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

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

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 minimum 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

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

The expression for density on the TF model,

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

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

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

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 $n = \nu$, 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.

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*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

$$u_c = -c_c \rho^{1/6}. \qquad (13)$$

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,

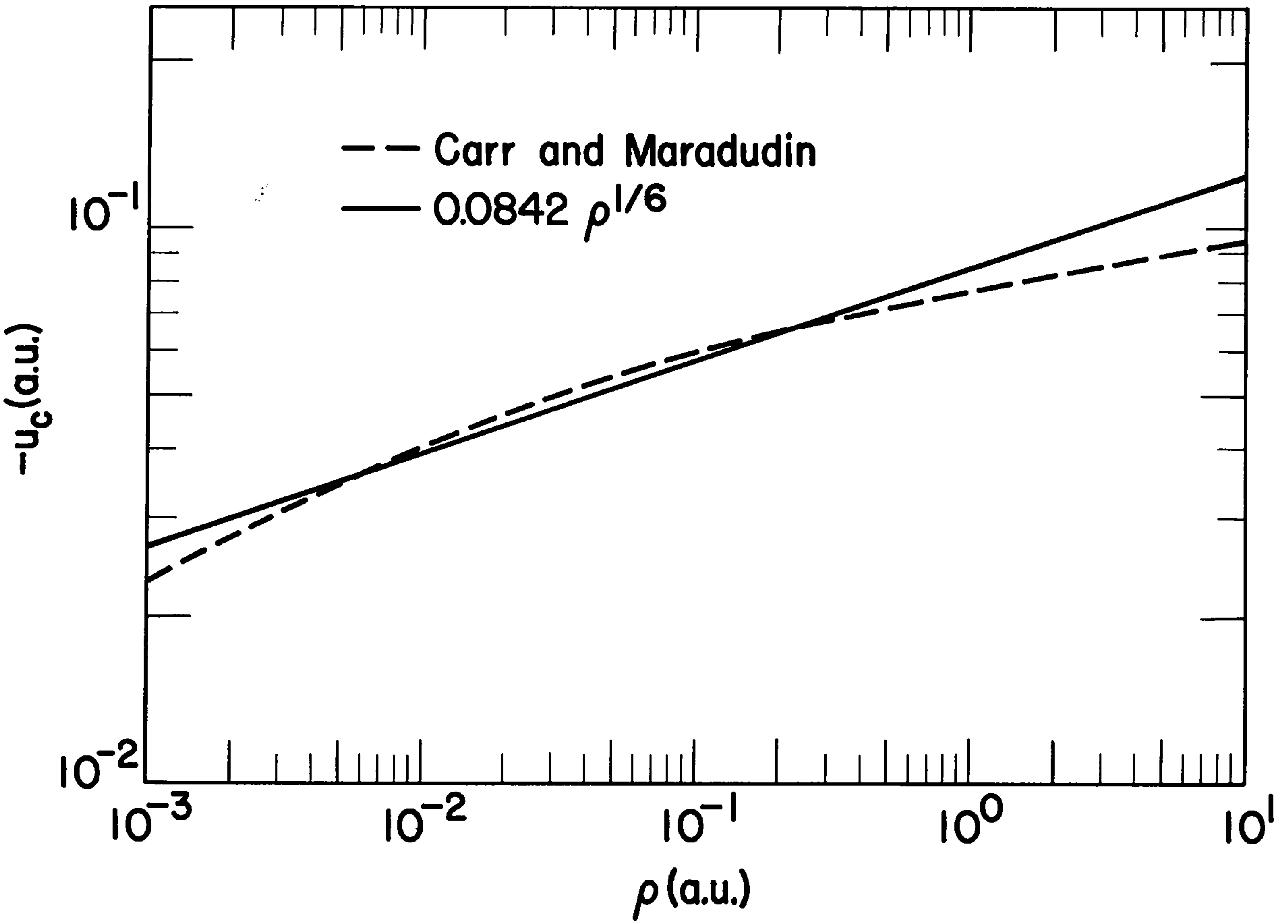


Figure 1. Correlation energy per electron.

but at ρ = 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. Derivation of the Equation

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:

$$y^3 + \tau_1 y^2 + Ry + (\tau_1 R - \upsilon_0^2) = 0. \tag{15}$$

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

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

In terms of ϕ,

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

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

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

Other energy integrals are, with an obvious notation,

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

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

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

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

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

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

where

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

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

$$\begin{aligned}\Delta^2\phi_0 &= (\phi_1-\phi_0) - (\phi_0-\phi_{-1})\\ &= \phi_1 - 2\phi_0 + \phi_{-1},\end{aligned}$$

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

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

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,

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

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

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

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 less 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

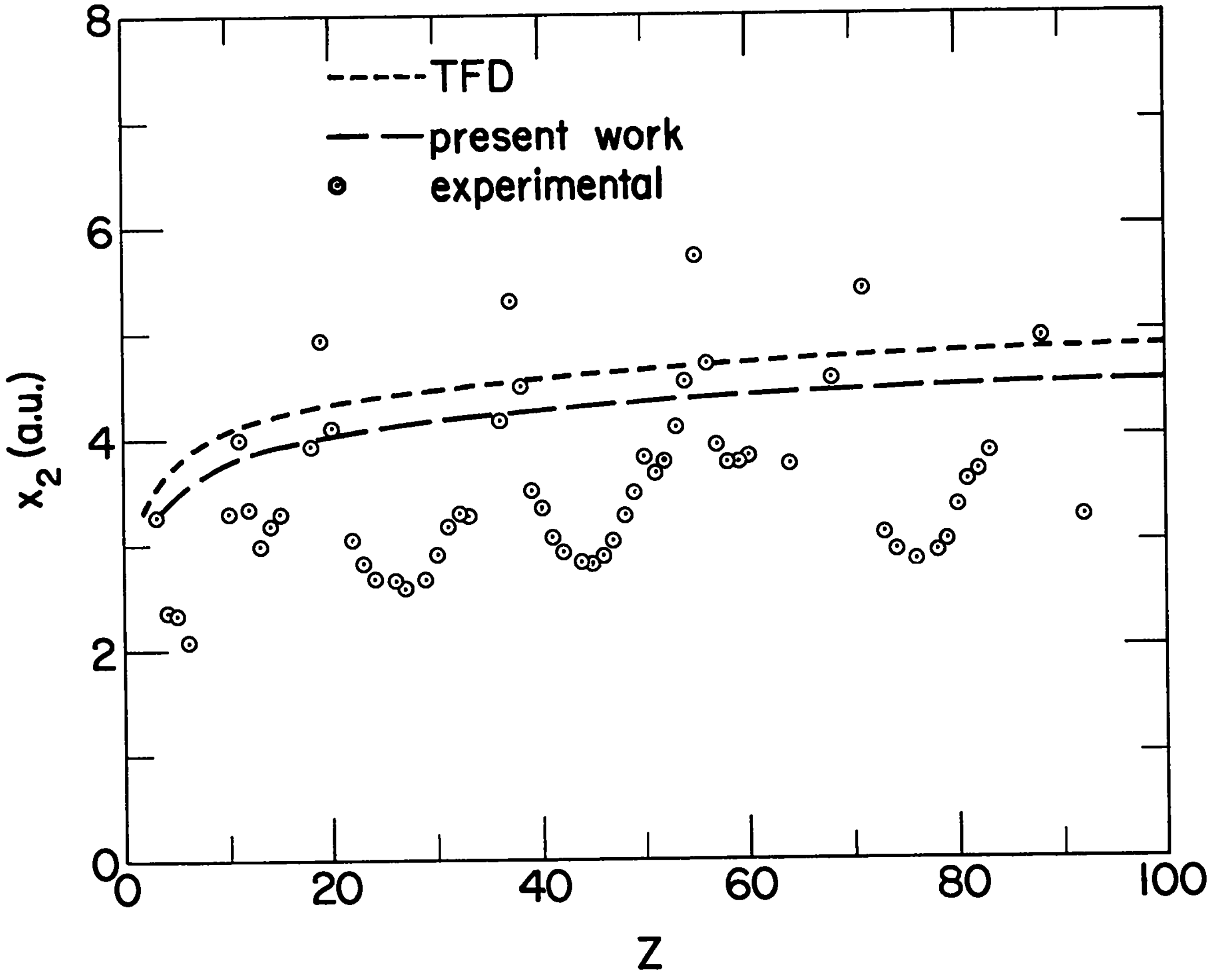
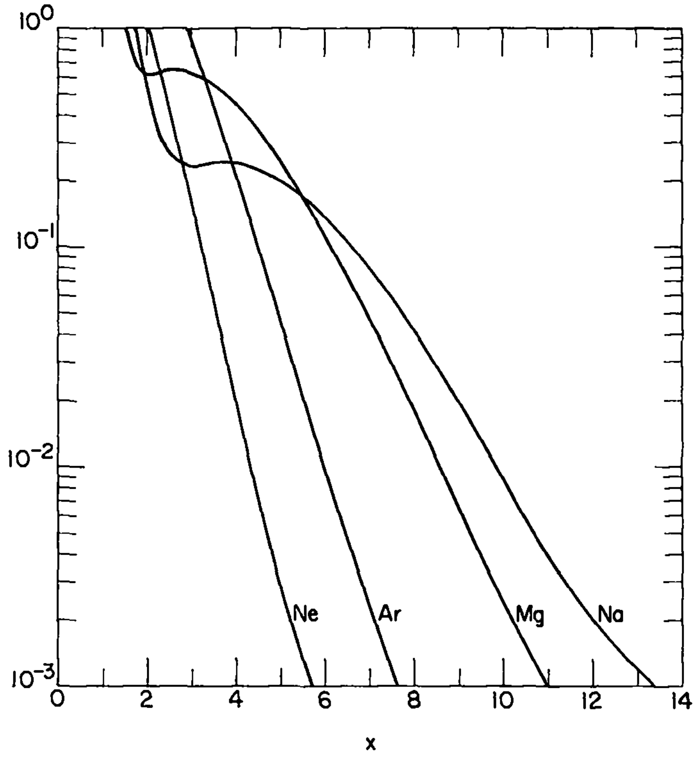


Figure 2. Lattice constant of the elements.



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

```
      DO 55 I=1,3                                                  MAINMTFO   000417
      FLI=I                                                        MAINMTFO   000420
      X(I)=(FLI-1.0)*H                                             MAINMTFO   000422
   55 PHI(I)=1.0+SLOPE*X(I)                                        MAINMTFO   000426
      IF(IPRTFG)56,600,56                                          MAINMTFO   000432
C     PRINT FIRST THREE POINTS                                     MAINMTFO   000432
   56 PRINT 60,(X(I),PHI(I),I=1,3)                                 MAINMTFO   000434
   60 FORMAT(2F12.8)                                               MAINMTFO   000460
  600 PHIM2=1.0                                                    MAINMTFO   000460
      PHIM1=PHI(2)                                                 MAINMTFO   000462
      PHIO=PHI(3)                                                  MAINMTFO   000464
      PHDPM2=0.0                                                   MAINMTFO   000466
      PHDPM1=0.0                                                   MAINMTFO   000470
      PHIDPO=0.0                                                   MAINMTFO   000472
      X0=X(3)                                                      MAINMTFO   000474
      INDXDB=1                                                     MAINMTFO   000476
      XM1=X1                                                       MAINMTFO   000500
      DO 61 J=1,8                                                  MAINMTFO   000502
   61 SUM(J)=0.0                                                   MAINMTFO   000503
      CALL FLINTS(X1,PHIX1,RHOX1)                                  MAINMTFO   000505
      DO 62 J=1,8                                                  MAINMTFO   000515
   62 FNT(2,J)=FLINT(J)                                            MAINMTFO   000516
C     ADVANCE ONE STEP IN X                                        MAINMTFO   000516
   65 CALL INTSEC(PHIM2,PHIM1,PHIO,PHDPM2,PHDPM1,PHIDPO,H,X0,A)     MAINMTFO   000520
      IF(X0-X1)70,75,75                                            MAINMTFO   000544
   70 IF(IPRTFG)71,72,71                                           MAINMTFO   000547
   71 PRINT 60,X0,PHIO                                             MAINMTFO   000551
   72 INDXDB=-INDXDB                                               MAINMTFO   000574
      GO TO 65                                                     MAINMTFO   000576
   75 RHO=RHOCON*PHIDPO/X0                                         MAINMTFO   000577
      IF(IPRTFG)76,810,76                                          MAINMTFO   000603
   76 PRINT 80,X0,PHIO,RHO                                         MAINMTFO   000605
   80 FORMAT(2F12.8,F17.7)                                         MAINMTFO   000635
  810 CALL FLINTS(X0,PHIO,RHO)                                     MAINMTFO   000635
      DO 81 J=1,8                                                  MAINMTFO   000645
      FNT(3,J)=FLINT(J)                                            MAINMTFO   000646
      SUM(J)=SUM(J)+.5*(FNT(2,J)+FNT(3,J))*(X0-XM1)                MAINMTFO   000650
   81 FNT(2,J)=FNT(3,J)                                            MAINMTFO   000661
      XM1=X0                                                       MAINMTFO   000663
      INDXDB=-INDXDB                                               MAINMTFO   000665
      IF(INDXDB)65,65,85                                           MAINMTFO   000667
   85 DO 86 J=1,8                                                  MAINMTFO   000671
   86 FNT(1,J)=FNT(3,J)                                            MAINMTFO   000672
      IF(H-.5*HMAX)90,94,94                                        MAINMTFO   000674
C     DOUBLE INTEGRATION INTERVAL                                  MAINMTFO   000674
   90 H=2.0*H                                                      MAINMTFO   000701
      PHIM1=PHIM2                                                  MAINMTFO   000704
      PHIM2=1.0                                                    MAINMTFO   000706
      PHDPM1=PHDPM2                                                MAINMTFO   000710
      PHDPM2=0.0                                                   MAINMTFO   000712
   91 CALL INTSEC(PHIM2,PHIM1,PHIO,PHDPM2,PHDPM1,PHIDPO,H,X0,A)     MAINMTFO   000714
      RHO=RHOCON*PHIDPO/X0                                         MAINMTFO   000740
      IF(IPRTFG)910,911,910                                        MAINMTFO   000744
  910 PRINT 80,X0,PHIO,RHO                                         MAINMTFO   000746
  911 CALL FLINTS(X0,PHIO,RHO)                                     MAINMTFO   000776
      DO 92 J=1,8                                                  MAINMTFO   001006
   92 FNT(3,J)=FLINT(J)                                            MAINMTFO   001007
      INDXDB=-INDXDB                                               MAINMTFO   001011
      IF(INDXDB)93,93,935                                          MAINMTFO   001013
   93 DO 931 J=1,8                                                 MAINMTFO   001015
  931 FNT(2,J)=FNT(3,J)                                            MAINMTFO   001016
```

```
      GO TO 91                                                          MAINMTFO      001020
  935 DO 936 J=1,8                                                      MAINMTFO      001021
  936 SUM(J)=SUM(J)+(H/3.0)•(FNT(1,J)+4.0•FNT(2.J)+FNT(3,J))            MAINMTFO      001022
      GO TO 85                                                          MAINMTFO      001034
C     INTEGRATION PROCEEDS WITH CONSTANT X INCREMENT                    MAINMTFO      001034
   94 DO 116 I=2,3                                                      MAINMTFO      001035
   95 CALL INTSEC(PHIM2,PHIM1,PHIO,PHOPM2,PHOPM1,PHIOPO.H,XO.A)         MAINMTFO      001036
C     TEST IF AUXILIARY CONDITIONS ON INTEGRATION                       MAINMTFO      001036
C      ARE SATISFIEC.  VIOLATION INDICATES INITIAL SLOPE                MAINMTFO      001036
C      IS TOO LARGE NEGATIVELY                                          MAINMTFO      001036
      YSQPLR=Y•Y+R                                                      MAINMTFO      001062
      IF(YSCPLR)98,96,96                                                MAINMTFO      001066
   96 IF(Y+TAU1)98,97,97                                                MAINMTFO      001070
   97 IF(TAU1-Y+2.0•SQRT(YSQPLR))98,10C,100                             MAINMTFO      001073
   98 PRINT 99,XG                                                       MAINMTFO      001103
   99 FORMAT(34H AUXILIARY CONDITION VIOLATED   X= F12.8)               MAINMTFO      001121
      GO TO 5                                                           MAINMTFO      001121
  10C RHO=RHOCON•PHIOPO/XO                                              MAINMTFO      001122
      CALL FLINTS(XO,PHIO,RHO)                                          MAINMTFO      001126
      DO 101 J=1,8                                                      MAINMTFO      001136
  101 FNT(I,J)=FLINT(J)                                                 MAINMTFO      001137
      IF(IPRTFG)105,11C,105                                             MAINMTFO      001141
  105 PRINT 80,XO,PHIO,RHO                                              MAINMTFO      001143
C     TEST IF OUTER BOUNDARY IS REACHED                                 MAINMTFO      001143
  110 G=(XO-.5•H)•(PHIO-PHIM1)/H-(PHIO+PHIM1)/2.0+DEGION/Z              MAINMTFO      001173
      IF(G)116,120,120                                                  MAINMTFO      001215
  116 CONTINUE                                                          MAINMTFO      001217
      DO 117 J=1,8                                                      MAINMTFO      001220
      SUM(J)=SUM(J)+(H/3.0)•(FNT(1,J)+4.0•FNT(2,J)+FNT(3,J))            MAINMTFO      001221
      FNT(1,J)=FNT(3,J)                                                 MAINMTFO      001233
  117 FNTTM(J)=FNT(3,J)                                                 MAINMTFO      001235
      XTRM=XO                                                           MAINMTFO      001237
      GO TO 94                                                          MAINMTFO      001241
C     OBTAIN OUTER RADIUS OF DISTRIBUTION                               MAINMTFO      001241
  120 X2=X2FNCT(PHIM2,PHIM1,PHIO,XO,H,DEGION)                           MAINMTFO      001242
      RHOX2=RHOCON•SOURCE(X2,PHIX2,A)/X2                                MAINMTFO      001261
      IF(IPRTFG)124,122,124                                             MAINMTFO      001274
  122 PRINT 123,X2                                                      MAINMTFO      001276
  123 FORMAT(7H    X2= F11.5)                                           MAINMTFO      001314
      GO TO 126                                                         MAINMTFO      001314
  124 PRINT 125,X2,PHIX2,RHOX2                                          MAINMTFO      001315
  125 FORMAT(//F8.4,F16.8.F17.7)                                        MAINMTFO      001345
C     CALC END POINT CORRECTIONS TO INTEGRALS                           MAINMTFO      001345
  126 CALL FLINTS(X2,PHIX2,RHOX2)                                       MAINMTFO      001345
      DO 13C J=1,8                                                      MAINMTFO      001355
  13C SUM(J)=SUM(J)+.5•(X2-XTRM)•(FNTTM(J)+FLINT(J))                    MAINMTFO      001356
C     CALC ENERGIES FROM INTEGRALS                                      MAINMTFO      001356
      EPRIME=(Z•PHIX2-DEGION)/X2-C2                                     MAINMTFO      001367
      FLNUM=C4•SUM(1)                                                   MAINMTFO      001375
      EPN=-Z•C4•SUM(4)                                                  MAINMTFO      001400
      EPEPRM=-Z•C4•SUM(5)                                               MAINMTFO      001404
      EF=CF•C4•SUM(3)                                                   MAINMTFO      001410
      EEX=-CEX•C4•SUM(2)                                                MAINMTFO      001414
      EQ=A•A•C4•SUM(6)/2.0                                              MAINMTFO      001420
      EC=-CC•C4•SUM(7)                                                  MAINMTFO      001426
      EPE=.5•(EPEPRM-EPN+FLNUM•(EPRIME+C2))                             MAINMTFO      001432
      E=EF+EPN+EPE+EEX+EQ+EC                                            MAINMTFO      001443
      PRINT 135,FLNUM                                                   MAINMTFO      001452
  135 FORMAT(//21H NUMBER OF ELECTRONS= F11.6)                          MAINMTFO      001470
      PRINT 136,EF,EQ                                                   MAINMTFO      001470
  136 FORMAT(//5H  EF= 1PE15.7,7H    EQ= 1PE15.7)                       MAINMTFO      001513
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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          001566
0C159          GO TO 5                                                                    MAINMTFD          001566
0C160          END                                                                        MAINMTFD          C01567

SUBPROGRAM •MAIN• - COMPILE TIME 000005 SECS. - NO. BINARY CARDS 000000 - LENGTH (8)001267 WORDS (=(10)000695)
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FORTRAN SYSTEM -- VERSION  07/15/64 - CORRECTION LEVEL  09/15/64


SUBTYPE,FORTRAN

        C      COMPUTE MODIFICATION FACTOR FROM INITIAL SLOPE                  AFNTMTFO
        C       BY NEWTON-RAPHSON METHOD                                       AFNTMTFO
00000          FUNCTION AFUNCT(SLCPE)                                          AFNTMTFO          000002
00001          COMMON Z,PI,PISQRD,C1,C2,C3,TAU1,CSLOPE,HMAX,R.Y.PHIX2,FLINT(8) AFNTMTFO          000002
0C002          CRIT=1.0E-14                                                    AFNTMTFO          000002
0G003          ALPHA=SQRT(Z/(2.0•ABS(SLOPE)))                                  AFNTMTFO          000004
0G004          ROOT1=SQRT(ALPHA)                                               AFNTMTFO          000010
00005          F1=3.0•ALPHA•ALPHA-.5                                           AFNTMTFO          000012
0C006          F2=ALPHA•ROOT1                                                  AFNTMTFO          000017
        C      INITIAL GUESS FOR NU                                            AFNTMTFO          000017
0C007          FLNU=ALPHA-.5                                                   AFNTMTFO          000022
0C008        5 ROOT2=SQRT(FLNU)                                                AFNTMTFO          000025
0C009          F=FLNU•(FLNU•(FLNU+1.5)+2.0•F2•ROOT2-F1)                        AFNTMTFO          000027
CC010          FPRIME=3.0•FLNU•(FLNU+1.0)+3.0•F2•ROOT2-F1                      AFNTMTFO          000042
0C011          IF(FPRIME)15,10,15                                              AFNTMTFO          000057
        C      ADJUST NU IF DERIVATIVE OF F IS ZERO                            AFNTMTFO          000057
00012       10 FLNU=.99999•FLNU                                                AFNTMTFO          000061
0C013          GO TO 5                                                         AFNTMTFO          000064
        C      CORRECT NU                                                      AFNTMTFO          000064
0C014       15 CORR=-F/FPRIME                                                  AFNTMTFO          000065
0C015          FLNU=FLNU+CORR                                                  AFNTMTFO          000070
0C016          ERROR=ABS(CORR/FLNU)                                            AFNTMTFO          000073
        C      TEST IF CRITERION IS MET                                        AFNTMTFO          000073
00017          IF(ERROR-CRIT)20,20,5                                           AFNTMTFO          000076
0C018       20 AFUNCT=ALPHA-SQRT(FLNU)•ROOT1                                   AFNTMTFO          000101
GC019          RETURN                                                          AFNTMTFO          000106
0C020          END                                                             AFNTMTFO          000107


SUBPROGRAM AFUNCT - COMPILE TIME 000003 SECS. - NO. BINARY CARDS 000000 - LENGTH (8)000135 WORDS (=(10)000093)
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FORTRAN SYSTEM -- VERSION  07/15/64 - CORRECTION LEVEL  09/15/64


SUBTYPE.FORTRAN
         C       COMPUTE INNER RADIUS OF ELECTRON DISTRIBUTION                               X1FNMTFO
00000            FUNCTION X1FNCT(SLOPE,A)                                                    X1FNMTFO       000002
00001            COMMON Z,PI.PISQRD,C1,C2,C3,TAU1,CSLOPE.HMAX.R,Y,PHIX2,FLINT(8)             X1FNMTFO       000002
00002            S=(1.0-PISQRD*Z*2.0*SLOPE)/(PISQRD*Z)                                       X1FNMTFO       000002
00003            X1FNCT=(1.0-SQRT(1.0-A*A*S/Z))/S                                            X1FNMTFO       000014
00004            RETURN                                                                      X1FNMTFO       000026
00005            END                                                                         X1FNMTFO       000027

SUBPROGRAM X1FNCT - COMPILE TIME 000002 SECS. - NO. BINARY CARDS 000000 - LENGTH (8)000067 WORDS (=(10)000055)
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FORTRAN SYSTEM -- VERSION  07/15/64 - CORRECTION LEVEL  09/15/64


SUBTYPE,FORTRAN
        C      COMPUTE OUTER RADIUS OF ELECTRON DISTRIBUTION                     X2FNMTF0
        C       AND INTERPOLATE FOR PHI AT OUTER BOUNDARY                        X2FNMTF0
00000          FUNCTION X2FNCT(PHIM2,PHIM1,PHI0,X0,H,DEGION)                     X2FNMTF0          000002
00001          COMMON Z,PI,PISQRD,C1,C2,C3,TAU1,CSLOPE,HMAX,R,Y,PHIX2,FLINT(8)   X2FNMTF0          000002
00002          SCRIPA=.5*(PHI0-2.0*PHIM1+PHIM2)/(H*H)                            X2FNMTF0          000002
00003          SCRIPB=(PHI0-PHIM1)/H-SCRIPA*(2.0*X0-H)                           X2FNMTF0          000014
00004          SCRIPC=PHI0-X0*(SCRIPA*X0+SCRIPB)                                 X2FNMTF0          000026
00005          X2=SQRT((SCRIPC-DEGION/Z)/SCRIPA)                                 X2FNMTF0          000034
00006          PHIX2=X2*(SCRIPA*X2+SCRIPB)+SCRIPC                                X2FNMTF0          000041
00007          X2FNCT=X2                                                         X2FNMTF0          000047
00008          RETURN                                                            X2FNMTF0          000051
00009          END                                                               X2FNMTF0          000052


SUBPROGRAM X2FNCT - COMPILE TIME 000002 SECS. - NO. BINARY CARDS 000000 - LENGTH (8)000115 WORDS (=(10)000077)
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FORTRAN SYSTEM -- VERSION  07/15/64 - CORRECTION LEVEL  09/15/64


SUBTYPE,FORTRAN

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


SUBPROGRAM INTSEC - COMPILE TIME 000003 SECS. - NO. BINARY CARDS 000000 - LENGTH (8)000255 WORDS (=(10)000173)
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FORTRAN SYSTEM -- VERSION  07/15/64 - CORRECTION LEVEL  09/15/64


SUBTYPE,FORTRAN

        C      COMPUTE SOURCE FUNCTION, WHICH IS EQUATED TO                    SRCEMTFO
        C       SECOND DERIVATIVE OF PHI                                       SRCEMTFO
00000          FUNCTION SOURCE(X,PHI,A)                                        SRCEMTFO              000002
00001          COMMON Z,PI,PISQRD.C1,C2,C3,TAU1,CSLOPE,HMAX,R,Y,PHIX2,FLINT(8) SRCEMTFO              000002
00002          CRIT=1.0E-14                                                    SRCEMTFO              000002
00003          N=0                                                             SRCEMTFO              000004
00004          NFLAG=0                                                         SRCEMTFO              000006
00005          R=C1•(Z•PHI/X-A•A/(2.0•X•X)-C2)                                 SRCEMTFO              000010
        C      EVALUATE Y BY NEWTON-RAPHSON METHOD                             SRCEMTFO              000010
00006          F2=TAU1•R-C3                                                    SRCEMTFO              000027
00007        5 F=Y•(Y•(Y+TAU1)+R)+F2                                           SRCEMTFO              000033
00008          FPRIME=Y•(3.0•Y+2.0•TAU1)+R                                     SRCEMTFO              000042
00009          IF(FPRIME)15,10,15                                              SRCEMTFO              000053
00010       10 Y=.99999•Y                                                      SRCEMTFO              000055
00011          GO TO 5                                                         SRCEMTFO              000060
00012       15 CORR=-F/FPRIME                                                  SRCEMTFO              000061
00013          Y=Y+CORR                                                        SRCEMTFO              000064
00014          ERROR=ABS(CORR/Y)                                               SRCEMTFO              000067
00015          IF(ERROR-CRIT)50,50,20                                          SRCEMTFO              000072
00016       20 N=N+1                                                           SRCEMTFO              000075
00017          IF(NFLAG)35,25,35                                               SRCEMTFO              000100
00018       25 IF(N-10)5,30,30                                                 SRCEMTFO              000102
00019       30 NFLAG=1                                                         SRCEMTFO              000105
00020          Y=0.13                                                          SRCEMTFO              000107
00021          N=0                                                             SRCEMTFO              000111
00022          GO TO 5                                                         SRCEMTFO              000113
00023       35 IF(N-10)5,40,40                                                 SRCEMTFO              000114
00024       40 PRINT 45                                                        SRCEMTFO              000117
00025       45 FORMAT(23H CRITERION ON Y NOT MET)                              SRCEMTFO              000130
00026       50 ROOT=SQRT(Y•Y+R)                                                SRCEMTFO              000130
00027          PSI=SQRT(Y+TAU1)•SQRT(-Y+TAU1+2.0•ROOT)                         SRCEMTFO              000134
00028          SOURCE=(.5•PI•X/Z)•(TAU1+PSI+ROOT)••3                           SRCEMTFO              000150
00029          RETURN                                                          SRCEMTFO              000165
00030          END                                                             SRCEMTFO              000166

SUBPROGRAM SOURCE - COMPILE TIME 000003 SECS. - NO. BINARY CARDS 00000C - LENGTH (8)000177 WORDS (=(10)000127)
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FORTRAN SYSTEM -- VERSION  07/15/64 - CORRECTION LEVEL  09/15/64


SUBTYPE,FORTRAN
        C      COMPUTE INTEGRANDS FOR ENERGY INTEGRALS AND TOTAL                  FLNTMTFO
        C       NUMBER OF PARTICLES CHECK                                         FLNTMTFO
00000          SUBROUTINE FLINTS(X,PHI,RHO)                                       FLNTMTFO             000002
00001          COMMON Z,PI,PISQRD,C1,C2,C3,TAU1,CSLOPE,HMAX,R.Y,PHIX2,FLINT(8)    FLNTMTFO             000002
00002          RTRHO=RHO**(1.0/3.0)                                               FLNTMTFO             000002
00003          FLINT(6)=RHO                                                       FLNTMTFO             000014
00004          FLINT(4)=RHO*X                                                     FLNTMTFO             000016
00005          FLINT(1)=FLINT(4)*X                                                FLNTMTFO             000021
00006          FLINT(8)=FLINT(1)*X*X                                              FLNTMTFO             000024
00007          FLINT(2)=FLINT(1)*RTRHO                                            FLNTMTFO             000030
00008          FLINT(3)=FLINT(2)*RTRHO                                            FLNTMTFO             000033
00009          FLINT(5)=PHI*FLINT(4)                                              FLNTMTFO             000036
00010          FLINT(7)=FLINT(1)*SQRT(RTRHO)                                      FLNTMTFO             000041
00011          RETURN                                                             FLNTMTFO             000045
00012          END                                                                FLNTMTFO             000046

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