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Universal Approximate Analytical Solution of the Thomas-Fermi Equation for Ions

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The great utility of the Thomas–Fermi (TF) theory of atoms lies in the fact that it gives a solution of the TF equation that is valid for for all neutral atoms. In contrast to this situation, the TF equation for positive ions has to be solved separately for each degree of ionization of each atom. Using a previously obtained approximate analytical solution of the TF equation for neutral atoms (which is based on a variational principle), and a series-expansion approach (which relates the parameters in the ionic solution to those in the neutral-atom solution), the present paper derives a universal approximate analytical solution of the TF equation for ions. This solution, in addition to being valid for positive ions, is also applicable for negative ions for which the original TF theory does not furnish a solution. Furthermore, the approximate solution obtained here is not associated with finite ionic radii, and gives an exponentially decreasing radial electron density, which is not the case in the original TF theory. For this reason, the electron densities and potentials of ions that result from the present work are expected to be in better agreement with the quantum-mechanical data for these quantities than the electron densities and potentials obtained with the original TF theory. To show that this is so, the accuracy of the universal approximate analytical solution is investigated by calculating the diamagnetic susceptibilities of singly and doubly charged positive and negative ions of noble-gas electron configurations. It is found that, in most cases, calculated and experimental values for ions of the Ar, Kr, and Xe electron configurations agree to within a factor of 2, while for ions of the Ne electron configuration the agreement is somewhat worse. This is about the same accuracy as that found using the Lenz-Jensen approximation to the TF theory which, like the universal approximation, also makes use of variational electron density but, unlike the universal approximation, has to be separately obtained for each particular ion. As a further check on the usefulness of the universal ionic solution, the diamagnetic susceptibilities of the isoelectronic ions Ga^{3+}, Ge^{4+}, and As^{5+} are also calculated and found to agree only slightly worse than within a factor of 2 with the experimental data. After further comparison with data obtained from more-refined statistical models, the conclusion is that the universal solution for ions may be useful in a variety of problems where quantum-mechanical accuracy may be traded for a simpler approach.

I. INTRODUCTION

In dealing with many physical problems, the statistical theory of atomic structure[1] is often used as an approximation to the more fundamental, but usually considerably more involved, quantum-mechanical description. In general, the approximate statistical theory is an attractive alternative to the exact quantum theory either when the accuracy of the latter is not required, or when the labor involved is not warranted. The basic, and also the simplest, formulation of the statistical theory of a neutral atom is embodied in the Thomas-Fermi (TF) model.[2] This is described by an ordinary nonlinear differential equation of the second order, the so-called TF equation, which possesses a universal solution for all neutral atoms. In terms of the universal solution, obtainable only in numerical form,[3] important physical quantities, such as the electric potential, and the electron density within the atom, can be expressed.

For positive ions, the situation is less favorable because for these the TF equation does not possess a universal solution, but has to be solved separately for each degree of ionization of each atom.[4]

Solutions of the TF equation for positive ions have been obtained by Fermi,[5] by Sommerfeld,[6] and more recently by Goudsmit and Richards.[7] While the functional form of the Fermi and Sommerfeld solutions is different, both types essentially consist of the universal solution for the neutral atom plus a correction function. The latter depends both on the atomic number Z, and the number N of electrons of the ion considered, so that it is specific to a given ion. As far as negative ions are concerned, they are not stable within the framework of the TF model,[8] chiefly because this model involves the electrostatic self-Coulomb interaction of the electrons.

In choosing the TF model as the basis of discussion of a particular physical problem, one must assess its reliability in the light of quantum-mechanical requirements. Dirac[9] has investigated the relationship between statistical theory and quantum mechanics, and he has shown that the TF model is the semiclassical equivalent of the Hartree approximation.[10] As a consequence of this relationship, they both share the same shortcoming of ignoring exchange effects between electrons of parallel spin.

A more serious shortcoming of the TF theory of a neutral atom lies in the fact that it leads to a radial electron density which, at large distances from the nucleus, decreases as the inverse fourth power of the distance from the nucleus,[11] whereas the Hartree approximation gives an exponential decrease. It has been possible to eliminate this undesirable feature from the TF model by replacing the TF equation by a variational principle.[12] By making use of the flexibility in imposing boundary conditions afforded by the variational approach, it has been possible to obtain a universal approximate analytical solution of the TF equation for neutral atoms which leads to an exponentially decreasing electron density. The variational approach is basically simple. Instead of merely requiring the proper behavior of the solution of the TF equation at large distances from the nucleus, one can furthermore specify by what functional form this limiting behavior of the solution is to be reached. That the variational approach does, indeed, represent an improvement over the original TF theory can be seen from the fact that physical quantities, such as the total ionization energies of neutral atoms, are in better agreement with the experimental data when calculated using the variational solution of the TF equation, than when obtained by using the numerical solution.[12] It therefore appeared advantageous to use the approximate variational solution for the neutral atom for deriving Fermi-type and Sommerfeld-type approximate analytical solutions of the TF equation for positive ions.[13] A calculation of the second ionization energies for the noble-gas atoms,[13] for instance, has shown that, with the exception of Ne, the variational approach led again to better agreement with the experimental data than the original Fermi or Sommerfeld approach. This improvement is due to the fact that, as a consequence of the use of an improved electron density for the neutral atom, the variational TF ion turns out to be more "compact" than the original one. In both of the above frameworks, however, the appeal of the TF model of a positive ion is marred by the fact that the theory associates a certain finite radius with each ion. Consequently, beyond the ionic radius the electron density abruptly drops to zero and the potential of the ion becomes the potential of a point charge. It appears, therefore, desirable to eliminate this discontinuous feature from the TF model and thereby to bring it into better agreement with the quantum-mechanical model of a positive ion. The present paper addresses itself to this task. It will be shown that this goal is, indeed, attainable. The result is a universal approximate analytical solution for both positive and negative ions.

II. THEORY

Since the approach for obtaining an approximate solution of the TF equation for ions makes use of the variational solution of the TF equation for a neutral atom,[12] some essentials of the latter solution are recapitulated first.

A. Neutral Atom

In terms of the dimensionless variable x, defined by

$$x = r/\mu\,, \tag{1}$$

where

$$\mu = \tfrac{1}{4}(\tfrac{9}{2})^{1/3}\pi^{2/3}Z^{-1/3}a_B\,, \tag{2}$$

the TF equation for a neutral atom is given by[1]

$$\frac{d^2\phi_0}{dx^2} = \phi_0^{3/2}/x^{1/2}\,, \tag{3}$$

where r stands for the distance from the atomic nucleus, measured in units of the Bohr radius a_B, and Z for the atomic number.

For a neutral atom, the differential equation is to be solved with the boundary conditions[2]

$$\phi_0(0) = 1\,, \tag{4}$$

and

$$\phi_0(\infty) = 0\,. \tag{5}$$

It is of interest to see the physical requirements from which these boundary conditions arise. In the TF model for a neutral atom, the total potential is expressed by[14]

$$V(r) = (Ze_0/r)\phi_0(x)\,, \tag{6}$$

where e_0 is the magnitude of the electronic charge. From the picture of a point nucleus, surrounded by a spatially extended electron cloud, it is obvious that in the immediate neighborhood of the nucleus, where there is no appreciable shielding of the nuclear charge by the electrons, the potential should be

$$V(r \approx 0) = Ze_0/r\,. \tag{7}$$

But Eq. (7) can only be obtained from Eq. (6) if $\phi_0(0) = 1$, which explains the boundary condition (4).

Now let us assume for a moment that a neutral atom has a finite radius r_0. Then, according to Eq. (6), as r approaches r_0, the potential becomes

$$V(r = r_0) = (Ze_0/r_0)\phi_0(x_0)\,. \tag{8}$$

We know, however, that outside the sphere of radius r_0, the potential is

$$V(r > r_0) = 0\,, \tag{9}$$

since in a neutral atom of finite radius there must be complete shielding of the nuclear charge for $r > r_0$. The requirement that the electric potential be continuous at the boundary now demands that the potential in Eq. (8) be equal to the potential in Eq. (9). This can only be achieved if $\phi_0(x_0) = 0$. We do not, however, want an electron density that terminates at r_0, but one that extends to infinity. With the choice of $r_0 = \infty$ we must therefore have $\phi_0(\infty) = 0$, which explains the boundary condition (5).

The boundary conditions themselves, Eqs. (4) and (5), are not sufficient to obtain physically realistic solutions of Eq. (3). They have to be augmented by the subsidiary condition that the electron density of the atom be normalized. In the TF model, the electron (number) density is given by[14]

$$\rho_0 = (4\pi)^{-1}(Z/\mu^3)(\phi_0/x)^{3/2}\,, \tag{10}$$

so that the subsidiary condition becomes

$$\int_\tau \rho_0\, d\tau = N\,, \tag{11}$$

where $N(=Z)$ stands for the number of electrons, and the integration is over all space τ whose volume element is $d\tau$. Now, instead of solving Eq. (3) exactly with the boundary conditions (4) and (5), and the subsidiary condition (11), we make use of the variational principle[15, 16]

$$L(\varphi_0) = \int_0^\infty F(\varphi_0, \varphi_0', x)\, dx\,, \tag{12}$$

where

$$F(\varphi_0, \varphi_0', x) = \tfrac{1}{2}(\varphi_0')^2 + \tfrac{2}{5}\varphi_0^{5/2} x^{-1/2}\,. \tag{13}$$

In Eqs. (12) and (13) φ_0' stands for $d\varphi_0/dx$ and, instead of ϕ_0 the symbol φ_0 has been chosen to signify that φ_0 is not an exact but an approximate solution of Eq. (3).

That the variational principle in Eq. (12) is equivalent to the differential equation (3) can be seen by substituting (13) into the Euler-Lagrange equation[17]

$$\frac{\partial}{\partial \varphi_0} F(\varphi_0, \varphi_0', x) - \frac{\partial}{\partial x}\frac{\partial}{\partial \varphi_0'} F(\varphi_0, \varphi_0', x) = 0\,. \tag{14}$$

When the operations indicated in Eq. (14) are performed, one finds that the TF equation (3) results.

Since, at large distances from the nucleus, we require an exponentially decreasing electron density, the problem is now to select a trial function which assures this behavior. It is obvious that the class of such functions is very large. In a previous paper[12] the trial function was chosen as

$$\varphi_0 = (a_0 e^{-\alpha_0 x} + b_0 e^{-\beta_0 x})^2\,, \tag{15}$$

where a_0, b_0, α_0, β_0 are as yet undetermined parameters. It is easy to see that if the boundary condition (4) is to be satisfied, then we must demand that

$$a_0 + b_0 = 1\,, \tag{16}$$

which means that there are only three independent parameters in φ_0.

Inspection of Eq. (15) also shows that with this choice for φ_0, the boundary condition (5) is also satisfied.

Using φ_0 given in Eq. (15), one now calculates F by means of Eq. (13), and then evaluates the integral in Eq. (12). Using the notation

$$L_1(a_0, \alpha_0, \beta_0) = \tfrac{1}{2}\int_0^\infty (\varphi_0')^2\, dx \tag{17}$$

and

$$L_2(a_0, \alpha_0, \beta_0) = \tfrac{2}{5}\int_0^\infty \varphi_0^{5/2} x^{-1/2}\, dx\,, \tag{18}$$

one finds[18] that

$$L_1(a_0, \alpha_0, n_0) = \alpha_0\left[\tfrac{1}{2}a_0^4 + 4a_0^3(1-a_0)\left(\frac{1+n_0}{3+n_0}\right) + a_0^2(1-a_0)^2\left(\frac{1+4n_0+n_0^2}{1+n_0}\right) + 4a_0(1-a_0)^3\left(\frac{n_0+n_0^2}{1+3n_0}\right) + \tfrac{1}{2}(1-a_0)^4 n_0\right]\,, \tag{19}$$

and

$$L_2(a_0, \alpha_0, n_0) = 2\pi^{1/2}\alpha_0^{-1/2}\left(\frac{a_0^5}{5^{3/2}} + \frac{a_0^4(1-a_0)}{(4+n_0)^{1/2}} + \frac{2a_0^3(1-a_0)^2}{(3+2n_0)^{1/2}} + \frac{2a_0^2(1-a_0)^3}{(2+3n_0)^{1/2}} + \frac{a_0(1-a_0)^4}{(1+4n_0)^{1/2}} + \frac{(1-a_0)^5}{5(5n_0)^{1/2}}\right)\,, \tag{20}$$

where, to facilitate numerical calculations a new variable defined by

$$n_0 = \beta_0/\alpha_0\,, \tag{21}$$

has been introduced.

According to Eq. (12), we now form the quantity

$$L(a_0, \alpha_0, n_0) = L_1(a_0, \alpha_0, n_0) + L_2(a_0, \alpha_0, n_0)\,, \tag{22}$$

which has to be extremalized with respect to the three independent parameters a_0, α_0, and n_0.

Furthermore, the extremalization is to be carried out subject to the subsidiary condition (11).

Substituting Eq. (10) into Eq. (11), and considering that in our spherically symmetric case $d\tau = 4\pi r^2\, dr$, the integration gives

$$\alpha_0^{-3/2}\left(\frac{a_0^3}{3^{3/2}}+\frac{3a_0^2(1-a_0)}{(2+n_0)^{3/2}}+\frac{3a_0(1-a_0)^2}{(1+2n_0)^{3/2}}+\frac{(1-a_0)^3}{(3n_0)^{3/2}}\right) = 2\pi^{-1/2}\frac{N}{Z}\cdot \tag{23}$$

We see from Eq. (23) that α_0 is a function of the parameters a_0 and n_0. We also see from Eq. (23) that α_0 is also a function of N/Z. For a neutral atom $N/Z=1$, and, for simplicity of notation, this dependence will not be shown explicitly at this stage.

Expressing α_0 from Eq. (23), and substituting the proper powers of α_0 into Eqs. (19) and (20), we can rewrite these equations as

$$L_1(a_0, n_0) = KX(a_0, n_0) \tag{24}$$

and

$$L_2(a_0, n_0) = 2\pi^{1/2}K^{-1/2}Y(a_0, n_0), \tag{25}$$

where the quantity

$$K = (2/\pi^{1/2})^{-2/3}(N/Z)^{-2/3} = K_0(N/Z)^{-2/3} \tag{26}$$

is a constant for a given ion. This step reduces by one the number of variables in L_1 and L_2. Furthermore, by substituting α_0 into L_1 and L_2, we have incorporated the normalization requirement for the electron density into the considerations that follow. Also, by this substitution, we have made $L(a_0, n_0)$ a function of N/Z, which is important when the ion problem will be discussed. The quantities X and Y, appearing in Eqs. (24) and (25), are defined by

$$X(a_0, n_0) = [A(a_0, n_0)]^{2/3}B(a_0, n_0) \tag{27}$$

and

$$Y(a_0, n_0) = [A(a_0, n_0)]^{-1/3}C(a_0, n_0), \tag{28}$$

where

$$A(a_0, n_0) = \frac{a_0^3}{3^{3/2}}+\frac{3a_0^2(1-a_0)}{(2+n_0)^{3/2}}+\frac{3a_0(1-a_0)^2}{(1+2n_0)^{3/2}}+\frac{(1-a_0)^3}{(3n_0)^{3/2}}, \tag{29}$$

$$\begin{aligned} B(a_0, n_0) = {} & \tfrac{1}{2}a_0^4 + 4a_0^3(1-a_0)\left(\frac{1+n_0}{3+n_0}\right) \\ & + a_0^2(1-a_0)^2\left(\frac{1+4n_0+n_0^2}{1+n_0}\right) + 4a_0(1-a_0)^3 \\ & \times\left(\frac{n_0+n_0^2}{1+3n_0}\right) + \tfrac{1}{2}(1-a_0)^4 n_0, \end{aligned} \tag{30}$$

$$\begin{aligned} C(a_0, n_0) = {} & \frac{a_0^5}{5^{3/2}}+\frac{a_0^4(1-a_0)}{(4+n_0)^{1/2}}+\frac{2a_0^3(1-a_0)^2}{(3+2n_0)^{1/2}}+\frac{2a_0^2(1-a_0)^3}{(2+3n_0)^{1/2}} \\ & + \frac{a_0(1-a_0)^4}{(1+4n_0)^{1/2}}+\frac{(1-a_0)^5}{5(5n_0)^{1/2}}\,. \end{aligned} \tag{31}$$

The expression for $L(a_0, n_0)$ in Eq. (22), is now to be extremalized with respect to the parameters a_0 and n_0. It is emphasized that the extremalization is carried out subject to the subsidiary condition in Eq. (11). This point is stressed, since previous attempts,[15, 16, 19] which paid no attention to the subsidiary condition, resulted in incorrectly normalized electron densities. (A detailed discussion of this problem is published elsewhere.[20]) The minimum of $L(a_0, n_0)$, to sixteen significant figures, is reached[21] when the parameters have the values

$$a_0 = 0.721\,8337, \quad n_0 = 9.869\,743\,. \tag{32}$$

[It would be desirable to introduce special symbols, such as a_{00} and n_{00}, for those values of the parameters a_0 and n_0 at which $L(a_0, n_0)$ is an extremum. This, however, is not done here for the sake of avoiding additional notational complexities.] It is found that L is a very slowly varying function of a_0 and n_0, as illustrated in Table I. With the parameter values in Eq. (32), one finds from Eq. (23) that[21]

$$\alpha_0 = 0.178\,2559\,. \tag{33}$$

Finally, using Eqs. (16) and (21), one obtains[21]

$$b_0 = 0.278\,1663\,, \quad \beta_0 = 1.759\,339\,. \tag{34}$$

B. Ionized Atom

When an atom loses (or gains) one (or more) electron(s), then the resulting ion's electron density, as we know from quantum mechanics, still

TABLE I. (a) The quantity $L(a_0, n_0)$ as a function of the parameter n_0 at a fixed value of a_0; (b) the quantity $L(a_0, n_0)$ as a function of the parameter a_0 at a fixed value of n_0. The asterisks refer to the values at the minimum of $L(a_0, n_0)$.

(a) a_0	n_0	$L(a_0, n_0)$
0.721 833 7	9.869 740	0.681 964 813 653 573 6
0.721 833 7	9.869 741	0.681 964 813 653 571 5
0.721 833 7	9.869 742	0.681 964 813 653 570 3
0.721 833 7*	9.869 743*	0.681 964 813 653 570 1*
0.721 833 7	9.869 744	0.681 964 813 653 570 7
0.721 833 7	9.869 745	0.681 964 813 653 572 3
0.721 833 7	9.869 746	0.681 964 813 653 574 8
(b) n_0	a_0	$L(a_0, n_0)$
9.869 743	0.721 833 4	0.681 964 813 653 583 8
9.869 743	0.721 833 5	0.681 964 813 653 576 4
9.869 743	0.721 833 6	0.681 964 813 653 571 9
9.869 743*	0.721 833 7*	0.681 964 813 653 570 1*
9.869 743	0.721 833 8	0.681 964 813 653 570 9
9.869 743	0.721 833 9	0.681 964 813 653 574 7
9.869 743	0.721 834 0	0.681 964 813 653 581 2

decreases exponentially at large distances from the nucleus. Furthermore, it seems reasonable to assume that, apart from very low Z atoms, the parameters describing the electron density distribution in a moderately ionized atom cannot differ drastically from the parameters describing the same in the neutral atom. This assumption is central to this paper. In other words, it seems reasonable to assume that the solution of the TF equation for an ion might also be of the form

$$\varphi_i = (a_i e^{-\alpha_i x} + b_i e^{-\beta_i x})^2 , \tag{35}$$

where, according to our assumption, the parameters for the ion should be related to the parameters for the neutral atom by

$$a_i \equiv a = a_0 + \Delta a , \tag{36}$$

$$b_i \equiv b = b_0 + \Delta b , \tag{37}$$

$$\alpha_i \equiv \alpha = \alpha_0 + \Delta \alpha , \tag{38}$$

$$\beta_i \equiv \beta = \beta_0 + \Delta \beta . \tag{39}$$

We can also write, in analogy with Eq. (21), that

$$n_i \equiv n = \beta / \alpha , \tag{40}$$

and assume also that

$$n = n_0 + \Delta n . \tag{41}$$

In Eqs. (36)–(39) and (41), the magnitudes of the corrections $\Delta a, \Delta b, \Delta \alpha, \Delta \beta$, and Δn are assumed to be small, so that we can write

$$|\Delta a| \ll a_0 , \tag{42}$$

$$|\Delta b| \ll b_0 , \tag{43}$$

$$|\Delta \alpha| \ll \alpha_0 , \tag{44}$$

$$|\Delta \beta| \ll \beta_0 , \tag{45}$$

$$|\Delta n| \ll n_0 . \tag{46}$$

Furthermore, we require that these corrections depend on both Z and N, so that Eq. (35) describes a particular degree of ionization of a particular atom.

Should we be able to obtain analytical expressions for the correction terms, Eqs. (36)–(39) and (41), then we will have obtained a universal approximate analytical solution of the TF equation for a given ion. In detail, the universal solution will still have the simple analytical form

$$\varphi_i(N/Z) = \big([a_0 + \Delta a(N/Z)] \exp\{-[\alpha_0 + \Delta \alpha(N/Z)]x\} + [b_0 + \Delta b(N/Z)] \exp\{-[\beta_0 + \Delta \beta(N/Z)]x\} \big)^2 , \tag{47}$$

where the subscript i refers to the word ion.

The approximate solution (47), in conjunction with the expressions for the electric potential V and the electron density ρ, Eqs. (6) and (10), is expected to be of practical value in a variety of physical problems.[22] Our task is now to obtain analytical expressions for the correction terms.

We know that when $L(a, n)$ is an extremum, then the following conditions must be met:

$$\frac{\partial L(a,n)}{\partial a} = 0 \tag{48}$$

and

$$\frac{\partial L(a,n)}{\partial n} = 0 . \tag{49}$$

We can rewrite Eqs. (48) and (49), by making use of Eqs. (36) and (41), as

$$\frac{\partial L(a_0 + \Delta a, n_0 + \Delta n)}{\partial a_0} \, \frac{\partial a_0}{\partial a} = 0 \tag{50}$$

and

$$\frac{\partial L(a_0 + \Delta a, n_0 + \Delta n)}{\partial n_0} \, \frac{\partial n_0}{\partial n} = 0 . \tag{51}$$

It follows from Eq. (36) that

$$\frac{\partial a_0}{\partial a} = 1 , \tag{52}$$

and from Eq. (41) that

$$\frac{\partial n_0}{\partial n} = 1 , \tag{53}$$

so that the two conditions for the extremum of $L(a, n)$, Eqs. (48) and (49), reduce to

$$\frac{\partial L(a_0 + \Delta a, n_0 + \Delta n)}{\partial a_0} = 0 \tag{54}$$

and

$$\frac{\partial L(a_0 + \Delta a, n_0 + \Delta n)}{\partial n_0} = 0 . \tag{55}$$

We now want to rewrite the two conditions in Eqs. (54) and (55) by making use of the Taylor-series expansion of $L(a, n)$. Keeping only those terms which are linear in Δa and Δn, the desired Taylor series is given by

$$L(a_0 + \Delta a, n_0 + \Delta n) = L(a_0, n_0) + \Delta a \, \frac{\partial L(a_0, n_0)}{\partial a_0} + \Delta n \, \frac{\partial L(a_0, n_0)}{\partial n_0} . \tag{56}$$

We may say that Eq. (56) expresses the idea mentioned before that the quantity $L(a, n)$, for an ion (for which $N \sim Z$ and $Z \gg 1$), is not too different from the quantity $L(a_0, n_0)$ for a neutral atom. Introducing the abbreviations

$$L_{a_0}(a_0, n_0) = \frac{\partial L(a_0, n_0)}{\partial a_0} \tag{57}$$

and

$$L_{n_0}(a_0, n_0) = \frac{\partial L(a_0, n_0)}{\partial n_0}, \tag{58}$$

and substituting Eq. (56) into Eqs. (54) and (55), we obtain

$$\frac{\partial}{\partial a_0}\,[L(a_0, n_0) + \Delta a L_{a_0}(a_0, n_0) + \Delta n L_{n_0}(a_0, n_0)] = 0\,, \tag{59}$$

and

$$\frac{\partial}{\partial n_0}\,[L(a_0, n_0) + \Delta a L_{a_0}(a_0, n_0) + \Delta n L_{n_0}(a_0, n_0)] = 0\,. \tag{60}$$

With the further abbreviations

$$L_{a_0a_0}(a_0, n_0) = \frac{\partial L_{a_0}(a_0, n_0)}{\partial n_0}, \tag{61}$$

$$L_{n_0n_0}(a_0, n_0) = \frac{\partial L_{n_0}(a_0, n_0)}{\partial n_0}, \tag{62}$$

$$L_{n_0a_0}(a_0, n_0) = \frac{\partial L_{n_0}(a_0, n_0)}{\partial a_0} = L_{a_0n_0}(a_0, n_0) = \frac{\partial L_{a_0}(a_0, n_0)}{\partial n_0}, \tag{63}$$

we can express Eqs. (59) and (60) as

$$\Delta a L_{a_0a_0}(a_0, n_0) + \Delta n L_{n_0a_0}(a_0, n_0) = -L_{a_0}(a_0, n_0) \tag{64}$$

and

$$\Delta a L_{a_0n_0}(a_0, n_0) + \Delta n L_{n_0n_0}(a_0, n_0) = -L_{n_0}(a_0, n_0)\,. \tag{65}$$

To first order in Δa and Δn, the above two equations satisfy the conditions for the extremum of $L(a, n)$ as displayed in Eqs. (48) and (49).

We can solve Eqs. (64) and (65) for Δa and Δn. The results are

$$\Delta a = \frac{L_{a_0}L_{n_0n_0} - L_{n_0}L_{n_0a_0}}{L^2_{n_0a_0} - L_{a_0a_0}L_{n_0n_0}} \tag{66}$$

and

$$\Delta n = \frac{L_{n_0}L_{a_0a_0} - L_{a_0}L_{a_0n_0}}{L^2_{n_0a_0} - L_{a_0a_0}L_{n_0n_0}}\,, \tag{67}$$

where the notation for the functional dependence of the L's on a_0 and n_0 has been dropped. Both of these expressions contain various first and second partial derivatives of $L(a_0, n_0)$. The detailed expressions for these quantities are somewhat involved and are given in the Appendix. When the various partial derivatives of $L(a_0, n_0)$ are evaluated, then Eqs. (66) and (67) assume the forms

$$\Delta a = \frac{p_1(N/Z)^{-4/3} + p_2(N/Z)^{-1/3} + p_3(N/Z)^{2/3}}{q_1(N/Z)^{-4/3} + q_2(N/Z)^{-1/3} + q_3(N/Z)^{2/3}} \tag{68}$$

and

$$\Delta n = \frac{r_1(N/Z)^{-4/3} + r_2(N/Z)^{-1/3} + r_3(N/Z)^{2/3}}{q_1(N/Z)^{-4/3} + q_2(N/Z)^{-1/3} + q_3(N/Z)^{2/3}}\,, \tag{69}$$

where the coefficients p_i, q_i, r_i, $(i = 1, 2, 3)$ of the various powers of N/Z are constants. To a limited number of figures, they are given by

$$\begin{aligned} &p_1 = 0.000\,270\,0475\,, \quad p_2 = -0.000\,600\,1717\,,\\ &p_3 = 0.000\,330\,1242\,, \quad q_1 = 0.001\,047\,4680\,,\\ &q_2 = -0.000\,344\,7563\,, \quad q_3 = -0.000\,827\,4575\,,\\ &r_1 = -0.016\,840\,11\,, \quad r_2 = 0.034\,227\,46\,,\\ &r_3 = -0.017\,387\,35\,. \end{aligned} \tag{70}$$

It should be mentioned here that the numerical values of the above coefficients depend on the extent to which $L(a_0, \alpha_0, n_0)$, Eq. (22), has been extremalized. With the parameter values displayed in Eqs. (32)–(34), we find from Eqs. (66) and (67) that

$$\Delta n(N/Z = 1) = 2.56\times 10^{-9}$$

and

$$\Delta a(N/Z = 1 = 1.46\times 10^{-10},$$

which, as it turns out for our purposes, is close enough an approximation of the requirements $\Delta n(N/Z = 1) = 0$ and $\Delta a(N/Z = 1) = 0$.

It should also be mentioned here that in some cases, depending on the values of N and Z, the accuracy of the coefficients in Eq. (70) may not be sufficient. This is so because there may be cancellation of significant figures in the numerators and denominators of Eqs. (68) and (69) due to the fact that the coefficients p_i, q_i, r_i do not all have the same sign. Should such a situation arise and cut down on the accuracy on Δa and Δn, then one has to further refine the parameters a_0, b_0, α_0, and β_0 by extremalizing Eq. (22) to more than sixteen figures and then recalculate the coefficients in Eq. (70) also to more significant figures. This can be done by making use of the expressions given in the Appendix for the various partial derivatives of $L(a_0, n_0)$.

As an example, anticipating some future use by the author, the relevant parameter values for three isoelectronic ions, Ge^{4+}, Ga^{3+}, As^{5+} have been calculated. (The first ion is the core of the Ge atom whose lattice forms a semiconductor. The other two ions correspond to the cores of the atoms Ga and As which, in the Ge lattice, correspond to a shallow acceptor and a shallow donor, respectively.) All three of these ions have a closed-shell electron configuration and, consequently, a spherically symmetric electron density as assumed in the TF model. All three of these ions have sufficiently high Z values, so that we may also assume that the requirements embodied in Eqs. (42)–(46) will be satisfied. Furthermore, we may consider these ions as being moderately ionized atoms.

At this point we can calculate the parameter a from Eq. (36), and then the parameter b from Eq. (16). For calculating the parameters α and β, we have two possibilities. The first possibility is the substitution of a and n into Eq. (23). This gives us α. We can then calculate β from Eq. (40). This procedure does not entail any further approximation beyond those already used in deriving Δa and Δn. It would, however, not lead to explicit expressions for the correction terms $\Delta\alpha$ and $\Delta\beta$ appearing in Eq. (47). The second possibility is that of obtaining explicit analytical expressions for these quantities, too, by making use of two further expansions. We can rewrite Eq. (23) as

$$\begin{aligned}\alpha(a,n) &= K[A(a,n)]^{2/3}\\ &= K_0(N/Z)^{-2/3}[A(a,n)]^{2/3} \qquad (71)\end{aligned}$$

and consider that $\alpha(a_0+\Delta a, n_0+\Delta n)$ can also be expanded. To terms linear in Δa and Δn, the Taylor series of $\alpha(a,n)$ is

$$\begin{aligned}\alpha(a_0+\Delta a, n_0+\Delta n) = \alpha(a_0,n_0) &+ \Delta a\,\alpha_{a_0}(a_0,n_0)\\ &+ \Delta n\,\alpha_{n_0}(a_0,n_0), \qquad (72)\end{aligned}$$

where the abbreviations

$$\alpha(a_0,n_0) = \alpha_0(N/Z)^{-2/3}, \qquad (73)$$

$$\alpha_{a_0}(a_0,n_0) = \frac{\partial\alpha(a_0,n_0)}{\partial a_0}, \qquad (74)$$

and

$$\alpha_{n_0}(a_0,n_0) = \frac{\partial\alpha(a_0,n_0)}{\partial n_0} \qquad (75)$$

have been used. Detailed expressions for these quantities are given in the Appendix.

Introducing the notation

$$\Delta\alpha = \Delta a\,\alpha_{a_0} + \Delta n\,\alpha_{n_0}, \qquad (76)$$

we can rewrite Eq. (72) as

$$\alpha = \alpha_0(N/Z)^{-2/3} + \Delta\alpha\,. \qquad (77)$$

Since we have found previously that both $\Delta a(N=Z) = 0$ and $\Delta n(N=Z)=0$, it follows from Eq. (76) that $\Delta\alpha(N=Z)=0$, which is the correct behavior for this quantity.

It remains now to calculate $\Delta\beta$. To first order, we can represent Eq. (40) as

$$\beta_0 + \Delta\beta = (n_0+\Delta n)[\alpha_0(N/Z)^{-2/3} + \Delta\alpha], \qquad (78)$$

from which, by neglecting the second-order term $\Delta n \Delta\alpha$, we obtain

$$\beta = \beta_0 + \Delta\beta\,, \qquad (79)$$

where

$$\Delta\beta = \alpha_0(N/Z)^{-2/3}\Delta n + n_0\Delta\alpha + \beta_0[(N/Z)^{-2/3} - 1]\,. \qquad (80)$$

It is seen from Eq. (80) that $\Delta\beta(N=Z)=0$, so $\Delta\beta$ also shows the correct behavior.

III. DISCUSSION

We have obtained approximate analytical solutions of the TF equation for the ions Ga^{3+}, Ge^{4+}, and As^{5+} of the form required by Eq. (47).

As a first and qualitative check of the correctness of these approximate solutions, the following consideration is suggested: Since all three ions have the same number of electrons, it is reasonable to assume that in an isoelectronic sequence the radial electron density, defined by

$$D(r) = 4\pi r^2 \rho(r)\,, \qquad (81)$$

should reflect the increasing Coulomb attraction between the nucleus and the electron cloud as one goes from Ga^{3+} to Ge^{4+}, and then from Ge^{4+} to As^{5+}. To simplify our considerations, let us look at the radial electron density at a "large enough" distance from the nucleus so that we can use the approximation

$$\varphi_i = (ae^{-\alpha x} + be^{-\beta x})^2 \approx a^2 e^{-2\alpha x} \equiv \varphi_{\mathrm{asy}}\,, \qquad (82)$$

where the subscript "asy" stands for asymptotic.

Using Eqs. (1) and (82), it follows from Eq. (10) that

$$\rho_{\mathrm{asy}} = Z(4\pi)^{-1} a^3 \mu^{-3/2} r^{-3/2} e^{-(3\alpha/\mu)r}\,. \qquad (83)$$

We expect that Ge^{4+} is a "tighter structure" than Ga^{3+}, so that at large enough a distance from the respective nuclei we should have

$$\delta = D_{\mathrm{asy}}(\mathrm{Ga}^{3+})/D_{\mathrm{asy}}(\mathrm{Ge}^{4+}) > 1\,. \qquad (84)$$

Using Eqs. (81) and (83), and considering Eq. (2), we can rewrite Eq. (84) as

$$\delta = \left(\frac{Z(\mathrm{Ga}^{3+})}{Z(\mathrm{Ge}^{4+})}\right)^{3/2} \left(\frac{a(\mathrm{Ga}^{3+})}{a(\mathrm{Ge}^{4+})}\right)^{3} \times \frac{\exp\{12(\tfrac{1}{2}\,9\pi^2)^{-1/3}\alpha(\mathrm{Ge}^{4+})[Z(\mathrm{Ge}^{4+})]^{1/3}(r/a_B)\}}{\exp\{12(\tfrac{1}{2}\,9\pi^2)^{-1/3}\alpha(\mathrm{Ga}^{3+})[Z(\mathrm{Ga}^{3+})]^{1/3}(r/a_B)\}}\,. \qquad (85)$$

Choosing the "large enough" distance, somewhat arbitrarily, as $r = 6a_B$ we find that Eq. (85) gives

$$\delta = 2.39\,, \qquad (86)$$

as anticipated.

Similarly, one also expects that As^{5+} is a "tighter structure" than Ge^{4+}, so that we should have

$$\delta' = D_{asy}(Ge^{4+})/D_{asy}(As^{5+}) > 1 . \qquad (87)$$

Indeed, making the proper changes in Eq. (85), one finds at $r = 6a_B$ that

$$\delta' = 1.90 , \qquad (88)$$

as anticipated. While the results in Eqs. (86) and (88) appear reasonable, one must resort to a more sensitive test to obtain supportive evidence for the correctness of the procedures used in establishing our model of a positive (and negative) TF ion.

As a more significant test of the validity and usefulness of the universal solution, the diamagnetic susceptibilities of singly and doubly charged positive and negative ions of noble-gas electron configurations are calculated. The susceptibilities are obtained from[23] the expression

$$\chi = -L(e_0^2/6m_0c^2)\langle r_0^2\rangle , \qquad (89)$$

where L is Avogadro's number, m_0 is the electron mass, c is the speed of light, and, for a spherically symmetric electron distribution,

$$\langle r_0^2\rangle = 4\pi \int_0^{r_0} \rho(r) r^4\, dr . \qquad (90)$$

Using Eq. (10), and considering that in the universal model $r_0 = \infty$, one finds[24] from Eq. (90) that

$$\langle r_0^2\rangle = \tfrac{15}{8}\pi^{1/2} Z\mu^2 [a^3(3\alpha)^{-7/2} + 3a^2b(2\alpha+\beta)^{-7/2} + 3ab^2(\alpha+2\beta)^{-7/2} + b^3(3\beta)^{-7/2}] . \qquad (91)$$

While the present paper discusses ions, it is of interest to see how neutral-atom susceptibilities, calculated with Eq. (15), compare with the experimental data, with quantum-mechanical data, and with data calculated from the TF model and its various modifications. For this reason, the susceptibilities for the noble-gas atoms Ne, Ar, Kr, Xe, and Rn have been obtained,[25] from Eqs. (89) and (91), and are listed in Table II(a) as χ(Pr), where Pr refers to the present work. Table II(a) also lists, under the heading χ(LJ), the susceptibility values[26] found by making use of the Lenz-Jensen (LJ) approximation[27] to the TF theory. The LJ approximation,[28] like the universal approximation, makes use of a variational electron density. This has the form

$$\rho_{LJ} = \left(\frac{N}{\Lambda}\right) y^{-3} e^{-y} \left(\sum_{i=0}^{m} d_i y^i\right)^3 , \qquad (92)$$

where N is again the number of electrons, Λ is a normalization constant, the d_i's are parameters obtainable from the minimization of the energy of a TF atom (or ion), and the variable y is defined by

$$y = \lambda^{1/2} Z^{1/6} (r/a_B)^{1/2} , \qquad (93)$$

with λ denoting another variational parameter.

In the first approximation, used to calculate the susceptibilities χ(LJ), the Lenz-Jensen electron density is

$$\rho_{LJ}^{(1)} = (N/\Lambda^{(1)}) y^{-3} e^{-y} (1 + d_1 y)^3 , \qquad (94)$$

where

$$\Lambda_1^{(1)} = 4\pi \left(\frac{a_B}{\lambda}\right)^3 \left(\frac{2}{Z}\right) \sum_{k=0}^{3} \binom{3}{k} (k+2)!\, d_1^k . \qquad (95)$$

TABLE II. (a) Diamagnetic susceptibilities per gram atom (in units of 1×10^{-6} cm^3) of the atoms listed as given by experiment and calculated by the various theories discussed in the text. (b) The calculated to experimental susceptibility ratios obtained from the data of Table IIa. For Rn no experimental susceptibility value is available. To calculate the ratios denoted by an asterisk, the experimental value for Rn has been "identified" with Clementi's calculated value of -59.3×10^{-6} cm^3 per gram atom.

(a) Atom	Z	χ(Expt)	χ(Pr)	χ(LJ)	χ(TF)	$\chi(\mathrm{TFD})_{\mathrm{Mod}}$	$\chi(\mathrm{TFDG})_{\mathrm{Mod}}$	χ(QM) (Clementi)	χ(QM) (others)
Ne	10	−6.74	−15.4	−20.3	−67.0	−13.7	−12.9	−5.77 to −5.86	−4.96 to −6.68
Ar	18	−19.6	−18.8	−24.7	−81.0	−22.0	−21.1	−17.4 to −18.3	−16.6 to −22.6
Kr	36	−28.8	−23.6	−31.1	−102.0	−36.4	−35.8	−26.8 to −27.9	−28.8 to −31.1
Xe	54	−43.9	−27.1	−35.6	−117.0	−48.5	−47.3	−38.9 to −42.6	−43.9 to −72.2
Rn	86	···	−31.6	−41.6	−136.7	···	···	−55.7 to −59.3	−14.6 to −117.2

(b) Atom	Z	$\frac{\chi(\mathrm{Pr})}{\chi(\mathrm{Expt})}$	$\frac{\chi(\mathrm{LJ})}{\chi(\mathrm{Expt})}$	$\frac{\chi(\mathrm{TF})}{\chi(\mathrm{Expt})}$	$\frac{\chi(\mathrm{TFD})_{\mathrm{Mod}}}{\chi(\mathrm{Expt})}$	$\frac{\chi(\mathrm{TFDG})_{\mathrm{Mod}}}{\chi(\mathrm{Expt})}$	$\frac{\chi(\mathrm{QM})}{\chi(\mathrm{Expt})}$ (Clementi)	$\frac{\chi(\mathrm{QM})}{\chi(\mathrm{Expt})}$ (others)
Ne	10	2.28	3.01	9.94	2.03	1.91	0.856 to 0.869	0.736 to 0.991
Ar	18	0.959	1.26	4.13	1.12	1.08	0.888 to 0.934	0.847 to 1.15
Kr	36	0.819	1.08	3.54	1.26	1.24	0.931 to 0.969	1.00 to 1.08
Xe	54	0.617	0.811	2.67	1.10	1.08	0.886 to 0.970	1.00 to 1.64
Rn	86	0.533*	0.702*	2.31*	···	···	···	0.246* to 1.98*

For neutral atoms, the parameters d_1 and λ are universal and have the values[29]

$$d_1 = 0.265, \quad \lambda = 10.91. \tag{96}$$

For ions the Lenz-Jensen parameters are not universal, but have to be obtained from the minimization of the energy of each particular ion.[30] While Eq. (94) shows that in the LJ approximation the radial electron density also goes to zero exponentially, as in the universal ionic approximation, the fact that for ions the LJ electron density has to be obtained separately makes it less advantageous than the universal ionic approximation.

Table II(b) compares the calculated to experimental susceptibility ratios. Inspection of the data permits several conclusions: First, both the universal variational solution,[12] and the LJ approximation,[28] represent significant improvement over the original TF theory, since the latter greatly overestimates the magnitude of the diamagnetic susceptibilities. This is attributed to the fact that, in the TF model, the radial electron density goes to zero as the inverse fourth power of the distance from the nucleus, and, for this reason, the TF model contributes too large an electron density at large values of r to the integral in Eq. (90). Consequently, $\langle r_0^2 \rangle$ and hence χ comes out too large. Second, the data in Table II(b) also show that both the universal ionic solution and the LJ approximation are of comparable accuracy, the latter being somewhat worse for Ne and Ar, and somewhat better for Kr, Xe, and Rn than the former. Third, we see from Table II(b) that, with the exception of Ne, the calculated and experimental susceptibility values agree to within a factor of 2. Fourth, the comparison of the $\chi(\mathrm{Pr})/\chi(\mathrm{Expt})$, and $\chi(\mathrm{QM})/\chi(\mathrm{Expt})$ ratios, where $\chi(\mathrm{QM})$ refers to quantum-mechanical data, also shows that, apart from Ne, the data obtained with the universal solution agree fairly well with the quantum-mechanical data.[31] This is all the more gratifying since the Clementi-type wave functions,[32] from which some of the quantum-mechanical data of Table II (a) have been obtained, are so constructed as to give the best agreement with the diamagnetic susceptibilities.[33] Other quantum-mechanical calculations are also available,[34] which, in some cases, show poorer agreement with the experimental data than those obtained with the Clementi-type wave functions. They are also included in Table II(a), even though the point on the accuracy of the universal variational approximation has already been made.

Before proceeding, it may be mentioned that, by considering Eqs. (2) and (91), we see that χ, Eq. (89), has a $Z^{1/3}$ dependence. When Eq. (91) is evaluated with the ionic parameters then, of course, $\langle r_0^2 \rangle$ has a much more complicated Z dependence but the dominant factor is still $Z^{1/3}$.

The diamagnetic susceptibilities, labeled $\chi(\mathrm{TFD})_{\mathrm{Mod}}$ and $\chi(\mathrm{TFDG})_{\mathrm{Mod}}$ in Table II(a), were obtained[35] by making use of the modified Thomas-Fermi-Dirac (TFD)[36] and Thomas-Fermi-Dirac-Gombás (TFDG)[37] models. In the TFD model the exchange effect, and in the TFDG model the exchange and correlation effects are included. In the modified TFD and TFDG models the Fermi-Amaldi correction[38] has been considered to cancel the self-Coulomb interaction of the electrons by the self-exchange interaction as best as possible in the outer regions of an atom or ion. Without this modification singly charged negative ions are not stable either in the TFD or in the TFDG theory. From the data in Table II(b) we see that, the successive refinements of the TF model do, indeed, lead to better and better agreement with the experimental data than the TF model.

Finally, our fifth conclusion is that for all neutral atoms considered the refined statistical models lead to susceptibilities which are in reasonable agreement with those obtained by using the universal ionic solution.

It was considered worthwhile to dwell at some length on the susceptibilities of the neutral atoms, since the universal variational solution for atoms is the backbone of the universal solution for ions. We may anticipate, therefore, that we shall encounter a favorable comparison also between calculated and experimental ionic susceptibilities.

Susceptibilities, calculated for the ions Na^+, K^+, Rb^+, and Cs^+, from the various models, are listed in Table III(a). Table III(b) shows the corresponding calculated to experimental susceptibility ratios. Inspection of the data in Table III(b) shows that, apart from Na^+, the data from the universal ionic solution are again in reasonable agreement with the more exact modified TFD and TFDG data,

TABLE III. (a) Diamagnetic susceptibilities per gram ion (in units of 1×10^{-6} cm^3) of the ions listed as given by experiment and calculated by the various theories discussed in the text. (b) Calculated-to-experimental susceptibility ratios obtained from the data of Table III (a).

(a) Ion	Z	$\chi(\mathrm{Expt})$	$\chi(\mathrm{Pr})$	$\chi(\mathrm{LJ})$	$\chi(\mathrm{TFD})_{\mathrm{Mod}}$	$\chi(\mathrm{TFDG})_{\mathrm{Mod}}$
Na^+	11	−5	−14.2	−14.5	−7.9	−7.3
K^+	19	−13	−12.3	−20.3	−14.5	−14.4
Rb^+	37	−20	−20.4	−28.2	−27.5	−26.8
Cs^+	55	−31	−24.5	−33.3	−37.5	−37.2

(b) Ion	Z	$\frac{\chi(\mathrm{Pr})}{\chi(\mathrm{Expt})}$	$\frac{\chi(\mathrm{LJ})}{\chi(\mathrm{Expt})}$	$\frac{\chi(\mathrm{TFD})_{\mathrm{Mod}}}{\chi(\mathrm{Expt})}$	$\frac{\chi(\mathrm{TFDG})_{\mathrm{Mod}}}{\chi(\mathrm{Expt})}$
Na^+	11	2.84	2.90	1.58	1.46
K^+	19	0.946	1.56	1.12	1.11
Rb^+	37	1.02	1.41	1.35	1.34
Cs^+	55	0.790	1.07	1.21	1.20

TABLE IV. (a) Diamagnetic susceptibilities per gram ion (in units of 1×10^{-6} cm^3) of the ions listed as given by experiment and calculated by the various theories discussed in the text. (b) Calculated-to-experimental susceptibility ratios obtained from the data of Table IV(a).

(a) Ion	Z	χ(Expt)	χ(Pr)	χ(LJ)	$\chi(\text{TFD})_{\text{Mod}}$	$\chi(\text{TFDG})_{\text{Mod}}$
F$^-$	9	−11	−21.6	−30.1	−26.5	−24.4
Cl$^-$	17	−26	−22.4	−30.6	−36.5	−34.6
Br$^-$	35	−36	−25.6	−34.6	−54.0	−51.2
I$^-$	53	−52	−28.4	−38.2	−66.5	−63.7

(b) Ion	Z	$\frac{\chi(\text{Pr})}{\chi(\text{Expt})}$	$\frac{\chi(\text{LJ})}{\chi(\text{Expt})}$	$\frac{\chi(\text{TFD})_{\text{Mod}}}{\chi(\text{Expt})}$	$\frac{\chi(\text{TFDG})_{\text{Mod}}}{\chi(\text{Expt})}$
F$^-$	9	1.96	2.74	2.41	2.22
Cl$^-$	17	0.862	1.18	1.40	1.33
Br$^-$	35	0.711	0.961	1.50	1.42
I$^-$	53	0.546	0.735	1.28	1.23

which appear in lieu of quantum-mechanical data. We also see that, with the exception of Cs$^+$, the universal ionic solution leads to better agreement with both the experimental data, and the data obtained from the more-refined statistical models than the LJ approximation.

Table IV(a) contains susceptibility data for the singly charged negative ions F$^-$, Cl$^-$, Br$^-$, and I$^-$. The calculated to experimental susceptibility ratios are compared in Table IV(b). Inspection of the susceptibility ratios shows that, with the exception of F$^-$, the data obtained from the universal ionic solution agree with the experimental data to within a factor of 2. This is a significant finding, since the validity of the universal ionic solution for singly charged negative ions could so far only be viewed as formal. We also see from Table IV(b) that, for the lighter ions F$^-$ and Cl$^-$, the universal ionic solution leads to data in better agreement with the experimental ones than the LJ approximation, while the opposite is true for the heavier ions Br$^-$ and I$^-$. Table IV(b) also shows that the present calculation underestimates, while the more refined statistical models overestimate the magnitude of the susceptibilities.

TABLE V. (a) Diamagnetic susceptibilities per gram ion (in units of 1×10^{-6} cm^3) of the ions listed as given by experiment and calculated by the various theories discussed in the text. (b) Calculated-to-experimental susceptibility ratios obtained from the data of Table V(a).

(a) Ion	Z	χ(Expt)	χ(Pr)	χ(LJ)	$\chi(\text{TFD})_{\text{Mod}}$	$\chi(\text{TFDG})_{\text{Mod}}$
Mg^{++}	12	−3	−9.79	−10.9	−5.2	−5.2
Ca^{++}	20	−8	−16.0	−17.0	−10.6	−10.6
Sr^{++}	38	−15	−15.6	−25.6	−21.5	−21.5
Ba^{++}	56	−32	−22.1	−31.2	−30.8	−30.8

(b) Ion	Z	$\frac{\chi(\text{Pr})}{\chi(\text{Expt})}$	$\frac{\chi(\text{LJ})}{\chi(\text{Expt})}$	$\frac{\chi(\text{TFD})_{\text{Mod}}}{\chi(\text{Expt})}$	$\frac{\chi(\text{TFDG})_{\text{Mod}}}{\chi(\text{Expt})}$
Mg^{++}	12	3.26	3.63	1.73	1.73
Ca^{++}	20	2.00	2.13	1.33	1.33
Sr^{++}	38	1.04	1.71	1.43	1.43
Ba^{++}	56	0.691	0.975	0.963	0.963

Table V(a) contains susceptibilities calculated for the doubly charged positive ions Mg^{++}, Ca^{++}, Sr^{++}, and Ba^{++}. The calculated to experimental susceptibility ratios are listed in Table V(b). We see again that, with the exception of Mg^{++}, the agreement of the universal ionic data with the experimental data is still within a factor of 2. We also see that, with the exception of Ba^{++}, the LJ approximation leads to poorer agreement with the experimental data than the universal ionic solution. We also see that the $\chi(\text{Pr})/\chi(\text{Expt})$ ratios agree quite well with the ratios obtained from the more refined statistical models.

It is of interest to see whether the universal ionic solution could also be applied to the calculation of the susceptibilities of the doubly charged negative ions O^{--}, S^{--}, Se^{--}, and Te^{--}. These ions are not stable, but in the present universal approximation (and in the LJ approximation) we can still formally obtain electron densities for them and thus calculate susceptibilities. The susceptibilities, together with the calculated to experimental ratios, are listed in Table VI. Again, from the data we see that, with the exceptions of O^{--} and Te^{--}, the agreement between the calculated and experimental susceptibility values is still within a factor of 2. This is considered as further evidence that the universal ionic model is applicable not only to positive but also to negative ions.

In all cases considered so far, we have seen that the agreement between calculated and experimental susceptibility values was the poorest for ions of Ne-like electron configuration. This is probably due to the fact that for ions with so few electrons the statistical theory is a poor approximation. This view is supported by the fact that for the Ne-like ions the ratios $\chi(\text{TFD})_{\text{Mod}}/\chi(\text{Expt})$, and $\chi(\text{TFDG})_{\text{Mod}}/\chi(\text{Expt})$ are also larger than for the heavier ions. Another factor, which may contribute to the relative poorness of the calculated susceptibility data for Ne-like ions, might be the fact that the magnitude of Δn, one of the basic

TABLE VI. Diamagnetic susceptibilities per gram ion (in units of 1×10^{-6} cm^3) of the ions listed as given by experiment and by the present theory and the calculated-to-experimental susceptibility ratios.

Ion	Z	χ(Expt)	χ(Pr)	$\frac{\chi(\text{Pr})}{\chi(\text{Expt})}$
O^{--}	8	−12	−31.6	2.63
S^{--}	16	−38(?)	−27.4	0.721
Se^{--}	34	−48(?)	−28.3	0.590
Te^{--}	52	−70	−29.2	0.417

correction terms, is much larger (about 2) for the Ne-like ions than for the heavier ions. Consequently, when compared with n_0, the correction term $|\Delta n|$ may no longer be considered small. This suggests that further improvement of the universal ionic solution for the light ions might be attainable by generalizing the theory to include higher than linear correction terms to n. (The Δa terms are small, a few % of a_0, so quadratic terms in Δa are not needed.)

The magnitude of the correction term Δn turns out to be also fairly large (somewhat smaller than 2) for the ions Ga^{3+}, Ge^{4+}, and As^{5+}. Susceptibility values calculated for these ions, together with the calculated to experimental ratios, are listed in Table VII. The agreement between the theoretical and experimental data is somewhat worse than a factor of 2, but still quite reasonable.

In judging the agreement between theoretical and experimental susceptibilities, we also have to consider that the experimental data[39] are not the results of straightforward measurements on particular ions but are deduced from measurements on compounds and resorting to more involved considerations.[40]

In judging the effect of the various refinements of the statistical theory, it is also customary to compare calculated and experimental polarizabilities. Such data can be calculated by making use either of second-order perturbation theory, formulated within the statistical framework,[41] or of the approximate Kirkwood-Vinti relation.[42] The latter states that the polarizability α_P can be related to the diamagnetic susceptibility, χ, by the equation

$$\alpha_P=\left(\frac{16m_0^2c^4}{L^2e_0^4a_B}\right)\frac{\chi^2}{N}, \qquad (97)$$

where N is again the number of electrons for a neutral atom $N=Z$, and χ has a $Z^{1/3}$ dependence. Consequently, we find from Eq. (97) that α_P has a $Z^{-1/3}$ dependence, i.e., decreases with increasing Z. This is in contradiction with the experimental data,[43] which show that α_P increases with Z. In view of the fact that for neutral atoms we do not have the correct Z dependence, we might anticipate that the same situation prevails for ions also. Calculation of α_P (not reproduced here), both from second-order perturbation theory, and from Eq. (97), has, indeed, substantiated this conclusion. The reason for this lies in the fact that the exchange and correlation effects are not considered in the TF model and in the various approximations to it. When these effects are included, then the calculated and experimental polarizabilities agree quite well.[44] The parameters used, for the ions considered, are listed in Table VIII.

TABLE VII. Diamagnetic susceptibilities per gram ion (in units of 1×10^{-6} cm^3) of the ions listed as given by experiment and by the present theory and the calculated-to-experimental susceptibility ratios.

Ion	Z	χ(Expt)	χ(Pr)	χ(Pr)/χ(Expt)
Ga^{3+}	31	−8	−19.1	2.38
Ge^{4+}	32	−7	−15.0	2.14
As^{5+}	33	−6	−14.6	2.43

One may ask at this stage what happens if one deals with a low Z atom, or with an atom so strongly stripped that we no longer have $N \lesssim Z$. In such cases one should go beyond the linear theory used here, and include higher-order terms in the Taylor-series expansion of $L(a_0+\Delta a, n_0+\Delta n)$ in Eq. (56). Such an extension of the present theory, while increasingly laborious, should not present unforeseen difficulties except that the resulting extended system of equations, corresponding to Eqs. (64) and (65), must then be solved by numerical techniques. Once higher-order terms, such as $(\Delta a)^2$ and $(\Delta n)^2$, are brought into the picture, the required modifications of the expressions for the

TABLE VIII. Parameter values in the universal approximate analytical solutions for the isoelectronic ions listed. For comparison the parameter values for the Ne, Ar, Kr, and Xe atoms are also shown.

Ion	Z	a	b	α	β	n
Mg^{++}	12	0.7173	0.2827	0.2047	1.595	7.758
Na^+	11	0.6674	0.3326	0.1717	1.339	7.998
Ne	10	0.7218	0.2782	0.1783	1.759	9.870
F^-	9	0.6917	0.3083	0.1535	1.643	10.641
O^{--}	8	0.6691	0.3309	0.1323	1.583	11.679
Ca^{++}	20	0.6814	0.3186	0.1785	1.672	8.090
K^+	19	0.8250	0.1750	0.2247	2.381	10.758
Ar	18	0.7218	0.2782	0.1783	1.759	9.870
Cl^-	17	0.7028	0.2972	0.1636	1.679	10.246
S^{--}	16	0.6892	0.3108	0.1511	1.636	10.747
Sr^{++}	38	0.8250	0.1750	0.2247	2.381	10.758
Rb^+	37	0.7412	0.2588	0.1894	1.864	9.840
Kr	36	0.7218	0.2782	0.1783	1.759	9.870
Br^-	35	0.7110	0.2890	0.1704	1.710	10.033
Se^{--}	34	0.7028	0.2972	0.1636	1.679	10.246
Ba^{++}	56	0.7535	0.2465	0.1953	1.936	9.918
Cs^+	55	0.7329	0.2671	0.1850	1.817	9.822
Xe	54	0.7218	0.2782	0.1783	1.759	9.870
I^-	53	0.7141	0.2859	0.1728	1.724	9.971
Te^{--}	52	0.7080	0.2920	0.1680	1.699	10.100
Ga^{3+}	31	0.6672	0.3228	0.1764	1.398	8.069
Ge^{4+}	32	0.7009	0.2991	0.1904	1.526	8.059
As^{5+}	33	0.7125	0.2877	0.1997	1.576	7.884

parameters a, b, α, and β can be made without difficulty on the basis of the material already presented.

One may also ask the question of just how good is the universal approximate solution φ_i that we have obtained here. Since the derivation of the approximate solution for an ion makes use of the approximate solution for a neutral atom, part of the question is essentially reduced to answering the problem of how good is φ_0, the solution for a neutral atom. This problem is quite involved and has been discussed elsewhere.[19,20] It suffices to say here that it is possible to formulate so-called complementary variational principles[45] which establish an upper bound and a lower bound for the energy belonging to a particular approximate solution of the TF equation for a neutral atom. Thus, if we have a number of approximate solutions φ_{01}, φ_{02}, φ_{03}, ..., each depending on more than one parameter,[46] then the best approximate solution should be the one for which the difference between the bounds is the smallest. It goes without saying that, eventually, practical considerations, such as the labor involved in minimizing L of Eq. (12) for a many-parameter function, will terminate the search for better and better approximate solutions. That this should be so is clear from the fact that the TF model itself is just the basic statistical model that still lacks effects such as the exchange between electrons of parallel spin, and correlation between electrons of antiparallel spin.

The fundamental constants used in the numerical calculations are those listed by Kittel.[47]

IV. CONCLUSIONS

It is concluded that the universal approximate analytical solution is physically realistic and may be used in a variety of problems when quantum-mechanical accuracy may be traded for a simpler approach.

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APPENDIX: EXPLICIT EXPRESSIONS FOR THE PARTIAL DERIVATIVES OF $L(a_0, n_0)$

Considering Eqs. (22), (24), and (25) we can express the partial derivatives of $L(a_0, n_0)$ as

$$L_{a_0} = KX_{a_0} + 2\pi^{1/2}K^{-1/2}Y_{a_0}, \tag{A1}$$

$$L_{a_0a_0} = KX_{a_0a_0} + 2\pi^{1/2}K^{-1/2}Y_{a_0a_0}, \tag{A2}$$

$$L_{n_0} = KX_{n_0} + 2\pi^{1/2}K^{-1/2}Y_{n_0}, \tag{A3}$$

$$L_{n_0n_0} = KX_{n_0n_0} + 2\pi^{1/2}K^{-1/2}Y_{n_0n_0}, \tag{A4}$$

$$L_{a_0n_0} = KX_{a_0n_0} + 2\pi^{1/2}K^{-1/2}Y_{a_0n_0}. \tag{A5}$$

From Eqs. (27) and (28) we obtain the partial derivatives of $X(a_0, n_0)$, and $Y(a_0, n_0)$ as

$$X_{a_0} = \tfrac{2}{3}BA_{a_0}A^{-1/3} + A^{2/3}B_{a_0}, \tag{A6}$$

$$Y_{a_0} = -\tfrac{1}{3}CA_{a_0}A^{-4/3} + A^{-1/3}C_{a_0}, \tag{A7}$$

$$X_{a_0a_0} = \tfrac{4}{3}A_{a_0}A^{-1/3}B_{a_0} + \tfrac{2}{3}BA^{-1/3}A_{a_0a_0} - \tfrac{2}{9}BA_{a_0}^2A^{-4/3} + A^{2/3}B_{a_0a_0}, \tag{A8}$$

$$Y_{a_0a_0} = -\tfrac{2}{3}A_{a_0}A^{-4/3}C_{a_0} - \tfrac{1}{3}CA^{-4/3}A_{a_0a_0} + \tfrac{4}{9}CA_{a_0}^2A^{-7/3} + A^{-1/3}C_{a_0a_0}, \tag{A9}$$

$$X_{n_0} = \tfrac{2}{3}BA_{n_0}A^{-1/3} + A^{2/3}B_{n_0}, \tag{A10}$$

$$Y_{n_0} = -\tfrac{1}{3}CA_{n_0}A^{-4/3} + A^{-1/3}C_{n_0}, \tag{A11}$$

$$X_{n_0n_0} = \tfrac{4}{3}A_{n_0}A^{-1/3}B_{n_0} + \tfrac{2}{3}BA^{-1/3}A_{n_0n_0} - \tfrac{2}{9}BA_{n_0}^2A^{-4/3} + A^{2/3}B_{n_0n_0}, \tag{A12}$$

$$Y_{n_0n_0} = -\tfrac{2}{3}A_{n_0}A^{-4/3}C_{n_0} - \tfrac{1}{3}CA^{-4/3}A_{n_0n_0} + \tfrac{4}{9}CA_{n_0}^2A^{-7/3} + A^{-1/3}C_{n_0n_0}, \tag{A13}$$

$$X_{a_0n_0} = \tfrac{2}{3}A^{-1/3}(A_{a_0}B_{n_0} + A_{n_0}B_{a_0}) + \tfrac{2}{3}BA^{-1/3}A_{a_0n_0} - \tfrac{2}{9}BA_{a_0}A_{n_0}A^{-4/3} + A^{2/3}B_{a_0n_0}, \tag{A14}$$

$$Y_{a_0n_0} = -\tfrac{1}{3}A^{-4/3}(A_{a_0}C_{n_0} + A_{n_0}C_{a_0}) - \tfrac{1}{3}CA^{-4/3}A_{a_0n_0} + \tfrac{4}{9}CA_{a_0}A_{n_0}A^{-7/3} + A^{-1/3}C_{a_0n_0}. \tag{A15}$$

The various partial derivatives of $A(a_0, n_0)$, $B(a_0, n_0)$, and $C(a_0, n_0)$, obtained from Eqs. (29)–(31), are given by the following expressions:

$$A_{a_0} = (3a_0^2)3^{-3/2} + (6a_0 - 9a_0^2)(2+n_0)^{-3/2} + 3(1 - 4a_0 + 3a_0^2)(1+2n_0)^{-3/2} + 3(-1 + 2a_0 - a_0^2)(3n_0)^{-3/2}, \tag{A16}$$

$$A_{a_0a_0} = (6a_0)3^{-3/2} + 6(1 - 3a_0)(2+n_0)^{-3/2} + 6(-2 + 3a_0)(1+2n_0)^{-3/2} + 6(1 - a_0)(3n_0)^{-3/2}, \tag{A17}$$

$$B_{a_0} = 2a_0^3 + 4(3a_0^2 - 4a_0^3)(1+n_0)(3+n_0)^{-1} + 2(a_0 - 3a_0^2 + 2a_0^3)(1 + 4n_0 + n_0^2)(1+n_0)^{-1} + 4(1 - 6a_0 + 9a_0^2 - 4a_0^3)(n_0 + n_0^2)(1+3n_0)^{-1} + 2(-1 + 3a_0 - 3a_0^2 + a_0^3)n_0, \tag{A18}$$

$$\begin{aligned} B_{a_0a_0} &= 6a_0^2+24(1-2a_0^2)(1+n_0)(3+n_0)^{-1}+2(1-6a_0+6a_0^2)(1+4n_0+n_0^2)(1+n_0)^{-1} \\ &\quad +24(-1+3a_0-2a_0^2)(n+n_0^2)(1+3n_0)^{-1}+6(1-2a_0+a_0^2)n_0\,, \end{aligned} \tag{A19}$$

$$\begin{aligned} C_{a_0} &= (5a_0^4)5^{-3/2}+(4a_0^3-5a_0^4)(4+n_0)^{-1/2}+2(3a_0^2-8a_0^3+5a_0^4)(3+2n_0)^{-1/2} \\ &\quad +2(2a_0-9a_0^2+12a_0^3-5a_0^4)(2+3n_0)^{-1/2}+(1-8a_0+18a_0^2-16a_0^3+5a_0^4)(1+4n_0)^{-1/2} \\ &\quad +(-1+4a_0-6a_0^2+4a_0^3-a_0^4)(5n_0)^{-1/2}\,, \end{aligned} \tag{A20}$$

$$\begin{aligned} C_{a_0a_0} &= (20a_0^3)5^{-3/2}+4(3a_0^2-5a_0^3)(4+n_0)^{-1/2}+4(3a_0-12a_0^2+10a_0^3)(3+2n_0)^{-1/2} \\ &\quad +4(1-9a_0+18a_0^2-10a_0^3)(2+3n_0)^{-1/2}+4(-2+9a_0-12a_0^2+5a_0^3)(1+4n_0)^{-1/2} \\ &\quad +4(1-3a_0+3a_0^2-a_0^3)(5n_0)^{-1/2}\,, \end{aligned} \tag{A21}$$

$$A_{n_0} = (-\tfrac{3}{2})[3a_0^2(1-a_0)(2+n_0)^{-5/2}+6a_0(1-a_0)^2(1+2n_0)^{-5/2}+3(1-a_0)^3(3n_0)^{-5/2}]\,, \tag{A22}$$

$$A_{n_0n_0} = (\tfrac{15}{4})[3a_0^2(1-a_0)(2+n_0)^{-7/2}+12a_0(1-a_0)^2(1+2n_0)^{-7/2}+9(1-a_0)^3(3n_0)^{-7/2}]\,, \tag{A23}$$

$$B_{n_0} = 8a_0^3(1-a_0)(3+n_0)^{-2}+a_0^2(1-a_0)^2(3+2n_0+n_0^2)(1+n_0)^{-2}+4a_0(1-a_0)^3(1+2n_0+3n_0^2)(1+3n_0)^{-2}+\tfrac{1}{2}(1-a_0)^4\,, \tag{A24}$$

$$B_{n_0n_0} = (-4)[4a_0^3(1-a_0)(3+n_0)^{-3}+a_0^2(1-a_0)^2(1+n_0)^{-3}+4a_0(1-a_0)^3(1+3n_0)^{-3}]\,, \tag{A25}$$

$$\begin{aligned} C_{n_0} &= (-\tfrac{1}{2})[a_0^4(1-a_0)(4+n_0)^{-3/2}+4a_0^3(1-a_0)^2(3+2n_0)^{-3/2}+6a_0^2(1-a_0)^3(2+3n_0)^{-3/2} \\ &\quad +4a_0(1-a_0)^4(1+4n_0)^{-3/2}+(1-a_0)^5(5n_0)^{-3/2}]\,, \end{aligned} \tag{A26}$$

$$\begin{aligned} C_{n_0n_0} &= (\tfrac{3}{4})[a_0^4(1-a_0)(4+n_0)^{-5/2}+8a_0^3(1-a_0)^2(3+2n_0)^{-5/2}+18a_0^2(1-a_0)^3(2+3n_0)^{-5/2} \\ &\quad +16a_0(1-a_0)^4(1+4n_0)^{-5/2}+5(1-a_0)^5(5n_0)^{-5/2}]\,, \end{aligned} \tag{A27}$$

$$A_{a_0n_0} = (-\tfrac{3}{2})[3(2a_0-3a_0^2)(2+n_0)^{-5/2}+6(1-4a_0+3a_0^2)(1+2n_0)^{-5/2}+9(-1+2a_0-a_0^2)(3n_0)^{-5/2}]\,, \tag{A28}$$

$$\begin{aligned} B_{a_0n_0} &= 8(3a_0^2-4a_0^3)(3+n_0)^{-2}+2(a_0-3a_0^2+2a_0^3)(3+2n_0+n_0^2)(1+n_0)^{-2} \\ &\quad +4(1-6a_0+9a_0^2-4a_0^3)(1+2n_0+3n_0^2)(1+3n_0)^{-2}+2(-1+3a_0-3a_0^2+a_0^3)\,, \end{aligned} \tag{A29}$$

$$\begin{aligned} C_{a_0n_0} &= (-\tfrac{1}{2})[(4a_0^3-5a_0^4)(4+n_0)^{-3/2}+4(3a_0^2-8a_0^3+5a_0^4)(3+2n_0)^{-3/2}+6(2a_0-9a_0^2+12a_0^3-5a_0^4)(2+3n_0)^{-3/2} \\ &\quad +4(1-8a_0+18a_0^2-16a_0^3+5a_0^4)(1+4n_0)^{-3/2}+5(-1+4a_0-6a_0^2+4a_0^3-a_0^4)(5n_0)^{-3/2}]\,. \end{aligned} \tag{A30}$$

The explicit expressions for the partial derivatives of $\alpha(a_0, n_0)$ are obtained from Eq. (71) and are given by

$$\alpha_{a_0} = \tfrac{2}{3}KA_{a_0}A^{-1/3} = 0.392\,2744(N/Z)^{-2/3} \tag{A31}$$

and

$$\alpha_{n_0} = \tfrac{2}{3}KA_{n_0}A^{-1/3} = -0.002\,267\,788(N/Z)^{-2/3}\,. \tag{A32}$$

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[1] For a comprehensive review of the subject, see (a) P. Gombás, in *Encyclopedia of Physics*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. XXXVI; (b) P. Gombás, *Die statistische Theorie des Atoms und ihre Anwendungen* (Springer-Verlag, Wien, 1949); (c) N. H. March, Adv. Phys. 6, No. 21 (1957).

[2] L. H. Thomas, Proc. Camb. Philos. Soc. 23, 542 (1926); E. Fermi, Z. Phys. 48, 73 (1928). For details see Ref. 1(a), p. 120ff and Ref. 1(b), p. 31ff.

[3] The most accurate numerical solution is given by S. Kobayashi, T. Matsukuma, S. Nagai, and K. Umeda, J. Phys. Soc. Jap. 10, 759 (1955).

[4] For details see Ref. 1(a), p. 129ff and Ref. 1(b), p. 47ff.

[5] For the original reference in Italian see Ref. 1(a), p. 230, item (20).

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[7] S. A. Goudsmit and P. I. Richards, Proc. Natl. Acad. Sci. USA 51, 664 (1964).

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[9] P. A. M. Dirac, Proc. Camb. Philos. Soc. 26, 376 (1930).

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[11] See Ref. 1(a), p. 132ff and Ref. 1(b), p. 54ff.

[12] P. Csavinszky, Phys. Rev. 166, 53 (1968).

[13] P. Csavinszky, J. Chem. Phys. 50, 1176 (1969).

[14] See Ref. 1(a), p. 125 and Ref. 1(b), p. 41.

[15] First given by M. G. Wesselow, Zh. Eksp. i. Teor. Fiz. 7, 829 (1937).

[16] Also given by S. Flügge and H. Marschall, *Rechenmethoden der Quanten theorie* (Springer-Verlag, Berlin, 1952), p. 262ff.

[17] R. Courant, *Differential and Integral Calculus* (Interscience, New York, 1951), Vol. II, p. 497ff.

[18] In Ref. 12 the expressions for L_1 and L_2 appeared with two misprints. In L_1 the first term in the bracket appeared as $(1/2)a_4$, while it should read $(1/2)a^4$. In L_2 the numerator of the third term in the bracket appeared as $2a^3b$, while the correct expression is $2a^3b^2$.

[19] N. Anderson, A. M. Arthurs, and P. D. Robinson, Nuovo Cimento 57, 523 (1968).

[20] P. Csavinszky, Phys. Rev. A 5, 2198 (1972).

[21] These parameter values differ somewhat from those given in Ref. 12. (There it was found that $n_0 = 9.5$, $a_0 = 0.7111$, $b_0 = 0.2889$, $\alpha_0 = 0.175$, $\beta_0 = 1.6625$). The reason for these is twofold: First, the data in Ref. 12 were obtained by using a desk calculator and minimizing L to less than 11 digits. Second, the actual numerical process of minimization is different here from that used in Ref. 12.

[22] An interesting problem in which the solution of the Thomas-Fermi (TF) equation for a positive ion is needed concerns the order in which electron shells are filled. Goudsmit and Richards have shown (see Ref. 7) that for ionized atoms the electron shells are filled in an order different from that of neutral atoms. In Ref. 7 an approximate analytical solution of the TF equation for positive ions is introduced which is based on an approximate analytical solution of the TF equation for neutral atoms [given by T. Tietz, Ann. Phys. 15, 186 (1955)]. In view of the fact that the approximate solution of Ref. 7 is associated with finite radii, while φ_i, Eq. (35), is not, little would be gained by comparing these two solutions as functions of x.

[23] For details see Ref. 1(a), p. 189ff and especially Ref. 1(b), p. 229ff.

[24] P. Csavinszky, J. Chem. Phys. 50, 3629 (1969). In this paper, under Eq. (7), there is a misprint. $\Gamma(7/2)$ is given as $(15/8)\pi$, while the correct expression is $(15/8)\pi^{1/2}$.

[25] For Ar, Kr, and Xe the susceptibilities were already given in Ref. 24.

[26] See Ref. 1(b), Table 29A, p. 233.

[27] W. Lenz, Z. Phys. 77, 713 (1932) and H. Jensen, Z. Phys. 77, 722 (1932).

[28] For details see Ref. 1(a), p. 138ff. and Ref. 1(b), p. 71ff.

[29] See Ref. 1(b), Table 7, p. 75.

[30] See Ref. 28. Parameters for several ions of noble-gas electron configurations are listed in the table mentioned in Ref. 29.

[31] J. T. Dehn and L. N. Mulay, J. Chem. Phys. 48, 4910 (1968).

[32] For literature references see Ref. 31.

[33] For a discussion of this subject see Ref. 31.

[34] For literature references see Ref. 31.

[35] See Ref. 23.

[36] See Ref. 1(a), p. 144ff. and Ref. 1(b), p. 92ff.

[37] See Ref. 1(a), p. 147ff. and Ref. 1(b), p. 105ff.

[38] For the original reference in Italian see Ref. 1(a), p. 230, item (22). With the Fermi-Amaldi correction the electrostatic self-Coulomb interaction of the electrons is partially eliminated from the TF model. For details see Ref. 1(a), p. 137ff, and Ref. 1(b), p. 65ff.

[39] L. N. Mulay, *Magnetic Susceptibility* (Interscience, New York, 1963), p. 1782.

[40] For details see Ref. 39.

[41] See Ref. 1(a), p. 191ff. and Ref. 1(b), p. 238ff.

[42] For details and literature references see Ref. 41.

[43] See Ref. 1(a), Table 8, p. 192 and Ref. 1(b), Table 30A, p. 240.

[44] See the tables cited in Ref. 43.

[45] A. M. Arthurs and P. D. Robinson, Proc. Camb. Philos. Soc. 65, 535 (1969).

[46] That the trial function must depend on more than one parameter is an important point, since single-parameter trial functions cannot lead to correctly normalized electron densities. For further discussion of this problem, see Ref. 20.

[47] C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1963), 2nd ed., p. 598.