beta-decay theory are not fulfilled in this decay process. Certainly all other experimental results support the former conclusion.

The authors wish to express their appreciation to the crews of the University of Illinois and the University of Chicago cyclotrons, who provided most of the Be[7] used in these experiments. They are also grateful for a very valuable discussion of the experiment with Dr. Raymond Davis of the Brookhaven National Laboratory, to a great deal of excellent advice on surface preparation given by Prof. C. W. Sherwin of the Department of Physics, University of Illinois.

# A Simplification of the Hartree-Fock Method

J. C. SLATER
Massachusetts Institute of Technology,* Cambridge, Massachusetts
(Received September 28, 1950)

It is shown that the Hartree-Fock equations can be regarded as ordinary Schrödinger equations for the motion of electrons, each electron moving in a slightly different potential field, which is computed by electrostatics from all the charges of the system, positive and negative, corrected by the removal of an exchange charge, equal in magnitude to one electron, surrounding the electron whose motion is being investigated. By forming a weighted mean of the exchange charges, weighted and averaged over the various electronic wave functions at a given point of space, we set up an average potential field in which we can consider all of the electrons to move, thus leading to a great simplification of the Hartree-Fock method, and bringing it into agreement with the usual band picture of solids, in which all electrons are assumed to move in the same field. We can further replace the average exchange charge by the corresponding value which we should have in a free-electron gas whose local density is equal to the density of actual charge at the position in question; this results in a very simple expression for the average potential field, which still behaves qualitatively like that of the Hartree-Fock method. This simplified field is being applied to problems in atomic structure, with satisfactory results, and is adapted as well to problems of molecules and solids.

## I. INTRODUCTION

THE Hartree-Fock equations[1] furnish the best set of one-electron wave functions for use in a self-consistent approximation to the problem of the motion of electrons in the field of atomic nuclei. However, they are so complicated to use that they have not been employed except in relatively simple cases. It is the purpose of the present paper to examine their meaning sufficiently closely so that we can see physically how to set up a simplification, which still preserves their main features. This simplified method yields a single potential in which we can assume that the electrons move, and we shall show the properties of this field for problems not only of single atoms but of molecules and solids, showing that it leads to a simplified self-consistent method for handling atomic wave functions, easy enough to apply so that we can look forward to using it even for heavy atoms.

## II. THE HARTREE-FOCK EQUATIONS AND THEIR MEANING

It is well known that the Hartree equations are obtained by varying one-electron wave functions $u_1(x)$,

$u_2(x)$, $\cdots u_n(x)$, in such a way as to make the energy $\int u_1^*(x_1)\cdots u_n^*(x_n)Hu_1(x_1)\cdots u_n(x_n)dx_1\cdots dx_n$ an extreme, where $H$ is the energy operator of a problem involving $n$ electrons in the field of certain nuclei, and where the functions $u_i$ are required to be normalized. Similarly the Hartree-Fock equations, as modified by Dirac,[2] are obtained by varying the $u_i$'s so as to make the energy

$$\frac{1}{n!}\int \begin{vmatrix} u_1^*(x_1)\cdots u_1^*(x_n) \\ \cdots\cdots\cdots\cdots\cdots \\ u_n^*(x_1)\cdots u_n^*(x_n) \end{vmatrix} H \begin{vmatrix} u_1(x_1)\cdots u_1(x_n) \\ \cdots\cdots\cdots\cdots\cdots \\ u_n(x_1)\cdots u_n(x_n) \end{vmatrix} dx_1\cdots dx_n$$

an extreme, where in this latter expression the $u$'s are assumed to be functions depending on coordinates and spin, and where the integrations over the $dx$'s are interpreted to include summing over the spins. The Hartree-Fock equations can then be written in the form

$$H_1u_i(x_1)+\left[\sum_{k=1}^n \int u_k^*(x_2)u_k(x_2)(e^2/4\pi\epsilon_0 r_{12})dx_2\right]u_i(x_1)$$

$$-\sum_{k=1}^n \left[\int u_k^*(x_2)u_i(x_2)(e^2/4\pi\epsilon_0 r_{12})dx_2\right]u_k(x_1)$$

$$=E_iu_i(x_1). \quad (1)$$

Here $H_1$ is the kinetic energy operator for the electron of coordinate $x_1$, plus its potential energy in the field of

[1] J. C. Slater, Phys. Rev. 35, 210 (1930); V. Fock, Z. Physik 61, 126 (1930); L. Brillouin, Les Champs Self-Consistents de Hartree et de Fock, Actualités Scientifiques et Industrielles No. 159 (Hermann et Cie., 1934); D. R. Hartree and W. Hartree, Proc. Roy. Soc. A150, 9 (1935); and many other references.

[2] P. A. M. Dirac, Proc. Cambridge Phil. Soc. 26, 376 (1930).

all nuclei; $e^2/4\pi\epsilon_0 r_{12}$ is the Coulomb potential energy of interaction between electrons 1 and 2, expressed in mks units; to get the corresponding formula in Gaussian units we omit the factor $4\pi\epsilon_0$, and to get it in atomic units we replace $e^2/4\pi\epsilon_0$ by 2. The $u_i$'s as before are assumed to depend on spin as well as coordinates, and the integrations over $dx_2$ include summation over spin, so that the exchange terms, the last ones on the left side of Eq. (1), automatically vanish unless the functions $u_i$ and $u_k$ correspond to spins in the same direction.

The Hartree-Fock equations in the form given present an appearance which seems to differ from the ordinary one-electron type of Schrödinger equation, and for this reason it is ordinarily thought that they cannot be given a simple physical interpretation. This assumption arises partly from the paper of Dirac[2], in which they are interpreted in a rather involved way. The second term on the left of (1) is simple: it is clearly the Coulomb potential energy, acting on the electron at position $x_1$, of all the electronic charge, including that of the $i$th wave function whose wave equation we are writing. The last term on the left, the exchange term, however, is peculiar, in that is is multiplied by $u_k(x_1)$ rather than by $u_i(x_1)$. It must somehow correct for the fact that the electron does not act on itself, which it would be doing if this term were omitted. In the Hartree, as opposed to the Hartree-Fock, equations, this is obvious. There the last term differs from that in the Hartree-Fock equations only in that all terms in the summation are omitted except the $i$th; the exchange term in that case then merely cancels the term in $k=i$ from the Coulomb interaction found in the second term. The main point of our discussion is to show that an equally simple interpretation of this term can be given in the Hartree-Fock equations.

Let us first state in words what the interpretation proves to be; then we can more easily describe the way in which the equations lead to it. We can subdivide the total density of all electrons into two parts, $\rho_+$ from those with plus spins, $\rho_-$ from those with minus spins; the two together add to the quantity $-e\sum(k=1\cdots n)$ $\times u_k^*(x)u_k(x)$, where $e$ is the magnitude of the electronic charge. Then we can show that the Hartree-Fock Eq. (1) for a wave function $u_i$ which happens to correspond to an electron with a plus spin is an ordinary Schrödinger equation for an electron moving in a perfectly conventional potential field. This field is calculated by electrostatics from all the nuclei, and from a distribution of electronic charge consisting of the whole of $\rho_-$, but of $\rho_+$ corrected by removing from the immediate vicinity of the electron, whose wave function we are finding, a correction or exchange charge density whose total amount is just enough to equal a single electronic charge. That is, this corrected charge distribution equals the charge of $n-1$ electrons, as it should. The exchange charge density equals just $\rho_+$ at the position of the electron in question, gradually

falling off as we go away from that point. We can get a rough idea of the distance in which it has fallen to a small value by replacing it by a constant density $\rho_+$ inside a sphere of radius $r_0$, zero outside the sphere. We have $\frac{4}{3}\pi r_0^3|\rho_+| = e$, or

$$r_0 = (3e/4\pi|\rho_+|)^{\frac{1}{3}}. \tag{2}$$

The situation is then much as if the corrected charge density equaled the actual total electronic charge density outside this sphere, but was only $\rho_-$ within the sphere; there is a sort of hole, sometimes called the Fermi[3] or exchange hole, surrounding the electron in question, consisting of a deficiency of charge of the same spin as the electron in question. Actually, of course, this exchange hole does not have a sharp boundary, but the charge density of the same spin as the electron in question gradually builds up as we go away from this electron. Similar statements hold for the field acting on an electron of minus spin.

The exchange hole clearly is different for wave functions of the two spins, provided $\rho_+$ and $\rho_-$ are different; examination proves further that it is different for each different wave function $u_i$. It is this difference which leads to the complicated form of the Hartree-Fock equation; and the simplification which we shall introduce in a later section is that of using sort of an averaged exchange hole for all the electrons. The difference between the exchange charge for two wave functions $u_i$ corresponding to the same spin is not great, however. We have already seen that the radius $r_0$ which we obtain by assuming a hole of constant density depends only on $\rho_+$ (for a plus spin), and hence is the same for all $u_i$'s of that spin. Thus the exchange holes for different $u_i$'s of the same spin will only show small differences. We shall later examine these differences for the case of a free electron gas, and show that they are really not large. It is this small dependence on $u_i$ which will make it reasonable to use an averaged exchange charge in the simplified method which we shall suggest later.

To agree with the qualitative description which we have just given, we then expect the exchange charge density at point $x_2$, producing a field acting on the electron at $x_1$ whose wave function $u_i(x_1)$ we are determining by the Hartree-Fock Eq. (1), to integrate over $dx_2$ to $-e$ (a single electronic charge), and to be equal when $x_2$ approaches $x_1$ to the quantity

$$-e \sum_{\substack{k=1 \\ \text{spin } k = \text{spin } i}}^{n} u_k^*(x_1)u_k(x_1). \tag{3}$$

We shall now show that this is the case.

[3] E. Wigner and F. Seitz, Phys. Rev. 43, 804 (1933); ibid. 46, 509 (1934). The discussion of Wigner and Seitz was one of the first to show a proper understanding of the main points taken up in the present paper, which must be understood to represent a generalization and extension of previously suggested ideas, rather than an entirely new approach. See also L. Brillouin, J. de Phys. et le Radium, 5, 413 (1934) for a discussion somewhat similar to the present one.

To show it; we rewrite (1) in the equivalent form[4]

$$H_1 u_i(x_1) + \left[ \sum_{k=1}^{n} \int u_k^*(x_2) u_k(x_2) (e^2/4\pi\epsilon_0 r_{12}) dx_2 \right] u_i(x_1)$$

$$- \left[ \sum_{k=1}^{n} \frac{\int u_i^*(x_1) u_k^*(x_2) u_k(x_1) u_i(x_2) (e^2/4\pi\epsilon_0 r_{12}) dx_2}{u_i^*(x_1) u_i(x_1)} \right] u_i(x_1)$$

$$= E_i u_i(x_1). \quad (4)$$

The exchange term now appears as the product of a function of $x_1$, times the function $u_i(x_1)$; thus it has the standard form of a potential energy term in a one-electron Schrödinger equation. This exchange potential energy is the potential energy, at the position of the first electron, of the exchange charge density,

$$- e \sum_{k=1}^{n} \frac{u_i^*(x_1) u_k^*(x_2) u_k(x_1) u_i(x_2)}{u_i^*(x_1) u_i(x_1)}, \quad (5)$$

located at the position $x_2$ of the second electron. We note as we expect that the exchange charge density depends on the position of the first electron, as well as the second, and also on the quantum state $i$ in which this first electron is located. We note, furthermore, that the total charge is that of a single electron. To show this, we integrate the exchange charge density (5) over $dx_2$, and find at once, on account of the orthogonality of the $u_i$'s (which follows from the Hartree-Fock equations) that the integral over all space is $-e$. Furthermore, as $x_2$ approaches $x_1$, we see at once that the exchange charge density approaches the correct value (3), where the restriction that the spins of $i$ and $k$ must be equal arises from (1), where an exchange term $u_k^*(x_2) u_i(x_2)$ is automatically zero unless this condition is satisfied. Thus we have shown that the exchange charge density (5) satisfies all the conditions necessary to justify our qualitative discussion of its behavior. In a later section, where we work out detailed values for the free-electron case, we can examine its properties more in detail.

The great difference between the Hartree and the Hartree-Fock methods is the fact that in the Hartree-Fock method the exchange hole or correction charge appropriate for an electron at $x_1$ moves around to follow that electron; in the Hartree method it does not, the correction charge depending only on the index $i$ of the wave function $u_i$. If our problem is a single atom, this is not very important, but in a crystal, for instance a metal, the difference is profound. Thus consider a periodic lattice, in which the one-electron functions $u_i$ are modulated plane waves, corresponding to $1/N$ of

an electronic charge on each of the $N$ atoms of the crystal. In the Hartree scheme, the potential acting on the electron in the wave function $u_i$ is that of all electrons, minus this charge corresponding to $1/N$ of an electron on each atom. This correction charge is so spread out that its effect on the potential field is completely negligible, and each electron acts as if it were in the field of all electrons, thus finding itself in the field of a neutral atom when near any of the nuclei of the metal. On the other hand, with the Hartree-Fock equations, the exchange charge is located near the position $x_1$ of the electron in question, moving around with it, so that when this electron is on a given atom, the exchange charge is removed largely from that atom, leaving it in the form of a positive ion, which, as our physical intuition tells us, is the correct situation.

## III. AVERAGED EXCHANGE CHARGE

We have seen that the exchange charges for different wave functions $u_i$ corresponding to the same spin are not very different from each other, since in every case they reduce to the same value when $x_2 = x_1$, and integrate to the same value over all space. Furthermore, in a system containing equal or approximately equal numbers of electrons with both spins, $\rho_+$ and $\rho_-$ will be at least approximately the same, so that exchange charges for different $u_i$'s even of opposite spins will be nearly the same. It then seems clear that we shall make no very great error if we use a weighted mean of the exchange charge density, weighting over $i$, for each value of $x_1$. The result of this will be that we shall have a single potential field to use for the Schrödinger equation for each $u_i$, simplifying greatly the application of the Hartree-Fock method. Let us first set up this average exchange charge and the consequent averaged exchange potential, then give some discussion of their properties and uses.

The probability that an electron at $x_1$ should be in the state $i$ is evidently $u_i^*(x_1) u_i(x_1)/[\sum_j u_j^*(x_1) u_j(x_1)]$. We can then use this quantity as a weighting factor to weight the exchange charge density (5). When we do this, we find as the average exchange charge density the quantity[5]

$$- e \frac{\sum_{j=1}^{n} \sum_{k=1}^{n} u_j^*(x_1) u_k^*(x_2) u_k(x_1) u_j(x_2)}{\sum_{j=1}^{n} u_j^*(x_1) u_j(x_1)}. \quad (6)$$

Using this average exchange charge density, we come to the following Schrödinger equations for the $u_i$'s, as

[4] J. C. Slater and H. M. Krutter, Phys. Rev. **47**, 559 (1935); particularly p. 564, where this same method is used in discussing the Thomas-Fermi method.

[5] J. C. Slater, Rev. Mod. Phys. **6**, 209 (1934), particularly p. 267, where this same expression is used for similar purposes, but without pointing out that it is the weighted mean of the exchange charge density found in the Hartree-Fock equations.

substitutes for the Hartree-Fock equations:

$$H_1u_i(x_1)+ \left\{ \sum_{k=1}^{n} \int u_k^*(x_2)u_k(x_2)(e^2/4\pi\epsilon_0 r_{12})dx_2 \right.$$

$$\left. - \frac{\sum_{j=1}^{n}\sum_{k=1}^{n} \int u_j^*(x_1)u_k^*(x_2)u_k(x_1)u_j(x_2)(e^2/4\pi\epsilon_0 r_{12})dx_2}{\sum_{j=1}^{n} u_j^*(x_1)u_j(x_1)} \right\} u_i(x_1)=E_iu_i(x_1). \quad (7)$$

The wave functions $u_i$, and energy values $E_i$, as determined from these equations, will not be quite so accurate as those determined from the Hartree-Fock equations; but they will at least be much better than those found from the Hartree equations, particularly for the case of the crystal, and they have the great advantage that they are all solutions of the same potential problem. This automatically brings one good feature, which the solutions possess in common with solutions of the Hartree-Fock equations, but which solutions of the Hartree equations do not have: the functions $u_i$ are all orthogonal to each other.

There is one aspect of Eqs. (7) which is very important. In the last few years there has been a great development of the energy-band theory of semiconductors. This is all based on the hypothesis that we can build up a model of a solid in which each electron moves independently in a potential field which is made up from the nuclei, and all other electrons except the one in question. The electric field derived from this potential is sometimes called the motive field acting on the electron. Each wave function corresponds to a definite energy level, and the Fermi statistics are applied to the distribution of the electrons in these levels. The soundest way to set up this potential acting on each electron is by the Hartree-Fock method, but we see by our present discussion that this implies a different potential energy or motive for each electron, or each $u_i$. If we wish to have a single motive field appropriate for all electrons, the best thing we can do is to use the weighted mean suggested in the present section. Thus Eqs. (7) may well be taken to be the basis of the ordinary form of the energy-band theory of solids.

In many problems, we are interested in cases of degeneracy, not merely in evaluating the wave function of a single nondegenerate stationary state. Thus we may be solving a problem of multiplet structure in an atom or molecule, or discussing ferromagnetism in a solid. In such a case we start with a number of degenerate or approximately degenerate energy levels, corresponding to different orientations of orbit or spin, or in some cases (as in the hybridization of atomic orbitals) corresponding to different total or azimuthal quantum numbers, and then carry out perturbations. If we take the Hartree-Fock scheme literally, we shall use different potentials for finding the $u_i$'s of each of these various unperturbed functions. It is highly desirable in such cases, in the interests of simplicity, to modify the method so as to use the same potential function for the calculation of each wave function. This may involve even more averaging than is contemplated in setting up Eqs. (6) and (7). As one illustration, Hartree's use of a spherical potential for discussing atomic structure is an example of this procedure; this involves averaging over all orientations of the various orbital angular momenta of electrons which are not in closed shells. Whether we are using the Hartree scheme or the present simplification of the Hartree-Fock scheme, such averaging over orientations seems certainly desirable. Again, in studying ferromagnetism, the potentials to use, according to the scheme of the present paper, will depend on the net magnetization, or on the number of electrons of each spin. It is much simpler to handle such a problem, however, by using a single potential function, and that will usually be chosen to be that representing the unmagnetized state, with equal numbers of plus and minus spins.

In all these cases which we have just been discussing, we use one-electron wave functions which are slightly less accurate than those found by the Hartree-Fock scheme. When we apply perturbation methods, we must remember this, computing the matrix components of the exact energy operator with respect to these somewhat incorrect wave functions, remembering the wave equation (for instance (7)) which they actually satisfy. Nondiagonal matrix components of energy between these somewhat inaccurate wave functions will be somewhat larger than those between exact Hartree-Fock functions. Nevertheless they will still not be very large, for the wave functions are still quite accurate; the slight decrease in exactness is much more than made up by the simplicity of the method. The energy values computed by averaging the exact energy operator over the wave function will be very nearly the same as for Hartree-Fock functions, on account of the theorem that the mean value of energy over an in-

correct wave function has errors only of the second order of small quantities.

## IV. THE EXCHANGE CHARGE FOR THE FREE-ELECTRON CASE

The calculations of exchange charge and exchange potential which we have been describing in general language can be carried out exactly for the case of a free-electron gas, as is well known. In this section we shall give the results, as an illustration of the general case. Then we shall point out in the next section that by using a free-electron approximation we can get an exchange potential much simpler than that of Eq. (7), which still is accurate enough for many purposes.

Let us have a free-electron gas with $n$ electrons in the volume $V$, half of them of each spin; the volume is assumed to be filled with a uniform distribution of positive charge, just enough to make it electrically neutral. The electrons are assumed to obey the Fermi statistics. Then by elementary methods we find that they occupy energy levels with uniform density in momentum space, out to a level whose energy is $P^2/2m = (h^2/2m)(3n/8\pi V)^{\frac{2}{3}}$, corresponding to a maximum momentum $P = h(3n/8\pi V)^{\frac{1}{3}}$. The de Broglie wavelength

$$d = h/P = (8\pi V/3n)^{\frac{1}{3}} \qquad (8)$$

FIG. 1. $F(\eta)$ as function of $\eta$ (from Eq. (11)).
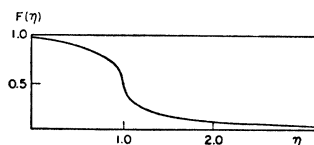
associated with this maximum momentum is clearly related to the radius $r_0$ of the exchange hole, which we introduced in Eq. (2). When we notice that $|\rho_+|$ which appeared there equals $ne/2V$, we see that

$$d = (4\pi/3)^{\frac{1}{3}} r_0. \qquad (9)$$

We can now state some of the principal results of the application of this model to the exchange charge density and exchange energy. The exchange potential energy can be conveniently stated in terms of the ratio $\eta = p/P$ of the magnitude of the momentum of the electron to the maximum momentum corresponding to the top of the Fermi distribution. It is[2]

exchange potential energy $= (e^2/4\pi\epsilon_0)(4P/h)F(\eta)$
$$\qquad\qquad = (6/\pi)^{\frac{1}{3}}(e^2/4\pi\epsilon_0 r_0)F(\eta), \quad (10)$$

where

$$F(\eta) = \frac{1}{2} + \frac{1-\eta^2}{4\eta} \ln[(1+\eta)/(1-\eta)]. \qquad (11)$$

The function $F(\eta)$ is shown in Fig. 1. It goes from unity when $\eta = 0$, for an electron of zero energy, to $\frac{1}{2}$ when $\eta = 1$, at the top of the Fermi distribution. We see that this exchange potential energy is of the form which we should expect. If we had a sphere of radius $r_0$, filled
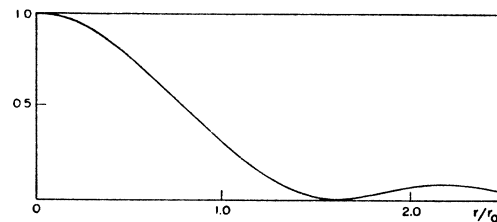
FIG. 2. Exchange charge density (divided by $\rho/2$) plotted as a function of $r/r_0$, from Eq. (12), where $r_0$ is given by Eq. (9).

with uniform charge density $|\rho_+| = ne/2V$, the potential energy of an electronic charge at the center of the sphere would be $\frac{3}{2}(e^2/4\pi\epsilon_0 r_0)$, while the value from Eq. (10) is $1.54(e^2/4\pi\epsilon_0 r_0)$ at the bottom of the Fermi band, half this value at the top. Thus this simple model of an exchange hole of constant charge density gives a qualitatively correct value for the exchange potential, and rather accurate quantitative value; and the extreme difference between top and bottom of the band corresponds only to a factor of 2 in the exchange potential.

If now we average over-all wave functions, we find that the properly weighted average of $F(\eta)$ is $\frac{3}{4}$. Thus the exchange potential energy of the averaged exchange charge[6] is $(\frac{3}{4})(6/\pi)^{\frac{1}{3}}(e^2/4\pi\epsilon_0 r_0)$. This can also be found from the averaged exchange charge density. This charge density is[3]

$$\frac{\rho}{2}\left[\frac{3\frac{\sin(r/d) - (r/d)\cos(r/d)}{(r/d)^3}}\right]^2, \qquad (12)$$

where $\rho$ is the total charge density of electrons, $d$ is given by Eqs. (8) and (9), and $r$ is the distance from point $x_1$, where the electron whose wave function we are computing is located, to $x_2$, where we are finding the exchange charge density. This function (12) is shown in Fig. 2, plotted as a function of $r/r_0$, and we see that it does in fact represent a density which equals $\rho/2$ when $r = 0$, and falls to small values at approximately $r = r_0$. The potential energy of an electron at the center of this averaged exchange charge distribution is just the value $(\frac{3}{4})(6/\pi)^{\frac{1}{3}}(e^2/4\pi\epsilon_0 r_0)$ previously given.

## V. USE OF THE FREE-ELECTRON APPROXIMATION FOR THE EXCHANGE POTENTIAL

From the argument of Sec. III, it is clear that the exchange charge density (6), and the corresponding potential appearing in (7), must depend on the density of electronic charge, but not greatly on anything else. Thus in no case will we expect it to be very different from what we should have in a free-electron gas of the same charge density. We may then make a further approximation and simplification, beyond that of Sec. III; we may approximate the averaged exchange potential by what we should have iń a free-electron gas

[6] F. Bloch, Z. Physik **57**, 545 (1929) gave the first derivation of this value.

of the same density, as given in Sec. IV.[7] Thus, combining (10) and (2), we have

exchange potential energy

$$= -\tfrac{3}{4}(6/\pi)^{\frac{1}{3}}(e^2/4\pi\epsilon_0 r_0)$$
$$= -3(e^2/4\pi\epsilon_0)(3n/8\pi V)^{\frac{1}{3}}, \quad (13)$$

where we are now to interpret $n/V$ as the local density of electrons, a function of position. If we recall that this is $\sum(k)u_k{}^*(x)u_k(x)$, we finally have as our simplified Schrödinger equation for the one-electron functions $u_i$, to replace (7),

$$H_1 u_i(x_1) + \left[\sum(k)\int u_k{}^*(x_2)u_k(x_2)(e^2/4\pi\epsilon_0 r_{12})dx_2\right.$$

$$\left. -3(e^2/4\pi\epsilon_0)\left\{\frac{3}{8\pi}\sum(k)u_k{}^*(x_1)u_k(x_1)\right\}^{\frac{1}{3}}\right]u_i(x_1)$$

$$= E_i u_i(x_1). \quad (14)$$

This equation is in practice a very simple one to apply. We solve it for each of the wave functions $u_i$, then find the total charge density arising from all these wave functions, and can at once calculate the potential energy, including the exchange term, to go into (14), so as to check the self-consistency of the solution. Here, as before, we change to Gaussian units by omitting $4\pi\epsilon_0$, and atomic units by changing $e^2/4\pi\epsilon_0$ to 2.

One result of this formulation of the self-consistent problem is of immediate interest. In a periodic potential problem such as a crystal, it is obvious that the total charge density will have the same periodicity as the potential. Thus the corrected potential of Eq. (14) will also be periodic, and hence the functions $u_i$ will be modulated according to Block's theorem. In other words, such modulated functions are the only type which can follow from a proper application of our simplification of the Hartree-Fock method to a periodic potential problem.

Our general method is applicable to any problem of atoms, molecules, or solids. It is easy to give it a very explicit formulation for the case of atoms, which can then be used for the self-consistent treatment of atomic

structure. Let the electrostatic potential of the nucleus, and of all electrons, at distance $r$ from the nucleus of a spherical atom, be $Z_p(r)e/4\pi\epsilon_0 r$. Then the charge density is given by Poisson's equation as $\rho = -\epsilon_0\nabla^2(Z_p e/4\pi\epsilon_0 r)$. When we express the Laplacian in spherical coordinates, this gives at once $\rho = -(e/4\pi)(1/r)d^2Z_p/dr^2$. This is the quantity which is expressed as $-e\sum(k) u_k{}^*(x)u_k(x)$. Thus the exchange potential energy becomes $-3(e^2/4\pi\epsilon_0)[(\tfrac{3}{32}\pi^2)(1/r)d^2Z_p/dr^2]^{\frac{1}{3}}$, and, finally, the total potential energy, for use in the Schrödinger equation for $u_i(x_1)$, is

$$-\frac{e^2}{4\pi\epsilon_0 r}\left[Z_p + 3\left(\frac{3}{32\pi^2}\right)^{\frac{1}{3}}\left(r^2\frac{d^2Z_p}{dr^2}\right)^{\frac{1}{3}}\right]. \quad (15)$$

To carry out a self-consistent solution for an atom, using this simplified method, we then find a $Z_p$ such that the wave functions $u_i$, determined from a single Schrödinger equation using the potential energy (15), determined from $Z_p$, add to give a charge density which would lead by Poisson's equation to a potential energy $-e^2 Z_p/4\pi\epsilon_0 r$.

In order to check the applicability of the method Mr. George W. Pratt is carrying out a self-consistent solution of the ion $Cu^+$ by this method. This ion was chosen, as being the heaviest one for which solutions by both the Hartree and the Hartree-Fock methods are available for comparison. The solution has gone far enough to show that the wave functions and energy parameters $E_i$ determined from it are not far from those found by the Hartree and the Hartree-Fock methods. The discrepancies come principally from large values of $r$, where the charge density is small, and our free-electron approximation for exchange is not very good. Over most of the range of $r$, however, the approximation seems very satisfactory. Detailed results will be reported later. The great advantages of this method for numerical calculation are clear from this example which has been worked out. Actual calculation is simpler than for the original Hartree scheme, since only one potential function need be computed, and can be used for all wave functions. The wave functions have the advantage of being orthogonal; and they possess a considerable part of the accuracy which the solutions of the Hartree-Fock equations possess, in contrast to the Hartree equations. It is to be hoped that they will make enough simplification so that it will be possible to carry out calculations for more complicated atoms than have yet been attempted by the Hartree-Fock method. At the same time the method should prove valuable in setting up solutions for molecules and solids.

---

[7] This method of treating the exchange potential as if the electrons formed part of a free-electron gas is similar to what is done in the Thomas-Fermi method with exchange (see Dirac (reference 2), Slater and Krutter (reference 4), and L. Brillouin, *L'Atome de Thomas-Fermi et la Méthode du Champ "Self-Consistent,"* Actualités Scientifiques et Industrielles No. 160 (Hermann et Cie., 1934)).