

## Analysis of the Statistical Density Matrix\*

K. M. KING AND L. H. THOMAS

*Watson Scientific Computing Laboratory, Columbia University, New York, New York*

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A generalized expression for the statistical field has been obtained which includes the Thomas-Fermi and Thomas-Fermi-Dirac fields as special cases. The behavior of the energy, charge density, boundary density, and electron groups has been investigated for various fields. Fields with exchange are obtained with behavior like the Thomas-Fermi field at the boundary. A singularity in the Thomas-Fermi-Dirac density matrix has been found which leads to an oscillation in the sign of the charge in high angular momentum states. This singularity is related to the necessity for terminating the Thomas-Fermi-Dirac distribution at a finite boundary. Comparison of the Fourier components and wave functions calculated from statistical density matrices for  $\text{Cu}^+$  with the corresponding Hartree-Fock values has revealed that it would not be useful to use the statistical density matrix as a starting point for a Hartree-Fock calculation.

### I. INTRODUCTION

DIRAC has shown that a statistical density matrix can be defined for an atom in its normal state, which is an approximation to the density matrix corresponding to a Hartree-Fock approximation.<sup>1</sup> The equations for the statistical field are then obtainable as the solution to a minimum problem similar to the minimum problem yielding the Hartree-Fock equations. From the density matrix, the number of electrons in each state may be calculated as well as the corresponding wavefunction, although the latter is not unique for an idempotent density matrix.

After a review of the theoretical background, a generalized statistical field is obtained which includes the Thomas-Fermi-Dirac and Thomas-Fermi fields as special cases. The behavior of the energy, charge density, and boundary density for various fields is then investigated. Fields with exchange are found which behave like the Thomas-Fermi field at the boundary.

Statistical fields for  $\text{Cu}^+$  are analyzed to find the number of electrons in each state and the corresponding wave function. This calculation reveals an oscillation in the sign of the charge in high angular momentum states for the Thomas-Fermi-Dirac field and the cause of this oscillation is traced to a singularity in the corresponding density matrix.

### II. THEORETICAL BACKGROUND

The quantum density operator  $\rho$ , for an  $N$ -electron system in the Hartree-Fock approximation to its ground state, may be defined by its representative as<sup>2</sup>

$$\langle \mathbf{r}_s | \rho | \mathbf{r}'_s \rangle = \sum_{j=1}^J \langle \mathbf{r}_s | j \rangle N_j \langle j | \mathbf{r}'_s \rangle, \quad (2.1)$$

where  $\langle \mathbf{r}_s | j \rangle$  is the wave function corresponding to the

$j$ th state of a set of  $J$  states accessible to an electron and  $N_j$  is equal to the number of electrons in the  $j$ th state. In Eq. (2.1),  $\mathbf{r}$  and  $\mathbf{r}'$  stand for the space coordinates of two electrons and  $s_z$  and  $s'_z$  the corresponding spin coordinates. The component states defining  $\rho$  are assumed to be orthonormal so that

$$\sum_{s_z} \langle i | \mathbf{r}_{s_z} \rangle d\mathbf{r} \langle \mathbf{r}_{s_z} | j \rangle = \delta_{ij}, \quad (2.2)$$

where  $\delta_{ij}$  is the Kronecker delta.

The eigenvalues of the density operator are the  $N_j$ 's, since

$$\sum_{s'_z} \int \langle \mathbf{r}_{s_z} | \rho | \mathbf{r}'_{s'_z} \rangle d\mathbf{r}' \langle \mathbf{r}'_{s'_z} | j \rangle = N_j \langle \mathbf{r}_{s_z} | j \rangle, \quad (2.3)$$

using Eqs. (2.1) and (2.2). The exclusion principle can be stated as the requirement that

$$\sum_{s_z'''} \int \langle \mathbf{r}_{s_z} | \rho | \mathbf{r}''_{s_z'''} \rangle d\mathbf{r}'' \langle \mathbf{r}''_{s_z'''} | \rho | \mathbf{r}'_{s'_z} \rangle = \langle \mathbf{r}_{s_z} | \rho | \mathbf{r}'_{s'_z} \rangle, \quad (2.4)$$

that is that  $\rho$  be idempotent. Equation (2.4) is equivalent to the requirement that the eigenvalues of  $\rho$ , the  $N_j$ 's, be equal to 0 or 1.

The particle density can be expressed in terms of the diagonal elements of the density matrix. The particle density in the neighborhood of  $\mathbf{r}$ , with  $z$  coordinate of spin equal to  $s_z$ , is  $\langle \mathbf{r}_{s_z} | \rho | \mathbf{r}_{s_z} \rangle d\mathbf{r}$ . Hence the trace of the density matrix,

$$\sum_{s_z} \int \langle \mathbf{r}_{s_z} | \rho | \mathbf{r}_{s_z} \rangle d\mathbf{r} = \sum_{j=1}^J N_j, \quad (2.5)$$

is equal to  $N$ , the total number of electrons in the atom.

### Density Matrix in the Central Field Approximation

For an electron in a central field a state can be specified by the usual elementary commuting constants of the motion  $n$ ,  $l$ ,  $m_l$ , and  $m_s$ . Taking

$$\langle j | = \langle nlm_l m_s |, \quad (2.6)$$

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<sup>1</sup> P. A. M. Dirac, Proc. Cambridge Phil. Soc. **26**, 376 (1930); **27**, 240 (1930).

<sup>2</sup> E. M. Corson, *Perturbation Methods in the Quantum Mechanics of  $n$ -Electron Systems* (Hafner Publishing Company, New York, 1950), pp. 71, 123.

the representative of the density operator becomes, using wave function notation,

$$\begin{aligned} \langle \mathbf{r} s_z | \rho | \mathbf{r}' s_z' \rangle &= \sum_{n,l,m_l,m_s} \psi_{nl}(\mathbf{r}) \psi_{nl}^*(\mathbf{r}') Y_{lm_l}(\theta, \phi) \\ &\quad \times Y_{lm_l}(\theta', \phi') N_{nlm_l m_s} \delta_{s_z m_s} \delta_{s_z' m_s}, \end{aligned} \quad (2.7)$$

where  $Y_{lm_l}(\theta, \phi)$  is a normalized spherical harmonic and  $\psi_{nl}(\mathbf{r})$  is normalized such that

$$\int_0^\infty \psi_{nl}(\mathbf{r}) \psi_{n'l}^*(\mathbf{r}) r^2 dr = \delta_{nn'}. \quad (2.8)$$

For a spherically symmetric atom

$$N_{nlm_l m_s} = N_{nl}, \quad (2.9)$$

and application of the addition theorem for Legendre polynomials gives

$$\begin{aligned} \langle \mathbf{r} s_z | \rho | \mathbf{r}' s_z' \rangle &= \sum_{n,l} \psi_{nl}(\mathbf{r}) \psi_{nl}^*(\mathbf{r}') P_l(\cos \Theta) \left( \frac{2l+1}{4\pi} \right) N_{nl} \delta_{s_z s_z'}. \end{aligned} \quad (2.10)$$

The trace of the density matrix defined by Eq. (2.10) is equal to  $\sum_{nl} 2(2l+1)N_{nl}$  and hence if  $\rho$  is idempotent,  $N_{nl}$  is equal to 0 or 1 depending upon whether the shell containing  $2(2l+1)N_{nl}$  electrons is empty or full.

### Hartree-Fock Density Matrix

The total electronic energy  $W$  of an  $N$ -electron atom can be expressed in the Hartree-Fock approximation as<sup>3</sup>

$$W = K + V + I + U, \quad (2.11)$$

where

$$K = \sum_{s_z s_z'} \iint \left\langle \mathbf{r} s_z \left| \frac{p^2}{2} \right| \mathbf{r}' s_z' \right\rangle d\mathbf{r}' \langle \mathbf{r}' s_z' | \rho | \mathbf{r} s_z \rangle d\mathbf{r}, \quad (2.12)$$

$$V = \sum_{s_z s_z'} \iint \left\langle \mathbf{r} s_z \left| -\frac{Z}{r} \right| \mathbf{r}' s_z' \right\rangle d\mathbf{r}' \langle \mathbf{r}' s_z' | \rho | \mathbf{r} s_z \rangle d\mathbf{r}, \quad (2.13)$$

$$\begin{aligned} I &= \frac{1}{2} \sum_{s_z s_z'} \iint \langle \mathbf{r} s_z | \rho | \mathbf{r} s_z \rangle \\ &\quad \times \frac{1}{|\mathbf{r} - \mathbf{r}'|} \langle \mathbf{r}' s_z' | \rho | \mathbf{r}' s_z' \rangle d\mathbf{r} d\mathbf{r}', \end{aligned} \quad (2.14)$$

and

$$\begin{aligned} U &= -\frac{1}{2} \sum_{s_z s_z'} \iint \langle \mathbf{r} s_z | \rho | \mathbf{r}' s_z' \rangle \\ &\quad \times \frac{1}{|\mathbf{r} - \mathbf{r}'|} \langle \mathbf{r}' s_z' | \rho | \mathbf{r} s_z \rangle d\mathbf{r} d\mathbf{r}'. \end{aligned} \quad (2.15)$$

<sup>3</sup> V. Fock, Z. Physik **61**, 126 (1930); **75**, 622 (1932); **81**, 195 (1933).

Equations (2.12) through (2.15) specify the total kinetic, potential, interaction, and exchange energy, respectively. The Hartree-Fock equations may be obtained for an  $N$ -electron atom by requiring that  $W$  be stationary, subject to the restrictions that the density matrix as specified by Eq. (2.10) be idempotent and the trace of the density matrix be equal to  $N$ . The solution of the Hartree-Fock equations determines  $\psi_{nl}(\mathbf{r})$  and the elements of the Hartree-Fock density matrix can then be calculated from Eq. (2.10).

### Statistical Approximation to the Hartree-Fock Density Matrix

In the statistical approximation, the representative of the density operator may be taken as

$$\begin{aligned} \langle \mathbf{r} s_z | \rho | \mathbf{r}' s_z' \rangle &= \sum_{s_z''} \int \langle \mathbf{r} s_z | \mathbf{p} s_z'' \rangle N(\mathbf{p}, s_z'') \langle \mathbf{p} s_z'' | \mathbf{r}' s_z' \rangle d\mathbf{p}, \end{aligned} \quad (2.16)$$

where  $N(\mathbf{p}, s_z'')$  is equal to the number of electrons with spin coordinate  $s_z''$  and with momentum in the neighborhood of  $\mathbf{p}$ . If we assume

$$N(\mathbf{p}, s_z'') = 1 \quad \text{for } |\mathbf{p}| \leq P(\xi), \quad (2.17)$$

and

$$N(\mathbf{p}, s_z'') = 0 \quad \text{for } |\mathbf{p}| > P(\xi), \quad (2.18)$$

where  $\xi$  is some average vector associated with  $\mathbf{r}$  and  $\mathbf{r}'$ , Eq. (2.16) becomes

$$\begin{aligned} \langle \mathbf{r} s_z | \rho | \mathbf{r}' s_z' \rangle &= \int_0^{P(\xi)} \int_0^\pi \int_0^{2\pi} \frac{1}{h^3} e^{(i/\hbar) \mathbf{p} \cdot (\mathbf{r} - \mathbf{r}')} p^2 \\ &\quad \times \sin \theta d\varphi d\theta dp \delta_{s_z s_z'}. \end{aligned} \quad (2.19)$$

We have taken

$$\langle \mathbf{r} s_z | \mathbf{p} s_z'' \rangle = \frac{1}{h^{\frac{3}{2}}} e^{(i/\hbar) \mathbf{p} \cdot \mathbf{r}} \delta_{s_z s_z''}. \quad (2.20)$$

Integration of Eq. (2.19) gives

$$\begin{aligned} \langle \mathbf{r} s_z | \rho | \mathbf{r}' s_z' \rangle &= \frac{1}{2\pi^2 r_{12}^3} \{ \sin[P(\xi) r_{12}] \\ &\quad - P(\xi) r_{12} \cos[P(\xi) r_{12}] \} \delta_{s_z s_z'}, \end{aligned} \quad (2.21)$$

where

$$r_{12} = |\mathbf{r} - \mathbf{r}'|, \quad (2.22)$$

and atomic units have been used. We must choose  $\xi(\mathbf{r}, \mathbf{r}')$  so that the density matrix is Hermitian and when  $\mathbf{r}$  equals  $\mathbf{r}'$ ,  $\xi$  must equal  $\mathbf{r}$  so that self-interaction terms between  $U$  and  $I$  cancel. The diagonal elements of this density matrix are

$$\langle \mathbf{r} s_z | \rho | \mathbf{r} s_z \rangle = P^3(r) / 6\pi^2. \quad (2.23)$$

The off-diagonal elements depend on the form taken for  $\xi(\mathbf{r}, \mathbf{r}')$ .

The statistical approximation to the Hartree-Fock density matrix is obtained by determining  $\langle \mathbf{r}s_z | \mathbf{p} | \mathbf{r}'s_z \rangle$  as given by Eq. (2.21), such that  $W$ , as given by Eqs. (2.12) through (2.15), is stationary, subject to the restriction that the trace of the density matrix is equal to  $N$ . The additional condition of idempotency imposed on the Hartree-Fock density matrix is not imposed in determining the statistical density matrix. This means that the statistical density matrix will not necessarily have the eigenvalues 0 or 1 as required by the exclusion principle. If the integral over  $\mathbf{p}$  in Eq. (2.19) is permitted to go to infinity, the representative of the density operator becomes

$$\langle \mathbf{r}s_z | \mathbf{p} | \mathbf{r}'s_z \rangle = \delta(\mathbf{r} - \mathbf{r}') \delta_{s_z s_z'}, \quad (2.24)$$

where  $\delta(\mathbf{r} - \mathbf{r}')$  is a Dirac delta function. With the representative of the density operator defined in this way, the idempotency condition is satisfied. However, if the integral over  $\mathbf{p}$  is restricted to a finite range as it must for a finite number of electrons, Eq. (2.21) is an approximation to an idempotent density matrix which is better the larger  $P(r)$ .

The energy terms in the statistical approximation can be evaluated by substituting Eq. (2.21) into Eqs. (2.12) through (2.15) and evaluating the integrals. To determine  $K$  and  $U$ , the form of  $\xi(\mathbf{r}, \mathbf{r}')$  must be specified. If we take

$$\xi = \frac{1}{2} |\mathbf{r} + \mathbf{r}'|, \quad (2.25)$$

the component terms of  $W$  become<sup>4</sup>

$$K = 2/5\pi \int P^5(r) r^2 dr, \quad (2.26)$$

$$V = -4Z/3\pi \int P^3(r) r dr, \quad (2.27)$$

$$I = 2 \int \int \frac{P^3(r)}{6\pi^2} \frac{1}{|\mathbf{r} - \mathbf{r}'|} \frac{P^3(r')}{6\pi^2} d\mathbf{r} d\mathbf{r}', \quad (2.28)$$

and

$$U = -1/\pi^2 \int P^4(r) r^2 dr. \quad (2.29)$$

The requirement that  $W$  be stationary, subject to the restriction that the trace of the statistical density matrix equals the number of electrons, leads to the differential equation

$$\nabla^2 \varphi(r) = (4/3\pi) P^2(r), \quad (2.30)$$

where  $\varphi(r)$  is the electrostatic potential

$$\begin{aligned} \varphi(r) &= \frac{Z}{r} - \int \frac{P^3(r')}{3\pi^2} \frac{d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} \\ &= P^2(r)/2 - P(r)/\pi - \gamma. \end{aligned} \quad (2.31)$$

This is the Thomas-Fermi-Dirac equation.<sup>1</sup>

<sup>4</sup> L. H. Thomas, J. Chem. Phys. **22**, 1758 (1954).

The Lagrangian multiplier  $\gamma$  corresponds to the requirement that the trace of the density matrix equal  $N$ . There is no universal agreement on the boundary conditions to be satisfied by Eq. (2.30). The Thomas-Fermi-Dirac potential distribution used in this paper was calculated by Thomas<sup>4</sup> and satisfies the boundary conditions:

$$[r\varphi(r)]_{r=0} = Z, \quad (2.32)$$

$$[r\varphi(r)]_{r=R} = Z - N, \quad (2.33)$$

and

$$P(R) = 5/4\pi. \quad (2.34)$$

Boundary condition (2.34) is due to Jensen.<sup>5</sup>

### III. GENERALIZED STATISTICAL MODEL

The form taken for  $\xi$  in determining the statistical density matrix can be generalized in a manner consistent with the fundamental assumptions of the theory. If one takes

$$\xi = (1 + b/2) \mathbf{r}_> + (1 - b/2) \mathbf{r}_<, \quad (3.1)$$

where

$$\begin{aligned} \mathbf{r}_> &= \mathbf{r} \quad \text{if } |\mathbf{r}| \geq |\mathbf{r}'|, \\ \mathbf{r}_> &= \mathbf{r}' \quad \text{if } |\mathbf{r}'| > |\mathbf{r}|, \end{aligned}$$

and

$$\begin{aligned} \mathbf{r}_< &= \mathbf{r} \quad \text{if } |\mathbf{r}| < |\mathbf{r}'|, \\ \mathbf{r}_< &= \mathbf{r}' \quad \text{if } |\mathbf{r}'| \leq |\mathbf{r}|, \end{aligned}$$

the density matrix remains Hermitian and  $\xi = \mathbf{r}$  when  $\mathbf{r} = \mathbf{r}'$ . For  $b=0$ ,  $\xi$  is of the form specified by Eq. (2.25). Choosing  $\xi$  as given by Eq. (3.1) does not alter the form of the representative of the statistical density matrix as given by Eq. (2.21) and the diagonal elements of this matrix are again given by Eq. (2.23). The off-diagonal elements will depend on the parameter  $b$ . We now obtain expressions for the energy terms and the differential equation for the field as a function of  $b$ .

#### Energy Terms

Since  $V$  and  $I$ , as given by Eqs. (2.13) and (2.14), depend on the diagonal elements of the density matrix only, a change in the form of  $\xi$  does not change them and they are again given by Eqs. (2.27) and (2.28).

The integral for the exchange energy can be written

$$U = - \int \int F^2(\xi, \mathbf{r}_{12}) \frac{1}{r_{12}} d\mathbf{r} d\mathbf{r}', \quad (3.2)$$

using Eqs. (2.15) and (2.21) where

$$\begin{aligned} F(\xi, \mathbf{r}_{12}) &= \frac{1}{2\pi^2 r_{12}^3} \{ \sin[P(\xi) r_{12}] \\ &\quad - P(\xi) r_{12} \cos[P(\xi) r_{12}] \}. \end{aligned} \quad (3.3)$$

If one integrates over the angles specifying the orienta-

<sup>5</sup> H. Jensen, Z. Phys. **93**, 232 (1935).

tion of the triangle formed by  $\mathbf{r}$ ,  $\mathbf{r}'$ , and  $\mathbf{r}_{12}$ , one obtains

$$U = -16\pi^2 \int_0^R \int_0^{\pi/2} \int_0^{\cos \varphi/b} \xi^2 r_{12} \sin \varphi F^2(\xi, r_{12}) d\xi d\varphi dr, \quad (3.4)$$

This integral can be transformed to

$$U = -16\pi^2 \int \int \int \xi^2 r_{12} \sin \varphi F^2(\xi, r_{12}) dr_{12} d\varphi d\xi, \quad (3.5)$$

where  $\varphi$  is the angle between  $\mathbf{r}_{12}$  and  $\xi$ . The limits on the  $r_{12}$  and  $\varphi$  integrals are determined by the requirement that

$$r_{>}^2 - r_{<}^2 \geq 0, \quad (3.6)$$

and hence

$$-br_{12}^2 + 2\xi r_{12} \cos \varphi \geq 0. \quad (3.7)$$

Thus for  $b \geq 0$ ,

$$U = -16\pi^2 \int_0^R \int_0^{\pi/2} \int_0^{2\xi \cos \varphi/b} \xi^2 r_{12} \sin \varphi F^2(\xi, r_{12}) dr_{12} d\varphi d\xi, \quad (3.8)$$

and for  $b \leq 0$

$$U = -16\pi^2 \int_0^R \int_0^{\pi/2} \int_0^\infty \xi^2 r_{12} \sin \varphi F^2(\xi, r_{12}) dr_{12} d\varphi d\xi \\ - 16\pi^2 \int_0^R \int_{\pi/2}^\pi \int_{2\xi \cos \varphi/b}^\infty \xi^2 r_{12} \sin \varphi F^2(\xi, r_{12}) dr_{12} d\varphi d\xi. \quad (3.9)$$

Integrating Eqs. (3.8) and (3.9) over  $r_{12}$  and  $\varphi$ , gives

$$U = -\frac{1}{\pi^2} \int_0^R P^4(r) r^2 dr, \quad (3.10)$$

for  $b=0$ , and

$$U = -1/\pi^2 \int_0^R P^4(r) r^2 dr + \frac{b|b|}{2\pi^2} \\ \times \int_0^R \sum_{\alpha=0}^\infty \frac{(-1)^\alpha (2\alpha+3)}{(2\alpha+1)(2\alpha+4)!} P^{2\alpha+4}(r) \\ \times \left(\frac{4r}{b}\right)^{2\alpha+2} dr, \quad (3.11)$$

for  $b \neq 0$ .

Equation (3.10) is the Dirac expression for the exchange energy. For  $b>0$ , the  $\alpha=0$  term in the second integral of Eq. (3.11) cancels the first integral, and  $U$  can be written

$$U = \frac{b^2}{2\pi^2} \int_0^R \left[ -\frac{16}{27} \frac{P^6 r^4}{b^4} + \dots \right] dr. \quad (3.12)$$

The kinetic energy integral, Eq. (2.12), can be written

$$K = 2 \int \int \int \langle \mathbf{r} | p^2/2 | \mathbf{p} \rangle d\mathbf{p} \langle \mathbf{p} | \mathbf{r}' \rangle d\mathbf{r}' \langle \mathbf{r}' | \mathbf{p} | \mathbf{r} \rangle d\mathbf{r}, \quad (3.13)$$

by summing over spin and introducing a projection operator. Integrating over the angles specifying the orientation of the triangle formed by  $\mathbf{r}$ ,  $\mathbf{r}'$ , and  $\mathbf{r}_{12}$  and transformation to  $\xi$ ,  $r_{12}$ , and  $\varphi$  gives

$$K = 8 \int \int \int \int \xi^2 r_{12} p^3 \sin(\varphi r_{12}) F(\xi, r_{12}) \\ \times \sin \varphi d\mathbf{p} dr_{12} d\varphi d\xi, \quad (3.14)$$

where again the limits of integration are determined by condition (3.7). The integral above can be written

$$K = -16\pi^2 \int \int \int \int \xi^2 \left\{ \frac{d^2}{dr_{12}^2} [r_{12} \delta(r_{12})] \right\} \\ \times F(\xi, r_{12}) \sin \varphi dr_{12} d\varphi d\xi, \quad (3.15)$$

where  $\delta(r_{12})$  is a Dirac delta function. Two integrations by parts, and use of the properties of the delta function, gives for all values of  $b$ ;

$$K = 2/5\pi \int P^5(r) r^2 dr. \quad (3.16)$$

Thus only the exchange energy is altered by the change in the form of  $\xi$  specified by Eq. (3.1).

### Differential Equation for the Field

The condition that the total energy be stationary, subject to the restriction that the trace of the density matrix equal the number of electrons in the atom, leads to

$$\varphi(r) = \frac{P^2}{2} - \frac{P}{\pi} - \gamma + \frac{b}{2\pi r} \int_0^{2Pr/|b|} \frac{\sin^2 z}{z^2} dz, \quad (3.17)$$

where the electrostatic potential  $\varphi(r)$  again satisfies the differential Eq. (2.30). Equation (3.17) is equal to the Thomas-Fermi-Dirac expression for the potential when  $b=0$ . For  $b>0$ , the potential can be written

$$\varphi(r) = \frac{P^2}{2} - \gamma - \frac{4P}{9\pi} \left[ \frac{P^2 r^2}{b^2} - \frac{8}{25} \frac{P^4 r^4}{b^4} \right. \\ \left. + \frac{16}{245} \frac{P^6 r^6}{b^6} - \frac{128}{14 \cdot 175} \frac{P^8 r^8}{b^8} + \dots \right]. \quad (3.18)$$

As  $b \rightarrow \infty$

$$\varphi(r) \rightarrow P^2/2 - \gamma, \quad (3.19)$$

which is the Thomas-Fermi potential.<sup>6,7</sup> For  $b < 0$ ,

$$\varphi(r) = \frac{P^2}{2} - \gamma - \frac{2P}{\pi} + \frac{4P}{9\pi} \left[ \frac{P^2 r^2}{b^2} - \frac{8}{25} \frac{P^4 r^4}{b^4} + \dots \right], \quad (3.20)$$

and as  $b \rightarrow -\infty$

$$\varphi(r) \rightarrow P^2/2 - 2P/\pi - \gamma. \quad (3.21)$$

As  $b \rightarrow -\infty$  the exchange term approaches twice the Dirac exchange term. For  $b > 0$  the differential equation has solutions at large distances of the form

$$P(r) \rightarrow 9\pi b^2/2(4+b^2)r^2, \quad (3.22)$$

and as  $b \rightarrow \infty$  the solutions at large distances behave like the solutions to the Thomas-Fermi differential equation. Thus the generalized distribution includes the Thomas-Fermi and Thomas-Fermi-Dirac distributions as special cases.

### Boundary Conditions

Two boundary conditions to be satisfied by the generalized potential are given by Eqs. (2.32) and (2.33). If one imposes as a third condition the Jensen requirement<sup>5</sup> that the total energy be stationary with respect to a variation of the boundary  $R$  of the distribution, subject to the restriction that the total number of electrons is constant, one obtains

$$P(R) = \frac{5}{4\pi} - \frac{10b}{\pi|b|} \left[ \frac{2 \sin^2(x/2)}{x^4} - \frac{\sin x}{x^3} + \frac{1}{2x^2} \right], \quad (3.23)$$

where

$$x = 4RP(R)/|b|. \quad (3.24)$$

For  $b < 0$ , Eq. (3.23) has only one root such that the boundary value of  $P$  varies from  $10/4\pi$  to  $5/4\pi$  as  $b$  varies from  $-\infty$  to 0. For  $b = 0$ , the boundary value of  $P$  is  $5/4\pi$  independent of  $R$ . For  $b > 0$  and  $R/b < 4.0716$ , there is only one root,  $P(R) = 0$ . For  $R/b = 4.0716$ , there is a root corresponding to  $P(R) = 0$  and  $P(R) = 0.2902$ . For  $R/b > 4.0716$  there are three roots, the largest of which approaches  $5/4\pi$  as  $R/b \rightarrow \infty$ . The energy is a minimum for the root which approaches  $5/4\pi$  as  $R/b \rightarrow \infty$ . There are consequently no solutions for neutral atoms satisfying the Jensen condition which go to infinity, except for  $b = \infty$ .

It is in fact impossible to impose the Jensen condition for neutral atoms on any solution other than those corresponding to  $b = \infty$ ,  $b = 0$ , and  $b = -\infty$ . For these three values of  $b$ , the Jensen condition leads to  $dP/dr = 0$  at the boundary for neutral atoms. For values of  $b$  other than these three,  $dP/dr$  is greater than zero at the boundary and solutions started there will connect to a solution satisfying the Jensen condition for a positive ion with a smaller radius. However there are non-

TABLE I. Energy and boundary parameters corresponding to various distributions for  $\text{Cu}^+$  for a range of values of  $b$ . Atomic units have been used.

$b$	$R$	$P(R)$	$-U$	$-V$	$K$	$\partial U/\partial b$
10	178.8	5.59805	0	$0.82 \times 10^{-6}$	4629.6	1986.3
2.09840	4.61649	0	14.7	4659.6	2000.8	10.02
1.01691	3.71174	0	31.9	4686.3	2017.6	21.53
0.913365	3.61709	0	34.2	4689.6	2019.9	22.92
0.864048	3.51803	0.290218	35.4	4691.2	2021.1	23.64
0	3.3052	0.397887	62.6	4726.4	2047.7	40.74
$-\infty$	2.42645	0.795775	130.0	4824.9	2112.2	0

minimum neutral atom solutions to the differential equation (2.30) for  $\varphi(r)$  given by Eq. (3.17) which go to infinity for  $b > 0$ .

### IV. STATISTICAL DISTRIBUTIONS FOR $\text{Cu}^+$ FOR VARIOUS VALUES OF $b$

The differential equation for the statistical field with  $\varphi(r)$  given by Eq. (3.17) has been integrated numerically for  $\text{Cu}^+$  for various values of  $b$ . In Table I the values of  $R$  and  $P(R)$ , corresponding to solutions for various values of  $b$ , are tabulated with the energy terms  $K$ ,  $V$ , and  $U$  of the corresponding distributions and the  $\partial U/\partial b$ . The Jensen boundary condition was imposed on these solutions. For  $b > 0.8640$ , the boundary value of  $P$  is zero. For  $b \leq 0.8640$ ,  $P(R)$  varies from 0.2902 to  $10/4\pi$ . The external radius of the distribution decreases as  $b$  decreases and the total energy increases. The minimum energy solution corresponds to  $b = -\infty$ .

In Fig. 1 the total radial charge density in atomic units has been plotted for  $\text{Cu}^+$  as a function of  $r$ , for  $b = -\infty$ ,  $b = 0$ , and  $b = \infty$ . The Hartree-Fock radial charge density has been included for comparison. In the region covered by Fig. 1, the radial charge density corresponding to  $b = -\infty$  is everywhere higher than the charge density for  $b = 0$ , which is everywhere higher than the charge density for  $b = \infty$ . It can be seen that the effect of decreasing  $b$  on the radial charge density is to raise the charge density rather uniformly and to contract the radius of the distribution. No improvement in the agreement of the Hartree-Fock and statistical charge densities is effected by altering  $b$ .

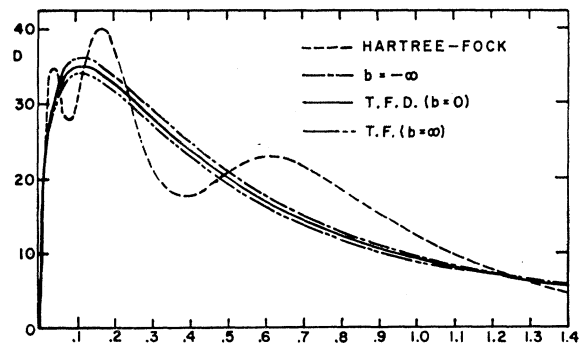


FIG. 1. The total radial charge densities  $D$  for  $\text{Cu}^+$  for  $b = -\infty$ , 0, and  $\infty$  are compared to the Hartree-Fock radial charge density. Density curves for  $b > 0$  lie between the Thomas-Fermi-Dirac curve and the Thomas-Fermi curve.

<sup>6</sup> L. H. Thomas, Proc. Cambridge Phil. Soc. 23, 542 (1927).

<sup>7</sup> E. Fermi, Z. Phys. 48, 73 (1928); 49, 550 (1928).

### V. EIGENVALUES AND FOURIER COMPONENTS OF THE DENSITY MATRIX

The elements of the density matrix in the central-field approximation can be written

$$\langle \mathbf{r} s_z | \rho | \mathbf{r}' s_z' \rangle = \sum_l C_l(\mathbf{r}, \mathbf{r}') P_l(\cos \Theta) \delta_{s_z, s_z'}, \quad (5.1)$$

where the Fourier component of the density matrix is

$$C_l(\mathbf{r}, \mathbf{r}') = \sum_n \psi_{nl}(\mathbf{r}) \psi_{nl}^*(\mathbf{r}') \left( \frac{2l+1}{4\pi} \right) N_{nl}, \quad (5.2)$$

using Eq. (2.10). We would like to compare the  $\psi_{nl}(\mathbf{r})$ 's, as determined from the various statistical density matrices, with the corresponding Hartree-Fock wave functions, but this is not useful since an idempotent density matrix does not determine a unique set of wave functions. This is a consequence of the fact that  $C_l(\mathbf{r}, \mathbf{r}')$  is invariant if one transforms to a new set of wave functions by means of a unitary transformation.<sup>8</sup> A density matrix does determine a unique  $C_l(\mathbf{r}, \mathbf{r}')$  matrix however, and therefore it is possible to compare the eigenvalues and Fourier components of the statistical and Hartree-Fock density matrices.

#### Fourier Analysis of the Density Matrix

For numerical calculation of the eigenvalues and Fourier components of a density matrix corresponding to a central field, it is convenient to define a matrix

$$G_{ij}(\Theta) = \frac{4\pi r_i r_j}{\lambda} [w_{ij} e^{\lambda(r_i + r_j)}]^{\frac{1}{2}} F(r_i, r_j, \Theta), \quad (5.3)$$

where

$$F(r, r', \Theta) = \sum_{s_z, s_z'} \langle \mathbf{r} s_z | \rho | \mathbf{r}' s_z' \rangle, \quad (5.4)$$

$\lambda$  is an arbitrary scale factor, and  $w_{ij}$  is an integration coefficient such that

$$\int_0^\infty e^{-\lambda r} f(r) dr \approx \sum_{i=1}^I \frac{w_{ii}^{\frac{1}{2}}}{\lambda} f(r_i). \quad (5.5)$$

Using Eqs. (5.3) and (5.5), we obtain

$$\sum_{i=1}^I G_{i,i}(0) \approx 4\pi \int_0^\infty r^2 F(r, r, 0) dr. \quad (5.6)$$

Thus, using Eqs. (2.5) and (5.4), the trace of  $G_{ij}(\Theta)$  is approximately equal to the total number of electrons in the atom.

The Fourier coefficients of  $G_{ij}(\Theta)$  form a discrete symmetric matrix

$$A_l(r_i, r_j) = \frac{2l+1}{2} \int_{-1}^1 G_{i,j}(\Theta) P_l(\cos \Theta) d \cos \Theta, \quad (5.7)$$

<sup>8</sup> See reference 2, p. 124.

such that

$$\sum_{i=1}^I A_l(r_i, r_i) \approx \sum_n 2(2l+1) N_{nl}. \quad (5.8)$$

Thus the trace of the symmetric discrete matrix  $A_l(r_i, r_j)$  is approximately equal to the total number of electrons with angular momentum  $l$ . The eigenvalues of  $A_l(r_i, r_j)$  are equal to  $2(2l+1) N_{nl}$ , with corresponding eigenvectors

$$\left( \frac{w_{ii}}{\lambda^2} \right)^{\frac{1}{2}} e^{\lambda r_i/2} r_i \psi_{nl}(r_i). \quad (5.9)$$

This follows from the fact that  $A_l(r_i, r_j)$  can be written

$$A_l(r_i, r_j) = \frac{8\pi r_i r_j}{\lambda} [w_{ij} e^{\lambda(r_i + r_j)}]^{\frac{1}{2}} \times \sum_n \psi_{nl}(r_i) \psi_{nl}^*(r_j) \left( \frac{2l+1}{4\pi} \right) N_{nl}, \quad (5.10)$$

using Eqs. (2.10), (5.4), and (5.7).

From the theory of Gauss-Laguerre integration,<sup>9</sup> if one sets

$$\lambda r_i = X_i^{(I)} \quad \text{and} \quad w_{ij} = \alpha_i^{(I)} \alpha_j^{(I)}, \quad (5.11)$$

where  $X_i^{(I)}$  is the  $i$ th root of the  $I$ th order Laguerre polynomial and  $\alpha_i^{(I)}$  is the corresponding weight factor, the numerical integration specified by Eq. (5.5) will be exact if  $f(r)$  is a polynomial of order  $2I-1$  or less. If  $f(r)$  is not a polynomial, Eq. (5.5) is an approximation corresponding to integrating Eq. (5.5) with  $f(r)$  replaced by the polynomial of order  $(2I-1)$ , which agrees with  $f(r)$  and its first derivative at the  $I$  roots of the  $I$ th order Laguerre polynomial. For a judicious choice of  $I$  and  $\lambda$ , Eq. (5.5) has been found to be a good approximation for Hartree-Fock wave functions.

The integral specified by Eq. (5.7) can be evaluated numerically as

$$A_l(r_i, r_j) \approx \frac{4\pi}{\lambda} r_i r_j [\alpha_i^{(I)} \alpha_j^{(I)} e^{\lambda(r_i + r_j)}]^{\frac{1}{2}} \times \sum_{k=1}^K w_k^{(K)} F(r_i, r_j, z_k^{(K)}) P_l(z_k^{(K)}), \quad (5.12)$$

where  $z_k^{(K)}$  is the  $k$ th root of the  $K$ th order Legendre polynomial and  $w_k^{(K)}$  is the corresponding weight factor for Gauss-Legendre integration.<sup>10</sup> Equation (5.12) will be exact if the integrand of Eq. (5.7) is a polynomial in  $\cos(\Theta)$  of degree  $2K-1$  or less. For a sufficiently large value of  $K$  Eq. (5.12) will be exact for Hartree-Fock functions, since the integral in that case involves the product of two Legendre polynomials only.

<sup>9</sup> F. B. Hildebrand, *Introduction to Numerical Analysis* (McGraw-Hill, Book Company, Inc., New York, 1956), p. 325.

<sup>10</sup> See reference 9, p. 323.

### The Eigenvalues of the Statistical Density Matrix

The  $A_l(r_i, r_j)$  matrix can be calculated from the statistical density matrix using Eq. (5.12) with

$$F(r, r', \Theta) = \frac{1}{\pi^2 r_{12}^3} \{ \sin[P(\xi)r_{12}] - P(\xi)r_{12} \cos[P(\xi)r_{12}] \}. \quad (5.13)$$

Using Eqs. (2.22) and (3.1), one can express  $r_{12}$  and  $\xi$  as a function of  $r$ ,  $r'$ , and  $\Theta$ , and  $P(\xi)$  can be calculated as the root of Eq. (3.17).

In Table II the trace of the  $A_l(r_i, r_j)$  matrices calculated from the statistical density matrices for  $\text{Cu}^+$  for various values of  $b$ , is compared with the corresponding Hartree-Fock values. The  $A_l(r_i, r_j)$  matrices were calculated with  $I=J=K=20$  and  $\lambda=0.0596$ . For these values the Hartree-Fock wave functions<sup>11</sup> for  $\text{Cu}^+$  satisfy Eq. (5.5) to the accuracy of the functions and Eq. (5.12) is exact. For large values of  $b$  the number of electrons with angular momentum  $l$  falls off gradually for large values of  $l$ . As  $b$  decreases, the number of electrons in shells with low  $l$  increases, and a sharp break occurs at  $l=3$ . As  $b \rightarrow 0$ , the number of electrons in shells for which  $l \geq 3$  begins to oscillate and the number of electrons in states with large  $l$  increases. The oscillations in the higher angular momentum states as  $b \rightarrow 0$  is present in heavier atoms as well. Values calculated for Hg for a Thomas-Fermi-Dirac field are presented at the bottom of Table II to illustrate this.

The oscillatory character of  $\sum_n 2(2l+1)N_{nl}$ , for large values of  $l$  as  $b \rightarrow 0$ , is a consequence of the form taken for  $\xi$ . This can be seen from the equation

$$\sum_n 2(2l+1)N_{nl} = 2(2l+1)\pi \int_0^\infty \int_{-1}^1 r^2 F(r, r, \Theta) \times P_l(\cos\Theta) d(\cos\Theta) dr, \quad (5.14)$$

obtained from Eqs. (2.8), (2.10), (2.21), and (5.13). For  $b=0$ , as  $\Theta \rightarrow \pi$  radians,  $\xi \rightarrow 0$  and  $P(\xi) \rightarrow \infty$ .  $F(r, r, \Theta)$  is consequently large and rapidly oscillating in the neighborhood of  $\Theta=\pi$ . This singularity leads to non-vanishing and in some cases negative values for the

TABLE II.  $\sum_n 2(2l+1)N_{nl}$  for  $\text{Cu}^+$  for various values of  $b$ , and for Hg for  $b=0$ . The Hartree-Fock values (H. F.) are included for comparison.

	$l=0$	$l=1$	$l=2$	$l=3$	$l=4$	$l=5$	$l=6$
H. F., $\text{Cu}^+$	6	12	10	0	0	0	0
$b=0$ , $\text{Cu}^+$	7.30	14.90	10.11	-0.39	-6.00	-0.51	0.51
$b=0.864$ , $\text{Cu}^+$	7.65	14.67	5.52	0.14	0.09	0.006	0.0009
$b=0.913$ , $\text{Cu}^+$	7.87	14.15	5.40	0.50	0.03	0.002	0.0004
$b=1.017$ , $\text{Cu}^+$	8.27	13.02	5.35	1.08	0.13	0.12	0.0008
$b=2.098$ , $\text{Cu}^+$	6.21	8.31	6.02	3.61	1.96	1.000	0.49
H. F., Hg	12	24	30	14	0	0	0
$b=0$ , Hg	11.55	27.88	28.58	19.60	-9.07	-2.39	3.61

<sup>11</sup> D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A157**, 490 (1936).

TABLE III. The eigenvalues of the  $A_l(r_i, r_j)$  matrices for  $\text{Cu}^+$  for  $b=0$  and 0.864, are compared with the corresponding Hartree-Fock values. These eigenvalues are equal to  $2(2l+1)N_{nl}$ .

		$l=0$	$l=1$	$l=2$	$l=3$
$n-l=1$	H. F.	2.0	6.0	10.0	0
	$b=0$	1.99	6.05	6.94	1.81
	$b=0.864$	3.10	4.86	1.63	0.09
$n-l=2$	H. F.	2.0	6.0	0	0
	$b=0$	2.07	4.30	2.96	-1.60
	$b=0.864$	1.85	2.92	1.03	0.06
$n-l=3$	H. F.	2.0	0	0	0
	$b=0$	1.47	2.47	0.93	-0.52
	$b=0.864$	1.03	1.85	0.70	-0.06
$n-l=4$	H. F.	0	0	0	0
	$b=0$	0.86	1.29	-0.58	0.50
	$b=0.864$	0.61	1.24	0.51	0.04
$n-l=5$	H. F.	0	0	0	0
	$b=0$	0.45	0.65	-0.48	0.45
	$b=0.864$	0.38	0.87	0.34	0.04

integral on the right hand side of Eq. (5.14) for large values of  $l$ . For  $b < 1$ , the minimum value of  $\xi$  for  $r=r'$  as a function of  $\Theta$  is  $br$  and one would expect the oscillations in the higher angular momentum states to become more pronounced as  $b \rightarrow 0$ . For  $b \geq 1$  and  $r=r'$ , the minimum value of  $\xi$  is  $r$  and as  $b \rightarrow \infty$ ,  $\xi \rightarrow \infty$  except for  $\Theta=0$ . Thus as  $b \rightarrow \infty$ ,  $F(r, r', \Theta) \rightarrow 0$  for  $r \neq r'$ . As  $b \rightarrow \infty$ , the integral of Eq. (5.14) will always be positive and consequently the Thomas-Fermi density matrix does not give a negative number of electrons in any angular momentum states. Golden has investigated the number of electrons in various angular momentum states for the Thomas-Fermi density matrix.<sup>12</sup>

The density matrix method of determining the angular momentum distribution is a quantum mechanical approach and leads to electrons in states with integral  $l$  only. Various other authors have calculated the angular momentum distribution for statistical atoms in a semi-classical manner by regarding the angular momentum as continuously distributed and assigning electrons within a certain interval to a definite angular momentum state.<sup>13-15</sup> All of these approaches, as well as the density matrix approach, lead to only moderate agreement with the experimental values. Fermi's calculations, for example, place about 7, 15, and 6 electrons in the  $s$ ,  $p$ , and  $d$  states of Cu, respectively.

In Table III the eigenvalues of the  $A_l(r_i, r_j)$  matrices for  $\text{Cu}^+$  are tabulated for  $b=0$  (the Thomas-Fermi-Dirac case),  $b=0.864$ , and the Hartree-Fock values. It can be seen that for low values of  $l$  and  $n$ , the eigenvalues corresponding to the Thomas-Fermi-Dirac density matrix agree quite well with the values corresponding to the Hartree-Fock density matrix. For large values of  $l$  and  $n$

<sup>12</sup> S. Golden, Phys. Rev. **110**, 1349 (1958).

<sup>13</sup> E. Fermi, Z. Physik **48**, 73 (1928).

<sup>14</sup> J. H. Jensen and J. M. Luttinger, Phys. Rev. **86**, 907 (1952).

<sup>15</sup> T. A. Oliphant, Jr., Phys. Rev. **104**, 954 (1956).

we again observe oscillations. The character of the eigenvalues of  $A_l(r_i, r_j)$  matrices for large values of  $b$  is indicated by the values corresponding to  $b=0.864$  in Table III. Even for low values of  $l$  and  $n$  these are a poor approximation to the Hartree-Fock eigenvalues. An interesting feature is the value of approximately 3 for the number of electrons in the  $K$  shell. It has been pointed out<sup>16,17</sup> that the discrepancy between the Thomas-Fermi potential and a Coulomb potential near the origin introduces a correction in the Thomas-Fermi energy of  $\frac{1}{2}Z^2$ . This is approximately the energy of an extra electron in the  $K$  shell and the distributions for large positive values of  $b$ , for which the eigenvalues have been calculated (up to  $b=2.098$ ), have approximately one extra electron in the  $K$  shell. No attempt has been made to determine the eigenvalues of the Thomas-Fermi density matrix by a limiting process.

The boundary condition difficulties of the Thomas-Fermi-Dirac equation are probably related to the oscillation in the sign of the charge in high angular momentum states. Since the sign of the charge in shells with high  $l$  oscillates, one would expect the sign of the charge density to oscillate at large distances. This is in fact what happens and the Thomas-Fermi-Dirac distribution must be cut off to prevent this oscillation. The only distribution for which the right hand side of Eq. (5.14) is definitely always positive is the Thomas-Fermi distribution, and this is the only distribution for which the minimum energy solution goes to infinity for neutral atoms.

<sup>16</sup> J. M. C. Scott, *Phil. Mag.* **43**, 859 (1952).

<sup>17</sup> N. H. March and J. J. Plaskett, *Proc. Roy. Soc. (London)* **A235**, 419 (1959).

A comparison of the Fourier components of the statistical density matrix for various values of  $b$  with the Fourier components of the Hartree-Fock density matrix, reveals rather poor agreement. The diagonal elements of the statistical and Hartree-Fock  $A_l(r_i, r_j)$  matrices agree about as well as the corresponding radial charge densities. Since the statistical density matrix is not idempotent, the wave functions calculated from the  $A_l(r_i, r_j)$  matrices are unique but prove to be a poor approximation to Hartree-Fock wave functions. It is evidently not worthwhile to compute the Fourier components of the statistical density matrix for use as a starting point for a Hartree-Fock calculation.

### CONCLUSION

A generalized expression for the statistical field has been obtained which includes the Thomas-Fermi and Thomas-Fermi-Dirac fields as special cases. The behavior of the energy, charge density, boundary density, and electron groups has been investigated for various fields. Fields with exchange are obtained which behave like the Thomas-Fermi field at the boundary. A singularity in the Thomas-Fermi-Dirac density matrix has been found which leads to an oscillation in the sign of the charge in high angular momentum states. This singularity is related to the necessity for terminating the Thomas-Fermi-Dirac distribution at a finite boundary.

A comparison of the Fourier components and wave functions calculated from statistical density matrices for  $\text{Cu}^+$  with the corresponding Hartree-Fock values has revealed that it would not be worthwhile to compute these components for use as a starting point for a Hartree-Fock calculation.