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On the Ground State of Lithium*

HUBERT M. JAMES AND ALBERT SPRAGUE COOLIDGE, *Harvard University*

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Wave functions of several forms have been applied to the treatment to the ground state of Li. It is found that errors in the representation of the K shell have but little effect on the computed ionization energy, and that a satisfactory orbital for the L electron can be constructed in a very simple form. The best wave function in which the relative positions of the K and L electrons are not taken into account gives an ionization energy in error by 0.05 ev. To take account of inter-shell polarization effects the Hylleraas method has been extended, and a wave function has been constructed which depends on the relative positions of all the electrons. A total energy in error by 0.068 ev (0.034 percent) has been computed, and the theoretical value of the ionization energy is fixed as 5.363 ± 0.007 ev against an observed 5.364 ev.

INTRODUCTION

THE lithium atom, a simple system with all the essential characteristics of the other more complicated and perhaps more interesting alkali metal atoms, has been the subject of several wave-mechanical investigations.[1] All these treatments have been characterized by the construction of the atomic wave function from one-electron orbitals, and may accordingly be considered as more or less satisfactory approximations to the Fock procedure.[2] In each case the computed atomic and ionic energies are in error by some 2.0 ev, while the errors in ionization energy (obtained as the difference of the computed atomic and ionic energies) are of the order of 0.1 ev. Wilson has reduced this error to 0.044 ev using for the K electrons the orbital $e^{-2.69r}$, and for the L electron $1.345re^{-0.665r}-e^{-1.5r}$. That so simple a method of treatment should yield such satisfactory values of the ionization energy is a matter of considerable interest. The reliability of these values must suffer, however, from their having been obtained as the difference of two quantities, each of which was much less accurately known; there is also no variation principle to assure us that the true value of the ionization energy is an upper limit monotonically approached by the calculated values as the wave functions improve.

We have therefore been interested in examining the effect on the ionization energy of various approximations in the atom and ion wave functions, in determining the theoretical ionization energy with considerable exactness, and in improving the determination of the energy and wave function of the complete three-electron system. Various steps in the passage from the Wilson function to the most flexible possible form readily suggest themselves. We have examined the following, which appear to be the most important: (a) improvement of the separate orbitals, for which Wilson used functions of somewhat limited flexibility, (b) improvement of the representation of the K electrons by removal of the requirement that they be represented by orbital functions, and (c) complete abandonment of orbitals in the construction of the wave functions of the systems. In the last two stages of our work we have employed the method of Hylleraas, which has been eminently successful in the treatment of the normal and first excited states of He,[3, 4, 5] which have many features in common with the ground state of Li. In principle the extension to the more complicated system is quite simple, but the practical difficulties encountered are rather serious. A description of the way in which these were overcome is reserved for later sections of this paper; we proceed now to a presentation and discussion of the results which we have obtained.

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* A preliminary notice of a portion of these results appeared in Phys. Rev. **47**, 700 (1935).

[1] E. B. Wilson, Jr., J. Chem. Phys. **1**, 210 (1933) and references given there.

[2] V. Fock, Zeits. f. Physik **61**, 126 (1930).

[3] E. A. Hylleraas, Zeits. f. Physik **54**, 347 (1929).

[4] E. A. Hylleraas and B. Undheim, Zeits. f. Physik **65**, 759 (1930).

[5] A. S. Coolidge and H. M. James (see paper in this issue, p. 676).

IMPROVEMENT OF THE ORBITAL FUNCTIONS

The wave functions hitherto used in treating Li have been of the form

$$\psi=\begin{vmatrix} K(1)\delta(\alpha/\sigma_1) & K'(1)\delta(\beta/\sigma_1) & L(1)\delta(\alpha/\sigma_1) \\ K(2)\delta(\alpha/\sigma_2) & K'(2)\delta(\beta/\sigma_2) & L(2)\delta(\alpha/\sigma_2) \\ K(3)\delta(\alpha/\sigma_3) & K'(3)\delta(\beta/\sigma_3) & L(3)\delta(\alpha/\sigma_3) \end{vmatrix},$$

where K, K' and L are the space parts of K and L orbitals, while $\delta(\alpha/\sigma_1)$, etc., are the spin functions introduced by Slater.[6] Actually $K(1)$ has always been taken to be identical with $K'(1)$, as would be the case in the ion, but is not required in the atom. Expanding the determinant above, we find $\psi=K'(1)\{K(2)L(3)-K(3)L(2)\}\delta(\beta/\sigma_1)\delta(\alpha/\sigma_2)\times\delta(\alpha/\sigma_3)+$two similar terms which differ by permutations which assign different spins to the electrons. Because of the different spin factors, no combination of two different terms can make any contribution to the matrix element of energy or unity corresponding to this function (so long as the Hamiltonian is assumed independent of the spin), so that these elements will be simply three times the contribution arising from any single term in combination with itself. Now this property can easily be seen to be a general one, possessed by any function having the symmetry appropriate to Li. We may write such a function

$$\begin{aligned}\psi=\varphi(1,\,2,\,3)\delta(\beta/\sigma_1)\delta(\alpha/\sigma_2)\delta(\alpha/\sigma_3)\\ +\varphi(2,\,3,\,1)\delta(\beta/\sigma_2)\delta(\alpha/\sigma_3)\delta(\alpha/\sigma_1)\\ +\varphi(3,\,1,\,2)\delta(\beta/\sigma_3)\delta(\alpha/\sigma_1)\delta(\alpha/\sigma_2),\end{aligned}$$

the only restriction upon $\varphi(1, 2, 3)$ being that it must be antisymmetrical in the coordinates of electrons 2 and 3. With this understanding, the whole discussion can be carried out on the basis of the function $\varphi(1, 2, 3)$.

For separate-orbital functions, we have

$$\varphi(1,\,2,\,3)=K'(1)\{K(2)L(3)-K(3)L(2)\}.$$

The Fock function is the best function of this form, and it is clear that Wilson's function is not a very close approximation to it. His K orbital in particular was rather inflexible, and a treatment of He using such orbitals gives decidedly poorer results than the Hartree method, and, *a fortiori*, the Fock method. In the next section we shall deal with even more radical changes of the core function than improvement of the orbitals involved, and it will become apparent that no appreciable change in the ionization energy is to be expected from such a modification of Wilson's function. We have therefore been interested only in the effect of increasing the flexibility of the L orbital, changes in which will be more strongly reflected in ionization energy. We find that with an L orbital of the form $L(1)=c_1r_1e^{-0.665r_1}+c_2e^{-1.25r_1}+c_3e^{-1.5r_1}+c_4e^{-1.75r_1}$ improvement of just 0.002 ev over Wilson's value could be obtained. An attempt to make a similar improvement in his function by replacing the term $r_1e^{-0.665r_1}$ by $c_1r_1e^{-\alpha_1r_1}+c_2r_1e^{-\alpha_2r_1}+c_3r_1e^{-\alpha_3r_1}$ gave no gain at all. Evidently Wilson's L orbital, though of very simple form, is about as good as any which might be used in functions of this type; of the residual error in his ionization energy only 0.002 ev can be attributed to lack of flexibility in this orbital.

IMPROVEMENT IN INNER SHELL REPRESENTATION

In the description of Li, the use of orbitals in connection with the K electrons is clearly inadequate, as it is in the treatment of the analogous He. The representation may be improved by similar methods, thus giving us a function of the separate-shell type, for which the general form is

$$\varphi(1,\,2,\,3)=KK(1,\,2)L(3)-KK(1,\,3)L(2),$$

where $KK(1, 2)$ is an unrestricted function of the relative coordinates of the two electrons, having the general nature of a wave function for Li^+, but not necessarily symmetrical in 1 and 2.

We have computed the energy of a number of functions of this form, both with the simple outer function $L=re^{-0.65r}$, and with the better one $L=1.4re^{-0.65r}-e^{-1.5r}$, which is nearly the same as Wilson's. Table I contains the results, as well as a description of the core functions investigated. With the exception of E, the core functions will be recognized as of the Hylleraas type, modified as discussed in our paper on excited He.

Function E is of a new type, which can be regarded as derived from a Hylleraas function by expanding the powers of r_{12} as functions of r_1, r_2, and $\cos\theta_{12}$, and then selecting a finite number of the resulting terms, with coefficients to be varied independently. In these terms there are dis-

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[6] J. C. Slater, Phys. Rev. **34**, 1293 (1929).

TABLE I. *Variation of ionization energy with inner shell functions.*
Energies in electron volts.

INNER FUNCTION ALONE			COMBINED WITH P		COMBINED WITH Q	
Symbol	Ion energy	Error	Atom	Error in ionization	Atom	Error in ionization
A	−192.89	+4.22	−198.19	−0.060	−198.27	+0.019
B	−195.49	+1.62	−200.78	−0.077	−200.83	−0.028
C	−195.53	+1.57	−200.82	−0.080	−200.85	−0.048
D	−196.30	+0.81	−201.56	−0.095	......	......
E	−197.02	+0.09	−202.28	−0.094	−202.32	−0.057
F	−197.05	+0.05	−202.32	−0.093	......	......
Ideal	−197.10	0.00	(−202.37)	(−0.093)	(−202.39)	(−0.056)

The functions used are as follows (not normalized):

A $e^{-3(r_1+r_2)}$.

B $e^{-3(r_1+r_2)}[c_1+c_2(r_1+r_2)]$.

C $e^{-2.6875(r_1+r_2)}$.

D $e^{-3(r_1+r_2)}[c_1+c_2(r_1+r_2)+c_3r_1r_2+c_4(r_1^2+r_2^2)]$.

E $e^{-3(s_{12}+g_{12})}[c_1+c_2g_{12}+c_3s_{12}^2g_{12}^{-1}+c_4g_{12}^2+c_5s_{12}+c_6s_{12}\cos\theta_{12}+c_7s_{12}^{-1}\cos^2\theta_{12}]$.

F $e^{-3(r_1+r_2)}[c_1+c_2(r_1+r_2)+c_3r_1r_2+c_4(r_1^2+r_2^2)+c_5r_{12}+c_6r_{12}^2]$.

P $r_3e^{-0.65r_3}$.

Q $1.4r_3e^{-0.65r_3}-e^{-1.5r_3}$.

The coefficients c_n were determined so as to minimize the ion energy. In constructing the atomic function, the same values were used.

The symbols g_{12} and s_{12} in function E represent, respectively, the greater and the smaller of r_1 and r_2.

The last row is an extrapolation, in which the error in the ion energy has been made to vanish.

continuities of derivative when $r_1=r_2$ which make finite contributions to the kinetic energy, but do not destroy their usefulness. We have applied such a function to the treatment of the ground state of He, and with the inclusion of nine terms have reduced the error in the computed energy to less than 0.02 ev. Since this error is some three times that given by Hylleraas' six-term function and the computations are no easier these functions are not recommended as a substitute under such conditions. It was found, however, that when it was desired to add a third electron to the system and to neglect polarization terms with this electron (as in the present case) the treatment was more conveniently carried out with this than with the Hylleraas function; hence the present computation. This ceases to be true, however, when inter-shell polarization effects must be included. Since functions of this type seem to be restricted in usefulness and the methods of handling them in the three-electron problem are quite complicated we omit any further description of them.

It is apparent from Table I that, for the given L orbitals, the ionization energy comes out almost independent of the representation of the inner shell, so long as the latter is not too bad, and that the small changes which do occur are similar with both orbitals. This would undoubtedly hold for any good L orbital. An obvious corollary is that when L has been given the best form for use in conjunction with some reasonably good core function, this will be very nearly the best form for any other good representation of the inner shell. As an example, we note that the linear coefficient in function Q is essentially the same whether it minimizes the atomic energy with core C or with core E. Now, computation with core function C has shown that Wilson's L function gives a result better than function Q by 0.004 ev, and that a further 0.002 ev can be gained by still further improving the outer orbital. In view of the above discussion we may confidently expect that the values in the last column of Table I (at least the last few entries, in which we are primarily interested) would be likewise raised by 0.006 ev if Q were replaced by the best possible L function.

The core functions from A to F are progressively better approximations to the true ion function. It is of interest to attempt an extrapolation to determine the energy which would be obtained by combining this function with various outer orbitals. The last row of Table I gives such estimates. In particular, if the best possible L function were used, the residual error would be very close to −0.050 ev, which is evidently the error inherent in the forced separation of the shells.

In the examples so far given the core function and the ion function have been identical, and there seems to be no doubt as to the propriety of computing the ionization energy as the difference of the computed energies of atom and ion. The best function for the atom core having a given form will, however, presumably differ from the best ion function of the same form; in fact, as has already been pointed out, the ion function has different symmetry properties from the best core function. Thus there arises the question as to how the ionization energy shall be determined. In order to investigate this point, we made computations differing from the $F-P$ combination of Table I in that, in the first case, the coefficients c_n were allowed to take on values minimizing the atomic energy, and, in the second case, in that this adjustment was made after separate coefficients were assigned to the terms in r_1 and r_2, and to those in r_1^2 and r_2^2. In the first case the energy was reduced by 0.0003 ev, while the second charge permitted a further improvement of 0.0002 ev. We conclude that there is no significant difference between the best ion function and the best core function obtainable with a given series of the sort which we use. This is fortunate, for it relieves us of the necessity of determining the coefficients of the ionic function and introducing them explicitly as restrictions upon the variation carried out to give the corresponding atomic function. We need only solve the secular equations for atomic and ionic problems, and take the difference as the ionization energy. It also enables us to save labor by assuming that terms which in the ionic function must have the same coefficient may be treated as preserving this relation in the atom, thereby forming, for purposes of variation, a single term.

Physical Interpretation

Qualitatively, these results are easy to understand. If we had complete flexibility in both KK and L, we should arrive, on minimizing the total energy, at a definite function of a rather interesting type, in which the relation between the L electron and the K shell taken as a whole is formally that between the L and K electrons in excited He, particularly in the $1s2s\,^3S$ state, according to the Fock approximation. In line with our discussion of the Fock function for the corresponding singlet state (no treatment of the triplet state being available), we may expect the defects of this function to be, speaking roughly, that it neglects the polarization of the core by the valence electron and the consequent contraction of the outer orbit, thereby yielding too high a total energy. We would also expect that the K shell function will be but slightly different from that of the free ion. Both the distortion of the ion function and the polarization effects should be less pronounced in Li than in $1s2s\,^3S$ He, because the core electrons are more firmly bound. Now, in $1s2s\,^1S$ He, we have found that the defects of the Fock function are responsible for an energy error of 0.078 ev; this should be less for the triplet state because the electrons are to some extent kept apart by the antisymmetry. The error in the total energy of the best separated-shell function (indicated by SS) for Li should then be a few hundredths of a volt only, and this will also be the error in the ionization energy if we disregard the difference between the correct ion function and the KK factor in our atomic function.

As computed for a separated-shell function the energy is roughly separable into energy of the core, energy of the valence electron in the average field of the core, and exchange energy, of which the last two parts give the ionization energy. Starting with the function SS, we may replace the core factor by another which may contain large errors with respect to the mutual relations of the core electrons, but which has substantially the same average field. While the total energy will be seriously affected, the ionization energy will be influenced only through the variation of the exchange term, a second-order effect which might be of either sign. On the other hand, if the L orbital is varied the change in the ionization energy will arise principally from modification of the energy of the valence electron, with the change in exchange energy making a second-order contribution. Thus the ionization energy is essentially a characteristic of the L orbital used, with a minor dependence on the core function through the exchange energy. When functions permitting separation of the shells give ionization energies in error by less than 0.05 ev, as in Wilson's work, this cannot be taken as evidence that the function is a good one; thus, it is clear from Table I that some combination of A and B could be found to give exactly the correct ionization energy. This effect is due to the compensating errors in the exchange energy which arise from a poor core function. To obtain a more accurate value for the ionization energy which is also reliable one must deal with the mutual polarization of the K and L shells. It is to this problem that the next section of this paper is devoted.

Inclusion of Polarization Effects Between the Shells

For the computations of this section, we have extended our modification of the Hylleraas method, constructing new terms in our trial series by multiplication of the terms already found most useful by powers of r_{13} and r_{23} and/or by suitable negative powers of r_3 (assigning the number 3 to the L electron). The new terms (as well as all of those previously discussed except those of the function E) can be specified as follows: We choose as variables $\rho_1=\kappa r_1, \cdots \rho_{23}=\kappa r_{23}$, in which a possible additional degree of flexibility is gained by introducing the scale-constant κ. Let

$$\zeta[k, m, n/\gamma, \delta, \delta] = (\kappa^9/4\pi)^{\frac{1}{2}} e^{-(\gamma\rho_3+\delta\rho_2+\delta\rho_1)} \rho_3{}^k \rho_2{}^m \rho_1{}^n,$$

$$\xi[k, m, n/\gamma, \delta, \delta] = (\kappa^9/4\pi)^{\frac{1}{2}} e^{-(\gamma\rho_2+\delta\rho_3+\delta\rho_1)} \rho_2{}^k \rho_3{}^m \rho_1{}^n.$$

Our terms in the series for $\varphi(1, 2, 3)$ then have the forms

$$f[k, m, n, p]=\rho_{23}{}^p\{\zeta[k, m, n/\gamma, \delta, \delta] - \xi[k, m, n/\gamma, \delta, \delta]\},$$

$$g[k, m, n, p]=\rho_{12}{}^p\zeta[k, m, n/\gamma, \delta, \delta] - \rho_{13}\xi[k, m, n/\gamma, \delta, \delta],$$

$$h[k, m, n, p]=\rho_{13}{}^p\zeta[k, m, n/\gamma, \delta, \delta] - \rho_{12}\xi[k, m, n/\gamma, \delta, \delta],$$

$$f[k^*, m, n, p]=\rho_{23}{}^p\{\zeta[k, m, n/\gamma^*, \delta, \delta] - \xi[k, m, n/\gamma^*, \delta, \delta]\}, \quad \text{etc.}$$

In the bulk of the work of this section, the constants had the values $\delta=3$, $\gamma=0.65$, $\gamma^*=1.5$, $\kappa=1$. We postpone for the present a discussion of their selection, as well as of the choice of appropriate terms. The most general extension of the Hylleraas method would, of course, require provision for terms with powers of two or three interelectronic distances occurring simultaneously, which could not be represented in the above notation. We have avoided this complication. We have also, in accordance with the results of the previous section, treated $\{g[k, m, n, p]+g[k, n, m, p]\}$ as a compound term with a single coefficient. It will be seen that the terms g are just those occurring in the previously discussed functions of the separate-shell type. The new terms f and h allow for detailed treatment of the reactions between the outer electron and the inner one having the same and the opposite spin, respectively.

It might appear that so long as one's interest is restricted to the ionization energy it would be possible to ignore the terms $g[k, m, n, p]$, $p\neq 0$, which permit an accurate treatment of the core. Thus one would regard the atomic function as constructed from a core function, depending on r_1 and r_2, and an L orbital depending on r_3, r_{13}, and r_{23}, and would argue from Table I that the ionization energy should be practically unaffected by change in the core function. But it must be noted that we have no guarantee that results parallel to those in Table I would be obtained if the outer function were freely variable. For r_{12}, r_{13} and r_{23} cannot take on their magnitudes with complete independence, and from this arises the possibility that (in a very awkward manner, to be sure) some defects in the core function might be compensated for by adjustment of the inter-shell polarization terms. Thus with a core function poor enough to bring this effect into play the calculated ionization energy might appreciably exceed the actual value. It is accordingly necessary to carry out the work with core and atomic functions so good that such second-order terms can be safely neglected, and this seems to require a fairly accurate treatment of the effects on each other of the K electrons.

As a basis for our work we have chosen the atomic function constructed from the Hylleraas core function F and the Wilson L orbital, omitting, however, four of the twelve terms with an estimated error of 0.001 ev. To this function we have added nine new terms designed to take account of the polarization effects, obtaining a total energy in error by 0.068 ev. It was possible to make a fairly definite estimate of the limit attainable by the inclusion of indefinitely many such terms, including those with higher powers of r_{13} and r_{23} and combinations of such powers, according to the general method which we have previously explained.[7] Such an estimate indicates a convergence limit in excess of the experimental value by 0.051 ± 0.007 ev. Now, this is, within the limit of uncertainty, exactly the error which we ascribed to the defective core factor of the function before the polarization terms were included,—that is to say, it is the error of the best free ion function which can be constructed out of the terms which remain when we write down the terms in our best atomic function and then strike out all factors referring to r_3, r_{13}, or r_{23}. It appears then that to a satisfactory degree of approximation, the core function retains its identity even in the correct, nonseparable atomic function; that our atomic function is so good an approximation that the errors due to imperfect representation of the inner shell and to incomplete treatment of the polarization are additive. To the extent that this is true, we may speak of the ionization energy corresponding to our func-

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[7] H. M. James, A. S. Coolidge and R. D. Present, J. Chem. Phys. **4**, 187 (1936).

tion, even though it is of a nonseparable type. Our best calculated ionization energy is thus 5.347 ev, and the extrapolated value 5.363 ±0.007 ev, as compared with the experimental 5.364 ev.

We have not determined the coefficients of our best 17-term function. We give here a comparatively simple normalized function which is very nearly as good.

$$\begin{aligned}\varphi(1,2,3) = {} & 8.70800g[1000]+0.46443\{g[1010]\\ & +g[1100]\}+3.74530\{g[1020]+g[1200]\}\\ & -2.25446g[1110]+4.66553g[1001]\\ & -0.60372g[1002]-7.76625g[0^*000]\\ & -1.85902\{g[0^*010]+g[0^*100]\}\\ & +1.57214f[0001]+1.93299h[0001].\end{aligned}$$

It will be recalled that the complete wave function is the sum of three such terms, differing by systematic permutations of the electron numbers, each multiplied by a different spin factor. Accordingly the above expression for $\varphi(1, 2, 3)$ has been normalized to 1/3.

The energy given by this function is as follows:

	Total energy, $R_{\mathrm{Li}}h$,	*Free ion,* $R_{\mathrm{Li}}h$,	*Ionization* (ev)
Experiment	−14.95784	−14.56160	5.364
Function	−14.95215	−14.55776	5.339
Error	0.00569	0.00384	−0.025
Percent	0.038	0.026	0.47

Of the total "polarization energy" of 0.05 ev about three-eighths comes from the pair of electrons with the same spin, and five-eighths from the other pair. This inequality is in agreement with the general rule that polarization is more important in singlet than in triplet states of two-electron systems.

METHOD OF CALCULATION

The calculation of the matrix components of energy and unity hinges upon the evaluation of the integrals

$$I(abcdef/\alpha\beta\gamma)=\int dV e^{-(\alpha r_1+\beta r_2+\gamma r_3)} r_1{}^a r_2{}^b r_3{}^c r_{23}{}^d r_{31}{}^e r_{12}{}^f.$$

Consider first the case that d, e, f are each either 0 or −1. If e (say) is 0, then the integral is readily evaluated by taking as variables of integration r_1, r_2, r_3, $\cos\theta_{12}$, $\cos\theta_{23}$, φ_{13} (the angle between the plane containing r_1 and r_2 and that containing r_3 and r_2) and three unspecified angles giving the orientation of the whole system in space. The last four variables do not enter the integrand. We set $1/r_{23}=\Sigma_n s_{23}{}^n g_{23}{}^{-n-1}P_n(\cos\theta_{23})$ and $1/r_{12}=\Sigma_n s_{12}{}^n g_{12}{}^{-n-1}\times P_n(\cos\theta_{12})$, where s_{ij}, g_{ij} mean, respectively, the smaller and the greater of r_i, r_j. Upon integration over the cosines, the terms for $n>0$ disappear, and we have, for example.

$$\begin{aligned}I(abc-10-1/\alpha\beta\gamma)=64\pi^3\{ & W_{a+2,\,b+1,\,c+1}(\alpha,\beta,\gamma)\\ & +W_{a+2,\,c+2,\,b}(\alpha,\gamma,\beta)+W_{b+2,\,a+1,\,c+1}(\beta,\alpha,\gamma)\\ & +W_{b+2,\,c+1,\,a+1}(\beta,\gamma,\alpha)+W_{c+2,\,a+2,\,b}(\gamma,\alpha,\beta)\\ & +W_{c+2,\,b+1,\,a+1}(\gamma,\beta,\alpha)\},\end{aligned}$$

where

$$W_{f,\,g,\,h}(\alpha,\beta,\gamma)=\int_0^\infty dx\int_x^\infty dy\int_y^\infty dz x^f e^{-\alpha x}y^g e^{-\beta y}z^h e^{-\gamma z}.$$

$$I(abc-100/\alpha\beta\gamma)=64\pi^3 A_{a+2}(\alpha)\{V_{b+2,\,c+1}(\beta,\gamma)+V_{c+2,\,b+1}(\gamma,\beta)\},$$

where
$$A_j(\alpha)=\int_0^\infty dx x^j e^{-\alpha x}$$

and
$$V_{m,\,n}(\beta,\gamma)=\int_0^\infty dy\int_y^\infty dz y^m e^{-\beta y}z^n e^{-\gamma z}.$$

We note that
$$A_j(\alpha)V_{m,\,n}(\beta,\gamma)=W_{j,\,m,\,n}(\alpha,\beta,\gamma)+W_{m,\,j,\,n}(\beta,\alpha,\gamma)+W_{m,\,n,\,j}(\beta,\gamma,\alpha).$$

If $d=e=f=-1$, it does not seem possible to find a symmetrical method of evaluating the integral. We have expanded $1/r_{13}$ as before in terms of $P_n(\cos\theta_{13})$, which, by the theorem of biaxial harmonics, can be replaced by $P_n(\cos\theta_{12})$ $P_n(\cos\theta_{23})$ plus terms which disappear upon integration over φ_{13}. We thus find

$$\begin{aligned}I(abc-1-1-1/\alpha\beta\gamma)= {} & 64\pi^3\Sigma_n(2n+1)^{-2}\\ & \times\{W_{a+2n+2,\,b+1,\,c-2n}(\alpha,\beta,\gamma)+W_{a+2n+2,\,c+1,\,b-2n}(\alpha,\gamma,\beta)\\ & +W_{b+2n+2,\,a+1,\,c-2n}(\beta,\alpha,\gamma)+W_{b+2n+2,\,c+1,\,a-2n}(\beta,\gamma,\alpha)\\ & +W_{c+2n+2,\,a+1,\,b-2n}(\gamma,\alpha,\beta)+W_{c+2n+2,\,b+1,\,a-2n}(\gamma,\beta,\alpha)\}.\end{aligned}$$

The final formula is thus symmetrical, and the summation converges rapidly.

Because of our not considering individual terms in which more than one interelectronic coordinate explicitly appear, we did not encounter the case that $e>0$. (This case could, however, be readily handled by extending the following method.) By means of the relation

$$r_{23}{}^2=r_2{}^2+r_3{}^2-2r_2r_3\cos\theta_{23}$$

it is possible to reduce any case of positive d by steps of two powers of r_{12} until one reaches either $d=0$ or $d=-1$. The resulting expressions will have the same form as the integral I, except that some of them will now contain powers of $\cos\theta_{23}$ in the integrand. These can readily be treated by the methods indicated above. The same reduction applies to the case that $f>0$. It was found advantageous to work out the explicit formulas, in terms of the W's, giving $I(abcdef/\alpha\beta\gamma)$ for every set of numbers d, e, f which we required, as this resulted in considerable cancellation, and also improved the rapidity of convergence when all three numbers were odd and a summation had to be used.

The first step in the calculation is the construction of tables of the integrals A, V, and W, according to the following definitions and recurrence relations. By the systematic use of the latter, the work can be made self-checking by verifying that two independent chains of calculations, in which the relations are applied in different order, lead to the same final value.

$$A_j(\alpha)=\int_0^\infty e^{-\alpha x}x^j dx,\quad j\geqq 0.$$

$$V_{mn}(\alpha,\beta)=\iint_{x<y} e^{-\alpha x}x^m e^{-\beta y}y^n dxdy,\quad m\geqq 0,\quad m+n\geqq -1.$$

$$W_{fgh}(\alpha,\beta,\gamma)=\iiint_{x<y<z} e^{-\alpha x}x^f e^{-\beta y}y^g e^{-\gamma z}z^h dxdydz,$$
$$f\geqq 0,\quad f+g\geqq -1,\quad f+g+h\geqq -2.$$

$$A_o(\alpha)=1/\alpha;$$

$$A_j(\alpha)=(1/\alpha)^j A_{j-1}(\alpha),\quad j\geqq 1.$$

$$V_{o,\,-1}(\alpha,\beta)=\frac{1}{\alpha}\log\frac{\alpha+\beta}{\beta};$$

$$^*V_{o,\,n}(\alpha,\beta)=(1/\alpha)[A_n(\beta)-A_n(\alpha+\beta)],\quad n\geqq 0;$$

$$V_{m,\,n}(\alpha,\beta)=(1/\alpha)[mV_{m-1,\,n}(\alpha,\beta)-A_{m+n}(\alpha+\beta)],$$
$$m\geqq 1,\quad m+n\geqq 0;$$

$$=(1/\beta)[A_{m+n}(\alpha+\beta)+nV_{m,\,n-1}(\alpha,\beta)],$$
$$m\geqq 0,\quad m+n\geqq 0;$$

$$=\frac{1}{\alpha+\beta}[mV_{m-1,\,n}(\alpha,\beta)+nV_{m,\,n-1}(\alpha,\beta)],$$
$$m\geqq 1,\quad m+n\geqq 0.$$

$$^*W_{o,\,g,\,h}(\alpha,\beta,\gamma)=(1/\alpha)[V_{g,\,h}(\beta,\gamma)-V_{g,\,h}(\alpha+\beta,\gamma)],$$
$$g\geqq 0,\quad g+h\geqq -1.$$

$$W_{f,\,g,\,h}(\alpha,\beta,\gamma)=(1/\alpha)[fW_{f-1,\,g,\,h}(\alpha,\beta,\gamma)$$
$$-V_{f+g,\,h}(\alpha+\beta,\gamma)],\quad f\geqq 1,\quad f+g\geqq 0,\quad f+g+h\geqq -1;$$

$$=(1/\beta)[gW_{f,\,g-1,\,h}(\alpha,\beta,\gamma)$$
$$+V_{f+g,\,h}(\alpha+\beta,\gamma)-V_{f,\,g+h}(\alpha,\beta+\gamma)],$$
$$f\geqq 0,\quad f+g\geqq 0,\quad f+g+h\geqq -1;$$

$$=(1/\gamma)[hW_{f,\,g,\,h-1}(\alpha,\beta,\gamma)$$
$$+V_{f,\,g+h}(\alpha,\beta+\gamma)],\quad f\geqq 0,\quad f+g\geqq -1,\quad f+g+h\geqq -1;$$

$$=\frac{1}{\alpha+\beta+\gamma}[fW_{f-1,\,g,\,h}(\alpha,\beta,\gamma)$$
$$+gW_{f,\,g-1,\,h}(\alpha,\beta,\gamma)+hW_{f,\,g,\,h-1}(\alpha,\beta,\gamma)],$$
$$f\geqq 1,\quad f+g\geqq 0,\quad f+g+h\geqq -1.$$

By reversing these recurrence relations, the functions can be computed for negative n, g, and h, within the limits for which they remain finite. It is well to avoid the relations marked,* as the computation of tables of all the W's required to construct all the I's for a given choice of α, β, γ, can then be based upon preliminary tables of $A(\alpha+\beta+\gamma)$ and of $V(\alpha,\beta+\gamma)$, $V(\beta,\alpha+\gamma)$, $V(\gamma,\alpha+\beta)$, $V(\alpha+\beta,\gamma)$, $V(\beta+\gamma,\alpha)$ and $V(\alpha+\gamma,\beta)$.

Each term in our trial series consists of two parts, but because of the symmetry of the Hamiltonian operator, the matrix elements of energy and unity between any two such terms contain but two components, each taken twice. These components are computed separately. The elements of unity need no further discussion. Those of energy are found to fall into two classes, according as the interelectronic distances specifically involved in the combining functions refer to the same or to different pairs of electrons. The first class gives rise to the integral

$$(2\kappa^9/64\pi^3)\int dV\{e^{-(\alpha'\rho_a+\beta'\rho_b+\gamma'\rho_c)}\rho_a{}^{k'}\rho_b{}^{m'}\rho_c{}^{n'}\rho_{ab}{}^{p'}\}$$
$$\times H\{e^{-(\alpha\rho_a+\beta\rho_b+\gamma\rho_c)}\rho_a{}^k\rho_b{}^m\rho_c{}^n\rho_{ab}{}^p\}=\kappa^2L+\kappa M;$$

$$L=-(\alpha^2+\beta^2+\gamma^2)I(000,\,000)+\alpha(2k+2+p)I(-100,\,000)$$
$$-k(k+1+p)I(-200,\,000)+\beta(2m+2+p)$$
$$\times I(0-10,\,000)-m(m+1+p)I(0-20,\,000)$$
$$+\gamma(2n+2)I(00-1,\,000)-n(n+1)I(00-2,\,000)$$
$$+p\{-(m+k+2+2p)I(000,00-2)-\alpha I(-120,00-2)$$
$$+\alpha I(100,00-2)+kI(-220,00-2)-\beta I(2-10,00-2)$$
$$+\beta I(010,\,00-2)+mI(2-20,\,00-2)\}.$$

$$M=I[000,\,-100]+I[000,\,0-10]+I[000,\,00-1]$$
$$-3I[-100,\,000]-3I[0-10,\,000]-3I[00-1,\,000].$$

In these formulas, $I[uvw,\ xyz]$ is an abbreviation for

$$I[k+k'+u,\ m+m'+v,\ n+n'+w,\ x,\ y,$$
$$p+p'+z/\alpha+\alpha',\ \beta+\beta',\ \gamma+\gamma'].$$

The second class of combinations produces the integral

$$(2\kappa^9/64\pi^3)\int dV\{e^{-(\alpha'\rho_a+\beta'\rho_b+\gamma'\rho_c)}\rho_a{}^{k'}\rho_b{}^{m'}\rho_c{}^{n'}\rho_{ab}{}^{p'}\}$$
$$\times H\{e^{-(\alpha\rho_a+\beta\rho_b+\gamma\rho_c)}\rho_a{}^k\rho_b{}^m\rho_c{}^n\rho_{bc}{}^p\}.$$

The value of this integral is represented by the same formula as before, provided that $I[uvw,\ xyz]$ is now understood to be an abbreviation for

$$I[k+k'+u,\ m+m'+v,\ n+n'+w,\ p'+x,\ y,$$
$$p+z/\alpha+\alpha',\ \beta+\beta',\ \gamma+\gamma'].$$

These formulas are not symmetrical; the coefficients of the I's are determined solely by one of the combining functions. This is in practice rather an advantage, since it provides two different methods of calculating the components, and thereby checking the rather treacherous step of picking out the coefficients. A symmetrical formula could, if desired, be worked out by a method which we have discussed in a previous paper.[8] The same paper contains a description of the process of setting up and solving the secular equation, and thereby determining the best function which can be constructed from a given selection of terms.

Choice of Parameters and Terms

It would be desirable to have a form of trial function permitting independent variation of the screening constants for the inner and outer electrons, but this degree of flexibility could not be combined with that secured by the use of many terms with adjustable coefficients without tremendously multiplying the labor of computation. With our definition of the trial function, the screening parameters are $s_1=\kappa\delta$ for the inner and $s_2=\kappa\gamma$, $s_2{}^*=\kappa\gamma^*$ for the outer orbital. The only practicable variation, that of κ, changes all three in the same ratio. It is therefore important to start with suitable ratios of δ, γ, and γ^*, and this can most easily be accomplished by making them equal to the values which s_1, s_2, and $s_2{}^*$ are expected to have, relying upon variation in κ only for slight additional improvement. Accordingly, γ and γ^* were fixed by rounding off Wilson's values, taking $\gamma=0.65$, $\gamma^*=1.5$. To fix δ, we investigated the energy of the ion as given by a six-term function similar to F of Table I but with variable screening parameter. Table II contains the results, which indicate that

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[8] H. M. James and A. S. Coolidge, J. Chem. Phys. **1**, 825 (1933).

TABLE II. *Computed energy of* Li^+, *as function of screening constant* s_1.

s_1	ION ENERGY, $R_{Li}h$	ERROR (ev)	s_1	ION ENERGY, $R_{Li}h$	ERROR (ev)
2.7	−14.55844	0.043	3.0	−14.55776	0.052
2.85	−14.55850	0.042	3.24	−14.55452	0.096

$s_1=2.79$ is the best value, and would give an energy error of 0.041 ev, or 0.020 percent, to be compared with the 0.014 percent error in Hylleraas' treatment of He, in which the same six terms were used. However, when many terms in the series are present, readjustment among the coefficients takes care of considerable variations in the screening constant, which therefore need not be very carefully chosen. We selected $\delta=3$ for ease in computing. A smaller value would have improved our total energy by 0.011 ev, but, in view of the results already presented, would not have affected our ionization energy appreciably.

With δ, γ, and γ^* so fixed, the effect of taking κ different from 1 can be anticipated. The outer orbital will be directly influenced by the change in s_2 and s_2^*, but since we have already chosen practically the best values for these constants, this will cause but a second-order change in the ionization energy. A poor choice of γ and γ^* could have been to a large degree corrected by varying κ. The effect on the core function of such a variation will be small, owing to readjustment of coefficients, and the residual effect will not be large enough sensibly to alter the ionization energy. We conclude that, so far as ionization energy is concerned, the chief usefulness of the variable κ is to correct errors in choice of γ and γ^*, and that in our case little gain could be expected. We have verified these relations by calculations with a single-term L orbital, for which our γ is not the best value of s_2.

In selecting terms, we first set up a function for the ion, using the terms occurring in Hylleraas' function for the analogous ground state of He. Upon multiplying these by the main term of the L orbital, re^{-s_2r}, we obtain the six terms $g[1000]$, $g[1010]+g[1100]$, $g[1020]+g[1200]$, $g[1110]$, $g[1001]$, and $g[1002]$, the best combination of which gives an ionization energy error of 0.093 ev ($F-P$ combination, Table I). To these terms there correspond six "star" terms, $g[0^*000]$, $g[0^*010]+g[0^*100]$, etc., arising from the minor term $e^{-s_2^*r}$ in the L orbital. From analogy with results with core function E, we should expect that inclusion of these terms would reduce the error to -0.056 ev. It was actually found that the first two star terms alone sufficed to carry us within 0.005 ev of this value, and we did not go to the labor of computing the matrix elements required for the remaining terms. We did find that inclusion of the additional terms $g[2000]$ and $g[1^*000]$ produced an improvement of 0.006 ev, leaving an error of -0.055 ev. This improvement is clearly due to perfecting the L orbital; it is exactly the same as was found with the crude core function C upon going from orbital Q to the best combination of six terms, which is a rather striking example of the degree to which corrections for different sorts of defects in the function are additive, and supports our conclusion that the ionization energy error for the best separate-shell function is -0.050 ev.

To take account of inter-shell polarization, we included the following additional terms: $f[0001]$, $f[1001]$, $f[0^*001]$, $h[0001]$, $h[0011]+h[0101]$, $h[1001]$, and $h[0^*001]$. The writers' discussion[5] of the most desirable form for polarization terms, when applied to this case, suggests the usefulness of $f[0001]$ and $h[0001]$, or modifications of these terms in which γ is somewhat increased. These are, indeed, the most helpful of the above terms. The terms $f[1001]$ and $h[1001]$, use of which would correspond to taking account of polarization by introducing the factor $(1+cr_{ij})$, are almost completely without value. However, as is also suggested by the argument just referred to, when $I[2000]$ is included in the function these terms are of some service, though not as helpful as the more compact $f[0001]$ and $h[0001]$. More compact even than these terms—indeed, apparently somewhat too compact—are $f[0^*001]$ and $h[0^*001]$. When correlated with $g[1^*000]$ these terms are less useful than $f[0001]$ and $h[0001]$, but not so poor as the other terms. As one would expect from the fact that none of the polarization terms are ideal in character, an appreciable further improvement is obtained by including all of them in the function.

All the above polarization terms were constructed from the principal term of the core function. In order to check that polarization could be satisfactorily treated in this way we introduced into the most complicated of our functions the term $h[0011]+h[0101]$, which corresponds to the important term $h[0001]$ in the treatment of the polarization, but is constructed on another term of the core function. Table I shows that this addition would markedly improve the representation of the core in connection with the polarization effect, yet the computed energy of the system is improved by just 0.001 ev. The introduction of other polarization terms of this type is apparently unnecessary.