

# Shells and Electron Groups in the Thomas-Fermi Atom\*

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Two prescriptions are given for the decomposition of the electron cloud of the Thomas-Fermi atom into charge domains that correspond to the shells and subshells of the wave-mechanical atom. Prescription 1 utilizes a rigorous analytical development of the Thomas-Fermi density function over three sets of indices identifiable with the quantum numbers:  $n$ ,  $l$ , and  $m$ . Prescription 2 is based on a semiempirical partitioning to fit the Bohr-Stoner table of electron configurations. Agreement with wave mechanics is moderate.

## 1. INTRODUCTION

THE statistical atom of Thomas<sup>1</sup> and Fermi<sup>2</sup> does not account for the electron shells and subshells of the wave mechanical atom. In this approximate model, the usual  $K$ ,  $L$ ,  $M$ ,  $\dots$  peaks of the wave mechanical electron distribution are smoothed out into a plain charge cloud devoid of orbital features. This lack of detail in the description of the electron configuration in the Thomas-Fermi (TF) atomic model restricts its application usually to problems dealing only with the average electron distribution or the gross charge effect of an atom.<sup>3</sup> The statistical method could, however, be employed in a more refined class of physical problems, if the TF electron cloud were simply broken down into electron groups that correspond to the shells and subshells of the wave mechanical picture. Such an extension of the TF method, in combination with the more recent improvements<sup>4-6</sup> in TF theory, could in fact facilitate the investigation of some of the intricate atomic problems, restricted up to now to standard but sometimes laborious wave mechanical methods.

The problem of portioning off the electron cloud of the TF atom into charge domains that have a spatial and physical correspondence with the electron groups of wave mechanics was partially solved by Fermi<sup>2</sup> as far back as 1928. Fermi separated the TF charge cloud into angular momentum groups by considering the velocity distribution of electrons around the nucleus. Some interesting applications of these angular momentum groups, have been made by Paneth,<sup>7</sup> Yang,<sup>8</sup> and others<sup>9</sup> to atomic and nuclear problems. Hellmann,<sup>9</sup>

and more recently, Golden,<sup>10</sup> and Tietz<sup>11</sup> have also investigated the angular momentum grouping of electrons in the TF atom, using the more sophisticated approach of spherical wave functions. This method leads to a quantized and essentially wave mechanical angular momentum distribution among the electrons, as contrasted with Fermi's distribution, which is continuous and subject to arbitrary quantization assignments.<sup>8</sup>

While quite a bit of work seems to have been done on the angular momentum groups, no really satisfactory suggestion has yet been made<sup>12</sup> on the construction of the more significant  $(n)$  groups, or  $(n,l)$  or  $(n,l,m)$  subgroups, from the TF density function. It seems to be a matter of some importance though, both from an academic and a practical viewpoint, that this decomposition of the TF atom into groups and subgroups be carried out. The present investigation is an attempt in that direction—it is aimed at devising rigorous as well as empirical methods of breaking down the electron cloud of the TF atom into charge domains that can be identified with the  $(n,l,m)$  set of quantized orbits in the wave mechanical atom. Two methods will be presented here. In method I, the TF density function will be expressed as a triple index series development, the indices being identifiable with the quantum numbers:  $n$ ,  $l$ , and  $m$ . The development itself will be shown to follow from a well-known spectral decomposition of a plane wave. In method II, which is semiempirical, the angular momentum groups are separated into  $(n,l)$  subgroups by utilizing a table of electron configuration, and certain ideas of Daudel<sup>13</sup> and Odier<sup>14</sup> on concentric, nonoverlapping electron orbitals. Some simple applications of the TF shells and subshells have then been considered for comparison with wave mechanics.

## 2. METHOD I

### 2.1 Series Development for the Density

It was shown by Alfred,<sup>6</sup> that the density in the unmodified TF system, viz.,

$$\rho(r) = (8\pi/3h^3)(2\mu)^{3/2}[\lambda - V]^{3/2}, \quad (2.1)$$

<sup>10</sup> S. Golden, Phys. Rev. **110**, 1349 (1958).

<sup>11</sup> T. Tietz, Nuovo cimento **11**, 121 (1959). L. P. Rapoport and S. G. Kadenskii, Soviet Phys.—JETP **10**, 929 (1960).

<sup>12</sup> P. Gombas, Acta. Physiol. Acad. Sci. Hung. **5**, 503 (1956).

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<sup>1</sup> L. H. Thomas, Proc. Cambridge Phil. Soc. **23**, 542 (1927).

<sup>2</sup> E. Fermi, Z. Physik **48**, 73 (1928).

<sup>3</sup> P. Gombas, *Die Statistische Theorie des Atoms und Ihre Anwendungen* (Springer-Verlag, Vienna, 1949).

<sup>4</sup> N. H. March, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1957), Vol. 6, p. 1.

<sup>5</sup> S. Golden, Phys. Rev. **105**, 604 (1957).

<sup>6</sup> L. C. R. Alfred, Phys. Rev. **121**, 1275 (1961).

<sup>7</sup> H. R. Paneth, Proc. Phys. Soc. (London) **A64**, 937 (1951). L. Yang, Proc. Phys. Soc. (London) **A64**, 632 (1951).

<sup>8</sup> S. I. Larin, Soviet Phys.—JETP **1**, 394 (1955). J. H. D. Jensen and J. M. Luttinger, Phys. Rev. **86**, 907 (1952). T. A. Oliphant, Jr., Phys. Rev. **104**, 954 (1956). P. Gombas, Acta. Physiol. Acad. Sci. Hung. **2**, 247 (1952).

<sup>9</sup> H. Hellmann, Acta Physiochim. U.S.S.R. **4**, 225 (1936). P. Gombas, Acta. Physiol. Acad. Sci. Hung. **1**, 295 (1952).

is a first approximation to the more general statistical density:

$$\rho(\mathbf{r}) = \frac{2}{h^3} \sum_{N=1}^{\infty} \frac{1}{2\pi i} \oint_{\gamma-i\infty}^{\gamma+i\infty} \frac{dz}{z} \psi_N^*(\mathbf{r}) \times \exp[z(\lambda - \mathbf{H})] \psi_N(\mathbf{r}), \quad (2.2)$$

where  $\mu$  is the mass of an electron,  $\lambda$  is the chemical potential,  $V$  the potential energy,  $\mathbf{H}$  the Hamiltonian operator, and  $\psi_N(\mathbf{r})$  is a plane wave. A simple way to obtain a series development for the TF density, is to substitute in the place of the wave function in (2.2) some suitable spectral decomposition. The expansion which is of interest here is that of Rayleigh,<sup>15</sup> viz.,

$$\exp(i\mathbf{p} \cdot \mathbf{r}/\hbar) = \sum_{l=0}^{\infty} (2l+1)(i)^l j_l(pr/\hbar) P_l(\cos\delta), \quad (2.3)$$

where  $j_l(x)$  is the spherical Bessel function

$$(\pi/2x)^{1/2} J_{l+1/2}(x),$$

$P_l(\cos\delta)$  the Legendre polynomial, and  $\delta$ , the angle  $(\mathbf{p}/\hbar, \mathbf{r})$ .

From the spherical harmonic addition theorem,<sup>16</sup> the Legendre polynomial  $P_l(\cos\delta)$  of (2.3) can be replaced by the more general expression:

$$P_l(\cos\delta) = \sum_{m=-l}^l \frac{(l-|m|)!}{(l+|m|)!} P_l^m(\cos\theta_r) P_l^m(\cos\theta_p) \times \exp(im\phi_r) \exp(-im\phi_p), \quad (2.4)$$

where  $P_l^m(x)$  is an associated Legendre polynomial;  $(r, \theta_r, \phi_r)$  and  $(p, \theta_p, \phi_p)$ , are coordinates in position and momentum space, respectively. The complete expansion for the plane wave is then

$$\exp(i\mathbf{p} \cdot \mathbf{r}/\hbar) = \sum_{l=0}^{\infty} \sum_{m=-l}^l (2l+1) \frac{(l-|m|)!}{(l+|m|)!} (i)^l \times j_l(pr/\hbar) Y_{lm}(\theta_r, \phi_r) Y_{lm}^*(\theta_p, \phi_p), \quad (2.5)$$

where  $Y_{lm}(\alpha, \beta)$  is the spherical harmonic  $P_l^m(\cos\alpha) \times \exp(im\beta)$ .

When the expression (2.5) is substituted in (2.2) for the plane wave, and the operation  $\exp(-z\mathbf{H}) \times \exp(i\mathbf{p} \cdot \mathbf{r}/\hbar)$  carried out<sup>6</sup> up to terms in the first

P. Gombas and K. Ladanyi, *ibid.* **5**, 313 (1955). K. M. King and L. H. Thomas, *Phys. Rev.* **124**, 785 (1961).

<sup>13</sup> R. Daudel, *Compt. rend.* **235**, 886 (1952).

<sup>14</sup> H. Brion and S. Odier, *Compt. rend.* **237**, 616 (1953). S. Odier, *ibid.* **237**, 1399 (1953).

<sup>15</sup> E. T. Whittaker and G. N. Watson, *A Course in Modern Analysis* (Cambridge University Press, New York, 1952), Chap. 18.

<sup>16</sup> P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1953), Chap. 10.

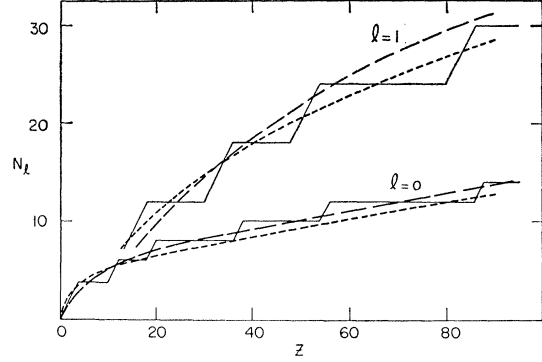


FIG. 1.  $N_l$  as a function of  $Z$ . — Wave mechanics; - - - Fermi; — — Present calculations.

power of  $\hbar$ , the result is

$$\rho(\mathbf{r}) = \frac{2}{h^3} \sum_{l=0}^{\infty} \sum_{m=-l}^l (2l+1)^2 \left[ \frac{(l-|m|)!}{(l+|m|)!} \right]^2 \times [P_l^m(\cos\theta_r)]^2 \frac{1}{2\pi i} \oint_{\gamma-i\infty}^{\gamma+i\infty} \frac{dz}{z} \exp[z(\lambda - V)] \times \int d\mathbf{p} \exp[-z(p^2/2\mu)] j_l^2(pr/\hbar) [P_l^m(\cos\theta_p)]^2. \quad (2.6)$$

Equation (2.6) can be shown to reduce to

$$\rho(\mathbf{r}) = \frac{8\pi}{h^3} \sum_{l=0}^{\infty} \sum_{m=-l}^l (2l+1) \frac{(l-|m|)!}{(l+|m|)!} \times [P_l^m(\cos\theta_r)]^2 \int_0^{p_0} dx x^2 j_l^2(xr/\hbar), \quad (2.7)$$

where  $p_0 = [2\mu(\lambda - V)]^{1/2}$ . It can be verified that the usual TF density of Eq. (2.1) is recovered from (2.7) on summing over  $m$  and  $l$ .

## 2.2 Quantum Groups

### 2.2.1. Angular Momentum Groups

Define

$$\rho(\mathbf{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^l \rho_{lm}(\mathbf{r}), \quad (2.8)$$

and

$$\rho_l(\mathbf{r}) = \sum_{m=-l}^l \rho_{lm}(\mathbf{r}), \quad (2.9)$$

where

$$\rho_{lm}(\mathbf{r}) = \frac{8\pi}{h^3} (2l+1) \frac{(l-|m|)!}{(l+|m|)!} \times [P_l^m(\cos\theta_r)]^2 \int_0^{p_0} dx x^2 j_l^2(xr/\hbar), \quad (2.10)$$

from Eq. (2.7).

It is easy to show by summing over  $m$ , that

$$\rho_l(\mathbf{r}) = \rho(\mathbf{r}) \left\{ 3(l + \frac{1}{2}) [j_l^2(y) - j_{l-1}(y)j_{l+1}(y)] \right\}, \quad (2.11)$$

where  $\rho(\mathbf{r})$  is the TF density of (2.1), and  $y = r[3\pi^2\rho(\mathbf{r})]^{1/3}$ . Expression (2.11) corresponds to the expression (4) of Golden,<sup>10</sup> for the density of electrons with angular quantum number  $l$ . This correspondence establishes the index  $l$  in (2.7) as the angular quantum number. A comparison of the total number of electrons  $N_l (= \int d\mathbf{v} \rho_l(\mathbf{r}))$  in the first two angular momentum states obtained from Eq. (2.11) and from wave mechanics, is made in Fig. 1. The curves for the distribution given by Fermi,<sup>2</sup> are also shown.

A connection can also be made in the scheme employed here with the angular momentum groups of Hellmann,<sup>9</sup> if the asymptotic form

$$(\hbar/pr) \sin(pr/\hbar - l\pi/2)$$

for the spherical Bessel function is used in (2.2) in the place of  $j_l(pr/\hbar)$ . Equation (2.6) then takes the form:

$$\begin{aligned} \rho'(\mathbf{r}) = & \frac{2}{\hbar^3} \sum_{l=0}^{\infty} \sum_{m=-l}^l (2l+1)^2 \left[ \frac{(l-|m|)!}{(l+|m|)!} \right]^2 [P_l^m(\cos\theta_r)]^2 \\ & \times \frac{1}{2\pi i} \int_{\gamma-i\infty}^{\gamma+i\infty} \frac{dz}{z} \exp \left[ z \left( \lambda - V - \frac{\hbar^2 l(l+1)}{2\mu r^2} \right) \right] \\ & \times \int d\mathbf{p} \exp[-z(p^2/2\mu)] \frac{\hbar^2}{p^2 r^2} \sin^2 \left( \frac{pr}{\hbar} - \frac{l\pi}{2} \right) \\ & \times [P_l^m(\cos\theta_p)]^2. \end{aligned} \quad (2.12)$$

Equation (2.12) can be shown to reduce to:

$$\rho'(\mathbf{r}) = \sum_{l=0}^{\infty} \rho'_l(\mathbf{r}), \quad (2.13)$$

where

$$\rho'_l(\mathbf{r}) = \frac{2l+1}{\hbar\pi r^2} \left[ p'_0 - \frac{\hbar}{2r} \sin(2p'_0 r/\hbar - l\pi) \right], \quad (2.14)$$

and

$$p'_0 = [2\mu(\lambda - V) - \hbar^2 l(l+1)/r^2]^{1/2}.$$

In the limit of  $r$  large, the second term in (2.14) can be neglected, and  $\rho'_l(\mathbf{r})$  then corresponds to the expression (17) of Hellmann<sup>9</sup> for the density of electrons with angular quantum number  $l$ .

### 2.2.2. Magnetic Quantum Groups

The angular part of the density expression (2.7) is

$$[P_l^m(\cos\theta_r)]^2. \quad (2.15)$$

There is no difficulty in recognizing (2.15) as the main angular term of the wave mechanical orbitals for a central force field.<sup>17</sup> A connection could be made here with the alternative forms for the orbitals, which

<sup>17</sup> L. Pauling and E. B. Wilson, Jr., *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935).

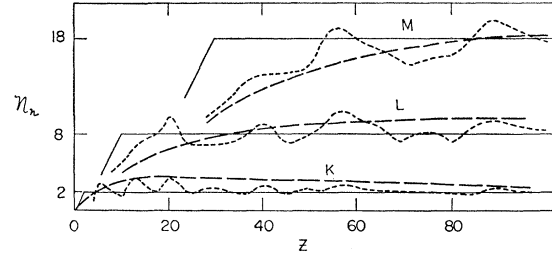


FIG. 2.  $\mathfrak{N}_n$  as a function of  $Z$ . — Wave mechanics; --- Rule (2.19); — Present calculations.

involve the cyclic coordinate  $\phi_r$ , if the function  $\exp(im\phi_r)$  were expressed as follows:

$$\exp(im\phi_r) = \cos(m\phi_r) + i \sin(m\phi_r). \quad (2.16)$$

With this modification, the plane wave gives rise in (2.7) to two sets of density terms with the standard angular dependence<sup>17</sup>:

$$[P_l^m(\cos\theta_r)]^2 \cos^2(m\phi_r), \quad (2.17a)$$

and

$$[P_l^m(\cos\theta_r)]^2 \sin^2(m\phi_r). \quad (2.17b)$$

The correspondence between the angular terms of the wave mechanical shells and those of the TF atom, coupled with the fact that the radial part of (2.7) corresponds (see Sec. 2.2.1) to the electrons in quantum state  $l$ , serves to identify the index  $m$  of (2.7) as the usual magnetic quantum number.

### 2.2.3. Principal Quantum Groups

The expression (2.11) for the angular momentum groups can be expanded with the help of well-known Bessel function expansion theorems,<sup>18</sup> as follows:

$$\begin{aligned} \rho_l(\mathbf{r}) = & \sum_{n=l+1}^{\infty} \rho(\mathbf{r}) \left\{ 9(l + \frac{1}{2})(n - l - \frac{1}{2}) \right. \\ & \times [j_l^2(y) - j_{l-1}(y)j_{l+1}(y)] \\ & \times [j_{n-l-1}^2(y) - j_{n-l-2}(y)j_{n-l}(y)] \} \\ & = \sum_{n=l+1}^{\infty} \rho_{ln}(\mathbf{r}). \end{aligned} \quad (2.18)$$

There are two reasons why the index  $n$  of (2.18), can be identified with the principal quantum number of wave mechanics: (a) the values for  $\mathfrak{N}_n [= \int d\mathbf{v} \sum_l \rho_{ln}(\mathbf{r})]$ , as illustrated in Fig. 2, tend to the values  $2n^2$  of wave mechanics, for large  $Z$ . (b) The relation (2.18) corresponds closely to a mathematical formulation of a rule that gives in the limit for  $Z$  large, a relation between  $\mathfrak{N}_n$  and the number of electrons

<sup>18</sup> G. N. Watson, *A Treatise on the Theory of Bessel Functions* (The MacMillan Company, New York, 1948) Chap. 5.

$N_l [= \int dv \rho_l(\mathbf{r})]$  in the angular momentum states, viz.

$$\mathfrak{N}_n = \frac{1}{Z} \sum_{l=0}^{n-1} (N_l N_{n-l-1}) \approx 2n^2; \quad Z \rightarrow \text{large}, \quad (2.19)$$

where  $Z$  is the atomic number. The rule (2.19) is illustrated in Fig. 2 for comparison with wave mechanics and TF.

### 3. METHOD II

Daudel<sup>13</sup> and Odiot<sup>14</sup> have experimented, with some success, with the construction of the principal electron shells in atoms by partitioning the charge cloud with concentric spherical surfaces. The  $K, L, M, \dots$  shells though, do not seem so well suited for such a straight wall partition scheme, because of the very sizeable overlap of neighboring shells. The adjacent subshells of the same  $l$  group, however, are known to overlap only slightly<sup>19</sup> and would approximate more closely to a tightly partitioned set of electron orbitals.

In the present prescription, the ideas of Daudel and Odiot are extended to effect the separation of the angular momentum groups of the TF atom into  $(n, l)$  subgroups. The expression (2.11) for the angular momentum distribution will be employed, and concentric spherical surfaces about the nucleus will section the distribution of each  $l$  state into cells, each cell containing  $2(2l+1)$  electrons (in accordance with the table of electron configurations<sup>20</sup>). Following this procedure, a typical subshell would be given by the expression:

$$\rho_{ln}(\mathbf{r}) = \rho_l(\mathbf{r}) \Big|_{r_{n-1,l}}^{r_{n,l}} = \rho(\mathbf{r}) \left\{ 3(l + \frac{1}{2}) [j_l^2(y) - j_{l-1}(y)j_{l+1}(y)] \right\} \Big|_{r_{n-1,l}}^{r_{n,l}}, \quad (3.1)$$

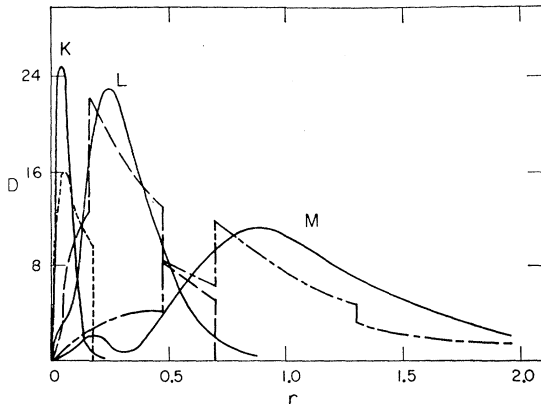


FIG. 3. Radial distribution for Cr;  $D = 4\pi r^2 \rho(r)$ , and  $r$  is in atomic units. — Wave mechanics; other curves: Thomas-Fermi.

<sup>19</sup> Landolt-Bornstein, *Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik, und Technik* (Springer-Verlag, Berlin, 1950) 1 Band, 1 Teil, p. 284–296.

<sup>20</sup> I. Kaplan, *Nuclear Physics* (Addison-Wesley Publishing Company, Inc., Cambridge, 1955), p. 130–133.

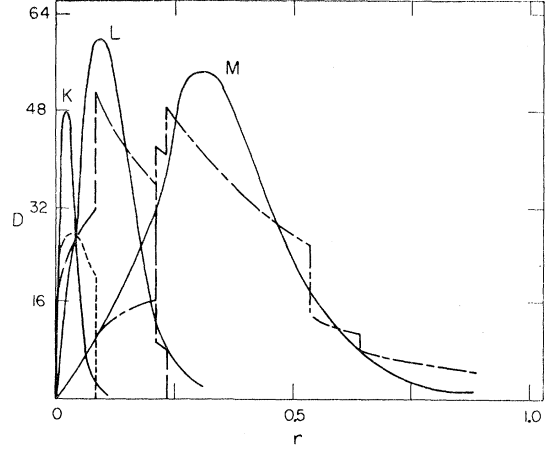


FIG. 4. Radial distribution for Ag;  $D = 4\pi r^2 \rho(r)$ , and  $r$  is in atomic units. — Wave mechanics; other curves: Thomas-Fermi.

where the bounding radii  $r_{n-1,l}$  and  $r_{n,l}$  are defined by the integral

$$\int_{r_{n-1,l}}^{r_{n,l}} dv \rho_l(\mathbf{r}) = 2(2l+1)$$

and  $r_{0,l} = 0$ . The last subshell of any particular  $l$  state will extend to the boundary of the atom and contain  $2(2l+1)$  or less electrons. Sets of tables or of curves for the bounding radii  $r_{n,l}$  for all the elements can be easily constructed. The magnetic quantum number  $m$  can be introduced here by incorporating the angular terms of (2.7) or (2.17a, b) with the expression (3.1).

The  $K, L, M, \dots$  shells obtained by this prescription for Cr and Ag, are shown in Figs. 3 and 4, and compared with the curves obtained by wave mechanics.<sup>21</sup>

### 4. APPLICATIONS

#### 4.1 Shell Contribution of X-ray Scattering Intensity

Waller and Hartree<sup>22</sup> have given for the total intensity of x-ray scattering by a monatomic gas, the formula:

$$I = I_e [(\sum_j f_{jj})^2 + Z - \sum_j f_{jj}^2 - \sum_{jk} (f_{jk})^2], \quad (4.1)$$

where  $I_e$  = intensity for scattering by a single electron,

$$f_{jk} = \int \psi_j^* \psi_k \frac{\sin \kappa r}{\kappa r} dv,$$

$\psi_i$  is the wave function of the  $i$ th electron,  $\kappa = 4\pi(\sin \frac{1}{2}\phi)/\lambda_R$ ,  $\phi$  is the scattering angle, and  $\lambda_R$  is the x-ray wavelength.

The contributions to the scattering intensity by the  $K, L$ , and  $M$  shells of argon, obtained from the pre-

<sup>21</sup> A. Porter, Proc. Manch. Phil. Soc. **79**, 75 (1935). R. Gaspar and K. Molnar-Ivanecsko, Acta. Physiol. Acad. Sci. Hung. **6**, 105 (1956).

<sup>22</sup> I. Waller and D. R. Hartree, Proc. Roy. Soc. (London) **A124**, 119 (1929).

TABLE I. Intensity of x-ray scattering for Ar.  
[ $(\sin \frac{1}{2}\phi)/\lambda_R = 1.566$ ].

	TF Method I	TF Method II	TF <sub>mod</sub> Method II	Wave mechanics <sup>a</sup>
$\sum_i f_{ii}$				
$\begin{cases} K \\ L \\ M_{eff} \end{cases}$	$\begin{cases} 1.04 \\ 0.96 \\ 0.36 \end{cases}$	$\begin{cases} 1.57 \\ 0.68 \\ 0.11 \end{cases}$	$\begin{cases} 1.40 \\ 0.64 \\ 0 \end{cases}$	$\begin{cases} 1.65 \\ 0.46 \\ 0.04 \end{cases}$
Total	2.36	2.36	2.04	2.15
$\sum_i f_{ii}^2$				
$\begin{cases} K \\ L \\ M_{eff} \end{cases}$	$\begin{cases} 0.32 \\ 0.15 \\ 0.01 \end{cases}$	$\begin{cases} 1.23 \\ 0.11 \\ 0 \end{cases}$	$\begin{cases} 0.98 \\ 0.10 \\ 0 \end{cases}$	$\begin{cases} 1.36 \\ 0.39 \\ 0 \end{cases}$
Total	0.48	1.34	1.08	1.75
$\sum_{jk} f_{jk}^2$	L	0	0	0.17
$Z^{-1}(I/I_e)$	1.28	1.23	1.17	1.15

<sup>a</sup> See reference 22.

scriptions of Secs. 2 and 3, have been evaluated for<sup>22</sup>  $(\sin \frac{1}{2}\phi)/\lambda_R = 1.566$ , and compared in Table I with the contributions obtained by Waller and Hartree for the wave mechanical shells. The contributions by shells constructed from a modified TF density (see Sec. 5 for details) are also shown.

## 4.2 Diamagnetic Susceptibility

The molar diamagnetic susceptibility of a monatomic gas is given by the expression<sup>23</sup>:

$$\chi = (-L\epsilon^2/6mc^2)\bar{r}^2, \quad (4.2)$$

where  $L$  is the Loschmidt number,  $c$  the velocity of light,  $\epsilon$  the charge of an electron and

$$\bar{r}^2 = \int dv r^2 \rho(\mathbf{r}) = \sum_n \sum_l \int dv r^2 \rho_{ln}(\mathbf{r}).$$

In Table II, the contribution to the diamagnetic susceptibility of argon from the shells of method II are compared with the wave mechanical values obtained by Hartree and Hartree.<sup>24</sup> It should be pointed out, however, that since it is a well known fact that the diamagnetic susceptibility of elements calculated from the TF density is in error by as much as a factor of ten,<sup>3</sup>

TABLE II. Diamagnetic susceptibility of Ar.

	TF Method II	TF <sub>mod</sub> Method II	Wave mechanics <sup>a</sup>	Exp. <sup>a</sup>
$\bar{r}^2$				
$\begin{cases} K \\ L \\ M_{eff} \end{cases}$	$\begin{cases} 0.03 \\ 2.76 \\ 99.8 \end{cases}$	$\begin{cases} 0.03 \\ 2.01 \\ 20.7 \end{cases}$	$\begin{cases} 0.02 \\ 1.44 \\ 24.56 \end{cases}$	$\begin{cases} \dots \\ \dots \\ \dots \end{cases}$
Total	102.6	23.5	26.03	$\dots$
$-\chi(10^6)$	81.0	18.2	20.6	19.5

<sup>a</sup> See reference 24.

<sup>23</sup> E. C. Stoner, *Magnetism and Matter* (Methuen and Company, Ltd., London, 1934), Chap. 9.

<sup>24</sup> D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A166**, 450 (1938).

the numbers in the TF column of Table II are not very significant; but they do bring out very sharply, in column three, the improvement which a modified TF density (see Sec. 5 for details) can make in the shells.

## 5. DISCUSSION

As can be seen from the tables and curves presented here, the TF shells and subshells bring out satisfactorily the general features of the electron orbitals of wave mechanics. A moderate agreement with wave mechanics is found for the x-ray scattering intensity, and only for shells of a modified TF density in the case of the diamagnetic susceptibility. Method II seems to be on the whole in better agreement with wave mechanics in these applications, than is method I. It should also be pointed out that though method I gives a reasonable indication of the number of electrons in the principal shells, the individual subshells themselves are not filled in the proper way, and certain modifications have to be made in the method to get better agreement.

It is well known that the electron distribution in the unmodified TF atom is significantly in error when compared with wave mechanics,<sup>3</sup> being too large, close to and far from the nucleus, and too low in the intermediate region. The shells and subshells constructed from the unmodified TF density are bound to contain these defects, and can agree with the wave mechanical electron orbitals only within the degree that the total TF density itself agrees with the total wave mechanical density. The main drawback in the way of a useful application of the TF shells and subshells lies, therefore, in the incorrect radial distribution obtained from the electrons. This shortcoming will lead to very significant divergences from wave mechanical results (see Table II, column 2) particularly in the types of problems like energy evaluation and electric polarizability, which depend on the higher powers or higher moments of the density.

In order to obtain good agreement with wave mechanics, it is essential that a good density be employed in the prescriptions. The densities obtained, for example, by Gombas<sup>25</sup> for the TF atom corrected for exchange and inhomogeneity have the proper behavior over the entire radial range and should lead to more interesting results than those obtained with the unmodified TF model. Corrections to the statistical atom can be incorporated in the present scheme with the formulation of a more elaborate theory on the lines of Secs. 2 and 3—these modifications will be presented in a later publication. For the moment, an idea of the improvement that is brought about by correcting the TF density, can be obtained quite easily, by employing in a formal way the densities of Gombas<sup>25</sup> in the expressions (4.1) and (4.2). As can be seen from Tables I and II, there is then a significant improvement on the results obtained with the unmodified TF model.

<sup>25</sup> P. Gombas, Acta. Physiol. Acad. Sci. Hung. **5**, 497 (1956).

## 6. CONCLUSIONS

Whether the prescriptions described in Secs. 2 and 3, are applied to a modified or an unmodified TF atom, they are still subject to three main criticisms which are: (a) The lack of uniqueness in the way the principal quantum number  $n$  is introduced in method II, and to a lesser degree in method I. (b) The shells obtained from a statistical atom are applicable strictly only to problems depending on the electron density rather than on the wave functions. Approximate wave functions, in the nature of Slater's<sup>26</sup> nodeless wave functions could, however, be obtained by taking the square root of the density. (c) Since the subshells of method II are separated by a straight wall partition, they are not applicable to problems like fine structure spectra, where the overlap of adjacent subshells is significant.

These criticisms, however, are easily offset by the many good points of the prescriptions. Among the interesting features that should be pointed out are: (a) That these prescriptions serve primarily to broaden

<sup>26</sup> J. C. Slater, Phys. Rev. **36**, 57 (1930).

the TF atom concept, by introducing a notion of shells, subshells and quantization, where there was just a plain cloud of electrons. (b) These prescriptions are formulated in a sufficiently flexible form as to be applicable to the partitioning of arbitrary density functions into shells—a point which may be of interest with experimentally determined densities, and in some nuclear problems. (c) While it is obvious that the shells obtained from these prescriptions cannot replace or do better than the standard wave mechanical wave functions where these are available, the facile qualities of the statistical method in the treatment of solid-state problems, or for dealing with systems under conditions of high temperature and high pressure,<sup>4</sup> could be an added advantage here. There may also be interesting possibilities in molecular work.

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