C. Froese Fischer and M. Wilson, Argonne National Laboratory, Report No. ANL-7404 (unpublished).

[14] The calculations reported here were obtained using a CDC-3600 at the Applied Mathematics Division of Argonne National Laboratory and an IBM-7094 at the Computing Center of The Johns Hopkins University.

[15] S. L. Ruby, G. M. Kalvius, G. B. Beard and R. E. Snyder, Phys. Rev. 159, 239 (1967); D. W. Hafemeister, G. DePasquali and H. deWaard, Phys. Rev. 135, B1089 (1964); W. H. Flygare and D. W. Hafemeister, J. Chem. Phys. 43, 789 (1965).

[16] G. J. Perlow and M. R. Perlow, J. Chem. Phys. 45, 2193 (1966); Hafemeister *et al.* (Ref. 15); Flygare *et al.* (Ref. 15).

[17] M. F. Crawford and A. L. Schawlow, Phys. Rev. 76, 1310 (1949).

[18] Kopfermann (Ref. 1). See Sec. 35.

[19] Unpublished calculations by the author.

[20] J. Blaise and A. Steudel, Z. Physik 209, 311 (1968); and unpublished data from M. Fred.

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Calculation of the ^1S State of the Beryllium Atom in Hylleraas Coordinates[*]

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The ^1S state of the Be atom is calculated in Hylleraas coordinates using a 25-term single-determinant wave function having the proper spin-angular-momentum symmetry. A ground-state energy of −29.3158 Ry is obtained, as compared with the experimentally observed value of −29.337 Ry and the best Hartree-Fock value of −29.14596 Ry, indicating that the application of the procedure to larger systems should be fruitful. Suggestions are given to improve the accuracy of the present method and to extend it to atoms of higher atomic number. Solutions of the integrals and procedures for manipulating them in storage are presented.

INTRODUCTION

It is well known that the main defect in using the Hartree-Fock formalism for an approximate solution of the many-electron Schrödinger equation is its failure to represent adequately the correlations between the motions of the individual electrons. Several methods have been employed in order to circumvent this failure. The simplest one, computationally, is the method of configuration interaction in which the wave function is approximated by a linear combination of hydrogen-like orbitals, the coefficients being chosen to minimize the energy. Although this method is readily applied to a great many multielectron problems (both atomic and molecular), difficulties with convergence have lead some investigators[1,2] to suggest as an alternative, a trial wave function which explicitly contains the interparticle coordinates r_{ij}. Recently generalized methods for including interparticle coordinates in the wave functions for atoms and molecules have been developed by Sinanoğlu[3] and Szasz.[4]

Hylleraas[5] applied this method to the helium atom. Using a six-term wave function depending on the variables $S = r_1 + r_2$, $t = r_2 - r_1$, and $u = r_{12}$ he calculated an energy within 0.02% of the experimental value. By carrying many more terms, more recent workers[6,7] have constructed wave functions that give energies within the current limits of experiment. However, when the method is extended to larger systems, extreme computational difficulties are encountered. James and Coolidge[8] calculated the ground-state energy of lithium using a wave function consisting of Slater-type orbitals multiplied by $r_{ij}^{\,n}$ (where $n = 0, 1, 2$) with the limitation that at most only one interelectronic separation coordinate is present in a given term. They did not, however, achieve the accuracy Hylleraas obtained for helium. As was later pointed out by James and Coolidge,[9] their wave function was not of pure doublet symmetry. Burke[10] has given an estimate of the error involved in this lack of proper symmetry. His calculation for lithium as well as the work of Berggren and Wood[11] and Smith and Larsson[12] have improved on the original results of James and Coolidge. All these workers used the correlated or Hylleraas-type wave function.

The purpose of the present investigation is to develop a simplified systematic approach for using the Hylleraas-type wave function to calculate the energy of a multielectron atom via the variational principle. The greatest problem in using the Hylleraas-type wave function is in the calculation of integrals involving several interelectronic separation coordinates. This problem is reduced by choosing a wave function which introduces at most only one r_{ij} per term as was done initially by James and Coolidge.[8] The justification of this choice has been discussed by several investigators.[3,4,13] Hence all the possible different types of integrals occurring in systems of larger atomic number will occur for beryllium. The present calculation is further simplified by choosing a basis set of Slater orbitals. The ground-state energy of beryllium is calculated using a correlated wave function with the proper spin angular-momentum symmetry. In the present paper:

(i) The choice of the trial wave function is discussed.

(ii) Formula for the matrix elements are presented.

(iii) A technique for manipulating the integrals in storage is described. This process should be readily extendible to larger systems and thereby remove a major difficulty in these calculations.

(iv) The integrals occurring and their evaluation are discussed in the Appendix.

WAVE FUNCTION

The wave function for a multielectron atom in the central-field approximation is given by

$$\Psi = \mathcal{A}\phi_1(1)\sigma(1)\phi_2(2)\sigma(2)\cdots\phi_N(N)\sigma(N), \tag{1}$$

where $\phi_i(q)$ is a normalized one-electron orbital, i standing for the set of quantum numbers n, l, and m and q for the space coordinates; σ is the spin coordinates α or β, and $\mathcal{A}$ is the antisymmetrizer

$$\mathcal{A} = (N!)^{-\frac{1}{2}}\sum_p(-1)^P P.$$

For beryllium Eq. (1) becomes

$$\Psi = (N!)^{-1/2}\sum_U U\psi_i(\alpha\beta\alpha\beta)_i, \tag{2}$$

where U is a permutation operator which permutes the spin functions. Thus for Be, U generates, in addition to $\alpha\beta\alpha\beta$, the spin configurations $\alpha\beta\beta\alpha$, $\alpha\alpha\beta\beta$, $\beta\alpha\alpha\beta$, $\beta\beta\alpha\alpha$, and $\beta\alpha\beta\alpha$. The function Ψ_i is given by

$$\psi_i = \sum_R(-1)^R R(\phi_1\phi_2\phi_3\phi_4)_i,$$

where R is a permutation operator which performs the appropriate permutations on $(\phi_1\phi_2\phi_3\phi_4)_i$. For example,

$$\Psi_1 = \phi_1\phi_2\phi_3\phi_4 - \phi_3\phi_2\phi_1\phi_4 - \phi_1\phi_4\phi_3\phi_2 + \phi_3\phi_4\phi_1\phi_2.$$

For a spin-independent Hamiltonian, no product of two terms with different spin factors will contribute to the energy and overlap matrix elements because of the orthogonality of the spin functions. Therefore the calculation can be carried out using any one of the spatial functions in Eq. (2).

One property a wave function must have beside that of antisymmetry is to be an eigenfunction of the operator of the square of the total-spin angular momentum. In order for a single-determinant wave function to fulfill this requirement, orbitals must be analytically the same in pairs. Thus for beryllium, electrons 1 and 2 must have identical analytic representations and so must electrons 3 and 4. To this end we introduce the operator Q which acts so that the resulting function will have the proper spin symmetry. Thus

$$Q[f(r_1)\phi_1\phi_1\phi_3\phi_3] = [f(r_1)+f(r_2)]\phi_1\phi_1\phi_3\phi_3.$$

This requirement and the restriction of at most one r_{ij} per term (to limit the complexity of a single term) determine the final form of the trial wave function. The unnormalized, properly symmetrized, singlet S function employed here is

$$\begin{aligned}\psi = \sum_{R,Q}(-1)^R RQ[&(c_1+c_3r_{12}+c_5r_{13}+c_7r_{34}+c_9r_{12}^2+c_{11}r_{13}^2+c_{13}r_{34}^2+c_{15}r_1+c_{17}r_3\\ &+c_{19}r_1^2+c_{21}r_3^2+c_{23}r_1r_{12}+c_{25}r_3r_{34})\phi_1\phi_1\phi_2\phi_2+(c_2+c_4r_{12}+c_6r_{13}+c_8r_{34}\\ &+c_{10}r_{12}^2+c_{12}r_{13}^2+c_{14}r_{34}^2+c_{16}r_1+c_{18}r_3+c_{20}r_1^2+c_{22}r_3^2+c_{24}r_1r_{12})\phi_1\phi_1\phi_3\phi_3],\end{aligned} \tag{3}$$

where $\phi_1(q)=e^{-\alpha r_q}$, $\phi_2(q)=r_q e^{-\beta r_q}$, and $\phi_3(q)=e^{-\gamma r_q}$ with $\alpha=4.0$, $\beta=1.0$, and $\gamma=2.0$. Note that whenever the coordinates q are not written explicitly in the above discussion the ordering 1 2 3 4 is understood.

FORMULATION

The time-independent Schrödinger equation for a many-electron atom is

$$H\Psi(\bar{q}_1,\sigma_1;\ldots;\bar{q}_n,\sigma_n)=E\Psi(\bar{q}_1,\sigma_1;\ldots;\bar{q}_n,\sigma_n), \tag{4}$$

where the $\bar{q}_i$ are the spatial coordinates and σ_i the spin coordinate of the ith electron. It is convenient to divide the Hamiltonian into kinetic and potential-energy operators and to calculate these quantities separately. Thus

$$H=T+V, \tag{5}$$

where $T=-\nabla_1^2-\nabla_2^2-\nabla_3^2-\nabla_4^2$ or[14] $T=-\nabla_{12}^2-\nabla_3^2-\nabla_4^2$, (6)

and

$$V=-2Z\sum_{i=1}^{4}\frac{1}{r_i}+2\sum_{i=1}^{4}\sum_{\substack{j=2\\ i\neq j}}^{4}\frac{1}{r_{ij}}. \tag{7}$$

With these operators the energy is expressed in units of rydbergs, $e^2/2a_0$.

There are three classes of matrix elements according as the interelectronic separation coordinates involved in the combining terms refer to the same pair of electrons (class I), to different pairs with an electron in common (class II) or to different pairs with no electron in common (class III). Thus

$$\begin{aligned}\int r_1^{k'} r_2^{l'} r_3^{m'} r_4^{n'} r_{ab}^{P'} &\exp[-(\alpha' r_1+\beta' r_2+\gamma' r_3+\delta' r_4)]H\\ &\times r_1^{k} r_2^{l} r_3^{m} r_4^{n} r_{12}^{p}\exp[-(\alpha r_1+\beta r_2+\gamma r_3+\delta r_4)]\,dV=T+V\end{aligned} \tag{8}$$

is a general matrix element; if $r_{ab}=r_{12}$ it is class I, if $r_{ab}=r_{14}$ it is class II, and if $r_{ab}=r_{34}$ it is Class III. With the definition

$$\begin{aligned}&J(k,l,m,n,s,t,u,v,w,x,a,b,c,d)\\ &=\int r_1^{k} r_2^{l} r_3^{m} r_4^{n} r_{12}^{s} r_{13}^{t} r_{14}^{u} r_{23}^{v} r_{24}^{w} r_{34}^{x}\exp[-(ar_1+br_2+cr_3+dr_4)]\,dV,\end{aligned} \tag{9}$$

we have for T and V:

$$\begin{aligned}T=&-(a^2+b^2+c^2+d^2)I(0000,000000)+a(2k+2+p)I(-1000,000000)\\ &-k(k+1+p)I(-2000,000000)+b(2l+2+p)I(0-100,000000)-l(l+1+p)I(0-200,000000)\\ &+c(2m+2)I(00-10,000000)-m(m+1)I(00-20,000000)+d(2n+2)I(000-1,000000)\\ &-n(n+1)I(000-2,000000)+p[-(k+l+2p+2)I(0000,-200000)\\ &+aI(1000,-200000)+bI(0100,-200000)-aI(-1200,-200000)\\ &-bI(2-100,-200000)+lI(2-200,-200000)+kI(-2200,-200000)],\end{aligned} \tag{10}$$

$$\begin{aligned}V=&-2Z[I(-1000,000000)+I(0-100,000000)+I(00-10,000000)\\ &+I(000-1,000000)+2I(0000,-100000)+I(0000,0-10000)\\ &+I(0000,00-1000)+I(0000,000-100)+I(0000,0000-10)+I(0000,00000-1)].\end{aligned} \tag{11}$$

These formulas hold for all three classes of matrix elements if one makes the following definition:

$$I(fghi,stuvwx)=J(k'+k+f,l'+l+g,m'+m+n,n'+n+i,S,t,U,v,w,X,a'+a,b'+b,c'+c,d'+d), \tag{12}$$

where $S=p'+p+s$, $U=u$, $X=x$ class I,
$S=p+s$, $U=P'+u'$ $X=x$ class II,
$S=p+s$, $U=u$, $X=p'+x$ class III.

The integrals arising in the matrix elements are discussed in the Appendix. The solution of the secular equation is described by Burke.[10] The necessary matrix diagonalizations were performed by the Jacobi method.[15] In performing the calculation, one term was added at a time, and the resulting secular equation was solved.

CALCULATIONS

The first step in the computation is to generate the wave function; to this end the R and Q operators have been programmed to handle functions of the general form

$$\prod_{i=j}^{4} r_i^{n_i} e^{-ar_i} r_{kl},$$

where r_{kl} is any one of the six interelectronic distances. The full 25-term function requires the evaluation of approximately 460 000 integrals, but since there is a great deal of repetition in this number, it was found expedient to devise a system to calculate each different integral but once and then store it for future use. In this way the number of integrals that must be calculated is reduced by a factor of about 25. An integral is fully specified by listing its 14 arguments [see Eq. (9)]. By transforming these 14 indicies into a 14 digit "code number" in which each digit stands for one index, one can represent an integral by a single number. Before carrying out this transformation, suitable interchances of the indicies are made so that, in an integral involving a single interelectronic separation coordinate, it is always an r_{12}. By arranging the other possible integral types into analogous "standard forms," one can determine what different integrals occur.

TABLE I. Energy improvement per term.

No. of terms	Energy ($e^2/2a_0$)	Term amplitudes C_n for 25 term function
1	−28.9155	0.172 550 0
2	−28.9292	0.832 739 9
3	−29.1787	0.052 718 6
4	−29.1811	1.464 382 0
5	−29.1867	0.113 312 9
6	−29.1873	2.131 037 2
7	−29.2247	0.073 721 1
8	−29.2265	2.178 467 9
9	−29.2265	−0.021 058 9
10	−29.2269	−1.396 010 6
11	−29.2326	−0.018 883 2
12	−29.2333	−1.470 658 6
13	−29.2376	−0.014 624 7
14	−29.2380	−1.287 734 9
15	−29.2637	−0.005 431 2
16	−29.2640	−0.658 256 6
17	−29.2778	−0.279 856 7
18	−29.2778	−5.198 012 7
19	−29.2948	0.054 207 1
20	−29.2948	0.098 717 2
21	−29.3076	0.037 829 3
22	−29.3081	3.191 755 1
23	−29.3082	0.010 832 1
24	−29.3085	0.534 066 1
25	−29.3158	0.014 160 5

RESULTS

The energies are listed in Table I as a function of the number of terms used. The c_n refer to the amplitudes of the terms in the 25-term function. Table II compares theoretical energies obtained by various authors. The experimental energy is taken from Moore.[16]

DISCUSSION

Using a 25-term wave function, an energy of −29.3158 Ry has been calculated. Compared to the experimental value of −29.334 86 Ry, this result is in error by about 0.06%. The even-numbered terms in the wave function impart some open-shell character to the $2s$ electrons. Roothaan's[17] analytic self-consistent-field calculation, suffers from the usual Hartree-Fock shortcoming of neglecting the details of the electronic repulsions. The present energy is considerably improved over the configuration interaction results of Boys[18] and Kibartas *et al.*,[19] who used seven and three configurations, respectively. It is slightly lower (0.001 Ry) than Watson's[20] result for 37 configurations, whereas Weiss's[1] energy is lower by 0.006 Ry; the latter work involved the superposition of 55 configurations demonstrating the slow convergence of the method. Kotchoubey and Thomas[21] used a 20-function basis, obtaining the expansion coefficients by an iterative procedure rather than by solving the secular equation directly. Kelly's[22] calculation by the Brueckner-Goldstone perturbation method has been modified recently, leading to a new energy of −29.328 16 Ry. Nesbet[13] has estimated that his result, arrived at from the variational solution of the third-order Bethe-Goldstone equations, is in error by approximately 0.004 Ry. Sinanoğlu's[23] result is closest to the experimental value, but Geller *et al.*[24] express some doubt

TABLE II. Comparison of various methods of energy calculations.

Reference	Method	Energy ($e^2/2a_0$)
Roothaan[17]	Hartree-Fock	−29.145 96
Boys[18]	Configuration interaction	−29.274
Iutsis[19]	Configuration interaction	−29.284
Kotchoubey[21]	Configuration interaction	−29.306 6
Watson[20]	Configuration interaction	−29.314 80
Weiss[1]	Configuration interaction	−29.321 80
Szasz[26]	Correlated wave function	−29.313 0
Present work	Correlated wave function	−29.315 8
Kelly[22]	Perturbation theory	−29.326 14
Nesbet[13]	Perturbation theory	−29.330 3
Geller[24]	Many electron theory	−29.328 77
Sinanoğlu[23]	Many electron theory	−29.334 68
Experimental[16]	Many electron theory	−29.337

as to this value. They have used the Sinanoğlu many-electron theory to calculate the ground-state energy of beryllium. Choosing a set of Hartree-Fock orbitals different from those used by Sinanoğlu, they obtained values for the $1s^2$ and $2s^2$ correlation energies in reasonable agreement with Sinanoğlu's results. They did not, however, calculate the $1s-2s$ correlation energy but used Kelly's[22] perturbation result of -0.00944 Ry which agrees fairly well with Watson's[20] value of -0.01010 Ry. Both these results are considerably higher than Sinanoğlu's corresponding value of 0.01296 Ry, arrived at by a "core-polarization" method.[25] Szasz's[26] work parallels most closely the current investigation but neglects the intershell correlation effects. The current wave function, utilizing one less parameter but including intershell correlation terms, yields a slightly improved energy. It would not be correct to attribute this improvement strictly to the $1s-2s$ correlation since (a) Szasz uses the Hartree-Fock orbitals of Roothaan[17] whereas simple Slater orbitals are used in this work, and (b) for many of Szasz's terms there are no comparable terms in the present wave function.

The numerical results arrived at in this investigation, reaffirm the already well-known fact that the Hylleraas-type wave function is capable of yielding energies at least comparable with, if not better than, those from a superposition of configurations, while using fewer terms than the latter. Examination of the energy decreases due to the r_{12} and r_{34} terms (terms 3, 4, 7, and 8) indicates that r_{12} is more effective than r_{34} in accounting for correlation in their respective shells. This would seem to imply that the 1s correlation differs significantly in nature from the 2s correlation, a fact in agreement with the previous conclusions of Watson,[20] Szasz,[26] and Linderberg and Shull.[27] The intershell correlation (terms 5, 6, 11, and 12) is fairly small for Be, but it is not negligible; one would expect it to be much more important for larger atoms since there are many more interactions to be considered.

Besides the specific calculation of Be, a principal aim of this work has been the development of generalized programming procedures for using Hylleraas-type wave functions in variational calculations of many-electron atoms. The results indicate that the application of the method to systems with atomic number greater than four should be feasible. With the approximation of at most one r_{ij} per term for the wave function of an arbitrary atom, only eight classes of integrals occur whose coordinates are not immediately separable. All eight classes occur in Be. Hence the programs for integral calculations used here are immediately applicable to any system. What remains then is the need to devise programs which, for an atom of arbitrary size, will determine to which of the eight classes a particular integral belongs. The programmed R and Q operators for the four electron system make it a simple matter to introduce new terms (obeying the previously mentioned restrictions) into the wave function. In extending the calculation to larger systems similar operators should be considered. Although the present results are not as close to experiment as those of others, it must be remembered that only simple Slater-type orbitals have been used as a basis here. At this point two methods for improving the procedure suggest themselves.

First, the basis could be improved by using Hartree-Fock orbitals or some other analytical approximation, in the hope of attaining the accuracy Pekeris[7] achieved for the helium atom. Secondly, it may be feasible to program the R and Q operators to generate multideterminant wave functions [the so-called Extended Hartree-Fock (EHF) functions], whose energies are much improved over the single-determinant representation. One or both of these approaches will be incorporated into the application of the procedure to atoms of higher atomic number in the near future.

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APPENDIX

All the integrals occurring in this calculation are evaluated by means of the following auxiliary functions:

$$A(k,a)=\int_0^\infty x^k e^{-ax}dx, \tag{13}$$

$$V(k,l,a,b)=\int_0^\infty dx\int_0^\infty dy\, x^k y^l e^{-(ax+by)}, \tag{14}$$

$$W(k,l,m,a,b,c)=\int_0^\infty dx\int_x^\infty dy\int_y^\infty dz\, x^k y^l z^m e^{-(ax+by+cz)}. \tag{15}$$

Recurrence relations, and the power limits for which they remain valid, are given by James and Coolidge[8]. It was found necessary to use double precision arithmetic[28] in evaluating these auxiliary functions, since for certain combinations of the exponential coefficients (a, b, and c) repeated application of the recurrence formulas caused a serious loss of significent figures. Ohrn and Nordling[29] have developed a scheme to circumvent this difficulty by evaluating the V and W integrals as infinite series. Geller, Taylor, and Levine[24] evaluate these partly in terms of incomplete gamma functions to avoid the use of recurrence relations altogether.

The integrals that occur in this work can be classified according to the manner in which the interelectronic separation coordinates enter. Thus, giving only the r_{ij}'s, we have

$$\text{(i) } r_{12}^{\,0} \qquad \text{(iii) } r_{12}^{-1} r_{13}^{-1} \qquad \text{(v) } r_{12}\, r_{23}/r_{13} \qquad \text{(vii) } r_{12}\, r_{34}/r_{23}$$

$$\text{(ii) } r_{12}^{-1} \qquad \text{(iv) } r_{12}^{-1} r_{34}^{-1} \qquad \text{(vi) } r_{12}\, r_{13}/r_{14} \qquad \text{(viii) } r_{12}\, r_{23}/r_{34}.$$

Because of the limits on the wave function three odd powers of the r_{ij}'s can occur only in one of the four ways v to viii. Any integral involving other than three odd powers of the interelectronic separation coordinates is expressible as a sum of one of the integrals i to iv. This is easily accomplished by expanding even powers of r_{ij} by the law of cosines; for odd powers, multiply numerator and denominator by that r_{ij}, expand the numerator by the law of cosines and the denominator by[30]

$$r_{12}^{-1} = \textstyle\sum_n r_{12<}^{\;n}/r_{12>}^{\;n+1} P_n(\cos\theta_{12}).$$

By the simple expedient of rotating the coordinate system when necessary, so that the Z axis is along the radius vector of one of the electrons, the θ integrations have the general form

$$f(g,n) = \int_0^{\pi} P_n(\cos\theta)\cos^g\theta \sin\theta d\theta\,. \tag{16}$$

With the notation

$$I\begin{pmatrix} s\ t\ u\ v\ w\ x \\ S\ T\ U\ V\ W\ X\end{pmatrix} = \int r_1^{\,k} r_2^{\,l} r_3^{\,m} r_4^{\,n} \exp[-(ar_1+br_2+cr_3+dr_4)]\, r_{12}^{\,s} r_{13}^{\,t} r_{14}^{\,u} r_{23}^{\,v} r_{24}^{\,w} r_{34}^{\,x}$$
$$\times\cos^S\theta_{12}\cos^T\theta_{13}\cos^U\theta_{14}\cos^V\theta_{23}\cos^W\theta_{24}\cos^X\theta_{34}\, dv_1\, dv_2\, dv_3\, dv_4\,, \tag{17}$$

we have for cases (i) to (iv):

$$I\begin{pmatrix}000000\\000000\end{pmatrix} = (4\pi)^4 A(k+2,a)A(l+2,b)A(m+2,c)A(n+2,d), \tag{18}$$

$$I\begin{pmatrix}-100000\\ S00000\end{pmatrix} = (4\pi)^4 A(m+2,c)A(n+2,d)\textstyle\sum_p \frac{1}{2}f(S,p)[V(l+p+2,k-p+1,b,a)+V(k+p+2,\,l-p+1,a,b)], \tag{19}$$

$$I\begin{pmatrix}-1-10000\\ S\ T0000\end{pmatrix} = (4\pi)^4 A(n+2,d)\textstyle\sum_p\sum_q \frac{1}{2}f(S,p)\frac{1}{2}f(T,q)[\,W(l+p+2,m+q+2,k-p-q,b,c,a)$$
$$+W(m+q+2,\,l+p+2,k-p-q,c,b,a)+W(m+q+2,k+p-q+1,\,l-p+1,c,a,b)$$
$$+W(l+p+2,k-p+q+1,m-q+1,b,a,c)+W(k+p+q+2,\,l-p+1,m-q+1,a,b,c)$$
$$+W(k+p+q+2,m-q+1,\,l-p+1,a,c,b)], \tag{20}$$

$$I\begin{pmatrix}-10000-1\\ S0000\ \ X\end{pmatrix} = (4\pi)^4\textstyle\sum_p\sum_q \frac{1}{2}f(S,p)\frac{1}{2}f(X,q)[V(l+p+2,k-p+1,b,a)+V(k+p+2,\,l-p+1,a,b)]$$
$$\times[\,V(m+q+2,n-q+1,c,d)+V(n+q+2,m-q+1,d,c)]\,. \tag{21}$$

The evaluation of the fifth integral has been discussed in detail by Burke.[31] His result multiplied by $4\pi A(n+2,d)$ obtains for the beryllium case. This is the only integral that is evaluated as an infinite series. (The first two or three terms usually suffice.) Bonham[32] avoids introducing the infinite series by means of Fourier transform techniques. However, for integrals involving other than 1s Slater-type orbitals, the method requires the taking of cumbersome derivatives. Roberts,[33] by means of Gaussian transformation techniques, has succeeded in obtaining a closed-form expression for this integral.

The evaluation of the three remaining integrals proceeds via an analysis analogous to that for case (v). We present only the results. Let us first make the following definitions:

$$J_{\alpha\beta}^{\gamma\delta}(k,l,m,n,i,j)=\int r_1^k r_2^l r_3^m r_4^n(\cos^i\theta_{\gamma\beta}\cos^j\theta_{12}r_{12}r_{\alpha\beta}r_{\gamma\sigma})$$

$$\times\exp[-(ar_1+br_2+cr_3+dr_4)]\,dv_1dv_2dv_3dv_4, \tag{22}$$

$$W1(k,l,m,a,b,c)=W(l+p+2,m+q+2,k-p-q-1,b,c,a)+W(m+q+2,l+p+2,k-p-q-1,c,b,a)$$

$$+W(m+q+2,k+p-q,l-p+1,c,a,b)+W(l+p+2,k-p+q,m-q+1,b,a,c)$$

$$+W(k+p+q+1,l-p+1,m-q+1,a,b,c)+W(k+p+q+1,m-q+1,l-p+1,a,c,b), \tag{23}$$

$$W2(k,l,m,a,b,c)=W(k+p+2,m+q-r+1,l-q-p,a,c,b)+W(m+q-r+1,k+p+2,l-q-p,c,a,b)$$

$$+W(m+q-r+1,l+p-q+1,k-p+1,c,b,a)+W(k+p+2,l+q-p+1,m-q,-r,a,b,c)$$

$$+W(l+p+q+2,k-p+1,m-q-r,b,a,c)+W(l+p+q+2,m-q-r,k-p+1,b,c,a). \tag{24}$$

With these definitions we have

Case (vi),

$$I\begin{pmatrix}11-1000\\00\ \ 0000\end{pmatrix}=J_{13}{}^{14}(k+4,l,m,n,0,0)+J_{13}{}^{14}(k+2,l+2,m,n,0,0)+J_{13}{}^{14}(k+2,l,m+2,n,0,0)$$

$$+J_{13}{}^{14}(k,l+2,m+2,n,0,0)-2[J_{13}{}^{14}(k+3,l+1,m,n,0,1)+J_{13}{}^{14}(k+1,l+1,m+2,n,0,1)$$

$$+J_{13}{}^{14}(k+3,l,m+1,n,1,0)+J_{13}{}^{14}(k+1,l+2,m+1,n,1,0)]+4J_{13}^{14}(k+2,l+1,m+1,n,1,1), \tag{25}$$

$$J_{13}{}^{14}(k,l,m,n,i,j)=(4\pi)^4\sum_p\sum_q\frac{f(j,p)}{2}\,\frac{f(i,q)}{2}\left(\frac{(n+2)!}{d^{n+3}}[W1(k,l,m,a,b,c)-W1(k,l,m,a+d,b,c)]\right.$$

$$\left.-(n+1)!\sum_{t=1}^{n+1}\frac{t}{(n+2-t)!d^{t+1}}W2(k+n-t+2,l,m,a+d,b,c)\right). \tag{26}$$

Case (vii),

$$I\begin{pmatrix}100-101\\000\ \ 000\end{pmatrix}=J_{34}{}^{23}(k+2,l,m+2,n,0,0)+J_{34}{}^{23}(k+2,l,m,n+2,0,0)+J_{34}{}^{23}(k,l+2,m+2,n,0,0)$$

$$+J_{34}{}^{23}(k,l+2,m,n+2,0,0)-2[J_{34}{}^{23}(k+2,l,m+1,n+1,1,0)+J_{34}{}^{23}(k,l+2,m+1,n+1,1,0)$$

$$+J_{34}{}^{23}(k+1,l+1,m+2,n,0,1)+J_{34}{}^{23}(k+1,l+1,m,n+2,0,1)]$$

$$+4J_{34}{}^{23}(k+1,l+1,m+1,n+1,1,1), \tag{27}$$

$$J_{34}{}^{23}(k,l,m,n,i,j)=(4\pi)^4\sum_p\sum_q\sum_r\tfrac{1}{2}f(j,p)\tfrac{1}{2}f(0,q)\tfrac{1}{2}f(i,r)R_R, \tag{28}$$

where $R_R=[(n+r+2)!/d^{n+r+3}]\,W2(k,l,m,a,b,c)$

$$+(n-r+1)!\sum_{t=0}^{t=n-r+1}\frac{1}{(n-r+1-t)!d^{t+1}}W2(k,l,m+n+r+2-t,a,b,c+d)$$

$$-(n+r+2)!\sum_{t=0}^{t=n+t+2}\frac{1}{(n+r+2-t)!d^{t+1}}W2(k,l,m+n+r+2-t,a,b,c+d). \tag{29}$$

Case (viii),

$$I\begin{pmatrix}10010-1\\00000\ \ 0\end{pmatrix}=J_{23}{}^{34}(k+2,l+2,m,n,0,0)+J_{23}{}^{34}(k,l+4,m,n,0,0)+J_{23}{}^{34}(k+2,l,m+2,n,0,0)$$

$$+J_{23}^{34}(k,l+2,m+2,n,0,0)-2[J_{23}^{34}(k+1,l+3,m,n,0,1)+J_{23}^{34}(k+1,l+1,m+2,n,0,1)$$

$$+J_{23}^{34}(k+2,l+1,m+1,n,1,0)+J_{23}^{34}(k,l+3,m+1,n,1,0)]+4J_{23}^{34}(k+1,l+2,m+1,n,1,1), \qquad (30)$$

$$J_{23}^{34}(k,l,m,n,i,j)=(4\pi)^4\sum_p\sum_q\sum_r \tfrac{1}{2}f(j,p)\tfrac{1}{2}f(i,q)\tfrac{1}{2}f(0,r)R_R, \qquad (31)$$

where R_R is given by Eq. (29).

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[1] A. W. Weiss, Phys. Rev. 122, 1826 (1961).

[2] C. Schwartz, Phys. Rev. 126, 1015 (1962).

[3] Oktay Sinanoğlu, Phys. Rev. 122, 493 (1960).

[4] L. Szasz, Z. Naturforsch. 14a, 1014 (1959); 15a, 909 (1960); J. Chem. Phys. 35, 1072 (1961); Phys. Rev. 126, 169 (1962); J. Math. Phys. 3, 1147 (1962); Phys. Rev. 132, 936 (1963); Z. Naturforsch. 22, 2109 (1967).

[5] E. A. Hylleraas, Z. Physik 54, 347 (1929).

[6] T. Kinoshita, Phys. Rev. 105, 1490 (1957); 115, 336 (1959).

[7] C. L. Pekeris, Phys. Rev. 112, 1649 (1958); 115, 1216 (1959).

[8] H. M. James and A. S. Coolidge, Phys. Rev. 49, 688 (1936).

[9] H. M. James and A. S. Coolidge, Phys. Rev. 55, 873 (1939).

[10] E. A. Burke, Phys. Rev. 130, 1871 (1963).

[11] K. F. Berggren and R. F. Wood, Phys. Rev. 130, 198 (1963).

[12] V. H. Smith, Jr., and S. Larsson, Uppsala University Quantum Chemistry Group Technical Report No. 186, 1967 (unpublished).

[13] R. K. Nesbet, Phys. Rev. 155, 51 (1967).

[14] See Ref. 8, Eq. (8).

[15] See, for example, S. S. Kuo, Numerical Methods and Computers (Addison-Wesley Publishing Co., Inc., Reading, Mass., 1965), Chap. 9.

[16] Atomic Energy Levels, National Bureau of Standards Circular No. 467, edited by C. E. Moore (U. S. Government Printing Office, Washington, D. C., 1949), Vol. 1. However, since relativistic and other minor effects have not been included in the determination of the wave function, it is more appropriate to compare the calculated energy to an "experimental" energy obtained by subtracting off these effects. In this way the "experimental" energy becomes −29.334 86 Ry. See C. W. Scherr, J. N. Silverman, and F. A. Matsen, Phys. Rev. 127, 830 (1962).

[17] C. C. J. Roothaan, L. M. Sachs, and A. W. Weiss, Rev. Mod. Phys. 32, 186 (1960).

[18] S. F. Boys, Proc. Roy. Soc. (London) A217, 136 (1953).

[19] V. V. Kibartas, V. I. Kavetskis, and A. P. Iutsis, Zh. Eksperim. i Teor. Fiz. 29, 623 (1955) [English transl.: Soviet Phys. – JETP 2, 481 (1956)].

[20] R. E. Watson, Phys. Rev. 119, 170 (1960).

[21] A. Kotchoubey and L. H. Thomas, J. Chem. Phys. 45, 3342 (1966).

[22] H. P. Kelly, Phys. Rev. 131, 684 (1963); 136, B896 (1964). An improved value of −0.089 76 Ry was found for the $2s^2$ correlation energy.

[23] D. F. Tuan and O. Sinanoğlu, J. Chem. Phys. 41, 2677 (1964).

[24] M. Geller, H. S. Taylor, and H. B. Levine, J. Chem. Phys. 43, 1727 (1965).

[25] O. Sinanoğlu and E. Mortenson, J. Chem. Phys. 34, 1078 (1961).

[26] L. Szasz and J. Byrne, Phys. Rev. 158, 34 (1967).

[27] J. Linderberg and H. Shull, J. Mol. Spectry 5, 1 (1960).

[28] For the CDC-6600 computer, which was used, single precision is 15 digits; double precision is 29 digits.

[29] Y. Öhrn and J. Nordling, J. Chem. Phys. 39, 1864 (1963).

[30] See, for example, H. Eyring, J. Walter, and G. E. Kimball, Quantum Chemistry (John Wiley & Sons, Inc., New York, 1944), p. 369.

[31] E. A. Burke, J. Math. Phys. 6, 1691 (1965). The numerical values of l and j in Eq. (5) and L and J in Eq. (21) should be interchanged.

[32] R. A. Bonham, J. Mol. Spectry 15, 112 (1965).

[33] P. J. Roberts, Proc. Phys. Soc. (London) 88, 53 (1966).