

Solution of the Thomas-Fermi Model with Quantum Corrections

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A new and more accurate numerical solution has been obtained to the differential equation which determines the first-order quantum-mechanical corrections to the Thomas-Fermi model of the atom. When used to calculate the diamagnetic susceptibility and atomic polarizability of the inert gases, it leads to a substantial improvement over the Thomas-Fermi model alone, and hence lends support to the validity of the quantum-mechanical corrections.

I. INTRODUCTION

The basic assumption of the Thomas-Fermi statistical model¹ is that the electrons surrounding the nucleus of an atom can be treated as a degenerate gas of noninteracting fermions at 0°K which occupy all the cells in phase space below a certain energy level and leave unoccupied all remaining cells. This is a semiclassical model of limited validity¹ because it neglects, among other things, an exchange correction due to repulsion among electrons of like spin because of the exclusion principle, an inhomogeneity correction due to the rapidly varying potential near the nucleus, and a correlation correction due to Coulomb repulsion among electrons of opposite spin. In an attempt to account for these effects, quantum-mechanical modifications have been introduced into the model, which involve expansions in powers of a small parameter that depends on Planck's constant and the atomic number. These effects were first properly calculated by Kompaneets and Pavlovskii² and Kirzhnits,³ using the Hartree-Fock self-consistent-field method and a modified electron-density matrix. They were then recalculated by Baraff and Borowitz,^{4,5} using a Green's-function method.

The model was used by Schey and Schwartz⁶ to numerically calculate values for various properties of atoms, such as energy eigenvalues and diamagnetic susceptibilities. These results showed little or no improvement over the values calculated using the Thomas-Fermi model alone, and, hence, the authors asserted that the quantum corrections may not be completely valid. However, an error has now been found in the solution of Schey and Schwartz, and so two of the most inaccurately predicted atomic properties, namely, the diamagnetic susceptibility and atomic polarizability, have been recalculated in this paper by using the correct solution, as obtained by a new numerical method, which shall be described. Substantial improvement over the Thomas-Fermi model and good agreement with the experimental values have been

obtained, lending support to the validity of the quantum-mechanical model.

II. CALCULATION OF THE POTENTIAL

According to the above theory, the Coulomb potential about a spherically symmetric neutral atom of atomic number Z , namely, $V(r) = -Ze^2/r$, is replaced by the modified potential

$$V(r) = -(Ze^2/bx)[\psi(x) + ay(x)], \quad (1)$$

where $r = bx$, $a = \frac{1}{8}(6\pi Z)^{-2/3}$, $b = (6\pi)^{2/3}a_B/8Z^{1/3}$, $a_B = \hbar^2/me^2$ is the Bohr radius for hydrogen, $\psi(x)$ is the solution of the Thomas-Fermi equation

$$\frac{d^2\psi}{dx^2} = x^{-1/2}\psi^{3/2}, \quad (2)$$

subject to the boundary conditions $\psi(0) = 1$ and $\psi(\infty) = 0$, and $y(x)$ is the solution to the quantum-mechanical equation of Kompaneets and Pavlovskii

$$\frac{d^2y}{dx^2} - \frac{3}{2}\left(\frac{\psi}{x}\right)^{1/2}y = 40\psi - \left(\frac{x^5}{\psi^3}\right)^{1/2}\left(\frac{d}{dx}\frac{\psi}{x}\right)^2, \quad (3)$$

subject to the boundary conditions $y(0) = 0$ and $y(\infty) = 0$.

We now solve (3) by using a procedure developed earlier to solve the Thomas-Fermi equation (2).⁷ We assume the solution near the origin has the form of a semiconvergent power series

$$y(x) = \sum_{n=0}^{\infty} b_n x^{n/2}. \quad (4)$$

In addition, we know the Thomas-Fermi equation has a power series solution near the origin given by^{7,8}

$$\psi(x) = \sum_{n=0}^{\infty} a_n x^{n/2}, \quad (5)$$

where

$$8i(i-2)a_i$$

$$= 16 \sum_{j=0}^{i-3} a_{i-j-3} \sum_{k=0}^j a_{j-k} a_k$$

$$-\sum_{j=0}^{i-5} (j+2)(j+4)(i-j-3)(i-j-1)a_{j+4}a_{i-j-1} \tag{6}$$

for $i \geq 6$, with $a_0 = 1, a_1 = 0, a_3 = \frac{4}{3}, a_4 = 0, a_5 = \frac{2}{5}a_2,$
 $a_6 = \frac{1}{3},$ and $a_2 = -1.5880710.$ ¹

Using (2) we can rewrite (3) as

$$\frac{d^2\psi}{dx^2} \left(\frac{d^2y}{dx^2} - 40\psi \right) = \frac{3}{2} \frac{\psi^2}{x} y - \left(x \frac{d}{dx} \frac{\psi}{x} \right)^2, \tag{7}$$

and substituting (4) and (5) into (7) and equating terms of equal powers in x , we obtain a recursion relationship for successive coefficients b_i in terms of a_2 and b_2 :

$$4i(i-2)b_i = 24b_{i-3} + 16(10i-9)(i-3)a_{i-1} + 24 \sum_{j=2}^{i-4} b_{i-j-3} \left(\sum_{k=0}^j a_{j-k} a_k \right)$$

$$-4 \sum_{j=3}^{i-3} (i-41j-3)(j-2)a_{i-j-1}a_j$$

$$-\sum_{j=5}^{i+2} (i-j+3)(i-j+1)j(j-2)b_{i-j+3}a_j \tag{8}$$

for $i \geq 6$, where $b_0 = 0, b_1 = 4, b_3 = 2a_2, b_4 = \frac{74}{3},$
 $b_5 = \frac{2}{5}b_2 - \frac{1}{2}a_2^2,$ and $b_6 = \frac{34}{5}a_2.$

We obtain the complete solution to (3) by using standard numerical integration techniques. We initiate the solution by using a power series formed from the first several terms in (4), where we assume an arbitrary value for b_2 . We continue the solution by simultaneously integrating the differential equations (2) and (3). The integration of (3) can be simplified by using an approximate analytic form of the well-known solution to (2),¹ such as⁹

$$\psi = \left(\frac{1 + 1.81061x^{1/2} + 0.60112x}{1 + 1.81061x^{1/2} + 1.39515x + 0.77112x^{3/2} + 0.21465x^2 + 0.04793x^{5/2}} \right)^2, \tag{9}$$

which has a maximum error of $\delta\psi < 1.2 \times 10^{-5}$. Since the integration procedure is most sensitive to error near the origin, we introduce a change of variables, $x = v^2$, and rewrite (3) as

$$\frac{d^2y}{dv^2} - \frac{1}{v} \frac{dy}{dv} - 6v\psi^{1/2}y = 160v^2\psi - \frac{1}{v\psi^{3/2}} \left(v \frac{d\psi}{dv} - 2\psi \right)^2 \tag{10}$$

From (4) we see that this means y and its derivatives

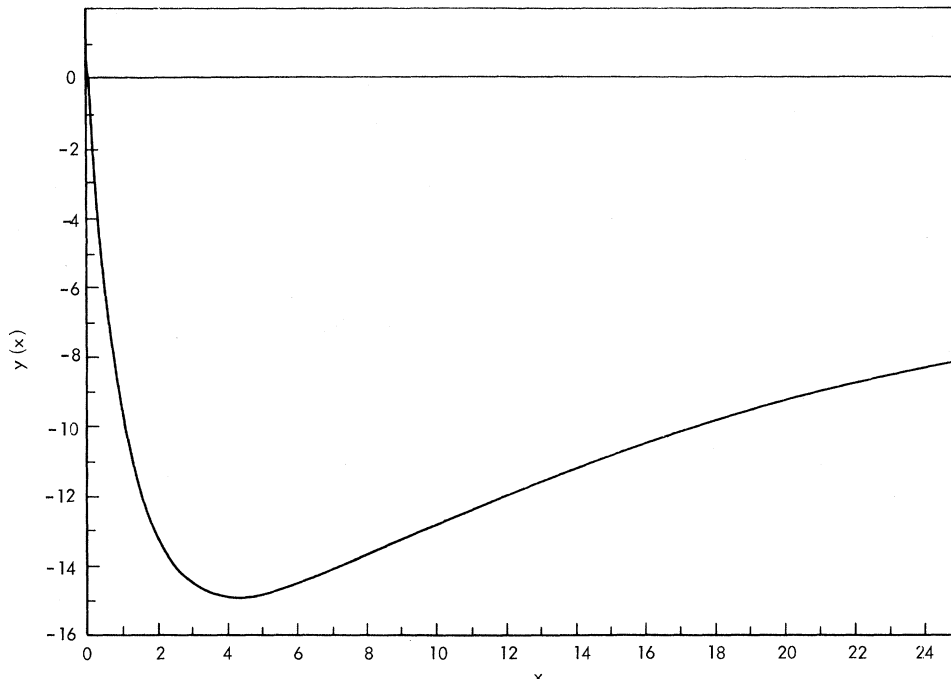


FIG. 1. Solution to the quantum-mechanical equation (3), $y(x)$ vs x .

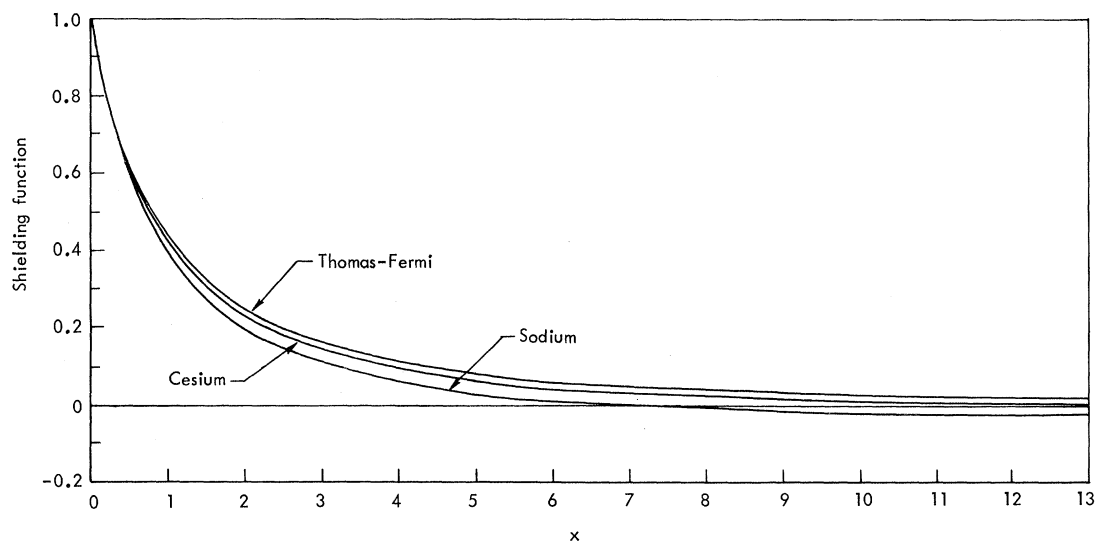


FIG. 2. Thomas-Fermi shielding function $\psi(x)$ and total shielding functions $[\psi(x) + ay(x)]$ for neutral sodium and cesium as functions of x .

with respect to v are now continuous near the origin. In order to satisfy the boundary condition $y(\infty) = 0$, it is necessary to vary b_2 until the solution converges to the axis. If b_2 is too negative, $y(\infty) = -\infty$, and if b_2 is too positive, $y(\infty) = +\infty$. We obtain a solution which satisfies $y(\infty) = 0$ by using a value of $b_2 = -22.56590$, with an error of $\delta b_2 < 5 \times 10^{-5}$. The range of validity of the power series (4) is obtained by determining the ratio of successive coefficients $R_n = b_n/b_{n-1}$. This has a limiting value of $R_n \sim -1.5$ for large n , which implies a radius of convergence of $x_c = |b_{n-1}/b_n|^2 = R_n^{-2} \sim 0.44$, which is the same as for the series (5).⁸

In the limit of very large x , the Thomas-Fermi equation has the exact solution¹

$$\psi = 144/x^3, \quad (11)$$

which is valid for $x \gg 12^{2/3}$. Assuming an exact limiting solution of (3) of the form $y = sx^t$, where s and t are constants, and substituting it and (11) into (3), we obtain

$$y = -348/x. \quad (12)$$

Note that for large values of x , y becomes the dominant term in the total potential shielding function $(\psi + ay)$, which hence becomes negative. Also, the x dependence of the solution (12) differs from that of the asymptotic solution obtained by Viswanathan and Narashari Achar¹⁰ and Venkatarangan,¹¹ which decreases as $x^{-1/2}$, but it agrees with the x dependence of the rederived solution of Tietz and Krzeminski.¹²

We have plotted $y(x)$ vs x in Fig. 1. Note that our solution is in basic agreement with the one obtained previously by Kompaneets and Pavlovskii using a different integration procedure, if their plot of $y(x)$ vs x is understood to be $y(x)/8(6\pi)^{2/3}$ vs x , as pointed out by Kalitkin.¹³ However, our solution is valid for much larger values of x . In Fig. 2 we have plotted the Thomas-Fermi shielding function $\psi(x)$ versus x , along with the total shielding function $[\psi(x) + ay(x)]$ versus x for the neutral atoms of sodium and cesium. Note that the total shielding function becomes negative at a radius x_0 , which depends upon Z . It remains negative for all x larger than x_0 , as noted from

TABLE I. Quantity $-10^6 \chi$, where χ is the diamagnetic susceptibility in cm^3 .

Atom	Thomas-Fermi model ^a	Former quantum model ^a	Radii		Present quantum model	Experiment ^b
			x_0	x_1		
Ne	64.1	46.1	6.32	10.5	14.7	6.74
Ar	78.1	63.3	8.23	13.2	22.3	19.6
Kr	89.3	86.6	11.1	17.4	35.5	28.8
Xe	113.0	103.0	13.2	20.2	45.7	43.9

^aReference 6.

^bReference 14.

TABLE II. Quantity $10^{24} \alpha$, where α is the atomic polarizability in cm^3 .

Atom	Thomas-Fermi model ^a	Quantum model	Experiment ^b
Neon	43.5	2.26	0.392
Argon	35.8	2.91	1.65
Krypton	28.4	3.67	2.50
Xenon	24.8	4.06	4.10

^aReference 15.

^bReference 1.

the asymptotic solutions (11) and (12). We define the radius of a neutral atom as the radius x_1 , where the electric field $E(r) = -dV(r)/dr$ first vanishes, or from (1),

$$\frac{d}{dx} (\psi + ay)_{x=x_1} = \left(\frac{\psi + ay}{x} \right)_{x=x_1}. \quad (13)$$

The radius x_1 is dependent on Z and is always larger than x_0 for a given Z . Our solution is in disagreement with the similar calculations of Schey and Schwartz,⁶ as shown in their Fig. 1, since their shielding functions for sodium and cesium appear to remain positive for all x . Furthermore, their value of $a = (24\pi Z)^{-2/3}$ is much larger than our value of $a = \frac{1}{8}(6\pi Z)^{-2/3}$, which is obtained from the original solution of Kompaneets and Pavlovskii.

III. CALCULATION OF ATOMIC PROPERTIES

Using our potential (1), we have calculated the diamagnetic susceptibilities of the inert gases. The diamagnetic susceptibility χ is a constant which determines the energy shift produced in a spherically symmetric charge distribution by the application of a uniform constant magnetic field,¹ and it is given by

$$\chi = - (N_0 e^2 / 6mc^2) \langle r^2 \rangle, \quad (14)$$

where N_0 is Avogadro's number and

$$\langle r^2 \rangle = \int r^2 \rho dV = 4\pi \int_0^\infty r^4 \rho dr, \quad (15)$$

where ρ is the electron charge density, which is given by Poisson's equation

$$\rho(r) = - (1/4\pi e^2) \nabla^2 V(r). \quad (16)$$

Schey and Schwartz obtain

$$\begin{aligned} \chi &= - \frac{e^2 b^2 N_0 Z}{6mc^2} \int_0^\infty x^3 \frac{d^2}{dx^2} [\psi(x) + ay(x)] dx \\ &= - 3.72 \times 10^{-6} Z^{1/3} \int_0^\infty x [\psi(x) + ay(x)] dx \text{ cm}^3. \end{aligned} \quad (17)$$

For our solution this becomes

$$\begin{aligned} \chi &= - 0.62 \times 10^{-6} Z^{1/3} \int_0^{x_1} x^3 \frac{d^2}{dx^2} \\ &\quad \times [\psi(x) + ay(x)] dx \text{ cm}^3. \end{aligned} \quad (18)$$

In Table I we have summarized the susceptibilities for Ne¹⁰, Ar¹⁸, Kr³⁶, and Xe⁵⁴. The second and third columns show the evaluation of (17), according to the Thomas-Fermi model ($a \equiv 0$) and according to the quantum-mechanical model [$a = (24\pi Z)^{-2/3}$], respectively, as given by Schey and Schwartz. The fourth and fifth columns show the radii x_0 and x_1 at which the potential and field, respectively, vanish. The sixth column shows our evaluation of (18) using $a = \frac{1}{8}(6\pi Z)^{-2/3}$. The final column shows

the current experimental values.¹⁴ Note that, except for neon, our values for the susceptibility are within 20% of the experimental values, and are a very substantial improvement over the values given by the Thomas-Fermi model. The quantum-mechanical values given by Schey and Schwartz are invalid because of their incorrect evaluation of the total shielding function.

We have also calculated the atomic polarizabilities of the inert gases using our potential (1). The atomic polarizability α is a constant which determines the energy shift produced in a spherically symmetric charge distribution by the application of a uniform constant electric field,¹ and it is given by

$$\alpha = (4/9Za_B) \langle r^2 \rangle^2, \quad (19)$$

which with (15) becomes¹⁵

$$\begin{aligned} \alpha &= \frac{4Zb^4}{9a_B} \left\{ \int_0^\infty x^3 \frac{d^2}{dx^2} [\psi(x) + ay(x)] dx \right\}^2 \\ &= 1.4565 \times 10^{-24} Z^{-1/3} \left\{ \int_0^\infty x [\psi(x) + ay(x)] dx \right\}^2 \text{ cm}^3. \end{aligned} \quad (20)$$

For our solution this becomes

$$\begin{aligned} \alpha &= 0.04046 \times 10^{-24} Z^{-1/3} \\ &\quad \times \left\{ \int_0^{x_1} x^3 \frac{d^2}{dx^2} [\psi(x) + ay(x)] dx \right\}^2 \text{ cm}^3. \end{aligned} \quad (21)$$

In Table II we have summarized the polarizabilities. The second column shows the evaluation of (20), according to the Thomas-Fermi model ($a \equiv 0$), as given by Kumar and Jain.¹⁵ The third column shows our evaluation of (21) and the last column shows the experimental values.¹ Note that our values for the polarizability are a substantial improvement over the values given by the Thomas-Fermi model, and the agreement with the experimental values becomes very good as Z increases.

Based on our results above and on the other successful predictions of the model, such as the total energy of an atom³ and various thermodynamic properties,¹³ this quantum-mechanical model is shown to be a valid first-order correction to the Thomas-Fermi model. The conjecture made by Schey and Schwartz and others⁶ that the model lacks certain important terms appears to be unjustified.

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- ¹P. Gombás, in *Encyclopedia of Physics*, edited by S. Flügge (Springer, Berlin, 1958), Vol. 36, p. 109.
- ²A. S. Kompaneets and E. S. Pavlovskii, Zh. Eksperim. i Teor. Fiz. 31, 427 (1956) [Sov. Phys. JETP 4, 328 (1957)].
- ³D. A. Kirzhnits, Zh. Eksperim. i Teor. Fiz. 32, 115 (1957) [Sov. Phys. JETP 5, 64 (1957)].
- ⁴G. A. Baraff and S. Borowitz, Phys. Rev. 121, 1704 (1961).
- ⁵G. A. Baraff, Phys. Rev. 123, 2087 (1961).
- ⁶H. M. Schey and J. L. Schwartz, Phys. Rev. 137, A709 (1965).
- ⁷R. P. Feynman, N. Metropolis, and E. Teller, Phys. Rev. 75, 1561 (1949).
- ⁸J. E. Enstrom, J. Chem. Phys. 46, 1213 (1967).
- ⁹J. C. Mason, Proc. Phys. Soc. (London) 84, 357 (1964).
- ¹⁰K. S. Viswanathan and B. N. Narahari Achar, Can. J. Phys. 42, 2332 (1964).
- ¹¹P. Venkatarangan, Can. J. Phys. 43, 1157 (1965).
- ¹²T. Tietz and S. Krzeminski, Acta Phys. Acad. Sci. Hung. 27, 161 (1969).
- ¹³N. N. Kalitkin, Zh. Eksperim. i Teor. Fiz. 38, 1534 (1960) [Sov. Phys. JETP 11, 1106 (1960)].
- ¹⁴*Handbook of Chemistry and Physics*, 51st ed. (Chemical Rubber, Cleveland, Ohio, 1970), p. E-127.
- ¹⁵S. Kumar and A. Jain, J. Phys. Soc. Japan 28, 1046 (1970).

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Obtaining the Optical Field Isotope Shifts of a Light Element*

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The problem of obtaining field isotope shifts for light elements is discussed, and it is shown to be possible, in principle, to extract this information solely from an optical-isotope-shift experiment. We attempted such an experiment with the even-even calcium isotopes: Ca 40, 42, 44, and 48. We found that an accuracy of $\sim 10^{-5}$ cm⁻¹ in the measurements would be required to effect the separation. Lacking that accuracy, we considered the conditions under which optical-isotope-shift measurements may be combined with those of other isotope-shift experiments. The even-even calcium isotopes fulfill these conditions, allowing the desired separation of optical mass- and field-effect isotope shifts to be accomplished by drawing on the results of muonic x-ray and electron-scattering experiments. The optical field-effect shifts thereby found are shown to corroborate the picture of the calcium nuclei derived from those experiments. A correlation between the relative isotope shift and the binding energy per nucleon, proposed by Gerstenkorn, is shown to apply to the calcium isotope shifts.

Isotope shifts in atomic spectrum lines of heavy elements are attributed mainly to isotopic differences in the nuclear charge distribution.¹ The shifts in a single line for a series of isotope pairs show the changes in the mean square radius of the nuclear ground-state charge distribution. Since there appear to be sharp changes in intrinsic nuclear shapes at magic neutron numbers,² it is particularly valuable to make such measurements on a series of nuclei containing a magic-number nucleus.

The same consideration applies to light elements, but both the experimental and interpretational problems are more difficult. For these elements the shifts due to mass differences in the nuclei cannot be neglected, and it is exceedingly difficult to separate the mass- and field-effect shifts. In fact, these can be opposite in sign, resulting in a net shift smaller than the Doppler widths of the spectral lines. However, it seems worthwhile to attempt this separation for calcium since the series of even-even isotopes both starts and ends with a doubly magic nucleus. Further, since the behavior of the

mean square radius of the nuclear charge distribution of the calcium isotopes is known (from muonic x-ray and electron-scattering experiments), we can determine when we have achieved a valid separation of the optical mass- and field-effect shifts.

Interest in calcium was spurred in 1963 when a measurement³ of the $2p$ - $1s$ muonic x-ray transition suggested that the addition of four neutrons to the Ca 40 nucleus results in a smaller proton volume—contrary to the widely held assumption (at that time) that the nuclear charge radius is proportional to $A^{1/3}$. Although later experiments⁴⁻⁶ have shown that Ca 44 does indeed have the larger charge radius, it is not so large as predicted from the $A^{1/3}$ law.

I. DEPENDENCE OF ISOTOPE SHIFTS ON ATOMIC AND NUCLEAR PROPERTIES

In isotope-shift calculations for hydrogenic atoms, the fact that the nucleus has finite mass is easily treated by use of the reduced electron mass μ . The result is that $E(\mu)$, the true energy eigenvalue, is equal to $(\mu/m_e)E(m_e)$, the energy eigen-