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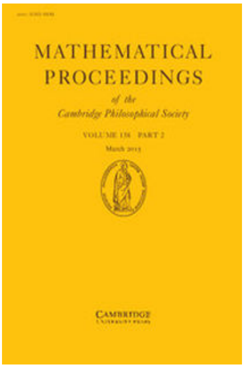

Wave Functions of Many-Electron Atoms

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Wave Functions of Many-Electron Atoms. By J. E. LENNARD-JONES, Ph.D., University of Bristol.

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1. The wave function of an atom containing many electrons has not yet been solved completely, even that of helium being as yet unknown. In the absence of a direct solution of the Schrödinger equation for the electrons in an atom, various attempts have been made to devise approximate methods of solution in particular cases. The particular case of helium, being the easiest, has received considerable attention and a number of approximate wave functions appropriate to the normal state have been constructed*. These functions usually contain empirical constants which are adjusted to make the energy of the system a minimum. Zener† has attempted the more ambitious programme of finding the wave functions of all the atoms in the first period of the Periodic Table (Lithium to Neon), and has made interesting discoveries as to the way in which the wave functions differ from atom to atom. This work also is based on the variation of parameters.

A different method has been developed by Hartree‡, which is equivalent to ascribing a definite orbit or state to each electron of the atom, consistent with the Exclusion Principle. Equations are constructed for each electron and solved numerically so as to make the distribution of charge in the atom reproduce the potential field already assumed. This method (the method of self-consistent fields) has been worked out for many atoms and has led to pictures of the charge distribution which have been extremely valuable in many physical problems. Fock has, however, shown that the Hartree equations are not really accurate since they neglect the important principle that electrons are identical and that interchanges may occur. This "exchange effect" leads to the introduction of new terms in the equations, as Fock§ and Dirac‖ have shown. Fock uses the Euler variation equation, to which the Schrödinger equation is equivalent, and, having assumed wave functions of the right symmetry properties, substitutes in the variation equation and thereby derives a system of linear differential equations, to which the

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* Hylleraas, *Zeits. f. Physik*, Vol. 54, p. 347 (1929); Slater, *Physical Review*, Vol. 32, p. 349 (1928).

† Zener, *Physical Review*, Vol. 36, p. 51 (1930); cf. also Slater, *Physical Review*, Vol. 36, p. 57 (1930).

‡ Hartree, *Proc. Camb. Phil. Soc.*, Vol. 24, pp. 89, 111 (1928).

§ Fock, *Zeits. f. Physik*, Vol. 61, p. 126 (1930).

‖ Dirac, *Proc. Camb. Phil. Soc.*, Vol. 26, p. 376 (1930).

Hartree equations are first approximations. Fock's method of deriving these equations is, however, not very attractive, and the object of this paper is to show that they can be obtained more briefly and elegantly by using the spin coordinates as well as the space coordinates.

2. The Schrödinger equation in atomic coordinates† for a nuclear charge N is

$$\left\{\sum_{j=1}^{N} H_j + \sum_{j>k=1}^{N} (1/r_{jk}) - E\right\}\Psi = 0 \quad \text{.........(2·01)},$$

where

$$H_j = -(\tfrac{1}{2})\nabla_j^2 - N/r_j \quad \text{..............(2·02)}.$$

One method of approximating to the solution of this equation is to choose another one which can be solved and use it as a basis for solving the actual equation. Let us suppose that an equation can be found of the type

$$\left\{\sum_{j=1}^{N} H_j^* - E\right\}\Psi = 0 \quad \text{..............(2·03)},$$

where

$$H_j^* = -(\tfrac{1}{2})\nabla_j^2 - v_j \quad \text{................(2·04)}$$

and v_j is a function of the jth set of coordinates alone. Then the equation (2·03) is separable and its solution can be expressed in terms of the solutions of

$$(H_j^* - \epsilon)\psi = 0 \quad \text{.................(2·05)},$$

which is an equation in the space coordinates of the jth electron alone.

Let the functions $\psi_1(j), \psi_2(j), \ldots$ be the solutions of the equation, where j is written for short for the space coordinates of the jth electron. These functions form an orthogonal set and may be taken to be normalised. Then a solution of (2·03) is of the type

$$\Psi = \psi_\alpha(1)\,\psi_\beta(2)\ldots\psi_\kappa(k)\ldots\psi_\nu(N) \quad \text{......(2·06)},$$

where $\psi_\alpha, \psi_\beta, \ldots$ are any members of the set of solutions of (2·05) and the coordinates of electrons 1, 2, ... are substituted in them. The corresponding energy is

$$E = \epsilon_\alpha + \epsilon_\beta + \ldots + \epsilon_\kappa + \ldots + \epsilon_\nu \text{...........(2·07)}.$$

There are many other wave functions like Ψ, with the same energy E, as is easily seen by permuting the coordinates 1, 2, ...

With each solution of equation (2·05) we may associate one or other of the two wave functions in the spin coordinate. These may

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† Unit of length equals the radius of the hydrogen Bohr orbit, and unit of energy equals twice that of normal hydrogen.

be denoted by $\alpha(\sigma)$ and $\beta(\sigma)$, the coordinate σ taking only the two values $\pm\frac{1}{2}$. These functions may be taken to be orthogonal and normalised so that

$$\sum_{\sigma}\bar{\alpha}(\sigma)\beta(\sigma)=0,\ \ \sum_{\sigma}\bar{\alpha}(\sigma)\alpha(\sigma)=\sum_{\sigma}\bar{\beta}(\sigma)\beta(\sigma)=1\ \ldots(2\cdot08).$$

The solutions of (2·05) may now be written as $\phi_1, \phi_2, \ldots$, the set containing twice as many as before, and still preserving the orthogonal property. Any member of the set, such as ϕ_κ, consists of a product such as $\psi_\kappa\alpha$ or $\psi_\kappa\beta$. A wave function of (2·03) is now

$$\Phi=\phi_\alpha(1)\,\phi_\beta(2)\ldots\phi_\kappa(k)\ldots\phi_\nu(N),$$

with the same energy as given by (2·07). Any linear expansion of the wave functions of this type, which have the same energy, is also a solution of equation (2·03). A wave function which incorporates the Exclusion Principle and the Principle of Identity of Electrons, as has been shown by Dirac* and used successfully by Slater†, is

$$\Phi=\mathrm{Det}\,\{\phi_\alpha(1)\,\phi_\beta(2)\ldots\phi_\nu(N)\},\ \ldots\ldots\ldots(2\cdot09),$$

the determinant containing $\phi_\alpha(1)\,\phi_\beta(2)\ldots\phi_\nu(N)$ as its leading term. This wave function is antisymmetric in the coordinates and no two of the functions $\phi_\alpha, \phi_\beta, \ldots$ are the same.

Slater‡ has shown that a wave function written in this way to include space and spin coordinates alike has many advantages over wave functions constructed in the space coordinates and the spin coordinates separately as has been the general practice. In particular it avoids many applications of the group theory, which were a necessary and unpleasant consequence of this method of attack.

It often happens that there are several such wave functions with the same energy. The excited states of a two-electron atom provide a simple example. Thus we may have

$$\left.\begin{aligned}\Phi_1&=\mathrm{Det}\,\{\psi_m(1)\,\alpha(\sigma_1),\ \psi_n(2)\,\alpha(\sigma_2)\},\\ \Phi_2&=\mathrm{Det}\,\{\psi_m(1)\,\alpha(\sigma_1),\ \psi_n(2)\,\beta(\sigma_2)\},\\ \Phi_3&=\mathrm{Det}\,\{\psi_m(1)\,\beta(\sigma_1),\ \psi_n(2)\,\alpha(\sigma_2)\},\\ \Phi_4&=\mathrm{Det}\,\{\psi_m(1)\,\beta(\sigma_1),\ \psi_n(2)\,\beta(\sigma_2)\},\end{aligned}\right\}\ \ldots(2\cdot10),$$

for since equation (2·03) does not contain the spin coordinates the latter have no influence on the energy to this approximation. All four have an energy $E=\epsilon_m+\epsilon_n$.

The degeneracy, which thus exists in such cases, is broken up when a perturbation is applied to the electronic system. Equation

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* Dirac, *Proc. Roy. Soc.*, Vol. 112, p. 661 (1926).

† Slater, *Phys. Review*, Vol. 34, p. 1293 (1929).

‡ Slater, *loc. cit.*

(2·01), which corresponds to the real atom, may be regarded as a perturbation of the artificial system (2·03), which up to now we have been considering. The real wave functions can then be expressed (to a first approximation) as linear expansions of the members of the degenerate set. Thus, in the two-electron atom, we find the wave functions to be Φ_1, $\Phi_2+\Phi_3$, Φ_4, each with the same energy (lower than $\epsilon_m+\epsilon_n$) and $\Phi_2-\Phi_3$ with an energy higher than $\epsilon_m+\epsilon_n$. The first three belong to the triplet set (ortho-helium) and the latter to the singlet set (parhelium). These new wave functions might be denoted by Ω_1, Ω_2, Ω_3 and Ω_4.

The important point is that, by considering an artificial system, we have arrived at wave functions of the real atom with definite symmetry properties, though these functions are only approximate. Three of the Ω's are antisymmetrical in the space coordinates and symmetrical in the spin coordinates, and vice versa for the fourth. These same symmetry properties may be expected to hold in the wave functions of a real atom, but we must no longer expect these functions to be expressible in the same simple explicit form. They may (and, in fact, probably do) contain as well the relative coordinates of the electrons r_{12}, r_{23}, ...

However, it will suffice for the present to suppose that the wave functions of the atom can be expressed in the same form as the Ω's. The problem then is to determine the component functions of which they are made up (ψ_m etc.) so as to satisfy Schrödinger's equation in the best possible way.

To sum up, we may say that an atomic system will give rise to a series of multiplets, and the number of wave functions associated with each energy level or state will be a measure of the multiplicity. The symmetry properties of these wave functions may be obtained from considerations of an artificial electron system such as that given by equation (2·03), and then wave functions of the real atom may be constructed by analogy.

3. Once suitable wave functions have been constructed, their actual determination may be made by the use of the variation method, as Fock* does. The Euler variation equation corresponding to the Schrödinger equation (2·01) is

$$\int \delta\overline{\Omega}\left\{\sum_j H_j+\sum_{j>k}(1/r_{jk})-E\right\}\Omega\,d\tau=0 \quad ......(3\cdot01),$$

where the integration is taken over the four coordinates of each electron. Now it may be shown that if

$$\Omega_1,\ \Omega_2,\ \ldots\ \Omega_\nu$$

all belong to the same term, that is, have the same energy, the

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[*] Fock, *loc. cit.*

substitution of any one of them in equation (3·01) leads to the same result*. In considering the triplet system of helium, for instance, we may substitute either

$$\Omega_1 = \begin{vmatrix} \psi_m(1)\,\alpha(\sigma_1) & \psi_n(1)\,\alpha(\sigma_1) \\ \psi_m(2)\,\alpha(\sigma_2) & \psi_n(2)\,\alpha(\sigma_2) \end{vmatrix}$$

or

$$\Omega_3 = \begin{vmatrix} \psi_m(1)\,\beta(\sigma_1) & \psi_n(1)\,\beta(\sigma_1) \\ \psi_m(2)\,\beta(\sigma_2) & \psi_n(2)\,\beta(\sigma_2) \end{vmatrix}$$

in the variation equation, and it will clearly be simpler to do so than to use Ω_2, which is a sum of two such determinants.

The theory of multiplets in atoms arising from a given configuration of electrons in an artificial system such as (2·03) has been worked out in a very elegant way by Slater†. He shows what had already been established by vector models by Hund‡, that the term of greatest multiplicity is usually lowest in energy. What is of greater interest from our point of view is that there are series of wave functions $\Omega_1, \Omega_2, \ldots \Omega_\nu$, of which the first and last can be expressed as single determinants, while the rest consist of sums of determinants. The configuration of the atom to which these two determinants correspond is that of a number of closed shells with electrons outside in different states or "orbits" but all having the same spin. In such a case, the wave function can be written

$$\Omega = \begin{vmatrix} \psi_1(1)\,\alpha(\sigma_1), & \psi_1(1)\,\beta(\sigma_1), & \ldots\,\psi_p(1)\,\alpha(\sigma_1), & \psi_p(1)\,\beta(\sigma_1), & \psi_{p+1}(1)\,\alpha(\sigma_1), & \ldots\,\psi_q(1)\,\alpha(\sigma_1) \\ \cdot & \cdot & \cdot\qquad\cdot & \cdot & \cdot & \cdot\qquad\cdot \\ \cdot & \cdot & \cdot\qquad\cdot & \cdot & \cdot & \cdot\qquad\cdot \\ \psi_1(N)\,\alpha(\sigma_N), & \psi_1(N)\,\beta(\sigma_N), & \ldots\,\psi_p(N)\,\alpha(\sigma_N), & \psi_p(N)\,\beta(\sigma_N), & \psi_{p+1}(N)\,\alpha(\sigma_N), & \ldots\,\psi_q(N)\,\alpha(\sigma_N) \end{vmatrix}$$

where the first $2p$ columns alternate with α and β spin, but the last $q-p$ columns have the same spin (either α or β). It is probably more convenient to re-arrange the determinant so that all the wave functions of the same spin are together. Thus we may write

$$\Omega = \operatorname{Det}\{\psi_1(1)\,\alpha(\sigma_1)\,.\,\psi_2(2)\,\alpha(\sigma_2)\ldots$$
$$\ldots\,\psi_q(q)\,\alpha(\sigma_q)\,.\,\psi_1(q+1)\,\beta(\sigma_{q+1})\ldots\,\psi_p(N)\,\beta(\sigma_N)\} \quad \ldots(3·02).$$

By suitable linear combinations of the *last* p columns a set of functions can be derived from $\psi_1, \ldots, \psi_p$, which are orthogonal to each other. The determinant Ω will not be altered in the process except perhaps by a numerical factor. Similar linear combinations of the *first* p columns may then be made. Finally linear combina-

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* Fock, *loc. cit.*, § 5.

† Slater, *loc. cit.*

‡ Hund, *Linienspektren u. periodisches System der Elemente*, Springer (1927).

tions of the first p functions so derived and of the functions $\psi_{p+1}, \ldots, \psi_q$ can be found so that the first q columns of the determinant contain functions which are mutually orthogonal. Since the first q columns are orthogonal to the last p columns because of the spin, every function in the determinant is orthogonal to every other function. Nothing in the process of making the functions mutually orthogonal has altered the fact that the first q columns have α spin and the last p columns β spin. Clearly each function may be normalised without altering the determinant except by a numerical constant. So we may regard the set of functions contained in Ω to be orthogonal and normalised. Such a wave function may be said to be "prepared." The wave functions of nearly all atoms in their normal state may be prepared in this manner.

4. The problem now is to determine the individual functions of which a prepared wave function like Ω is composed. By substituting in the variation equation (3·01) a number of linear differential equations in three coordinates only may be obtained, instead of the Schrödinger equation in its many coordinates, to which (3·01) is equivalent.

Let the prepared wave function be

$$\Omega = \text{Det}\,\{\phi_1(1) \ldots \phi_q(q) \ldots \phi_N(N)\} \quad \ldots\ldots(4{\cdot}01),$$

where the functions ϕ_1 to ϕ_q contain an α-spin factor and the functions ϕ_{q+1} to ϕ_N (where $N = p + q$) contain a β-spin factor.

Substituting in equation (3·01) we find

$$\int \Big(\sum_i \bar{\delta}_i\Big)\Big(\sum_j H_j + \sum_{j>k} (1/r_{jk})\Big)\rho\, d\tau = E \int \Big(\sum_i \bar{\delta}_i\Big)\rho\, d\tau \ldots(4{\cdot}02),$$

where

$$\rho = \bar{\Omega}\Omega = \begin{vmatrix} \rho(1,1) & \rho(1,2) & \ldots & \rho(1,N) \\ \rho(2,1) & \rho(2,2) & \ldots & \rho(2,N) \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \rho(N,1) & \rho(N,2) & \ldots & \rho(N,N) \end{vmatrix} \ldots\ldots(4{\cdot}03),$$

and

$$\rho(1,2) = \sum_{l=1}^{N} \bar{\phi}_l(1)\,\phi_l(2) \ldots\ldots\ldots\ldots\ldots(4{\cdot}04).$$

We have adopted the convention that $\bar{\delta}_i$ operates only on the coordinates of the ith electron when they appear in terms such as $\rho(i,j)$, but not in terms like $\rho(j,i)$.

Further,
$$\bar{\delta}_i\,\rho(i,j) = \sum_{l=1}^{N} \delta_i\bar{\phi}_l(i)\,.\,\phi_l(j) \quad \ldots\ldots\ldots\ldots(4{\cdot}05).$$

Similarly H_j operates only on $\rho(i, j)$ and not on $\rho(j, i)$ and

$$H_j \rho(i, j) = \sum_{l=1}^{N} \bar{\phi}_l(i) H_j \phi_l(j) \quad \text{...........(4·06).}$$

Thus

$$(\bar{\delta}_i H_j) \rho = \begin{vmatrix} \rho(1,1), & \dots H_j \rho(1,j), & \dots \rho(1,N) \\ \cdot & \cdots \quad \cdot & \cdots \quad \cdot \\ \bar{\delta}_i \rho(i,1), & \dots \bar{\delta}_i H_j \rho(i,j), & \dots \bar{\delta}_i \rho(i,N) \\ \cdot & \cdots \quad \cdot & \cdots \quad \cdot \\ \rho(N,1), & \dots H_j \rho(N,j), & \dots \rho(N,N) \end{vmatrix} \quad \text{...(4·07).}$$

The determinant ρ has many remarkable properties. It may be integrated with respect to any of its variables with great ease. For example, to integrate with respect to the coordinates of the Nth electron, we note that these variables occur only in the last row and column of the determinant. The determinant may easily be expanded as a sum of terms each containing one element from the last row and column. A typical term is $\rho(i, N)\rho(N, j)$ multiplied by minus the cofactor of $\rho(i, j)$ in the minor of $\rho(N, N)$. Now

$$\int \rho(i, N) \rho(N, j) \, d\tau_N = \rho(i, j) \quad \text{...........(4·08),}$$

owing to the orthogonal properties of the ϕ's, and by a known theorem on determinants,

$$\rho = \rho(N, N) \rho_{N-1} - \sum_i \sum_j \rho(i, N) \rho(N, j) \{\text{cofactor of } \rho(i, j) \text{ in } \rho_{N-1}\} \quad \text{......(4·09),}$$

where ρ_{N-1} is the determinant obtained from ρ by omitting the Nth row and column. Hence

$$\begin{aligned} \int \rho \, d\tau_N &= N \rho_{N-1} - (N-1) \rho_{N-1} \quad \text{........(4·10)} \\ &= \rho_{N-1}, \end{aligned}$$

since

$$\int \rho(N, N) \, d\tau_N = N \quad \text{................(4·11),}$$

because of the normal properties of the ϕ's.

Similarly

$$\int \rho_{N-1} \, d\tau_{N-1} = N \rho_{N-2} - (N-2) \rho_{N-2} = 2 \rho_{N-2} \quad \text{...(4·12),}$$

$$\int \rho \, d\tau_{q+1} \dots d\tau_N = (N-q)! \, \rho_q \quad \text{...................(4·13),}$$

$$\int \rho \, d\tau_1 \dots d\tau_N = N! \quad \text{...............................(4·14).}$$

A number of other properties of the determinant may be demonstrated, though they must be omitted as they are not needed in the present paper. A typical result may be quoted. If the factor of the expression

$$\begin{vmatrix} \rho(x_k, x_j) & \rho(x_k, x_l) \\ \rho(x_i, x_j) & \rho(x_i, x_l) \end{vmatrix}$$

in the determinant ρ is integrated over all the variables except those of $d\tau_i d\tau_j d\tau_k d\tau_l$, the result is

$$\{(N-2)!/2!\}\begin{vmatrix} \rho(x_j, x_k) & \rho(x_l, x_k) \\ \rho(x_j, x_i) & \rho(x_l, x_i) \end{vmatrix}$$

when i, j, k and l are all unequal. When $l = k$ the expression can be integrated over the range of $d\tau_{lk}$ and $d\tau_l$ as well and the result is

$$-\{(N-1)!/2!\}\,\rho(x_j, x_i).$$

In view of the results (4·12)—(4·14) we may say that ρ is *integrable along the diagonal**. In the same way, it may be shown that $(\delta_i H_j)\,\rho$, when its rows and columns are suitably rearranged, is integrable $(N-2)$ times along the diagonal.

We thus find

$$\begin{aligned}\int \bar{\delta}_i H_j \rho\, d\tau_1 \ldots d\tau_N & \\ &= (N-2)!\int \bar{\delta}_i \rho(i,i)\, d\tau_i \int H_j \rho(j,j)\, d\tau_j \\ &\qquad - (N-2)!\int \rho(j,i)\,\bar{\delta}_i H_j \rho(i,j)\, d\tau_i d\tau_j \\ &= (N-2)!\left\{\left(\sum_m H_{mm}\right)\int \delta\bar{\psi}_n \,.\, \psi_n\, dx - \underset{m,n}{S}\, H_{mn}\int \delta\bar{\psi}_n \,.\, \psi_m\, dx\right. \qquad \ldots\ldots(4{\cdot}15),\end{aligned}$$

where

$$H_{mn} = \int \bar{\psi}_m H \psi_n\, dx \qquad \ldots\ldots\ldots\ldots\ldots\ldots(4{\cdot}16).$$

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* In a paper which has just appeared (*Proc. Camb. Phil. Soc.* Vol. 27, p. 240 1931) Dirac gives a simple interpretation of the function ρ. The expression $\rho\, d\tau_1 \ldots d\tau_N$ is the probability that an electron shall be found in $d\tau_1$, another in $d\tau_2$, … and so on; in other words, it gives the probability of a specified configuration. The probability of finding $N-1$ electrons in a prescribed configuration irrespective of the position of the Nth may therefore be obtained by integrating ρ over the variables of the Nth electron, and is therefore ρ_{N-1}. The probability of finding q of the electrons in prescribed elements of volume may be obtained by integrating over the variables $d\tau_{q+1} \ldots d\tau_N$ in such a way that each configuration appears only once. Thus the configuration $q+1 = (q+1)'$, $q+2 = (q+2)'$, … $N = N'$, and any permutation of $(q+1)'$, $(q+2)'$, … N' among the variables $q+1, q+2, \ldots N$ must be counted as the same. The result is just ρ_q.

The special sign $\mathop{S}\limits_{m,n}$ is used to denote a summation over those pairs of wave functions m and n, *which have the same spin factor*. Those which have opposite spin factor are orthogonal and disappear on integration over $d\tau_i$ and $d\tau_j$. The ordinary summation $\sum\limits_{m}$ used in (4·15) implies that m ranges over all values 1 to N irrespective of spin factors. The integration of H_{mn} and those contained in (4·15) are with respect to space coordinates only.

Similarly

$$\int \bar{\delta}_i H_i \rho \, d\tau = (N-1)! \sum_n \int \delta \overline{\psi}_n . H \psi_n \, dx \quad \text{......(4·17)},$$

so that

$$\int \left(\sum_i \bar{\delta}_i\right) \left(\sum_j H_j\right) \rho \, d\tau = N! \sum_n \int \delta \overline{\psi}_n \left\{ H\psi_n - \mathop{S^{(n)}}_{m} H_{mn} \psi_m + \left(\sum_m H_{mm}\right) \psi_n \right\} dx \quad \text{......(4·18)},$$

where $\mathop{S^{(n)}}\limits_{m}$ is a summation over all those ψ's which are associated with the same spin factor as ψ_n in Ω.

Again

$$\int (\bar{\delta}_i / r_{jk}) \rho \, d\tau = (N-3)! \int (\bar{\delta}_i / r_{jk}) \begin{vmatrix} \rho(i,i) & \rho(i,j) & \rho(i,k) \\ \rho(j,i) & \rho(j,j) & \rho(j,k) \\ \rho(k,i) & \rho(k,j) & \rho(k,k) \end{vmatrix} d\tau_i d\tau_j d\tau_k \quad \text{......(4·19)}.$$

There are $N(N-1)(N-2)/2$ terms of this type, since the number of pairs j, k with $j > k$ is $N(N-1)/2$ and the number of ways of choosing i to be different from either of them is $N-2$. We thus find

$$\int \left(\sum_i \bar{\delta}_i\right) \left(\sum_{j>k} (1/r_{jk})\right) \rho \, d\tau \div N!$$

$$= \tfrac{1}{2} \left\{ \sum_{l,m} (lm \,|\, G \,|\, lm) - \mathop{S}_{l,m} (lm \,|\, G \,|\, ml) \right\} \sum_n \int \delta \overline{\psi}_n . \psi_n \, dx$$

$$- \left\{ \sum_l . \mathop{S}_{m,n} (lm \,|\, G \,|\, ln) - \mathop{S}_{l,m,n} (lm \,|\, G \,|\, nl) \right\} \int \delta \overline{\psi}_n . \psi_m \, dx \quad \text{...(4·20)}.$$

The summation $\mathop{S}\limits_{l,m,n}$ is over those sets of ψ-functions which are associated with the same spin factor in the wave function Ω, and we have used the notation

$$(\kappa\lambda \,|\, G \,|\, \mu\nu) = \int \overline{\psi}_\kappa(j) \overline{\psi}_\lambda(k) \psi_\mu(j) \psi_\nu(k) (1/r_{jk}) \, dx_j dx_k \quad \text{...(4·21)}.$$

The case of $i=j$ or $i=k$ can be dealt with similarly. The result is

$$\sum_i \sum_{j\neq i} \int (\bar{\delta}_i/r_{ij})\, \rho\, d\tau \div N! = \int \delta\bar{\psi}_n \psi_n V(x)\, dx - \mathop{S}_{m,n} \int \delta\bar{\psi}_n \psi_m G_{mn}(x)\, dx \qquad \text{......(4·22)},$$

where
$$G_{mn}(x) = \int \bar{\psi}_m(x')\, \psi_n(x')\, (1/r)\, dx' \qquad \text{.........(4·23)},$$

and
$$V(x) = \sum_n G_{nn}(x) \qquad \text{.....................(4·24)}.$$

The right-hand side of equation (4·02) is easily found to be

$$E \sum_i \int \bar{\delta}_i \rho\, d\tau = (N!)\, E \sum_n \int \delta\bar{\psi}_n . \psi_n\, dx \qquad \text{.........(4·25)},$$

and from the Schrödinger equation (2·01), we find

$$\begin{aligned} E &= \int \Big(\sum_j H_j + \sum_{j>k} 1/r_{jk} \Big) \rho\, d\tau \div \int \rho\, d\tau \\ &= \sum_n H_{nn} + \tfrac{1}{2} \int (1/r_{jk}) \begin{vmatrix} \rho(j,j) & \rho(j,k) \\ \rho(k,j) & \rho(k,k) \end{vmatrix} d\tau_j\, d\tau_k \\ &= \sum_n H_{nn} + \tfrac{1}{2} \Big\{ \sum_{l,m} (lm\,|\,G\,|\,ml) - \mathop{S}_{l,m} (lm\,|\,G\,|\,ml) \Big\} \qquad \text{...(4·26)}. \end{aligned}$$

The variation equation (4·02) thus consists of a number of differentials $\delta\bar{\psi}_n$ and the factors of each can be equated separately to zero. The result is a series of equations of the type

$$\begin{aligned} [H + V(x)]\, \epsilon_n \psi_n(x) - \mathop{S^{(n)}}_{m} \Big\{ G_{mn}(x) + H_{mn} + \sum_l (lm\,|\,G\,|\,ln) \Big\} \psi_m \\ + \mathop{S^{(n)}}_{l,m} (lm\,|\,G\,|\,nl)\, \psi_m = 0 \qquad \text{...............(4·27)}, \end{aligned}$$

where ϵ_n is the number of times ψ_n occurs in Ω, and may be either 1 or 2. These are the required equations for the functions ψ_n.

Special Cases. When the atom consists of p pairs and $q-p$ outer electrons in different states but possessing the same spin, then ψ_n may be associated with either α-spin or β-spin, when $n<p$. In this case $\epsilon_n = 2$,

$$\mathop{S^{(n)}}_{m} = \sum_{m=1}^{p} + \sum_{m=1}^{q},$$

and
$$\mathop{S^{(n)}}_{l,m} = \sum_{l=1}^{p} \sum_{m=1}^{p} + \sum_{l=1}^{q} \sum_{m=1}^{q}.$$

But when $p < n < q$, we have

$$\epsilon_n = 1, \quad \underset{m}{S^{(n)}} = \sum_{m=1}^{q}, \quad \underset{l,m}{S^{(n)}} = \sum_{l=1}^{q} \sum_{m=1}^{q}.$$

The asymmetry in Fock's results† is thus explained. Equation (4·27) has the advantage of bringing both of them within the same scheme.

Hartree's equations are obtained from (4·27) by neglecting (i) the factors of every ψ_m for which $m \neq n$ and (ii) the non-diagonal matrix elements $(ln|G|nl)$. The equation then becomes

$$\left\{H + \sum_n{}' G_{nn}(x)\right\} \psi_n(x) = \left\{H_{nn} + \sum_l{}' (ln|G|ln)\right\} \psi_n(x).$$

The term $\sum_n{}' G_{nn}(x)$ is the potential of the nth electron due to the Coulomb fields of all the other electrons averaged over their respective probability charge distributions; H_{nn} is the energy of the nth electron in the field of the nucleus alone, and $\sum_l{}' (ln|G|ln)$ is its energy due to the presence of all the other electrons. Hartree has solved these equations numerically by assuming the fields $G_{nn}(x)$ to be spherically symmetrical, then by making an assumption as to their form and adjusting them until the solutions of the ψ's obtained reproduce the field. These solutions might be used as a basis for the solution of the equations (4·27), but the disadvantage of the method is that the solutions can only be obtained in a numerical form. Perturbation methods cannot be applied because the excited states of the system would have to be found as well and the arithmetical labour of doing so would be prohibitive.

Another method of attack is to find an equation which is separable and which is yet a good representation of the actual system. Suppose that $V_n^*(x)$ were such a potential and that

$$(H + V_n^* - E)\psi_n(x) = 0 \quad \text{..............(4·28)}$$

could be solved completely (just as the hydrogen atom can be, where $V_n^* = -1/r$), giving a set of wave functions $\psi_l, \psi_m, \psi_n, \ldots$. These could then be substituted in equation (4·27) and

$$V_n^* - \sum_n{}' G_{nn}(x) \quad \text{....................(4·29)}$$

could be regarded as a perturbation of (4·28).

The assumed function $V_n^*(x)$ should approach N/r as $r \rightarrow 0$ and should approximate to $1/r$ as $r \rightarrow \infty$. A function of this type is

$$V_n^* = -\{1 + (N-1)e^{-ar}\}/r,$$

where a is any suitable constant. A solution of equation (4·28) with such a form for V_n^* would be a valuable step towards a solution of the wave functions of complex atoms.

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† Fock, *loc. cit.*, equations (83) and (84).

Note added in proof.

When the wave functions occurring in Ω are not orthogonal to each other, it is more convenient to use another expansion for $\bar{\Omega}\Omega$ than that used above. It is easy to show that

$$\bar{\Omega}\Omega = \sum_P P \begin{vmatrix} \bar{\phi}_1(1)\,\phi_1(1), & \bar{\phi}_1(2)\,\phi_2(2), & \dots & \bar{\phi}_1(N)\,\phi_N(N) \\ \cdot & \cdot & \dots & \cdot \\ \bar{\phi}_N(1)\,\phi_1(1), & \bar{\phi}_N(2)\,\phi_2(2), & \dots & \bar{\phi}_N(N)\,\phi_N(N) \end{vmatrix},$$

where the summation is over all permutations of the electron coordinates among the columns of the determinant. There are obviously $N!$ such determinants.

Integration with respect to any variable can be carried out with great ease, as each variable occurs in only one column of the determinant; thus integration with respect to all the coordinates except those of electron 1 is given by

$$\int \bar{\Omega}\Omega\, d\tau_2 \dots d\tau_N = (N-1)! \sum_{k=1}^{N} \begin{vmatrix} a_{11}, & a_{12}, & \dots & \bar{\phi}_1(1)\,\phi_k(1), & \dots & a_{1N} \\ a_{21}, & a_{22}, & \dots & \bar{\phi}_2(1)\,\phi_k(1), & \dots & a_{2N} \\ \cdot & \cdot & \dots & \cdot & \dots & \cdot \\ a_{N1}, & a_{N2}, & \dots & \bar{\phi}_N(1)\,\phi_k(1), & \dots & a_{NN} \end{vmatrix},$$

where
$$a_{jk} = \int \bar{\phi}_j(x)\,\phi_k(x)\,dx.$$

If H is an operator such that

$$H = \sum_k H_k,$$

and H_k operates on the coordinates of electron k only, we find

$$\int \bar{\Omega} H \Omega\, d\tau_1 \dots d\tau_N = N! \sum_{k=1}^{N} \begin{vmatrix} a_{11}, & a_{12}, & \dots & H_{1k}, & \dots & a_{1N} \\ \cdot & & \dots & \cdot & \dots & \cdot \\ \cdot & \cdot & \dots & \cdot & \dots & \cdot \\ a_{N1}, & a_{N2}, & \dots & H_{Nk}, & \dots & a_{NN} \end{vmatrix}.$$

Similar results for $\int \delta\bar{\Omega}\,.\,\Omega\, d\tau_1 \dots d\tau_N$ can also be deduced.