

Wave Functions for $1s2s\ ^1S$ Helium

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(Received February 24, 1936)

The $1s2s\ ^1S$ state of He has been treated with a variant of Hylleraas' variational method, and a wave function has been determined which gives an error of only 0.005 ev in the energy of the system. The properties of desirable functions for use in this method are discussed. Wave functions of the Hartree and Fock types, and a more flexible function not involving r_{12} , are also determined by simple variational processes. The properties of the resulting functions are compared, and are discussed in the light of the polarization method of Hylleraas and Bethe, properly applicable to more highly excited states. The computations by the polarization method have been extended, and the results are compared with those given by the variational procedure.

INTRODUCTION

ONE of the most interesting of the singly excited states of He, as well as one of the most difficult to treat, is the $2s$ state of parahelium. The difficulty arises from the fact that in the treatment of the moderately excited S states of He, methods of approximation which are satisfactory elsewhere tend to break down. This forces one to rely on variational methods, which are in general not so easily applied to excited states as to ground states. The best previously found wave function for this state is that of Hylleraas and Undheim.¹ The agreement of their energy with the experimental value is markedly poorer than that given by the Hylleraas method for the normal or the $2s$ *ortho* state of the atom.² In the study of this state of He, as a preliminary to the treatment of the ground state of lithium, we have therefore attempted to extend and improve the method by increasing its flexibility with respect to the radial coordinates, introducing two modifications. The first and more important consists of the use of two sets of terms with different values of the exponent applying to the "outer" electron. This corresponds to the work of Wilson³ and others who have constructed single orbitals for excited electrons by superposing terms with different exponentials, finding that only a very few terms are required. The second consists in forming the wave function as a sum of terms which differ somewhat in form from those used by Hylleraas

and Undheim, which may be constructed as sums and differences of our terms. Use of these terms somewhat mars the elegance of the mathematical treatment, but contributes to the clarity of the physical picture. It also tends to reduce the number of terms needed to attain a given accuracy in the treatment of the system.

Having thus produced a considerable increase in the accuracy with which this state can be treated we have chosen it as one suitable for a detailed consideration of the way in which atomic wave functions vary with the distance between the electrons, and for a comparison of the successes obtained by various simpler methods of attacking the problem. For this purpose it is particularly satisfactory in that the relation of the electrons is similar to that obtaining in interesting atoms such as Li, Na, etc., while this system is much easier to treat accurately.

FORM OF WAVE FUNCTIONS

The wave functions employed were of the form $\psi = \sum_{mnp} C_{mnp} [mnp]$, where $[m, n, p] = (\kappa^3/4\pi) \{ e^{-\nu\kappa r_1} (\kappa r_1)^m e^{-\delta\kappa r_2} (\kappa r_2)^n + e^{-\nu\kappa r_2} (\kappa r_2)^m e^{-\delta\kappa r_1} (\kappa r_1)^n \} (\kappa r_{12})^p$. κ is here a scale constant, δ and ν are parameters, and the distances which define a configuration are represented in the usual way. Other terms were also introduced, which we designate by $[m^*np]$, in which the * is not an adjunct of the m , but indicates that in these terms ν has been replaced by another parameter, ν^* . While the best value of κ could easily be determined during the final variation, we desired to base all our computations upon a single set of tables computed for fixed values of

¹ E. A. Hylleraas and B. Undheim, *Zeits. f. Physik* **65**, 759 (1930).

² E. A. Hylleraas, *Zeits. f. Physik* **54**, 347 (1929).

³ E. B. Wilson, *J. Chem. Phys.* **1**, 210 (1933).

the parameters δ , ν , ν^* , and after experimenting with some simple functions (of the type later called $F\Phi$), selected the following as suitable: $\delta=2$, $\nu=0.55$, $\nu^*=1$. Thus, δ is characteristic of a one-quantum orbital about the bare nucleus, ν corresponds to a two-quantum orbital governed by a highly shielded nucleus, and the star terms are useful in dealing with the region in the atom where the outer electron makes a close approach to the nucleus, penetrating a region where the shielding is less effective.

One advantage of the form chosen for terms in our wave function appears in the ease with which orbital functions can be represented. Thus, such a function as that employed by Zener⁴ is simply $[100]+c[000]$. The terms used by Hylleraas and Undheim are linear combinations of ours, $[100]\pm[010]$, $[200]\pm 2[110]+[020]$, $[200]-[020]$, etc.; it would require three of these to give the Zener function. This advantage is only partially lost in going to more general functions, for the helpful terms are those which are not too different from the ones occurring in the product functions. Our method enables these terms to be introduced by themselves, whereas in Hylleraas and Undheim's functions the helpful terms are linked with harmful ones, which can be removed only by using additional terms in order to cancel them out. For example, in constructing our best function, we can do as well by the inclusion of $[200]$ and $[110]$ alone as with the last three of the above combination terms; the term $[020]$ is harmful and must be eliminated.

The form of trial function adopted enabled us to determine analytical approximations to several simplified functions as well as to the correct function, permitting various interesting comparisons. The four functions which our approximations approach as limits are:

The Hartree function ($H\Phi$); the best function expressible in the form $K(r_1)\times L(r_2)$, where $K(r)$ and $L(r)$ are single-electron functions of the general character of $1s$ and $2s$ orbitals.

The Fock function ($F\Phi$); the best function which can be expressed as $K(r_1)\times L(r_2)+K(r_2)\times L(r_1)$, where $K(r)$ and $L(r)$ are similar to but not identical with those occurring in the $H\Phi$.

The Best Radial function ($R\Phi$); the best function of any form containing only r_1 and r_2 , which must enter symmetrically.

The Correct function ($C\Phi$); a function of r_1 , r_2 , and r_{12} , the first two entering symmetrically.

(The above abbreviations will be applied also

to our analytical approximations where no confusion will result.)

It must be clearly understood that these four limiting functions have a definite existence independent of the method used to approximate them. Thus $R\Phi$ is the exact solution of a differential equation obtained from the Schrödinger equation upon replacing $1/r_{12}$ at each point in configuration-space by its mean value over all points having the same values of r_1 and r_2 , i.e., by $1/g_{12}$ where g_{12} is the greater of r_1 and r_2 . There results an equation involving only r_1 and r_2 , but it cannot be separated and solved by a product of single-electron functions. The equations solved by $F\Phi$ and $H\Phi$ are sufficiently well known.

In the ensuing discussion we shall distinguish between two forms of atomic wave function constructed from the Hartree single orbitals. The first, which we shall designate $H_0\Phi$, is that already described, which neglects the requirement of symmetry in electron coordinates. The second, $H_x\Phi$, meets this requirement by the addition of exchange terms: it has thus the same form as $F\Phi$, but the coefficients are those determined by minimizing the energy of $H_0\Phi$. To find the energy of $H_x\Phi$ requires an additional computation, using these coefficients explicitly.

In using the variational method to find approximations for the various types of limiting function, we have simply to observe certain restrictions on the character of the terms used or the way in which they enter. The product functions $H\Phi$ and $F\Phi$ must have the form

$$\sum_m \sum_n c_m c_n' [m, n, 0] + \sum_m \sum_n c_m^* c_n' [m^*, n, 0]$$

corresponding to $K(r) = e^{-\delta r} \sum c_n' r^n$, $L(r) = e^{-\nu r} \sum c_m r^m + e^{-\nu^* r} \sum c_m^* r^{m^*}$, (taking $\kappa=1$). In determining $H\Phi$, of course, the exchange terms have to be omitted from the definitions of the functions and from the matrix formulas. Corresponding to the conventional way of determining these functions, we first assume that $K(r) = e^{-2r}$, the He^+ $1s$ function; we thus determine preliminary values of the c and c^* by variation among all terms having $n=0$, $p=0$. The next stage of approximation improves $K(r)$, determining the c' by a variation among individual terms each in the form $\sum_m \{c_m [m, n, 0] + c_m^* [m^*, n, 0]\}$. The c and c^* can then be readjusted if necessary,

⁴ C. Zener, Phys. Rev. 36, 51 (1930).

holding the c' constant, and so on until self-consistent results are reached. $R\Phi$ is obtained by an unrestricted variation among all terms having $p=0$; the removal of this specialization gives $C\Phi$.

In none of these variations (except that determining the $K(r)$ factor in the product functions $H\Phi$ and $F\Phi$) were we seeking an absolute minimum value of the energy parameter. Hylleraas and Undheim have shown, however, that the second root of the secular equation can never lie lower than the second characteristic energy value of the problem, and approaches that value as a limit as the terms in the series are improved, even though the lowest root may be at the same time a very poor approximation to the lowest energy value. The only precaution in using the method is, therefore, to be sure that one has the proper root.

INTRODUCTION OF r_{12}

There has been considerable experimentation to determine the most practical way of introducing r_{12} into the wave function. It will not do, (as Hylleraas and Undheim point out) merely to multiply a function of the $R\Phi$ type by $(1+cr_{12})$. Inspection of Table I will show that we find no tendency for the coefficients of the terms $[m, n, 1]$ to be proportional to those of the corresponding terms $[m, n, 0]$, a result likewise noticed by Hylleraas and Undheim. A possible guide to the selection of r_{12} terms can be derived by applying a method due to Hassé and Lennard-

Jones.⁵ We regard $R\Phi$ as the solution of an unperturbed equation, and introduce as a perturbation the quantity $1/r_{12}-1/g_{12}$. Then the Hassé approximation to $C\Phi$ is

$$R\Phi\{1+c[1/r_{12}-1/g_{12}]\},$$

c being a constant to be determined by variation. The energy corresponding to this function is not integrable over small r_{12} , but this is a defect in the approximation and not a property of the function which we desire to represent. Upon multiplication of the perturbation term by r_{12}/g_{12} we remove this defect and obtain an expression which is but little different from the Hassé approximation in regions where one r is much greater than the other, these regions being those where the approximation itself is valid, and simultaneously those in which the factor $R\Phi$ takes on its largest values. In a wave function for an excited atom, it is a small approximation to replace g_{12} by r_1 and r_2 , respectively, in the terms in which electron 1 and electron 2 are assigned the more diffuse distribution. From each term $[m, n, 0]$ of $R\Phi$ we thus derive $[m, n, 0] + c\{[m-1, n, 0]-[m-2, n, 1]\}$. The argument not being rigorous, we can in general get the best results by introducing the new terms with free coefficients to be determined by variation, rather than adhering to the relations between the coefficients which the Hassé approximation prescribes. Nevertheless we should expect definite cooperation between the terms which in the theory occur in pairs; each term in r_{12} may be most helpful only when a corresponding term, which behaves in nearly the same way for large r , is included in the series to be varied.

Terms suggested by this reasoning cannot be used for $m < 2$, for they would not be properly integrable. It may therefore be necessary to employ, say, the terms $[m, n, 0]$ and $[m-1, n, 1]$. Moreover, terms such as $[m+1^*, n, 0]$ and $[m^*, n, 1]$, are always available, and may to a certain extent take the place of $[m-1, n, 0]$ and $[m-2, n, 1]$, since both sets have the common feature of representing more compact distributions than the term $[m, n, 0]$ from which they are derived. We believe that this explains the fact that the introduction of star terms is more

TABLE I. *Computed wave functions and energies.*

FUNCTION	$H_0\Phi$	$H_2\Phi$	$F\Phi$	$R\Phi$	$C\Phi$
Energy, in $2R\hbar$	-2.13915	-2.14309	-2.14407	-2.14580	
Energy error (ev)	0.185	0.078	0.052	0.005	
$\frac{\kappa}{r^2}$ per electron	14.447	14.223	16.756	16.485	16.036
COEFFICIENTS OF TERMS IN NORMALIZED FUNCTIONS					
(000)	25.21939	8.41368	4.88925		
(100)	-6.32769	-2.75611	-0.02948		0.35368
(010)		-0.00725	-85415		-69387
(110)		.00237	.23488		.14042
(200)	0.28620	.05770	.09866		.12251
(020)		.03635	.03271		
(210)		-.00005			
(120)		-.01191			
(220)		-.00025			
(0*00)	-20.80546	-5.66385	-7.17757		-2.30134
(1*00)	-7.90329	-2.14445	-2.26128		0.47626
(0*10)		.00488	1.39627		1.08184
(1*10)		.00185			
(0*20)		-.02447			
(1*20)		-.00926			
(001)					0.63432
(101)					-.08422
(011)					.07633
(0*01)					-1.21923

⁵ J. E. Lennard-Jones, Proc. Roy. Soc. **A129**, 598 (1930); H. R. Hassé, Proc. Camb. Phil. Soc. **26**, 542 (1930).

helpful in constructing the function with r_{12} than when the terms with r_{12} are omitted.

The importance of a given term is by no means indicated by the magnitude of its coefficient in the series, partly because the terms as we define them are very differently normalized, and partly because it may happen that two fairly similar terms enter with large coefficients of opposite sign, the net result being a very small alteration of the function which might be ignored without serious effects. (In such a case it is not worth while to consider the corresponding terms in r_{12} .) A principal and indispensable term (as indicated by its effect on the computed energy) may thus have a relatively small coefficient, and serve as the basis for the construction of useful r_{12} terms, while other terms with larger coefficients are ignored for this purpose.

EVALUATION OF MATRIX COMPONENTS

The required matrix elements can all be found in terms of the integrals

$$J(f, g, h/\alpha, \beta) = (1/16\pi^2) \int dV r_1^f e^{-\alpha r_1} r_2^g e^{-\beta r_2} r_{12}^h.$$

$$J(m, n, -1) = V_{m+2, n+1}(\alpha, \beta) + V_{n+2, m+1}(\beta, \alpha),$$

$$J(m, n, 0) = V_{m+2, n+2}(\alpha, \beta) + V_{n+2, m+2}(\beta, \alpha) \\ = A_{m+2}(\alpha) \times A_{n+2}(\beta),$$

$$J(m, n, 1) = V_{m+2, n+3}(\alpha, \beta) + V_{n+2, m+3}(\beta, \alpha) \\ + \frac{1}{3} [V_{m+4, n+1}(\alpha, \beta) + V_{n+4, m+1}(\beta, \alpha)],$$

$$J(m, n, 2) = V_{m+2, n+4}(\alpha, \beta) + V_{n+2, m+4}(\beta, \alpha) \\ + V_{m+4, n+2}(\alpha, \beta) + V_{n+4, m+2}(\beta, \alpha) \\ = A_{m+2}(\alpha) \times A_{n+4}(\beta) + A_{m+4}(\alpha) \times A_{n+2}(\beta).$$

Here $A_n(\alpha) = \int_0^\infty e^{-\alpha\lambda} \lambda^n d\lambda$

and $V_{nm}(\alpha, \beta) = \int_0^\infty \lambda^n e^{-\alpha\lambda} d\lambda \int_\lambda^\infty \mu^m e^{-\beta\mu} d\mu.$

The latter quantities are conveniently computed by using formulas given by the writers.⁶

Consider two terms $[m, n, p]$ and $[m', n', p']$; as either or both may carry stars we must distinguish between the possibly different values ν and ν' which occur, whereas κ and δ must be the same in both terms. Between these terms the

matrix element of unity is

$$2J(m+m', n+n', p+p'/\nu+\nu', 2\delta) \\ + 2J(m+n', n+m', p+p'/\nu+\delta, \nu'+\delta);$$

which may be abbreviated to $2J(000) + 2J'(000)$, the general scheme of abbreviation being such that $J(a, b, c)$ stands for $J(m+m'+a, n+n'+b, p+p'+c/\nu+\nu', 2\delta)$ and $J'(a, b, c)$ is similarly formed from the "exchange" term. The matrix element of the energy, in units of $2R_\infty h$, is the sum of two terms involving J and J' , respectively, with identical coefficients as follows:

$$\kappa^2 \{ -(\nu^2 + \delta^2)J(000) + \nu(2m+p+2)J(-100) \\ - m(m+1+p)J(-200) + \delta(2n+p+2)J(0-10) \\ - n(n+1+p)J(0-20) + p[-2(p+1)-m-n] \\ \times J(00-2) + \nu J(10-2) - \nu J(-12-2) \\ + mJ(-22-2) + \delta J(01-2) - \delta J(2-1-2) \\ + nJ(2-2-2) \} + 2\kappa \{ J(00-1) - 2J(0-10) \\ - 2J(-100) \}.$$

It will be noted that these coefficients depend only on the first of the two combining terms. A symmetrical formula could of course be obtained; but the unsymmetrical form has the advantage of permitting a check against the alternative calculation in which the terms are interchanged.

RESULTS

In Table I will be found the wave functions and energies obtained in our best computations with functions of the various types.

The energies stated are those for the fixed nucleus problem, in units of $2R_\infty h = 27.074$ ev. Hylleraas² has shown that, to the approximation in which one can neglect the dependence of the wave functions on r_{12} , these numbers also give the energies of the corresponding approximate solutions of the free nucleus problem in units of $2R_{He} h = 27.070$ ev. Bethe⁷ has shown that for the ground state the correction for dependence on r_{12} of the function is a fifth of that above. In the present computations this further correction has been neglected, for the dependence of $C\Phi$ on r_{12} is much less important; the error in the energy arising from neglect of r_{12} terms is less than a tenth of that found for the ground state. The errors given in Table I are then differences between the corrected energies and the observed energy of the system.

⁶ H. M. James and A. S. Coolidge, Phys. Rev. 49, 688 (1936).

⁷ H. Bethe, Handbuch der Physik, Vol. 24/1.

A discussion of these results falls naturally into two parts; in the first we are concerned with the reliability of the approximations which the variation method yields, taking the four limiting functions and their corresponding energies as standards of perfection, while in the second it is these limiting functions themselves which interest us, and which we regard as sufficiently well represented by our approximations.

ACCURACY OF RESULTS OBTAINED BY THE VARIATIONAL PROCEDURE

Hylleraas and Undheim estimate that the limiting energy obtainable by a function of the radial type is -2.14400 . We have barely surpassed this, reaching -2.14407 . There appears to be no calculation of the function itself available for comparison. This is also true of the correct function.

As measured against experiment, the error in our approximation to the energy of $C\Phi$ is only about one-sixth of that associated with the six-term function of Hylleraas and Undheim, the best previously available. The essential difference between the two functions is the addition of the ν^* terms, to be discussed later. Other terms were introduced, but discarded as being of no value. The explorations made were, however, not sufficiently extensive to permit an accurate estimate of the convergence limit, in accordance with the procedure outlined elsewhere.⁸

In the case of the Hartree function, it is possible to make a direct comparison between the results of the variation method and those obtained by accurate numerical integration by Wilson and Lindsay⁹ at the first stage of the calculation, in which the $1s$ orbital is taken as e^{-2r} . The energy parameter ϵ for the $2s$ orbital we find to be $\epsilon_2 = 0.3054$, and Wilson informs us that they obtained precisely the same value, this proving the effectiveness of our variational procedure. In view of the existence of their complete solution, we have not carried out any further stages of approximation. In any case, the differences between our function and their final one are so small that we shall use our function in the following discussions.

⁸ H. M. James, A. S. Coolidge and R. D. Present, *J. Chem. Phys.* **4**, 187 (1936).

⁹ W. S. Wilson and R. B. Lindsay, *Phys. Rev.* **47**, 681 (1935).

The value given by Wilson¹⁰ for the energy of this state is, however, very different from ours, his computed ionization energy being less than that observed by 0.81 ev, while ours is in error by only 0.184 ev. Wilson calculated the energy of the atom by introducing into the formulas of Slater¹¹ values which he obtained for the integrals using his Hartree orbitals. In doing so he neglected the nonorthogonality of his orbitals; his value is accordingly not the energy associated with a wave function constructed from the Hartree orbitals, as ours is, and his computed ionization energy is not comparable with other results of the Hartree method.

Our approximate Fock function was obtained as a second approximation, varying each factor once. A further variation gave no appreciable change in the $2s$ orbital; this function thus represents the best approximation to the Fock function obtainable with the terms included. It may be compared with that computed by Hylleraas,¹² likewise by the variation method, but with a different series, and without varying the $1s$ orbital. Taking $\nu = 0.5$, he finds with the three terms $[m00]$, $m = 0, 1, 2$, the energy -2.14275 , which sinks to -2.14294 upon inclusion of two more terms of the same series. Judging by the smallness of the improvement given by the fifth term, he accepts this value as substantially the limit of convergence. With the same three terms as Hylleraas (but with $\nu = 0.55$) we find the energy -2.14285 ; putting $[0^*00]$ in place of $[200]$ gives us -2.14293 , illustrating the usefulness of the star terms. With $[200]$ and $[1^*00]$ in addition, we reached the value -2.14307 , appreciably lower than Hylleraas' apparent convergence limit. The value given in Table I, -2.14309 , shows the minute improvement resulting from variation of the $1s$ orbital, and justifies Hylleraas in neglecting this step. Comparison of numerical values of his $2s$ orbital with ours shows typical discrepancies of one or two percent; in view of the lower energy, we believe our result is superior. Our complete atomic function should be more reliable than that of Hylleraas also because we have improved the $1s$ factor.

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

¹¹ J. C. Slater, *Phys. Rev.* **34**, 1293 (1929).

¹² E. A. Hylleraas, *Zeits. f. Physik* **83**, 739 (1933).

COMPARATIVE ACCURACY OF THE METHODS
OF APPROXIMATION

The functions $H_x\Phi$ to $C\Phi$ which we have obtained may be considered as successive steps in the determination of an accurate function, in which approximations are successively removed. The approximations in $H_x\Phi$ consist of neglect of exchange in determining the function and failure to give a detailed treatment of the interelectronic repulsion. In $F\Phi$ the first of these is removed, while $R\Phi$ and $C\Phi$ represent two steps in taking better account of the electronic interaction. For comparison with our results on this state there appear in Table II certain corresponding values for the ground states of He and Be.

The exchange effects in $1s2s\ ^1S$ He and $(1s)^2(2s)^2$ Be are comparable with regard to the quantum numbers of the states involved; in Be, however, there are twice as many exchange terms. That the exchange effects in these two states differ by roughly a factor of 2 in absolute magnitude is thus not surprising. The percent of error in $H_x\Phi$ due to the neglect of exchange is, however, very different from that in Be, where there is not only an error due to neglect of the polarizing effect of the outer electron on the core, which has its analog in the excited He, but also a very large error due to failure to treat the interactions of the 2s electrons in a detailed manner. In such a case as this the Fock method does not offer a significant improvement over the Hartree method.

Abandonment of the orbital idea, the difference between $F\Phi$ and $R\Phi$, permits a partial adjustment of the relative positions of the electrons. In both of the states of He a third of the error of the Fock function is thus removed. This may be taken as a rough measure of the general effectiveness of this modification. Thus, for instance, a function similar to $R\Phi$ applied to the treatment of Be might give an error in the first two ionization energies as small as 1.0 ev. Further reduction of this error, associated principally with the treatment of the 2s electrons,

TABLE II. Errors in computed energy necessary for removal of two electrons.

	$(1s)^2\ ^1S$ He	$1s2s\ ^1S$ He	$(1s)^2(2s)^2$ Be
$H_x\Phi$	} 1.14 ⁽¹⁰⁾	0.185	1.95 ⁽¹³⁾
$F\Phi$		0.078	1.61 ⁽¹³⁾
$R\Phi$		0.052	

would require the very difficult step of introducing explicitly the distance between the 2s electrons.

RADIAL CHARGE DENSITIES

It is something of a problem to find a satisfactory method for portraying the wave functions of the different types, with the special object of facilitating intercomparisons. Fig. 1 shows the total radial charge densities; in order to avoid confusion due to overlapping, we have plotted a single curve for our best function, and indicated by an enlarged difference plot how the other values deviate from this. $C\Phi$ gives a charge density of the form $\rho_r = r^2 \sum_{\sigma, \tau} C_{\sigma\tau} e^{-\delta_{\sigma\tau} r}$. The coefficients are shown in Table III. Though useful for certain purposes, the total density is not adequate for a careful study of the functions, since it suppresses the most interesting characteristics of the better functions, which take into account in detail the interaction of the electrons. Thus, although the total density given by $R\Phi$ is much better than any of the others without r_{12} , it would be a mistake to conclude that $R\Phi$ is itself a correspondingly close approximation to the correct function, as consideration of the errors in the energy will show. On the other hand, in cases where only the charge density is of interest it may be a helpful simplification to use functions of this type. Improvement of the dependence of the functions on interelectronic distance will be seen to result in an increase in the charge density for the smaller values of r , when the electronic repulsions are most important. This is probably a general behavior.

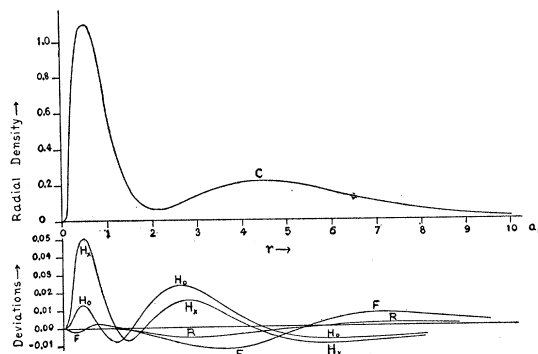


FIG. 1. Total radial charge densities. Upper figure shows values for $C\Phi$. Lower figure shows values for other functions minus those for $C\Phi$. Normalized to 2 on integration over r .

TABLE III. Constants in formula for total charge density of $C\Phi$ $\rho_r = r^2 \sum_{\sigma, \tau} e^{-\delta_{\sigma\tau}} C_{\sigma\tau} r^{\tau}$.

σ	δ_{σ}	$C_{\sigma, -1}$	$C_{\sigma 0}$	$C_{\sigma 1}$	$C_{\sigma 2}$	$C_{\sigma 3}$	$C_{\sigma 4}$
1	1.155	-0.02237	0.07185	-0.10055	0.10313	0.00738	0.00013
2	1.6275	.01346	-.01260	-.19053	-.14547	-.00476	
3	2.1	.03986	.23617	.16818	.04403		
4	2.6775	.18754	-.12678	-.16386	-.10751	.05943	.00199
5	3.15	-.19766	.70711	.19377	-.01275	-.03667	
6	4.2	-.06098	37.37703	2.90319	1.26657	.02744	.02464
7	5.355	-12.83385	-8.66312	-2.91047	-.57610	.01630	
8	5.8275	14.76190	6.80816	1.54834	.72437		
9	6.3	-1.88790	1.48937	1.68280			

On the other hand it cannot be expected in general that, as is observed here, the true radial density will be between those given by $H\Phi$ and $F\Phi$, for as we shall see, the relation between these functions varies with the system treated.

COMPARISON OF HARTREE AND FOCK FUNCTIONS

The product functions $H\Phi$ and $F\Phi$ can be compared by plotting or tabulating their separate $1s$ and $2s$ factors. Table IV gives the results for $F\Phi$, the quantities tabulated being the "radial amplitudes" $c_{1r}K(r)$ and $c_{2r}L(r)$, with c_1 and c_2 so chosen that each factor separately will be normalized with respect to integration over r alone. Since these two factors are not orthogonal, these normalization constants are not the proper ones for constructing a normalized atomic function; for the same reason, caution should be observed in comparing these orbitals with those given by other authors who have used the Fock method in problems where the symmetry was such as to permit solution in terms of orthogonal orbitals. In such cases comparison should be based on the complete atomic functions. Fig. 2 shows our $2s$ factors of $H\Phi$ and $F\Phi$; the $1s$ factors would on this scale be imperceptibly different from the He^+ orbital, and are not shown. The figure shows that the $2s$ factor of $F\Phi$ is more diffuse than that of $H\Phi$; this difference of course

carries over into the total charge density, since that due to the $1s$ factor and to the exchange is nearly the same in both cases. Fig. 1 shows that the total charge density due to $F\Phi$ is somewhat excessive at large r , while both $H_0\Phi$ and $H_x\Phi$ err more seriously in the opposite direction. These results contrast with those of Hartree and Hartree,¹³ who find for Be that the Fock density is more compact than that given by the self-consistent field theory, and surmise that this is a general relation. The origin of the difference is not far to seek. In the case of excited He, the exchange term occurs with a positive sign, just as in the Heitler-London treatment of two attracting H atoms; and for the same reason: there exists a degeneracy of configurations of the same total spin. In Be, and in general in atoms where the inner shells are filled, the situation resembles that of two repelling He atoms, in which there is no degeneracy of configurations and the exchange terms have negative coefficients. It is not surprising that the effects of considering exchange should be of opposite character in these contrasting cases. Similar remarks apply to the mean values of r^2 corresponding to $F\Phi$ and $H_x\Phi$. We find the former some 16 percent greater (see Table I), while in Be it is 11 percent smaller. (The Hartrees give 8.42 and 9.54 as the respective contributions from each electron in the $2s$ orbit. A rough numerical integration of their $1s$ function gives 0.23 as the corresponding r^2 , making the mean values per electron 4.32 for $F\Phi$ and 4.88 for $H_x\Phi$.) This result, however, is to be expected only in excited atoms, and therefore is hardly an objection to the general usefulness of the statement made by the Hartrees, that wave functions calculated by the method of the self-

TABLE IV. Radial functions in $F\Phi$.

r	$c_{1r}K(r)$	$c_{2r}L(r)$	r	$c_{1r}K(r)$	$c_{2r}L(r)$	r	$c_{2r}L(r)$
0.2	0.756	0.1033	2.4	0.114	-0.2487	6.4	-0.3787
0.4	1.014	0.1513	2.6	0.083	-0.2890	7.2	-0.3205
0.6	1.021	0.1601	2.8	0.061	-0.3261	8.0	-0.2615
0.8	0.913	0.1422	3.0	0.043	-0.3582	9.0	-0.1949
1.0	0.766	0.1066	3.4	0.022	-0.4071	10.0	-0.1406
1.2	0.617	0.0608	3.8	0.011	-0.4406	11.0	-0.0987
1.4	0.484	0.0086	4.2	0.005	-0.4573	12.0	-0.0671
1.6	0.372	-0.0459	4.6	0.003	-0.4602	13.0	-0.0456
1.8	0.281	-0.1006	5.0		-0.4533	14.0	-0.0302
2.0	0.210	-0.1528	5.4		-0.4388	15.0	-0.0197
2.2	0.155	-0.2026	5.8		-0.4181		

¹³ D. R. Hartree and W. Hartree, Proc. Roy. Soc. A150, 9 (1935).

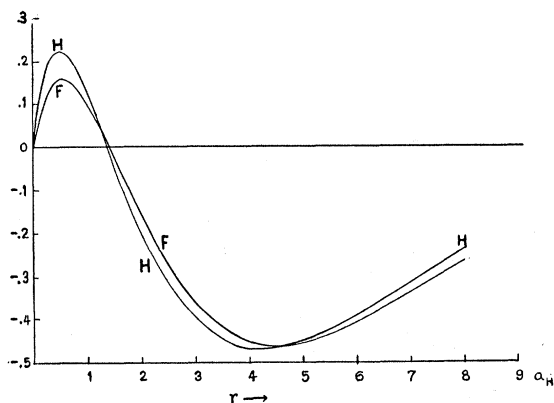


FIG. 2. $2s$ orbitals of Hartree function (H) and Fock function (F). Curves show $rL(r)$, normalized to 1 on integration over r .

consistent field appear always to give too large a value for the diamagnetic susceptibility.

THE POLARIZATION METHOD

The relation between the Fock function and those which are not restricted to the orbital form may be qualitatively understood with the aid of the polarization theory developed by Hylleraas¹⁴ and Bethe.⁷ The method, primarily applicable to highly excited atoms, makes use of a separation of variables similar to that generally used in molecular problems. The outer electron is regarded as moving so slowly in comparison with the inner that the motion of the latter is essentially that of a particle about two fixed centers, and may be represented by a wave function $u_2(1)$, a solution of the differential equation

$$\left(-\frac{1}{2}\nabla_1^2 - Z/r_1 - Z/r_2 + 1/r_{12}\right)u_2(1) = E_2u_2(1),$$

which is regarded as a function of the coordinates of electron 1 only, those of electron 2 entering as parameters. This function will differ from $K(1)$, the Hartree inner orbital, by being shifted in a direction away from the instantaneous position of the outer electron, so that its repulsive effect upon the latter is reduced. The outer electron is in turn considered as moving in the field of the thus polarized inner distribution plus that of the nucleus; its motion will be described by $v(2)$, a solution of a non-Coulomb central field problem. Clearly $v(2)$ will be more

compact than the corresponding Hartree orbital, in determining which the polarization of the inner orbital was neglected. As an approximate solution of the wave equation one then takes the definite function $\psi = u_2(1)v(2)$; there are no further steps of successive approximation, so long as polarization is dealt with in this manner.

In the case of a moderately excited atom the reasoning loses sharpness. In the first place, there is a considerable probability of the electrons being at comparable distances, so that neither can be regarded as almost stationary. In such configurations, we must (in terms of the classical analogy) think of the orbit of each electron as somewhat polarized by the instantaneous proximity of the other, but to only a fraction of the extent which would be caused by a stationary electron, since the actual electron does not occupy any given position long enough for the full effect to develop. The polarization correction as given by the Hylleraas-Bethe theory will therefore be excessive in the region of penetration. In the second place, the exchange terms required by symmetry are not negligible, and their interpretation is not clear. It is assumed that $\psi = u_2(1)v'(2) + u_1(2)v'(1)$, in which $u_2(1)$ is the function obtained above, while $v'(2)$ is the solution of the variational problem in which the energy of the complete function is minimized. To a first approximation the corrections due to exchange will be independent of the polarization corrections, and one may expect $v(2)$ and $v'(2)$ to be related in the same way as the outer orbitals given by the Hartree and Fock methods, respectively.

We shall now show that even in the comparatively little excited state which we are now considering, the qualitative, and to some extent the quantitative, properties of our functions are those indicated by this theory.

An exact calculation of $u_2(1)$ would be very difficult. Bethe⁷ and Ludwig¹⁵ have applied a perturbation method, starting with the simple He^+ function $u^0(1)$, and calculating the first-order perturbation produced as the outer electron moves in from infinity. They use an expansion in surface harmonics, and obtain only the terms in P_1 and P_2 , the first being much the more important. We have obtained a general formula for

¹⁴ E. A. Hylleraas, *Zeits. f. Physik* **66**, 453 (1930).

¹⁵ G. Ludwig, *Helv. Phys. Acta* **7**, 273 (1934).

these terms, and have included in our computations terms in P_0 and P_3 . (Details are reserved for a separate section.) The new terms are small except when the second electron is only slightly beyond the first, or even inside it,—that is, for configurations for which the basic ideas of the method break down anyway.

The function $v(2)$ has received practically no discussion by previous authors, who have been concerned primarily with determining energy values, for which purpose they have used Fock or even hydrogenic outer orbitals, as being sufficiently good in the case of highly excited states. We have not attempted to determine $v(2)$ directly, but have investigated an “empirical” $v(2)$ of form so chosen that, when combined with our approximate values of $u_2(1)$, it reproduced $C\Phi$ as well as possible. In the outer regions, this function is well defined by the total radial density; since the exchange terms are negligible here and $u_2(1)$ is normalized for integration over $d\tau_1$, the density gives immediately the square of $v(2)$. In the inner region, the choice of $v(2)$ becomes increasingly arbitrary; no values can be found which give consistent agreement, and those selected will serve as well as any to show the magnitude and nature of the discrepancies.

In Table V are indicated values of the assumed $v(2)$, the corresponding atomic function $P\Phi$, and $C\Phi$, for several configurations. We also include the angle variations (differences in the function for configurations with the same r_1 and r_2 , but minimum and maximum values of r_{12} , compared with the mean value over all values of r_{12}). This table shows that, as expected, the function $v(2)$, in the region where it is well defined, is appreciably more compact than the Fock outer orbital, and that it leads to an atomic function in quite satisfactory agreement with the correct function, both in absolute magnitude and in angle variation. The angle variation furnishes a particularly good test of the polarization theory, since the values calculated are only slightly dependent upon the form assumed for $v(2)$. In the inner region, on the other hand, the agreement becomes much worse, and the angle variation according to the polarization computation is much too large, likewise as expected.

Reasoning similar to that above can be applied to the determination of the function $R\Phi$. The

inner function $u_2(1)$ now describes the motion of the first electron in the field of a second electron distributed over a sphere with radius r_2 ; the first-order correction is given by the term in P_0 of the complete polarization theory. The “polarization” takes the form of an increasing diffuseness of $u_2(1)$ as r_2 becomes smaller. It must also result in some contraction of the outer function $v(2)$, compared with $L(2)$, but the smallness the P_0 term in the polarization correction indicates that this should be insignificant, except for very small r_2 .

COMPARISON OF THE FOCK FUNCTION WITH MORE ACCURATE FORMS

Except for the complication introduced by the exchange terms, we have now a basis for comparison between $R\Phi$ and $F\Phi$. In Fig. 3, we have plotted $r_1 r_2 R\Phi$ in the form of a series of curves for fixed values of r_1 , which we may regard as cross sections of the surface representing $r_1 r_2 R\Phi$ as a function of r_1 and r_2 . These cross sections are practically indistinguishable on this scale from those corresponding to $F\Phi$. For small r_1 , they have essentially the character of a 2s orbital, while, as r_1 increases, they pass over into the 1s orbital form. The exchange effect, a necessary consequence of the symmetry of the function, largely masks that due to polarization. It happens, however, that, for $r_1=0.2$, $F\Phi$ gives $r_1 K(1)=0.756$, $r_1 L(1)=0.1033$, while for $r_1=1.0$ we find $r_1 K(1)=0.766$, $r_1 L(1)=0.1066$. A comparison of the corresponding cross sections for $R\Phi$ and $F\Phi$ therefore practically eliminates the exchange effect, since the amounts of 1s and 2s orbitals present in $F\Phi$ are almost the same in both cases, and the exchange effect is supposed independent of the polarization correction. These cross sections are shown in Fig. 4. For large r_2 and small r_1 , both $F\Phi$ and $R\Phi$ reduce practically to the single terms $K(1)L(2)$ and $u_2(1)v(2)$. Further, $u_2(1)$ is, as shown by computation, practically indistinguishable from $K(1)$, so that in this region we are essentially comparing $v(2)$ with $L(2)$; it is seen that the difference between $R\Phi$ and $F\Phi$ is practically the same for both values of r_1 and corresponds to a slight contraction in the outer function. On the other hand, when both r 's are small the two terms in the function

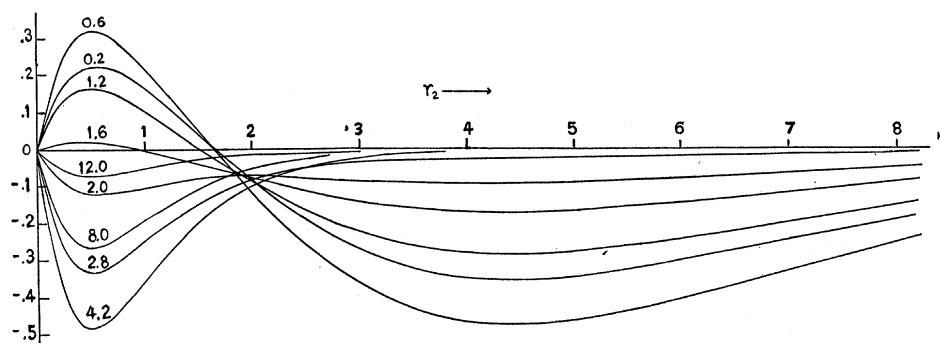


FIG. 3. Values of best function of r_1 and r_2 . Curves give $r_1 r_2 R\Phi$ as functions of r_2 for the indicated values of r_1 . On the scale shown, $R\Phi$ is normalized to $16\pi^2$ on integration over coordinate space.

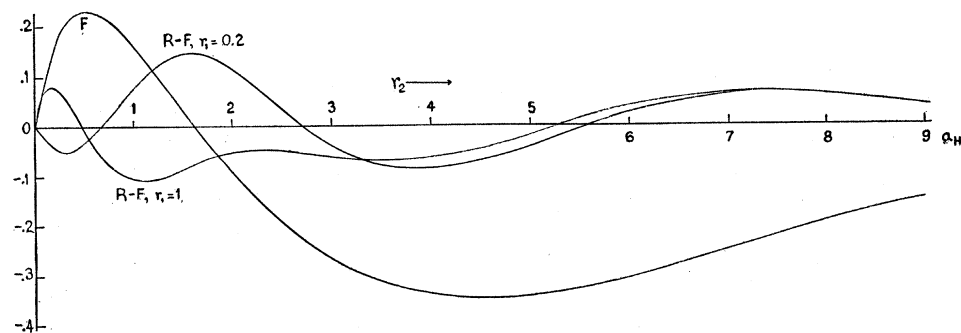


Fig. 4. Comparison of $R\Phi$ and $F\Phi$. Curve F shows values of $r_2 F\Phi$, for $r_1=0.2$ and for $r_1=1.0$, the values being too close together for separate representation. The other curves show, ten times enlarged, the values of $r_2(R\Phi - F\Phi)$ for r_1 as indicated. Normalization as in Fig. 3.

are of comparable importance, and both must be somewhat affected by polarization. We might represent $R\Phi$ as $K(1)L(2)g(1, 2) + L(1)K(2)h(1, 2)$, where the factors $g(1, 2)$ and $h(1, 2) = g(2, 1)$ have, both separately and in combination, the character of moving the average distribution of electron 2 in or out, respectively, accordingly as the known position of electron 1 moves out or in. In the Fock function $L(2)$ and $K(2)$ are distributions in the field of the average distribution of electron 1. In $R\Phi$, however, $L(2)g(1, 2)$, as a function of 2, is more diffuse than this if the fixed electron (considered as a K electron) is at an unusually small $r(0.2)$ and less diffuse if it is at a greater than average $r(1.0)$. On the other hand, $K(2)h(1, 2)$ is in both cases more diffuse than the Fock orbital $K(2)$, since 0.2 and 1.0 are both much smaller than the average distance of an L electron. The term $K(1)L(2)g(1, 2)$ is the principal part of the function for intermediate values of r_2 , and it may therefore be expected that the Fock cross section should lie between

the other two in this region. For still smaller distances the polarization idea breaks down completely and the theory ceases to be helpful; it remains true, however, that the Fock cross section lies between the other two.

$C\Phi$ differs from $F\Phi$, to an even greater extent than does $R\Phi$, in assigning a larger probability to the appearance of the two electrons at approximately the same r . This is, of course, not correlated with a corresponding increase in the indicated chance of the two electrons approaching each other, for the favored configurations place the electrons on opposite sides of the nucleus. At large r the charge density is distinctly more compact than for $F\Phi$ and $R\Phi$, as indicated by the polarization theory. In our diagram their difference in form between $R\Phi$ and $C\Phi$, really more pronounced than that between $F\Phi$ and $R\Phi$, is somewhat disguised by the different normalization of the outer parts of the distributions.

Table V will illustrate the importance of the dependence of $C\Phi$ on r_{12} , particularly for the

smaller values of r_1 and r_2 . Here the differences in $C\Phi$ with varying r_{12} are much greater than the differences between $R\Phi$ or $F\Phi$, and $\overline{C\Phi}$, the mean value of $C\Phi$ for given r_1 and r_2 . $R\Phi$ is in fact a fairly good approximation to $\overline{C\Phi}$ everywhere; from this the satisfactory agreement of the charge densities for $R\Phi$ and $C\Phi$ follows.

COMPLETE DETERMINATION OF FIRST-ORDER POLARIZATION OF THE CORE

We require a solution of the equation

$$\left(\frac{1}{2}\nabla_1^2 + E(r_2) + Z/r_1 + Z/r_2 - 1/r_{12}\right)u_2(1) = 0, \quad (1)$$

where r_2 is considered as a fixed parameter, and $u_2(1)$ is a function of the coordinates of electron 1 which depends upon the position of electron 2. We regard $(1/r_{12} - 1/r_2)$ as a perturbation term, small of the first order. Then, in terms of the new variables

$$\rho = Zr_1, \quad R = Zr_2,$$

we find the zeroth approximations for solution and energy to be

$$u^0(1) = (Z/2)ce^{-\rho}, \quad c^2 = 4Z/\pi; \quad E^0(R) = -\frac{1}{2}Z^2 - Z(Z-1)/R.$$

To the first order, the energy is $E^0(R) + \epsilon_1(R)$; where $\epsilon_1(R) = -Ze^{-2R}(1+1/R)$. The first approximation for the solution is assumed to have the form

$$u_2(1) = u^0(1) \left\{ 1 + \sum_{n=0}^{\infty} f_n(1, 2) P_n(\cos \theta_{12}) \right\}. \quad (2)$$

To determine the $f_n(1, 2)$, we expand $1/r_{12}$ in spherical harmonics, substitute (2) in (1), and equate terms of corresponding order of smallness and involving the same harmonics. Let $u^0(1)f_n(1, 2) = \varphi_n(\rho)$. There result the equations

$$\begin{aligned} \varphi_0'' - \varphi_0 + 2(\varphi_0' + \varphi_0)/\rho \\ = ce^{-\rho} \begin{cases} e^{-2R}(1+1/R) & \text{for } \rho < R, \\ [e^{-2R}(1+1/R) + 1/\rho - 1/R] & \text{for } \rho > R. \end{cases} \end{aligned} \quad (3)$$

$$\begin{aligned} \varphi_n'' - \varphi_n + 2(\varphi_n' + \varphi_n)/\rho - n(n+1)/\rho^2 \\ = ce^{-\rho} \begin{cases} \rho^n/R^{n+1}, & \rho < R, \\ R^n/\rho^{n+1}, & \rho > R, \end{cases} \quad n > 0. \end{aligned} \quad (4)$$

Ludwig gives the solutions of these equations for $n=1, 2$. (Through an error, he introduces a factor 2 on the right side, but his solutions are correct except that in his Eq. (15a) $(1+R^2)$ should read $(1+R)^2$.) The general solution for $n > 0$ may be obtained in the same way.

The case $n=0$ presents some interesting peculiarities. For the region $\rho < R$, a particular solution, everywhere finite, is found to be

$$\varphi_{in} = \frac{1}{2}e^{-2R}(1+1/R)ce^{-\rho} [Ei(2\rho) - \log(2\rho) - \rho - (e^{2\rho} - 1)/2\rho]. \quad (5)$$

To this may be added a constant, $\alpha(R)$, times that solution of the homogeneous equation which remains finite for $\rho \rightarrow 0$. Similarly, for $\rho > R$ a particular solution, vanishing properly at infinity, is

$$\begin{aligned} \varphi_{out} = \frac{1}{2}ce^{-\rho} \{ [e^{-2R}(1+1/R) + 1 - 1/R] \\ \times [1/2\rho - \log(2\rho) - \rho] + \rho \}. \end{aligned} \quad (6)$$

To this may be added a constant, $\beta(R)$, times that solution of the homogeneous equation which vanishes properly for $\rho \rightarrow \infty$. One would expect the constants α and β to be determined by the conditions that the two solutions and their derivatives must have the same values at $\rho=R$. However, it turns out that the two required solutions of the homogeneous equation are identical, namely, $u^0(1)$ itself. Continuity of function requires

$$\beta - \alpha = \beta^0 = (1/Z) \{ (e^{-2R}Ei(2R) - 1)(1+1/R) + \log(2R)(1-1/R) \}, \quad (7)$$

and it is found that this relation also leads to continuity of derivative.

There are therefore an infinite number of solutions of the complete equation which satisfy the boundary conditions. The one desired is that which is orthogonal to the unperturbed solution (a requirement which does not need to be considered when $n > 0$, since orthogonality is assured by the presence of the factor $P_n(\cos \theta_{12})$). We have, therefore, (since $u^0(1)$ is normalized),

$$\begin{aligned} \alpha(R) = - (4\pi/Z^3) \left[\int_0^R \varphi_{in} u^0 \rho^2 d\rho \right. \\ \left. + \int_R^\infty (\varphi_{out} + \beta^0 u^0) u^0 \rho^2 d\rho \right]. \end{aligned} \quad (8)$$

The final expressions for $f_n(1, 2)$ may be conveniently thrown into the form:

$$\text{For } \rho < R, f_n = - (1/Z) \{ A_n(\rho) B_n(R) + [C_n(\rho) - D_n(\rho)] E_n(R) + H_n(R) \}.$$

$$\text{For } \rho > R, f_n = - (1/Z) \{ C_n(\rho) [E_n(R) - F_n(R)] - G_n(\rho) R^n + K_n(R) \}.$$

For $n=0$, we find

$$\begin{aligned} A_0(x) &= 1 & B_0(x) &= 0 \\ C_0(x) &= 1/2x - x - \log(2x) & D_0(x) &= e^{2x}/2x - Ei(2x) \\ E_0(x) &= -e^{-2x}(x+1)/x & F_0(x) &= (x-1)/x \\ G_0(x) &= x \\ H_0(x) &= e^{-2x} \{ x + 2C - \frac{3}{2} + (2C-1)/x \\ & \quad + (1+1/x) \log(2x) + (1-1/x)e^{2x}Ei(-2x) \}. \\ K_0(x) &= H_0(x) - \{ (e^{-2x}Ei(2x) - 1)(1+1/x) \\ & \quad + \log(2x)(1-1/x) \}. \end{aligned}$$

C represents Euler's constant.

For $n > 0$, we let $n(n+1)/2 = m$; then

$$\begin{aligned} A_n(x) &= (n+1)x^n + nx^{n+1}, & B_n(x) &= 1/2mx^{n+1}. \\ C_n(x) &= 1/m + 1/x + m/2!x^2 + m(m-1)/3!x^3 \\ & \quad + m(m-1)(m-3)/4!x^4 \\ & \quad + m(m-1)(m-3)(m-6)/5!x^5 + \dots \\ D_n(x) &= \frac{1}{2}e^{2x}(-1)^{n+1} \{ 1/x^2 - (m-1)/x^3 \\ & \quad + (m-1)(m-3)/2!x^4 - \dots \}. \\ E_n(x) &= \frac{1}{2}e^{-2x}(-1)^{n+1}(2n+1)(1+x) \{ 1/x \\ & \quad + m/x^2 + m(m-1)/2!x^3 + \dots \}. \\ F_n(x) &= -\frac{1}{2}(2n+1)(1+x) \{ 1/x - m/x^2 \\ & \quad + m(m-1)/2!x^3 - \dots \}. \\ G_n(x) &= (n+(n+1)x)B_n(x). \\ H_n(x) &= 0, & K_n(x) &= 0. \end{aligned}$$