AN EXTENSION OF THE STATISTICAL MODEL OF THE ATOM

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ABSTRACT

The statistical model of the atom is extended within the semi-classical framework to include the correlation energy of the electron gas, obtained by an interpolation formula which reproduces the known high and low density limits exactly. The basic equations of the model are derived, and general theoretical results valid for all free atoms and ions are obtained. These include the determination of the electron density at the edge of the atom, a virial theorem for the atom, an estimate for the correlation energy as a function of Z, and a treatment of the Fermi-Amaldi correction. The theory of the compressed atom is also treated, and an equation of state as well as a virial theorem for atoms under pressure is derived. The equations of the model are solved in terms of a Thomas-Fermi-Dirac - like approximation, in terms of a semi-convergent expansion for the potential near the nucleus, and numerically for the atoms Argon, Chromium, Krypton, Xenon, and Uranium on the Burroughs Computer. Complete tables of the solutions obtained are given. The solutions of the model are illustrated in detail for the case of Argon, including a calculation of the energy terms of the Argon atom. Finally, the extended model is applied to the calculation of equations of state, the cross-section for small-angle scattering of medium-energy electrons from atoms, and atomic polarizabilities and diamagnetic susceptibilities. It is found that the extended model leads to improved agreement with experimental values.

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I. INTRODUCTION AND BACKGROUND

A. Introduction

The so-called semi-classical statistical model of the atom, originated independently by Thomas (1) and Fermi (2), has proved to be a simplified, albeit fruitful and versatile approach to the many electron system of the atom. Since its inception, this model has been extensively elaborated by numerous authors, and has been made the basis for the calculation of a large variety of atomic properties. Comprehensive reviews of the theory and applications of the statistical model have been given by Corson (3) and Gombas (4).

The model is based on a number of simplifying assumptions which we shall sketch briefly. To begin with, it is assumed that the electrons surround the nucleus with a spherically symmetric density distribution. The basis of the model lies in assuming further that the volume of the atom can be divided into subvolumes $4\pi r^2 dr$ over which the potential is approximately constant but which still contain a sufficiently large number of electrons. Finally, the electrons occupying each subvolume at a distance r from the nucleus are considered to constitute a totally degenerate electron gas at zero temperature, whose energy density ϵ depends solely on the electron density $\rho(r)$ and the nuclear potential at r. The energy of the atom as a whole is then obtained by integrating both the potential energy and the electron gas energy density over the volume of the atom. The above model is semi-classical in the sense that quantum

mechanics enters only into the expression for the energy density of the electron gas.

In the spirit of the above model it is clearly desirable to write the best possible expression for ϵ. In the original formulation of Thomas and Fermi, which has come to be called the Thomas-Fermi model (henceforth abbreviated as TF), ϵ was taken simply to be the kinetic energy density of the degenerate electron gas. Thus, all electron interactions with the exception of the classical electrostatic Coulomb interaction were neglected. It was found that the electron density calculated on the basis of this model decreased too slowly with distance far from the nucleus, and thus led to appreciable errors in the calculation of effects which depend critically on the electron density in the outer regions of the atom. Examples of such are atomic polarizabilities and diamagnetic susceptibilities, the cross-section for small-angle electron scattering from atoms, and equations of state.

The first step toward extending the model was taken by Dirac (5) who, in addition to the kinetic energy density, included in ϵ the exchange energy density of the electron gas. The corresponding model is known as the Thomas Fermi-Dirac model (henceforth abbreviated as TFD).

Within the framework of the semi-classical statistical approach outlined above, the next obvious extension of the model is to include in ϵ the correlation energy density of the electron gas in addition to the kinetic and exchange energy densities. The chief difficulty is that the electron density in an atom ranges from very small values at the edge of the atom to very large values

close to the nucleus. Consequently, it is necessary to have an expression for the correlation energy of an electron gas valid for the whole range of electron densities. Expressions for the correlation energy of an electron gas have been obtained at the low density limit by Wigner (6,7), and at the high density limit by Gell-Mann and Brueckner (8); it has so far been impossible to derive theoretically an expression valid at intermediate densities, which correspond to intermediate coupling (Cf. Gell-Mann, ref. 9) in the perturbation approach to electron interactions.

A first attempt to take into account the correlation energy in the statistical model of the atom was made in 1943 by Gombas (10) based on an approximate expression for the correlation energy due to Wigner (7), which, however, is valid only for reasonably small densities and thus not realistic for the atom as a whole. More recently, Lewis (11) treated the same problem, starting with an analytical interpolation formula for the correlation energy which allegedly reproduces the known exact expressions at the low and high density limits. In view of the lack of a satisfactory theoretical expression at intermediate densities, this appears to be a reasonable way to approach the problem from a practical viewpoint. However, the work of Lewis includes some unsatisfactory aspects which it is our intention to obviate. In the first place, there is a fundamental error made by confusing the average energy per electron with the energy of an electron at the top of the Fermi sea. Secondly, the interpolation is unnecessarily crude and can easily be improved in order to reproduce both the high and low density limits correctly.

Further, as has been pointed out by Gell-Mann, there are some missing terms in Lewis' expression connecting the potential with the density. This arises partly from the fact that the interpolation is not carried out between the known high and low density limits for the energy density ϵ, but rather for $d\epsilon/d\rho$, with the result that the known limits of ϵ are not reproduced. Finally, the work of Lewis is only preliminary in that he merely derives the Fermi-Thomas equation corresponding to his expression for the correlation energy density, but does not solve the resulting equation. Nor does he attempt to develop the theory much further beyond obtaining an expansion for the potential near the origin and a virial theorem for the atom, both of which are also in error as can be seen from the fact that they do not reduce to the TFD limit in the case of vanishing correlation. The former of these is presumably due to an algebraic error, while the latter arises from a misunderstanding of the work of Feynman, Metropolis, and Teller (12).

It therefore appears worthwhile to reattempt the problem of including the correlation energy density in the statistical model of the atom, and to investigate fully the implications of this extension of the model, to which task the present work is devoted. In keeping with the preliminary work of Gombas and Lewis, we shall remain strictly within the semi-classical framework in the sense outlined above, and neglect the so called 'quantum corrections' to the model, which are essentially inhomogeneity corrections. The latter were first discussed in 1935 by Weizsaecker (13), and most recently by Baraff and Borowitz (14). It is well known that in the outer regions

of the atom, which are of paramount interest to us; the quantum corrections are negligible.

In the remainder of Part I we collect some basic results from the theory of degenerate gases and from Fermi-Thomas theory for purposes of background and later reference. In Part II we derive an interpolation formula for the correlation energy density of the electron gas, which reproduces the known exact high and low density limits. In Part III we derive the Fermi-Thomas equation corresponding to our expression for the correlation energy density, and reexpress it in dimensionless variables. Part IV is devoted to a full development of the theory of the free atom on the basis of our model, i.e. to those features of the model which can be obtained without resorting to a numerical solution of the equations. Part V treats the case of the compressed atom. In Part VI we discuss methods for the solution of the basic equations of the model. The equations have been solved on a computer for the cases of Argon, Chromium, Krypton, Xenon, and Uranium. In the way of illustration, the solution for Argon is discussed in detail in Part VII. In Part VIII we present various applications of our model, and compare our results to the corresponding TF and TFD results, wherever possible, also to experiment. The applications considered are equations of state, small angle scattering of medium energy electrons from atoms, and the calculation of atomic polarizabilities and diamagnetic susceptibilities. Finally, in the Appendix we include complete tables of the numerical solutions obtained.

B. Resume of Basic Formulae

For purposes of background and convenient reference we collect in this section some well known results from the theory of degenerate electron gases and from the statistical model of the atom.

(i) Electron Gas

We consider a completely degenerate electron gas at zero temperature, consisting of N electrons confined in a volume V, and define the uniform density $\rho = N/V$. We now ask for the energy of the ground state of the system.

In the first approximation we take into account only the kinetic energy of the electrons. Then a simple quantum-mechanical calculation yields for the average energy per electron:

$$\left.\begin{aligned} \bar{u} &= \alpha_k \rho^{2/3} \\ \alpha_k &= (3/10)\,(3\pi^2)^{2/3}\, e^2 a_0 = 2.871\, e^2 a_0 \end{aligned}\right\} \quad \text{(I-1)}$$

where

The kinetic energy density of the electron gas is consequently given by

$$\epsilon_k = \rho \bar{u}_k = \alpha_k \rho^{5/3} \qquad \text{(I-2)}$$

and the highest energy electron at the top of the Fermi sea has the energy:

$$u_{kf} = (p_{kf}^2)/(2m) = (5/3)\,\bar{u}_k \qquad \text{(I-3)}$$

If we include effects of exchange, the total energy density of the electron gas becomes

$$\epsilon = \epsilon_K + \epsilon_e \tag{I-4}$$

where ϵ_e is the exchange energy density term given by

$$\left.\begin{aligned} \epsilon_e &= -\alpha_e \rho^{4/3} \\ \text{where} \\ \alpha_e &= (3/4)\ (3/\pi)^{1/3}\ e^2 = 0.7386\ e^2 \end{aligned}\right\} \tag{I-5}$$

Thus, the total energy density of the electron gas, I-4, has the explicit form:

$$\epsilon = \alpha_k \rho^{5/3} - \alpha_e \rho^{4/3} \tag{I-6}$$

Finally, for quick reference , we note the following definitions which are frequently employed in the statistical model of the atom:

$$r_s = (3/4\pi)^{1/3}\ \rho^{-1/3}\ ;\quad a_o = \hbar^2/(me^2)\ ;\quad (Ry) = e^2/2a_o \tag{I-7}$$

(ii) The statistical model

The basic assumptions underlying the statistical model of the atom were outlined in the introduction. The elementary Thomas-Fermi equation can be derived from simple physical considerations; however, for purposes of later extension, it is advisable to follow a systematic approach.

On the basis of the statistical model, the total energy of an atomic system consisting of a nucleus of charge Ze surrounded by

N electrons can be written in the form:

$$E = \int \epsilon(\rho) dv - \int e V_N \rho dv + \frac{e^2}{2} \iint \frac{\rho(r)\rho(r')}{|\vec{r} - \vec{r}'|} dv\, dv' \qquad \text{(I-8)}$$

The first term on the right of I-8 arises from the energy density $\epsilon(\rho)$ of the electron gas; the second integral represents the energy of the electron gas in the nuclear potential V_N, and the third is due to the electrostatic Coulomb interaction of the electrons.

The electron density is now determined from the condition that the density be such as to minimize the total energy of the atom, subject to the side condition that the atom contain N electrons:

$$\int \rho\, dv = N \qquad \text{(I-9)}$$

Expressed formally, this condition becomes

$$\delta(E + N e V_0) = 0 \qquad \text{(I-10)}$$

where V_0 is an as yet undetermined Lagrange multiplier. If the kinetic energy density I-2 is substituted for ϵ in expression I-8, and the variation indicated by I-10 is performed, one obtains the equation

$$\frac{5}{3} \alpha_k \rho^{2/3} = (V - V_0) e \qquad \text{(I-11)}$$

where V represents the total potential at r. When this is combined with Poisson's equation:

$$\nabla^2 (V - V_0) = 4\pi \rho e \qquad \text{(I-12)}$$

one is led directly to the Thomas-Fermi equation:

$$\nabla^2(V-V_0) = 4\pi e \left(\frac{3e}{5K_K}\right)^{3/2} (V-V_0)^{3/2} \qquad \text{(I-13)}$$

Equations I-8 through I-13 represent the basic theory of the TF statistical model. The boundary conditions on the potential are given by

$$\lim_{r \to 0} \; r\,(V - V_0) = Ze \qquad \text{(I-14)}$$

$$-\,dV/dr\Big|_{r=R} = (Z - N)\, e/R^2 \qquad \text{(I-15)}$$

where R represents the radius of the atom. Equation I-13 is customarily expressed in terms of dimensionless variables defined by:

$$\psi(x) = \frac{r}{Ze}\,(V-V_0) \qquad \text{(I-16)}$$

$$x = r/\mu \quad ; \quad \mu = \frac{a_0}{4}\left(\frac{9\pi^2}{2Z}\right)^{1/3} \qquad \text{(I-17)}$$

In terms of these variables, equation I-13 and the boundary conditions I-14,15 take the form:

$$\psi''(x) = \frac{\psi^{3/2}}{x^{1/2}} \qquad \text{(I-18)}$$

$$\left.\begin{aligned} \psi(0) &= 1 \\ \psi(X) - X\psi'(X) &= \frac{Z-N}{Z} \end{aligned}\right\} \qquad \text{(I-19)}$$

where $X = R/\mu$. Thus, in dimensionless form, the Thomas-Fermi equation and its boundary conditions are independent of Z, so that a single solution applies to all atoms, the scale being given by the definitions I-16,17. The solution of I-18,19 can only be obtained numerically.

In order to obtain the Thomas-Fermi-Dirac equation it is merely necessary to substitute in equation I-8 the expression I-6 for the energy density of the electron gas and again determine $\rho(r)$ from the condition I-10. If this is done, equation I-11 becomes replaced by

$$\frac{5}{3}\alpha_K \rho^{2/3} - 4/3\,\alpha_e \rho^{1/3} = (V-V_0)\,e \qquad \text{(I-20)}$$

It is again possible to solve this equation explicitly for $\rho\,(V-V_0)$ and substitute it into Poisson's equation, yielding in place of I-13 the TFD equation:

$$\nabla^2(V-V_0+\tau^2) = 4\pi e\left(\frac{3e}{5\alpha_K}\right)^{3/2}\left[(V-V_0+\tau^2)^{1/2}+\tau\right]^3 \qquad \text{(I-21)}$$

where

$$\tau = \left(\frac{1}{2\pi^2}\,\frac{e}{a_0}\right)^{1/2}$$

If analogously we define the dimensionless variables:

$$\varphi_e(x) = \frac{r}{Ze}\,(V-V_0+\tau^2)$$

$$x = r/\mu \qquad \text{(I-22)}$$

the equation corresponding to I-18 becomes:

$$\psi_e''(x) = x\left[\left(\frac{\psi_e}{x}\right)^{1/2} + \kappa\right]^3 \qquad \text{(I-23)}$$

with

$$\kappa = \frac{2\kappa_e}{3e^2(4\pi Z^2)^{1/3}}$$

The boundary conditions corresponding to I-19 in this case take the form:

$$\left.\begin{aligned} \psi_e(0) &= 1 \\ \psi_e(X) &= \frac{\kappa^2}{16} X \\ \psi_e(X) - X\psi_e'(X) &= \frac{Z-N}{Z} \end{aligned}\right\} \qquad \text{(I-24)}$$

Unlike in the case of the TF atom, here Z is involved both in the equation for $\psi_e(x)$ and its boundary conditions. Consequently, a separate numerical solution becomes necessary for each value of Z and N.

II. INTERPOLATION FORMULA FOR THE CORRELATION ENERGY OF AN ELECTRON GAS.

There is some ambiguity in the literature in the usage of the term 'correlation energy' for an electron gas. The correlation energy is defined by some authors to be the difference between the exact energy and the kinetic plus exchange energies; whereas, particularly since the advent of field-theoretic methods for treating many body problems, the term is frequently applied simply to the e^4 term in the perturbation expansion. Here we shall use the term interchangeably, the difference between the two definitions clearly consisting of terms of order e^6 and higher.

As we have pointed out previously, the atom as a physical system encompasses a wide range of electron densities, whereas exact expressions for the correlation energy of an electron gas are known only in the high and low density limits. In order to include the correlation energy in the statistical model of the atom it therefore becomes necessary to first obtain a reasonable interpolation expression which can be assumed to be approximately valid in the intermediate density range.

The high density limit has been derived by Gell-Mann and Brueckner (8) who obtain the following expression for the average correlation energy per electron of an electron gas in a uniform positive background:

$$\bar{\mu}_c = \frac{2}{\pi^2}(1-\ln 2)\ln\left(\frac{r_s}{a_0}\right) - 0.096 \qquad \text{(II-1)}$$

where $\bar{u}_c$ is expressed in Rydbergs. We write this in terms of a dimensionless variable $\xi = a_0 \rho^{1/3}$, obtaining:

$$\bar{u}_c = -\frac{2}{\pi^2}(1-\ln 2)\ln\xi - \left[\frac{2}{\pi^2}(1-\ln 2)\ln\left(\frac{9\pi}{3}\right)^{1/3} + 0.096\right] \qquad \text{(II-2)}$$

After calculating the numbers, this becomes

$$\left.\begin{aligned} \bar{u}_c\ (Ry) &= -\beta \ln\xi - C' \quad , \quad \xi \gg 1 \\ \beta &= 0.06218 \quad , \quad C' = 0.1257 \end{aligned}\right\} \qquad \text{(II-3)}$$

The corresponding low density limit has been calculated by Wigner (6,7) starting from the assumption that as $\rho \to 0$ the electrons crystallize into a cubic body-centered lattice, which has a lower energy than any alternative lattice. The calculations of Wigner have recently been redone by Coldwell-Horsfall and Maradudin (15) who obtain for the total energy per electron the expression:

$$\bar{u}_{tot} = -0.89593\ e^2/r_s \qquad \text{(II-4)}$$

The correlation energy per electron is obtained from the above by subtracting the exchange energy per electron, ϵ_e/ρ , where ϵ_e is given by equation I-5. Consequently, we have:

$$\bar{u}_c = \bar{u}_{tot} - \epsilon_e/\rho \qquad \text{(II-5)}$$

If we express this in terms of the dimensionless variable ξ and in units of Rydbergs, we obtain:

$$\left.\begin{aligned} \bar{\mu}_c\,(Ry) &= -\gamma\xi \quad , \quad \xi \ll 1 \\ \gamma &= 2\,(0.89593)\left(\frac{4\pi}{3}\right)^{1/3} - \frac{3}{2}\left(\frac{3}{\pi}\right)^{1/3} = 1.412 \end{aligned}\right\} \qquad \text{(II-6)}$$

Our aim is now to find some analytic interpolation formula for $\bar{u}_c$ which reproduces the above high and low density limits. An obvious first attempt (essentially equivalent to Lewis (11)) would be to try

$$\bar{\mu}_c = a \ln(1+b\xi) + C \qquad \text{(II-7)}$$

which has the limits

$$\bar{\mu}_c = \begin{cases} a \ln \xi + a \ln b + C & , \xi \gg 1 \\ ab\xi + C & , \xi \ll 1 \end{cases} \qquad \text{(II-8)}$$

In order to satisfy the low density limit II-6, we must have

$$C = 0 \quad , \quad ab = -\gamma$$

and the high density limit requires

$$a = -\beta \quad , \quad a \ln b = -C'$$

The above four equations constitute an overdetermined set. If we choose to reproduce the low density limit exactly, we must take

$$C = 0 \quad , \quad a = -\beta \quad , \quad b = \gamma/\beta$$

which means that we cannot reproduce the constant C' in the high density limit. Although the absolute value of C' is irrelevant in the statistical theory of the atom, the difference between $-a \ln b = \beta \ln(\gamma/\beta)$ and C' gives a general measure

of the error of the interpolation formula. In this case we have $\beta \ln(\gamma/\beta) = 0.195$ compared to $C' = 0.126$.

However, we can improve upon this result and require that both the high and low density limits be satisfied exactly. This can be accomplished by adding to our trial function II-7 a function $f(\xi)$ with the following properties:

$$f(\xi) \longrightarrow \begin{cases} \text{constant}, & \xi \gg 1 \\ 0, & \xi \ll 1 \end{cases}$$

A simple function of this type is $f(\xi) = c\,\xi\,(\xi + d)^{-1}$. Consequently; we shall replace II-7 by the trial function

$$\bar{\mu}_c = a \ln(1+\xi) + \frac{c\,\xi}{\xi + d} \tag{II-9}$$

which has the limits:

$$\bar{\mu}_c = \begin{cases} a \ln \xi + c, & \xi \gg 1 \\ \left(a + \frac{c}{d}\right)\xi, & \xi \ll 1 \end{cases} \tag{II-10}$$

It can now easily be shown that both the limits, II-3 and II-6, can be satisfied exactly by choosing

$$a = -\beta, \quad c = -C', \quad d = \frac{C'}{\gamma + \beta} \tag{II-11}$$

If we calculate the necessary numbers we find that with II-11 our proposed interpolation formula II-9 for the correlation energy then becomes:

$$\bar{\mu}_c\,(Ry) = -0.06218 \ln(1+\xi) - \frac{0.1257\,\xi}{\xi + 0.09311} \tag{II-12}$$

Finally, for later use, we write explicitly the corresponding expression for the correlation energy density ϵ_c in the form:

$$\epsilon_c = -\alpha_c \left[\rho \ln(1+a_0\rho^{1/3}) + \frac{\sigma a_0 \rho^{4/3}}{\tau + a_0\rho^{1/3}} \right] \qquad \text{(II-13)}$$

where

$$\alpha_c = 0.03109 \frac{e^2}{a_0} \quad , \quad \sigma = 2.0216 \quad , \quad \tau = 0.09311$$

In order to assess the reasonableness of our interpolation formula we have made a numerical comparison of II-12 with an approximate extrapolated expression obtained by Wigner (7) for reasonably low densities. It was found that II-12 agrees with Wigner's expression well within the accuracy claimed for the latter. Thus, our interpolation formula can be considered satisfactory from the point of view that it reproduces both the high and low density limits exactly, and agrees with an independently obtained approximate expression over the range of validity of the latter.

If desired, the interpolation procedure could be carried out to higher orders by making use of known higher order corrections to both the high and low density limits. Thus, the next term in the high density limit II-1 is of the form $r_s \ln(r_s/a_0)$ while the next term in the low density limit II-4 is proportional to $r_s^{-3/2}$. An interpolation corresponding to II-12 exact to those orders is found to lead to a set of eight non-linear simultaneous equations. While it is possible to solve these, it is felt that the inherent inaccuracy of the interpolation procedure does not warrant the additional complications involved, particularly in later work.

III. THE THOMAS-FERMI EQUATION INCLUDING CORRELATION

We now proceed to derive the fundamental equation of the statistical atom model based on our interpolation expression II-13. In section A we obtain the analogue of the TF or TFD equation, given, respectively, by I-13 or I-21, and carry out the conversion to dimensionless variables in section B.

A. Derivation of the Equation.

We begin by including the interpolation formula II-13 in the expression for the total energy density ϵ of the electron gas, and thus write:

$$\epsilon = \alpha_k \rho^{5/3} - \alpha_e \rho^{4/3} - \alpha_c \left[\rho \ln(1 + a_0 \rho^{1/3}) + \frac{\sigma a_0 \rho^{4/3}}{\tau + a_0 \rho^{1/3}} \right] \qquad \text{(III-1)}$$

The total energy of the atom can then be written in the form:

$$E = E_1 + E_2 + E_3 \qquad \text{(III-2)}$$

where

$$\left.\begin{aligned} E_1 &= \int \epsilon(\rho)\, dv \\ E_2 &= \frac{e^2}{2} \iint \frac{\rho(r)\rho(r')}{|\vec{r} - \vec{r}'|}\, dv\, dv' \\ E_3 &= -e \int \rho V_N\, dv \end{aligned}\right\} \qquad \text{(III-3)}$$

The term E_1 represents the contribution of the electron gas energy, while E_2 and E_3 are the electrostatic energies due to the electron Coulomb interaction and the nuclear potential, respectively. We must now perform the variation indicated by I-10. i.e.

$$\delta(E + N e V_0) = 0 \qquad \text{(III-4)}$$

Taking the variation of the individual terms of III-3, we obtain in view of III-1:

$$\delta E_1 = \int \delta\rho\, dv \left\{ \frac{5}{3}\alpha_k \rho^{2/3} - \frac{4}{3}\alpha_e \rho^{1/3} - \alpha_c \left[\ln(1+a_0\rho^{1/3}) + \right.\right.$$

$$\left.\left. + \frac{1}{3}\frac{a_0\rho^{1/3}}{1+a_0\rho^{1/3}} + \frac{4}{3}\frac{\sigma a_0\rho^{1/3}}{\tau + a_0\rho^{1/3}} - \frac{1}{3}\frac{\sigma(a_0\rho^{1/3})^2}{(\tau+a_0\rho^{1/3})^2} \right] \right\}$$

$$\delta E_2 = e^2 \iint \frac{[\delta\rho(r)]\rho(r')\, dv dv'}{|\vec{r}-\vec{r}'|} = -e\int \delta\rho\, dv \int \frac{-e\rho(r')\, dv'}{|\vec{r}-\vec{r}'|}$$

$$= -e\int \delta\rho\, dv\, V_e$$

(III-5)

$$\delta E_3 = -e\int \delta\rho\, dv\, V_N$$

and

$$\delta N = \int \delta\rho\, dv$$

where V_e, as is apparent from the above, is the potential at r due to all the electrons of the atom. If we denote the total potential by $V = V_N + V_e$ and substitute the expressions III-5 into III-4 we obtain the desired local relation between V and ρ :

$$(V-V_0)e = \frac{5}{3}\alpha_k\rho^{2/3} - \frac{4}{3}\alpha_e\rho^{1/3} - \alpha_c\left[\ln(1+a_0\rho^{1/3}) + \right.$$

$$\left. + \frac{1}{3}\frac{a_0\rho^{1/3}}{1+a_0\rho^{1/3}} + \frac{4}{3}\frac{\sigma a_0\rho^{1/3}}{\tau+a_0\rho^{1/3}} - \frac{1}{3}\frac{\sigma(a_0\rho^{1/3})^2}{(\tau+a_0\rho^{1/3})^2}\right] \qquad \text{(III-6)}$$

Together with Poisson's equation

$$\nabla^2(V-V_0) = 4\pi\rho e \qquad \text{(III-7)}$$

and the physical boundary conditions

$$\lim_{r\to 0} r(V-V_0) = Ze \qquad \text{(III-8)}$$

$$V(R) = \frac{(Z-N)e}{R} \qquad \text{(III-9)}$$

$$-\left.\frac{dV}{dr}\right|_{r=R} = \frac{(Z-N)e}{R^2} \qquad \text{(III-10)}$$

our model is then completely defined. If in equation III-6 we set $\alpha_c = 0$ we reproduce the TFD model given by I-20; if we set both $\alpha_c = \alpha_e = 0$ we regain the TF model described by I-11,13.

Unlike with both the TF and TFD models, in our case it is manifestly impossible to solve equation III-6 explicitly for $\rho(V - V_0)$ and substitute it into Poisson's equation in order to obtain a differential equation involving only the single dependent variable $(V - V_0)$. This circumstance causes considerable analytical complications in the actual solution of the system of equations defining our model, but presents no fundamental difficulties.

B. Conversion to Dimensionless Variables.

In order to express the equations of our model in terms of dimensionless variables corresponding to I-18 or L-23, we may proceed in two alternative ways.

We again define the dimensionless variables $\psi(x)$ and x by means of

$$\psi(x) = \frac{r}{ze}\left[V(r) - V_0\right] \qquad \text{(III-11)}$$

$$x = r/\mu \quad ; \quad \mu = \frac{a_0}{4}\left(\frac{9\pi^2}{2z}\right)^{1/3} \qquad \text{(III-12)}$$

If we now further define the variable $\lambda(x)$ by

$$\lambda(x) = k\, x^{1/2}\rho^{1/3} \quad ; \quad k = \mu\left(\frac{4\pi}{z}\right)^{1/3} \qquad \text{(III-13)}$$

then Poisson's equation in terms of these variables takes the form:

$$\frac{d^2\psi}{dx^2} = \frac{\lambda^3}{x^{1/2}} \qquad \text{(III-14)}$$

i.e. it becomes a second order differential equation in the two dependent variables ψ, λ. The algebraic relation connecting ψ (x) and λ (x) can be obtained by expressing equation III-6 in terms of the above dimensionless variables. Thus we find

$$\psi(x) = \lambda^2 - \beta x^{1/2}\lambda - \gamma x\, f\left(\frac{\epsilon\lambda}{x^{1/2}}\right) \qquad \text{(III-15)}$$

where

$$f(s) = \ln(1+s) + \frac{1}{3}\frac{s}{1+s} + \frac{4}{3}\frac{\sigma s}{\gamma+s} - \frac{1}{3}\frac{\sigma s^2}{(\gamma+s)^2} \qquad \text{(III-16)}$$

and

$$\epsilon = \frac{2}{\pi}\left(\frac{4Z^2}{9}\right)^{1/3} \quad , \quad \beta = \left(\frac{3}{4\pi^2 Z^2}\right)^{1/3}$$

$$\gamma = \frac{\alpha_e \mu}{Z e^2} = \frac{(1-\ln 2)}{4\pi^2 Z}\left(\frac{9\pi^2}{2Z}\right)^{1/3}$$

We must now express the boundary conditions as well in dimensionless form. Since $\psi(x)$ was defined exactly as in the TF case (Equations I-16,17), the boundary conditions corresponding to III-8 and III-10 are likewise identical to those of the TF case, i.e. we have

$$\psi(0) = 1 \tag{III-17}$$

$$\psi(x) - x\psi'(x) = \frac{Z-N}{Z} \tag{III-18}$$

The boundary condition III-9 becomes in view of the defining equation III-11:

$$\psi(x) = x\left[\frac{\mu}{Ze}\left(V(R) - V_0\right)\right] \tag{III-19}$$

Referring back to III-6 we see that the term in brackets on the right-hand side of III-19 is a function only of Z and the density $\rho_0 \equiv \rho(R)$ at the outer radius of the atom. As we shall show next in Part IV(A), for the case of a free atom, ρ_0 is an invariant for all atoms and ions. Consequently, III-19 can be written in the simple form

$$\psi(x) = x\,C(\rho_0) \tag{III-20}$$

where $C(\rho_0)$ is a constant given explicitly (Cf. equation IV-20) by

$$C(\rho_0) = -\frac{0.08933}{4Z}\left(\frac{9\pi^2}{2Z}\right)^{1/3} \tag{III-21}$$

Thus, in dimensionless form, our model is represented by the differential equation III-14 with ψ and λ connected by III-15,16, and where ψ must satisfy the boundary conditions III-17,18,20.

The advantage of this form is that the differential equation itself is simple in form, and the boundary conditions are likewise relatively simple and directly obtained from physical considerations. The disadvantage is analytical in that we must deal with a system of equations rather than with a single differential equation. As in the TFD case, it is necessary to obtain a separate solution for each atom and ion since both Z and N enter into the equation and its boundary conditions.

Alternatively, we may try to obtain a single differential equation in a single dependent variable. This can be achieved by substituting III-15 into III-14 and performing the indicated differentiation. Thus we obtain after considerable simplification:

$$2\lambda\lambda'' + 2(\lambda')^2 - \left[x^{1/2}\lambda'' + \frac{\lambda'}{x^{1/2}} - \frac{\lambda}{4x^{3/2}}\right]\left[\beta + \gamma\epsilon\, \mathcal{F}'\left(\frac{\epsilon\lambda}{x^{1/2}}\right)\right] -$$

$$-\gamma x\, \mathcal{F}''\left(\frac{\epsilon\lambda}{x^{1/2}}\right)\left[\frac{\epsilon(2x\lambda' - \lambda)}{2x^{3/2}}\right]^2 = \frac{\lambda^3}{x^{1/2}} \qquad \text{(III-22)}$$

where the primes denote differentiation with respect to the argument and $\mathcal{F}'(\mathfrak{x})$ and $\mathcal{F}''(\mathfrak{x})$ are given in their simplest form by

$$\left.\begin{aligned} f'(x) &= \frac{4}{3}\frac{1}{1+x} - \frac{1}{3}\frac{x}{(1+x)^2} + \frac{4}{3}\frac{\sigma}{\tau+x} - \frac{2\sigma x}{(\tau+x)^2} + \frac{2}{3}\frac{\sigma x^2}{(\tau+x)^3} \\ f''(x) &= -\frac{5}{3}\frac{1}{(1+x)^2} + \frac{2}{3}\frac{x}{(1+x)^3} - \frac{10}{3}\frac{\sigma}{(\tau+x)^2} + \frac{16}{3}\frac{\sigma x}{(\tau+x)^3} - \frac{2\sigma x^2}{(\tau+x)^4} \end{aligned}\right\} \quad \text{(III-23)}$$

Equation III-22 together with III-23 constitutes a differential equation in the single dependent variable $\lambda(x)$, albeit a very complicated one. Its only advantages are analytical in that we obviate the necessity for dealing with a system of equations and have freed the equation from troublesome logarithms, contained originally in III-15. Also, once a solution for λ is obtained, the corresponding value of $\psi(x)$ is obtained relatively simply from III-15, while the reverse is not true.

It remains to express the boundary conditions III-17,18,20 directly in terms of $\lambda(x)$. The boundary condition corresponding to III-8 cannot be obtained directly from that for $\psi(x)$. Instead, we proceed from the observation that since correlation will not appreciably affect $\rho(r)$ near the nucleus, the behaviour of ρ as $r \to 0$ will have the same character as in the TF and TFD cases, namely

$$\rho(r) \longrightarrow \frac{Z}{4\pi\mu^{3/2}} \frac{1}{r^{3/2}} \quad ; \quad r \to 0 \qquad \text{(III-24)}$$

If this is expressed in terms of λ, we find

$$\lambda(0) = 1 \qquad \text{(III-25)}$$

At the outer edge of the atom, the boudary condition corresponding to III-20 follows directly from the definition of λ, and we have

$$\lambda(X) = k\rho_0^{1/3} X^{1/2} \qquad \text{(III-26)}$$

where, as mentioned previously, ρ_0 and k are known constants. Finally, the condition corresponding to III-18 can be obtained by substituting III-15 into III-18 which yields the complicated relation:

$$\lambda_0^2 - \frac{\beta}{2} X^{1/2}\lambda_0 + \beta X^{3/2}\lambda_0' - 2X\lambda_0\lambda_0' + \qquad \text{(III-27)}$$

$$+ \frac{\gamma\epsilon}{2} X^{1/2}(2X\lambda_0' - \lambda_0) F'\left(\frac{\epsilon\lambda_0}{X^{1/2}}\right) = \frac{Z-N}{Z}$$

where

$$\lambda_0 = \lambda(X) \quad , \quad \lambda_0' = \left.\frac{d\lambda}{dx}\right|_{x=X}$$

Thus, our model can be described in dimensionless form alternatively by the system of equations III-14,15,17,18,20 or by the system III-22,23,25,26,27.

IV. THEORY OF THE FREE ATOM

This part is devoted to the development of what we consider to be the basic theory of our model defined in Part III, i.e. to those features which can be obtained without resorting to a numerical solution of the basic equations of the model. The most important of these are the determination of the undetermined Lagrange multiplier V_0 and the electron density $\rho_0 = \rho(R)$ at the edge of the atom. These are obtained in section A. In section B we derive a virial theorem for our model. Section C is devoted to establishing an approximate expression for the correlation energy of the atom as a whole. Finally, in section D we investigate the well-known Fermi-Amaldi correction (16) in the framework of our model. Our considerations in this part will pertain exclusively to the case of the free atom, defined by zero pressure at the boundary. The corresponding situation when this requirement is relaxed will be treated in Part V.

A. Determination of V_0 and ρ_0.

The most important result of our model which can be obtained without explicitly solving the system of equations III-(6-10) is the value of the electron density at the edge of the atom, which in turn serves to determine the previously undetermined Lagrange multiplier V_0. We have obtained the fundamental equation III-6 by requiring that the electron density as a function of r be such as to minimize the total energy of the atom. If analogous to the TFD case we assume that the electron density in our model is given by $\rho(r)$ up to the edge $r = R$ of the atom and vanishes

thereafter, it is then clear by referring to the boundary conditions III-8,9,10 that the total energy of the atom is a function of the hitherto undetermined atomic radius R. We can now in turn obtain a condition on R by requiring likewise that R will adjust itself such as to make the energy of the atom a minimum, i.e. by requiring the fulfillment of the condition

$$\frac{\delta E}{\delta R} = 0 \qquad \text{(IV-1)}$$

In the above variation we must remember that ρ must simultaneously satisfy the equation III-15, obtained by our previous variation of E with respect to ρ while keeping R constant. We shall find that the condition IV-1 leads to an equation for the determination of ρ_0.

We begin by rewriting the expressions III-2,5 for the total energy of the atom in the form:

$$E = \int_0^R 4\pi r^2 dr \left\{ \alpha_K \rho^{5/3} - \alpha_e \rho^{4/3} - \alpha_c \left[\rho \ln(1+a_0\rho^{1/3}) + \right.\right.$$

$$\left.\left. + \frac{\sigma a_0 \rho^{4/3}}{\tau + a_0 \rho^{1/3}} \right] - e\rho V_N(r) - \frac{e}{2}\rho V_e(r) \right\} \qquad \text{(IV-2)}$$

In performing the variation IV-1 on the expression IV-2 we must keep in mind that both the limits of the integral IV-2 as well as the functions V_e and $\rho(r)$ in the integrand are functions of R. Following the usual rules for differentiating an integral, and writing $\rho_0 = \rho(R)$ we then obtain:

$$\frac{\delta E}{\delta R} = \int_0^R \Big\{ \frac{5}{3}\alpha_K \rho^{2/3} - \frac{4}{3}\alpha_e \rho^{1/3} - \alpha_c \Big[\ln(1+a_0\rho^{1/3}) + \frac{4}{3}\frac{\sigma a_0 \rho^{1/3}}{\tau + a_0\rho^{1/3}} - \frac{1}{3}\frac{\sigma (a_0\rho^{1/3})^2}{(\tau + a_0\rho^{1/3})^2} \Big] - e V_N(r) - \frac{e}{2} V_e(r) \Big\} \frac{\partial \rho}{\partial R} 4\pi r^2 dr -$$

$$- \int_0^R \frac{e}{2} \rho \frac{\partial V_e(r)}{\partial R} 4\pi r^2 dr + 4\pi R^2 \Big\{ \alpha_K \rho_0^{5/3} - \alpha_e \rho_0^{4/3} - \alpha_c \Big[\rho_0 \ln(1+a_0\rho_0^{1/3}) + \frac{\sigma a_0 \rho_0^{4/3}}{\tau + a_0\rho_0^{1/3}} \Big] - e\rho_0 V_N(R) - \frac{e}{2}\rho_0 V_e(R) \Big\} = 0 \qquad \text{(IV-3)}$$

In order to simplify this expression, we start by considering the following expression:

$$V_e(r) = -e \int \frac{\rho(r')\, dv'}{|\vec{r} - \vec{r}'|} \qquad \text{(IV-4)}$$

from which we can obtain:

$$\frac{\partial V_e(r)}{\partial R} = -e \iint_{S:\,|\vec{r}^*| = R} \frac{\rho(R)\, dS}{|\vec{r} - \vec{r}^*|} - e \int \frac{1}{|\vec{r} - \vec{r}'|} \frac{\partial \rho(r')}{\partial R} dv' \qquad \text{(IV-5)}$$

where the first integral on the right of IV-5 arises from the differentiation of IV-4 with respect to the upper limit of the integral, and is an integral over the surface of the sphere $|\vec{r}^*| = R$. We now form the expression:

$$2\pi e \int_0^R \frac{\partial V_e}{\partial R} \rho \, r^2 dr = \frac{e}{2} \int \frac{\partial V_e}{\partial R} \rho \, dv \qquad \text{(IV-6)}$$

By substituting equation IV-5 into IV-6 and exchanging the order of integration in both terms on the right-hand side, we find

$$\frac{e}{2} \int \frac{\partial V_e}{\partial R} \rho \, dv = \frac{e}{2} \left[\int_{S:|\vec{r}^*|=R} dS \int \frac{-e\rho(R)\rho(r)dv}{|\vec{r}-\vec{r}^*|} + \int \frac{\partial \rho(r')}{\partial R} dv' \int \frac{-e\rho(r)dv}{|\vec{r}-\vec{r}'|} \right]$$

$$= \frac{e}{2} \left[\int_S \rho_0 V_e(r^*) dS + \int V_e(r') \frac{\partial \rho(r')}{\partial R} dv' \right]$$

$$= \frac{e}{2} \left[4\pi R^2 V_e(R) \rho_0 + \int_0^R \frac{\partial \rho(r')}{\partial R} V_e(r') 4\pi r'^2 dr' \right]$$

(IV-7)

In the last integral on the right of IV-7, the dummy variable r' may be replaced by r; if we then substitute IV-7 into IV-3, the latter becomes

$$\frac{\delta E}{\delta R} = 4\pi R^2 \left\{ \alpha_k \rho_0^{5/3} - \alpha_e \rho_0^{4/3} - \alpha_c \left[\rho_0 \ln(1+a_0\rho_0^{1/3}) + \right.\right.$$

$$\left.\left. + \frac{\sigma a_0 \rho_0^{4/3}}{\tau + a_0\rho_0^{1/3}} \right] - e\rho_0 V_N(R) - e\rho_0 V_e(R) \right\} +$$

$$+ \int_0^R 4\pi r^2 dr \frac{\partial \rho}{\partial R} \left\{ \frac{5}{3}\alpha_k \rho^{2/3} - \frac{4}{3}\alpha_e \rho^{1/3} - \alpha_c \left[\ln(1+a_0\rho^{1/3}) + \right.\right.$$

$$\left.\left. + \frac{1}{3}\frac{a_0\rho^{1/3}}{1+a_0\rho^{1/3}} + \frac{4}{3}\frac{\sigma a_0 \rho^{1/3}}{\tau + a_0\rho^{1/3}} - \frac{1}{3}\frac{\sigma (a_0\rho^{1/3})^2}{(\tau + a_0\rho^{1/3})^2} \right] - eV_N - eV_e \right\} \quad \text{(IV-8)}$$

Referring back to the equation III-6 connecting V and ρ, and noting that $V_N = V_e + V$, it is seen that the complicated integral on the right-hand side of IV-8 is simply equal to

$$-e \int 4\pi r^2 V_0 \frac{\partial \rho}{\partial R} dr \quad \text{(IV-9)}$$

However, since

$$N = \int 4\pi r^2 \rho \, dr \quad \text{(IV-10)}$$

we have, for a fixed number of electrons

$$\frac{dN}{dR} = 0 = 4\pi R^2 \rho_0 + \int_0^R 4\pi r^2 \frac{\partial \rho}{\partial R} dr$$

with which the integral IV-9 reduces simply to:

$$4\pi R^2 \rho_0 e V_0$$

Substituting this result into the complicated integral-differential equation IV-8, we obtain the much simpler form:

$$\frac{\delta E}{\delta R} = 0 = 4\pi R^2 \left\{ \alpha_k \rho_0^{5/3} - \alpha_e \rho_0^{4/3} - \alpha_c \left[\rho_0 \ln(1+a_0\rho_0^{1/3}) + \right.\right.$$

$$\left.\left. + \frac{\sigma a_0 \rho_0^{1/3}}{\tau + a_0\rho_0^{1/3}} \right] - e\rho_0 V(R) + e\rho_0 V_0 \right\} \qquad \text{(IV-11)}$$

This can be further simplified by substituting into the above for $V(R) - V_0$ the expression obtained from III-15 with ρ_0 in place of ρ. Thus, we are finally led to

$$\frac{\delta E}{\delta R} = 4\pi R^2 \left\{ -\frac{2}{3}\alpha_k \rho_0^{5/3} + \frac{1}{3}\alpha_e \rho_0^{4/3} + \alpha_c \left[\frac{1}{3} \frac{a_0 \rho_0^{4/3}}{1+a_0\rho_0^{1/3}} + \right.\right.$$

$$\left.\left. + \frac{1}{3} \frac{\sigma a_0 \rho_0^{4/3}}{\tau + a_0\rho_0^{1/3}} - \frac{1}{3} \frac{\sigma (a_0\rho_0^{1/3})^2 \rho_0}{(\tau + a_0\rho_0^{1/3})^2} \right] \right\} = 0 \qquad \text{(IV-12)}$$

which is simply an algebraic expression for the single unknown ρ_0. Since the solutions $R = 0$ or $\rho_0 = 0$ are ruled out by the requirement that with $\alpha_c = 0$ our model must reduce to the TFD case for which both R and ρ_0 are known to be finite, we can freely divide the above equation through by R and ρ_0. If we consequently divide the last equation through by $R^2\rho_0$, reexpress it in terms of the dimensionless parameter $z_0 = a_0\rho_0^{1/3}$ and adopt the definitions

$$\beta_e = \left(\frac{\alpha_e}{\alpha_k}\right) a_0 \quad , \quad \beta_c = \left(\frac{\alpha_c}{\alpha_k}\right) a_0^2$$

we find, after some algebra, that the simplest form of the determining equation for ξ_0 is a quartic given by

$$f(\xi_0) = 0 = \xi_0^4 + a\xi_0^3 + b\xi_0^2 + c\xi_0 + d \qquad \text{(IV-13)}$$

where the known constants a,b,c,d are as follows:

$$\left.\begin{aligned} a &= 1 + 2\tau - \frac{\beta_e}{2} \\ b &= 2\tau + \tau^2 - \frac{\beta_e}{2}(1+2\tau) - \frac{\beta_c}{2} \\ c &= \tau^2 - \frac{\beta_e}{2}(2\tau+\tau^2) - \frac{\beta_c}{2}(2\tau+\tau\sigma) \\ d &= -\frac{\beta_e}{2}\tau^2 - \frac{\beta_c}{2}(\tau^2+\tau\sigma) \end{aligned}\right\} \qquad \text{(IV-14)}$$

The necessary numerical values are calculated to be:

$$\beta_e = 0.2573\,, \qquad \beta_c = 0.01083$$

$$a = 1.058, \quad b = 0.03690, \quad c = -.01843, \quad d = -.002180$$

A cursory analysis of the function $f(\xi_0)$ reveals that it has a unique zero on the positive ξ_0-axis. In order to obtain ξ_0 we have solved equation IV-13 numerically by Newton's iterative method, finding

$$\xi_0 = 0.15048 = a_0\rho_0^{1/3} \qquad \text{(IV-15)}$$

which yields the value

$$\rho_0 = \frac{3.4075 \times 10^{-3}}{a_0^3} \qquad \text{(IV-16)}$$

As is apparent from the generality of the above derivation, the electron density ρ_0 at the edge of the atom is an invariant for all atoms and ions in this model. The same is true for the TFD model for which

$$\rho_{0\,TFD} = \frac{2.127 \times 10^{-3}}{a_0^{\,3}} \qquad \text{(IV-17)}$$

We see that the effect of including the correlation energy density increases the value of ρ_0 by some 60 per cent over the TFD value. It does not follow, however, that the effect of correlation on other parameters of the atom, such as for example the energy, will be of the same order of magnitude. In the simple TF model, $\rho_0 = 0$ which implies an infinite radius R, and consequently leads to a too slowly decreasing electron density for large r, and to considerable errors in applications of the model to situations for which the density in the outer regions of the atom is significant.

The above result has as its consequence that the value of R for a given atom or ion in our model will be smaller than the corresponding TFD value, although ---- unlike ρ_0 --- R cannot be found without first solving the equations completely.

Finally, we determine the Lagrange multiplier V_0. We proceed by writing the basic equation III-6 for $r = R$ and $\rho = \rho_0$. By then taking cognizance of the boundary condition III-9, we have

$$-V_0 e = -\frac{(Z-N)e^2}{R} + \frac{5}{3}\frac{\kappa_K}{a_0^{\,2}}\eta_0^{\,2} - \frac{4}{3}\frac{\kappa_e}{a_0}\eta_0 - \kappa_c\left[\ln(1+\eta_0) + \frac{1}{3}\frac{1}{1+\eta_0} + \frac{4}{3}\frac{\sigma\eta_0}{\tau+\eta_0} - \frac{1}{3}\frac{\sigma\eta_0^{\,2}}{(\tau+\eta_0)^2}\right] \qquad \text{(IV-19)}$$

With $\mathcal{I}_0$ given by IV-15, the terms involving $\mathcal{I}_0$ in IV-8 can be evaluated, and we obtain:

$$V_0 e = \frac{(Z-N)e^2}{R} + 0.08933 \frac{e^2}{a_0} \qquad \text{(IV-19)}$$

Equation IV-19 shows that for neutral atoms V_0 is a universal constant, while for ions it is a function of the degree of ionization and the radius R of the ion. In both cases we have, again by reference to the boundary condition III-8 the relation

$$(V(R) - V_0)\, e = -0.08933 \frac{e^2}{a_0} \qquad \text{(IV-20)}$$

It is this relation which permits us to write the universal dimensionless boundary condition III-20,21.

We have thus accomplished our purpose of finding exact expressions for ρ_0 and V_0 directly from the basic equations of our model. We shall find these to be very useful in the development to follow.

B. Virial Theorem

Our purpose in this section is to derive a virial theorem for the atom based on our model.

The corresponding virial theorems for the TF and TFD models are given, respectively, by

$$2\ E_k + E_p = 0 \qquad \text{(IV-21)}$$

$$2\ E_k + E_p + E_e = 0 \qquad \text{(IV-22)}$$

where E_k, E_p and E_e represent the total kinetic, potential, and exchange energy of the atom, respectively.

We shall use as our starting point an approach due to Fock (17) which is based essentially on a similarity transformation. In this method, we let ρ be the density which minimizes the energy of the atom, i.e. the density which satisfies the basic equations III-6,7. We then consider a family of neighboring densities ρ_λ obtained by contracting all distances by a factor λ. These are given explicitly by

$$\rho_\lambda = \lambda^3 \rho(\lambda r) \qquad \text{(IV-23)}$$

which for $\lambda = 1$ becomes the correct density. Next, the energy of the atom is calculated as a function of λ. The varational principle then gives the condition

$$\lim_{\lambda=1} \frac{dE(\lambda)}{d\lambda} = 0 \qquad \text{(IV-24)}$$

For our model, the total energy of the atom as a function of λ is given formally by

$$E(\lambda) = E_k(\lambda) + E_p(\lambda) + E_e(\lambda) + E_c(\lambda) \qquad \text{(IV-25)}$$

where E_c represents the total correlation energy of the atom. It can easily be shown (17) that

$$E_k(\lambda) = \lambda^2 E_k, \quad E_p(\lambda) = \lambda E_p, \quad E_e(\lambda) = \lambda E_e \qquad \text{(IV-26)}$$

By substituting these expressions into IV-25 and applying the condition IV-24 we are led to the formal virial theorem:

$$2E_k + E_p + E_e = -\lim_{\lambda \to 1} \frac{dE_c(\lambda)}{d\lambda} \qquad \text{(IV-27)}$$

The correlation energy E_c can be obtained from II-13; thus we have

$$E_c = -\alpha_c \int_0^R \rho \left[\ln(1+a_0\rho^{1/3}) + \frac{\sigma a_0 \rho^{1/3}}{\tau + a_0\rho^{1/3}} \right] 4\pi r^2 dr \qquad \text{(IV-28)}$$

With IV-23 we then obtain for $E_c(\lambda)$:

$$E_c(\lambda) = -\alpha_c \int_0^{R/\lambda} \lambda^3 \rho(\lambda r) \left[\ln(1+a_0\lambda\rho^{1/3}(\lambda r)) + \frac{\sigma a_0 \lambda \rho^{1/3}(\lambda r)}{\tau + a_0\lambda\rho^{1/3}(\lambda r)} \right] 4\pi r^2 dr \qquad \text{(IV-29)}$$

We note that we do not obtain a simple expression analogous to IV-26 since the correlation energy, unlike the kinetic, potential, and exchange energies, is not a homogeneous function of ρ ------ consequently $E_c(\lambda)$ cannot be written as a function of λ times the original correlation energy E_c.

If in IV-29 we make the change of variable $r' = \lambda r$, we obtain:

$$E_c(\lambda) = -\alpha_c \int_0^R \rho \left[\ln(1+a_0\lambda\rho^{1/3}) + \frac{\sigma a_0 \lambda \rho^{1/3}}{\tau + a_0 \lambda \rho^{1/3}} \right] 4\pi r'^2 dr' \qquad \text{(IV-30)}$$

where $\rho = \rho(r')$. Differentiating and taking the limit indicated by IV-27 we are led to:

$$-\lim_{\lambda=1} \frac{dE_c(\lambda)}{d\lambda} = \alpha_c \int \rho \left[\frac{a_0\rho^{1/3}}{1+a_0\rho^{1/3}} + \frac{\sigma a_0 \rho^{1/3}}{\tau + a_0\rho^{1/3}} - \frac{\sigma (a_0\rho^{1/3})^2}{(\tau + a_0\rho^{1/3})^2} \right] dv \qquad \text{(IV-31)}$$

By comparing IV-27 with IV-22 we see that it is the above expression which must be added to the TFD virial theorem due to the inclusion of correlation in our model. However, this would lead to a very awkward and physically unclear virial theorem; we are thus motivated to simplify the expression IV-31.

Consequently, we go back to the basic equation III-6 which we recast in the form:

$$\alpha_c \left[\frac{a_0\rho^{1/3}}{1+a_0\rho^{1/3}} - \frac{\sigma(a_0\rho^{1/3})^2}{(\tau+a_0\rho^{1/3})^2} \right] = 5\alpha_k \rho^{2/3} - 4\alpha_e \rho^{1/3} - 3(V-V_0)e - \alpha_c \left[\frac{4\sigma a_0 \rho^{1/3}}{\tau + a_0\rho^{1/3}} + 3\ln(1+a_0\rho^{1/3}) \right] \qquad \text{(IV-32)}$$

If IV-32 is substituted into IV-31 we obtain

$$-\lim_{\lambda\to 1} \frac{dE_c(\lambda)}{d\lambda} = \alpha_c \int \rho \left[\frac{-3\sigma a_0 \rho^{1/3}}{\tau + a_0\rho^{1/3}} - 3\ln(1+a_0\rho^{1/3}) \right] dv + \int \left[5\alpha_k \rho^{5/3} - 4\alpha_e \rho^{4/3} - 3V\rho e + 3V_0 \rho e \right] dv \qquad \text{(IV-33)}$$

which at first sight is even more complicated. However, unlike in IV-31 we can readily identify all terms in IV-33. Thus, comparing with IV-28 we see that the first integral on the right of IV-33 is in fact simply three times the correlation energy E_c. We can similarly identify the remaining terms in IV-33 by noting that

$$E_k = \int \alpha_k \rho^{5/3} dv \quad , \quad E_e = -\alpha_e \int \rho^{4/3} dv \qquad \text{(IV-34)}$$

$$-\int V \rho e\, dv = -\int (V_N + V_e) \rho e\, dv = -e \int \rho (V_N + \tfrac{1}{2} V_e) dv - \frac{e}{2} \int \rho V_e dv$$

$$= E_p + E_{ep} \qquad \text{(IV-35)}$$

where E_p is the total potential energy while E_{ep} is the potential energy due to the electron Coulomb interaction alone. With these identifications, equation IV-33 then reduces to

$$-\lim_{\lambda=1} \frac{dE_c(\lambda)}{d\lambda} = 3\,E_c + 5\,E_k + 4\,E_e + 3\,E_p + 3\,E_{ep} + 3\,V_o e\,N \qquad \text{(IV-35)}$$

By combining this with equation IV-27 we finally obtain the exact virial theorem for our model as follows:

$$3\,E_k + 2\,E_p + 3\,E_e + 3\,E_{ep} + 3\,E_c + 3\,V_o e\,N = 0 \qquad \text{(IV-37}$$

The above represents the generalization of IV-21,22, and must reduce to the TFD virial theorem if we neglect correlations, i.e. if we go to the limit $E_c = 0$, $V_o = V_{oTFD}$. In this limit IV-37 takes the form:

$$3\,E_k + 2\,E_p + 3\,E_e + 3\,E_{ep} + 3\,V_{o_{TFD}} e\,N = 0 \qquad \text{(IV-38)}$$

Comparing with IV-22 we find that the equivalence is by no means apparent. In order to establish the equivalence, we proceed from the TFD virial theorem IV-22. If we now return to the basic TFD equation I-20, multiply it by 3ρ and integrate term by term, we obtain

$$5\alpha_K \int \rho^{5/3} dv - 4\alpha_e \int \rho^{4/3} dv - 3\int (V - V_{0TFD}) e\rho dv = 0 \qquad \text{(IV-39)}$$

Identifying the individual terms by means of IV-34,35, equation IV-39 becomes

$$5\,E_k + 4\,E_e + 3\,E_p + 3\,E_{ep} + 3\,V_{0TFD} e\,N = 0 \qquad \text{(IV-40)}$$

If we now subtract IV-22 from IV-40, or alternately substitute IV-40 into IV-38 and compare with IV-22, we observe that the equivalence is established so that our virial theorem does indeed reduce to the correct TFD limit.

Our final virial theorem IV-37 is somewhat unsatisfactory from a practical viewpoint since, unlike the TF and TFD virial theorems, it unavoidably involves E_{ep} explicitly in addition to E_p. This circumstance arose fundamentally from the fact that E_c is not a homogeneous function of ρ. Once the numerical solution for ψ or ρ is obtained, all energy terms entering into the virial theorem can be directly calculated, with the exception of E_{ep}. We find it possible, however, to eliminate E_{ep} in terms of E_p and the boundary conditions of the solution $\psi(x)$ for a given atom.

To show how this is done, we proceed by writing

$$E_p = E_{np} + E_{ep} \qquad \text{(IV-41)}$$

where E_{np} is the potential energy of the atom due to the interaction of the electrons with the nuclear potential, and is given explicitly by

$$E_{np} = -Ze^2 \int \frac{\rho}{r} dv \qquad \text{(IV-42)}$$

From the differential equation III-14 together with the definition of $\lambda(x)$ we have for ρ the expression

$$\rho = \frac{Z}{4\pi\mu^3} \frac{\psi''(x)}{x} \qquad \text{(IV-43)}$$

where $\psi(x)$ and x are defined by III-11,12. If this is substituted into IV-42, we obtain

$$E_{np} = -\frac{Z^2e^2}{\mu} \int_0^X \psi''(x)\,dx = -\frac{Z^2e^2}{\mu}\left[\tilde{\psi}'(X) - \psi'(0)\right] \qquad \text{(IV-44)}$$

It is possible to simplify this further by making use of the boundary conditions II-18 and II-9, and the definition of ψ. With these we find

$$\psi'(X) = -\frac{\mu}{Ze} V_0 \qquad \text{(IV-45)}$$

and by denoting the initial slope $\psi'(0)$ of the solution for a particular atom or ion by a_1, equation IV-44 becomes, after using IV-41 to eliminate E_{ep}:

$$3E_k + 5E_p + 3E_e + 3E_c - \frac{3Z^2e^2 a_1}{\mu} - 3eV_0(Z-N) = 0 \qquad \text{(IV-46)}$$

For neutral atoms (N = Z) this reduces simply to

$$3\,E_k + 5\,E_p + 3\,E_e + 3\,E_c - \frac{3\,Z^2e^2\,a_1}{\mu} = 0 \qquad \text{(IV-47)}$$

Equation IV-46 represents the desired formulation of the basic virial theorem IV-37 in which E_{ep} has been eliminated in terms of the boundary value a_1. Both are, of course, equally valid. However, once a solution $\psi(x)$ is obtained for a particular atom, a_1 is known automatically, so that the form IV-46, or alternatively IV-47 is more convenient for practical calculations.

We note in passing that while above we were able to obtain E_{np} exactly in terms of the boundary values of ψ at $x = 0$ and $x = X$, this does not appear to be possible for the other energy terms. For the TF case this can indeed be accomplished by a series of partial integrations; however, in our model the complicated nature of the expression III-15 relating ψ and λ precludes this possibility.

C. The Correlation Energy of the Atom.

We desire to obtain an estimate of the total correlation energy of the atom. By this we can mean two different things. On the one hand, we can define the correlation energy of the atom through equation IV-28 where $\rho(r)$ is to be obtained from the solution of our model. It is this meaning which was attached to E_c in our development of the virial theorem. Alternatively, we can define the correlation energy of the atom to be the difference between the total energies of the atom in our model and the TFD model. It can be shown that in actuality the difference between these two definitions is very small, inasmuch as the values of the kinetic, potential, and exchange energies are not appreciably changed from their TFD values by including correlations. The method which we use below to obtain an estimate of E_c implicitly assumes the second of the above definitions.

In order to arrive at an estimate for E_c we shall use as our starting point a technique due to Hulthen (18). Thus we form the derivative dE/dZ where N/Z is kept constant and E is the total energy of the atom:

$$E = \int \epsilon \, dv - Ze^2 \int \frac{\rho}{r} dv - \frac{e}{2} \int \rho V_c dv \qquad \text{(IV-48)}$$

We write:

$$\left.\frac{dE}{dZ}\right|_{\frac{N}{Z}} = \frac{\partial E}{\partial Z} + \frac{\partial E}{\partial N} \frac{dN}{dZ} \qquad \text{(IV-49)}$$

With IV-48, equation IV-49 becomes

$$\left.\frac{dE}{dZ}\right|_{N/Z} = -\int \frac{\rho e^2}{r}\, dv + \frac{\partial E}{\partial N}\,\frac{N}{Z} \qquad \text{(IV-50)}$$

On the other hand, from III-4 we can infer

$$\frac{\partial E}{\partial N} = -V_0 e \qquad \text{(IV-51)}$$

with which IV-50 takes the form:

$$\left.\frac{dE}{dZ}\right|_{N/Z} = -e^2 \int \frac{\rho}{r}\, dv - V_0 e \frac{N}{Z} \qquad \text{(IV-52)}$$

The relation IV-52 holds equally well for the TFD and for our model. If we let unprimed variables represent the values for our model and use primes to denote the corresponding values for the TFD model, we can thus write:

$$\left.\frac{dE_c}{dZ}\right|_{\frac{N}{Z}} = \left.\frac{d(E-E')}{dZ}\right|_{\frac{N}{Z}} = -e^2\left[\int \frac{\rho}{r}\, dv - \int \frac{\rho'}{r}\, dv\right] - \frac{Ne}{Z}(V_0 - V_0') \qquad \text{(IV-53)}$$

The last term on the right-hand side of IV-53 we can evaluate immediately since we have previously calculated V_0, which is given by equation IV-19. The corresponding value V_0' for the TFD model is given by

$$V_0' e = \frac{(Z-N)e^2}{\mu \delta'} + 0.0474\,\frac{e^2}{a_0} \qquad \text{(IV-53')}$$

Inasmuch as we do not know the values of X or X' without recourse to a numerical solution, we shall restrict our attention to the case of neutral atoms. For these, the last term on the right of IV-53 then becomes:

$$-\frac{N}{Z}\, e\, (V_0 - V_0') = -0.0419\, \frac{N}{Z}\, \frac{e^2}{a_0} \qquad \text{(IV-54)}$$

We now turn our attention to the more complicated term in brackets on the right-hand side of IV-53. In order to estimate this term we shall make two assumptions: (1) In Part VI(A) we show that for purposes of calculating the density our model can be approximately represented by a TFD-like equation with a changed value of α_e. We shall assume that this is a sufficiently good approximation for our immediate purpose, so that the term we wish to estimate consists of the difference of two TFD-like terms; (2) for the density we shall make use of an approximate expression derived by Jensen (19) on the basis of the Ritz variational principle.

For the Thomas-Fermi atom Jensen proceeds from the basic equation:

$$\delta(E + N\, e\, V_0) = 0, \qquad N = \int \rho\, dv \qquad \text{(IV-55)}$$

where, in our notation:

$$E = E_p + \alpha_k \int \rho^{5/3} dv \qquad \text{(IV-56)}$$

He then makes the following Ansatz for the density:

$$\rho = \frac{N}{A}\frac{e^{-x}}{x^3}\left(1 + c_1 x + c_2 x^2 + \dots\right)^3$$

with

$$x = \left(\frac{r\lambda}{a_0}\right)^{1/2} Z^{1/6} \qquad \text{(IV-57)}$$

The above density has the desired properties that it decreases exponentially for large r and behaves as $r^{-3/2}$ near the origin. The undetermined coefficients λ, a_1, a_2, etc. are to be determined by the Ritz variational principle. The constant A is fixed by the normalization condition IV-55 and can be written in the form

$$A = \frac{4\pi a_0^3}{\lambda^3 N} P(c_i) \qquad \text{(IV-58)}$$

where $P(c_i)$ is a polynomial of the coefficients c_i alone and does not involve λ :

$$P(c_i) = 2\int_0^\infty e^{-x}\left(1 + c_1 x + c_2 x^2 + \dots\right)^3 x^2 dx \qquad \text{(IV-59)}$$

Jensen found that he obtains a very satisfactory solution by retaining oly c_1 and c_2 in the series IV-57; in fact, c_2 is found to vanish. By substituting IV-57 into IV-56, the total energy for neutral atoms takes the form:

$$E = \left(F_k \lambda^2 - F_p \lambda\right) Z^{7/3} \frac{e^2}{a_0} \qquad \text{(IV-60)}$$

where F_k and F_p are independent of λ, depending only on the coefficients c_i. The coefficients c_1 and λ are finally determined from the extremal relations:

$$\frac{\partial E}{\partial c_1} = 0 \quad , \quad \frac{\partial E}{\partial \lambda} = 0 \qquad \text{(IV-61)}$$

The second of these gives immediately:

$$\lambda = \frac{F_p}{2 F_k} \qquad \text{(IV-62)}$$

For a neutral atom, Jensen found the values $c_1 = 0.265$, $\lambda = 10.91$, $F_p = 0.140$.

Jensen (20) has further extended this method to the TFD atom for which IV-56 is replaced by

$$E = E_p + \alpha_k \int \rho^{5/3} dv - \alpha_e \int \rho^{4/3} dv \qquad \text{(IV-63)}$$

By substituting the density IV-57 into IV-63 it is found that added to the energy expression IV-60 is an exchange term, the total energy now being:

$$E = \left(F_k \lambda^2 - F_p \lambda - \frac{\lambda \alpha_e F_e}{e^2 Z^{2/3}} \right) Z^{7/3} \frac{e^2}{a_0} \qquad \text{(IV-64)}$$

where F_e is found to be given by:

$$F_e = \frac{2}{(4\pi)^{1/3} [P(c_1)]^{4/3}} \int_0^\infty e^{-\frac{4}{3}x} (1 + c_1 x)^4 x \, dx \qquad \text{(IV-65)}$$

Jensen now further assumes that c_1 remains approximately unchanged so that the effect of exchange is manifested only by a changed value of λ. The second of the conditions IV-61 applied to IV-64 gives for the new value of λ :

$$\lambda' = \frac{F_p + \frac{\alpha_e F_e}{e^2 Z^{2/3}}}{2 F_k} = \lambda_0 \left(1 + \frac{\alpha_e}{e^2 Z^{2/3}} \frac{F_e}{F_p} \right) \qquad \text{(IV-66)}$$

where λ_0 corresponds to the TF value given by IV-62. The parameter F_e is calculated to be $0.021\ e^2/\varkappa_e$ with $c_1 = 0.265$.

As outlined above, our approach will now consist of representing our model by the TFD-like approximation discussed in Part VI(a). Further, we shall assume for the density Jensen's expression, where for our case λ is given by:

$$\lambda = \lambda_0 \left(1 + \frac{\varkappa_e'}{e^2 Z^{2/3}} \frac{F_e}{F_\rho} \right) \tag{IV-67}$$

and where $\varkappa_e'$ is defined by equation VI-6. Accordingly, in the expression IV-53 we shall assume both ρ and ρ' to be of the form IV-57 with λ given by IV-67 and IV-66, respectively.

We must now evaluate the integral:

$$J = e^2 \int \frac{\rho}{r} dv \tag{IV-68}$$

Substituting for ρ and r from IV-57, we obtain

$$J = \frac{2e^2}{a_0} Z^{4/3} \lambda \frac{I(c_1)}{P(c_1)} \tag{IV-69}$$

where

$$I(c_1) = \int_0^\infty e^{-x} (1+c_1 x)^3 dx = \sum_{\nu=0}^{3} \binom{3}{\nu} c_1^\nu \int_0^\infty x^\nu e^{-x} dx$$

$$= \sum_{\nu=0}^{3} \binom{3}{\nu} c_1^\nu \nu! \tag{IV-70}$$

and

$$P(c_1) = 2\int_0^\infty e^{-x} (1+c_1 x)^3 x^2 dx = 2 \sum_{\nu=0}^{3} \binom{3}{\nu} c_1^\nu (\nu+2)! \tag{IV-71}$$

With the result IV-69 we can thus write:

$$-e^2\left[\int \frac{\rho}{r}dv - \int \frac{\rho'}{r}dv\right] = -\frac{Ze^2}{a_0} Z^{4/3} \frac{I(c_1)}{P(c_1)} (\lambda - \lambda') \qquad \text{(IV-72)}$$

which in view of the relations IV-66,67 becomes:

$$-e^2\left[\int \frac{\rho}{r}dv - \int \frac{\rho'}{r}dv\right] = -\frac{Z}{a_0} Z^{2/3} \frac{I(c_1)}{P(c_1)} \lambda_0 \frac{Fe}{F_p}\left(\frac{\alpha_e'}{\alpha_e} - 1\right)\alpha_e \qquad \text{(IV-73)}$$

With $c_1 = 0.265$, we calculate $I(c_1) = 2.328$, $P(c_1) = 28.12$, and putting in the remaining numerical parameters calculated previously we obtain explicitly:

$$-e^2\left[\int \frac{\rho}{r}dv - \int \frac{\rho'}{r}dv\right] = -0.0924\, Z^{2/3}\ [Ry] \qquad \text{(IV-74)}$$

By substituting the results IV-54 and IV-74 into IV-53, and integrating, we finally obtain

$$E_c = -(0.0554\, Z^{5/3} + 0.0838\, Z) \quad Ry \qquad \text{(IV-75)}$$

The above formula gives the total correlation energy of the atom in the framework of our approximation. The exchange energy of the atom in the TFD model is calculated to be:

$$E_e = -0.46\ Z^{5/3} \quad Ry$$

We observe that the correlation energy is of the order of 13 to 30 per cent of the exchange energy, the actual ratio being a function of Z.

In conclusion, we note that if the expression IV-53 is substituted into the virial theorem IV-37 and the resulting expression is compared with the TFD virial theorem IV-38, the only additional term arises from the term in brackets of equation IV-53; the second term involving the V_0's gives no contribution. That this must be true can also be seen in a very simple way. For neutral atoms, the term involving the V_0's corresponds to a part E' of the correlation energy which is proportional to Z, i.e.

$$E_c' = \kappa' Z = \kappa' \int \rho \, dv$$

However, this term is unchanged by the similarity transformation, so that

$$E_c'(\lambda) = E_c', \qquad \frac{dE_c'(\lambda)}{d\lambda} = 0$$

and consequently it can give no additional contribution to the virial theorem.

D. The Fermi-Amaldi Correction.

One of the basic inadequacies of the original Thomas-Fermi model is that the electrons interact with themselves, i.e. in computing the energy the potential V_e acting on a particular electron is taken to be the potential due to all electrons including the particular electron in question.

In order to correct this situation, at least in a crude way, Fermi and Amaldi (16) simply assign to each electron of the atom the individual density ρ/N, where ρ is the total electron density within the atom, and then assume that the potential acting on a particular electron is that due to the other N-1 electrons. Thus, the electron potential $V_e^*(r)$ acting on each electron is written as

$$V_e^*(r) = \frac{N-1}{N} V_e(r) \qquad \text{(IV-78)}$$

where $V_e(r)$ is the total electron potential as defined before by equation I-8 or IV-4. The result of incorporating this modification into the TF theory in the standard manner outlined in Part I(B) is that in place of I-11 we now obtain the equation:

$$(V - V_0)\, e - e\frac{V_e}{N} = \frac{5}{3} \alpha_K \rho^{2/3} \qquad \text{(IV-79)}$$

where V, as before, is defined by $V = V_N + V_e$. In this approach, it is thus the additional potential term $-e\,V_e/N$, known as the Fermi-Amaldi correction, which serves to eliminate the electron self-interaction. Without going into detail, it can easily be

shown that the equation corresponding to I-13 becomes

$$\nabla^2(V^*-V_0) = 4\pi e\left(\frac{3e}{5\alpha_K}\right)^{3/2}\frac{N-1}{N}(V^*-V_0)^{3/2} \qquad \text{(IV-80)}$$

where

$$V^* = V_N + V_e^* = V - \frac{1}{N}V_e \qquad \text{(IV-81)}$$

By now applying the transformations:

$$\varphi(x) = \frac{r}{ze}(V^*-V_0) \qquad \text{(IV-82)}$$

$$x = r/\mu^* \quad , \quad \mu^* = \mu\left(\frac{N}{N-1}\right)^{2/3} \qquad \text{(IV-83)}$$

equation IV-80 becomes:

$$\varphi'' = \frac{\varphi^{3/2}}{x^{1/2}} \qquad \text{(IV-84)}$$

which is formally equivalent to the original TF equation I-18, but differs from the former in that φ and x are related differently to V and r. The boundary conditions for φ take the form

$$\varphi(0) = 1 \quad , \quad \varphi(\chi) = 0 \qquad \text{(IV-85)}$$

$$\varphi(\chi) - \chi\varphi'(\chi) = \frac{Z-N}{Z} + \frac{1}{Z} \qquad \text{(IV-86)}$$

Equation IV-84 together with IV-85, 86 and the definitions IV-81,82,83 constitutes the so-called Fermi-Amaldi equation. The Fermi-Amaldi equation, in view of the boundary condition IV-85, possesses the same family of solutions as the TF equation; however, the particular

solution for a given atom will be different due to the difference in the boundary conditions I-19 and IV-86. Further, the potential and radius are related differently to φ and x. In fact, it is to be noted from IV-82 that the potential V(r) is not directly obtainable from $\varphi(x)$, ulike in the TF case. The same is not true of the density which is given explicitly by

$$\rho = \frac{Z}{4\pi\mu^{*3}} \frac{N}{N-1} \frac{\varphi''}{x} \qquad \text{(IV-87)}$$

Fermi and Amaldi (16) proceed to solve equation IV-84 approximately by making the Ansatz

$$\varphi = \varphi_0 + k\eta_0 \qquad \text{(IV-87')}$$

where φ_0 is the ordinary TF solution, and $\eta_0(x)$ is a known tabulated function (Cf. for example ref. 4) with the properties $\eta_0(0) = 0$, $\eta_0'(0) = 1$. The coefficient k is then to be determined from the boundary conditions at X.

If we now progress to the TFD model, the situation is somewhat different. For an extended electron gas of sufficiently high density, the exchange energy includes a self-exchange term which cancels the electrostatic self-interaction discussed previously. Thus, in the interior of the TFD atom the electrostatic self-interaction is compensated by inclusion of the exchange energy in the model, so that we can no longer justify the Fermi-Amaldi correction. However, at the edge of the atom where the electron density is low this compensation is not complete, and the Fermi-

Amaldi term again becomes necessary in order to eliminate the self-interaction. Jensen (21) has described a way to combine these effects for the case of the TFD model, which we shall here sketch in outline. To this purpose, he replaces the exchange energy term I-5 by a function which in the interior of the atom is equal to the exchange energy term, but at the edge approaches the Fermi-Amaldi term. Thus, in essence, the atom is described by the usual TFD equation I-21 in the interior, but by the Fermi-Amaldi equation IV-80 near the outer edge of the atom. The value of the electron density $\rho_0 = \rho(r)$ at the edge of the atom is assumed to be maintained at the original TFD model value; the value of R changes, however. Then, as far as the calculation of the density is concerned, one can to a sufficient degree of accuracy replace the TFD equation with the Fermi-Amaldi equation with suitably changed boundary conditions. However, any other parameters of the atom, which depend significantly on the interior of the atom, such as the energy, must be calculated from the original TFD equation. An extended discussion of the justification of this procedure is to be found in the paper of Jensen (21).

The considerations of Jensen apply equally well to our model, since the exchange and correlation energies are physically similar in nature, both describing the tendency of electrons to stay away from each other with a consequent lowering of the energy. We can therefore incorporate the Fermi-Amaldi correction in an exactly analogous manner, and calculate the density on the basis of the Fermi-Amaldi equation IV-84 with the boundary conditions:

$$\varphi(0) = 1 \tag{IV-88}$$

$$\varphi(X) = \gamma X \quad ; \quad \gamma = \frac{5}{3}\,\frac{\alpha_k \mu^*}{z e^2}\,\rho_0^{2/3} \tag{IV-89}$$

$$\varphi(X) - X\varphi'(X) = \frac{z-N}{z} + \frac{1}{z} \tag{IV-90}$$

The boundary condition IV-89, in which ρ_0 is to be replaced by the previously calculated value IV-16, is obtained directly from IV-82 and IV-79.

Equation IV-84, as in the TF and TFD cases, can approximately be solved by the Ansatz IV-87, in terms of which the above boundary conditions become

$$\psi_0(X) + k\eta_0(X) = \gamma X \tag{IV-91}$$

$$\psi_0(X) - X\psi_0'(X) + k\left[\eta_0(X) - X\eta_0'(X)\right] = \frac{z-N+1}{z} \tag{IV-92}$$

Equations IV-91,92 represent two simultaneous equations for the unknown parameters k and X.

It is evident that the Fermi-Amaldi correction is of less importance in our model than in the TFD and particularly in the TF model, since the effect of the correlation term is in the same direction as that of the exchange term and thus helps to compensate for the self-interaction of the electrons, whose removal was the original raison-d'être of the Fermi-Amaldi correction.

V. THEORY OF THE COMPRESSED ATOM.

Our considerations up to this point have dealt exclusively with the isolated free atom, defined by zero pressure at the boundary. In this part we shall show how the solutions of the model may be adapted to apply to matter in bulk under pressure, and derive formulas for the pressure and compressibility of elements as a function of mass density. Finally, we shall obtain the generalization of the virial theorem for atoms under external pressure.

We consider matter in bulk but restrict our attention to the region of very high pressures. In this region the valence electrons are little distinguished from the core electrons so that all electrons can be treated together by the statistical method. The latter is particularly suited for this case inasmuch as the shell structure of the electrons becomes relatively unimportant; also, since the electron density is everywhere high, the statistical assumption of many electrons per unit volume is better satisfied.

At very high pressures the atoms, both in the solid and liquid state, assume a very symmetric distribution. Consequently, as is usually done, we can attribute to each atom a spherical elementary cell of radius R and reduce the problem of matter in bulk to the consideration of the elementary cell. We shall further consider each cell as electrically neutral, i.e. confine our attention to unionized matter. For a specified mass density, the problem is then to find $V(r)$ and $\rho(r)$ for each cell, and to derive a relation between the large-scale properties of pressure and mass density.

The main difference between this case and the case of the free atom is that by specifying the mass density of the bulk matter, we specify the radius R of the elementary cell so that R is no longer determined by the minimum condition for the total energy, i.e. by IV-1, or the boundary condition III-20.

As before, the potential V(r) in the cell must satisfy the boundary condition

$$\lim_{r \to 0} r\, V(r) = Z e \qquad \text{(V-1)}$$

and the condition obtained from symmetry:

$$\left.\frac{dV}{dr}\right|_{r=R} = 0 \qquad \text{(V-2)}$$

Thus, the solutions for the elementary cell are again obtained from the equations III-14,15,16:

$$\psi''(x) = \frac{\lambda^3(x)}{x^{1/2}} \qquad \text{(V-3)}$$

with the now changed boundary conditions:

$$\psi(0) = 1, \qquad X\,\psi'(X) = \psi(X) \qquad \text{(V-4)}$$

For a given mass density, X is specified, and the correct solution of the family of solutions of $\psi(x)$ obtained previously for the free atom is the one which satisfies the second of the boundary conditions V-4 for the specified value of X.

The potential is related to $\psi(x)$ by

$$V = \frac{Ze}{r}\,\psi(x) + V_0 \qquad \text{(V-5)}$$

As we have seen in Part IV(A), V_o was determined for the free atom from the minimum condition $\delta E/\delta R = 0$ which now no longer applies. Following Slater and Krutter (22), we shall determine V_o for the compressed atom from the condition that at the nucleus the potential $V(r)$ must be independent of R, and hence of the pressure. If, for a given value of Z, we let $\psi_f(x)$, V_{of} represent the solution for a free neutral atom, and ψ, V_o the corresponding values for the compressed atom, and write the expansion of $\psi(x)$ near the origin (Cf. equation VI-17 in part VI(A)) in the form:

$$\psi(x) = 1 + \psi'(o)\, x + 0\,(x^2) \qquad (V\text{-}6)$$

this condition becomes

$$\frac{Ze}{\mu x} + V_o + \frac{Ze}{\mu}\psi'(0) = \frac{Ze}{\mu x} + V_{of} + \frac{Ze}{\mu}\psi_f'(0)$$

or

$$V_o = V_{of} + \frac{Ze}{\mu}\left[\psi_f'(0) - \psi'(0)\right] \qquad (V\text{-}7)$$

For a specified value of X for the cell, $\psi'(o)$ is known once the solution determined by the boundary conditions V-4 is obtained, and V_o and the potential can then be found by equations V-7 and V-5, respectively.

The pressure of a system can be defined in general by

$$P = -\frac{dE}{dV} \qquad (V\text{-}8)$$

where dV represents an adiabatic expansion, and E is the total

energy. If we apply this to our elementary cell, we obtain the pressure at the edge of the cell as:

$$P = -\frac{1}{4\pi R^2}\frac{dE}{dR} \qquad \text{(V-9)}$$

where R is the radius of the cell. The expression dE/dR for our model we have calculated previously in part IV(A). If we compare V-9 and IV-12, we obtain the following expression for the pressure:

$$P = \frac{2}{3}\alpha_k \rho_0^{5/3} - \frac{1}{3}\alpha_e \rho_0^{4/3} - \alpha_c\left[\frac{1}{3}\frac{a_0\rho_0^{4/3}}{1+a_0\rho_0^{1/3}} + \right.$$

$$\left. + \frac{1}{3}\frac{\sigma a_0 \rho_0^{4/3}}{\tau + a_0\rho_0^{1/3}} - \frac{1}{3}\frac{\sigma a_0^2 \rho_0^{5/3}}{(\tau + a_0\rho_0^{1/3})^2}\right] \qquad \text{(V-10)}$$

where ρ_0 is the electron density at the edge of the cell, which, however, is no longer given by the value IV-16 for a free atom.

This completes the theoretical development. In order to obtain an explicit equation of state between the bulk properties of pressure and mass density, we must proceed as follows. The mass density ρ_m expressed in g/cc is related to the radius of the elementary cell by:

$$R = \left(\frac{3A}{4\pi\mathcal{N}}\right)^{1/3}\frac{1}{\rho_m^{1/3}} \qquad \text{(V-11)}$$

where A is the atomic weight of the particular element and $\mathcal{N}$ is Avogadro's numer. Equation V-11 defines R for a given value of ρ_m. We find X simply from

$$X = R/\mu \qquad \text{(V-12)}$$

With this value of X , the density of electrons ρ_0 at the edge of the cell is then obtained from

$$\rho_0 = \frac{Z}{4\pi\mu^3} \frac{\psi''(X)}{X} \qquad \text{(V-13)}$$

where $\psi(x)$ is that solution of the family of solutions of V-3 which satisfies the conditions V-4 for the given value of X. By substituting the value of ρ_0 found by V-13 into V-10, we finally obtain the pressure corresponding to the mass density ρ_m.

We can further find the compressibility as a function of ρ_m or of the pressure in a similar manner. The compressibility κ is defined by

$$\frac{1}{\kappa} = - V \frac{dP}{dV} \qquad \text{(V-14)}$$

which, in terms of X, becomes

$$\frac{1}{\kappa} = - \frac{X}{3} \frac{dP}{dX} \qquad \text{(V-15)}$$

Above we have outlined how to obtain P(X). The derivative dP/dX is probably best found numerically once we have obtained P(X). However, it is possible to give an explicit expression for κ in terms of the solution $\psi(x)$. To this purpose we write

$$\frac{dP}{dX} = \frac{dP}{d\rho_0} \frac{d\rho_0}{dX} \qquad \text{(V-16)}$$

which in view of V-13 allows us to write V-15 in the form:

$$\frac{1}{K} = \frac{-Z}{12\pi\mu^3}\left(\frac{dP}{d\rho_0}\right)\left[\psi'''(x) - \frac{\psi''(x)}{x}\right] \qquad \text{(V-17)}$$

The derivative $dP/d\rho_0$, can be found straightforwardly from equation V-10, and we are thus able to find the compressibility of elements as a function of either density or pressure.

Finally, we shall obtain the generalization of the virial theorem IV-37 for the case of compressed matter, and show that it becomes:

$$3\,E_k + 2\,E_p + 3\,E_e + 3\,E_{ep} + 3\,E_c + 3\,V_o eN = -3\,P\,v \qquad \text{(V-18)}$$

where all quantities apply to the elementary cell. In order to demonstrate V-18, we proceed in a fashion similar to that of Part IV(B). We again form the family $E(\lambda)$:

$$E(\lambda) = E(\rho_\lambda)$$

where ρ_λ and $E(\rho_\lambda)$ are as defined in Part IV(B). Next, we find the limit $\lim_{\lambda=1} dE(\lambda)/d\lambda$ which from equations IV-25,27,36 is known to be

$$\left.\frac{dE(\lambda)}{d\lambda}\right|_{\lambda=1} = -3\,E_k - 2\,E_p - 3\,E_e - 3\,E_{ep} - 3\,E_c - 3\,V_o e\,N \qquad \text{(V-19)}$$

On the other hand, we can also write

$$\left.\frac{dE(\lambda)}{d\lambda}\right|_{\lambda=1} = \lim_{\lambda=1}\frac{dE(\lambda)}{d(R/\lambda)}\frac{d(R/\lambda)}{d\lambda} = \lim_{\lambda=1}\frac{-R}{\lambda^2}\frac{dE(\lambda)}{d(R/\lambda)} \qquad \text{(V-20)}$$

If we now assume that in the last expression of V-20 we can interchange

the limiting and differential operations, V-20 becomes simply

$$\left.\frac{dE(\lambda)}{d\lambda}\right|_{\lambda=1} = -R\frac{dE}{dR} \qquad \text{(V-21)}$$

which, together with V-19 and V-9 immediately leads to the desired virial theorem V-18. However, it is by no means obvious that the differential and limiting operations are in fact interchangeable; consequently we shall derive V-18 in a more circuitous but less ambiguous manner.

Written out explicitly, $E(\lambda)$ becomes

$$E(\lambda) = \int_0^{R/\lambda}\Big\{\alpha_k\rho_\lambda^{5/3} - \alpha_e\rho_\lambda^{4/3} - \alpha_c\Big[\rho_\lambda \ln(1+a_0\rho_\lambda^{1/3}) + \frac{\sigma a_0\rho_\lambda^{4/3}}{\tau + a_0\rho_\lambda^{1/3}}\Big] - V_N e\rho_\lambda\Big\}dv + \frac{e^2}{2}\int_0^{R/\lambda}\int_0^{R/\lambda}\frac{\rho_\lambda(r)\rho_\lambda(r')}{|\vec{r}-\vec{r}'|}\,dv\,dv' \qquad \text{(V-22)}$$

Differentiating, we obtain by the usual rules for differentiating an integral:

$$\frac{dE(\lambda)}{d\lambda} = -\frac{R}{\lambda^2}\frac{dE(\lambda)}{d(R/\lambda)} = -4\pi\left(\frac{R}{\lambda}\right)^2\frac{R}{\lambda^2}\Big\{\alpha_k\rho_\lambda^{5/3} - \alpha_e\rho_\lambda^{4/3} - \alpha_c\Big[\rho_\lambda\ln(1+a_0\rho_\lambda^{1/3}) + \frac{\sigma a_0\rho_\lambda^{4/3}}{\tau + a_0\rho_\lambda^{1/3}}\Big] - e\rho_\lambda(V_N + V_e(\lambda))\Big\}_{r=R}^{+}$$

$$+\int_0^{R/\lambda}\frac{\partial\rho_\lambda}{\partial\lambda}\Big\{\frac{5}{3}\alpha_k\rho_\lambda^{2/3} - \frac{4}{3}\alpha_e\rho_\lambda^{1/3} - \alpha_c\Big[\frac{1}{3}\frac{a_0\rho_\lambda^{1/3}}{1+a_0\rho_\lambda^{1/3}} + \ln(1+a_0\rho_\lambda^{1/3}) + \frac{4}{3}\frac{\sigma a_0\rho_\lambda^{1/3}}{\tau + a_0\rho_\lambda^{1/3}} - \frac{1}{3}\frac{\sigma a_0^2\rho_\lambda^{2/3}}{(\tau + a_0\rho_\lambda^{1/3})^2}\Big] - V_N e - V_e(\lambda)e\Big\}dv \qquad \text{(V-23)}$$

where we have made use of IV-4. For $\lambda = 1$, the integral of expression V-23 becomes

$$\int_0^R \left|\frac{\partial \rho_\lambda}{\partial \lambda}\right|_{\lambda=1} \left\{ \frac{5}{3}\kappa_K \rho^{2/3} - \frac{4}{3}\kappa_e \rho^{1/3} - V_e - \kappa_c \left[\frac{1}{3}\frac{a_0 \rho_\lambda^{1/3}}{1+a_0\rho_\lambda^{1/3}} + \right.\right.$$

$$\left.\left. + \ln(1+a_0\rho^{1/3}) + \frac{4}{3}\frac{\sigma a_0 \rho^{1/3}}{\tau + b_0 \rho^{1/3}} - \frac{1}{3}\frac{\sigma a_0^2 \rho^{2/3}}{(\tau + a_0\rho^{1/3})^2} \right] \right\} dV \qquad \text{(V-24)}$$

Referring back to III-6, we see that V-24 is simply equal to

$$-4\pi V_0 e \int_0^R \left|\frac{\partial \rho_\lambda}{\partial \lambda}\right|_{\lambda=1} r^2 dr \qquad \text{(V-25)}$$

If we now take note of the normalization condition

$$\int_0^{R/\lambda} 4\pi r^2 \rho_\lambda \, dr = Z \qquad \text{(V-26)}$$

and differentiate V-26 with respect to λ, we obtain

$$-\frac{4\pi R^3}{\lambda^4}\rho_\lambda(R/\lambda) + \int_0^{R/\lambda} 4\pi r^2 \frac{\partial \rho_\lambda}{\partial \lambda} dr = 0 \qquad \text{(V-27)}$$

Taking the limit $\lambda = 1$ of equation V-27, we find that the expression V-25 becomes

$$-4\pi V_0 e R^3 \rho_0 \qquad \text{(V-28)}$$

On the other hand, after taking the limit $\lambda = 1$ of the first term on the right-hand side of V-23, we have

$$-4\pi R^3 \left\{ \alpha_k \rho_0^{5/3} - \alpha_e \rho_0^{4/3} - \alpha_c \left[\rho_0 \ln\left(1 + a_0 \rho_0^{1/3}\right) + \right.\right.$$

$$\left.\left. + \frac{\sigma a_0 \rho_0^{4/3}}{\tau + a_0 \rho_0^{1/3}} \right] - V(R) e \rho_0 \right\} \qquad \text{(V-29)}$$

By now referring back to IV-11 we see that V-29 becomes

$$4 \pi R^3 e \, V_0 \rho_0 = R \frac{dE}{dR} \qquad \text{(V-30)}$$

Substituting V-30 and V-28 into V-23, we finally obtain

$$\left. \frac{dE(\lambda)}{d\lambda} \right|_{\lambda=1} = -R \frac{dE}{dR} \qquad \text{(V-31)}$$

which is identical to the relation V-21 which we set out to prove, and which as shown leads to the desired virial theorem V-18.

A similar calculation shows that V-18 reduces to the correct TFD limit for a compressed atom, namely:

$$2 E_k + E_p + E_e = 3 P v \qquad \text{(V-32)}$$

VI. METHODS OF SOLUTION

We now proceed to the problem of obtaining the solution of the system of basic equations describing our model. An approximate method for solving the equations is discussed in Section A. In section B we derive a semi-convergent expansion for $\Psi(x)$ which is valid near the origin. In the final analysis, the system III-(14-20) must be solved numerically; this has been done on the Burroughs computer for five selected elements. A few comments regarding the numerical solution procedure are included in section C; complete tables of the solutions obtained are to be found in the Appendix.

A. Approximate Solution.

The exact system of equations III-(14-20) based on our expression II-12 for the correlation energy is very complicated. In order to gain an idea of the general effect of correlation, we shall here obtain an approximate solution, showing that to first order our model is equivalent to a TFD model with a changed value of χ_e.

This method is based on an observation of Gombas (10) that, as far as the calculation of the electron density is concerned, the effect of correlation is appreciable only in the outermost region of the atom and can be neglected in the inner regions where even exchange effects which are larger do not appreciably influence $\rho(r)$. The principle of the method is then to replace

the function $\bar{u}_c$ given by I-12 by an analytically simpler expression which is valid at $r = R$ or $\rho = \rho_0$.

Thus, we expand $\bar{u}_c$ in a Taylor series about ξ_0, keeping only first order terms, i.e. we replace $\bar{u}_c(\xi)$ by an approximation $\bar{w}_c(\xi)$ given by

$$\bar{w}_c(\xi) = \bar{u}_c(\xi_0) + \zeta_0(\xi - \xi_0)$$

where (VI-1)

$$\zeta_0 = \zeta(\xi_0) = \left.\frac{d\bar{u}_c(\xi)}{d\xi}\right|_{\xi=\xi_0}$$

and where ξ_0 represents the value of $\xi = a_0\rho^{1/3}$ at the edge of the atom and is given for our model by equation IV-15.

Equation VI-1 can be written in the more convenient form:

$$\bar{w}_c(\xi) = \zeta_0\xi + k \quad ; \quad k = \bar{u}_c(\xi_0) - \zeta_0\xi_0 \qquad \text{(VI-2)}$$

We have thus approximated the function II-12 simply by a straight line, namely the slope of $\bar{u}_c(\xi)$ at $\xi = \xi_0$. However, in so doing, we have used the exact theory to determine ξ_0.

The total energy density of the electron gas corresponding to VI-2 becomes

$$\varepsilon = \alpha_k\rho^{5/3} - \alpha_e\rho^{4/3} + \zeta_0 a_0\rho^{4/3} + k\rho \qquad \text{(VI-3)}$$

As can easily be verified, the corresponding approximation to the model equation III-6 becomes

$$(V - V_0)e = \frac{5}{3}\alpha_k\rho^{2/3} - \frac{4}{3}\alpha_e\rho^{1/3} + \frac{4}{3}\zeta_0 a_0\rho^{1/3} + k \qquad \text{(VI-4)}$$

It is now seen that the term k is irrelevant since it can be absorbed in the undetermined Lagrange multiplier by writing

$$V_0' = V_0 + k/e \qquad \text{(VI-5)}$$

which then changes the value of V_0 from that previously obtained. Alternatively, it is clear physically that the term k will not affect the solution for $\rho(r)$ since it corresponds to a constant background potential k/e. If we now define

$$\alpha_e' = \alpha_e - \zeta_0 a_0 \qquad \text{(VI-6)}$$

equation VI-4 becomes

$$(V - V_0')\, e = \frac{5}{3}\alpha_K \rho^{2/3} - \frac{4}{3}\alpha_e' \rho^{1/3} \qquad \text{(VI-7)}$$

which is seen to be formally equivalent to the TFD equation I-20, but with α_e replaced by α_e'. Thus, in this approximation, we can avail ourselves of all previous results obtained for the TFD atom in order to derive results for corresponding atoms in our model.

The quantity ζ_0 can be calculated from the known expression for u_c and the previously derived value of β_0. The result is

$$\zeta_0 = -0.1255\ \frac{e^2}{a_0} \qquad \text{(VI-8)}$$

and thus

$$\alpha_e' = 0.8641\, e^2 \qquad \text{(VI-9)}$$

The above approximation must now be checked for internal consistency. Thus, for the TFD atom, $\rho_{0\,TFD}$ is given by

$$\rho_{0\,TFD}^{1/3} = \frac{\alpha_e}{2\alpha_k} \qquad \text{(VI-10)}$$

If the above approximation is to be self-consistent, the value for ρ_0 previously obtained for our model and given by IV-16 must also be reproduced by VI-10 with α_e again replaced by α_e'. We note that the transformation $\alpha_e \rightarrow \alpha_e'$ obtains already in the expression VI-3 for $\mathcal{E}$. If VI-3 is now used to determine ρ_0 by the method of Part IV(A), the term $k\rho$ corresponding to the constant potential naturally does not contribute so that $\rho_{0\,TFD}$ is indeed given by VI-10 with α_e replaced by α_e'. Thus, the approximation is self-consistent.

Since α_e enters into the TFD equation, every known solution of the TFD equation corresponds to a solution of our model represented by the above approximation. Referring to I-23,24 we observe that the equivalence can be written as

$$\frac{2\alpha_e}{3e^2(4\pi Z^2)^{1/3}} = \frac{2\alpha_e'}{3e^2(4\pi Z'^2)^{1/3}}$$

Consequently, a TFD solution for the density $\rho(r)$ for an atom of atomic number Z corresponds within the framework of the above approximation to the solution in our model for an atom with atomic number

$$Z' = Z\left(\frac{\alpha_e'}{\alpha_e}\right)^{3/2} \qquad \text{(VI-11)}$$

The simplification gained is of course enormous. However the approximation is admittedly crude. Furthermore, it can be used only for the calculation of the density; in order to obtain the energy and similar parameters of the atom, the exact expressions are required.

Inasmuch as it is our intention to solve the exact system of equations numerically, we shall not pursue the above approximation further. The purpose for including it here is to elucidate the nature of the correlation correction, and to be able to use it in approximate estimates.

B. Expansion near the Origin.

For the purpose of the numerical integration of the equation III-14 it is convenient to have available an expansion for $\psi(x)$ near the origin, since the second derivative $\psi''(x)$ diverges near the origin as $x^{-\frac{1}{2}}$. Such an expansion will also show how correlation affects the potential near the nucleus.

For reference and later comparison we cite the known expansions for the TF and TFD solutions to order x^3, the latter being obtained from Feynman et al (12):

$$\psi_{TF} = 1 + a_1 x + \frac{4}{3} x^{3/2} + \frac{2}{5} a_1 x^{5/2} + \frac{1}{3} x^3 \qquad \text{(VI-12)}$$

$$\psi_{TFD} = 1 + a_1 x + \frac{4}{3} x^{3/2} + \frac{3}{4} \beta x^2 + \left(\frac{2}{5} a_1 + \frac{\beta^2}{5}\right) x^{5/2} + \left(\frac{1}{3} + \frac{a_1 \beta}{4} + \frac{\beta^3}{48}\right) x^3 \qquad \text{(VI-13)}$$

where β is as defined in equation III-15, and a_1 in both cases is the arbitrary slope at the origin which is not defined by the second-order differential equation or the boundary conditions at the origin.

The above expansions can be obtained simply by making an Ansatz for $\psi(x)$ as a series in half-powers of x with undetermined coefficients, and determining the coefficients by substituting into the TF or TFD equation. The solution thus obtained is strictly formal, and nothing is known about its uniqueness or convergence. On the other hand, as shown by the author (23), both the uniqueness

and convergence is automatically demonstrated if the solution is obtained by extending the well-known Picard method in the theory of first order differential equations.

We begin by integrating equation III-14 twice with respect to x and obtain in view of III-17:

$$\psi(x) = 1 + a_1 x + \int_0^x \int_0^\xi \frac{\lambda^3(\eta)}{\eta^{1/2}} \, d\xi \, d\eta \qquad \text{(VI-14)}$$

where a_1 is the arbitrary slope $\psi'(0)$ at the origin. By making use of the following identity which can be verified by a simple integration by parts:

$$\int_0^x \int_0^\xi g(\eta) \, d\eta \, d\xi = \int_0^x (x-\eta) g(\eta) \, d\eta \qquad \text{(VI-15)}$$

we obtain:

$$\psi = 1 + a_1 x + \int_0^x \frac{(x-\eta)}{\eta^{1/2}} \lambda^3(\eta) \, d\eta \qquad \text{(VI-16)}$$

By substituting successive approximations of λ into the integrand of VI-16 we can thus obtain successive approximations of ψ. The advantage of this method for generating successive approximations for ψ from those of λ lies in the fact that we obtain three higher orders than if we calculated ψ directly from λ by means of equation III-15.

Since we know $\lambda(0) = 1$, we can use $\lambda = 1$ as the zero-order approximation for $\lambda(x)$. Substituting this into VI-16

and performing the integration leads to:

$$\psi = 1 + a_1 x + \frac{4}{3} x^{3/2} \qquad \text{(VI-17)}$$

to order $x^{3/2}$. To find the next term in the expansion for λ we can go back to the horribly complicated equation III-22. If we solve III-22 for $\lambda''(x)$ and then substitute the zero-order behaviour $\lambda(0) = 1$, we find after much tedious algebra:

$$F'(\xi) \to \frac{x^{1/2}}{\epsilon} \quad , \quad F''(\xi) \to -\frac{x}{\epsilon^2} \quad , \quad \lambda''(x) \to \frac{-\beta}{8 x^{3/2}} \qquad \text{(VI-18)}$$

as $x \to 0$. Knowing the behaviour of $\lambda''(x)$ in the limit $x \to 0$ we can thus write the next order for $\lambda(x)$:

$$\lambda(x) = 1 + \frac{\beta}{2} x^{\frac{1}{2}} \qquad \text{(VI-19)}$$

If we in turn substitute this into VI-16, expand to order $\eta^{\frac{1}{2}}$ and integrate, we find the next order term for the ψ-expansion:

$$\psi = 1 + a_1 x + \frac{4}{3} x^{3/2} + \frac{3}{4} \beta x^2 \qquad \text{(VI-20)}$$

It would now appear to be reasonable to make an Ansatz for λ of the form

$$\lambda = 1 + \frac{\beta}{2} x^{\frac{1}{2}} + b_2 x + b_3 x^{3/2} + \ldots \qquad \text{(VI-21)}$$

To determine the coefficients, we can proceed by differentiating III-15 and using the resulting equation together with III-15 to eliminate the divergent logarithmic term. In this manner we obtain the equation:

$$\psi'(x) = 2\lambda\lambda' - \beta x^{1/2}\lambda' + \frac{\psi}{x} - \frac{\lambda^2}{x} + \frac{\beta\lambda}{2x^{1/2}} -$$

$$- \gamma \in \mathfrak{F}'(\xi)\frac{(2x\lambda' - \lambda)}{2x^{1/2}} \qquad \text{(VI-22)}$$

Since ψ is known to a higher order than λ, we can expand VI-22 consistently to any given order of λ and hope to determine the coefficients of the λ-expansion. It is found, however, that when VI-21 and VI-20 are substituted into VI-23, we obtain for the constant term the inconsistent equation $\gamma = 0$. This shows that the Ansatz VI-21 is analytically inconsistent. In fact, it is found that the expression for $\lambda(x)$ must include in addition to $b_2 x$ another term giving a constant first derivative. Such a term is provided by $(x \ln x)$. Consequently, we shall instead of VI-21 make the Ansatz

$$\lambda(x) = 1 + \frac{\beta}{2} x^{\frac{1}{2}} + x(b_2 + b_3 \ln x) + x^{3/2}(b_4 + b_5 \ln x) \qquad \text{(VI-23)}$$

where we have included a trial function for the next order as well. The coefficients are calculated as follows. First, we substitute the above expression into VI-16, expand $\lambda^3(\eta)$ to order $\eta^{3/2}$ and perform the integrations to obtain ψ, which after much algebra is found to be

$$\psi(x) = 1 + a_1 x + \frac{4}{3} x^{3/2} + \frac{3\beta}{4} x^2 + x^{5/2}\left[\frac{\beta^2}{5} + \frac{4}{5} b_2 - \frac{64}{75} b_3\right] +$$
$$+ \frac{4}{5} b_3 x^{5/2} \ln x + x^3\left[\frac{\beta^3}{48} + \frac{\beta b_2}{2} + \frac{b_4}{2} - \frac{5}{12}(\beta b_3 + b_5)\right] +$$
$$+ x^3 \ln x\left[\frac{b_5}{2} + \frac{\beta}{2} b_3\right] \qquad \text{(VI-24)}$$

Next, we calculate ψ from equation III-15, viz.:

$$\psi = \lambda^2 - \beta x^{1/2}\lambda - \gamma x \mathcal{F}\left(\frac{\epsilon\lambda}{x^{1/2}}\right) \qquad \text{(VI-25)}$$

where $\mathcal{F}(\xi)$ is given by III-16. With λ given by VI-23, we find the following auxiliary expansions to the required orders:

$$\ln\left(1+\frac{\epsilon\lambda}{x^{1/2}}\right) = \ln\epsilon - \frac{1}{2}\ln x + \mu_0 x^{1/2}$$

$$\frac{\epsilon\lambda x^{-1/2}}{1+\epsilon\lambda x^{-1/2}} = 1 + \left(\frac{\beta}{2} - \mu\right)x^{1/2}$$

$$\frac{\epsilon^2\lambda^2 x^{-1}}{(1+\epsilon\lambda x^{-1/2})^2} = 1 + (\beta - 2\mu)x^{1/2}$$

$$\mathcal{F}(\epsilon\lambda x^{-1/2}) = \left(\ln\epsilon + \frac{1}{3} + \sigma\right) - \frac{1}{2}\ln x + \left[\mu_0 + \frac{1}{3}\left(\frac{\beta}{2} - \mu_0\right) + \right.$$

$$\left. + \frac{2}{3}\sigma\left(\frac{\beta}{2} - \mu\right)\right] x^{1/2}$$

where

$$\mu = \left(\frac{1}{\epsilon} + \frac{\beta}{2}\right), \quad \mu_0 = \left(\frac{1}{\epsilon} + \frac{\beta}{2}\right) \qquad \text{(IV-26)}$$

If the remaining terms in VI-25 are similarly expanded, we obtain for $\psi(x)$:

$$\psi(x) = 1 + \left[2b_2 - \frac{\beta^2}{4} - \gamma\left(\ln\epsilon + \frac{1}{3} + \sigma\right)\right] x + \left(2b_3 + \frac{\gamma}{2}\right) x\ln x +$$

$$+ \left\{2b_4 - \gamma\left[\mu_0 + \frac{1}{3}\left(\frac{\beta}{2} - \mu_0\right) + \frac{2}{3}\sigma\left(\frac{\beta}{2} - \mu\right)\right]\right\} x^{3/2} +$$

$$+ 2b_5 x^{3/2}\ln x \qquad \text{(IV-27)}$$

We then determine the coefficients b_k by requiring that the two expressions for ψ as given by VI-24 and VI-27 be identical to the orders involved, which leads to:

$$b_2 = \frac{1}{2}\left[a_1 + \frac{\beta^2}{4} + \gamma\left(\ln\epsilon + \frac{1}{3} + \sigma\right)\right]$$

$$b_3 = -\frac{\gamma}{4} \qquad \text{(VI-26)}$$

$$b_4 = \frac{2}{3} + \frac{\gamma}{2}\left[\frac{2}{3\epsilon} + \frac{\beta}{2} - \frac{2}{3}\frac{\sigma\tau}{\epsilon}\right]$$

$$b_5 = 0$$

The fact that we can determine the coefficients consistently means that the Ansatz VI-23 is analytically consistent. If we now substitute the coefficients VI-26 into VI-24 we finally obtain after considerable simplification the expansion of $\psi(x)$ consistent to order x^3, which is given by:

$$\psi(x) = 1 + a_1 x + a_2 x^{3/2} + a_3 x^2 + a_4 x^{5/2} + a_5 x^{5/2} \ln x + a_6 x^3 + a_7 x^3 \ln x \qquad \text{(VI-27)}$$

with

$$a_2 = \frac{4}{3}$$

$$a_3 = \frac{3\beta}{4}$$

$$a_4 = \frac{\beta^2}{5} + \frac{2}{5}\left(a_1 + \frac{\beta^2}{4}\right) + \frac{2}{5}\gamma\left(\ln\epsilon + \frac{1}{3} + \sigma\right) + \frac{16}{75}\gamma$$

$$a_5 = -\frac{\gamma}{5}$$

$$a_6 = \frac{\beta^3}{48} + \frac{\beta}{4}\left(a_1 + \frac{\beta^2}{4}\right) + \frac{\beta\gamma}{4}\left(\ln\epsilon + \frac{1}{3} + \sigma\right) +$$

$$+ \frac{1}{3} + \frac{\gamma}{4}\left(\frac{2}{3\epsilon} + \frac{\beta}{2} - \frac{2}{3}\frac{\sigma_T}{\epsilon}\right) + \frac{5}{48}\beta\gamma$$

$$a_7 = -\frac{\beta\gamma}{8}$$

The corresponding expansion for $\lambda(x)$ is provided by VI-23 with the coefficients determined by VI-26.

The above can be shown to have the correct TFD limit VI-13 for $\gamma = 0$ if account is taken of the fact that $\psi(x)$ was defined differently in the two cases (Cf. equations III-11 and I-22). Because of the extreme complexity of the differential equation for $\lambda(x)$ (Equations III-22,23) we have avoided dealing with it directly, and have thus not followed the Picard method rigorously. However, we have checked the first few terms of the expansion by applying the extended Picard approach directly to the λ-equation.

We note from the expansion VI-27 that exchange effects ---- represented by β ----- are involved already in the x^2 term, while correlation first makes an appearance in the $x^{5/2}$ term.

C. Numerical Solution

The basic system of equations III(14-20) describing our model was solved numerically for the five elements: Argon, Krypton, Xenon, Chromium and Uranium.

The systematics of the numerical solution is as follows. For each value of Z a family of solutions $\psi(x)$ corresponding to different values of the starting slope $a_1 = \psi'(o)$ is obtained. The point X at which each solution intersects the straight line $\psi = Cx$ where C is given by III-21 defines the edge of the particular atom or ion. This solution then corresponds to an ion with atomic number Z and degree of ionization:

$$\frac{Z - N}{Z} = \psi(X) - X\,\psi'(X) \qquad \text{(VI-28)}$$

where $\psi(x)$ is the particular solution in question, and X is as defined above. Thus, in order for the solution to correspond to a physical system, the starting slope a_1 must be such that the value of the right-hand side of VI-28 lies between zero and one. Solutions which do not intersect the line $\psi = Cx$ do not correspond to any free atom or ion. The value of the right-hand side of VI-28 is found to be extremely sensitive to the starting slope a_1; for example, in the case of Xenon the values of a_1 for the neutral and singly ionized atom differ only in the seventh place. This means that in order to find the solution for the neutral atom for which the right-hand side of VI-28 must vanish, the corresponding a_1 must be found to the full eight-place accuracy of the computer.

In the actual integration procedure the basic equation III-14 was transformed by the change of variable $x = w^2$ with which III-14 takes the form

$$\frac{d^2\psi}{dw^2} = \frac{1}{w}\frac{d\psi}{dw} + 4 w \lambda^3 (w) \qquad \text{(VI-29)}$$

The advantage of this transformation is two-fold. In the first place, unlike the differential equation for $\psi(x)$, the above equation contains no terms which diverge at the origin, thereby making a more accurate numerical integration possible for small x or w. Secondly, for a given interval Δw, the transformation automatically decreases the interval for Δx when $w \ll 1$ for which $\psi(w)$ varies relatively rapidly, and increases it for large values of w at which $\psi(w)$ is slowly varying.

Equation III-15 in terms of w becomes

$$\psi(w) = \lambda^2 - \beta w \lambda - \gamma w^2 \mathcal{F}\left(\frac{\epsilon\lambda}{w}\right) \qquad \text{(VI-30)}$$

where $\mathcal{F}(\xi)$, as before, is given by III-16.

In obtaining the solutions, the power series VI-27 was used out to $x = 0.01$ with the coefficients computed for each Z by VI-27 and III-16. From $x = 0.01$ onward, the solution was obtained numerically with a step size $\Delta w = 0.01$. The integration was carried out by means of the standard Adams-Moulton procedure. At each step of the integration it is necessary to invert equation VI-30 to find $\lambda[\psi, w]$. This was done by Newton's method, and it was found on the average that by using the value of $\lambda(w)$ from the

previous step as an initial guess, three interations sufficed to obtain λ with seven-place accuracy. In some cases it was found to be necessary to diminish the step size near the edge of the atom due to the circumstance that equation VI-30 has real solutions for $\lambda(w)$ only barely beyond the edge of the atom. The truncation error per step was found to be $< 10^{-7}$.

Four solutions were obtained for each value of Z. Among these the solution for the neutral atom was pinpointed within the accuracy of the computer. To a lesser degree of accuracy (in (Z-N)/Z) we have also tried to obtain the solutions describing the singly and doubly ionized atom. For the solutions obtained the values of $\psi(x)$, $\psi'(x)$, and $\psi''(x)$ are given to seven significant figures in Tables VL-X of the Appendix. In the course of the trial and error procedure for determining the value of the correct starting slope a_1 for the neutral atom, a number of sets of values of a_1, X, and (Z-N)/Z was found for each value of Z. These are useful for interpolation and are presented in the summary tables I-V of the Appendix.

VII. DISCUSSION OF THE SOLUTION FOR ARGON.

In the way of illustrating the general nature of the results obtained, we shall here discuss in some detail the solution for Argon ($Z = 18$).

In figure 1 we illustrate the family of solutions of equation III-14 for the case of Argon. The three curves shown represent three solutions $\psi(x)$ corresponding to different starting slopes $a_1 = \psi'(0)$. On the scale of this graph, the boundary line $\psi = Cx$ coincides with the x-axis for all practical purposes.

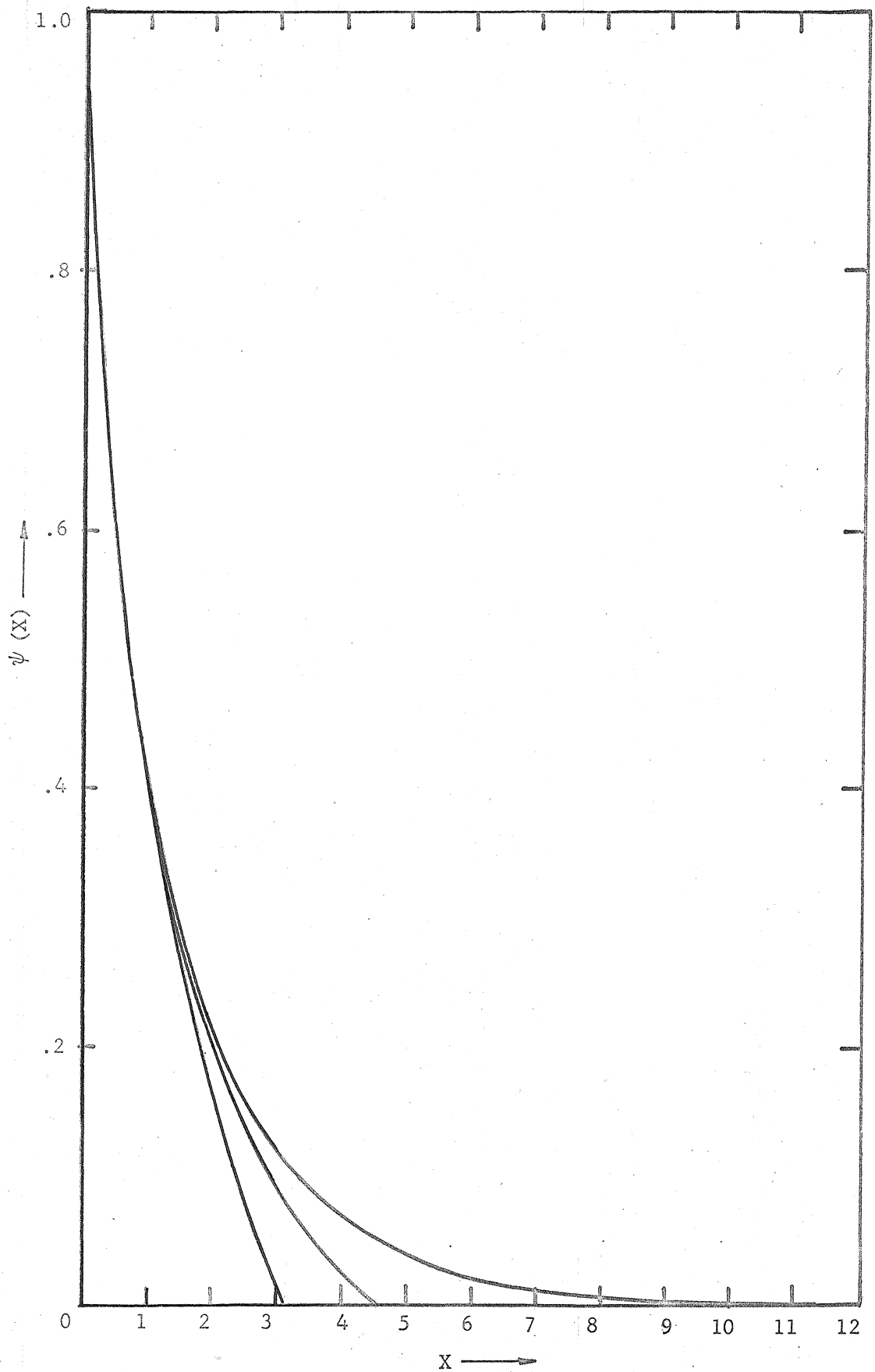
Within the limits of accuracy of the computer, the solution closest to that of the neutral atom corresponds to the starting slope $a_1 = -1.6376553$, which is associated with the values $(Z-N)/Z = 0.00345$, $X = 11.39$. The associated values of X and $(Z-N)/Z$ for different starting slopes are summarized in Table I of the Appendix. An extrapolation of this data yields for the free atom with $Z-N = 0$ the value $X = 11.52$. Comparing this with the TFD model result $X_{TFD} = 12.7$, we see that in our model the radius of the Argon atom is smaller by some 10%. As computed previously, the electron density at the edge of the atom is larger than the TFD value by some 60%.

For Argon, the value of μ, defined by III-12, is found to be

$$\mu = 0.337805\ a_0 \qquad \text{(VII-1)}$$

Figure 1

Family of Solutions $\psi(x)$ of Equation III-14, Z = 18. (Cf. also Table VI of the Appendix).


1.0
.8
.6
.4
.2
0
1
2
3
4
5
6
7
8
9
10
11
12
ψ (X)
X

with which the radius of the free neutral Argon atom in our model becomes $R = 3.89\ a_0$, where a_0 is the Bohr radius. The electron density in terms of the solution $\psi(x)$ is given by equation IV-43:

$$\rho = \frac{Z}{4\pi\mu^3}\,\frac{\psi''}{x} \qquad \text{(VII-2)}$$

from which we calculate the explicit formula

$$4\pi r^2 \rho a_0 = (53.285)\, x\, \psi''(x) \qquad \text{(VII-3)}$$

This function, computed from the values of Table VI of the Appendix, is plotted in figure 2, and compared with the TF and TFD models. From this figure it can be seen that the difference between the density distributions of the TFD and of our model is significant only in the outer regions of the atom, where our model leads to higher densities and a smaller overall radius.

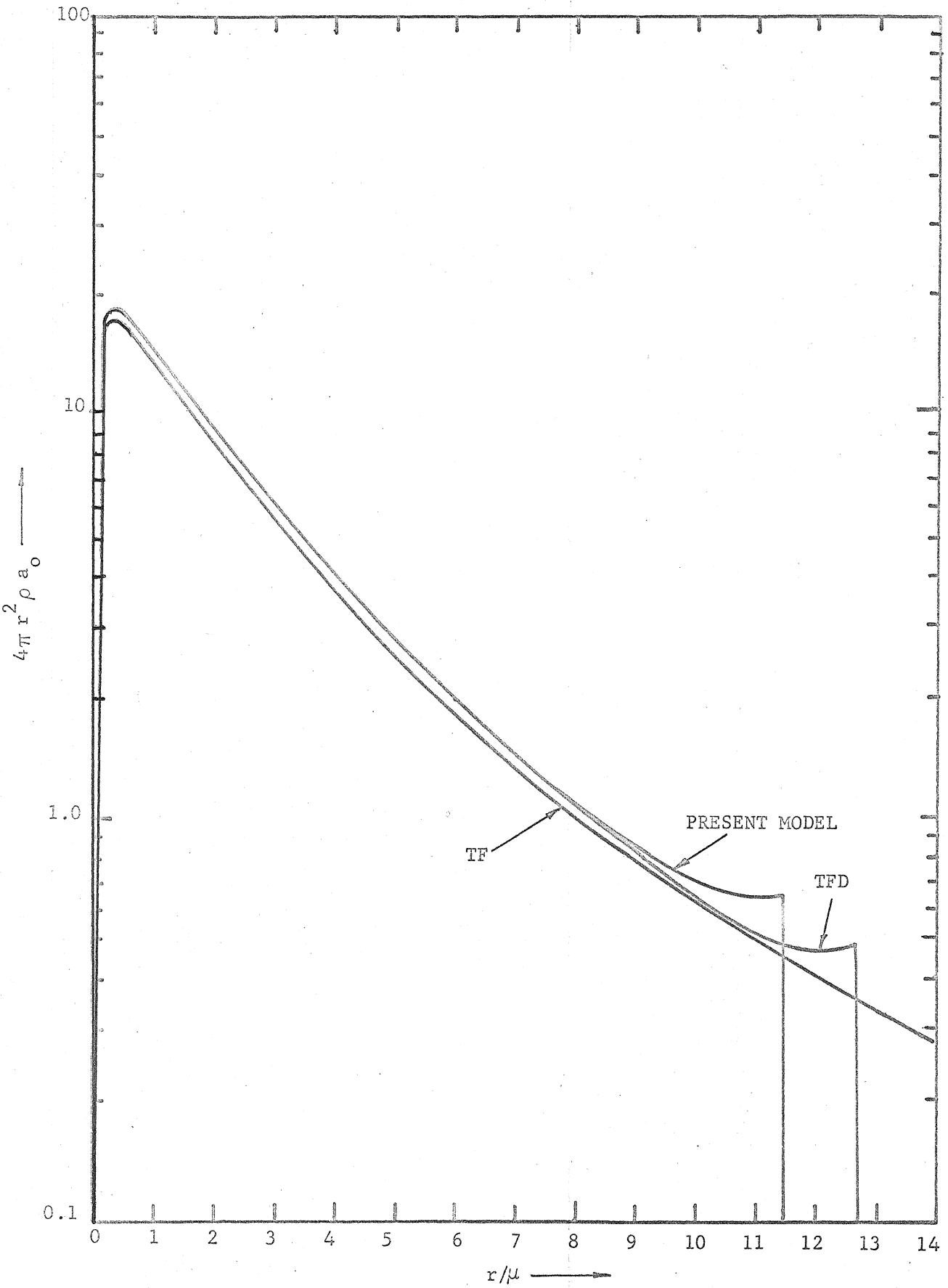
By comparing the density ρ_0 at the dege of the atom computed by VII-2 with the exact value IV-16 derived on theoretical grounds, we are provided with an independent check of the accuracy of our numerical solution. The two values thus computed are found to be identical to within the four-place accuracy of the computation.

We now proceed to the calculation of the energy terms of the Argon atom. For the kinetic energy of the Argon atom we have from IV-34:

$$E_k = \kappa_k \int \rho^{5/3} dv$$

Figure 2

Comparison of the electron density of Argon, expressed as $4\pi r^2 \rho a_o$ as a function of r/μ, for the TF, TFD and present models.


100
10
1.0
0.1
$4\pi r^2 \rho a_o$ ⟶
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14
r/μ ⟶
TF
PRESENT MODEL
TFD

which with VII-2 becomes

$$E_k = \frac{Z^{5/3} K_k}{\mu^2 (4\pi)^{2/3}} \int_0^X \psi''^{5/3} x^{1/3} dx \qquad \text{(VII-4)}$$

In order to evaluate E_k, the above integral must be obtained numerically with the values of ψ'' taken from Table VI of the Appendix. A difficulty is presented, however, by the fact that near the origin the integrand diverges like $x^{-\frac{1}{2}}$. This difficulty can be circumvented by using the expansion VI-27 near the origin in order to calculate ψ''. If this is done out to a value $x = \kappa$ and the integral computed numerically from then on, VII-4 becomes replaced by

$$E_k = \frac{Z^{5/3} K_k}{\mu^2 (4\pi)^{2/3}} \left[2\kappa^{1/2} + \frac{10}{3} a_3 \kappa + \frac{2}{3}\left(\frac{25}{4} a_4 + \frac{20}{9} a_3\right) \kappa^{3/2} + \int_\kappa^X \psi''^{5/3} x^{1/3} dx \right] \qquad \text{(VII-5)}$$

where a_3 and a_4 are given by VI-27.

The exchange energy of the atom is given by IV-34, which in view of VII-2 can be written in the form:

$$E_e = \frac{-K_e Z^{4/3}}{(4\pi)^{1/3} \mu} \int_0^X x^{2/3} \psi''^{4/3} dx \qquad \text{(VII-6)}$$

In this case there are no divergence problems at the origin so that VII-6 may be directly evaluated numerically with the data of Table VI of the Appendix.

For the purpose of computing the potential energy, we first write:

$$E_p = -e\int V_N \rho\, dv - \frac{e}{2}\int V_e \rho\, dv \qquad \text{(VII-7)}$$

$$= -\frac{1}{2}\int e V \rho\, dv - \frac{1}{2}\int e V_N \rho\, dv \qquad \text{(VII-8)}$$

In order to express the first integral on the right of VII-8 in terms of the solution $\psi(x)$, we note that

$$V = \frac{Ze}{r}\psi(x) + V_0$$

where V_0 is given explicitly by equation IV-19. The second integral is simply half the nuclear potential energy which we previously obtained in equation IV-44 in terms of the boundary values of ψ. With these relations, the expression VII-8 for neutral atoms takes the explicit form:

$$E_p = \frac{-e^2Z^2}{2\mu}\left[\int_0^X \psi\psi''\,dx + \psi'(X) - \psi'(0)\right] - \frac{e}{2}V_0 Z \qquad \text{(VII-9)}$$

As in the case of the kinetic energy, the integrand of the integral appearing in VII-9 diverges like $x^{-\frac{1}{2}}$ near the origin so that we must again have recourse to the expansion VI-27 in order to carry out the integral near the origin.

The nuclear potential energy is given by

$$E_{np} = -\frac{Z^2e^2}{\mu}\left[\psi'(X) - \psi'(0)\right] \qquad \text{(VII-10)}$$

With VII-10 and VII-9, the electron potential energy is then obtained from

$$E_{ep} = E_p - E_{np} \qquad \text{(VII-11)}$$

Finally, the correlation energy E_c is best obtained from the approximate expression IV-76, although in principle it can be obtained from the virial theorem IV-46 once the remaining energy terms have been calculated. The latter presents practical difficulties, however, since the small correlation energy is obtained as the difference between large numbers, which must therefore be known very accurately in order to give a reliable value for E_c.

For the neutral Argon atom we have calculated the above energy terms, evaluating the necessary integrals numerically or by combined series-numerical integration, as required. The values of $\psi(x)$, $\psi'(x)$, and $\psi''(x)$ for the Argon solution corresponding to $a_1 = -1.6376553$ were taken from Table VI of the Appendix. The results, accurate to the figures stated, are:

$$
\begin{aligned}
E_k &= 675 \ e^2/a_o \\
E_{ep} &= 241 \ e^2/a_o \\
E_{np} &= -1569 \ e^2/a_o \\
E_p &= -1328 \ e^2/a_o \\
E_e &= -28.7 \ e^2/a_o \\
E_c &= -6.47 \ e^2/a_o
\end{aligned}
\qquad \text{(VII-12)}
$$

We note that the correlation energy is very small compared to the kinetic and potential energies, but amounts to some 23% of the exchange energy. A check reveals that the above values satisfy the exact virial theorem IV-47 to within the accuracy of the above energy values.

With the values VII-12 the total energy of the Argon atom in our model becomes

$$E = -688 \ e^2/a_0 \qquad \text{(VII-13)}$$

compared to the TF value $E_{TF} = -653 \ e^2/a_0$. The negative of the value VII-13 at the same time represents the total ionization energy of the Argon atom. Without further laborious computation we can also obtain the energy necessary to ionize the atom down to the K-shell, which is of some astrophysical interest. The energy of an ion containing only two K-shell electrons has been obtained for reasonably large Z by Hylleraas (24), who finds:

$$E_k = -(Z^2 - \tfrac{5}{8} Z) \ e^2/a_0 \qquad \text{(VII-14)}$$

The energy necessary to ionize the Argon atom down to the K-shell is then simply given by the difference of the two expressions VII-14 and VII-13, and is found to be $375 \ e^2/a_0$.

Other results pertaining to the Argon atom, such as the polarizability, diamagnetic susceptibility, and small-angle electron scattering cross-section are presented together with those of other atoms in Part VII dealing with applications of our model.

VIII. SELECTED APPLICATIONS OF THE THEORY.

The theory of the model developed in the previous sections is generally applicable to the calculation of all atomic properties which can be treated on the basis of the statistical model of the atom. In this part we shall investigate briefly the application of our model to selected problems. In doing so, our purpose is not primarily to obtain a large body of specific data, but more to illustrate the general nature of the effect of including the correlation energy in the framework of the semi-classical statistical atom model. Accordingly, we shall limit our calculations to representative examples. The specific applications considered are equations of state of the elements, the cross-section for the small-angle scattering of medium-energy electrons from atoms, and atomic polarizabilities and diamagnetic susceptibilities. The results are compared with previous models and with experiment, wherever possible. It is found that our model leads in general to improved agreement with experiment, although the agreement is not quantitative.

A. Equations of State

As we have shown in Part V dealing with the theory of the compressed atom, the statistical model of the atom can be made the basis for the calculation of the equation of state of elements. The results of Part V are strictly applicable only at zero absolute temperature since the development was based on the assumption of

total degeneracy of the electron gas. However, it is well known that the degeneracy criterion for an electron gas is:

$$\frac{h^2}{8m}\left(\frac{3}{\pi}\right)^{2/3}\frac{\rho^{2/3}}{kT} \gg 1 \qquad \text{(VIII-1)}$$

In Part IV(A) we found that for our model, even for a free atom, the lowest value of the density is given by

$$\rho_0 = \frac{3.4075 \times 10^{-3}}{a_0^3} \qquad \text{(VIII-2)}$$

If this is substituted into VIII-1, we calculate

$$\frac{h^2}{8m}\left(\frac{3}{\pi}\right)^{2/3}\frac{\rho_0^{2/3}}{kT} \simeq \frac{34,200^\circ K}{T} \qquad \text{(VIII-3)}$$

For matter under pressure the electron density at the edge of the atom becomes larger than the value VIII-2 so that the assumption of degeneracy is valid to higher temperatures. We see from VIII-3 that for the practical calculation of equations of state, the electron gas can be considered as totally degenerate up to quite high temperatures. In fact, the degeneracy criterion VIII-3 is well enough satisfied for the pressures and temperatures existing at the earth's core.

We choose as examples the elements of Iron and Carbon in order to be able to compare our results to those previously obtained by Jensen (25) and Feynman, Metropolis and Teller (12), respectively. For purposes of simplicity, our calculations will be based on the Fermi-Amaldi equation applicable to our model, which

was discussed in Part IV(D).

We summarize briefly the procedure for the calculation of a point on the mass density versus pressure curve for a given element. To begin with, we choose an arbitrary value of x and calculate R from

$$R = \mu^* X \tag{VIII-4}$$

where μ^* is given by IV-83. The corresponding mass density is obtained from

$$\rho_m = \frac{3A}{4\pi N} \frac{1}{R^3} \tag{VIII-5}$$

For solution of the applicable Fermi-Amaldi equation at X we make as usual the Ansatz

$$\varphi(X) = \psi_0(X) + k\eta_0(X) \tag{VIII-6}$$

and determine k from the condition

$$k = \frac{-1/2 + [\psi_0(X) - X\psi_0'(X)]}{X\eta_0'(X) - \eta_0(X)} \tag{VIII-7}$$

As discussed previously, the functions ψ_0, η_0 are known tabulated functions, and are given for example in ref. 4. Next we determine the parameter

$$\xi_0 = \left(\frac{Z}{4\pi}\right)^{1/3} \frac{a_0}{\mu^*} \left[\frac{\varphi(X)}{X}\right]^{3/2} \tag{VIII-8}$$

and write our expression V-10 for the pressure in the form

$$P = \frac{2}{3} \frac{N_K}{a_0^5} \xi_0^5 g(\xi_0) \tag{VIII-9}$$

where

$$g(\mathfrak{Z}_0) = 1 - \left(\frac{\kappa_e a_0}{2\kappa_k}\right)\frac{1}{\mathfrak{Z}_0} - \left(\frac{\kappa_c a_0^2}{2\kappa_k}\right)\frac{1}{\mathfrak{Z}_0}\left[(1+\mathfrak{Z}_0)^{-1} + \frac{2\sigma}{(\tau+\mathfrak{Z}_0)^2}\right] \qquad \text{(VIII-10)}$$

By going through the above steps for each chosen value of X, we obtain a corresponding point on the P - ρ_m curve.

It has become customary in the literature (Cf. for example Feynman et. al., ref. 12) to present the results in terms of a function $f(\mathfrak{Z})$ (where $\mathfrak{Z}$ is not identical with our previously defined variable $\mathfrak{Z}$). Thus, the pressure is written in the form

$$P = \bar{P} f^{5/3}(\mathfrak{Z}) \qquad \text{(VIII-11)}$$

where $\bar{P}$ is the pressure due to the uniform distribution of all electrons of the material throughout the volume of the material, given by

$$\bar{P} = \frac{2}{3}\kappa_k \bar{\rho}^{5/3} \quad , \quad \bar{\rho} = \frac{3Z}{4\pi R^3} \qquad \text{(VIII-12)}$$

and the variable $\mathfrak{Z}$ is defined by

$$\mathfrak{Z} = \frac{a_0 \bar{\rho}^{1/3}}{Z^{2/3}} \qquad \text{(VIII-13)}$$

It is a simple matter to convert the data of equations VIII-(4-10) to the form VIII-(11-13).

We have calculated $f(\mathfrak{Z})$ for Carbon, and plot our results in figure 3. The curves corresponding to the TF and TFD models were

taken from fig. 1 of Feynman et. al. (12), although the actual numbers were recomputed for the TF and TFD cases from formulas given there. The points at which the $f(s)$ curves intersect the s -axis correspond to zero pressure, i.e. the free atom. It is seen that the effect of correlation is not negligible. At the high pressures at which the statistical model of compressed matter can be considered applicable, no data is available for a direct comparison with experiment.

By means of the equations VIII-(4-10) we have also calculated the equation of state for iron in terms of the absolute units of dynes/cm^2 and g/cc. The results are presented in figure 4 and compared with the TF model.

Figure 3

The pressure - density function $f(\beta)$ (Cf. equations VIII-11,13) for Carbon compared for the TF, TFD and present models.

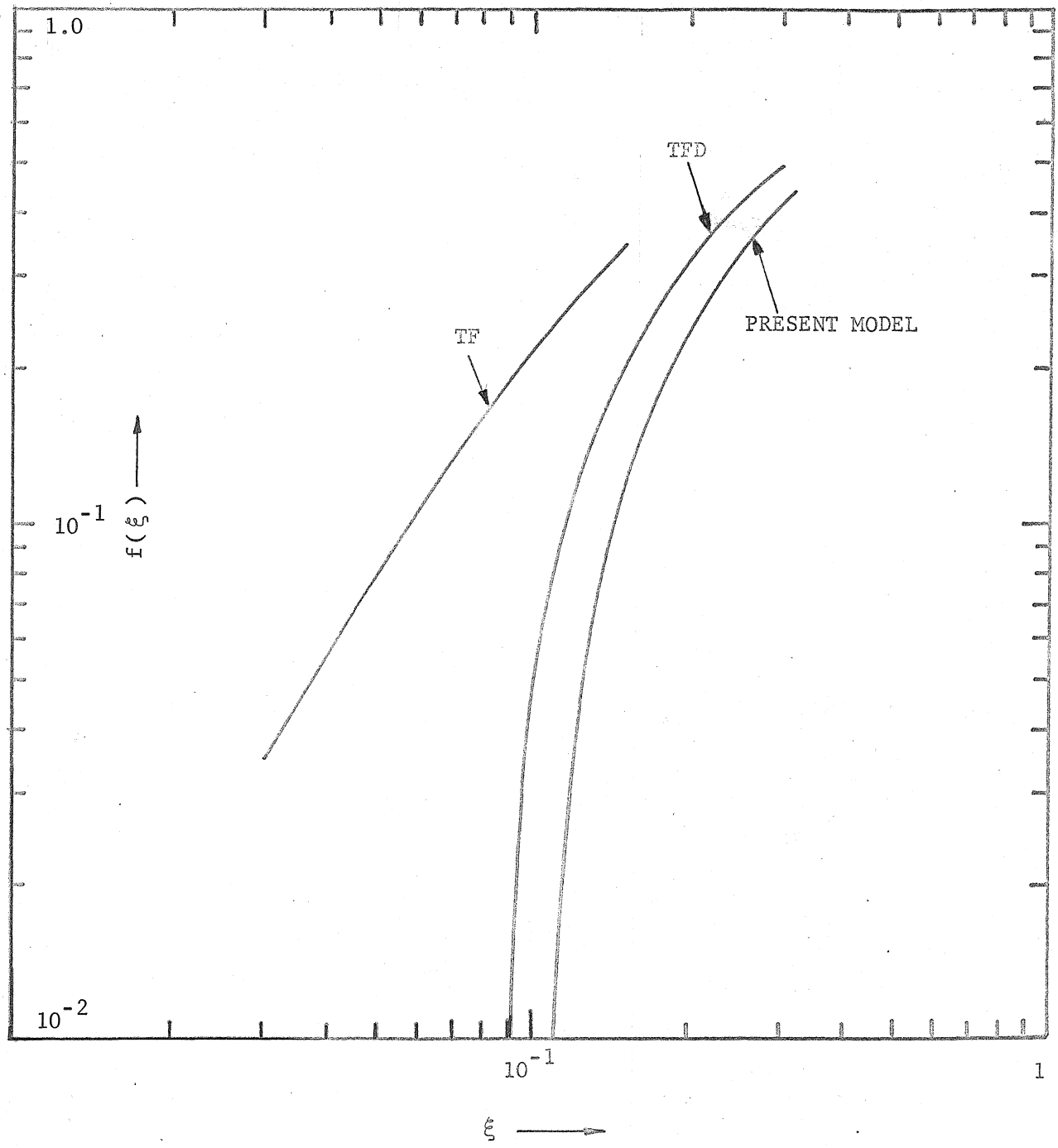
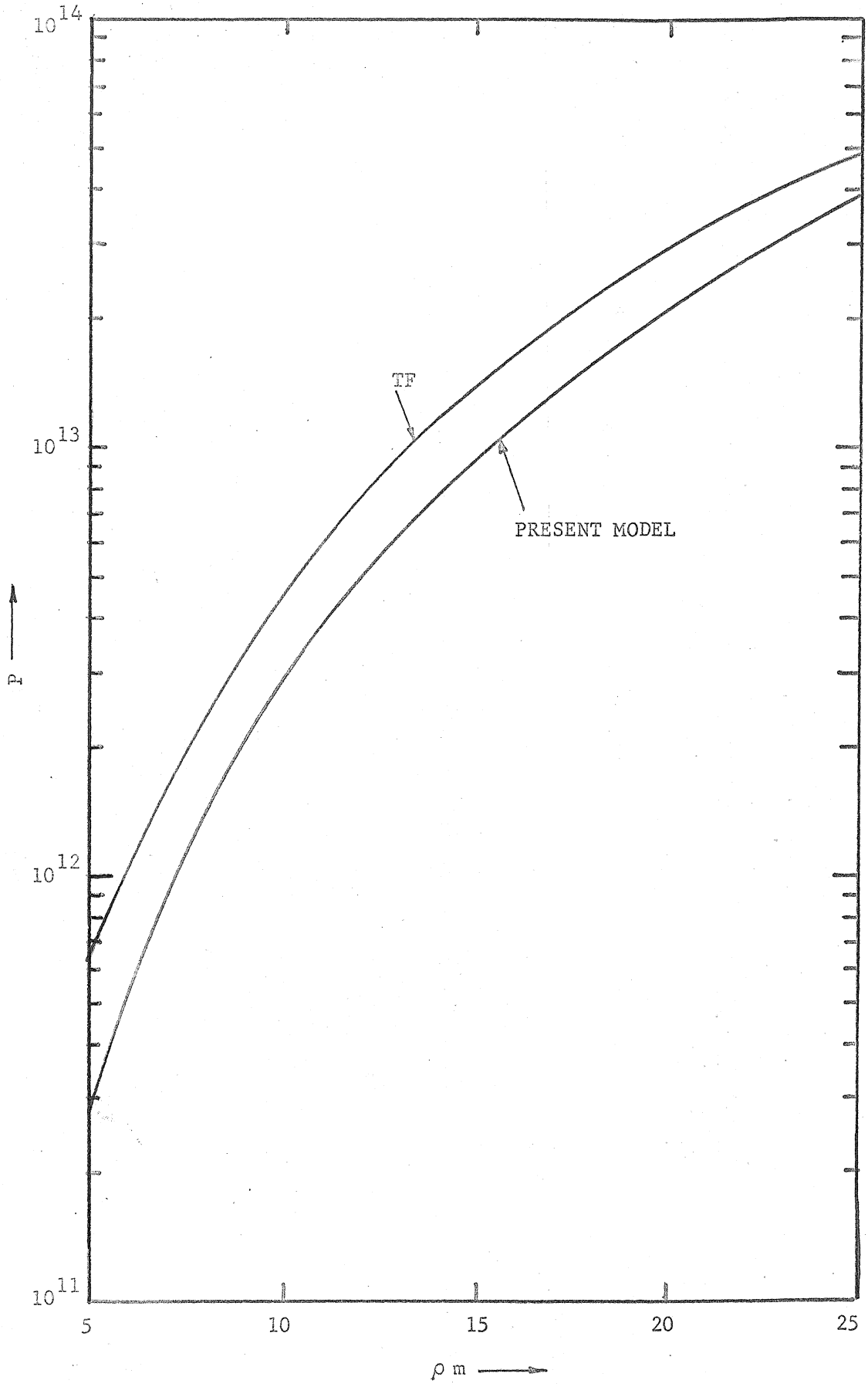

1.0
TFD
TF
PRESENT MODEL
10^{-1}
f(ξ)
10^{-2}
10^{-1}
1
ξ

Figure 4

The pressure P (dynes/cm^2) as a function of ρ_m (g/cc) for iron. Theoretical curves for the TF and present models.


10^{14}
10^{13}
10^{12}
10^{11}
ρ_i
TF
PRESENT MODEL
5
10
15
20
25
ρ m

B. Electron Scattering.

We shall here investigate the scattering of electrons from atoms in the framework of our model. We restrict our considerations to very small scattering angles ($\theta = 10^{-4} - 10^{-2}$) and electron energies of the order of 50 kev for which the Born approximation is valid and relativistic effects may be neglected to a good approximation. It is this region which is of paramount importance for contrast formation in electron microscopy (Cf. Lenz, ref. 26). The scattering of electrons from atoms has been treated on the basis of the Thomas-Fermi model by a number of authors: e.g. v.Borries (27), Heisenberg (28), Lenz (26). It is found that while the TF model leads to generally satisfactory results for scattering angles of the order of 10° and above, at the very small angles of interest in electron microscopy the scattering function $\textcircled{4}$ (defined below in equation VIII-21) given by the TF model is too large by a factor of 4 to 5. This leads to elastic scattering cross-sections which are 25 times too large, and to inelastic cross-sections 5 times larger than those obtained by experiment or on the basis of cumbersome Hartree-Fock calculations (Cf. ref. 29). The reason for the agreement at large angles and simultaneous disagreement at very small angles lies in the fact that for the former the interior of the atom is important, while the latter depend on the outer regions of the atom which are not satisfactorily described by the TF model. It is the hope of improving this situation which constituted the original motivation for the present investigation.

We consider first the cross-section for elastic scattering. On the basis of the Born approximation, the cross-section for the elastic scattering of electrons from an atom of atomic number Z is given by the well-known Mott (30) equation:

$$\frac{d\sigma_{el}}{d\Omega} = \frac{4}{a_0^2 q^4} (Z-F)^2 \qquad \text{(VIII-14)}$$

where $d\Omega$ is the solid angle element, $q = |\vec{k} - \vec{k}'|$ is the magnitude of the electron wave vector difference before and after scattering, and F is the atomic form factor given by:

$$F = \int \rho(r)\, e^{i\vec{q}\cdot\vec{r}}\, dv \qquad \text{(VIII-15)}$$

i.e. the Fourier transform with respect to $\vec{q}$ of the electron density $\rho(r)$ of the atom. For elastic scattering, q can be written as

$$q = \frac{4\pi}{\lambda} \sin\frac{\theta}{2} \qquad \text{(VIII-16)}$$

where λ is the electron wavelength and θ the scattering angle. After the integration over the angular variables is performed, the form factor VIII-15 takes the form

$$F = \frac{4\pi}{q} \int_0^\infty r\rho(r) \sin(qr)\, dr \qquad \text{(VIII-17)}$$

The application of the statistical model of the atom to the calculation of electron scattering cross-sections now simply consists of using in VIII-17 for $\rho(r)$ the value obtained on the basis of the

statistical model. Thus, for the TF model, we have with IV-43:

$$F = \frac{Z}{q\mu} \int_0^X \psi_0''(x) \sin(q\mu x)\, dx \qquad \text{(VIII-18)}$$

where $\psi_0(x)$ is the TF function defined by I-16. If this is integrated twice by parts and use is made of the TF boundary conditions $X = \infty$, $\psi_0(0) = 1$, $\psi_0'(X) = \psi_0(X) = 0$ obtained for the neutral atom, one can write:

$$F = Z - Zq\mu \int_0^\infty \psi_0(x) \sin(q\mu x)\, dx \qquad \text{(VIII-19)}$$

For small q, i.e. small scattering angles, the above can be expanded to yield

$$F = Z - Z(q\mu)^2 \int_0^\infty x\, \psi_0(x)\, dx + O(q^4) \qquad \text{(VIII-20)}$$

By defining the dimensionless variable $\eta = qa_0$ and using the definition I-17, equation VIII-20 is finally written in the form

$$F = Z - \frac{\Theta_{TF}}{6} \eta^2 + O(\eta^4) \qquad \text{(VIII-21)}$$

where the TF scattering function Θ_{TF} is defined by

$$\Theta_{TF} = 6Z\frac{\mu^2}{a_0^2} \int_0^\infty x\, \psi_0(x)\, dx \qquad \text{(VIII-22)}$$

Referring back to VIII-14, we find that in terms of Θ and η the elastic scattering cross-section is given by:

$$\frac{d\sigma_{el}}{d\Omega} = \frac{a_0^2 \Theta_{TF}^2}{q} + O(\eta^2) \qquad \text{(VIII-23)}$$

For the TF model, Θ_{TF} has been computed by Lenz (26), who finds

$$\Theta_{TF} = 43.6\, Z^{1/3} \qquad \text{(VIII-24)}$$

As discussed above, the above value of Θ_{TF} is too large by a factor of 4 to 5 when compared to experiment (29).

We now progress to our model. Here again, F is given by equation VIII-18, but where $\psi(x)$ now represents the solution corresponding to our model, which for a neutral atom satisfies the boundary conditions

$$\psi(0) = 1 \quad , \quad \psi'(X) = \frac{\psi(X)}{X} \quad , \quad \psi(X) = CX \qquad \text{(VIII-25)}$$

with C as defined by III-20. If we again integrate VIII-18 twice by parts and use the boundary conditions VIII-25, we obtain in place of VIII-19 the more complicated formula:

$$F = Z - \frac{Z}{q\mu}\left[(q\mu)^2 \int_0^X \psi \sin(q\mu x)\,dx - \psi(X)\left\{\frac{\sin(q\mu X)}{X} - q\mu\cos(q\mu X)\right\}\right] \qquad \text{(VIII-26)}$$

In order to assess the effect of our model it is sufficient to consider only very small scattering angles; accordingly, we expand the above expression for small q and obtain in terms of $\eta = q a_0$ the expression

$$F = Z - Z\frac{\mu^2}{a_0^2}\eta^2\left[\int_0^X x\psi(x)\,dx - \frac{\psi(X)X^2}{3}\right] + O(\eta^3) \qquad \text{(VIII-27)}$$

Finally, by making use of the last of the boundary conditions VIII-25, the above can be simplified to

$$F = Z - \frac{Z\mu^2\eta^2}{a_0^2}\left[\int_0^X x\psi(x)\,dx - \frac{CX^3}{3}\right] + O(\eta^9) \qquad \text{(VIII-28)}$$

Comparing VIII-28 with VIII-21 we see that for our model we can define an analogue Θ of the TF scattering function in the form:

$$\Theta = \frac{6Z\mu^2}{a_0^2}\left[\int_0^X x\psi(x)\,dx - \frac{CX^3}{3}\right] \qquad \text{(VIII-29)}$$

which when substituted into VIII-23 in place of Θ_{TF} gives the elastic cross-section for our model. We note that unlike the TF function Θ_{TF}, Θ, in our model is not a simple function of Z since both X and $\psi(x)$ are implicit functions of Z.

We now turn our attention to inelastic scattering. The total scattering cross-section, including both elastic and inelastic scattering is given by the familiar Morse (31) formula:

$$\frac{d\sigma}{d\Omega} = \frac{4}{a_0^2 q^4}\left[(Z-F)^2 + S\right] \qquad \text{(VIII-30)}$$

which differs from VIII-14 by the addition of the inelastic scattering function S. At small angles, we can use for the latter a formula derived by Compton (32) on classical grounds:

$$S = Z - \frac{F^2}{Z} \qquad \text{(VIII-31)}$$

where F is again given by VIII-15. Wyrwich and Lenz (29) have

shown that to order η^2 the Compton formula VIII-31 agrees with the exact quantum mechanical expression of Morse (31), and can thus be used at the very small angles of interest to us.

Substituting VIII-21 into VIII-31, we find to order :

$$S = \frac{\Theta}{3}\eta^2 \qquad \text{(VIII-32)}$$

With the relations VIII-32 and VIII-23 the problem of calculating the electron scattering cross-sections at very small angles in the framework of the statistical theory of the atom is thus reduced to the calculation of the scattering function Θ .

In order to calculate the functions Θ for our model, the integral appearing in equation VIII-29 must be evaluated numerically with the values of X and $\psi(x)$ obtained from the numerical solutions for each particular atom. We have calculated Θ from the data of Tables VI-X of the Appendix for the neutral atoms for which we have obtained solutions. The results are presented in Table 1 and compared with the TF value Θ_{TF} given by equation VIII-24. We see that the values of Θ given by our model are indeed much smaller than the TF values Θ_{TF}, the reduction factor ranging from 4.4 for Argon to 2.6 for Uranium.

We have further carried out calculations for Chromium, and computed the total scattering cross-section at very small angles for electrons with energy 60 kev. The results are shown in figure 5 and compared to the corresponding TF results, and to the experimental data of Biberman et. al. (33). It is seen that the agreement with

experiment is markedly improved. In fact, the theoretical values are now slightly too small, which is probably due to contributions by the valence electrons of the Chromium foil which are inadequately represented by the statistical model of the atom.

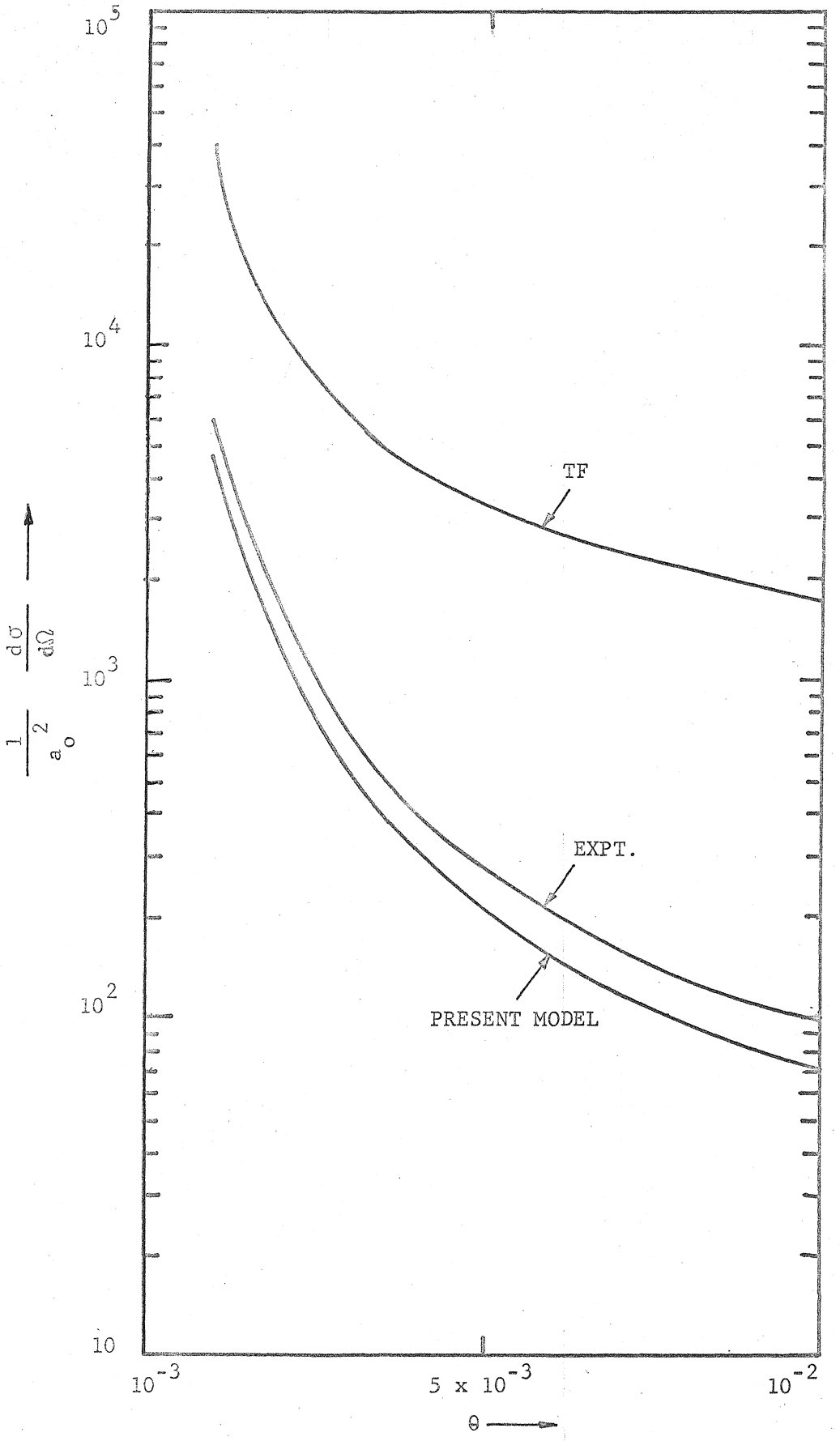
Table 1

Electron scattering functions Θ for the present model and for the TF model (Θ_{TF}) for various elements.

Atom	Θ_{TF}	Θ
Ar	114.36	26.36
Kr	144.0	41.66
Xe	164.8	55.05
U	196.8	74.79

Figure 5

Total cross-sections $\frac{1}{a_0^2}\frac{d\sigma}{d\Omega}$ for the scattering of 60 kev electrons from Chromium. Theoretical curves computed for the TF model and the present model; experimental curve from the data of Biberman et. al. (37); θ in radians.


10^5
10^4
10^3
10^2
10
$\frac{1}{a_o^2}\frac{d\sigma}{d\Omega}$
TF
EXPT.
PRESENT MODEL
10^{-3}
5×10^{-3}
10^{-2}
θ

C. Atomic Polarizabilities and Diamagnetic Susceptibilities.

As a final illustration of the application of our model we consider the calculation of atomic polarizabilities and diamagnetic susceptibilities.

The diamagnetic susceptibility χ and polarizability α of an atom are given, respectively, by the well-known formulae (Cf. ref. 34):

$$\chi = -\mathcal{N}\frac{e^2}{6mc^2}\overline{\langle r^2\rangle} \qquad \text{(VIII-33)}$$

$$\alpha = \frac{4}{9Za_0}\left[\overline{\langle r^2\rangle}\right]^2 \qquad \text{(VIII-34)}$$

where $\mathcal{N}$ is Avogadro's number, m the mass of the electron, and $\overline{\langle r^2\rangle}$ is given by

$$\overline{\langle r^2\rangle} = \int r^2\rho(r)\,dv = 4\pi\int_0^R r^4\rho\,dr \qquad \text{(VIII-35)}$$

Substituting for ρ and r form IV-43 and III-12, we obtain for $\overline{\langle r^2\rangle}$:

$$\overline{\langle r^2\rangle} = Z\mu^2\int_0^{\mathcal{I}} x^3\psi''(x)\,dx \qquad \text{(VIII-36)}$$

After integrating twice by parts and using the boundary conditions VIII-25, we find that VIII-36 can be written in the form

$$\overline{\langle r^2\rangle} = a_0^{\,2}\,\textcircled{H} \qquad \text{(VIII-37)}$$

where $\textcircled{H}$ has been previously obtained in connection with the

electron scattering problem and is given explicitly by equation VIII-29 for our model, and by VIII-24 for the TF model. The values of Θ for the atoms for which we obtained numerical solutions were calculated in the previous section and are given there in Table 1. On the basis of these we can calculate χ and α by the formulas VIII-33 and VIII-34, respectively.

In tables 2 and 3 we present the results obtained with our model andcompare them with available results of calculations based on the TF model, on the Hartree self-consistent field, and with experiment. The Hartree self-consistent field values were taken from Hartree (35). The experimental results for the diamagnetic susceptibility were obtained from Mann (36), those for the polarizability from Fajans and Joos (37). From Tables 2 and 3 we see that while the unmodified TF model is hopelessly inadequate for calculating atomic polarizabilities and diamagnetic susceptibilities, our model obtained by including both exchange and correlation leads to reasonable agreement with experiment, although the agreement is not quantitatively precise. In fact, as can be seen from the results for Argon, the calculations based on our model lead to much the same values as those obtained by the much more cumbersome method of the Hartree self-consistent field.

In general, we can conclude that for the calculation of atomic properties which depend critically on the electron density in the outermost region of the atom, our model leads to improved agreement with experiment. For those properties which depend primarily on the density in the interior of the atom, the correlation correction has little effect.

Table 2

Magnetic susceptibilities χ (10^{-6} cm^3) for stoms of various elements.

	Ar	Cr	Kr	Xe	U
TF model	81.0	--	102.0	117.0	--
Present model	20.88	25.96	33.00	43.61	59.25
Hartree field	20.6	--	--	--	--
Experimental	19.5	--	28.0	42.4	--

Table 3

Atomic Polarizabilities α (10^{-24} cm^3) for atoms of various elements.

	Ar	Cr	Kr	Xe	U
TF model	47.78	43.41	37.92	33.13	27.74
Present model	2.54	2.95	3.17	3.70	4.00
Hartree field	2.47	--	--	--	--
Experimental	1.65	--	2.50	4.10	--

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X. APPENDIX

The Appendix consists of tables of numerical solutions obtained for the elements Argon, Chromium, Krypton, Xenon , and Uranium.

Tables I - V are summary tables giving corresponding values of a_1 , X and $(Z-N)/Z$ for each element . For the values of a_1 preceded by a star complete solutions are given in tables VI - X. The values of a_1 preceded by + and ++ correspond approximately to the singly and doubly ionized atom in each case. The value of X listed for $(Z-N)/Z = 0$ is extrapolated from the remaining data.

Four complete solutions $\psi(x)$, $\psi'(x)$, $\psi''(x)$, were obtained for each element . These are presented in Tables VI - X.

SUMMARY TABLES I - V

TABLE I

Argon

	$-a_1$	X	(Z-N)/Z
	* 1.65	3.045	.4359
	* 1.64	4.478	.2724
	1.638	6.300	.1464
	1.6379	6.656	.1299
	1.6377	8.237	.0679
+	* 1.637685	8.570	.05949
	163767	9.181	.04777
	1.63766	9.9225	.02818
	1.637657	10.489	.01782
	1.637656	10.780	.01228
	1.6376556	11.089	.008227
	1.6376554	11.15	.0072
	* 1.6376553	11.39	.00345
		11.52	0

TABLE II

Chromium

$-a_1$	X	(Z-N)/Z
* 1.635	3.662	.3675
1.629	6.407	.1567
1.62875	7.450	.1120
1.62868	8.108	.0896
1.62867	8.227	.0853
++ * 1.628665	8.323	.0831
1.62864	8.806	.0698
1.628627	9.180	.0602
1.628613	9.839	.0461
+ * 1.6286105	10.011	.0427
1.6286	11.594	.0173
1.6285992	12.076	.0113
1.6285989	12.360	.00811
* 1.6285987	12.85	.00294
	13.10	0

TABLE III

Krypton

	$= a_1$	X	(Z-N)/Z
*	1.623	4.1083	0.333
	1.619	6.72	0.159
	1.6188	7.56	0.126
	1.6187	8.43	0.098
	1.61865	9.36	0.075
++ *	1.618625	10.27	0.056
	1.618620	10.62	0.051
	1.618610	11.69	0.035
+ *	1.6186077	12.11	0.029
	1.618605	13.25	0.0175
*	1.6186039	15.26	0.0019
		15.49	0

TABLE IV

Xenon

	$-a_1$	X	$(Z-N)/Z$
*	1.614	4.62	.298
	1.6115	6.91	.163
	1.6111	11.76	.047
++ *	1.611095	12.457	.03886
	1.61109	13.91	.025
+ *	1.6110889	14.554	.01981
	1.611088	15.83	.0116
	1.6110877	16.83	.006275
*	1.6110876	17.372	.003988
		18.15	0

TABLE V

Uranium

	$-a_1$	X	$(Z-N)/Z$
*	1.61	3.94	.368
	1.604	10.14	.085
	1.60397	11.35	.0656
	1.60395	13.65	.0398
++ *	1.6039448	16.01	.0228
	1.6039445	16.34	.0210
+ *	1.6039434	18.68	.0106
*	1.6039432	19.91	.0066
		21.9	0

TABLE VI

SOLUTIONS FOR ARGON

$a_1 = -1.65$

X	$\psi(x)$	$-\psi'(x)$	$\psi''(x)$
.0100	.9848393	1.450626	9.864423
.0225	.9673932	1.353521	6.434106
.0400	.9445816	1.258430	4.679281
.0900	.8865212	1.078520	2.866782
.1600	.8171128	..9153542	1.925161
.2500	.7416178	..7708467	1.349441
.3600	.6641068	.6453919	.9673567
.4900	.5875366	.5383262	.7019585
.6400	.5138910	.4483284	.5125129
.8100	.4493455	.3737379	.3748673
1.000	.3794292	.3127871	.2735680
1.210	.3191680	.2637577	.1982183
1.440	.2632009	.2250773	.1415952
1.613	.2262359	.2034121	.1102985
1.796	.1515960	.1699218	.0598874
2.190	.1228550	.1608797	.0445350
2.496	.0753575	.1506279	.0235920
2.993	.0024419	.1448915	.0018273
3.04468	-.0050582	.1448358	.0002923
3.04503	-.0051087	.1448357	.0002779

$a_1 = -1.64$

x	$\psi(x)$	$-\psi'(x)$	$\psi''(x)$
.0100	.9849393	1.440616	9.865933
.0225	.9676181	1.343488	6.436339
.0400	.9449825	1.248351	4.682241
.0900	.8874304	1.068255	2.871148
.1600	.8187524	.9047338	1.930876
.2500	.7442384	.7596506	1.356466
.3600	.6680042	.6333494	.9756813
.4900	.5930737	.5251137	.7116080
.6400	.5215238	.4335630	.5235514
.8100	.4546551	.3569685	.3873970
1.000	.3931610	.2934819	.2877278
1.210	.3372794	.2412902	.2141782
1.440	.2869194	.1987105	.1595453
1.613	.2547890	.1738115	.1297562
1.796	.2250550	.1524251	.1053839
2.0164	.1937721	.1317638	.0828222
2.190	.1720251	.1186065	.0688873
2.496	.1386393	.1005564	.0501195
2.993	.0939495	.0811497	.0296378
4.000	.0226652	.0641916	.0068491
4.4779	-.0074883	.0625103	.0004158
4.4821	-.0077529	.0625087	.0003318

$a_1 = -1.637685$

x	$\psi(x)$	$-\psi'(x)$	$\psi''(x)$
.0100	.9849625	1.438299	9.866280
.0225	.9676702	1.341165	6.436857
.0400	.9450753	1.246017	4.682926
.0900	.8876409	1.065878	2.872160
.1600	.8191321	.9022752	1.932200
.2500	.7448450	.7570585	1.358094
.3600	.6689065	.6305612	.9776119
.4900	.5943557	.5220540	.7138482
.6400	.5232912	.4301425	.5261181
.8100	.4570428	.3530815	.3903176
1.000	.3963424	.2890027	.2910404
1.210	.3414776	.2360692	.2179325
1.440	.2924221	.1925686	.1638035
1.613	.2614193	.1668993	.1344109
1.796	.2330283	.1446228	.1104767
2.0164	.2035967	.1227760	.0884728
2.190	.1835014	.1085955	.0750005
2.496	.1534784	.0885442	.0570970
2.993	.1156742	.0652985	.0381506
3.497	.0870505	.0492751	.0263434
4.000	.0652404	.0380613	.0187625
4.4944	.0484926	.0301001	.0137555
5.018	.0344446	.0239188	.0100952
5.5225	.0235396	.0199879	.0075905

$a_1 = -1.637685$

x	$\psi(x)$	$-\psi'(x)$	$\psi''(x)$
6.0025	.0149874	.0162869	.0058291
6.5025	.0075105	.0137372	.0044310
7.0225	.0009122	.0117389	.0032989
7.5076	-.0044294	.0103532	.0024394
8.0089	-.0093461	.0093269	.0016680
8.5264	-.0139837	.0086646	.0008689
8.5849	-.0144892	.0086170	.0007575

$a_1 = -1.6376553$

x	$\psi(x)$	$-\psi'(x)$	$\psi''(x)$
.0100	.9849628	1.438269	9.866285
.0225	.9676709	1.341135	6.436862
.0400	.9450675	1.245987	4.682936
.0900	.8876436	1.106585	2.872173
.1600	.8191369	.9022436	1.932217
.2500	.7448528	.7570252	1.358115
.3600	.6689181	.6305254	.9776368
.4900	.5943722	.5220146	.7138771
.6400	.5233139	.4300986	.5261511
.8100	.4570735	.3530315	.3903551
1.000	.3963833	.2889451	.2910830
1.2100	.3415315	.2312553	.2118125
1.440	.2924924	.1964618	.1685749
1.613	.2615045	.1668103	.1344711
1.796	.2331308	.1445223	.1105426
2.016	.2037231	.1226601	.0885462
2.190	.1836491	.1084663	.0750802
2.496	.1536695	.0883888	.0571885
2.993	.1159546	.0650923	.0382643
3.497	.0874504	.0490050	.0264839
4.000	.0657952	.0377128	.0189348
4.494	.0942423	.0296575	.0139654
5.018	.0354565	.0233542	.0101006
5.5225	.0248712	.0187792	.0079052

$a_1 = -1.6376553$

x	$\psi(x)$	$-\psi'(x)$	$\psi''(x)$
6.0025	.0166986	.0154118	.0062099
6.5025	.0097101	.0126511	.0048969
7.0225	.0037443	.0103827	.0038772
7.5076	-.0008664	.0086847	.0031545
8.0089	-.0048494	.0072542	.0025774
8.5264	-.0082802	.0060447	.0021171
9.0000	-.0109186	.0051230	.0017881
9.4864	-.0132100	.0043204	.0015225
10.0489	-.0154125	.0035322	.0012922
10.4976	-.0168721	.0029836	.0016048
11.0224	-.0182832	.0024003	.0010664
11.3569	-.0190276	.0020502	.0010441
11.4244	-.0191636	.0019797	.0010436

TABLE VII

Solutions for Chromium

$a_1 = -1.635$

x	$\psi(x)$	$-\psi'(x)$	$\psi''(x)$
.0100	.9849885	1.435773	9.850513
.0225	.9677265	1.338833	6.421379
.0400	.9451701	1.243953	4.667837
.0900	.8878204	1.064545	2.897945
.1600	.8193708	.90190442	1.918876
.2500	.7450644	.7578485	1.345568
.3600	.6689646	.6326915	.9657181
.4900	.5940377	.5256998	.7023774
.6400	.5222983	.4354996	.5148349
.8100	.4549775	.3603503	.3789737
1.000	.3926897	.2984533	.2793817
1.210	.3355794	.2480246	.2057021
1.440	.2384438	.2074288	.1507428
1.613	.2496729	.1840800	.1206152
1.796	.2179080	.1644015	.0958206
2.016	.1837430	.1459140	.0726846
2.496	.1205988	.1198960	.0386274
2.993	.0648358	.1065166	.0169266
3.497	.0126446	.1017440	.0031950
3.6622	-.0041492	.1014704	.0001970
3.6626	-.0041880	.1014704	.0001878

$a_1 = -1.628665$

x	$\psi(x)$	$-\psi'(x)$	$\psi''(x)$
.0100	.9850519	1.429432	9.851473
.0225	.9678691	1.332477	6.422791
.0400	.9454241	1.237568	4.669709
.0900	.8883965	1.058043	2.860704
.1600	.8204096	.8951773	1.922484
.2500	.7467244	.7507584	1.349998
.3600	.6714330	.6250678	.9709639
.4900	.5975440	.5173391	.7084538
.6400	.5271303	.4261533	.5217819
1.000	.4013658	.2862662	.2882825
1.210	.3470195	.2338485	.2157478
1.440	.2984213	.1907952	.1620734
1.613	.2677006	.1654018	.1329398
1.796	.2395599	.1433735	.1092229
2.016	.2103754	.1217799	.0874231
2.496	.1606274	.0879737	.0563450
2.993	.1230220	.0650537	.0375742
3.497	.0944533	.0492933	.0258656
4.000	.0725760	.0383060	.0183333
4.494	.0556557	.0305522	.0133418
5.018	.0413143	.0245886	.0096729
5.5225	.0300164	.0203771	.0071411
6.0025	.0209843	.0174008	.0053400

$a_1 = -1.628665$

x	$\psi(x)$	$-\psi'(x)$	$\psi''(x)$
6.5025	.0128871	.0151086	.0038878
7.0225	.0054993	.0134102	.0026869
7.5076	-.0007279	.0123391	.0017515
8.0089	-.0067305	.0116817	.0008762
8.3203	-.0094733	.0111293	.0004365
8.3261	-.0095376	.0111269	.0004228

$a_1 = -1.6286105$

x	$\psi(x)$	$-\psi'(x)$	$\psi''(x)$
.0100	.9850524	1.429377	9.851478
.0225	.9678703	1.332422	6.422804
.0400	.9454262	1.237513	4.669725
.0900	.8884014	1.058987	2.860727
.1600	.8204184	.8951194	1.922515
.2500	.7467386	.7506974	1.350036
.3600	.6714542	.6250023	.9710089
.4900	.5975741	.5172672	.7085059
.6400	.5271718	.4260730	.5218416
.8100	.4615580	.3496599	.3869252
1.000	.4014511	.2861535	.2883704
1.210	.3471304	.2337162	.2158459
1.440	.2985654	.1906390	.1621836
1.613	.2678734	.1652257	.1330597
1.796	.2397669	.1431745	.1093536
2.016	.2106297	.1215505	.0875684
2.190	.1907346	.1075150	.0742350
2.496	.1610097	.0876670	.0565235
2.993	.1235801	.0646485	.0377935
3.497	.0952455	.0487657	.0261334
4.000	.0736699	.0376298	.0186577
4.494	.0571260	.0296999	.0137313
5.018	.0432874	.0235119	.0101433
5.5225	.0325968	.0190403	.0077035

$a_1 = -1.6286105$

x	$\psi(x)$	$-\psi'(x)$	$\psi''(x)$
6.0025	.0242749	.0157701	.0060051
6.5025	.0170813	.0131148	.0046788
7.0225	.0108439	.0109655	.0036351
7.5076	.0059209	.0093924	.0028798
8.0089	.0015468	.0081105	.0022569
8.5264	-.0023727	.0070825	.0017328
9.0000	-.0055485	.0063605	.0013250
9.4864	-.0085006	.0058092	.0009458
9.9856	-.0112989	.0054349	.0005406
10.0489	-.0116418	.0054026	.0004767

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$a_1 = -1.6285987$

x	$\psi(x)$	$-\psi'(x)$	$\psi''(x)$
.0100	.9850525	1.429365	9.851480
.0225	.9678705	1.332411	6.422807
.0400	.9454267	1.237501	4.669728
.0900	.8884024	1.057975	2.860733
.1600	.8204204	.8951070	1.922521
.2500	.7467417	.7506843	1.350044
.3600	.6714587	.6249882	.9710186
.4900	.5975805	.5172518	.7085172
.6400	.5271807	.4260558	.5218545
.8100	.4615701	.3496403	.3869399
1.000	.4014672	.2861309	.2883870
1.210	.3471516	.2336899	.2158647
1.440	.2985932	.1906081	.1622049
1.613	.2679068	.1651910	.1330829
1.796	.2398071	.1431354	.1093790
2.016	.2106791	.1215054	.0875966
2.190	.1907924	.1074648	.0742655
2.496	.1610843	.0876068	.0565584
2.993	.1236892	.0645691	.0378364
3.496	.0954005	.0486623	.0261858
4.000	.0738839	.0374973	.0187214
4.494	.0574139	.0295328	.0138078
5.018	.0436740	.0233006	.0102361
5.5225	.0331026	.0187776	.0078148

$a_1 = -1.6285987$

x	$\psi(x)$	$-\psi'(x)$	$\psi''(x)$
6.0025	.0249203	.0154491	.0061374
6.5025	.0179048	.0127213	.0048372
7.0225	.0118948	.0104814	.0038263
7.5076	.0072305	.0088068	.0031084
8.0089	.0031806	.0073988	.0025333
8.5264	-.0003310	.0062123	.0020717
9.0000	-.0030540	.0053130	.0017382
9.4864	-.0054440	.0045368	.0014638
10.0489	-.0077784	.0037868	.0012134
10.4976	-.0093610	.0032791	.0010547
11.0224	-.0109439	.0027661	.0009068
11.4921	-.0121471	.0023653	.0008044
12.0409	-.0133288	.0019491	.0007184
12.5316	-.0142009	.0016089	.0006734
12.8164	-.0146320	.0014190	.0006628
12.8881	-.0147320	.0013715	.0006621

TABLE VIII

Solutions for Krypton

$\varepsilon_1 = -1.623$

x	$\psi(x)$	$-\psi'(x)$	$\psi''(x)$
.0100	.9851076	1.423942	9.834268
.0225	.9679919	1.327198	6.406125
.0400	.9456368	1.232574	4.653688
.0900	.8888395	1.053813	2.846072
.1600	.8211140	.8919210	1.909235
.2500	.7476701	.7486343	1.338013
.3600	.6725422	.6241993	.9600534
.4900	.5986765	.5178299	.6983896
.6400	.5280786	.4281045	.5123202
.8100	.4619840	.3532763	.3777522
1.000	.4010254	.2914986	.2793048
1.210	.3453818	.2409745	.2066552
1.440	.2949016	.2000476	.1526443
1.613	.2624385	.1763147	.1231476
1.796	.2321381	.1561167	.0989661
2.016	.1998848	.1368581	.0765156
2.190	.1771561	.1247956	.0626016
2.496	.1415816	.1086749	.0437800
2.993	.0920728	.0924577	.0231325
3.497	.0477803	.0844328	.0096772
4.000	.0061236	.0818723	.0012798
4.1047	-.0024416	.0817993	.0001403
4.1087	-.0027731	.0817988	.0000864

$a_1 = -1.6186250$

x	$\psi(x)$	$-\psi'(x)$	$\psi''(x)$
.0100	.9851514	1.419563	9.834925
.0225	.9680904	1.322808	6.407100
.0400	.9458123	1.228164	4.654979
.0900	.8892373	1.049323	2.847971
.1600	.8218313	.8872762	1.911715
.2500	.7488163	.7437399	1.341056
.3600	.6742464	.6189387	.9636510
.4900	.6010966	.5120643	.7025510
.6400	.5314126	.4216699	.5170706
.8100	.4664835	.3459801	.3831340
1.000	.4070126	.2831142	.2853777
1.210	.3532692	.2312344	.2134957
1.440	.3052178	.1886358	.1603452
1.613	.2748462	.1635140	.1315143
1.796	.2470281	.1417217	.1080557
2.016	.2181820	.1203572	.0865057
2.190	.1984793	.1064933	.0733203
2.496	.1690275	.0868928	.0558103
2.993	.1319046	.0641697	.0372990
3.497	.1037550	.0484987	.0257766
4.000	.0822726	.0375188	.0183878
4.494	.0657532	.0297076	.0135165
5.018	.0518831	.0236217	.0099651
5.5225	.0411153	.0192342	.0075466

$a_1 = -1.6186250$

x	$\psi(x)$	$-\psi'(x)$	$\psi''(x)$
6.0025	.0326828	.0160363	.0058597
6.5025	.0253382	.0134520	.0045390
7.0225	.0189066	.0113750	.0034963
7.5076	.0137686	.0098696	.0027391
8.009	.0091374	.0086590	.0021131
8.526	.0049147	.0077061	.0015867
9.000	.0014273	.0070532	.0011806
9.486	-.0018786	.0065697	.0008138
10.049	-.0054663	0062238	.0004152
10.240	-.0066490	.0061585	.0002636
10.304	-.0070432	.0061436	.0001978

$a_1 = -1.6186077$

x	$\psi(x)$	$-\psi'(x)$	$\psi''(x)$
.0100	.9851515	1.419546	9.834928
.0225	.9680907	1.322791	6.407103
.0400	.9458129	1.228147	4.654984
.0900	.8892388	1.049305	2.847978
.1600	.8218341	.8872579	1.911725
.2500	.7488208	.7437206	1.341067
.3600	.6742531	.6189181	.9636651
.4900	.6011061	.5120416	.7025674
.6400	.5314257	.4216446	.5170893
.8100	.4665012	.3459515	.3831552
1.000	.4070361	.2830813	.2854016
1.2100	.3533002	.2311961	.2135227
1.440	.3052583	.1885909	.1603757
1.613	.2748949	.1634636	.1315475
1.796	.2470866	.1416650	.1080919
2.016	.2182540	.1202921	.0865458
2.496	.1691357	.0868062	.0558594
2.993	.1320623	.0640561	.0373589
3.497	.1039781	.0483518	.0258491
4.000	.0825793	.0373319	.0184750
4.494	.0661636	.0294738	.0136197
5.018	.0524308	.0233288	.0100881
5.5225	.0418275	.0188738	.0076917

$a_1 = -1.6186077$

x	$\psi(x)$	$-\psi'(x)$	$\psi''(x)$
6.0025	.0335856	.0156600	.0060288
6.5025	.0264812	.0129246	.0047370
7.0225	.0203521	.0107359	.0037290
7.5076	.0155529	.0091088	.0030093
8.0089	.0112290	.0077518	.0024282
8.5264	.0076303	.0066221	.0019564
9.0000	.0046998	.0057804	.0016096
9.4864	.0020666	.0050709	.0013171
10.0489	-.0005929	.0044109	.0010387
10.4976	-.0024740	.0039879	.0008507
11.0224	-.0044589	.0035933	.0006572
11.492	-.0060800	.0033222	.0004981
12.041	-.0078375	.0031001	.0003067
12.1104	-.0080523	.0030798	.0002783
12.1801	-.0082663	.0030614	.0002468

$a_1 = -1.6186039$

X	$\Psi(x)$	$-\Psi'(x)$	$\Psi''(x)$
.0100	.9851516	1.419542	9.834930
.0225	.9680908	1.322787	6.407104
.0400	.9458131	1.228143	4.654984
.0900	.8892392	1.049301	2.847980
.1600	.8218348	.8872538	1.911727
.2500	.7488218	.7437163	1.341070
.3600	.6742546	.6189134	.9636685
.4900	.6011083	.5120364	.7025712
.6400	.5314287	.4216388	.5170936
.8100	.4665053	.3459449	.3831601
1.000	.4070415	.2830737	.2854071
1.210	.3533074	.2311873	.2135289
1.440	.3052676	.1885805	.1603827
1.613	.2749062	.1634520	.1315551
1.796	.2471001	.1416519	.1081003
2.016	.2182706	.1202771	.0865550
2.190	.1985826	.1064042	.0733735
2.496	.1691607	.0867863	.0558707
2.993	.1320986	.0640300	.0373728
3.497	.1040294	.0483180	.0258658
4.000	.0826499	.0372889	.0184950
4.494	.0662581	.0294200	.0136435
5.018	.0525569	.0232614	.0101166
5.5225	.0419915	.0187907	.0077252

$a_1 = -1.6186039$

x	$\psi(x)$	$-\psi'(x)$	$\psi''(x)$
6.0025	.0337935	.0155000	.0060680
6.5025	.0267445	.0128030	.0047829
7.0225	.0206853	.0105883	.0037830
7.5076	.0159644	.0089328	.0030723
8.0089	.0118470	.0075416	.0025020
8.5264	.0082574	.0063704	.0020434
9.0000	.0054565	.0054842	.0017109
9.4864	.0029799	.0047213	.0014360
10.0489	.0005372	.0039877	.0011826
10.4976	-.0011388	.0034948	.0010193
11.0224	-.0028401	.0030025	.0008626
11.492	-.0041596	.0026251	.0007477
12.0409	-.0054935	.0022461	.0006377
12.5316	-.0065222	.0019534	.0005577
13.0321	-.0074330	.0016916	.0004910
13.542	-.0082348	.0014555	.0004366
14.0625	-.0089348	.0012400	.0003942
14.516	-.0094577	.0010675	.0003681
15.0544	-.0099800	.0008745	.0003515
15.210	-.0101118	.0008200	.0003498
15.288	-.0101748	.0007927	.0003496

TABLE IX

SOLUTIONS FOR XENON

$a_1 = -1.614$

x	$\psi(x)$	$-\psi'(x)$	$\psi''(x)$
.0100	.9851969	1.415071	9.821885
.0225	.9681909	1.318475	6.394506
.0400	.9459867	1.224047	4.642916
.0900	.8896030	1.045779	2.837034
.1600	.8224193	.8844567	1.901893
.2500	.7496198	.7417558	1.332254
.3600	.6753168	.6178717	.9557236
.4900	.6021409	.5119792	.6953236
.6400	.5323905	.4226270	.5103601
.8100	.4672036	.3480465	.3767581
1.000	.4072262	.2863739	.2791607
1.210	.3526615	.2357977	.2072707
1.440	.3033947	.1946472	.1539538
1.613	.2718872	.1706476	.1249161
1.796	.2426542	.1500853	.1011791
2.016	.2117907	.1302825	.0792256
2.190	.1902490	.1177162	.0656796
2.496	.1569946	.1005597	.0474636
2.993	.1120061	.0822928	.0276759
3.497	.0734432	.0718109	.0148156
4.000	.0387930	.0666506	.0062708
4.494	.0063595	.0649952	.0009114
4.6195	-.0017660	.0649368	.0000503
4.6199	-.0017939	.0649368	.0000465

$a_1 = -1.6110950$

X	$\psi(x)$	$-\psi'(x)$	$\psi''(x)$
.0100	.9852260	1.412163	9.822325
.0225	.9682563	1.315561	6.395152
.0400	.9461032	1.221120	4.643771
.0900	.8898672	1.042798	2.838292
.1600	.8228956	.8813729	1.903535
.2500	.7503808	.7385070	1.334266
.3600	.6763481	.6143810	.9580997
.4900	.6037472	.5081550	.6980693
.6400	.5346028	.4183617	.5134907
.8100	.4701883	.3432138	.3803003
1.000	.4111957	.2808255	.2831523
1.210	.3578878	.2293588	.2117604
1.440	.3102256	.1871119	.1590013
1.613	.2800985	.1622024	.1303951
1.796	.2525025	.1405965	.1071272
2.016	.2238838	.1194161	.0857595
2.190	.2043342	.1056716	.0726896
2.496	.1751070	.0862385	.0553387
2.993	.1382589	.0637022	.0370052
3.497	.1103132	.0481474	.0256017
4.000	.0889893	.0372335	.0182959
4.494	.0726023	.0294522	.0134849
5.018	.0588638	.0233691	.0099844
5.5225	.0482280	.0189611	.0076076

$a_1 = -1.6110950$

x	$\psi(x)$	$-\psi'(x)$	$\psi''(x)$
6.0025	.0399349	.0157251	.0059571
6.5025	.0327597	.0130829	.0046734
7.0225	.0265400	.0109258	.0036701
7.5076	.0216418	.0093267	.0029525
8.0089	.0173115	.0079981	.0023717
8.5264	.0134677	.0068978	.0018987
9.0000	.0104001	.0060839	.0015501
9.4864	.0076121	.0054039	.0012552
10.0489	.0047554	.0047795	.0009742
10.4976	.0027023	.0043859	.0007847
11.0224	.0004994	.0040259	.0005918
11.4921	-.0013320	.0037847	.0004375
12.0409	-.0033517	.0035912	.0002683
12.3201	-.0045927	.0035169	.0001534
12.4609	-.0048403	.0035071	.0001251

$a_1 = -1.6110889$

x	$\psi(x)$	$-\psi'(x)$	$\psi''(x)$
.0100	.9852260	1.412157	9.822325
.0225	.9682564	1.315555	6.395153
.0400	.9461034	1.221113	4.643772
.0900	.8898677	1.104279	2.838294
.1600	.8228965	.8813666	1.903538
.2500	.7503823	.7385003	1.334270
.3600	.6763504	.6143739	.9581045
.4900	.6037504	.5081472	.6980748
.6400	.5346072	.4183531	.5134970
.8100	.4701943	.3432040	.3803074
1.000	.4112037	.2808142	.2831603
1.210	.3578984	.2293458	.2117695
1.440	.3102394	.1870966	.1590115
1.613	.2801151	.1621853	.1304063
1.796	.2525225	.1405773	.1071393
2.016	.2239083	.1193939	.0857729
2.190	.2043627	.1056741	.0727040
2.496	.1751438	.0862093	.0553550
2.993	.1383123	.0636640	.0370251
3.497	.1103885	.0480982	.0256255
4.000	.0890925	.0371712	.0183242
4.494	.0727399	.0293748	.0135182
5.018	.0590469	.0232727	.0100237
5.5225	.0484649	.0188433	.0076535

$a_1 = -1.6110889$

x	$\psi(x)$	$-\psi'(x)$	$\psi''(x)$
6.0025	.0402340	.0155835	.0060100
6.5025	.0331364	.0129129	.0047345
7.0225	.0270138	.0107216	.0037410
7.5076	.0222234	.0090856	.0030336
8.0089	.0180247	.0077133	.0024649
8.5264	.0143414	.0065613	.0020061
9.000	.0114458	.0056931	.0016721
9.4864	.0088629	.0049497	.0013943
10.0489	.0062849	.0042407	.0011362
10.4976	.0044906	.0037698	.0009679
11.0224	.0026376	.0033062	.0008038
11.4921	.0011686	.0029584	.0006806
12.0409	-.0003589	.0026194	.0005585
12.5316	-.0015808	.0023688	.0004647
13.0321	-.0027119	.0021578	.0003802
13.5424	-.0037669	.0019840	.0003020
14.0625	-.0047614	.0018467	.0002257
14.5161	-.0055782	.0017600	.0001542
14.5924	-.0057121	.0017489	.0001401

$a_1 = -1.6110876$

x	$\psi(x)$	$-\psi'(x)$	$\psi''(x)$
.0100	.9852260	1.412156	9.822325
.0225	.9682564	1.315553	6.395153
.0400	.9461034	1.221112	4.643773
.0900	.8898678	1.042790	2.838295
.1600	.8228967	.8813652	1.903539
.2500	.7503826	.7384988	1.334271
.3600	.6763508	.6143723	.9581055
.4900	.6037511	.5081455	.6980759
.6400	.5346082	.4183511	.5134984
.8100	.4701956	.3432018	.3803090
1.000	.4112055	.2808117	.2831621
1.210	.3579007	.2293428	.2117716
1.440	.3102424	.1870932	.1590138
1.613	.2801188	.1621814	.1304088
1.796	.2525269	.1405729	.1071420
2.016	.2239138	.1193891	.0857759
2.190	.2043691	.1056417	.0727072
2.496	.1751519	.0862028	.0553587
2.993	.1383242	.0636555	.0370295
3.497	.1104053	.0480873	.0256308
4.000	.0891155	.0371574	.0183305
4.494	.0727706	.0293576	.0135256
5.018	.0590876	.0232513	.0100324
5.5225	.0485176	.0188170	.0076637
6.0025	.0403005	.0155521	.0060217
6.5025	.0332202	.0128751	.0047481

$a_1 = -1.6110876$

x	$\psi(x)$	$-\psi'(x)$	$\psi''(x)$
7.0225	.0271192	.0106761	.0037568
7.5076	.0223529	.0090319	.0030518
8.0089	.0181834	.0076498	.0024858
8.5264	.0195359	.0064862	.0020302
9.0000	.0116787	.0056058	.0016995
9.4864	.0091417	.0048481	.0014257
10.0489	.0066260	.0041201	.0011730
10.4976	.0048897	.0036316	.0010095
11.0224	.0031152	.0031445	.0008521
11.4921	.0017278	.0027724	.0007359
12.0409	.0003112	.0024004	.0006236
12.5316	-.0007951	.0021154	.0005405
13.0321	-.0017893	.0018632	.0004693
13.5424	-.0026818	.0016398	.0004083
14.0625	-.0034819	.0014414	.0003561
14.5161	-.0041004	.0012888	.0003174
15.0544	-.0047501	.0011288	.0002785
15.5236	-.0052502	.0010050	.0002450
16.0000	-.0057016	.0008920	.0002252
16.4836	-.0061075	.0007883	.0002044
17.0569	-.0065270	.0006770	.0001850
17.3056	-.0066897	.0006318	.0001784
17.3889	-.0067517	.0006170	.0001765

TABLE X

SOLUTIONS FOR URANIUM

$a_1 = -1.61$

x	$\psi(x)$	$-\psi'(x)$	$\psi''(x)$
.0100	.9852362	1.411200	9.809288
.0225	.9682775	1.314758	6.382326
.0400	.9461365	1.220538	4.631226
.0900	.8899142	1.042827	2.826389
.1600	.8229120	.8822123	1.892283
.2500	.7502769	.7403303	1.323588
.3600	.6759801	.6713526	.9478608
.4900	.6029073	.5124379	.6880988
.6400	.5330088	.4241317	.5035986
.8100	.4674701	.3506730	.3702873
1.000	.4068778	.2902152	.2728157
1.210	.3513668	.2409718	.2008981
1.440	.3007399	.2013041	.1474134
1.613	.2679828	.1784512	.1181833
1.796	.2372105	.1591411	.0941992
2.016	.2041746	.1409161	.0719077
2.190	.1806704	.1296476	.0580788
2.496	.1434014	.1148935	.0393666
2.993	.0902686	.1008187	.0189444
3.497	.0412497	.0947775	.0060988
3.9438	-.0007453	.0936206	.0000144
3.9442	-.0007825	.0936206	.0000101

$a_1 = -1.6039448$

x	$\psi(x)$	$-\psi'(x)$	$\psi''(x)$
.0100	.9852968	1.405139	9.810203
.0225	.9684137	1.308682	6.383670
.0400	.9463793	1.214436	4.633004
.0900	.8904647	1.036613	2.829004
.1600	.8239046	.8757847	1.895692
.2500	.7518629	.7335611	1.327761
.3600	.6783376	.6100817	.9527850
.4900	.6062538	.5044765	.6937805
.6400	.5376164	.4152583	.5100658
.8100	.4736836	.3406288	.3775892
1.000	.4151371	.2786974	.2810222
1.210	.3622328	.2276264	.2100977
1.440	.3149286	.1857168	.1577109
1.613	.2850246	1610113	.1293181
1.796	.2576293	.1395851	.1062306
2.016	.2292136	.1185828	.0850350
2.190	.2097985	.1049457	.0720737
2.496	.1807644	.0856861	.0548716
2.993	.1441405	.0633378	.0367023
3.497	.1163450	.0479067	.0254057
4.000	.0951205	.0370725	.0181713
4.494	.0788001	.0293400	.0134096
5.018	.0651119	.0232858	.0099471
5.5225	.0545146	.0188893	.0075984

$a_1 = -1.6039448$

x	$\psi(x)$	$-\psi'(x)$	$\psi''(x)$
6.0025	.0462558	.0156524	.0059693
6.5025	.0391192	.0129992	.0047049
7.0225	.0329482	.0108210	.0037196
7.5076	.0281073	.0091940	.0030179
8.0089	.0238525	.0078284	.0024536
8.5264	.0201082	.0066813	.0019981
9.0000	.0171550	.0058163	.0016666
9.4864	.0145117	.0050750	.0013909
10.0489	.0118627	.0043674	.0011349
10.4976	.0100115	.0038967	.0009682
11.0224	.0080920	.0034325	.0008061
11.4921	.0065641	.0030831	.0006850
12.0409	.0049690	.0027408	.0005660
12.5316	.0036885	.0024857	.0004759
13.0321	.0025005	.0022679	.0003966
13.5424	.0013917	.0020838	.0003261
14.0625	.0003490	.0019311	.0002626
14.5161	-.0005016	.0018235	.0002124
15.0544	-.0014552	.0017243	.0001571
15.5236	-.0022487	.0016615	.0001103
16.0000	-.0030296	.0016209	.0000578
16.0801	-.0031592	.0016168	.0000456

$a_1 = -1.6039434$

x	$\psi(x)$	$-\psi'(x)$	$\psi''(x)$
.0100	.9852968	1.405137	9.810203
.0225	.9684138	1.308681	6.383671
.0400	.9463794	1.214434	4.633005
.0900	.8904648	1.036611	2.829004
.1600	.8239048	.8757832	1.895613
.2500	.7518632	.7335595	1.327762
.3600	.6783381	.6100801	.9527861
.4900	.6062545	.5044747	.6937818
.6400	.5376174	.4152563	.5100673
.8100	.4736850	.3406265	.3775908
1.000	4151389	.2786984	.2810240
1.210	.3622353	.2276234	.2100998
1.440	.3149318	.1857133	.1577132
1.613	.2850285	.1610074	.1293206
1.796	.2576339	.1395807	.1062333
2.016	.2292192	.1185778	.0850380
2.496	.1807729	.0856794	.0548753
2.993	.1441528	.0633291	.0367068
3.497	.1163623	.0478957	.0254110
4.000	.0951442	.0370584	.0181776
4.494	.0788315	.0293225	.0134170
5.018	.0651536	.0232642	.0099557
5.5225	.0545683	.0188630	.0076083
6.0025	.0463234	.0156210	.0059807
6.5025	.0392040	.0129617	.0047178
7.0225	.0330542	.0107763	.0037345

$a_1 = -1.6039434$

X	$\psi(x)$	$-\psi'(x)$	$\psi''(x)$
7.5076	.0282368	.0091417	.0030347
8.0089	.0240104	.0077671	.0024726
8.5264	.0203005	.0066096	.0020197
9.0000	.0173838	.0057337	.0016908
9.4864	.0147835	.0049800	.0014180
10.0489	.0121925	.0042561	.0011658
10.4976	.0103944	.0037708	.0010024
11.0224	.0085460	.0032874	.0008448
11.4921	.0070906	.0029189	.0007280
12.0409	.0055924	.0025514	.0006148
12.5316	.0044109	.0022710	.0005305
13.0321	.0033375	.0020242	.0004578
13.5424	.0023613	.0018071	.0003950
14.0625	.0014723	.0016162	.0003405
14.5161	.0007728	.0014712	.0002994
15.0544	.0000221	.0013217	.0002571
15.5236	-.0005710	.0012088	.0002248
16.0000	-.0011225	.0011088	.0001956
16.4836	-.0016369	.0010208	.0001690
17.0596	-.0021959	.0009322	.0001405
17.4724	-.0025717	.0008778	.0001213
18.0625	-.0030701	.0008140	.0000949
18.6624	-.0035430	.0007654	.0000665
18.7489	-.0036090	.0007598	.0000618

$a_1 = -1.6039432$

x	$\psi(x)$	$-\psi'(x)$	$\psi''(x)$
.0100	.9852968	1.405137	9.810203
.0225	.9684138	1.308681	6.383671
.0400	.9463794	1.214434	4.633004
.0900	.8904648	1.036611	2.829004
.1600	.8239049	.8757830	1.895693
.2500	.7518633	.7335594	1.327762
.3600	.6783381	.6100799	.9527862
.4900	.6062546	.5044745	.6937819
.6400	.5376175	.4152560	.5100675
.8100	.4736852	.3406262	.3775910
1.0000	.4151391	.2786945	.2810243
1.210	.3622356	.2276230	.2101000
1.440	.3149322	.1857129	.1577135
1.613	.2850289	.1610069	.1293209
1.796	.2576345	.1395801	.1062337
2.016	.2292199	.1185771	.0850384
2.190	.2098059	.1049484	.0720773
2.496	.1807739	.0856786	.0548757
2.993	.1441543	.0633280	.0367073
3.497	.1163644	.0478943	.0254116
4.000	.0951471	.0370567	.0181783
4.494	.0788353	.0293204	.0134178
5.018	.0651587	.0232615	.0099567
5.5225	.0545749	.0188598	.0076095

$a_1 = -1.6039432$

X	$\Psi(x)$	$-\Psi'(x)$	$\Psi''(x)$
6.0025	.0463316	.0156172	.0059821
6.5025	.0392143	.0129572	.0047194
7.0225	.0330671	.0107709	.0037363
7.5076	.0282526	.0091353	.0030367
8.0089	0.240296	.0077596	.0024749
8.5264	.0203240	.0066008	.0020223
9.0000	.0174117	.0057236	.0016937
9.4864	.0148167	.0049684	.0014213
10.0489	.0122328	.0042425	.0011696
10.4976	.0104412	.0037554	.0010067
11.0224	.0086014	.0032697	.0008495
11.4921	.0071549	.0028988	.0007333
12.0409	.0056686	.0025282	.0006208
12.5316	.0044992	.0022447	.0005372
13.0321	.0034399	.0019943	.0004654
13.5424	.0024800	.0017730	.0004036
14.0625	.0016099	.0015774	.0003502
14.5161	.0009290	.0014278	.0003103
15.0544	.0002033	.0012721	.0002694
15.5236	-.0003651	.0011530	.0002387
16.0000	-.0008884	.0010460	.0002114
16.4836	-.0013705	.0009497	.0001871
17.0569	-.0018856	.0008499	.0001618

$a_1 = -1.6039432$

x	$\psi(x)$	$-\psi'(x)$	$\psi''(x)$
17.4724	-.0022253	.0007861	.0001456
18.0625	-.0026650	.0007064	.0001249
18.4900	-.0029560	.0006559	.0001113
19.0096	-.0032825	.0006022	.0000959
19.5364	-.0035872	.0005556	.0000809
19.8916	-.0037796	.0005287	.0000706
19.9809	-.0038266	.0005225	.0000679