \tag{12}$$

The reduced matrix elements R_i, P_i, S_i are bilinear functionals of their arguments. R_i and P_i are two-dimensional integrals involving the functions $d(\xi, \eta)$ and $d'(\xi, \eta)$, and S_i is a one-dimensional integral involving $e(\theta)$ and $e'(\theta)$.

Symmetry Properties of Reduced Matrix Elements

The expansions [12] for R_i, P_i, and S_i have a certain symmetry, which can be used to save a factor of two in computing time.

The quantities R_i have the property that

$$R_i(d, d') = R_i(d', d), \qquad (i = 1, 2, 3).$$

The other reduced matrix elements have slightly more complicated properties. The interchange of d and d' must be accompanied by a permutation π which interchanges the pairs of indices (6, 8) and (7, 9):

$$P_i(d, d') = P_{\pi(i)}(d', d),$$

$$S_i(e, e') = S_{\pi(i)}(e', e),$$

where $\pi(6) = 8$, $\pi(7) = 9$, $\pi(8) = 6$, $\pi(9) = 7$, and $\pi(i) = i$ for $1 \leqslant i \leqslant 5$.

Expansion of Supermatrices

The supermatrices (9) can be expanded in terms of reduced matrix elements, according to (12). The relevant reduced matrix elements are $R_i(a_j c_l, a_{j'} c_{l'})$, $P_i(a_j c_l, a_{j'} c_{l'})$, and $S_i(e_n, e_{n'})$. We abbreviate these by $R_{ijlj'l'}$, $P_{ijlj'l'}$, and $S_{inn'}$, respectively. The expansions are then expressed as follows:

$$\begin{aligned} U_{jnlj'n'l'} &= 8\pi^2 \sum_{i=1}^{3} R_{ijlj'l'} S_{inn'}, \\ H_{jnlj'n'l'} &= 8\pi^2 \sum_{i=1}^{9} P_{ijlj'l'} S_{inn'}. \end{aligned} \tag{13}$$

Expansion of Matrices

The matrices (10), (11) can also be expanded in terms of reduced matrix elements, as is clear from (13). Substitution of (13) into (11) yields the expressions

$$\begin{aligned} U_{jn,j'n'} &= 8\pi^2 \sum_{i=1}^{3} \tilde{R}_{ijj'} S_{inn'}, \\ H_{jn,j'n'} &= 8\pi^2 \sum_{i=1}^{9} \tilde{P}_{ijj'} S_{inn'}, \end{aligned} \tag{14}$$

where $\tilde{R}_{ijj'}$ and $\tilde{P}_{ijj'}$ are the following partial sums:

$$\begin{aligned} \tilde{R}_{ijj'} &= \sum_{l} \sum_{l'} Y_l Y_{l'} R_{ijlj'l'} \, , \\ \tilde{P}_{ijj'} &= \sum_{l} \sum_{l'} Y_l Y_{l'} P_{ijlj'l'} \, . \end{aligned} \tag{15}$$

Similarly, substituting (13) into (10), we obtain

$$\begin{aligned} U_{ll'} &= 8\pi^2 \sum_{i=1}^{3} \sum_{j} \sum_{j'} R_{ijlj'l'} \tilde{S}_{ijj'} \, , \\ H_{ll'} &= 8\pi^2 \sum_{i=1}^{9} \sum_{j} \sum_{j'} P_{ijlj'l'} \tilde{S}_{ijj'} \, , \end{aligned} \tag{16}$$

where

$$\tilde{S}_{ijj'} = \sum_{n} \sum_{n'} X_{jn} X_{j'n'} S_{inn'} \, . \tag{17}$$

The summations over j in (16) include each value j for which there exists an n such that the pair j, n occurs in (6). The first summation in (17) includes each value of n for which the pair j, n is summed over in (6). Summations over primed variables are defined similarly to those over unprimed variables in (16) and (17). Caution must be exercised to insure that the substitution of (17) into (16) will yield sums over pairs j, n (and j', n') which agree with the summations in Eq. (10).

Fewer arithmetic operations are required to compute large matrices via (14)–(17), than directly by (10) and (11). It was pointed out in Sec. III that $2\mathcal{N}^4$ operations are required to evaluate (10) or (11), in the case that F and G each have $\mathcal{N}$ terms. A similar estimate shows that the time required to evaluate (14) and (15), or (16) and (17), is proportional to $\mathcal{N}^3$, which is comparable to the time required for the numerical solution of the matrix eigenvalue problem. The coefficient of proportionality of $\mathcal{N}^3$ depends on the indices summed over in (6). In any case, one can save a factor of two by making use of the symmetry of the partial sums $\tilde{R}$, $\tilde{P}$, $\tilde{S}$, their symmetry-properties being identical with (and an immediate consequence of) the symmetry of the reduced matrix elements.

V. NUMERICAL EXAMPLES

The iterative method described above has been applied to several bound states of muonic molecules. In this section we describe the specific calculations which have been made and present the numerical results. All computations were carried out on a CDC-6600 computer. The usefulness of the iterative method of Secs. II–IV is tested by a comparison of these results with those of previous adiabatic and variational calculations.

Hylleraas Basis

The overall trial function (5) was of the Hylleraas type: polynomial times exponential in (linear combinations of) the interparticle distances. The exponential part of ψ, and the values assumed for the masses of the particles, were the same as in a previous calculation [9]. The functions F and G were also polynomials times exponentials, with the exponential part of ψ equal to the product of the exponential parts of F and G, as required by (5).

The functions $a_j(\xi)$, $e_n(\theta)$, $c_l(\xi, \eta)$ were chosen to be mononomials times exponentials, so that X_{jn} and Y_l were the polynomial coefficients in F and G, respectively. At each stage in the iteration, the number $\mathcal{N}$ of terms in F was taken to be the same as the number of terms in G. The number $\mathcal{N}$ was determined by placing an upper limit K on the sum of the powers of the two variables in F (and in G).

Thus e.g., in (6) the two indices j, n (the powers of ξ and θ) were allowed to take on all nonnegative values such that the sum $j + n$ did not exceed K; hence, $\mathcal{N} = (K + 1)(K + 2)/2$.

We began arbitrarily with $\mathcal{N} = 6$ and $G(\xi, \eta) = 1$, and varied first the X's, then the Y's, and so on. After every ten iterations (five for F and five for G) we would increment K by 1. Table I shows the computed dissociation energy of $p\mu d$ at each iteration, covering several values of $\mathcal{N}$. For a given $\mathcal{N}$ the convergence of

TABLE I

$p\mu d$ ENERGY AT EACH ITERATION (SMALL $\mathcal{N}$)

Number of Iterations For given $\mathcal{N}$	Computed Values of Dissociation Energy (eV)		
	With $\mathcal{N} = 6$	With $\mathcal{N} = 10$	With $\mathcal{N} = 15$
1	−15.941	210.968	216.523
2	159.936	213.455	220.182
3	173.359	213.652	220.274
4	175.884	213.798	220.311
5	178.335	213.925	220.331
6	180.759	214.042	220.350
7	184.302	214.147	220.366
8	187.354	214.243	220.382
9	190.524	214.328	220.397
10	192.171	214.406	220.411

the energy with the number of iterations is evidently slow. It does not appear that an increase beyond ten in the number of iterations (for a given $\mathcal{N}$) would be useful.

Table II shows the binding and dissociation energies of $p\mu d$ for a larger number of values of $\mathcal{N}$ than in Table I. For each $\mathcal{N}$, only the result of the tenth iteration is shown in Table II. The binding energy is the absolute value of the Rayleigh quotient (1), whereas the dissociation energy is that needed to remove the less massive of the two nuclei. The convergence with $\mathcal{N}$ in Table II is rapid. The

TABLE II

$p\mu d$ Energy at Last Iteration for Each Value of $\mathcal{N}$

Number of terms in F (or in G) $\mathcal{N}$	Total Binding Energy (a.u.)	Dissociation energy (eV)
6	104.933 977	192.171
10	105.751 127	214.406
15	105.971 823	220.411
21	106.001 105	221.208
28	106.008 365	221.405
36	106.009 935	221.448
45	106.010 127	221.453
55	106.010 192	221.455
66	106.010 225	221.456
78	106.010 236	221.456

TABLE III

$p\mu p$ Energy at Last Iteration for Each $\mathcal{N}$

Number of terms in F (or in G) $\mathcal{N}$	Total Binding Energy (a.u.)	Dissociation Energy (eV)
6	101.238 853	226.330
10	101.956 244	245.851
15	102.196 971	252.401
21	102.215 959	252.917
28	102.220 542	253.042
36	102.221 453	253.067
45	102.221 581	253.070
55	102.221 620	253.071

$\mathcal{N} = 28$ entry is more accurate than the best previously published value [9] which corresponds to an 84-term wavefunction.

Similar data for $p\mu p$ are shown in Table III. The best dissociation energy in Table III is within 0.1 eV of the value 253.13 computed by Delves and Kalotas [8] with a 100-term wavefunction. These values also agree with [9] to within 0.1 eV.

An accuracy of 0.1 eV or better is evidently obtainable with the trial function (5), for which $p\mu p$ and $p\mu d$ are the most severe test cases among muonic molecules. Even higher accuracy could be obtained with a trial function of the form (4) with $N > 1$, but this has not been attempted.

Pseudo-Wavefunction

Besides computing the energy level, we have also computed the pseudo-wavefunction $\Phi(r_3)$ of the $p\mu d$ ground state. This function is defined [10] as follows:

$$\Phi(r_3) = \left[\int \psi^2 \, d^3r_\mu\right]^{1/2}, \tag{18}$$

where ψ is normalized so that the denominator of (1) is unity, and where d^3r_μ is the two-center volume element for the muon. The integration is over the coordinates r_1, r_2, which describe the position of the muon relative to the nuclei. The function $\Phi(r_3)$ is the square root of a probability density, and is expected (on theoretical grounds) to resemble an adiabatic wavefunction for the relative motion of the nuclei. The normalization of Φ is such that the integral of Φ^2 is unity with respect to the volume element $4\pi r_3^2 \, dr_3$. Kolos [11] apparently normalizes the integral with respect to $r_3^2 \, dr_3$, so that his pseudo-wavefunction differs from (18) by a factor of $\sqrt{(4\pi)}$.

The function $\Phi(r_3)$ has been plotted previously by Carter [10] and by Kolos [11], with dissimilar results for small values of r_3. The quantity $\Phi(0)$ is important, because it controls the fusion rates [15], and because of the *hfs* interaction term discussed by Zwanziger [16]. Therefore, an intensive study of the properties of ψ (or of Φ) at small values of r_3 is justified.

Figure 1 shows the curve $\Phi(r_3)$ obtained from the last (tenth) iteration, for each of several values of $\mathcal{N}$. These curves resemble S-wave Coulomb wavefunctions, in that they increase monotonically for small r_3. To show the convergence with $\mathcal{N}$ more clearly we have divided the function $\Phi(r_3)$ by the S-wave Coulomb wavefunction $\Phi_C(\rho, \eta)$, and plotted the quotient in Fig. 2. Here $\rho = kr_3$ and $\eta = e^2/\hbar v$ are the usual dimensionless variables. (This η should not be confused with that of Sec. III.) The power series [17] for Φ_C is normalized to unity at $\rho = 0$; so the curves in Figs. 1 and 2 have the same values at $r_3 = 0$ for given $\mathcal{N}$.

The quantities k, v are determined by the relations $\hbar k = \mu v$ and $E = \frac{1}{2}\mu v^2$, where μ is the reduced mass of the two nuclei, and E is the energy of their relative motion when they are close together. According to the adiabatic approximation E

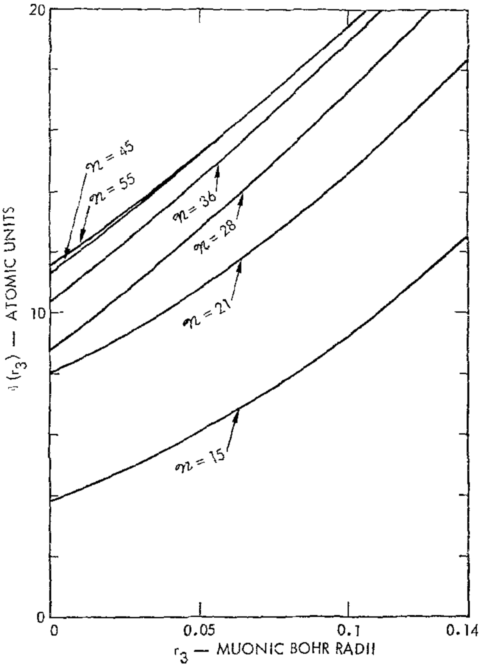

FIG. 1. Pseudo-wavefunction Φ for tenth iterations with $15 \leqslant \mathcal{N} \leqslant 55$.

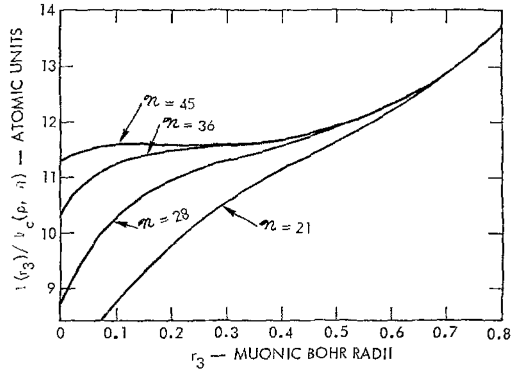

FIG. 2. Ratio Φ/Φ_C for tenth iterations with $21 \leqslant \mathcal{N} \leqslant 45$.

is the difference between the energies of the $p\mu d$ molecule and the $\mathrm{He}^3\mu$ atom. This difference is approximately 8 keV. The corresponding value $\eta = 1.446$ was used in evaluating the Coulomb wavefunction Φ_C.

The limiting value of $\Phi(0)$ for large $\mathcal{N}$ appears to be about 11.5 a.u., according to Figs. 1 and 2. This is in fair agreement with the value 12 a.u. of Ref. [10], but is inconsistent with the results obtained by Kolos [11], whose curves do not resemble Coulomb wave functions.

Figures 3–6 show Φ/Φ_C for four large values of $\mathcal{N}$. In each figure the top curve corresponds to the 9th, and the bottom curve to the 10th iteration (for given $\mathcal{N}$).

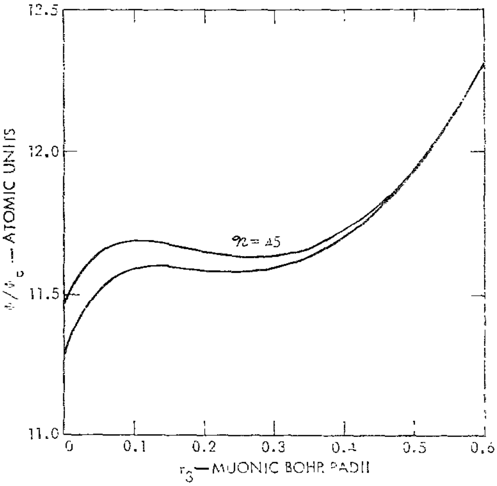

Fig. 3. Ratio Φ/Φ_C for ninth and tenth iterations with $\mathcal{N} = 45$.

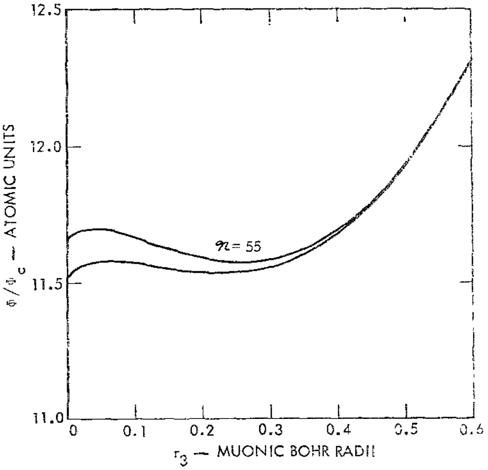

Fig. 4. Ratio Φ/Φ_C for ninth and tenth iterations with $\mathcal{N} = 55$.

The slopes of these curves at $r_3 = 0$ appear to be approaching zero, as they should, as $\mathcal{N}$ increases. The limit of $\Phi(0)$ as $\mathcal{N} \rightarrow \infty$ seems to be 11.4 ± 0.1, according to Figs. 3–6.

Similar curves (not shown) for $p\mu p$ yield $\Phi(0) = 18.5$, compared to the value 20 a.u. of Ref. [10].

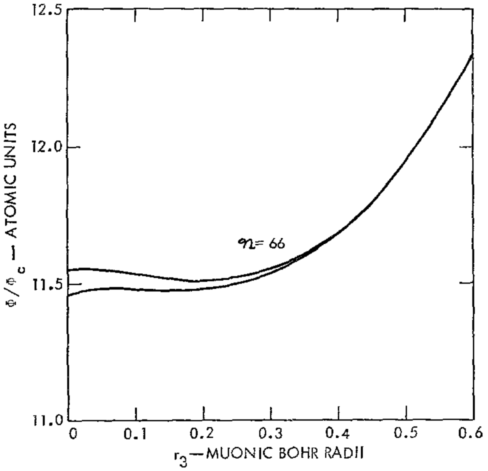

FIG. 5. Ratio Φ/Φ_C for ninth and tenth iterations with $\mathcal{N} = 66$.

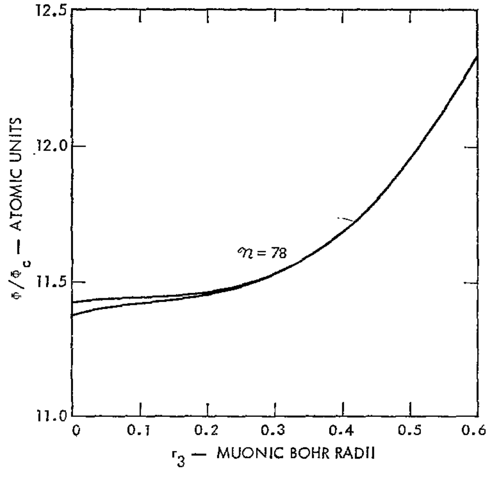

FIG. 6. Ratio Φ/Φ_C for ninth and tenth iterations with $\mathcal{N} = 78$.

P States

A state of nonzero orbital angular momentum L can be calculated with perfectly general trial functions of various kinds [18, 19]. But such calculations involve different and more complicated matrix elements than those for S states. Here we replace (5) by a trial function of the restricted form $\xi^{L} F G Y_{LM}$, where Y_{LM} is a spherical harmonic of the angles describing the direction of one nucleus from the other. This is a special case of the trial function discussed in Appendix A, where we show that only a trivial modification of the S-state matrix elements is required in order to calculate states of arbitrary L. In fact, Eqs. (6)–(8), (10), (11), and (13)–(17) are retained, and the only modification is the inclusion of $2L$ more powers of ξ in the basic integrals [12] on which the reduced matrix elements R_i, P_i depend.

Our numerical results for three P states ($L = 1$) are shown in Table IV, along with comparable results of previous adiabatic and variational calculations. The last row of Table IV was computed with $\mathcal{N} = 36$ terms in F, and 36 terms in G. But Table IV includes only homonuclear molecules, for which the 16 odd powers of η in (7) have vanishing coefficients. The total number of non-zero coefficients is therefore only 56.

TABLE IV

ODD-PARITY *P*-STATES

Reference	Dissociation Energy (eV) $p\mu p$	$d\mu d$	$t\mu t$
Wessel and Phillipson [4]	102.2		
Belyaev *et al.* [3]	109[a]	226	288
Halpern [5]	107.23	226.55	288.72
Scherr and Machacek [7]	106.8	226.3	288.8
Kabir [6]	104.9		
Cohen, Judd and Riddell [2]	93	223	
Patterson and Becker [1]	101.5	224.6	287.7
This work	105.74	226.14	288.80

[a] This value is not a variational bound, because of the approximation involving a Morse Potential in Ref. [3].

The accuracy of our computed dissociation energies is limited, both by the form of the trial function, and by the number of parameters in F and G. The two kinds of error have opposite dependence on the nuclear reduced masses, which are approximately in the proportion 1, 2, 3 for $p\mu p$, $d\mu d$, $t\mu t$, respectively. As the nuclei become less massive, the error due to the restricted functional form *increases*, whereas the effect of the limited number of parameters *decreases*. (These comments apply also to Tables I–III.) A comparison with other variational calculations [5, 7] in Table IV suggests that our results become less accurate as the nuclei become lighter, so that the major source of error is probably the restricted form of the trial function. The error is no more than 1.5 eV in any case.

APPENDIX A—SIGMA-STATE APPROXIMATION

In this appendix we discuss a simple modification of S-state calculations, to treat states of arbitrary orbital angular momentum in the sigma-state approximation. This approximation consists of using a trial function of a restricted form (see below), for which the matrix elements are equivalent to slightly-modified S-state matrix elements. The derivation given here is more general than its application in Sec. V, in that no assumption is made here concerning the functional form of the S-states.

This appendix is mostly self-contained, and the notation for coordinates and other quantities does not, in general, agree with the notation of Secs. I–V.

Coordinates

We number the three particles 1, 2, 3, and assume that particle 3 is the muon. Particles 1 and 2 are the nuclei. The vector $\mathbf{R} = (X, Y, Z)$ is the displacement of particle 2 from particle 1, and $\mathbf{r} = (x, y, z)$ is the displacement of particle 3 from the center of mass (CM) of 1 and 2. The internuclear distance is $R = |\mathbf{R}|$, and the distance from the CM of the nuclei to the muon is $r = |\mathbf{r}|$. The inner product

$$s = \mathbf{R} \cdot \mathbf{r} = Xx + Yy + Zz = Rr \cos \theta \tag{A-1}$$

depends only on the shape of the triangle formed by the three particles, and not on its orientation in space. An S-state wavefunction can always be written as a function of the internal coordinates R, r, and s, since these three quantities determine the interparticle distances.

It is convenient to introduce here the unit vectors $\hat{R} = \mathbf{R}/R$ and $\hat{r} = \mathbf{r}/r$, which will appear in operator equations.

We also introduce spherical polar coordinates R, Θ, Φ for $\mathbf{R}$. The polar and Cartesian coordinates are related in the usual way: $X = R \sin \Theta \cos \Phi$, $Y = R \sin \Theta \sin \Phi$, and $Z = R \cos \Theta$. For $\mathbf{r}$ we introduce polar coordinates r, θ, ϕ, which are similarly related to the components x', y', z' of $\mathbf{r}$ in a rotated coordinate system.

To be consistent with the definition (A-1) of θ, the rotation connecting the primed and unprimed components of $\mathbf{r}$ must be such that $\hat{R}$ points along the positive z' axis. We represent one such rotation in the usual manner, as the product of two rotations about coordinate axes. The first is a rotation by the angle Φ about the z axis: $x'' = x \cos \Phi + y \sin \Phi$, $y'' = y \cos \Phi - x \sin \Phi$, $z'' = z$. The second is a rotation about the y'' axis (one of the axes defined by the first rotation) by the angle Θ: $x' = x'' \cos \Theta - z'' \sin \Theta$, $y' = y''$, $z' = x'' \sin \Theta + z'' \cos \Theta$. That the z axis lies along $\hat{R}$ can be checked by setting $\mathbf{r} = \hat{R}$, in which case the coordinate transformations yield $x' = y' = 0$ and $z' = 1$.

Operators

We proceed now to derive expressions for some differential operators, which will be applied later to states of nonzero angular momentum.

In atomic units, the momentum operators conjugate to $\mathbf{R}$, $\mathbf{r}$ are $-i\nabla_R$, $-i\nabla_r$, respectively. Here ∇_R is the gradient with components $\partial/\partial X$, $\partial/\partial Y$, $\partial/\partial Z$: and ∇_r has components $\partial/\partial x$, $\partial/\partial y$, $\partial/\partial z$. The relative orbital angular momentum of the nuclei is

$$\mathbf{L} = -i\mathbf{R} \times \nabla_R . \tag{A-2}$$

The orbital angular momentum of the muon, relative to the CM of the nuclei, is

$$\mathbf{L}' = -i\mathbf{r} \times \nabla_r . \tag{A-3}$$

The total internal orbital angular momentum of the three-body system is

$$\mathbf{L}_{\text{tot}} = \mathbf{L} + \mathbf{L}'. \tag{A-4}$$

Of particular importance for the classification of molecular states is the projection Λ of $\mathbf{L}_{\text{tot}}$ onto the internuclear axis. A short calculation yields several equivalent expressions for Λ:

$$\Lambda = \hat{R} \cdot \mathbf{L}_{\text{tot}} = \hat{R} \cdot \mathbf{L}' = L'_{z'} = -i\partial/\partial\phi, \tag{A-5}$$

where the partial with respect to ϕ is with the other Euler angles, as well as the internal coordinates, held constant. (In general, partial derivatives in this appendix refer either to the Cartesian coordinates (X, Y, Z, x, y, z), or to the set of internal coordinates plus Euler angles (R, r, s, Θ, Φ, ϕ).)

The Hamiltonian (see below) does not commute with Λ. A perfectly general trial function of angular momentum l must contain terms with eigenvalues of Λ which range from $-l$ to l. The terms with $\Lambda = 0$, ± 1, ± 2, etc. are usually designated sigma, pi, delta, etc., respectively. A reasonable approximation, which we adopt here, is to use a trial function containing only the sigma term.

The spinless, nonrelativistic Hamiltonian operator takes the form

$$H = \frac{-\nabla_R{}^2}{2M} + \frac{-\nabla_r{}^2}{2M'} + V(R, r, s), \tag{A-6}$$

where V is the electrostatic potential energy. The reduced masses M, M' are related to the masses of the three particles by well-known formulas: $M = m_1m_2/(m_1 + m_2)$ and $M' = (m_1 + m_2)\, m_3/(m_1 + m_2 + m_3)$.

To calculate matrix elements of the first term in (A-6), it will help to use the formula for the Laplacian operator $\nabla_R{}^2$ in spherical coordinates. That formula, with the aid of (A-2), can be written as follows:

$$\nabla_R{}^2 = R^{-1}(\partial/\partial R)^2\, R - \mathbf{L}^2/R^2. \tag{A-7}$$

This completes the necessary list of expressions for differential operators. The next step is to apply some of these operators to two special classes of functions, S states and spherical harmonics, in terms of which the trial function will be defined.

Operators Applied to S *States*

The gradients act on the internal coordinates as follows:

$$\begin{aligned} \nabla_R R &= \hat{R}, & \nabla_R s &= \mathbf{r}, \\ \nabla_r r &= \hat{r}, & \nabla_r s &= \mathbf{R}. \end{aligned} \tag{A-8}$$

Using these relations (A-8) and the chain rule of partial differentiation, we obtain

$$\begin{aligned} \nabla_R f(R, r, s) &= \hat{R}\frac{\partial f}{\partial R} + \mathbf{r}\frac{\partial f}{\partial s}, \\ \nabla_r f(R, r, s) &= \hat{r}\frac{\partial f}{\partial r} + \mathbf{R}\frac{\partial f}{\partial s}, \end{aligned} \tag{A-9}$$

where f is an arbitrary function of its arguments. Next we substitute (A-9) into the definitions (A-2, A-3) of $\mathbf{L}$ and $\mathbf{L}'$, and obtain

$$\mathbf{L}f = -\mathbf{L}'f = i\mathbf{r} \times \mathbf{R}\frac{\partial f}{\partial s}. \tag{A-10}$$

It follows from (A-10) and (A-4) that $\mathbf{L}_{\text{tot}}$ annihilates f, which is just another way of saying that f is an S-state. This result becomes

$$[\mathbf{L}_{\text{tot}}, f] = 0, \tag{A-11}$$

when we think of (multiplication by) f as an operator.

Operators Applied to Spherical Harmonics

Consider a function $Y(\hat{R})$ which is proportional to $Y_{lm}(\Theta, \Phi)$. From the elementary properties of spherical harmonics, and from the definition (A-2) of $\mathbf{L}$, we have

$$\begin{aligned} \mathbf{L}^2 Y &= l(l + 1)Y, \\ L_z Y &= mY. \end{aligned} \tag{A-12}$$

Since Y does not depend on $\mathbf{r}$, we have

$$\mathbf{L}'Y = 0. \tag{A-13}$$

Furthermore, since $[\mathbf{L}, \mathbf{L}'] = 0$, we have $\mathbf{L}_{\text{tot}}^2 = \mathbf{L}^2 + 2\mathbf{L} \cdot \mathbf{L}' + \mathbf{L}'^2$, and

$$\begin{aligned} \mathbf{L}_{\text{tot}}^2 Y &= l(l+1)Y, \\ L_{\text{tot}_z} Y &= mY. \end{aligned} \tag{A-14}$$

Sigma-state Trial Function

We consider now a trial function of the form

$$\psi = Y(\hat{R})\, f(R, r, s), \tag{A-15}$$

where f is a real function which falls off exponentially at large distances (to allow integration by parts), and where

$$Y(\hat{R}) = (4\pi)^{1/2}\, Y_{lm}(\Theta, \Phi). \tag{A-16}$$

Since (A-15) does not involve ϕ, Eq. (A-5) implies that $\Lambda\psi = 0$, and ψ is indeed a sigma state.

From (A-11), (A-14), and (A-15), we obtain

$$\begin{aligned} \mathbf{L}_{\text{tot}}^2 \psi &= f \mathbf{L}_{\text{tot}}^2 Y = l(l+1)\psi, \\ L_{\text{tot}_z} \psi &= f L_{\text{tot}_z} Y = m\psi. \end{aligned}$$

Therefore, ψ is a valid trial function (though not a perfectly general one) for a state with angular-momentum quantum numbers l, m. The parity of ψ is that of Y, namely $(-1)^l$. Only states with this parity can be approximated by trial functions of the form (A-15).

Matrix Element of Unity

The matrix elements which appear in (1) are six-dimensional integrals with respect to the volume element $d\tau = d\mathbf{R}\, d\mathbf{r}$, where $d\mathbf{R} = dX\, dY\, dZ$ and $d\mathbf{r} = dx\, dy\, dz$. We have $d\mathbf{R} = R^2\, dR\, d\Omega$ and $d\mathbf{r} = r^2\, dr\, d\omega$ in polar coordinates, where $d\Omega = \sin\Theta\, d\Theta\, d\Phi$ and $d\omega = \sin\theta\, d\theta\, d\phi$. In general, our approach is to equate matrix elements involving ψ with S-state matrix elements involving only f, by integrating first over $d\Omega$ to get rid of Y. The problem of calculating matrix elements for $l \neq 0$ will thus be reduced to the problem of calculating S-state matrix elements

The matrix element of unity is

$$\langle\psi\psi\rangle = \int \psi^* \psi\, d\tau. \tag{A-17}$$

The normalization of Y has been chosen such that (A-16) reduces to $Y = 1$ when $l = m = 0$. In this special case we have $\psi = f$, and hence,

$$\langle\psi\psi\rangle = \langle ff\rangle. \tag{A-18}$$

By using polar coordinates, one can carry out the integration over $d\Omega$ in (A-17), and show that the value of $\langle\psi\psi\rangle$ is independent of l and m. Therefore, (A-18) holds not just for $l = m = 0$, but for all values of l and m.

Matrix Element of the Hamiltonian

According to (A-6), the matrix element of H can be written as

$$\langle\psi H\psi\rangle = T/2M + T'/2M' + \langle\psi V\psi\rangle, \tag{A-19}$$

where T, T' are the matrix elements of $-\nabla_R{}^2$, $-\nabla_r{}^2$, respectively.

By the same argument used to obtain (A-18), we may replace ψ by f in the matrix element of any quantity which does not involve Θ or Φ. This argument obviously applies to the matrix element $\langle\psi V\psi\rangle$, and also applies indirectly to T'. Integration by parts yields

$$T' = \int |\, Y\,|^2 \, (\nabla_r f)^2 \, d\tau,$$

and (A-9) shows that the quantity $(\nabla_r f)^2$ in the integral above depends only on R, r, and s. We have shown that

$$T' = -\langle\psi\nabla_r{}^2\psi\rangle = -\langle f\nabla_r{}^2 f\rangle.$$

We use (A-7) to expand the remaining term of (A-19) as follows:

$$T = -\langle\psi\nabla_R{}^2\psi\rangle = T_1 + T_2 + T_3\,,$$

$$T_1 = -\int d\tau\psi^* Y\nabla_R{}^2 f,$$

$$T_2 = \int d\tau\psi^* f R^{-2}\mathbf{L}^2 Y,$$

$$T_3 = 2\int d\tau\psi^* R^{-2}(\mathbf{L}f)\cdot(\mathbf{L}Y).$$

One can use (A-9) to show that $\nabla_R{}^2 f$ is a function of R, r, and s; hence, $T_1 = -\langle f\nabla_R{}^2 f\rangle$. From (A-12) we obtain $T_2 = l(l+1)\langle fR^{-2}f\rangle$. We use (A-10) to write

$$T_3 = \int d\mathbf{R}\, Y^*(\mathbf{L}Y)\cdot\left[-2iR^{-2}\mathbf{R}\times\int \mathbf{r}f\frac{\partial f}{\partial s}\,d\mathbf{r}\right].$$

Because of its symmetry about $\hat{R}$, the inner integral must be a multiple of $\hat{R}$; hence, $T_3 = 0$.

Combining the results for the various terms in H, we obtain

$$\langle\psi H\psi\rangle = \langle f \,|\, H + \frac{l(l+1)}{2MR^2} \,|\, f\rangle. \tag{A-20}$$

The centrifugal potential on the right-hand-side of (A-20) is the same potential that would appear in the radial Schrödinger equation (for the relative motion of the two nuclei) if the muon were not present. By analogy with the usual treatment of radial equations, we may set $f = R^l g$, and rewrite the matrix elements (A-18), (A-20) in terms of $g(R, r, s)$. After some algebra, we obtain

$$\begin{aligned} \langle\psi\psi\rangle &= \int R^{2l} g^2 \, d\tau, \\ \langle\psi H\psi\rangle &= \int R^{2l} \left[\sum_{i=1}^{3} \frac{(\nabla_i g)^2}{2m_i} + V g^2 \right] d\tau, \end{aligned} \tag{A-21}$$

where ∇_i is the gradient with respect to the position of particle i. Equations (A-21) are identical to the matrix elements for the S-state $g(R, r, s)$, except for the extra factor R^{2l}. The results for P states in Sec. V were obtained by means of (A-21), which represents a trivial change in the basic integrals I, J of Ref. [12].

REFERENCES

1. M. R. Patterson and R. L. Becker, Oak Ridge Nat'l Lab. Report No. ORNL-TM-1850 (1967).
2. S. Cohen, D. L. Judd, and R. J. Riddell, Jr., *Phys. Rev.* **119**, 384 (1960).
3. V. B. Belyaev, S. S. Gershtein, B. N. Zakhar'ev, and S. P. Lomnev, Zh. Eksperim. i Teor. Fiz. **37**, 1652 (1959) [English transl.: *Soviet Phys.-JETP* **10**, 1171 (1960)].
4. W. R. Wessel and P. Phillipson, *Phys. Rev. Letters* **13**, 23 (1964).
5. A. Halpern, *Phys. Rev. Letters* **13**, 660 (1964).
6. P. K. Kabir, *Z. Physik* **191**, 447 (1966).
7. C. W. Scherr and M. Machacek, *Phys. Rev.* **138**, A371 (1965)
8. L. M. Delves and T. Kalotas, *Aust. J. Phys.* **21**, 1 (1968).
9. B. P. Carter, *Phys. Rev.* **165**, 139 (1968).
10. B. P. Carter, *Phys. Rev.* **141**, 863 (1966).
11. W. Kolos, *Phys. Rev.* **165**, 165 (1968).

[redacted]

15. E. J. Bleser, E. W. Anderson, L. M. Lederman, S. L. Meyer, J. L. Rosen, J. E. Rothberg, and I.-T. Wang, *Phys. Rev.* **132**, 2679 (1963). References to other fusion experiments are given here and in Ref. 10.
16. D. Zwanziger, *Phys. Rev.* **151**, 1337 (1966).

17. M. ABRAMOWITZ, "Coulomb Wave Functions" in *Handbook of Mathematical Functions* (ed. by M. Abramowitz and I. A. Stegun), Nat. Bur. of Standards Appl. Math. Ser. 55, pp 537 ff.
18. G. BREIT, *Phys. Rev.* **35**, 569 (1930). For a similar treatment with symmetric Euler angles, see A. K. Bhatia and A. Temkin, *Revs. Mod. Phys.* **36**, 1050 (1964); *Phys. Rev.* **137**, A1335 (1965).
19. C. SCHWARTZ, *Phys. Rev.* **123**, 1700 (1961), Appendix I.