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# Thomas-Fermi revisited: The outer regions of the atom

Berthold-Georg Englert and Julian Schwinger*
*Institute for Theoretical Physics, University of Tübingen, Tübingen, Federal Republic of Germany*

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The consequences of exchange and the first quantum kinetic-energy correction are extrapolated outward in the statistical atom, up to a sharp boundary. Possible locations of that boundary are considered, and two are tested in the context of the diamagnetic susceptibility of neutral and ionized atoms with closed-shell configurations. The comparisons with experimental values and with Hartree-Fock (HF) calculations are reasonably successful, favoring one of the boundary options. An appendix presents, for neutral-atom energies, the detailed comparison between the HF calculations at integer $Z$ values and the continuous curve of the statistical theory, with its known coefficients of $Z^{7/3}$, $Z^{6/3}$, and $Z^{5/3}$. The deviation between the two oscillates smoothly, with decreasing amplitude and lengthening period as $Z$ increases; there is no striking evidence of shell structure. An asymmetry between positive and negative deviations suggests an additional, small multiple of $Z$. It produces agreement between the statistical and HF calculations to better than 0.1%, for $Z \geq 32$.

The original Thomas-Fermi (TF) statistical model of the atom—a semiclassical treatment requiring large numbers of electrons—produced some remarkable quasiquantitative results, particularly for the total binding energies of neutral atoms.[1] This invites attempts at quantitative improvement, which naturally focus on the two regions where the semiclassical approximation fails, and explicit quantum considerations are required: the neighborhood of the nucleus and the outer reaches of the atom. Of these, the necessary changes in the treatment of the strongly bound electrons near the nucleus are clearer and also immediately rewarding,[2] for the correct quantum description of such essentially hydrogenic electrons is, of course, well known. Guiding the search for a more realistic approach to the weakly bound electrons at the fringes of the atom is the need to preserve the major appeal of the TF method—simplicity. This has led to an "experimental" program[3] in which the effects of the leading exchange and kinetic-energy quantum corrections are extrapolated into the outer regions, where such effects are of controlling importance. The merits of a particular extrapolation are judged by its success in improving the poor performance shown by TF in computing such properties as the diamagnetic susceptibility of closed-shell atoms—the inert gases. One such extrapolation has already been described[4]; it gave a significant, but hardly overwhelming improvement. This paper is concerned with another attempt, which produces somewhat more gratifying results, both for neutral and ionized atoms.

## MODIFIED TF THEORY

In the following we adopt atomic units: length, the Bohr radius $a_0$, and energy, $e^2/a_0$, twice the binding energy of hydrogen. We shall also make temporary use of an additional factor in specifying energy and particle number, which is illustrated for the particle density $n$ by

$$\tilde{n} = 3\pi^2 n \ . \tag{1}$$

The various contributions to the energy $\tilde{E}$ are then exhibited as

$$\tilde{E} = \int (d\vec{r}) \left\{ \frac{3}{10}\tilde{n}^{5/3} - \frac{3}{4\pi}\tilde{n}^{4/3} + \frac{1}{72}\frac{(\vec{\nabla}\tilde{n})^2}{\tilde{n}} + \tilde{n}V - \frac{3\pi}{8}\left[\vec{\nabla}\left[V + \frac{Z}{r}\right]\right]^2 + \zeta\tilde{n} \right\} - \zeta\tilde{N} + \cdots \ , \tag{2}$$

where the ellipsis represents the injunction to make the necessary correction for strongly bound electrons. Successively displayed here are the TF kinetic energy, the leading exchange correction, the first quantum correction to the kinetic energy, the two terms that express the electrostatic energy of the charges in terms of the single-particle interaction energy $V(\vec{r})$, and, last, the relation between particle density and particle number, as conveyed with the aid of the Lagrange multiplier $\zeta$.

Both $\tilde{n}(\vec{r})$ and $V(\vec{r})$ are variables in this energy expression. They obey the equations supplied by the stationary property of $\tilde{E}$. That produces the second-order Poisson differential equation for $V$,

$$-\nabla^2\left[V+\frac{Z}{r}\right]=\frac{4}{3\pi}\tilde{n}\ (=4\pi n)\ , \tag{3}$$

and also a second-order differential equation for $\tilde{n}$. The resulting fourth-order differential equation for $V$ is too complicated, and there is the danger of taking too seriously the initial terms of an infinite series of quantum corrections. The first attempt at a simple extrapolation[3] ignored the quantum corrections to the density; the TF density ($\zeta=0$)

$$\tilde{n}_{\mathrm{TF}}=(-2V)^{3/2} \tag{4}$$

was inserted in $\tilde{E}$ to produce a functional of the single variable

$$\overline{V}=V+\frac{1}{6\pi}(-2V)^{1/2}\ . \tag{5}$$

Now we try to incorporate some effects of the quantum corrections. To that end, we write

$$\tilde{n}=\tilde{\rho}+\tfrac{1}{8}\nabla^2\tilde{\rho}^{1/3}\ , \tag{6}$$

which, under the assumption of a small difference between $\tilde{n}$ and $\tilde{\rho}$, is such that

$$\int(d\vec{r})\left[\tfrac{3}{10}\tilde{n}^{5/3}+\tfrac{1}{72}\frac{(\vec{\nabla}\tilde{n})^2}{\tilde{n}}\right]\cong\int(d\vec{r})\tfrac{3}{10}\tilde{\rho}^{5/3}\ . \tag{7}$$

A further consequence of (6) is given by

$$\int(d\vec{r})\tilde{n}(V+\zeta)=\int(d\vec{r})\left[\tilde{\rho}(V+\zeta)-\tfrac{1}{8}\vec{\nabla}\tilde{\rho}^{1/3}\cdot\vec{\nabla}\left[V+\frac{Z}{r}\right]\right]\ , \tag{8}$$

together with an additional singular term:

$$\tfrac{1}{8}\int(d\vec{r})\vec{\nabla}\tilde{\rho}^{1/3}\cdot\vec{\nabla}\frac{Z}{r}=\tfrac{1}{2}\pi Z\tilde{\rho}^{1/3}\quad(\vec{r}=0)\ , \tag{9}$$

which is completely deleted on removing the incorrect contribution of strongly bound electrons, in the manner of Ref. 3. Then we combine the field energy density term of (2) with the related structure in (8) to produce

$$-\frac{3\pi}{8}\left[\vec{\nabla}\left[V+\frac{Z}{r}\right]\right]^2-\tfrac{1}{8}\vec{\nabla}\tilde{\rho}^{1/3}\cdot\vec{\nabla}\left[V+\frac{Z}{r}\right]\cong-\frac{3\pi}{8}\left[\vec{\nabla}\left[\overline{V}+\frac{Z}{r}\right]\right]^2\ , \tag{10}$$

in which

$$\overline{V}=V+\zeta+\frac{1}{6\pi}\tilde{\rho}^{1/3} \tag{11}$$

incorporates the constant $\zeta$. Accordingly, we have

$$\tilde{\rho}(V+\zeta)=\tilde{\rho}\overline{V}-\frac{1}{6\pi}\tilde{\rho}^{4/3}\ , \tag{12}$$

and, as already found in Ref. 3, the additional density-dependent term that emerges here is just two-ninths of the exchange contribution (for which we are content to write $\tilde{n}^{4/3}\cong\tilde{\rho}^{4/3}$).

The resulting energy functional of the variables $\tilde{\rho}(\vec{r})$ and $\overline{V}(\vec{r})$ is (tentatively)

$$E-\tfrac{1}{2}Z^2=\frac{1}{3\pi^2}\int(d\vec{r})\left\{\tfrac{3}{10}\tilde{\rho}^{5/3}-\frac{11}{9}\frac{3}{4\pi}\tilde{\rho}^{4/3}+\tilde{\rho}\overline{V}-\frac{3\pi}{8}\left[\vec{\nabla}\left[\overline{V}+\frac{Z}{r}\right]\right]^2\right\}-\zeta\tilde{N}\ . \tag{13}$$

The Poisson equation produced by varying $\overline{V}$,

$$-\nabla^2\left[\overline{V}+\frac{Z}{r}\right]=\frac{4}{3\pi}\tilde{\rho}\ , \tag{14}$$

is entirely consistent with Eq. (3), for the difference of the two versions,

$$\nabla^2(\overline{V}-V)=\frac{4}{3\pi}(\tilde{n}-\tilde{\rho})\ , \tag{15}$$

is obeyed, both sides having the value $(1/6\pi)\nabla^2\tilde{\rho}^{1/3}$. The related consequence that the volume integrals of $\tilde{\rho}$ and $\tilde{n}$ are equal,

$$\tilde{N}=\int(d\vec{r})\tilde{\rho}(\vec{r})\ , \tag{16}$$

also follows from the stationary property with respect to infinitesimal variations of $\zeta$. The definition (11) shows that

$$\delta\overline{V}=\delta\zeta\ , \tag{17}$$

and therefore

$$\delta\tilde{E}=\delta\zeta\left[\int(d\vec{r})\tilde{\rho}-\tilde{N}\right]=0\,. \tag{18}$$

The variation of $\tilde{\rho}$ in Eq. (13) produces the algebraic equation

$$\tilde{\rho}^{2/3}-\frac{11}{9}\frac{2}{\pi}\tilde{\rho}^{1/3}=-2\bar{V}\,, \tag{19}$$

which is solved by

$$\tilde{\rho}^{1/3}=\frac{11}{9\pi}\pm\left[-2\bar{V}+\left(\frac{11}{9\pi}\right)^2\right]^{1/2}. \tag{20}$$

In the TF region, where $\tilde{n}$ and $\tilde{\rho}$ differ relatively little and $-\bar{V}$ is a large number in our units, only the positive root in Eq. (20) is physically acceptable. If one extrapolates that choice toward smaller values of $-\bar{V}$, a qualitatively new situation is first encountered for $-\bar{V}=0$, where

$$-\bar{V}=0:\ \tilde{\rho}^{1/3}=\frac{11}{9\pi}\pm\frac{11}{9\pi}=2\frac{11}{9\pi};0\,. \tag{21}$$

Here is a possible model of an atom with a definite boundary, outside of which $\tilde{\rho}$, and $\tilde{n}$, can be set equal to zero. We shall take it somewhat seriously. Another possibility consists in the further continuation of the positive-root solution to its ultimate real number limit,

$$\bar{V}=\tfrac{1}{2}\left(\frac{11}{9\pi}\right)^2:\ \tilde{\rho}^{1/3}=\frac{11}{9\pi}\,, \tag{22}$$

beyond which the statistical model is replaced by $\tilde{\rho}=0$.

The Thomas-Fermi-Dirac equation, not surprisingly, involves an equation analogous to (19), with $\frac{11}{9}$ replaced by unity. Neither of the above possibilities (*mutatis mutandis*) is usually adopted in the literature of this equation.[5] Instead, an appeal is made to the physical requirement that the total energy be a minimum at the correct position of the boundary—a statement related to the continuity of the energy density at that boundary. But, in doing this, the energy forms applicable in the dense interior of the atom are extrapolated to the boundary, without regard to the possible occurrence of additional, otherwise innocuous terms, that could, for example, assure the boundary continuity of the energy density independently of the position of that boundary. We develop this point in the context of the provisional energy expression (13), now rewritten, for a spherically symmetrical system, by employing (19) to reexpress $\tilde{\rho}\bar{V}$:

$$E-\tfrac{1}{2}Z^2=\frac{4}{3\pi}\int_0^\infty dr\,r^2\left\{-\tfrac{1}{5}\tilde{\rho}^{5/3}+\frac{11}{9}\frac{1}{4\pi}\tilde{\rho}^{4/3}-\frac{3\pi}{8}\left[\frac{d}{dr}\left(\bar{V}+\frac{Z}{r}\right)\right]^2\right\}-\zeta N\,. \tag{23}$$

To begin, observe that the volume integral of the Poisson equation (14), extended up to the atomic radius $r_0$, gives

$$-4\pi r_0^2\frac{d}{dr}\left(\bar{V}+\frac{Z}{r}\right)\bigg|_{r_0}=\frac{4}{3\pi}\tilde{N}=4\pi N\,, \tag{24}$$

or

$$\frac{d}{dr}\left(\bar{V}+\frac{Z-N}{r}\right)\bigg|_{r_0}=0\,, \tag{25}$$

which supplies the limiting value of $d\bar{V}/dr$ for $r\rightarrow r_0-0$. On the other side of the boundary, according to (17), we have

$$r>r_0:\ \bar{V}=V+\zeta=-\frac{Z-N}{r}+\zeta\,, \tag{26}$$

displaying the net charge of an atom with nuclear charge $Z$ and $N$ electrons. The comparison of (25) and (26) shows that $d\bar{V}/dr$ is continuous across the boundary, as expected from the boundedness of $\tilde{\rho}$ in the Poisson equation. The inference that $\bar{V}$ is also continuous, with the boundary value

$$\bar{V}_b=\bar{V}(r_0)\,, \tag{27}$$

supplies the form of $\zeta$ in terms of the characteristics of the boundary:

$$\zeta=\frac{Z-N}{r_0}+\bar{V}_b\,. \tag{28}$$

Note that, in the examples (21) and (22), $\bar{V}_b$ is independent of $r_0$. We restrict ourselves to this situation.

The contribution to $E$ [Eq. (23)], associated with (apart from a minus sign) the electrostatic energy of the electrons for $r>r_0$, is the radial integral

$$-\tfrac{1}{2}\int_{r_0}^\infty dr\,r^2\left(\frac{d}{dr}\frac{N}{r}\right)^2=-\frac{N^2}{2r_0}\,. \tag{29}$$

That combines with $-\zeta N$ to produce

$$\frac{N^2-2NZ}{2r_0}-N\bar{V}_b\,. \tag{30}$$

Now we use the rearrangement

$$-\frac{1}{2}\left[r\frac{d}{dr}\frac{r\bar{V}+Z}{r}\right]^2=-\frac{1}{2}\left[\frac{d}{dr}r(\bar{V}-\bar{V}_b)\right]^2+\frac{d}{dr}\frac{[r(\bar{V}-\bar{V}_b)+Z]^2}{2r} \tag{31}$$

to express the part of this negative electrostatic energy that occupies the interior of the atom, $0<r<r_0$. The radial integral of the last term in (31) equals

$$Z^2/2r_0\,, \tag{32}$$

provided that

$$r\to 0:\ r\bar{V}(r)+Z\to 0\,, \tag{33}$$

more rapidly than $r^{1/2}$ (which is consistent with the Poisson equation that $\bar{V}$ obeys). We use the abbreviation

$$\mathscr{E}(\tilde{\rho})=\frac{4}{3\pi}\left[-\frac{1}{5}\tilde{\rho}^{5/3}+\frac{11}{9}\frac{1}{4\pi}\tilde{\rho}^{4/3}\right] \tag{34}$$

to convey the present position concerning $E$:

$$E-\tfrac{1}{2}Z^2=\int_0^{r_0}dr\left[r^2[\mathscr{E}(\tilde{\rho})-\mathscr{E}(\tilde{\rho}_b)]-\frac{1}{2}\left[\frac{d}{dr}r(\bar{V}-\bar{V}_b)\right]^2\right]+\frac{(Z-N)^2}{2r_0}-N\bar{V}_b\,, \tag{35}$$

*except* that we have taken the liberty of adding a constant:

$$-\tfrac{1}{3}r_0^3\mathscr{E}(\tilde{\rho}_b)\,,$$

$$\tilde{\rho}_b^{1/3}=\frac{11}{9\pi}+\left[-2\bar{V}_b+\left[\frac{11}{9\pi}\right]^2\right]^{1/2}. \tag{36}$$

It is intended as a conceivable example of effects that are associated with the boundary, rather than the interior of the atom.

The introduction of this constant in no way affects the derivation of the differential equation obeyed by $\bar{V}(r)$, in consequence of the stationary property of $E$. Indeed, from the property of $\tilde{\rho}$ expressed by

$$\delta\mathscr{E}(\tilde{\rho})=\frac{4}{3\pi}\left[-\tilde{\rho}^{4/3}+\frac{11}{9\pi}\tilde{\rho}\right]\delta\tilde{\rho}^{1/3}=\frac{4}{3\pi}\tilde{\rho}\delta\bar{V}\,, \tag{37}$$

we again deduce the Poisson equation

$$-\frac{1}{r}\frac{d^2}{dr^2}(r\bar{V})=\frac{4}{3\pi}\tilde{\rho}=\frac{4}{3\pi}\left\{\left[-2\bar{V}+\left[\frac{11}{9\pi}\right]^2\right]^{1/2}+\frac{11}{9\pi}\right\}^3. \tag{38}$$

And, inasmuch as $\tilde{\rho}_b$ [Eq. (36)] is a fixed number for a given boundary condition, and $r_0^3$ increases even less rapidly than $Z$ (see Table I), the additional energy constant is far below the level of the leading asymptotic terms, of orders $Z^{7/3}$, $Z^{6/3}$, and $Z^{5/3}$ (which are compared with Hartree-Fock calculations for neutral atoms in the Appendix).

In computing $\partial E/\partial r_0$, we must take into account the induced change of $\tilde{\rho}$. But that is removed by the stationary property, except for the boundary term

$$-r_0\delta\bar{V}(r_0)r_0\frac{d\bar{V}}{dr}(r_0)=\left[r_0\frac{d\bar{V}}{dr}(r_0)\right]^2, \tag{39}$$

which evaluation expresses the maintenance of the boundary value $\bar{V}_b$:

$$(\bar{V}+\delta\bar{V})(r_0+\delta r_0)=\bar{V}(r_0)\,. \tag{40}$$

This piece is added to the contribution of the explicit $r_0$ dependence in (35) to give

TABLE I. Values of $y_0$ for inert atoms and related ions. The left- and right-hand columns refer to the boundary conditions (1) and (2), respectively, of Eq. (48).

| $N$ | $Z=N$ | | $Z=N+1$ | | $Z=N+2$ | |
|---|---|---|---|---|---|---|
| 10 | 2.805 | 3.737 | 2.296 | 2.569 | 1.928 | 2.050 |
| 18 | 3.010 | 3.957 | 2.551 | 2.865 | 2.206 | 2.359 |
| 36 | 3.231 | 4.191 | 2.821 | 3.179 | 2.504 | 2.692 |
| 54 | 3.349 | 4.316 | 2.964 | 3.343 | 2.662 | 2.868 |

$$\frac{\partial E}{\partial r_0}=r_0^2[\mathscr{E}(\tilde{\rho}_b)-\mathscr{E}(\tilde{\rho}_b)]+\frac{1}{2}\left[r_0\frac{d\bar{V}}{dr}(r_0)\right]^2-\frac{1}{2}\left[\frac{Z-N}{r_0}\right]^2=0\,. \tag{41}$$

The cancellation of the last two terms on the right-hand side, according to the boundary condition (25), conveys the continuity of the electrostatic energy density derived from $\bar{V}(r)$. The cancellation of the first two terms on the right-hand side exhibits the continuity (with the null external value) of the $\mathscr{E}$ part of the energy density, which has been achieved by the supplemental term (36) independently of the value of $r_0$. Had we not included that otherwise innocuous term, the inference would be

$$\begin{gathered}\mathscr{E}(\tilde{\rho}_b)=0,\ \tilde{\rho}_b^{1/3}=\frac{11}{9}\frac{5}{4\pi}\,,\\ \bar{V}_b=\frac{15}{16}\frac{1}{2}\left[\frac{11}{9\pi}\right]^2.\end{gathered} \tag{42}$$

Indeed, with the substitution $\frac{11}{9}\rightarrow 1$, this value of $\tilde{\rho}_b$ becomes the one ordinarily cited for the TFD equation.

The point of the preceding discussion is simply that the sharp boundary of the semiclassical TFD theory (modified by the first quantum correction to the kinetic energy) involves more than what is known about the interior of the atom, and no clear-cut basis for locating that boundary exists. Of course, a sharp boundary is a fiction; it does not occur in a proper quantum-mechanical treatment—a subject to which we shall return elsewhere. We proceed here in an experimental way, by examining how the diamagnetic susceptibility, of atoms and ions having inert-gas electronic configurations, depends on the choice of boundary. The possibilities will be limited to (21) and (22)—the option of (42) is essentially indistinguishable numerically from the latter.

## DIAMAGNETIC SUSCEPTIBILITY

First we simplify matters by adopting new scales for $r$ and $\bar{V}$,

$$\begin{gathered}y=\frac{4}{3\pi}\left[\frac{11}{2}\right]^{1/2}r=0.995\,34r\,,\\ -\bar{V}+\frac{1}{2}\left[\frac{11}{9\pi}\right]^2=\frac{1}{2}\left[\frac{11}{3\pi}\right]^2\frac{\phi(y)}{y}\,.\end{gathered} \tag{43}$$

The differential equation (38) now reads

$$\frac{d^2\phi}{dy^2}=y\left[\left[\frac{\phi}{y}\right]^{1/2}+\frac{1}{3}\right]^3. \tag{44}$$

Under the circumstances $(\phi/y)^{1/2}\gg\frac{1}{3}$ it reduces to the form of the TF equation. Retaining the first two terms of an expansion in powers of $\frac{1}{3}$ replaces (44) with

$$\frac{d^2\phi}{dy^2}=\frac{\phi^{3/2}}{y^{1/2}}+\phi\,, \tag{45}$$

which is the equation introduced in Ref. 3.

The boundary condition at the origin, conveying (33), is

$$\phi(0)=6\pi(11/2)^{-3/2}Z=1.461\,36Z\,, \tag{46}$$

while Eq. (25), referring to the atomic edge, becomes

$$-y_0\frac{d\phi}{dy}(y_0)+\phi(y_0)=\left[1-\frac{N}{Z}\right]\phi(0)\,. \tag{47}$$

As for the individual outer boundary values of $\phi$, they are given by

$$\begin{gathered}(1)\ \text{Eq. (21):}\ \phi/y(y_0)=\tfrac{1}{9}\,,\\ (2)\ \text{Eq. (22):}\ \phi/y(y_0)=0\,.\end{gathered} \tag{48}$$

Values of $y_0$ produced by numerical integration of the differential equation, for these two boundary conditions, are listed in Table I. The numbers refer to the purely diamagnetic closed-shell neutral atoms Ne, Ar, Kr, and Xe, along with the singly and doubly charged positive ions having those electronic configurations.

The molar diamagnetic susceptibility can be written

$$-\chi=\left[\frac{1}{\text{'}137\text{'}}\right]^2N_Aa_0^3I=4.752\times10^{-6}I\,, \tag{49}$$

where, expressed in atomic units,

$$I=\tfrac{1}{6}\int(d\vec{r})r^2n\,. \tag{50}$$

In view of the $r^2$ factor here, no error is introduced on modifying Eq. (3) as indicated by

$$\begin{aligned}I&=\tfrac{1}{6}\int(d\vec{r})r^2\left[-\frac{1}{4\pi}\right]\nabla^2\left[V+\frac{Z-N}{r}\right]\\ &=\frac{1}{4\pi}\int(d\vec{r})\left[-V-\frac{Z-N}{r}\right];\end{aligned} \tag{51}$$

the latter rearrangement exploits the null value of $V+(Z-N)/r$ outside the atom. The replacement of $V$ by $\bar{V}$, in accordance with (11) and (28), converts this into

$$I=\int_0^{r_0} dr\, r^2 \left[ -\bar{V}+\bar{V}_b-\frac{Z-N}{r} + \frac{Z-N}{r_0}+\frac{1}{6\pi}\tilde{\rho}^{1/3}\right] . \quad (52)$$

Then the introduction of such relations as

$$-\bar{V}+\bar{V}_b=\frac{1}{2}\left[\frac{11}{3\pi}\right]^2\left[\frac{\phi(y)}{y}-\frac{\phi(y_0)}{y_0}\right] ,$$
$$\tilde{\rho}^{1/3}=\frac{11}{3\pi}\left[\left[\frac{\phi}{y}\right]^{1/2}+\tfrac{1}{3}\right] , \quad (53)$$
$$\frac{1}{r}=\frac{4}{3\pi}\left[\frac{11}{2}\right]^{1/2}\frac{1}{y}$$

yields the final form for numerical integration:

$$I=\frac{3\pi}{32}\left[\frac{11}{2}\right]^{1/2}\left[\int_0^{y_0} dy\, y\phi+\tfrac{1}{11}\int_0^{y_0} dy\, y(y\phi)^{1/2}-\tfrac{1}{3}y_0^3\left[\frac{\phi(y_0)}{y_0}-\frac{1}{33}\right]-\pi(\tfrac{11}{2})^{-3/2}y_0^2(Z-N)\right] . \quad (54)$$

The overall numerical coefficient has the value 0.6907; the multiple of $y_0^2(Z-N)$ equals 0.2436.

While the experimental values of the susceptibility are well established for the neutral atoms,[6] those for the ions[7] are unavoidably uncertain owing to the necessity of measuring them in ionic crystals. An independent input is provided by Hartree-Fock calculations.[8] For the neutral atoms those calculated values exceed the accurately measured ones by amounts ranging from 5 to 13% (Ne: 9.9%, Ar: 5.3%, Kr: 8.7%, Xe: 13.0%). We have assumed, quite arbitrarily, that the HF numbers are in excess by fractional amounts that are characteristic of the electronic configuration alone—the same for all $Z$ with a given $N$. The adjusted Hartree-Fock (AHF) numbers thus produced are listed in Table II, along with the experimental values and the two sets of theoretical predictions, which are displayed in the same manner as in Table I.

Looking at the results for neutral atoms, one gets the distinct impression that boundary condition (1) has outperformed boundary condition (2); and, the agreement with experiment is to within 3 percent for $Z=18$ and 54. (A larger error for $Z=10$ is understandable; $Z=36$ seems to exhibit a quantum oscillation.) That same level of accuracy applies to all six numbers for $N=18$ and 54, when compared with the experimental values. Agreement with the AHF numbers appears at roughly the 10% level for the 9 entries of $N=18$, 36, 54.

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TABLE II. Comparison of adjusted HF and experimental values for $I$ with Eq. (54) predictions. Left- and right-hand columns refer to the boundary conditions (1) and (2), respectively, of Eq. (48).

| $N$ | $Z$ | AHF | Expt. | Theor. | | AHF/Theor. (%) | | Expt./Theor. (%) | |
|---|---|---|---|---|---|---|---|---|---|
| 10 | 10 | 1.42 | 1.42 | 2.71 | 3.32 | 52 | 43 | 52 | 43 |
| | 11 | 0.97 | 1.28 | 1.75 | 1.85 | 55 | 52 | 73 | 69 |
| | 12 | 0.72 | 0.91 | 1.22 | 1.24 | 59 | 58 | 75 | 73 |
| 18 | 18 | 4.12 | 4.12 | 4.24 | 5.00 | 97 | 82 | 97 | 82 |
| | 19 | 3.09 | 3.07 | 3.04 | 3.19 | 102 | 97 | 101 | 96 |
| | 20 | 2.44 | 2.25 | 2.30 | 2.35 | 106 | 104 | 98 | 96 |
| 36 | 36 | 6.06 | 6.06 | 6.91 | 7.83 | 88 | 77 | 88 | 77 |
| | 37 | 4.88 | 4.63 | 5.42 | 5.66 | 90 | 86 | 85 | 82 |
| | 38 | 4.09 | 3.79 | 4.42 | 4.51 | 93 | 91 | 86 | 84 |
| 54 | 54 | 9.24 | 9.24 | 9.01 | 10.04 | 103 | 92 | 103 | 92 |
| | 55 | 7.75 | 7.39 | 7.37 | 7.66 | 105 | 101 | 100 | 96 |
| | 56 | 6.71 | 6.10 | 6.22 | 6.33 | 108 | 106 | 98 | 96 |

TABLE III. Comparison of nonrelativistic HF with statistical calculations of total atomic binding energy, for various values of $Z$.

| $Z$ | $-E_{\text{HF}}/\frac{1}{2}Z^2$ | $-E_{\text{stat}}/\frac{1}{2}Z^2$ | $(E_{\text{HF}}/E_{\text{stat}}-1)$ (%) |
|---|---|---|---|
| 2 | 1.4308 | 1.3656 | 4.8 |
| 4 | 1.8216 | 1.7807 | 2.3 |
| 6 | 2.0922 | 2.0909 | 0.063 |
| 8 | 2.3365 | 2.3449 | −0.36 |
| 10 | 2.5709 | 2.5630 | 0.31 |
| 12 | 2.7724 | 2.7558 | 0.60 |
| 16 | 3.1053 | 3.0885 | 0.54 |
| 20 | 3.3838 | 3.3723 | 0.34 |
| 24 | 3.6220 | 3.6221 | −0.003 |
| 28 | 3.8439 | 3.8465 | −0.068 |
| 32 | 4.0534 | 4.0513 | 0.052 |
| 36 | 4.2470 | 4.2402 | 0.16 |
| 42 | 4.5073 | 4.4997 | 0.17 |
| 48 | 4.7440 | 4.7362 | 0.16 |
| 54 | 4.9603 | 4.9542 | 0.12 |
| 60 | 5.1577 | 5.1570 | 0.014 |
| 66 | 5.3450 | 5.3470 | −0.037 |
| 72 | 5.5252 | 5.5260 | −0.014 |
| 80 | 5.7528 | 5.7502 | 0.045 |
| 88 | 5.9644 | 5.9601 | 0.072 |
| 96 | 6.1617 | 6.1579 | 0.062 |
| 104 | 6.3492 | 6.3451 | 0.065 |
| 112 | 6.5271 | 6.5232 | 0.060 |
| 120 | 6.6948 | 6.6930 | 0.027 |

## APPENDIX

The asymptotic expansion of the nonrelativistic total binding energy, for neutral atoms, has the following leading terms in the statistical theory[2,3]:

$$-E_{\text{stat}}(Z)=0.768\,75Z^{7/3}-\tfrac{1}{2}Z^{6/3}+0.2699Z^{5/3}\,. \qquad (55)$$

TABLE IV. Percentage deviation between HF energies and the statistical energy curve of Eq. (59).

| $Z$ | % | $Z$ | % |
|---|---|---|---|
| 2 | −0.68 | 42 | 0.089 |
| 4 | 0.19 | 48 | 0.099 |
| 6 | −1.1 | 54 | 0.067 |
| 8 | −1.1 | 60 | −0.035 |
| 10 | −0.28 | 66 | −0.080 |
| 12 | 0.15 | 72 | −0.052 |
| 16 | 0.24 | 80 | 0.013 |
| 20 | 0.12 | 88 | 0.044 |
| 24 | −0.18 | 96 | 0.036 |
| 28 | −0.21 | 104 | 0.042 |
| 32 | −0.064 | 112 | 0.039 |
| 36 | 0.062 | 120 | 0.008 |

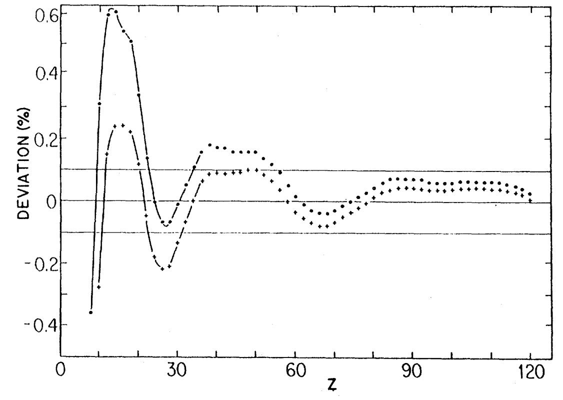

FIG. 1. Graphical presentation of Table III (dots) and Table IV (crosses).

It is interesting to compare these values with the accurate HF nonrelativistic calculations,[8] in order to see the degree of agreement, and the nature of the deviation, between calculations that refer to specific, integer values of $Z$, and those inferred from the continuous curve of the statistical theory. That is presented in Table III, where $\frac{1}{2}Z^2$ is adopted as an energy unit, so that

$$\frac{-E_{\text{stat}}}{\frac{1}{2}Z^2}=1.5375Z^{1/3}-1+0.5398Z^{-1/3}\,, \qquad (56)$$

which has the advantage of limiting the range of variation over the usual periodic table from roughly one to six.[9]

It is seen that $E_{\text{HF}}$ oscillates quite smoothly about $E_{\text{stat}}$. (That is even more striking when the complete set of $Z$ values is examined; see Fig. 1.) The oscillations decrease in amplitude (with an exception to be noted later) and increase in period as $Z$ grows larger. In particular, nothing at all dramatic occurs at the positions of closed-shell atoms,[10] which encourages a hope that further refinement of the statistical model could incorporate those oscillations. We also remark that for $Z>54$ the oscillation amplitude is below the 0.1% level.

The exception cited above concerns the negative excursions for $Z>10$, which are smaller in amplitude than both the preceding and following positive swings. This suggests that $-E_{\text{stat}}$ is slightly too small; matters might be improved by including yet another term in the asymptotic expansion. In this connection we remark that rewriting the differential equation of (44) in TF units, according to the transformations

$$y=(6\pi)^{-1/3}(\tfrac{11}{2})^{1/2}Z^{-1/3}x\ ,$$
$$\phi(y)=6\pi(\tfrac{11}{2})^{-3/2}Zf(x)\ , \qquad (57)$$

yields

$$\frac{d^2f}{dx^2}=x\left[\left[\frac{f}{x}\right]^{1/2}+\tfrac{11}{6}(6\pi)^{-2/3}Z^{-2/3}\right]^3 . \qquad (58)$$

exhibiting the expansion parameter $Z^{-2/3}$. We therefore expect that the next contribution in (56) is a multiple of $Z^{-1}$. As an example, we exhibit in Table IV the fractional deviation between $-E_{\mathrm{HF}}/\frac{1}{2}Z^2$ and[11]

$$\frac{-E_{\mathrm{stat}}}{\frac{1}{2}Z^2}=1.5375Z^{1/3}-1+0.5398Z^{-1/3}+0.15Z^{-1}\ . \qquad (59)$$

Once past $Z=4$, the maximum amplitudes of the successive swings do decrease steadily with increasing values of Z. And, now, one is already below the 0.1% level at $Z=32$.

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*Permanent address: Department of Physics, University of California, Los Angeles, California 90024.

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[2] J. Schwinger, Phys. Rev. A 22, 1827 (1980); J. Scott, Philos. Mag. 43, 859 (1952).

[3] J. Schwinger, Phys. Rev. A 24, 2353 (1981).

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[5] See Ref. 1. A recent review article, E. Lieb, Rev. Mod. Phys. 53, 603 (1981), contains, among other related topics, a highly mathematized discussion of the Thomas-Fermi-Dirac theory. We looked eagerly for a useful new insight into the troublesome boundary problem—we did not find it.

[6] *Handbook of Chemistry and Physics* (Chemical Rubber Co., Cleveland, Ohio, 1979/80).

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[8] S. Fraga, J. Karwowski, and K. Saxena, *Handbook of Atomic Data* (Elsevier, Amsterdam, 1976); J. P. Desclaux, At. Data Nucl. Data Tables 12, 311 (1973).

[9] Large values of Z have been used by R. Shakeshaft, L. Spruch, and J. Mann, J. Phys. B 14, L121 (1981) who attack a different problem, that of finding numerically the best choice for the coefficients of the various powers of Z. This analysis lends further support to the leading terms of the asymptotic expansion, Eq. (56).

[10] This is contrary to the expectation of R. Shakeshaft and L. Spruch, Phys. Rev. A 23, 2118 (1981), that quantum discontinuities associated with shell structure would terminate the utility of the statistical model. More congenial is a recent [J. Phys. Paris (in press)] paper of I. K. Dimitrieva and G. I. Plindov, who suggest that quantum oscillations would supplement Eq. (56) [or Eq. (59)] by a term of order $Z^{-2/3}$, multiplied by a periodic function of a numerical multiple of $Z^{1/3}$, which certainly is in accord with the decrease in amplitude and increase in period as Z grows.

[11] The large-Z numerical work of Shakeshaft *et al.*, cited in Ref. 9, also confirms the absence of any significant constant multiple of $Z^{-2/3}$ in Eq. (59). Note also that if the last term of (59) is regarded as producing a slightly Z-dependent coefficient of $Z^{-1/3}$, namely, $0.5398+0.15Z^{-2/3}$, the range of values the latter exhibits for the large-Z atoms considered by Shakeshaft *et al.*—0.548 to 0.543—is consistent with their best fit—$0.55\pm0.005$.