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Modified Quantum-Statistical Calculations for Atomic Electron Densities

Jerry Goodisman
Department of Chemistry, Syracuse University, Syracuse, New York 13210

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We attempt to overcome one of the shortcomings in the Thomas-Fermi and related theories for atoms by connecting a quantum-mechanical electron density for the region near the nucleus to a density given by a statistical model. The joining may be done in a nonarbitrary manner: All parameters are determined. It suffices to use a very crude and easily calculated approximation to the density to start with, so the calculation is quite easy. The resulting electron density is in much better agreement with reality than that from the unmodified theories.

I. INTRODUCTION

The statistical [Thomas-Fermi (TF), Thomas-Fermi-Dirac (TFD), Thomas-Fermi-Dirac-Gombás (TFDG)] theories[1] for atoms and molecules lead to a differential equation in three spatial coordinates from the solution of which the electron density may be determined. This constitutes a great simplification over the full quantum-mechanical treatment, wherein one first must deal with a $3N$-dimensional differential equation for the N-electron wave function, which gives the one-electron density by integration over the coordinates of all but one electron. Furthermore, the statistical methods are expected to be more accurate for systems with more electrons, while the difficulty of the quantum-mechanical methods increases rapidly with N. The problem is that the statistical theories give only a very rough approximation to the electron density, even for atoms of large atomic number. This is due to the breakdown of the assumptions of the theory at very small and very large distances from the nucleus. In the former case, the potential becomes Coulombic and hence too rapidly varying with r (the theory assumes that the potential is constant in a small region about each point in space, so that the density and potential may be related as for a gas of free electrons); in the latter case, the density is too low (the theory assumes all free-particle states below the Fermi surface filled for each point in space). As a result, the TF theory for atoms gives a radial density D ($D = 4\pi r^2 \rho$, ρ is the density in electrons per unit volume) which goes to zero as $r^{1/2}$ rather than r^2 for small r and as r^{-4} rather than exponentially for large r.

The Von Weizsäcker[2] kinetic-energy correction leads to the correct behavior at both small and large r, but numerical results are poor and its reliability has been questioned.[3,4] Related treatments[4,5] are of questionable theoretical validity.[5] It must be noted that Gombás's modification[4] of the kinetic-energy correction gives impressive results and maintains the correct behavior of the Weizsäcker theory. However, the theoretical basis is problematic and a complicated differential equation is obtained. Yonei and Tomishima[6] found that by multiplying the Weizsäcker correction by 0.2 they obtained a density which was correct near the nucleus and which led to good energies, while using the full Weizsäcker correction led to good densities for large r.

It is possible to correct the large-r behavior by working with the variational principles which lead to the TF, TFD, TFDG equations. For instance, the energy in the TF theory is given in terms of ρ by[1]

$$E = \kappa_k \int \rho^{5/3}\, d\tau - e \int V_n \rho\, d\tau + \tfrac{1}{2} \iint \rho(\tau_1)\, \rho(\tau_2)\, r_{12}^{-1}\, d\tau_1\, d\tau_2 \quad , \tag{1}$$

the terms representing kinetic energy, electron-nuclear attraction energy (V_n is the Coulomb potential of the nucleus), and interelectronic repulsion energy. κ_k is a known constant. If ρ is varied to minimize E with $\int \rho\, d\tau$ fixed (normalization), an equation for ρ, which leads to the TF equation for the potential, is obtained. The distance at which ρ must become zero may also be obtained by varying E with respect to this distance. Lenz and Jensen[7] and recently, Csavinszky[8] consider trial functions for ρ which guarantee exponential behavior at large r as well as normalization and vary parameters in them to make E stationary. The electron densities are improved – in particular, calculated diamagnetic susceptibilities (expectation values of r^2) are in closer agreement with experiment.[8,9]

For many purposes, the incorrect behavior at small r is the more serious deficiency. The electron-nuclear attraction energy is given by $-Ze^2$ (Z is the nuclear charge) times the expectation value of r^{-1}, which is sensitive to the behavior of the electron density near the nucleus. In fact, one can show[10] that for neutral atoms

$$\left(\frac{dE}{dZ}\right)_{\rm neu} = -e^2\int \rho r^{-1}\,d\tau = -e^2\int D r^{-1}\,dr \ , \qquad (2)$$

so that the expectation value of r^{-1} determines the energy by

$$E(Z) = \int_0^Z \frac{dE}{dZ}\,dZ = -e^2\int_0^Z dZ\int_0^\infty dr\,D(r,Z)\,r^{-1} \ . \qquad (3)$$

Equation (2) holds exactly in the TF, and approximately in the TFD and TFDG cases. The TF theory (see below) overestimates the expectation value and leads to energies which are much too large. Going to TFD or TFDG makes things worse, since the energy is decreased by exchange and correlation terms.[1]

One could hope to improve the small-r behavior by going back to the variational principle as was done for the problem at large r. One would take a trial function for D which guaranteed r^2 behavior for small r, exponential behavior for large r, and normalization. With reference to such methods, we believe that one can get arbitrarily close to the TF density over any finite region of r with a function going as r^2 for $r \to 0$ and dying off exponentially for $r \to \infty$. Most expectation values then would be no better than those from the exact solution to the TF equation, i. e., bad. Good results from such a method mean the trial function had only limited flexibility, and are in a sense due to a fortuitous cancellation of errors.

In this paper, we consider joining a quantum-mechanical density for small r onto a statistical density at some $r = r_c$ in order to produce a density which is better at small and intermediate r than what one gets from the statistical models alone. Only neutral atoms are considered. The work involved is hardly more than that required by the statistical model, and a real improvement is obtained. In all cases, r_c can be determined *a priori* and is *not* a parameter to be adjusted for good results.

The TF case is considered in Sec. II, the TFD and the TFDG cases in Sec. III. It is clear that the procedure is of little interest if one has to do a quantum-mechanical calculation to get the density for small r in the first place. We show in Sec. IV how one can easily get a sufficiently accurate small-r density from very simple considerations. Results using this density, as well as the accurate density, are given for neon, not a particularly favorable case for statistical methods. In Sec. V, the methods of the preceding sections are tested, using the approximate small-r density, for atoms of higher atomic number to demonstrate the accuracy obtainable.

II. THOMAS-FERMI

In the TF theory, one considers the interelectronic repulsion, the electron-nuclear attraction, and a contribution from a kinetic-energy which is proportional to the $\frac{5}{3}$ power of the electron density ρ. The density is obtainable in terms of a function ϕ, defined as r/Ze times the potential, which satisfies the well-known TF equation

$$\phi'' = \phi^{3/2}/x^{1/2} \ . \qquad (4)$$

Here, x is related to the distance from the nucleus by

$$x = r/\mu \ , \qquad (5a)$$

$$\mu = \tfrac{1}{4}(3\pi)^{2/3}(2Z)^{-1/3}a_0 \ , \qquad (5b)$$

where a_0 is the Bohr radius. For neon, $\mu^{-1} = 2.433\,450\,8 a_0^{-1}$. Equation (4), of course, assumes spherical symmetry. For a neutral atom, ϕ must obey the boundary conditions (i) $\phi(0) = 1$ and (ii) $\phi \to 0$ as $x \to \infty$. The electron density is related to ϕ by

$$\rho = (Z/4\pi\mu^3)(\phi/x)^{3/2} = (Z/4\pi\mu^3)(\phi''/x) \ . \qquad (6)$$

Normalization of ρ, i. e.,

$$\int_0^\infty 4\pi r^2 \rho\,dr = N = Z \ ,$$

is assured by the boundary conditions on ϕ. It is important to note that ϕ is a universal function which is tabulated[1] so that $\rho(r)$, for any neutral atom, is immediately available. All expectation values are obtained from ϕ. For instance

$$\langle r^{-1}\rangle = \int_0^\infty D r^{-1}\,dr = -Z\mu^{-1}\phi'(0) \ , \qquad (7)$$

where $D = 4\pi r^2\rho$, the radial density. Note that we define $\langle f(r)\rangle$ as N times $\langle f(r_i)\rangle$.

The initial slope of ϕ required to satisfy the boundary conditions is -1.588. Then (7) gives $\langle r^{-1}\rangle = 1.794\,Z^{4/3}a_0^{-1}$, and (3) gives the TF energy formula

$$E = -0.7689\,Z^{7/3}e^2/a_0$$
$$= -20.92 Z^{7/3}\,\text{eV}.$$

While the $Z^{7/3}$ behavior is roughly correct, the energies are much too large.[11] For neon, the TF theory predicts $\langle r^{-1}\rangle = 38.7 a_0^{-1}$, while a correct quantum-mechanical treatment[12] gives $\langle r^{-1}\rangle = 31.1 a_0^{-1}$. Improvements on the theory give even worse values for $\langle r^{-1}\rangle$, except for the Weizsäcker and related corrections.

We not consider the electron density to be given from $r=0$ to some distance r_c. We use $\bar{\rho}(r)$ and $\bar{D}(r)$ to denote the given density and radial density. The density for $r>r_c$ is to be obtained from a solution to the TF equation with appropriate boundary conditions. It seems reasonable to demand that, as for a neutral atom in the TF theory, ρ go to zero for $r\to\infty$ and also that ρ be continuous for $r=r_c$. In fact, if one considers the energy formula (1) and varies $\rho(r)$ (for $r>r_c$ only) to make E stationary, one finds that ρ should be derived from ϕ of Eq. (4) with $\phi\to 0$ as $x\to\infty$. In this calculation, the nuclear charge for V_n must be the true charge diminished by the electronic charge within r_c. This is given by

$$\mathscr{g}=\int_0^{r_c}\bar{D}\,dr \quad . \tag{8}$$

A final necessary boundary condition is normalization:

$$Z=\mathscr{g}+\int_{r_c}^{\infty}D\,dr \quad . \tag{9}$$

Now the continuity of ρ gives the initial value for ϕ:

$$\begin{aligned}\phi_c&=[4\pi\bar{\rho}(r_c)/Z]^{2/3}\mu^2x\\&=0.88534\,Z^{-1}[\bar{D}(r_c)^2/r_c]^{1/3} \quad .\end{aligned} \tag{10}$$

The boundary condition (9) gives the initial slope:

$$\begin{aligned}Z-\mathscr{g}&=Z\int_{x_c}^{\infty}x\phi_{xx}\,dx\\&=Z[-x_c\phi'(x_c)+\phi(x_c)]\ ,\end{aligned}$$

where we have used the fact that ϕ and ϕ' go to zero as $x\to\infty$. Thus, we obtain

$$\phi'(x_c)=\frac{\phi(x_c)-1+\mathscr{g}/Z}{x_c} \quad , \tag{11}$$

where $x_c=r_c/\mu$. Starting at x_c with (10) and (11), one can integrate the differential equation (4) outward. In general, ϕ will *not* approach zero for large x, but will either cut the x axis or turn upward [note that (4) makes ϕ concave upward everywhere]. This makes it possible to determine x_c, the joining point.

We have employed a Runge-Kutta procedure[13] for integration of (4) for different x_c, changing x_c until a value was found such that the resultant ϕ went to zero for large x. In fact, all solutions of (4) which go to zero at infinity approach $144/x^3$ [an exact solution to (4) which has unacceptable behavior for small x.[14]] Some of these have vertical asymptotes for $x>0$, and some cut the $x=0$ axis. It can be shown[15] that by a scaling transformation any such solution can be transformed into one of two master solutions. Tables of these were given, but could not be used for the small-x values with which we were concerned.

In our calculations, we, in fact, find one value of x_c which gives a solution ϕ_1 cutting the x axis and one slightly higher which gives a solution ϕ_2 going unbounded. The correct x_c is between the two. Table I gives the initial conditions for ϕ_1. Unfortunately, we cannot get upper and lower bounds on the expectation values, since in

$$\langle f(r)\rangle=\int_0^{r_c}\bar{D}f(r)\,dr+\int_{r_c}^{\infty}Df(r)\,dr \tag{12}$$

the second integral does not converge when ϕ_2 is used. If we calculate (12) with ϕ_1, expectation values will be underestimated because of the missing tail of the electron density. This is of course more important for properties emphasizing the density at large r.

The electron density $\bar{D}$ for $r<r_c$ is calculated from the approximate self-consistent-field (SCF) function given by Clementi.[16] In Table I, several moments of the calculated distribution are given. The difference of the normalization $\langle 1\rangle$ from 10 is a measure of the size of the tail. Its contribution to $\langle r\rangle$ will be considerably larger than its contribution to $\langle 1\rangle$ and its contribution to $\langle r^2\rangle$ large enough to make the number in Table I correct only to an order of magnitude, while $\langle r^{-2}\rangle$ and $\langle r^{-1}\rangle$ are essentially not affected. Numerical integration was used to obtain all the results of Table I. For $\langle r^{-1}\rangle$, we can also use Eq. (7) (which assumes

TABLE I. Corrected TF results for neon.

r_c	$\phi(x_c)$	$\phi'(x_c)$	$\mathscr{g}$	$\langle r^{-2}\rangle(a_0^{-2})$	$\langle r^{-1}\rangle(a_0^{-1})$	$\langle 1\rangle$	$\langle r\rangle(a_0)$	$\langle r^2\rangle(a_0^2)$
$0.04680a_0$	0.8759	−0.9720	0.13465	391.2	28.30	9.662	11.5	28.0
Unmodified TF				∞	38.64	⋯	14.8[a]	84.6[b]
Quantum mechanical				414.8[c]	31.09[d]	10.0	7.634[c]	9.35[d]

[a] Calculated from $4\pi\int_0^{\infty}\rho r^3\,dr=\mu Z\int_0^{\infty}\phi''x^2dx=2\mu Z\int_0^{\infty}\phi\,dx$.

[b] Reference 1, p. 233.

[c] Computed from LCAO-SCF function of Clementi, Ref. 16.

[d] S. Fraga and G. Malli, *Many-Electron Systems: Properties and Interactions* (Saunders, Philadelphia, 1968).

$\phi \to 0$ for $x \to \infty$). This has the advantage that $\langle r^{-1}\rangle$ for the true solution to our problem can be bounded by using the initial slopes for ϕ_1 and ϕ_2. This enables us to write $28.33a_0^{-1} < \langle r^{-1}\rangle < 28.35_0^{-1}$.

We expect $\langle r\rangle$ and $\langle r^2\rangle$ to be too high because the TF theory leads to a density dying off too slowly at large r. Our method has apparently compensated for this somewhat, although we were attempting mainly to correct the small-r behavior. In this connection, we note the improvement in $\langle r^{-1}\rangle$ and $\langle r^{-2}\rangle$ (it must be admitted that most of $\langle r^{-2}\rangle$ comes from $r < r_c$). Electron exchange should give a contraction of the electron density and improve the agreement. For Ne, going from TF to TFD (with no small-r correction) cuts $\langle r^2\rangle$ by a factor of 3.[9] The effect of exchange on $\langle r^{-1}\rangle$ in our case may be estimated from the following not quite legitimate argument.

The exchange energy in the statistical theories is given by $-\kappa_a \int \rho^{4/3} d\tau$, with $\kappa_a = 0.7386e^2$. We calculate this with our present density and obtain about 26 e^2/a_0. The lowering in the energy by this amount must be accompanied by a lowering in the potential energy by twice this amount (virial theorem). If the electron repulsion energy is lowered by $26e^2/a_0$, the electron-nuclear potential energy $-Ze^2\langle r^{-1}\rangle$ must also be lowered by $26e^2/a_0$, which means $\langle r^{-1}\rangle$ is increased by about $2.6a_0^{-1}$. Our corrected value for $\langle r^{-1}\rangle$ of $30.9a_0$ differs by a fraction of a percent from that calculated quantum mechanically. If the TF density, which becomes larger than the quantum-mechanical density close to the nucleus, were used for this calculation, $\langle r^{-1}\rangle$ would be increased beyond the quantum-mechanical value, as, in fact, turns out to be the case in Sec. III.

III. THOMAS-FERMI-DIRAC AND THOMAS-FERMI-DIRAC-GOMBÁS

The TFD theory includes the exchange interaction by adding a term $-\int \nu_a \rho^{4/3} d\tau$ to (1). Making E stationary with respect to variations in ρ gives an equation for ρ in terms of the potential which, together with Poisson's equation, leads to the TFD equation

$$\psi'' = x[(\psi/x)^{1/2} + \beta_0]^3 \ . \tag{13}$$

Here ψ is related to the potential, and the density is given in terms of ψ by

$$(4\pi\mu^3\rho/Z)^{1/3} = (\psi/x)^{1/2} + \beta_0 \ . \tag{14}$$

Equations (13) and (14) go over to Eqs. (4) and (6) for $\beta_0 = 0$ (no exchange). The constant β_0 depends on Z:

$$\beta_0 = \tfrac{1}{2}(3/4\pi^2)^{1/3} Z^{-2/3} \quad , \tag{15}$$

so Eq. (13) is different for each atom, unlike the TF equation. A more important difference, for our purposes, between the TF and TFD equations is the change in boundary condition. Since ρ can never vanish, the electron density must be cut off at a finite radius x_0. If this is determined to minimize the energy, the boundary condition on ψ is

$$\psi(x_0)/x_0 = \tfrac{1}{16}\beta_0^2 \quad , \tag{16}$$

which means that

$$\rho_0 = Z(4\pi\mu^3)^{-1}(\tfrac{5}{4}\beta_0)^3 \ .$$

Given an electron density out to some distance r_c from the nucleus, one can fix $\rho(x_c)$ by the continuity of ρ and demand that E (including the exchange term) be stationary to variations in ρ. This leads to the TFD equations. Demanding that E be stationary to variations in the boundary radius again yields (16).

Thus our procedure would be to integrate (13) from some x_c to x_0 determined by (16). $\psi(x_c)$ is fixed using (14). As the initial slope is increased, the intersection of ψ with the line $\psi = \frac{1}{16}\beta_0^2 x$ is pushed out further, the area under ψ and hence $\int_{x_c}^{x_0} \rho \, d\tau$ increasing. The initial slope may thus be determined by the normalization condition

$$1 - Z^{-1}\mathscr{g} = x_0\psi_0' - \psi_0 - x_c\psi_c' + \psi_c \ . \tag{17}$$

We use subscripts 0 and c to indicate evaluation at x_0 and x_c. But it appears that this may be done for a range of x_c, so an additional condition is necessary. (Actually, for certain x_c, such as near the TF x_c in the neon case, increasing ψ_c' leads to a rapidly increasing ψ, which never touches $\psi = \frac{1}{16}\beta_0^2 x$, before the normalization condition can be fulfilled.) We choose to demand continuity of the derivative of D with r at the joining point x_c. The derivative D_r is obtained from the quantum-mechanical density, and, from (14), the initial slope of ψ is given by

$$\psi'(x_c) = \psi_c/x_c + \tfrac{2}{3}(\mu/Z\overline{D}^2 x_c^5)^{1/3}(x_c\psi_c)^{1/2}(r_c\overline{D}_r - 2\overline{D}) \ . \tag{18}$$

For a given x_c, $\psi(x_c)$ and $\psi'(x_c)$ are then known. We integrate (13) to x_0 determined according to (16) and check the normalization. The joining point x_c is determined as the one for which (17) is fulfilled.

In the first line of Table II, the results of such a calculation for neon are given. Clementi's approximate SCF density was again used for $\overline{D}$. The closeness of $\langle 1\rangle$ to 10 reflects how well we have determined x_c. The value given for x_c is correct to 0.000 01, but $\langle 1\rangle$ is very sensitive to x_c. By

TABLE II. Corrected TFD and TFDG results.

Calculation	$r_c(a_0)$	$\psi(x_c)$	$\psi'(x_c)$	g	$\langle r^{-2}\rangle\,(a_0^{-2})$	$\langle r^{-1}\rangle\,(a_0^{-1})$	$\langle 1\rangle$	$\langle r\rangle\,(a_0)$	$\langle r^2\rangle\,(a_0^2)$
Corrected TFD	0.09542	0.905864	−0.997045	0.58912	425.9	34.93	9.9265	6.643	6.740
Corrected TFDG	0.9529	0.90087	−0.9914	0.58804	442.8	35.81	9.9253	6.459	6.465
Unmodified TFD	0	...	...	...	∞	40.76[a]	...	...	25.6[b]
Quantum mechanical	∞	...	...	...	414.8[c]	31.09[d]	10.0	7.634	9.35[d]

[a] Estimated initial slope for Ne of 1.675 was used (cf. Ref. 1, p. 86).

[b] Reference 1, p. 233.

[c] Computed from the linear combination of atomic orbital function of Clementi, Ref. 16.

[d] S. Fraga and G. Malli, *Many-Electron Systems: Properties and Interactions* (Saunders, Philadelphia, 1968).

numerical integration, the moments of the distribution given in the table were calculated. Ordinary TFD and quantum-mechanical results are given for comparison. Because of the great change in x_c from the TF case, comparison with the results of Sec. III does not seem meaningful.

We note that all the moments are now in qualitative agreement with the quantum-mechanical results. The improvement over the unmodified TFD results is quite evident. It must again be noted that the good agreement in $\langle r^{-2}\rangle$ is not really that impressive, since $\frac{3}{4}$ of $\langle r^{-2}\rangle$ comes from $r < r_c$.

Gombás[17] has added the correlation energy into the TFD theory. In this theory (which we refer to as TFDG), an additional term of the form $-\int g(\rho^{1/3})\rho\, d\tau$ is added to the energy, g being a known function of $\rho^{1/3}$. The equations to which this leads can be put in the form of the TFD equations when certain approximations are made, except that β_0 in Eqs. (13), (14), and (16) is replaced by

$$\beta_0' = 1.1303\beta_0 \ . \qquad (19)$$

The solutions to the TFDG problem are similar to those for the TFD problem. In our case, the discussion given above for TFD is applicable.

The change in results due to the change in Eq. (19) is slight although in the wrong direction. These results are included in Table II. Because of the approximations in the method, and because of the closeness of the results to those from TFD, we do not consider TFDG further.

IV. APPROXIMATE SMALL-r DENSITY

Obviously, a method which requires the SCF density and then proceeds to approximate it is of little interest. However, we here require only the electron density for small r, i.e., $r < 0.1a_0$ for neon. In this region, only the 1s electrons contribute. For r very small, these electrons see the Coulombic potential of the nucleus and each other's Coulombic potential, the former being much more important. The density of the outer electrons is negligible here, so they contribute only a constant term to the potential (outer shielding) which does not affect the wave function of the 1s electrons. We approximate the 1s atomic orbitals as hydrogenic orbitals, so the small-r electron density becomes

$$\overline{D} \simeq 8Z^3 r^2 e^{-2Zr} \ . \qquad (20)$$

Z may be taken as the true nuclear charge, although it is well known[18] that the interaction between the 1s electrons may be taken into account approximately by putting $Z = Z_{\text{nuc}} - \frac{5}{16}$. This should give a better density for r near the Bohr radius (0.1a_0 for neon), but since the $\frac{5}{16}$ becomes increasingly unimportant as Z increases, we simply put $Z = Z_{\text{nuc}}$ in (20) from here on. The radial density given by (20), with and without the correction to Z, is compared with the approximate SCF density in Table III. It seems reasonable that $\overline{D}$ can be taken from Eq. (20) for use with the procedures of Secs. II and III. In fact, the TF procedure here makes $r_c = 0.4552a_0$, $\phi(x_c) = 0.8786$, $\phi'(x_c) = -0.9795$, close to the results with the exact $\overline{D}$ (Table I).

For the TFD procedure, which we shall employ for calculations on heavier atoms, the results are given in Table IV. We here report two calculations, for one of which r_c is lower, for the other

TABLE III. Approximate radial densities [Eq. (20)] compared to SCF density for neon.

$r(a_0)$	$D_{\text{SCF}}\,(a_0^{-1})$	$D_{Z=10}\,(a_0^{-1})$	$D_{Z=9.6875}\,(a_0^{-1})$
0.01	0.638	0.655	0.599
0.02	2.090	2.145	1.975
0.03	3.856	3.951	3.660
0.04	5.624	5.751	5.361
0.05	7.214	7.358	6.901
0.06	8.533	8.674	8.188
0.07	9.459	9.667	9.181
0.08	10.261	10.337	9.880
0.09	10.697	10.711	10.302
0.10	10.889	10.827	10.478

TABLE IV. Final results.

			σ ($10^{-5}\,a_0^{-1}$)[a]				χ (10^{-6} cm^3/mole)[b]			
Z	$r_c(a_0)$	$\langle 1\rangle$	Calc	SCF[c]	Derived[d]	TF	Calc	SCF	Expt[e]	TF
10	0.091 462	9.962	59.9	55.2	55.2	68.6	5.35	5.9[f]	6.74	67.0
10	0.091 460	10.030	63.4				6.09	7.4[c]		
20	0.042 769	19.707	154.2	142.3	142.3	172.9	12.87	24.8[c]		
20	0.042 768	20.631	155.2				13.46			
30	0.027 717 9	29.228	265.0	252.2	251.0	296.8	13.8	25.3[f]		
30	0.027 717 8	30.219	265.6				16.1	27.7[c]		
36	0.022 852 72	35.837	338.3	324.6	324.0	378.6	15.7	27.9[f]	28.8	102.0
36	0.022 852 70	36.050	338.4				17.6	31.3[c]		
54	0.014 932 865	53.905	582.1	563.9	564.0	650.0	25.0	38.9[f]	43.9	117.0
54	0.014 932 853	54.963	582.8				27.0	44.9[c]		
80	0.009 926 037	79.214	985.0		972.0	1098.0	31.9	50.8		
80	0.009 926 034	80.280	985.9				36.6			

[a] Diamagnetic shielding.
[b] Diamagnetic susceptibility.
[c] Reference 9.
[d] Derived from atomic energies according to Eqs. (21)–(23).
[e] J. T. Dehn and L. N. Mulay, J. Chem. Phys. 48, 4910 (1968).
[f] Reference e, calculated from Clementi's functions.

higher, than the correct value. This is seen from the expectation values $\langle 1\rangle$, the correct value for neon being 10. The various expectation values obtained from the two calculations then bracket that from the calculation for which $\langle 1\rangle = 10$. In this table, we report the nuclear magnetic shielding and diamagnetic susceptibilities (obtained from $\langle r^{-1}\rangle$ and $\langle r^2\rangle$, respectively) and compare with experiment and with SCF calculations. The results for neon differ little from those in the first line of Table II, where an accurate $\bar{D}$ was used.

V. RESULTS AND CONCLUSIONS

Table IV includes also the results calculated by our method for the atoms with $Z = 20$, 30, 36, 54, and 80. We here summarize this method. (a) For the atom of nuclear charge Z we calculate a small-r density from (20). (b) Assuming a value of r_c, we obtain $\psi(x_c)$ and $\psi'(x_c)$ from $\bar{D}$ using (14) and (18). (c) The TFD equation (13) is integrated out to x_0 determined by (16) and the normalization is checked according to (17). It ψ' becomes positive before (16) is fulfilled, we need a larger x_c. (d) The correct r_c is that for which the normalization is satisfied. The density and its slope are continuous at r_c.

In this table, we have given $\langle r^{-1}\rangle$ and $\langle r^{-2}\rangle$ as well as $\langle 1\rangle$ for two values of r_c, such that $\langle l\rangle$ brackets the correct number of electrons. The values of $\langle r^{-1}\rangle$ and $\langle r^{-2}\rangle$ then bracket the values predicted by the method. For $\langle r^{-1}\rangle$ we have converted to diamagnetic shielding and for $\langle r^2\rangle$ to diamagnetic susceptibility. In fact, $\langle r^{-1}\rangle$ is not directly measurable from nuclear magnetic resonance spectra, but can be calculated from atomic energies.

By the Hellmann-Feynman theorem, we find

$$\left(\frac{\partial E}{\partial Z}\right)_N = -\langle r^{-1}\rangle\,, \tag{21}$$

where N is the number of electrons. The left-hand side of (21) may be approximated as

$$\left(\frac{\partial E}{\partial Z}\right)_N \sim \frac{E(Z+\delta Z, N) - E(Z, N)}{\delta Z}\,, \tag{22}$$

where δZ is small. We have to be satisfied in reality with $\delta Z = \pm 1$. Taking the average [corresponding to fitting $E(Z+1, N)$, $E(Z, N)$, and $E(Z-1, N)$ to a parabola] gives

$$\langle r^{-1}\rangle_Z \sim \tfrac{1}{2}[E(Z-1, N) - E(Z+1, N)]. \tag{23}$$

Unfortunately, tables of atomic energies derived from experimental data are not available for large Z. Since correlation energies do not change with Z to a first approximation, we use SCF energies[16] for the atoms and ions with $N = 10$ and 20. For higher N we use calculated nonrelativistic energies[19] for the neutral atoms in conjunction with measured ionization potentials and electron affinities.[20]

The expectation values of r^{-1} as computed by our method are in much closer agreement with the correct values than those from the TF theory. Those of the TFD theory would be worse than those of the TF theory because of the contraction of the charge density permitted by exchange. The expectation values of r^{-2} could hardly be worse than those from TF where they diverge. In fact, they agree quite well with quantum-mechanical calculations, partly because of the large contribution of the density for $r < r_c$. We have thus succeeded in correcting the small-r behavior of the quantum-statistical densities by the simple expedient of joining a solution to the TFD equation to an approximate quantum-mechanical density at r_c. We emphasize that r_c is not arbitrary, but determined by the requirements that the density be continuous and of continuous slope at r_c, and that the normalization be correct. It appears that the large-r behavior (as evidenced in $\langle r^2 \rangle$) is also improved somewhat. In fact, TFD gives much better results here than TF. In any case, $\langle r^2 \rangle$ in our method as in other quantum-statistical methods increases too slowly with Z. It would be interesting to compare in greater detail our density with the correct and statistical densities for several atoms.

Finally, we derive an expression for the energies of neutral atoms from our results. The TF formula $E(Z) = -0.7689 Z^{7/3}$ a.u. has already been cited. According to various arguments,[11] a formula in descending powers of $Z^{1/3}$ starting from a $Z^{7/3}$ term seems indicated. March and Plaskett[11] have given

$$E(Z) = -0.7687\, Z^{7/3} + \tfrac{1}{2} Z^2 - 0.266\, Z^{5/3} \;, \qquad (24)$$

which seems to work well. To get such an expression, we put

$$\langle r^{-1} \rangle = aZ^{4/3} + bZ + cZ^{2/3}$$

and obtain a, b, and c by least-squares fitting our calculated $\langle r^{-1} \rangle$ for the six cases of Table IV. We find that $a = 1.683$, $b = -0.473$, and $c = 0.709$. Then Eq. (3) gives, in a.u.,

$$E(Z) = -0.72 Z^{7/3} + 0.24 Z^2 - 0.43 Z^{5/3} \,. \qquad (25)$$

Energies from (24) and (25) are compared in Table V.

TABLE V. Energies [negative values in 10^2 (a.u.)].

Z	Eq. (24)	Eq. (25)
10	1.281	1.51
20	6.74	7.5
30	17.80	19.2
40	35.39	37.6
50	60.3	63.4
60	92.7	97.0
70	134.0	139.0
80	184.0	190.0

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