Self-Consistent Field, with Exchange, for Beryllium

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1—INTRODUCTION

Except for the lightest atoms, most calculations of approximate wave functions and fields for many-electron atoms have been carried out by the method of the " self-consistent field," of which the principle is, shortly, the determination of a set of one-electron wave functions such that each represents a stationary state of an electron in the field of the nucleus and the Schrödinger charge distribution of the electrons occupying the other wave functions of the set.[†] This method has been found quite practicable for numerical work, even for the heaviest atoms.

As so far applied, it involves three main approximations, namely, (*a*) neglect of relativity and spin effects, (*b*) neglect of exchange effects, and (*c*) treatment of the wave function of the whole atom as built up of functions of the co-ordinates of the individual electrons only, its dependence on the mutual distances between every pair of electrons being neglected; or, in other words, each electron is replaced by a statistical average distribution, in calculating its effect on the other electrons on the atom.

Spin and relativity effects are not likely to be considerable except for the heavier atoms. There seems no difficulty in principle or in practice in taking them into account, to a certain approximation, in the " self-consistent field " method, although they would make somewhat heavier the numerical work, which is already rather laborious for heavy atoms; but no quantitative work on these lines has yet been done.

The third approximation appears difficult to dispense with at present, except for the very lightest atoms. It is implied in the usual practice of describing atomic configurations in terms of one-electron wave functions, each of which is regarded as occupied by an electron; and though departure from this practice must certainly be made in order to obtain an accurate description of the structure of an atom, the resulting description is likely to be more elaborate, less easily visualized, and more difficult to work out and apply quantitatively. So it seems desirable to proceed as far as possible along the lines of improving the approximation

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[†] D. R. Hartree, ' Proc. Camb. Phil. Soc.,' vol. 24, pp. 89, 111 (1928).

without such a departure from the usual practice of describing atomic configurations, and the main possible improvement (except perhaps for the heavier atoms) is the inclusion of exchange effects. When the work described in this paper was begun, it was thought probable that the neglect of exchange effects was the most important of the three approximations made in the self-consistent field method; the results of the present paper show that this is not so, at least according to one way of estimating the relative importance of different approximations, but even so, the inclusion of exchange effects is worth carrying out if possible.

The principles and general theory of a method for including exchange effects have already been given some years ago by Fock†; they were suggested independently about the same time by Slater.‡ But the practical handling of Fock's equations is a problem of numerical technique altogether more complex than the solution of the self-consistent field problem without exchange, and, as far as we are aware, the only complete solution yet obtained for any case in which the main features of the problem are fully shown§ is that of sodium, for which the results, and methods used to obtain them, have quite recently been given by Fock and Petrashen.‖ The solution of Fock's equations given in the present paper had been completed, and the subsidiary calculations of energy values were in progress, when this paper appeared. The methods we have used differ considerably from those of Fock and Petrashen and appear simpler for practical work; for example, we make no use of analytical approximations which are usually not so convenient to handle numerically as they might appear, or of the Green's function constructed by them.

† 'Z. Physik,' vol. 61, p. 126, and vol. 62, p. 795 (1930).

‡ 'Phys. Rev.,' vol. 35, p. 210 (1929). This note will be referred to as Slater I.

§ L. P. Smith (' Phys. Rev.,' vol. 42, p. 176 (1932)) has obtained solutions of Fock's equations for the highly excited S states of neutral He. But this is altogether an exceptionally simple case, as the (1*s*) wave function can be taken to be hydrogen-like, unperturbed by the electron in the excited wave functions, and the problem reduces effectively to a one-electron problem; also various analytical approximations, not available in the general case, can be made here.

‖ 'Phys. Z. Sowjet.,' vol. 6, p. 368 (1934). The solution for the ion Na^+ is fully worked out, but the solutions for the states of the neutral atom are strictly speaking, not complete, as the perturbation of the core by the series electron is neglected. In the self-consistent field without exchange, this perturbation is not large, but it is appreciable for the lowest states of the series electron; the results of the present work show that, at least in the case here considered, the perturbation of the core by the series electrons, although not zero, is considerably smaller when exchange effects are included than when they are neglected, and this result may be regarded as a partial justification of the neglect of this perturbation by Fock and Petrashen.

2—FOCK'S EQUATIONS

Fock's equations are obtained by applying the variation principle to determine the best approximation, of a particular type, to the wave function for a whole atom. The type of wave function contemplated is

$$\Psi = \begin{vmatrix} \psi(\alpha|1) & \psi(\alpha|2) & \psi(\alpha|3) \ldots \\ \psi(\beta|1) & \psi(\beta|2) & \psi(\beta|3) \ldots \\ \psi(\gamma|1) & \psi(\gamma|2) & \psi(\gamma|3) \ldots \\ \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots \end{vmatrix}. \tag{1}$$

where the Greek letters α, β, ... are labels of the one-electron wave functions ψ, and the numbers 1, 2, 3, .. stand for the co-ordinates of the various electrons. Further, the one-electron wave functions ψ are taken to be of the central-field type

$$\psi(\alpha|j) = \frac{1}{r} \mathrm{P}(n_\alpha l_\alpha|r_j)\,\mathrm{S}(l_\alpha m_\alpha|\theta_j\phi_j)\,\chi(s_\alpha|s_j), \tag{2}$$

where n_α, l_α, m_α, s_α are the three spatial and one-spin quantum numbers specifying the wave function α, and r_j, θ_j, ϕ_j, s_j are the three spatial and one-spin co-ordinate of electron j; S is a spherical harmonic of degree l_α, and χ is the spin wave function.

The criterion of the "best" approximate wave function given by (1) and (2) is that the approximate value E of the energy, given by

$$\mathrm{E} = \int \Psi^* \mathrm{H} \Psi d\tau \Big/ \int \Psi^* \Psi d\tau \tag{3}$$

should be a minimum for arbitrary small variations of the radial wave functions P.

The most simple and direct method of deriving Fock's equations, for any given atomic state, seems to be to use the results of Slater† for the evaluation of E given by (3), when Ψ is taken as a determinant (1) of central field one-electron wave functions (2), and then to apply the variation principle to obtain the differential equations for the radial wave functions P. This method follows closely the original suggestion of Slater,‡ and has been used by Brown§ to obtain Fock's equations for neon-like atoms and neutral fluorine.

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† 'Phys. Rev.,' vol. 34, p. 1293 (1929). This paper will be referred to as Slater II.

‡ *See* Slater I.

§ 'Phys. Rev.,' vol. 44, p. 214 (1933).

It is not necessary to carry out the work from the beginning for the normal state of neutral Be with which this paper is concerned, since Fock's equations for this state can be obtained from those given by Fock for sodium, or from those given by Brown for the cases considered by him, by retaining only the terms involving the (1*s*) and (2*s*) wave functions.

For the analytical work of evaluating E, and of applying the variation principle, and for theoretical discussions, it is most convenient to regard the one-electron wave functions ψ as orthogonal and normalized; this places no restriction on the wave function Ψ of the whole atom, but is a condition imposed in the interests of analytical convenience and simplicity. In the numerical work, however, it is inconvenient to be restricted to working explicitly with normalized wave functions. To avoid misunderstanding, we shall distinguish between unnormalized and normalized functions, denoting the latter by a suffix N, so that

$$\mathrm{P_N}(\alpha|r) = \mathrm{P}(\alpha|r) \bigg/ \left[\int_0^\infty \mathrm{P}^2(\alpha|r)\,dr\right]^{\frac{1}{2}}. \tag{4}$$

It is convenient to use the functions

$$\mathrm{Z}_k(\alpha\beta|r) = \int_{r_1=0}^{r} \mathrm{P_N}(\alpha|r_1)\,\mathrm{P_N}(\beta|r_1)\quad (r_1/r)^k\,dr_1 \tag{5}$$

$$\mathrm{Y}_k(\alpha\beta|r) = \int_{r_1=0}^{r} \mathrm{P_N}(\alpha|r_1)\,\mathrm{P_N}(\beta|r_1)\,(r_1/r)^k\,dr_1 + \int_{r_1=r}^{\infty} \mathrm{P_N}(\alpha|r_1)\,\mathrm{P_N}(\beta|r_1)\,(r/r_1)^{k+1}\,dr_1 \tag{6}$$

already introduced in another context,† and the integrals‡

$$\mathrm{I}(\alpha) = -\tfrac{1}{2}\int_0^\infty \mathrm{P_N}(\alpha|r)\left[\frac{d^2}{dr^2} + \frac{2\mathrm{N}}{r} - \frac{l_a(l_a+1)}{r^2}\right]\mathrm{P_N}(\alpha|r)\,dr \tag{7}$$

$$\mathrm{F}_k(\alpha\beta|r) = \int_0^\infty \mathrm{P_N}^2(\alpha|r)\,\mathrm{Y}_k(\beta\beta|r)r^{-1}\,dr = \int_0^\infty \mathrm{P_N}^2(\beta|r)\,\mathrm{Y}_k(\alpha\alpha|r)r^{-1}\,dr \tag{8}$$

$$\mathrm{G}_k(\alpha\beta|r) = \int_0^\infty \mathrm{P_N}(\alpha|r)\,\mathrm{P_N}(\beta|r)\,\mathrm{Y}_k(\alpha\beta|r)\,r^{-1}\,dr. \tag{9}$$

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† Hartree and Black, 'Proc. Roy. Soc.,' A, vol. 139, p. 311 (1933). The function $\mathrm{Y}_k(\alpha\beta/r)$ is that written $\mathrm{Z}_{vk}{}^{\alpha\beta}$ by Brown (*loc. cit.*), and is $(1/r)$ times the function written $\mathrm{F}_k{}^{\alpha\beta}(r)$ by Fock and Petrashen (*loc. cit.*) and by Brown. The functions Y_k seem more convenient for practical work than the functions F_k, and the notation of the present paper is used to avoid a multiplicity of suffixes and indices.

‡ *See* Slater II, and Hartree and Black, *loc. cit.*

For the normal state $[(1s)^2\,(2s)^2\,{}^1S_0]$ of neutral Be, the conditions of orthogonality reduce to

$$\int_0^\infty P\,(1s|r)\,P\,(2s|r)\,dr = 0, \tag{10}$$

the expression for E, which we shall require later, is

$$\begin{aligned} E = 2I\,(1s) + 2I\,(2s) + F_0\,(1s,\,1s) + 4F_0\,(1s,\,2s) \\ + F_0\,(2s,\,2s) - 2G_0\,(1s,\,2s), \end{aligned} \tag{11}$$

and Fock's equations for the orthogonal, but unnormalized, radial wave functions become

$$\begin{aligned} \left[\frac{d^2}{dr^2} + \frac{2N - 2Y_0\,(1s,\,1s|r) - 4Y_0\,(2s,\,2s|r)}{r} - \varepsilon_{11}\right] P\,(1s|r) \\ + \frac{1}{K^2}\left[\frac{2KY_0\,(1s,\,2s|r)}{r} - K\varepsilon_{12}\right] P\,(2s|r) = 0 \end{aligned} \tag{12}$$

$$\begin{aligned} \left[\frac{d^2}{dr^2} + \frac{2N - 4Y_0\,(1s,\,1s|r) - 2Y_0\,(2s,\,2s|r)}{r} - \varepsilon_{22}\right] P\,(2s|r) \\ + \left[\frac{2KY_0\,(1s,\,2s|r)}{r} - K\varepsilon_{12}\right] P\,(1s|r) = 0, \end{aligned} \tag{13}$$

where

$$K = \left[\int_0^\infty P^2\,(2s|r)\,dr \Big/ \int_0^\infty P^2\,(1s|r)\,dr\right]^{\frac{1}{2}} \tag{14}$$

and ε_{11}, ε_{12}, ε_{22} are Lagrange multipliers introduced in the course of the application of the variation principle. The equations have been written here in the form found suitable for numerical work.

The equations of the self-consistent field are given by omitting the second term in each of these equations, and are

$$\left[\frac{d^2}{dr^2} + \frac{2N - 2Y_0\,(1s,\,1s|r) - 4Y_0\,(2s,\,2s|r)}{r} - \varepsilon_{11}\right] P(1s|r) = 0 \tag{15}$$

$$\left[\frac{d^2}{dr^2} + \frac{2N - 4Y_0\,(1s,\,1s|r) - 2Y_0\,(2s,\,2s|r)}{r} - \varepsilon_{22}\right] P(2s|r) = 0 \tag{16}$$

(the values of the Lagrange multipliers ε_{11}, ε_{22} for equations (15), (16) will generally be different from these for equations (12), (13)).

3—ARBITRARINESS OF THE SOLUTIONS OF FOCK'S EQUATION

Since the determinant (1) is unchanged by the replacement of the ψ's by any set of independent linear combinations of them, it follows that the form of equations (12), (13) is unaffected by orthogonal transformation of the functions P. Thus if P (1*s*), P (2*s*) are the normalized solutions of (12), (13), the functions Y_0 in these equations being related to these P's by (4), (6), then, for any constant value of γ, the orthogonal pair of functions

$$\left.\begin{aligned} P'(1s) &= P(1s) + (\gamma/K)\,P(2s) \\ P'(2s) &= P(2s) - \gamma K\,P(1s) \end{aligned}\right\} \tag{17}$$

are solutions of equations of the form (12), (13), in which the functions Y_0 are replaced by functions Y'_0 related to the wave functions P′ in the same way as the functions Y_0 are related to the wave functions P, and in which the values ε of the Lagrange multipliers are replaced by other values ε'. Thus the functions P′ are also solutions of the self-consistent field problem including exchange, so that this problem has not a unique solution but a set of linearly related solutions given by (17) with different values of γ.

This invariance of the form of equations (12), (13) under the transformation (17) can also be shown by direct substitution in the equations, and this also gives the transformation formulæ for the ε's, namely,

$$\left.\begin{aligned} \varepsilon'_{11} &= (\varepsilon_{11} + 2\gamma\varepsilon_{12} + \gamma^2\varepsilon_{22})/(1+\gamma^2) \\ \varepsilon'_{22} &= (\varepsilon_{22} - 2\gamma\varepsilon_{12} + \gamma^2\varepsilon_{11})/(1+\gamma^2) \end{aligned}\right\} \tag{18}$$

$$\varepsilon'_{12} = [(1-\gamma^2)\,\varepsilon_{12} + \gamma\,(\varepsilon_{22} - \varepsilon_{11})]/(1+\gamma^2). \tag{19}$$

The last of these is important, as it shows that there is one, and essentially only one,† value of γ for which $\varepsilon'_{12} = 0$, namely, that for which

$$(\varepsilon_{11} - \varepsilon_{12})\,\gamma = (1-\gamma^2)\,\varepsilon_{12}, \tag{20}$$

so that the condition $\varepsilon'_{12} = 0$ selects a single pair of functions P′ out of the set of pairs (17) with different values of γ.

The pair of functions so selected will be regarded as the standard solution of Fock's equations and will be distinguished by a suffix $_f$, thus $P_f(\alpha/r)$. Koopmans‡ has shown generally that such functions are the most convenient ones to use in describing an atomic configuration, and the equations from which Fock and Petrashen start their numerical work contain no ε_{12}.

In the method we have used for the solution of the equations, it is most convenient to include ε_{12} as one of the parameters adjustable to satisfy

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† Equation (20) has two roots, but they only differ in interchanging the two functions P′.

‡ 'Physica,' vol. 1, p. 105 (1934).

the conditions of orthogonality and normalization, that is to say, directly for the purpose for which it is introduced in the application of the variation principle, and the details of the procedure were planned to give a series of approximations converging to one of the solutions of (12), (13), but not necessarily to the particular one for which $\varepsilon_{12} = 0$. But from any solution of (6), (12), (13) with $\varepsilon_{12} \neq 0$, the standard solution can be obtained by solving (20) for γ and then using (17).

4—PROCESS OF SOLUTION OF FOCK'S EQUATIONS

So far as the coefficients of $P(1s)$, $P(2s)$ in (12), (13) involve the Y_0 functions which themselves depend on the solutions of the equations, Fock's equations are similar to those of the self-consistent field, and the same process of successive approximation can be used to deal with this feature; but Fock's equations are more complex than those of the self-consistent field in two respects.

Firstly, for *given* Y_0 functions, the self-consistent field equations (15) and (16) are independent, the Lagrange multipliers ε can be determined separately and, more important, the solutions of the two equations can be normalized independently, whereas Fock's equations are simultaneous equations so that the values of the normalization integrals appear in the equations themselves through the constant K. Secondly, in Fock's equations there appears the cross-multiplier ε_{12}, which has to be chosen so that the condition of orthogonality is satisfied by the functions $P(1s)$, $P(2s)$ which are solutions of (12), (13) with the appropriate value of K,† or alternatively, if ε_{12} is omitted, some other adjustment must be made to secure orthogonality.‡ We have used equations (12), (13) as they stand, and have adopted a trial-and-error method of determining both K and ε_{12}, carrying out (directly and indirectly) the solution for different values of both these constants, and interpolating for the values for which the solution satisfies the conditions (10) and (14) simultaneously. It should be noted here that the values of ε_{11} and ε_{22} may not be exactly the same

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† In the self-consistent field calculation without exchange, it would be possible to impose an orthogonality condition on the P's; this would give equations which included the ε_{12} terms of (12), (13), but did not include the $Y_0(1s, 2s|r)$ terms. There would, however, be no object in imposing such a condition, as, besides making the numerical problem much more complex, it would be placing an additional restriction on the wave function for the whole atom, so that the solution of the more complicated problem would actually give a worse approximation. With a wave-function for the whole atom of the type (1), on the other hand, the condition of orthogonality is no restriction.

‡ Fock and Petrashen (*loc. cit.*), working with equations with no ε_{12}, use a process of orthogonalization which has the result that the orthogonalized functions are no longer solutions of the equations.

for the different trial values of K and ε_{12}, so that the determination of the solution of (12), (13) for each trial pair of values of K and ε_{12} includes the determination of the appropriate values of ε_{11} and ε_{22}.

It is worth emphasizing that the difficulty of handling Fock's equations does not lie in the numerical process of evaluation of a single solution of (12), (13) for given functions of Y_0, and given values of K and ε_{12}, which is not to any serious extent more difficult or laborious than the evaluation of a solution of the self-consistent field equations (15), (16) for given Y_0's, but arises from the need for satisfying the additional conditions of orthogonality and normalization, and the greater number of trial solutions which may be required before these conditions are satisfied.

The general scheme used for the numerical treatment of Fock's equations is very similar to that already developed for the solution of the equations of the self-consistent field, and can be indicated shortly as follows:—

I. Estimate functions $Z_0(\alpha\beta|r)$, (*cf.* (5)).
II. Calculate the functions $Y_0(\alpha\beta|r)$ from estimated $Z_0(\alpha\beta|r)$'s.
III. Evaluate solution of equations (12), (13) with these Y_0's.
IV. Calculate functions $Z_0(\alpha\beta|r)$ from this solution.

If these calculated or " final " Z_0's agree with the estimated or " initial " Z_0's, the wave functions and field derived from them can be called " self-consistent," including exchange, in the same sense as the term was originally applied to describe the physical idea which was the basis of the " self-consistent field " without exchange.

Stage III in this scheme includes the determination of K and ε_{12} to satisfy the conditions of orthogonality and normalization, as well as the determination of ε_{11} and ε_{22}, and it is here that the main difference from the self-consistent field without exchange appears. Another difference, of much less importance, occurs for atomic configurations involving one-electron wave functions with $l \neq 0$, when Fock's equations involve functions $Y_k(\alpha\beta|r)$ with $k \neq 0$, whereas the self-consistent field without exchange only involves Y_k functions with $k = 0$: in such cases, the relevant Z_k's would be estimated at Stage I, and calculated at Stage IV, and compared with the estimates. The calculation of Y_k from Z_k required in Stage II has already been discussed elsewhere†; for $k = 0$ it is usually most convenient to do it by inward integration of

$$\frac{dY_0}{dr} = \frac{Y_0 - Z_0}{r}, \tag{21}$$

as has been the usual practice in self-consistent field calculations.

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† *See* Hartree and Black, *loc. cit.*

It seemed most convenient to take $\left(\frac{dP}{dr}\right)_{r=0}$ the same for P $(1s)$ and P $(2s)$. Then the maximum P is of the same order of magnitude for both, and K^2 is quite large (it is actually about 30), so that it is clear on inspection of equations (12), (13) that the effect of the "exchange" terms on P $(1s)$ is likely to be much smaller than their effect on P $(2s)$, and also probably does not depend greatly on the exact behaviour of P $(2s)$. So it appeared best not to try to solve the equations simultaneously, but first to solve (13) for P $(2s)$, taking P $(1s)$ the same as for the self-consistent field, for which preliminary results were available when this work was begun, and then, using this P $(2s)$, and also the values of K and ε_{12} found from the equation for P $(2s)$, to solve (12) for P $(1s)$, and then to use this P $(1s)$, and improved Y_0 functions, for a further approximation to P $(2s)$.

It was also found convenient to treat K and $(K\varepsilon_{12})$, rather than K and ε_{12} itself, as the adjustable parameters to be determined to fulfil the conditions of orthogonality and normalization. We shall call the value of K used in a solution of (13) the "initial" value of K for this solution, and the value calculated by (14) from this solution the "final" value; for the solution required, these must agree.

The first estimates of the Z_0's were based on the self-consistent field wave functions, and equation (13) for P $(2s)$ was treated as a variation on the self-consistent field equation (16). No attempt was made at this stage to obtain more than a rough solution, as it was expected that the estimated Z_0's would have to be changed appreciably, as was found to be the case. The self-consistent field gives the solution of (13) when $K = 0$, $K\varepsilon_{12} = 0$; solutions were carried out for $K = 12$, $K\varepsilon_{12} = 0$ and for $K = 0$, $K\varepsilon_{12} = 1$, and approximate values of K and $K\varepsilon_{12}$ to satisfy the conditions of orthogonality and normalization were found by linear interpolation in the two variables K and $(K\varepsilon_{12})$. The validity of linear interpolation over the large range involved being quite uncertain at this stage, a solution was then carried out for these approximate values of K and $K\varepsilon_{12}$, which proved to be not far wrong, showing that the departures of the final K and of $\int_0^\infty P(1s)\,P(2s)\,dr$ from linear variation with initial K and $K\varepsilon_{12}$ were not large. A further linear interpolation then gave

$$K = 5{\cdot}62, \quad K\varepsilon_{12} = -0{\cdot}43 \tag{22}$$

and final $Z_0\,(1s, 2s)$ and $Z_0\,(2s, 2s)$ were then calculated.

It would be possible to take these final Z_0's of one approximation as the initial Z_0's of the next, but experience of the self-consistent field calculations has shown that this purely iterative process does not always converge, and that, when it does, the convergence can usually be hastened considerably by taking, as the initial Z_0's of one approximation, the final Z_0's of the previous approximation with judicious modifications. An attempt at similar modifications was made in this case, and, by good luck more than anything else, the revised estimates of the Z_0's made at this stage happened to be rather good approximations, and this considerably shortened the work.

For this second approximation and subsequent ones, the usual practice was to evaluate numerically (*a*) the solution of (13) as it stands, for one pair of values of initial K and of $K\varepsilon_{12}$, and (*b*) variations of the solution (13) for variation of K (for $K\varepsilon_{12}$ constant) and for variation of $K\varepsilon_{12}$ (for K constant); or, if it seemed advisable, for variations of both. Typical results are the following, for the second approximation:—

Initial K	$K\varepsilon_{12}$	Final K	$\int_0^\infty P(1s)\,P(2s)dr$	ε_{22}
5·5	0	5·484	$-0{\cdot}0087$	$0{\cdot}6179$
5·5	0·1	5·411	$-0{\cdot}0024_5$	$0{\cdot}6178_5$
5·4	0·1	5·403	$+0{\cdot}0004_5$	$0{\cdot}6167$

(23)

whence bilinear interpolation for the values of initial K and $K\varepsilon_{12}$ for which

$$\text{initial } K = \text{final } K \text{ (normalization condition)}$$

and

$$\int_0^\infty P(1s)\,P(2s)\,dr = 0 \text{ (orthogonality condition)}$$

gives

$$K = 5{\cdot}406, \quad K\varepsilon_{12} = +\,0{\cdot}095. \tag{24}$$

Using the second estimate of the Z_0's, the solution of (13) was carried out, still taking P (1*s*) as unaffected by the " exchange " terms. It was found (as shown by the results given above) that the value of K was not greatly altered by the change of estimated Z_0's, so that initial values over a much smaller range were adequate and linear interpolation was much more reliable; on the other hand, $K\varepsilon_{12}$ was considerably affected, being even changed in sign.

The approximation to P (2*s*) at this stage appeared good enough to use to investigate the effect of exchange terms on P (1*s*), using equation (12). This effect turned out to be larger than was anticipated, and led to the unexpected result that the P (1*s*) given by the solution of Fock's equation is nearer to the P (1*s*) of the self-consistent field of Be^{++} than to that of neutral Be; consequently it was necessary to revise the estimate of $Z_0(1s, 1s)$, and the function $P(1s)$ to use in solving equation (13) for $P(2s)$, and the value of $\int_0^\infty P^2(1s)\,dr$ to use in evaluating the final K (the change of this integral was more than 1%, and so affected the second decimal in K).

The solution of the equation for $P(2s)$ for two further approximations, and of that for $P(1s)$ for one, then brought the maximum difference between initial and final Z_0's down to 0·001. This degree of approximation was aimed at, as the approximation to the self-consistent field without exchange had been taken to a similar stage, and also because a good approximation to "self-consistency" greatly simplifies the calculation of energy (*cf.* § 8). The final values of K, $K\varepsilon_{12}$ were

$$K = 5\cdot442, \quad K\varepsilon_{12} = +\,0\cdot063. \tag{25}$$

At this stage, the value of the energy (11) was calculated (*see* § 8), and as this work was in progress, the paper of Fock and Petrashen came to our notice, and suggested a further development in the integration of the equations, as a general check on the work.

The value of γ required to make $\varepsilon'_{12} = 0$ was determined from (20), and the standard pair of functions

$$\left.\begin{aligned} P_f(1s) &= [P(1s) + (\gamma/K)\,P(2s)]/(1 + \gamma/K) \\ P_f(2s) &= [P(2s) - \gamma K\,P(1s)]/(1 - \gamma K) \end{aligned}\right\} \tag{26}$$

which, by § 3, should give a solution of (6), (12), (13) with $\varepsilon_{12} = 0$, were constructed; these functions are unnormalized, and are arranged to have the same value of $(dP/dr)_{r=0}$ as $P(1s)$ and $P(2s)$ as is convenient for numerical work and for comparison purposes.

Then, as a final check, new estimates of Z_0 were constructed from the P_f functions (26) by (6), and, using these estimates, a complete independent solution of (12), (13), including the determination of the values of K and $K\varepsilon_{12}$ to satisfy the conditions of orthogonality and normalization, was carried through. The value of $K\varepsilon_{12}$ found to be required was 0·006, and the final Z_0's nowhere differed from the estimates by 0·001. The small departure of $K\varepsilon_{12}$ from the expected value zero is probably due firstly, to the fact that the previous approximation was not exactly "self-consistent," and secondly, to accumulation of rounding-off errors at various stages of the work.

A new pair of standard functions P_f to give a solution of (6), (12) and (13) with $\varepsilon'_{12} = 0$ was then found from this later approximation, again using (26), and are tabulated in Table I; four decimal places in P were kept throughout the calculations, the values actually tabulated were obtained by multiplying by 2 and rounding off the fourth decimal. The maximum differences from similar values of P_f given by the previous approximation are $0 \cdot 001$ for P (1*s*) and $0 \cdot 003$ for P (2*s*); these differences occur near the main maxima of the wave functions and are less than $0 \cdot 1\%$ of these maxima. Since the two determinations of P_f were made by completely separate solutions of the equations, with different values of the constant occurring in them, this close agreement of the final results provides a very close check on the overall accuracy of the work.

5—SOME DETAILS CONCERNING THE SOLUTION OF EQUATIONS

One or two points arising in the numerical solution of equations (12) and (13) for given Y_0's, K, and $K\varepsilon_{12}$ are worth putting on record.

The solution of (13) for P (2*s*) was carried out in the usual way by integrating outwards from $r = 0$, and inwards from a large r (actually $r = 10$) and determining ε_{22} so that the solutions joined smoothly (*i.e.*, $\frac{1}{P}\frac{dP}{dr}$ was the same for both) at some convenient intermediate radius (actually $r = 3 \cdot 6$), which was chosen so that the term in (13) involving P (1*s*) was negligible outside it, so that the inward integration could be carried out, using the first order equation for the quantity $\eta = -\frac{d}{dr}(\log P)$.

This process, however, is not feasible for the (1*s*) equation (12), since the term in P (2*s*) is appreciable over the whole range unless $\varepsilon_{12} = 0$. Outward integration of (12) over the whole range was tried, and was found possible, but not satisfactory on account of the very rapid exponential increase, for large r, of the effects of any error (including, of course, the inevitable rounding-off errors involved in working to a finite number of significant figures) which masked the real behaviour of the " tail " of the (1*s*) wave function.

The difficulty at this point can be avoided, or at least much lessened, by working with the equations with $\varepsilon_{12} = 0$, and satisfying the condition of orthogonality in some other way. But the use of ε_{12} as an adjustable parameter seemed the simplest and most direct way of satisfying this condition, and a similar difficulty may arise in other cases in which there is no adjustable constant like ε_{12} here, so an alternative method seemed desirable, and a quite satisfactory one was found, which does not require the construction of the Green's function used by Fock and Petrashen.

When solving (12) for P (1*s*), P (2*s*) is regarded as given, so that (12) is an inhomogeneous linear equation for the one function P (1*s*). Let *p* (1*s*) be any particular integral of this equation which tends to 0 as $r \to \infty$; any complementary function which tends to 0 as $r \to \infty$ must be a multiple of $e^{-\int \eta dr}$, where η satisfies the first order equation

$$\frac{d\eta}{dr} = \eta^2 + \frac{2N - 2Y_0(1s, 1s|r) - 4Y_0(2s, 2s|r)}{r} - \varepsilon_{11} \tag{27}$$

as in the self-consistent field calculations, and for the inward integration this equation is quite convenient. A particular integral *p* (1*s*) can also be evaluated by integration inwards; it was found that an adequate approximation to initial conditions for this inward integration was given by putting $d^2P(1s)/dr^2 = 0$ in (12), at a sufficiently large value of *r*. Different initial conditions give particular integrals differing by multiples of the complementary function $e^{-\int \eta dr}$, and this increases very rapidly as *r* decreases, so that slightly different initial conditions may give solutions *p* (1*s*) which vary considerably, but it does not matter to the final result which one of these is taken.

The inward integration of (12) for the particular integral *p* (1*s*), and the integration of (27), are taken as far as the radius at which the outward and inward integrations are compared. If the result P (1*s*) of the outward integration is a solution of (12) which tends to 0 as $r \to \infty$, as is required, then $P(1s) - p(1s)$ must be a multiple of the complementary function $e^{-\int \eta dr}$; that is $-\frac{d}{dr}[P(1s) - p(1s)]/[P(1s) - p(1s)]$ must agree with the value of η obtained by inward integration of (27). The value of ε_{11} is adjusted until this is the case, and when P (1*s*), *p* (1*s*) and η have been found for this value of ε_{11}, the solution P (1*s*) for *r* greater than r_0, the radius at which the join of the two solutions is made, is given by

$$P(1s|r) = p(1s|r) + [P(1s|r_0) - p(1s|r_0)]\, e^{-\int_{r_0}^{r} \eta dr}. \tag{28}$$

6—AN ALTERNATIVE METHOD OF HANDLING THE EQUATIONS

Another kind of method for the numerical solution of Fock's equations was tried, and though it did not seem so satisfactory as the method outlined in the previous two sections, this may have been due partly to comparative lack of familiarity with methods of this kind.

This alternative method was suggested by Torrance's method† of handling the equations of the self-consistent field; the particular characteristic of this method is that the field is built up from the radial wave functions concurrently with the solution of the equations for the behaviour of the wave functions in the field, whereas in the more usual way of handling the equations of the self-consistent field, the processes of constructing the field, and finding the wave functions in it, are two separate stages, which are carried out alternately and not concurrently. Torrance's method of approach is clearly applicable to Fock's equations; its application can be illustrated adequately by considering the solution of (13) for P (2*s*), regarding P (1*s*), and so $Y_0\,(1s,\ 1s)$, as given; it can be extended to apply to (12), (13), regarded as simultaneous equations with none of the Y_0's given.

To avoid elaboration, we shall assume the given P (1*s*) to be normalized, so that $K = \left[\int_0^\infty P^2\,(2s/r)\,dr\right]^{\frac{1}{2}}$. Then from (6) it follows that

$$\frac{d^2}{dr^2}Y_0\,(1s,\ 2s|r) = -\frac{P\,(1s|r)\,P\,(2s|r)}{Kr} \tag{29}$$

$$\frac{d^2}{dr^2}Y_0\,(2s,\ 2s|r) = -\frac{P^2\,(2s|r)}{K^2r}, \tag{30}$$

and these equations enable the Y_0 functions occurring in (13) to be built up from $P\,(2s\mid r)$ as the solution of (13) proceeds. In other words, (13), (29), (30) can be solved as a set of simultaneous equations: that they are non-linear is, of course, no difficulty in numerical work. There are three parameters ε_{22}, K, ε_{12}, to be determined so that the solution P (2*s*) of these three equations satisfies three conditions, namely:—

(*a*) $P\,(2s) \rightarrow 0$ as $r \rightarrow \infty$,

(*b*) $\int_0^\infty P^2\,(2s)\,dr = K^2$,

(*c*) $\int_0^\infty P\,(1s)\,P\,(2s)\,dr = 0$.

One apparent difficulty is that the initial conditions for the solution of (29), (30) are not fully known, for from (6), $Y_0\,(\alpha\beta|0) = 0$, but

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† 'Phys. Rev.,' vol. 46, p. 388 (1934). One of us (D. R. H.) is indebted to Dr. Torrance for an interesting account and discussion of his method, and for an advance copy of his paper. A similar method has been used by Caldwell for solving the equations of the self-consistent field for helium-like atoms, using the differential analyser of Dr. Bush.

$dY_0(\alpha\beta|0)/dr = \int_0^\infty P_N(\alpha|r)\,P_N(\beta|r)\,r^{-1}\,dr$ which is unknown at the start of the integration. On the other hand, solutions of (30) (for example), differing in the value of $dY_0(2s, 2s|0)/dr$ adopted, differ only by a term proportional to r, whose coefficient can be incorporated in ε_{22} when the Y_0, determined by integration of (30), is used in (13), and similarly for the solution of (29). This way of avoiding the difficulty, however, only raises another, for the Lagrange multipliers ε_{12} and ε_{22} may then contain unknown (and perhaps quite large) contributions from this source, and estimation of appropriate values for which to make trial solutions becomes rather speculative; also it is difficult to estimate the effect, for example, of a change in K on the value of ε_{22} required to give P the right asymptotic behaviour.

Further, the outward integration for large r is unsatisfactory for the reason, mentioned in § 6 in connection with P (1*s*), that the solution of (13) becomes very sensitive to small errors, and in this case this reacts on the functions Y_0, through equations (29), (30). Inward integration for the simultaneous equations does not appear to be practicable.

As Torrance points out, a method of this kind only involves the estimation of *parameters*, and so may be expected to provide a simpler process of approximation than the more usual method of handling the equations of the self-consistent field which involves the estimation of *functions* (the Z_0's), and, in the case of Fock's equations, some parameters also. It seemed at first sight a method of attack particularly suitable for Fock's equations; but, as far as our experience goes, an extension of the original self-consistent field method seems in practice the easier to carry out, though it is possible that greater familiarity with Torrance's method would modify this opinion.

7—RESULTS AND DISCUSSION

In comparing the solution of Fock's equations (12), (13) with that of the self-consistent field equations (15), (16), it is convenient to distinguish by a suffix f the radial wave functions forming the standard solution of Fock's equations, as defined in § 3, and quantities derived from them, and by a suffix s the radial wave functions of the self-consistent field and derived quantities.

The wave functions $P_f(1s)$, $P_f(2s)$ are necessarily orthogonal, but $P_s(1s)$, $P_s(2s)$ are not, and it is often convenient to form from them an orthogonal pair. Taking $P_s(1s)$ and $P_s(2s)$ to have the same value of $(dP/dr)_{r=0}$, we shall write $P_s(2s)$ for the linear combination of them which is orthogonal to $P_s(1s)$ and has the same value of $(dP/dr)_{r=0}$, that is

$$P_{s'}(2s) = [P_s(2s) - \beta P_s(1s)]/(1 - \beta), \tag{31}$$

where

$$\beta = \int_0^\infty P_s(1s)\, P_s(2s)\, dr \Big/ \int_0^\infty P_s^2(1s)\, dr, \tag{32}$$

the value of β in this case is 0·2878.

The results of the calculation of the solutions of Fock's equations are given in Table I; the radial wave functions P are not normalized, but have $(dP/dr)_{r=0} = 20$, as for the solution of the self-consistent field equations already published,[†] with which the present results should be compared. The $Z_0(\alpha\beta|r)$ functions, or rather functions derived from them, which are more convenient to use in practical work, are also given in Table I; in comparing these results for the corresponding ones for the self-consistent field, it should be remembered that for the Schrödinger charge distribution of the $(ns)^2$ group, $2[1 - Z_0(ns, ns|r)]$ is the total charge lying outside a radius r, and that a decrease of this quantity, for given r, indicates a contraction of that group.

TABLE I

	Radial Wave Functions				
r	P (1s)	P (2s)	$2[1 - Z_0(1s, 1s)]$	$2Z_0(1s, 2s)$	$2[1 - Z_0(2s, 2s)]$
0·00	0·000	0·000	2·000	0·000	2·000
0·02	0·369	0·369	1·999	0·000	2·000
0·04	0·682	0·681	1·993	0·001	2·000
0·06	0·946	0·941	1·978	0·004	1·999
0·08	1·166	1·156	1·954	0·008	1·998
0·10	1·347	1·329	1·920	0·014	1·997
0·12	1·496	1·466	1·876	0·022	1·996
0·14	1·615	1·570	1·824	0·032	1·994
0·16	1·709	1·645	1·764	0·042	1·992
0·18	1·781	1·694	1·699	0·054	1·990
0·20	1·834	1·719	1·628	0·066	1·988
0·25	1·898	1·698	1·440	0·097	1·983
0·30	1·889	1·580	1·246	0·128	1·978
0·35	1·831	1·391	1·059	0·155	1·974
0·40	1·742	1·150	0·887	0·178	1·971
0·45	1·633	0·873	0·733	0·194	1·970
0·50	1·515	0·572	0·600	0·206	1·969
0·55	1·392	0·256	0·486	0·212	1·968
0·60	1·270	−0·068	0·391	0·213	1·968

[†] Hartree and Hartree, 'Proc. Roy. Soc.,' A, vol. 149, p. 210 (1935).

TABLE I—*continued*

r	P (1s)	P (2s)	$2[1 - Z_0(1s,1s)]$	$2Z_0(1s, 2s)$	$2[1 - Z_0(2s, 2s)]$
0·7	1·038	−0·717	0·247	0·204	1·967
0·8	0·834	−1·343	0·153	0·186	1·963
0·9	0·661	−1·926	0·093	0·162	1·954
1·0	0·518	−2·454	0·056	0·137	1·937
1·1	0·403	−2·922	0·033	0·113	1·911
1·2	0·311	−3·328	0·019	0·091	1·876
1·3	0·239	−3·674	0·011	0·072	1·832
1·4	0·183	−3·962	0·006	0·056	1·780
1·6	0·105$_5$	−4·379	0·002	0·033	1·654
1·8	0·060	−4·615	0·001	0·019	1·509
2·0	0·034	−4·704		0·010	1·353
2·2	0·019	−4·680		0·005$_5$	1·195
2·4	0·011	−4·571		0·003	1·041
2·6	0·006	−4·401		0·001$_5$	0·897
2·8	0·003$_5$	−4·189		0·001	0·765
3·0	0·001$_8$	−3·950		0·000$_5$	0·646
3·2	0·000$_9$	−3·695			0·542
3·4	0·000$_5$	−3·434			0·451
3·6	0·000$_2$	−3·174			0·373
3·8	0·000$_1$	−2·919			0·306
4·0		−2·674			0·250
4·5		−2·112			0·149
5·0		−1·639			0·086
5·5		−1·254			0·048
6·0		−0·949			0·027
7		−0·529			0·008
8		−0·287			0·002
9		−0·152			0·001
10		−0·079			
12		−0·021			
14		−0·005			
16		−0·001			
ε	9·466$_5$	−0·6186			
$\int_0^\infty P^2\,dr$	1·858$_4$	55·94			

The difference between $P_f(1s)$ and $P_s(1s)$ is small but appreciable; it is too small to be shown graphically, and is most easily seen from the tables. $P_f(1s)$ is slightly the more compact and, as already mentioned, agrees more closely with $P_s(1s)$ for Be^{++} than for Be, so that, in this case at least, the perturbation of the core by the "series" electrons is considerably smaller when exchange is included than when it is not.

A graphical comparison of the various (2*s*) wave functions is made in two different forms in figs. 1 and 2, fig. 1 showing unnormalized P's, all having the same value of $(dP/dr)_{r=0}$, such as are convenient to use in the numerical integration of the equations, and in some applications, and fig. 2 showing normalized P^2's, which have a direct physical interpretation as radial charge densities, and which are also useful in some other applications.

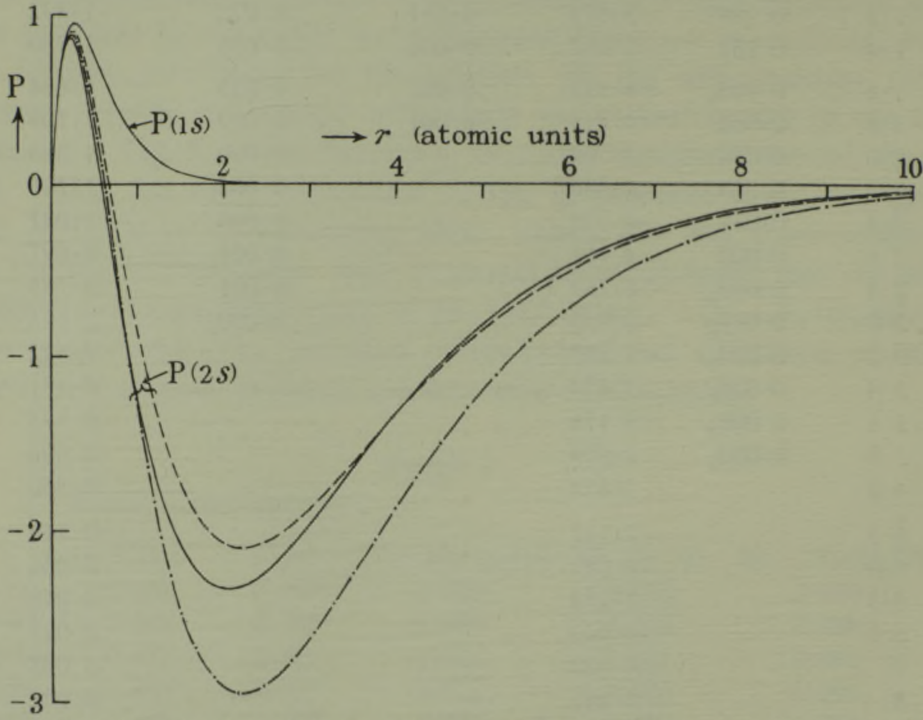

FIG. 1—Unnormalized radial wave functions P (1*s*), P (2*s*), for Be. —— from solutions of Fock's equations, (P_f). – – – – from solution of equations of self-consistent field, (P_s). — · — · — P (2*s*) from solution of equations of self-consistent field, modified so as to be orthogonal to P (1*s*), ($P_{s'}$). $\left(\frac{dP}{dr}\right)_{r=0} = 10$ in all cases. The difference between P_f (1*s*) and P_s (1*s*) is too small to be shown on the scale of the figure.

The difference between P_f (2*s*) and P_s (2*s*) is considerable; it can be expressed in general terms by saying that, compared to P_s (2*s*), P_f (2*s*) is more compact, and also smaller near the origin compared to its value for large *r*. Further, it might be thought that the (2*s*) wave function $P_{s'}$ (2*s*), made orthogonal to (1*s*), would be a better approximation than P_s (2*s*) to P_f (2*s*), but the results show that this is hardly the case. If the wave functions are compared as in fig. 1, then P_s (2*s*) is definitely the better approximation to P_f (2*s*), and if compared, as in fig. 2, $P_{s'}$ (2*s*) is only slightly the better approximation to $P_f(2s)$ in the neighbourhood of the main maximum of P^2, and near the origin it is too small by a greater factor than $P_s(2s)$ is too large. This is shown in another way by the values of the normalization integral when the functions are compared as in fig. 1, which are

$$\int_0^\infty P^2\,dr \qquad \left.\begin{array}{ll} \text{for } P_s\ (2s) & 47\cdot 0 \\ \text{for } P_f\ (2s) & 55\cdot 9 \\ \text{for } P_{s'}\ (2s) & 92\cdot 3 \end{array}\right\} \qquad (33)$$

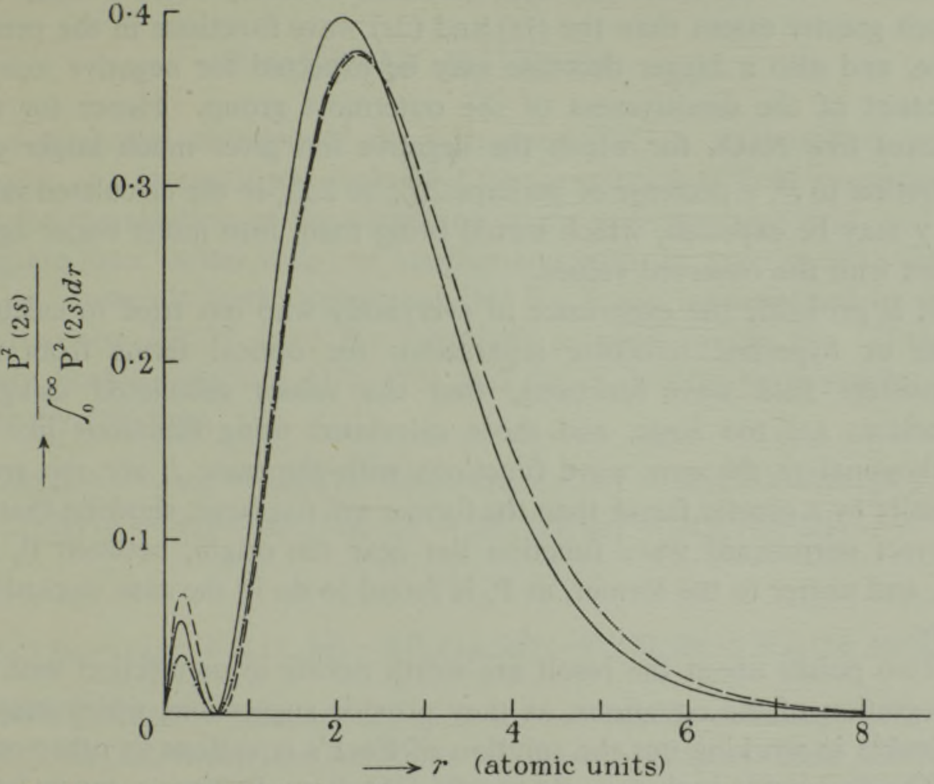

FIG. 2—Normalized $P^2(2s)$ for Be. ——— from solution of Fock's equations, (P_f^2). - - - - from solution of equations of self-consistent field, (P^2). —·—·— ditto, modified so that $P(2s)$ is orthogonal to $P(1s)$, $(P_{s'}^2)$.

The general nature of these differences between $P_f(2s)$ and $P_s(2s)$ suggests that the solution of Fock's equations is likely to give a considerably better agreement between calculated and observed atomic properties than the solutions of the equations of the self-consistent field, though no quantitative comparison can be made in this particular case.

Two properties which are rather simply related to the behaviour of the wave functions are the diamagnetic susceptibility χ, which depends on the average value of r^2, and the spin and hyperfine structure separations of terms of the optical spectrum, which depend on the relation between the behaviour of the wave function for small and large r.

Wave functions calculated by the method of the self-consistent field appear always to give too large a value for χ,[†] and the contraction of the wave functions brought about by the inclusion of exchange terms will certainly lessen the disagreement in this respect. The values of $\overline{r^2}$ for the (2*s*) wave function in this case are $(\overline{r^2})_s = 9\cdot54$, $(\overline{r^2})_f = 8\cdot42$, a decrease of about 12%. A bigger decrease may be expected for atoms with complete shells,[‡] for which there are exchange terms between wave functions with the same principal quantum number, which overlap to a much greater extent than the (1*s*) and (2*s*) wave functions in the present case, and also a bigger decrease may be expected for negative ions on account of the sensitiveness of the outermost group. Hence for substances like NaCl, for which the negative ion gives much larger contribution to $\overline{r^2}$, a decrease of perhaps 20% to 25% in the calculated values of χ may be expected, which would bring them into much better agreement with the observed values.

It is probably the experience of everybody who has tried to calculate spin or hyperfine structure separations for optical terms from self-consistent field wave functions, that the values calculated using P_s functions are too large, and those calculated using functions like $P_{s'}$, orthogonal to the core wave functions with the same *l*, are too small, usually by a greater factor than the former are too large, showing that the correct normalized wave function lies near the origin, between P_s and $P_{s'}$, and nearer to the former, as P_f is found to do in the case worked out here.

Two points about the result are worth noting in connection with the integration of the equations, as they provide suggestions which may be valuable in working out the solution of Fock's equations in other cases.

The first point is that, as the results (31) show, P_s gives a much better approximation than $P_{s'}$ to the value of the normalization integral using P_f: this is relevant in connection with the choice of an initial trial value of K in (13).

The second point is that the solution of (13) with $\varepsilon_{12} = 0$ already gives a function P (2*s*), which is much more nearly orthogonal to P (1*s*) than P_s (2*s*) is. This is shown by comparing the value

$$\int_0^\infty \mathrm{P}\,(1s)\,\mathrm{P}\,(2s)\,dr = -\,0\cdot0045$$

[†] *See*, for example, Hoare, ' Proc. Roy. Soc.,' A, vol. 147, p. 88 (1934).

[‡] For Na$^+$ the corresponding decrease, calculated from Fock and Petrashen's results, is about 13%; for a given configuration, the effect of the exchange terms would be expected to be smaller the greater the net positive charge of the system concerned.

for $K = 5\cdot5$, $K\varepsilon_{12} = 0$, in the results (24), with the value $0\cdot1349$ for the self-consistent field; the inclusion of the term $[2KY_0(1s, 2s|r)/r]\,P(1s)$ alone has actually altered the sign of $\int_0^\infty P(1s)\,P(2s)\,dr$.

8—ENERGY VALUES

In view of the use of the approximate energy value

$$E = \int \Psi^* H \Psi \, d\tau \Big/ \int \Psi^* \Psi d\tau$$

as an analytical criterion of the " goodness " of an approximate wave function, it is interesting to evaluate it for the solution of Fock's equations, and for the solution of the equations of the self-consistent field, and to compare these values with one another and with the experimental value.

The I integrals in the expression (11) for E can be simplified by substitution for d^2P/dr^2 from the equations satisfied by the P's. If these satisfy Fock's equations (12), (13) and the Y_0's in those equations are given by (6), then

$$\left.\begin{aligned} 2I(1s) &= -\varepsilon_{11} - 2F_0(1s, 1s) - 4F_0(1s, 2s) + 2G_0(1s, 2s) \\ 2I(2s) &= -\varepsilon_{22} - 4F_0(1s, 2s) - 2F_0(2s, 2s) + 2G_0(1s, 2s) \end{aligned}\right\} \quad (34)$$

and

$$E = -\varepsilon_{11} - \varepsilon_{22} - F_0(1s, 1s) - 4F_0(1s, 2s) - F_0(2s, 2s) + 2G_0(1s, 2s). \quad (35)$$

If the Y_0's used in solving (12), (13) are not exactly consistent with the $P_f(1s)$, $P_f(2s)$ which are solutions of these equations, these formulæ will not be exact, and it is partly in order that they should be sufficiently exact that the process of approximation to " self-consistent " Y_0's was carried as far as it was.

If the P's satisfy the equations (22), (23) of the self-consistent field, a similar substitution can be carried out, but does not lead to such a simple result; the details of the calculation of energy values for such a case have already been discussed elsewhere,† and need not be repeated here.

The values of the I, F, G integrals and of the E, for the solutions of Fock's equations,‡ and of those for the self-consistent field, for neutral

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† *See* Hartree and Black, *loc. cit.*

‡ These integrals were evaluated using the solution of Fock's equations giving the result (25), not with the standard solution P_f for which $\varepsilon_{12} = 0$. This does not affect the value of E, but the separate contributions to E may be slightly affected.

Be, and also for Be^{++} (for which the solutions are the same since there are no exchange terms) are given in Table II. The values of I_f were calculated from (34); those of I_s involved integrations independent of those for the F_0's.

TABLE II—CALCULATED CONTRIBUTIONS TO ENERGY, AND TOTAL ENERGY, OF NORMAL STATES OF Be AND Be^{++}

	Be neutral			
	S.C.f.	Fock		Be^{++}
$2I(1s)$	−15·873	−15·882		$-15{\cdot}895_5$
$2I(2s)$	−2·993	$-3{\cdot}179_5$		
$F_0(1s, 1s)$	+2·266	+2·273		2·278
$4F_0(1s, 2s)$	$1{\cdot}757_5$	$1{\cdot}926_5$		
$F_0(2s, 2s)$	0·320	$0{\cdot}343_5$		
$-2G_0(1s, 2s)$	−0·035	−0·052		
2E	−29·115	−29·140		−27·235
$2E(Be^{+2}) - 2E(Be)$ calc.	1·880	1·905	$2E(Be^{+3}) - 2E(Be^{+2})$	11·235
Ditto obs.	2·024		Ditto obs.	11·307 ± 0·008
Obs.-calc.	0·144	0·119		0·072 ± 0·008

The numerical work involved in the calculation of the energy values E is difficult to check thoroughly; the available checks, such as evaluation of $F_0(1s, 2s)$ by the two alternative forms indicated in (8), were used, but it seemed desirable to make a completely independent check of the whole set of calculations, especially as the energy difference $E_f - E_s$ came out much smaller than was anticipated.

Such a check is provided by a direct calculation of this energy difference in terms of the differences between the wave functions P_f and P_s: the stationary property of E used to give Fock's equations enables this energy difference to be put in a comparatively simple form.

It is convenient now to work with normalized wave functions. Let $P_N(1s|r)$, $P_N(2s|r)$ form a normalized solution of Fock's equations (not necessarily with $\varepsilon_{12} = 0$), and let $P_N(\alpha|r) + \delta P_N(\alpha|r)$ (with $\alpha = 1s$ and $2s$) any other pair of normal orthogonal functions. Then evaluating the variations δE of E for the variations of the radial wave functions P, retaining all terms and not only those of the first order, we obtain two integrals involving the δP's linearly, and a number of others involving squares and products of the δP's. The first two integrals vanish to the first order, since this is the condition from which Fock's equations are obtained, but on substitution of (12), (13) in them some second order terms remain, and these with the other integrals give finally an expression for δE which can be written as the sum of nine integrals which are listed in Table III; this expression is exact, not only second order. The values of these integrals when the varied wave functions $P_N + \delta P_N$ are the normalized orthogonal pair derived from the self-consistent field, are also given in Table III. It will be seen that these are all of much smaller magnitude than most of those occurring in the evaluation of the separate energy values E, given in Table II, and are comparatively easy to evaluate numerically, since for most of them two-figure accuracy is already sufficient to give a fourth decimal in δE. A point to be noted is that the terms $\int_0^\infty \left[\frac{d}{dr}(\delta P)\right]^2 dr$ in δE arise from one integration by parts of $-\int_0^\infty \delta P \frac{d^2}{dr^2}(\delta P)\, dr$; numerical differentiation of the comparatively small quantity δP is practicable, whereas use of a corresponding transformation of the I integrals in the evaluation of E would probably not be satisfactory, unless dP/dr were obtained by integra-

Table III—Contributions to Difference between Energy Values Calculated using Solutions of Fock's Equations and those of s.c.f. Equations

(All integrals are from $r = 0$ to ∞)

$\int \left[\frac{d}{dr}\delta P(1s)\right]^2 dr$	$+0{\cdot}0003_3$
$+ \int \left[\frac{d}{dr}\delta P(2s)\right]^2 dr$	$+0{\cdot}0386_5$
$- \int \left[\frac{2N - 2Y_0(1s, 1s) - 4Y_0(2s, 2s)}{r} - \varepsilon_{11}\right] [\delta P(1s)]^2\, dr$	$-0{\cdot}0001_1$
$- \int \left[\frac{2N - 4Y_0(1s, 1s) - 2Y_0(2s, 2s)}{r} - \varepsilon_{22}\right] [\delta P(2s)]^2\, dr$	$-0{\cdot}0269_6$
$- 2\int \left[\frac{2Y_0(1s, 2s)}{r} - \varepsilon_{12}\right] \delta P(1s)\, \delta P(2s)\, dr$	$-0{\cdot}0000_3$
$+ \int \frac{\delta Y_0(1s, 1s)}{r}\, \delta[P^2(1s)]\, dr$	$+0{\cdot}0000_3$
$+ 4\int \frac{\delta Y_0(1s, 1s)}{r}\, \delta[P^2(2s)]\, dr$	$+0{\cdot}0001_6$
$+ \int \frac{\delta Y_0(2s, 2s)}{r}\, \delta[P^2(2s)]\, dr$	$+0{\cdot}0015_5$
$- 2\int \frac{\delta Y_0(2s, 2s)}{r}\, \delta[P(1s)\, P(2s)]\, dr$	$-0{\cdot}0017_5$
Total	$0{\cdot}0118_7$

tion of d^2P/dr^2, which would involve a good deal of additional computing, rather than by numerical differentiation of P, which would be difficult to carry out to the accuracy required.

The value of δE obtained from the sum of the terms in Table III is 0·0119, which is probably correct to 1 or 2 in the fourth decimal, in excellent agreement with the difference of E values obtained from Table II, which is $0 \cdot 012_5$ and is not certain to 1 in the third decimal. This provides a complete check on the calculation of the energy values.

The values of 2E in Table II are the calculated total energies of the whole atomic system, expressed as multiples of the ionization energy of the hydrogen atom ($\frac{1}{2}$ atomic unit). The differences of the values of 2E for neutral Be and that for Be^{++} are the energies, in terms of this unit, required to remove two electrons from the normal state; that is to say, they are the values of the sum of the ionization energies of Be and Be^+. This sum is a quantity for which an accurate experimental value is available,† since the spectra of both these ions have been fully analysed. Also the value of 2E for Be^{+++} is -16, so $-16 - 2E(Be^{++})$ is the ionization energy, in the same units, of Be^{++}, for which there is an approximate spectroscopic value.† The absolute value of the difference between calculated and observed values of the latter ionization energy is very similar to the corresponding difference (0·077) for helium.

It will be seen that for neutral Be the solutions of Fock's equations give a smaller value of the total energy than that given by the solutions of the equations of the self-consistent field, as must be the case. But the improvement in the calculated value for the sum of the ionization energies of Be and Be^+ is disappointingly small, being only about 20% of the whole difference between the value calculated for the self-consistent field and the observed value. This shows that if the energy value is used as the criterion in judging the importance of the various approximations made in the self-consistent field method, the neglect of exchange is not the most important of them. On the other hand, the considerations of the previous section suggest that there is a considerable improvement of the wave function regarded as a basis for calculation of other atomic properties. So that, as far as one can judge from the present results, it seems that the inclusion of exchange terms improves the wave function considerably, though not in a way which has much effect on the energy; this is rather surprising in view of the use of the energy as the criterion for the "best" wave function of the kind assumed.

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† The observed values have been taken from the Tables in Bacher and Goudsmit's "Atomic Energy States" (McGraw Hill, 1932).

9—SUMMARY

Fock's equations for the self-consistent field of an atom, including exchange effect, have been completely solved numerically for the normal state of neutral Be.

The main features of the process of their solution are described and the results and energy values calculated from them discussed. In connection with the numerical calculations of energy values, which are difficult to check thoroughly, a new check, depending on the direct calculation of the difference of energy values calculated using the solution of Fock's equations and using any other wave functions, is developed and applied.

The inclusion of the exchange terms has a small but appreciable effect on the ($1s$) wave function, which becomes more like that for the Be^{++} ion, and a considerable effect on the ($2s$) wave function, which contracts, and also becomes smaller near the origin compared to its maximum value. It is shown that these changes are qualitatively of a kind to bring calculated values of certain atomic properties into better accord with experiment, though no quantitative comparison can be made in this case.

The calculated energy value is found to be brought into slightly better accord with observation, though the improvement is not great.