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A Proposed Modification of the Available Momentum Region in Thomas-Fermi Theory

John F. Barnes

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A PROPOSED MODIFICATION OF THE AVAILABLE MOMENTUM REGION IN THOMAS-FERMI THEORY

By

John F. Barnes

A Dissertation

Submitted in Partial Fulfillment of the

Requirements for the Degree of

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DATE

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INTRODUCTION

The statistical model of the atom, first propounded by Fermi (Ref. 1) and Thomas (Ref. 2) has proved a most useful approximation to the self-consistent field method in calculating electron distributions and fields in atoms. Because of its relative simplicity, it has found wide application as a means of predicting properties of free atoms and of solids. The original theory has been the subject of many modifications and refinements,[1] some of which are reviewed in this paper.

Of particular interest here are the binding energies of atoms as obtained by the statistical theory, and the calculated equation of state of compressed materials. It should be mentioned here that the temperature is taken as zero degrees absolute unless stated otherwise.

Electron distributions calculated on the basis of the model suffer, broadly, from two faults. The first is that only a smoothly varying "average" distribution is obtained, as opposed to a distribution which reveals the grouping of electrons into shells, such as is obtained by

---

[1] For a concise development of the relation of the Thomas-Fermi approximation to the general many-body problem one may refer to Ref. 3. Comprehensive accounts of the applications and improvements are found in Refs. 4 and 5, while references are given in the text for the specific points treated.

the self-consistent field treatment. Thus the applicability of the results of the theory is limited to those properties which do not depend on the presence of a shell structure. In particular, in compressed matter, the influence of the outer shells of electrons is thought to be unimportant only at pressures of the order of 10^{13} dyne/cm^2 and above, so that the pressure-compression relations predicted by the statistical theory are reliable only at these quite high pressures. In the vicinity of normal material density, where the model is not valid, the Thomas-Fermi pressures are substantially above the experimental values.

The second fault is that an infinite electron density is obtained at the nucleus, causing the calculated atomic binding energies to be considerably too large.

In the Thomas-Fermi approximation the only interaction considered between electrons is in the mean screening of the nuclear charge by the electron cloud. A better estimate of the interaction is achieved through the introduction of the exchange energy, which leads to the Thomas-Fermi-Dirac model of the atom (Ref. 6). The exchange energy accounts in some measure for the tendency of electrons of parallel spin to keep apart as required by the Fermi-Dirac statistics. However, although the pressure calculated on this model is lessened, and thereby ostensibly improved, the binding energy is increased, or made worse. Furthermore, a more accurate treatment of the electron interaction makes the binding energy greater yet. This procedure is to introduce the correlation energy, which is meant to account for the tendency of electrons, regardless of

spin, to stay apart because of their Coulomb repulsion. Both of these effects lower the pressure and increase the binding energy by tending to contract the electron cloud about the nucleus, the density at the nucleus remaining infinite.

Numerical evaluations of the equation of state on both the Thomas-Fermi model and the Thomas-Fermi-Dirac model have been performed (see, e.g., Refs. 7, 8, 9). Prior to proceeding with the primary task of the paper we compute the correlation-corrected equation of state for a pair of metals, using the equations suggested by Lewis (Ref. 10).

We might consider the correlation energy to be one of the two effects neglected by the Thomas-Fermi-Dirac model of the atom. The other would be of the nature of the so-called inhomogeneity energy, which is essentially a correction for the nonclassical behavior of the electrons. It is the purpose of this paper to develop a "quantum correction" of the statistical theory, effective primarily near the nucleus, which is based on placing a lower limit on the momentum an electron is allowed to possess at a given distance from the nucleus. We derive a modified statistical equation, the solutions of which can be obtained by an iterative procedure similar to that employed in the self-consistent field method. An approximation method is developed whereby the solutions follow without iteration; the results of these calculations are described. The most significant numerical result is the excellent agreement obtained between the calculated atomic binding energies and the experimental values. We also evaluate the effect of this modification on the equation of state.

Part I contains the background material for the modification which is developed and discussed in Parts II and III. In addition, we have attempted to make Part I a fairly complete, if brief, account of other work which bears on the results we have obtained. Specifically, a section on Scott's correction to the binding energy is included since it is a correction based on a somewhat similar (Coulomb field) approximation to that which we have used, and the points of agreement and disagreement are of interest. There is a section on the Weizsäcker kinetic energy correction, with which it is interesting to compare our kinetic energy correction. There is also a brief note on one treatment of the density matrix, mainly for the expository purpose of indicating the quantum-mechanical origin of the various corrections of the statistical theory.

The numerical work has been performed on the Los Alamos IBM type 704 digital computers.

PART I

THE THOMAS-FERMI AND THOMAS-FERMI-DIRAC EQUATIONS

1. The Thomas-Fermi Equation

In an assembly of particles which obey the Pauli exclusion principle, such as electrons, the Fermi distribution law (see, e.g., Ref. 11) states that the probability of a particle occupying a state of energy E_j is given by

$$n_j = \frac{1}{e^{\beta(E_j-\mu)}+1}, \tag{1.1}$$

where μ, the chemical potential, is a function of temperature and the total number of particles in the assembly, say N. β is $1/kT$, where k is Boltzmann's constant and T is the absolute temperature. At $T = 0$, (1.1) reduces to $n_j = 1$ for E_j less than μ, and to $n_j = 0$ for E_j greater than μ. The value of μ at zero temperature may be designated as the Fermi energy, E'.

The number of energy states available for particles of spin $\frac{1}{2}$ in a range of kinetic energy ΔW is easily evaluated as

$$\frac{8\pi m\Omega}{h^3}(2mW)^{1/2}\Delta W,$$

where m is the particle mass, Ω is the volume of coordinate space occupied by the assembly, and h (= $2\pi\hbar$) is Planck's constant. Expressed in other terms, it follows that there are $2/h^3$ states in a volume of phase space equal to the product

$$\Delta x\Delta y\Delta z\Delta p_x\Delta p_y\Delta p_z,$$

where p_x is the x-component of the momentum $\vec{p}$, etc.

At the absolute zero of temperature, from the above considerations it is clear that the number of occupied states per unit volume of phase space is $2/h^3$ for those points of phase space representing energy less than E', and zero otherwise. If the potential energy is V, it follows that points within a sphere in momentum space of radius

$$P = [2m(E'-V)]^{1/2} \tag{1.2}$$

are filled, and points outside the sphere are empty. P is the Fermi momentum. The particle density in coordinate space is then given by an integration over momentum space:

$$\rho = \frac{2}{h^3}\int_0^P 4\pi p^2 dp$$

$$= \frac{8\pi}{3h^3}P^3$$

$$= \frac{8\pi}{3h^3}\,[2m(E'-V)]^{3/2}. \qquad (1.3)$$

The simplest derivation of the Thomas-Fermi equation (Refs. 1,2) proceeds by assuming that the potential field in an atom varies sufficiently slowly that the fractional change in an electron's deBroglie wave length, defined by $\lambda = h/p$, is small over a distance equal to the wave length. If one also assumes that there are many electrons in a region whose volume is of the order of λ^3, then one can apply the statistics to the distribution, and the density at a point is given by (1.3). The field in which each electron moves is taken to be the average field due to the nucleus, of charge Ze, and the electron distribution itself. With r measuring the distance from the nucleus, Poisson's equation,

$$\frac{1}{-e}\nabla^2 V = 4\pi e\rho,$$

becomes

$$\frac{d^2V}{dr^2} + \frac{2}{r}\frac{dV}{dr} = -\frac{32\pi^2 e^2}{3h^3}\,[2m(E'-V)]^{3/2}. \qquad (1.4)$$

Only the derivatives with respect to r have been retained in the Laplacian, since the charge distribution is spherically symmetric.

New independent and dependent variables are now chosen. The unit of length is taken as

$$r_o = a_o\left(\frac{9\pi^2}{128Z}\right)^{1/3}, \tag{1.5}$$

where

$$a_o = \frac{\hbar^2}{me^2}$$

is the first Bohr radius. Distances from the nucleus are then measured in terms of $x = r/r_o$. The new dependent variable, the Thomas-Fermi "potential" function[2] ϕ, is defined by the relation

$$Ze^2\phi = (E'-V)r. \tag{1.6}$$

With these changes, (1.4) reduces to the Thomas-Fermi equation,

$$\phi'' = \frac{\phi^{3/2}}{x^{1/2}}. \tag{1.7}$$

The prime denotes differentiation with respect to x.

---

[2]Hereafter the quotation marks will be omitted in referring to the potential function.

distribution. There is, however, a tendency for electrons of like spin to stay apart, because of the exclusion principle; this is partially accounted for by the inclusion of the exchange energy in the total energy of the system of free electrons.

Exchange effects were first introduced into the statistical model by Dirac (Ref. 6). However, we shall outline here a method due to Jensen (Ref. 12), because it lends itself very simply to a later application. The method consists of minimizing the total energy of the system, where the energy is written as a volume integral of a function of density.

The exchange energy density, or exchange energy per unit volume, of a system of free electrons has been calculated by Bloch (Ref. 13), and is equal to

$$-c_{ex}\rho^{4/3},$$

where

$$c_{ex} = \frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} e^2.$$

The kinetic energy density is obtained by calculating the average squared momentum of particles distributed according to the Fermi statistics. We have

$$\overline{p^2} = \frac{1}{(8\pi/3h^3)P^3}\,\frac{2}{h^3}\int_0^P p^2\, 4\pi p^2 dp$$

$$= \frac{3}{5}\,P^2.$$

The average kinetic energy per particle is therefore

$$\frac{3}{10m}\,P^2,$$

producing a kinetic energy density of

$$\frac{3}{10m}\,P^2\rho.$$

By introducing the constant

$$c_f = \frac{3}{10}(3\pi^2)^{2/3}\,e^2 a_o, \tag{2.1}$$

and substituting for the Fermi momentum, the kinetic energy density is written as

$$c_f\rho^{5/3}.$$

The electrostatic potential energy density is considered to be the sum of two terms, the electron-nuclear potential energy density

$$-ev^n\rho,$$

where v^n is the potential due to the nucleus of charge Ze, and the electron-electron potential energy density

$$-\frac{1}{2}ev^e\rho.$$

Here v^e is the potential due to the electrons in the distribution, and the factor 1/2 is inserted to avoid counting each pair of electrons twice.

The total energy is now given by

$$E = \int_0^{r_2} [c_f\rho^{5/3} - c_{ex}\rho^{4/3} - e(v^n + \frac{1}{2}v^e)\rho]4\pi r^2 dr. \qquad (2.2)$$

The Thomas-Fermi-Dirac equation is obtained by minimizing E subject to the auxiliary condition that the total number of particles, which is

$$N = \int_0^{r_2} \rho 4\pi r^2 dr, \qquad (2.3)$$

remains constant. In the Appendix it is shown that this procedure leads to the equation

$$\frac{5}{3}c_f\rho^{2/3} - \frac{4}{3}c_{ex}\rho^{1/3} + (V-E') = 0, \qquad (2.4)$$

which is a second degree equation in $\rho^{1/3}$. Solving for ρ yields

$$\rho = \sigma_o[\tau_o+(E'-V+\tau_o^2)^{1/2}]^3, \tag{2.5}$$

where

$$\sigma_o = \left(\frac{3}{5c_f}\right)^{3/2} = \frac{8\pi}{3h^3}(2m)^{3/2}, \tag{2.6}$$

and

$$\tau_o = \left(\frac{4c_{ex}^2}{15c_f}\right)^{1/2} = \frac{e^2}{h}(2m)^{1/2}. \tag{2.7}$$

The positive sign of the square root is chosen so that the density agrees with the Thomas-Fermi expression if the exchange, represented by τ_o, is neglected.

The Thomas-Fermi-Dirac potential function[3] ϕ is now defined by

$$Ze^2\phi = (E'-V+\tau_o^2)r. \tag{2.8}$$

Distances are measured in the same units as in the Thomas-Fermi equation, so that again, with reference to (1.5), we put $x = r/r_o$. The introduction of the potential function into Poisson's equation, using (2.5) for the

---

[3]It is customary to denote this potential function by ψ, but we choose to use ϕ with a subscript "T-F" or "T-F-D", if necessary, to differentiate between the Thomas-Fermi and Thomas-Fermi-Dirac potential functions.

density, now results in the Thomas-Fermi-Dirac equation

$$\phi'' = x[\epsilon+(\frac{\phi}{x})^{1/2}]^3, \tag{2.9}$$

where

$$\epsilon = \tau_o\left(\frac{r_o}{Ze^2}\right)^{1/2} = \left(\frac{3}{32\pi^2}\right)^{1/3} Z^{-2/3}.$$

The boundary conditions on the solutions are the same as for the Thomas-Fermi equation.

An important difference between (1.7) and (2.9) is that the solutions of the Thomas-Fermi equation are valid for all values of atomic number, whereas (2.9) obviously must be solved separately for each element.

3. Solutions of the Thomas-Fermi and Thomas-Fermi-Dirac Equations

The Thomas-Fermi and the Thomas-Fermi-Dirac equations are nonlinear differential equations which must be solved numerically. The procedure is to assume a solution in the form of a power series expansion about the origin, and to start the numerical integration from the series solution. Upon setting $\phi(0) = 1$, the series coefficients of the solution may be evaluated in terms of the (arbitrary) initial slope of the potential function. Each value of the initial slope then gives rise to a particular potential curve. Figure 1 illustrates a few solutions of the Thomas-Fermi equation.

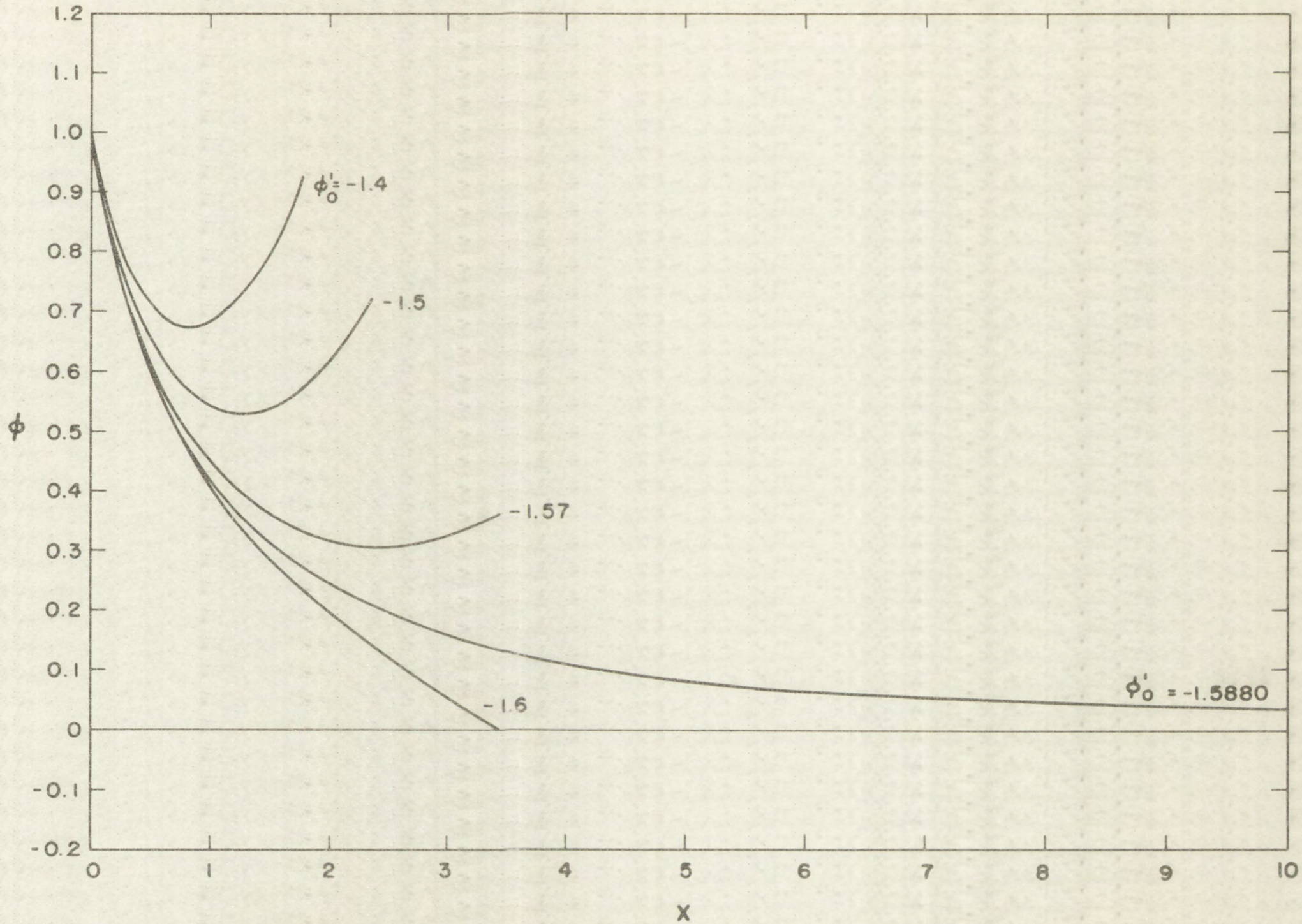

Figure 1. Various solutions of the Thomas-Fermi equation

The Thomas-Fermi equation possesses a solution which becomes tangent to the x axis at infinity. This solution has an initial slope which has been determined accurately by Latter (Ref. 14):

$$(\phi_o')_I = -1.58807102. \tag{3.1}$$

This particular solution, for which the electron density extends to infinity, and for which it develops that the calculated pressure is zero, is taken to represent the isolated atom. A potential curve starting with a slope algebraically less than (3.1) intersects the x axis. There are then less than Z electrons in the distribution and the solution represents a positive ion.

Application of the Thomas-Fermi method to metals (see, e.g., Refs. 15, 16) follows by surrounding each nucleus in a metal by a cell which contains just Z electrons. The boundaries of the cell are planes which perpendicularly bisect the lines joining each nucleus with the nearest or next nearest neighbors. Because of the high order of symmetry of the charge distribution, the electric field at points outside the cell should then be very small and drop off rapidly with distance. The approximation is then made that the field outside the cell can be neglected, and the polyhedron is replaced by a spherically symmetric distribution of charge having the same volume as that of the polyhedron. The solutions of the Thomas-Fermi equation for which x_2 is finite are thus capable of describing the metal in various states of compression.

The solutions of the Thomas-Fermi-Dirac equation have the same general form as those of the Thomas-Fermi equation with the exception that there is no solution in the exchange case which extends to infinity. For each Z there is a potential curve which becomes tangent to the x axis at a finite distance, but for this solution, as for all solutions of the Thomas-Fermi-Dirac equation, the electron density at the boundary of the cell is nonzero. Thus there is no adequate representation of the isolated atom, although the solution for which the pressure equals zero is frequently taken to represent such an atom. (See Ref. 17 for a discussion of this point.)

With the determination of the potential function, various physical quantities may be calculated. The particle density is given by

$$\rho_{T-F} = \frac{1}{3\pi^2}\left(\frac{2Z}{a_o}\right)^{3/2}\left(\frac{\phi_{T-F}}{r}\right)^{3/2}, \tag{3.2}$$

or

$$\rho_{T-F-D} = \sigma_o\left[\tau_o + \left(\frac{Ze^2\phi_{T-F-D}}{r}\right)^{1/2}\right]^3. \tag{3.3}$$

In Figure 2 the density functions, multiplied by r^2, are plotted for the isolated hydrogen atom (the zero-pressure atom in the Thomas-Fermi-Dirac case). For comparison, the quantum-mechanical radial distribution function $r^2\psi^*\psi$ is plotted in the same units.

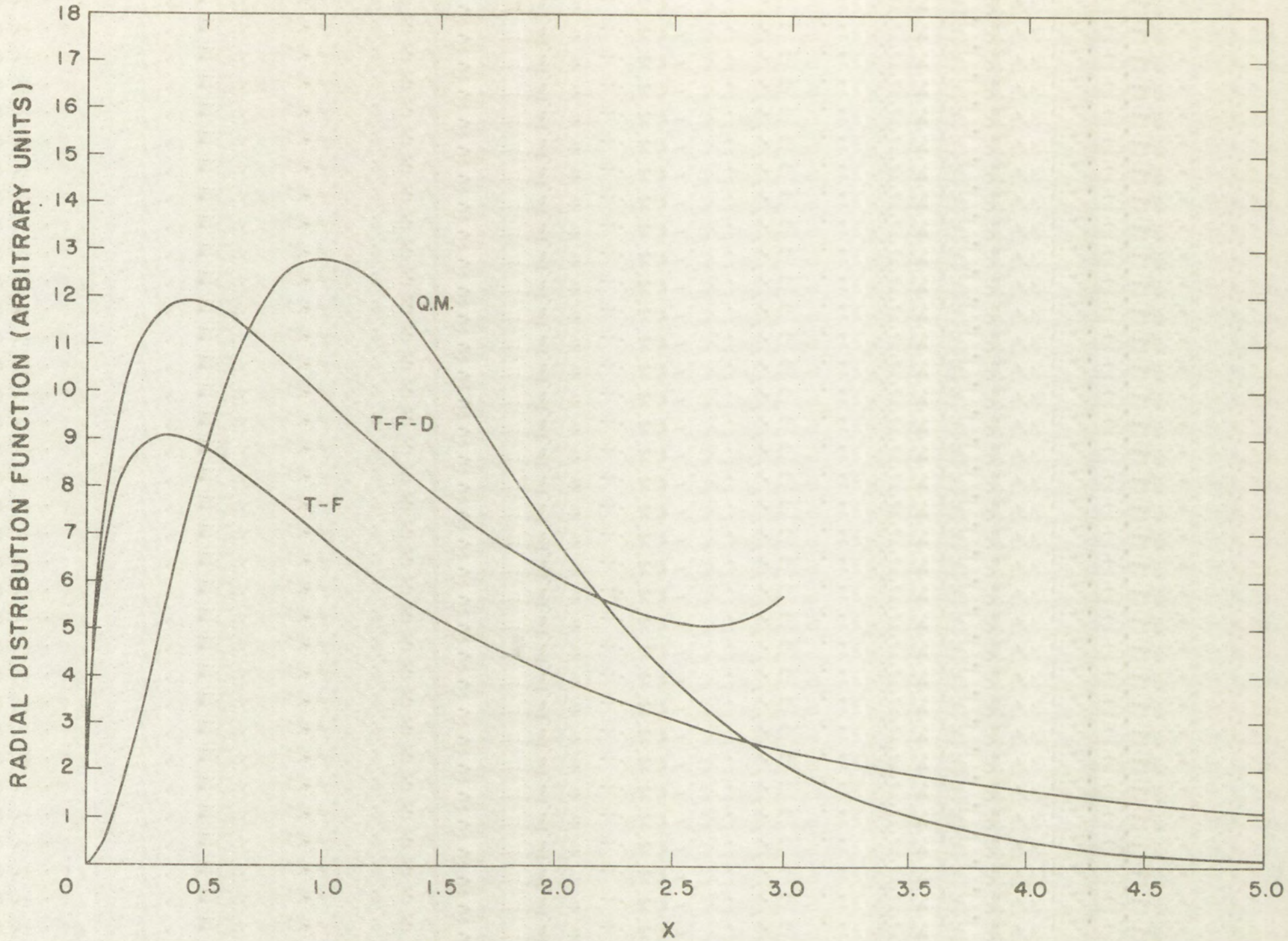

Figure 2. The statistical and quantum-mechanical radial distribution functions for the normal state of the hydrogen atom

The total energy may be calculated from (2.2), with, of course, the exchange term omitted in the Thomas-Fermi case. In evaluating the electrostatic potential terms, we can write for the potential due to the nucleus

$$v^n = \frac{Ze}{r},$$

since any additive constant can be absorbed by the potential due to the electrons, v^e. Then we have, from (1.6) and the relation $V = -e(v^n+v^e)$,

$$v^e = \frac{Ze}{r}(\phi-1) - \frac{E'}{e} . \tag{3.4}$$

It has become the convention to set the potential at the boundary of the neutral atom equal to zero; this serves to fix the arbitrary constant which is originally present in both the potential energy and the Fermi energy. In the Thomas-Fermi case, again from (1.6),

$$E' = \frac{Ze^2\phi(r_2)}{r_2} ,$$

so that, substituting into (3.4),

$$v^e = \frac{Ze}{r}(\phi-1) - \frac{Ze\phi(r_2)}{r_2} .$$

When the exchange energy is considered, (2.8) leads to

$$\mathcal{P} = \frac{2}{3}c_f[\rho(r_2)]^{5/3}, \qquad \text{(Thomas-Fermi)}, \tag{3.8}$$

and

$$\mathcal{P} = \frac{2}{3}c_f[\rho(r_2)]^{5/3} - \frac{1}{3}c_{ex}[\rho(r_2)]^{4/3}, \text{ (Thomas-Fermi-Dirac)}. \tag{3.9}$$

These equations are obtained by forming the derivative of (2.2) with respect to r_2 and writing (3.7) as

$$\mathcal{P} = -\frac{1}{4\pi r_2^2}\frac{dE}{dr_2}.$$

In Section 17 this procedure is employed in finding the pressure on the modified model.

An alternative method of calculating the pressure is by means of the virial theorem (see, e.g., Ref. 19), which has been proven to hold for the statistical atom (Refs. 7, 20, 21). This theorem states that

$$\mathcal{P}\Omega = \frac{2}{3}E_{kin} + \frac{1}{3}E_{pot},$$

E_{kin} being the total kinetic energy of the electron distribution, and E_{pot} the total potential energy, including the exchange energy if applicable.

4. Comparison with Experiment

There have been many attempts to improve the statistical model; some of these are mentioned in the sections to follow. The modifications have been prompted by at least two observations. The first is the knowledge that the discrepancy is quite large between the observed energy and that calculated by the statistical theories. These values are given for the low Z elements, for which experimental values have been obtained, in the listing below. The Thomas-Fermi energies have been calculated according to the formula due essentially to Milne (Ref. 22):

$$E_{T-F} = -20.92\ Z^{7/3} \text{ev.} \tag{4.1}$$

The Thomas-Fermi-Dirac energies have been obtained from the paper of Cowan and Ashkin (Ref. 8), and the experimental values are from Moore (Ref. 23).

Z	$-E_{T-F}$(ev)	$-E_{T-F-D}$(ev)	$-E_{Exp}$(ev)
1	20.92	28.07	13.60
2	105.4	126.7	78.98
3	271.5	312.4	203.4
4	531.3	596.3	399.0
5	894.3	987.5	670.8
6	1369.	1494.	1030.
7	1961.	2122.	1486.
8	2678.	2878.	2043.

The second shortcoming of the statistical theory is the rather poor agreement between the calculated pressure-compression curves and the experimental values which have been obtained for several metals. In Figures 3 and 4 are shown the calculated and experimental pressure curves for copper (Z=29), and lead (Z=82), respectively. The upper two theoretical curves of each figure are the Thomas-Fermi and Thomas-Fermi-Dirac pressures; the third theoretical curve is discussed in the next section. Experimental data are from a paper by McQueen and Marsh (Ref. 24). The compression, η, is defined as the normal specific volume divided by the specific volume of the compressed material.

The primary reason for the considerable discrepancy in pressure at volumes near normal is the total lack of any form of chemical binding in the theory. On the Thomas-Fermi model there is no stable crystal at all since, as we have mentioned, the solution for which the pressure is zero represents the infinite atom. When the exchange energy is included there is a zero-pressure solution representing an atom of finite extent, the proper interpretation of which would seem to be as an atom of a crystal. This is pointed out in Ref. 17, to which we have already referred. The disagreement between measured pressures and those calculated on the Thomas-Fermi-Dirac theory arises because the theoretical zero pressure solution occurs for a volume which is, in general, too large.

The usual method of estimating the pressure corresponding to compressions near unity is to extrapolate from the experimental values along a curve which smoothly intersects the Thomas-Fermi or Thomas-Fermi-Dirac

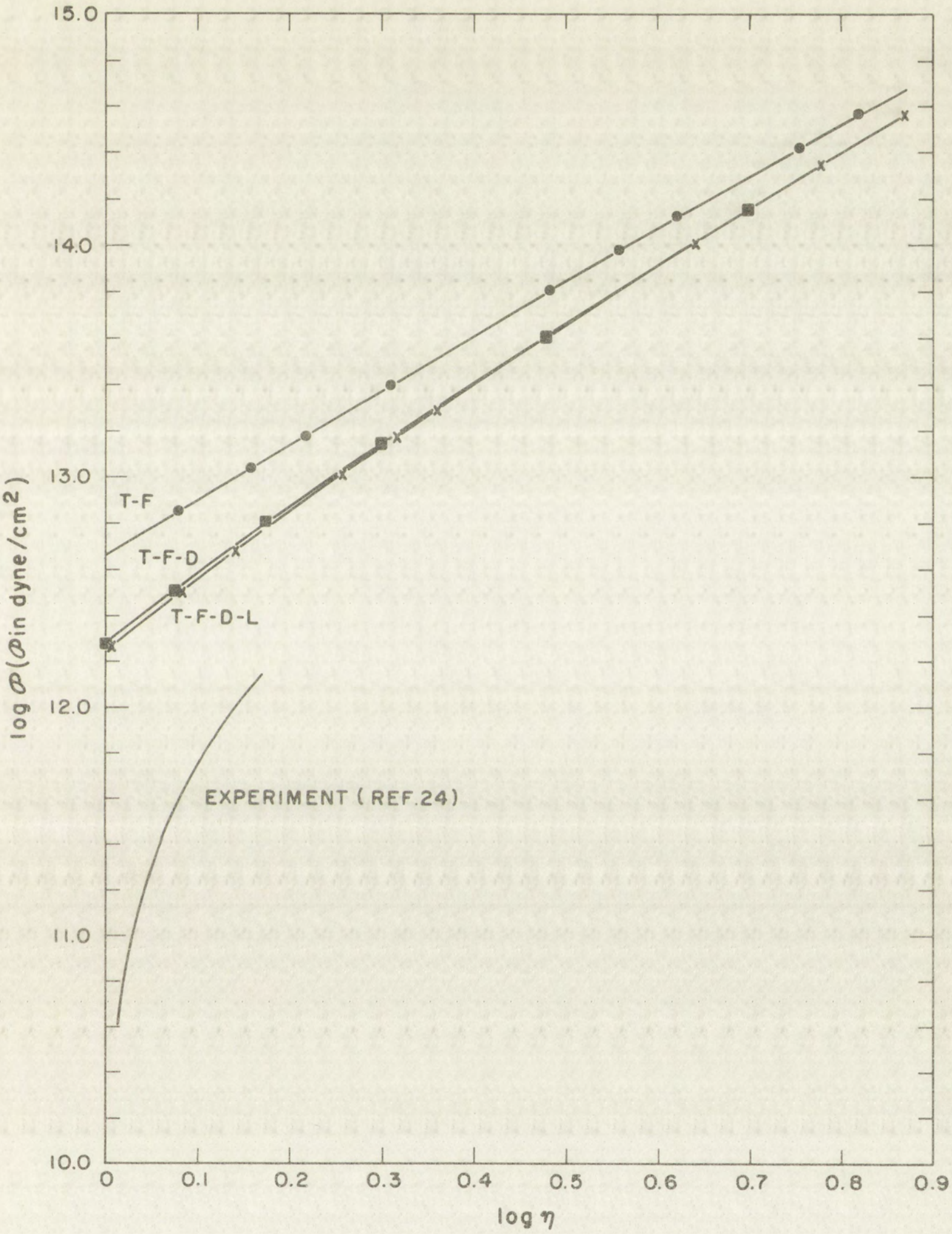

Figure 3. Theoretical and experimental pressure-compression curves for copper

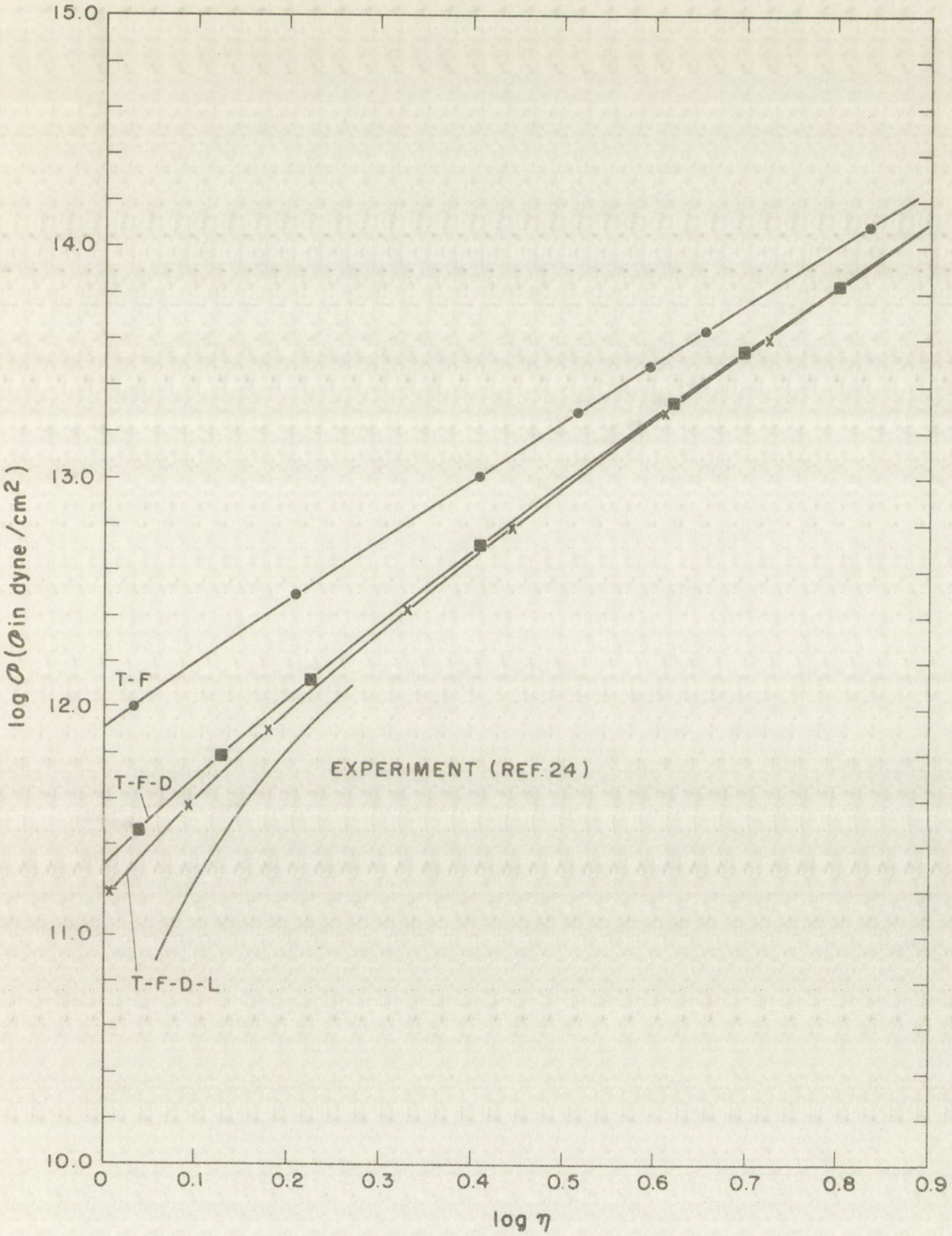

Figure 4. Theoretical and experimental pressure-compression curves for lead

curve (Refs. 25, 26, 27). Although the neglect of interatomic forces precludes the theoretical reproduction of the experimental equation of state curves, it is nevertheless of interest to observe the effect on the pressure caused by modification of the theory. The inference is, of course, that one might expect the pressures calculated according to a "corrected" statistical model to be lower, and thus in improved agreement with experiment. In the following section such a correlation-corrected equation of state is considered.

5. The Correlation Energy

As mentioned in Section 2, the introduction of exchange energy into the original Thomas-Fermi model takes into account the tendency for electrons of parallel spin to stay away from each other, but there is also a tendency for electrons of any spin to stay apart because of their Coulomb repulsion. The effects of correlation and exchange being in the same direction, it is obvious that consideration of the correlation energy will not improve the situation regarding the binding energy (see Section 4 listing). However, we wish here to evaluate the correlation-corrected equation of state.

Lewis (Ref. 10) has suggested an interpolation formula for the correlation energy which at low density approaches the value for electrons crystallized into a body-centered cubic lattice. The latter can be calculated exactly (Ref. 28). At high density the interpolated value approaches that derived by Gell-Mann and Brueckner (Ref. 29). Lewis has

then obtained the following coupled equations[4] for $\phi(x)$ and a function $v(x)$:

$$\phi'' = v^3 x^{-1/2},$$

$$\phi = v^2 - avx^{1/2} - \rho a^2 x \ln(\sigma a + vx^{-1/2}), \tag{5.1}$$

where ϕ is the modified potential function in the usual sense, and x is related to r in the same way as in the unmodified Thomas-Fermi or Thomas-Fermi-Dirac equations. The function v(x) is defined by

$$v = \frac{Pa_o}{\hbar} \frac{\pi a x^{1/2}}{2},$$

where P is the Fermi momentum. Also,

$$a = \left(\frac{2\beta}{\pi^2 Z}\right)^{1/2},$$

$$\beta = \left(\frac{9\pi^2}{128Z}\right)^{1/3},$$

$$\rho = \frac{1}{2}(1 - \ln 2),$$

$$\sigma = \frac{1 - \ln 2}{2(0.89\alpha\pi - 1)},$$

[4] Many of the symbols in these equations are used in other parts of the text in some other sense. The equations of this section are not referred to elsewhere, however, so there is no chance of confusion.

and

$$\alpha = \left(\frac{4}{9\pi}\right)^{1/3}.$$

The boundary conditions are the standard ones:

$$\phi(0) = 1,$$

and

$$x_2\phi'(x_2) = \phi(x_2),$$

with the addition of

$$v(0) = 1.$$

The present writer has solved the system (5.1) using techniques described for the most part in Part III. From the conditions at the surface of the cell the pressure has been determined using the equation given by Lewis:

$$\mathcal{P} = \frac{\hbar^2}{ma_0^5}\frac{w^5}{15\pi^2}\left(1 - \frac{5}{4\pi w} - \frac{0.052}{w^2}\right),$$

where

$$w = \frac{2v(x_2)}{\pi a x_2^{1/2}} .$$

The pressure-compression curve which results from applying this Thomas-Fermi-Dirac-Lewis theory to copper and lead may be compared with the pressure curves computed without the correlation correction in Figures 3 and 4. It is seen that the pressure is indeed lowered by the correlation effect,[5] but certainly, at least for these two elements, the lack of agreement with experiment is still very much in evidence.

In the second of the two equations (5.1), the second and third terms on the right side represent, respectively, the exchange and the correlation contributions. For small values of x, these two terms become negligible and (5.1) reduces to the Thomas-Fermi equation. Therefore we may regard the correlation correction, in particular, as an improvement affecting the outer regions of the atom. This view is substantiated by the work of Tomishima (Ref. 30) who, using a different form for the correlation energy, has computed electron distributions for several atoms. The only discernible modification appears to be to the outer part of the distribution.

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[5] We should point out that comparable numerical methods have been used in obtaining the different theoretical curves, so that the differences in the curves should not be attributed to different calculational techniques.

6. Scott's Correction to the Energy

We wish now to direct our efforts toward a modification of the electron distribution near the nucleus in an attempt to improve the calculated binding energies. In this connection it is of interest to consider a method due to Scott (Ref. 31), in which a correction is based on the determination of the amount contributed to the potential at the nucleus by the Thomas-Fermi electron distribution, as compared to that computed from the quantum-mechanical solution. Scott has first shown that it is possible to obtain Milne's formula (4.1) by such a potential calculation, in the following manner.

Consider the nuclear charge increased by an incremental amount δZ. This may be considered to give rise to a perturbation potential $\delta Z/x$.[6] The change in the energy of the ground state is obtained by applying first order perturbation theory, and we have

$$\delta E_{T-F} = \int \psi^* \left(\frac{-\delta Z}{x}\right) \psi d\tau,$$

where ψ is the unperturbed product wave function for which $|\psi|^2$ corresponds to the Thomas-Fermi density, and the integral is taken over the volume of the distribution. Now

[6] It is convenient in this discussion and in the derivation of certain quantities in Part II to use atomic units. In this system of units, $e = \hbar = m = 1$. The unit of length is a_o, the first Bohr radius, in which units we have already introduced x as the measure of distance. The atomic unit of energy, 1 au, is e^2/a_o.

$$-\int \frac{\psi^*\psi}{x}\, d\tau$$

is just the contribution made to the potential at the nucleus by the electron cloud, say v. Therefore we have

$$\frac{dE_{T-F}}{dZ} = v.$$

But

$$v = \lim_{x \to 0} v^e ,$$

or, writing (3.4) in atomic units and putting E' = 0 for the infinite atom,

$$v = \lim_{x \to 0} \frac{Z}{x}(\phi - 1)$$

$$= Z(\phi_o')_I \left(\frac{128Z}{9\pi^2}\right)^{1/3} .$$

Using the value of $(\phi_o')_I$ given by (3.1) we have

$$v = -1.794\, Z^{4/3}.$$

The total energy is then given by

$$E_{T-F} = -0.7689\ Z^{7/3} \quad \text{au}$$

$$= -20.92\ Z^{7/3} \quad \text{ev},$$

in agreement with (4.1).

In calculating the error in the formula, Scott's procedure is to determine the contribution to the potential at the nucleus made by that part of the distribution which corresponds to the K shell, the L shell, etc. Thus, in atomic units, the number of electrons per unit volume with energy between V and E_n is

$$\frac{2^{3/2}}{3\pi^2}(E_n-V)^{3/2}.$$

The number of electrons whose energy lies between these limits and which are located within a spherical shell of thickness dx is therefore

$$\frac{8\cdot 2^{1/2}}{3\pi}(E_n-V)^{3/2}\ x^2dx.$$

E_n is now chosen so that there are just two electrons of lower energy according to the statistical model. Call this value of energy E_K. We then have

$$2 = \frac{8\cdot 2^{1/2}}{3\pi}\int_0^{x_{2,K}}(E_K-V)^{3/2}\ x^2dx,$$

where the upper limit is the point at which the integrand vanishes. In terms of the Thomas-Fermi potential function,

$$2 = \frac{8\cdot 2^{1/2}}{3\pi}\int_{o}^{x_{2,K}} \left(\frac{Z\phi}{x} + E_K\right)^{3/2} x^2 dx.$$

On the idealized model used by Scott, wherein Z is allowed to become infinite, ϕ can be replaced by one. The integration is then easily performed with the result

$$2 = \frac{Z^3}{3\cdot 2^{1/2}(-E_K)^{3/2}},$$

so that

$$E_K = -\frac{1}{2\cdot 3^{2/3}} Z^2. \tag{6.1}$$

The potential at the nucleus due to electrons of energy equal to or less than E_K is

$$v_K = -\frac{8\cdot 2^{1/2}}{3\pi}\int_{o}^{x_{2,K}} \frac{(Z/x + E_K)^{3/2}}{x} x^2 dx$$

$$= -\frac{2^{1/2} Z^2}{(-E_K)^{1/2}}$$

$$= -2\cdot 3^{1/3} Z. \tag{6.2}$$

The actual potential due to the two K-electrons, calculated quantum-mechanically, is -2Z. The K shell correction to the potential at the nucleus is thus

$$2Z(3^{1/3}-1) \approx 0.88Z.$$

Repetition of the calculation with the additional inclusion of the eight L-electrons leads to the correction

$$2Z(15^{1/3}-2) \approx 0.93Z.$$

Now in the limit as the number of electron shells is allowed to become infinite, the correction is found to become equal to Z. The correction to the total energy, obtained by performing an integration over Z, is therefore

$$\frac{1}{2} Z^2 \text{ au},$$

or

$$13.6050 \; Z^2 \text{ ev}.$$

In the following list, the energies obtained by adding Scott's correction to the energies calculated on the Thomas-Fermi-Dirac model are

compared with the experimental values.

Z	$-E_{Scott}$(ev)	$-E_{Exp}$(ev)
1	14.46	13.60
2	72.28	78.98
3	190.0	203.4
4	378.6	399.0
5	647.4	670.8
6	1004.	1030.
7	1455.	1486.
8	2007.	2043.

Scott's correction is important to the present work because of the evidence it presents that the bulk of the discrepancy in total energy apparently occurs within such a distance from the nucleus that the field is approximately Coulombic. It is on this basis that the modification term derived in Part II of this paper is evaluated for a pure Coulomb field.

7. The Inhomogeneity Correction

In using the statistical equations, one is assuming that within a small volume, whose extensions are of the order of an electron wave length, the particle density is approximately constant. The particle eigenfunctions used are plane waves. This is certainly a poor approximation in the rapidly changing field near the nucleus, and upon taking the deviation from plane wave eigenfunctions into account a correction

to the kinetic energy density arises. One form of this correction is the so-called inhomogeneity energy of von Weizsäcker (Ref. 32).

In von Weizsäcker's derivation, the individual wave functions are written in the form

$$\psi = \frac{1}{\sqrt{\omega}} (1+\vec{b}\cdot\vec{\xi})\, e^{(i/\hbar)\vec{p}\cdot\vec{\xi}},$$

where ω is a normalizing volume and the wave function is localized in the neighborhood of $\vec{\xi} = 0$. The vector $\vec{b}$, which is assumed to be small, can here depend upon $\vec{p}$, the particle momentum. From differentiation under the integral sign of the expression for the density within the volume ω, namely,

$$\rho = \frac{1}{\omega}\int^{P} \frac{\omega d\vec{p}\; 2}{h^3} \int_{\omega} d\vec{\xi}\; \psi^*\psi,$$

one obtains

$$\nabla\rho = \frac{4}{h^3}\int^{P} \vec{b}(\vec{p})d\vec{p},$$

which is considered to be the defining equation for $\vec{b}(\vec{p})$.

The kinetic energy per unit volume is given by

$$U_k = \frac{1}{\omega}\int^{P} \frac{\omega\, d\vec{p}\, 2}{h^3} \int_{\omega} d\vec{\xi}\; \psi^*\left(-\frac{\hbar^2}{2m}\right)\nabla^2\psi$$

$$= \frac{1}{\omega}\int^{P} \frac{\omega\, d\vec{p}}{h^3}\; \frac{\hbar^2}{m} \int_{\omega} d\vec{\xi}(\nabla\psi^*)\cdot(\nabla\psi)$$

$$= \frac{4\pi}{5}\,\frac{P^5}{mh^3} + \frac{1}{4\pi^2 hm}\int^{P} |\vec{b}(\vec{p})|^2 d\vec{p}.$$

The requirement that the energy belonging to a given density distribution be a minimum has been shown by von Weizsäcker to yield

$$\vec{b} = \text{constant}.$$

Therefore we have

$$\nabla\rho = \frac{16\pi}{3h^3}\, P^3\vec{b}$$

$$= 2\rho\vec{b},$$

and

$$U_k = \frac{4\pi}{5}\,\frac{P^5}{mh^3} + \frac{|\vec{b}|^2}{3\pi hm}\, P^3,$$

which may be written in the form

$$U_k = c_f\rho^{5/3} + c_i\,\frac{|\nabla\rho|^2}{\rho}\,. \qquad (7.1)$$

The coefficient c_f has been defined in (2.1), and

$$c_i = \frac{\hbar^2}{8m} .$$

The first term in (7.1) is the Fermi kinetic energy density; the second is the Weizsäcker correction.

By use of (7.1) as the expression for the total kinetic energy density, the total energy may be minimized by a variational procedure entirely similar to that used in deriving the Thomas-Fermi-Dirac equation. The result is the Weizsäcker equation:

$$4c_i \nabla^2 \chi - \frac{5}{3} c_f \chi^{7/3} + \frac{4}{3} c_{ex} \chi^{5/3} + (E'-V)\chi = 0,$$

where

$$\chi = \rho^{1/2}.$$

An investigation into the validity of the Weizsäcker equation has been carried out by Berg and Wilets (Ref. 33), who have solved the equation for the case of a three-dimensional isotropic harmonic oscillator, and for a potential which is constant in the y and z directions but possessing a step in the x direction. It is their conclusion that the Weizsäcker kinetic energy term is too great, but that a good improvement in energy over the Thomas-Fermi solution can be obtained by reducing

the term by a factor which depends upon the potential.

A kinetic energy correction of magnitude somewhat smaller than the Weizsäcker term is obtained in Part II. As applied to the electron distribution in an atom, a reduction of the Weizsäcker term by a factor of about ten would seem to be indicated.

The work of Swiatecki (Ref. 34) might also be mentioned in connection with the inhomogeneity correction. He has obtained a modified relation between density and potential which takes into account the gradient of the potential at the point in question. However, the infinite electron density near the nucleus is not remedied by this treatment.

8. The Effect of Imposing a Cut-off Momentum

In the previous two sections we have dealt with topics which will be of interest once the form of the modification of the statistical theory is developed. In the modification a quantity is obtained which we shall evaluate for a Coulomb field, thus utilizing Scott's results, and a kinetic energy correction is obtained which may be compared to the Weizsäcker correction.

We wish now to suggest a possible approach to "improving" the electron density near the nucleus. We recall that the binding energy as computed by the statistical theories is much too great, clearly the result of the very large density of electrons which is obtained at small distances from the nucleus. It is seen from (3.2) or (3.3) that the electron density becomes infinite at $r = 0$.

The large density in coordinate space may be regarded as a consequence of the vanishing density in momentum space, due, of course, to the very large volume of occupied momentum space. However, the cell to which the electrons are confined is, in general, of finite size. Since the deBroglie wave associated with a very low momentum electron is very large, it might be reasonable to restrict in some manner the lowest available momentum state.[7] Let us therefore investigate briefly the possibility of "improving" the electron distribution by imposing a cut-off momentum, p_c.

Let us first assume that at any radial distance r, no momentum state is available below a value

$$p_c = K/r,$$

where K is some undetermined constant. Then the density of particles is given by

$$\rho = \frac{2}{h^3}\int_{p_c}^{P} 4\pi p^2 dp$$

$$= \frac{8\pi}{3h^3}(P^3 - p_c^3). \qquad (8.1)$$

[7] A paper by Fradkin (Ref. 35) should be mentioned. In it a lower limit to allowed electron energies is proposed, from the observation that the lower bound of the atomic levels does not lie below the lowest level of a hydrogen-like atom with nuclear charge Ze.

From (1.2) it is seen that P varies as $r^{-1/2}$ near the nucleus. Since p_c varies as r^{-1}, the electron density according to (8.1) must be set equal to zero for r less than the value, say r_1, at which p_c becomes equal to P. We obtain

$$r_1 = \frac{K^2}{2mZe^2},$$

which we may label as the "inner density cut-off distance." If we should demand that for an electron to be at r, its wavelength

$$\lambda \geqq 2\pi r,$$

then $K = \hbar$. The electron density would then vanish inside

$$r_1 = \frac{a_o}{2Z},$$

a fairly large distance equal to one-half the radius of the first Bohr orbit for the hydrogen-like atom. In this connection it might be mentioned that Golden has found an inner boundary to the electron cloud in his formulation of the problem, which is discussed in Section 9. (Golden's values of the inner density cut-off distance are graphed along with those derived later in this study in Figure 13, Part III, Section 19.)

Let us now choose the distribution of states in momentum space to produce a density at the nucleus equal to the quantum-mechanical

probability distribution function for the hydrogen atom in its normal state. At $r = 0$ the latter is given by

$$\psi^*\psi = \frac{1}{\pi a_0^3} . \tag{8.2}$$

We introduce a function $g(p,p_c)$ such that $g = 0$ for $p = 0$, $g = 1$ for $p \geq p_c$, and

$$\rho = \frac{8\pi}{h^3}\int_0^P g(p,p_c)p^2dp.$$

We are interested now in evaluating the density at radial distances less than r_1. In this region p_c is greater than P and g is less than one. The simplest form for g which is dimensionless and satisfies the above requirements is

$$g = \left(\frac{p}{p_c}\right)^\nu , \qquad p < p_c ,$$

where ν is nonnegative. We therefore write, for $r < r_1$,

$$\rho = \frac{8\pi}{h^3}\int_0^P \left(\frac{p}{p_c}\right)^\nu p^2dp.$$

Performing the integration,

$$\rho = \frac{8\pi}{h^3(\nu+3)} \frac{P^{\nu+3}}{p_c^\nu} .$$

As $r \to 0$ we can write

$$\rho \sim \frac{(1/r^{1/2})^{\nu+3}}{(1/r)^{\nu}} ,$$

which remains finite and nonzero if we take $\nu = 3$. We then have

$$\rho = \frac{4\pi}{3h^3}\left(\frac{P^2}{p_c}\right)^3, \qquad p_c > P. \tag{8.3}$$

Now equating (8.3) to (8.2) and solving for p_c we get

$$p_c = \frac{2a_o}{h}\left(\frac{\pi^2}{6}\right)^{1/3} P^2, \qquad p_c > P,$$

or, as $r \to 0$,

$$p_c = \frac{2a_o}{h}\left(\frac{\pi^2}{6}\right)^{1/3}\frac{2me^2}{r}$$

$$= \frac{h}{(6\pi^4)^{1/3}}\ \frac{1}{r}.$$

The wavelength corresponding to this momentum is

$$(6\pi^4)^{1/3} r \approx 8.4\ r.$$

In the above derivation p_c is the cut-off momentum in the sense that for momenta less than p_c, the momentum states have a probability less

than unity of being filled. We have thus shown that by requiring a reduction in the probability of finding an electron located approximately at r with wavelength greater than 8.4r, the density at the nucleus is reduced from infinity to the result obtained by quantum theory.

A modified Thomas-Fermi equation has been obtained by utilizing (8.3) and a corresponding modified form of the density in the region in which $p_c \leq P$. The results are not particularly impressive; the density function for the isolated hydrogen atom drops off too rapidly with distance from the nucleus, causing the binding energy to be over-corrected. The major contribution to the energy occurs in the region where ρr^2 is near its maximum, say at a radial distance of the order of a few tenths of a Bohr radius, and the density has not been "corrected" in this region.

It is evident that such discussions of imposing a lower limit on the available momentum states, or of reducing the probability of their occupation, emphasize the apparent contradictions of the simple statistical theory. Electron waves in the atom are not well localized, and it is not necessarily true that many electrons are located in a region with extensions of the order of a wavelength. In order to obtain a satisfactory modification of the statistical theory based on a cut-off momentum, it is necessary to go beyond what might be called this "classical" approach, and to view the theory as the quasi-classical approximation to quantum mechanics. In Part II, Section 12, a proposed cut-off momentum is derived from a slight modification of the derivation of the

Thomas-Fermi energy equation as given by March and Plaskett. Their method of derivation, which is covered in detail in Section 10, demonstrates clearly the connection between the statistical theory and the Wentzel-Kramers-Brillouin (WKB) method of quantum mechanics.

9. The Density Matrix Formulation

That there is a connection between the statistical method and the quasi-classical WKB approximation has been known for some time (Refs. 36, 37, 38). For completeness we wish to mention a more general approach to the origin of the statistical theory, based on the density matrix of von Neumann and Dirac (see, e.g., Ref. 39), which has been utilized recently by several workers (Refs. 40, 41, 42). Golden's paper (Ref. 41) is of particular interest, since the modified electron density distribution which he has obtained is at least qualitatively similar to that obtained in the present work.

Golden has started from the density matrix, defined by

$$\rho(\vec{r}\,',\vec{r}) = \sum_j w_j \psi_j^*(\vec{r}\,')\psi_j(\vec{r}), \tag{9.1}$$

where, in the case under consideration, the statistical weights w_j are given by

$$w_j = \frac{1}{e^{\beta(E_j-\mu)}+1},$$

normalized, through the choice of μ, so that

$$\sum_j w_j = N,$$

the number of particles in the assembly. The ψ_j are one-electron wave functions, which are taken to be momentum eigenfunctions.

The statistical weight is now considered to be an operator, operating on ψ_j, E_j being replaced by the effective single particle Hamiltonian in the form

$$H_j = \frac{1}{2m} P_j^2 + V(\vec{r}).$$

Here P_j is the operator $-i\hbar\nabla_j$, which operates on the components of the jth particle.

Golden has developed a means of expanding (9.1), written in operator form, in a series in powers of $\hbar/i$. The electron density is obtained from the diagonal elements of the density matrix, and to terms of the second order in $\hbar$ it is found to be given by

$$\rho \approx \frac{2\pi(2m)^{3/2}}{h^3}\left[(kT)^{3/2}F_{1/2}(\zeta) - \frac{\hbar^2}{12m(kT)^{1/2}}\nabla^2 V\, F''_{1/2}(\zeta)\right.$$

$$\left. + \frac{\hbar^2}{24m(kT)^{3/2}}\nabla V\cdot\nabla V\, F'''_{1/2}(\zeta)\right], \qquad (9.2)$$

where the function

$$F_{1/2}(\zeta) = \int_0^\infty \frac{y^{1/2}dy}{e^{y-\zeta}+1}$$

is one of a class of "Fermi-Dirac functions" (Ref. 43). We have used the symbols

$$y = \frac{p^2}{2mkT},$$

and

$$\zeta = -\frac{1}{kT}[V(\vec{r})-\mu].$$

The term of zero order in $\hbar$ in (9.2) is the usual expression for density obtained in the extension of the Thomas-Fermi theory to nonzero temperature (see, e.g., Refs. 7, 9).[8] The higher order terms arise because the momentum and potential energy operators are no longer assumed to commute. Thus, the higher order terms are considered to be specifically quantum-mechanical in origin.

For application to the spherically symmetric atom at zero temperature, Golden has obtained a quantum-corrected Thomas-Fermi equation,[9] i.e., corrected to order $\hbar^2$, by setting up Poisson's equation in the usual way. From the solutions of this equation the density distributions

[8] The density as given by (9.2) pertains to spinless electrons.

[9] Actually, it is a quantum-corrected Thomas-Fermi-Amaldi equation, but this need not concern us here.

10. March and Plaskett's Derivation of the Thomas-Fermi Energy Equation

Of particular interest in illustrating the approximations underlying the statistical theory is the paper of March and Plaskett (Ref. 37). Since the modification derived in Part II of this paper is based on an extension of their derivation, the derivation is reviewed here in some detail.

The WKB method may be applied to the problem of a particle in a one-dimensional potential well, whereupon application of the boundary conditions leads to "half integral" quantization of the Sommerfeld phase integral. That is, the energy eigenvalues, which we shall now denote by E_n, are given by the solutions of the equation

$$2\int_{x_1(E)}^{x_2(E)} p(E,x)dx = 2\int_{x_1(E)}^{x_2(E)} \left\{2m[E-V(x)]\right\}^{1/2} dx = (n+1/2)h, \quad n=0,1,2,\ldots, \tag{10.1}$$

where x_1 and x_2 are the classical turning points. Here $p(E,x)$ is the local momentum and $V(x)$ is the potential energy.

We are interested in the sum of the first N eigenvalues, say

$$E = \sum_{n=0}^{N-1} E_n .$$

Clearly this is equivalent to summing the areas of rectangles of height E_n and unit width, the rectangles being centered at integral values of n.

If we regard n as a continuous variable and consider the function E(n), we can approximate the sum by an integral between the limits to which the rectangles extend along the n axis. We then have

$$E = \int_{-1/2}^{N-1/2} E(n)dn. \tag{10.2}$$

We now consider (10.1) to define the inverse function n(E), and obtain

$$dn = \frac{2}{h}\int_{x_1(E)}^{x_2(E)} \frac{dp}{dE}\, dEdx$$

$$= \frac{2m}{h}\int_{x_1(E)}^{x_2(E)} p^{-1} dEdx.$$

There is no contribution from differentiating the endpoints of the integration, since the integrand vanishes there. Substituting this expression for dn into (10.2), we have

$$E = \int_{E(-1/2)}^{E(N-1/2)} \int_{x_1(E)}^{x_2(E)} \frac{2m}{h} E\, p^{-1}\, dxdE.$$

Changing the order of integration and letting E(N-1/2) = E', we have

$$E = \int_{x_1(E')}^{x_2(E')} \int_{E=V(x)}^{E'} \frac{2m}{h} E\, p^{-1}\, dEdx \quad (=)$$

$$= \int_{x_1(E')}^{x_2(E')} \int_{E=V(x)}^{E'} \frac{2m}{h} E[2m(E-V)]^{-1/2} \, dE dx.$$

The shaded portion of Figure 5 illustrates the region of integration.

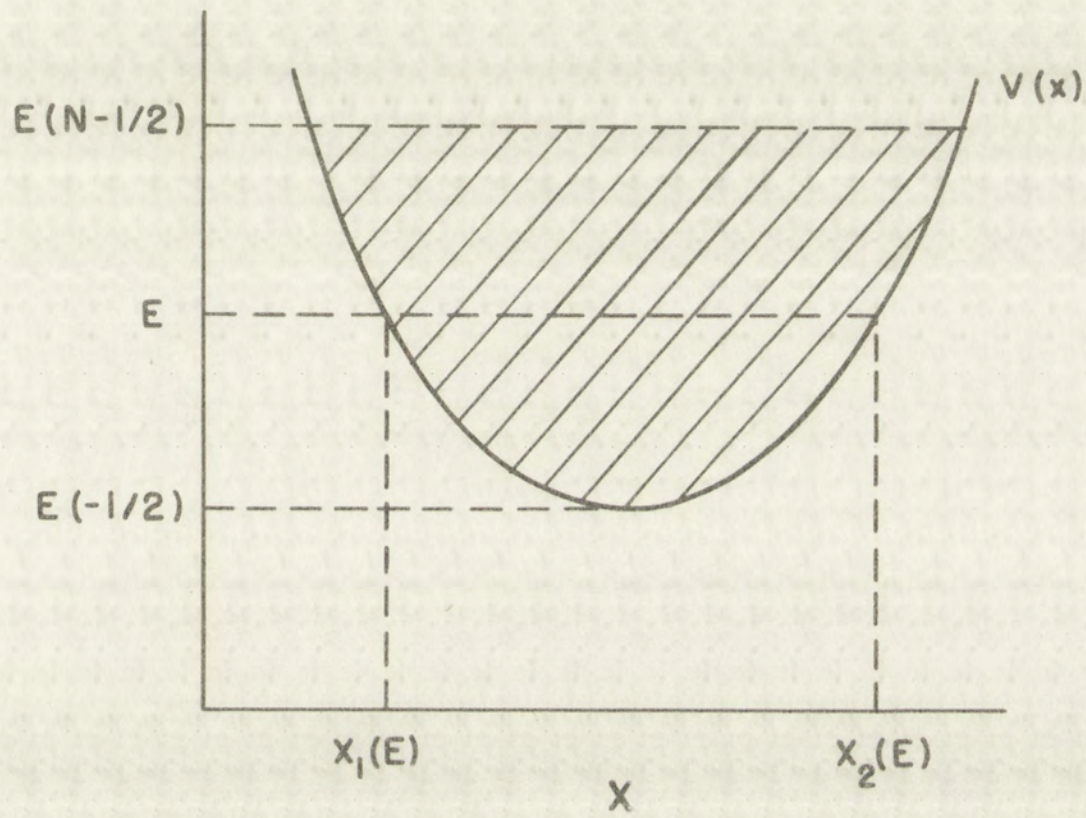


Figure 5. The (E,x) plane for the one-dimensional case (from Ref. 37)

Performing the integration over E, we get

$$E = \int_{x_1(E')}^{x_2(E')} \frac{(2m)^{1/2}}{h} \frac{2}{3} [(E'+2V)(E'-V)^{1/2}] dx,$$

or, writing $P = p(E',x)$,

$$E = \int_{x_1(E')}^{x_2(E')} \left(\frac{1}{3} \frac{P^2}{2m} + V\right) \frac{2}{h} P \, dx. \tag{10.3}$$

E' is determined by the total number of eigenstates by substituting the maximum value of n into (10.1):

$$\int_{x_1(E')}^{x_2(E')} \frac{2}{h} P \, dx = N,$$

whereupon 2P/h is identified with the particle density of the Thomas-Fermi method, P being the Fermi momentum. Equation (10.3) is the Thomas-Fermi energy equation in one dimension. It is not an expression of the total energy, however, since the potential energy term contains twice the potential energy of interaction between the electrons.[10]

Turning to three dimensions, Langer has shown (Ref. 44) that the correct WKB equation for the eigenvalues $E_{n_r,\ell}$ in a spherically symmetric potential is

$$2\int_{r_1^{\ell}(E)}^{r_2^{\ell}(E)} \left\{2m[E-V(r)-\frac{\hbar^2}{2m}\frac{(\ell+1/2)^2}{r^2}]\right\}^{1/2} dr = (n_r+1/2)h, \qquad (10.4)$$

where $r_1^{\ell}(E)$ and $r_2^{\ell}(E)$ are the roots of the equation

$$V(r) + \frac{\hbar^2}{2m}\frac{(\ell+1/2)^2}{r^2} = E,$$

that is, the turning points, for a given ℓ, in the fictitious one-dimensional potential. The radial quantum number is denoted by n_r, and ℓ is the orbital quantum number.

---

[10] We are using the symbol "E" to represent both the total energy and sum of eigenvalues. The meaning in a particular case is clear from the context.

The sum of the eigenvalues is now given by

$$E = \sum_{\substack{n_r, \ell \\ \text{integers} \geq 0}} (2\ell+1)\, E_{n_r, \ell} \,,$$

for all n_r, ℓ satisfying the condition $E_{n_r, \ell} \leq E''$, where E'' is determined by the number of levels being considered. The factor $(2\ell+1)$ accounts for there being $(2\ell+1)$ independent eigenstates with given values of n_r and ℓ. Now we again replace the sum of eigenvalues by an integral and write

$$E = \int\int (2\ell+1) E(n_r, \ell)\, dn_r\, d\ell, \tag{10.5}$$

and likewise replace the number of states over which we are summing by an integral over the same region:

$$N = \int\int (2\ell+1)\, dn_r\, d\ell. \tag{10.6}$$

The region of integration in both (10.5) and (10.6) is bounded by

$$n_r = -1/2, \ \ell = -1/2, \text{ and } E(n_r, \ell) = E',$$

where E' is chosen so that N in (10.6) is equal to the total number of states being considered. The region of integration in the (n_r, ℓ) plane is illustrated by Figure 6. One of the approximations involved is

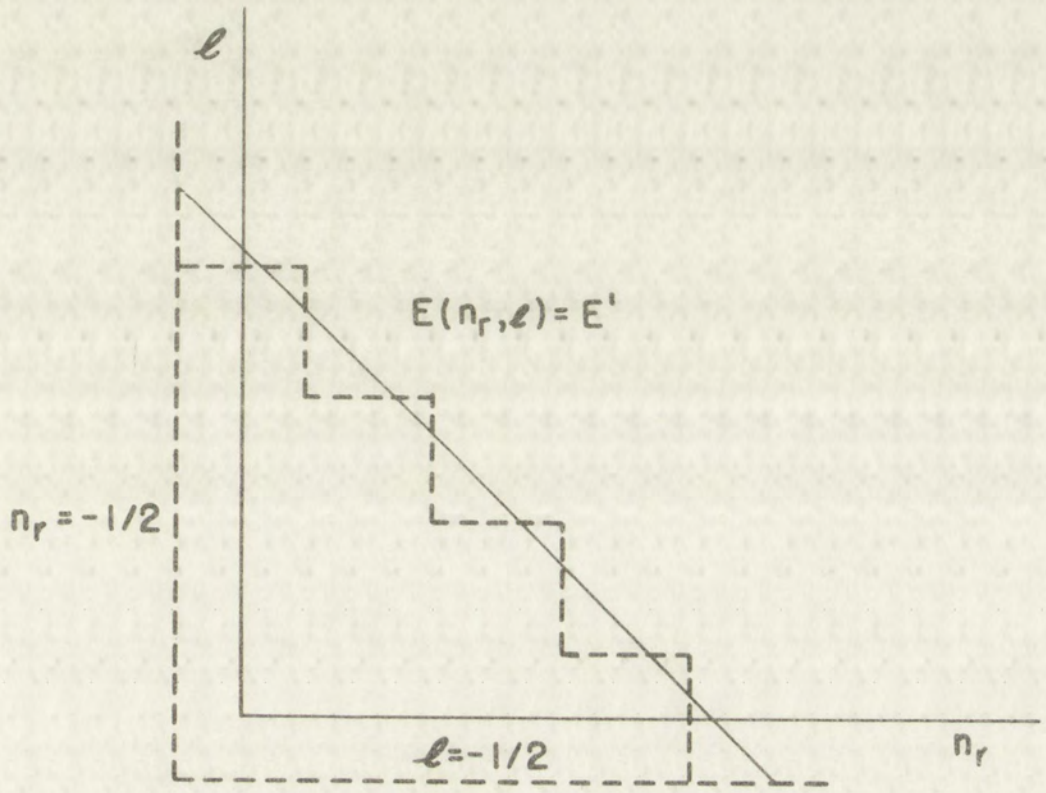


Figure 6. The (n_r, ℓ) plane illustrating the regions of integration in a central field problem (from Ref. 37)

apparent upon comparing the aforementioned region with the correct region of integration which is bounded by $E_{n_r,\ell} = E''$, where E'' has been introduced previously. This correct region is indicated by the dashed lines at half integral values of n_r and ℓ.

We now perform the integration with respect to n_r in (10.5). Holding ℓ constant we obtain, in a manner analogous to that used in deriving (10.3),

$$\int_{-1/2}^{n_r'(\ell,E')} E(n_r,\ell)dn_r = \int_{r_1^{\ell}(E')}^{r_2^{\ell}(E')} \left[\frac{1}{3}\frac{p_\ell^2(E',r)}{2m} + V + \frac{\hbar^2}{2m}\frac{(\ell+1/2)^2}{r^2}\right]\frac{2}{h}\,p_\ell(E',r)dr,$$

where

$$p_\ell(E',r) = \left\{2m\left[E'-V-\frac{\hbar^2}{2m}\frac{(\ell+1/2)^2}{r^2}\right]\right\}^{1/2}, \tag{10.7}$$

and $n_r'(\ell,E')$ is the solution of $E(n_r,\ell) = E'$ for n_r. We now have

$$E = \int_{-1/2}^{E(n_r,\ell)=E'}\int_{-1/2}^{} (2\ell+1)E(n_r,\ell)dn_r d\ell$$

$$= \frac{2}{h}\int_{-1/2}^{\ell_{max}}\int_{r_1^{\ell}(E')}^{r_2^{\ell}(E')} (2\ell+1)\left\{\frac{1}{3}\frac{p_\ell^3(E',r)}{2m} + \left[V+\frac{\hbar^2}{2m}\frac{(\ell+1/2)^2}{r^2}\right]p_\ell(E',r)\right\}drd\ell$$

$$= \frac{2}{h}\int_{-1/2}^{\ell_{max}}\int_{r_1^{\ell}(E')}^{r_2^{\ell}(E')} (2\ell+1)\left[-\frac{2}{3}\frac{p_\ell^3(E',r)}{2m} + E'p_\ell(E',r)\right]drd\ell. \tag{10.8}$$

Here ℓ ranges from -1/2 to the maximum value, ℓ', which from Figure 6 is the solution of $E(-1/2,\ell) = E'$.

Changing the order of integration we obtain

$$E = \frac{2}{h}\int_{r_1^{-1/2}(E')}^{r_2^{-1/2}(E')}\int_{-1/2}^{\ell_{max}(r)} (2\ell+1)\left[-\frac{2}{3}\frac{p_\ell^3(E',r)}{2m} + E'\ p_\ell(E',r)\right]d\ell dr.$$

The quantity $\ell_{max}(r)$ is obtained by solving

$$V(r) + \frac{\hbar^2}{2m}\frac{(\ell+1/2)^2}{r^2} = E',$$

and $r_1^{-1/2}(E')$ and $r_2^{-1/2}(E')$ are the roots of $E' = V(r)$. Substituting

now for $p_\ell(E',r)$ from (10.7), and changing the variable of integration from ℓ to $(\ell+1/2)^2$, the equation can be integrated with respect to ℓ, giving

$$E = \int_{r_1^{-1/2}(E')}^{r_2^{-1/2}(E')} \left(\frac{3}{5}\frac{P^2}{2m} + V\right) \frac{4\pi P^3}{3h^3} 4\pi r^2 dr, \tag{10.9}$$

where

$$P = [2m(E'-V)]^{-1/2}.$$

From (10.6),

$$N = \int_{-1/2}^{E(n_r,\ell)=E'} \int_{-1/2} (2\ell+1) dn_r d\ell$$

$$= \int_{-1/2}^{\ell_{max}} (2\ell+1)\frac{2}{h} \int_{r_1^{\ell}(E')}^{r_2^{\ell}(E')} \left\{2m\left[E'-V-\frac{\hbar^2}{2m}\frac{(\ell+1/2)^2}{r^2}\right]\right\}^{1/2} dr d\ell, \tag{10.10}$$

where the integration over n_r has been carried out by referring to (10.4). Now again reversing the order of integration and integrating over ℓ, we get

$$N = \int_{r_1^{-1/2}(E')}^{r_2^{-1/2}(E')} \frac{4\pi P^3}{3h^3} 4\pi r^2 dr. \tag{10.11}$$

Equation (10.9) is the Thomas-Fermi energy equation for three dimensions, where the density ρ is identified from (10.11) as

$$\rho = \frac{4\pi P^3}{3h^3}.$$

If the spin degeneracy had been taken into account, so that every level is doubly filled, a factor of two would have appeared throughout the development and the density would be found to be given by

$$\rho = \frac{8\pi P^3}{3h^3}.$$

PART II

A PROPOSED MODIFICATION OF THE STATISTICAL EQUATIONS

11. The Coulomb Field Correction

It has been shown by March and Plaskett's derivation that the sum of eigenvalues is approximated in the Thomas-Fermi method by an integral of the WKB eigenvalues over a particular region of the (n_r, ℓ) plane. When the potential is known, the evaluation of the Thomas-Fermi approximation to the sum is simply effected by the use of (10.5) and (10.6). In the case of a Coulomb field, Scott's results (Section 6) are obtained in correcting from the approximate sum to the correct value. To show this we write the WKB expression for the eigenvalues in a Coulomb field, which is, in atomic units,

$$E_{n_r,\ell} = -\frac{Z^2}{2(n_r+\ell+1)^2} . \tag{11.1}$$

The formula is, of course, identical to the result obtained by solving Schrödinger's equation exactly. The Thomas-Fermi approximation to the sum of the energies of the lowest N states is found by using (11.1)

together with (10.5) and (10.6). We introduce for convenience

$$\alpha = \left(-\frac{Z^2}{2E'}\right)^{1/2}, \tag{11.2a}$$

or, from (11.1),

$$\alpha = (n_r+\ell+1)_{\text{outer boundary}}, \tag{11.2b}$$

the subscript referring to the outer boundary of the region of integration in the (n_r,ℓ) plane.

We now have, from (10.6),

$$\begin{aligned} N &= 2\int_{\ell=-1/2}^{n_r+\ell+1=\alpha}\int_{n_r=-1/2}(2\ell+1)dn_r d\ell \\ &= 2\int_{\ell=-1/2}^{\alpha-1/2}\int_{n_r=-1/2}^{\alpha-\ell-1}(2\ell+1)dn_r d\ell \\ &= \frac{2}{3}\alpha^3. \end{aligned} \tag{11.3}$$

If we consider the K shell electrons only, we put N = 2 and obtain

$$\alpha = 3^{1/3}.$$

From (10.5),

$$E = 2\int_{\ell=-1/2}^{n_r+\ell+1=\alpha}\int_{n_r=-1/2} (2\ell+1)\left[\frac{-Z^2}{2(n_r+\ell+1)^2}\right]dn_r\,d\ell$$

$$= -Z^2\alpha. \tag{11.4}$$

With the above value of α, we have

$$E = -3^{1/3}Z^2,$$

which is identical to the result obtained by Scott for the K shell.

If we consider the levels filled from $n = 1$ to $n = \nu$, where n is the total quantum number defined by

$$n = n_r + \ell + 1,$$

then the number of states is given by

$$N = \sum_{1}^{\nu} 2n^2$$

$$= \frac{\nu(\nu+1)(2\nu+1)}{3}, \tag{11.5}$$

since each level is $2n^2$ - fold degenerate. Therefore, from (11.3),

$$\frac{1}{3}\,\nu(\nu+1)(2\nu+1) = \frac{2}{3}\alpha^3,$$

or

$$\alpha = [\tfrac{1}{2}\nu(\nu+1)(2\nu+1)]^{1/3}.$$

Substituting this value of α into (11.4), we have as the Thomas-Fermi approximation to the sum of eigenvalues the expression

$$E = -Z^2[\tfrac{1}{2}\nu(\nu+1)(2\nu+1)]^{1/3}. \tag{11.6}$$

Scott's value for the correction, $(1/2)Z^2$, is obtained by subtracting (11.6) from the correct sum of eigenvalues, $-Z^2\nu$, and letting ν tend to infinity.

Let us now consider the following modification of the available electron states. Let us change the lower limit of ℓ and the value of α so that the correct total energy of the filled states results, in the particular case of the Coulomb field, when integrations such as the preceding are performed over the modified region.[11] We shall denote the lower limit of ℓ by ℓ_{min}, which is, in general, now different from -1/2. It is convenient also to introduce the quantity

$$a = \ell_{min} + 1/2, \tag{11.7}$$

[11] Although the results of this section can be obtained from a change in the lower limit of either ℓ or n_r, the modifications which are derived in the following section do not follow from altering the minimum value of n_r.

which we shall call the "modification factor." An evaluation of a, ℓ_{min}, and α for the K shell follows.

To include two states in the region of integration we require that

$$2 = 2\int_{\ell=a_K-1/2}^{n_r+\ell+1=\alpha_K}\int_{n_r=-1/2} (2\ell+1)dn_r d\ell$$

$$= 2\int_{a_K-1/2}^{\alpha_K-1/2} (2\ell+1)(\alpha_K-\ell-1/2)d\ell$$

$$= 2(\frac{1}{3}\alpha_K^3-\alpha_K a_K^2+\frac{2}{3}a_K^3). \qquad (11.8)$$

The condition that the total energy of the two K-electrons be the correct value yields

$$2\left(\frac{-Z^2}{2}\right) = 2\int_{\ell=a_K-1/2}^{n_r+\ell+1=\alpha_K}\int_{n_r=-1/2} (2\ell+1)\left[\frac{-Z^2}{2(n_r+\ell+1)^2}\right]dn_r d\ell$$

$$= -\frac{Z^2}{\alpha_K}\int_{a_K-1/2}^{\alpha_K-1/2} (2\alpha_K-2\ell-1)d\ell$$

$$= -\frac{Z^2}{\alpha_K}(\alpha_K^2-2\alpha_K a_K+a_K^2).$$

Thus we have two equations in α_K and a_K:

$$\frac{1}{3}\alpha_K^3 - \alpha_K a_K^2 + \frac{2}{3}a_K^3 = 1, \qquad (11.9)$$

$$\alpha_K^2 - 2\alpha_K a_K + a_K^2 = \alpha_K. \tag{11.10}$$

From (11.10) we obtain

$$a_K = \alpha_K \pm \alpha_K^{1/2}, \tag{11.11}$$

which, when substituted into (11.9), gives

$$\alpha_K^2 \pm \frac{2}{3}\alpha_K^{3/2} - 1 = 0. \tag{11.12}$$

There is one positive real root to (11.12) when written with either sign, according to Descartes' rule of variation of sign. The respective roots have been obtained by the Newton-Raphson process, and are summarized below, where the plus and minus signs indicate the sign taken in (11.12). The corresponding value of $\ell_{min,K}$ is also given.

Sign	α_K	a_K	$\ell_{min,K}$
+	0.75189460	1.6190132	1.1190132
-	1.4856820	0.26679643	-0.23320357

The solution given in the upper row of the listing is not of interest, as can be seen immediately upon evaluating ℓ for $n_r = -1/2$. We have, for the plus solution,

$$-\frac{1}{2} + \ell + 1 = \alpha_K \approx 0.75,$$

which yields a value of ℓ of about 0.25. This is smaller than the lowest value of ℓ to be considered in the region, $\ell_{min,K}$, which is approximately 1.12. The appropriate solution is therefore that of the lower row of the listing, and corresponds to taking the negative sign in (11.11) and (11.12).

Putting $\nu = 2$, a similar calculation for the ten states of lowest energy results in the following values:

$$\alpha_L = 2.4915790, \qquad a_L = 0.25928018, \qquad \ell_{min,L} = -0.24071982.$$

As the number of filled shells becomes very large, ℓ_{min} does indeed tend toward the unmodified Thomas-Fermi value of -1/2. To show this we again consider the general case in which shells from n = 1 to n = ν are filled. The number of electron states is given by (11.5),

$$N = \frac{\nu(\nu+1)(2\nu+1)}{3}$$

$$\approx \frac{2}{3}\nu^3,$$

where ν is very large compared to one. Comparison with (11.3) then allows us to write

$$\alpha = \nu, \qquad \nu >> 1.$$

The equation which in the general case of ν filled shells corresponds to (11.11), written with the negative sign, is

$$a = \alpha - (\alpha\nu)^{1/2} . \tag{11.13}$$

Substituting $\alpha = \nu$ we have $a = 0$, or from (11.7), $\ell_{min} = -1/2$.

In Section 14 we define a Coulomb problem to replace the actual atomic problem. The modification to the (n_r, ℓ) plane is then computed for this equivalent Coulomb problem. In general there is a nonintegral number of filled shells, so that an interpolation is necessary in order to determine the appropriate values of the quantities involved in the modification. A simple way of performing the interpolation is to adapt (11.5) as the definition of $N(\nu)$ for any nonnegative value of ν, consider ν a continuous variable, and perform the calculation of ℓ_{min} exactly as if ν were an integer. In Figure 7 we have graphed ℓ_{min} as a function of ν.

Actually, in the equivalent Coulomb problem the quantity which is given is α rather than ν, and it develops that a is more convenient to use than ℓ_{min}. To evaluate a when α is given, we make use of the generalization of (11.8) to include N states, which is

$$N = \frac{\nu(\nu+1)(2\nu+1)}{3} = 2(\tfrac{1}{3}\alpha^3 - \alpha a^2 + \tfrac{2}{3}a^3).$$

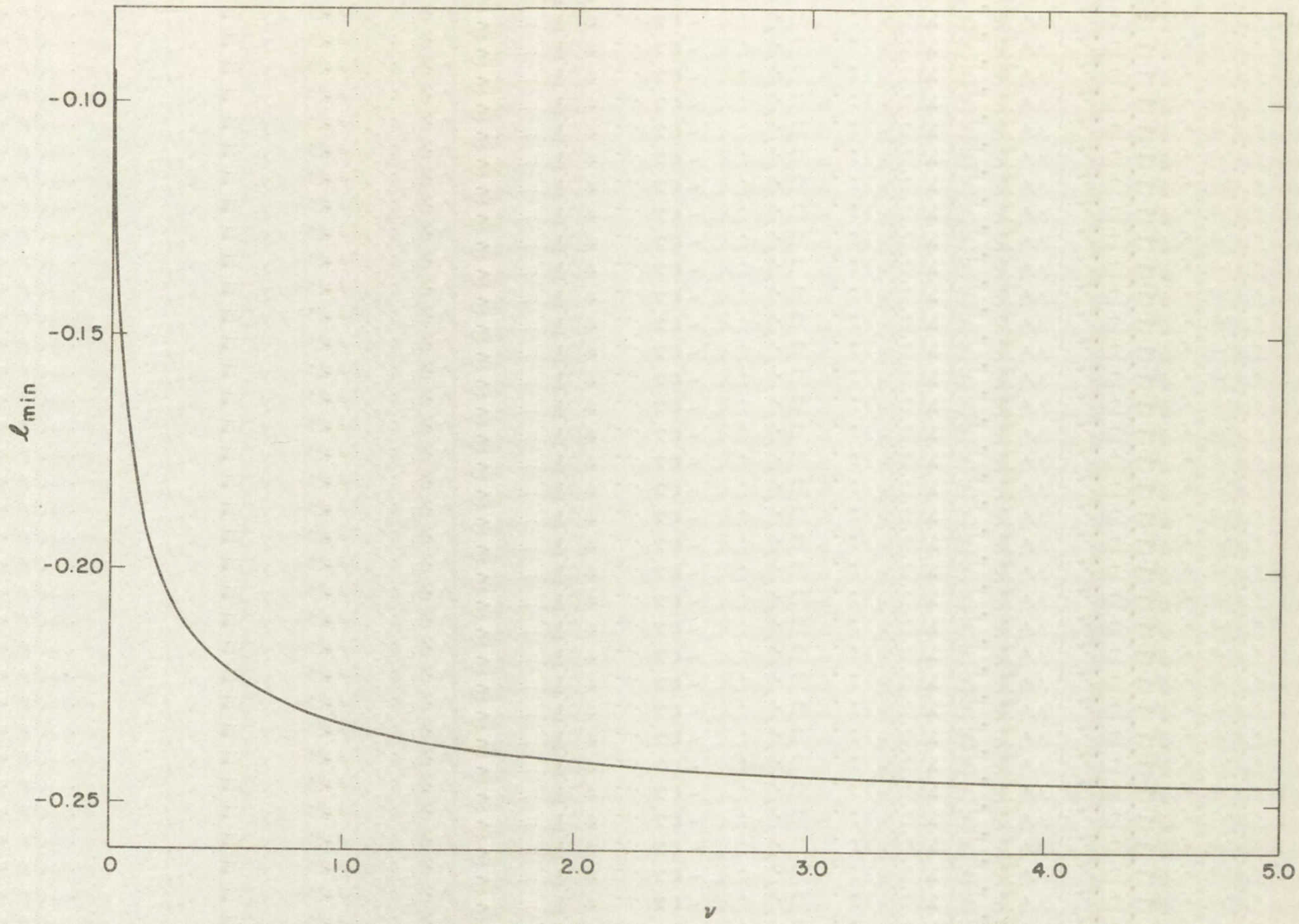


Figure 7. The corrected lower limit of ℓ vs. the number of filled shells in a Coulomb field

Using (11.11) to eliminate a, we have

$$\frac{\nu(\nu+1)(2\nu+1)}{3} = 2[\alpha^2\nu - \frac{2}{3}(\alpha\nu)^{3/2}],$$

which may be written as

$$\nu^2 + \frac{3}{2}\nu + 2\alpha^{3/2}\nu^{1/2} - (3\alpha^2 - 1/2) = 0. \qquad (11.14)$$

If α is known, (11.14) may be solved by numerical means for ν. Using (11.13), the quantity a is then determined. In other words, one can calculate, from the Fermi energy of particles in a Coulomb field, the correction to be applied to the lower limit of the orbital quantum number.

Finally, we note that as the region of integration tends to zero, from (11.2b),

$$\alpha \to -1/2 + \ell_{min} + 1 = a.$$

Letting ν go to zero in (11.14) we then obtain

$$3a^2 - 1/2 = 0,$$

or,

$$a = 6^{-1/2}$$
$$= 0.40824829.$$

In Figure 8 we have plotted a as a function of α.

12. A Minor Generalization of March and Plaskett's Integrations

If one performs the integrations indicated in (10.5) and (10.6) of Part I, with the general value ℓ_{min} replacing -1/2 as the lower limit of ℓ, the result is a modified Thomas-Fermi energy equation and a modified formula for the density. In this section we shall obtain these modified forms. We shall then show that it is possible to interpret them as a consequence of regarding the electrons as behaving classically (except for their obeying the Fermi statistics), as in the simple derivation of the Thomas-Fermi equation, but having a nonzero lower limit to their available angular momentum. This is, of course, what one would expect from the change which has been brought about in the lower limit of the orbital quantum number.

In deriving the modified energy equation to replace (10.9), we note that the integration over n_r proceeds as before. Therefore, we may merely rewrite (10.8) with ℓ_{min} as the lower limit of ℓ. We have

$$E = \frac{2}{h}\int_{\ell_{min}}^{\ell_{max}} \int_{r_1^{\ell}(E')}^{r_2^{\ell}(E')} (2\ell+1)\left[- \frac{2}{3}\frac{p_\ell^3(E',r)}{2m} + E'p_\ell(E',r)\right] dr d\ell,$$

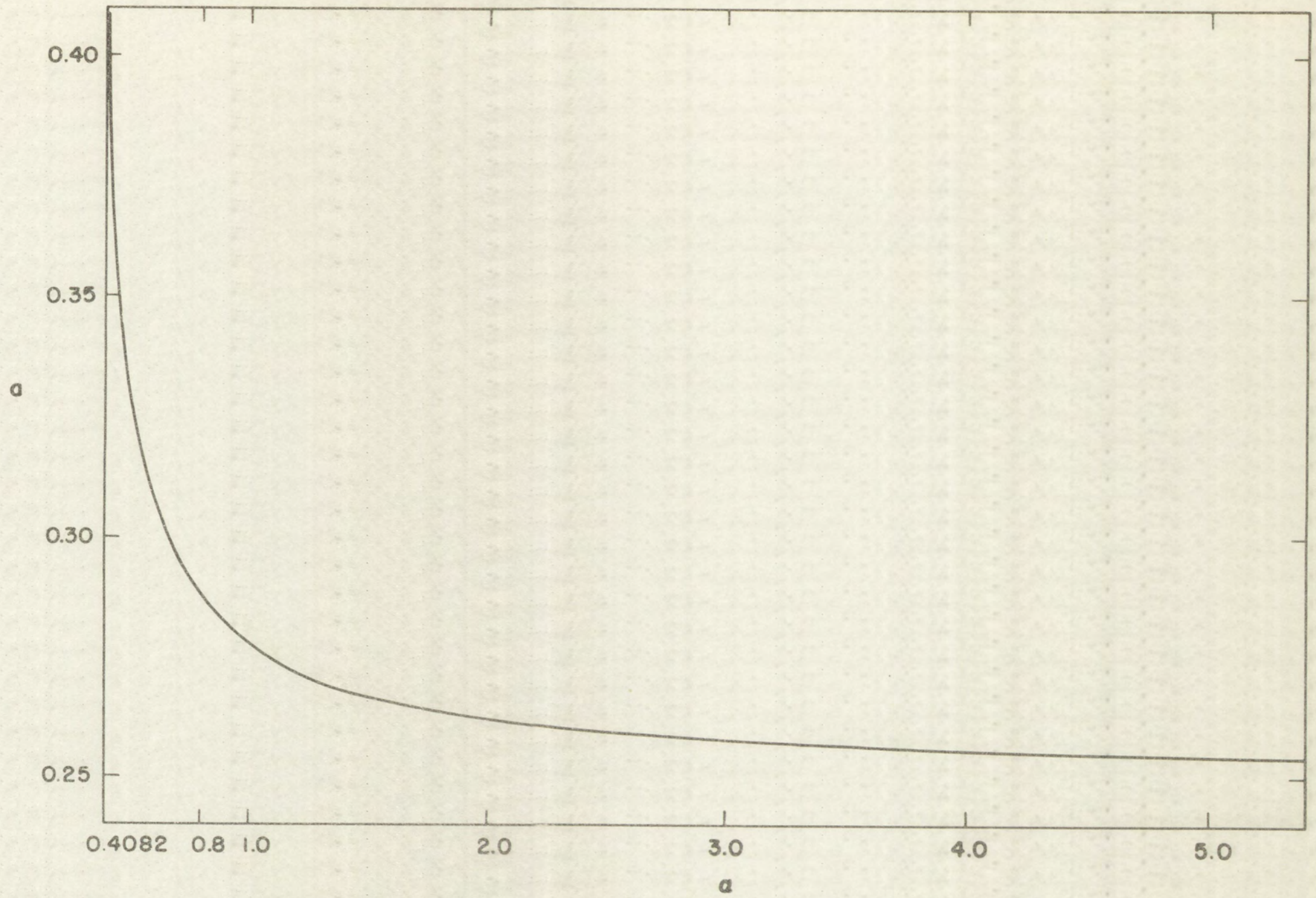


Figure 8. The relation between the boundaries of the corrected region of integration in the (n_r, ℓ) plane

where, again, ℓ_{max} is the solution of $E(-1/2,\ell) = E'$. Changing the order of integration yields

$$E = \frac{2}{h}\int_{r_1(E',\ell_{min})}^{r_2(E',\ell_{min})}\int_{\ell_{min}}^{\ell_{max}(r)}(2\ell+1)\left[-\frac{2}{3}\frac{p_\ell^3(E',r)}{2m} + E'p_\ell(E',r)\right]d\ell dr.$$

As before, $\ell_{max}(r)$ is the solution of

$$V(r) + \frac{\hbar^2}{2m}\frac{(\ell+1/2)^2}{r^2} = E',$$

but now $r_1(E',\ell_{min})$ and $r_2(E',\ell_{min})$ are the roots[12] of

$$V(r) + \frac{\hbar^2}{2m}\frac{(\ell_{min}+1/2)^2}{r^2} = E'. \tag{12.1}$$

Integrating with respect to ℓ, we obtain

$$E = \int_{r_1(E',\ell_{min})}^{r_2(E',\ell_{min})}\left[\frac{3}{5}\frac{P^2}{2m} + V + \frac{\hbar^2}{5m}\frac{(\ell_{min}+1/2)^2}{r^2}\right]\rho\, 4\pi r^2 dr, \tag{12.2}$$

where P, the Fermi momentum, is defined by

$$P = [2m(E'-V)]^{1/2},$$

---

[12] It should be noted that in application to compressed atoms, there is only one root of (12.1) between zero and r_2, where r_2 is the outermost point to which the integration is carried. This root is to be identified as $r_1(E',\ell_{min})$, and r_2 replaces $r_2(E',\ell_{min})$ as the upper limit of the energy integral.

in agreement with the unmodified theory. The electron density ρ has been identified from the corresponding modification of (10.11), which is found by writing (10.10) with the general lower limit of ℓ. We have

$$N = \int_{\ell_{min}}^{\ell_{max}} (2\ell+1) \frac{2}{h} \int_{r_1^{\ell}(E')}^{r_2^{\ell}(E')} \left\{ 2m\left[E'-V- \frac{\hbar^2}{2m} \frac{(\ell+1/2)^2}{r^2} \right] \right\}^{1/2} dr d\ell.$$

Reversing the order of integration and integrating over ℓ as before, we obtain

$$N = \int_{r_1(E',\ell_{min})}^{r_2(E',\ell_{min})} \frac{4\pi}{3h^3} \left\{ 2m\left[E'-V- \frac{\hbar^2}{2m} \frac{(\ell_{min}+1/2)^2}{r^2} \right] \right\}^{3/2} 4\pi r^2 dr. \qquad (12.3)$$

The spin degeneracy contributes another factor of two to the right side of (12.3), and the modified Thomas-Fermi density is therefore given by

$$\rho = \frac{8\pi}{3h^3} \left[2m\left(E'-V- \frac{\hbar^2}{2m} \frac{a^2}{r^2} \right) \right]^{3/2}, \qquad r \geq r_1(E',\ell_{min}), \qquad (12.4)$$

and zero otherwise. In writing (12.4), the modification factor a has been substituted for $(\ell_{min}+1/2)$.

The effect of the generalization of the lower limit of the orbital quantum number is thus two-fold. First, the density formula contains an extra term in the radical as compared with the formula

$$\rho = \frac{8\pi}{3h^3} [2m(E'-V)]^{3/2}. \qquad (1.3)$$

Second, an additional form of energy has been introduced into the Thomas-Fermi approximation to the sum of eigenvalues as given by the integral (12.2). We wish now to show that these results can be formulated in terms of a cut-off momentum such as described in Section 8.

We have seen that the lower limit of the orbital quantum number in the unmodified Thomas-Fermi theory is -1/2. This corresponds to an orbital angular momentum of zero, provided that we assume the orbital motion to be governed by half-integral quantization of the phase integral. Thus, let us write for a particle moving with constant angular momentum of magnitude L,

$$\oint L \, d\Phi = (\ell+1/2)h,$$

where Φ is the polar angle, and the integration is over a complete cycle of Φ from zero to 2π. Integrating,

$$L = (\ell+1/2)\hbar,$$

so that for $\ell = -1/2$ we have $L = 0$. If now the lower limit of ℓ is written as ℓ_{min}, then states with angular momentum between zero and

$$L_c = (\ell_{min}+1/2)\hbar \tag{12.5}$$

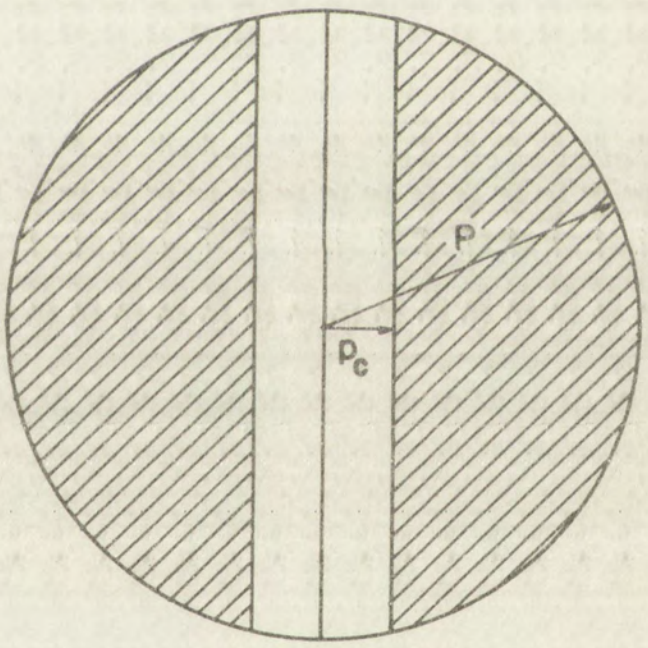
are not available for occupation. L_c can thus be designated as a cut-off

value for the orbital angular momentum.

Let us now consider the distribution of states in momentum space when we impose the condition that the angular momentum of an electron located approximately at r be no less than

$$L_c = p_c r, \tag{12.6}$$

where p_c is the lower limit to the allowed linear momentum. The distribution of available states in momentum space is then as shown by the shaded portion of the figure below, the complete figure representing a sphere of radius P. There is removed from the sphere a circularly cylindrical portion of radius p_c, whose longitudinal axis passes through the center of the sphere, and the spherical segments on the ends of the cylinder. The axis of the figure is the radial momentum axis.



The electron density which results from the momentum distribution under discussion is found by multiplying the volume represented by the shaded portion of the figure by $2/h^3$. If the angle θ is measured

from the axis shown in the figure, and Φ is here the azimuthal angle, then the volume is

$$2\int_{\Phi=0}^{2\pi}\int_{\theta=\sin^{-1}p_o}^{\pi/2}\int_{p=\frac{p_c}{\sin\theta}}^{P} p^2\,dp\,\sin\theta\,d\theta d\Phi.$$

We have introduced into the notation the dimensionless quantity $p_o = p_c/P$. Upon integrating we find the volume to be

$$\frac{4}{3}\pi(P^2-p_c^2)^{3/2},$$

so that the density is

$$\frac{8\pi}{3h^3}(P^2-p_c^2)^{3/2}.$$

Comparison with (12.4) allows us to identify the cut-off momentum,

$$p_c = \frac{\hbar a}{r}, \tag{12.7}$$

in agreement with that obtained by solving (12.5) and (12.6). It follows that r_1 is the inner point at which $p_c = P$. At radial distances less than r_1, momenta are prohibited over the entire range from zero to P, so that the electron density vanishes.

We shall now calculate the kinetic energy density at a point in the spatial distribution. The average squared momentum is given by

$$\overline{p^2} = \frac{1}{(8\pi/3h^3)(P^2-p_c^2)^{3/2}} \frac{2}{h^3} \int_{\theta=\sin^{-1}p_o}^{\pi/2} \int_{p=p_c/\sin\theta}^{P} p^2\, 4\pi p^2 dp \sin\theta\, d\theta$$

$$= \frac{3}{5}P^2 + \frac{2}{5}p_c^2.$$

The average kinetic energy per particle is therefore

$$\frac{3}{5}\frac{P^2}{2m} + \frac{2}{5}\frac{p_c^2}{2m},$$

and the kinetic energy density is given by

$$U_k = \left(\frac{3}{5}\frac{P^2}{2m} + \frac{2}{5}\frac{p_c^2}{2m}\right)\rho, \tag{12.8}$$

which allows the identification of the third term in the integral (12.2) as a factor contributing to the kinetic energy. We now rewrite (12.8) as

$$U_k = \left[\left(\frac{3}{5}\frac{P^2}{2m} - \frac{3}{5}\frac{p_c^2}{2m}\right) + \frac{p_c^2}{2m}\right]\rho$$

$$= \frac{3}{10}(3\pi^2)^{2/3}\, e^2 a_o \rho^{5/3} + \frac{p_c^2}{2m}\rho$$

$$= c_f \rho^{5/3} + \frac{\hbar^2}{2m}\frac{a^2}{r^2}\rho.$$

The constant c_f has been defined previously by (2.1), and we have made

use of (12.7). The first term on the right side is the usual expression for the Fermi kinetic energy density. The second term is a correction which we shall call the quantum-correction energy density, U_q. If we define

$$c_q = \frac{\hbar^2}{2m} a^2, \tag{12.9}$$

we can write

$$U_q = \frac{c_q}{r^2} \rho. \tag{12.10}$$

The modification of the density formula and the quantum-correction energy are more fully discussed in later sections. We turn now to the derivation of the equations for the potential functions.

13. The Modified Thomas-Fermi and Thomas-Fermi-Dirac Equations

The modified Thomas-Fermi and Thomas-Fermi-Dirac equations follow very simply from the results of the previous section. In the no-exchange case, the density is given by

$$\rho = \frac{8\pi}{3h^3}\left[2m\left(E'-V-\frac{\hbar^2}{2m}\frac{a^2}{r^2}\right)\right]^{3/2}, \qquad r \geq r_1(E', \ell_{min}), \tag{12.4}$$

and the modified equation for the potential function is obtained directly from Poisson's equation, just as in the derivation of the unmodified

Thomas-Fermi equation. Again we introduce the potential function ϕ defined by

$$Ze^2\phi = (E'-V)r,$$

so that we have for the Laplacian

$$\frac{d^2V}{dr^2} + \frac{2}{r}\frac{dV}{dr} = -\frac{Ze^2}{r}\frac{d^2\phi}{dr^2}.$$

Then from Poisson's equation and the above expression for the density we obtain

$$\frac{d^2\phi}{dr^2} = \frac{32\pi^2}{3h^3}\frac{r}{Z}\left(\frac{2mZe^2}{r}\phi - \frac{\hbar^2a^2}{r^2}\right)^{3/2}, \qquad r \geq r_1, \tag{13.1}$$

where r_1 is the inner radius at which the expression in the parentheses vanishes. For $r < r_1$, since the density is set equal to zero,

$$\frac{d^2\phi}{dr^2} = 0. \tag{13.2}$$

We now choose as the unit of length the first Bohr radius, and write[13]

$$x = \frac{r}{a_o}, \tag{13.3}$$

[13] There is little chance of confusion in using the same notation for the distance variable as in the unmodified theories.

in terms of which (13.1) and (13.2) become

$$\phi'' = \frac{4x}{3\pi Z}\left(\frac{2Z\phi}{x} - \frac{a^2}{x^2}\right)^{3/2}, \qquad x \geq x_1,$$
$$= 0, \qquad x < x_1. \tag{13.4}$$

This is the modified Thomas-Fermi equation. The boundary conditions, determined respectively by the potential as r tends to zero, and the vanishing of the electric field at the outer boundary, are again

$$\phi(0) = 1,$$

and

$$x_2\phi'(x_2) = \phi(x_2).$$

The modified Thomas-Fermi-Dirac equation is obtained by the variational principle discussed in the Appendix. The procedure is exactly as described there, except that in the total energy integral there is the additional contribution of the quantum-correction energy. The total energy is now written as

$$E = \int_{r_1}^{r_2}\left[c_f\rho^{5/3} - c_{ex}\rho^{4/3} - e(v^n + \frac{1}{2}v^e)\rho + \frac{c_q}{r^2}\rho\right]4\pi r^2 dr. \tag{13.5}$$

Minimization of the integral leads to the equation

$$\frac{5}{3}c_f\rho^{2/3} - \frac{4}{3}c_{ex}\rho^{1/3} + \frac{c_q}{r^2} + (V-E') = 0. \tag{13.6}$$

Solving for ρ and using the constants defined by (2.6)and (2.7), we have the density given by

$$\rho = \sigma_o\left[\tau_o+(E'-V-\frac{c_q}{r^2}+\tau_o^2)^{1/2}\right]^3, \qquad r \geqq r_1. \tag{13.7}$$

We again choose r_1 as the radius at which

$$E' - V - \frac{c_q}{r^2}$$

vanishes. At $r = r_1$ the density is therefore $8\sigma_o\tau_o^3$, while again we set

$$\rho = 0, \qquad r < r_1.$$

As in the derivation of the unmodified Thomas-Fermi-Dirac equation, the potential function is defined by the relation

$$Ze^2\phi = (E'-V+\tau_o^2)r, \tag{13.8}$$

in terms of which

$$\rho = \sigma_o\left[\tau_o + \left(\frac{Ze^2\phi}{r} - \frac{c_g}{r^2}\right)^{1/2}\right]^3. \tag{13.9}$$

With x defined by (13.3), the modified Thomas-Fermi-Dirac equation is now derived in the customary way, with the result

$$\begin{aligned} \phi'' &= \frac{4\pi}{Z} a_o^3 x\rho \\ &= \frac{4x}{3\pi^4 Z}\left[1+\pi\left(\frac{2Z}{x}\phi - \frac{a^2}{x^2}\right)^{1/2}\right]^3, \qquad x \geq x_1, \\ &= 0, \qquad x < x_1. \end{aligned} \tag{13.10}$$

The familiar boundary conditions apply:

$$\phi(0) = 1,$$

$$x_2\phi'(x_2) = \phi(x_2). \tag{13.11}$$

The Fermi energy is again fixed by setting V = 0 at the cell boundary. This gives us

$$E' = \frac{Ze^2\phi(r_2)}{r_2} - \tau_o^2,$$

the same as given by (3.5) on the unmodified model.

14. The Equivalent Coulomb Problem

In performing the integrations of (13.4) or (13.10), the modification factor, a, must be specified. In Section 11 we have described the evaluation of a for a Coulomb field, and it is under the approximation that the electrons are moving in a pure Coulomb field that the numerical work described in this paper is performed. We note, however, that the method is perfectly general, and that it is possible in theory to determine the correct region of integration for any potential field. The potential in which we are interested is, of course, that due to the nucleus of charge Ze partially shielded by the surrounding cloud of electrons.

The eigenvalues in the shielded potential will not have an analytic form, but must be evaluated numerically by use of the WKB formula (10.4). The sum of the lowest N eigenvalues computed in this fashion, where N is the number of electrons, is then to be compared with the sum of eigenvalues determined by adding an amount of energy equal to the electron-electron potential energy to the total energy of the distribution, as found by (13.5). No calculations of this type have been performed, but we can conjecture that there should be some value of the modification factor, for each initial slope of the potential function, for which the two calculations of the sum of eigenvalues agree. This would be found by an iterative procedure.

The similarity between this process and the self-consistent field method of Hartree (Ref. 45) is apparent. In the present case we demand that the resultant field be such that the <u>sum</u> of eigenvalues computed by

the two means at our disposal is consistent. In the Hartree method each individual wave function and eigenvalue is consistent with the field created by the nuclear charge and the charge density of all the other electrons.

The calculations which we have performed employ, as already indicated, a further approximation in the determination of the modification factor, which greatly simplifies the numerical effort. A Coulomb field approximation is suggested by the success of Scott's correction (Section 6) in yielding the atomic binding energies. In calculating a, then, we shall replace the actual problem by an "equivalent Coulomb problem," in which there is a small, in general nonintegral, number of electrons moving in the pure Coulomb field of the nucleus.

The defining equation for ϕ, neglecting exchange, is

$$Ze^2\phi = (E'-V)r. \tag{14.1}$$

It is easily seen that in a pure Coulomb field ϕ takes the form

$$\phi = 1 + \frac{d\phi}{dr} r,$$

for if we substitute this into (14.1) we obtain

$$V = -\frac{Ze^2}{r} + E' - Ze^2 \frac{d\phi}{dr}, \tag{14.2}$$

and we are always free to add constants to the potential energy. The eigenvalues for this system are given by (11.1) if we let the Fermi energy of the equivalent Coulomb problem be determined by the relation

$$E' = Ze^2 \frac{d\phi}{dr} .$$

Writing this in atomic units and identifying the slope with the initial slope used in starting a solution of the actual problem, we have

$$E' = Z\phi_o' .$$

Therefore, with the help of (11.2a),

$$\alpha = \left(- \frac{Z}{2\phi_o'} \right)^{1/2} .$$

With α determined, the modification factor can be found by the method set forth in Section 11.

The validity of the Coulomb field approximation is investigated for a special case in the following two sections.

15. The Modification of the Electron Density

The methods used in obtaining solutions of the modified Thomas-Fermi-Dirac equation (13.10) are described in Part III of this paper, together with the resulting total energies of the atoms and the effect

of the modification on the equation of state. Here we wish to utilize some of the results in considering the effect on the radial distribution function ρx^2. The Thomas-Fermi-Dirac and the present modification of the Thomas-Fermi-Dirac radial distribution functions are plotted for the "isolated"[14] copper atom in Figure 9. In comparing the two distributions, it is seen that the difference becomes quite insignificant for radial distances beyond about 0.2 Bohr radius, although, of course, the displaced electron density must lead to an increased outer radius of the atom.

The result of the density modification is a lowering (in magnitude) of the electron-nuclear potential energy, or equivalently, of the contribution by the electrons to the potential at the nucleus. For convenient comparison with Scott's results, we shall discuss the effect in terms of the potential at the nucleus. However, the final results are expressed as a correction of the electron-nuclear potential energy.

Since a pure Coulomb field has been used as the basis for correcting the region of integration in the (n_r, ℓ) plane, it is of interest to compute the distance from the nucleus at which the potential at the nucleus is essentially corrected by use of the modified density formula. If the correction of the potential at the nucleus, and any other consequence of the modification of the region of integration, is confined to the spatial

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[14] As with the unmodified Thomas-Fermi-Dirac equation, there is really no solution which adequately represents the isolated atom. The distribution plotted is that for which the calculated pressure is very small; within the precision of the graph this distribution would correspond to that of an isolated atom solution, if such a solution did exist.

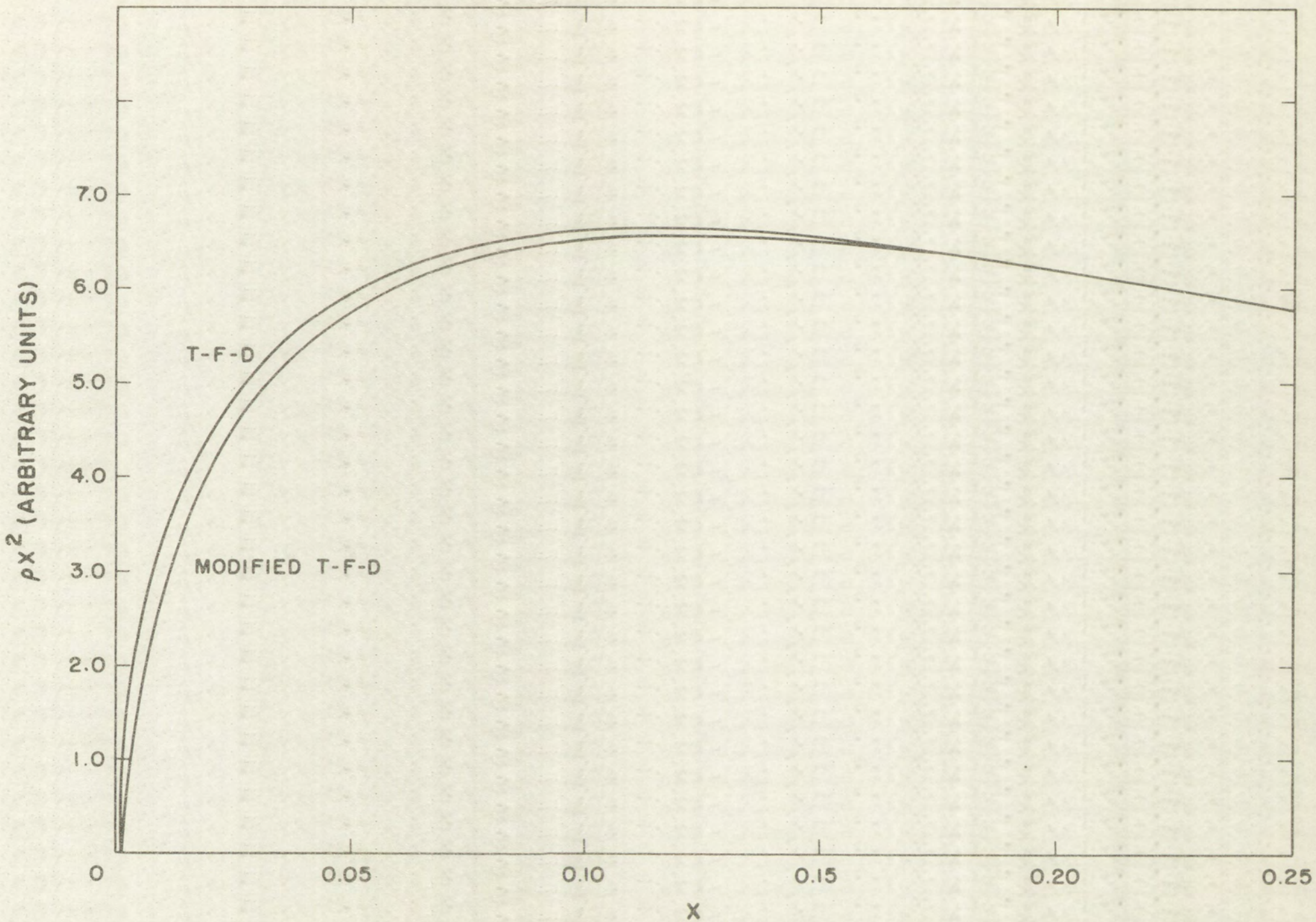

Figure 9. The radial distribution function for the "isolated" copper atom

region in which the field is essentially a pure Coulomb field, then for the modification the equivalent Coulomb problem truly represents the actual atomic problem. The other consequence which we must consider is the calculation of the quantum-correction energy, which is taken up in the next section.

An indication of the distance required for correction of the potential at the nucleus can be obtained by calculating that due to the K shell electrons in a Coulomb field. Let us first consider the unmodified Thomas-Fermi density. In atomic units we have the density of the K shell electrons given by

$$\rho_{K,T-F} = \frac{2^{3/2}}{3\pi^2}(E_K - V)^{3/2}, \tag{15.1}$$

where

$$E_K = -\frac{1}{2\cdot 3^{2/3}} Z^2 . \tag{6.1}$$

E_K has been determined by the requirement that there be just two electrons of lower energy in the statistical distribution.

It has been shown in the previous section that with the proper choice of the Fermi energy we can write, in atomic units,

$$V = -\frac{Z}{x}.$$

Therefore (15.1) becomes

$$\rho_{K,T-F} = \frac{2^{3/2}}{3\pi^2}\left(\frac{Z}{x} + E_K\right)^{3/2}.$$

This is the same expression as used by Scott, but he has obtained it by choosing $E' = \phi_0' = 0$, which implies the presence of an infinite number of particles in the Coulomb field.

For a given value of Z, the contribution to the potential at the nucleus by that portion of the K shell electron density located within a distance x of the nucleus is

$$v_{K,T-F}(x) = -\int_0^x \frac{\rho_{K,T-F}}{x} 4\pi x^2 dx$$

$$= -\frac{2^{7/2}}{3\pi}\int_0^x \left(\frac{Z}{x} + E_K\right)^{3/2} x dx$$

$$= -\frac{32\cdot 3^{1/3}}{3\pi} Z\left(\frac{3\theta_K}{8} + \frac{\sin 2\theta_K}{4} + \frac{\sin 4\theta_K}{32}\right), \qquad (15.2)$$

where

$$\theta_K = \sin^{-1}\left(\frac{Zx}{2\cdot 3^{2/3}}\right)^{1/2},$$

and we have made use of (6.1) in eliminating E_K.

On the other hand, the modified Thomas-Fermi density of K shell electrons is given in atomic units by

$$\rho_K = \frac{2^{3/2}}{3\pi^2}\left(\frac{Z}{x} + \mathcal{E}_K - \frac{a_K^2}{2x^2}\right)^{3/2}, \tag{15.3}$$

where $\mathcal{E}_K$ is the energy value which corresponds to E_K in the unmodified case. That is, for two electrons we have from (11.2a),

$$\mathcal{E}_K = -\frac{Z^2}{2\alpha_K^2}.$$

We now form

$$v_K(x) = -\int_{x_{1,K}}^{x} \frac{\rho_K}{x} 4\pi x^2 dx,$$

where $x_{1,K}$ is the lower value of x at which (15.3) vanishes, or

$$\frac{-Z + (Z^2+2\mathcal{E}_K a_K^2)^{1/2}}{2\mathcal{E}_K}.$$

Substituting for the density, we obtain

$$v_K(x) = -\frac{2^{7/2}}{3\pi}\int_{x_{1,K}}^{x}\left(\frac{Z}{x} + \mathcal{E}_K - \frac{a_K^2}{2x^2}\right)^{3/2} x dx$$

$$= -\frac{4}{3\pi}\left[-\frac{X^{3/2}}{x} + AX^{1/2} + B(\Theta_1 - \frac{\pi}{2}) + C(\Theta_2 + \frac{\pi}{2})\right]. \tag{15.4}$$

The quantities within the brackets are defined by the following relations:

$$A = \frac{9}{2}Z - 3e_K Z^2 x \ ,$$

$$B = -3Z \frac{2e_K a_K^2 + 1}{2^{3/2}\ e_K^{1/2}} \ ,$$

$$C = -3Za_K \ ,$$

$$\Theta_1 = \sin^{-1} \frac{1 - 2e_K Zx}{(1-2e_K a_K^2)^{1/2}} \ ,$$

$$\Theta_2 = \sin^{-1} \frac{Zx - a_K^2}{Zx(1-2e_K a_K^2)^{1/2}} \ ,$$

$$X = -2e_K Z^2 x^2 + 2Zx - a_K^2,$$

where

$$e_K = -\frac{\varepsilon_K}{Z^2} = \frac{1}{2\alpha_K^2} \ . \qquad (15.5)$$

If the integrals in (15.2) and (15.4) extend in each case to include the entire K shell electron distribution, we obtain Scott's value for the correction to the contribution by the K shell electrons to the potential at the nucleus. Thus, for the unmodified case the angle

$$\Theta_K = \sin^{-1}(1)$$

$$= \frac{\pi}{2},$$

and

$$v_{K,T-F} = -\frac{32\cdot 3^{1/3}}{3\pi} Z\left(\frac{3\pi}{16}\right)$$

$$= -2\cdot 3^{1/3} Z. \tag{6.2}$$

In the modified case, we have

$$x_{2,K} = \frac{-Z - (Z^2+2\mathcal{E}_K a_K^2)^{1/2}}{2\mathcal{E}_K}$$

$$= \frac{1 + (1-2e_K a_K^2)^{1/2}}{2e_K Z}.$$

For $x = x_{2,K}$,

$$\theta_1 = -\frac{\pi}{2}$$

and

$$\theta_2 = \frac{\pi}{2},$$

while

$$X = 0.$$

Therefore (15.4) becomes simply

$$v_K = \frac{4}{3}(B-C).$$

By use of the definitions of B and C with (15.5) and (11.11), this reduces to

$$v_K = \frac{4}{3}(-\frac{3}{2}Z)$$

$$= -2Z, \tag{15.6}$$

in agreement with the quantum-mechanical value. The difference between (15.6) and (6.2) is, of course, Scott's value for the correction.

If now the respective integrals are taken to a value of x less than that which contains the entire K shell distribution, the correction can be evaluated as a function of x. As a measure of the amount of correction that occurs within a radial distance x for a given atom, we define the K shell "electron-nuclear potential energy correction factor"

$$\delta_K(x) = \frac{v_K(x) - v_{K,T-F}(x)}{2(3^{1/3}-1)Z},$$

which can be generalized in an obvious way to include electrons of other shells. At $x = 0$, δ_K is zero, and it is equal to unity for values of x large enough to contain the entire K shell electron distribution.

In Figure 10 we have plotted $\delta_K(x)$ for Z = 29, and, from the figure, it is seen that 90% of the correction to the electron-nuclear potential energy occurs in this case within a distance from the nucleus of 0.008 Bohr radius.

If we calculate the potential energy of an electron a x = 0.01 Bohr radius, using the modified Thomas-Fermi-Dirac solution for the isolated copper atom, we obtain the value

$$V = -2905 \text{ au.}$$

Calculation of the same quantity in the pure Coulomb field of the nucleus yields

$$V = -2900 \text{ au.}$$

In this case, then, the potential differs from that of a pure Coulomb field by only about five parts in 3000 within the radial distance in which nearly all of the correction to the electron-nuclear potential energy occurs. If the potential energy is evaluated from the Thomas-Fermi solution, the deviation from the pure Coulomb field value is slightly greater because of the large density of electrons near the nucleus. Nevertheless, the deviation is still only about 25 parts in 3000.

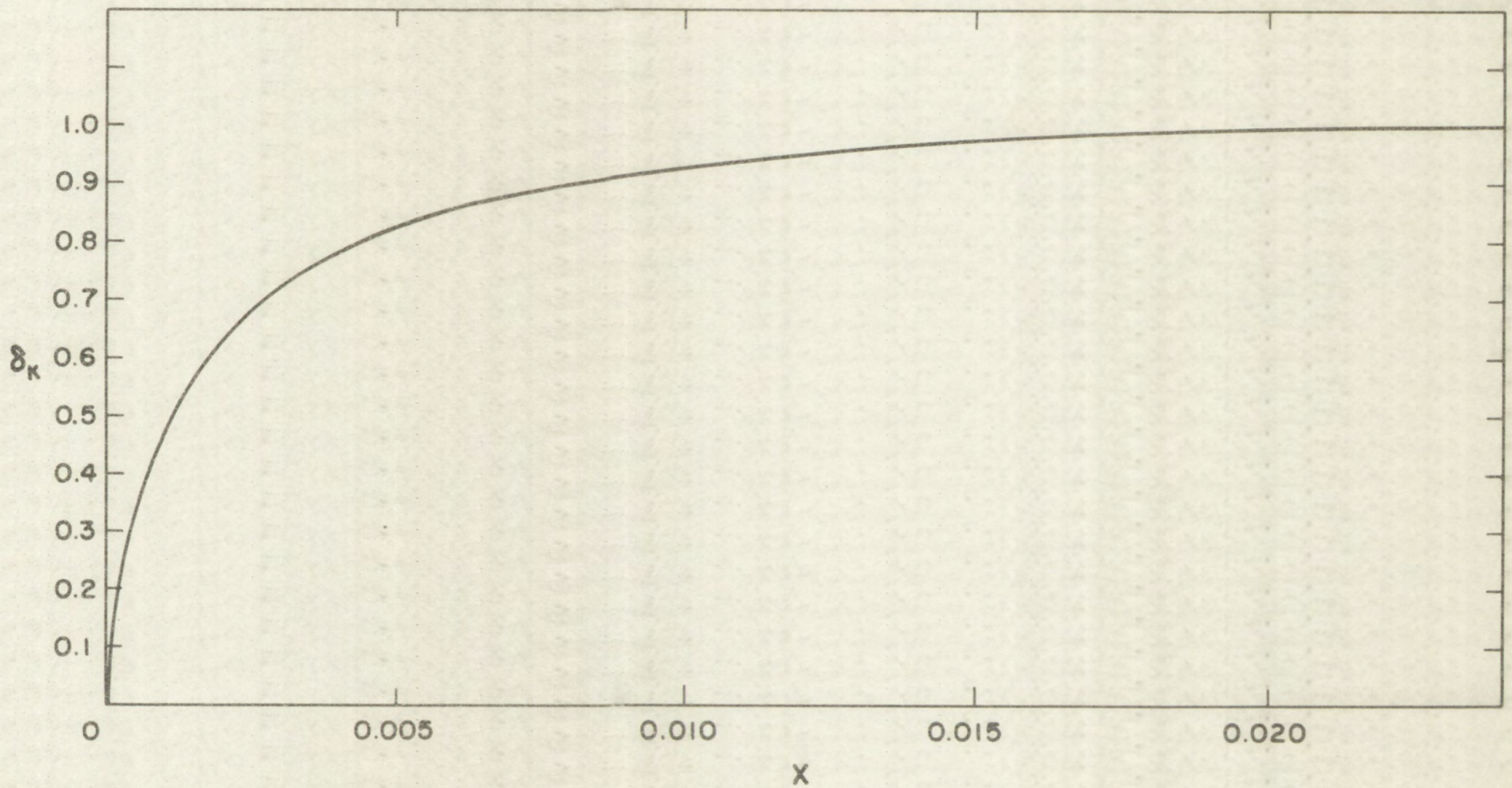

Figure 10. The electron-nuclear potential energy correction factor for the K shell, with Z = 29

Since the great bulk (88% -- see Section 6) of the correction to the electron-nuclear potential energy pertains to the K shell, the above illustration of the small deviation from a pure Coulomb field which occurs can be taken to apply with only slight additional error to the region in which the total electron-nuclear potential energy is substantially corrected. Hence the use of the Coulomb field approximation in evaluating the modification factor appears to be reasonably consistent with the density modification which results.

We have used Z = 29 for quantitative discussion of the correction. For smaller values of Z the general effect is that the radial distance required for correction is greater, but the deviation from the pure Coulomb field within a given distance from the nucleus is less. Naturally the opposite is true for larger values of atomic number.

16. The Quantum-Correction Energy

In the previous section we have been concerned with the correction of the electron-nuclear potential energy which results from the derived modification of the electron distribution. The second effect of the modification of the region of integration in the (n_r, ℓ) plane is the introduction into the theory of a correction to the kinetic energy density. This has been named the quantum-correction energy density, and is given by

$$U_q = \frac{c_q}{r^2} \rho, \tag{12.10}$$

where

$$c_q = \frac{\hbar^2 a^2}{2m} . \tag{12.9}$$

Just as most of the correction of the electron-nuclear potential energy occurs within a region in which the Coulomb field approximation is quite good, the bulk of the contribution to the quantum-correction energy similarly occurs fairly near the nucleus. The Coulomb field approximation is not as well substantiated, however, in this case. It develops that in the case of the "isolated" copper atom, 90% of the contribution occurs within 0.06 Bohr radius, but the deviation of the electrostatic potential from the pure Coulomb value at this distance is about 7%. Although it is thus with somewhat less consistency that the quantum-correction energy is evaluated using the Coulomb field modification factor, the quantum-correction energy is a relatively small part of the total energy, and slight errors in its calculation are of little consequence in determining the total energy of the atom.

It is interesting to compare the present correction to the kinetic energy density with that of Weizsäcker. Using the electron distribution for the "isolated" copper atom, which is summarized in Part III, Table II, we have made an approximate calculation of the Weizsäcker and the quantum-correction energy densities. We have then plotted in Figure 11 the Weizsäcker energy density U_i (multiplied by a rather arbitrary factor of 1/10), the quantum-correction energy density U_q, and the

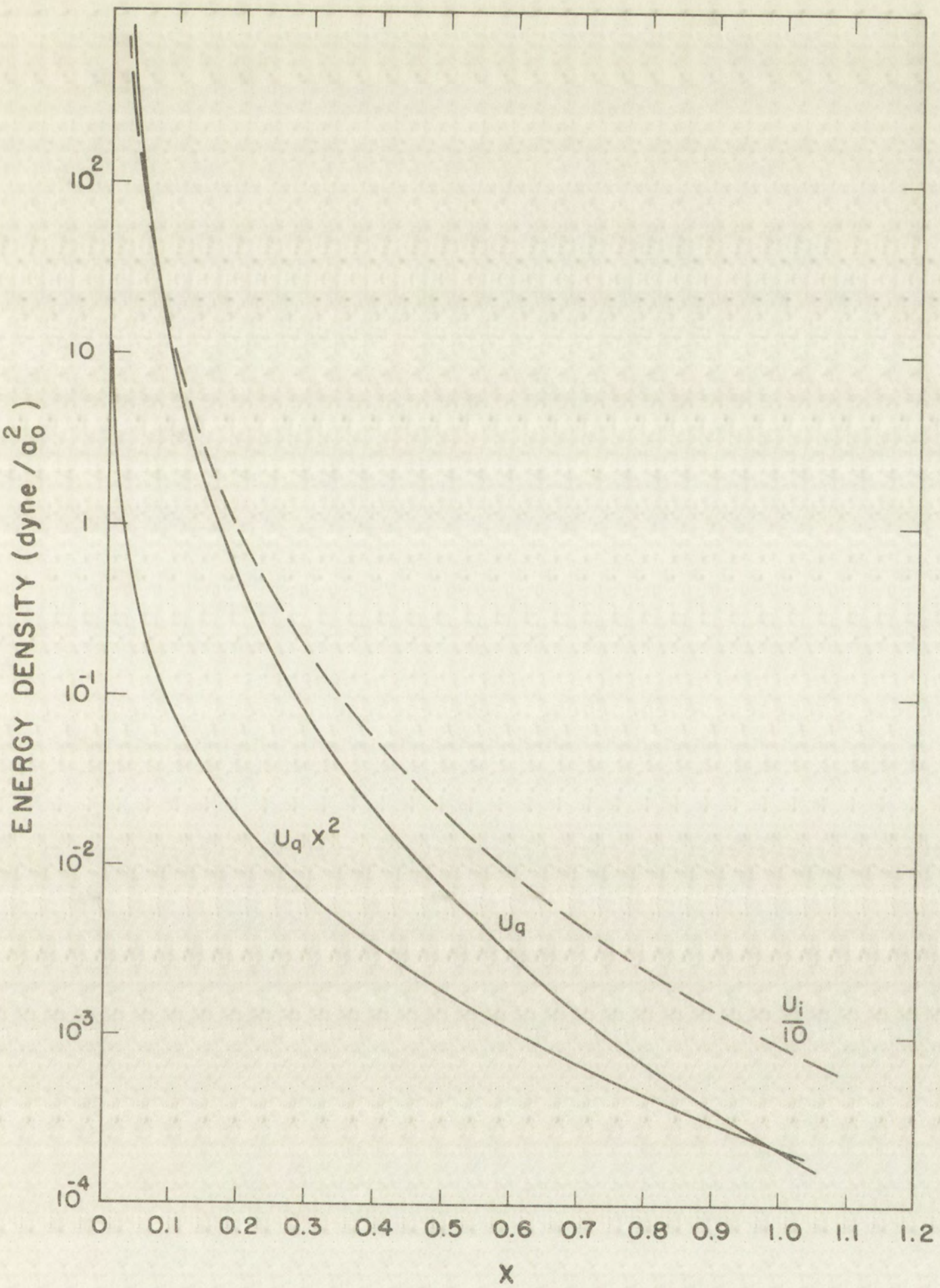

Figure 11. A comparison of the quantum-correction energy density and the Weizsäcker inhomogeneity energy density for the "isolated" copper atom

corresponding radially weighted quantity $U_q x^2$. It is seen that the former two curves differ by less than an order of magnitude over the spatial region in which $U_q x^2$, which measures the contribution to the quantum-correction energy at a given radius, varies by several orders of magnitude. Very near the nucleus the correspondence breaks down, however, since the Weizsäcker energy possesses a zero at the radius at which the electron density has its maximum value.

17. The Modified Pressure-Compression Relation

The pressure is related to the particle density at the boundary of the cell by an expression similar to (3.8) and (3.9). The relation is obtained by an extension of the method described in Ref. 18, by which the total energy, which is now given by

$$E = \int_{r_1}^{r_2} \left[c_f \rho^{5/3} - c_{ex} \rho^{4/3} - e(v^n + \tfrac{1}{2} v^e)\rho + \frac{c_q}{r^2} \rho \right] 4\pi r^2 dr, \qquad (13.5)$$

is differentiated with respect to r_2. This yields

$$\frac{dE}{dr_2} = \left[c_f \rho^{5/3} - c_{ex} \rho^{4/3} - e(v^n + \tfrac{1}{2} v^e)\rho + \frac{c_q}{r^2} \rho \right]_{r=r_2} 4\pi r_2^2$$

$$- \left[c_f \rho^{5/3} - c_{ex} \rho^{4/3} - e(v^n + \tfrac{1}{2} v^e)\rho + \frac{c_q}{r^2} \rho \right]_{r=r_1} 4\pi r_1^2 \frac{dr_1}{dr_2} \quad (+)$$

$$+\int_{r_1}^{r_2}\left\{\left[\frac{5}{3}c_f\rho^{2/3}-\frac{4}{3}c_{ex}\rho^{1/3}-e(v^n+\frac{1}{2}v^e)+\frac{c_q}{r^2}\right]\frac{\partial\rho}{\partial r_2}-\frac{1}{2}e\frac{\partial v^e}{\partial r_2}\rho+\frac{dc_q}{dr_2}\frac{\rho}{r^2}\right\}4\pi r^2dr. \tag{17.1}$$

To evaluate the next to last term of the integral we write

$$v^e(r) = -e\int\frac{\rho(r')}{|\overrightarrow{r-r'}|}d\vec{r}'$$

$$= -e\int_{r_1}^{r_2}dr'\int_{\text{all angles}}\frac{\rho(r')}{|\overrightarrow{r-r'}|}dS',$$

from which we obtain

$$\frac{\partial v^e(r)}{\partial r_2} = -e\int_{r'=r_2}\frac{\rho(r')}{|\overrightarrow{r-r'}|}dS' + e\frac{dr_1}{dr_2}\int_{r'=r_1}\frac{\rho(r')}{|\overrightarrow{r-r'}|}dS' - e\int\frac{\partial\rho(r')}{\partial r_2}\frac{1}{|\overrightarrow{r-r'}|}d\vec{r}'.$$

We then have, with some interchanging of integration variables,

$$-\frac{1}{2}e\int_{r_1}^{r_2}\rho\frac{\partial v^e}{\partial r_2}4\pi r^2dr = -2\pi r_2^2ev^e(r_2)\rho(r_2) + \frac{dr_1}{dr_2}2\pi r_1^2ev^e(r_1)\rho(r_1)$$

$$-\frac{1}{2}e\int_{r_1}^{r_2}\frac{\partial\rho}{\partial r_2}v^e4\pi r^2dr. \tag{17.2}$$

Substituting (17.2) into (17.1) and combining terms, we have

$$\frac{dE}{dr_2} = \left(c_f\rho^{5/3} - c_{ex}\rho^{4/3} - ev\rho + \frac{c_q}{r^2}\rho\right)_{r=r_2} 4\pi r_2^2$$

$$- \left(c_f\rho^{5/3} - c_{ex}\rho^{4/3} - ev\rho + \frac{c_q}{r^2}\rho\right)_{r=r_2} 4\pi r_1^2 \frac{dr_1}{dr_2}$$

$$+ \int_{r_1}^{r_2} \left(\frac{5}{3}c_f\rho^{2/3} - \frac{4}{3}c_{ex}\rho^{1/3} - ev + \frac{c_q}{r^2}\right)\frac{\partial\rho}{\partial r_2} 4\pi r^2 dr + \frac{dc_q}{dr_2}\int_{r_1}^{r_2} 4\pi\rho dr. \tag{17.3}$$

We also note that, from (13.6),

$$\frac{5}{3}c_f\rho^{2/3} - \frac{4}{3}c_{ex}\rho^{1/3} + \frac{c_q}{r^2} - ev = E',$$

so that (17.3) may be written as

$$\frac{dE}{dr_2} = \left(-\frac{2}{3}c_f\rho_2^{5/3} + \frac{1}{3}c_{ex}\rho_2^{4/3} + E'\rho_2\right)4\pi r_2^2$$

$$- \left(-\frac{2}{3}c_f\rho_1^{5/3} + \frac{1}{3}c_{ex}\rho_1^{4/3} + E'\rho_1\right) 4\pi r_1^2 \frac{dr_1}{dr_2}$$

$$+ E' \int_{r_1}^{r_2} \frac{\partial\rho}{\partial r_2} 4\pi r^2 dr + \frac{dc_q}{dr_2}\int_{r_1}^{r_2} 4\pi\rho dr. \tag{17.4}$$

We have introduced the notation $\rho(r_1) = \rho_1$, and $\rho(r_2) = \rho_2$ for brevity.

Equating the total number of electrons to the atomic number for the neutral atom, we have

$$Z = \int_{r_1}^{r_2} \rho 4\pi r^2 dr,$$

so that, differentiating,

$$\frac{dZ}{dr_2} = 4\pi r_2^2 \rho_2 - 4\pi r_1^2 \rho_1 \frac{dr_1}{dr_2} + \int_{r_1}^{r_2} \frac{\partial \rho}{\partial r_2} 4\pi r^2 dr.$$

The number of electrons must remain constant as the volume of the atom is varied, and therefore

$$\frac{dZ}{dr_2} = 0,$$

or

$$\int_{r_1}^{r_2} \frac{\partial \rho}{\partial r_2} 4\pi r^2 dr = -4\pi r_2^2 \rho_2 + 4\pi r_1^2 \rho_1 \frac{dr_1}{dr_2}.$$

With this substitution, (17.4) simplifies to

$$\frac{dE}{dr_2} = \left(-\frac{2}{3} c_f \rho_2^{5/3} + \frac{1}{3} c_{ex} \rho_2^{4/3}\right) 4\pi r_2^2$$

$$- \left(-\frac{2}{3} c_f \rho_1^{5/3} + \frac{1}{3} c_{ex} \rho_1^{4/3}\right) 4\pi r_1^2 \frac{dr_1}{dr_2} + \frac{dc_q}{dr_2} \int_{r_1}^{r_2} 4\pi \rho dr. \tag{17.5}$$

The pressure is given by

$$\mathcal{P} = -\frac{1}{4\pi r_2^2}\frac{dE}{dr_2},$$

or, using (17.5),

$$\mathcal{P} = \frac{2}{3}c_f\rho_2^{5/3} - \frac{1}{3}c_{ex}\rho_2^{4/3} + \gamma\left(\frac{r_1}{r_2}\right)^2\frac{dr_1}{dr_2} - \frac{1}{r_2^2}\frac{dc_q}{dr_2}\int_{r_1}^{r_2}\rho dr, \qquad (17.6)$$

where we have introduced the constant

$$\gamma = -\frac{2}{3}c_f\rho_1^{5/3} + \frac{1}{3}c_{ex}\rho_1^{4/3}$$

$$= \frac{1}{60\pi^7}\frac{e^2}{a_o^4}. \qquad (17.7)$$

In order to express the pressure as a function of compression, we make use of the formula

$$\eta = \frac{3}{4\pi}\frac{M}{LD_o r_2^3},$$

where η is the compression, M is the molecular weight of the substance, L is Avogadro's number, and D_o is the normal material density.

The first two terms of the right side of (17.6) constitute the usual expression for the pressure on the Thomas-Fermi-Dirac model, as given by (3.9). The third term is very small and can in practice be

ignored. The final term may be regarded as providing the possibility of lowering the pressure-compression curve from the unmodified case. However, in Part III, Section 19, it is shown that, for a given compression, the first two terms are larger in the modified than in the unmodified case, and the remaining term is not of sufficient magnitude to produce an over-all reduction in pressure, at least at the low-compression end of the curves of Figures 3 and 4.

The virial theorem, mentioned briefly in Section 3 as furnishing an alternate method of calculating the pressure, can be shown by an extension of previous work (Refs. 20, 21) not to be valid within the present modification of the Thomas-Fermi-Dirac theory. To do this we write twice the Fermi kinetic energy E_f in terms of the particle density:

$$2E_f = 2c_f \int \rho^{5/3} d\vec{r}, \tag{17.8}$$

where

$$\rho = \sigma_o \left[\tau_o + \left(E' - V - \frac{c_q}{r^2} + \tau_o^2 \right)^{1/2} \right]^3, \tag{13.7}$$

and the integral is taken over the entire electron cloud. For convenience let

$$\mathcal{V} = \left[\tau_o + \left(E' - V - \frac{c_q}{r^2} + \tau_o^2 \right)^{1/2} \right]^2, \tag{17.9}$$

whereupon we obtain on substituting into (17.8),

$$2E_f = 2c_f\sigma_o^{5/3}\int \mathcal{V}^{5/2}d\vec{r}. \tag{17.10}$$

Consider now the vector field

$$\vec{F} = \vec{r}\,\mathcal{V}^{5/2}.$$

Using a vector identity and setting div $\vec{r} = 3$, we have

$$\text{div}\,\vec{F} = \vec{r}\cdot\text{grad}\,\mathcal{V}^{5/2} + 3\mathcal{V}^{5/2},$$

and it follows from Gauss's theorem that

$$\int \mathcal{V}^{5/2}d\vec{r} = \frac{1}{3}\left(\int \mathcal{V}^{5/2}\vec{r}\cdot d\vec{S} - \int \vec{r}\cdot\text{grad}\,\mathcal{V}^{5/2}d\vec{r}\right). \tag{17.11}$$

The surface integral is over the two spherical surfaces at r_1 and r_2 which bound the electron distribution. By manipulating (17.9) we obtain, referring to the second term on the right side of (17.11),

$$\int \vec{r}\cdot\text{grad}\,\mathcal{V}^{5/2}d\vec{r} = \frac{5}{4}\,\tau_o\int \vec{r}\cdot\text{grad}\,\mathcal{V}^2 d\vec{r} + \frac{5}{2\sigma_o}\int \rho\vec{r}\cdot\text{grad}\left(-V - \frac{c_q}{r^2}\right)d\vec{r},$$

where we have made use of (13.7) in writing the last integral in terms of ρ.

We now note that, again by Gauss's theorem,

$$\int \vec{r}\cdot \text{grad}\, \mathcal{V}^2 d\vec{r} = \int \mathcal{V}^2 \vec{r}\cdot d\vec{S} - 3\int \mathcal{V}^2 d\vec{r}\,.$$

Also, since

$$\text{grad}(-V - \frac{c_q}{r^2}) = e\ \text{grad}\ v^e + Ze^2\ \text{grad}\ \frac{1}{r} - \text{grad}\ \frac{c_q}{r^2}\,,$$

we have

$$\int \rho\vec{r}\cdot \text{grad}(-V - \frac{c_q}{r^2})d\vec{r} = e\int \rho\vec{r}\cdot \text{grad}\ v^e d\vec{r}$$

$$+ Ze^2 \int \vec{r}\cdot \text{grad}\ \frac{1}{r}\ d\vec{r} - \int \rho\vec{r}\cdot \text{grad}\ \frac{c_q}{r^2}\ d\vec{r}. \qquad (17.12)$$

Using the vector identity

$$\vec{r}\cdot \text{grad}_r \frac{1}{|\overrightarrow{r-r'}|} + \vec{r}'\cdot \text{grad}_{r'} \frac{1}{|\overrightarrow{r-r'}|} = -\frac{1}{|\overrightarrow{r-r'}|}\,,$$

it follows from the form of v^e that

$$\int \rho\vec{r}\cdot \text{grad}\ v^e d\vec{r} = -\frac{1}{2}\int \rho v^e d\vec{r}.$$

Thus (17.12) becomes

$$\int \rho\vec{r}\cdot \mathrm{grad}\left(-V-\frac{c_q}{r^2}\right)d\vec{r} = \frac{1}{2}E_p^e + E_p^n + 2E_q$$

$$= E_p + 2E_q,$$

the notation for the various forms of energy being obvious.

Finally, it can be shown that

$$\frac{5}{2}c_f\sigma_o^{5/3}\tau_o\int \nu^2 d\vec{r} = c_{ex}\int \rho^{4/3}d\vec{r}$$

$$= -E_{ex}.$$

Collecting terms we may write (17.10) in the form

$$2E_f + 2E_q + E_p + E_{ex} = \int\left(\frac{2}{3}c_f\rho^{5/3} - \frac{1}{3}c_{ex}\rho^{4/3}\right)\vec{r}\cdot d\vec{S}$$

$$= \left(\frac{2}{3}c_f\rho_2^{5/3} - \frac{1}{3}c_{ex}\rho_2^{4/3}\right)4\pi r_2^3 + \gamma 4\pi r_1^3, \tag{17.13}$$

making use of (17.7). Noting that

$$4\pi r_2^3 = 3\Omega,$$

where Ω is the volume of the atomic cell, (17.13) becomes

$$2E_f + 2E_q + E_p + E_{ex} = \left(\frac{2}{3}c_f\rho_2^{5/3} - \frac{1}{3}c_{ex}\rho_2^{4/3} + \gamma\frac{r_1^3}{r_2^3}\right)3\Omega.$$

If the quantity in parentheses were equal to the pressure, we would conclude that the virial theorem is satisfied. The pressure on this model, however, is given by (17.6), quite a different expression. Therefore the virial theorem is not satisfied, and the pressure must be calculated directly from (17.6) for equation of state purposes.

PART III

COMPUTATIONS AND RESULTS

18. Numerical Methods

The method which has been employed in obtaining solutions of the modified Thomas-Fermi-Dirac equation, (13.10), an equation which is of the form $\phi'' = f(x,\phi)$, is described fully by Hartree (Ref. 46). Briefly, it is a finite difference scheme in which the approximation is made that

$$\Delta^2\phi_o = (\Delta x)^2(\phi_o'' + \frac{1}{12}\Delta^2\phi_o''), \tag{18.1}$$

the subscripted quantities being associated with the point $x = x_o$, to which the integration is assumed to have progressed.[15] The quantity

$$\Delta^2\phi_o = (\phi_1 - \phi_o) - (\phi_o - \phi_{-1})$$

$$= \phi_1 - 2\phi_o - \phi_{-1} ,$$

[15] These subscripts are not to be confused with those used to denote evaluation at the inner boundary (x_1) or outer boundary (x_2) of the electron distribution, or evaluation at the origin of coordinates in the case of ϕ_o'.

is the second difference in the function $\phi(x)$. The integration step is represented by Δx, and $\Delta^2\phi''_o$ is the second difference in the second derivative of $\phi(x)$.

At this point in the integration the pertinent quantities which are known are ϕ_o, $\phi''_o = f(x_o, \phi_o)$, and the backward difference $\phi_{-1/2}$. To proceed in the integration, an estimate of $\Delta^2\phi''_o$ is made, and an approximation to $\Delta^2\phi_o$ is found from (18.1). From this value of $\Delta^2\phi_o$, the forward first difference in ϕ, $\Delta\phi_{1/2}$, is obtained, and thence ϕ_1. Now ϕ''_1 is given by $\phi''_1 = f(x_1, \phi_1)$ so that, forming differences, another value of $\Delta^2\phi''_o$ is obtained. This is then compared with the estimate with which the integration step was initiated; if the two quantities agree within the error allowed in the calculation, the integration proceeds to the next step. If this is not the case, then the step is repeated with a revised estimate of $\Delta^2\phi''_o$.

In the calculations which we have performed, the integration criterion is that

$$\left|\frac{(\Delta^2\phi''_o)_{\text{estimated}} - (\Delta^2\phi''_o)_{\text{predicted}}}{\phi_o}\right| \leq \iota ,$$

and setting $\iota = 10^{-6}$ seems to be adequate to produce the desired eight decimal precision in ϕ. This may be checked by noting that, according to (18.1), an absolute error of $\iota\phi_o$ in $\Delta^2\phi''_o$ ultimately produces an error of $(1/12)(\Delta x)^2\iota\phi_o$ in ϕ_1. We therefore demand that, throughout the calculation,

$$\frac{1}{12}(\Delta x)^2\ 10^{-6}\phi \leq \frac{1}{2}\cdot 10^{-8},$$

or,

$$(\Delta x)^2\ \phi \leq 6\cdot 10^{-2}.$$

If this condition is not satisfied, t should be decreased.

In starting the integration, two values of ϕ and ϕ'' are needed, but for the purpose of estimating $\Delta^2\phi''$ three values are used in practice. In contrast to starting the integration of the ordinary Thomas-Fermi or Thomas-Fermi-Dirac equations, where a series solution of from nine to eleven terms is required,[16] the integration of the modified Thomas-Fermi-Dirac equation is started from values of ϕ lying along a straight line. This is seen from (13.10). If the starting values are confined to $x < x_1$, we have

$$\phi'' = 0,$$

or

$$\phi = 1 + \phi_o' x. \tag{18.2}$$

[16] Integration of the Thomas-Fermi-Dirac-Lewis coupled equations, reviewed in Section 5, is similarly initiated from a series solution.

To determine the interval of integration we first calculate x_1, given by

$$x_1 = \frac{1 - (1-a^2 s/Z)^{1/2}}{s},$$

where

$$s = -2\phi_o' + \frac{1}{\pi^2 Z},$$

and, for the calculations presented here, the modification factor, a, has been computed from the value chosen for ϕ_o' by the Coulomb approximation described in Section 14. An initial integration interval, Δx_{in}, is now chosen such that

$$2\Delta x_{in} \leq x_1, \tag{18.3}$$

thus guaranteeing three starting values of ϕ and ϕ'' in the region of zero density.

In satisfying (18.3) an annoyance is encountered. If Δx_{in} is too small, the starting values of ϕ, which are calculated from (18.2), will not reflect changes in ϕ_o' to anything approaching the full eight figure precision which the digital computer employed is capable of handling. A variation in ϕ_o' of $\delta\phi_o'$ produces a variation in the value of ϕ at the point x, where $x < x_1$, of

$$\delta\phi = \delta\phi'_o x.$$

Let us consider as an example the solution for Z = 29 which is summarized in Table II. If the value of ϕ'_o is varied by $1 \cdot 10^{-6}$ we have, at $x = 2\Delta x$,

$$\delta\phi = (1 \cdot 10^{-6})(2)(3.125 \cdot 10^{-4})$$

$$\approx 6 \cdot 10^{-10}.$$

Since ϕ is of the order of unity for small x, it is clear that this change in ϕ'_o does not affect, within eight significant figures, any of the values of ϕ which are used in starting the integration. Therefore the same solution is obtained as before this particular variation in ϕ'_o is performed. This restriction of possible solutions is particularly annoying in the region of the zero-pressure solution. For example, the nearest approach to the "isolated" copper atom solution in the calculations as performed is the one of Table II, for which the calculated pressure is about $1.4 \cdot 10^{10}$ dyne/cm^2.[17]

There is an additional restriction placed on the choice of Δx_{in}. To increase the speed of the integration, the integration interval is doubled a number of times in proceeding outward from the nucleus, and

[17] It should be pointed out that the binding energies tabulated in Table IV are probably precise to the number of significant figures presented, even though they are not strictly obtained from "isolated" atom solutions.

it is convenient to have ϕ evaluated at integral values of x, half-integral values, and so on. In order that this will occur, the maximum Δx, Δx_{max}, which is used over most of the integration, is typically chosen to have a value such as 0.01 or 0.02. Of course, Δx_{max} must also be small enough that precision in the integration is retained. Having chosen Δx_{max}, we then require that

$$\Delta x_{in} = \frac{\Delta x_{max}}{2^b}$$

where b is the number of times the interval is to be doubled. For the reasons given above, a value of b is picked so that Δx_{in} is as large as possible consistent with (18.3). For simplicity, the integration interval is doubled on alternate steps until Δx_{max} is reached, this value of Δx then being retained until the outer boundary of the integration is achieved.

The outer boundary of the atom is determined by noting that the tangent to the curve $\phi(x)$ cuts the axis at x = 0 at positive x prior to reaching the boundary, and at negative x after passing the boundary. The quantity

$$g = \left(x_o - \frac{\Delta x}{2}\right)\left(\frac{\phi_o - \phi_{-1}}{\Delta x}\right) - \frac{\phi_o + \phi_{-1}}{2}$$

thus first becomes positive somewhere in the vicinity of the boundary x_2, while at the boundary

$$x_2\phi'(x_2) = \phi(x_2). \tag{13.11}$$

At the step in the integration at which g becomes positive, a parabola is passed through the three points ϕ_{-2}, ϕ_{-1}, and ϕ_o. In doing this we have, of course, approximated ϕ by

$$\phi = \mathcal{A}x^2 + \mathcal{B}x + \mathcal{C}.$$

Under the further approximation that

$$\phi'' = \frac{\Delta^2\phi}{(\Delta x)^2},$$

the coefficients $\mathcal{A}$, $\mathcal{B}$, and $\mathcal{C}$ are easily evaluated.

We now write

$$\phi(x_2) = \mathcal{A}x_2^2 + \mathcal{B}x_2 + \mathcal{C}, \tag{18.4}$$

and

$$\phi'(x_2) = 2\mathcal{A}x_2 + \mathcal{B}.$$

The boundary condition (13.11) becomes

$$2\mathcal{A}x_2^2 + \mathcal{B}x_2 = \mathcal{A}x_2^2 + \mathcal{B}x_2 + \mathcal{C},$$

and therefore the outer radius of the atom is simply given by

$$x_2 = \left(\frac{c}{a}\right)^{1/2}.$$

Once x_2 is determined, no further interpolations are required to fix the values of other quantities at the boundary, for (18.4) and (13.9) serve to determine the boundary density from which the other quantities follow directly.

The integrals yielding the total energies of the various forms are evaluated by a method equivalent to a Simpson's 1/3 Rule integration with unequally spaced arguments (Ref. 47). As a check on the precision of the integration of the differential equation and of the calculation of the atom boundary, the total number of electrons is also computed by integrating the charge density over the volume of the distribution. In the calculations which have been performed, this number agrees with Z typically to about one part in 30,000.

Table I contains the values of the physical constants used in the calculations.

19. Results Obtained from the Modified Thomas-Fermi-Dirac Equation

In Table II there is summarized an illustrative solution of the modified Thomas-Fermi-Dirac equation. The solution, representing a copper atom under very low compression, is used as the basis for several quantitative discussions in earlier sections of this paper.

Tables IIIa and IIIb contain information from certain solutions which represent, for several values of Z, atoms at volumes not too different from normal. For the lower values of atomic number the pressures associated with these solutions are quite low, and the solutions are therefore fairly close to what we are taking as representing an isolated atom. If it were so desired, it would be possible at these lower values of Z to obtain solutions yielding pressures nearer yet to zero, but this has not been deemed necessary here.

For the atoms of higher atomic number, we encounter, in general, the problem mentioned in the previous section. Unless we are fortunate, the solutions are so restricted that, with the number of figures we have carried in the calculations, a very low pressure solution cannot be obtained. The energies, however, depend very slightly on the minor variations of initial slope, and we have considered the energies from the solutions tabulated in Tables III to pertain to the isolated atoms in all cases.

The calculated total energies may be compared with the experimental values for the isolated atoms, using Table IV. For atomic numbers above eight the experimental values do not exist, but comparison may be made with energies computed according to a formula due to Foldy (Ref. 48),[18] which is based on results of Hartree calculations. It may be seen that the agreement is quite good for the entire range of Z. Overlooking

[18] Foldy's results have been altered slightly to correspond to the values of atomic constants used in the present calculations.

$Z = 1$, the agreement with experiment is within 2%, and the agreement with Foldy's values is nowhere worse than to within 1.5%, with most discrepancies well under 1%. Even in the case of hydrogen, the calculated energy of -15.50 ev is a considerable improvement over the Thomas-Fermi-Dirac value of -28.07 ev.

It is of some interest in comparing these results with those of Scott to take note of the predicted number of filled shells in the equivalent Coulomb problem. This curve is shown in Figure 12. It will be recalled that Scott's analysis is on the basis of an infinite number of shells in a Coulomb field.

The value of x_1, the inner density cut-off distance, naturally plays a large role in the correction of the binding energies. In Golden's formulation of the problem, discussed in Section 9, an inner cut-off of the particle distribution is also obtained. In his paper the quantities are given from which this radius may be calculated for the ground states of the atoms with $Z = 1$, 2, and 8. In Figure 13 we have plotted x_1 as a function of Z as given by the present calculations, and have included a curve drawn from Golden's data for low Z. From the curves it is apparent that the cut-off distance obtained in the present calculations ranges from about three times Golden's value at low Z to about 1.5 times his (projected) value at high Z. Thus in the present modification the inner boundary of the electron cloud is further removed from the nucleus, and one might therefore expect the binding to be less than that obtained by Golden. However, the situation is obviously more complicated, since

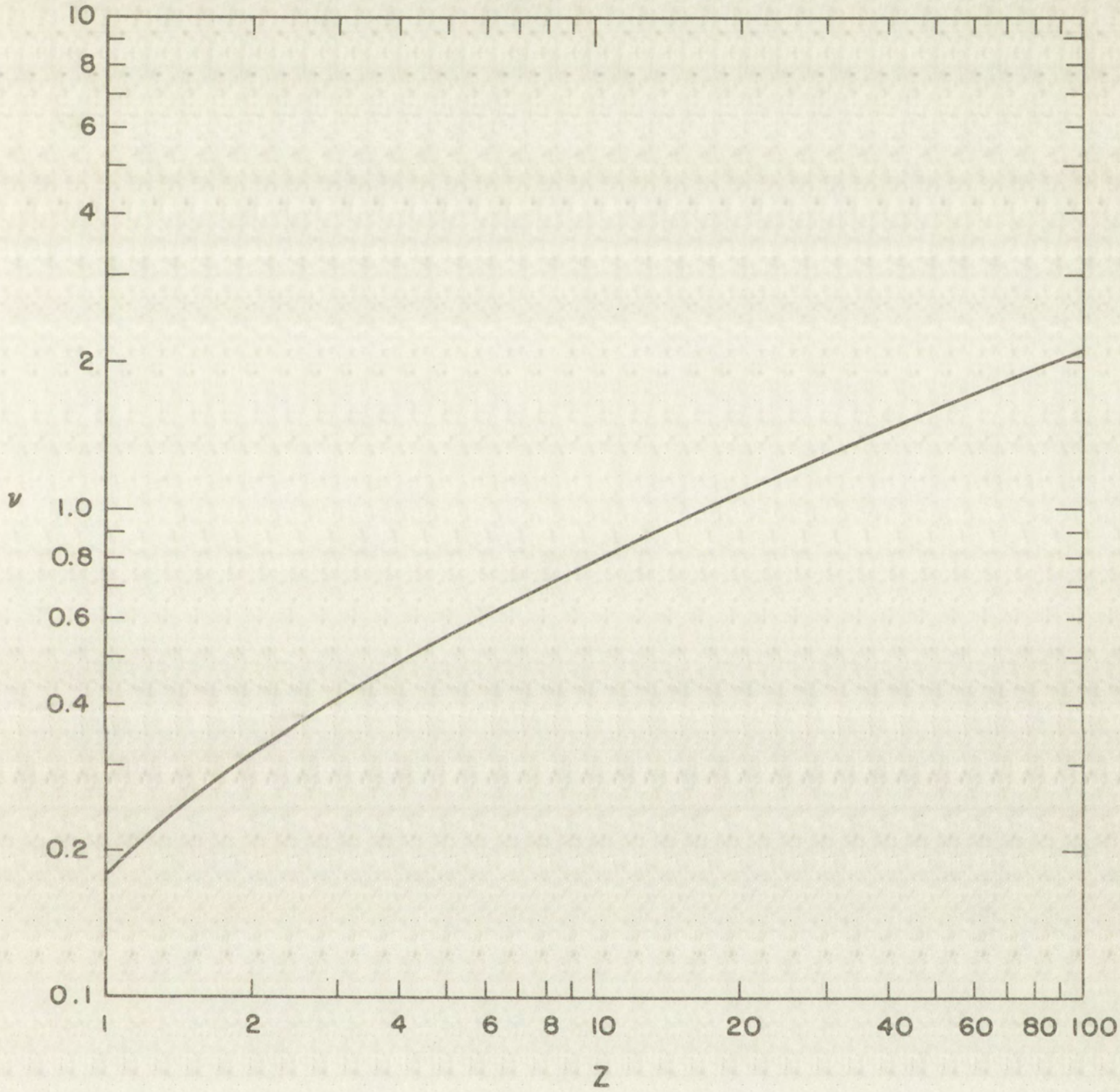

Figure 12. The number of filled shells in the equivalent Coulomb problem for the "isolated" atoms

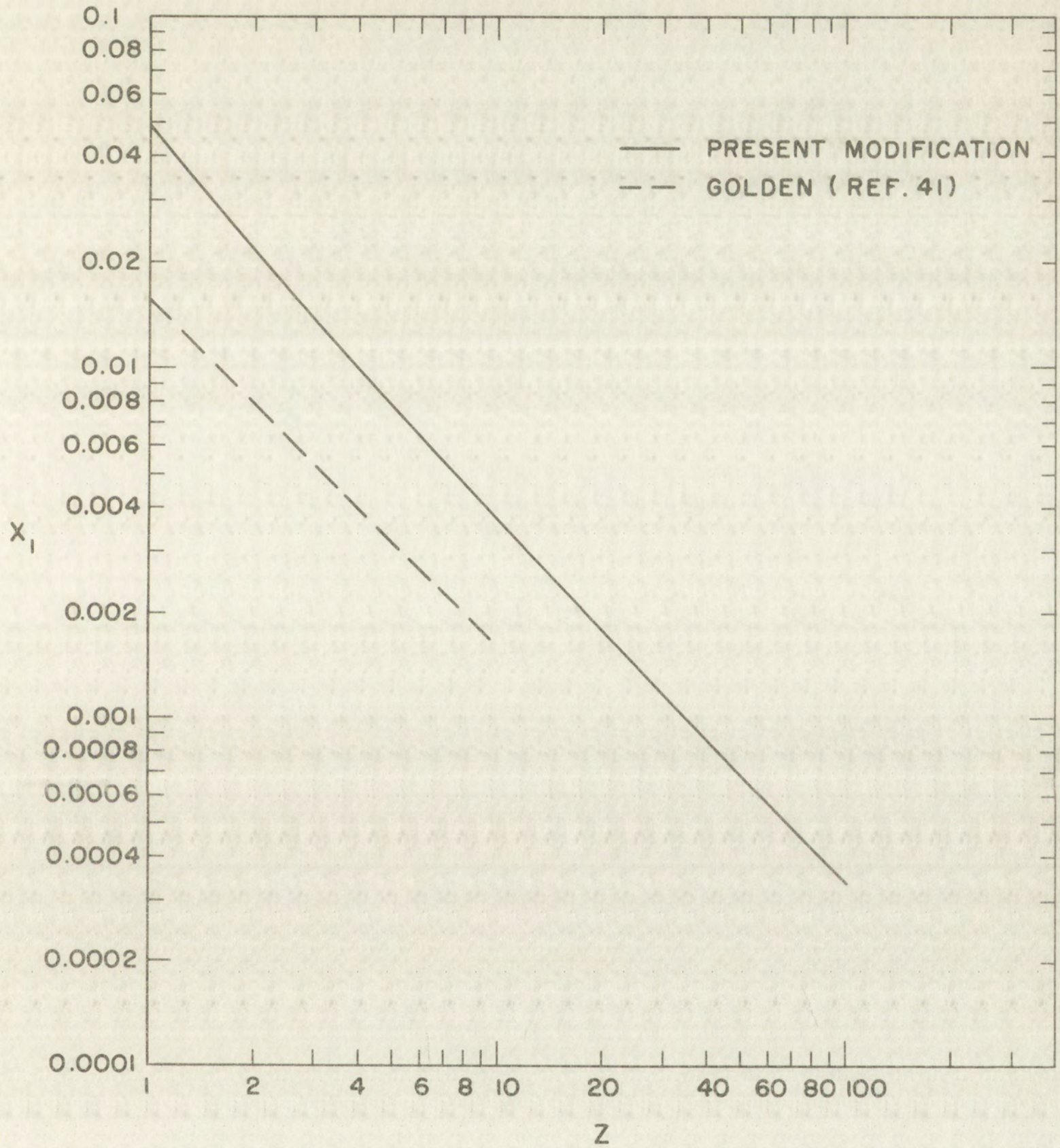

Figure 13. The inner density cut-off distance for the "isolated" atoms

Golden reports less binding for Z = 1, greater binding for Z = 2, and, again, less for Z = 8 than in the present work.

The formula for the pressure, derived in Section 17, is

$$\mathcal{P} = \frac{2}{3}c_f\rho_2^{5/3} - \frac{1}{3}c_{ex}\rho_2^{4/3} - \frac{1}{r_2^2}\frac{dc_q}{dr_2}\int_{r_1}^{r_2}\rho dr,$$

where the term that was mentioned there as being negligible has been omitted. Using the definition of c_q, and expressing distance in terms of the variable x, the above may be written as

$$\mathcal{P} = \frac{2}{3}c_f\rho_2^{5/3} - \frac{1}{3}c_{ex}\rho_2^{4/3} - \frac{\hbar^2}{ma_o^2}\frac{a}{x_2^2}\frac{da}{dx_2}\int_{x_1}^{x_2}\rho dx, \qquad (19.1)$$

the form in which it is evaluated numerically.

It is to be observed that a value of the pressure cannot be calculated from one solution of the modified Thomas-Fermi-Dirac equation alone, because of the presence of the derivative da/dx_2. The latter is calculated by obtaining a number of solutions of the differential equation corresponding to various compressions over the region of interest. In Figure 14 the modification factor is shown as a function of the outer radius of the cell. One possibility for the evaluation of the derivative of the function is a graphical determination of the slope, but a more precise evaluation may be made in the following way.

It is noticed that a small range of ϕ_o' produces a large range of compression, and therefore the fractional change in the modification

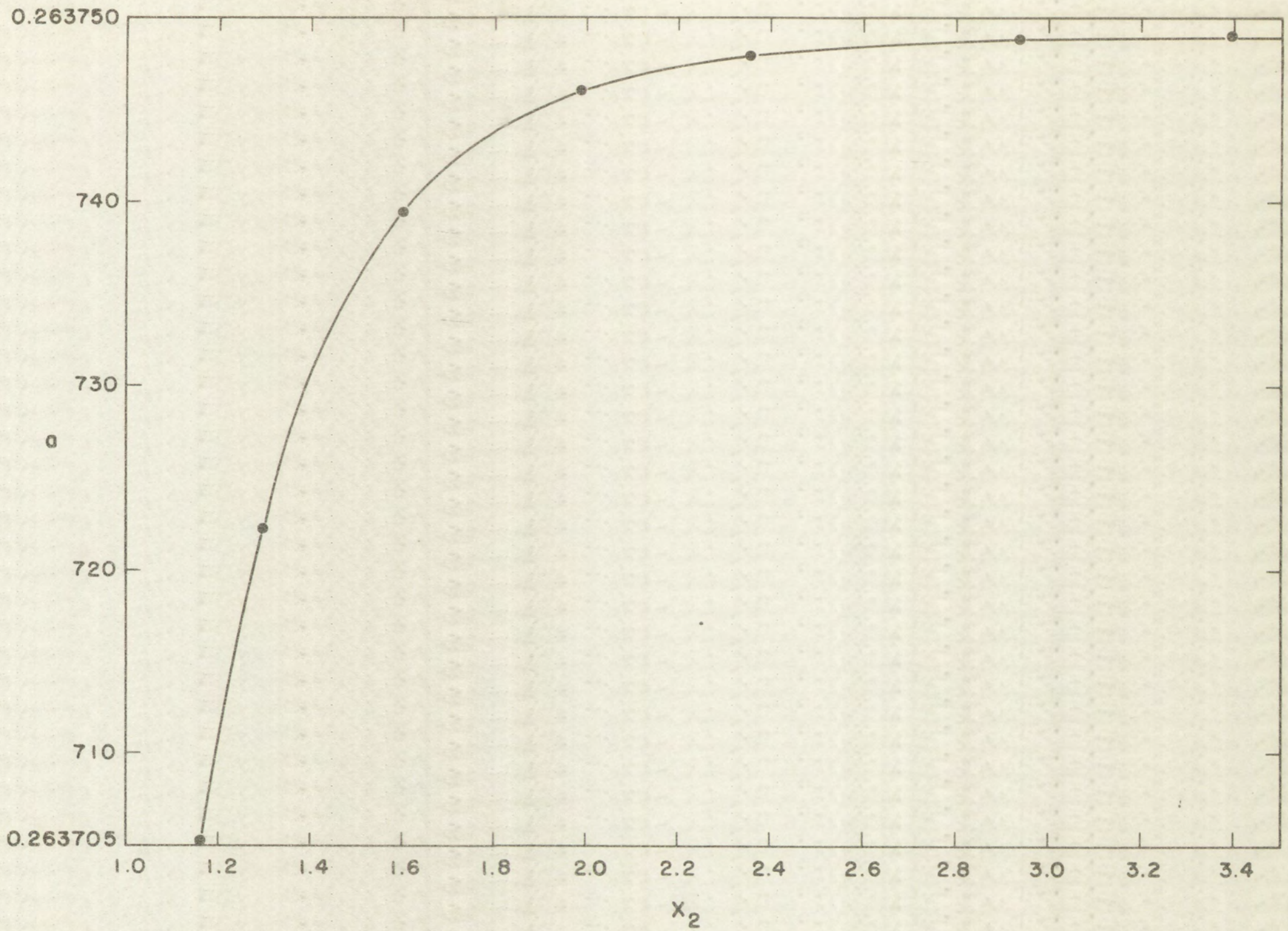

Figure 14. The modification factor vs. the outer radius of the compressed copper atom

factor is small over solutions which are of interest. This is illustrated by the following quantities taken from solutions representing the copper atom. The compressions are rounded to two decimals.

η	$-\phi'_o$	a
9.42	4.658	0.26371886
5.54	4.668	0.26373594
1.00	4.67535	0.26374849
0.37	4.675625	0.26374893

Because a is so slowly varying, if one obtains a number of solutions in a much smaller range of compression, such as between 0.9 and 1.1, by varying ϕ'_o by equal increments, it turns out that the modification factor also changes by equal increments from solution to solution. This makes it possible to calculate dx_2/da with high precision by utilizing differences in x_2 of any number of orders. The reciprocal of this derivative is the quantity sought.

For our calculations based on the Coulomb field approximation, it is not necessary to evaluate the slope with great precision, since the term in which it is a factor in (19.1) contributes only slightly to the pressure. For example, again using solutions representing the copper atom, at normal volume the third term in (19.1) is about $-0.0053 \cdot 10^{12}$ dyne/cm^2, while the calculated pressure is $2.0137 \cdot 10^{12}$ dyne/cm^2. As a consequence of this contribution being so small in general, the pressure on this model is not greatly different from that calculated

without the modification. The modified pressure is slightly higher because the particle density at the boundary, ρ_2, is increased by a small amount over the value in the unmodified case for the same compression. In the example used above, the density at the boundary is increased by about 2%.

In Figure 15 we have plotted the modified pressure-compression curve for copper, and indicated a few values from the unmodified Thomas-Fermi-Dirac solutions. Pressures under the present modification are about 2% higher than the unmodified values at a compression near unity. The greatest deviation occurs for volumes above normal, the difference in pressures being about 5% for a compression of about 0.6.

It is perhaps somewhat surprising that, although in the case of the copper atom the total energy has been multiplied by a factor of 0.81, the pressure modification is so slight. In view of this result we have not carried out more extensive equation of state calculations.

We wish also to point out that abandoning the Coulomb field approximation, while retaining the concept of correcting the statistical distribution of quantum states, cannot greatly "improve" the pressure. Referring again to Figure 3, we might say that at normal volume a predicted pressure of $3 \cdot 10^{11}$ dyne/cm^2 ($\log 3 \cdot 10^{11} \approx 11.5$) would constitute such an "improvement." Neglecting the density change at the boundary, which seems to be small for any reasonable value of the modification factor, this would require a value of da/dx_2 about 300 times as large as that calculated in the Coulomb approximation.

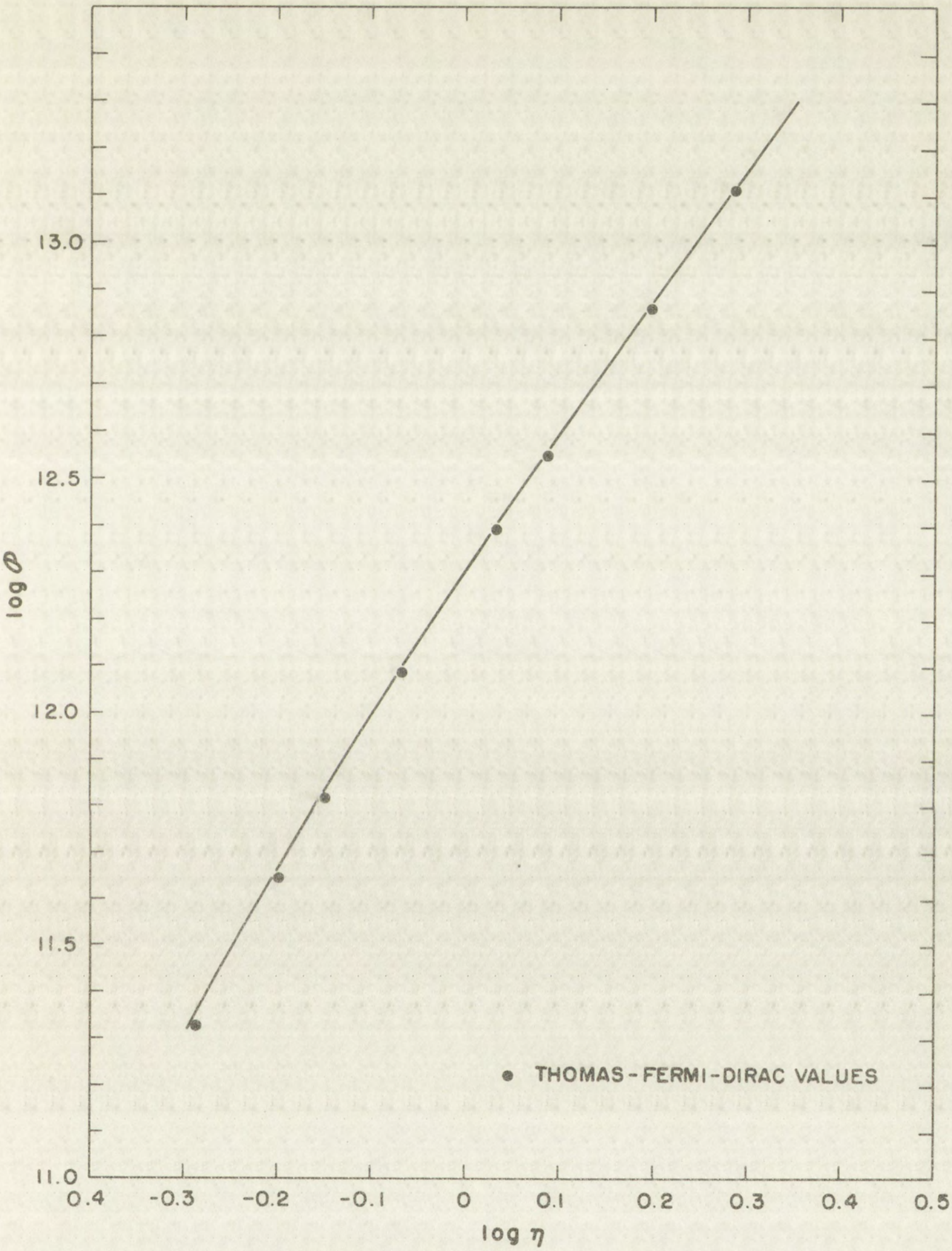

Figure 15. The modified pressure-compression curve for copper

Finally, we should note the work of Kalitkin (Ref. 27). Using the corrections obtained essentially by the methods described in Section 9, he has calculated corrections to various thermodynamic functions, and has presented a modified pressure-compression curve for iron which falls below the Thomas-Fermi-Dirac curve. However, he has performed the calculations using the standard Thomas-Fermi electron distribution with the attendant large density of electrons near the nucleus. Other treatments, not to mention the present one, demonstrate that a rather marked change in the electron distribution occurs when quantum effects are considered. (See, e.g., Refs. 40, 41.)

20. Extension to Nonzero Temperature

Essentially all of the preceding discussion has pertained to the zero temperature case. However, an extension of the modification to nonzero temperature is possible, and will be outlined here. Exchange effects will be neglected.

We write for the total kinetic energy of a particle in the jth state

$$E_{kin,j} = \frac{p_j^2}{2m} + \text{a quantum correction},$$

where p_j is the local momentum at the point at which the particle is assumed to be localized, and the quantum correction must be apportioned from the total quantum-correction energy for the system. The correct

apportionment may be calculated by writing the corresponding energy density,

$$U_q = \frac{c_q}{r^2} \rho \ , \tag{12.10}$$

or, from (12.7), and (12.9), in terms of the cut-off momentum,

$$U_q = \frac{p_c^2}{2m} \rho \ .$$

Consider now a variation $\delta\rho$ in the particle density within a spherical shell with bounding radii r and r + dr. Under such a variation, the resulting change in U_q within the shell is just

$$\frac{p_c^2}{2m} \delta\rho \ , \tag{20.1}$$

and the added electrons have momenta which are, of course, governed by the Fermi distribution pertinent to conditions at that radius. The momenta of these electrons are therefore dependent upon the density within the cell; the higher the density, the greater must be the momenta of the added electrons. However, according to (20.1), the added quantum-correction energy depends only on the change in density, not on the density itself. This indicates that the quantum-correction energy is independent of particle momentum, and therefore may be thought of as being shared equally by each electron, irrespective of momentum. For

the total kinetic energy of a particle in the state j we therefore write

$$E_{kin,j} = \frac{p_j^2}{2m} + \frac{p_c^2}{2m} .$$

It has been shown in Section 12 that we may express the spatial density of electron states in the form

$$\frac{8\pi}{3h^3}(P^2-p_c^2)^{3/2} .$$

The number of states per unit volume with momentum between p and p + dp is found by differentiation, the result being

$$\frac{8\pi}{h^3}(p^2-p_c^2)^{1/2}\ pdp.$$

Since the probability of a state being occupied is given by

$$n_j = \frac{1}{e^{\beta(E_j-\mu)}+1} , \qquad (1.1)$$

the electron density

$$\rho = \frac{8\pi}{h^3}\int_{p_c}^{\infty} \frac{(p^2-p_c^2)^{1/2}pdp}{e^{\beta[(p^2/2m)+(p_c^2/2m)+V-\mu]}+1} \qquad (20.2)$$

Introducing a new momentum variable defined by

$$(p')^2 = p^2 - p_c^2,$$

(20.2) becomes

$$\rho = \frac{8\pi}{h^3} \int_0^\infty \frac{(p')^2 dp'}{e^{\beta\left\{[(p')^2/2m]+[p_c^2/m]+V-\mu\right\}}+1}.$$

The integral is of the form which is mentioned in Section 9 as a "Fermi-Dirac function" provided we define

$$y = \beta \frac{(p')^2}{2m}$$

and

$$\zeta = -\beta\left(\frac{p_c^2}{m} + V - \mu\right).$$

The electron density, written in terms of the function $F_{1/2}(\zeta)$, becomes

$$\rho = \frac{4\pi}{h^3} (2mkT)^{3/2} F_{1/2}(\zeta), \tag{20.3}$$

where β has been replaced by $1/kT$.

Using (20.3) with Poisson's equation, the equation for the potential function could be set up and solved exactly as described, for example, in Ref. 9. The solutions would differ from those obtained in the reference only because of the term containing the cut-off momentum in the argument of the Fermi-Dirac function.

The evaluation of p_c, or equivalently of the modification factor, should proceed just as in the zero temperature case.

21. Summary

We have derived a modification of the statistical theory of the atom that is based on correcting a region of integration in the (n_r, ℓ), or quantum number, plane, where the quantum numbers are treated as continuous variables. This region labels the states which are occupied by the atomic electrons. Out of the number of ways in which the region of integration can be corrected, we have chosen to increase by a constant the original constant lower limit of the orbital quantum number. The difference between the new limit and the old limit we have called the modification factor.

By correcting the region of integration in this manner we have imposed a nonzero lower limit on the allowed orbital angular momentum of an electron. At a given distance from the nucleus the distribution of allowed states in momentum space is anisotropic, and we may identify a cut-off at the low end of the allowed linear momentum. The cut-off momentum is very simply related to the modification factor.

Using the new lower limit of the orbital quantum number, we have performed those integrations over the quantum number plane which, in the unmodified case, lead to the Thomas-Fermi energy equation. The results of the revised integrations are a modified expression for the Thomas-Fermi density, and an energy correction which we have called the quantum-correction energy. We have then used the modified density expression, evaluated the modification factor for a pure Coulomb field, and shown that the electron-nuclear potential energy is corrected from the erroneous Thomas-Fermi value within a very small distance from the nucleus. The small deviation from a pure Coulomb field at this distance supports the use of the Coulomb approximation.

The quantum-correction energy shows a similarity to the Weizsäcker correction, but is smaller by a factor of the order of 10. The ratio is not a constant, but changes by an order of magnitude only over a wide range of variation of the corrections.

We have derived a modified Thomas-Fermi-Dirac equation by adding the quantum-correction energy to the other forms on the Thomas-Fermi-Dirac model, and minimizing the resultant integral. Solutions have been obtained which yield atomic binding energies in much better agreement with experimental values than those of the unmodified theory.

A modified pressure-compression relation has been derived, and the pressures on this model have been shown to be only slightly different from those on the unmodified model. In addition, numerical values have been obtained for a correlation-corrected equation of state. Considering

the effect of this correction and of the quantum correction which we have obtained, we must conclude that the chemical binding does indeed play a major role in the equation of state at compressions in the neighborhood of unity.

We have also outlined how we could proceed with a more general determination of the modification factor than that based on a Coulomb field, and the manner in which the modification could be extended to the nonzero temperature case.

TABLE I

CONSTANTS AND CONVERSION FACTORS[a]

Electronic charge	$e = 4.80294 \cdot 10^{-10}$ esu
Planck's constant	$h = 6.6254 \cdot 10^{-27}$ erg sec
	$\hbar = 1.05446 \cdot 10^{-27}$ erg sec
Electron rest mass	$m = 9.1086 \cdot 10^{-28}$ gm
Avogadro's number	$L = 6.0247 \cdot 10^{23}$ mole^{-1}
First Bohr radius	$a_o = \hbar^2/me^2 = 5.29173 \cdot 10^{-9}$ cm
Fermi kinetic energy coefficient	$c_f = (3/10)(3\pi^2)^{2/3}\, e^2 a_o$
	$= 3.50494 \cdot 10^{-27}$ erg cm^2
Exchange energy coefficient	$c_{ex} = (3/4)(3/\pi)^{1/3}\, e^2$
	$= 1.70372 \cdot 10^{-19}$ erg cm
Thomas-Fermi-Dirac density constants	$\sigma_o = (8\pi/3h^3)(2m)^{3/2}$
	$= 2.23978 \cdot 10^{39}$ erg$^{-3/2}$cm^{-3}
	$\tau_o = (e^2/h)(2m)^{1/2}$
	$= 1.48608 \cdot 10^{-6}$ erg$^{1/2}$
Electron volt	1 ev $= 1.60209 \cdot 10^{-12}$ erg
Atomic unit of energy	1 au $= e^2/a_o = 4.35930 \cdot 10^{-11}$ erg
	$= 27.2101$ ev

[a]Values of atomic constants are from Ref. 49.

TABLE II

SUMMARY OF A SOLUTION OF THE MODIFIED THOMAS-FERMI-DIRAC EQUATION

$Z = 29$ $\quad M = 63.54$ gm/mole $\quad D_o = 8.94$ gm/cm^3

$\phi'_o = -4.675627$ $\quad \alpha = 1.7610192$ $\quad a = 0.26374895$

$x_1 = 0.0012061760$ $\quad \Delta x_{in} = 0.0003125$ $\quad \Delta x_{max} = 0.01$

x	ϕ	ρ (cm^{-3})	$4\pi a_o^2 \rho x^2$ (cm^{-1})
0.0	1.00000000	0.0	0.0
0.0012061760	0.99436038	$5.8806640 \cdot 10^{22}$	$3.0106026 \cdot 10^{1}$
0.001250	0.99415551	$1.5051692 \cdot 10^{28}$	$8.2758197 \cdot 10^{6}$
0.001875	0.99123467	$2.6086452 \cdot 10^{29}$	$3.2271802 \cdot 10^{8}$
0.0025	0.98832564	2.9469033	6.4811423
0.00375	0.98256500	2.3876938	$1.1815357 \cdot 10^{9}$
0.005	0.97689300	1.8204068	1.6014527
0.0075	0.96581786	1.1350161	2.2466229
0.01	0.95508390	$7.7896420 \cdot 10^{28}$	2.7410891
0.015	0.93452690	4.4015579	3.4849343
0.02	0.91503406	2.8686920	4.0378444
0.03	0.87871565	1.5238525	4.8260420
0.04	0.84535428	$9.5252407 \cdot 10^{27}$	5.3629235
0.06	0.78565117	4.7523891	6.0203279
0.08	0.73334713	2.8238963	6.3596670
0.10	0.68688411	1.8517088	6.5159591
0.12	0.64519994	1.2941467	6.5577021
0.15	0.58999001	$8.1945594 \cdot 10^{26}$	6.4880440
0.20	0.51317459	4.3941848	6.1850607
0.30	0.39874237	1.6917982	5.3579259
0.40	0.31784322	$8.0716142 \cdot 10^{25}$	4.5444987
0.50	0.25808917	4.3656850	3.8405904
0.60	0.21256199	$2.5680294 \cdot 10^{25}$	$3.2531797 \cdot 10^{9}$

TABLE IV

CALCULATED AND EXPERIMENTAL TOTAL BINDING ENERGIES

Z	$-E_{calc}$(ev)	$-E_{exp}$(ev)	$-E_{Foldy}$(ev)
1	15.50	13.595	13.60
2	77.52	78.983	78.69
3	201.8	203.43	202.2
4	399.4	399.03	400.6
5	679.1	670.79	677.3
6	1049.	1029.8	1042.
7	1515.	1485.6	1507.
8	2084.	2043.3	2070.
10	3548.		3538.
20	$1.856 \cdot 10^4$		$1.834 \cdot 10^4$
30	4.881		4.815
40	9.682		9.597
50	$1.646 \cdot 10^5$		$1.638 \cdot 10^5$
60	2.539		2.534
70	3.662		3.666
80	5.030		5.053
90	6.651		6.710
100	8.540		8.585

APPENDIX

MINIMIZATION OF THE THOMAS-FERMI-DIRAC ENERGY INTEGRAL

The total energy is given on the Thomas-Fermi-Dirac model by the equation

$$E = \int_0^{r_2} \left[c_f \rho^{5/3} - c_{ex} \rho^{4/3} - e(v^n + \frac{1}{2} v^e)\rho \right] 4\pi r^2 dr, \qquad (2.2)$$

which we may write as

$$E = \int_0^{r_2} f[\rho(r), r] dr.$$

The determination of the differential equation which must be satisfied by the density function $\rho(r)$, when it is subject to the auxiliary condition that the total number of particles

$$N = \int_0^{r_2} \rho(r) 4\pi r^2 dr,$$

is an isoperimetric problem in the field of the calculus of variations (see, e.g., Ref. 50).

In the standard methods of a variational problem we consider the derivative of an integral with respect to a parameter, say ϵ, which is introduced to distinguish the various members of the family of possible functions $\rho'(r)$, and whose value is chosen as zero for the particular function $\rho(r)$ which leads to a minimum for the integral. For an extreme value of the integral the derivative with respect to ϵ is equal to zero.

In an isoperimetric problem it is necessary to introduce a two parameter family of comparison functions. That is, different members are distinguished by ϵ_1 and ϵ_2, the comparison functions being written as

$$\rho'(r) = \rho(r) + \epsilon_1\eta_1(r) + \epsilon_2\eta_2(r),$$

where η_1 and η_2 are arbitrary differentiable functions which must, however, vanish at the endpoints of the integration.

The electron-electron potential energy portion of the energy integral presents the only difficulty in the minimization procedure. Written in terms of the comparison functions we have

$$E_p^e = \frac{1}{2}e^2 \int\int \frac{\rho'(r)\rho'(r')}{|\overrightarrow{r-r'}|}\, d\vec{r}'\, d\vec{r}.$$

Then, with $j = 1, 2$,

$$\frac{\partial E_p^e}{\partial \epsilon_j} = \frac{1}{2}e^2 \int \left\{ \left[\frac{\partial}{\partial \rho'(r)} \int \frac{\rho'(r)\rho'(r')}{|\overrightarrow{r-r'}|} d\vec{r}' \right] \frac{\partial \rho'(r)}{\partial \epsilon_j} \right.$$

$$\left. + \left[\frac{\partial}{\partial \rho'(r')} \int \frac{\rho'(r)\rho'(r')}{|\overrightarrow{r-r'}|} d\vec{r}' \right] \frac{\partial \rho'(r')}{\partial \epsilon_j} \right\} d\vec{r}$$

$$= \frac{1}{2}e^2 \left[\iint \frac{\rho(r')\eta_j(r)}{|\overrightarrow{r-r'}|} d\vec{r}' d\vec{r} + \iint \frac{\rho(r)\eta_j(r')}{|\overrightarrow{r-r'}|} d\vec{r}' d\vec{r} \right]$$

$$= e^2 \iint \frac{\rho(r')\eta_j(r)}{|\overrightarrow{r-r'}|} d\vec{r}' d\vec{r} \ .$$

Writing the other terms of (2.2) in terms of the comparison functions, carrying out the differentiations, and introducing -E' as an undetermined Lagrangian multiplier, we obtain as the conditions for an extremum,

$$\left(\frac{\partial E}{\partial \epsilon_j}\right)_{\epsilon_j=0} = \int_0^{r} 2\left[\frac{5}{3}c_f\rho^{2/3} - \frac{4}{3}c_{ex}\rho^{1/3} - ev^n + e^2 \int \frac{\rho(r')}{|\overrightarrow{r-r'}|} d\vec{r}' - E' \right] \eta_j 4\pi r^2 dr$$

$$= \int_0^{r} 2\left[\frac{5}{3}c_f\rho^{2/3} - \frac{4}{3}c_{ex}\rho^{1/3} + V - E' \right] \eta_j 4\pi r^2 dr.$$

In writing the last line we have made use of the relation $V = -e(v^n + v^e)$. By virtue of the arbitrariness of the η's we can write, upon setting the integrals equal to zero,

$$\frac{5}{3}c_f\rho^{2/3} - \frac{4}{3}c_{ex}\rho^{1/3} + (V - E') = 0,$$

which is the desired equation (2.4) of the text.

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