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FOCK EXPANSION FOR THE WAVE FUNCTIONS OF A SYSTEM OF CHARGED PARTICLES

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The method with which Fock[1] investigated the wave function of the ^1S state of helium is generalized to an arbitrary system of charged particles and to states of any symmetry.

1. In 1954, Fock[1] established the fact that the wave function of the ^1S state of helium and helium-like ions could be expanded in a double series of integral powers of $r = \sqrt{r_1^2 + r_2^2}$ and $\ln r$, where r_1 and r_2 are the distances of the first and second electrons from the nucleus. In this case, the proof was made by a method of successive determination of the expansion coefficients, which were homogeneous functions of zeroth order in the cartesian coordinates of the electrons (if the origin of the coordinates is fixed in the nucleus). We shall show that an expansion of this type, which we shall call a Fock expansion, has a very general character and is valid for any system composed of an arbitrary number of charged particles; there is also no need of placing any restrictions on the symmetry of the wave function.

As an example, we consider an N-electron atom (generalization of the results to more complicated systems presents no difficulties and is discussed below). The Schrödinger equation for the wave function of a stationary state (in atomic units) then has the form

$$H\psi = \left[-\frac{1}{2}\Delta_{3N} + U(x_1, x_2, \ldots, x_{3N})\right]\psi = E\psi. \qquad (1)$$

Here $x_1, \ldots, x_{3N}$ are the cartesian coordinates of the electrons, Δ_{3N} is the Laplace operator in the configuration space of 3N variables, while the potential energy U contains the Coulomb interaction of the electrons with the nucleus and between themselves, and is a homogeneous function of the coordinates of order −1. We introduce spherical coordinates in the configuration space. Then Eq. (1) takes the form

$$\left[\frac{1}{r^{3N-1}}\frac{\partial}{\partial r}\left(r^{3N-1}\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\Delta^*_{3N}\right]\psi + \frac{2V}{r}\psi = 2E\psi, \qquad (2)$$

where $r = (x_1^2 + \ldots + x_{3N}^2)^{1/2}$, Δ^*_{3N} is the Laplace operator on a sphere in a space of 3N dimensions, and V is a vector function of 3N − 1 spherical angles.

We shall now seek a solution of this equation in the form of a series

$$\psi = \sum_n \sum_p a_{np} r^n (\ln r)^p, \qquad (3)$$

where a_{np} are certain functions of the spherical angles which must be determined, and the subscripts n and p can take on integer values only. Substituting this expansion in Eq. (2), we obtain a system of equations for a_{np}:

$$\begin{gathered}\Delta^*_{3N} a_{np} + n(n + 3N - 2)a_{np} \\ = -(p+1)(2n + 3N - 2)a_{n,p+1} - (p+1)(p+2)a_{n,p+2} \\ + 2Va_{n-1,p} - 2Ea_{n-2,p}.\end{gathered} \qquad (4)$$

We shall carry out further investigation of this system by a method which was assumed by Fock for the helium atom, and we shall not therefore give the details of all the analysis.

First, we note that the factor $n(n + 3N - 2)$ on the left-hand side is precisely the eigenvalue of the operator Δ^*_{3N}. If we set the right-hand side of Eq. (4) equal to zero, then its solution will be a linear combination of the generalized spherical functions Φ_n of order n on the sphere in the 3N-dimensional space (we shall call them, here and below, spherical harmonics). With accuracy up to the same linear combination, both the solutions of Eq. (4) are determined; however the solution exists in this or that case only when the right-hand side of the equation is orthogonal to all spherical harmonics of order n.*

Another important property of the system (4) is that the coefficients a appear on the right hand side of the equation for the coefficient a_{np} for which either the first index is smaller than n, or the second index is larger than p. It then follows

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*The function V on the right-hand side of Eq. (4) contains singularities; however, these singularities are weak and do not affect the finiteness and continuity of the coefficients a_{np}.

that if the coefficients a_{np} are known for sufficiently small n and sufficiently large p, then, as a consequence of the "triangularity" of the system, we can determine the a_{np} successively for any n and p. To satisfy these conditions we can, in the first place, require that all the terms of the series (3) be finite at $r = 0$. For this, it is necessary to set all the a_{np} equal to zero for $n < 0$, and all the a_{0p} equal to zero for $p > 0$. In the second place, we must require that, for any fixed n, but for sufficiently large p, the coefficients a_{np} must vanish. This condition is necessary in order that the expansion be single-valued.

We can then solve the system (4) successively for $n = 0, 1, 2, \ldots$, and for each fixed n, beginning with the largest p for which the coefficient a_{np} is different from zero. Setting $n = p = 0$, we obtain $a_{00} = \text{const}$. Further, let $a_{1,p+1}$, $a_{1,p+2}, \ldots$ be equal to zero. Then, successively solving the equations for $a_{1,p}, a_{1,p-1}, \ldots, a_{10}$, and satisfying the conditions of orthogonality, we obtain $a_{1,p} = a_{1,p-1} = \ldots = a_{10} = 0$; the coefficient a_{11} is uniquely determined, and a_{10} — with accuracy up to a linear combination of spherical harmonics of first order. Then, solving Eq. (4) for $n = 2, 3, \ldots$, we obtain the expansion

$$\psi = \sum_{n=0}^{\infty} \sum_{p=0}^{n} a_{np} r^n (\ln r)^p, \tag{5}$$

where the coefficients a_{n0} are determined with accuracy up to a linear combination of spherical harmonics of order n, and all the remaining coefficients are established uniquely. All the a_{np} for $p < 0$ vanish, due to the presence of the factors $p+1$ and $(p+1)(p+2)$ on the right side of equation (4) for the coefficients $a_{n,p+1}$ and $a_{n,p+2}$, respectively. The Fock expansion for the wave function has such a form if we do not set any considerations of symmetry on the potential energy U.

We can further take into account the fact that the energy operator is invariant relative to inversion (i.e., change of sign of all coordinates), and, consequently, the solutions of Eq. (1) must be either even or odd. Then, in a number of cases, the parity of the right side of Eq. (4) and of the spherical harmonic of order n will be different; the orthogonality condition will be satisfied automatically, and certain coefficients a_{np} vanish. Furthermore, let us consider that some of the first terms of the expansion with $n = 0, 1, \ldots, k-1$, can be equal to zero. For this reason, the coefficients a_{np} again vanish and we obtain the expansion

$$\psi = \sum_{n=0}^{\infty} \sum_{p=0}^{[n/2]} a_{n+k,\,p}\, r^{n+k} (\ln r)^p, \tag{6}$$

in which only the coefficients $a_{k,0}, a_{k+2,0}, \ldots$ are determined non-uniquely, with accuracy up to linear combinations of spherical harmonics of $k, k+2, \ldots$, respectively. The parity of the function (6) coincides with the parity of the number k, which can take on the values $0, 1, 2, \ldots$. If $k > 0$, then the wave function ψ vanishes for $r = 0$. The expansion is of just this type for the two electron system and for $k = 0$ was obtained in reference 1. Comparing the exact functions considered here with the approximate functions, obtained by the method of separation of variables, it is easy to become convinced that the number k is equal to the sum of the azimuthal quantum numbers of all the electrons.

The solution of the Eq. (1) in the form (4) is obtained nonuniquely. For each fixed n, there remain arbitrary coefficients for the terms $r^n \Phi_{n\ldots}$, where $\Phi_{n\ldots}$ is the set of spherical harmonics of order n. Such a lack of uniqueness is obtained also in the solution of the Laplace equation in 3N dimensional space — its character is determined only by the differential part of the operator and is not connected in explicit fashion with the potential energy U. In our case, as also for the Laplace equation, this non-uniqueness is removed by the imposition of boundary conditions, i.e., by giving the asymptotic form of ψ for $r \to \infty$.

In our consideration, the spherical symmetry of the problem (in ordinary three dimensional space) has not been taken into account. Thanks to this symmetry, we can look for a general eigenfunction of the energy operator H and the operator of the square of the total angular momentum $\mathbf{m}^2$. Then the dependence of the coefficients a_{np} on those angles which characterize the simultaneous rotation of all the N electrons around the nucleus can be investigated independently of the explicit form of the operator H for each of the eigenvalues of the operator $\mathbf{m}^2$. For example, the function ψ does not generally depend (for the S state) on these angles, and thus the number of arguments in a_{np} is decreased by three. For the case $N = 2$, which was investigated by Fock, a_{np} depends only on two parameters: the angle θ between the radius vectors of the two electrons, and the ratio of the lengths of these vectors r_1/r_2. It is easy to become convinced that if we change to the variables $R = r^2$, θ, $\alpha = 2 \arctan (r_1/r_2)$ in Eqs. (2) and (3), then we get the Fock equation (3.10) of reference 1.*

If the potential energy of the interaction between

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*A correction must be made in Eqs. (3.09) and (3.10) of reference 1: in the second term of the right hand side of Eq. (3.09) we must add the factor k, and in the first term of the right side of Eq. (3.10), we must add the factor $k + 1$.

the electrons is neglected in the energy operator H, then the variables are separated and the problem can be solved exactly; the wave functions can be expanded in integral powers of r and thus the logarithmic terms in the expansion (3) should be absent. Actually, it is not difficult to show that in this special case the expression $2Va_{n-1,0} - 2Ea_{n-2,0}$ is orthogonal to all the spherical harmonics of order n, whence it follows that all the coefficients a_{np} with $p > 0$ vanish.

So far, we have assumed that the potential energy $U = U_{-1}$ is a homogeneous function of order -1. However, if it happens that the function U can be represented in the form of a series

$$U = U_{-1} + U_0 + U_1 + \dots = r^{-1} V_{-1} + V_0 + rV_1 + \dots, \qquad (7)$$

where U_i are homogeneous functions of order i, while the functions V_i depend only on the spherical angles, then on the right side of Eq. (4), the term $2Va_{n-1,p}$ must be replaced by the expression

$$2(V_{-1} a_{n-1,p} + V_0 a_{n-2,p} + V_1 a_{n-3,p} + \dots), \qquad (8)$$

in this case all the characteristics of the set (4) are preserved, and the solution can be obtained in the same way in the form (5). It is then evident that the expansion (5) remains valid for the potential energy of very general form, in particular, for the presence of an external electric field or for the placing of the origin of the coordinates of the nucleus at an arbitrary point of space.

It is also evident that similar considerations are applicable to an equation of the type (1), if a differential operator with constant coefficients, which can be transformed into a Laplace operator by a linear transformation of coordinates, replaces the Laplace operator.

This, for example, takes place for a quantum system of charged particles with different masses. In this case the role of the parameter r is played by the quantity

$$(m_1 r_1^2 + m_2 r_2^2 + \dots + m_N r_N^2)^{1/2}. \qquad (9)$$

As is well known, this very same quantity is widely used in the classical consideration of the many body problem.

Thus the Fock expansion is valid for a very wide class of equations in partial derivatives. It is a generalization of the well known expansion of the solution of ordinary differential equations in the vicinity of a regular singular point which contains a logarithm only in the first degree.

Consideration of the Fock expansion for a wave function of a many-electron system is evidently necessary in the case when the functions are computed with a high degree of accuracy, for example, for two electron systems by the Ritz method in high approximation. The attempt at multiple calculations[2,3] shows that if the test functions do not take into account the behavior of the wave function close to the nucleus, then it is extremely difficult to obtain the accuracy required for a comparison of the relativistic and radiative corrections with experiment.

In some cases, the matrix elements are strongly dependent on the behavior of the wave function close to the nucleus; the calculation of the Fock expansion is then especially necessary. Thus, for example, this is the case in the calculation of the matrix elements of the operator H^2, and for just this reason the estimate below for the energy of the ground state of helium in references 3 and 4 is much worse than the corresponding estimate above by the Ritz method. It is also evident that the behavior of the wave function close to the nucleus is important in the calculations of the interaction of the electronic shell with the nucleus.

It must therefore be expected that the Fock expansion, which takes into consideration the behavior of the wave function in this important region finds application in a wide variety of atomic calculations.

A detailed investigation of the solution of the set (4), the connection of the Fock expansion with other types of expansions of wave functions of helium, the possible generalization of this expansion, and also certain other problems will be set forth in a paper by A. M. Ermolaev, which will appear in the "Herald" (Vestnik) of Leningrad University.

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