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The Self-Consistent Field Equations in an Atom

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The Thomas-Fermi equations for the potential in an atom are obtained from the Fock self-consistent field method, together with all corrections of order $Z^{-2/3}$, where Z is the atomic number of the element. It is shown that the correction put forward earlier by Weizsäcker was too large by a factor of 9. The exchange correction found by Dirac is in principle correct only if it is small in comparison with the main term in the potential.

1. THE EQUATION FOR THE DENSITY MATRIX

As is well known, the best method for finding the terms of the many-electron atom is that due to V. A. Fock. Fock's method is based on the fact that the integral $\int \Psi^* H \Psi dq$ is stationary for all eigenvalues of the Hamiltonian H of the atom. In particular, this integral has an absolute minimum for the ground state of the atom (q denotes the set of all space and spin coordinates of the atom). The wave function is subject to the condition

$$\int |\Psi|^2 dq = 1. \tag{1}$$

In the Fock method the wave equation is chosen in the form of a symmetrized product of the wave functions of the individual electrons $\psi_i(q)$:

$$\Psi = (Z!)^{-1/2} \sum_P (-)^P \cdot \prod_i \psi_i(Pq) \tag{2}$$

(P denotes a permutation of the variables of the individual electrons).

The wave functions $\psi_i(q_i)$ can always be regarded as mutually orthogonal and normalized, since they can be orthogonalized by a method of linear substitution. If the function ψ is chosen in the form (2), then it is possible, without further limitation of generality, to introduce, as an additional condition on the wave function,

$$\int \psi_i^*(q)\psi_k(q)dq = \delta_{ik} \tag{3}$$

in place of the earlier requirement (1).

Before varying the energy integral, we put it in a special form, making use of the fact that the Hamiltonian contains only terms that refer to the individual electrons and to their pairwise interaction,

$$H = \sum_i U(q_i) + \frac{1}{2}\sum_{i,\,k\neq i} V(q_i, q_k), \tag{4}$$

where the function V is symmetric relative to both variables entering into it. In the atom, U is the sum of the kinetic and potential energies of the electron in the field of the nucleus, V is the energy of electrostatic interaction of the electrons. Substituting (2) and (4) in the expression $\int \Psi^* H \Psi\, dq$, and making use of Eq. (3), we get

$$\int \Psi^* H \Psi dq = \sum_i \int \psi_i^* U \psi_i dq + \sum_{i,\,k<i} \iint \psi_i^*(q')\psi_k^*(q) V(q,q')[\psi_i(q')\psi_k(q) - \psi_i(q)\psi_k(q')]dqdq'. \tag{5}$$

Here q on the left refers to the entire atom, while on the right it refers to the individual electron. The variation of Eq. (5) is given by

$$\begin{aligned}\int \delta\Psi^* H \Psi dq &= \sum_i \int \delta\psi_i^*(q)dq\Big\{U\psi_i(q) + \sum_{k<i}\int \psi_k^*(q')V(q,q')[\psi_i(q)\psi_k(q') - \psi_i(q')\psi_k(q)]dq'\Big\} \\ &\equiv \sum_i \int \delta\psi_i^*(q)dq\Big[U\psi_i(q) + B(q)\psi_i(q) - \sum_k B_{ik}(q)\psi_k(q)\Big],\end{aligned} \tag{6}$$

where the following abbreviating notation is used:

$$B_{ik}(q) \equiv \int \psi_k^*(q')V(q,q')\psi_i(q')dq', \qquad B(q) \equiv \sum_k B_{kk}(q). \tag{7}$$

Multiplying the additional condition (3) by the variation parameter a_{ik} and adding the variation of Eq. (3) to the variation of the energy integral, we get a system of equations for the desired wave functions ψ_i:

$$U(q)\psi_i(q) + B(q)\psi_i(q) - \sum_k B_{ik}(q)\psi_k(q) + \sum_k a_{ik}\psi_k(q) = 0. \tag{8}$$

It is essential that the term in which $i = k$ is not excluded.

It is easy to express the parameters a_{ik} in terms of integrals of U, B and B_{ik}, making use of the condition (3). That is,

$$a_{ik} = \int \psi_k^* U \psi_i dq + \int \psi_k^* B \psi_i dq - \sum_l \int \psi_k^* B_{il} \psi_l dq. \tag{9}$$

Making use of the definitions, it can be shown that the matrix a_{ik} is Hermitian: $a_{ik} = a_{ki}^*$.

Equations (8) can be rewritten in very compact form if we introduce the density matrix $\rho(q, q')$, which is defined in the following form[1]:

$$\rho(q, q') = \sum_i \psi_i(q)\psi_i^*(q'). \tag{10}$$

Here the wave functions $\psi_i(q)$ are excluded from the equations.

In order to arrive at the density matrix $\rho(q, q')$, we write down, along with Eq. (8), the equation for the complex conjugate function $\psi_i^*(q')$:

$$U^*(q')\psi_i^*(q') + B^*(q')\psi_k^*(q') - \sum_k B_{ik}^*(q')\psi_k^*(q') + \sum_k a_{ik}^*\psi_k^*(q') = 0. \tag{8*}$$

We now multiply Eq. (8) by $\psi_i^*(q')$ and Eq. (10) by $\psi_i(q)$, sum over i and subtract (8*) from (8). Terms containing a_{ik} and a_{ik}^* vanish in this case since

$$\sum_k a_{ik}\psi_k(q)\psi_i^*(q') - \sum_k a_{ik}^*\psi_k^*(q')\psi_i(q) = \sum_k a_{ik}\psi_k(q)\psi_i^*(q') - \sum_k a_{ki}^*\psi_i^*(q')\psi_k(q) = 0$$

by virtue of the Hermitian character of the matrix a_{ik}.

The terms in U and B involve the matrix $\rho(q,q')$. The expression containing B_{ik} can also be described with the aid of ρ. Actually, we get in Eq. (8)

$$\sum_k B_{ik}(q)\psi_k(q)\psi_i^*(q') = \sum_{ik}\int \psi_k^*(q'')V(q, q'')\psi_i(q'')dq''\psi_k(q)\psi_i^*(q') = \int V(q, q'')\rho(q, q'')dq''\rho(q'', q') \tag{11}$$

and in the analogous transformation of (8*),

$$\sum_{i,k}\psi_i(q)\psi_k^*(q')\int \psi_k(q'')V(q', q'')\psi_i^*(q'')dq'' = \int \rho(q, q'')dq''\rho(q'', q')V(q'', q'). \tag{11*}$$

If we introduce the operator

$$A_{qq''} \equiv \rho(q, q'')V(q, q''), \tag{12}$$

then Eq. (11) is rewritten as

$$\sum_{i,k} B_{ik}(q)\psi_k(q)\psi_i^*(q') = \int A_{qq''}dq''\rho(q'', q'), \tag{13}$$

while (11*) has the form

$$\sum_{i,k} B_{ik}^*(q')\psi_i(q)\psi_k^*(q') = \int \rho(q, q'')dq''A_{q''q'}, \tag{13*}$$

where use is made of the obvious symmetry of the interaction operator V:

$$V(q', q'') = V(q'', q').$$

Terms which derive from B can also be expressed in terms of the density matrix:

$$B\sum_i \psi_i(q)\psi_i^*(q') = \left(\int \rho(q'', q'')V(q, q'')dq''\right)\rho(q, q').$$

Introducing the operators

$$B_{qq''} = \delta(q - q'')\int \rho(q''', q''')V(q, q''')dq'''; \tag{14}$$

$$U_{qq''} = \delta(q - q'')U,$$

we get an equation for the density matrix in the form

$$\int dq''[(U_{qq''} + B_{qq''} - A_{qq''})\rho(q'', q') - \rho(q, q'')(U_{q''q'} + B_{q''q'} - A_{q''q'})] = 0. \tag{15}$$

This latter equation represents the Poisson bracket between the operators

$$H_{qq''} \equiv U_{qq''} + B_{qq''} - A_{qq''} \qquad (16)$$

and the density matrix:

$$H\rho - \rho H = 0. \qquad (17)$$

In other words, H is the effective Hamiltonian operator. In this operator, the term B corresponds to the self-consistent field which is associated with the electron density distribution , while the term A is the so-called exchange energy operator.

It is evident in these equations, therefore, that the antisymmetrized wave function Ψ [see Eq. (2)] was taken, from the very beginning, in accordance with the Pauli principle for the electron system. Equation (17) differs somewhat from the usual equations of quantum mechanics by the fact that the Hamiltonian operator H itself depends on the density ρ.

We now eliminate the spin variable, making use of the fact that the initial Hamiltonian (4) did not depend on the spins. The density matrix is diagonal relative to the spin variable since, in the sum over i, one can substitute the entire system of spin functions. Therefore, the exchange operator is also diagonalized in the spin variables. The operator $B_{qq''}$ contains, in comparison with $A_{qq''}$, an additional integration over q''', which also includes summation over the spins. This gives an additional factor of 2 in $B_{qq''}$ in comparison with $A_{qq''}$ (Dirac[2] first wrote the A with the extra factor of 2, which was latter corrected by Jensen[3]).

Thus we need no longer describe all the quantities by the total set of variables q but only by the space variable r, because all the expressions are diagonal relative to the spin variable:

$$A_{\mathbf{rr}''} = \frac{e^2}{|\mathbf{r}-\mathbf{r}''|}\,\rho(\mathbf{r}-\mathbf{r}''), \qquad (18)$$

$$B_{\mathbf{rr}''} = 2\delta(\mathbf{r}-\mathbf{r}'')\,e^2\int \frac{\rho(\mathbf{r}''',\mathbf{r}''')}{|\mathbf{r}-\mathbf{r}'''|}\,d\mathbf{r}'''. \qquad (19)$$

2. TRANSITION TO THE QUASICLASSICAL APPROXIMATION

Dirac[2] has pointed out that, by way of a transition to the quasiclassical approximation one can obtain the well-known Thomas-Fermi potential distribution in the atom from Eq. (17). In this case the Dirac exchange operator gave a term in the equation for the potential which was less than the other terms in the ratio $Z^{-2/3}$, where Z is the atomic number of the element. This exchange term is treated by many authors[3-5] not as a small correction relative to the equation itself, but on a level with all the other terms of the equation. We shall show that it is not possible to treat it in this fashion.

The limiting transition to the quasiclassical approximation in the work of Dirac consisted of the fact that the quantum Poisson bracket for the density matrix $\rho(r, r')$ was simply the substitution of the classical Poisson bracket for the Fourier coefficient of the density matrix. Meanwhile it appears that if we do not restrict ourselves to this approximation, but find the term of next order of smallness, a correction appears that is proportional to $Z^{-2/3}$, and also an "exchange term", omitted by Dirac in the equation. As will be shown below, this additional term, proportional to $Z^{-2/3}$, enters with a numerical coefficient that is small in comparison with the exchange term. But in each case it is appropriate to solve the equation with the "exchange term" accurately. Each term proportional to $Z^{-2/3}$ must be considered only as a correction of the corresponding order to the usual Thomas-Fermi equation.

It should be pointed out that Weizsäcker[6] attempted to improve the Thomas-Fermi equation by introducing other correction terms in it of order $Z^{-2/3}$ in addition to the exchange terms. But the method used by Weizsäcker is not convincing. In fact, it is shown that the correct expression, corresponding to corrections following from Eqs. (17), is less than Weizsäcker's by a factor of 9. From this it follows that the exchange correction is predominant in comparison with the other terms of order $Z^{-2/3}$, so that in the numerical expression, the corrections, thus far produced, of the usual Thomas-Fermi equation must be considered valid. But this conclusion is correct only so long as the exchange correction term is small in comparison with the fundamental. The latter condition is not always fulfilled: for example, at great distances from the nucleus the correction already surpasses the fundamental term.

We now perform the transition to the quasiclassical approximation. For this purpose we first represent the matrix elements $\rho(x, x')$ and $H(x, x')$ in the form of expansions in Fourier integrals in the difference of the arguments $x - x'$:

$$\rho(x, x') = \int \rho\left(p, \frac{x+x'}{2}\right) e^{ip(x-x')}dp, \tag{20}$$

$$H(x, x') = \int H\left(p, \frac{x+x'}{2}\right) e^{ip(x-x')}dp, \tag{21}$$

where all the arguments are vectors, so that x stands for **r**, etc. We substitute these expansions in the Poisson bracket:

$$\begin{aligned} H\rho - \rho H &= \int dx'' \left[H(x, x'')\rho(x'', x') - \rho(x, x'')H(x'', x')\right] \\ &= \iiint dx'' dp dp_1 \left[H\left(p_1, \frac{x+x''}{2}\right)\rho\left(p, \frac{x''+x'}{2}\right) - \rho\left(p_1, \frac{x+x''}{2}\right)H\left(p, \frac{x''+x'}{2}\right)\right] \\ &\quad \times \exp\{ip_1(x-x'') + ip(x''-x')\}. \end{aligned} \tag{22}$$

In the first component of this integral we make the following change in variables: $x'' = x + \zeta + \Delta$, $x' = x - \Delta$, $p_1 = p - q$. In the second component we exchange the designations p and p_1 and set $x'' = x + \zeta$, $x' = x - \Delta$, $p_1 = p + q$. After these changes, the Poisson bracket takes on the form

$$\begin{aligned} &\int dp e^{ip\Delta} \iint dq d\zeta e^{iq(\zeta+\Delta)} \rho\left(p, x + \frac{\zeta}{2}\right) \\ &\times \left[H\left(p - q, x + \frac{\zeta}{2} + \frac{\Delta}{2}\right) - H\left(p + q, x + \frac{\zeta}{2} - \frac{\Delta}{2}\right)\right] = 0. \end{aligned} \tag{23}$$

In the transition to the quasiclassical approximation we must consider the region of motion and the momentum in the integral (23) to be large. In other words, we have a large momentum p and coordinate ζ because ζ enters only in the combination $x + \zeta/2$ (we set $\hbar = 1$, and we also employ $e = 1$ and $m = 1$ in what follows, i.e., we shall use atomic units). But if the coordinate ζ is large, then the momentun difference q is correspondingly small, since the product $q\zeta$ appears in the exponent. The difference in coordinates Δ must also be regarded as small because it enters into the exponent multiplied by a large momentum p. Consequently, the difference of Hamiltonians under the integral sign can be expanded in a power series in q and Δ. We limit ourselves to the third term of the expansion. It is evident that the zeroth and second terms vanish, leaving only the first and the third. We shall first write the formulas without tensor notation, which is easily inserted in the final result. The expansion is as follows[7]:

$$\begin{aligned} &H\left(p - q, x + \frac{\zeta}{2} + \frac{\Delta}{2}\right) - H\left(p + q, x + \frac{\zeta}{2} - \frac{\Delta}{2}\right) = -2q\frac{\partial H}{\partial p} + \Delta\frac{\partial H}{\partial x} \\ &+ \frac{1}{3}\left[-q^3\frac{\partial^3 H}{\partial p^3} + 3q^2\frac{\Delta}{2}\frac{\partial^3 H}{\partial p^2 \partial x} - 3q\left(\frac{\Delta}{2}\right)^2\frac{\partial^3 H}{\partial p \partial x^2} + \left(\frac{\Delta}{2}\right)^3\frac{\partial^3 H}{\partial q^3}\right]. \end{aligned} \tag{24}$$

It is easy to get rid of the factors q and Δ by integration by parts, replacing $qe^{i\zeta q}$ and $\Delta e^{ip\Delta}$ by $-i(\partial/\partial\zeta)e^{iq\zeta}$ and $-i(\partial/\partial p)e^{ip\Delta}$. Equating the Fourier coefficient to zero, we obtain (upon integration by parts) the following expression, written in tensor form:

$$\begin{aligned} &\frac{\partial H}{\partial p_i}\frac{\partial \rho}{\partial x_i} - \frac{\partial H}{\partial x_i}\frac{\partial \rho}{\partial p_i} \\ &+ \frac{1}{24}\left(\frac{\partial^3 H}{\partial x_i \partial x_k \partial x_l}\frac{\partial^3 \rho}{\partial p_i \partial p_k \partial p_l} - 3\frac{\partial^3 H}{\partial x_i \partial x_k \partial p_l}\frac{\partial^3 \rho}{\partial p_i \partial p_k \partial x_l} \right. \\ &\quad + 3\frac{\partial^3 H}{\partial x_i \partial p_k \partial p_l}\frac{\partial^3 \rho}{\partial p_i \partial x_k \partial x_l} \\ &\quad \left. - \frac{\partial^3 H}{\partial p_i \partial p_k \partial p_l}\frac{\partial^3 \rho}{\partial x_i \partial x_k \partial x_l}\right) = 0. \end{aligned} \tag{25}$$

The first two terms in this equation represent the classical Poisson bracket of the Fourier coefficient of the density ρ, while the remaining terms give the quantum correction to the Poisson bracket. The study of this correction is a fundamental purpose of the present research.

3. INVESTIGATION OF THE SELF-CONSISTENT FIELD IN THE QUASICLASSICAL APPROXIMATION

In the simplest approximation, the Fourier coefficient of the density matrix has the form

$$\rho_0 = \rho_0(p - p_0(r)) = \begin{cases} 1, & p \leqslant p_0(r), \\ 0, & p > p_0(r) \end{cases} \tag{26}$$

In other words, all states in which the momentum is less than a certain limiting momentum $p_0(r)$ are occupied, while the states for which $p > p_0(r)$ are unoccupied. With the help of ρ_0 one can determine the Fourier coefficients of the various terms of the Hamiltonian (we are dealing here with the Fourier coefficients relative to the difference in arguments $x - x'$, so that the coordinate dependence enters into them through half sums of the arguments).

The self-consistent potential B [see Eq. (19)] gives the following expression for the Fourier coefficient:

$$B = \frac{2}{(2\pi)^3} \int \frac{d\mathbf{r}''}{\mathbf{r} - \mathbf{r}''} \int \rho_0 (p - p_0)\, d\mathbf{p} \tag{27}$$

$$= \frac{1}{3\pi^2} \int \frac{d\mathbf{r}''}{\mathbf{r} - \mathbf{r}''}\, p_0^3 (r').$$

Here $(2\pi)^{-3}$ is the Fourier coefficient of the δ-function $\delta(r - r')$, and the inner integral is equal to $4\pi p_0^3/3$ according to the definition of the function ρ_0. The spin states lack the factor 2 entering into B.

The exchange operator is transformed as follows:

$$A_p = \int \frac{e^{i\mathbf{p}(\mathbf{r}-\mathbf{r}')}}{|\mathbf{r} - \mathbf{r}'|} \frac{d\mathbf{r}'}{(2\pi)^3} \int d\mathbf{p}' \rho_0 (p' - p_0)\, e^{-i\mathbf{p}'(\mathbf{r}-\mathbf{r}')} \tag{28}$$

$$= \frac{1}{(2\pi)^3} \int d\mathbf{p}' \rho_0 (p' - p_0) \int \frac{d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|}\, e^{i(\mathbf{p}-\mathbf{p}',\, \mathbf{r}-\mathbf{r}')}.$$

As is known, the inner integral is equal to $4\pi|\mathbf{p} - \mathbf{p}'|^{-2}$. Subsequent integration over $d\mathbf{p}'$ is elementary and yields

$$A_p = \frac{1}{2\pi}\left(\frac{p_0^2 - p^2}{p} \ln \frac{p_0 + p}{p_0 - p} + 2p_0\right). \tag{29}$$

In comparison with B, A_p has the smaller order of magnitude, which will be shown later after transition to Thomas-Fermi units. Therefore, in this approximation, the Hamiltonian is

$$H_0 = \frac{p^2}{2} - \frac{Z}{r} + B \tag{30}$$

$$= \frac{p^2}{2} - \frac{Z}{r} + \frac{1}{3\pi^2} \int \frac{d\mathbf{r}''}{|\mathbf{r} - \mathbf{r}''|}\, p_0^3 (r'').$$

In accordance with Eq. (25), the function ρ_0 in this approximation should cause the vanishing of the classical Poisson bracket:

$$\frac{\partial H_0}{\partial p_i} \frac{\partial \rho_0}{\partial x_i} - \frac{\partial H_0}{\partial x_i} \frac{\partial \rho_0}{\partial p_i} = 0.$$

From the expressions for H_0 and ρ_0 we get

$$\frac{\partial H_0}{\partial p_i} = p_i; \quad \frac{\partial H_0}{\partial x_i} = \frac{x_i}{r} \frac{d}{dr}\left(\frac{1}{3\pi^2} \int \frac{d\mathbf{r}''}{|\mathbf{r} - \mathbf{r}''|}\, p_0^3 (r'') - \frac{Z}{r}\right);$$

$$\frac{\partial \rho_0}{\partial p_i} = \frac{p_i}{p} \rho_0'; \quad \frac{\partial \rho_0}{\partial x_i} = -\frac{x_i}{r} \frac{dp_0}{dr} \rho_0',$$

so that the Poisson bracket has the following form:

$$\frac{(\mathbf{p},\, \mathbf{r})}{pr} \rho_0' \left[p \frac{dp_0}{dr} + \frac{d}{dr}\left(\frac{1}{3\pi^2} \int \frac{d\mathbf{r}''}{|\mathbf{r} - \mathbf{r}''|}\, p_0^3 (r'') - \frac{Z}{r}\right)\right] = 0. \tag{31}$$

The function ρ_0' differs from zero only for $p = p_0$. Consequently, for this value of p, the expression in the square brackets vanishes:

$$p_0 \frac{dp_0}{dr} + \frac{d}{dr}\left(\frac{1}{3\pi^2} \int \frac{p_0^3 (r'')}{|\mathbf{r} - \mathbf{r}''|} d\mathbf{r}'' - \frac{Z}{r}\right) = 0. \tag{32}$$

This equation is directly integrated; from the condition at inifnity, the integration constant must be set equal to zero:

$$\frac{p_0^2}{2} + \frac{1}{3\pi^2} \int \frac{p_0^3}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' - \frac{Z}{r} = 0. \tag{33}$$

The expression on the left side of this equation is the energy computed for the limiting value of the momentum p_0. As we see, it is equal to zero. Therefore, the function ρ_0 can be written in the following form, which is very useful for further calculations:

$$\rho_0 = \rho_0 (E_0) = \begin{cases} 1, & E_0 \leqslant 0, \\ 0, & E_0 > 0. \end{cases} \tag{34}$$

It is easy to transform Eq. (33) to its usual form. Actually, setting

$$\varphi_0 = -\frac{1}{3\pi^2} \int \frac{p_0^3 (r'')}{|\mathbf{r} - \mathbf{r}''|} d\mathbf{r}'' + \frac{Z}{r}, \tag{35}$$

we see that

$$\Delta\varphi_0 = 4\pi p_0^3 / 3\pi^2. \tag{36}$$

But, according to Eq. (33), $p_0^2 = 2\varphi_0$, so that the potential satisfies the Thomas-Fermi equation:

$$\Delta\varphi_0 = (2^{7/2}/3\pi)\, \varphi_0^{3/2}. \tag{37}$$

We now proceed to the equations of first approximation. For this case we write the density matrix and the potential in the form of expansions

$$\rho = \rho_0 + \rho_1 = \rho_0 (E_0) + \rho_1, \qquad \varphi = \varphi_0 + \varphi_1. \tag{38}$$

Here φ_0 is by definition the sum of the potential of the nucleus and the self-consistent field of zeroth approximation. The function $\rho_0(E_0)$ is determined by Eq. (34). We shall substitute the correction terms φ_1 and ρ_1 only in the Poisson bracket of zero approximation; in all the remaining terms of Eq. (25) and in the exchange operator, we shall use the zeroth approximation.

If we substitute the Hamiltonian H_0 according to Eq. (30) in the part of Eq. (25) which contains third derivatives, then it is easy to become convinced that there remains only the first term in the square brackets. Actually, all the mixed derivatives of H_0 with respect to x_i and p_i are equal to zero; moreover, H_0 has only a derivative with respect to p_i no higher than second order. Calculating the derivatives, we have

$$\frac{\partial^3 H_0}{\partial x_i \partial x_k \partial x_l} = -x_i x_k x_l \frac{d}{dr}\frac{1}{r}\frac{d}{dr}\frac{1}{r}\frac{d\varphi_0}{dr} - (\delta_{ik}x_l + \delta_{il}x_k + \delta_{kl}x_i)\frac{d}{dr}\frac{1}{r}\frac{d\varphi_0}{dr}, \tag{39}$$

$$\frac{\partial^3 \rho_0}{\partial p_i \partial p_k \partial p_l} = (\delta_{ik}p_l + \delta_{kl}p_i + \delta_{il}p_k)\frac{d^2\rho_0}{dE_0^2} + p_i p_k p_l \frac{d^3\rho_0}{dE_0^3}.$$

It is useful to split off the factor $(\mathbf{p}, \mathbf{r})$ and, in the remaining part, to change the independent variables entering into the problem: instead of p, r and $(\mathbf{p}\ \mathbf{r})$ we introduce the variables

$$E_0 = {}^1/_2\, p^2 - \varphi_0, \qquad M^2 = [\mathbf{r}, \mathbf{p}]^2 = p^2r^2 - (\mathbf{p}\ \mathbf{r})^2 \tag{40}$$

and r. In the new variables, the third derivatives take the form

$$\frac{\partial^3 H_0}{\partial x_i \partial x_k \partial x_l}\frac{\partial^3 \rho_0}{\partial p_i \partial p_k \partial p_l} = -\frac{(\mathbf{pr})}{r}\frac{\partial}{\partial r}\left\{\frac{d^3\rho_0}{dE_0^3}\left[2E_0\frac{d^2\varphi_0}{dr^2} + 2\left(\varphi_0\frac{d^2\varphi_0}{dr^2} - \frac{1}{2}\left(\frac{d\varphi_0}{dr}\right)^2\right) - M^2\frac{1}{r}\frac{d}{dr}\frac{1}{r}\frac{d\varphi_0}{dr}\right] + 3\frac{d^2\rho_0}{dE_0^2}\left(\frac{d^2\varphi_0}{dr^2} + \frac{2}{r}\frac{d\varphi_0}{dr}\right)\right\} \equiv -\frac{(\mathbf{pr})}{r}\frac{\partial I}{\partial r}, \tag{41}$$

where the meaning of I is obvious.

It follows that the exchange energy A [see Eq. (29)] is substituted only in the Poisson bracket of zeroth approximation:

$$\frac{\partial A}{\partial p_i}\frac{\partial \rho_0}{\partial x_i} - \frac{\partial A}{\partial x_i}\frac{\partial \rho_0}{\partial p_i} = -\frac{(\mathbf{pr})}{pr}\frac{dp_0}{dr}\left(\frac{\partial A}{\partial p} + \frac{\partial A}{\partial p_0}\right)_{p=p_0}\frac{\partial \rho_0}{\partial p} = -\frac{(\mathbf{pr})}{r}\frac{1}{\pi}\frac{dp_0}{dr}\frac{d\rho_0}{dE_0} = -\frac{(\mathbf{pr})}{r}\frac{1}{\pi}\frac{d}{dr}\sqrt{2\varphi_0}\,\frac{d\rho_0}{dE_0}. \tag{42}$$

We shall assume that the correction to the density is given in terms of E_0, M^2 and r. As is well known, the classical Poisson bracket of any integral of motion or of any function of integrals of motion reduces to zero. Therefore, upon substitution of ρ_1 into the Poisson bracket of zeroth approximation, only that term fails to vanish which has a derivative with respect to r. This term is equal to

$$\frac{\partial H_0}{\partial p_i}\frac{\partial \rho_1}{\partial x_i} = \frac{(\mathbf{pr})}{r}\frac{\partial \rho_1}{\partial r}. \tag{43}$$

The correction to the potential φ_1 depends, by definition, only on r. Therefore, it yields the term

$$\frac{(\mathbf{rp})}{r}\frac{d\varphi_1}{dr}\frac{\partial \rho_0}{\partial E_0}. \tag{44}$$

All the expressions entering into Eq. (25), after contraction to $\mathbf{p}\ \mathbf{r}/r$, have the form of derivatives with respect to r of the different expressions:

$$\frac{\partial \rho_1}{\partial r} + \frac{d\varphi_1}{dr}\frac{d\rho_0}{dE_0} = -\frac{1}{\pi}\frac{d}{dr}\left(\sqrt{2\varphi_0}\right)\frac{d\rho_0}{dE_0} + \frac{1}{24}\frac{\partial I}{\partial r}. \tag{45}$$

Since ρ_0 does not depend on r, this equation can be integrated immediately, setting the arbitrary additive function of E_0 and M^2 equal to zero because of the condition at infinity. This integration with respect to r is possible because of the choice of the independent variables E_0, M^2 and r. Thus,

$$\rho_1 + \varphi_1\frac{d\rho_0}{dE_0} = -\frac{\sqrt{2\varphi_0}}{\pi}\frac{d\rho_0}{dE_0} + \frac{1}{24}\frac{d^3\rho_0}{dE_0^3}\left[2E_0\frac{d^2\varphi_0}{dr^2} + 2\varphi_0\frac{d^2\varphi_0}{dr^2} - \left(\frac{d\varphi_0}{dr}\right)^2 - M^2\frac{1}{r}\frac{d}{dr}\frac{1}{r}\frac{d\varphi_0}{dr}\right] + \frac{1}{8}\frac{d^2\rho_0}{dE_0^2}\left(\frac{d^2\varphi_0}{dr^2} + \frac{2}{r}\frac{d\varphi_0}{dr}\right). \tag{46}$$

The other equation, which connects φ_1 and ρ_1, is the Poisson equation for the potential:

$$\Delta\varphi_1 = \frac{1}{\pi^2}\int \rho_1 d\mathbf{p}. \tag{47}$$

Although the corrections to ρ_0 are large for $E_0=0$, they enter integrally into the potential, and therefore, the resultant addition to the potential is small.

It is useful to carry out integration by parts in Eq. (47). In this case the terms which do not depend on angle acquire a factor of 4π, while the terms proportional to M^2 gain the factor $4\pi(2/3) \times r^2p^2$ because M^2 is proportional to the square of the sine of the angle between **r** and **p**. With the help of Eq. (40), the expression in the square brackets in Eq. (46), after integration over the angular variables, has the form

$$\frac{8\pi}{3}(E_0+\varphi_0)\left(\frac{d^2\varphi_0}{dr^2}+\frac{2}{r}\frac{d\varphi_0}{dr}\right)-4\pi\left(\frac{d\varphi_0}{dr}\right)^2.$$

It is easy to carry out integration over p if we make use of the definition of ρ_0 in Eq. (34).

Actually, we write $\sqrt{2(E_0+\varphi_0)}\,dE_0$ in place of p^2dp and make use of the fact that $d\rho_0/dE_0 = -\delta(E_0)$. The integrals of the second and third derivatives of ρ_0 are obtained with the aid of the well-known formula

$$\int f(E_0)\frac{d^{n+1}}{dE_0^{n+1}}\rho_0(E_0)\,dE_0 = (-1)^n\left(\frac{d^n}{dE_0^n}f(E_0)\right)_{E_0=0}. \tag{48}$$

Substituting ρ_1 from (46) in Eq. (47), we get

$$\Delta\varphi_1-\frac{4}{\pi}\sqrt{2\varphi_0}\,\varphi_1=\frac{8}{\pi^2}\varphi_0+\frac{1}{12\pi\sqrt{2\varphi_0}}\left[4\Delta\varphi_0-\frac{1}{\varphi_0}\left(\frac{d\varphi_0}{dr}\right)^2\right]. \tag{49}$$

This is also the equation for the correction to the potential. Here the first component on the right takes exchange into account, and the second follows from the addition to the classical Poisson bracket. If we substitute the expression $\Delta\varphi_0$ in the right side of Eq. (49), then we get the value $(8/9\pi^2)\varphi_0$, which is nine times smaller than the exchange term. In numerical integration it is shown that the ratio of both corrections to the potential is of the same order. We now transform to the dimensionless Thomas-Fermi variables, which are based on m, e and h:

$$r=\frac{(3\pi)^{2/3}}{2^{7/3}}\frac{x}{Z^{1/3}}\frac{\hbar^2}{me^2}; \tag{50}$$

$$\varphi_0=\frac{Ze^2}{r}\chi;\quad \varphi_1=\frac{Z^{2/3}}{(6\pi)^{4/3}}\frac{y}{x}\frac{me^4}{h^2}.$$

Then the dimensionless potential in zero approximation satisfies the well-known equation

$$d^2\chi/dx^2=\chi^{3/2}x^{-1/2}, \tag{51}$$

and the dimensionless correction y is found from the linear inhomogeneous equation

$$\frac{d^2y}{dx^2}-\frac{3}{2}\sqrt{\frac{\chi}{x}}\,y=\left[40\chi-\sqrt{\frac{x^5}{\chi}}\left(\frac{d}{dx}\frac{\chi}{x}\right)^2\right]. \tag{52}$$

We note that the potential in zeroth approximation is proportional to $Z^{4/3}$, and in first approximation, it is proportional to $Z^{2/3}$. Consequently, the relative order of the correction is $Z^{-2/3}$ (the numerical coefficient $40/(6\pi)^{4/3}$ differs but slightly from unity).

4. INTEGRATION OF THE EQUATION FOR THE CORRECTION TO THE POTENTIAL

The boundary conditions for Eq. (51) are $\chi(0) = 1$, $\chi(\infty) = 0$, because the potential is purely Coulombic in the immediate vicinity of the nucleus, but at large distances from the nucleus, the potential falls more rapidly than Coulombic (due to electron screening). The condition at infinity for y is evidently $y(\infty) = 0$, and at zero, $y(0) = 0$, inasmuch as the value of the potential in the neighborhood of $x = 0$ is described by the function $\chi(x)$.

On the other hand, Eq. (52) is invalid both in the immediate neighborhood of the nucleus and also at large distances from the nucleus. One can raise the question: is it valid to integrate Eq. (52) with the boundary conditions $y(0) = y(\infty) = 0$ if these conditions are applied outside the region of applicability of the equation*?

Let us first consider the solution for small values of x, of the order of the radius of the K-shell. In the region of the K-shell, the quasiclassical approximation assumed in the work is known to be inapplicable. But the charge included in this shell is of the order of unity, so that its effect on the potential of the self-consistent field in the atom is of order $1/Z$ relative to the total potential.

Further, the accuracy assumed by us is $Z^{-2/3}$ so that a correction of the order of $1/Z$ ought to be neglected. Also, it is evident that $Z^{-2/3}$ is the highest approximation compatible with the classical approach to the problem.

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* This question was raised and answered for us by L. D. Landau.

Therefore, one does not integrate the "exact" equation, in which terms proportional to $Z^{-2/3}$ are considered on a par with the main term (as, for example, Jensen does[3]). It suffices to integrate the equation for the first approximation (52) only *once*, as also the main equation (51), and for different atoms, to consider the dependence of the potential on Z only according to Eq. (50).

We can estimate [directly, by Eq. (52)] the order of magnitude of those distances from the nucleus (on the side of small x), where the correction is comparable with the zeroth approximation. A more suitable estimate can be obtained if we compare not the potentials but the fields which are produced from the given density distribution of electronic charge. We shall also make this comparison. The function near the origin of the coordinates has the form $\chi = 1 - 1.589x + 4/3\,x^{3/2}$, as is well known. The number one appearing in the first part corresponds to the potential of the nucleus, and is not of interest to us in the computation of the field. The field due to the electrons, in zeroth approximation, is

$$\mathcal{E}_0 = -Z^{4/3}\frac{d}{dx}\frac{\chi-1}{x} = -\frac{2}{3}Z^{4/3}x^{-1/2}.$$

The expression y for very small x is easily obtained by setting $\chi = 1$ on the right-hand side of Eq. (52), which gives $y = 4\sqrt{x}$ or, in accord with Eq. (50),

$$\mathcal{E}_1 = \frac{4}{(6\pi)^{4/3}}Z^{2/3}\frac{d}{dx}\frac{1}{\sqrt{x}} = 0.04Z^{2/3}x^{-3/2}.$$

Comparing $\mathcal{E}_0$ and $\mathcal{E}_1$, we see that $\mathcal{E}_1$ is of order of $\mathcal{E}_0$ when $x_{\min} \sim 0.06\,Z^{-2/3}$, $r_{\min} \sim 0.07h^2/Zme^2$, i.e., $\sim$ 0.07 of the radius of the *K*-shell.

In this way, extrapolating the boundary condition for y to the point $x = 0$, we commit an error whose relative order is $1/Z$, with a small numerical coefficient.

Now let us consider the applicability of the boundary condition $y = 0$ for large x. As is well known, the asymptotic form of the solution of $\chi(x)$ for large x is $144/x^3$. In practice, however, this form of the solution is not obtained. It is therefore appropriate to assume that the function $\chi(x)$ (for large x) is $A^2(x)x^{-3}$, where $A(x)$ is a slowly changing function of x. Correspondingly, we determine the asymptotic solution of the homogeneous equation

$$y_0'' - {}^3/_2\,y_0\sqrt{\chi/x} = 0.$$

We shall seek y_0 in the form $y_0 = x^{\lambda(x)}$, neglecting the derivatives $d\lambda/dx$. Then,

$$\lambda_{1,2} = -{}^1/_2 \pm \sqrt{(3A/2) + {}^1/_4}.$$

One solution, y_{01}, vanishes at infinity as x^{λ_1}, and the other solution, y_{02}, goes to infinity as x^{λ_2}.

One can choose an arbitrary solution of the inhomogeneous equation (52) in the form of the quadrature of the right-hand side, with the help of the solutions y_{01} and y_{02}. But the right side is known to us, not for arbitrary values of x, but only for such x in which the correction is still small in comparison with the main solution. Let us assume that, beginning with each $x = x_0$ and larger, the function on the right side of Eq. (52) is some unknown $F(x)$. We shall show that the solution $y(x)$ for $x < x_1$ does not depend on this function $F(x)$ if $y(x_1)$ is sufficiently large that the solution vanishing at infinity is already small. This means that we can set $y(\infty) = 0$ without making any error.

We denote the known right side of Eq. (52) by $f(x)$. Then the solution for $x < x_1$ can be written in the following form:

$$y(x) = C_1 y_{01}(x) + C_2 y_{02}(x) + \int_0^x f(x')\left(y_{01}(x')\,y_{02}(x) - y_{01}(x)\,y_{02}(x')\right)dx', \tag{53}$$

if the solution y_{02} is connected with y_{01} by the well-known relation $y_{02} = y_{01}\int y_{01}^{-2}\,dx$. There exists a relation between the coefficients C_1 and C_2 that is determined from the boundary condition at zero. This dependence has the form $C_2 = \beta C_1$, where the coefficient β is independent of the values $x = x_1$ chosen, and is not connected with the function $F(x)$.

For large x the solution runs as

$$y(x) = C_3 y_{01}(x) + C_4 y_{02}(x) + \int_{x_1}^x F(x')\left(y_{01}(x')\,y_{02}(x) - y_{01}(x)\,y_{02}(x')\right)dx'. \tag{54}$$

In order that the solution remain finite at infinity, it is necessary to impose on C_3 the condition

$$C_3 = \int_{x_1}^{\infty} F(x)\, y_{02}(x)\, dx. \tag{55}$$

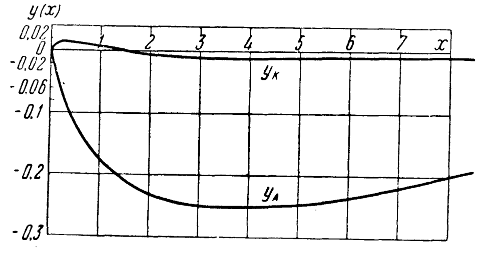
The solutions of Eqs. (53) and (54) must join smoothly for $x = x_1$, i.e., the functions and their derivatives must be equal. This yields

$$C_1 = \int_0^{x_1} f(x')\, y_{02}(x')\, dx' + \int_{x_1}^{\infty} F(x')\, y_{02}(x')\, dx' \tag{56}$$

But this also means that for large x_1 it is possible to set $x_1 = \infty$, if only to provide that the function $F(x)$ does not increase to infinity, which is quite natural. But then the solution of Eq. (52) for $x \leq x_1$ generally ceases to depend on the value of x_1 and on the unknown function $F(x)$. Consequently, we can assume that the condition $y(\infty) = 0$ applies in the region of applicability of Eq. (52).

Equation (52) has been integrated numerically by the method of Numerov[8]. In this method a new unknown function $y(x) - (a^2/12)y''$ is chosen in place of the unknown function $y(x)$. Here a is the interval in the numerical integration. The second derivative of the new unknown differs from the second difference by a quantity of sixth order relative to a. Thanks to this method of Numerov, it was possible to integrate equations numerically, solved relative to the second derivative, by choosing a large interval.

In order to satisfy the condition at infinity, we must proceed in the following fashion. We first determine by the method of numerical integration the solution of the homogeneous equation, which is equal to zero for $x = 0$; then, also by numerical integration, we find the similar solution of the inhomogeneous equation (52). The ratio of the two solutions tends toward a constant value for $x = 0$. Then, if we subtract from the solution of the inhomogeneous equation the solution of the homogeneous equation, multiplied by this constant ratio, we obtain a solution which satisfies both the boundary conditions.



For comparison with the calculations carried out by other authors, we have divided the right-hand side into two components: the purely "exchange" correction, equal to 36χ, and the remainder, the "quantum" part, which is found in the present work. The corresponding components are labeled y_A and y_K. The curves y_A and y_K are plotted separately on the graph. As a consequence of the large numerical coefficient, y_A dominates for all x; therefore, the results of Jensen are practically valid, but only so long as the exchange correction in them is small in comparison with the main term. The final condition of Jensen was not observed for large x.

As far as the quantum correction is concerned, it is shown to be 9 times smaller than predicted by Weizsäcker. We can therefore consider it as finally established that only the exchange correction is appreciable in the Thomas-Fermi potential.

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