



Modern Ab-initio Calculations Based on Tomas-Fermi-Dirac Theory with High-Pressure Environment

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Abstract: Thomas-Fermi theory is an approximate method, which is widely used to describe the properties of matter at various hierarchical levels (atomic nucleus, atom, molecule, solid, etc.). Special development achieved using Thomas-Fermi theory to the theory of extreme states of matter appearing under high pressures, high temperatures or strong external fields. Relevant sections of physics and related sciences (astrophysics, quantum chemistry, a number of applied sciences) determine the scope of Thomas-Fermi theory. Popularity Thomas-Fermi theory is related to its relative simplicity, clarity and versatility. The latter means that result of the calculation by Thomas-Fermi theory applies immediately to all chemical elements: the transition from element to element is as simple scale transformation. These features make it highly convenient tool for qualitative and, in many cases, quantitative analysis.

Keywords: Quantum Mechanics, Ab-initio Calculations, Thomas-Fermi Theory, Material Science, Temperature and Pressure Environment, Supercomputer Calculations, Nanostructures, Ab-initio Molecular Dynamics, Numerical Methods

1. Introduction

Thomas-Fermi theory was originally proposed by Thomas and Fermi [1-4] to describe the electron shell of a heavy atom, which is characterized by a relatively uniform distribution of the electron density.

Thomas-Fermi theory is the semi-classical (or Wentzel-Kramers-Brillouin) limit in relation to self-consistent Hartree field equations, and therefore modification of this model are associated with a more detailed account of the correlation, exchange, quantum and multi-shell effects.

Initial approximate nature of Thomas-Fermi theory has a dual nature. Remain outside the model, firstly, correlation effects, reflecting the inaccuracy of the Hartree method and the associated self-consistent difference (average) true interaction from the true physical interaction. Secondly, in Thomas-Fermi theory, quantum effects are not considered responsible approximate nature of the semi-classical description of the atom. The report examines the theory of these effects, allowing to find the limits of applicability of Thomas-Fermi theory in its original form and generalize the model beyond the scope of its applicability.

The presence of correlation corrections are caused by difference of self-consistent field of the actual field inside the atom. These corrections are the result of the anti-symmetry of the electron wave functions and are interpreted as the exchange correlation effects. Additionally, appear also the effects of the power correlation.

We begin by considering the effects of correlation, which in turn are divided into two classes. This is primarily the effects of statistical correlation (exchange effects), describing the effect of the Pauli principle on the interaction of particles. Electrons with parallel spins are hold at a greater distance from each other than in the singlet state, and the radius of such a correlation coincides with the de Broglie wavelength of an electron.

Correlation effects of the second class (called correlation effects of power or simply correlation effects) reflect the inaccuracy of the principle of independent particles, i.e., the inability to talk about the state of a single electron in the effective average field of the other particles because of their mutual influence, beyond the self-consistent description. Being the power effects, this kind of correlation effects are characterized by a dimensionless parameter equal to the ratio of perturbation theory of the average energy of the coulomb

interaction between pairs of particles to their average kinetic energy. In Thomas-Fermi [3, 4] theory introduced accounting Dirac's correlation effects [2], this expansion has been called the theory of Thomas-Fermi-Dirac.

The report shows that the total energy of the electrons can be expressed in terms of the spatial dependence of the electron density according to the Thomas-Fermi-Dirac theory. In this calculations, the energy of the atom is based on nuclear-electron and electron-electron interactions (which can also be represented as a function of the electron density).

Quantum corrections arise from the use of the semi-classical formalism and reflect the presence of non-local electron density communication to the potential in consequence of the "uncertainty principle".

2. Theoretical Procedures

A variational technique can be used to derive the Thomas-Fermi equation, and an extension of this method provides an often-used and simple means of adding corrections to the statistical model [5, 6]. Thus, we can write the Fermi kinetic energy density of a gas of free electrons at a temperature of zero degrees absolute in Eq. (1).

$$U_f = c_f \rho^{\frac{5}{3}} \quad (1)$$

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 Eq. (2).

$$E_p = U_p^n + U_p^e = -(v^n + \frac{v^e}{2})\rho \quad (2)$$

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 Eq. (3).

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

The expression for density on the Thomas-Fermi model:

$$\rho = \sigma_0 (E' - V)^{3/2} \quad (4)$$

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

Eqs. (4) and (5) are obtained by minimizing Eq. (3) subject to the auxiliary condition that the total number of particles N , remains constant.

The potential 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 Thomas-Fermi equation follows from Eq. (4) and Poisson's equation.

The tendency for electrons of like spin to stay apart because of exclusion principle is accounted for by the inclusion in Eq. (3) of exchange energy, the volume density of which is given by Eq. (6).

$$U_{ex} = -c_{ex} \rho^{\frac{4}{3}} \quad (6)$$

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

Minimization of the total energy now leads to Eq. (7).

$$\frac{5}{3} c_f \rho^{\frac{2}{3}} - \frac{4}{3} c_{ex} \rho^{\frac{1}{3}} - (E' - V) = 0 \quad (7)$$

Eq. (7) is quadratic in $\rho^{1/3}$. From Eq. (7), we get Eq. (8).

$$\rho = \sigma_0 (\tau_0 + \sqrt{(E' - V + \tau_0^2)j^3}) \quad (8)$$

Where,

$$\tau_0 = \sqrt{\frac{4c_{ex}^2}{15c_f}} \quad (9)$$

Now Poisson equation with the density given by Eq. (9) leads to the TFD (Thomas-Fermi-Dirac) equation. In the following two slides, we propose additional energy terms to be included in Eq. (3). The incorporation of these terms leads to a simple quantum- and correlation-corrected TFD equation.

The quantum-correction energy density follows from a slight change in the derivation due to March and Plaskett [6]. March and Plaskett have demonstrated that the TF (Thomas-Fermi) approximation to the sum of one-electron eigenvalues in a spherically symmetric potential is given by the integral:

$$I = 2 \iint (2l+1) E(n_r, l) dn_r dl \quad (10)$$

Where, the number of states over which the sum is carried is written as Eq. (11).

$$N = 2 \iint (2l+1) dn_r dl \quad (11)$$

where, $E(n_r, l)$ is the expression for the semi-classic eigen-values considered as functions of continuous variables [1, 6]; n_r is the radial quantum number; l is the orbital quantum number; the region of integration is bounded by $n_r = -1/2$, $l = -1/2$, and $E(n_r, l) = E'$.

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. (11) gives the total number of states being considered, the N electrons occupying the N lowest states.

$$I = \int (\frac{3}{5} \frac{P^2}{2} + V) \frac{P^3}{3\pi^2} 4\pi x^2 dx \quad (12)$$

With considerable manipulation, Eq. (10) becomes TF energy Eq. (12) and Eq. (11) reveals the TF density through Eq. (13).

$$N = \int \frac{P^3}{3\pi^2} 4\pi x^2 dx \quad (13)$$

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 Eq. (14).

$$P = \sqrt{2(E' - V)} \quad (14)$$

It is pertinent to examine the error in the TF sum of eigen-values, as given by Eq. (12), for case of pure Coulomb field. The WKB eigen-values in Coulomb field is given by Eq. (15).

$$E_{n_r, l} = \left(-\frac{Z}{2(n_r + l + 1)} \right)^2 \quad (15)$$

And let us consider the levels filled from $n = 1$ to $n = \nu$, where n is the total quantum number defined by $n = n_r + l + 1$. Then, for any value of ν , we can evaluate the error in the TF approximation to the sum of eigen-values, comparing always with the correct value, $-Z^2\nu$. Scott correction to the total binding energy is obtained by letting ν become very large.

Although the sum of one-electron eigen-values 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", we obtain, after more manipulation, slightly different expressions corresponding to Eqs. (12) and (13).

$$a = l_{min} + \frac{1}{2} \quad (16)$$

From these revised expressions, we can identify a quantum-corrected TF density expression as Eq. (17), and corrected kinetic energy density as Eq. (18).

$$\rho = \sigma_0 \left(E' - V - \frac{a^2}{2x^2} \right)^{\frac{3}{2}} \quad (17)$$

$$U_k = c_f \rho^{\frac{5}{3}} + \frac{a^2}{2x^2} \rho \quad (18)$$

Revised lower limit on the volume integrals, say x_l , is the lower root of:

$$E' - V - \frac{a^2}{2x^2} = 0 \quad (19)$$

For $x < x_l$, ρ must vanish (stay zero), and we have thus termed x_l the "inner density cutoff distance".

We can call the second term on the right-hand side of Eq. (18) the "quantum-correction energy density" and write it in

the more consistent form as Eq. (20).

$$U_q = \frac{c_q}{x^2} \quad (20)$$

Where, c_q is defining as Eq. (21):

$$c_q = \frac{a^2}{2} \quad (21)$$

The modification factor a , is determined by the initial slope of the potential function.

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

Since the lower limit $l = -1/2$ 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. (17) in terms of the Fermi momentum and cutoff momentum:

$$\rho = \frac{\sigma_0}{2^{\frac{3}{2}}} (P^2 - P_c^2)^{\frac{3}{2}} \quad (22)$$

At radial distances less than x_l , 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. (14), 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. (19), but it is not correct to demand that the density vanish at the upper root. Instead, we require only that the density is real.

Correlation correction [1, 5, 6], 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.

In extensions of the statistical model, there have been suggested at least two different expressions, 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, Gombas and Tomishima [6] 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 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 interesting and fortunate that over density range of interest it is apparently possible to approximate the correlation energy per particle quite closely by an expression of form:

$$u_c = -c_c \rho^{1/6} \quad (23)$$

where, we have set $c_c = 0.0842$, and compared this approximation with the values due to Carr and Maradudin [5].

So, Thomas-Fermi and the Thomas-Fermi-Dirac equations are nonlinear differential equations which must be solved numerically. The procedure is to assume a solution in the form of a power series, and to start the numerical integration from the series solution. The series coefficients of the solution may be evaluated in terms of the initial slope of the potential function. Each value of the initial slope then gives rise to a particular potential curve.

The TFD equation possesses a solution which becomes tangent to the x axis at infinity. This solution has an initial slope which has been determined for He by Latter. Application of the TFD method follows by surrounding each nucleus in by a cell which contains just Z electrons. The boundaries of the cell are planes which perpendicularly bisect the lines joining each nucleus with the nearest or next nearest neighbors. Because of the high order of symmetry of the charge distribution, the electric field at points outside the cell should then be very small and drop off rapidly with distance.

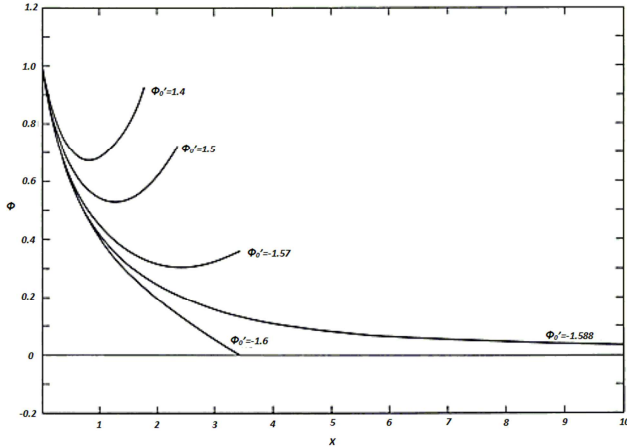


Figure 1. Various TFD solutions.

The approximation is then made that the field outside the cell can be neglected, and the polyhedron is replaced by a spherically symmetric distribution of charge having the same volume as that of the polyhedron. The solutions of the Thomas-Fermi equation for finite border are thus capable of describing the element in various states of compression (pressure), figure 1.

3. Derivation and Discussion

From the results of the preceding slides, we can now express the total energy per unit volume of the charge

distribution in the form:

$$U = c_f \rho^{5/3} - c_{ex} \rho^{4/3} - c_c \rho^{7/6} - (v^n + \frac{v^e}{2}) \rho + \frac{c_q}{x^2} \rho \quad (24)$$

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 Eq. (25).

$$\rho^{2/3} - \tau_1 \rho^{1/3} - v_0 \rho^{1/6} - \frac{R}{4} = 0 \quad (25)$$

$$\text{Where, } \tau_1 = \frac{4}{5} \frac{c_{ex}}{c_f}, \quad v_0 = \frac{7}{6} c_c \sigma_0^{2/3},$$

The electron density is found as a function of R by solving Eq. (23), a quartic in $\rho^{1/6}$.

To accomplish this we write a “resolvent cubic equation” in terms of another variable, say y :

$$y^3 + \tau_1 y^2 + R y + (\tau_1 R - v_0^2) = 0 \quad (26)$$

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:

$$\rho = \frac{1}{8} (\tau_1 + \psi + \sqrt{y^2 + R})^3 \quad (27)$$

Where,

$$\psi = \sqrt{\tau_1 + y(\tau_1 - y + 2\sqrt{y^2 + R})} \quad (28)$$

We note that ψ vanishes when correlation is neglected, since $y = -\tau_1$ is then root of Eq. (26). In the familiar manner we now define a modified TFD potential function θ by Eq. (29), and from Poisson equation and Eq. (27) we obtain Eq. (30).

$$Z\theta = (E' - V + \tau_0^2) x \quad (29)$$

$$\theta'' = \begin{cases} \frac{\pi x}{2Z} (\tau_1 + \psi + \sqrt{y^2 + R})^3; & x \geq x_1, \\ 0; & x < x_1. \end{cases} \quad (30)$$

In terms of θ :

$$R = 4\sigma_0^{2/3} \left(\frac{Z\theta}{x} - \frac{a^2}{2x^2} - \tau_0^2 \right) \quad (31)$$

Eqs. (26), (28), (30) and (31) constitute the differential relationship to be satisfied at each step in the integration. We could, of course, write immediately the solutions of Eq. (26) 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. (30) are:

- 1 As nucleus approached the potential must become that nucleus alone, or $\theta(0) = 1$;
- 2 At outer boundary x_2 , of distribution of N electrons:

$$N = \int_{x_1}^{x_2} \rho 4\pi x^2 dx = Z \int_{x_1}^{x_2} \theta'' x dx \quad (32)$$

Integration by parts yields:

$$\theta(x_1) = 1 + x_1 \theta'(x_1), \quad (\theta' x - \theta)_{x_1}^{x_2} = \frac{N}{Z}, \quad \text{and since we have}$$

the usual condition:

$$\theta(x_2) = x_2 \theta'(x_2) + \frac{Z - N}{Z} \quad (33)$$

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:

$$V = -\frac{Z - N}{x_2} \quad (34)$$

The defining relation, Eq. (34), now gives at the boundary:

$$Z\theta(x_2) = (E' + \frac{Z - N}{x_2} + \tau_0^2)x_2 \quad (35)$$

Or solving for the Fermi energy,

$$E' = Z \frac{\theta(x_2)}{x_2} - \frac{Z - N}{x_2} - \tau_0^2 \quad (36)$$

The total electron-nuclear potential energy given by

$$E_p^n = -\int_{x_1}^{x_2} \frac{Z}{x} \rho 4\pi x^2 dx \quad (37)$$

While for the electron-electron potential energy we have:

$$E_p^e = \frac{1}{2} \int_{x_1}^{x_2} v^e \rho 4\pi x^2 dx \quad (38)$$

From Eq. (29) and the relation $V = -(v_n + v_e)$, this becomes:

$$E_p^e = \frac{1}{2} (-E_p^n + \tau_0^2 N + E'N - \int_{x_1}^{x_2} \frac{Z\theta}{x} \rho 4\pi x^2 dx) \quad (39)$$

Other energy integrals are, with an obvious notation:

$$E_f = c_f \int \rho^{5/3} 4\pi x^2 dx \quad (40)$$

$$E_q = c_q \int \frac{\rho}{x^2} 4\pi x^2 dx \quad (41)$$

$$E_{ex} = -c_{ex} \int \rho^{4/3} 4\pi x^2 dx \quad (42)$$

$$E_c = -c_c \int \rho^{7/6} 4\pi x^2 dx \quad (43)$$

4. Results and Conclusions

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 DFT (density functional theory) calculations [5].

Multi-shells effects reflect irregularities physical quantities due to the discrete energy spectrum, but in the case of the continuous spectrum of these effects may occur as a result of interference of de Broglie waves and allow the model to take into account the shells structure of the atom. Multi-shells effects associated with the discrete spectrum of bound electrons in atomic systems (atom, ion, atomic cell, etc.).

Multi-shells effects, unlike quantum-exchange effects, affect the chemical potential E' , but practically have no effect on the value of self-consistent potential V [7]. Therefore, when they accounting for the calculation of a corresponding shells correction, is not necessary to solve the Poisson's equation. Just use the normalization condition with the same self-consistent potential in TFD model.

For shell corrections E'_{sh} primary role of shell effects reduces to a shift of the chemical potential E' [8].

$$E'_{sh} = \frac{1}{\pi} \sum_{k=1}^{\infty} -1^k \frac{\sin(2\pi k v(\lambda))}{k} \quad (44)$$

Where, $v = n_r + 1/2$, $\lambda = l + 1/2$.

Software implementation of this modified Thomas-Fermi theory and calculations (for example, rare gas atoms, Table 1 and Figure 2) taking into account quantum, exchange and correlation corrections showed that the corrections really lead to a rapprochement and converge results with experimental data, and also the results obtained by the DFT approximation [5]. Total energy calculations by Thomas-Fermi, DFT and experimental data are shown in the summary Table 1. Next step of this work include program realization for multi-shell and gradient corrections also [1, 6].

Table 1. Results comparisons.

Z	E_{TFD} (a.u.)	E_{DFT} (a.u.)	E_{exp} (a.u.)
2	-2.96	-2.89	-2.90
10	-7.60	-7.23	-7.48
18	-14.95	-14.56	-14.67
36	-25.32	-24.08	-24.65
54	-38.99	-37.08	-37.85
86	-56.23	-53.59	-54.60

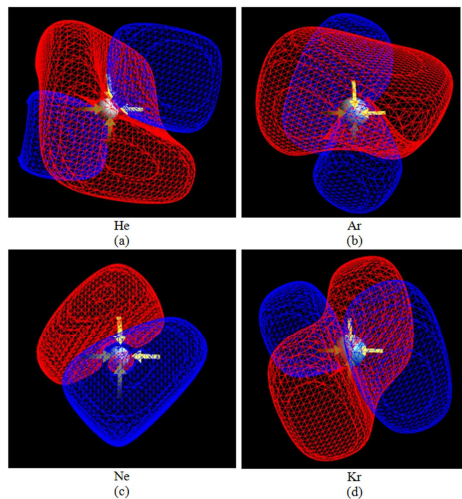


Figure 2. The electron density(external shells) of the rare atoms—(a) helium (He), (b) argon (Ar), (c) neon (Ne) and (d) krypton (Kr), computed on the present model agree closely with their crystal radii.

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