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Correlation Energy in the Ground State of He I†

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With a view of examining the effects of configuration interaction in a simple case, the three term and six term expressions given by Hylleraas for the ground-state wave function of He I 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 r_1 and r_2, the distances of the two electrons from the nucleus. The various component functions are presented, together with the coefficients with which these functions enter the expansions, and their contributions to the total energy. A discussion is given of the method of estimating the magnitude of the correlation, or configuration interaction, energy. Evidence is presented that the total correlation energy is at least $-0.129R_{\mathrm{He}}hc$ and may be even more negative. Of this amount it is estimated that $-0.056R_{\mathrm{He}}hc$ is associated with the radial part of the correlation energy, $-0.075R_{\mathrm{He}}hc$ with the angular part, and $+0.002R_{\mathrm{He}}hc$ with the mixed part.

THE importance of configuration interaction in atomic spectra has long been recognized,[1] and a number of calculations dealing with such interactions have been made.[2–6] In general, some improvement in term separations has been obtained when superposition was included but in the two most thorough treatments of such effects by self-consistent field methods, the work of Hartree[2] on O, O^+, and O^{++} and the work of Jucys[3] on C, the results were disappointing. It therefore seemed valuable to investigate the effects of configuration interaction by considering a relatively simple case in some detail. As a consequence in an earlier paper[5] two of the present authors together with others undertook the expansion of two of the Hylleraas wave functions for the $^1S_0$ ground state of He I in series of central field wave functions representing the various configurations.[7] In total five configurations were considered: $1s^2$, $1s2s$, $1s3s$, $2s^2$ and $2p^2$. The wave functions in each case were taken as symmetrized products of self-consistent field wave functions for the individual electrons. For the $1s^2$ and $1s2s$ configurations a second set of expansion coefficients was also calculated using analytic variationally determined wave functions. One of the results of this work was to show that for the self-consistent field wave functions the nonspherically symmetric $2p^2$ was the second largest contributor to the ground-state wave function among the configurations considered.

However, in this earlier work the coefficient of the $1s2s$ configuration was markedly different for the self-consistent field wave functions and for the analytic ones. It seemed entirely possible that the same might also be true for the $2p^2$ as well as the other excited configurations. This would mean in the case of the $2p^2$ that the angular dependence which would be found for the Hylleraas functions would depend on the particular kind of radial functions used in the expansion. This of course would not be true if a sufficiently large number of orthogonal functions were used so that they could be considered as forming a fair approximation to a complete set for the purpose in hand. However, to obtain such a set and to expand in terms of it might well be a heavy task.

To avoid this difficulty it was decided to use an expansion of the form[8]

$$\Psi_H{}^N = \sum_i c_i \Phi_i{}^N P_i{}^N \tag{1}$$

where $\Psi_H{}^N$ is the normalized Hylleraas wave function, the $\Phi_i{}^N$'s are normalized functions [whose functional form is to be determined from Eq. (1)] of the distances r_1 and r_2 of the two electrons from the nucleus, and the $P_i{}^N$'s are the normalized Legendre functions of the various orders i of the cosine of the angle between the two radius vectors. More precisely, $\Psi_H{}^N$ 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, and θ and φ, the Euler angles specifying the direction of r_2 with respect to r_1. $\Phi_i{}^N$ is normalized with respect to integration over r_1, θ_1, φ_1, r_2, and φ. From Eq. (1) it then follows that $\Phi_i{}^N$ is given by the

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[1] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1935), Chap. XV.

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

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

[4] For references to the earlier literature see reference 5 below. In addition one should mention A. Jucys and V. J. Kavetskis, Zhur. Eksptl. i Teort. Fiz. (U.S.S.R.) **21**, 1139 (1951); G. F. Koster, Phys. Rev. **86**, 148 (1952); J. Lennard-Jones and J. A. Pople, Phil. Mag. **43**, 581 (1952); A. Brickstock and J. A. Pople, Phil. Mag. **43**, 1090 (1952); N. Rosenzweig, Phys. Rev. **88**, 580 (1952).

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

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

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

[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.

expression

$$\Phi_i^N = \frac{1}{c_i}\int \Psi_H{}^N P_i{}^N \sin\theta d\theta, \tag{2}$$

and c_i by the expression

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

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

It is clear that the c_i's depend on the particular form which is used for $\Psi_H{}^N$. Therefore to obtain an indication of their stability for small variations in $\Psi_H{}^N$, expansions of the type given in Eq. (1) were carried out for both the three and the six constant expressions given by Hylleraas. The three term wave function has the form

$$\Psi_H{}^N = Ne^{-Zs}(1+a_1u+a_2t^2),$$

and the six term wave function the form

$$\Psi_H{}^N = Ne^{-Zs}(1+a_1u+a_2t^2+a_3s+a_4s^2+a_5u^2),$$

where $s=r_1+r_2$, $t=r_1-r_2$, and $u=r_{12}$, and the r's are expressed in atomic units. The values which were used for the constants in the three term expression were $N=1.321350$, $Z=1.816$, $a_1=0.30$, $a_2=0.13$, and in the six term expression $N=1.381890$, $Z=1.818$, $a_1=0.353$, $a_2=0.128$, $a_3=-0.101$, $a_4=0.033$, $a_5=-0.032$. The three term wave function gives -5.80488 $R_{\mathrm{He}}hc$ for the energy and the six term one gives -5.80648 $R_{\mathrm{He}}hc$. An empirical value for this quantity can be found by adding the ionization energies for He I and He II (-1.80734 ± 0.00014) $R_{\mathrm{He}}hc$ and -4.00018 $R_{\mathrm{He}}hc$, respectively, to give (-5.80752 ± 0.00014) $R_{\mathrm{He}}hc$.[9] The two expressions are therefore quite similar and both give excellent values of the energy. Table I gives the values of the c_i's found in the two expansions. Column two gives the values of the c_i's in the expansion of the three term Hylleraas expression and column three the values in the expansion of the six term expression. The final line of the table gives the value of $\sum_i c_i^2$. If the expansions were complete and the normalization constants were exact, this sum should be one. The stability of the c_i's is indicated by the similarity of their values in the two expansions.

TABLE I. Values of c_i in the expansion $\Psi_H{}^N = \Sigma_i c_i \Phi_i{}^N P_i{}^N$.

	Three term $\Psi^N{}_H$	Six term $\Psi^N{}_H$
c_0	0.997535	0.997945
c_1	0.069227	0.062583
c_2	0.010398	0.012739
c_3	0.003528	0.004322
$\Sigma_i c_i^2$	0.999989	0.999991

The most interesting result which appears in Table I is the large contribution to the ground-state wave function of components which are not spherically symmetric. Thus the coefficients of the $P_1{}^N$, $P_2{}^N$, and $P_3{}^N$ terms are approximately 7 percent, 1 percent and 0.4 percent of the coefficient of the $P_0{}^N$ term.

From Eq. (2) one may find the form of the $\Phi_i{}^N$'s. For those associated with the three term expression one obtains

$$\Phi_0{}^N = \sqrt{2}N\frac{1}{c_0}e^{-Z(r_1+r_2)}\left\{1+\tfrac{1}{3}a_1r_>\left(\frac{r_<^2}{r_>^2}+3\right)+a_2(r_>-r_<)^2\right\},$$

and for $i=n>0$,

$$\Phi_n{}^N = \sqrt{2}N\frac{1}{c_n}e^{-Z(r_1+r_2)}\left\{\frac{a_1}{(2n+3)(2n+1)^{\frac{1}{2}}}\frac{r_<^n}{r_>^{n-1}} \times\left(\frac{r_<^2}{r_>^2}-\frac{2n+3}{2n-1}\right)\right\}$$

where $r_<$ is the lesser, and $r_>$ the greater, of r_1 and r_2. For the $\Phi_i{}^N$'s associated with the six-term expression one finds for $i=0$ and 1,

$$\Phi_0{}^N = \sqrt{2}N\frac{1}{c_0}e^{-Z(r_1+r_2)}\left\{1+\tfrac{1}{3}a_1r_>\left(\frac{r_<^2}{r_>^2}+3\right)+a_2(r_>-r_<)^2 +a_3(r_1+r_2)+a_4(r_1+r_2)^2+a_5(r_1^2+r_2^2)\right\},$$

$$\Phi_1{}^N = \sqrt{2}N\frac{1}{c_1}e^{-Z(r_1+r_2)}\left\{\frac{a_1}{5\sqrt{3}}\left(\frac{r_<^3}{r_>^2}-5\right)-\frac{2a_5}{\sqrt{3}}r_1r_2\right\}.$$

The $\Phi_i{}^N$'s for $i>1$ for the three and six term expressions are identical except for the values of the c_i's, a_i's and N and Z.

It is interesting now to see how much the various angular components of the ground-state wave function contribute to the total energy of the state. Therefore we have listed in Table II for the three and six constant functions the contributions to the total energy of the various terms in the integral

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

where $d\tau$ indicates the volume element with respect to all six variables.

The first column of Table II gives the various terms in the integrand, where (i) is written for $c_i\Phi_i{}^N P_i{}^N$. The second and fourth columns give the contributions to the energy in units of $R_{\mathrm{He}}hc$ of these terms for the cases of the three- and six-constant Hylleraas wave functions, respectively. The third and fifth columns give

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[9] The values of the ionization energies and R_{He} in cm^{-1} were taken from Charlotte E. Moore, *Atomic Energy Levels*, National Bureau of Standards Circular 467 (U. S. Government Printing Office, Washington, D. C., 1949), pp. 4, 6.

TABLE II. Contributions to the total energy of the terms in $E=\int\Sigma_i(c_i\Phi_i^NP_i^N)^*H\Sigma_i(c_i\Phi_i^NP_i^N)d\tau$ in units of $R_{\mathrm{He}}hc$.

	3-constant Hylleraas wave function		6-constant Hylleraas wave function	
Terms	Contributions of the terms	Contributions of the angular components of the wave function	Contributions of the terms	Contributions of the angular components of the wave function
$(0)^*H(0)$	−5.72823	−5.72823	−5.73371	−5.73371
$(1)^*H(1)$	+0.01700	−0.06992	+0.01921	−0.06527
$(1)^*H(0)+(0)^*H(1)$	−0.08692		−0.08448	
$(2)^*H(2)$	+0.00179	−0.00478	+0.00269	−0.00545
$(2)^*H(0)+(0)^*H(2)$	−0.00790		−0.00969	
$(2)^*H(1)+(1)^*H(2)$	+0.00133		+0.00155	
$(3)^*H(3)$	+0.00044	−0.00110	+0.00066	−0.00121
$(3)^*H(0)+(0)^*H(3)$	−0.00192		−0.00235	
$(3)^*H(1)+(1)^*H(3)$	+0.00030		+0.00035	
$(3)^*H(2)+(2)^*H(3)$	+0.00008		+0.00013	
Sum	−5.80403	−5.80403	−5.80564	−5.80564
$\int\Psi_H^{N*}H\Psi_H^Nd\tau$	−5.80488		−5.80648	

the contributions of the various angular components of these wave functions to the energy if all of the angular components of lower order are also present. The next to last line of Table II gives the sum of the contributions to the energy of the first four angular components, and the final line gives the energy found by Hylleraas for the complete wave function.

An examination of Table II shows that the spherically symmetric term accounts for 98.7 percent of the total energy given by the three-constant wave function and for 98.8 percent of that given by the six-constant wave function. The addition of a cosine term allows one to pick up 91.2 percent and 89.7 percent of the remaining energy, respectively. The terms containing the second-order Legendre polynomial account for 71.0 percent and 72.6 percent of what then remains, and the terms containing the third-order Legendre polynomial account for 55.9 percent and 59.1 percent, respectively, of what is still left after the spherically symmetric component and the first two angular components have been included. The first four components together account for 99.9851 percent and 99.9855 percent, respectively, of the total energies given by the three-constant and six-constant wave functions.

A comparison of the results given in Tables I and II shows that the ratios of the contributions of the non-spherically symmetric components to those of the spherically symmetric ones are much larger for the wave function than for the energy. Thus the contributions of the P_1^N, P_2^N, and P_3^N components to the energy are only 1.22 percent, 0.083 percent, and 0.019 percent of the contribution of the P_0^N component in the case of the three constant wave function and only 1.14 percent, 0.095 percent, and 0.021 percent in the case of the six-constant function. 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 therefore roughly 6, 13, and 19 times as large as the corresponding ratios of the contributions to the energy. This result emphasizes the difficulty of obtaining a high accuracy wave function by minimizing the energy.

One may use the data in Table II, together with the results of earlier work, to estimate the magnitude of the correlation energy, that is, the configuration interaction energy, and its component parts for the ground state of He I. The correlation energy is sometimes taken to be the difference between the experimental value of the energy and the energy as found by the Hartree-Fock procedure, without any consideration of configuration interaction. However, the correlation energy as computed in this way does not have the simple physical significance which one would like to associate with this term. We can see that this is the case by considering the physical situation which leads to the introduction of the concept of correlation energy. If a wave function is to take into account the repulsion between electrons and the consequent low probability that two of them will be found in the same small volume, it must be small whenever two electrons are close together. The Hartree and the Hartree-Fock wave functions are in general the only high accuracy wave functions available for complex atoms. Of these two types the Hartree-Fock wave functions are the superior since exchange effects are included in their derivation, and we shall limit our further discussion to functions of this type. However, Hartree-Fock functions are not necessarily small when two electrons are close together. They take the electron repulsion into account only in the average. As a result the energies obtained from such functions are higher than the observed energies because they include the positive repulsive potential energies from the increased electron interactions. It would therefore seem to be more meaningful physically to define the correlation energy (the configuration interaction energy) as the difference between the energy given by an exact solution of the Schrödinger equation for the particular problem and the energy given by the Hartree-Fock component in an expansion of the exact solution. This expansion of the exact solution is to be made in terms of some orthonormal set of functions of which the Hartree-Fock function is the first member. The reasons for suggesting this definition will be presented in the following paragraph.

If we are to use this definition for the correlation energy, the method of computing this quantity which was mentioned first can yield only a lower limit and this limit, at least for the case of the ground state of He I, is considerably smaller than the true value. The reason for this is the following: To build an exact solution from a Hartree-Fock wave function it is necessary to superpose the Hartree-Fock solutions for other configurations or to include multiplicative functions of the r_{ij}'s. The energy found for such a solution would be lower than that found for the Hartree-Fock solution alone. However, the new wave function must be normalized, and the contribution of the Hartree-Fock component to the total energy will be less than if this component were the only one. Therefore the difference between the observed energy and the Hartree-Fock energy is a smaller quantity than the correlation energy as defined above. The proper procedure to determine this energy would be to find the difference between the energy given by the exact solution and the energy given by the Hartree-Fock component of the exact solution where the Hartree-Fock wave function is that of the configuration making the largest contribution to the energy of the state. To obtain the latter quantity one would multiply the ordinary Hartree-Fock energy by the square of the coefficient of the Hartree-Fock wave function in an expansion of the exact solution in terms of some orthonormal set of functions of which the Hartree-Fock function was the first member. Unfortunately, it will usually be the case that neither the exact solution nor any close approximation to it will be known. One may then take the experimental energy as the energy which would be given by an exact solution if one were known, but there would seem to be no way of determining the needed expansion coefficient. Under these circumstances one can only turn to the first method of estimating the correlation energy mentioned above, which assumes it to be the difference between the experimental and the Hartree-Fock energy, recognizing that this method yields only a lower limit.

Fortunately in the case of the ground state of He I the data are more complete. The three- and six-constant Hylleraas ground-state wave functions are both excellent approximations to the exact solution of the Schrödinger equation of the problem. The three-constant function gives the observed energy to better than 0.05 percent and the six-constant function to better than 0.02 percent. For this state the self-consistent field wave functions with and without exchange are identical and the energy has been found to be $-5.723\ R_{\mathrm{He}}hc$.[10] In addition, in earlier work[5] the three- and six-constant Hylleraas wave functions were expanded in terms of symmetrized products of self-consistent field wave functions, and the coefficients of the $1s^2$ configuration were found to be 0.99550 and 0.99606, respectively. The largest contribution which these wave functions can yield to the energy given by the Hylleraas expressions can therefore be found by multiplying the energy obtained using only these wave functions by the square of their expansion coefficients. This procedure gives $-5.672 R_{\mathrm{He}}hc$ and $-5.678\ R_{\mathrm{He}}hc$ for the three- and six-term wave functions, respectively. However, the three-term Hylleraas expression yields an energy $0.003\ R_{\mathrm{He}}hc$ above the experimental value and the six-term expression an energy $0.001\ R_{\mathrm{He}}hc$ higher than the experimental. It is not clear what part of these differences between the Hylleraas and the experimental energies should be assigned to the correlation energy. If we assume that none of it should be so assigned, we obtain the smallest estimates of the size of the correlation energy, $-0.133\ R_{\mathrm{He}}hc$ and $-0.129\ R_{\mathrm{He}}hc$, respectively. These values are considerably larger than the value $-0.073\ R_{\mathrm{He}}hc$ found by Taylor and Parr.[6] The discrepancy is accounted for by their use of an older value of the Hartree-Fock energy[11] and by the fact that they did not employ an expansion coefficient to determine a correction factor, so that they took no cognizance, in the manner suggested above, of the reduction of this energy which would result if terms were included in the wave function to take account of the correlation in the position of the electrons.

In general, it is clear that the choice of the correction factor will depend on the particular approximation to the exact wave function which has been employed. Thus the coefficients of the $1s^2$ configuration in the expansions of the two Hylleraas functions were different. However, if one employs approximate wave functions which give good values of the energy and which are of sufficiently general form, the expansion coefficient of the $1s^2$ configuration should be relatively stable. It might seem that if the correlation energy is introduced by the addition of terms in the interelectron distances it would only be necessary to set the coefficients of such terms equal to zero to find the noncorrelation part of the energy. This is not the case, however, since when r_{ij} terms are introduced they will take up part of the average interelectron distance effect. Thus, in the case of the three-constant He I ground-state wave function, the contribution of the terms not involving the interelectron distance is only $-3.11084\ R_{\mathrm{He}}hc$.

It is interesting now to estimate what part of the total correlation energy is radial, what part angular, and what part may be classified as mixed. One may take the radial correlation energy for the ground state of He I as the difference between the contribution to the total energy from the purely radial terms of a wave function which gives a good value of the energy and contains both radial and angular terms and the Hartree-

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[10] W. S. Wilson, Phys. Rev. 48, 536 (1935).

[11] H. Bethe, *Handbuch der Physik* (Julius Springer, Berlin, 1933), second edition, Vol. 24/1, p. 370.

Fock energy corrected as in the preceding paragraphs. Similarly the angular part of the correlation energy may be taken as the difference between the contribution from the Hartree-Fock component plus the nonspherically symmetric components and the corrected Hartree-Fock energy. Finally, the mixed part of the correlation energy may be taken as the contribution from the cross-product terms between those parts of the purely radial terms which do not belong to the Hartree-Fock wave function and the nonspherically symmetric terms. We should therefore take the difference between the energy given in Table II for the spherically symmetric component and the corrected Hartree-Fock energy as the radial correlation energy. This quantity is $-0.056\ R_{\mathrm{He}}hc$ for both the three- and six-term wave functions. It is not possible from the data at hand to compute a value strictly according to the tentative definition given above for the angular correlation energy. This results from the fact that, in calculating the contribution of the nonspherically symmetric components, the cross-product terms have been found using Φ_0^N instead of the Hartree-Fock part of Φ_0^N. However, the correct calculation has been made for the cross product involving the first angular component Φ_1^N of the Hylleraas three-term expression, with the result that the value found was $-0.08896\ R_{\mathrm{He}}hc$ instead of $-0.08692\ R_{\mathrm{He}}hc$ as given in line 3 of Table II. This indicates, as was to be expected, that the mixed part of the correlation energy amounts to only a few percent of the radial and angular parts. If one accepts this result as applicable to the other angular components, which have not been specifically investigated, one would estimate the angular correlation energy as a few percent more than the difference between the energy given by one of the Hylleraas expressions and that given by its Φ_0^N component. The angular correlation energy is therefore probably a few percent more than $-0.077\ R_{\mathrm{He}}hc$ and $-0.073\ R_{\mathrm{He}}hc$, perhaps $-0.079\ R_{\mathrm{He}}hc$ and $-0.075\ R_{\mathrm{He}}hc$, for the three- and six-term wave functions, respectively. In accordance with this argument we estimate the mixed correlation energy very roughly as $+0.002\ R_{\mathrm{He}}hc$. These values for the parts of the correlation energy assume that the entire difference between the experimental ground-state energy and the values given by the Hylleraas functions should be attributed to that part of the energy which does not depend on the correlation of the positions of the electrons. Without this assumption the above values of the correlation energies would be slightly increased, but just how these small differences should be divided between the noncorrelation energy and the various parts of the correlation energy is not clear.

In summary the present work gives the results of the expansion of the three-term and the six-term expressions given by Hylleraas for the ground-state wave function of He I in series of normalized Legendre functions times normalized functions of r_1 and r_2. The coefficients in these expansions decrease with increasing order of the Legendre functions but not so rapidly as might have been expected. Thus the coefficient of the term involving the Legendre function of order one is 7 percent of the coefficient of the spherically symmetric term. The contribution of the various terms to the total energy falls off more rapidly. A definition of total correlation energy is suggested, and on the basis of this definition, the value of the total correlation energy is found to be at least $-0.129\ R_{\mathrm{He}}hc$ for the He I ground state. The total correlation energy is further divided into radial, angular, and mixed parts of estimated size $-0.056\ R_{\mathrm{He}}hc$, $-0.075\ R_{\mathrm{He}}hc$, and $+0.002\ R_{\mathrm{He}}hc$, respectively.