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A Quantum- and Correlation-Corrected Thomas-Fermi-Dirac Equation with a FORTRAN Code

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by

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ABSTRACT

In a previously published report (LA-2750, A Proposed Modification of the Available Momentum Region in Thomas-Fermi Theory) a "quantum correction" to the statistical model of the atom was derived in detail. In the present work we use these results and a very simple approximation to the correlation energy in deriving a quantum- and correlation-corrected Thomas-Fermi-Dirac (TFD) equation. One expects the radial density distribution and potential calculated from this equation to be improved over those on the TFD model, both near the nucleus and near the outer boundary of the atom or ion. Minimum-energy (that is, zero boundary pressure) solutions for rare-gas atoms possess values of cell radius in good agreement with those calculated from experimental values of the lattice parameter.

A FORTRAN code is included in an Appendix to the report.

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I. INTRODUCTION

Many properties of free atoms and of solids are predicted with considerable accuracy by the statistical atom model of Thomas, Fermi, and Dirac.[1-4] The accuracy of the method has probably helped inspire the deeper investigation into its foundations; for if one considers only the premises upon which the original model is based, he would hardly expect more than very rough agreement with experiment or with the predictions of a more refined theory. Yet, to give some examples, the radial density distribution function for a given element calculated from either the Thomas-Fermi (TF) or the Thomas-Fermi-Dirac (TFD) equation appears to be, for any but the very lightest elements, in good agreement with that obtained from self-consistent field calculations. The shell structure is not reproduced, but there appears to be a reasonable averaging of the relative maxima and minima. One-electron energy levels computed in the TF or TFD fields are remarkably close to experimental term values, and the atomic number at which electrons of a given angular momentum make their "first appearance" are predicted correctly to the nearest integer.

The correctness of these predictions would have to be regarded as fortuitous, when they result from a theory which presumes that (1) the potential field in an atom varies sufficiently slowly that the fractional change in an electron's de Broglie wave length λ is small over a distance comparable to λ; and (2) there are a great many electrons in a region having a volume of the order of λ^3. However, Fényes showed that the TF energy and density expressions follow from quasi-classical arguments as well as from a strictly classical viewpoint.[5] Later, March and Plaskett succeeded in deriving the TF energy equation from an integral of the

WKB eigenvalues over a particular region of the quantum-number plane.[6] Thus, the validity of the statistical model seems to depend upon that of the WKB approximation, and Langer showed that the WKB phase integral, at least in one dimension, is applicable under quite broad conditions on the potential even for small quantum numbers.[7]

Since it is known that the statistical theory rests on more than the classical arguments, it appears well worthwhile to attempt those improvements that can be made with little complication of the equations to be solved. The derivation of March and Plaskett provides the basis for a "quantum correction" of the statistical model reported earlier[8,9] and outlined below.

We have stressed the general success of the TF and TFD equations. There are, nevertheless, some areas in which the calculations do not agree well with experiment. A very apparent discrepancy is in the total binding energy of the electron cloud. The electron density predicted at the nucleus is infinite on either the TF or the TFD model; consequently, the calculated binding energy is considerably too large. The previously derived quantum correction modifies the density in the region near the nucleus and produces binding energies in much better agreement with experimental values and with those obtained from self-consistent field calculations.

A further area for attempting improvement is suggested by the rather large errors in the calculated pressure-compression curves. These relationships are influenced mainly by the outermost parts of the electron distribution. In this region of low density the correlation energy, neglected in the original models, becomes important.

In the present work we incorporate the quantum correction and a very simple form for the correlation energy in the derivation of an easily applied quantum- and correlation-corrected TFD equation. One expects the density distribution and potential calculated from this equation to be improved over those on the TFD model, both near the nucleus and near the outer boundary of the atom or ion.

The numerical procedures used in obtaining solutions of the equation are discussed, and a few calculational results are summarized. It is found that the inclusion of the correlation energy should not greatly change the pressure-compression curves for most elements. However, minimum-energy (that is, zero boundary pressure) solutions for rare-gas atoms possess values of cell radius in good agreement with those calculated from experimental values of the lattice parameter. These results suggest the interpretation of minimum-energy solutions as representing isolated atoms, rather than atoms in crystals, since the rare gases are known to be bound in crystals by the very weak van der Waals forces.

Numerical work was performed on an IBM 7030 computer. A FORTRAN code, version "F4", is listed in the Appendix, but we should caution that certain changes, mainly in the Input-Output statements, might have to be made before using the code with other computer systems. Also, it is necessary to carry more than eight-figure precision throughout the calculations in order to obtain accurately the solutions possessing mimimum energy. We have attempted to carry our calculations to about thirteen figures, and while the 7030 word size is equivalent to about 16 decimal digits, it would be necessary to perform the calculations in double-precision arithmetic on a smaller machine. Eight-figure precision is certainly sufficient, however, to obtain general solutions corresponding to arbitrary degrees of compression.

II. A QUANTUM- AND CORRELATION-CORRECTED TFD EQUATION

A. The TF and TFD Equations

A variational technique can be used to derive the TF equation, and an extension of this method provides an often-used and simple means of adding corrections to the statistical model. Thus, we can write the Fermi kinetic energy density of a gas of free electrons at a temperature of zero degrees absolute in the form

$$U_f = c_f \rho^{5/3},$$

where

$$c_f = (3/10)(3\pi^2)^{2/3}.*$$

The electrostatic potential energy density is the sum of the electron-nuclear and the electron-electron terms. We can write this as

$$U_p = U_p^n + U_p^e = -(v^n + v^e/2)\rho,$$

where v^n is the potential due to the nucleus of charge Z; v^e is the potential due to the electrons; and the factor of 1/2 is included in the electron-electron term to avoid counting each pair of electrons twice. With x denoting distance from the nucleus, the total energy of the spherical distribution is given by

$$E = \int [c_f \rho^{5/3} - (v^n + v^e/2)\rho] 4\pi x^2 dx. \quad (1)$$

The expression for density on the TF model,

$$\rho = \sigma_0 (E' - V)^{3/2}, \quad (2)$$

with

$$\sigma_0 = (3/5c_f)^{3/2},$$

is obtained by minimizing Eq. (1) subject to the auxiliary condition that the total number of particles, N, remains constant. The potential

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*Throughout this work we shall use atomic units (a.u.), in which $e = \hbar = m = 1$. The unit of length is a_0, the first Bohr radius for hydrogen; and the unit of energy is e^2/a_0.

energy, V, is a function of position in the electron distribution; E' is the Fermi energy, or chemical potential, and is constant throughout a given distribution. The TF equation follows from Eq. (2) and Poisson's equation.

The tendency for electrons of like spin to stay apart because of the exclusion principle is accounted for by the inclusion in Eq. (1) of the exchange energy, the volume density of which is given by

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

where

$$c_{ex} = (3/4)(3/\pi)^{1/3}.$$

Minimization of the total energy now leads to the equation

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

which is quadratic in $\rho^{1/3}$. From this equation we get

$$\rho = \sigma_0[\tau_0+(E'-V+\tau_0^2)^{1/2}]^3, \tag{3}$$

where

$$\tau_0 = (4c_{ex}^2/15c_f)^{1/2}.$$

Now Poisson's equation with the density given by Eq. (3) leads to the TFD equation.

In the following two sections we propose additional energy terms to be included in Eq. (1); the incorporation of these terms leads to a simple quantum- and correlation-corrected TFD equation.

B. The Quantum Correction

The quantum-correction energy density follows from a slight change in the derivation due to March and Plaskett; the development will be only briefly outlined here.

March and Plaskett have demonstrated that the TF approximation to the sum of one-electron eigenvalues in a spherically symmetric potential is given by the integral

$$I = 2\int\int (2\ell+1)E(n_r,\ell)dn_r d\ell, \tag{4}$$

where the number of states over which the sum is carried is written as

$$N = 2\int\int (2\ell+1)dn_r d\ell. \tag{5}$$

Here $E(n_r,\ell)$ is the expression for the WKB eigenvalues considered as functions of continuous variables; n_r is the radial quantum number; ℓ is the orbital quantum number; and the region of integration is bounded by $n_r = -1/2$, $\ell = -1/2$, and $E(n_r,\ell) = E'$. We have included a factor of two in these equations to account for the spin degeneracy of the electronic states. The Fermi energy E' is chosen so that Eq. (5) gives the total number of states being considered, the N electrons occupying the N lowest states. With considerable manipulation, Eq. (4) becomes the TF energy equation

$$I = \int (\frac{3}{5}\frac{P^2}{2} + V)\frac{P^3}{3\pi^2} 4\pi x^2 dx, \tag{6}$$

and Eq. (5) reveals the TF density through the expression

$$N = \int \frac{P^3}{3\pi^2} 4\pi x^2 dx, \tag{7}$$

both integrals being taken between the roots of $E' = V(x)$. We have written these results in atomic units, so that P, the Fermi momentum, is defined by

$$P = 2^{1/2}(E'-V)^{1/2}. \qquad (8)$$

It is pertinent to examine the error in the TF sum of eigenvalues, as given by Eq. (6), for the case of the pure Coulomb field. The WKB eigenvalues in a Coulomb field are given by

$$E_{n_r,\ell} = -Z^2/2(n_r+\ell+1)^2,$$

and let us consider the levels filled from n = 1 to n = ν, where n is the total quantum number defined by

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

Then, for any value of ν we can evaluate the error in the TF approximation to the sum of eigenvalues, comparing always with the correct value, $-Z^2\nu$. Scott's correction to the total binding energy[10] is obtained by letting ν become very large.

Although the sum of one-electron eigenvalues is not the total energy of the statistical atom because of the electron-electron interaction being counted twice, we might expect to improve the calculated binding energy greatly by correcting this sum in some manner, since the chief cause of the discrepancy is certainly the large error in the electron-nuclear potential energy. This correction can be performed by imposing a new lower limit on ℓ in the integrations above. When we introduce a new lower limit ℓ_{min} and a related quantity which we call the "modification factor,"

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

we obtain, after more manipulation, slightly different expressions corresponding to Eqs. (6) and (7). From these revised expressions we can identify a quantum-corrected TF density expression,

$$\rho = \sigma_0(E'-V-a^2/2x^2)^{3/2}, \tag{9}$$

and a corrected kinetic energy density,

$$U_k = c_f\rho^{5/3} + (a^2/2x^2)\rho. \tag{10}$$

The revised lower limit on the volume integrals, say x_1, is the lower root* of

$$E' - V - a^2/2x^2 = 0; \tag{11}$$

for $x < x_1$, ρ must vanish, and we have thus termed x_1 the "inner density cutoff distance." We can call the second term on the right-hand side of Eq. (10) the "quantum-correction energy density" and write it in the more consistent form

$$U_q = (c_q/x^2)\rho, \tag{12}$$

by defining

$$c_q = a^2/2.$$

The modification factor, a, is determined by the initial slope of the potential function, as described in Part III of this report.

For interpreting these results it is helpful to consider just what we have done in changing the lower limit of the orbital quantum number.

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*In application to the atomic problem, there is only one root of Eq. (11) between zero and the outer boundary of the atom or ion. This root is identified as x_1, and x_2 is then determined by the usual TF boundary condition.

Since the lower limit $\ell = -1/2$ must correspond to an orbital angular momentum of zero, we have, clearly, eliminated states with angular momentum of magnitude between zero and a cutoff value $L_c = a\hbar$. Corresponding to L_c at every radial distance is now a linear cutoff momentum

$$p_c = a\hbar/x,$$

and we can rewrite Eq. (9) in terms of the Fermi momentum and cutoff momentum:

$$\rho = (\sigma_0/2^{3/2})(P^2-p_c^2)^{3/2}.$$

At radial distances less than x_1, momenta are prohibited over the entire range from zero to P, so the electron density vanishes.

This interpretation must be modified somewhat when exchange and correlation effects are included; for then the Fermi momentum is no longer simply given by Eq. (8), except very near the nucleus. We can define x_1 as in the absence of interactions, i.e., as the lower of the roots of Eq. (11), but it is not correct to demand that the density vanish at the upper root. Instead, we require only that the density be real.

C. The Correlation Correction

The original TF equation describes a system of independent* particles, while the introduction of exchange energy, which leads to the TFD equation, represents a correction for the correlated motion of electrons of like spin. The remainder of the energy of the electron gas is termed the correlation energy; by its inclusion we are recognizing that electrons, regardless of spin orientation, tend to avoid one another.

*The particles are "independent" in the sense that there is no correlation among their positions. They do interact with each other, however, in establishing the potential field in which each particle moves.

In extensions of the statistical model there have been suggested at least two different expressions[11,12] for the correlation energy that approach, in the appropriate limits, Wigner's low-density formula and the expression due to Gell-Mann and Brueckner at high densities. In addition to these, Gombás[13] and Tomishima[14] have utilized expansions of the correlation energy per particle in powers of $\rho^{1/3}$ about the particle density encountered at the outer boundary of the atom or ion. In this expansion, the term of first-order can be considered as a correction to the exchange energy, and it follows that the TFD solutions for a given Z then correspond to correlation-corrected solutions for a modified value of Z. Aside from the rather poor approximation of the correlation energy, a drawback to this procedure is that the TFD solutions must be at hand. If solutions representing specified degrees of compression are desired, the method would appear to be impractical.

It is, however, interesting and fortunate that over the density range of interest it is apparently possible to approximate the correlation energy per particle quite closely by an expression of the form

$$u_c = -c_c \rho^{1/6}. \tag{13}$$

This is shown in Fig. 1, where we have set $c_c = 0.0842$, and compared this approximation with the values due to Carr and Maradudin.[15] The latter are obtained as a higher-order correction to Gell-Mann and Brueckner's formula at the high densities (say $\rho \geq 0.25$ a.u.), and are again reasonable interpolated values at the lower electron densities.

There is no need to be concerned with the correlation energy outside the limited range of density shown in Fig. 1. The lowest density that can be obtained in solutions of the "corrected" TFD equation to be derived is about 0.002 a.u., and at densities above 1.0 a.u. the correlation energy becomes small compared with the exchange energy. Near the lower limit of density, the magnitude of the correlation energy computed from Eq. (13) is about one-third as large as the exchange energy,

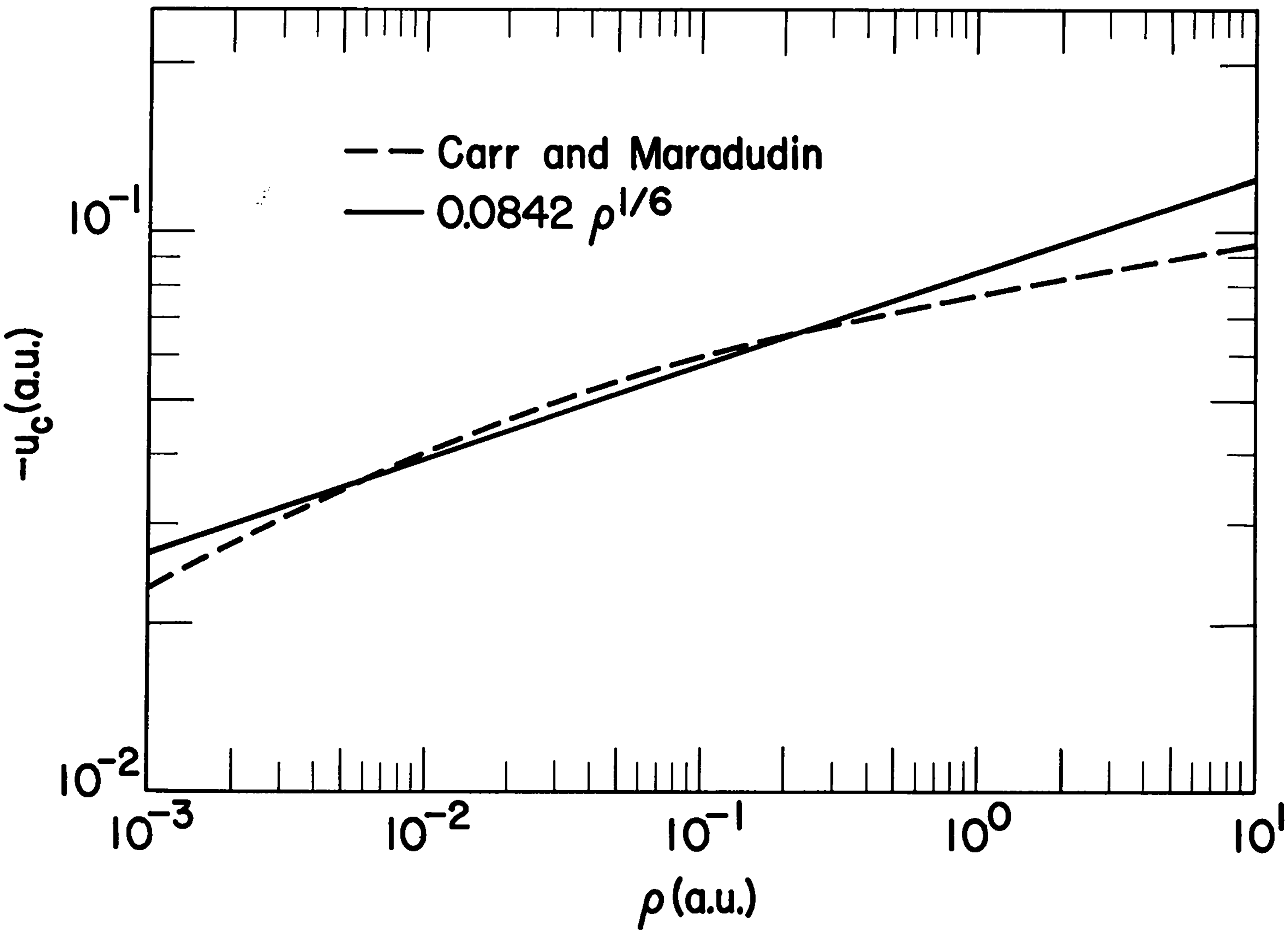


Figure 1. Correlation energy per electron.

but at $\rho = 2.0$ a.u. it is only 10% as large. For, say, $\rho = 10^5$ the ratio is 1% and the exchange energy itself is only 0.01% of the Fermi kinetic energy.

We shall, then, approximate the correlation energy density with

$$U_c = -c_c \rho^{7/6}$$

and, in atomic units,

$$c_c = 0.0842.$$

D. <u>Derivation of the Equation</u>

From the results of the preceding paragraphs, we can now express the total energy per unit volume of the charge distribution in the form

$$U = c_f \rho^{5/3} - c_{ex} \rho^{4/3} - c_c \rho^{7/6} - (v^n + v^e/2)\rho + (c_q/x^2)\rho,$$

where all quantities appearing in the equation have been previously defined. By minimizing the integral of U over the volume occupied by the charge, while requiring that the total number of electrons be fixed, we obtain the following equation:

$$\rho^{2/3} - \tau_1 \rho^{1/3} - \upsilon_0 \rho^{1/6} - R/4 = 0, \qquad (14)$$

where

$$\tau_1 = (4/5)(c_{ex}/c_f),$$

$$\upsilon_0 = (7/6) c_c \sigma_0^{2/3},$$

$$R = 4\sigma_0^{2/3}(E' - V - c_q/x^2).$$

The electron density is found as a function of R by solving Eq. (14), a quartic in $\rho^{1/6}$. To accomplish this we write a "resolvent cubic equation" in terms of another variable, say y:

$$y^3 + \tau_1 y^2 + Ry + (\tau_1 R - \nu_0^2) = 0. \tag{15}$$

Let us use the same symbol, y, to denote any real root of this cubic equation. We can then express the four roots of the quartic, and hence four expressions for the electron density, in terms of y. One of these expressions possesses the proper behavior in reducing to previously obtained results in the neglect of correlation and exchange effects, namely,

$$\rho = (1/8)[\tau_1+\psi+(y^2+R)^{1/2}]^3, \tag{16}$$

where

$$\psi = (\tau_1+y)^{1/2}[\tau_1-y+2(y^2+R)^{1/2}]^{1/2}. \tag{17}$$

We note that ψ vanishes when correlation is neglected, since $y = -\tau_1$ is then a root of Eq. (15).

In the familiar manner we now define a modified TFD potential function ϕ by the relation

$$Z\phi = (E'-V+\tau_0^2)x, \tag{18}$$

and from Poisson's equation and Eq. (16) we obtain

$$\begin{aligned} \phi'' &= (\pi x/2Z)[\tau_1+\psi+(y^2+R)^{1/2}]^3, \qquad & x \geq x_1, \\ &= 0, & x < x_1. \end{aligned} \tag{19}$$

In terms of ϕ,

$$R = 4\sigma_0{}^{2/3}(Z\phi/x - a^2/2x^2 - \tau_0^2). \tag{20}$$

Eqs. (20), (15), (17), and (19) constitute the differential relationship to be satisfied at each step in the integration. We could, of course, write immediately the solutions of Eq. (15) in analytic form, but it proves convenient in the numerical treatment to obtain a root by the Newton-Raphson method, since a good first guess in the iteration is available from the previous integration step.

The boundary conditions on Eq. (19) are: (1) As the nucleus is approached the potential must become that of the nucleus alone, or

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

and (2) at the outer boundary, x_2, of the distribution of N electrons,

$$N = \int_{x_1}^{x_2} \rho \, 4\pi x^2 dx$$

$$= Z \int_{x_1}^{x_2} \phi'' x dx.$$

Integration by parts yields

$$(\phi' x - \phi)\Big|_{x_1}^{x_2} = N/Z,$$

and since

$$\phi(x_1) = 1 + x_1 \phi'(x_1),$$

we have the usual condition:

$$\phi(x_2) = x_2\phi'(x_2) + (Z-N)/Z. \tag{21}$$

In addition to potential and density distributions, total binding energies of atoms are of special interest to us here. For the proper evaluation of energies, the arbitrary constant that is present originally in both the electrostatic potential energy and the Fermi energy must be specified. The state of infinite separation of the constituent particles is normally taken to have zero energy; we therefore follow the usual convention and fix the potential at the edge of the neutral atom at zero for all values of x_2. For an ion the potential energy of an electron at the boundary is taken as

$$V = -(Z-N)/x_2.$$

The defining relation, Eq. (18), now gives at the boundary

$$Z\phi(x_2) = [E'+(Z-N)/x_2+\tau_0^2]x_2,$$

or, solving for the Fermi energy,

$$E' = Z\phi(x_2)/x_2 - (Z-N)/x_2 - \tau_0^2.$$

The total electron-nuclear potential energy is given by

$$E_p^n = -\int_{x_1}^{x_2} (Z/x)\rho\, 4\pi x^2 dx,$$

while for the electron-electron potential energy we have

$$E_p^e = (1/2)\int_{x_1}^{x_2} V^e\rho\, 4\pi x^2 dx.$$

From Eq. (18) and the relation $V = -(v^n+v^e)$, this becomes

$$E_p^e = (1/2)\left[-E_p^n+\tau_0^2 N+E'N-\int_{x_1}^{x_2}(Z\phi/x)\rho\, 4\pi x^2 dx\right].$$

Other energy integrals are, with an obvious notation,

$$E_f = c_f\int \rho^{5/3}\, 4\pi x^2 dx,$$

$$E_q = c_q\int (\rho/x^2) 4\pi x^2 dx,$$

$$E_{ex} = -c_{ex}\int \rho^{4/3}\, 4\pi x^2 dx,$$

$$E_c = -c_c\int \rho^{7/6}\, 4\pi x^2 dx.$$

III. NUMERICAL PROCEDURES

For a given atomic number Z, a family of solutions of the corrected TFD equation, corresponding to different degrees of compression of the element, is obtained by varying the slope of the potential function at the origin. Several parameters of the integration are determined directly by this initial slope, which we denote by ϕ_0'. From the discussion of Eq. (11) we conclude that the electron density, and hence ϕ'', vanishes for x less than

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

where

$$s = -2\phi_0' + 1/\pi^2 Z.$$

In starting the stepwise numerical integration, three values of ϕ and ϕ'' are used, including those at the origin. If we therefore choose an initial interval h_{in} such that

$$2h_{in} < x_1, \tag{22}$$

then ϕ is linear in this region, and it is trivial to generate the starting values. For practical reasons h_{in} is chosen as the largest interval which satisfies both Eq. (22) and the condition

$$h_{in} = 0.02/2^b, \tag{23}$$

where b is an integer. This is done so that upon doubling the space interval a number of times (not necessarily b times) ϕ is evaluated at convenient values of x.

In the earlier work, justification was presented for determining the modification factor, a, through an "equivalent Coulomb problem."[8] In following this procedure we consider a number of electrons interacting with the charged nucleus but not at all with each other, even to the extent of providing a partial screening of the nuclear charge. Under these conditions we would define ϕ through the equation

$$Z\phi = (E'-V)x.$$

Here, in contrast to the situation in the actual atomic problem, the potential energy distribution is known. We have

$$V = -Z/x. \tag{24}$$

It can be established by direct substitution that for the Coulomb problem, ϕ is linear throughout the distribution, or

$$\phi = 1 + x\phi'.$$

In order for Eq. (24) to be satisfied with no additive constant, we must let the Fermi energy of the Coulomb problem be given by

$$E' = Z\phi'. \tag{25}$$

Correction of the region of integration in the quantum-number plane is based on the above value of the Fermi energy, where for ϕ' we use the initial slope of the actual atomic problem, i.e., ϕ_0'. The outer boundary of the region defines a quantity α through the relation

$$\alpha = (n_r+\ell+1)_{\text{outer boundary}}.$$

The Fermi energy given by Eq. (25) is the maximum eigenvalue in the Coulomb field. From the form of these eigenvalues we obtain

$$\alpha = (-Z/2\phi_0').$$

In correcting the integration region for the Coulomb field we derive the expression for the modification factor,

$$a = \alpha - (\alpha\nu)^{1/2},$$

where ν is the (generally non-integral) number of filled shells obtained as the solution of the equation

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

Thus the initial slope of ϕ determines the inner density cutoff distance x_1, the initial interval of integration h_{in}, and the modification factor a.

The quantum- and correlation-corrected TFD equation is of the form

$$\phi'' = f(x,\phi), \tag{26}$$

a form which can be integrated simply and rapidly by a finite-difference method described by Hartree.[16] In this method the approximation is made that

$$\Delta^2\phi_0 = h^2(\phi_0''+\Delta^2\phi_0''/12), \tag{27}$$

the subscripted quantities here being associated with the point $x = x_0$ to which the integration has progressed. In the usual notation, Δ^2 is the second difference operator, such that

$$\Delta^2\phi_0 = (\phi_1-\phi_0) - (\phi_0-\phi_{-1})$$

$$= \phi_1 - 2\phi_0 + \phi_{-1},$$

and h is the existent integration interval.

To proceed in the integration an estimate is made of $\Delta^2\phi_0''$, and from Eq. (27) we find $\Delta^2\phi_0$. From the backward first difference and $\Delta^2\phi_0$ we can predict ϕ at the next step. Eq. (26) then furnishes the predicted value of ϕ'', from which the predicted $\Delta^2\phi_0''$ follows. This predicted value is compared with the original estimate to determine whether the integration is to be allowed to proceed to the next step, or whether it must be repeated with a revised estimate of $\Delta^2\phi_0''$. The criterion for this decision is discussed below.

Some modification of the integration procedure seems advisable in the vicinity of x_1, where an abrupt change in ϕ'' occurs. A table of differences in ϕ'' of second-order and above reveals that the assumption that leads to Eq. (27), namely, that the terms involving differences higher than second-order can be neglected, is not too well justified for x close to x_1. We can attempt to do a little better by adding one more term and writing

$$\Delta^2\phi_0 = h^2(\phi_0''+\Delta^2\phi_0''/12-\Delta^4\phi_0''/240). \quad (28)$$

The extra term is retained for only a few integration steps for which the changes in ϕ'' are relatively large; in practice it is dropped upon reaching the point at which h has achieved its maximum value. We note that, for that portion of the integration in which Eq. (28) is utilized, it is necessary at each step to estimate $\Delta^4\phi_0''$; but we can get an estimate of ϕ'' at the forward steps of sufficient accuracy to compute this difference by merely extending ϕ linearly from the origin, thereby obtaining the arguments for Eq. (26).

The integration interval, starting at h_{in}, is doubled on alternate steps until a certain maximum value is obtained, and then is kept constant out to the outer boundary of the charge distribution. This maximum value is selected by requiring that the precision in each integration be independent of Z, the precision being that of a chosen test run. A convenient check on the precision is furnished by the relative discrepancy between the total number of particles N which enters the boundary condition, Eq. (21), and the volume integral of the calculated electron density. It is thus apparent that there are two conditions on the integration. With h given, the criterion on proceeding to the next step in integrating the differential equation is that

$$\left|\frac{(\Delta^2\phi_0'')_{\text{estimated}}-(\Delta^2\phi_0'')_{\text{predicted}}}{6\phi_0}\right| h^2 \le 10^{-n},$$

where n is the number of significant digits carried in the calculation of ϕ. This condition arises from requiring that an error in $\Delta^2\phi_0''$ ultimately cause an error in ϕ_1 of no more than 1/2 in the least significant digit. However, the precision of the integration, as measured by the calculated number of particles, also depends upon h. We might expect this error to be dependent to a large degree upon the magnitudes of $\Delta^2\phi$ encountered in the integration, and results seem to bear this out. We require, then, as a rough measure of the error,

$$h_{max}^2 \phi''_{max} \approx \text{ constant},$$

and seek to estimate ϕ''_{max} as a function of Z and ϕ'_0.

In the neglect of exchange and correlation effects we have

$$\phi'' = (4x/3\pi Z)(2Z\phi/x - a^2/x^2)^{3/2}.$$

With Z and a given, the condition for a maximum of $\phi''(x)$ is easily derived as

$$2a^2/x - Z(\phi - 3\phi' x) = 0;$$

and since the maximum occurs at a small value of x, it is adequate for this discussion to put $\phi = 1$ and to neglect $3\phi' x$ in comparison with it. We then obtain the result that the maximum is at a position

$$x \approx 2a^2/Z,$$

from which there follows

$$\phi''_{max} \approx (3^{1/2}/\pi)Z/a.$$

We then have the requirement

$$h_{max}^2 \approx \text{constant}\cdot(\pi/3^{1/2})a/Z.$$

It is found, moreover, that a varies but slightly with Z and ϕ_0'. We can treat it as a constant here. It is also found in our calculations that an interval $h_{max} = 0.00125$ produces a respectably small error in number of particles of about four parts in 10^6 for Z = 54, with a modification factor of about 0.261. If h_{max} is chosen as the largest value obtained by doubling h_{in} subject to the condition

$$h_{max} < 0.018/Z^{1/2},$$

a fairly uniform error of a few parts in 10^6 results for all integrations, although for very small Z the error tends to be somewhat larger, say one part in 10^5.

The outer boundary of the electron distribution, x_2, is determined by Eq. (21). We define a quantity

$$g = (x_0-h/2)(\phi_0-\phi_{-1})/h - (\phi_0+\phi_{-1})/2 + (Z-N)/Z,$$

which first becomes positive somewhere in the vicinity of x_2. At the integration step at which this occurs, a parabola is passed through the points ϕ_{-2}, ϕ_{-1}, and ϕ_0. We then have for this limited region the approximation

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

and the coefficients $\mathcal{A}$, $\mathcal{B}$, and $\mathcal{C}$ are evaluated under the condition that

$$\phi'' = \Delta^2\phi/h^2.$$

Thus,

$$\mathcal{A} = \phi''/2,$$

$$\mathcal{B} = (\phi_0 - \phi_{-1})/h + h\mathcal{A} - 2x_0,$$

$$C = \phi_0 - \mathcal{A}x_0^2 - \mathcal{B}x_0.$$

The boundary condition becomes

$$\mathcal{A}x_2^2 + \mathcal{B}x_2 + C = 2\mathcal{A}x_2^2 + \mathcal{B}x_2 + (Z-N)/Z,$$

and hence

$$x_2 = [(ZC-Z+N)/Z\mathcal{A}]^{1/2}.$$

Integrals yielding the total energies of the various forms and the total number of electrons are evaluated by the Simpson "1/3" rule, with boundary corrections at x_1 and x_2 computed by the trapezoidal rule.

IV. RESULTS

It was pointed out in the Introduction that the quantum-corrected TFD equation yields atomic binding energies in good agreement with experimental values and with the results of Hartree-type calculations. It is of interest to know whether the agreement is retained when correlation energy is included. We also wish to ascertain the effect that inclusion of correlation has on the radii of the minimum-energy solutions. The pressure-compression curves on the TFD model suffer from this radius being too large for almost all elements, and correlation effects are known within the statistical theory to contract the electron cloud.

Table I presents summaries of minimum-energy solutions for a number of neutral atoms. We should mention here that the correlation energy for the low-Z elements is roughly twice that given by Clementi.[17]

Table II compares the calculated total energies with Hartree-Fock-Slater non-relativistic values, and, for low-Z elements, with experimental

TABLE I

MINIMUM-ENERGY SOLUTIONS

A. THE INITIAL SLOPES, MODIFICATION FACTORS, AND INNER AND OUTER RADII

Z	$-\phi_0'$	a	x_1	x_2
2	1.662286185	.28930262	.021720161	3.1500
3	1.944982019	.28290387	.013707739	3.3149
4	2.179156982	.27921366	.015083695	3.4274
5	2.372918675	.27665497	.0077987352	3.5175
6	2.548968232	.27480082	.0063976318	3.5925
7	2.705926337	.27334467	.0054165521	3.6525
8	2.852616885	.27218124	.0046931340	3.7075
10	3.108618420	.27036059	.0036973067	3.7925
20	4.063980433	.26564491	.0017783697	4.0387
30	4.745875374	.26359841	.0011645068	4.1787
40	5.289883861	.26226632	.00086374273	4.2637
50	5.752752881	.26133199	.00068564904	4.3387
60	6.158923349	.26062552	.00056803471	4.3893
70	6.520766586	.26006289	.00048462240	4.4306
80	6.852574996	.25960300	.00042243370	4.4729
90	7.157896787	.25921554	.00037429564	4.4972
100	7.440332217	.25888199	.00033593916	4.5293

TABLE I -- Continued

B. THE VARIOUS FORMS OF ENERGY (a.u.)

Z	E_f	E_q	E_p^n	E_p^e	E_{ex}	E_c	E
2	2.2270	0.67061	-6.5965	1.5881	-0.73537	-0.11198	-2.9582
3	5.9421	1.5576	-17.415	3.9161	-1.4135	-0.18777	-7.6005
4	11.962	2.8506	-34.693	7.4654	-2.2572	-0.27172	-14.944
5	20.611	4.5210	-59.182	12.345	-3.2519	-0.36243	-25.319
6	32.149	6.5894	-91.534	18.646	-4.3867	-0.45896	-38.995
7	46.827	9.0707	-132.36	26.453	-5.6544	-0.56071	-56.225
8	64.846	12.030	-182.22	35.838	-7.0479	-0.66715	-77.217
10	111.73	19.085	-310.64	59.605	-10.193	-0.89269	-131.31
20	602.82	80.184	-1625.0	292.06	-32.214	-2.2164	-684.37
30	1609.6	185.67	-4269.1	743.60	-63.280	-3.7829	-1797.3
40	3225.3	334.76	-8461.7	1445.6	-102.22	-5.5329	-3563.9
50	5523.5	529.12	-14378.	2422.7	-148.31	-7.4337	-6058.2
60	8566.6	771.39	-22167.	3696.1	-201.05	-9.4648	-9343.2
70	12409.	1057.3	-31953.	5283.9	-260.02	-11.611	-13474.
80	17100.	1386.9	-43849.	7202.5	-324.94	-13.861	-18498.
90	22683.	1764.7	-57964.	9466.8	-395.53	-16.206	-24461.
100	29200.	2186.9	-74392.	12090.	-471.58	-18.639	-31405.

TABLE II

COMPARISON OF CALCULATED AND EXPERIMENTAL TOTAL BINDING ENERGIES (a.u.)

Z	$-E_{calc}$	$-E_{HFS}$	$-E_{exp}$
2	2.9582	2.8779	2.9027
3	7.6005	7.2262	7.4761
4	14.944	14.255	14.665
5	25.319	24.079	24.652
6	38.995	37.079	37.846
7	56.225	53.587	54.598
8	77.217	73.938	75.092
10	131.31	127.48	
20	684.37	674.02	
30	1797.3	1773.6	
40	3563.9	3532.6	
50	6058.2	6014.6	
60	9343.2	9273.6	
70	13474.	13380.	
80	18498.	18395.	
90	24461.	24343.	
100	31405.	31264.	

values.[18] The Hartree-Fock-Slater results through Z = 30 were reported by Snow, et al,[19] as computed from the code published by Herman and Skillman,[20] while for larger Z the values were calculated by Cowan[21] with a modification of the same code. In comparing with experiment, the binding energies on the corrected TFD model are seen to be not much worse than those calculated by the self-consistent field method, and in some cases are better. At high Z the two methods give energies differing by roughly one-half of one percent. It should be mentioned, however, that the agreement is slightly better on the model that includes the quantum correction but no correlation. This is especially true for lower Z. Correlation increases the discrepancies with experimental energies from about 2% to about 3% for atomic numbers 6, 7, and 8, but at high Z it causes a change in energy of only about 0.1%.

The radius of minimum-energy solutions as a function of atomic number is shown in Fig. 2; this radius is the "lattice constant" if the atoms are considered to be bound in a solid. Also shown are the corresponding TFD values computed by Thomas,[22] and spherical cell radii calculated from the observed normal crystal densities. The inclusion of correlation produces a cell radius which represents a somewhat better average to the experimental points in the variation with Z, but quite obviously the equation of state for many metals will not be greatly improved.

Although in equation of state calculations a zero boundary pressure solution is tacitly considered to represent an atom bound in a crystal of normal density, the calculated radii of such solutions actually support their interpretation as representing isolated atoms. One might object that, with reference again to Fig. 2, the calculated cell radius of some elements, notably most of the alkalis and alkaline earths, is <u>less</u> than the observed crystal radius. This result is not surprising for these elements, as can be seen from the sketch on page 35. Here are shown the radial distribution functions, as calculated by the self-consistent field code of Boyd, et al,[23] for the ground states of neon, sodium, magnesium, and argon. The long "tail" of the distribution, apparent especially for

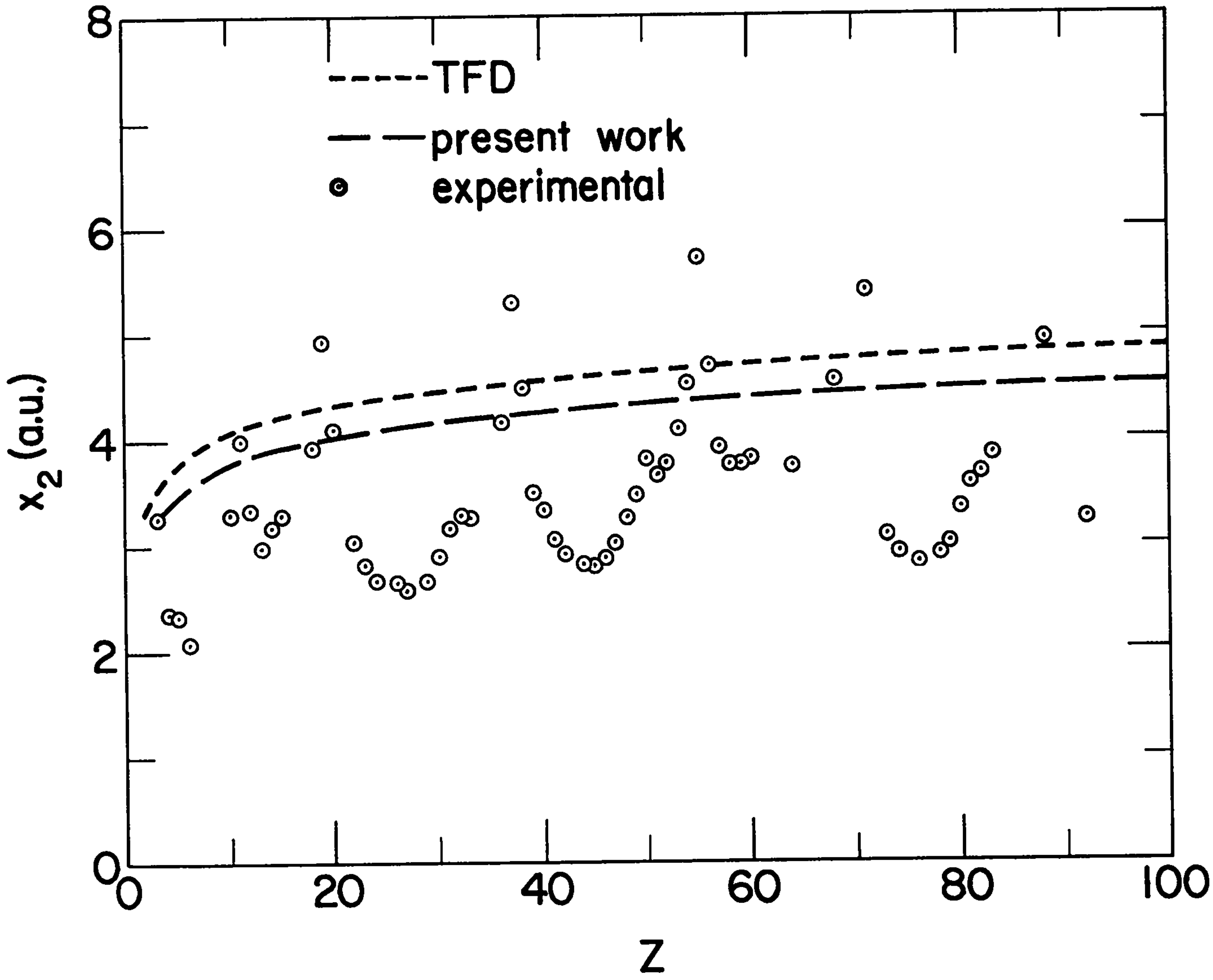
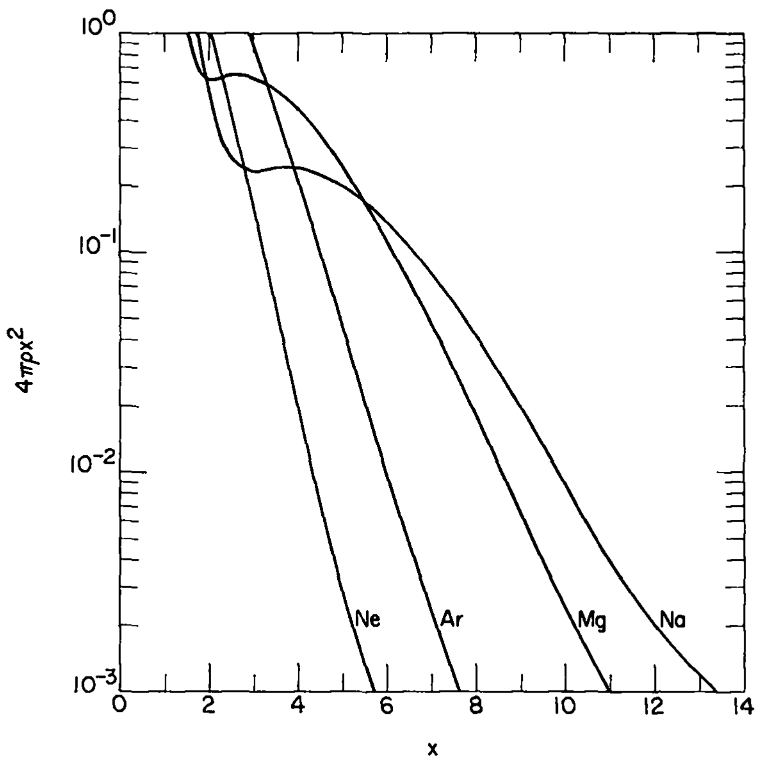


Figure 2. Lattice constant of the elements.



sodium, and to a lesser extent for magnesium, is not obtained on the statistical model. The statistical density distributions have an abrupt cutoff, and thus much more closely resemble those of the rare gases.

The radii of the rare-gas atoms neon, argon, krypton, and xenon, computed on the present model agree closely with their crystal radii. This comparison is made in Table III, where the "experimental" values are computed from the experimental lattice constants given in the recent review article by Pollack.[24] The rare gases are bound in crystals only by the very weak van der Waals forces; if we were to ascribe a finite radius to the isolated atom, it should be for the solid rare gases that such a radius would most nearly equal its crystal radius. Since the corrected statistical model predicts close to these values for the rare-gas atomic radii, it would appear that the correct interpretation of minimum-energy, or zero boundary pressure, solutions is as representing isolated atoms.

TABLE III

LATTICE CONSTANTS OF THE SOLID RARE GASES (a.u.)

Element	$(x_2)_{calc}$	$(x_2)_{exp}$
Neon	3.79	3.30
Argon	4.00	3.92
Krypton	4.23	4.17
Xenon	4.36	4.53

APPENDIX

A FORTRAN CODE TO INTEGRATE THE QUANTUM- AND CORRELATION-CORRECTED TFD EQUATION

The FORTRAN machine code listed here in "F4" language generates a single solution of the quantum- and correlation-corrected TFD equation for a given atomic number, initial slope of the potential function, and degree of ionization. The minimum-energy solutions were stressed in this report, and the code as actually used contains a feature that searches for the solutions possessing the lowest energy by adjusting ϕ_0' and performing a series of integrations. However, there seems little virtue in complicating the present write-up by including a number of code statements that are unnecessary for the task to which a potential user may put the code.

The input data consists of any number of sets of Z, ϕ_0', degree of ionization, and a print flag that indicates whether the entire solution is to be printed, or whether summary information only is desired. Each set is entered by a data card, the layout of which is as follows:

Columns	Data
1 - 4	Atomic number Z
5 - 18	Initial slope ϕ_0'
19 - 23	Degree of ionization
24	Print flag

All but the print flag are floating point numbers. For example, to obtain and print the complete solution corresponding to the free neutral lithium atom, one would prepare the following card:

Columns	Data
1 - 4	003.
5 - 18	-1.94498201900
19 - 23	0000.
24	1

If only summary information were desired, column 24 would contain a 0 punch.

As a further example, a solution corresponding to a compressed O^{--} ion of radius 2.5203 a.u. is obtained with the input

Columns	Data
1 - 4	008.
5 - 18	-2.84800000000
19 - 23	-002.
24	1

The output contains a listing of Z and ϕ_0', and the computed value of a. There follows, unless suppressed by the presence of a 0 in column 24 of the input card: x_1, $\rho(x_1)$, and a tabulation of ϕ and ρ for each x value. Immediately following the tabulation is the computed outer radius of the distribution, x_2, and the interpolated values of $\phi(x_2)$ and $\rho(x_2)$. Also printed out are the total calculated number of electrons within the distribution, and the various energies. If the printing is suppressed, then x_1, $\rho(x_1)$, and the table of $\phi(x)$ and $\rho(x)$ are not printed.

The code consists of a main program and a number of FUNCTION and SUBROUTINE subprograms. "Comment" cards make the purpose of the programs evident; no further explanation of their purpose is required here. However, an attempt will be made to clarify a few items that might prove puzzling:

In the SOURCE subprogram, note that after 10 attempts to find y by iteration, y being a solution of Eq. (15) of the text, the initial guess is changed; and 10 more attempts can be made. This can occur only once in each integration, where the density decreases below about 0.0123. At this point there becomes only one real root of the cubic equation, this root being approximately 0.13, whereas the iteration procedure utilizing the solution on the previous step of the integration as a first guess attempts to find a solution near y = -0.18.

Another item is an apparently extraneous integral that is calculated and never used. This is calculated through FLINT(8) in the integrand routine, and SUM(8) in the main routine. The integral is

$$\int_{x_1}^{x_2} \rho x^4 dx,$$

from which the diamagnetic susceptibility and other quantities of possible interest can be calculated if desired. It should be mentioned that, indeed, the susceptibility has been calculated on this model for the rare gases. The agreement with experiment is slightly better than on the uncorrected TFD model; but the latter values are already in quite good agreement, and the improvement is small.

In addition to the possible necessity of altering the Input-Output statements of the code, it may also be necessary to change the iteration criteria used in the AFUNCT, INTSEC, and SOURCE subprograms.

FORTRAN SYSTEM -- VERSION 07/15/64 - CORRECTION LEVEL 09/15/64

SUBTYPE,FORTRAN

```
        C      MAIN PROGRAM TO INTEGRATE THOMAS-FERMI-DIRAC EQUATION                     MAINMTFD
        C       WITH QUANTUM AND CORRELATION CORRECTIONS                                 MAINMTFD
00000          DIMENSION X(3),PHI(3),FNT(3,8),SUM(8),FNTTM(8)                            MAINMTFD      000002
00001          COMMON Z,PI,PISQRD,C1,C2,C3,TAU1,CSLOPE,HMAX,R,Y,PHIX2,FLINT(8)           MAINMTFD      000002
        C      CONSTANTS                                                                 MAINMTFD      000002
00002          PI=3.14159265                                                             MAINMTFD      000002
00003          PISQRD=PI*PI                                                              MAINMTFD      000004
00004          CON1=3.0**(1.0/3.0)                                                       MAINMTFD      000007
00005          CON2=PI**(1.0/3.0)                                                        MAINMTFD      000021
00006          CF=.3*PI*CON1*CON1*CON2                                                   MAINMTFD      000033
00007          CEX=.75*CON1/CON2                                                         MAINMTFD      000041
00008          CC=.0842                                                                  MAINMTFD      000045
00009          C1=8.0/(3.0*PISQRD)**(2.0/3.0)                                            MAINMTFD      000047
00010          C2=.5/(PISQRD)                                                            MAINMTFD      000065
00011          C3=(49.0/36.0)*CC*CC*4.0/(3.0*PISQRD)**(4.0/3.0)                          MAINMTFD      000070
00012          C4=4.0*PI                                                                 MAINMTFD      000114
00013          TAU1=2.0/(3.0*PI**5)**(1.0/3.0)                                           MAINMTFD      000117
        C      READ PROBLEM INPUT                                                        MAINMTFD      000117
00014        5 READ 10,Z,SLOPE,DEGION,IPRTFG                                             MAINMTFD      000142
00015       10 FORMAT(F4.0,F14.0,F5.0,I1)                                                MAINMTFD      000177
00016          CSLOPE=SLOPE                                                              MAINMTFD      000177
00017          RHOCON=Z/C4                                                               MAINMTFD      000201
        C      OBTAIN MODIFICATION FACTOR                                                MAINMTFD      000201
00018       15 A=AFUNCT(SLOPE)                                                           MAINMTFD      000204
        C      OBTAIN INNER RADIUS OF ELECTRON DISTRIBUTION                              MAINMTFD      000204
00019          X1=X1FNCT(SLOPE,A)                                                        MAINMTFD      000211
00020          PHIX1=1.0+SLOPE*X1                                                        MAINMTFD      000220
        C      INITIAL GUESS FOR Y                                                       MAINMTFD      000220
00021          Y=-.19                                                                    MAINMTFD      000224
00022          RHOX1=(RHOCON/X1)*SOURCE(X1,PHIX1,A)                                      MAINMTFD      000226
        C      RESTORE PAPER AND PRINT PROBLEM DATA                                      MAINMTFD      000226
00023          PRINT 20                                                                  MAINMTFD      000243
00024       20 FORMAT(1H1)                                                               MAINMTFD      000254
00025          PRINT 22,Z                                                                MAINMTFD      000254
00026       22 FORMAT(7H      Z= I5)                                                     MAINMTFD      000272
00027          PRINT 24,SLOPE                                                            MAINMTFD      000272
00028       24 FORMAT(7H SLOPE= F16.10)                                                  MAINMTFD      000310
00029          PRINT 26,A                                                                MAINMTFD      000310
00030       26 FORMAT(7H      A= F16.10)                                                 MAINMTFD      000326
00031          IF(IPRTFG)261,36,261                                                      MAINMTFD      000326
00032      261 PRINT 28,X1                                                               MAINMTFD      000330
00033       28 FORMAT(7H     X1= F16.10)                                                 MAINMTFD      000346
00034          PRINT 30,RHOX1                                                            MAINMTFD      000346
00035       30 FORMAT(7H RHOX1=F13.7////)                                                MAINMTFD      000364
        C      PRINT COLUMN HEADINGS                                                     MAINMTFD      000364
00036          PRINT 35                                                                  MAINMTFD      000364
00037       35 FORMAT(8H       X,13H          PHI,16H             RHO//)                 MAINMTFD      000375
        C      COMPUTE INITIAL AND FINAL INTEGRATION INTERVALS                           MAINMTFD      000375
00038       36 SPLIT=1.0                                                                 MAINMTFD      000375
00039       40 IF(SPLIT-.04/X1)45,45,50                                                  MAINMTFD      000377
00040       45 SPLIT=SPLIT*2.0                                                           MAINMTFD      000404
00041          GO TO 40                                                                  MAINMTFD      000407
00042       50 H=.02/SPLIT                                                               MAINMTFD      000410
00043          HMAX=.018/SQRT(Z)                                                         MAINMTFD      000413
        C      CALCULATE INITIAL VALUES FOR INTEGRATION                                  MAINMTFD      000413
```

```
00044          DO 55 I=1,3                                             MAINMTFD     000417
00045          FLI=I                                                   MAINMTFD     000420
00046          X(I)=(FLI-1.0)*H                                        MAINMTFD     000422
00047       55 PHI(I)=1.0+SLOPE*X(I)                                   MAINMTFD     000426
00048          IF(IPRTFG)56,600,56                                     MAINMTFD     000432
        C      PRINT FIRST THREE POINTS                                MAINMTFD     000432
00049       56 PRINT 60,(X(I),PHI(I),I=1,3)                            MAINMTFD     000434
00050       60 FORMAT(2F12.8)                                          MAINMTFD     000460
00051      600 PHIM2=1.0                                               MAINMTFD     000460
00052          PHIM1=PHI(2)                                            MAINMTFD     000462
00053          PHIO=PHI(3)                                             MAINMTFD     000464
00054          PHDPM2=0.0                                              MAINMTFD     000466
00055          PHDPM1=0.0                                              MAINMTFD     000470
00056          PHIDPO=0.0                                              MAINMTFD     000472
00057          XO=X(3)                                                 MAINMTFD     000474
00058          INDXDB=1                                                MAINMTFD     000476
00059          XM1=X1                                                  MAINMTFD     000500
00060          DO 61 J=1,8                                             MAINMTFD     000502
00061       61 SUM(J)=0.0                                              MAINMTFD     000503
00062          CALL FLINTS(X1,PHIX1,RHOX1)                             MAINMTFD     000505
00063          DO 62 J=1,8                                             MAINMTFD     000515
00064       62 FNT(2,J)=FLINT(J)                                       MAINMTFD     000516
        C      ADVANCE ONE STEP IN X                                   MAINMTFD     000516
00065       65 CALL INTSEC(PHIM2,PHIM1,PHIO,PHDPM2,PHDPM1,PHIDPO,H,XO,A)   MAINMTFD     000520
00066          IF(XO-X1)70,75,75                                       MAINMTFD     000544
00067       70 IF(IPRTFG)71,72,71                                      MAINMTFD     000547
00068       71 PRINT 60,XO,PHIO                                        MAINMTFD     000551
00069       72 INDXDB=-INDXDB                                          MAINMTFD     000574
00070          GO TO 65                                                MAINMTFD     000576
00071       75 RHO=RHOCON*PHIDPO/XO                                    MAINMTFD     000577
00072          IF(IPRTFG)76,810,76                                     MAINMTFD     000603
00073       76 PRINT 80,XO,PHIO,RHO                                    MAINMTFD     000605
00074       80 FORMAT(2F12.8,F17.7)                                    MAINMTFD     000635
00075      810 CALL FLINTS(XO,PHIO,RHO)                                MAINMTFD     000635
00076          DO 81 J=1,8                                             MAINMTFD     000645
00077          FNT(3,J)=FLINT(J)                                       MAINMTFD     000646
00078          SUM(J)=SUM(J)+.5*(FNT(2,J)+FNT(3,J))*(XO-XM1)           MAINMTFD     000650
00079       81 FNT(2,J)=FNT(3,J)                                       MAINMTFD     000661
00080          XM1=XO                                                  MAINMTFD     000663
00081          INDXDB=-INDXDB                                          MAINMTFD     000665
00082          IF(INDXDB)65,65,85                                      MAINMTFD     000667
00083       85 DO 86 J=1,8                                             MAINMTFD     000671
00084       86 FNT(1,J)=FNT(3,J)                                       MAINMTFD     000672
00085          IF(H-.5*HMAX)90,94,94                                   MAINMTFD     000674
        C      DOUBLE INTEGRATION INTERVAL                             MAINMTFD     000674
00086       90 H=2.0*H                                                 MAINMTFD     000701
00087          PHIM1=PHIM2                                             MAINMTFD     000704
00088          PHIM2=1.0                                               MAINMTFD     000706
00089          PHDPM1=PHDPM2                                           MAINMTFD     000710
00090          PHDPM2=0.0                                              MAINMTFD     000712
00091       91 CALL INTSEC(PHIM2,PHIM1,PHIO,PHDPM2,PHDPM1,PHIDPO,H,XO,A)   MAINMTFD     000714
00092          RHO=RHOCON*PHIDPO/XO                                    MAINMTFD     000740
00093          IF(IPRTFG)910,911,910                                   MAINMTFD     000744
00094      910 PRINT 80,XO,PHIO,RHO                                    MAINMTFD     000746
00095      911 CALL FLINTS(XO,PHIO,RHO)                                MAINMTFD     000776
00096          DO 92 J=1,8                                             MAINMTFD     001006
00097       92 FNT(3,J)=FLINT(J)                                       MAINMTFD     001007
00098          INDXDB=-INDXDB                                          MAINMTFD     001011
00099          IF(INDXDB)93,93,935                                     MAINMTFD     001013
00100       93 DO 931 J=1,8                                            MAINMTFD     001015
00101      931 FNT(2,J)=FNT(3,J)                                       MAINMTFD     001016
```

```
          GO TO 91                                              MAINMTFD   001020
      935 DO 936 J=1,8                                          MAINMTFD   001021
      936 SUM(J)=SUM(J)+(H/3.0)*(FNT(1,J)+4.0*FNT(2,J)+FNT(3,J)) MAINMTFD   001022
          GO TO 85                                              MAINMTFD   001034
C         INTEGRATION PROCEEDS WITH CONSTANT X INCREMENT        MAINMTFD   001034
       94 DO 116 I=2,3                                          MAINMTFD   001035
       95 CALL INTSEC(PHIM2,PHIM1,PHIO,PHDPM2,PHDPM1,PHIDPO,H,XO,A) MAINMTFD 001036
C         TEST IF AUXILIARY CONDITIONS ON INTEGRATION           MAINMTFD   001036
C          ARE SATISFIED.  VIOLATION INDICATES INITIAL SLOPE    MAINMTFD   001036
C          IS TOO LARGE NEGATIVELY                              MAINMTFD   001036
          YSQPLR=Y*Y+R                                          MAINMTFD   001062
          IF(YSQPLR)98,96,96                                    MAINMTFD   001066
       96 IF(Y+TAU1)98,97,97                                    MAINMTFD   001070
       97 IF(TAU1-Y+2.0*SQRT(YSQPLR))98,100,100                 MAINMTFD   001073
       98 PRINT 99,XO                                           MAINMTFD   001103
       99 FORMAT(34H AUXILIARY CONDITION VIOLATED   X= F12.8)   MAINMTFD   001121
          GO TO 5                                               MAINMTFD   001121
      100 RHO=RHOCON*PHIDPO/XO                                  MAINMTFD   001122
          CALL FLINTS(XO,PHIO,RHO)                              MAINMTFD   001126
          DO 101 J=1,8                                          MAINMTFD   001136
      101 FNT(I,J)=FLINT(J)                                     MAINMTFD   001137
          IF(IPRTFG)105,110,105                                 MAINMTFD   001141
      105 PRINT 80,XO,PHIO,RHO                                  MAINMTFD   001143
C         TEST IF OUTER BOUNDARY IS REACHED                     MAINMTFD   001143
      110 G=(XO-.5*H)*(PHIO-PHIM1)/H-(PHIO+PHIM1)/2.0+DEGION/Z  MAINMTFD   001173
          IF(G)116,120,120                                      MAINMTFD   001215
      116 CONTINUE                                              MAINMTFD   001217
          DO 117 J=1,8                                          MAINMTFD   001220
          SUM(J)=SUM(J)+(H/3.0)*(FNT(1,J)+4.0*FNT(2,J)+FNT(3,J)) MAINMTFD  001221
          FNT(1,J)=FNT(3,J)                                     MAINMTFD   001233
      117 FNTTM(J)=FNT(3,J)                                     MAINMTFD   001235
          XTRM=XO                                               MAINMTFD   001237
          GO TO 94                                              MAINMTFD   001241
C         OBTAIN OUTER RADIUS OF DISTRIBUTION                   MAINMTFD   001241
      120 X2=X2FNCT(PHIM2,PHIM1,PHIO,XO,H,DEGION)               MAINMTFD   001242
          RHOX2=RHOCON*SOURCE(X2,PHIX2,A)/X2                    MAINMTFD   001261
          IF(IPRTFG)124,122,124                                 MAINMTFD   001274
      122 PRINT 123,X2                                          MAINMTFD   001276
      123 FORMAT(7H    X2= F11.5)                               MAINMTFD   001314
          GO TO 126                                             MAINMTFD   001314
      124 PRINT 125,X2,PHIX2,RHOX2                              MAINMTFD   001315
      125 FORMAT(//F8.4,F16.8,F17.7)                            MAINMTFD   001345
C         CALC END POINT CORRECTIONS TO INTEGRALS               MAINMTFD   001345
      126 CALL FLINTS(X2,PHIX2,RHOX2)                           MAINMTFD   001345
          DO 130 J=1,8                                          MAINMTFD   001355
      130 SUM(J)=SUM(J)+.5*(X2-XTRM)*(FNTTM(J)+FLINT(J))        MAINMTFD   001356
C         CALC ENERGIES FROM INTEGRALS                          MAINMTFD   001356
          EPRIME=(Z*PHIX2-DEGION)/X2-C2                         MAINMTFD   001367
          FLNUM=C4*SUM(1)                                       MAINMTFD   001375
          EPN=-Z*C4*SUM(4)                                      MAINMTFD   001400
          EPEPRM=-Z*C4*SUM(5)                                   MAINMTFD   001404
          EF=CF*C4*SUM(3)                                       MAINMTFD   001410
          EEX=-CEX*C4*SUM(2)                                    MAINMTFD   001414
          EQ=A*A*C4*SUM(6)/2.0                                  MAINMTFD   001420
          EC=-CC*C4*SUM(7)                                      MAINMTFD   001426
          EPE=.5*(EPEPRM-EPN+FLNUM*(EPRIME+C2))                 MAINMTFD   001432
          E=EF+EPN+EPE+EEX+EQ+EC                                MAINMTFD   001443
          PRINT 135,FLNUM                                       MAINMTFD   001452
      135 FORMAT(//21H NUMBER OF ELECTRONS= F11.6)              MAINMTFD   001470
          PRINT 136,EF,EQ                                       MAINMTFD   001470
      136 FORMAT(//5H  EF= 1PE15.7,7H    EQ= 1PE15.7)           MAINMTFD   001513
```

```
CC155          PRINT 137,EPN,EPE,EEX,EC                                                              MAINMTFD          001513
00156      137 FORMAT(5H EPN= 1PE15.7,7H   EPE= 1PE15.7,7H   EEX= 1PE15.7,                           MAINMTFD          001550
              1 7H    EC= 1PE15.7)                                                                   MAINMTFD          001550
00157          PRINT 138,E                                                                           MAINMTFD          001550
0C158      138 FORMAT(5H    E= 1PE18.10//)                                                           MAINMTFD          0C1566
0C159          GO TO 5                                                                               MAINMTFD          0C1566
0C160          END                                                                                   MAINMTFD          C01567
```

SUBPROGRAM *MAIN* - COMPILE TIME 000005 SECS. - NO. BINARY CARDS 000000 - LENGTH (8)001267 WORDS (=(10)000695)

FORTRAN SYSTEM -- VERSION 07/15/64 - CORRECTION LEVEL 09/15/64

SUBTYPE,FORTRAN

```
        C      COMPUTE MODIFICATION FACTOR FROM INITIAL SLOPE                    AFNTMTFD
        C       BY NEWTON-RAPHSON METHOD                                         AFNTMTFD
00000          FUNCTION AFUNCT(SLCPE)                                            AFNTMTFD    000002
00001          COMMON Z,PI,PISQRD,C1,C2,C3,TAU1,CSLOPE,HMAX,R,Y,PHIX2,FLINT(8)   AFNTMTFD    000002
0C002          CRIT=1.0E-14                                                      AFNTMTFD    000002
0C003          ALPHA=SQRT(Z/(2.0*ABS(SLOPE)))                                    AFNTMTFD    000004
0C004          ROOT1=SQRT(ALPHA)                                                 AFNTMTFD    000010
00005          F1=3.0*ALPHA*ALPHA-.5                                             AFNTMTFD    000012
0C006          F2=ALPHA*ROOT1                                                    AFNTMTFD    000017
        C      INITIAL GUESS FOR NU                                              AFNTMTFD    000017
0C007          FLNU=ALPHA-.5                                                     AFNTMTFD    000022
0C008        5 ROOT2=SQRT(FLNU)                                                  AFNTMTFD    000025
0C009          F=FLNU*(FLNU*(FLNU+1.5)+2.0*F2*ROOT2-F1)                          AFNTMTFD    000027
CC010          FPRIME=3.0*FLNU*(FLNU+1.0)+3.0*F2*ROOT2-F1                        AFNTMTFD    000042
0C011          IF(FPRIME)15,10,15                                                AFNTMTFD    000057
        C      ADJUST NU IF DERIVATIVE OF F IS ZERO                              AFNTMTFD    000057
00012       10 FLNU=.99999*FLNU                                                  AFNTMTFD    000061
0C013          GO TO 5                                                           AFNTMTFD    000064
        C      CORRECT NU                                                        AFNTMTFD    000064
00014       15 CORR=-F/FPRIME                                                    AFNTMTFD    000065
0C015          FLNU=FLNU+CORR                                                    AFNTMTFD    000070
CC016          ERROR=ABS(CORR/FLNU)                                              AFNTMTFD    000073
        C      TEST IF CRITERION IS MET                                          AFNTMTFD    000073
00017          IF(ERROR-CRIT)20,20,5                                             AFNTMTFD    000076
0CC18       20 AFUNCT=ALPHA-SQRT(FLNU)*ROOT1                                     AFNTMTFD    000101
CC019          RETURN                                                            AFNTMTFD    000106
0C020          END                                                               AFNTMTFD    000107
```

SUBPROGRAM AFUNCT - COMPILE TIME 000003 SECS. - NO. BINARY CARDS 000000 - LENGTH (8)000135 WORDS (=(10)000093)

FORTRAN SYSTEM -- VERSION 07/15/64 - CORRECTION LEVEL 09/15/64

SUBTYPE,FORTRAN

```
      C     COMPUTE INNER RADIUS OF ELECTRON DISTRIBUTION                      X1FNMTFD
            FUNCTION X1FNCT(SLOPE,A)                                           X1FNMTFD     000002
            COMMON Z,PI,PISQRD,C1,C2,C3,TAU1,CSLOPE,HMAX,R,Y,PHIX2,FLINT(8)    X1FNMTFD     000002
            S=(1.0-PISQRD*Z*2.0*SLOPE)/(PISQRD*Z)                              X1FNMTFD     000002
            X1FNCT=(1.0-SQRT(1.0-A*A*S/Z))/S                                   X1FNMTFD     000014
            RETURN                                                             X1FNMTFD     000026
            END                                                                X1FNMTFD     000027
```

SUBPROGRAM X1FNCT - COMPILE TIME 000002 SECS. - NO. BINARY CARDS 000000 - LENGTH (8)000067 WORDS (=(10)000055)

FORTRAN SYSTEM -- VERSION 07/15/64 - CORRECTION LEVEL 09/15/64

SUBTYPE,FORTRAN

```
      C     COMPUTE OUTER RADIUS OF ELECTRON DISTRIBUTION               X2FNMTFD
      C      AND INTERPOLATE FOR PHI AT OUTER BOUNDARY                  X2FNMTFD
            FUNCTION X2FNCT(PHIM2,PHIM1,PHIO,XO,H,DEGION)               X2FNMTFD   000002
            COMMON Z,PI,PISQRD,C1,C2,C3,TAU1,CSLOPE,HMAX,R,Y,PHIX2,FLINT(8)  X2FNMTFD   000002
            SCRIPA=.5*(PHIO-2.0*PHIM1+PHIM2)/(H*H)                      X2FNMTFD   000002
            SCRIPB=(PHIO-PHIM1)/H-SCRIPA*(2.0*XO-H)                     X2FNMTFD   000014
            SCRIPC=PHIO-XO*(SCRIPA*XO+SCRIPB)                           X2FNMTFD   000026
            X2=SQRT((SCRIPC-DEGION/Z)/SCRIPA)                           X2FNMTFD   000034
            PHIX2=X2*(SCRIPA*X2+SCRIPB)+SCRIPC                          X2FNMTFD   000041
            X2FNCT=X2                                                   X2FNMTFD   000047
            RETURN                                                      X2FNMTFD   000051
            END                                                         X2FNMTFD   000052
```

SUBPROGRAM X2FNCT - COMPILE TIME 000002 SECS. - NO. BINARY CARDS 000000 - LENGTH (8)000115 WORDS (=(10)000077)

FORTRAN SYSTEM -- VERSION 07/15/64 - CORRECTION LEVEL 09/15/64

SUBTYPE,FORTRAN

```
              C      SUBROUTINE WHICH INTEGRATES SECOND ORDER DIFFERENTIAL EQUATION       INTGMTFD
              C       BY HARTREE (STOERMER) METHOD, WITH A CORRECTION TERM                 INTGMTFD
              C       INVOLVING AN ESTIMATE OF FOURTH DIFFERENCE IN PHI                    INTGMTFD
              C       DOUBLE PRIME WHEN THIS QUANTITY IS LARGE                             INTGMTFD
00000                SUBROUTINE INTSEC(PHIM2,PHIM1,PHIO,PHDPM2,PHDPM1,PHIDPO,H,XO,A)      INTGMTFD   000002
00001                COMMON Z,PI,PISQRD,C1,C2,C3,TAU1,CSLOPE,HMAX,R,Y,PHIX2,FLINT(8)      INTGMTFD   000002
00002                CRIT=1.0E-13                                                         INTGMTFD   000002
00003                N=0                                                                  INTGMTFD   000004
00004                XP1=XO+H                                                             INTGMTFD   000006
              C      TEST IF TO APPLY CORRECTION                                          INTGMTFD   000006
00005                IF(H-.5*HMAX)10,5,5                                                  INTGMTFD   000011
00006             5  IF(PHDPM2)15,10,15                                                   INTGMTFD   000016
              C      CALCULATE FOURTH ORDER TERM                                          INTGMTFD   000016
00007            10  XP2=XO+2.0*H                                                         INTGMTFD   000020
00008                ESPHP1=1.0+CSLOPE*XP1                                                INTGMTFD   000024
00009                ESPHP2=1.0+CSLOPE*XP2                                                INTGMTFD   000030
00010                EPDPP1=SOURCE(XP1,ESPHP1,A)                                          INTGMTFD   000034
00011                EPDPP2=SOURCE(XP2,ESPHP2,A)                                          INTGMTFD   000045
00012                FOURTH=(EPDPP2-4.0*EPDPP1+6.0*PHIDPO-4.0*PHDPM1+PHDPM2)/240.0        INTGMTFD   000056
00013                GO TO 20                                                             INTGMTFD   000074
00014            15  FOURTH=0.0                                                           INTGMTFD   000075
              C      ESTIMATE SECOND DIFFERENCE IN PHI DOUBLE PRIME                       INTGMTFD   000075
00015            20  D2PDPE=PHIDPO-2.0*PHDPM1+PHDPM2                                      INTGMTFD   000077
              C      CALCULATE PREDICTED VALUE FOR COMPARISON                             INTGMTFD   000077
00016            25  D2PHI=(H*H)*(PHIDPO+(D2PDPE/12.0)-FOURTH)                            INTGMTFD   000104
00017                PHIP1=2.0*PHIO-PHIM1+D2PHI                                           INTGMTFD   000115
00018                PHDPP1=SOURCE(XP1,PHIP1,A)                                           INTGMTFD   000122
00019                D2PDPP=PHDPP1-2.0*PHIDPO+PHDPM1                                      INTGMTFD   000133
              C      TEST FOR CONVERGENCE                                                 INTGMTFD   000133
00020                ERROR=ABS((D2PDPP-D2PDPE)/PHIO)*H*H/6.0                              INTGMTFD   000140
00021                IF(ERROR-CRIT)45,45,30                                               INTGMTFD   000150
00022            30  D2PDPE=D2PDPP                                                        INTGMTFD   000153
00023                N=N+1                                                                INTGMTFD   000155
00024                IF(N-10)25,35,35                                                     INTGMTFD   000160
00025            35  PRINT 40                                                             INTGMTFD   000163
00026            40  FORMAT(30H INTEGRATION CRITERION NOT MET)                            INTGMTFD   000174
00027                GO TO 45                                                             INTGMTFD   000174
00028            45  PHIM2=PHIM1                                                          INTGMTFD   000175
00029                PHIM1=PHIO                                                           INTGMTFD   000177
00030                PHIO=PHIP1                                                           INTGMTFD   000201
00031                PHDPM2=PHDPM1                                                        INTGMTFD   000203
00032                PHDPM1=PHIDPO                                                        INTGMTFD   000205
00033                PHIDPO=PHDPP1                                                        INTGMTFD   000207
00034                XO=XP1                                                               INTGMTFD   000211
00035                RETURN                                                               INTGMTFD   000213
00036                END                                                                  INTGMTFD   000214
```

SUBPROGRAM INTSEC - COMPILE TIME 000003 SECS. - NO. BINARY CARDS 000000 - LENGTH (8)000255 WORDS (=(10)000173)

```
FORTRAN SYSTEM -- VERSION  07/15/64 - CORRECTION LEVEL  09/15/64


SUBTYPE,FORTRAN

      C       COMPUTE SOURCE FUNCTION, WHICH IS EQUATED TO                    SRCEMTFD
      C        SECOND DERIVATIVE OF PHI                                       SRCEMTFD
              FUNCTION SOURCE(X,PHI,A)                                        SRCEMTFD       000002
              COMMON Z,PI,PISQRD,C1,C2,C3,TAU1,CSLOPE,HMAX,R,Y,PHIX2,FLINT(8) SRCEMTFD       000002
              CRIT=1.0E-14                                                    SRCEMTFD       000002
              N=0                                                             SRCEMTFD       000004
              NFLAG=0                                                         SRCEMTFD       000006
              R=C1*(Z*PHI/X-A*A/(2.0*X*X)-C2)                                 SRCEMTFD       000010
      C       EVALUATE Y BY NEWTON-RAPHSON METHOD                             SRCEMTFD       000010
              F2=TAU1*R-C3                                                    SRCEMTFD       000027
            5 F=Y*(Y*(Y+TAU1)+R)+F2                                           SRCEMTFD       000033
              FPRIME=Y*(3.0*Y+2.0*TAU1)+R                                     SRCEMTFD       000042
              IF(FPRIME)15,10,15                                              SRCEMTFD       000053
           10 Y=.99999*Y                                                      SRCEMTFD       000055
              GO TO 5                                                         SRCEMTFD       000060
           15 CORR=-F/FPRIME                                                  SRCEMTFD       000061
              Y=Y+CORR                                                        SRCEMTFD       000064
              ERROR=ABS(CORR/Y)                                               SRCEMTFD       000067
              IF(ERROR-CRIT)50,50,20                                          SRCEMTFD       000072
           20 N=N+1                                                           SRCEMTFD       000075
              IF(NFLAG)35,25,35                                               SRCEMTFD       000100
           25 IF(N-10)5,30,30                                                 SRCEMTFD       000102
           30 NFLAG=1                                                         SRCEMTFD       000105
              Y=0.13                                                          SRCEMTFD       000107
              N=0                                                             SRCEMTFD       000111
              GO TO 5                                                         SRCEMTFD       000113
           35 IF(N-10)5,40,40                                                 SRCEMTFD       000114
           40 PRINT 45                                                        SRCEMTFD       000117
           45 FORMAT(23H CRITERION ON Y NOT MET)                              SRCEMTFD       000130
           50 ROOT=SQRT(Y*Y+R)                                                SRCEMTFD       000130
              PSI=SQRT(Y+TAU1)*SQRT(-Y+TAU1+2.0*ROOT)                         SRCEMTFD       000134
              SOURCE=(.5*PI*X/Z)*(TAU1+PSI+ROOT)**3                           SRCEMTFD       000150
              RETURN                                                          SRCEMTFD       000165
              END                                                             SRCEMTFD       000166

SUBPROGRAM SOURCE - COMPILE TIME 000003 SECS. - NO. BINARY CARDS 000000 - LENGTH (8)000177 WORDS (=(10)000127)
```

FORTRAN SYSTEM -- VERSION 07/15/64 - CORRECTION LEVEL 09/15/64

SUBTYPE,FORTRAN

```
 C      COMPUTE INTEGRANDS FOR ENERGY INTEGRALS AND TOTAL                  FLNTMTFD
 C       NUMBER OF PARTICLES CHECK                                         FLNTMTFD
        SUBROUTINE FLINTS(X,PHI,RHO)                                       FLNTMTFD     000002
        COMMON Z,PI,PISQRD,C1,C2,C3,TAU1,CSLOPE,HMAX,R,Y,PHIX2,FLINT(8)    FLNTMTFD     000002
        RTRHO=RHO**(1.0/3.0)                                               FLNTMTFD     000002
        FLINT(6)=RHO                                                       FLNTMTFD     000014
        FLINT(4)=RHO*X                                                     FLNTMTFD     000016
        FLINT(1)=FLINT(4)*X                                                FLNTMTFD     00C021
        FLINT(8)=FLINT(1)*X*X                                              FLNTMTFD     000024
        FLINT(2)=FLINT(1)*RTRHO                                            FLNTMTFD     000030
        FLINT(3)=FLINT(2)*RTRHO                                            FLNTMTFD     000033
        FLINT(5)=PHI*FLINT(4)                                              FLNTMTFD     00C036
        FLINT(7)=FLINT(1)*SQRT(RTRHO)                                      FLNTMTFD     000041
        RETURN                                                             FLNTMTFD     000045
        END                                                                FLNTMTFD     000046
```

SUBPROGRAM FLINTS - COMPILE TIME 000002 SECS. - NO. BINARY CARDS 000000 - LENGTH (8)000105 WORDS (=(10)000069)

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