

*A Theory of Hartree's Atomic Fields.* By J. A. GAUNT, B.A.,  
Trinity College. (Communicated by Mr R. H. FOWLER.)

[Received 20 February, read 27 February 1928.]

### 1. *Introduction.*

In a recent communication to this Society\* Dr Hartree has put forward a method for calculating the field of an atom containing many electrons. Each orbit—to borrow a metaphor from the old quantum theory—is related to a wave-function  $\psi$  which obeys Schrödinger's equation. The potential energy used in this equation is due partly to the field of the nucleus, and partly to the fields of the electrons in the other orbits. The latter are calculated upon Schrödinger's interpretation of the wave-function, that  $|\psi|^2$  is the density of charge, measured in electronic charges per unit volume. It is not the purpose of this paper to discuss the practical methods of obtaining wave-functions which reproduce the fields from which they are derived; but to relate these wave-functions and their energy parameters to those of the accepted theory.

Hartree's assumptions, in common with those of many good physical theories, are simple and picturesque, but from a rigorous point of view are open to several objections. When the interactions of the electrons are not neglected, there are not so many separate orbits, each related to its own wave-function; but the atom must be described as a whole by means of one complete wave-function. Nor is this wave-function, even in the case of no interaction, a mere product of orbital wave-functions, but a combination of such products having one of the forms demanded by Heisenberg's resonance theory. It will be shown, however, that the complete wave-function lies very near to such a combination of Hartree's functions.

Again, although when the complete wave-function is a combination of orbital wave-functions the total mean density at any point is  $\Sigma |\psi|^2$  summed over all the orbital wave-functions, and it is no doubt reasonable to attribute each  $|\psi|^2$  to the corresponding orbit, yet whether the effect of one orbit on another is that of the stationary mean distribution of charge is not at once obvious. In fact, the point which gave rise to the present investigation is that in Hartree's method the mutual potential energy of each pair of electrons is counted twice over. Ought, then, his interaction terms to be halved?

In any case, it seems desirable to relate Hartree's equations to the complete wave-equation of the atom, as is done in the following

\* D. R. Hartree, *Proc. Camb. Phil. Soc.* xxiv, pp. 89–132 (1928).

sections. The comparison is by means of ordinary perturbation theory, which is carried to the first order for the wave-functions and to the second order for the energies. The efficacy of this theory depends on the smallness of the perturbing potential energy, or rather its matrix-components. A certain result for the helium atom suggests that in this case we are nearing the limit of its validity.

Section 2 deals with the simplest case—the normal state of an atom with two point electrons. The remaining sections concern the general case of an atom with many electrons. In these sections the spin-coordinate of each electron is used along with the position-coordinates, because then the complete wave-function is known to be anti-symmetrical; whereas when spin is omitted it may have various symmetry-characters. The spin-coordinate does not otherwise alter the appearance of the formulae, and their interpretation presents no difficulty. The notation can be interpreted, if it is so desired, as including the spin interaction energies and relativity effects. But in comparisons with Hartree's work both of these are neglected, as in his paper they are inserted only as final corrections.

The description of Hartree's method with which this section opens omits one part of the process. Hartree always averages his fields over spherical surfaces so as to keep them symmetrical about the nucleus. The effect of this averaging is not considered here, though the formulae obtained could be used in order to estimate it.

## 2. *The Normal Helium Atom.*

We write the wave-equation of a single electron in the field of the nucleus alone as

$$[H - E] \psi = 0 \dots\dots\dots(2\cdot00),$$

where  $H$  is a 'Hamiltonian operator'—for a helium nucleus and a point electron the operator

$$-\frac{1}{2} \nabla^2 + 1/r$$

in Hartree's units.

The equation used by Hartree is then

$$[H + V - E] \psi = 0 \dots\dots\dots(2\cdot01),$$

where  $V$  is the potential energy of a point electron in the electrostatic field of a distribution of density  $|\psi_0|^2$ . (The suffix 0 refers to the solution of (2·01) which has the lowest energy; the general characteristic and wave-function will be given a suffix  $t$  or  $u$ .) Hartree's potential energy is

$$V(x) = \int |\psi_0(x')|^2 e^2/r' dx' \dots\dots\dots(2\cdot02),$$

where  $x, x'$  are abbreviations for  $x, y, z; x', y', z'$ ; and  $dx'$  for  $dx' dy' dz'$ ; the integration is over all space;  $r'$  is the distance from the point  $x$  to the point  $x'$ ; and  $-e$  is the charge on an electron. In future we shall use the notation

$$G(x, x') \equiv e^2/r' \dots\dots\dots(2\cdot03)$$

and

$$G_0(x) \equiv \int G(x, x') |\psi_0(x')|^2 dx' \dots\dots\dots(2\cdot04).$$

Thus Hartree's  $V$  is equal to  $G_0$ .

In a precise application of the wave-mechanics, the two orbits of the helium atom cannot be separated. There is one complete wave-function  $\Psi$ , a function of the coordinates  $x_1$  and  $x_2$  of both the electrons, which satisfies the equation

$$[H_1 + H_2 + G(x_1, x_2) - E] \Psi(x_1, x_2) = 0 \dots\dots(2\cdot10).$$

Here  $H_1$  and  $H_2$  are the result of writing  $x_1$ , etc. and  $x_2$ , etc. instead of  $x$ , etc. in  $H$ ;  $G$ , as defined in (2·03), is the mutual potential energy of the electrons. The characteristic and solution of (2·10) are given the suffix  $\alpha$  when they refer to the normal state, and in other cases the suffix  $\beta$ .

For comparison with (2·10) the equations (2·01) for the two orbits may be combined into the single equation

$$[H_1 + H_2 + V(x_1) + V(x_2) - E'] \Psi'(x_1, x_2) = 0 \dots(2\cdot11).$$

Corresponding solutions of (2·10) and (2·11) are given the same suffixes. (2·11) is symmetrical in the two electrons, so that resonance effects can be preserved. Evidently

$$E_{\alpha'} = 2E_0 \dots\dots\dots(2\cdot12),$$

$$\Psi_{\alpha'}(x_1, x_2) = \psi_0(x_1) \psi_0(x_2) \dots\dots\dots(2\cdot13),$$

and more generally

$$E_{\beta'} = E_t + E_u \dots\dots\dots(2\cdot14),$$

$$\Psi_{\beta'}(x_1, x_2) = \frac{1}{\sqrt{2}} \{ \psi_t(x_1) \psi_u(x_2) \pm \psi_u(x_1) \psi_t(x_2) \} \quad (t \neq u) \quad (2\cdot15)$$

$$= \psi_t(x_1) \psi_t(x_2) \quad (t = u) \quad (2\cdot16).$$

We have put the wave-function in the form which is suitable for a first approximation to  $\Psi_{\beta}$ . We propose, in fact, to consider (2·10) as a perturbation of (2·11), with a perturbing potential energy

$$A(x_1, x_2) \equiv G(x_1, x_2) - V(x_1) - V(x_2) \dots\dots(2\cdot17).$$

If the matrix components of  $A$  are small, as we assume, then  $E_{\alpha'}, E_{\beta'}, \Psi_{\alpha'}, \Psi_{\beta'}$  are respectively first approximations to

$$E_{\alpha}, E_{\beta}, \Psi_{\alpha}, \Psi_{\beta}.$$

Let us consider the first order perturbation of the wave-function

$$\Psi_a = \Psi_a' + \sum_{\beta} \frac{(\alpha | A | \beta)'}{E_a' - E_{\beta}'} \Psi_{\beta}' + \dots \dots \dots (2.20),$$

where we are using Dirac's notation for a matrix-component,

$$(\alpha | A | \beta) \equiv \iint \Psi_{\alpha}'(x_1, x_2) A(x_1, x_2) \overline{\Psi_{\beta}'(x_1, x_2)} dx_1 dx_2 \quad (2.21),$$

the bar denoting the conjugate complex function. These matrix-components fall into two groups. If the suffixes  $t$  and  $u$  of (2.14) both differ from 0, the functions  $V$  in (2.17) contribute nothing, and

$$\begin{aligned} (\alpha | A | \beta) &= \sqrt{2} \begin{Bmatrix} (00 | G | tu) & (t \neq u) \\ (00 | G | tt) & (t = u) \end{Bmatrix} \quad t, u \neq 0 \dots (2.22), \end{aligned}$$

where

$$(00 | G | tu) \equiv \iint \psi_0(x_1) \psi_0(x_2) G(x_1, x_2) \overline{\psi_t(x_1)} \overline{\psi_u(x_2)} dx_1 dx_2 \dots (2.23).$$

The symmetrical wave-function (2.15) contributes the above, the anti-symmetrical function makes no contribution to (2.21).

When, however,  $u = 0, t \neq 0$ , using (2.04),

$$(\alpha | A | \beta) = \sqrt{2} (0 | G_0 - V | t) \quad (u = 0, t \neq 0) \dots (2.24),$$

where  $(0 | F | t) \equiv \int \psi_0(x) F(x) \overline{\psi_t(x)} dx \dots \dots \dots (2.25).$

Substituting in (2.20)

$$\begin{aligned} \Psi_a &= \Psi_a' + \sum_t \frac{(0 | G_0 - V | t)}{E_0 - E_t} \{\psi_0(x_1) \psi_t(x_2) + \psi_t(x_1) \psi_0(x_2)\} \\ &\quad + \sum_{\beta} \frac{(\alpha | A | \beta)''}{E_a' - E_{\beta}'} \Psi_{\beta}' + \dots \dots \dots (2.26), \end{aligned}$$

where the double dash denotes that in  $\beta$  both  $t$  and  $u$  differ from 0.

Now the matrix (2.23) will be much smaller when both  $t$  and  $u$  differ from 0 than when  $u = 0$ , and it reduces to  $(0 | G_0 | t)$ ; for in the latter case the  $\psi_0(x_1)$  and its conjugate reinforce one another\*. The second sum in (2.26) is therefore comparatively unimportant. A good choice of  $V$ , the potential energy in (2.01), would be one which reduced the first sum. Hartree's choice of  $V = G_0$  reduces this sum to zero. No other choice of  $V$  of any practical simplicity would make  $\Psi_a'$  so likely to be a good approximation to  $\Psi_a$ .

\* This argument is borne out by calculations with the symmetrical wave-functions of the hydrogen atom. Denoting each state by its principal quantum number, and using Hartree's units, we have

$$\begin{aligned} (11 | G | 11) &= 0.63, & (11 | G | 12) &= 0.09, & (11 | G | 13) &= 0.04, \\ (11 | G | 22) &= 0.02, & (11 | G | 23) &= 0.01. \end{aligned}$$

Having established the accuracy of Hartree's wave-function, we proceed to consider the energy. Here, second order perturbations are of interest,

$$E_a = E_a' + (\alpha | A | \alpha) + \sum_{\beta}' \frac{(\alpha | A | \beta)^2}{E_a' - E_{\beta}'} + \dots \quad (2.30).$$

The matrix-component

$$(\alpha | A | \alpha) = (0 | G_0 | 0) - 2(0 | V | 0) \dots \dots (2.31).$$

The other matrix-components have already been dealt with; and  $E_a'$  is given by (2.12). Thus

$$\begin{aligned} E_a = 2E_0 - (0 | 2V - G_0 | 0) + 2 \sum_t' \frac{(0 | G_0 - V | t)^2}{E_0 - E_t} \\ + \sum_{\beta}'' \frac{(\alpha | A | \beta)^2}{E_a' - E_{\beta}'} + \dots \quad (2.32). \end{aligned}$$

Again  $V = G_0$  reduces the second order corrections to a sum containing only the smaller matrix-components. We may write with considerable accuracy

$$E_a = 2E_0 - (0 | G_0 | 0) - \dots \quad (2.33),$$

$(0 | G_0 | 0)$  is the mean mutual potential energy of the two electrons. Its appearance was to be expected, since in using (2.01) for each orbit, we have counted the mutual potential energy twice over.

The best way of calculating the first ionisation potential of helium would seem to be to use (2.33), and subtract from it the energy of the normal state of ionised helium. This differs from Hartree's suggestion that  $-E_0$  is the first ionisation potential. Let  $E_0'$  be the energy of the ionised atom. Considering (2.00) as a perturbation of (2.01), we have

$$E_0' = E_0 - (0 | V | 0) + \sum_t' \frac{(0 | V | t)^2}{E_0 - E_t} + \dots \quad (2.34).$$

Thus the first ionisation potential, with a negative sign, would be

$$E_a - E_0' = E_0 - \sum_t' \frac{(0 | V | t)^2}{E_0 - E_t} - \dots \quad (2.35).$$

It differs from  $E_0$  by a small term of the second order, which, however, might be expected to be larger than the second order term omitted from (2.33).

In practice, the method I should recommend is less accurate than Hartree's. He obtains, in his units,  $E_0' = -1.835$ , which compares very favourably with an observed first ionisation energy of 1.81.  $(0 | G_0 | 0)$  is 1.98\*, so that (2.33) gives for the total energy  $-5.75$ . The second ionisation energy is 4.00, leaving only 1.75 for

\* Dr Hartree kindly calculated this for me.

the first ionisation—about 3 % too little. Perhaps this error is not unreasonable, and the accuracy of  $E_0$  is a piece of good fortune attributable to the terms of higher order in (2'34).

### 3. *The General Case—Notation.*

In dealing with an atom containing many electrons—such as ionised rubidium treated by Hartree—it is worth our while to resort to some subtlety of notation.

The number of electrons is  $n$ . Each electron has three co-ordinates of position and one of spin. These will be summarised by  $x_a$  or  $x_b$  ( $a, b = 1, 2, \dots n$ );

$$\int \dots dx_a$$

denotes an integration over all positions of the  $a$ th electron, and summation over both (or all) its orientations.

As before we take the equation of a single electron in the field of the nucleus to be

$$[H - E] \psi = 0 \dots\dots\dots(3'00),$$

but now the Hamiltonian operator includes the spin term.  $H_a$  is the modification of  $H$  obtained by replacing  $x$  by  $x_a$ .

The mutual potential energy of two electrons is called, as before,  $G(x_a, x_b)$ . In comparisons with Hartree's work we neglect the interactions of the spins, and give  $G$  its previous form (2'03).

The stationary state of the system whose energy and wave-function we are calculating is denoted by a suffix  $\alpha$ , any other state the suffix  $\beta$ . Approximations to these wave-functions and energies are given the corresponding suffixes.

In an approximate description of the stationary state under consideration we speak of various 'orbits,' each of which is described by a set of four (or in Dirac's latest theory three) quantum numbers. This set is summarised by one of the suffixes  $p, q, r$ , which are reserved for the orbits actually under consideration. Other possible orbits are given suffixes  $t, u$ ; while the suffix  $m$  will denote an orbit which may or may not be contained in the set  $\alpha$ . 'Orbit' includes the orientation of the electron, so that in nature—and in this theory—no two orbits are the same in any stationary state.

$\sum_p$  denotes a sum over only those orbits which occur in the state of the atom with which we are dealing (similarly for  $q, r$ ).  $\sum_{pq}$  denotes a sum over pairs of such orbits, each pair being counted once.  $\sum_t$  denotes a sum over all orbits which do not occur in  $\alpha$  (similarly for  $u$ ).  $\sum_{tu}$  denotes a sum over pairs of such orbits.  $\sum_m$  denotes a sum over all possible orbits.

Hartree's equation for the wave-function of the  $p$ -orbit is written

$$[H + V_p - {}_pE] {}_p\psi = 0 \quad \dots\dots\dots(3\cdot01).$$

A different potential energy appears in each of these equations, and a corresponding prefix is used where necessary, but is often dropped. The characteristic and wave-function calculated by Hartree are  ${}_pE_p, {}_p\psi_p$ ; but (3·01) has other solutions  ${}_pE_q, {}_p\psi_q$ ;  ${}_pE_t, {}_p\psi_t$ .

The exact equation for the complete wave-function is

$$[\sum_a H_a + \sum_{ab} G(x_a, x_b) - E] \Psi(x_1 \dots x_n) = 0 \quad \dots(3\cdot02).$$

Intermediate between (3·01) and (3·02) we introduce wave-functions satisfying

$$[\sum_a H_a + \sum_a V(x_a) - E'] \Psi'(x_1 \dots x_n) = 0 \quad \dots\dots(3\cdot03),$$

where  $V$  is a function introduced to preserve symmetry and deal with resonance effects, but which will eventually cancel out. (3·03) splits into  $n$  identical equations

$$[H + V - E'] \psi' = 0 \quad \dots\dots\dots(3\cdot04).$$

Various matrix-components are denoted as follows,  $F$  being any function of  $x_1 \dots x_n$ ,  $f$  any function of  $x$ , and  $\phi$  any function of  $x$  and  $x'$ .

$$(\alpha | F | \beta) \equiv \int \dots \int \Psi_\alpha F \overline{\Psi_\beta} dx_1 \dots dx_n \quad \dots\dots\dots(3\cdot10),$$

$$(\alpha | F | \beta)' \equiv \int \dots \int \Psi_\alpha' F \overline{\Psi_\beta'} dx_1 \dots dx_n \quad \dots\dots\dots(3\cdot11),$$

$$(p | f | m)_q \equiv \int {}_q\psi_p f {}_q\overline{\psi_m} dx \quad \dots\dots\dots(3\cdot12),$$

$$(p | f | m)' \equiv \int \psi_p' f \overline{\psi_m'} dx \quad \dots\dots\dots(3\cdot13),$$

$$(pq | \phi | tu)_r \equiv \iint {}_r\psi_p(x) {}_r\psi_q(x') \phi(x, x') {}_r\overline{\psi_t}(x) {}_r\overline{\psi_u}(x') dx dx' \quad \dots\dots(3\cdot14),$$

$$(pq | \phi | tu)' \equiv \iint \psi_p'(x) \psi_q'(x') \phi(x, x') \overline{\psi_t'}(x) \overline{\psi_u'}(x') dx dx' \quad \dots\dots(3\cdot15).$$

The dashes and suffixes are dropped when the distinctions they preserve are of no importance.

(3·02) is considered as a perturbation of (3·03), with a perturbing potential energy

$$A(x_1 \dots x_n) \equiv \sum_{ab} G(x_a, x_b) - \sum_a V(x_a) \quad \dots\dots\dots(3\cdot20).$$

Also we use

$$G_p(x) \equiv \int G(x, x') |{}_p\psi_p(x')|^2 dx' \dots\dots\dots (3\cdot21),$$

$$G_{pq} \equiv (q | G_p | q)_q \equiv G_{qp} \quad (p \neq q) \dots (3\cdot22),$$

$$U_p(x) \equiv \sum_{q \neq p} G_q(x) \dots\dots\dots (3\cdot23).$$

$G_p$  may be interpreted as the field due to the  $p$ -orbit,  $G_{pq}$  as the mean mutual potential energy of the  $p$ - and  $q$ -orbits,  $U_p$  as the field due to all orbits but  $p$ . Hartree's  $V_p$  is a central field derived from  $U_p$  by averaging over concentric spheres.

$$g_{pq} \equiv \iint {}_p\psi_p(x) {}_q\psi_q(x') \overline{G(x, x') {}_q\psi_q(x) {}_p\psi_p(x')} dx dx' \dots (3\cdot24).$$

$\Psi'_a$ , being a first approximation to  $\Psi_a$ , will be anti-symmetrical in the electrons. It is derived from  $\psi'_p(x_1)\psi'_q(x_2)\dots\psi'_s(x_n)$  by permuting the variables  $x_1, \dots, x_n$ , prefixing a minus sign when the permutation is odd, adding, and dividing by the normalising factor  $\sqrt{n}$ . The corresponding function, with  $\psi'_p, \psi'_q \dots$  replaced by  ${}_p\psi_p, {}_q\psi_q \dots$ , is denoted by  $\Psi_H$ . This is the complete wave-function obtained from equations (3\cdot01). A function derived from  $\Psi'_a$  or  $\Psi_H$  by replacing  $\psi'_p$  by  $\psi'_t$  or  ${}_p\psi_p$  by  ${}_p\psi_t$  is denoted by  $(p, t) \Psi'_a$  or  $(p, t) \Psi_H$  respectively. Similarly the operator  $(pq, tu)$  replaces  $p$  and  $q$  by  $t$  and  $u$  respectively.

#### 4. The Wave-Function.

We compare the exact equation (3\cdot02) with Hartree's equation (3\cdot01) in two stages. First the equations (3\cdot04), into which (3\cdot03) break up, are considered as perturbations of (3\cdot01); then (3\cdot02) as a perturbation of (3\cdot03).

The difference between the potential energies of (3\cdot04) and (3\cdot01) is  $V - V_p$ . Therefore

$$\psi'_p = {}_p\psi_p + \sum_{m \neq p} \frac{(p | V - V_p | m)_p}{{}_pE_p - {}_pE_m} {}_p\psi_m + \dots \dots (4\cdot00).$$

For a first order perturbation the prefixes may be omitted in the sum. If  $S$  denote a summation over all permutations of  $x_1 \dots x_n$ ,

$$\begin{aligned} \Psi'_a &= \frac{1}{\sqrt{n}} S \pm \psi'_p(x_a) \psi'_q(x_b) \dots \\ &= \frac{1}{\sqrt{n}} S \pm {}_p\psi_p(x_a) {}_q\psi_q(x_b) \dots \\ &\quad + \frac{1}{\sqrt{n}} S \sum_p \sum_{m \neq p} \pm \frac{(p | V - V_p | m)}{{}_pE_p - {}_pE_m} \psi_m(x_a) \psi_q(x_b) \dots + \dots \\ &= \Psi_H + \sum_{p, t} \frac{(p | V - V_p | t)}{{}_pE_p - {}_tE_t} (p, t) \Psi_H + \dots \dots\dots (4\cdot01), \end{aligned}$$

for the terms for which  $m$  occurs in  $\alpha$  cancel each other.



Considering (3.02) as a perturbation of (3.03),

$$\Psi_{\alpha} = \Psi_{\alpha}' + \sum \frac{(\alpha | A | \beta)'}{E_{\alpha}' - E_{\beta}'} \Psi_{\beta}' + \dots \quad (4.10).$$

First suppose that  $\beta$  differs from  $\alpha$  in respect of only one orbit; e.g.  $p$  is replaced by  $t$ . Only the anti-symmetrical  $\Psi_{\beta}'$  contributes anything, and it may be taken to be

$$\Psi_{\beta}' = (p, t) \Psi_{\alpha}' \quad (4.11).$$

The integral expression (3.11) for the matrix-component, when expanded in terms of the  $\Psi'$ 's, contains  $n^2$  products of which many contribute nothing. The relevant products are of two kinds. First, the product of any term in  $\Psi_{\alpha}'$  and the corresponding term in  $\Psi_{\beta}'$ . These terms have the same sign, and the contribution of their product is

$$\frac{1}{n} (p | \sum_{q \neq p} G_q - V | t)'$$

This must be multiplied by  $n$ , giving

$$(p | U_p - V | t)' \quad (4.12).$$

The second kind of relevant product is that of any term in  $\Psi_{\alpha}'$  and the term of  $\Psi_{\beta}'$  which is obtained by changing  $p$  into  $q$  and  $q$  into  $t$ . These terms have opposite signs, and the contribution of their product is

$$-\frac{1}{n} (pq | G | qt)'$$

This must be multiplied by  $n$  and summed for  $q$ , giving

$$-\sum_{q \neq p} (pq | G | qt)' \quad (4.13).$$

Now suppose that  $\beta$  differs from  $\alpha$  in respect of two orbits;  $p, q$ , being replaced by  $t, u$ .

$$\Psi_{\beta}' = (pq, tu) \Psi_{\alpha}' \quad (4.14).$$

Again there are two kinds of relevant products in (3.11). The products of corresponding terms give altogether

$$(pq | G | tu)' \quad (4.15),$$

and the products of terms of  $\Psi_{\alpha}'$  with those obtained by replacing  $p$  by  $u$  and  $q$  by  $t$  give

$$-(pq | G | ut)' \quad (4.16).$$

In substituting (4.11) to (4.16) in (4.10), we can drop the dashes, and replace  $\Psi_a'$  by  $\Psi_H$ ,

$$\begin{aligned}\Psi_a = \Psi_a' + \sum_p \sum_t \frac{(p | U_p - V | t) - \sum_{q \neq p} (pq | G | qt)}{E_p - E_t} (p, t) \Psi_H \\ + \sum_{pq} \sum_{tu} \frac{(pq | G | tu) - (pq | G | ut)}{E_p + E_q - E_t - E_u} (pq, tu) \Psi_H + \dots \quad (4.17).\end{aligned}$$

Substituting for  $\Psi_a'$  from (4.01),

$$\begin{aligned}\Psi_a = \Psi_H + \sum_p \sum_t \frac{(p | U_p - V_p | t) - \sum_{q \neq p} (pq | G | qt)}{E_p - E_t} (p, t) \Psi_H \\ + \sum_{pq} \sum_{tu} \frac{(pq | G | tu) - (pq | G | ut)}{E_p + E_q - E_t - E_u} (pq, tu) \Psi_H + \dots \quad (4.20).\end{aligned}$$

As in section 2, we argue that matrix-components such as  $(pq | G | qt)$  and  $(pq | G | tu)$  are particularly small, so that  $\Psi_H$  is a good approximation to  $\Psi_a$  if  $V_p = U_p$ . If we restrict ourselves to central fields, Hartree's method is probably the best.

## 5. The Energy.

By the usual perturbation formula, including the second order,

$$E_a = E_a' + (\alpha | A | \alpha)' + \sum_{\beta} \frac{(\alpha | A | \beta')^2}{E_a' - E_{\beta}'} + \dots \quad (5.00).$$

$$\text{Also } E_a' = \sum_p E_p' \quad (5.01)$$

$$\text{and } E_p' = {}_p E_p + (p | V - V_p | p)_p + \sum_{m \neq p} \frac{(p | V - V_p | m)^2}{E_p - E_m} + \dots \quad (5.02).$$

The suffix (or prefix)  $p$  has been omitted in the second order terms.

The matrix-component  $(\alpha | A | \alpha)'$  is calculated by means of an integral like (3.11). Expressed in terms of the  $\psi$ 's, it involves  $n^2$  products, only some of which make any contribution. The product of any term of  $\Psi_a'$  with its conjugate gives

$$\frac{1}{n} \left\{ \sum_{pq} (pq | G | pq)' - \sum_p (p | V | p) \right\} \quad (5.10).$$

The product of any term of  $\Psi_a'$  with the conjugate of the term in which  $p$  and  $q$  are interchanged gives

$$-\frac{1}{n}(pq|G|qp)' \dots\dots\dots (5.11).$$

(5.10), (5.11) have to be multiplied by  $n$ , and the latter summed for all pairs  $pq$ . Thus

$$(\alpha|A|\alpha)' = \sum_{pq} \{(pq|G|pq)' - (pq|G|qp)'\} - \sum_p (p|V|p)' \quad (5.12).$$

The matrix-components in this expression are given by integrals like (3.15), (3.13). In these integrals we replace the  $\psi$ 's by  $\psi$ 's by means of the equation (4.00). Neglecting terms of higher order than the second, we have

$$(pq|G|pq)' = G_{pq} + \sum_{m \neq p} 2R(p|V - V_p|m)(m|G_q|p)/E_p - E_m \\ + \sum_{m \neq q} 2R(q|V - V_q|m)(m|G_p|q)/E_q - E_m \dots (5.13),$$

$$(pq|G|qp)' = g_{pq} + \sum_{m \neq p} 2R(p|V - V_p|m)(mq|G|qp)/E_p - E_m \\ + \sum_{m \neq q} 2R(q|V - V_q|m)(mp|G|pq)/E_q - E_m \dots (5.14),$$

$$(p|V|p)' = (p|V|p)_p + \sum_{m \neq p} 2R(p|V - V_p|m)(m|V|p)/E_p - E_m \\ \dots (5.15),$$

where  $R$  denotes the real part. Thus

$$(\alpha|A|\alpha)' = \sum_{pq} \{G_{pq} - g_{pq}\} - \sum_p (p|V|p)_p \\ + \sum_p \sum_{m \neq p} 2R \frac{(p|V - V_p|m)}{E_p - E_m} \{ (m|U_p - V|p) - \sum_{q \neq p} (mq|G|qp) \} \\ \dots (5.16).$$

The remaining matrix-components in (5.00) are given by (4.12), (4.13); (4.15), (4.16). The dashes may be omitted in this approximation,

$$\sum_{\beta} \frac{(\alpha|A|\beta)|^2}{E_{\alpha} - E_{\beta}} = \sum_p \sum_t \{ (p|U_p - V|t) - \sum_{q \neq p} (pq|G|qt) \}^2 / E_p - E_t \\ + \sum_{pq} \sum_{tu} \{ (pq|G|tu) - (pq|G|ut) \}^2 / E_p + E_q - E_t - E_u \\ \dots (5.20).$$

Adding (5.02) for all  $p$ , (5.16) and (5.20), we obtain after some adjustments due to the difference in meaning between  $t$  and  $m$

$$\begin{aligned}
 E_a = & \sum_p \{ {}_p E_p - (p | V_p | p) \} + \sum_{pq} \{ G_{pq} - g_{pq} \} \\
 & + \sum_p \sum_{m \neq p} \{ | (p | U_p - V_p | m) |^2 \\
 & - 2R(p | U_p - V_p | m) \sum_{q \neq p} (mq | G | qp) \} / E_p - E_m \\
 & - \sum_{pr} \{ | (p | G_p | r) |^2 - | (r | G_r | p) |^2 \\
 & + 2R(p | G_p - G_r | r) \sum_{q \neq p, r} (rq | G | qp) \} / E_p - E_r \\
 & + \sum_p \sum_t \sum_{q \neq p} (pq | G | qt) |^2 / E_p - E_t \\
 & + \sum_{pq tu} | (pq | G | tu) - (pq | G | ut) |^2 / E_p + E_q - E_t - E_u + \dots \\
 & \dots (5.21).
 \end{aligned}$$

The last three lines of this equation are probably unimportant since they contain matrix-components involving more than two orbits. The second and third lines vanish on putting  $V_p = U_p$ . The remaining terms are then

$$\begin{aligned}
 E_a = & \sum_p E_p - \sum_{pq} \{ G_{pq} + g_{pq} \} \\
 & - \sum_{pr} \{ | (p | G_p | r) |^2 - | (r | G_r | p) |^2 \} / E_p - E_r + \dots \dots (5.22).
 \end{aligned}$$

The second order terms in this equation occur in pairs of opposite sign, and probably cancel each other sufficiently. At least we can say that it is difficult to think of a better choice for the potential energies of (3.01) than  $V_p = U_p$ .

A point in connection with the helium atom is perhaps worth noting. If we are dealing with two different orbits, neglecting spin throughout, the symmetrical wave-function as well as the anti-symmetrical must be considered. The expression for its energy reduces to (5.22) with different signs for  $g_{pq}$  and the last sum. Thus the mean between the energies of para- and ortho-states should be given by

$$\bar{E} = {}_p E_p + {}_q E_q - G_{pq} \dots \dots \dots (5.23),$$

from which the second order corrections have dropped out.

## 6. The Series Electron.

Let us now suppose that the orbits  $p, q, r \dots$  form the core or an electron, to which is added a series electron in an orbit  $s$ . If we consider the whole as forming a set of orbits, we have to solve the equations corresponding to (3.01),

$$\begin{aligned}
 [H + V_p' - {}_p E'] {}_p \psi' &= 0 \dots \dots \dots (6.00), \\
 [H + V_s' - {}_s E'] {}_s \psi' &= 0 \dots \dots \dots (6.01).
 \end{aligned}$$

The best choice for the potential energies is

$$V_p' = \sum_{q \neq p} G_q' + G_s' \dots\dots\dots (6\cdot02),$$

$$V_s' = \sum_p G_p' \dots\dots\dots (6\cdot03),$$

where  $G_p'$  is given by (3·21), with  ${}_p\psi_p'$  in place of  ${}_p\psi_p$ .

To a first approximation  $G_p' = G_p$ , and (if  $V_p = U_p$ )

$$V_p' = V_p + G_s' + \dots\dots\dots (6\cdot10).$$

Hence, considering (6·00) as a perturbation of (3·01),

$${}_p\psi_p' = {}_p\psi_p + \sum_{m \neq p} \frac{({}_p | G_s' | m)}{E_p - E_m} \psi_m + \dots\dots\dots (6\cdot11).$$

Substituting in the integral for  $G_p'$ ,

$$G_p' = G_p + \sum_{m \neq p} 2R({}_p | G_s' | m) \Gamma_{mp}/E_p - E_m + \dots\dots\dots (6\cdot12),$$

$$\text{where} \quad \Gamma_{mp}(x) \equiv \int G(x, x') \psi_m(x') \overline{\psi_p(x')} dx' \dots\dots\dots (6\cdot13).$$

By (6·13), (3·21),

$$({}_p | \Gamma_{mq} | p) \equiv (m | G_p | q) \dots\dots\dots (6\cdot14).$$

By (6·02), (6·12), we have to the second order,

$$V_p' = V_p + G_s' + \sum_{q \neq p} \sum_{m \neq q} 2R(q | G_s' | m) \Gamma_{mq}/E_q - E_m + \dots\dots\dots (6\cdot15).$$

Again considering (6·00) as a perturbation of (3·21),

$$\begin{aligned} {}_pE_p' &= {}_pE_p + ({}_p | G_s' | p)_p + \sum_{q \neq p} \sum_{m \neq q} 2R(q | G_s' | m) (m | G_p | q)/E_q - E_m \\ &\quad + \sum_{m \neq p} |({}_p | G_s' | m)|^2/E_p - E_m + \dots\dots\dots (6\cdot16). \end{aligned}$$

Let  $G_{pq}'$ ,  $g_{pq}'$  denote the analogues to  $G_{pq}$ ,  $g_{pq}$ , using wave-functions which satisfy (6·00). Then by (3·22), (6·11),

$$\begin{aligned} G_{pq}' &= (q | G_p' | q)_q + \sum_{m \neq q} 2R(q | G_s' | m) (m | G_p | q)/E_q - E_m \\ &= G_{pq} + \sum_{m \neq p} 2R(p | G_s' | m) (m | G_q | p)/E_p - E_m \\ &\quad + \sum_{m \neq q} 2R(q | G_s' | m) (m | G_p | q)/E_q - E_m + \dots\dots\dots (6\cdot17), \end{aligned}$$

using (6·12), (6·14). By (3·24), (6·11),

$$\begin{aligned} g_{pq}' &= g_{pq} + \sum_{m \neq p} 2R(p | G_s' | m) (mq | G | qp)/E_p - E_m \\ &\quad + \sum_{m \neq q} 2R(q | G_s' | m) (mp | G | pq)/E_q - E_m + \dots\dots\dots (6\cdot18). \end{aligned}$$

The last two sums contain matrix-components of the kind which we neglect. Similarly,

$$G_{sp}' = (p | G_s' | p)_p + \sum_{m \neq p} 2 | (p | G_s' | m) |^2 / E_p - E_m \dots (6.19),$$

and the difference between  $g_{sp}'$  and  $g_{sp}$  is negligible.

Now Hartree's method is to calculate separately the distribution of the core, by means of equations (3.01) (with  $V_p = U_p$ ), and then to use for the series electron an equation like (6.01) in which  $G_p'$  is replaced by the already calculated  $G_p$ . That is

$$[H + V_s - {}_sE] {}_s\psi = 0 \dots \dots \dots (6.20)$$

with 
$$V_s = \sum_p G_p \dots \dots \dots (6.21).$$

In our notation (6.20) will be looked upon as related to (3.01), just as (6.01) is related to (6.00).

By (6.03), (6.12),

$$V_s' = V_s + \sum_p \sum_{m \neq p} 2R(p | G_s' | m) \Gamma_{mp} / E_p - E_m \dots (6.22),$$

so that, using (6.14),

$${}_sE_s' = {}_sE_s + \sum_p \sum_{m \neq p} 2 | (p | G_s' | m) |^2 / E_p - E_m + \dots \quad (6.23).$$

The equation for the energy corresponding to (5.22) is

$$\begin{aligned} E' = & \sum_p E_p' + {}_sE_s' - \sum_{pq} \{G_{pq}' + g_{pq}'\} - \sum_p \{G_{sp}' + g_{sp}'\} \\ & - \sum_{pr} \{ | (p | G_p | r) |^2 - | (r | G_r | p) |^2 \} / E_p - E_r \\ & - \sum_p \{ | (p | G_p | s) |^2 - | (s | G_s | p) |^2 \} / E_p - E_s + \dots \quad (6.30), \end{aligned}$$

where some dashes have been omitted in second order terms.

Using (6.16), (6.17), (6.18), (6.19), (6.23), this gives

$$\begin{aligned} E' = & E_a + {}_sE_s - \sum_p g_{sp} + \sum_p \sum_t | (p | G_s' | t) |^2 / E_p - E_t \\ & - \sum_p \{ | (p | G_p | s) |^2 - | (s | G_s | p) |^2 \} / E_p - E_s + \dots \quad (6.31). \end{aligned}$$

This ionisation energy is  $E_a - E'$ . Hartree uses  $-{}_sE_s$ . (6.31) gives other terms, of which the first is of the order of the difference in energy between symmetrical and anti-symmetrical states. The second arises from (6.16), and represents the change in the energy of the core owing to the field of the series electron; this effect is mentioned by Hartree in § 7 of his second paper. The last contains pairs of terms of opposite signs, and may well be negligible.

The same equations apply to the X-ray terms, if  $s$  refers to the orbit whose electron is removed from the core, and the series electron is included in the set of orbits  $a$ . The only difference is that, owing to the closer interaction of the core electrons in comparison with their interaction with the series electron, the last three terms of (6.31) are much more important when  $s$  belongs to the core, than when it is an outer orbit.

## 7. Conclusion.

It appears that of all methods of approximating to the wave-function and energy of a complicated atom by solving equations for the individual orbits, Hartree's (apart from his spherical averaging) is the most generally effective in reducing the first order error in the wave-function and the second order error in the energy. It would be a mistake to follow the suggestion of halving his interaction potential energies, for the double counting of mutual potential energies is easily allowed for by means of first order corrections to the energy (see (2.33), (5.22)). The value  $V_p = U_p$  removes important terms from corrections of the higher orders also. For in the perturbation of (3.03) by  $A$  the most important matrix-components are those related to a single electron-jump, and they reduce to the form  $(p|U_p - V|m)$ . Since  $V$  must disappear from the final formula, this will generally become  $(p|U_p - V_p|m)$ , though some other suffix is possible.

The smallness or vanishing of the matrix-components provide the justification for the use of perturbation theory to obtain (2.26), (2.32), (4.20), (5.22). This is more doubtful in the cases of (2.34), and of (6.11), (6.16) when  $s$  is an inner orbit; and I am inclined to be more surprised at the agreement of the orbital energy-parameter with the ionisation energy in helium than at its errors in the X-ray terms of ionised rubidium. In the latter case there is again a discrepancy between Hartree's results and the formulae of this paper. (6.31) seems to indicate an ionisation energy greater than  $-_sE_s$ , whereas Hartree's results in Table III exceed the observed values. This may be due to the intrusion of third order terms.

To sum up, the expressions for the total energy of the atom are theoretically more sound than those for the separate X-ray terms, though of less practical value. Hartree's wave-functions have been shown to be good approximations.