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Correlation Energies and Angular Components of the Wave Functions of the Ground States of H$^-$, He I, and Li II*

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With a view to examining the effects of configuration interaction in the ground state of the three simple atomic systems, H$^-$, He I, and Li II, a three-parameter variational function invcvling a symmetrized exponential in the nuclear distances and a linear factor in the interelectron distance has been obtained for He I and Li II. These functions together with the one of the same type already in existence for H$^-$ have been expanded in series of Legendre functions of the cosine of the angle between the two radius vectors. The coefficients in these expansions are functions of the nuclear distances of the two electrons. The various component functions are presented, together with the coefficients with which they enter the expansions, and their contributions to the total energies. A discussion is given of the method of estimating the magnitude of the total correlation, or configuration interaction, energy and its radial, angular, and mixed parts. A table is given of the values of the correlation energy and its various parts for H$^-$, He I, and Li II.

THE great body of theoretical atomic spectroscopy is based on central-field wave functions. The fact that this method of approach gives results in good agreement with the classification of atomic energy states, as worked out more or less independently by the experimental spectroscopists, indicates that the central-field approximation is a good one. Furthermore, it is clear how the simple theory should be extended in a higher approximation to include the effects of exchange and configuration interaction. On the other hand, in those cases in which the theory has been most completely worked out, something is left to be desired. Hartree, Hartree, and Sirles[1] have superposed the $1s^22p^{q+2}$ and the $1s^22s^22p^q$ configurations for O III, O II, and O I, using wave functions with exchange. Jucys[2] has superposed the $1s^22s^22p^2$, $1s^22p^4$, $1s^22s^22p3p$, and the $1s^22s2p^23s$ for C I using self-consistent field wave functions without exchange. In both cases some slight improvement in the energies was found. The cause of this disappointing outcome is suggested by work on the ground state of He I,[3] which indicates that to obtain good results it would be necessary to superpose a large number of configurations.

In contrast to the wave functions derived on the central-field approximation are those which contain terms or functions in the interelectron distances r_{ij}. The Hylleraas[4] and the Baber and Hassé[5] wave functions for He I are of this type. With only a few exceptions[6] very little has been done on the more complex spectra with wave functions involving the r_{ij}'s. However, in two electron spectra, which are almost the only ones which have been worked out in detail, the inclusion in the wave function of fairly simple terms in r_{12} has yielded good values of the energy. On the other hand, there are certain disadvantages to using the r_{ij}'s. No simple combination of elementary functions of r_{ij} is an eigenfunction of any large part of the energy operator. In addition the r_i's and r_{ij}'s do not form an orthogonal coordinate system. The energy operator is therefore rather involved. This is true also of many of the integrals which arise when the minimum principle is applied.

Fortunately one may take advantage of the accuracy offered by the solutions involving the r_{ij}'s to learn something of the form which solutions in central-field wave functions would have to possess if they were to be of equal accuracy. To do so, one expands the r_{ij} solutions in series of central-field solutions. The latter should form complete orthogonal sets. The individual members of a set may be constructed from one-electron wave functions in such a way as to have the desired symmetry and exchange properties. That is, the individual members of the set may be chosen to represent particular levels arising from particular electron configurations. The coefficients in the expansion then show just what configurations must be superposed, and with what weight, to obtain a solution in the central-field approximation equivalent to the r_{ij} solution.[7]

The present paper takes the first step in the direction of such an expansion in the case of a relatively simple type of expression for the ground-state wave functions of H$^-$, He, and Li$^+$. This first step consists in expanding the solution involving r_{12} in terms of a series of normalized Legendre functions of the cosine of the angle between the two radius vectors. It is wise to begin the expansions in this way because some interesting results with regard to the relative importance of the various

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[1] Hartree, Hartree, and Swirles, Trans. Roy. Soc. (London) **A238**, 229 (1939).

[2] A. Jucys (sometimes transliterated A. Yutsis), J. Exptl. Theoret. Phys. (U.S.S.R.) **19**, 565 (1949).

[3] Green, Mulder, Ufford, Slaymaker, Krawitz, and Mertz, Phys. Rev. **85**, 65 (1952).

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

[5] T. D. H. Baber and H. R. Hassé, Proc. Cambridge Phil. Soc. **33**, 253 (1937).

[6] H. M. James and A. S. Coolidge, Phys. Rev. **49**, 688 (1936); E. Conwell, Phys. Rev. **74**, 268 (1948); R. M. Thaler, Phys. Rev. **83**, 131 (1951).

[7] The possibility of investigating configuration interaction in He I in this manner was suggested to one of us (L.C.G.) by Dr. G. Breit.

angular components of the wave functions appear at once. Besides the results of the more detailed expansions into configurations which might follow will depend on the particular type of function chosen for the radial components of the central-field wave functions.[8] The coefficients of the Legendre functions in the expansion are themselves functions of r_1 and r_2, the distances of the two electrons from the nucleus. We then have

$$\Psi^N(r_1,r_2,r_{12})=\sum_i c_i\Phi_i^N(r_1,r_2)P_i^N(\cos\theta), \qquad (1)$$

where Ψ^N is the normalized function involving r_{12} which is to be expanded, P_i^N is the normalized Legendre polynomial of order i, and the Φ_i^N's are normalized functions of r_1 and r_2 whose form is to be determined from Eq. (1). Ψ^N is normalized with respect to integration over r_1, θ_1, and φ_1, the coordinates of the first electron, r_2 for the second electron, r_{12}, and φ, the Euler angle which together with r_{12} specifies the direction of $\mathbf{r}_2$ with respect to $\mathbf{r}_1$. The Φ_i^N's are normalized with respect to integration over r_1, θ_1, φ_1, r_2, and φ. From Eq. (1) it then follows that Φ_i^N is given by the expression

$$\Phi_i^N=\frac{1}{c_i}\int\Psi^N P_i^N \sin\theta d\theta, \qquad (2)$$

and c_i by the expression

$$c_i=\left\{\int\left[\int\Psi^N P_i^N \sin\theta d\theta\right]^2 d\tau'\right\}^{\frac{1}{2}}, \qquad (3)$$

where $d\tau'$ indicates the volume element with respect to r_1, θ_1, φ_1, r_2, and φ.

Expansions of the type described in the above paragraph have already been carried through[9] using for Ψ^N the three and the six constant expressions for the ground state of He I given by Hylleraas.[4] However, these two Ψ^N's are of quite similar form so that, although the c_i's did not vary much between the two expansions, there was still some possibility of doubt as to the validity of the conclusions with regard to the relative importance of the various angular components of the ground-state wave function and to the size of the components of the correlation energy. It therefore seemed wise to repeat the foregoing work using a ground-state wave function containing terms in r_{12} but of a somewhat different functional form from those of Hylleraas. At the same time it was felt that it would be distinctly interesting to examine the variation in the importance of the correlation energy, together with its various parts, and of the different angular components of the ground-state wave function as one passes from the negative ion H^-, to the neutral atom He I, and on to the positive ion Li II. For such a comparison to be of the most interest it seemed that the same type of ground-state wave function should be used for the expansion in all three cases.

TABLE I. Values of the constants in Eq. (4) and of the computed energies (in units of R_Zhc).

	H^-	He I	Li II
N	0.0312241	0.675135	2.88811
Z_1	0.478[a]	1.436	2.362
Z_2	1.075[a]	2.208	3.299
α	0.3121[a]	0.2924	0.2770
E(cal)	−1.05184[a]	−5.80284	−14.55435
E(exp)	−1.05512[b]	−5.80752	−14.56079

[a] Taken from Chandrasekhar; see reference 10.
[b] Best calculated value, due to Henrich; see reference 11.

The best available three-parameter wave function for H^- is that due to Chandrasekhar.[10] It is of the form

$$\Psi^N=N(e^{-Z_1r_1-Z_2r_2}+e^{-Z_2r_1-Z_1r_2})(1+\alpha r_{12}), \qquad (4)$$

where r_1, r_2, and r_{12} are measured in atomic units and Z_1, Z_2, and α are chosen to give the lowest energy. This simple function gives an energy only 0.31 percent above that given by the best function now known, Henrich's eleven-parameter function.[11] The expression for Ψ^N in Eq. (4) is of a distinctly different form from the three- and six-parameter functions of Hylleraas for He I,[4] which were used in the earlier expansions.[9] The functions given by Hylleraas use the same effective nuclear charge for both electrons and the symmetrized exponential therefore does not appear. Furthermore, Hylleraas includes quadratic terms in r_1, r_2, and r_{12} in the final factor. It seemed therefore that if a function of the form given by Eq. (4) should prove to give good values of the energy for He I and Li II as well as for H^-, it would be plausible to take this as the type of function to be expanded.

The first task was, therefore, to obtain the values of the parameters in Eq. (4) which would give the lowest energies for the ground states of He I and Li II. The values found for these parameters as well as the energies which they yield are given in Table I together with the results of Chandrasekhar for H^-. In the first line is given the ion; in the second, the normalization constant; in the third, fourth, and fifth, the values of the parameters in Eq. (4); in the sixth the energy calculated from the energy integral using these values of the parameters and units of R_Hhc, $R_{He}hc$, and $R_{Li}hc$ for H^-, He, and Li^+, respectively; in the first column of the seventh line the value of the H^- energy found by Henrich,[11] and in the second and third columns the experimental values of the energies for He I and Li II.[12] As already indicated Chandrasekhar's wave function gives an energy only 0.31 percent above Henrich's

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[8] The value of an expansion in terms of Legendre functions was pointed out to two of us (L.C.G. and M.M.M.) by Dr. E. U. Condon.

[9] Green, Mulder, and Milner, Phys. Rev. **91**, 35 (1953).

[10] S. Chandrasekhar, Astrophys. J. **100**, 176 (1944).

[11] L. R. Henrich, Astrophys. J. **99**, 59 (1944).

[12] The values of the ionization energies and Rydberg constants were taken from Charlotte E. Moore, *Atomic Energy Levels*, National Bureau of Standards Circular 467 (U. S. Government Printing Office, Washington, D. C., 1949).

value. For He I the energy given by the wave function of Eq. (4) exceeds the experimental value by 0.081 percent and for Li II by 0.044 percent. All three wave functions are therefore quite good. It is interesting to note for comparison that with the Hylleraas three-parameter wave function,† the energy for H^- is 0.44 percent above Henrich's value and for He I it is 0.045 percent above the experimental value.

If one examines the values of the parameters in Table I, several points of interest emerge. As one passes from H^- to Li^+, the difference between the true nuclear charge and Z_1, the effective nuclear charge for the outer electron, shows the expected increase toward one. In other words, as the nuclear charge increases, the shielding of the outer electron by the inner becomes more complete. Chandrasekhar[10] has already pointed out that in H^- if α is set equal to zero, $Z_1=0.283$ and $Z_2=1.039$ so that dropping the r_{12} term increases the shielding of the outer electron by 0.195 unit. In He I for $\alpha=0$, one finds[13] $Z_1=1.19$ and $Z_2=2.18$ so that dropping the r_{12} term increases the shielding by 0.25 unit. In Li II setting $\alpha=0$ yields $Z_1=2.08$ and $Z_2=3.29$, so that in this case dropping the r_{12} term increases the shielding of the outer electron by 0.28 unit.

If the values of Z_2 in Table I are divided by the nuclear charges, one obtains a slowly varying number, which already in the case of Li^+ seems to be decreasing toward one, as was to be expected. A more interesting result is found in the values of α. One might at first expect that the relative importance of the r_{12} term would decrease sharply with increasing nuclear charge. However, Table I shows a rather slow decline for α, which we may attribute to the fact that the increasing nuclear charge pulls the electrons into a smaller volume and thereby increases their interaction.

When the values of the parameters in Eq. (4) had been found, the Ψ^N's were substituted into Eq. (3) and the values of the c_i's were obtained. Table II gives the values of the c_i's. The final line of the table gives the values of $\sum_i c_i^2$. If the expansions were complete and the normalization constants were exact, this sum should be one. Above all else Table II shows how far the ground-state wave functions for these atomic structures are from spherically symmetric. The coefficients of the P_1^N terms are 12 percent, 7 percent, and 5 percent of the coefficients of the P_0^N term for H^-, He I, and Li II, respectively. If the values of the c_i's for He I in Table II are compared with those found earlier[9] for the Hylleraas three- and six-parameter wave functions, one finds that the coefficients for the two three-parameter functions differ on the average, for the four coefficients given, by less than 0.6 percent. On the other hand, the coefficients of the two Hylleraas functions differ by almost 12 percent. These averages might vary markedly if a different number of coefficients were considered. However, in view of the difference in functional form of the three-parameter solutions and the similarity in form of the Hylleraas solutions, it is surprising that for not one of the coefficients computed does the difference between the three-parameter functions amount to as much as one-sixth of the difference of the two Hylleraas functions.

TABLE II. Values of c_i in the expansion $\Psi^N=\sum_i c_i\Phi_i^NP_i^N$.

	H^-	He I	Li II
c_0	0.993206	0.997467	0.998806
c_1	0.115067	0.070256	0.048251
c_2	0.016245	0.010387	0.007179
c_3	0.005375	0.003501	0.002426
$\sum_i c_i^2$	0.999991	0.999996	0.999998

With the values of the c_i's known, one can write from Eq. (2) explicit expressions for the Φ_i^N's. For $i=0$ these take the form

$$\Phi_0^N=\frac{\sqrt{2}N}{c_0}(e^{-Z_1r_1-Z_2r_2}+e^{-Z_2r_1-Z_1r_2})\left\{1+\frac{\alpha}{3}\left(\frac{r_<^2}{r_>}+3r_>\right)\right\},$$

and for $i=n>0$:

$$\Phi_n^N=\frac{\sqrt{2}N}{c_n}(e^{-Z_1r_1-Z_2r_2}+e^{-Z_2r_1-Z_1r_2})\times\left\{\frac{\alpha}{(2n+3)(2n+1)^{\frac{1}{2}}}\frac{r_<^n}{r_>^{n-1}}\left(\frac{r_<^2}{r_>^2}-\frac{2n+3}{2n-1}\right)\right\}.$$

When the Φ_i^N's are known, one may proceed to find the contribution to the total energies of the various components of the ground-state wave functions. For this purpose the terms in the integral

$$E=\int\sum_i(c_i\Phi_i^NP_i^N)^*H\sum_i(c_i\Phi_i^NP_i^N)d\tau,$$

where $d\tau$ indicates the volume element with respect to all six variables, have been computed separately and the results are presented in Table III. The first column of Table III gives the various terms in the integrand, where (i) is written for $c_i\Phi_i^NP_i^N$. The second, fourth and sixth columns give the contributions of these terms to the energy in units of R_Hhc, $R_{He}hc$, and $R_{Li}hc$ for H^-, He I, and Li II, respectively. The third, fifth, and seventh columns give the contributions of the various angular components to the energy if all of the angular components of lower order are also present. The next to the last line of Table III gives the sum of the contributions to the energy of the first four angular components, and the final lines gives the energy found for the complete wave function.

It is interesting to note from Table III that the spherically symmetric terms in the wave functions account for 96.0 percent, 98.7 percent, and 99.4 percent of the total energy given by the wave function in the

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† H. Bethe, Z. Physik **57**, 815 (1929) and E. A. Hylleraas, Z. Physik **60**, 624 (1930).

[13] G. R. Taylor and R. G. Parr, Proc. Natl. Acad. Sci. U. S. **38**, 154 (1952).

TABLE III. Contributions to the total energy of the terms in $E=\int\sum_i(c_i\Phi_i^NP_i^N)^*H\sum_i(c_i\Phi_i^NP_i^N)d\tau$.

	H$^-$		He I		Li II	
Terms	Contributions of the terms	Contributions of the angular components of the wave functions	Contributions of the terms	Contributions of the angular components of the wave functions	Contributions of the terms	Contributions of the angular components of the wave functions
$(0)^*H(0)$	-1.00925	-1.00925	-5.72603	-5.72603	-14.46774	-14.46774
$(1)^*H(1)$	$+0.01003$	-0.03968	$+0.01700$	-0.07014	$+0.01731$	-0.07855
$(1)^*H(0)+(0)^*H(1)$	-0.04971		-0.08714		-0.09586	
$(2)^*H(2)$	$+0.00082$	-0.00215	$+0.00176$	-0.00480	$+0.00198$	-0.00576
$(2)^*H(0)+(0)^*H(2)$	-0.00428		-0.00787		-0.00872	
$(2)^*H(1)+(1)^*H(2)$	$+0.00131$		$+0.00131$		$+0.00098$	
$(3)^*H(3)$	$+0.00019$	-0.00046	$+0.00043$	-0.00109	$+0.00049$	-0.00135
$(3)^*H(0)+(0)^*H(3)$	-0.00102		-0.00190		-0.00212	
$(3)^*H(1)+(1)^*H(3)$	$+0.00029$		$+0.00030$		$+0.00022$	
$(3)^*H(2)+(2)^*H(3)$	$+0.00008$		$+0.00008$		$+0.00006$	
Sum	-1.05154	-1.05154	-5.80206	-5.80206	-14.55340	-14.55340
$\int\Psi^{N*}H\Psi^Nd\tau$	-1.05184		-5.80284		-14.55435	

cases of H$^-$, He I, and Li II, respectively. Similarly the terms containing $\cos\theta$ account for 93.2 percent, 91.3 percent, and 90.7 percent of what remains of the total energy after the spherically symmetric terms have been removed. The terms containing the second-order Legendre polynomial account for 73.9 percent, 72.0 percent, and 71.5 percent of what is then left. Finally using all the figures available, one finds that the terms containing the third-order Legendre polynomial account for 59.2 percent, 58.6 percent, and 58.3 percent of what remains after the terms containing the Legendre polynomials of lower order have been removed.

From Tables II and III one can also see that the ratios of the contributions of the nonspherically symmetric components to those of the spherically symmetric ones are much larger for the wave function than for the energy. For H$^-$ the ratios of the contributions to the wave function of the P_1^N, P_2^N, and P_3^N components to that of the P_0^N component are roughly 3, 8, and 12 times as large as the corresponding ratios of the contributions to the energy. For He I the similar set of numbers is 6, 12, and 18, and for Li II one finds 9, 18, and 26. These numbers give a clear illustration of the fact that a wave function chosen by minimizing the energy will in general yield an energy which is much closer to the true energy than the wave function itself is to the true wave function.

The figures in Tables II and III may also be used to obtain rough maximum and minimum estimates of the energies which purely radial wave functions may be expected to give for the ground state of H$^-$, He I, and Li II. Since such wave functions are often used in approximate calculations, it will be worthwhile to see how close a few of the better known purely radial functions come to yielding the estimated maximum energy. The energies given in Table III for the P_0^N components are those which are found when all the other angular components are also present. However if the P_0^N component is the only one present in the expansion given by Eq. (1), that is, if all the Φ_i^N's for $i>0$ are set equal to zero, as they must be in a purely radial function, then c_0 will be 1 and the energy is $1/c_0^2$ times the value given for the P_0^N component in Table III. Such estimates of the values of the energies given by spherically symmetric functions may be regarded as rough maximum estimates because the functions used to compute the quantities in Table III do not, of course, give total energies as low as the experimental values. On the other hand if one attributes the entire difference between the experimental values and the computed total energies to the energies of the spherically symmetric components, one obtains rough minimum estimates of the energy. Quantities computed in these ways are listed in Table IV together with the energies given by three of the better known spherically symmetric functions and by one worked out by the present authors to use in connection with the computations of the correlation energies below. The energies for each element in Table IV are given in units of the Rydberg constant for that element times hc. The first line gives the energy as computed from the simple exponential. The second line gives the energy as computed from the three parameter function

$$\Psi^N=(c_1e^{-Z_1r_1}+c_2e^{-Z_2r_1})(c_1e^{-Z_1r_2}+c_2e^{-Z_2r_2}), \qquad (5)$$

where Z_1, Z_2, and the ratio of c_1 and c_2 have been chosen to yield the minimum energy.[14] The third line of Table IV gives the Hartree-Fock energy and the fourth the energy as found from the symmetrized exponential. The last two lines of Table IV give the maximum and minimum estimates of the energy to be expected from spherically symmetric wave functions computed as sug-

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[14] A paper will appear in *The Physical Review* **93**, February 15 (1954) dealing with this function and a two-parameter one, both of which are of the product type, and both of which compare favorably with the Hartree $1s^2$ function for He I-like ions.

TABLE IV. Energies given by spherically symmetric ground-state wave functions.

Functions	H^-	He I	Li II
$Ne^{-Z(r_1+r_2)}$	-0.9453	-5.6953	-14.4453
3-parameter [see Eq. (5)]	-0.9756	-5.7233	-14.4728
Hartree-Fock		-5.723[b]	-14.42[d]
$N\{e^{-Z_1r_1-Z_2r_2}+e^{-Z_2r_1-Z_1r_2}\}$	-1.0266[a]	-5.7513[c]	-14.4975
Estimated maximum	-1.0231	-5.7552	-14.5024
Estimated minimum	-1.0264	-5.7599	-14.5088

[a] From S. Chandrasekhar, see reference 10.
[b] From W. S. Wilson, see reference 15.
[c] From G. R. Taylor and R. G. Parr, see reference 13.
[d] From V. Fock and M. J. Petrashen, see reference 16 below. This value appears to be a misprint since it does not give energies even as low as the simple exponential in the first line of this table.

gested above. For He I it is possible to obtain similar maximum and minimum estimates from earlier work on the three- and six-parameter Hylleraas wave functions.[9] These values are $-5.7566\ R_{\mathrm{He}}hc$ and $-5.7592\ R_{\mathrm{He}}hc$ from the three parameter function and $-5.7574\ R_{\mathrm{He}}hc$ and $-5.7584\ R_{\mathrm{He}}hc$ from the six-parameter function, respectively. Examination of Table IV shows that only for the symmetrized exponential does the calculated energy approach the estimates of what is possible even with just spherically symmetric functions to closer than 0.02 unit. This result is, of course, a consequence of the fact that the first three wave functions are of the simple product type and therefore do not take into account any configuration interaction even among spherically symmetric terms, that is, they do not take into account any radial correlation in the positions of the electrons except in the average. For He I and Li II, even the symmetrized exponential is seen to leave something to be desired in the way of radial correlation. The fact that for H^- the symmetrized exponential gives a value a little lower than the estimated minimum energy would appear to mean that when angular components are added to the wave function the parameters in the spherically symmetric component must change considerably to yield the minimum total energy.

The data in Table III together with earlier work may be used to estimate the size of the correlation energy and its various component parts for the three atomic systems under consideration. It was suggested in an earlier paper[9] that for the purpose of examining the correlation energy one should write the wave function for the ground state of these simplest systems in the form

$$\Psi^N = c_{HF}\Phi_{HF}{}^N P_0{}^N + c_R\Phi_R{}^N P_0{}^N + c_A\chi_A{}^N. \qquad (6)$$

In Eq. (6) $\Phi_{HF}{}^N$ is the Hartree-Fock wave function for the particular configuration and term, namely $1s^2\,{}^1S$, making the largest contribution to the energy of the ground state. $\Phi_R{}^N$ includes all the remaining terms in Ψ^N which are not angularly dependent. $\chi_A{}^N$ consists of all the angularly dependent terms in Ψ^N. The relation of the various quantities in Eq. (6) to those in Eq. (1) is given by the following set of equations:

$$c_{HF} = \int (c_0\Phi_0{}^N P_0{}^N)^* \Phi_{HF}{}^N P_0{}^N d\tau,$$

$$c_R = (1-c_{HF}{}^2)^{\frac{1}{2}},$$

$$\Phi_R{}^N = (c_0\Phi_0{}^N - c_{HF}\Phi_{HF}{}^N)/c_R,$$

$$\chi_A{}^N = \sum_{i=1} c_i\Phi_i{}^N P_i{}^N \Big/ \sum_{i=1} c_i^2,$$

$$c_A = \sum_{i=1} c_i^2.$$

The Hartree-Fock wave functions should be the best function which takes account of the electron interaction only in the average, that is, the best wave function which takes no account of the correlation in the position of the electrons except in the average. It includes no terms which depend on the instantaneous value of the interlectron distance. It is suggested that if $\Phi_R{}^N$ and $\chi_A{}^N$ are of sufficiently general form so that Ψ^N may be considered to be a good approximation to an exact solution of the Schrödinger equation, then the total correlation energy and its various parts may be found from the different terms obtained when Ψ^N as given in Eq. (6) is substituted into the energy integral,

$$\begin{aligned}
\int \Psi^{N*} H \Psi^N d\tau = {} \\
& + \left\{ c_{HF}{}^2 \int (\Phi_{HF}{}^N P_0{}^N)^* H \Phi_{HF}{}^N P_0{}^N d\tau \right\} \\
& + \left\{ c_{HF}c_R \int (\Phi_{HF}{}^N P_0{}^N)^* H \Phi_R{}^N P_0{}^N d\tau + c_R c_{HF} \int (\Phi_R{}^N P_0{}^N)^* H \Phi_{HF}{}^N P_0{}^N d\tau + c_R{}^2 \int (\Phi_R{}^N P_0{}^N)^* H \Phi_R{}^N P_0{}^N d\tau \right\} \\
& + \left\{ c_{HF}c_A \int (\Phi_{HF}{}^N P_0{}^N)^* H \chi_A{}^N d\tau + c_A c_{HF} \int (\chi_A{}^N)^* H \Phi_{HF}{}^N P_0{}^N d\tau + c_A{}^2 \int (\chi_A{}^N)^* H \chi_A{}^N d\tau \right\} \\
& + \left\{ c_R c_A \int (\Phi_R{}^N P_0{}^N)^* H \chi_A{}^N d\tau + c_A c_R \int (\chi_A{}^N)^* H \Phi_R{}^N P_0{}^N d\tau \right\}. \qquad (7)
\end{aligned}$$

The different terms in the energy integral fall into four types. These four types have been separately bracketed in Eq. (7). First, there is a term which involves only Ψ_{HF}^N. This term yields an energy which is equal to c_{HF}^2 times the energy of the Hartree-Fock solution and is the part of the total energy which does not depend on the correlation in the position of the electrons except in the average. Second, there is a group of three terms which yield that part of the energy which appears because terms arising from the radial correlation in the position of the electrons are included in the wave function. It is reasonable to refer to this part of the energy as the radial correlation energy. Third, there is a group of three terms which yield that part of the energy which appears because terms arising from the angular correlation in the position of the electrons are included in the wave function. This part of the energy is, therefore, referred to as the angular correlation energy. Fourth, there are two terms still remaining which yield that part of the energy which appears because terms arising from both the radial and the angular correlation in the position of the electrons are included in the wave function. This part of the energy may be called the mixed correlation energy.

TABLE V. Correlation energies in the ground states of H$^-$, He I, and Li II. The values are given in units of $R_H hc$, $R_{He} hc$, and $R_{Li} hc$ for H$^-$, He I, and Li II, respectively.

	H$^-$	He I	Li II
Radial	−0.0930	−0.0608	−0.0492
Angular	−0.0547	−0.0788	−0.0880
Mixed	+0.0121	+0.0020	+0.0014
Total corr.	−0.1356	−0.1376	−0.1358

The extension of the above discussion to other states and other atomic systems would seem to be clear.

If one adopts the definitions suggested above, one can estimate the value of the total correlation energy and its various parts for any of the three atomic systems considered here for which Hartree-Fock wave functions are known. Wilson[15] has given such a solution for He I and Fock and Petrashen[16] have given the solution for Li II, but unfortunately no solution for H$^-$ seems to be available. In view of the lack of a Hartree-Fock solution for H$^-$ it was decided to use the analytic product type wave function of Eq. (5) for all three atomic systems. This wave function has been compared with the available Hartree-Fock solutions for He I, Li II, Be III,[17] and C V.[18] It was found that it gave energies which were very close to the Hartree-Fock energies, and that with the exception of C V for which the Hartree-Fock function seems to be somewhat less accurate, the maximum difference between the normalized analytic and numerical wave functions was 1.2×10^{-3}.[14] Using this wave function, the values of c_{HF} were found to be 0.969074, 0.994907, and 0.998124 for H$^-$, He I, and Li II, respectively. With these values for c_{HF} and the values of the energy for this function as given in the second line of Table IV the correlation energies have been computed. The results are recorded in Table V. Table V gives the values of the total correlation energy and its component parts, the radial, angular, and mixed correlation energies. The values are given in units of $R_H hc$, $R_{He} hc$, and $R_{Li} hc$ for H$^-$, He I, and Li II, respectively. The radial correlation energy was computed by subtracting c_{HF}^2 times the Hartree-Fock energy, taken as suggested above from the second line of Table IV, from the energy given in the first line of Table III for the spherically symmetric component of the ground-state wave function. The mixed correlation energy was computed directly from the integrals listed in Eq. (7). The angular correlation energy was then computed by subtracting the energy of the spherically symmetric component and the mixed correlation energy from the total energy given by the ground-state wave function. Finally, the total correlation energy was computed by subtracting c_{HF}^2 times the Hartree-Fock energy, taken as above from the second line of Table IV, from the total energy given by the ground-state wave function for the particular atomic system.

The results given in Table V may be compared with those obtained earlier[9] for He I using the three- and six-parameter wave functions of Hylleraas. There the radial, angular, mixed, and total correlation energies were found to be −0.056, −0.079, +0.002, and −0.133 unit and −0.056, −0.075, +0.002, and −0.129 unit, respectively, for the three- and six-parameter functions. In making use of the results in Table V and in comparing them with the results of the earlier work, it must be remembered that all of the ground-state wave functions employed give energies above the experimental values. These differences amount to 0.0033, 0.0047, and 0.0064 unit for H$^-$, He I, and Li II, respectively, using a wave function of the form given in Eq. (4) and to 0.0026 and 0.0010 unit for the three- and six-parameter Hylleraas functions. These small differences represent corrections to the values of the energies given in Table V and in the earlier work, but just how these small quantities should be divided between the noncorrelation energy and the various parts of the correlation energy is not clear.

The most striking characteristic of the values in Table V is the remarkable similarity of the total correlation energies for the three atomic systems. Perhaps more significant is the fact that the total correlation energy accounts for 12.9 percent, 2.4 percent, and 0.9 percent of the energy of the ground-state wave function for H$^-$, He I, and Li II, respectively. Next one notices the downward trend of the magnitude of the radial and

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the mixed correlation energies with increasing atomic number and the corresponding increasing importance of the angular correlation energy. A quantitative discussion of these results will be presented in a later paper.

In summary the present work gives the correlation energies in the ground states of H^-, He I, and Li II and the importance of the various angular components of the ground-state wave functions both in the total wave functions and in the energies computed from them. First the values of the three parameters in the ground-state wave function given by Eq. (4) were determined variationally for He I and Li II. These functions together with the one of the same type already in existence for H^- were then expanded in series of Legendre functions of the cosine of the angle between the two radius vectors. The size of the coefficients in these expansions indicate the importance of the nonspherically symmetric components of the ground-state wave functions. That is, the size of the coefficients indicate the importance of configuration interaction with configurations which are not spherically symmetric. This importance decreases as one passes from H^- to Li II. On a percentage basis the contribution of the various components to the ground-state energy is less important than their contribution to the wave function. This contribution to the energy becomes larger in absolute value but smaller relatively as one passes from H^- to Li II. On the basis of the size of the contribution of the spherically symmetric component to the total energy and to the wave function for the ground state, the accuracy of various spherically symmetric ground-state wave functions is considered. Definitions are given for the total correlation or configuration interaction energy and its radial, angular, and mixed parts. Making use of an excellent analytic approximation to the Hartree-Fock ground-state wave functions, the definitions of the configuration interaction energies are applied to the three atomic systems under consideration. The total configuration interaction energies are found to be remarkably similar in absolute value but of decreasing relative importance with increasing atomic number. The absolute value of the radial and mixed correlation energy decreases from H^- to Li II and the absolute value of the angular configuration interaction energy increases.

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