Variational Calculation of the Ground State of the Lithium Atom

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The ground state of the lithium atom is calculated using wave functions containing interelectronic separation terms. A 13-term properly symmetrized variational function is employed yielding a ground-state energy of -14.9559 in units of $e^2/2a_0$ as compared to the previous best value of -14.9542 using the superposition of 45 configurations and the experimental value of -14.9561. A brief discussion of applications and extensions of the present work is given along with solutions of the integrals which occur.

INTRODUCTION

THE principal defect in most approximations to the wave functions for many-electron atoms is the failure of such methods to account sufficiently for the relative motions of the electrons with each other. Thus, such solutions introduce the so-called correlation effect errors. Various methods have been introduced to compensate for these errors. The simplest approach analytically is to add configurations of hydrogen-like orbitals of the same symmetry as the atom under consideration. The amplitudes of the configurations are obtained from the Rayleigh-Ritz variational principle and by this principle the approximate wave function converges to the exact wave function with the addition of configurations. It has been shown by many authors,[1-3] however, that for configurations of hydrogen-like orbitals the convergence is quite slow. It is reasonable, then, to investigate other configurations which although possibly more complex may converge rapidly enough to make the resulting wave functions more compact and, hence, more useful for general applications.

Recently there has been considerable interest in the use of wave functions containing interelectronic separations terms for two electron atoms and ions.[4,5] The convergence is rapid and Pekeris[6] has been able to calculate measurable quantities within the limits of the presently known experimental deviations. It is only recently, however, that computer technology has reached the stage where calculations involving interelectronic separation configurations for three electron atoms can be performed so as to improve the monumental work of James and Coolidge.[7]

The present paper extends the work of James and Coolidge on the ground state of the lithium atom and considers possible extensions of the method to more complex atoms. Calculations of quantities other than the ground-state energy are briefly discussed along with the possible application of the wave function to solid-state phenomena. A discussion of the integrals involved

and the method of computation are discussed in an Appendix.

CHOICE OF FUNCTION

Neglecting nuclear motion, the nonrelativistic Hamiltonian for many-electron atoms with the energy in units of $e^2/2a_0$ is given by

$$H = \sum_i -\nabla_i^2 - (2Z/r_i) + (\sum_{j>i} 2/r_{ij}). \quad (1)$$

By choosing a real wave function normalized to unity we are concerned with the calculation of $\int \phi H \phi d\tau = T + V$. The quantities T and V represent, respectively, the kinetic and potential energy contributions to the total energy.

Apart from electron spin, the approximate wave function employed here may be represented generally as

$$\phi = \sum C(i,j,k,l,m,n,\alpha,\beta,\gamma) r_1{}^i r_2{}^j r_3{}^k r_{23}{}^l r_{13}{}^m r_{12}{}^n$$
$$\times \exp[-(\alpha r_1 + \beta r_2 + \gamma r_3)]. \quad (2)$$

Due to the complexity of the invidual terms, it is judicious to make limitations on the summing indices Thus, following James and Coolidge,[7] choose l, m, n so that at least two of them are always zero. Then, at most, only one interelectronic separation coordinate enters any given term. Further, consider the three-electron atom as composed of a two-electron core interacting with a third electron. Choose Hylleraas'[8] two-electron core. Combine this with Wilson's[9] representation of the third electron and then add interelectronic separation terms between the core orbitals and the outer orbital. In this way one arrives at the James and Coolidge[7] wave function approximation. The powers of the radial coordinates and of the coordinate coefficients in the exponential are tabulated in Table I for this wave function.

The first improvement considered is that of the proper spin angular momentum symmetry and has been discussed by James and Coolidge in a paper[10] subsequent to their initial calculation. In principle, the terms within the sum of Eq. (2) may in turn be written as sums of products of terms each involving only the

[1] Charles Schwartz, Phys. Rev. **126**, 1015 (1962).
[2] A. W. Weiss, Phys. Rev. **122**, 1826 (1961).
[3] R. K. Nesbet and R. E. Watson, Phys. Rev. **110**, 1073 (1958).
[4] C. L. Pekeris, Phys. Rev. **112**, 1649 (1958); **115**, 1216 (1959).
[5] Charles Schwartz, Phys. Rev. **128**, 1146 (1962).
[6] C. L. Pekeris, Phys. Rev. **126**, 1470 (1962).
[7] H. M. James and A. S. Coolidge, Phys. Rev. **49**, 688 (1936).

[8] E. A. Hylleraas, Z. Physik **54**, 347 (1929).
[9] E. B. Wilson, J. Chem. Phys. **1**, 210 (1933).
[10] H. M. James and A. S. Coolidge, Phys. Rev. **55**, 873 (1939).

TABLE I. James and Coolidge wave-function parameters.

Terms[a]	i	j	Powers[b] k	l	m	n	Coefficients[b] $(\alpha=\beta=3.0)$ γ
1	0	0	1	0	0	0	0.65
2	1	0	1	0	0	0	0.65
2	0	1	1	0	0	0	0.65
3	2	0	1	0	0	0	0.65
3	0	2	1	0	0	0	0.65
4	1	1	1	0	0	0	0.65
5	0	0	1	0	0	1	0.65
6	0	0	1	0	0	2	0.65
7	0	0	0	0	0	0	1.5
8	1	0	0	0	0	0	1.5
8	0	1	0	0	0	0	1.5
9	0	0	0	1	0	0	0.65
10	0	0	0	0	1	0	0.65

[a] Identical numbering of terms means they have identical amplitudes as a result of symmetry.
[b] Powers and coefficients correspond to the representation

$$r_1{}^i r_2{}^j r_3{}^k r_{23}{}^l r_{13}{}^m r_{12}{}^n \exp[-(\alpha r_1+\beta r_2+\gamma r_3)].$$

coordinates of a single electron. This may be done by expanding first the interelectronic separation terms by the law of cosines then the cosine of the angle between two radii by the rules of spherical trigonometry. Consider a single term of an inner sum. Denote it by $K(1)K'(2)L(3)$. The total wave function is constructed by taking a product function of this spatial representation with a spin function of the proper symmetry.

Two linearly independent spin functions with eigenvalues of $3/4\hbar^2$ and $1/2\hbar$ for S^2 and S_z, respectively, are[11]

$$2^{-1/2}[\alpha(1)\beta(2)\alpha(3)-\beta(1)\alpha(2)\alpha(3)],$$

$$6^{-1/2}[2\alpha(1)\alpha(2)\beta(3)-\alpha(1)\beta(2)\alpha(3)-\beta(1)\alpha(2)\alpha(3)]. \quad (3)$$

By combining the spin and spatial functions and antisymmetrizing the result, one obtains

$$\begin{aligned}
\phi_i=&[(A_1-A_2)L(1)K'(2)L(3)-(A_1-A_2)L(1)K'(2)K(3)-(A_1+A_2)L(1)K(2)K'(3)+(A_1+A_2)K'(1)K(2)L(3)\\
&+2A_2K'(1)L(2)K(3)-2A_2K(1)L(2)K'(3)]\alpha(1)\beta(2)\alpha(3)+[(A_1-A_2)K'(1)L(2)K(3)\\
&-(A_1-A_2)K'(1)K(2)L(3)-(A_1+A_2)K(1)K'(2)L(3)+(A_1+A_2)K(1)L(2)K'(3)+2A_2L(1)K(2)K'(3)\\
&-2A_2L(1)K'(2)K(3)]\beta(1)\alpha(2)\alpha(3)+[(A_1-A_2)L(1)K(2)K'(3)-(A_1-A_2)K(1)L(2)K'(3)\\
&-(A_1+A_2)K'(1)L(2)K(3)+(A_1+A_2)L(1)K'(2)K(3)+2A_2K(1)K'(2)L(3)-2A_2K'(1)K(2)L(3)]\\
&\times\alpha(1)\alpha(2)\beta(3). \quad (4)
\end{aligned}$$

A_1 and A_2 are variational parameters multiplying, respectively, the two linearly independent spin functions. It will be observed that any term which is enclosed by a square bracket may be obtained from any other term within a square bracket merely by a permutation of electrons and since the spin functions are orthonormal and not operated on by the Hamiltonian, then, for purposes of computation, one need only consider any one of the three spatial functions within the square brackets.

Consider the first square bracket. Let the analytic form of K and K' be identical. Thus, we have

$$\phi_i=2A_1[K(1)K(2)L(3)-L(1)K(2)K(3)]$$

$\times\alpha(1)\beta(2)\alpha(3)+$terms which differ only in

permutation of electrons. (5)

Now K and K' have identical analytic forms if two terms within the inner sums of Eq. (2) become identical when the numbering 1 and 2 is interchanged in either of the terms. This may be accomplished without resorting to expansions of the interelectronic separation terms by the simple expedient of requiring that those terms of Eq. (2) which differ only in the permutation of the 1 and 2 indices have the same amplitude factor. Thus, a single determinant wave function requires that the core orbitals have identical analytic representations to satisfy symmetry restrictions. This is not the case for the James and Coolidge function for it will be observed

that all the terms have the proper symmetry. (The four from Table I that from symmetry criteria terms 9 and 10 should then be a single term. From Table II it is seen terms listed as 13 could have been grouped in two sets combining the first and last and the middle two terms and still satisfy symmetry criteria. They were combined in order to be able to write the individual terms as functions of the sum or product of r_1 and r_2.)

Additional improvement may be obtained by adding more terms representing the outer electron with the addition of interelectronic terms between the core orbitals and the improved outer orbital representations. Furthermore, one may introduce a scaling parameter κ such that $\rho=\kappa r$ and the equation to be solved becomes $\int\phi H\phi d\tau=\kappa^2 T+\kappa V$. It has been shown[12] that the scaling parameter may, in principle, be easily determined. However, in the present calculation the use of a scaling parameter is circumvented by choosing the exponential coefficients of Eq. (2) from Wilson's[9] calculation and from Slater's rules.[13] Then set $\kappa=1$.

The final form of the wave function as determined from the previous considerations but reduced in size by calculation restrictions is given in Table II.

[11] L. I. Schiff, Quantum Mechanics (McGraw-Hill Book Company, Inc., New York, 1955), p. 235.
[12] Per-Olov Löwdin, J. Mol. Spectr. 3, 46 (1959).
[13] J. C. Slater, Phys. Rev. 36, 57 (1930).

TABLE II. Wave function parameters of present calculations.

Terms[a]	i	j	Powers[b] k	l	m	n	Coefficients[b] $(\alpha=\beta=2.69)$ γ
1	0	0	1	0	0	0	0.64
2	0	0	1	0	0	2	0.64
3	1	0	1	0	0	0	0.64
3	0	1	1	0	0	0	0.64
4	1	1	1	0	0	0	0.64
5	0	0	1	0	0	1	0.64
6	0	0	0	0	0	0	1.5
7	1	0	0	0	0	0	0.64
7	0	1	0	0	0	0	0.64
8	0	0	0	1	0	0	0.64
8	0	0	0	0	1	0	0.64
9	0	0	2	0	0	0	0.64
10	0	0	1	0	0	0	1.5
11	0	0	1	1	0	0	0.64
11	0	0	1	0	1	0	0.64
12	0	0	0	1	0	0	1.5
12	0	0	0	0	1	0	1.5
13	1	0	0	1	0	0	0.64
13	1	0	0	0	1	0	0.64
13	0	1	0	1	0	0	0.64
13	0	1	0	0	1	0	0.64

[a] Identical numbering of terms means they have identical amplitudes as a result of symmetry.
[b] Powers and coefficients correspond to the representation

$$r_1{}^i r_2{}^j r_3{}^k r_{23}{}^l r_{13}{}^m r_{12}{}^n \exp[-(\alpha r_1 + \beta r_2 + \gamma r_3)].$$

METHOD OF CALCULATION

The first step in the calculation is to break up the Hamiltonian into kinetic and potential energy operators and then perform the indicated operations. Thus,

$$T = -\nabla_1{}^2 - \nabla_2{}^2 - \nabla_3{}^2 \qquad (6)$$

or

$$T = -\nabla_{12}{}^2 - \nabla_3{}^2. \qquad (7)$$

Now

$$\nabla_{12}{}^2 = \frac{2}{r_1}\frac{\partial}{\partial r_1} + \frac{2}{r_2}\frac{\partial}{\partial r_2} + \frac{\partial^2}{\partial r_1{}^2} + \frac{\partial^2}{\partial r_2{}^2} + \frac{4}{r_{12}}\frac{\partial}{\partial r_{12}} + \frac{2\partial^2}{\partial r_{12}{}^2}$$

$$+ \frac{r_{12}{}^2 + r_1{}^2 - r_2{}^2}{r_1 r_{12}}\frac{\partial^2}{\partial r_1 \partial r_{12}} + \frac{r_{12}{}^2 - r_1{}^2 + r_2{}^2}{r_2 r_{12}}\frac{\partial^2}{\partial r_2 \partial r_{12}}. \qquad (8)$$

The latter expression has been given by Hylleraas[8] and may be obtained by expressing the Laplacian and the r_1, r_2, r_{12} coordinates in cartesian coordinates.

One must now calculate the kinetic energy, potential energy, and overlap matrix elements. A matrix element of an operator Ω is given by

$$\langle\Omega\rangle_{kk'} = \int \phi_k \Omega \phi_{k'} d\tau, \qquad (9)$$

where ϕ_k and $\phi_{k'}$ are any two terms, aside from the amplitude factor, of Eq. (2). The resulting integrations are discussed in the Appendix.

Denoting the ij energy and overlap matrix elements by H_{ij} and S_{ij}, respectively, one is then led via the variational principle to the 13 secular equations

$$\sum_j H_{ij} C_{jk} = \sum_j S_{ij} C_{jk} E_k, \quad i=1, \cdots, 13, \qquad (10)$$

where C_{ij} is the jth amplitude factor for the kth eigenvalue and E_k is the kth eigenvalue. The latter equation may be written in the usual matrix notation as $HC=SCE$, where E is a diagonal matrix. In this application H and S are real symmetric and S is positive definite. The procedure then is to diagonalize S via the unitary transformation U_S, forming the diagonal matrix S'. Applying a similarity transformation with U_S on $(S')^{-1/2}$ one obtains $S^{-1/2}$. A matrix $H'=S^{-1/2} \times HS^{-1/2}$ is formed and then diagonalized to the matrix E via the unitary transformation U_H. Finally, $C=S^{-1/2} \times U_H$ yields the associated amplitudes of the various eigenvalues.[14]

Jacobi's method of matrix diagonalization is employed here. A unit matrix U is formed and a two-dimensional rotation on the ij, ii, jj, ji elements is performed rotating U into U'. Then the transformation $U'H$ (where H is to be diagonalized) is restricted to the case for which the ijth element and its symmetric counterpart are zero. This determines the transformation. The rotation of U and H is continued until H is diagonal.[15]

In the actual calculations, one term at a time was added and the associated eigenvalue computed. However, at the completion of the calculation of an 11-term function a precision check in the program noted that the desired precision of 6 digits was lost. Thus, the first 10 terms with their associated amplitudes were combined into a single term and the remaining three terms of Table II were added one at a time (without varying the relative amplitudes of the first ten terms) and the associated eigenvalues computed.

RESULTS

The final form of Eq. (2) as determined by this calculation is

$$\phi = 1.03670(19.0146\phi_1 - 2.02248\phi_2 - 2.08637\phi_3$$
$$-0.142702\phi_4 + 7.02797\phi_5 - 9.82786\phi_6 - 0.562915\phi_7$$
$$-0.296473\phi_8 - 2.19970\phi_9 - 3.45488\phi_{10})$$
$$-0.0913939\phi_{11} + 1.94123\phi_{12} + 0.00994224\phi_{13}, \qquad (11)$$

where the subscripted ϕ's refer to the terms of Eq. (2) without the amplitudes. The parameters of the ϕ's are listed in Table II.

Table III lists the energy values obtained as a function of the number of terms used.

Table IV compares the theoretical values obtained here with those of Weiss[2] and of James and Coolidge.[7]

[14] This solution of the secular determinant is due to Fred J. Quelle, Jr., of the Solid State and Molecular Theory Group at MIT and has been written by that group as MIT SSMTG Programming Note No. 17.
[15] This diagonalization procedure has been programmed in FORTRAN for the IBM 70 series machines. A more complete description is available from MIT in Computer Center Report CC29 written by Miss M. Merwin.

TABLE III. Ground-state energy of the Li atom using terms containing interelectronic separation coordinates.

No. of terms	Energy ($e^2/2a_0$)
1	−14.8358
2	−14.8396
3	−14.8849
4	−14.9102
5	−14.9345
6	−14.9345
7	−14.9363
8	−14.9370
9	−14.9370
10	−14.9541
11	−14.9549
12	−14.9559
13	−14.9559
∞ [a]	−14.9561

[a] See reference 15.

The experimental energy is taken from the compilation of Scherr et al.[16]

This table also includes comparisons of the energy values for equal numbers of terms in order to provide a clearer comparison between the different methods employed.

TABLE IV. A comparison of ground-state energies of the Li atom as determined by various authors.

No. of terms	Author	Method	Energy ($e^2/2a_0$)
45	Weiss[a]	superposition of configurations	−14.9542
10	James and Coolidge[b]	interelectronic separation coordinates	−14.9522
10	This paper	interelectronic separation coordinates	−14.9541
13	This paper	interelectronic separation coordinates	−14.9559
...		experimental[c]	−14.9561

[a] See reference 2.
[b] See reference 7.
[c] See reference 15.

DISCUSSION

The advantage of using configurations containing interelectronic separation terms is apparent from Table IV. The convergence towards the experimental energy arrives very close to the experimental value with the addition of comparatively few terms. Also Weiss's best 45-term superposition of configurations is as good as a 10-term function of the type used here.

The error introduced by using improper symmetry is

[16] Charles W. Scherr, J. N. Silverman, and F. A. Matsen, Phys. Rev. 127, 830 (1962). The experimental energy is the nonrelativistic energy as obtained by these authors and combines two-electron theoretical energies with experimental ionization energies taking into account relativistic and nuclear motion corrections.

also clear in the results tabulated in Table IV. It is observed that the James and Coolidge[7] 10-term function and the 10-term function used here are quite different with the latter function lower by 0.002 $e^2/2a_0$. Although these two functions are not the same (see Tables I and II), they do have identical interelectronic separation terms. Thus, as is expected proper symmetry of the wave function yields a better representation of the system.

It is worthwhile to consider the continuation of this calculation until one arrives at the accuracy achieved by Pekeris[4] for helium. On the surface it might appear that a wave function that requires 3 hours running time on an IBM 7090 and at the same time extends the previouscalculation by only three terms is not worth continuing. It must be pointed out, however, that the present program is written in such a way that a great deal of calculation is unnecessarily repeated. With the initial program written and tested, numerical checks are now available to decrease, substantially, the required running time. Furthermore, although only three terms of different symmetry have been added to the function of James and Coolidge[7] it will be observed by reference to Tables I and II that the present calculation employs 21 terms as compared to 13 terms for the earlier calculation.

With the completion of refinements of the present program it would be interesting to apply the general approach to other atoms. Beryllium, being spherically symmetric, should not present any great difficulties. Terms containing only one interelectronic separation term each would be used and then basic integral programs for lithium could once more be applied.

Since the energy value is not a very good criterion of the "goodness" of a wave function and since the present energy value is still outside of experimental limits, it was considered unnecessary to calculate any other quantities. With the improvement of the wave function, however, such things as ionization potential and electron density at the nucleus for use in hyperfine structure calculations should certainly be ascertained. Application of the wave function to solid-state phenomena should also be considered especially for applications using the orthogonalized plane-wave representations.

ACKNOWLEDGMENTS

APPENDIX

The following integrals occur:

$$A(h,\alpha) = \int_0^\infty x^h e^{-\alpha x} dx, \quad h \geqslant 0 \qquad (12)$$

$$V(g,\alpha/h,\beta) = \int_0^\infty dx \int_x^\infty dy\, x^g y^h e^{-(\alpha x + \beta y)};$$
$$g \geqslant 0, \quad h + g \geqslant -1, \quad (13)$$

$$W(a,b,c,/d,e,f) = \int_0^\infty dx \int_x^\infty dy \int_y^\infty dz\, x^a y^b z^c e^{-(dx+ey+fz)},$$
$$a \geqslant 0, \quad a+b \geqslant -1, \quad a+b+c \geqslant -2. \quad (14)$$

All of the integrations which occur in the present calculation may be put into one of the three aforementioned forms via the general relationship

$$\int_a^b dy \int_a^y dx\, g(y)f(x) = \int_a^b dx \int_x^b dy\, f(x)g(y). \quad (15)$$

The limits on the powers of the V and W integrals are obtained via Taylor series expansions. Thus,

$$V(g,\alpha/h,\beta) = \sum_{k=0}^\infty \frac{(-1)^k \alpha^k}{k!} \int_0^\infty \frac{y^{h+g+k+1}}{g+k+1} e^{-\beta y} dy. \quad (16)$$

From $g+k+1 \neq 0$ one obtains $g \geqslant 0$. From $h+g+k+1 \geqslant 0$ one obtains $h+g \geqslant -1$. The power limitations for the W integrals are obtained in the same manner.

Recurrence relationships between the A, V, and W integrals are given by James and Coolidge.[7]

The general form of the integrals evaluated here is

$$J(a,b,c,d,e,f/\alpha,\beta,\gamma)$$
$$= \int r_1{}^a r_2{}^b r_3{}^c r_{23}{}^d r_{13}{}^e r_{12}{}^f e^{-(\alpha r_1 + \beta r_2 + \gamma r_3)} d\tau_1 d\tau_2 d\tau_3. \quad (17)$$

If the interelectronic separations have even powers, they are simply expanded by the law of cosines. If the powers are odd, then numerator and denominator are multiplied by that term and the numerator is expanded by the law of cosines and the denominator expanded in the usual way by Neumann's expansion in terms of Legendre polynomials.

By rotating, where necessary, the coordinate systems of one or two of the electrons in such a way that the z axis is along the radius vector of another electron the θ integrations have the general form

$$f(g,n) = \int_0^\pi P_n(\cos\theta)\cos^g(\theta)\sin\theta d\theta \quad (18)$$

for all cases of odd powers of interelectronic separation

TABLE V. Values of $f(g,n) = \int_0^\pi P_n(\cos\theta)\cos^g\theta \sin\theta d\theta$.

g	n	$f(g,n)$
0	0	2
1	1	2/3
2	0	2/3
2	2	4/15
3	1	2/5
3	3	4/35
4	0	2/5
4	2	8/35
4	4	16/315

terms of Eq. (17). Some values of these integrals as determined by Barnett[17] are listed in Table V.

Using the notation

$$I(a,b,c/d,e,f) = \int r_1{}^k r_2{}^l r_3{}^m e^{-(\alpha r_1 + \beta r_2 + \gamma r_3)}$$
$$\times \frac{\cos^a(\theta_{23})}{r_{23}{}^d} \frac{\cos^b \theta_{13}}{r_{13}{}^e} \frac{\cos^c \theta_{12}}{r_{12}{}^f} d\tau_1 d\tau_2 d\tau_3, \quad (19)$$

we have

$$I(0,0,0|0,0,0) = 64\pi^3 A(k+2,\alpha) A(l+2,\beta)$$
$$\times A(m+2,\gamma), \quad (20)$$

$$I(0,g,0|0,1,0) = 64\pi^3 A(l+2,\beta) \sum_n \frac{f(g,n)}{2}$$
$$\times [V(m+2+n,\gamma|k-n+1,\alpha)$$
$$+ V(k+2+n,\alpha|m+1-n,\gamma)], \quad (21)$$

$$I(h,0,g|1,0,1) = 64\pi^3 \sum_n \sum_p \frac{f(h,n)}{2} \frac{f(g,p)}{2}$$

$$\times [W(l+p+n+2, m+n+1, k-p+1|\beta,\gamma,\alpha)$$
$$+ W(m+n+2, l+p-n+1, k-p+1|\gamma,\beta,\alpha)$$
$$+ W(k+p+2, l+n-p+1, m-n+1|\alpha,\beta,\gamma)$$
$$+ W(k+p+2, m+n+2, l-p-n|\alpha,\gamma,\beta)$$
$$+ W(m+n+2, k+p+2, l-p-n|\gamma,\alpha,\beta)$$
$$+ W(l+p+n+2, k-p+1, m-n+1|\beta,\alpha,\gamma)]. \quad (22)$$

The integrals represented thus far are reducible from terms containing 0, 1, or 2 odd powers of interelectronic separations. The general form of the reduced integral for three odd powers of interelectronic separations is $I(h,0,g/1,1,1)$ and this becomes a rapidly converging infinite series. However, by the choice of wave function employed here three odd powers of the interelectronic separations may occur in only one way, viz.,

$$K = \int r_1{}^k r_2{}^l r_3{}^m \frac{r_{23} r_{12}}{r_{13}} e^{-(\alpha r_1 + \beta r_2 + \gamma r_3)} d\tau_1 d\tau_2 d\tau_3, \quad (23)$$

[17] M. P. Barnett, University of Wisconsin Naval Research Laboratory Report WIS-ONR-30, 1958 (unpublished).

which reduces to 16 infinite series of the type $I(0,0,0/-1,0,-1)$. Each of these series converges to the desired accuracy within three or four terms. It is found to be more expedient, computationally, to combine all 16 series into a single series for which convergence is

obtained in two or three terms. The computation of this integral required double-precision arithmetic tabulating. It is the only place in the entire calculation which such precision is required.

By the definition

$$WW(K,M,N,A,B,C,L,J,q) = W(M-2+2q+L+J, N+3-L, K-2q+2-J, B, C, A)$$
$$+W(N+2q+L, M+1-L+J, K-2q+2-J, C, B, A)+W(N+2q+L, K-1+J, M+4-L-J-2q, C, A, B)$$
$$+W(M-2+2q+L+J, K+3-J, N-2q+2+L, B, A, C)+W(K+2q+J, M+1-J+L, N-2q+2-L, A, B, C)$$
$$+W(K+2q+J, M+1-J+L, N-2q+2-L, A, B, C)+W(K+2q+J, N-1+L, M-2q+4-L-J, A, C, B),$$

$$(24)$$

one obtains

$$K = 64\pi^3 \sum_q \frac{1}{(2q+1)^2} \Big\{ [WW(K+2, M+2, N, A, B, C, 2, 2, q)+WW(K, M+4, N, A, B, C, 2, 2, q)$$

$$+WW(K+2, M, N+2, A, B, C, 2, 2, q)+WW(K, M+2, N+2, A, B, C, 2, 2, q)]$$

$$-\frac{2q}{(2q-1)}[WW(K+1, M+3, N, A, B, C, 1, 2, q)+WW(K+1, M+1, N+2, A, B, C, 1, 2, q)$$

$$+WW(K+2, M+1, N+1, A, B, C, 2, 1, q)+WW(K, M+3, N+1, A, B, C, 2, 1, q)]$$

$$-\frac{2(q+1)}{(2q+3)}[WW(K+1, M+3, N, A, B, C, 3, 2, q)+WW(K+1, M+1, N+2, A, B, C, 3, 2, q)$$

$$+WW(K+2, M+1, N+1, A, B, C, 2, 3, q)$$

$$+WW(K, M+3, N+1, A, B, C, 2, 3, q)]+\frac{4q^2}{(2q-1)^2}WW(K+1, M+2, N+1, A, B, C, 1, 1, q)$$

$$+\frac{4(q+1)^2}{(2q+3)^2}[WW(K+1, M+2, N+1, A, B, C, 1, 3, q)+WW(K+1, M+2, N+1, A, B, C, 3, 1, q)]\Big\}.$$

$$(25)$$

Equation (25) is obtained from Eq. (23) in the following way:

1. Multiply by $r_{23}r_{12}/r_{23}r_{12}$.
2. Expand numerator by law of cosines.
3. Expand denominator by Neumann expansion.
4. Rotate Z_1 and Z_3 along r_2. Hence, $\theta_{12}=\theta_2$.
5. Apply the addition theorem[18] for Legendre poly-

nomials to $P_q(\cos\theta_{13})$. Thus, we have

$$P_q(\cos\theta_{13}) = P_q(\cos\theta_1)P_q(\cos\theta_3)+f(\psi_{13}). \quad (26)$$

Upon integration over ψ_{13}, $f(\psi_{13})$ vanishes.

6. Integrate r_2 between the limits $(0,r_{<13})$, $(r_{<13},r_{>13})$, and $(r_{>13},\infty)$, and integrate r_3 between the limits $(0,r_1)$ and (r_1,∞).

7. Finally express the resulting integrations in terms of the W integrals.[19]

[18] P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1953), p. 1274.

[19] A more detailed discussion of the evaluation of this integral and a discussion of convergence properties is available on request.