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THE SELF CONSISTENT FIELD AND THE STRUCTURE OF ATOMS

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Abstract

The method proposed by Hartree for the solution of problems in atomic structure is examined as to its accuracy as a method of solving Schrödinger's equation. A wave function is set up at once from his method, and the matrix of the energy computed with respect to it. The non-diagonal terms are shown to be small, indicating that the function is a good approximation to a real solution. The energy levels are found by perturbation theory from this matrix, and are compared with the term values as found by Hartree. His values should be corrected for three reasons: he has neglected the fact that electron distributions are not really spherical; he has not considered the resonant interactions between electrons; and he has made an approximation which amounts to neglecting the polarization energy. The sizes of these corrections are estimated, and they are found to be of the order of the errors actually present in the numerical cases he has worked out.

HARTREE[1] has recently proposed a method of approximate solution of problems in atomic structure by using central fields defined in a certain way, which he calls "self-consistent" fields. He has justified his method only by qualitative arguments and by the agreement of his calculations with experiment (particularly in the case of Rb, the atom which he has investigated in greatest detail). It is the purpose of the present paper to show to what extent his method is really a solution of the problem by wave mechanics, and to estimate the errors which should be present in it. It appears that Hartree's procedure has in fact a good theoretical foundation, and that the estimated errors are in general of the order of magnitude of the discrepancy between his calculations and experiment.

Hartree's method is the following: he sets up a separate wave function for each electron of the atom; he assumes the individual electrons to have charge density corresponding to their $\psi\psi^*$'s, averaged over different directions to give a spherical distribution of density; he adds these distributions for all the electrons but one, and finds the electric potential of the resulting charge; then he subjects the wave function of the remaining electron to the condition that it be a solution, with proper quantum numbers, of the wave equation connected with the central field so defined. By applying this condition to each electron of the atom, the problem becomes determinate. Finally, he takes the sum of the density distributions of all the electrons to be the real density distribution in the atom; and he assumes the characteristic numbers of his various central field problems to be the energy values of the corresponding terms of the spectrum. The latter agree well with the observed terms, except in the optical case, in which there is a discrepancy

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[1] D. R. Hartree, Proc. Camb. Phil. Soc., 24, 89 (1928).

which he assumes due to the polarization of the core by the valence electron. Hartree considers this agreement to be only empirically justified, since it is not obvious that the method takes into account the rearrangement of the electrons in the ion when one electron is removed.

One can set up a wave function for the problem by taking the product of Hartree's functions for the individual electrons. The resulting function proves to be in fact a good approximation to a solution of Schrödinger's equation, which we verify by computing the non-diagonal terms of the matrix of the energy referred to these wave functions, and by showing that they are remarkably small. To a lower order of accuracy, we can set up a wave function for the ion found by removing an electron, merely by leaving the wave function of that electron out of the product. Then by perturbation theory we can calculate the various ionization potentials. These prove to differ from the term values of the one-electron problem (which Hartree takes as representing them) on three distinct accounts: first, there is a term arising because the process of averaging densities over different directions to produce a central field is not strictly justified; second, there is a term on account of resonance between the electrons. These two corrections are in close relation to each other; they are more important for x-ray electrons, except *s* electrons, than for optical electrons; and they can be estimated, and prove not to be much larger than the divergences between Hartree's calculation and experiment. Finally there is a term which arises because the wave function of the ion is of a lower order of accuracy than that of the atom, and appreciable second-order terms in the energy arise from it. For the x-ray spectra, this is of opposite sign to the errors mentioned above, and may reasonably cancel part of them. For the optical terms, it proves to be a polarization term, of just the sort demanded to bring Hartree's calculations into better agreement with experiment.

2. The first step in discussing Hartree's method is to formulate his process mathematically. Let the separate wave function of the ith electron be u_i, a function of the coordinates x_i of this electron. The density of charge connected with this electron is u_i^2 (neglecting for simplicity the possibility that u_i may be complex). Let this density averaged over all orientations, viz., $(1/4\pi)\int u_i^2(r,\theta,\phi)\sin\theta d\theta d\phi$ be $\bar{u}_i^2$. The density of all the electrons but the ith is $\Sigma_{(k,k\neq i)}\bar{u}_k^2$ (where here, and always unless otherwise stated, all summations are assumed to be over all the electrons of the atom). The potential energy of the ith electron in this field, and in the field of the nucleus of charge Z units, is then $-Z/r_i+\Sigma_{(k,k\neq i)}\int(\bar{u}_k^2/r_{ik})dv_k$, where r_i is the distance of the ith electron from the nucleus, r_{ik} the distance between ith and kth. Thus the wave equation for this electron becomes[2]

$$\nabla_i^2u_i+(\epsilon_i-2\sum_{(k,k\neq i)}\int(\bar{u}_k^2/r_{ik})dv_k+2Z/r_i)u_i=0 \tag{1}$$

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[2] Here and elsewhere we shall measure distances in terms of a_0, the radius of the first hydrogen orbit, and energies in terms of Rh. This accounts for the factor 2 in all potential energy terms.

Hartree finds u_i's and ϵ_i's so that these equations are satisfied for each i. Each equation is obviously that of an electron in a central field; and in each case he chooses the particular solution of the central field problem given by the quantum numbers he wishes to assign to the corresponding electron.

Next we inquire what differential equation is satisfied by the product of all the u_i's, which we shall call ψ: $\psi = u_1 \cdots u_n$. We have at once, multiplying Eq. (1) by all the other u's, recalling that each u_k is a function only of x_k, and then adding the equations so obtained,

$$\nabla^2\psi + \left(\sum_i \epsilon_i - \sum_{(i,k;i\neq k)} \int 2\bar{u}_k^2/r_{ik}dv_k + Z \sum_i 2/r_i\right)\psi = 0 \tag{2}$$

This is an equation which, as we shall show, is not very different from the true equation for ψ, which is $H\psi = E\psi$, where

$$H = -\nabla^2 + \tfrac{1}{2} \sum_{(i,k;i\neq k)} 2/r_{ik} - Z \sum_i 2/r_i \tag{3}$$

(where the factor $\frac{1}{2}$ is inserted because we wish each pair of electrons to be counted once, instead of twice, as the sum $\Sigma_{(i,\,k;\,i\neq k)}$ would give).

Having found the differential Eq. (2) satisfied by Hartree's function ψ, we can compute the matrix of H with respect to it by integrating the operator (3) over the function. That is, the component connected with a transition $\psi' \rightarrow \psi''$ is, using (2),

$$H'{}'' = \int \psi' H \psi'' = \int \psi'\psi'' \left[\sum_i \epsilon_i + \tfrac{1}{2} \sum_{(i,k;\,i\neq k)} \left(2/r_{ik} - 2\int 2\bar{u}_k''^2/r_{ik}dv_k\right)\right] \tag{4}$$

We shall show the non-diagonal components of this matrix, at least those connected with one-electron transitions, to be very small. For to an approximation, in a one-electron transition, say of the jth electron, only u_j changes, the other u's remaining unchanged; u_j' and u_j'', on the other hand, are approximately orthogonal to each other, so that ψ' and ψ'' are orthogonal. We readily see that the only terms of Eq. (4) which survive are

$$H'{}'' = \tfrac{1}{2} \sum_{(k,k\neq j)} \left(\int 4u_j'u_j''u_k''^2/r_{jk}dv_{jk} - \int 4u_j'u_j''\bar{u}_k''^2/r_{jk}dv_{jk}\right) \tag{5}$$

Plainly this differs from zero only to the small extent to which $\Sigma_{(k,\,k\neq j)}\int u_k''^2/r_{jk}dv_k$ differs from $\Sigma_{(k,\,k\neq j)}\int \bar{u}_k''^2/r_{jk}dv_k$; a difference which we shall show later to be very small, appreciable in first order terms, but negligible in second order terms. Thus the second order energy, which involves squares of these non-diagonal components, is quite negligible. It is instructive to compare this result with what we should have if in the unperturbed wave function the mutual shielding effect of the electrons were not taken into account by Hartree's method. Then the last term of Eq. (5) would be absent, and the almost exact cancellation which we have here would not occur. From the nature of the cancellation in Eq. (5), it seems highly probable that Hartree's method is the best method using central fields that can be found, from the standpoint of making the non-diagonal terms of H small.

For comparison with Hartree's results, we wish, not the energy of the stationary state, but the ionization potentials, the differences between the energy of the atom and that of the ion with a particular electron removed. To do this, we must solve also for the energy of such an ionic state, and subtract. Following Hartree, we shall not assume the problem of the ion to be separately solved (except in the case of optical spectra, for which the procedure is somewhat different, and will be explained later). Rather we take as an approximate solution of the ionic problem the product of the atomic wave functions of all the electrons except that which is removed. This neglects the rearrangement of the orbits when one electron is removed, on account of the lost shielding of that electron. We may therefore expect this wave function to be a much less accurate solution of the ionic problem than the complete function is of the atomic problem; an expectation which is verified when we compute the energy, for now the non-diagonal terms of the matrix, and the second order term of E computed from them, are of an altogether larger order of magnitude than before.

The energy operator for the ion with the ith electron removed is

$$H^i = -\nabla^2 + \tfrac{1}{2}\sum\nolimits_{(j,k;j\neq k;j,k\neq i)} 2/r_{jk} - Z\sum\nolimits_{(j,j\neq i)} 2/r_j \tag{6}$$

where this ∇^2 does not include derivatives with respect to the coordinates of the ith electron. That is,

$$H - H^i = -\nabla_i^2 + \sum\nolimits_{(k,k\neq i)} 2/r_{ik} - 2Z/r_i \tag{7}$$

This operator, averaged over the wave function in the proper fashion, will give the negative of the ionization potential which we desire. We should properly average H over the wave function of the atom, H^i over that of the ion; but as H^i does not involve the coordinates x_i in any way, the terms in u_i merely integrate to unity. Thus we may find the matrix of the ion by integrating H^i over the atomic wave function. Then

$$(H - H^i)'\,'' = \int \psi'(-\nabla_i^2 + \sum\nolimits_{(k,k\neq i)} 2/r_{ik} - 2Z/r_i)\psi'' dv \tag{8}$$

This may be put in different form by using Eq. (1); for from it

$$(-\nabla_i^2 + \sum\nolimits_{(k,k\neq i)} 2/r_{ik} - 2Z/r_i)\psi'' = \left[\epsilon_i + \sum\nolimits_{(k,k\neq i)}\left(2/r_{ik} - \int 2\bar{u}_k''^2/r_{ik} dv_k\right)\right]\psi''.$$

Thus

$$(H - H^i)'\,'' = \int \psi'\psi'' dv \epsilon_i + \sum\nolimits_{(k,k\neq i)} \int \psi'\psi''\left(2/r_{ik} - \int 2\bar{u}_k''^2/r_{ik} dv_k\right) dv \tag{9}$$

From Eq. (9), one can see to what extent Hartree's assumption is justified, that $-\epsilon_i$ measures the ionization potential of the ith electron. The true ionization potential is determined from (9) as the sum of, first, the diagonal term; second, a combination of terms involving resonant interchanges between two electrons; third, second and higher order terms coming from products of non-diagonal terms. Now if the ψ's corresponding to different states, and to states with interchange of electrons, were orthogonal (as they nearly are), the first term of (9) would give just $-\epsilon_i$ for the ionization potential. Thus the error in Hartree's assumption comes principally from the second term. This term leads to contributions of the types mentioned earlier in the paper: (1) its diagonal terms are not zero, because $u_k''^2$ and $\bar{u}_k''^2$ are not the same; (2) its terms corresponding to resonant interchange of electrons are not zero, on account of the non-vanishing of $\int\psi'\psi''2/r_{ik}dv$; (3) its non-diagonal terms are not zero, resulting in a second-order term in the ionization potential. We see, however, that there is no large first order error coming from the use of an incorrect wave function for the ion; the process of averaging H^i over the wave function has made correction for this to the first order, only the second order error remaining. This is an instructive example of the value of the perturbation method of averaging H over an unperturbed orbit. The average, say, of the potential energy over the incorrect wave function would show considerable errors, on account of the excessive size of the outer shells as described by the incorrect wave function; but the average of the kinetic energy compensates this, to the first order, leaving an error of smaller order in the whole energy.

3. In investigating Hartree's method more closely, we next try to estimate the size of the various errors discussed above. In the present section we shall compute the first-order terms in the ionization potential. First is the diagonal term. This, from (9), is

$$(H-H^i)''=\epsilon_i+\sum_{(k,k\neq i)}\int u_i^2dv_i\int 2(u_k^2-\overline{\overline{u_k^2}})/r_{ik}dv_k \tag{10}$$

The second term of (10), arising from the fact that u_k^2 is not spherically symmetrical, contains many terms which cancel each other, and in some cases it is strictly zero. For, as Unsöld[3] has shown, and as Hartree mentions, in any closed shell, the total distribution is spherically symmetrical. Thus if we write this term as $\int u_i^2dv_i\Sigma_{(k,k\neq i)}\int 2(u_k^2-\bar{u}_k^2)/r_{ik}dv_k$, and take the sum over all the electrons of a closed shell not including the ith electron, we shall have zero. The only contribution, then, comes from the other electrons in the same shell with the ith electron. Now the charge of these electrons, increased by that of the ith, must add to make a spherical shell, by what we have just said; thus they by themselves have charge in excess of the average where the ith electron is deficient, and have a deficiency where the ith has excess charge. Thus the density represented by $\Sigma_{(k,k\neq i)}(u_k^2-\bar{u}_k^2)$ is negative where the ith electron has large density, and positive where the ith has small density. In computing the integral, then, the regions where r_{ik} is small, and the integrand is large, will make negative contributions to

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[3] A. Unsöld, Ann. d. Phys., **85**, 355 (1927).

the integral, while those with small integrands will make positive contributions; as a result, the integral is negative. It then results in a decrease in ϵ_i or an increase in ionization potential.

In two important cases, the second term vanishes exactly. These are first the case of a valence electron outside closed shells (so that this error is not met in Hartree's calculation of optical terms); and second the case of an s electron, where the other electron in the same shell has exactly a spherically symmetrical distribution. Thus this term is not met in the K shell, or the L_1 or M_1. On the other hand, in the L_2 shell, and other similar ones, such a term would be present. To estimate its importance, it has been calculated for the 2_2 shell of Rb, using Hartree's values of the field. The actual wave functions are the function of r given by Hartree, multiplied by certain spherical harmonics of the angles. Taking account of them, we find that the second term of (10) is respectively—1/25 and—4/25 times 5.46 (in terms of Rh) for the transitions in which a 2_2 electron with $m=1$ or $m=0$ is removed from the L shell. The first term (1/25 or 4/25) comes from integration of the spherical harmonics, and is of course different in the two cases because the states with $m=1$ and 0 have different distributions of charge; the second term (5.46) comes from an integration over the functions of r, an integration which should give a result resembling the interaction energy of one 2_2 electron on itself (which, as Hartree states, is about 12 units), but should be decidedly smaller.

In addition to the diagonal terms of the matrix (9), there are other terms entering the first order energy, arising from resonant interchanges of pairs of electrons. Suppose one denote the matrix component of H, connected with an interchange of the mth and nth electron, as H_{mn}. Then one can show, by the group theory developed by Wigner, Hund, Heitler[4] and others, that for an atom consisting of closed shells of electrons, except for a possible excess or deficiency of one electron (the only kind we need consider), the first order energy is the diagonal term of the matrix, decreased by the sum of the H_{mn}'s for all pairs of electrons which have spins in the same direction. In the difference between the energy of atom and ion, then, will appear, with a negative sign, the sum of all terms H_{mn} connected with interchange of the electron which is removed, and other electrons with spins in the same direction. Thus we have for the first order ionization energy the diagonal term (10), already found, with additional correction for the resonance terms:

$$E-E^i=(H-H^i)''-\sum_{(k,k\neq i;\ \text{spin } k \text{ par. to spin } i)} H_{ik}. \tag{11}$$

The last term in (11), arising from resonant interchange of electrons, can be shown to be small, though not strictly zero, in several important cases. One has

$$H_{ik}=\int 2u_i'u_i''u_k'u_k''/r_{ik}dv_{ik} \tag{12}$$

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[4] E. Wigner, Zeits. f. Phys., **40,** 883; **43,** 624 (1927).
F. Hund, Zeits. f. Phys., **43,** 788 (1927).
W. Heitler, Zeits. f. Phys., **46,** 47 (1927).

where u_i' and u_k'' mean the same function, but of different arguments, and similarly u_i'' and u_k' mean the same function, although different from the previous one. Obviously this term, then, can be large only for interaction between electrons whose wave functions overlap considerably. Now the K electrons on the one hand, and the valence electron on the other, do not spend any large fraction of their time in a region where there are other electrons; thus the interaction terms for them are small. There is no term for interaction of one K electron with the other, because their spins are antiparallel. For electrons between the two extremes, however—the L, M, N shells, etc.—the resonance terms can be of considerable importance. Naturally the largest terms of this kind will come from the interchange of two electrons in the same shell, for their wave functions differ only in the spherical harmonic part; for two electrons in different shells, the wave functions differ also in the function of r, so that these terms are less important. As an estimate, the resonance terms for a 2_2 electron of Rb, coming from interaction with other 2_2's, have been calculated. These prove to be the product of—9/25 or—6/25 (the first for the removal of an electron with $m=1$, the second with $m=0$) with the same quantity 5.46 found above.

The sum of the two first order correction terms, for the L shell of Rb, is thus $(-1/25-9/25)\times 5.46$ for an electron with $m=1$, or $(-4/25-6/25)\times 5.46$ for an electron with $m=0$; that is, in either case, $2/5\times 5.46=2.2$ units. We should expect the correct ionization potential of a 2_2 electron to be, then, what Hartree finds (about 137 units), increased by 2.2 units. As a matter of fact, Hartree's value itself is in almost perfect agreement with experiment; but this seems to be a coincidence, to judge from his other figures, and the errors seem to be of the order of one or two units, so that the value we have found appears to be of the actual order of the errors of Hartree's method. For M electrons, and others, we should naturally suppose the errors from these terms to be less than for L orbits (on account of the smaller interaction of an M electron on itself); thus it seems likely that the errors introduced by the extra terms in the first order energy are in any case of the order of magnitude of the discrepancy between Hartree's calculations and experiment. It does not seem to be true, however, that one improves the agreement with experiment by making these corrections.

One fact of great theoretical interest was met in the last paragraph: the fact that, when both sorts of first order corrections are taken into account, the ionization potential for either an electron of $m=1$ or $m=0$ is the same. This means that the ion has the same energy, whatever kind of 2_2 electron is missing from the completed shell. The ionized shell is degenerate, and degenerate in just the same way that a single 2_2 electron would be. It is this fact that leads to the result that the interaction of a shell lacking one electron with the spins is just like the interaction of a single electron with its spin, so that the L terms of x-rays are doublet terms. The degeneracy in this case, however, does not seem to be obvious, as it is with a single electron; one can see this by noting that the remaining electrons of the shell provide an axis in a definite direction, or by remembering the way in which the interaction energy is built up, of terms which separately are different for the different values of m.

4. In the last section, we discussed the first order ionization potentials, and showed the extent of the error which Hartree makes in his assumption as to the value of these quantities. Now we must consider the remaining error, arising from the second order energy. In finding this, which is a quadratic term, it is not at once allowable to use the matrix components of $H-H^i$, from (9); we should rather find separately the non-diagonal components of the separate matrices for H and H^i, work out their individual second-order terms, and subtract. But as we saw earlier, the non-diagonal terms of H are small compared with those of H^i, so that the non-diagonal terms derived from (9) are essentially those of H^i itself. Since this appears with negative sign, we are justified in computing the second order energy in the usual way from the matrix of (9), except that we must use the opposite sign to the usual one. Thus we have, from ordinary perturbation theory,

$$(E-E^i)_2 = -\sum{}''\left\{(H-H^i)'{}''(H-H^i)''{}'/(E'-E'')\right\}. \tag{13}$$

In one other respect, this problem differs from the ordinary one of perturbation theory: the matrix of $H-H^i$ is not the integral of one given function over the wave functions; the function is different (on account of the term $\int 2\bar{u}_k''^2/r_{ik}dv_k$) for each stationary state. Closer examination shows that this is to be taken care of by using $\bar{u}_k'^2$ in each of the components occurring in (13).

In finding the matrix components $(H-H^i)'{}''$ from (9), one notes first that the essential contributions come from the second term of (9), since ψ' and ψ'' are practically orthogonal; next, only those transitions for which some other electron than the ith changes its quantum number, have large components. For if the ith alone changes, ψ' and ψ'' differ essentially only in having different factors u_i' and u_i''. The summation in (9) then is $\int u_i'u_i''dv_i\Sigma_{(i,k,i\neq k)}\int 2(u_k^2-\bar{u}_k^2)/r_{ik}dv_k$. On account of the small difference between the actual distribution of charge and a spherical distribution (a difference of zero if the ith electron is the valence electron) this is small. We then consider only transitions of the electrons other than the ith. If, say, the pth has a transition, we have

$$(H-H^i)'{}'' = \int u_i^2dv_i\int u_p'u_p''\left(2/r_{ip} - \int 2\bar{u}_p'^2/r_{ip}dv_p\right)dv_p \tag{14}$$

We shall be able to interpret this term better after considering the optical case, in which it has a simple meaning.

For the valence electron, Hartree proceeds somewhat differently from what he does in other cases. He does not carry through a calculation of his problem for each energy level; instead, he solves the problem of the ion, and uses the central field determined from it for the atomic computation, neglecting therefore the reaction of the valence electron on the ion. The second-order error in the problem then comes in the energy E of the atom, rather than in the E^i of the ion. For this electron, then, we need make no change in (13) except to change the sign. With this change, we shall show that the term represents, in a somewhat unsatisfactory way, the energy change on account of polarization of the ion by the valence electron. To demonstrate this, we may most conveniently consider a non-penetrating orbit, in which u_i^2 is not appreciable except for large values of r_i. Then, since $\bar{u}_p'^2$ represents a distribution which is spherical, and is practically all inside the radius r_i, we have very closely

$$2/r_{ip}-\int 2\overline{u_p''^2}/r_{ip}dv_p=2/r_{ip}-2/r_i.$$

We can next expand $2/r_{ip}$ in series in $1/r_i$:

$$2/r_{ip}=2/r_i+2r_p\cos(r_i,r_p)/r_i^2\cdots.$$

Since the first of these terms cancels, we have essentially the second left, giving

$$(H-H^i)'\,''=\int 2u_i^2/r_i^2dv_i\int u_p'u_p''r_p\cos(r_ir_p)dv_p. \tag{15}$$

Thus the second order energy is

$$(E-E^i)_2=1/2\left[\int 2u_i^2/r_i^2dv_i\right]^2$$
$$\sum''\left\{2\left[\int u_p'u_p''r_p\cos(r_i,r_p)dv_p\right]^2/\,(E'-E'')\right\} \tag{16}$$

The second term is recognized as the polarizibility of the ion; the first is, not the average of $1/r_i^4$, as we should expect, but the square of the average of $1/r_i^2$ (the numerical factor 2 in $2/r_i^2$ arises from our units). With this difference, the term is just the sort of polarization term that Hartree wished, to explain the discrepancy between observation and experiment. It results, one notices, in a decrease of $E-E'$ (on account of the negative sign of all terms $E'-E''$) or an increase of ionization potential.

The fact that this introduces a polarization term depending on the square of the average of $1/r_i^2$, instead of on the average of $1/r_i^4$, is to be interpreted as an error inherent in the method. The effect depends on the distortion of the inner orbits by the valence electron; and since the wave function we use is one obtained by separation of variables, so that the function for the inner electrons must not depend on the instantaneous position of the valence electron, the distortion effect must be the average of that produced by the valence electron at the different points of its orbit, giving the average of $1/r_i^2$. Thus when we average the change of energy on account of this distortion, over the orbit of the valence electron, we find the other factor $1/r_i^2$. When one calculates, it is found that for the important optical orbits $(\overline{1/r_i^2})^2$

and $\overline{1/r_i{}^4}$ differ by about a factor of 2, so that this difference makes a considerable error in the method, even when carried to the second order. That the correct polarization energy involves $\overline{1/r}{}^4$ is shown by the success of Waller's[5] calculations for helium.

Having seen that the second order term for the valence electron refers to polarization, we can return to the case of the other electrons. There evidently the same physical situation exists, the term representing the polarization of the atom, now not by an outer electron, but by one inside it. Since the electron is so much closer the atom, it might seem that the $1/r^4$ term would make the effect very large; but it is easy to see, directly from (14), that after a variable electron penetrates a shell, the polarization energy of this shell does not increase much more when the electron approaches the nucleus. It is possible to estimate the size of the energy actually present in such a case, by approximating to the polarizibility of the various shells; and it is found that the total correction for this effect, for the inner electrons, is of the same order of magnitude as the corrections found in section 3; not only that, but they are of the opposite sign, making a decrease in ionization potential (on account of the fact that the summation in (13), which is itself negative, has a negative sign). Thus it seems actually possible that the two effects, the first order and second order corrections, partly cancel, and that Hartree's excellent agreement in the x-ray terms arises in this way. Whether this is true or not, we see that none of the corrections to Hartree's terms are really much larger than the order of magnitude of his discrepancies from experiment, so that his good agreement with observations is justified.

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May 31, 1928.

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[5] I. Waller, Zeits. f. Phys., 38, 635 (1926).