

If  $r < a/\sqrt{2}$ , then instability may generally cause a redistribution of currents over the cross-section of the cylinder.

The dependence of  $n$ ,  $T$  and  $H$  upon  $r$  may similarly be obtained in other cases.

In conclusion the author wishes to express his profound gratitude to N. N. Bogoliubov for his assistance in this analysis.

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<sup>1</sup> M. Kruskal and M. Schwarzschild, Proc. Roy. Soc. (London) A223, 348 (1954).

<sup>2</sup> K. A. Brueckner and K. M. Watson, Phys. Rev. 102, 19 (1956).

<sup>3</sup> This is similar to the method used by Watson, Phys. Rev. 102, 12 (1956), to obtain the distribution function for a low density plasma.

<sup>4</sup> L. D. Landau, J. Exptl. Theoret. Phys. (U.S.S.R.) 16, 574 (1946)

<sup>5</sup> Equation (20) was obtained and analyzed by N. N. Bogoliubov.

<sup>6</sup> L. D. Landau and E. M. Lifshitz, *The Mechanics of Continuous Media*, Moscow, 1953.

<sup>7</sup> A Schlüter, Z. Naturforsch. 5a, 72 (1950).

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## Quantum Corrections to the Thomas–Fermi Equation

D. A. KIRZHITS

*P. N. Lebedev Physical Institute, Academy of Sciences, USSR*

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The operator form of the Hartree–Fock equation is considered. The Thomas–Fermi and the Thomas–Fermi–Dirac equations are obtained in the zeroth approximation in terms of  $\hbar$ . Quantum corrections were found by the operator method for the Thomas–Fermi equations of 2nd and 4th order in  $\hbar$ . The correction of 2nd order is compared with the Weizsacker correction and it is shown that the latter is 9 times larger than the quantum theory value. The resultant equations are applied to the computation of the total energy of the atom.

### 1. INTRODUCTION

THE Thomas–Fermi method<sup>1</sup> is one of the methods of the statistical description of systems consisting of a large number of identical particles, and finds wide application in different areas of physics. On the basis of this method, the idea is presented of electrons (if an atom is under discussion) moving classically but with the additional condition that in each cell of phase space there be located no more than two particles. Interaction of particles is considered here by the introduction of the self-consistent field (with or without exchange).

The method under consideration is approximate, for which reason attempts have repeatedly been made at making it more precise in various ways by the introduction of corresponding corrections.<sup>1</sup> In their number we include the quantum correction (or, what amounts to the same thing, the correction for heterogeneity) which reflects the fact of the smearing out of the trajectory of the particle.

This correction was first found by Weizsacker<sup>2</sup> by a variational method; however, in its quantitative behavior, it has been subjected to criticism, both in principle and in a comparison of its value with experiment.<sup>3–7</sup> It was established that the Weizsacker correction was too large a quantity, in which connection, it was improved in a series of researches<sup>3,6</sup> by the introduction of a constant coefficient less than unity. In the present work, a stepwise quantum–mechanical derivation of the quantum corrections of second and fourth order in  $\hbar$  is deduced from the Hartree–Fock equation. In this case it is appropriate to use the operator formulation of the problem. A study of the non-relativistic equation of Hartree–Fock in operator form is given in Sec. 2. This form is especially convenient in the relativistic case, and also for interactions which depend on the spin or on the isotopic spin. In the neglect of the non-commutability of the operators for the potential and kinetic energies, we obtain the Thomas–Fermi and the Thomas–Fermi–Dirac equations.

The quantum corrections correspond to a consideration of the commutators of these operators,

in which the corrections of higher order are connected with the more complicated commutators. This problem is considered in Sec. 3 and in the Appendix.

In Sec. 4, the resultant correction is used for evaluation of the total energy of the atoms of the noble gases. In this case, the disagreement with experiment is reduced from 25–35% (without account of quantum corrections) and 20–35% (with account of the Weizsacker correction) down to 5–7%.

## 2. OPERATOR FORMULATION OF THE HARTREE-FOCK EQUATION

The quantum-mechanical equations of particles interacting according to the potential  $V(|q' - q''|)$  have, in the Hartree-Fock approximation, the form:<sup>8</sup>

$$\int dq''' \{ (q' | U + B - A | q''') (q''' | \rho | q'') - (q' | \rho | q''') (q''' | U + B - A | q'') \} = 0. \quad (1)$$

Here  $\rho$  is the density matrix

$$(q' | \rho | q'') = \sum_n \rho_n \psi_n(q') \bar{\psi}_n(q''), \quad (2)$$

where  $\rho_n$  is the average occupation number;  $U$  is the total kinetic and potential energy in the external field;  $B$  is the potential energy of the direct interaction of the particles:

$$(q' | B | q'') = \int V(|q' - q'''|) \cdot (q''' | \rho | q''') dq''' \cdot \delta(q' - q''); \quad (3a)$$

$A$  is the exchange energy<sup>1</sup>:

$$(q' | A | q'') = 1/2 V(|q' - q''|) (q' | \rho | q''). \quad (3b)$$

Equation (1) corresponds to the stationary case.

It is appropriate to formulate the problem in operator form, starting out from the matrix elements for the corresponding operators. The advantage of such an approach is connected with the independence of the resultant equation of the type of representation, and also with a significant simplification of the computations. The transition to the operators is brought about with the help of the following equivalent relations:

$$\hat{Q} f(q') = \int (q' | Q | q'') f(q'') dq'', \quad (4a)$$

$$({}_{a,b} - {}_{b,a}) \varrho({}_{a',b'}) \hat{\rho} = ({}_{a,b} [\hat{\rho}] {}_{b'}) \quad (4b)$$

The operator  $\hat{p}'$  which is contained in the latter equation, acts both on the  $\delta$ -function and on the coordinate  $q'$  that enters into  $\hat{Q}$ . Therefore, it can be written in the form  $\hat{p}' = -i\hbar \partial / \partial q' + \hat{p}'_{\delta}$ , where the subscript  $\delta$  indicates the object of operation of  $\hat{p}'$ . Making use of the integral representation of the  $\delta$ -function, we obtain the relations

$$(q' | Q | q'') = \frac{1}{(2\pi\hbar)^3} \quad (4c)$$

$$\times \int \hat{Q}(q', p - i\hbar \frac{\partial}{\partial q'}) \exp\left[\frac{ip}{\hbar}(q' - q'')\right] dp,$$

which, if we neglect the differential operator in  $\hat{Q}$  [and also carry out the substitution  $q' \rightarrow (q' + q'')/2$ ], goes over into the well known equation of compound representation.

To find the operator which corresponds to the density matrix, we introduce the filling-factor operator, whose spectrum is the mean value of the filling factor:

$$\hat{\rho}(q, \hat{p}) \psi_n(q) = \rho_n \psi_n(q). \quad (5)$$

Then (2) has the form:

$$(q' | \rho | q'') = \hat{\rho}(q', \hat{p}') \quad (6)$$

$$\times \sum_n \psi_n(q') \bar{\psi}_n(q'') = \hat{\rho}(q', \hat{p}') \delta(q' - q'').$$

The latter equation follows from the completeness theorem. It follows from Eq. (6), along with (4b), that the filling-factor operator  $\hat{\rho}$  is precisely the operator whose matrix elements coincide with the density matrix.

As far as the operators which correspond to the different parts of the Hamiltonian are concerned, the operator which yields  $(q' | U | q'')$  is simply

$$\hat{U} = \hat{p}^2 / 2M + V_e(q), \quad (7)$$

where  $V_e$  is the potential for the external field. For  $(q' | B | q'')$ , we get from Eqs. (4b), (4c) and (6):

$$\begin{aligned} \hat{B}(q') &= \int V(|q' - q'''|) (q''' | \rho | q''') dq''' \quad (8) \\ &= \frac{1}{(2\pi\hbar)^3} \int V(|q' - q'''|) dq''' \int \hat{\rho}(q''', p - i\hbar \frac{\partial}{\partial q'''}) dp. \end{aligned}$$

Finally, we get for  $A$ , by means of several transformations,

$$\hat{A}(q', p') = \frac{1}{2} \int \hat{\rho}(q', p - i\hbar \frac{\partial}{\partial q'}) V_{(p'-p)\hbar} dp,$$

where  $V_k$  is the Fourier component of the function  $V(|q' - q''|)$ .

Equation (1) takes the following form in operator notation:

$$[\hat{H}, \hat{\rho}] = 0, \quad \hat{H} = \hat{U} + \hat{B} - \hat{A} \quad (10)$$

and represents the condition for stationarity of the distribution. It then follows that  $\hat{\rho}$  ought to be a function of operators which commute with the Hamiltonian, i.e., of integrals of the motion.

For a system in which all the degenerate states which correspond to a given energy value have their identical filling factors (for example, for an atom with all shells filled), we can consider that

$$\hat{\rho} = \hat{\rho}(\hat{H}). \quad (11)$$

Concrete form of this function should be given additionally. Thus, if we are interested in a non-degenerate Fermi gas, then

In the case of a degenerate gas, which will be considered below,

$$\hat{\rho} = 2 \left[ \exp \left( \frac{\hat{H} - E_0}{kT} \right) + 1 \right]^{-1}. \quad (12)$$

Here  $E_0$  is the upper limit of filling, which is determined by the total charge of the system; moreover, the possibility is considered of two spin orientations.

Going on to the case of electrostatic interaction of the particles  $V(|q' - q''|) = e^2 / |q' - q''|^2$ ,  $V_e = -e\varphi_e$ , we get operator equations equivalent to (1):

$$\Delta\Phi(\mathbf{r}) = -4\pi\rho_e(\mathbf{r}) + \frac{4\pi e^2}{(2\mu\hbar)^3} \int \hat{\rho}[\hat{H}] d\mathbf{p}, \quad (13)$$

$$\hat{A}(\mathbf{r}, \mathbf{p}) = \frac{e^2}{2\pi\hbar} \int \hat{\rho}[\hat{H}'] \frac{d\mathbf{p}'}{|\mathbf{p} - \mathbf{p}'|^2},$$

$$\hat{H} = \frac{\hat{p}^2}{2M} - e\Phi(\mathbf{r}) - A(\mathbf{r}, \mathbf{p});$$

$$\hat{\rho}[\hat{H}] = \hat{\rho}[\hat{H}(\mathbf{r}, \mathbf{p} - i\hbar\nabla)].$$

Here  $\Phi$  is the self-consistent field:  $\Phi = \varphi_e - B/e$ ,  $\rho_e$  is the external charge.

The system (13) is an explicit solution of Eq. (1); the ease of obtaining it is compensated by the fact that the argument  $\hat{\rho}$  is itself the sum of non-commuting quantities. The center of difficulty of the calculation is thus transferred to the realization of the function from the sum of non-commuting arguments. In cases in which we can neglect this lack of commutation, i.e., in the quasi-classical case, the Thomas-Fermi and the Thomas-Fermi-

Dirac equations follow from the system (13) [in place of a proof, we refer to Ref. 1, Sec. 16, where the equations are written in  $c$ -numbers which coincide with (13) in the quasi-classical case].

### 3. QUANTUM CORRECTIONS TO THE THOMAS-FERMI EQUATION OF ORDER $\hbar^2$ AND $\hbar^4$

In the computation of the quantum corrections by means of the expansion of  $\hat{\rho}[\hat{H}]$  in Eq. (13) in a series of the commutator components of the Hamiltonian use is made of the formula (see Appendix E):

$$\begin{aligned} f(\hat{a} + \hat{b}) &= f(\overline{a + b}) \\ &+ f''(\overline{a + b}) \cdot [ab] / 2 + f'''(\overline{a + b}) \cdot [[ab]b] / 6 \\ &+ f'''(\overline{a + b}) \cdot [a[ab]] / 6 + f^{IV}(\overline{a + b}) [ab]^2 / 8, \end{aligned} \quad (14)$$

where the bar over  $a + b$  signifies that  $a$  and  $b$  must be considered as commuting (i.e.,  $i\hbar\nabla$  is to be omitted in the argument). Considering the degenerate gas (12), and expanding the operator  $\epsilon[(\mathbf{p} - i\hbar\nabla)^2 - 2Me\Phi]$  in Eq. (13), we take

$$a = (\mathbf{p} - i\hbar\nabla)^2, \quad b = -2Me\Phi$$

which gives for the commutators

$$[ab] = -4i\hbar eM \mathbf{p} \nabla \Phi \quad (15)$$

$$+ 2\hbar^2 eM \Delta\Phi + 4\hbar^2 M (\nabla\Phi\nabla),$$

$$[ab]^2 = -16\hbar^2 e^2 M^2 (\mathbf{p}\nabla\Phi)^2 + \dots,$$

$$[[ab]b] = -8\hbar^2 e^2 M^2 (\nabla\Phi)^2 + \dots,$$

$$[a[ab]] = -8\hbar^2 M (\mathbf{p}\nabla)^2 \Phi + \dots$$

Consideration of more complicated commutators in this approximation is unnecessary since it gives terms  $\sim \hbar^3$  and higher. Upon substitution of (14) and (15) in the first equation of (13), and after integration of the  $\delta$ -function and its derivatives arising here, we get the Thomas-Fermi equation with the quantum corrections\*

$$\Delta\Phi + 4\pi\rho_e = 4\pi e\rho(\Phi, \nabla\Phi, \Delta\Phi, \dots) \quad (16)$$

$$= (4e / 3\pi\hbar^3) [2M(e\Phi + E_0)]^{3/2}$$

$$- (e^3 M^2 / 6\pi\hbar) [2M(e\Phi + E_0)]^{-3/2}$$

$$\times [(\nabla\Phi)^2 - 4(\Phi + E_0/e)\Delta\Phi].$$

\*As has been pointed out by the author, Eq. (16) was also obtained by A. S. Kompaneets and E. S. Pavlov by means of a method essentially different from that given in the present work.

Here  $\rho$  is the density of the electron cloud;  $E_0$  must be taken equal to zero in the case of a neutral system. Equation (16) is simplified in the case

$$e\Phi + E_0 < 0,$$

since here the functions

$$1 - \varepsilon, \delta, \delta'$$

and so forth are identically equal to zero. This gives for any finite order of  $\hbar$

$$\Delta\Phi + 4\pi\rho_e = 0. \quad (16a)$$

Correction terms of the order of  $\hbar$  (and generally of any odd order) are absent, as also follows from the real nature of  $\rho$ .

Let us find the correction to the energy which is determined by quantum effects. According to the general formula for the approximation of a self-consistent field,

$$E = \sum_n E_n - E_{\text{int}},$$

$$E_{\text{int}} = \frac{e^2}{2} \int \frac{\rho(r_1)\rho(r_2)}{|r_1 - r_2|} dr_1 dr_2$$

we get

$$E = \frac{1}{(2\pi\hbar)^3} \int \left( \frac{\hat{p}^2}{2M} - e\Phi \right) \times \left[ 1 - \varepsilon \left( \frac{\hat{p}^2}{2M} - e\Phi - E_0 \right) \right] dp dr - E_{\text{int}}, \quad (17)$$

where

$$\hat{p} = p - i\hbar\nabla.$$

Instead of taking (17) into account and using Eqs. (14) and (15), we can establish the connection between the energy corrections and the density  $\rho$ . For this purpose, we note that for any order of  $\hbar$  ( $f$  is an arbitrary function),

$$\int_0^\infty f\left(\frac{\hat{p}^2}{2M} - A\right) p^2 dp, \quad A = e\Phi + E_0,$$

is represented in the form of an expansion only in half-integer (positive and negative) powers of  $A$  [in this connection, see Eq.(23)]. This statement is based on the parity of the half-integral expression relative to  $p$  and  $\hat{p}$ , and can be proved by induction. Let us transform (17) to the form

$$E = E_1 + E_0 \int \rho dr - E_{\text{int}},$$

$$E_1 = \frac{1}{(2\pi\hbar)^3} \int (\hat{H} - E_0) [1 - \varepsilon (\hat{H} - E_0)] dp dr. \quad (18)$$

Differentiating  $E_1$  with respect to  $E_0$  we obtain

$$\partial E_1 / \partial E_0 = - \int \rho \cdot dr$$

Integrating this expression, we take it into account that  $\rho$  depends only on the combination

$$e\Phi + E_0$$

and on commutators which do not contain  $E_0$ . Therefore, we can carry out the integration with  $E_0$  over  $e\Phi$ , taking the commutators to be constant.

This gives for the energy correction

$$\delta E = - e \int d\Phi \int \delta\rho(\Phi, \nabla\Phi \dots) dr + E_0 \int \delta\rho(\Phi, \nabla\Phi \dots) dr. \quad (19)$$

The arbitrary constant of integration ought to be so chosen that the result did not contain any powers of

$$e\Phi + E_0,$$

$e\Phi + E_0$  beside the half-integral ones, and in particular, that

$$e\Phi + E_0$$

be absent in the zeroth power.

In the second order of  $\hbar$ , with account of (16), we get (for  $E_0 = 0$ ):

$$\delta_2 E = - \frac{e^2 M}{24\pi^2 \hbar} \int dr (2Me\Phi)^{-1/2} [(\nabla\Phi)^2 + 4\Phi\Delta\Phi]. \quad (20)$$

Transforming to atomic units  $e = M = \hbar = 1$

we express  $\delta_2 E$  in terms of  $\rho$  by Eq.(16). This gives, in the approximation under consideration

$$\delta_2 E = \frac{1}{72} \int dr \frac{(\nabla\rho)^2}{\rho} - \frac{\pi}{3} \lim_{\varepsilon \rightarrow 0} \frac{\partial\rho}{\partial r} r^2 \Big|_\varepsilon. \quad (21)$$

The first term of this expression coincides in form with the well known correction of Weizsacker<sup>2</sup> for the inhomogeneity of the density, but is numerically smaller by a factor of 9. The second term is not important if we put in (21) the density distribution of Hartree-Fock (or a distribution with a suitable behavior at zero; see below, Sec.4).

In conclusion, let us establish the dependence on  $Z$  of the quantum correction for an atom with a nuclear charge  $Z$ . Starting out from the estimates

$$r \sim Z^{-1/3}, \quad \rho \sim Z/r^3 \sim Z^2,$$

we find

$$\delta_2 E \sim Z^{1/3}, \quad (22)$$

while in the quasi-classical case,

$$E_0 \sim Z^{1/3}.$$

Thus, expansion in  $\hbar^2$  is at the same time an expansion in  $Z^{-1/3}$ . This corresponds to the fact that the Thomas-Fermi equation is the more accurate the larger the value of  $Z$ .

Let us proceed to the quantum corrections of fourth order. The technique of computation in this case is the same as above, but in place of (14) we use a formula which contains more complicated commutators [see Appendix, Eq. (1)]. In the process of calculation, the relation

$$\int_0^\infty \left(\frac{p^2}{2M}\right)^m \frac{\partial^n}{\partial (p^2/2M)^n} \varepsilon \left(\frac{p^2}{2M} - e\Phi\right) p^2 dp \quad (23)$$

$$= \frac{(-1)^{n-1}}{2^{n-1}} (2M)^{1/2} (2m+1)(2m-1)$$

$$\dots (2m-2n+5) (e\Phi)^{m-n+3/2}.$$

is useful. As a result, we obtain the following expression for the correctness of fourth order to the density:

$$\delta_4 \rho = (32e^4 M^4 \hbar / 15\pi^2) (2Me\Phi)^{-1/3} \quad (24)$$

$$\times \{64\Phi^3 \Delta^2 \Phi - 192\Phi^2 \nabla \Phi \cdot \nabla \Delta \Phi$$

$$- 64\Phi^2 (\nabla_i \nabla_k \Phi)^2 - 80(\Delta \Phi)^2 \Phi^2$$

$$+ 200\Phi \Delta \Phi \cdot (\nabla \Phi)^2$$

$$+ 240\Phi \nabla_i \Phi \cdot \nabla_i \nabla_k \Phi \cdot \nabla_k \Phi - 175(\nabla \Phi)^4\}.$$

Expressing the energy correction in terms of  $\rho$ , we obtain in the given approximation [taking also into consideration the terms of the same order from Eq. (20)],

\*The dimensionless parameter

$$\hbar^2 / p^2 r^2$$

has the order of

$$\rho^{-2/3} r^{-2} \sim Z^{-2/3}.$$

$$\delta_4 E = - \frac{1}{4320 (3\pi^2)^{1/3}} \quad (25)$$

$$\times \int \frac{dr}{\rho^{11/3}} \{8(\nabla \rho)^4 - 27\rho(\nabla \rho)^2 \Delta \rho + 24\rho^2 (\Delta \rho)^2\}.$$

The estimate of the dependence of Eq. (26) on  $Z$  gives

$$\delta_4 E \sim Z \quad (26)$$

corresponding to the fact that the  $Z^{-3/2}$  appears as the expansion parameter.

In conclusion, we note that consideration of the quantum corrections of fourth order to the Thomas-Fermi equation requires, generally speaking, a simultaneous consideration of the corrections of second order to the Thomas-Fermi-Dirac equation, i.e., to quantum corrections in the exchange. This problem has a whole series of specific peculiarities and will be set forth in a separate paper.

#### 4. ENERGY OF THE ATOM IN THE STATISTICAL MODEL

It is known from experiment, and from quantum-mechanical calculations, that the total energy of an atom  $E$  is a monotonic function of the ordinal number  $Z$ . This bears witness to the weak dependence of  $E$  on the details of the internal structure of the atom, and permits us to hope for a successful application of the semi-classical statistical model to the calculation of  $E$ . However, calculation of  $E$  by means of the Thomas-Fermi model, which leads to the expression  $E = -0.769 Z^{7/2}$  gives much too large a value (in absolute magnitude) to the energy. This is connected with the fact that the density in the Thomas-Fermi model varies as  $r^{-2/3}$  at the origin while quantum mechanics leads to a finite value of  $\rho$  at  $r \sim 0$ . In view of this fact, there is an excess of electrons in the neighborhood of the nucleus in the given model in comparison with their actual distribution. This fact leads to a lower value of the kinetic energy of the electron cloud and to a higher value (in absolute magnitude) of the total energy\*. The reason for this is clear and is contained in the inapplicability of the quasi-classical Thomas-Fermi equation in the vicinity of

the nucleus, since the quantum effects in this region must be especially strong. Therefore, we can hope that calculation of the Weizsacker quantum correction improves the position with respect to the energy of the atom. This is evident if only from the fact that for  $\rho \sim r^{3/2}$ , the integral (21) tends to  $\infty$ , i.e., the energy in each case does not have a minimum (a growth of  $\rho$  at zero that is weaker than  $r^{-1}$  is acceptable). However, calculations of N. Sokolov<sup>3</sup> have shown that although the Weizsacker correction also leads to a decrease (in absolute value) of the total energy of the atom, this decrease is so great that divergence from experiment is obtained just as in the quasi-classical case, but with different sign. This, and also a series of other considerations<sup>3-7</sup> leads to the conclusion that the Weizsacker correction has too large a value. One of the reasons is the circumstance that the test function chosen by Weizsacker in the variational method was excessively rough and therefore gives a higher value of the energy.

It was established above that quantum-mechanical considerations lead to a quantum correction of second order which is 9 times smaller than that of Weizsacker. The correction we found has been used by us in the calculation of the total energy of the atom by the Lenz-Jensen method. This method, in application to the present problem, has been described in Ref. 3, where the calculations are carried out with the Weizsacker correction: therefore the details of the calculation are omitted below.

The method just mentioned is not connected with the solution of the differential equation for the potential  $\Phi$ , but derives from the expression for the energy which is expressed in terms of the density  $\rho$ :

$$E = \frac{3}{10} (3\pi^2)^{2/3} \int \rho^{5/3} d\mathbf{r} - Z \int \frac{\rho}{r} d\mathbf{r} \quad (27)$$

$$+ \frac{1}{2} \int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

$$- \frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3} \int \rho^{4/3} d\mathbf{r} + \delta_2 E + \dots$$

Here the first term is the kinetic energy, the second and the third are potential terms, the fourth is exchange (without quantum corrections), and, finally, the remaining terms are the quantum corrections of the 2nd, 4th, . . . orders. Carrying out the calculations for second order in  $\hbar$ , we limit ourselves to writing down five terms and seek a minimum of (27) by substitution of different test functions of  $\rho$ . Here it is shown (see also Ref. 3) that, within an accuracy of 3-4% of the quantity  $E$ , this minimum is realized by the class of functions

$$\rho(r) = c \exp\{- (\lambda r)^{1/\beta}\}, \quad (28)$$

where  $\lambda$  and  $\beta$  are variation parameters and  $C$  is determined by normalization. Upon substitution of Eq. (28) in  $\delta_2 E$ , we can discard the second term in (21) and the Weizsacker correction, decreased by a factor of 9, will figure in (27).

Departure of the total energy,

$$\delta = (E - E_{\text{emp}}) E_{\text{emp}}^{-1}$$

from the empirical (and semi-empirical) values which are taken from Ref. 4, and also the values of the parameters are listed in the Table where, moreover we give the values of  $\delta$  for the Thomas-Fermi and Thomas-Fermi-Dirac equation with the Weizsacker correction.

For argon ( $Z=18$ ), we have carried out estimates of the fourth order corrections of (26). In this connection, it is important to note that just as the density obtained from the solution of the Thomas-Fermi equation cannot be used for estimating the second order correction because of the notably higher divergence, the density (28) is unsuitable, for the same reason, for estimating the fourth order correction. It is necessary to set up the variational problem for the function included in (26), and we must limit the class of test functions to functions which do not lead to the divergencies of (26). Moreover, for an approximate estimate, we must substitute in Eq. (26) the exact solution of the Hartree equation.<sup>9</sup> This leads to the estimate

$$\delta_4 E \approx -3\%$$

It is evident from the Table above that the second order quantum correction contributes a term to the energy  $\sim 20-30\%$ ; this bears witness to the excellent convergence of the approximation process. In addition, for accurate determination of the fourth order correction, it is necessary to take into account quantum-exchange corrections (see the end of Sec. 3) and also to make use of a much wider class of test functions with the purpose of improving the accuracy of the result.

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REALIZATION OF A FUNCTION FROM NON-COMMUTING ARGUMENTS

In a number of problems of quantum theory, one deals with functions of the sum of non-commuting operators, the rule of operation with which has recently been clarified by a number of researches.<sup>10</sup> These methods, which appear to be sufficiently general, can be applied to the problem considered above of the expansion in powers of  $\hbar$ , but have a much more useful special property which stems from the fact that an expansion in powers of  $\hbar$  is simultaneously a computation of more complicated commutators.

As early as 1933, the first terms of an expansion of functions of the sum of operators were described by Peierls but the method used by him in the problem of finding the coefficients of expansion was extremely crude. A much simpler method is considered below, with the help of which an expansion up to four commutators was obtained.

For a sufficiently wide class of functions  $f(a+b)$ , where  $\hat{a}$  and  $\hat{b}$  are non-commuting arguments, we can use a Fourier expansion\* and thus work with exponential functions  $\exp[i(a+b)\tau]$

Let us represent it in the form

$$\exp[i(a+b)\tau] = \exp(ib\tau) K \exp(ia\tau), \quad (\text{a})$$

here  $K$  depends on the commutators of  $\hat{a}$  and  $\hat{b}$  on  $\tau$ , and is determined by an equation which is obtained upon differentiation of Eq. (a) with respect to  $\tau$

$$\partial K / \partial \tau = i \exp(-i\tau[b]a) K - iKa$$

$$\exp(-i\tau[b]a) \equiv e^{-i\tau b} a e^{i\tau b} \quad (\text{b})$$

$$= \sum_{n=0}^{\infty} \frac{(-i\tau)^n}{n!} [b \overbrace{[b \dots [ba] \dots]}^n \dots].$$

Starting out from  $K_0 = 1$ , we find

$$\partial K_1 / \partial \tau = \tau [ba], \quad K_1 = \tau^2 [ba] / 2.$$

Similarly, limiting ourselves to two commutators and to the square of one of them, we get the expression

(c)

$$K_2(\tau) = (i\tau^3/6) \{[a[ba]] - [b[ba]]\} + (\tau^4/8) [ba]^2.$$

In Eq. (a), the operators  $K$  and  $e^{ia\tau}$  no longer act on  $e^{ib\tau}$ , as a consequence of which the latter can be moved to the right:

$$\exp[i(a+b)\tau] = K(\tau) \exp[i\overline{(a+b)}\tau], \quad (\text{d})$$

where the bar denotes that  $a$  and  $b$  must be considered as commuting operators, and  $K(\tau)$  ought not to act on the function following it. Transforming from the Fourier form to the initial function, we get\*

$$\begin{aligned} f(a+b) &= f(\overline{a+b}) \\ &+ f''(\overline{a+b}) [ab] / 2 + f'''(a+b) \{[[ab]b] \\ &+ [a[ab]]\} / 6 + f^{IV}(\overline{a+b}) [ab]^2 / 8. \end{aligned} \quad (\text{e})$$

Consideration of more complicated commutators is carried out similarly. Introducing the notation

$$Q_n^m = \underbrace{[a[a \dots [a]}_m \underbrace{[b[b \dots [ba] \dots]}_n \dots], \quad (\text{f})$$

we obtain the remaining terms of the expansion  $K(\tau)$  up to four commutators inclusively in the form:

$$\begin{aligned} K_3(\tau) &= (\tau^4/24) (Q_2^1 - Q_1^2 - Q_3^0) \\ &+ (i\tau^5/120) (7Q_1^0 Q_1^1 - 4Q_1^0 Q_2^0 - 6Q_2^0 Q_1^0 \\ &+ 3Q_1^1 Q_1^0) + (\tau^6/48) (Q_1^0)^3, \\ K_4(\tau) &= (i\tau^5/120) (Q_4^0 + Q_2^2 - Q_1^3 - Q_3^1) \\ &+ (\tau^6/720) (-3Q_1^2 Q_1^0 - 10(Q_1^1)^2 \\ &- 12Q_1^0 Q_1^2 + 4Q_1^1 Q_2^0 \\ &+ 9Q_1^0 Q_2^1 - 5Q_1^0 Q_3^0 + 16Q_2^0 Q_1^1 \\ &- 10(Q_2^0)^2 - 10Q_3^0 Q_1^0 \\ &+ 6Q_2^1 Q_1^0) + (i\tau^7/1680) (5Q_1^1 (Q_1^0)^2 \\ &+ 11Q_1^0 Q_1^1 Q_1^0 + 19(Q_1^0)^2 Q_1^1 \\ &- 8(Q_1^0)^2 Q_2^0 - 12Q_1^0 Q_2^0 Q_1^0 \\ &- 15Q_2^0 (Q_1^0)^2) + (\tau^8/384) (Q_1^0)^4 \dots \end{aligned} \quad (\text{g})$$

(h)

\*For the functions  $\epsilon(a+b)$ , we must use the discontinuous integral of Dirichlet.

\*The quantity  $\tau$  plays the role of the differentiation operator with respect to  $a \mp b$ .

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## Capture of Conduction Electrons by Charged Defects in Ionic Crystals

IU. E. PERLIN

*Kishinev State University*

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Capture of conduction electrons by charged defects of an ionic crystal lattice is regarded as a one-quantum thermal transition from the continuous spectrum to an excited state of the discrete spectrum. The role of the perturbation is played by the nonconfigurational interaction which in an ideal crystal leads to ordinary polaron scattering. The capture probability as a function of polaron velocity has been computed and the temperature dependence of current-carrier lifetime has been established.

### 1. INTRODUCTION

IN the phenomenological theory of semiconductors, the recombination coefficients of conduction electrons with "impurity centers" such as ion vacancies or excess interstitial ions are usually regarded as parameters to be determined by comparing the theory with experiment. The large number of such parameters endows the formulas of the phenomenological theory with excessive approximational flexibility so that the comparison of the theory with experiment is sometimes inconclusive. Therefore, calculation of the probability of electron capture by an impurity center using the methods of a microscopic theory is of considerable interest.

We shall not in this article attempt a complete review of the theoretical work on this problem. We shall, however, indicate that a treatment of the problem very similar to ours was first published by Adirovich,<sup>1</sup> who regarded electron capture as a quantum transition induced by the nonconfigurational interaction of an electron with ion motions (the violation of adiabaticity). Adirovich's proposed model of a pulsating double layer enabled him to make a qualitative estimate of capture probability.

A theoretical formula for the recombination coefficient which does not contain undetermined parameters and which permits comparison of the theory with experiment was obtained by Pekar,<sup>2</sup> who divided the process of electron capture by an impurity center into the diffusion of an electron to a lattice defect and direct thermal transition to a discrete energy level. In crystals where conduction electron mobility is low, the first part of the process can play the deciding role.

Pekar and the present author<sup>3</sup> made a comparison of the recombination coefficient calculated on this hypothesis with experimental data on electron capture by *F* centers in alkali halide crystals and obtained satisfactory results. Nevertheless, without a quantum mechanical calculation of the thermal transition probability (of an electron) to a discrete level, the "diffusion" theory of recombinations is of uncertain applicability. There are undoubtedly cases in which the second stage of the process rather than the first, plays the deciding role.

The present article attempts a quantum mechanical calculation of the probability for electron capture by a positively charged ionic crystal lattice defect (such as a negative ion vacancy). Such a



ERRATA TO VOLUME 5

We are indebted to Mr. D. A. Kirzhnits of the P. N. Lebedev Physics Institute, Academy of Sciences, U.S.S.R. for calling our attention to a few regrettable errors in the translation of his article "Quantum Corrections to the Thomas-Fermi Equation" [Soviet Phys. JETP 5, 64-71 (August, 1957); original in J. Exptl. Theoret. Phys. (U.S.S.R.) 32, 115-123 (January, 1957)].

P. 66, column 1—the text following Eq. (11) should read

Concrete form of this function should be given additionally. Thus, if we are interested in a non-degenerate Fermi gas, then

$$\hat{\rho} = 2 \left[ \exp \left( \frac{\hat{H} - E_0}{kT} \right) + 1 \right]^{-1}.$$

In the case of a degenerate gas, which will be considered below

$$\hat{\rho} = 1 - \varepsilon(\hat{H} - E_0), \quad \varepsilon(x) = x/|x|. \quad (12)$$

Additional errata are:

- P. 68, column 1, 9 lines above Eq. (23)                      reads  $Z^{-2/3}$                                       should read  $Z^{-2/3}$
- P. 68, column 2, first line after Eq. (26)                      reads  $Z^{-3/2}$                                       should read  $Z^{-2/3}$
- P. 68, column 2, 14th line from bottom                      reads  $E = -0.769 Z^{7/2}$                       should read  $E = -0.769 Z^{7/3}$
- P. 68, column 2, 10th line from bottom                      reads  $r^{-2/3}$                                       should read  $r^{-3/2}$
- P. 69, column 2, the following table was omitted

Atomic Number Z	$\delta$ , Thomas-Fermi	$\delta$ , Thomas-Dirac	$\delta$ , Thomas-Dirac with Weizsaecker correction	$\delta$ , from Eq. (27)	Variational parameters	
					$\beta$	$\lambda \cdot 10^{-4}$
10	-28	-36	+34	-7	4.0	0.24
18	-25	-30	+29	-6	4.3	0.56
36	-21	-25	+24	-6	4.7	3.5
54	-20	-23	+21	-5	5.0	7.6

Other Errata

Page	Column	Line	Reads	Should Read
<b>Volume 4</b>				
38	1	Eq. (3)	$\dots \frac{\pi r^2 \rho^2 \rho_n^2}{\rho_s^2},$	$\dots \frac{\pi r^2 \rho^2 \rho_n}{\rho_s^2},$
196		Date of submittal	May 7, 1956	May 7, 1955
377	1	Caption for Fig. 1	$\delta_{35} = \eta - 21 \cdot \eta^5$	$\delta_{35} = -21 \eta^5.$
377	2	Caption for Fig. 2	$\alpha_3 = 6.3^\circ \eta$	$\alpha_3 = -6.3^\circ \eta$
516	1	Eq. (29)	$s^2/c^2 \dots$	$s/c$
516	2	Eqs. (31) and (32)	Replace $A_1 s^2/c^2$ by $A_1$	
497		Date of submittal	July 26, 1956	July 26, 1955
900	1	Eq. (7)	$\dots \frac{i}{4\pi} \sum_{c, \alpha} \frac{\partial w_a(t, P)}{\partial P^\alpha} \dots$	$\dots 2\pi^2 i \sum_{c, \alpha} \dots$
			(This causes a corresponding change in the numerical coefficients in the expressions that result from the calculation of the effects of the plasma particles on each other).	
804	2	Eq. (1)	$\dots \exp \{-(\bar{T} - V')\}$	$\dots \exp \{-(\bar{T} - V')\tau^{-1}\}$

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59	1	Eq. (6)	$v_l (l \partial F_0 / \partial x) + \dots$ where $E_l$ is the projection of the electric field $E$ on the direction $l$	$\overline{(v \partial F_0 / \partial x)} + \dots$ where the bar indicates averaging over the angle $\theta$ and $E_l$ is the projection of the electric field $E$ along the direction $l$
91	2	Eq. (26)	$\Lambda = 0.84 (1 + 22/A)$	$\Lambda = 0.84 / (1 + 22/A)$
253		First line of summary	$T_1^{204, 206}$	$T_1^{203, 205}$
318	1	Figure caption	$\dots e^2 mc^2 = 2.8 \cdot 10^{-23} \text{ cm},$	$\dots e^2 / mc^2 = 2.8 \cdot 10^{-13} \text{ cm},$
398		Figure caption	$\dots$ to a cubic relation. A series of points etc.	$\dots$ to a cubic relation, and in the region 10–20°K to a quadratic relation. A series of points ●, coinciding with points ○, have been omitted in the region above 10°K.