# Chapter 5

# STATISTICAL MODELS

In the previous chapter we discussed the self-consistent field method for finding energy levels and wave functions for atoms. We saw that any numerical calculation is very cumbersome, especially for atoms with many electrons. For these, there exists a simpler method to obtain at least a fair approximation. Developed by Thomas and Fermi, it is based on Fermi-Dirac statistics. The results admittedly are less accurate than those of the Hartree-Fock calculations. The Thomas-Fermi method nevertheless is very useful for calculating form factors and for obtaining effective potentials which can be used as initial trial potentials in the self-consistent field method. It is also applicable to the study of nucleons in nuclei and electrons in a metal. Exchange is not treated in the Thomas-Fermi model. However, a statistical model for the exchange effects can be given also. We discuss this at the end of this chapter, after the presentation of the model without exchange.

## THOMAS-FERMI MODEL

The goal of the Thomas-Fermi statistical method is to obtain the effective potential energy which is experienced by an infinitesimal test charge, and to find the electron density $\rho(r)$ around the nucleus of an atom.

Consider a number of electrons moving in a volume $\Omega_0$, subject to a spherically symmetric potential energy $V(r)$ which varies sufficiently slowly with r so that the system can be treated by Fermi-Dirac free particle statistics. The electrons are supposed to interact with each other sufficiently to establish statistical equilibrium, but still so little that we can speak of the kinetic and potential energy of each individual electron. We assume $\lim_{r \to \infty} V(r) = 0$. The distribution function f is





$$f = \frac{1}{e^{(E-\zeta)/kT} + 1} \tag{5-1}$$

Here $\zeta$ is the chemical potential, k is Boltzmann's constant, and T is the absolute temperature. If we assume that $T = 0$,

$$f = \begin{cases} 1 & E < \zeta \\ 0 & E > \zeta \end{cases} \tag{5-2}$$

In the zero-temperature limit, therefore, $\zeta$ is the energy of the most energetic electrons; the Pauli principle forces the electrons to occupy all states from the ground state to the state of energy $\zeta$. $\zeta$ is not a function of r; if it were, electrons would migrate to that region of space where $\zeta$ is smallest, because this would make the total energy of the system decrease. By this process, $\zeta$ would tend to equalize. Clearly,

$$\zeta = V(r) + \frac{p_F^2(r)}{2m} \tag{5-3}$$

(In this and subsequent chapters we use ordinary units.) Here $p_F(r)$ is the maximum momentum of the electrons, the so-called Fermi momentum, which must depend on r to make $\zeta$ constant.

We can obtain an expression connecting $p_F$ with $\rho$ by considering the number of quantum states of translational motion of a completely free electron with a momentum whose absolute value lies between p and $p + dp$. For this purpose we consider the electron as moving in a box of volume $\Omega$ without any forces. Then the number of quantum states is equal to

$$2\frac{\Omega}{(2\pi)^3} 4\pi k^2 \, dk \tag{1-18}$$

where $\hbar k = p$ and the factor 2 is due to the two spin orientations that an electron can have. We integrate the above from 0 to $k_F$ and this must equal N, the total number of electrons within the box.

$$2\frac{\Omega}{(2\pi)^3}\frac{4\pi}{3}k_F^3 = N \qquad k_F^3 = 3\pi^2\rho \qquad \rho = \frac{N}{\Omega} \tag{5-4}$$

It is then assumed that we can construct such a box with volume $\Omega$, within the big volume $\Omega_0$ originally considered, which is large enough to make (5-4) valid, and yet small enough that the potential energy does not vary too much within the box. Then we may consider (5-4) and (5-3) simultaneously valid. We now perform a gauge transformation on the potential energy

$$V - \zeta \to V_1 \tag{5-5}$$

From (5-3) and (5-4) it then follows that

$$\rho = \frac{1}{3\pi^2}\,\frac{(2m)^{3/2}}{\hbar^3}\,(-V_1)^{3/2} \tag{5-6}$$

The Poisson equation connects the electrostatic potential $-(1/e)V$ with the charge density $-e\rho$. With suitable rearrangement this is

$$\nabla^2 V_1 = -4\pi e^2 \rho \tag{5-7}$$

Combining (5-6) with (5-7) we get

$$\frac{1}{r}\,\frac{d^2}{dr^2}(rV_1) = -\frac{4e^2}{3\pi\hbar^3}\,(2m)^{3/2}\,(-V_1)^{3/2} \tag{5-8}$$

For $r \to 0$ the leading term of V must be $-Ze^2/r$. Hence (5-8) is supplemented by the boundary condition

$$\lim_{r \to 0} (rV_1) = -Ze^2 \tag{5-9}$$

We make the change of variable

$$r = xb \qquad rV_1 = -Ze^2\Phi$$

$$b = \frac{(3\pi)^{2/3}}{2^{7/3}}\,\frac{\hbar^2}{me^2}\,Z^{-1/3} = 0.885 a_0 Z^{-1/3} \tag{5-10}$$

with $a_0 = \hbar^2/me^2$, the Bohr radius. Therefore the equation we must solve is

$$\frac{d^2\Phi}{dx^2} = \frac{\Phi^{3/2}}{\sqrt{x}} \tag{5-11}$$

$$\Phi(0) = 1 \tag{5-12}$$

This is the *Thomas-Fermi* equation.

Physically (5-11) holds only for positive $\Phi$; for negative $\Phi$ the electron density vanishes because there is no state with $E > \zeta$, c.f. (5-2) and (5-6). The correct differential equation for negative $\Phi$ is therefore $d^2\Phi/dx^2 = 0$ ($\Phi < 0$). If $x_0$ is the point where $\Phi$ crosses the x axis, we have $\Phi = A(x - x_0)$, where A is a negative constant which by continuity is equal to $\Phi'(x_0)$. Thus the solution is completely determined if we know it for $\Phi > 0$, and we therefore consider only this portion of it. At $x_0$, $\Phi(x_0) = 0$, and $\Phi'(x_0)$ cannot vanish; for if it did, equation (5-11) indicates that $\Phi''$ and all higher derivatives would vanish, giving the unacceptable trivial solution $\Phi = 0$.



## SOLUTIONS OF THE THOMAS-FERMI EQUATION

Equation (5-11) is a second-order, nonlinear, differential equation. It is important to notice that it is independent of Z. Evidently, we shall obtain a whole family of solutions, since we have specified only one boundary condition. These solutions can be classified according to the initial slope, which is clearly arbitrary in the differential equation (5-11).

Certain properties of the solutions can be obtained by examining (5-11). All solutions are initially concave upward. Hence if a particular solution doesn't become zero, it will remain concave upward, and will either diverge for large x or approach the x axis asymptotically. If a solution becomes zero for finite $x = x_0$, the differential equation (5-11) stops being valid as explained above. Finally, we note that $\Phi$ does not have a Taylor expansion in x about 0 since $\Phi''(0)$ diverges. The behavior of the various possible solutions is illustrated in Figure 5-1.

Numerical integration of equation (5-11) for various initial slopes indicates that the solutions can be expressed in a semiconvergent series

$$\Phi = 1 - a_2 x + a_3 x^{3/2} + a_4 x^2 + \ldots$$

with

$$a_3 = \tfrac{4}{3} \qquad a_4 = 0 \qquad \Phi'(0) = -a_2 \tag{5-13}$$

Three distinct types of solutions are found as predicted above. One class consists of solutions which vanish for finite $x = x_0$. These have $a_2$ larger than a critical value. With $a_2$ smaller than the critical value, another class of solutions is found, which do not vanish anywhere and diverge for large x. Finally when $a_2$ is precisely at the critical value, a unique solution is obtained which is asymptotic to the x axis. Numerical determination of the critical initial slope gives $a_2 = -\Phi'(0) = 1.5880710\ldots \approx \pi/2$, and this critical solution

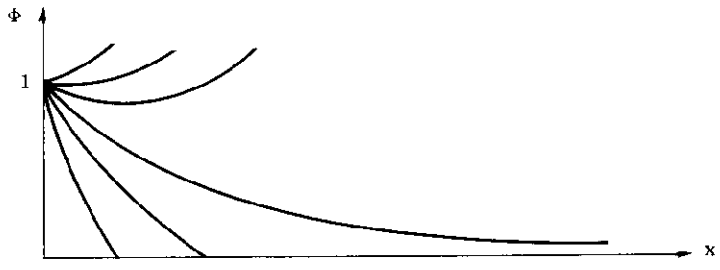


**Figure 5-1**
Behavior of the solutions to (5-12)

has been tabulated (Landau and Lifshitz[1], p. 261). These three different types of solutions correspond to different physical circumstances for the atom, which we now discuss.

## DETERMINATION OF ADDITIONAL BOUNDARY CONDITIONS

Further analysis of specific physical situations leads to a determination of additional boundary conditions on $\Phi$, which in turn determine unique solutions. We examine several such situations.

Let the electronic configuration of a neutral atom or charged ion under consideration be confined to a sphere of radius $r_0$. The total number of electrons N in the electronic configuration is given by

$$N = 4\pi \int_0^{r_0} \rho r^2 \, dr = -\frac{1}{e^2} \int_0^{r_0} r \frac{d^2}{dr^2} (rV_1) \, dr$$

$$= Z \int_0^{x_0} x \Phi'' \, dx$$

$$\frac{N}{Z} = (\Phi' x - \Phi)\Big|_0^{x_0} \tag{5-14a}$$

Using the boundary condition at $x = 0$ this reduces to

$$\Phi(x_0) - x_0 \Phi'(x_0) = \frac{Z - N}{Z} = \frac{z}{Z} \tag{5-14b}$$

where z is the net charge of the neutral atom or charged ion. (For a neutral atom $z = 0$.)

[1] L.D. Landau and E.M. Lifshitz, *Quantum Mechanics*, 3rd ed., Pergamon, Oxford, 1977.



Let us first consider free atoms or ions, viz., systems not subject to external pressure. In this case $\rho = 0$ at $r = r_0$ which implies

$$\Phi(x_0) = 0 \tag{5-15a}$$

$$x_0 \Phi'(x_0) = -\frac{z}{Z} \tag{5-15b}$$

For neutral atoms, $z = 0$ and (5-15) has the consequence that

$$\Phi(x_0) = 0 \tag{5-16a}$$

$$x_0 \Phi'(x_0) = 0 \tag{5-16b}$$

If $x_0$ is a finite number, (5-16) gives $\Phi(x_0) = \Phi'(x_0) = 0$. Since no nontrivial solutions with this property exist, a solution for a free neutral atom with finite radius cannot be obtained. To achieve a solution for a free neutral atom, we must assume that the surface of the atom lies at infinity and interpret (5-16) as

$$\lim_{x \to \infty} \Phi = 0 \tag{5-17a}$$

$$\lim_{x \to \infty} x\Phi' = 0 \tag{5-17b}$$

(5-17a) by itself determines a unique solution, the only solution which is asymptotic to the x axis. This is the critical solution mentioned earlier. Since the function $\Phi$ vanishes only at infinity, the neutral free atom has no boundaries in the Thomas-Fermi model.

It can be verified that $144\, x^{-3}$ satisfies the differential equation, as well as the bounding conditions (5-17). The boundary condition at the origin is not satisfied. Sommerfeld showed that this solution is the asymptotic form of the correct solution for a free neutral atom.

For free ions ($z \neq 0$), the boundary condition (5-15a) indicates that the solutions of (5-11) which vanish at finite $x = x_0$ correspond to ions of radius $r_0$. Boundary condition (5-15b) gives the net charge of the ion. Since the slope of $\Phi$ must be negative at $x_0$ (see Figure 5-1), (5-15) implies that the theory cannot handle negative free ions.

Next, we consider neutral atoms under pressure. We do not concern ourselves with ions under pressure, since an assembly of many ions under pressure would lead to physical difficulties, because of the large, cumulative Coulomb forces. When the atom is subject to an external pressure, $\rho(x_0)$ no longer equals zero, and we must remain with (5-14b). Evidently the solutions that do not vanish for any x correspond to this

case. Equation (5-14b) determines $x_0$ and therefore the radius of such systems. Since atoms are neutral, (5-14b) becomes

$$\frac{\Phi(x_0)}{x_0} = \Phi'(x_0) \tag{5-18}$$

This defines the point $x_0$ at which the tangent to $\Phi$ passes through the origin. For $x > x_0$ the differential equation (5-12) is no longer a description of the physical situation.

## APPLICATIONS

All atoms in the Thomas-Fermi model have the same electron distribution, except for a different scale of length and total number of electrons. Equations (5-10) show that the length scale for any atom is proportional to $Z^{-1/3}$. Thus the radius of the entire atom decreases as $Z^{-1/3}$. However it can be shown that the radius of the sphere which contains all but one electron is roughly proportional to $Z^{1/6}$.

An interesting application of the Thomas-Fermi method is to calculate for which Z bound atomic states with a given angular momentum first appear. We consider the reduced radial equation

$$\frac{d^2\mathcal{R}}{dr^2} + \frac{2m}{\hbar^2}(E - V_r)\mathcal{R} = 0$$

$$V_r = V(r) + \frac{\hbar^2}{2m}\frac{(\ell + \frac{1}{2})^2}{r^2} \tag{5-19}$$

[We have made the usual WKB substitution $\ell(\ell + 1) \rightarrow (\ell + \frac{1}{2})^2$.] Bound states exist only if $E - V_r > 0$ for some range of r. Since $E < 0$, this means we must have

$$-\frac{2m}{\hbar^2}V(r)\,r^2 > (\ell + \tfrac{1}{2})^2$$

$$\frac{2me^2}{\hbar^2}Zr\Phi = 0.885\,Z^{2/3}\,2x\Phi > (\ell + \tfrac{1}{2})^2 \tag{5-20}$$

for some range of r.

The following broad maximum is found in $2x\Phi$.

| $\sqrt{2x}$ | 1 | 1.96 | 2.04 | 2.12 | 2.20 | 3.0 |
|---|---|---|---|---|---|---|
| $2x\Phi$ | 0.607 | 0.972 | 0.973 | 0.968 | 0.968 | 0.829 |



A necessary condition for (5-20) to hold is that

$$0.885Z^{2/3}\,\mathrm{Max}(2x\Phi) > (\ell + \tfrac{1}{2})^2$$

$$0.861Z^{2/3} > (\ell + \tfrac{1}{2})^2$$

$$Z > 0.157(2\ell + 1)^3 \tag{5-21a}$$

This formula determines the value of Z for which an electron with a given $\ell$ is first bound. We should expect that we can change the "greater" sign in (5-21a) to an "equal" sign if we increase the coefficient somewhat. If we take 0.17 instead of 0.157:

$$Z = 0.17(2\ell + 1)^3 \tag{5-21b}$$

we get

| for $\ell$ = | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Z = | 4.6 | 21.25 | 58.3 | 123.9 |

Rounding to the nearest integer we obtain 5, 21, 58, 124. Comparing with experiment, we find the first three results to be correct and the last one predicting that g electrons can appear only in the $124^{th}$ element. This is six places beyond the predicted noble gas Z = 118, with the heaviest element so far discovered having Z = 103.

The maximum of $Vr^2$ was found above to be quite flat. We expect therefore that there will be close cancellation between V(r) and the centrifugal potential term for the largest $\ell$ which can be bound by a given atom. In this situation a small change in Z would effect a large change in the wave function; see pp. 81.

## VALIDITY OF THE THOMAS-FERMI METHOD

The Fermi model is useful for calculating properties that depend on the average electron such as form factor (see Chapter 13), total energy of all electrons, electrostatic potential produced by all electrons at the nucleus, and average excitation potential. The latter occurs in the theory of atomic stopping power and is defined by

$$\log E_{AV} = \frac{1}{Z}\sum_j \log E_j$$

where $E_j$ is the average excitation potential of the $j^{th}$ orbital. The Thomas-Fermi method, even when corrected for exchange effects (as discussed below), is very poor for calculating properties that depend on the outer electrons, such as the ionization potential, or the mean square radius of the atom, which is important for diamagnetism.

Because of the statistical nature of this model, best results are obtained for large Z. Experience shows that calculations for $Z < 10$ are unreliable.

For fixed Z, the Thomas-Fermi results are inaccurate for large and small r. For large r the electron density is overestimated. Indeed, we saw that the Thomas-Fermi atom has no boundaries, with the electron density $\rho \sim (\Phi/r)^{3/2}$ decreasing as $1/r^6$ at large distance. On the other hand, we expect the electron density of a physical atom should decrease exponentially. For small r the Thomas-Fermi density diverges as $1/r^{3/2}$ rather than remaining finite.

## CORRECTION FOR EXCHANGE; THE THOMAS-FERMI-DIRAC EQUATION

The Thomas-Fermi equation (5-11) does not take into account the exchange interaction. This was done by Dirac. We shall here give a simple derivation of this correction.

We recall the exchange term in the Hartree-Fock theory,

$$\int U(\mathbf{r}_1, \mathbf{r}_2)\, u_1(\mathbf{r}_2)\, d\tau_2$$

$$U(\mathbf{r}_1, \mathbf{r}_2) = -\frac{e^2}{r_{12}}\, \rho(\mathbf{r}_1, \mathbf{r}_2)$$

$$\rho(\mathbf{r}_1, \mathbf{r}_2) = \sum_j u_j^*(\mathbf{r}_2)\, u_j(\mathbf{r}_1)$$

In the spirit of the Thomas-Fermi method we consider the electrons to be free (subject to a constant potential). Thus we set

$$u_j(\mathbf{r}_1) = \Omega^{-1/2} e^{i\mathbf{k}_j \cdot \mathbf{r}_1} \tag{5-22}$$

$$\rho(\mathbf{r}_1, \mathbf{r}_2) = \Omega^{-1} \sum_j e^{i\mathbf{k}_j \cdot (\mathbf{r}_1 - \mathbf{r}_2)}$$

$$\approx \frac{1}{(2\pi)^3} \int e^{i\mathbf{k} \cdot \mathbf{r}_{12}}\, d^3k \qquad (\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2)$$



$$= \frac{4\pi}{(2\pi)^3} \int_0^{k_F} \frac{\sin kr_{12}}{kr_{12}}\, k^2\, dk$$

$$= \frac{1}{2\pi^2} \frac{1}{r_{12}^3} (\sin k_F r_{12} - k_F r_{12} \cos k_F r_{12}) \tag{5-23}$$

which verifies (4-60).

In the expression (5-23) for $\rho(\mathbf{r}_1, \mathbf{r}_2) k_F$ depends on position in the following fashion; see also footnote 4 in Chapter 4. When $\mathbf{r}_1$ and $\mathbf{r}_2$ are sufficiently close together so that they lie in the same cell $\Omega$ in which we take the potential to be constant, $k_F$ is evaluated at the radius vector of that cell, which we may take to be $\frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2)$. When $\mathbf{r}_1$ and $\mathbf{r}_2$ lie in different cells, we may assume $|\mathbf{r}_1 - \mathbf{r}_2|$ to be large. In that case the dependence of $k_F$ on position may be ignored as $\rho(\mathbf{r}_1, \mathbf{r}_2)$ goes rapidly to zero. In evaluating integrals over $r_2$, which involve $\rho(r_1, r_2)$, we may take $k_F$ to be a function of $r_1$ only, hence constant in the integration.

It is seen that

$$\rho(\mathbf{r}, \mathbf{r}) = \frac{k_F^3}{6\pi^2} = \frac{1}{2}\rho \tag{5-24}$$

The factor $\frac{1}{2}$ is present due to the fact that the density matrix $\rho(\mathbf{r}, \mathbf{r})$ is defined as a sum of $|u_i(\mathbf{r})|^2$ taken over all orbitals with the same value of the spin projection, while the density $\rho$ is the sum of $|u_i(\mathbf{r})|^2$ over all orbitals with both spin projections. In the absence of interactions half the electrons will be in one spin state and half in the other.

We recall that for the $i^{th}$ electron

$$V_{eff}(\mathbf{r}_1) = -\int e^2 \frac{\rho(\mathbf{r}_1, \mathbf{r}_2)}{r_{12}} \frac{u_i(\mathbf{r}_2)}{u_i(\mathbf{r}_1)}\, d\tau_2 \tag{4-39}$$

Hence in the Thomas-Fermi spirit

$$V_{eff}(\mathbf{r}_1) = -e^2 \int \frac{\rho(\mathbf{r}_1, \mathbf{r}_2)}{r_{12}}\, e^{i\mathbf{k}_i \cdot \mathbf{r}_{21}}\, d\tau_2 \tag{5-25a}$$

This integral is evaluated to be

$$V_{eff}(\mathbf{r}_1) = -2\left(\frac{3}{\pi}\rho\right)^{1/3} e^2 F(\eta)$$

$$= -\frac{2}{\pi} e^2 k_F F(\eta) \tag{5-25b}$$

where

$$\eta = \frac{k_i}{k_F}$$

$$F(\eta) = \frac{1}{2} + \frac{1-\eta^2}{4\eta} \log\frac{1+\eta}{1-\eta} \tag{5-26}$$

$F(0) = 1$, $F(1) = \frac{1}{2}$, and F decreases from 1 to $\frac{1}{2}$ monotonically as $\eta$ goes from 0 to 1.

We now must determine a relation between V, the electrostatic potential energy, and $\rho$. The simplest argument is that the total energy of the most energetic electron is now, instead of (5-3),

$$\zeta = V(r) - \frac{2}{\pi} e^2 k_F F(1) + \frac{p_F^2}{2m} = V(r) - \frac{e^2}{\pi}(3\pi^2\rho)^{1/3} + \frac{\hbar^2}{2m}(3\pi^2\rho)^{2/3} \tag{5-27}$$

Here the effective exchange potential energy has been added to V(r); $V_{eff}$ depends on the momentum according to (5-25). In our case of the most energetic electron, $\eta = 1$ and $F(1) = \frac{1}{2}$, according to (5-26). The result (5-27) is identical with (5-30) to be derived below.

For variety, we shall now derive (5-27) in another fashion. We shall consider the total energy E of the system of electrons, vary this quantity as a function of $\rho$, and obtain the desired relations from the requirement that E be stationary. This variational approach could have been used in deriving the Thomas-Fermi model.

The total energy is the sum of the kinetic energy $E_k$ and potential energy $E_p$. The total kinetic energy of the electrons can be obtained by multiplying the number of states by $\hbar^2k^2/2m$, integrating over all momenta from 0 to $k_F$, and then integrating over all volume. The result is easily found to be

$$E_k = \int d\tau \left[\frac{3}{5}\frac{\hbar^2\pi^2}{2m}\left(\frac{3}{\pi}\rho\right)^{2/3}\rho\right] \tag{5-28}$$

The potential energy is

$$E_p = \int \left[\left(-\frac{Ze^2}{r}\right)\rho + \left(\frac{1}{2}\int d\tau_2 \frac{e^2}{r_{12}}\rho(r_2)\right)\rho - \frac{3}{4}e^2\left(\frac{3\rho}{\pi}\right)^{1/3}\rho\right] d\tau \tag{5-29}$$



The first term is due to the nuclear charge; the second term is due to the interelectron interaction, the factor $\frac{1}{2}$ being inserted to avoid counting the electron pairs twice. The third term is the exchange energy, already computed when the Thomas-Fermi approximation was applied to the Hartree-Fock theory; see (4-66).

We now set the arbitrary variation of $E = E_k + E_p$ with respect to $\rho$ equal to 0 and obtain

$$a_0 e^2 \frac{\pi^2}{2}\left(\frac{3}{\pi}\rho\right)^{2/3} + V \quad e^2\left(\frac{3\rho}{\pi}\right)^{1/3} = 0$$

$$V(r_1) = -\frac{Ze^2}{r_1} + \int d\tau_2 \frac{e^2}{r_{12}}\rho(r_2) \qquad a_0 = \frac{\hbar^2}{me^2} \tag{5-30}$$

[In point of fact, the variation of E is not totally unrestricted, since we must also have $\int \rho\, d\tau = N$, the total number of electrons. We can introduce this subsidiary condition by the Lagrange multiplier method. This adds a term $\lambda$ to (5-30), where $\lambda$ is the multiplier. We now can make a gauge transform $V + \lambda \to V$ and obtain (5-30).]

We now solve (5-30) for the density. Setting $y = a_0(3\rho/\pi)^{1/3} = (a_0/\pi)k_F$, we get

$$y = \frac{1}{\pi^2}\left(1 + \sqrt{1 - 2\pi^2\frac{Va_0}{e^2}}\right) \tag{5-31}$$

The plus sign is chosen in front of the radical to assure agreement with the Thomas-Fermi theory and to avoid negative density. With

$$\Psi = \frac{1}{2\pi^2} - \frac{Va_0}{e^2} \tag{5-32}$$

we obtain

$$y = \frac{\sqrt{2}}{\pi}\left(\sqrt{\Psi} + \frac{1}{\pi\sqrt{2}}\right) \tag{5-33}$$

Poisson's equation now gives

$$\frac{d^2}{dr^2}(r\Psi) = 4\pi a_0 \rho r = \frac{4\pi^2}{3a_0^2} y^3 r$$

$$\frac{d^2}{dr^2}(r\Psi) = \frac{2^{7/2}}{3a_0^2\pi} r\left(\sqrt{\Psi} + \frac{1}{\pi\sqrt{2}}\right)^3 \tag{5-34}$$

Finally, changing variables as in (5-10),

$$r = xb \qquad r\Psi = a_0 Z \Phi \qquad b = 0.885 a_0 Z^{-1/3}$$

we obtain

$$\Phi'' = x\left(\sqrt{\frac{\Phi}{x}} + \beta\right)^3$$

$$\beta = \sqrt{\frac{b}{a_0 Z}}\,\frac{1}{\pi\sqrt{2}} = 0.2118 Z^{-2/3} \tag{5-35}$$

This is the *Thomas-Fermi-Dirac* equation. Unlike (5-12), it depends on Z through $\beta$. We see that for $Z \to \infty$, (5-35) becomes (5-11) Indeed it can be shown quite rigorously that the Thomas-Fermi model becomes exact as $Z \to \infty$. Moreover, there are non-asymptotic corrections, present at finite Z, which fall off more slowly with Z than the exchange term.[2]

The boundary conditions for the Thomas-Fermi-Dirac equation are the following:

$$\Phi(0) = 1$$

$$\Phi(x_0) - x_0 \Phi'(x_0) = \frac{Z - N}{Z} = \frac{z}{Z} \tag{5-36}$$

For free atoms and ions we can no longer define the surface by $\rho(x_0) = 0$, since it is seen from (5-33) that $\rho$ never vanishes. However, we can define $x_0$ by requiring that the pressure vanish there. To do this we write the specific energy $\epsilon$ (energy per particle) from (5-28) and (5-29). [There is actually some problem about the electrostatic interaction of the electrons, but (5-37) gives the correct result.]

$$\epsilon = \frac{3}{5}\frac{\pi^2}{2}\frac{e^2}{a_0} y^2 + V(r) - \frac{3}{4}\frac{e^2}{a_0} y \tag{5-37}$$

The pressure $P = -(\partial \epsilon / \partial v)_S$, where v is the specific volume and S is the entropy. Since (5-37) has been derived for T = 0, the entropy is equal to zero, hence already constant, so we merely need to differentiate with respect to v. Recalling $y = [(3/\pi)\rho]^{1/3} a_0$, $v = 1/\rho$, we obtain

$$P = \rho \frac{e^2}{a_0}\left[\frac{\pi^2 y^2}{5} - \frac{y}{4}\right] \tag{5-38}$$

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[2] A systematic study of corrections to the Thomas-Fermi theory, as well as an assessment of its validity may be found in E.H. Lieb, Rev. Mod. Phys. *53*, 603(1981).



**Table 5-1**
Comparison of Energy Levels of Ag as Calculated by Hartree-Fock Method and Thomas-Fermi-Dirac Method (Values are given in Ry)

| | Hartree-Fock | Thomas-Fermi-Dirac |
|---|---|---|
| 1s | 1828 | 1805 |
| 2s | 270 | 263 |
| 2p | 251 | 245 |
| 3d | 29.8 | 29.2 |
| 4s | 8.46 | 7.95 |

This vanishes at

$$y = \frac{5}{4\pi^2}$$

or

$$\rho(x_0) = 2.13 \times 10^{-3} a_0^{-3} \tag{5-39}$$

Had we not included the exchange effect, P would vanish at y = 0, implying $\rho(x_0) = 0$ as before. A lower density than (5-39) is unphysical in the Thomas-Fermi-Dirac model since this would correspond to negative pressure. Substituting (5-39) in (5-33) we find with some algebra that

$$\frac{\Phi(x_0)}{x_0} = \frac{\beta^2}{16} \tag{5-40}$$

These results imply that in the Thomas-Fermi-Dirac theory atoms as well as ions have a finite radius. Equation (5-40) does not apply of course to systems under external pressure, since then the density can be larger than that given in (5-39). [No solution which goes to zero at $x = \infty$ exists, as can be seen from (5-35). This causes no difficulty since atomic solutions no longer satisfy (5-17).] As before, the differential equation applies only to $x \le x_0$. Moreover, from numerical calculations it is found that in the Thomas-Fermi-Dirac model negative free ions are not treated.

One can solve the radial, one-electron Schrödinger equation for all normally occupied orbitals n, $\ell$ for many atoms, using as the potential that given by the Thomas-Fermi-Dirac method. This gives both energy levels and wave functions for these orbitals. From these wave functions, one could then construct a potential using the Hartree-Fock prescription, and this should be very good starting data for

a Hartree-Fock calculation. For atoms for which no Hartree-Fock solution is available, the one-electron Thomas-Fermi-Dirac wave functions are the best available. That they are indeed very good is shown by comparing their eigenvalues with the Hartree-Fock results. We list these for a few orbitals in silver for which both types of calculation exist in Table 5-1.

## PROBLEMS

1. Derive the Thomas-Fermi equation, using the variation principle as in the derivation of the Thomas-Fermi-Dirac theory.
2. A solvable Hartree-Fock problem: Consider a N electron "gas" moving in a large box of volume $\Omega$ in which there is a background positive charge density of $eN/\Omega$. The electrons interact with this background through a potential of the form

$$-e^2 \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, d\tau' \tag{1}$$

where $\rho$ is the density of the electron gas.

$$\rho = \frac{N}{\Omega} \tag{2}$$

They also interact with each other through the usual Coulomb interaction. Assume the number of spin up (down) electrons is $N_+$ ($N_-$).

$$N_+ + N_- = N \tag{3}$$

Let the spin up (down) electrons be described by individual wave functions $u_i^+ \alpha (u_i^- \beta)$, where $u_i^+ (u_i^-)$ is the space part, and $\alpha(\beta)$ the spin part of the wave function. Write down the Hartree-Fock equations for $u_i^\pm$. Show that they are solved by plane waves

$$u_i^\pm(\mathbf{r}) = \frac{1}{\sqrt{\Omega}}\, e^{i\mathbf{k}_i \cdot \mathbf{r}} \tag{4}$$

Procedure: Assume the solution is of the form (4). Evaluate the direct and exchange interactions



$$V(\mathbf{r}) = e^2 \int \sum_i \frac{|u_i^+(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|}\, d\tau' + e^2 \int \sum_i \frac{|u_i^-(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|}\, d\tau'$$

$$U_+(\mathbf{r}, \mathbf{r}') = -e^2 \sum_i \frac{u_i^{+*}(\mathbf{r}')\, u_i^+(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \qquad \text{for spin up electrons}$$

$$U_-(\mathbf{r}, \mathbf{r}') = -e^2 \sum_i \frac{u_i^{-*}(\mathbf{r}')\, u_i^-(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \qquad \text{for spin down electrons} \tag{5}$$

The sums over i are performed with the usual assumption that the spin up (down) electrons fill up the available spaces up to the Fermi momentum $k_F^+$ ($k_F^-$). [Recall equations (5-23) to (5-26).] Thus, show the following:

$$V(\mathbf{r}) = e^2 \int \frac{\rho_+}{|\mathbf{r} - \mathbf{r}'|}\, d\tau' + e^2 \int \frac{\rho_-}{|\mathbf{r} - \mathbf{r}'|}\, d\tau'$$

$$\rho_\pm = \frac{N_\pm}{\Omega} = \frac{k_F^{\pm 3}}{6\pi^2}$$

$$U_\pm(\mathbf{r}_1, \mathbf{r}_2) = \frac{-e^2 \rho_\pm(\mathbf{r}_1, \mathbf{r}_2)}{r_{12}}$$

$$= \frac{-e^2}{2\pi^2} \frac{1}{r_{12}^4} \left[ \sin k_F^\pm r_{12} - k_F^\pm r_{12} \cos k_F^\pm r_{12} \right]$$

$$\int U_\pm(\mathbf{r}_1, \mathbf{r}_2)\, u_i(\mathbf{r}_2)\, d\tau_2$$

$$= -\frac{2}{\pi} e^2 k_F^\pm F(\eta^\pm)\, u_i^\pm(\mathbf{r}_1)$$

$$F(\eta) = \tfrac{1}{2} + \frac{1 - \eta^2}{4\eta} \log \frac{1 + \eta}{1 - \eta}$$

$$\eta^\pm = \frac{k}{k_F^\pm} \tag{6}$$

(Many of the integrals that arise in this problem are evaluated in Chapter 5.) Noting that the direct interaction potential $V(\mathbf{r})$ cancels the interaction with the background (1), show that the Hartree-Fock eigenvalue is

$$\epsilon_{\mathbf{k}}^{\pm} = \frac{\hbar k^2}{2m} - \frac{2e^2 k_F^{\pm}}{\pi} F(\eta^{\pm})$$

and the expectation value of the Hamiltonian is

$$\langle H \rangle = E = \frac{\Omega}{(2\pi)^3} \left\{ \frac{2\pi\hbar^2}{5m} (k_F^{+5} + k_F^{-5}) - e^2 (k_F^{+4} + k_F^{-4}) \right\}$$

(This provides a plausible, but not very accurate, picture of valence electrons in a conducting metal.)

3. Show directly from the Thomas-Fermi equation (5-12), that a solution which remains finite at infinity must go to zero, rather than to a constant.
4. Verify the manipulations leading to (5-11).
5. Assuming a solution to (5-11) of the form (5-13), verify that $a_2$ is undetermined, $a_3 = 4/3$, $a_4 = 0$.