($\Delta F=0, \pm 1, \Delta m=0, \pm 1$) are given in Table IX. A prime added to the transition designation as *CE′* indicates a transition for which $\Delta m=0$. The oscillating field inducing such transitions must be parallel to the external field.

In intermediate fields the transition frequencies can be obtained by differencing the values of Tables VI and VII. The results of such a procedure are plotted in Figs. 3, 4, 5, and 6. Lines which are dotted along either their upper or lower halves indicate transitions forbidden in either the strong or weak field limit. The quantum numbers associated with each transition can be obtained by correlating the quantum numbers with the transition designation with the aid of Tables III and IV.

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Superposition of Configurations in the Ground State of He I*

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To obtain some understanding of the role played by various configurations in configuration interaction, the Hylleraas six-term expression for the ground-state wave function of He I has been expanded in series of orthogonal functions. To determine the degree of dependence of the coefficients of the expansion on the specific function used for the ground state, the Hylleraas three-term expression was also expanded. Two sets of orthogonal functions were used. One set consisted of orthogonalized symmetrized product type wave functions where the functions for the individual electrons were found from a Hartree self-consistent field without exchange. The second set consisted of orthogonalized variationally determined analytic wave functions. The results emphasize the large number of configurations which would have to be considered if the Hylleraas wave function were to be represented with high accuracy. After $1s^2$ the largest contributors among the configurations considered were $2p^2$ and $2s^2$.

IT has long been recognized[1] that the method of the self-consistent field involves three principal approximations: (a) the neglect of relativity effects, (b) the neglect of exchange effects, and (c) the neglect of the nonseparability of the wave functions. Relativity effects should be small for the lighter atoms. Exchange effects have been extensively investigated, principally by Hartree using Fock's equations. The inclusion of exchange improves the wave functions considerably and usually improves the energies somewhat. However, something is left to be desired. For example in O, O^+, and O^{++} the average difference between the observed and the calculated energies for the three lowest states are found to be 0.188, 0.088, and 0.114 respectively in units of the ionization energy of hydrogen when self-consistent field wave functions without exchange are used with Slater's integrals.[2] If wave functions with exchange are employed, the values obtained are 0.198, 0.086, and 0.080 with no improvement in the ratio of the multiplet separations.[3] To obtain further improvement one may attempt to remove the approximation involved in the neglect of the nonseparability of the wave functions. This has usually been done by considering the effects of superposition of configurations. A number of calculations of this sort have been made.[4] In general some improvement in multiplet 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[3] on O, O^+, and O^{++} and the work of Jucys[5] on C, the results were disappointing. Hartree, by the superposition of $1s^2 2p^{q+2}$ on $1s^2 2s^2 2p^q$, obtained for the average difference between the observed and calculated energies for the same lowest states of O, O^+, and O^{++} mentioned above 0.180, 0.108, and 0.090 respectively using wave functions with exchange to determine the effects of the configuration interaction. The ratio of the multiplet separations was considerably improved for O and somewhat improved for O^+ and O^{++}. Jucys, by superposing $1s^2 2s^2 2p^2$, $1s^2 2p^4$, $1s^2 2s^2 2p 3p$, and $1s^2 2s 2p^2 3s$ for CI reduced the average difference between the observed

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[4] C. W. Ufford, Phys. Rev. **44**, 732 (1933). R. E. Trees, Phys. Rev. **83**, 756 (1951). A. A. Schweizer, Phys. Rev. **80**, 1080 (1950). E. Trefftz, Z. Astrophys. **26**, 240 (1949) and **28**, 67 (1950). H. H. Marvin, Phys. Rev. **47**, 521 (1935). A. Many, Phys. Rev. **70**, 511 (1946). F. Rohrlich, Phys. Rev. **74**, 1372 (1948). J. N. P. Hume and M. F. Crawford, Phys. Rev. **84**, 486 (1951).

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TABLE I. Coefficients for the expansions of Hylleraas functions for the ground state of He I in terms of symmetrized product type functions.

	Self-consistent field functions				Analytic functions	
Configurations	Six-term Ψ_H		Three-term Ψ_H		Three-term Ψ_H	
	Non-Or.	Orthog.	Non-Or.	Orthog.	Non-Or.	Orthog.
$1s^2$	+0.9966	+0.9961	+0.9955	+0.9955	+0.9873	+0.9928
$1s2s$	−0.0020	−0.0023	−0.0004	−0.0005	+0.0556	+0.0553
$1s3s$	−0.0018	−0.0018	−0.0012	−0.0012		
$2s^2$	−0.0263	−0.0263				
$2p^2$ [a]	−0.0273	−0.0273	−0.0223	−0.0223		
Sum of squares of coefficients	+0.9947	+0.9936	+0.9915	+0.9915	+0.9779	+0.9887

[a] Spin and angular part chosen with signs as follows: $-6^{-\frac{1}{2}}(\alpha_1\beta_2-\beta_1\alpha_2)\times\{Y(1,1|1)Y(1,-1|2)-Y(1,0|1)Y(1,0|2)+Y(1,-1|1)Y(1,1|2)\}$.

and calculated energies for the three terms of the lowest configuration, $1s^22s^22p^2$, from 0.556 to 0.482 using self-consistent field wave functions without exchange, but the ratio of the multiplet separations became somewhat poorer.

In view of these results it seemed wise to investigate the effects of superposition by considering a relatively simple case in some detail. Consequently it was decided to expand certain of the Hylleraas wave functions for the ground state of He I in terms of sets of functions representing the various configurations.[6]

The six-term Hylleraas wave function gives the energy of the ground state of He I to one part in 6600. This accuracy was thought to be adequate for a preliminary survey. It also seemed wise to expand the Hylleraas three-term function at the same time in order to gain some knowledge of the dependence of the coefficients of the expansion on the specific function used for the ground state. This function reproduces the experimentally determined energy to one part in 2300. The two functions used for the ground state were therefore

$$\Psi_H=N_6e^{-Z_6s}(1+a_1u+a_2t^2+a_3s+a_4s^2+a_5u^2)$$

and

$$\Psi_H=N_3e^{-Z_3s}(1+b_1u+b_2t^2),$$

where $s=\rho_1+\rho_2$, $t=\rho_1-\rho_2$, and $u=\rho_{12}$, and the ρ's are expressed in atomic units. The values which were used for the constants were: $N_6=1.38189$, $Z_6=1.818$, $a_1=0.353$, $a_2=0.128$, $a_3=-0.101$, $a_4=0.033$, $a_5=-0.032$, and $N_3=1.32135$, $Z_3=1.816$, $b_1=0.30$, $b_2=0.13$.

The more critical choice is that of what type of functions to use in the expansion. Since more complicated atoms can be treated with moderate success only in the central field approximation, it seemed wise to test the effect of superposition in the present case by using sets of functions whose individual members were identifiable with particular solutions of the central field problem. The best functions of this type for He I are those for the self-consistent field without exchange given by Wilson and Lindsay.[7] Among the configurations which they give, we have used the following $1s^2$, $1s2s$, $2s^2$, and $2p^2$. To these we have added $1s3s$. Since the coefficients in the expansion depend on the set of functions used, it was thought desirable to see how the coefficients changed when a second set of functions was used. For this purpose analytic functions were chosen. For the $1s^2$ configuration the function $\exp[-1.6875(\rho_1+\rho_2)]$ was used, and for $1s2s$ the variationally determined function given by Morse, Young, and Haurwitz.[8]

The number of configurations which need to be considered in the present case is considerably reduced by the fact that superposition of configurations can only occur between configurations of the same parity.[9] Among the configurations involving electrons with smaller l-values we are thus limited to those of types: *nsms*, *npmp*, *nsmd*, and *ndmd*. Further, in pure Russell-Saunders coupling, only terms with the same L and S interact.[9] In He I the term intervals of the $1s2p\ ^3P$ are of the order 1 cm^{-1} whereas the separation of the ^3P and the ^1P is of the order of 2050 cm^{-1}. The coupling would therefore appear to be almost purely Russell-Saunders in character. Since the ground state is certainly primarily $1s^2\ ^1S$, the configuration *nsmd* can be eliminated. In addition it is only necessary to consider the ^1S terms of the remaining configurations. From the numerical wave functions given by Wilson and Lindsay, symmetrized products were made up and these were the functions used in the expansion. Morse's variational wave function for the $1s2s\ ^1S$ state was already in the symmetrized form.

The results of the present work are collected in Table I. The meaning of the various columns is clear except for the headings of Non-Or. and Orthog. to whose explanation we now turn. If the Hylleraas wave function, Ψ_H, is written

$$\Psi_H=c_1\psi(1s^2)+c_2\psi(1s2s)+\cdots, \tag{1}$$

where the ψ's are the symmetrized product functions described above, we are at once faced with the fact that these ψ's are not orthogonal except for the $2p^2$ function which is orthogonal to all *nsms* functions. In view of this, two sets of coefficients are given in Table I for each of the expansions which have been made. One set is determined using the non-orthogonal functions. In this case we assume that (for the numerical functions) the five configurations considered, namely $1s^2$, $1s2s$, $1s3s$, $2s^2$, and $2p^2$, are the only ones which make any contribution to the ground state. One can then solve the system of simultaneous linear equations obtained from Eq. (1) by multiplication of both sides by the various ψ's and integration over all space for the different c's.

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

[7] W. S. Wilson and R. B. Lindsay, Phys. Rev. **47**, 681 (1935). We are indebted to these authors for supplying us with more complete tables of their wave functions than were published.

[8] Morse, Young, and Haurwitz, Phys. Rev. **48**, 948 (1935).

[9] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, London, 1935), p. 366.

It was felt that if the values obtained for the various coefficients did not change appreciably as the series was broken off after three, four, and five terms, considerable confidence could be placed in the values obtained even from this limited expansion. In the worst case, that of $1s^2$, in going from the three to the four term expression the change was only 0.0004 so that some measure of stability seems to have been obtained in the values of these coefficients.

Another possible way of dealing with the fact that our ψ's are not orthogonal is, of course, to build from them by the Schmidt process[10] a new set of functions which are orthogonal. This has also been done and the results are given in Table I. However, such a procedure is open to some criticism, for the different members of the set of self-consistent field functions are not solutions of the same differential equation and of course this is also true of the analytic functions. After orthogonalization the nature of the new functions is somewhat obscure. On the other hand, it is clear from the similarity of the coefficients for the orthogonal and non-orthogonal functions in Table I that the effect of orthogonalization is small, that is, the ψ's were almost orthogonal initially. This would of course account for the stability of the coefficients of the ψ's noted above. As far as the effect of orthogonalization on the functions is concerned, it would therefore seem that the results in Table I can be taken with some confidence.

If now the coefficients in Table I are examined, the importance of the $1s^2$ configuration appears in every column. This is, of course, no surprise in view of the fact that the energy of $1s^2$, as found for example by Wilson[11] differs by only 1.4 percent from the experimentally determined value and the contribution to the ground state energy of this configuration should be roughly proportional to the square of its coefficient in Table I.

Perhaps the second most noticeable point in Table I is the large size of the coefficients for $2s^2$ and $2p^2$. These are so much larger than the coefficients for other excited states considered that it was thought wise, in spite of the agreement of the customary checking computations, to repeat the whole calculation for at least one of them using different numerical methods. The result obtained for $2s^2$ was 0.0266, somewhat larger but less accurate than before. It might appear possible that the large size of this coefficient was the result of not having orthogonalized this function to all the various possible members of the $1sms$ set of functions. An examination of the effect on this coefficient of orthogonalizing $2s^2$ to $1s^2$, $1s2s$, and $1s3s$ shows that the largest effect arises from $1s^2$ but that even here it is necessary to subtract only 0.01648 of $1s^2$ from Wilson and Lindsay's $2s^2$ to obtain a $2s^2$ orthogonal to $1s^2$. It therefore seems unlikely, but not certain, that the coefficient for $2s^2$ would be radically changed by orthogonalization to all members of the $1sms$ set. To check the coefficients of $2p^2$ further, the value of the constants in an arbitrary linear combination of $1s^2\,{}^1S$ and $2p^2\,{}^1S$ using hydrogenic functions with $Z=2$ have been determined by the variational method. The coefficient of the $2p^2\,{}^1S$ proved to be 0.0271 in as good agreement as could be expected with the value given in Table I for the six-term Hylleraas function. Since $2p^2$ is orthogonal to all $nsms$ wave functions and is the lowest member of the $npmp$ set, there is no possibility of any reduction in the size of its coefficient through orthogonalization.

It is also clear from Table I that the values of the coefficients for the configurations making the smaller contribution are sensitive to whether the three or the six term Hylleraas function is used. The indication is, however that the larger coefficients are relatively stable.

Finally it should be noted that if the expansions represented the Hylleraas function accurately, the sum of the squares of the expansion coefficients of the orthogonal functions would be one. Since the coefficients of all configurations considered other than $1s^2$ are small and therefore make a still smaller contribution to the sum of the squares, it is highly probable that it would be necessary when using self-consistent field functions to consider a large number of configurations if the ground-state wave function or energy is desired to high accuracy.

In summary, the present work emphasizes (a) the large contribution of $1s^2$ to the ground state wave function, (b) the surprisingly large size of the $2s^2$ and $2p^2$ contributions, and (c) the very large number of configurations which would have to be considered if a high accuracy wave function or energy were desired.

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[10] D. Jackson, *Fourier Series and Orthogonal Polynomials* (Carus Monograph No. 6, the Mathematical Association of America, Oberlin, Ohio, 1941), p. 151.

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