

## Thomas-Fermi Theory of the Atom as a Solution of the Density-Matrix Hierarchy\*†

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In this paper we show that the Thomas-Fermi (TF) theory for a neutral atom is the zeroth-order solution of the full  $N$ -body problem if (a) the following assignments of smallness are made:  $N^{-1/3} = \epsilon$ ,  $e = e_0 \epsilon^{3/2}$ ,  $m = m_0/\epsilon^2$ ,  $\epsilon \rightarrow 0$ ; (b) the singlet density matrix in the  $x$  representation,  $\rho_1(x', x)$ , is a fast oscillating function of the off-diagonal elements, of the type  $\sin[(x' - x)/\epsilon]$ ; (c) the higher-order density matrices are determinants of the singlet density matrix as  $\epsilon \rightarrow 0$ . The higher-order approximations, however, cannot be obtained by a simple power-series expansion in  $\epsilon$ , since the solutions contain  $\epsilon$  in a nonanalytical fashion. Taking into account the exclusion principle to zeroth order in  $\epsilon$ , and solving the equations of motion for the singlet density matrix to the next-higher-(second-) order approximation, we obtain the equations found by Kompaneets and Pavlovskii, and Baraff and Borowitz. These contain the Dirac and Weizsäcker corrections. Finally, we offer some conjectures about possible improvements of the approximation scheme.

### 1. INTRODUCTION

THE Thomas-Fermi (TF) model of the atom is the most successful attempt to account in simple terms for the characteristic features of complex atoms.

Many papers deal with the application of this theory to different systems, and with its heuristic improvements.<sup>1</sup> However, relatively little attention has been paid to the *systematic construction* of a statistical theory of complex atoms. The original derivation of the TF model was heuristic, and it is hard to tell what are the approximations involved, and how one can improve upon them. Such a more systematic treatment can be obtained in two different ways: expansion in terms of a small parameter, or a variational treatment.

There were three major efforts utilizing an expansion technique, all starting essentially from the Hartree-Fock (HF) scheme, expanding (1) in Planck's constant,  $\hbar^2$ ; (2) in inverse powers of the number of electrons ( $N$ ) in the atom<sup>2</sup>; (3) in the off-diagonal elements of the density matrix.<sup>4</sup>

There are, however, two major difficulties associated with any of these attempts. First, it is not clear in what sense one should take  $\hbar$ ,  $1/N$ , or the magnitude of the off-diagonal elements of the density matrix as small. It cannot mean that in the limit when the chosen parameter tends to zero we obtain a rigorous solution, since if  $\hbar$  goes to zero the exclusion principle must become inoperative, and if  $N$  goes to infinity the atom acquires an infinite radius. Clearly, a coupled limiting process is involved and one has to determine which parameters

tend to zero and at what rate. Second, starting with the HF scheme the following objections are left unanswered. (A) One can show at most in this way that in some limit the TF model is as good as the HF scheme; actually it might turn out to be better. (B) We may indeed find that in some limit we obtain from the HF scheme the TF solutions; it also may happen that in this limit the HF scheme itself is a very poor approximation to the actual  $N$ -body problem. (C) If we intend to improve systematically the TF model starting with the HF scheme we have no assurance that the correction terms found are not of the same order of magnitude as the error committed by starting with the HF scheme in the first place.

Another very popular approach makes use of the fact that the HF scheme can be obtained as the Euler equations of a variational principle.<sup>5</sup> Write out the energy of the atom as a functional of the one-particle density matrix. Stipulate as auxiliary conditions that the one-particle density matrix or singlet density matrix normalized to  $N$  has a fixed trace and is idempotent. The Euler equations of this variational problem give the HF scheme. One is then tempted to go into this variational problem with a suitable trial function and determine its best form in the usual manner. However, a very serious trouble occurs (apart from the fact that the accuracy of the approximation cannot be assessed). The one-particle density matrix and hence the trial function has to obey an additional condition which cannot be given a simple mathematical form without solving the whole  $N$ -body problem: The singlet density matrix is to be of the form which can be obtained by integrating  $N-1$  times the  $N$ -particle density matrix. While it is obvious that for the trial function this implies "smoothness" in some sense, it is by no means clear how to formalize this condition. Without satisfying it, however, the variational approximations obtained can be void of any physical meaning.

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† Invited paper at the Washington meeting of the American Physical Society, April 1963.

<sup>1</sup> P. Gombas, *Die Statistische Theorie des Atoms und ihre Anwendungen* (Springer-Verlag, Vienna, 1949); *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1958), Vol. 36, p. 109.

<sup>2</sup> P. A. M. Dirac, Proc. Cambridge Phil. Soc. 26, 376 (1930); G. A. Baraff and S. Borowitz, Phys. Rev. 121, 1704 (1961).

<sup>3</sup> A. S. Kompaneets and E. S. Pavlovskii, Zh. Eksperim. i Teor. Fiz. 31, 427 (1956) [English transl.: Soviet Phys.—JETP 4, 328 (1957)].

<sup>4</sup> M. A. Naqui, Nucl. Phys. 10, 256 (1959).

<sup>5</sup> J. E. Mayer, J. Chem. Phys. 100, 1579 (1955); H. Koppe, Z. Physik 148, 135 (1957).

For this reason we decided to investigate the possibility of an expansion in terms of a small parameter. Of course, it is possible that the wisest approach will eventually combine both methods. Throughout this paper we confine our interest to neutral atoms.

## 2. OUTLINE

Our plan will be as follows: First, we find the small parameter involved; then we show heuristically that in the limit when this parameter goes to zero the TF model is to be expected to give a rigorous solution of the  $N$ -body problem in question, and we assess the orders of magnitude of the different correction terms usually appended to the original TF theory (see Ref. 1). Then we start from first principles, set up the appropriate equations and symmetry conditions and show that indeed to zeroth order in this parameter we *rigorously* obtain the conventional TF theory. Next we shall show that the actual solutions are nonanalytical in the small parameter, hence the next approximation cannot be obtained by a simple power-series expansion. If, notwithstanding we attempt to do this in an inconsistent fashion, by improving the solutions of the differential equations to the next order, while satisfying the exclusion principle only to zeroth order, we obtain the usual exchange (Dirac) and inhomogeneity (Weizsäcker) correction. This will demonstrate, then, that these correction terms are probably not quite correct, and that for a consistent improvement over the original TF results it is necessary to devise an approximation method which can be used if the solution is nonanalytical in the small parameter.

## 3. THE SMALL PARAMETER

### Characteristic Quantities

To construct the small parameter we shall first need the characteristic quantities involved in the TF theory. A short, dimensional analysis will accomplish this. Assume that the electron cloud around the nucleus is confined to a volume  $L^3$ ; let this be accomplished entirely by an electrostatic potential  $U$  in cooperation with the exclusion principle. (This, of course, may not be possible, but if it is, the argument runs as follows.) Let there be  $N$  electrons confined; denote the maximum momentum at a given point inside  $L^3$  by  $p_0$ , the mass and charge of an electron by  $m$  and  $e$ . Then, from Poisson's equation

$$U/L^2 \approx e^2 N/L^3, \quad (1)$$

since the density is  $\approx N/L^3$ . The condition that  $p_0$  is the maximum momentum reads

$$p_0^2/2m \approx U. \quad (2)$$

The exclusion principle stipulates that each phase cell should contain at most one electron with a given spin; the condition that the atom be in its lowest energy state requires that no phase cell having momentum

less than  $p_0$  be empty. The two conditions together give

$$p_0^3/h^3 \approx N/L^3. \quad (3)$$

From (1) and (2) it follows that

$$U \approx Ne^2/L \approx p_0^2/2m, \quad (4)$$

while (2) and (3) give

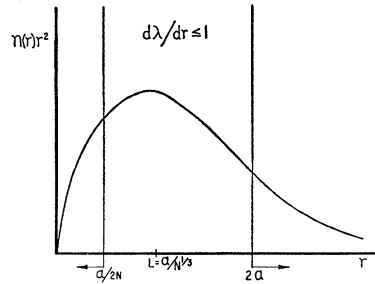
$$p_0 L \approx hN^{1/3}, \quad L \approx a/N^{1/3}; \quad (a = \text{Bohr radius}).$$

Thus, we obtained the three characteristic quantities  $p_0$ ,  $U$ , and  $L$  as functions of  $N$ . (Observe that the  $1/N^{1/3}$  dependence is connected with the three-dimensional nature of the problem. One- and two-dimensional atoms, composed of charged sheets, or charged filaments, respectively, would have characteristic quantities with a different  $N$  dependence.)

### Assessment of the TF Approximation

Suppose you have solved the TF differential equations. How can you tell whether the answer is, or is not, a correct solution of the full  $N$ -body problem? The problem is not trivial since the TF solutions do not furnish immediately the wave function or the density matrix of the  $N$ -body problem. There are two avenues open. First, the TF solution gives the number of electrons with given positions and momenta; from this we may construct in the well-known manner the singlet density matrix. In turn, from this we may construct the density matrix of the whole system, provided further assumptions are made about the relation of the singlet density matrix to the complete density matrix. Once this is obtained, we may verify how far this matrix obeys the equations of motion and the exclusion principle. This method has the advantage that both the satisfaction of the equations of motion and the exclusion principle can be tested. However, from the TF theory it is not immediately clear what are those further assumptions necessary to construct the density matrix from the singlet density matrix. For this reason we choose the second approach. This will test to a certain degree the satisfaction of the equations of motion, but not that of the exclusion principle. The TF theory is semiclassical theory, consequently it assumes that the local de Broglie wavelength varies slowly from point to point. Is this assumption satisfied everywhere by the solution? If we plot according to the TF theory the number of electrons contained in a spherical shell of radius  $r$  and unit-thickness around the nucleus,  $n(r)4\pi r^2$ , where  $n(r)$  is the density at the point  $r$ , we find a function as shown in Fig. 1. For small values of  $r$  the function starts as  $\sqrt{r}$ , it has a single maximum at about  $a/N^{1/3} = L$ , where  $a$  is the Bohr radius and  $N$  is the number of electrons in the neutral atom; for large values of  $r$  the function goes to zero as  $r^{-3/2}$ . Associated with this density there is an electric potential energy  $U(r)$  which goes as  $Ne^2/r$  if  $r \ll L$ , and as  $e^2 a^3/r^4$  for  $r \gg L$ . Finally we can define a local momentum

FIG. 1. Qualitative graph showing number of electrons on a shell of radius  $r$  as given by the Thomas-Fermi theory. Approximation good within region where the rate of change of the local de Broglie wavelength is small.



$p(r) = [2m(U-E)]^{1/2}$ . The validity of the semiclassical approximation requires that  $d\lambda/dr \ll 1$ , with  $\lambda = \hbar/p$ . Write  $d\lambda/dr = \lambda d \ln p/dr$ ; put approximately  $\ln p \sim \frac{1}{2} \ln U + \text{const}$  with  $U \sim r^{-n}$ ;  $n=1$ ,  $r \ll L$ ,  $n=4$ ,  $r \gg L$ . This gives  $\lambda n/2r \ll 1$  as our condition. The latter is certainly violated if  $\frac{1}{2}n(\lambda/r) \equiv \frac{1}{2}n(\hbar/pr)$  is equal to 1. There are two roots to this equation:  $a/2N$  and  $2a$ . Between them lies the maximum of the charge distribution (see Fig. 1). Hence we may say that for the majority of the electrons the TF solution is a good approximation to the Schrödinger equation.

Is the exclusion principle satisfied? Seemingly yes, since the solution was so constructed that one, or no, electrons of a given spin occupy each phase cell. However, this elementary form of the exclusion principle does not hold any longer if density gradients are present within the system and a more complicated condition has to be satisfied in its place. The derivation of this condition requires more preparation. In Sec. 7 we will show what this condition is, and how well the TF solutions satisfy it.

### Construction of the Small Parameter

Now let us find the small parameter of the problem. Obviously we seek a limiting process such that in this limit the equations and the exclusion principle should be satisfied everywhere, while keeping the characteristic features of the solution unchanged. The usual solution is believed to be correct for  $a/2N < r < 2a$ . The characteristic features of the atom represented by this solution are the radius of the atom  $L$ , and the energy per electron  $Ne^2/L$ . (According to the virial theorem for charged particles the kinetic and the potential energies, hence the total energy have the same order of magnitude.) Thus we seek a limiting process where  $a/N$  goes to zero,  $a$  goes to infinity, while  $L$  and  $Ne^2/L$  is being kept fixed. If we keep  $\hbar$  fixed, this can only be accomplished by letting  $N$  go to infinity,  $e$  going to zero as  $N^{-1/2}$ , and  $m$  going to infinity as  $N^{2/3}$ , thus  $N \rightarrow \infty$ ,  $e = e_0 N^{-1/2}$ ,  $m = m_0 N^{2/3}$ ,  $e_0, m_0$  being the original values of  $e$  and  $m$ . In this limit then the equations are satisfied everywhere, and, as we shall show, so is the exclusion principle. Formally, we may consider  $\hbar$  as variable, instead of  $m$ . Then the same result can be obtained by letting  $\hbar$  go to zero as  $N^{-1/3}$ , i.e.,  $N \rightarrow \infty$ ,  $e = e_0 N^{-1/2}$ ,  $\hbar = \hbar_0 N^{-1/3}$ . Since we are employing a limiting process

in which  $N$  tends to infinity, the question arises as to the computation of extensive quantities. The rule is as follows. First, compute the value of the associated intensive quantity in the limit as  $N$  tends to infinity. (E.g., if you are interested in the total energy, compute first the energy per particle as  $N$  tends to infinity.) Next, multiply this quantity by the actual number of particles.

Finally, we would like to stress that this selection of a small parameter was specifically designed for the purposes of the TF problem in such a manner as to make the semiclassical approximation valid for the entire atom in the zeroth order. For this reason it has less generality than the usual method where one treats the difference between the actual and the self-consistent potential as small; on the other hand, because of the more specific nature of the choice it tells us more about the approximation.

### Orders of Magnitude of the Correction Terms

The usual exchange correction to the energy per electron is given by  $\approx e^2 p_0/\hbar$ , i.e., the Coulomb interaction between two electrons at a de Broglie wavelength  $\hbar/p_0$  apart. The ratio of this quantity to  $p_0^2/m$  is of the order  $1/N^{2/3} = \epsilon^2$ . The inhomogeneity correction to the energy per electron is given by  $\approx e^2 a [\text{grad} \ln n]^2$ ; its ratio to  $p_0^2/m$  is again  $\epsilon^2$ . Thus, if we accept  $\epsilon$  as a relevant small parameter, these terms are correction terms of second-order smallness. The Fermi-Amaldi correction, replacing  $N$  with  $N-1$ , gives obviously a correction of order  $1/N = \epsilon^3$ , a term of third-order smallness. Finally, the correlation correction, introduced by Gombás,  $\sim e^2 n^{1/3}/(an^{1/3} + 10^{-1})$  is of the order  $\epsilon^4 p_0^2/m$ .

### 4. THE BASIC EQUATIONS

In this section we derive the basic equations of the theory, the equations of motion for the reduced density matrices. We shall work with density matrices for the following reason. The basic aim is to set up expressions in which the coordinates of one or two electrons appear only, the coordinates of the other electrons being integrated out. However, the state of one electron interacting with the others cannot be described by a wave function (not being a pure state) while it can be described by a density matrix; hence the latter is the proper tool.

Envisage a neutral atom with  $N$  electrons, and a fixed nucleus with charge number  $N$ . The Hamiltonian of the system is given by

$$H = \sum_{r=1}^N (K_r + V_r) + \sum_{1 \leq i < j \leq N} \Phi(x_i - x_j),$$

$$K_r = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x_r \partial x_r}; \quad \Phi(x) = e^2/|x|; \quad (5)$$

$$V_r = -N\Phi(x_r).$$

The state of the system is described by the antisymmetrical wave function  $\Psi(x_1, \dots, x_N, t)$ . (In principle the spin coordinates should also be included; however, the absence of spin variables in the Hamiltonian has the effect that the existence of the spin coordinates changes only certain factors in the equations. These can be put in any time, practically by inspection. Hence, for simplicity, we omit them throughout the paper, and shall point out when necessary which terms acquire different factors.) The density matrix for the whole atom in a pure state is defined as

$$\rho_N(x'_1, \dots, x'_N; x_1, \dots, x_N, t) = \Psi^*(x'_1, \dots, x'_N, t) \Psi(x_1, \dots, x_N, t). \quad (6)$$

Differentiate (6) with respect to  $t$  and express the time derivative of  $\Psi$  through the Schrödinger equation. We obtain

$$i\hbar \partial \rho_N / \partial t = (H - H') \rho_N, \quad (7)$$

where  $H'$  acts only on the  $x'$  variables. (This equation holds true even if  $\rho_N$  does *not* represent a pure state.)

Define now the reduced density matrices  $\rho_s$  by

$$\rho_s(x'_1, \dots, x'_s, x_1, \dots, x_s, t) = \int d^3 x_{s+1} \dots \times \int d^3 x_N \rho_N(x'_1, \dots, x'_s, x_{s+1}, \dots, x_N; x_1, \dots, x_s, \dots, x_{s+1}, \dots, x_N, t). \quad (8)$$

Contrary to the usual definition we do not include any combinatorial factors in the definition of the  $\rho_s$ . Consequently, all the density matrices  $\rho_s$  ( $s=1, 2, \dots, N$ ) are normalized to unity. The reason for this departure is due to the fact that an  $N$ -dependent normalization would make a limiting process  $N \rightarrow \infty$  more unpleasant. In Eq. (7) put  $x_{s+1}' = x_{s+1}$ ,  $x_{s+2}' = x_{s+2}$ ,  $\dots$ ,  $x_N' = x_N$ , and integrate over these variables. We get

$$i\hbar \frac{\partial \rho_s}{\partial t} = \sum_{r=1}^s [(K_r - K_r') + (V_r - V_r')] \rho_s + \sum_{1 \leq i < j \leq s} [\Phi(x_i - x_j) - \Phi(x_i' - x_j')] \rho_s + (N - s) \times \sum_{1 \leq i \leq s} \int d^3 x_{s+1} [\Phi(x_i - x_{s+1}) - \Phi(x_i' - x_{s+1})] \times \rho_{s+1}(x'_1, \dots, x'_s, x_{s+1}; x_1, \dots, x_s, x_{s+1}). \quad (9)$$

If the atom is in a stationary state, the time derivative is equal to zero. The exclusion principle is incorporated in the symmetry conditions on the  $\rho_s$ ; an interchange of any two primed coordinates, reproduces the function with the opposite sign. (Since we shall discuss stationary states we may choose, if we so desire, all density matrices real.)

Define now the new dimensionless variables

$$y_k = (x_k' + x_k) / 2L, \quad z_k = (x_k' - x_k) / L, \quad (k=1, 2, \dots, N),$$

and the new dimensionless functions of these variables

$$\rho_s(x'_1, \dots, x'_s; x_1, \dots, x_s) = R_s(y_1, \dots, y_s; z_1, \dots, z_s) / L^{3s}.$$

Equation (8) becomes

$$R_s(y_1, \dots, y_s; z_1, \dots, z_s) = \int d^3 y_{s+1} R_{s+1}(y_1, \dots, y_s, y_{s+1}; z_1, \dots, z_s, 0).$$

Write  $\Phi(x) = e^2 \phi / L$  and observe that  $K_r(x) - K_r(x') = \hbar^2 / mL^2 (\partial^2 / \partial y_r \partial z_r)$ . Substitute all these back in Eq. (9), and divide by  $N e^2 / L$ ; we obtain (putting  $\partial \rho_s / \partial t = 0$ )

$$\begin{aligned} & \sum_{1 \leq i \leq s} \{ (a/LN) (\partial^2 / \partial y_i \partial z_i) \\ & + [\phi(y_i + z_i/2) - \phi(y_i - z_i/2)] \} R_s \\ & - 1/N \sum_{1 \leq i < j \leq s} \{ \phi[y_i - y_j + (z_i - z_j)/2] \\ & - \phi[y_i - y_j - (z_i - z_j)/2] \} R_s - (1 - s/N) \\ & \times \sum_{1 \leq i \leq s} \int d^3 y_{s+1} [\phi(y_i - y_{s+1} + z_i/2) \\ & - \phi(y_i - y_{s+1} - z_i/2)] R_{s+1}(y_1, \dots, y_s, y_{s+1}; \\ & z_1, \dots, z_s, 0) = 0. \end{aligned}$$

Introduce  $N = \epsilon^{-3}$  and  $L/a = \epsilon$  according to the previous section. The first term acquires the factor  $\epsilon^2$ . Absorb one  $\epsilon$  in the new variable  $\zeta = z/\epsilon$ , and divide with the other  $\epsilon$ . This way finally we obtain the set of equations,  $\epsilon^{-3}$  in number, we shall work with:

$$\begin{aligned} & \sum_{1 \leq i \leq s} \left\{ \frac{\partial^2}{\partial y_i \partial \zeta_i} + (1/\epsilon) [\phi(y_i + \epsilon \zeta_i/2) - \phi(y_i - \epsilon \zeta_i/2)] \right\} \\ & \times R_s(y_1, \dots, y_s; \epsilon \zeta_1, \dots, \epsilon \zeta_s | \epsilon) \\ & - \epsilon^3 \sum_{1 \leq i < j \leq s} (1/\epsilon) \{ \phi[y_i - y_j + \epsilon(\zeta_i - \zeta_j)/2] \\ & - \phi[y_i - y_j - \epsilon(\zeta_i - \zeta_j)/2] \} R_s(y_1, \dots, y_s; \\ & \epsilon \zeta_1, \dots, \epsilon \zeta_s | \epsilon) - (1 - \epsilon^3 s) \sum_{1 \leq i \leq s} \int d^3 y_{s+1} (1/\epsilon) \\ & \times [\phi(y_i - y_{s+1} + \epsilon \zeta_i/2) - \phi(y_i - y_{s+1} - \epsilon \zeta_i/2)] \\ & \times R_{s+1}(y_1, \dots, y_s, y_{s+1}; \epsilon \zeta_1, \dots, \epsilon \zeta_s, 0 | \epsilon) = 0, \\ & (s=1, 2, \dots, 1/\epsilon^3). \quad (10) \end{aligned}$$

Here we have explicitly indicated the fact that the  $R$  functions now can depend on  $\epsilon$  in two different ways; first, due to the change of variables from  $z$  to  $\zeta$ , and second, on account of the fact that originally  $\rho_s$ , and hence  $R_s$ , involved  $N (= 1/\epsilon^3)$  parametrically (since they were obtained from  $\rho_N$  or  $R_N$  by integration). We

rewrite Eq. (10) in a more transparent form. Introduce the difference operator  $D_r$ ; it acts on the argument  $y_r$  of a function  $F$  to which it is applied;

$$D_r F(y_1, y_2, \dots, y_r, \dots) - (1/\epsilon)[F(y_1, y_2, \dots, y_r + \epsilon \zeta_r/2, \dots) - F(y_1, y_2, \dots, y_r - \epsilon \zeta_r/2, \dots)].$$

Thus in the limit  $\epsilon \rightarrow 0$  it gives  $\zeta_r \cdot \partial F / \partial y_r$ . Equation (10) reads now as

$$\sum_{1 \leq i \leq s} \left[ \frac{\partial^2}{\partial y_i \partial \zeta_i} + D_i \phi(y_i) \right] f_s - \epsilon^3 \sum_{1 \leq i < j \leq s} [(D_i + D_j) \phi(y_i - y_j)] f_s - (1 - \epsilon^3 s) \sum_{1 \leq i \leq s} \int d^3 y_{s+1} \int d^3 \zeta_{s+1} \delta(\zeta_{s+1}) \times [(D_i + D_{s+1}) \phi(y_i - y_{s+1})] f_{s+1} = 0. \quad (11)$$

For sake of symmetry we introduced the delta function  $\delta(\zeta_{s+1})$  and an additional integration over  $\zeta_{s+1}$ . The functions  $f_s$  are defined as:

$$R_s(y_1, \dots, y_s; \epsilon \zeta_1, \dots, \epsilon \zeta_s | \epsilon) = f_s(y_1, \dots, y_s; \zeta_1, \dots, \zeta_s | \epsilon).$$

These equations must be supplemented by conditions on the  $f_s$  functions. These are the recursion relations:

$$f_s(y_1, \dots, y_s; \zeta_1, \dots, \zeta_s | \epsilon) = \int d^3 y_{s+1} f_{s+1} \times (y_1, \dots, y_s, y_{s+1}; \zeta_1, \dots, \zeta_s, 0 | \epsilon); \quad (12)$$

the normalization conditions:

$$\int d^3 y_1 \dots \int d^3 y_s f_s(y_1, \dots, y_s; 0, \dots, 0 | \epsilon) = 1; \quad (13)$$

the symmetry conditions:

$$f_s \left( \frac{x'_1 + x_1}{2L}, \dots, \frac{x'_s + x_s}{2L}; \frac{x'_1 - x_1}{\epsilon L}, \dots, \frac{x'_s - x_s}{\epsilon L} \middle| \epsilon \right) \quad (14)$$

must change its sign upon interchange of  $x_k$  and  $x_r$ , or  $x'_k$  and  $x'_r$ ,  $k \neq r$ .

We wrote out the latter in terms of the variables  $x, x'$ , to simplify the conditions. Equations (12) and (13) are not independent. If we define  $f_0 = 1$ , the normalization conditions are the consequence of (12) for  $s = 0$ . Hence, in the future we need not mention (13) explicitly.

Then our aim is to solve the equation-system (11) for the set of  $f_s$  functions satisfying conditions (12), (13), and (14) in the limit  $\epsilon \rightarrow 0$ ; moreover, if possible, to devise a scheme of successive approximations for small, nonzero  $\epsilon$ . In addition we may require that the solution should give the lowest possible value for the

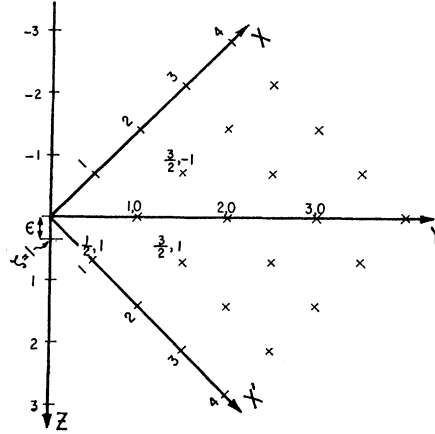


FIG. 2. Relation between old  $(x',x)$  and new  $(y,z)$  labeling of elements of singlet density matrix  $\rho_1(x',x)$ .

mean energy per electron. In that case we seek the solution for the lowest energy state of the neutral atom. If the atom is at temperature  $T = 0$ , we must require that  $\rho_N$ , or the associated  $f_N$  should represent a pure state as indicated by (6). [For nonzero temperatures all equations remain unchanged except for (6).] The purpose of the new variables  $y, z$ , and  $\zeta$  is the following: Envisage  $\rho_1(x',x)$  defined at the lattice points in the  $(x',x)$  plane, then the  $y, z$  labeling of these points corresponds to a  $45^\circ$  rotation, and a change in scales (see Fig. 2);  $y$  labels a distance along lines parallel to the diagonal,  $z$  the perpendicular distance from the diagonal. Since our limiting process shifts the problem in the semiclassical region, the off-diagonal elements must decrease in size and oscillate fast; thus only small values of  $z$  become of importance. For this reason we introduce the new variable  $\zeta = z/\epsilon$ , which amounts to introducing a new unit of length along the  $z$  axis, which is  $\epsilon$  times the previous one, using thereby a yardstick more adapted to the problem. This is also evident from the fact that in terms of these variables the coefficients in the equation-system (11) contain positive powers of  $\epsilon$ , and as  $\epsilon \rightarrow 0$  the coefficients become independent of  $\epsilon$ . (At this stage one could take the Fourier transform with respect to  $z$  or  $\zeta$ , a natural step to do for oscillatory functions; this introduces the so-called Wigner functions. However, the general treatment seems to be simpler without this step, and consequently we shall formulate the theory in terms of the  $f$  functions, and will use Fourier transforms only as a tool to solve the resulting equations.)

**5. CHARACTERISTIC FEATURES OF THE EQUATION SYSTEM AND THE SUPPLEMENTARY CONDITIONS; NONANALYTICITY DIFFICULTIES**

The solution of (11) subject to conditions (12), (13), and (14) is equivalent to the full, correct solution of the problem; in order to obtain an approximate solution we must study the characteristic features of the

problem for small  $\epsilon$ . As  $\epsilon$  tends to zero, in (11) all coefficients of  $f_s$  and  $f_{s+1}$  become independent of  $\epsilon$ ; moreover, we observe that there are no terms linear in  $\epsilon$ , and two of the terms proportional to  $\epsilon^3$  disappear entirely. These terms have a simply physical interpretation. The set of  $s$  particles described by  $f_s$  interact with the external field [second term of (11)], with each other, and with the  $N-s$  other particles; as  $\epsilon$  tends to zero the interaction *within* the set of  $s$  particles becomes negligible compared with the other interactions, being proportional to  $\epsilon^3$ ; consistently with this the interaction with the  $N-s$  other particles can be approximated with the interaction of  $N$  other particles. Because of this, the  $s$  particles within the group behave as if they would move independently of each other, their behavior being determined by the interaction of each with the particles outside the group. Thus we expect that up to and including order  $\epsilon^2$  the  $f_s$  functions should be expressible in terms of  $f_1$ . Thus the structure of the Eqs. (11) suggests that (a) using the variables  $y$  and  $\zeta$ ,  $f_s$  will depend only on positive powers of  $\epsilon$  (this, of course, was just reason to introduce these variables); (b) there shall be no terms linear in  $\epsilon$ ; (c) up to  $\epsilon^2$ ,  $f_s$  shall be expressible in terms of  $f_1$ . Introduce now functions  $f_s^{(k)}(y_1, \dots, y_s, \zeta_1, \dots, \zeta_s)$  independent of  $\epsilon$ , where  $k$  denotes the order of the approximation. Then our expectations can be formulated in the expression

$$f_s(y_1, \dots, y_s; \zeta_1, \dots, \zeta_s | \epsilon) = \sum_{k=0} \epsilon^k f_s^{(k)}, \quad (15)$$

with  $f_s^{(0)} = F[f_1^{(0)}]$ ,  $f_s^{(1)} \equiv 0$ ,  $f_s^{(2)} = G[f_1^{(2)}]$ ;  $F$  and  $G$  are unknown functionals, independent of  $\epsilon$ .

The following questions are to be faced: (a) Does (11) have solutions of this form at all; (b) if so, are these solutions compatible with the supplementary conditions; (c) if so, how to determine  $F$  and  $G$  together with  $f_1^{(0)}$ ,  $f_1^{(2)}$  from the equations and supplementary conditions? The difficulty we encounter in answering these questions is due to the fact that the introduction of the small parameter gives no clue as to the construction of the functions  $F$  and  $G$ , while the existence of the solutions will depend on this construction. Omitting in (11) the term containing the double sum on  $i$  and  $j$ , which is proportional to  $\epsilon^3$ , we see that the equation contains only a sum of operators each acting on one set of  $y, \zeta$  variables with a given index. This, then suggests that the functionals should simply be the product of their argument functions each carrying variables with a given index. Indeed, it is easy to show that one can find such solutions to (11) [see next section, Eq. (27)], however, they violate the symmetry conditions (4) for  $s > 1$ , since they correspond to solutions which obey Boltzmann statistics.<sup>6</sup> It is natural that the symmetry condition will cause trouble if we

<sup>6</sup> It is rather interesting that such a solution should still exist, since in constructing the small parameter  $\epsilon$  we made already explicit use of the exclusion principle.

use the variables  $y, \zeta$ . In term of these variables it is impossible to express the exclusion principle in an  $\epsilon$ -independent way. Thus the variables most suited for the discussion of the equations of motion are not so useful when it comes to express the conditions implied by the exclusion principle. Indeed the command: exchange  $x_1'$  and  $x_2'$ , keep  $x_1, x_2$  fixed, amounts to replacing  $y_1$  with  $\frac{1}{2}(y_1+y_2) + \frac{1}{4}\epsilon(\zeta_1-\zeta_2)$ ;  $y_2$  with  $\frac{1}{2}(y_1+y_2) - \frac{1}{4}\epsilon(\zeta_1-\zeta_2)$ ;  $\zeta_1$  with  $(y_2-y_1)/\epsilon + \frac{1}{2}(\zeta_1+\zeta_2)$ ;  $\zeta_2$  with  $-(y_2-y_1)/\epsilon + \frac{1}{2}(\zeta_1+\zeta_2)$ . This explicit appearance of  $\epsilon$  casts doubt on the possibility of expressing  $f_s(|\epsilon)$  as a power series in  $\epsilon$  with only positive powers, if the symmetry condition is to be satisfied. Indeed, for  $s=2$  the symmetry condition reads

$$\begin{aligned} f_2(y_1, y_2; \zeta_1, \zeta_2 | \epsilon) &= -f_2[\frac{1}{2}(y_1+y_2) + (\epsilon/4)(\zeta_1-\zeta_2), \frac{1}{2}(y_1+y_2) \\ &\quad - (\epsilon/4)(\zeta_1-\zeta_2); (1/\epsilon)(y_2-y_1) + \frac{1}{2}(\zeta_1+\zeta_2), \\ &\quad - (1/\epsilon)(y_2-y_1) + \frac{1}{2}(\zeta_1+\zeta_2)]. \quad (16) \end{aligned}$$

Now we see why  $f_2$  cannot be a power series involving only positive powers of  $\epsilon$ , with coefficients which are functions of  $y$  and  $\zeta$  only.  $f_2$  will be oscillatory in  $\zeta_1$ , and  $\zeta_2$ , i.e., in the third and fourth variables. On account of (16), this means that it must also be oscillatory in  $(y_1-y_2)/\epsilon$  thus it will have to contain, in general, arbitrarily high negative powers of  $\epsilon$ . This does not preclude the possibility that there should be a solution of  $\epsilon \rightarrow 0$ ; it only asserts that the  $\epsilon$  dependence of the solution cannot be analytic around  $\epsilon=0$  if it also satisfies the exclusion principle. This squashes our hopes of finding a solution of the form (15), and we must go about the solution differently. First, let us see whether there is a solution for  $\epsilon=0$ ; next, investigate the possibility of an approximation scheme which is not a simple power-series expansion in  $\epsilon$ . In the remainder of the paper we will discuss the  $\epsilon=0$  approximation and only touch upon the more difficult problem of the approximation scheme.

## 6. THE ZERO-ORDER APPROXIMATION

### The Reduction of the Hierarchy

For  $\epsilon \rightarrow 0$ ,  $D_r \rightarrow \zeta_r(\partial/\partial y_r)$ , and the equations read

$$\begin{aligned} \left\{ \frac{\partial^2}{\partial y_1 \partial \zeta_1} + \zeta_1 \frac{\partial \phi(y_1)}{\partial y_1} \right\} f_1(y_1, \zeta_1) \\ - \int d^3 y \left[ \zeta_1 \frac{\partial}{\partial y_1} \phi(y_1 - y_2) \right] f_2(y_1, y_2; \zeta_1, 0) = 0, \quad (17a) \end{aligned}$$

$$\begin{aligned} \sum_{1 \leq i \leq s} \left\{ \frac{\partial^2}{\partial y_i \partial \zeta_i} + \zeta_i \frac{\partial \phi(y_i)}{\partial y_i} \right\} f_s(y_1, \dots, y_s; \zeta_1; \dots, \zeta_s) \\ \times \sum_{1 \leq i \leq s} \int d^3 y_{s+1} \left[ \zeta_i \frac{\partial \phi(y_i - y_{s+1})}{\partial y_i} \right] \\ \times f_{s+1}(y_1, \dots, y_s, y_{s+1}; \zeta_1, \dots, \zeta_s, 0) = 0, \\ (s=2, 3, \dots); \quad (17b) \end{aligned}$$

with

$$f_s(y_1, \dots, y_s; \zeta_1, \dots, \zeta_s) = \int d^3 y_{s+1} f_{s+1} \times (y_1, \dots, y_s, y_{s+1}; \zeta_1, \dots, \zeta_s, 0); \quad (18a)$$

where

$$f_s\left(\frac{x'_1+x_1}{2L}, \dots, \frac{x'_s+x_s}{2L}; \frac{x'_1-x_1}{\epsilon L}, \dots, \frac{x'_s-x_s}{\epsilon L}\right) \quad (18b)$$

must change its sign if we interchange any two primed variables,  $x'_i, x'_j$ , say ( $i=1, \dots, s; j=1, \dots, s; i \neq j$ ), or any two unprimed variables,  $x_i, x_j$ , say; all  $f_s$  must be normalized to unity, the  $f_s$  must describe a pure state, the energy must be a minimum.

Now we construct the functional  $F$ , guided by the Hartree-Fock scheme. To do this we temporarily return to the density matrices  $\rho_s$ . Let  $f_1^{(0)}(y_1, \zeta_1)$  be independent of  $\epsilon$ , *qua* function of  $y$  and  $\zeta$ ; a  $\rho_1(x', x)$  is now defined by

$$L^3 \rho_1(x', x) = f_1^{(0)}\left(\frac{x'_1+x_1}{2L}, \frac{x'_1-x_1}{\epsilon L}\right).$$

$\rho_1$ , of course, will depend on  $\epsilon$  in a complicated way. We proceed to  $f_s$  and  $\rho_s$ , ( $s > 1$ ) in a similar manner. With  $f_s(y_1, \dots, y_s; \zeta_1, \dots, \zeta_s | \epsilon)$  a  $\rho_s(x'_1, \dots, x'_s; x_1, \dots, x_s)$  is associated by

$$f_s(y_1, \dots, y_s; \zeta_1, \dots, \zeta_s | \epsilon) = L^{3s} \rho_s(x'_1, \dots, x'_s; x_1, \dots, x_s),$$

where

$$x'_k/L = y_k + \frac{1}{2}\epsilon\zeta_k, \quad x_k = y_k - \frac{1}{2}\epsilon\zeta_k.$$

The functional relation is now obtained as follows:

First, construct  $\rho_s$  as a determinant,

$$\rho_s(x'_1, \dots, x'_s; x_1, \dots, x_s) = \frac{N^s(N-s)!}{N!} \begin{vmatrix} \rho_1(x'_1, x_1) & \dots & \rho_1(x'_1, x_s) \\ \vdots & & \vdots \\ \rho_1(x'_s, x_1) & \dots & \rho_1(x'_s, x_s) \end{vmatrix}. \quad (19)$$

Next, express all the  $x$ 's through  $y$  and  $\zeta$ , and put  $N = \epsilon^{-3}$ . Finally, let  $\epsilon \rightarrow 0$  wherever it still appears, after everything is expressed in terms of  $y$  and  $\zeta$  (not  $x$ !). The resulting  $f_s^{(0)}$  will be our zeroth approximation. (The appearance of the  $N^s$  factor in addition to the more usual combinational term is due to the fact that here  $\rho_1$  is normalized to unity and not to  $N$ . This way, as  $N \rightarrow \infty$  the combinatorial factor goes to one.) These functions should satisfy the supplementary conditions and the equations of motion. Let us start with the supplementary conditions. The recursion relation between  $\rho_2$  and  $\rho_1$  reads as

$$\int \rho_2(x'_1, x'_2; x_1, x_2) d^3 x_2 = \rho_1(x'_1, x_1).$$

According to (19),  $\rho_2$  is given by

$$\rho_2(x'_1, x'_2; x_1, x_2) = [N/(N-1)] [\rho_1(x'_1, x_1)\rho_1(x'_2, x_2) - \rho_1(x'_1, x_2)\rho_1(x'_2, x_1)].$$

Substituting this in the previous equation we obtain the integral condition

$$N \int d^3 x'' \rho_1(x', x'') \rho_1(x'', x) = \rho_1(x', x). \quad (20)$$

Now we show that if (20) is fulfilled, the other recursion relations for  $s \geq 2$  are also satisfied. Take  $\rho_s$  with  $x'_s = x_s$  and expand the determinant according to elements in the  $s$ th column; multiply the coefficients into the last row and integrate over  $x_s$ . The integration can be performed using (20) and we indeed obtain  $\rho_{s-1}$  as defined by (19). This shows that all recursion relations are fulfilled if (20) is satisfied. Let us demonstrate now that if (20) is satisfied the system is in a pure state, i.e., it is at the temperature zero. The system is in a pure state if  $\rho_N$  is idempotent, i.e., if

$$\int d^3 x_1'' \dots d^3 x_N'' \rho_N(x'_1, \dots, x_N'; x_1'', \dots, x_N'') \times \rho_N(x_1'', \dots, x_N''; x_1, \dots, x_N) = \rho_N(x'_1, \dots, x_N'; x_1, \dots, x_N).$$

Again, we can perform the integrations using (20) and we find that  $\rho_N$  is idempotent. Thus, the only conditions not yet satisfied through (20) are the normalization condition on  $f_1$ , and the minimal condition on the energy. We now express (20) and the normalization condition in terms of  $f_1^{(0)}$ . Substitute in (20)  $\rho_1 = f_1^{(0)}(y, \zeta)/L^3$  with  $x'/L = y + \frac{1}{2}\epsilon\zeta$ ,  $x/L = y - \frac{1}{2}\epsilon\zeta$  and put  $N = \epsilon^{-3}$ . Change the integration variables from  $x''$  to  $s$  by  $(x'' - x)/\epsilon L = s$ ; one gets

$$\int d^3 s f_1^{(0)}(y + \frac{1}{2}\epsilon s, \zeta - s) f_1^{(0)}[y - \frac{1}{2}\epsilon(\zeta - s), s] = f_1^{(0)}(y, \zeta). \quad (21)$$

Letting  $\epsilon \rightarrow 0$ , we obtain

$$\int d^3 s f_1^{(0)}(y, \zeta - s) f_1^{(0)}(y_1, s) = f_1^{(0)}(y, \zeta). \quad (22)$$

The normalization condition reads

$$\int f_1^{(0)}(y, 0) d^3 y = 1. \quad (23)$$

Thus, our problem is reduced to show that the so constructed  $f_s^{(0)}$  functions satisfy (17), (22), (23), and the minimal condition on the energy. We shall accomplish this in two steps. First, we show that the  $f_s^{(0)}$  functions for  $s > 1$  satisfy (17b) if  $f_1^{(0)}$  satisfies (17a); next, we show that the set of equations (17b), (22), and (23) for

$f_1^{(0)}$ , coupled with the minimum condition is nothing else but the TF theory. To accomplish the first step we need the  $f_s^{(0)}$  functions in terms of  $f_1^{(0)}$ . Let us start with  $f_2^{(0)}$ . Before going to the limit  $\epsilon \rightarrow 0$ , we get from (19)

$$f_2(y_1, y_2; \zeta_1, \zeta_2 | \epsilon) = \frac{1}{1 - \epsilon^3} \left\{ f_1^{(0)}(y_1, \zeta_1) f_1^{(0)}(y_2, \zeta_2) - f_1^{(0)} \left( \frac{1}{2}(y_1 + y_2) + \frac{\epsilon}{4}(\zeta_1 - \zeta_2), \frac{y_1 - y_2}{\epsilon} + \frac{1}{2}(\zeta_1 + \zeta_2) \right) \times f_1^{(0)} \left( \frac{y_1 + y_2}{2} - \frac{\epsilon}{4}(\zeta_1 - \zeta_2); - \frac{(y_1 - y_2)}{\epsilon} + \frac{1}{2}(\zeta_1 + \zeta_2) \right) \right\}. \quad (24)$$

In the semiclassical region the off-diagonal elements of  $\rho_1$  decrease in size and oscillate fast. In terms of  $f_1$  this means that  $f_1$  for a fixed value of  $y$  must tend to zero and oscillate fast as  $\zeta$  tends to infinity. Thus we seek solutions for which  $f_1(y, \infty) = 0$ . Now let  $\epsilon$  tend to zero. The second term is then always zero, unless  $y_1 = y_2$  in which case it has the finite value

$$f_1^{(0)}[y_1, \frac{1}{2}(\zeta_1 + \zeta_2)] f_1^{(0)}[y_2, \frac{1}{2}(\zeta_1 + \zeta_2)].$$

Hence,

$$f_2^{(0)}(y_1, y_2; \zeta_1, \zeta_2) = \lim_{\epsilon \rightarrow 0} f_1^{(0)}(y_1, \zeta_1) f_1^{(0)}(y_2, \zeta_2) - \delta_{y_1 - y_2, 0} f_1^{(0)}[y_1, \frac{1}{2}(\zeta_1 + \zeta_2)] f_1^{(0)}[y_2, \frac{1}{2}(\zeta_1 + \zeta_2)], \quad (25)$$

where  $\delta_{k,0}$  is a Kronecker  $\delta$  and not a Dirac  $\delta$ . [We must add the stipulation  $\epsilon \rightarrow 0$  since the symmetry properties required by the exclusion principle are expressed through the variables  $x'$ ,  $x$  and their relation to  $y$ ,  $\zeta$  involves  $\epsilon$ . This makes  $\epsilon$  appear each time explicitly in the right-hand side of (25) whenever we interchange  $x'$  and  $x$ .] This result can be easily generalized for the higher  $f_s^{(0)}$  functions. The rule is as follows. Think of the expanded determinant in (19); each term in the sum will contain  $s\rho_1$  factors; of these, some  $\rho_1$  factors will have the same index on both the primed and unprimed  $x$  variables, e.g.,  $\rho_1(x'_k, x_k)$ ; the others will carry variables where the two indices differ, e.g.,  $\rho_1(x'_k, x_l)$ . To get the corresponding  $f_s^{(0)}$ , replace each  $\rho_1$  where the indices are the same, say  $k$ , by  $f_1^{(0)}(y_k, \zeta_k)$ , and replace each  $\rho_1(x'_k, x_l)$ , where the indices on the two variables are different ( $k$  and  $l$ , say) by  $\delta_{y_k - y_l, 0} f_1^{(0)} \times (y_k, \frac{1}{2}(\zeta_k + \zeta_l))$ . Now we are prepared to solve (17) in the limit  $\epsilon \rightarrow 0$ . Write (17a) as

$$A_1 f_1(1) + J_{1,2} [f_2(1,2)] = 0 \quad (26)$$

where  $A_1$  is the operator  $\partial^2 / \partial y_1 \partial \zeta_1 + \zeta_1 (\partial \phi / \partial y_1)$ , and  $J_{1,2}$  is the operator  $(-1) \int d^3 y_2 \int d^3 \zeta_2 \delta(\zeta_2) \zeta_1 [\partial \phi(y_1 - y_2) / \partial y_1]$ . The arguments in the  $f$  functions are indicated by the index of the argument, e.g.,

$$f_2(1,2) = f_2(y_1, y_2; \zeta_1, \zeta_2).$$

The set (17b) reads then

$$\sum_{r=1}^s A_r f_s(1, \dots, s) + \sum_{r=1}^s J_{r,s+1} [f_{s+1}(1, \dots, s+1)] = 0. \quad (27)$$

We first show that (27) is satisfied if  $f_s$  is a product of  $f_1^{(0)}$ 's, provided  $f_1^{(0)}$  satisfies (26). [By (25)  $f_s$  is this product if all  $y$ 's are different.] Then  $f_s(1, \dots, s) = f_1^{(0)}(1) \dots f_1^{(0)}(s)$ , and  $J_{r,s+1} [f_{s+1}(1, \dots, s+1)] = f_1^{(0)}(1) \dots f_1^{(0)}(s) J_{r,s+1} [f_1^{(0)}(s+1)]$ . Equations (26) and (27) become

$$A_1 f_1^{(0)}(1) + f_1^{(0)}(1) J_{1,2} [f_1^{(0)}(2)] = 0; \quad (28)$$

$$1 f_1^{(0)}(2) \dots f_1^{(0)}(s) \{ A_1 f_1^{(0)}(1) + f_1^{(0)}(1) J_{1,s+1} [f_1^{(0)}(s+1)] + f_1^{(0)}(1) 1 f_1^{(0)}(3) \dots f_1^{(0)}(s) \{ A_2 f_1^{(0)}(2) + f_1^{(0)}(2) J_{2,s+1} [f_1^{(0)}(s+1)] + \text{same for index } 3 + \dots + \text{same for index } s \} \} = 0. \quad (29)$$

Thus, if  $f_1^{(0)}(1)$  satisfies (28), then (29) is automatically satisfied for any  $s$ . If the  $y$ 's are not all different, we proceed as follows. First, we observe that in (26) the second term in  $f_2$  [see (25)] does contribute nothing, since we integrate a function, which is zero everywhere except at a point, where it is finite.<sup>7</sup> Next, we observe that for the same reason the integral in (27) contributes nothing as long as in the integrand there is a Kronecker  $\delta$  present which carries a  $y_{s+1}$ . All such terms must carry a factor  $f_1^{(0)}(s+1)$  according to the construction; thus they must be  $\rho_1(x_{s+1}', x_{s+1})$  times the minor of  $\rho_1(x_{s+1}', x_{s+1})$  in the determinant. Consequently, under the operator  $J_{r,s+1}$  we can write  $f_{s+1}(1, \dots, s+1) = f_s(1, \dots, s) f_1^{(0)}(s+1)$ , and (27) becomes

$$\sum_{r=1}^s A_r f_s(1, \dots, s) + f_s(1, \dots, s) \times \sum_{r=1}^s J_{r,s+1} [f_1^{(0)}(s+1)] = 0, \quad (s=1, 2, \dots). \quad (30)$$

[This expression also contains the product of all the diagonal elements, for which we have already shown the truth of (30).] Now interpret  $\delta_{y,0}$  as an even function of  $y$ , then its derivative is zero, and  $A_r$  does not act on the deltas in the product; this makes all deltas a multiplicative factor in (30). If all the  $y$ 's are not equal to each other, this factor is zero, and the equation is satisfied; if all the  $y$ 's have the same value, cancel the  $\delta$  factors, and we are to satisfy the set (30) with the

<sup>7</sup> It is easy to see that the  $(y_1 - y_2)^{-2}$  type of singularity due to  $\partial \phi(y_1 - y_2) / \partial y_1$  does not affect this argument.



stipulation  $y_1=y_2=\dots=y_s$ . Now again, as before, the equation breaks up into a sum of terms, each of which vanishes, if (30) is satisfied for  $s=1$ . This is, however, satisfied if we require (28) to be true. Thus, in the limit  $\epsilon=0$  we have solved the whole hierarchy of equations if we can solve (28) for  $\epsilon=0$ .

**The Reduced Hierarchy and the Dirac Scheme**

The problem is then solved if we find a solution of (28), (22), and (23) which minimizes the energy. Equation (28) is the equation of motion of the singlet density matrix; (22) expresses the two auxiliary conditions that the exclusion principle should be satisfied, and that the system should be in a pure state; (23) is a normalization condition. This set of equations are related to the set which formed the starting point of Dirac's investigations.<sup>2</sup> Dirac introduces a singlet density matrix, normalized to  $N$ , and stipulates that this density matrix should be a solution of the Hartree-Fock scheme with the subsidiary condition that the singlet density matrix should be idempotent, and that the energy be a minimum. Then he proceeds to solve this set of equations in the limit as Planck's constant tends to zero. Equation (28) is related to the equation of motion in the Hartree-Fock scheme, (22) to the idempotency condition, (23) to the normalization condition. However, in the further development there appears a disparity. Dirac solves in this limit the idempotency condition by an heuristic assumption on the form of the singlet density matrix; using the so resulting density matrix in the equations of motion he finds the TF solution, *amended by exchange terms, but with no other corrections*. This is astonishing for two reasons. First, according to our estimates in Sec. 3, the exchange terms are second-order corrections. Second, there is another second-order correction, the Weizsäcker correction. Thus, either no correction term should appear, or both. (Indeed, one of the more mysterious features of the Weizsäcker correction has always been that it somehow failed to appear in Dirac's approximation.) The inconsistency arises through the heuristic assumption used in solving the idempotency condition. This is a correct lower-order approximation; however, to this approximation the exchange terms in the equations of motion do also vanish [see (25)], the same way as the terms containing the Weizsäcker correction, and which indeed were tacitly put equal to zero by Dirac, when he equated the kinetic-energy term with its classical limit,  $p^2/2m$ .

For this reason in the next section we shall analyze the solution of our set of equations with somewhat greater care as usual, to demonstrate that in zeroth order the TF solutions are only obtained. To accomplish this aim we solve the equations in a manner which exhibits the similarities with the usual TF derivation as much as possible, instead of striking out along the path suggested by Dirac.

**7. THE THOMAS-FERMI SOLUTION**

We seek the solution of (28), (22), (23) which makes the energy a minimum. Let us start with (22) and (23). Fourier analyze  $f_1^{(0)}$  in  $\zeta$ :

$$f_1^{(0)}(y,\zeta) = (2\pi)^{-3} \int d^3k w(y,k) e^{ik \cdot \zeta}. \tag{31}$$

Equation (22) asserts that

$$w(y,k)^2 = w(y,k), \tag{32}$$

or

$$w(y,k) = 1, \text{ or } 0. \tag{33}$$

The location of the boundary  $h(y,k)=0$  separating the  $w=1$  and  $w=0$  domains (which can be multiply connected) is left undetermined by (22), while the normalization condition (23) merely requires that the volume of the  $w=1$  region be  $(2\pi)^3$ . Observe that the determination of the boundary  $h=0$  completes the solution of the problem. This is furnished by Eq. (28) and the minimal condition. Equation (28) written out in full reads:

$$\left\{ \frac{\partial^2}{\partial y \partial \zeta} + \zeta \frac{\partial \phi(y)}{\partial y} \right\} f_1^{(0)}(y,\zeta) - f_1^{(0)}(y,\zeta) \int d^3y_2 \zeta \frac{\partial \phi(y-y_2)}{\partial y} f_1^{(0)}(y_2,0) = 0. \tag{34}$$

Substitute (31) into (34) and observe that  $w \zeta e^{ik \cdot \zeta} \equiv -i w (\partial e^{ik \cdot \zeta} / \partial k) \rightarrow i (\partial w / \partial k) e^{ik \cdot \zeta}$  by partial integration. We obtain:

$$k (\partial w / \partial y) - (\partial \Psi / \partial y) (\partial w / \partial k) = 0, \tag{35a}$$

$$\Psi(y) = -\phi(y) + \int d^3y_2 \phi(y-y_2) \int d^3k_2 w(y_2, k_2); \tag{35b}$$

$$w(y,k) = 1, \text{ or } 0.$$

Equation (35) is the same as the classical Liouville equation for a one-particle distribution function  $w(y,k)$ ,  $k$  being a dimensionless momentum variable,  $y$  a dimensionless position variable, and  $\Psi$  a dimensionless potential energy. The latter is a self-consistent potential since it depends on  $\int d^3k w(y,k)$ , which is proportional to the (yet unknown) density: thus (32) is the self-consistent field problem of Thomas and Fermi. Equation (35a) gives the equation of motion, (35b) the exclusion principle at  $T$  equal to zero. This is to be solved with the auxiliary condition that the total energy  $\int d^3k \times \int d^3y (\frac{1}{2}k^2 + \Psi) w$  be a minimum. What restrictions are placed by (35a) on the location of the boundary  $h=0$ ? A straightforward substitution shows that  $w(y,k)$  can only be a function of the combination  $\frac{1}{2}k^2 + \Psi(y)$ . (In a stationary state the distribution function can only be a function of the constants of

motion; the angular momentum being by hypothesis zero, only the energy  $E = \frac{1}{2}k^2 + \Psi$  remains.) Hence, the boundary  $h=0$  must be a  $E = \text{const}$  surface, or several different energy surfaces pieced together.

To determine the boundary we must know (a) which energy surface, or surfaces, will be used, i.e., the determination of the constants in the  $E = \text{const}$  equation; (b) the potential energy  $\Psi$ .

We first answer (a). In the 6-dimensional  $(y, k)$  space (Fig. 3) one constructs the  $E = \text{const}$  surfaces; they will be spherically symmetrical in both the  $k$  three-space, and  $y$  three-space. The former is a consequence of  $E$  containing  $k^2$  only; the latter is due to the fact that  $\Psi$  can only depend on  $|y|$ , since  $\phi$  is a function of  $|y|$ , and so is  $\int d^3k w(y, k)$  by symmetry. Were the angular momentum of the atom different from zero, a preferred plane would exist. (In the one-dimensional situation depicted in Fig. 3. This symmetry means that the  $E = \text{const}$  surfaces are symmetrical with respect to both the  $y$  and  $k$  axis.) By assumption only bound states should exist; thus  $w(k, y) = W(E)$  must be zero if  $E > 0$ ; for  $E < 0$   $W(E)$  must be zero or one. In other words, we could have a  $W$  which consists of layers of 0 and 1, each layer bounded by  $E = \text{const}$  surfaces. (E.g., we could have on Fig. 2  $W = 1$  between the  $E = 0, E = E'$  surfaces,  $W = 0$  between the  $E = E'$  and  $E = E''$  surfaces, etc.)

Now, it is possible to show that (a) the minimum energy obtains if there are no gaps, thus  $W(E) = 1$  if  $E \leq E_c \leq 0$ , where  $E_c$  is a critical energy; (b) the equations have no solution unless  $E_c = 0$ . (The layered distributions correspond to excited states.) Thus

$$\begin{aligned} W(E) &= 1 & E \leq 0, \\ W(E) &= 0 & E > 0, \\ E &= \frac{1}{2}k^2 + \Psi(y). \end{aligned} \tag{36}$$

To answer (b) we proceed as follows: Take the Laplacian of  $\Psi$  with respect to  $y$ . We obtain

$$\Delta \Psi = 4\pi \delta(y) - 4\pi \int w(y, k) d^3k, \tag{37}$$

since  $\Delta \phi = \Delta(1/|y|) = -4\pi \delta(y)$ . The integral over  $w$  can be simply performed. Fix  $y$ ; for each  $y$ ,  $k$  can range over all values less than or equal to  $k_m(y)$  defined by  $\frac{1}{2}k_m^2 + \Psi = 0$ ; for all these values of  $k$ ,  $w$  is equal to one; hence the integral is  $(4\pi/3)k_m^3$ . (The shaded area is

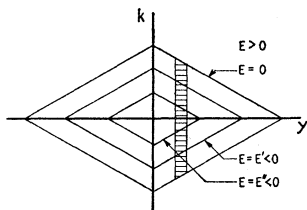


FIG. 3. Qualitative picture of  $(k, y)$  space, reduced  $\mu$  space of electron,  $k$ -reduced momentum,  $y$ -reduced position; several constant-energy surfaces are shown.

Fig. 2.) Thus we get the two equations

$$\begin{aligned} \Delta \Psi &= -4\pi \delta(y) - 4\pi(4\pi/3)k_m^3(y), \\ \frac{1}{2}k_m^2 + \Psi &= 0. \end{aligned} \tag{38}$$

Equation (38) constitutes the standard set of Thomas-Fermi equations in dimensionless variables. The numerical factors are different. This is due to two trivial causes. First, we did not scale out  $4\pi$ 's and other numbers with our choice of  $L$ ; second, as we mentioned, we omitted the factor 2 arising from the additional summation to be performed over the spin states. This then shows that in the limit  $\epsilon \rightarrow 0$  the TF theory is a rigorous solution of the  $N$ -body problem.

### 8. THE INCONSISTENT NEXT APPROXIMATION

We have seen that the simple power-series expansion (15) does not exist. In spite of this it may be worthwhile to pretend temporarily its existence, in order to observe through what anomalies the equations inform us that we are attempting the impossible.

The pattern is clear. First, we have to assume a functional  $G$  which connects the  $f_s$  with  $f_1$  to the next order in  $\epsilon$ , still satisfying the exclusion principle. This, with the recursion relations gives a condition on  $f_1$  which must be solved together with the equations of motion for the  $f_s$ . Let us assume that  $G$  is of the same form as  $F$ ; thus, we extend to second order in  $\epsilon$  the determinantal construction of the  $f_s$  from  $f_1$ . Then the recursion relations give again Eq. (21) as a condition, with  $f_1(y, \zeta) = f_1^{(0)}(y, \zeta) + \epsilon^2 f_1^{(2)}(y, \zeta)$  in place of  $f_1^{(0)}$ , and with  $y + \frac{1}{2}\epsilon \zeta$ ,  $y - \frac{1}{2}\epsilon \zeta$  appearing in the arguments. Expanding it to second order in  $\epsilon$  and equating the coefficient of  $\epsilon^2$  to zero, we get an inhomogeneous linear integral equation for  $f^{(2)}$ , where the homogeneous equation has only zero as its solution. Hence the inhomogeneous equation has, at most, one solution. This means that if a solution exists we have found  $f_1$  to second order without ever investigating the equations of motion to second order. It is clear, however, that such a solution must be incompatible with the equations of motion for the following reason. We can modify the functional  $G$  in an infinite number of ways to give the same relation between  $f_1$  and  $f_2$ , but different relations between  $f_1$  and  $f_3, f_4$ , etc. This leaves the hypothetical solution unchanged but will modify the equations of motion. Thus, this specification of  $G$  is too restrictive. The solution, however, does not exist. If we formally solve the equation we find that the solution diverges. An inconsistent solution can be obtained, however. Assume that  $f_2$  is a determinant, put

$$f_1(y, \zeta | \epsilon) = f_1^{(0)}(y, \zeta) + \epsilon^2 f_1^{(2)}(y, \zeta)$$

and expand it to second order in  $\epsilon^2$ . Insert it in the equation of motion for  $f_1$ , and equate to zero separately the coefficient of  $\epsilon^2$ . This way we obtain the previous zeroth-order equations for  $f_1^{(0)}$ , and an inhomogeneous equation for  $f_1^{(2)}$ . This equation is the one found by

Kompaneets and Pavlovskii, and Baraff and Borowitz, containing the correction terms introduced earlier in a more heuristic way by Dirac (exchange correction) and by Weizsäcker (inhomogeneity correction). As we see, this result is then inconsistent in the sense that the exclusion principle is satisfied to zeroth order, while the equation of motion for  $f_1$  is satisfied to second order; moreover it is left open how far the other equations of motion for  $f_s$  with  $s > 1$  are satisfied, since this involves a decision about the functional dependence of  $f_s$  on  $f_1$ .

### 9. CONJECTURES

As we see, the solution of the hierarchy of equations for the reduced density matrices involves three steps: the discovery of the proper small parameter; the establishment of a functional relation between the singlet density matrix and the higher density matrices; the invention of a calculational scheme to improve the approximations. We shall now comment on each step, bearing in mind what we have shown before. First, we observe the general difficulty that there is no general, all embracing postulate from which all three steps would necessarily follow. We first picked a small parameter such that in zeroth order we should recover the TF model; this of course does not make the small parameter unique. However, the parameter of smallness gives no clue as to the construction of the functional connecting the higher density matrices with the singlet density matrix. Moreover, this functional relation (chosen in such a way as to satisfy the exclusion principle) forces the small parameter already picked to appear in a nonanalytical manner. What we are missing is a postulate which connects the two separate assumptions about the small parameter and the functional relation. The basic feature of the TF model is that the energy is a functional of the density only. This unique feature should be incorporated from the beginning in some manner, as for example to seek those solutions of the hierarchy for which the singlet density matrix is a functional of the density (its diagonal elements) only, the pair density matrix a functional of the singlet density matrix, etc., and trying to determine the unknown functionals through the expansion in terms of a small parameter. Sidestepping this basic predicament, the present treatment suggests two basic improvements. We observe that the present small parameter essentially expresses the smallness of the off-diagonal elements of the singlet density matrix, but it does so in a very crude way. Think of the singlet density matrix in the  $x$  representation; our expansion says that only those elements are of importance which lie along the diagonal in a strip of *uniform* width  $\epsilon$ . In reality this strip will be far from being uniform. As we go (in the  $x$  representation) along the diagonal, the diagonal elements  $\rho(x,x)$  give the density as a function of the radial distance from the nucleus. The heuristic considerations in Sec. 3 show that the TF approximation is good around a

distance  $L$  from the nucleus but poor everywhere else. Close to the nucleus the field is changing too rapidly; far away the density is insufficient. Thus, this strip is rather wide at both ends, becoming narrow in between. Thus, it is unwise to assign the small parameter  $\epsilon$  uniformly in the  $(y,\zeta)$  space; most likely there will be different asymptotic regions in this space with different correct assignment of smallness. One way to accomplish this is to introduce the unknown density distribution in the scale, and hence in the small parameter. Thus the small parameter must be specified implicitly. This already may make the nonanalyticity difficulties disappear. However, it seems to us that another remedy may also be required. In the present scheme, as it is usual, we insisted that the temperature of the atom is absolute zero. This may be too restrictive a stipulation. For, is it not rather preposterous to state, that you wish to determine the energy of the atom within an accuracy of, say, 20%, and at the same time to insist that you know its temperature exactly and not only to the same accuracy as you know the energy? It is likely that a coupled limiting process is required, in which the temperature is treated as an additional small parameter. Preliminary work suggests that this does indeed eliminate some of the difficulties, since at finite temperatures Eq. (22) acquires an additional term  $kT\partial f/\partial\mu$  ( $\mu$  being the chemical potential). Thus, we have essentially a "boundary layer" problem in  $\mu$  around the Fermi surface,  $kT$  being the thickness of the boundary layer. It is a well-known fact of asymptotic analysis that one must *not* treat such cases by putting simply the boundary thickness equal to zero, since this obliterates the highest derivative in the equation.

### 10. SUMMARY AND CONCLUSIONS

We have shown then, that there exists a small parameter and a functional relation between the singlet and higher density matrices such that in the limit as this small parameter tends to zero, the TF solutions are exact solutions of the full  $N$ -body problem, for neutral atoms at absolute zero temperature. One surmises that the same would hold for ions as well, if under ionization we mean that a fraction of the total number of electrons are removed (and not a given number). The problem, however, involves the small parameter in question in a nonanalytical fashion and for this reason a simple power-series expansion cannot be used to go to the next approximation. If we are content to satisfy the exclusion principle to zeroth order, and the equations of motion of the singlet density matrix to next order, we obtain the equations found by Kompaneets and Pavlovskii, and Baraff and Borowitz, which contain the exchange and inhomogeneity correction terms. Finally, we suggest possible steps one could take to get rid of the difficulty generated by the nonanalyticities.

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## Theory of Core-Electron Contributions to Hyperfine Interactions\*

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A convenient method is devised for the calculation of magnetic hyperfine constants in atoms, molecules, and metals taking into consideration the exchange interaction between the core electrons and the unpaired valence electrons. In this method, the core-electron wave functions are perturbed by the nuclear magnetic moment via the Fermi contact term, and the energy of the system is then calculated in the Hartree-Fock approximation using the perturbed core wave functions. The present method is closely related to the exchange perturbation method of Cohen, Goodings, and Heine. However, the former has the advantage of being more flexible in the sense that the same perturbed core-electron functions may be used for the ground and excited states of the atom and for metals without significant error. For lithium atom  $1s^2 2s$  and  $1s^2 2p$  states, we obtained values for the core contribution to the hyperfine constant  $a$  (in  $\text{aI}\cdot\text{S}$ ) of 83.76 Mc/sec and  $-8.9$  Mc/sec in good agreement with the earlier values of Cohen, Goodings, and Heine. We have applied this method to a calculation of the core-polarization correction to the Knight shift in lithium metal using recent wave functions of Kohn and Callaway. The core-polarization corrections produced by the  $s$  and  $p$  parts of the conduction-electron wave function are nearly equal but opposite in sign, while that produced by the  $d$  part is an order of magnitude smaller. This results in a net correction of about  $-5.3\%$  of the direct contribution to the Knight shift from the conduction electrons.

## I. INTRODUCTION

A NUMBER of recent detailed and careful investigations<sup>1-10</sup> of the magnetic hyperfine interaction in atoms and paramagnetic ions have clearly demonstrated the important role of exchange polarization of the core electrons in contributing to the magnetic hyperfine interaction constant. In all these investigations, the method that has been employed has come to be known generally as the unrestricted Hartree-Fock (UHF) method. In keeping with the recent attempt of standardization of nomenclature,<sup>11</sup> we shall call the unrestricted Hartree-Fock method the spin polarized

method (SP). Similarly, the projected unrestricted Hartree-Fock method will be denoted as the projected spin polarized method (PSP).<sup>12</sup> Some of the investigators<sup>2-4,6,9</sup> have handled the SP method self-consistently, while others have used a perturbation approach. To avoid confusion we shall refer to the method of treating the exchange potential as a perturbation, the exchange perturbation method (EP). In recent papers, Nesbet,<sup>7</sup> Marshall,<sup>8</sup> and Heine<sup>13</sup> have discussed possible errors that can occur in the results of calculation by the SP method, because the many-electron wave function used in the SP method is not an eigenfunction of  $\mathbf{S}^2$ , where  $\mathbf{S}$  is the total spin of the atom. From the investigations of these authors, one arrives at the conclusion, that for paramagnetic ions and atoms, this limitation of the SP method is not a serious source of error; but in extending the SP method to metals and molecules, one has to be more careful about the influence of this source of error.

In this paper we are interested in a perturbation method which has the advantage of flexibility over the EP method while not sacrificing accuracy. The accuracy

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<sup>12</sup> The PSP method should be distinguished from the SPP method. In the SPP method one applies the projection operator after an SP calculation is performed to obtain an eigenfunction of  $\mathbf{S}^2$ .

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