of the c axis at low temperatures had been previously observed by Banister et al.[10] No orthorhombic distortion is observed in the ferromagnetic state since the sinusoidal variation in the a-b plane is retained. Application in the ferromagnetic state of fields sufficient to collapse the helical component should lead to orthorhombic distortion comparable to that observed for terbium.

CONCLUSIONS

Expansion of the hexagonal axis with decreasing temperature observed for terbium and erbium, and for the other heavy rare earths, demonstrates a positive sign for the rate of change of the effective exchange integral with distance. The magnitude of $\partial J/\partial c$ for terbium is of the same order as that found for dysprosium and holmium. The temperature dependences

of the c axes may be semiquantitatively explained by an interaction of the form $\mathbf{M} \cdot \mathbf{M}$, in agreement with ideas of coupling between magnetic and elastic forces proposed by Kittel and by Rocher[11]. The magnitude of $\partial J/\partial a$ for terbium is found to be comparable to $\partial J/\partial c$.

The orthorhombic distortion or magnetostriction of terbium is found to be easily observable by x rays. The changes in linear dimensions at 77° are -3.2×10^{-3} for $\Delta a/a$ and 4.6×10^{-3} for $\Delta b/b$.

[10] J. R. Banister, S. Legvold, and F. H. Spedding, Phys. Rev. 94, 1140 (1954).

[11] Y. A. Rocher, J. Phys. Chem. Solids, 23, 759 (1962); Advan. Phys., 11, 233 (1962).

Extension of the Statistical Model of the Atom

Victor A. Erma*

Giannini Scientific Corporation, Santa Ana, California

The statistical model of the atom is extended within the semiclassical framework to include the correlation energy of the electron gas, obtained by an interpolation formula which reproduces the known high- and low-density limits exactly. The basic equations of the model are derived, and general theoretical results valid for all free atoms and ions are obtained. These include the determination of the electron density at the edge of the atom, a virial theorem for the atom, and a treatment of the Fermi-Amaldi correction. The equations of the model are solved in terms of a Thomas-Fermi-Dirac-like approximation, in terms of a semiconvergent expansion for the potential near the nucleus, and numerically on a computer for the atoms argon, chromium, krypton, xenon, and uranium. The solutions of the model are illustrated in detail for the case of argon, including a calculation of the energy terms of the argon atom. Finally, the application of the extended model is illustrated by a calculation of atomic polarizabilities and diamagnetic susceptibilities and the results are compared with experiment.

I. INTRODUCTION

THE so-called semiclassical statistical model of the atom, originated independently by Thomas[1] and Fermi,[2] has proved to be a simplified, albeit fruitful and versatile approach to the many electron system of the atom, and has been made the basis for the calculation of a large variety of atomic properties. Comprehensive reviews of the theory and applications of the statistical model have been given by Corson,[3] Gombas,[4] and March.[5]

The model is based on a number of simplifying assumptions which we shall sketch briefly. To begin with, it is assumed that the electrons surround the nucleus with a spherically symmetric density distribution. The basis of the model lies in assuming further that the volume of the atom can be divided into subvolumes $4\pi r^2 dr$ over which the potential is approximately constant, but which still contain a sufficiently large number of electrons. Finally, the electrons occupying each subvolume at a distance r from the nucleus are considered to constitute a totally degenerate gas at zero temperature, whose energy density ϵ depends solely on the

[1] L. H. Thomas, Proc. Cambridge Phil. Soc. 23, 542 (1927).
[2] E. Fermi, Z. Physik 48, 73 (1928).
[3] M. Corson, Perturbation Methods in the Quantum Mechanics of n-Electron Systems (Hafner Publishing Company, Inc., New York, 1950).
[4] P. Gombas, Die statistische Theorie des Atoms und ihre Anwend-

ungen (Springer-Verlag, Vienna, 1949). A more up-to-date, though more abbreviated version of the same work is contained in P. Gombas, in Handbuch der Physik, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 36, p. 109.
[5] N. H. March, Suppl. Phil. Mag. 6, 1 (1957).

electron density $\rho(r)$ and the nuclear potential at r. The energy of the atom as a whole is then obtained by integrating both the potential energy and the electron gas energy density over the volume of the atom. The above model is semiclassical in the sense that quantum mechanics enters only into the expression for the energy density of the electron gas.

In the spirit of the above model it is clearly desirable to write the best possible expression for ϵ. In the original formulation of the model by Thomas and Fermi (henceforth abbreviated as TF) ϵ was taken simply to be the kinetic energy density of the degenerate electron gas, thereby neglecting all electron interactions with the exception of the classical electrostatic Coulomb interaction. It was found that the electron density calculated on the basis of this model decreased too slowly with distance far from the nucleus, and thus led to appreciable errors in the calculation of effects which depend critically on the electron density in the outer regions of the atom. Examples of such are atomic polarizabilities and diamagnetic susceptibilities, the cross section for small-angle electron scattering from atoms, and equations of state.

The first step toward extending the model was taken by Dirac[6] who, in addition to the kinetic energy density, included in ϵ the exchange energy density of the electron gas. The corresponding model is known as the Thomas-Fermi-Dirac model (henceforth abbreviated as TFD).

Within the framework of the semiclassical statistical approach outlined above, the next obvious extension of the model is to include in ϵ the correlation energy density of the electron gas in addition to the kinetic and exchange energy densities. The chief difficulty is that the electron density in an atom ranges from very small values at the edge of the atom to very large values near the nucleus. Expressions for the correlation energy density of an electron gas have been obtained at the low density limit by Wigner,[7,8] and at the high-density limit by Gell-Mann and Brueckner[9]; however, it has so far been impossible to derive theoretically an expression valid at intermediate densities, which correspond to intermediate coupling[10] in the perturbation approach to electron interactions.

A first attempt to take into account the correlation energy in the statistical model of the atom was made in 1943 by Gombas[11] based on an approximate expression for the correlation energy due to Wigner[8] which, however, is valid only for reasonably small densities and thus not realistic for the atom as a whole. More recently, the problem has been given renewed attention by several

authors.[12] The most significant step was taken by Lewis[13] who treated the same problem, starting with an analytical interpolation formula for the correlation energy designed to reproduce the known exact expressions at the low and high density limits. In view of the lack of a satisfactory theoretical expression at intermediate densities, this appears to be a reasonable way to approach the problem from a practical viewpoint. However, the work of Lewis is merely preliminary in that he only derives the Thomas-Fermi equation corresponding to his expression for the correlation energy but does not solve the resulting equations.[14] Nor does he attempt to develop the theory much farther beyond obtaining an expansion for the potential near the nucleus and a virial theorem for the atom, both of which are in error inasmuch as they do not reduce to the correct TFD limit in the case of vanishing correlation. Finally, the expression for the correlation energy used by Lewis is unsatisfactory in several respects.[15]

It therefore appears worthwhile to reattempt the problem of including the correlation energy density in the statistical model of the atom, and to investigate fully the implications of this extension of the model, to which task the present work is devoted. In keeping with the preliminary work of Gombas and Lewis, we shall remain strictly within the semiclassical framework in the sense outlined above, and neglect the so-called 'quantum corrections' to the model, which are essentially inhomogeneity corrections. The latter were first discussed in 1935 by Weizsäcker[16] and more recently by Baraff and Borowitz.[17] In the outer regions of the atom, which are of paramount interest to us, the quantum corrections are of minor importance, particularly for neutral atoms whose potential gradient vanishes at the edge of the atom.

In Part II we obtain an analytical interpolation formula for the correlation energy density of a degenerate electron gas, which reproduces the known high- and low-density limits exactly. In Part III we derive

[6] P. A. M. Dirac, Proc. Cambridge Phil. Soc. 26, 376 (1930).

[7] E. Wigner, Phys. Rev. 46, 1002 (1934).

[8] E. Wigner, Trans. Faraday Soc. (London) 34, 678 (1938).

[9] M. Gell-Mann and K. Brueckner, Phys. Rev. 106, 364 (1957).

[10] Cf. M. Gell-Mann, Topics in Theoretical Physics, Lecture Notes, California Institute of Technology, 1959 (unpublished).

[11] P. Gombas, Z. Physik 121, 523 (1943).

[12] Cf. P. Noziéres and D. Pines, Phys. Rev. 111, 442 (1958); and Y. Tomishima, Progr. Theoret. Phys. (Kyoto) 22, 1 (1959).

[13] H. Lewis, Phys. Rev. 111, 1554 (1958).

[14] Following the completion of the present paper, the author's attention was drawn to the fact that the equations obtained by Lewis were solved approximately by Gombas [Ann. Physik 7, 1 (1961)], who also offered serious criticisms of the work of Tomishima cited in the previous footnote. However, the solutions obtained by Gombas are based on a very crude approximation to the equations of Lewis; furthermore, none of the errors inherent in the original equations of Lewis were corrected (cf. Ref. 15).

[15] In the first place, in the low-density limit there is some confusion between the average energy per electron and the energy of an electron at the top of the Fermi sea. Secondly, the interpolation formula gives only the low-density limit exactly, and can easily be improved to reproduce both the complete Gell-Mann and Brueckner high-density limit and the low-density limit correctly. Finally, there are some missing terms in the Lewis expression connecting the potential with the density. This arises partly from the fact that the interpolation is carried out for $d\epsilon/d\rho$ (i.e., the energy at the top of the Fermi sea) directly, with the result that the known limits of ϵ are not reproduced.

[16] C. F. v. Weizsäcker, Z. Physik 96, 431 (1935).

[17] G. A. Baraff and S. Borowitz, Phys. Rev. 121, 1704 (1961).

the corresponding Thomas-Fermi equation and re-express it in dimensionless variables. Part IV is devoted to those features of the model which can be obtained without resorting to a numerical solution of the equations. In Part V we consider various methods for the solution of the basic equations of the model. The equations have been solved on a computer for the cases of argon, chromium, krypton, xenon, and uranium. In the way of illustration, the solution for argon is discussed in some detail in Sec. VI. As an example of the application of the model, we present calculations of the atomic polarizabilities and diamagnetic susceptibilities of neutral atoms in Sec. VII.

II. INTERPOLATION FORMULA FOR THE CORRELATION ENERGY

The 'correlation energy' of a degenerate electron gas is customarily defined as the difference between the exact energy and the kinetic plus exchange energies. On the other hand, since the advent of field-theoretic methods for treating many-body problems, the term is frequently applied simply to the e^4-term in the perturbation expansion of the energy. Here we shall use both definitions interchangeably, the difference between them consisting of terms of order e^6 and higher.

The high-density limit has been derived by Gell-Mann and Brueckner,[9] whose result for the average correlation energy $\bar{u}_c$ per electron of an electron gas in a uniform positive background we rewrite in the form,

$$\bar{u}_c(\text{Ry}) = -\beta \ln\xi - C', \qquad (1)$$

where we have defined the dimensionless variable $\xi = a_0\rho^{1/3}$ ($a_0 \sim$ first Bohr radius, $\rho \sim$ density of the electron gas) and where $\bar{u}_c$ is expressed in units of Rydbergs ($\text{Ry} = e^2/2a_0$). The constants β and C' have the values $\beta = 0.06218$, $C' = 0.1257$.

The corresponding low density limit has been calculated by Wigner[7,8] starting from the assumption that as $\rho \to 0$ the electrons crystallize into a cubic body-centered lattice, which has a lower energy than any alternative lattice. The calculations of Wigner have recently been redone by Coldwell-Horsfall and Mara-dudin[18] who obtain for the total energy per electron the expression,

$$\bar{u}_{\text{tot}} = -0.89593e^2/r_s, \qquad (2)$$

where $r_s = (3/4\pi)^{1/3}\rho^{-1/3}$. If we subtract from the above the exchange energy per electron $u_e = -\frac{3}{4}(3/\pi)^{1/3}e^2\rho^{1/3}$ and re-express the result in units of Rydbergs and in terms of our dimensionless variable ξ, we obtain for the correlation energy per electron in the low-density limit the expression

$$\bar{u}_c(\text{Ry}) = -\gamma\xi, \qquad \gamma = 1.412. \qquad (3)$$

Our aim is now to find a suitable analytic interpolation formula for $\bar{u}_c$ which reproduces the above high-

and low-density limits. An obvious first attempt (essentially equivalent to Lewis[13]) would be to try $\bar{u}_c = a \ln(1+b\xi)$. However, it is clear that if the constants are chosen such as to satisfy the low density limit (3) exactly, it is impossible to reproduce the constant term in the high density limit (1).[19] This situation may be easily remedied, however, by adding a function which vanishes for $\xi \to 0$ and approaches a constant in the limit of high ξ. Accordingly, we shall choose an interpolation expression of the form.

$$\bar{u}_c = a \ln(1+\xi) + [C\xi/(\xi+d)], \qquad (4)$$

which has the limits

$$\begin{aligned}\bar{u}_c &\to a \ln\xi + C, \qquad & \xi \gg 1 \\ &\to [a+(C/d)]\xi, \qquad & \xi \ll 1. \end{aligned} \qquad (5)$$

It is now apparent that both the known limits (1) and (3) can be satisfied exactly by choosing

$$a = -\beta, \quad C = -C', \quad d = C'/(\gamma-\beta).$$

After calculating the necessary numbers, we then obtain the following explicit interpolation formula for the correlation energy density of an electron gas:

$$\epsilon_c(\rho) = -\alpha_c\left[\rho \ln(1+a_0\rho^{1/3}) + \frac{\sigma a_0\rho^{4/3}}{\tau+a_0\rho^{1/3}}\right], \qquad (6)$$

where $\alpha_c = 0.03109e^2/a_0$, $\sigma = 2.0216$, and $\tau = 0.09311$.

The above formula has been compared with an approximate extrapolated expression obtained by Wigner[8] for reasonably low densities, and was found to agree with Wigner's expression well within the accuracy claimed for the latter. Expression (6) for the correlation energy density forms the basis for our extension of the Thomas-Fermi-Dirac model.[20]

III. THE THOMAS-FERMI EQUATION INCLUDING CORRELATION

In order to obtain the Thomas-Fermi equation corresponding to our extended model, we begin as usual[4] by writing the total energy of the atom in the form,

$$E = \int \epsilon(\rho)dv - e\int \rho V_N dv + \frac{e^2}{2}\int\int \frac{\rho(r)\rho(r')dvdv'}{|\mathbf{r}-\mathbf{r'}|}, \qquad (7)$$

where $\epsilon(\rho)$ is the total energy density of the electron gas, $\rho(r)$ is the electron density within the atom, $V_N = (Ze)/r$ is the nuclear potential, and all integrations

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[18] R. A. Coldwell-Horsfall and A. A. Maradudin, J. Math. Phys. **1**, 395 (1960).

[19] While the constant term does not enter into the final Thomas-Fermi equation, the degree to which it is reproduced by any proposed interpolation formula is nevertheless a general measure of the accuracy of the latter.

[20] If desired, the interpolation procedure could be carried out to higher orders by making use of known higher order corrections to both the high-, and low-density limits. However, it is felt that the inherent inaccuracy of the interpolation procedure does not warrant the additional complications involved, particularly in later work.

extend over the volume of the atom. In view of (6), the total energy density $\epsilon(\rho)$ becomes

$$\epsilon(\rho) = \alpha_k \rho^{5/3} - \alpha_e \rho^{4/3} - \alpha_c \left[\rho \ln(1 + a_0 \rho^{1/3}) + \frac{\sigma a_0 \rho^{4/3}}{\tau + a_0 \rho^{1/3}} \right], \quad (8)$$

where

$$\alpha_k = \tfrac{3}{10}(3\pi^2)^{2/3} e^2 a_0 = 2.871 e^2 a_0 ,$$

$$\alpha_e = \tfrac{3}{4}(3/\pi)^{1/3} e^2 = 0.7386 e^2. \quad (9)$$

The first and second terms in expression (8) represent the kinetic and exchange energy densities of the degenerate electron gas, respectively.

The Thomas-Fermi relation connecting the density with the potential at each point within the atom is now obtained from the condition that the density be such as to minimize the total energy of the atom, subject to the normalization that the atom contain N electrons:

$$\int \rho dv = N. \quad (10)$$

Expressed formally, this condition becomes

$$\delta(E + NeV_0) = 0, \quad (11)$$

where V_0 is a suitable undetermined Lagrange multiplier. If we substitute expressions (8) and (7) into (11) and perform the indicated variation, we are led to the desired local relation between the total potential $V = V_e + V_N$ and the density ρ:

$$(V - V_0)e = \frac{5}{3}\alpha_k \rho^{2/3} - \frac{4}{3}\alpha_e \rho^{1/3}$$

$$- \alpha_c \left[\ln(1 + a_0 \rho^{1/3}) + \frac{1}{3}\frac{a_0 \rho^{1/3}}{1 + a_0 \rho^{1/3}} \right.$$

$$\left. + \frac{4}{3}\frac{\sigma a_0 \rho^{1/3}}{\tau + a_0 \rho^{1/3}} - \frac{1}{3}\frac{\sigma(a_0 \rho^{1/3})^2}{(\tau + a_0 \rho^{1/3})^2} \right]. \quad (12)$$

Together with Poisson's equation,

$$\nabla^2(V - V_0) = 4\pi \rho e; \quad (13)$$

and the physical boundary conditions,

$$\lim_{r \to 0} r(V - V_0) = Ze, \quad (14)$$

$$V(R) = \frac{(Z - N)e}{R}, \quad (15)$$

$$-\frac{dV}{dr}\bigg|_{r=R} = \frac{(Z - N)e}{R^2}, \quad (16)$$

where R represents the as yet undetermined radius of the atom, our model is then completely defined. If in Eq. (12) we set $\alpha_c = 0$ we reproduce the TFD model; if

we set both $\alpha_c = \alpha_e = 0$, we regain the original TF model.

Unlike with both the TF and TFD models, in our case it is manifestly impossible to solve Eq. (12) explicitly for ρ as a function of $(V - V_0)$ and substitute it into Poisson's equation in order to obtain a single differential equation involving only the one dependent variable $(V - V_0)$. This circumstance causes considerable analytical complications in the actual solution of the system of equations defining our model, but presents no fundamental difficulties.

For purposes of the actual solution of the equations of our model it is convenient to express them in terms of dimensionless variables. Accordingly, we define the customarily employed dimensionless variables[4] $\Psi(x)$ and x by means of

$$\Psi(x) = \frac{r}{Ze}[V(r) - V_0], \quad (17)$$

$$x = \frac{r}{\mu}, \quad \mu = \frac{a_0}{4}\left(\frac{9\pi^2}{2Z}\right)^{1/3}. \quad (18)$$

If we further define the variable $\lambda(x)$ by

$$\lambda(x) = kx^{1/2}\rho^{1/3}, \quad k = \mu\left(\frac{4\pi}{Z}\right)^{1/3}, \quad (19)$$

then Poisson's equation in terms of these variables takes the form,

$$\frac{d^2\Psi(x)}{dx^2} = \frac{\lambda^3}{x^{1/2}}, \quad (20)$$

i.e., it becomes a second-order differential equation in the two dependent variables $\Psi(x)$, $\lambda(x)$. The algebraic relation connecting $\Psi(x)$ and $\lambda(x)$ is obtained by expressing Eq. (12) in terms of the above dimensionless variables, which leads to

$$\Psi(x) = \lambda^2 - \beta x^{1/2}\lambda - \gamma x F\left(\frac{e\lambda}{x^{1/2}}\right), \quad (21)$$

where

$$F(\xi) = \ln(1 + \xi) + \frac{1}{3}\frac{\xi}{1 + \xi} + \frac{4}{3}\frac{\sigma\xi}{\tau + \xi} - \frac{1}{3}\frac{\sigma\xi^2}{(\tau + \xi)^2}; \quad (22)$$

and

$$\epsilon = \frac{2}{\pi}\left(\frac{4Z^2}{9}\right)^{1/3}, \quad \beta = \left(\frac{3}{4\pi^2 Z^2}\right)^{1/3}, \quad (23)$$

$$\gamma = \frac{\alpha_c \mu}{Ze^2} = \frac{(1 - \ln 2)}{4\pi^2 Z}\left(\frac{9\pi^2}{2Z}\right)^{1/3}. \quad$$

It remains to express the boundary conditions in dimensionless form. With the definitions (17) and (18), the boundary conditions (14) and (16) become

$$\Psi(0) = 1 \quad (24)$$

$$\Psi(X) - X\Psi'(X) = (Z - N)/Z, \quad (25)$$

where X corresponds to the edge of the atom, $X=R/\mu$. The boundary condition corresponding to (15) becomes

$$\Psi(X)=X\left\{\frac{\mu}{Ze}[V(R)-V_0]\right\}. \tag{26}$$

Referring back to (12) we see that the term in brackets on the right-hand side of (26) is a function only of Z and the density $\rho_0\equiv\rho(R)$ at the outer radius of the atom. As we shall show in the next section, for the case of a free atom ρ_0 is an invariant for all atoms and ions. Consequently, the condition (26) can be written in the simple form

$$\Psi(X)=XC(\rho_0), \tag{27}$$

where $C(\rho_0)$ is a constant given explicitly [cf. Eq. (33)] by

$$C(\rho_0)=-(0.08933/4Z)(9\pi^2/2Z)^{1/3}. \tag{28}$$

For future reference, we finally also note the boundary condition,

$$\lambda(0)=1, \tag{29}$$

which can be obtained from (21) and (24), or from the observation that the inclusion of correlation in the model will not affect the limiting behavior of $\rho(r)$ near the nucleus.

The equations of our model are thus given by the system (20) and (21) together with the boundary conditions (24), (25), and (27). Alternatively, we could obviate the necessity for dealing with a system of equations by substituting (21) into (20) and thus obtain a single, although exceedingly cumbersome, differential equation in the single dependent variable $\lambda(x)$. As in the case of the TFD model, it is necessary to obtain a separate solution for each atom and ion, since both Z and N enter into the system of equations and its boundary conditions.

IV. THEORY OF THE FREE ATOM

In this part we shall treat those features of the model which can be discussed without solving the equations of the model explicitly. Our considerations will pertain exclusively to free atoms and ions, defined by zero pressure at the boundary.

A. Determination of ρ_0 and V_0

We have obtained the fundamental Eq. (12) by requiring that the electron density $\rho(r)$ be such as to minimize the total energy of the atom. If analogous to the TFD model we assume that the electron density in our model is given by $\rho(r)$ up to the edge $r=R$ of the atom and vanishes thereafter, it is clear that the total energy of the atom is a function of the hitherto undetermined atomic radius R. In the usual manner,[4] a condition on R can now be obtained by requiring that R likewise will adjust itself such as to make the energy of the atom a minimum, i.e., by requiring the fulfillment of the condition

$$\delta E/\delta R=0. \tag{30}$$

In performing the above variation we must keep in mind that both the limits and the integrands of the integrals of Eq. (7) defining E are functions of R, and that simultaneously $\rho(r)$ must satisfy the Eq. (12) obtained from our previous variation. If the energy E is expressed in the form (7) and the variation indicated by (30) is performed, we finally obtain, after a series of manipulations,[21]

$$\frac{\delta E}{\delta R}=4\pi R^2\left\{-\tfrac{2}{3}\alpha_k\rho_0^{5/3}+\tfrac{1}{3}\alpha_e\rho_0^{4/3}+\alpha_c\left[\frac{1}{3}\frac{a_0\rho_0^{4/3}}{1+a_0\rho_0^{1/3}}\right.\right.$$
$$\left.\left.+\frac{1}{3}\frac{\sigma a_0\rho_0^{4/3}}{\tau+a_0\rho_0^{1/3}}-\frac{1}{3}\frac{\sigma\rho_0(a_0\rho_0^{1/3})^2}{(\tau+a_0\rho_0^{1/3})^2}\right]\right\}. \tag{31}$$

If (31) is substituted into (30), we are then led simply to a quartic equation in the unknown $\xi_0=a_0\rho_0^{1/3}$.[22] After calculating the necessary coefficients and solving the quartic by Newton's method, we obtain the density at the edge of the atom as

$$\rho_0=0.0034075/a_0^3. \tag{32}$$

As is apparent from the derivation, ρ_0 is an invariant for all free atoms and ions in our model. Comparing the above result with the corresponding TFD value $a_0^{-3}\rho_0=0.002127$, we observe that the inclusion of the correlation energy density has the effect of increasing the value of ρ_0 by some 60% over the TFD value. It does not follow, however, that the effect of correlation on other parameters of the atom, such as for example the energy, will be of a similar order of magnitude. As a consequence of the above result, the value of R for a given atom or ion in our model will be smaller than the corresponding TFD value, although—unlike ρ_0—R cannot be found without first solving the equations completely.

If the numerical value (32) for ρ_0 is now substituted into (12) for $r=R$, we obtain

$$[V(R)-V_0]e=-0.08933e^2/a_0. \tag{33}$$

Together with the boundary condition (15), the Lagrange multiplier V_0 is thus determined, and is given by

$$eV_0=\frac{(Z-N)e^2}{R}+0.08933e^2/a_0. \tag{34}$$

The practical importance of the result (33) is that it permits us to write the boundary condition (15) in the universal form (27).

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[21] For details, see for example, Ref. 4.
[22] The solutions $R=0$ or $\rho_0=0$ are ruled out by the requirement that with $\alpha_c=0$ our model must reduce to the TFD model for which both R and ρ_0 are known to be nonvanishing. (e.g., cf. Ref. 4).

B. Virial Theorem

In order to derive a virial theorem for the atom and ions of our model, we shall use as a starting point an approach due to Fock[23] which is based essentially on a similarity transformation. We let ρ be the density which minimizes the energy of the atom, i.e., the density which satisfies Eqs. (12) and (13). We then consider a family of neighboring densities ρ_λ obtained by contracting all distances by a factor λ. These are given explicitly by

$$\rho_\lambda = \lambda^3 \rho(\lambda r), \qquad (35)$$

which for $\lambda = 1$ becomes the correct density, and which for all λ satisfies the normalization condition (10). If the total energy $E(\lambda) = E(\rho_\lambda)$ is calculated as a function of λ, the variational principle then gives the condition

$$\lim_{\lambda=1} \frac{dE(\lambda)}{d\lambda} = 0. \qquad (36)$$

For our model, the total energy of the atom as a function of λ is given formally by

$$E(\lambda) = E_k(\lambda) + E_p(\lambda) + E_e(\lambda) + E_c(\lambda), \qquad (37)$$

where

$$E_k = \int \alpha_k \rho^{5/3} dv, \quad E_e = -\int \alpha_e \rho^{4/3} dv, \quad E_c = \int \epsilon_c(\rho) dv, \qquad (38)$$

with α_k and α_e given by (9) and $\epsilon_c(\rho)$ given by the last term on the right of (8). We also note the relation,

$$-\int V \rho e \, dv = -e \int \rho (V_N + \tfrac{1}{2} V_e) dv$$

$$-\frac{e}{2} \int \rho V_e dv = E_p + E_{ep}, \qquad (39)$$

where E_p is the total potential energy of the atom while E_{ep} is the potential energy due to the electron-electron Coulomb interaction alone. It can easily be shown[23] that

$$E_k(\lambda) = \lambda^2 E_k, \quad E_p(\lambda) = \lambda E_p, \quad E_e(\lambda) = \lambda E_e. \qquad (40)$$

By substituting (40) into (37) and applying the condition (36) we are then led to the formal virial theorem

$$2E_k + E_p + E_e = -\lim_{\lambda=1} [dE_c(\lambda)/d\lambda]. \qquad (41)$$

The total correlation energy $E_c(\lambda)$ of the atom is

$$E_c(\lambda) = -\alpha_c \int_0^{R/\lambda} \lambda^3 \rho(\lambda r) \left\{ \ln[1 + a_0 \lambda \rho^{1/3}(\lambda r)] \right.$$

$$\left. + \frac{\sigma a_0 \lambda \rho^{1/3}(\lambda r)}{\tau + a_0 \lambda \rho^{1/3}(\lambda r)} \right\} 4\pi r^2 dr. \qquad (42)$$

We note that unlike the kinetic, potential, and exchange

[23] V. Fock, Physik. Z. Sowietunion 1, 747 (1932).

energies, $E_c(\lambda)$ is not a simple function of λ times the original E_c; this is a consequence of the fact that the correlation energy density is not a homogeneous function of ρ. If in the above integral we make the change of variable $r' = \lambda r$ and differentiate the result with respect to λ, we obtain after taking the limit

$$-\lim_{\lambda=1} \frac{dE_c(\lambda)}{d\lambda}$$

$$= \alpha_c \int \rho \left[\frac{a_0 \rho^{1/3}}{1 + a_0 \rho^{1/3}} + \frac{\sigma a_0 \rho^{1/3}}{\tau + a_0 \rho^{1/3}} - \frac{\sigma (a_0 \rho^{1/3})^2}{(\tau + a_0 \rho^{1/3})^2} \right] dv. \qquad (43)$$

The virial theorem for our model is then formally given by substituting (43) into (41). However, this form of the virial theorem is physically unclear and awkward for purposes of computation; we are thus motivated to simplify expression (43). This can be achieved by combining (43) with equation (12), which leads to

$$-\lim_{\lambda=1} \frac{dE_c(\lambda)}{d\lambda} = -3\alpha_c \int \rho \left[\frac{\sigma a_0 \rho^{1/3}}{\tau + a_0 \rho^{1/3}} + \ln(1 + a_0 \rho^{1/3}) \right] dv$$

$$+ \int (5\alpha_k \rho^{5/3} - 4\alpha_e \rho^{4/3} - 3V\rho e + 3V_0 \rho e) dv. \qquad (44)$$

While this at first sight seems more complicated than the original expression (43), it has the advantage that we can readily identify all terms by means of the relations (38) and (39). If we use the latter to identify the individual terms of (44) and combine the result with (41), we finally obtain the desired virial theorem for our model in the form

$$3E_k + 2E_p + 3E_e + 3E_{ep} + 3E_c + 3V_0 eN = 0. \qquad (45)$$

Starting with (41) and (12), it is a relatively straightforward matter to verify that (45) reduces to the correct TFD limit ($E_c = 0$ and $V_0 = V_{0\text{ TFD}}$) given by expression (41) with the right-hand side set equal to zero.

Unlike the corresponding TF and TFD virial theorems, the virial theorem (45) for our model unavoidably involves the energy E_{ep} in addition to E_p. This is undesirable from a practical viewpoint, inasmuch as E_{ep} cannot be readily obtained once the solution $\Psi(x)$ for a given atom is known. We find it possible, however, to eliminate E_{ep} in terms of E_p and the boundary values of the solution $\Psi(x)$ for a given atom, which are known once the relevant solution has been obtained. We proceed by writing

$$E_p = E_{np} + E_{ep}, \qquad (46)$$

where E_{np} is the potential energy of the atom due to the interaction of the electrons with the nuclear potential, and is given explicitly by

$$E_{np} = -Ze^2 \int (\rho/r) \, dv. \qquad (47)$$

From the differential Equation (20) together with the definition of $\lambda(x)$, we have for ρ the expression

$$\rho = \frac{Z}{4\pi\mu^3}\frac{\Psi''(x)}{x},\qquad(48)$$

which, if substituted into (47), yields

$$E_{np} = \frac{-Z^2e^2}{\mu}\int_0^X \Psi''(x)dx$$
$$= \frac{-Z^2e^2}{\mu}[\Psi'(X)-\Psi'(0)].\quad(49)$$

This may be simplified further by making use of the boundary conditions (25) and (26) and the definition of Ψ. With these we find

$$\Psi'(X) = \frac{-\mu}{Ze}V_0.\qquad(50)$$

If we now denote the initial slope $\Psi'(0)$ of a particular solution by a_1 and use (46) to eliminate E_{ep}, the virial theorem (45) takes the form,

$$3E_k+5E_p+3E_e+3E_c-\frac{3Z^2e^2a_1}{\mu}-3eV_0(Z-N)=0.\quad(51)$$

Both forms (45) and (51) of the virial theorem are of course equally valid, although the latter is more suited to practical computations.

C. The Fermi-Amaldi Correction

One of the basic inadequacies of the original Thomas-Fermi model is that the electrons interact with themselves. In order to correct this situation, at least in a crude way, Fermi and Amaldi[24] simply assign to each electron of the atom the individual density ρ/N, where ρ is the total electron density within the atom, and then write the potential $V_e^*(r)$ acting on a particular electron as that due to the other $N-1$ electrons of the atom

$$V_e^*(r) = \frac{(N-1)}{N}V_e(r),\qquad(52)$$

where $V_e(r)$ is the total electron potential as defined previously. The result of incorporating this modification into the simple TF theory leads to the so-called Fermi-Amaldi equation

$$\varphi'' = x^{-1/2}\varphi^{3/2},\qquad(53)$$

where

$$V = V_N+V_e\qquad(53)$$

$$\varphi(x) = \frac{r}{Ze}(V^*-V_0);\quad V^*=V_N+V_e^*=V-\frac{1}{N}V_e,\quad(54)$$

$$x = \frac{r}{\mu^*};\qquad \mu^* = \mu\left(\frac{N}{N-1}\right)^{2/3}\qquad(55)$$

and where $\varphi(x)$ satisfies the boundary conditions

$$\varphi(0)=1,\quad \varphi(X)-X\varphi'(X)=(Z-N+1)/Z.\quad(56)$$

The Fermi-Amaldi equation possesses the same family of solutions as the original Thomas-Fermi equation; however, the boundary conditions for $\varphi(x)$ are different and the potential $V(r)$ is related differently to the dimensionless solution $\varphi(x)$. Equation (53) is customarily solved by making the ansatz,

$$\varphi(x) = \Psi_0(x)+k\eta_0(x)\qquad(57)$$

where $\Psi_0(x)$ is the ordinary Thomas-Fermi solution, k is a constant to be determined by the boundary conditions, and where to first order $\eta_0(x)$ is a universal function.

In our model which includes both exchange and correlation the situation is somewhat more involved, since in the interior of the atom where the electron density is high the electrostatic self-interaction is compensated by the inclusion of exchange in the model so that the simple Fermi-Amaldi correction is justified only in the low electron-density outer regions of the atom. In order to take into account both exchange and correlation as well as the Fermi-Amaldi correction in the regions where they are significant we follow a procedure developed by Jensen[25] for the TFD model. Thus, we shall replace the exchange and correlation terms in Eq. (7) by a function which in the interior of the atom is equal to the exchange plus correlation terms, but at the edge approaches the Fermi-Amaldi term. The atom is then described by Eq. (12) in the interior, but by the Fermi-Amaldi Eq. (53) near the outer edge of the atom. The electron density ρ_0 at the edge of the atom is assumed to be maintained at the original value given by (32); the value of R changes, however. Then, as far as the calculation of the density (which in the interior is unaffected by the various correction terms) is concerned, one can to a sufficient degree of accuracy replace the basic Eq. (20) of our model simply by the Fermi-Amaldi Eq. (53) with suitably changed boundary conditions. For our model, modified in this way by the Fermi-Amaldi correction, the boundary conditions for $\varphi(x)$ as defined in (55) are then given by (56) and the additional boundary condition corresponding to (15) which can be directly obtained from (53):

$$\varphi(x)=\gamma X;\quad \gamma = \frac{5}{3}\frac{\alpha_k\mu^*}{Ze^2}\rho_0^{2/3}.\qquad(58)$$

Equation (53) may again be solved by making the ansatz (57). The boundary conditions (56) and (58) then yield two simultaneous equations for the unknown parameters k and X. This method is sufficiently accurate for calculating the density; however, any parameters which depend significantly on the interior of the

[24] E. Fermi and E. Amaldi, Mem. Accad. Italia **6**, 117 (1934).
[25] H. Jensen, Z. Physik **101**, 141 (1935) (cf. also Gombas, Ref. 4).

atom, such as the energy, must be calculated from the original Eq. (20). For a detailed justification of this procedure we refer to the original paper by Jensen[25] whose considerations apply equally well to our model.

It is evident that the Fermi-Amaldi correction is of less importance in our model than in the TFD and particularly in the TF model, since the effect of the correlation term is in the same direction as that of the exchange term and thus helps to compensate for the self-interaction of the electrons, whose removal was the original *raison-d'être* of the Fermi-Amaldi correction.

IV. METHODS OF SOLUTION

A. Approximate Thomas-Fermi-Dirac-like Solution

The exact system of Eqs. (20)–(27) based on our expression (6) for the correlation energy density is rather complicated. In order to gain an idea of the general effect of correlation, we can follow a method introduced by Gombas[11] which is based on the observation that in the calculation of the electron density the effect of correlation is appreciable only in the outermost regions of the atom and may be neglected in the inner regions where even the larger exchange effects do not appreciably influence $\rho(r)$. The principle of the method is then to replace the function $\bar{u}_c(\xi)$ given by (4) by an analytically simpler expression which remains valid at $r=R$ or $\rho=\rho_0$.

This may be accomplished by expanding $\bar{u}_c(\xi)$ in a Taylor series about $\xi_0 = a_0\rho_0^{1/3}$, keeping only first-order terms. Equation (8) for the total energy density then takes the simpler form,

$$\epsilon(\rho) = \alpha_k\rho^{5/3} - \alpha_e\rho^{4/3} + \delta_0 a_0\rho^{4/3} + \theta_0\rho, \qquad (59)$$

where

$$\delta_0 = \frac{d\bar{u}_c(\xi)}{d\xi}\bigg|_{\xi=\xi_0}, \qquad \theta_0 = \bar{u}_c(\xi_0) - \delta_0\xi_0. \qquad (60)$$

We have thus replaced the function (4) simply by the slope of $\bar{u}_c(\xi)$ at $\xi=\xi_0$. However, in so doing, we have used the exact theory to determine the value of ξ_0. We now observe from (59) that the third term on the right —representing correlation—is of the same analytic form as the exchange term.[26] Consequently, our model in this approximation is equivalent to a TFD model with a new value of α_e given by

$$\alpha_e' = \alpha_e - \delta_0 a_0. \qquad (61)$$

The equation analogous to (12) now becomes

$$(V - V_0')e = (5/3)\alpha_k\rho^{2/3} - \tfrac{4}{3}\alpha_e'\rho^{1/3};$$

$$V_0' = V_{0\,\mathrm{TFD}} + \frac{\theta_0}{e}. \qquad (62)$$

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[26] The term $k\rho$ in Eq. (59) is equivalent to a constant background potential and does not affect $\rho(r)$.

It may readily be verified that the above relation leads to the same value of ρ_0 as that originally assumed, so that the approximation is self-consistent.

In this approximation, our model has thus been reduced to a TFD-like model. Consequently, an equivalence exists between the solutions of the TFD model and those of our model in the above reduced form. The equivalence can be expressed by the fact that the same solution $\rho(r)$ describes a TFD atom of atomic number Z and in the above approximation an atom in our model of atomic number Z', where Z' and Z are related by

$$Z' = Z(\alpha_e'/\alpha_e)^{3/2}. \qquad (63)$$

The simplification gained is of course enormous; however, the approximation is admittedly crude. Furthermore, it can be used only for the calculation of the density; in order to obtain the energy and similar parameters of the atom, the exact expressions are required. The purpose for including it here is to elucidate the nature of the correlation correction and to be able to use it in rough estimates.

B. Expansion near the Origin

For purposes of the numerical integration of Eq. (20) it is convenient to have available an expansion for $\Psi(x)$ near the origin, since the second derivative $\Psi''(x)$ diverges near the origin as $x^{-1/2}$. Such an expansion will also reveal how correlation affects the potential near the nucleus.

If Eq. (20) is integrated twice with respect to x, making use of (24) and the easily verified identity,

$$\int_0^x \int_0^\zeta g(\eta)d\eta d\zeta = \int_0^x (x-\eta)g(\eta)d\eta$$

we obtain

$$\Psi = 1 + a_1 x + \int_0^x \frac{(x-\eta)}{\eta^{1/2}}\lambda^3(\eta)d\eta, \qquad (64)$$

where a_1 is the arbitrary slope $\Psi'(0)$ at the origin. A preliminary analysis of the analytic nature of the system of Eqs. (20)–(22) together with (29) reveals that the expansion of $\lambda(x)$ near the origin has the form,

$$\lambda(x) = 1 + \tfrac{1}{2}\beta x^{1/2} + x(b_2 + b_3\ln x)$$
$$+ x^{3/2}(b_4 + b_5\ln x) + \cdots. \qquad (65)$$

The coefficients may be determined by substituting the above expression for $\lambda(x)$ both into (64) and (21), expanding to the required order, performing the necessary integrations, and equating the coefficients of the two resulting expressions for $\Psi(x)$. The advantage of using the integral Eq. (64) rather than the differential Eq. (20) lies in the fact that once $\lambda(x)$ is known to a given order, expression (64) determines $\Psi(x)$ to three higher half-orders than can be obtained from (20). In this way,

we find after much tedious labor

$$b_2 = \frac{1}{2}[a_1 + \frac{1}{4}\beta^2 + \gamma(\ln\epsilon + \frac{1}{3} + \sigma)]$$
$$b_3 = -\frac{1}{4}\gamma$$
$$b_4 = \frac{2}{3} + \frac{1}{2}\gamma[(2/3\epsilon) + \frac{1}{2}\beta - \frac{2}{3}(\sigma\tau/\epsilon)]$$
$$b_5 = 0.$$
(66)

The corresponding expansion for $\Psi(x)$ is given by

$$\Psi(x) = 1 + a_1 x + a_2 x^{3/2} + a_3 x^2 + a_4 x^{5/2}$$
$$+ a_5 x^{5/2} \ln x + a_6 x^3 + a_7 x^3 \ln x, \quad (67)$$

with the coefficients given by

$$a_2 = \frac{4}{3},$$
$$a_3 = \frac{3}{4}\beta,$$
$$a_4 = \frac{1}{5}\beta^2 + \frac{2}{5}(a_1 + \frac{1}{4}\beta^2)$$
$$+ \frac{2}{5}\gamma(\ln\epsilon + \frac{1}{3} + \sigma) + (16/75)\gamma,$$
$$a_5 = -\frac{1}{5}\gamma,$$
$$a_6 = (\beta^3/48) + \frac{1}{4}\beta(a_1 + \frac{1}{4}\beta^2) + \frac{1}{4}\beta\gamma(\ln\epsilon + \frac{1}{3} + \sigma) + \frac{1}{3}$$
$$+ \frac{1}{4}\gamma[(2/3\epsilon) + \frac{1}{2}\beta - \frac{2}{3}(\sigma\tau/\epsilon)] + (5/48)\beta\gamma,$$
$$a_7 = -\frac{1}{8}\beta\gamma.$$
(68)

The above expansion for $\Psi(x)$ reduces to the correct TFD limit given by Feynman et al.[27] once account is taken of the fact that Ψ was defined differently in the two cases. We note from expression (67) together with (68) that exchange effects—represented by β—are involved already in the x^2 term, while correlation—represented by γ—first makes an appearance in the $x^{5/2}$ term.

C. Numerical Integration

The basic system of Eqs. (20)–(27) describing our model was solved numerically on a computer for the five elements: argon, chromium, krypton, xenon, and uranium. The systematics of the numerical solution proceeds by obtaining for each Z a family of solutions $\Psi(x)$ corresponding to different values of the starting slope $a_1 = \Psi'(0)$. The point X at which each solution intersects the straight line $\Psi(x) = Cx$, where C is given by (28), defines the edge of the particular atom or ion. This solution then corresponds to an ion with atomic number Z and degree of ionization $(Z-N)/Z = \Psi(X) - X\Psi'(X)$. Solutions which do not intersect the line $\Psi = Cx$ represent atoms under external pressure. The value of a_1 corresponding to the free neutral atom was pinpointed in each case to within the eight-place accuracy of the computer. To a lesser degree of accuracy in $(Z-N)/Z$ we have also tried to obtain the solutions corresponding to the singly and doubly ionized atoms for each Z.

In the actual integration procedure, Eq. (20) was transformed by the change of variable $x = w^2$. The power series (67) was used out to $x = 0.01$ with the coefficients computed for each Z by (68) and (23). From $x = 0.01$ onward, the solution was obtained numerically with a step size $\Delta w = 0.01$. The integration was carried out by means

of the standard Adams-Moulton procedure. At each step of the integration it is necessary to invert Eq. (21) to find $\lambda(\Psi,x)$. This was done by Newton's method and was found to require use of a smaller step size Δw near the edge of the atom, inasmuch as (21) has real solutions only barely beyond the edge of the atom. The truncation error per step was found to be less than 10^{-7}.

A number of sets of corresponding values of a_1, X, and $(Z-N)/Z$, which are useful for interpolation, were found for each value of Z. Four complete solutions (corresponding to different degrees of ionization) $\Psi(x)$, $\Psi'(x)$, $\Psi''(x)$ were obtained for each of the elements considered. Because of space limitations, tables of the numerical solutions cannot be presented here.[28]

V. DISCUSSION OF THE SOLUTION FOR ARGON

In the way of illustrating the general nature of the results obtained, we shall here discuss in some detail the solution for $Z = 18$.

The solution closest to that of the neutral atom corresponds to the starting slope $a_1 = -1.6376553$ which is associated with the values $(Z-N)/Z = 0.00345$, $X = 11.39$. An extrapolation of the X versus $(Z-N)/Z$ data yields for the free neutral atom with $Z-N=0$ the value $X = 11.52$ which gives $R = 3.89a_0$ for the radius of the Argon atom. Comparing this with the TFD model result $X_{\text{TFD}} = 12.7$, we see that in our model the radius of the argon atom is smaller by some 14%.

The density may be computed from Eq. (48) with μ given by (18). In Fig. 1 we show a graph of $4\pi r^2 \rho a_0$ as a function of r/μ and compare the results of our model with those of the TF and TFD models. It can be seen that the difference between the density distributions of the TFD and of our model is significant only in the outer regions of the atom, where our model leads to higher densities and a smaller over-all radius.

We now proceed to a calculation of the energy terms of the argon atom. If expression (48) for the density is substituted into the energy expressions (38), we obtain

$$E_k = \frac{Z^{5/3}\alpha_k}{\mu^2(4\pi)^{2/3}} \int_0^X (\Psi'')^{5/3} x^{1/3} dx,$$

$$E_e = \frac{-\alpha_e Z^{4/3}}{\mu(4\pi)^{1/3}} \int_0^X x^{2/3}(\Psi'')^{4/3} dx_p.$$
(69)

By writing

$$E_p = E_{ep} + E_{np} = -\frac{1}{2}\int eV\rho dv - \frac{1}{2}\int eV_N\rho dv,$$

[27] R. P. Feynman, N. Metropolis, and E. Teller, Phys. Rev. **75**, 1561 (1949).

substituting for V from (17), and taking note of (49), E_p in terms of the solution $\Psi(x)$ becomes

$$E_p = \frac{-e^2 Z^2}{2\mu}\left[\int_0^X \Psi\Psi'' dx + \Psi'(X) - \Psi'(0)\right] - \frac{e}{2}V_0 Z. \quad (70)$$

The nuclear potential energy E_{np} is given by (49); the correlation energy E_c of the atom may be computed directly from the last of expressions (38) with $\epsilon_c(\rho)$ given by (6).

In performing the actual numerical integration of the integrals occurring in expressions (69) and (70) for E_k and E_p, some difficulty is encountered due to the fact that near the origin the integrands diverge like $x^{-1/2}$. It therefore becomes necessary to use the series expansion (67) near the origin out to some value m and begin the numerical integration at m. Thus, for example, after substitution of the power series, expansion of the integrand to a consistent order, and integration, the energy E_k becomes explicitly

$$E_k = \frac{Z^{5/3}}{\mu^2(4\pi)^{2/3}}\left\{\int_m^X x^{1/3}(\Psi'')^{5/3}dx + 2m^{1/2} + \frac{10}{3}a_3 m\right.$$

$$+ m^{3/2}\left(\frac{95}{9}a_5 + \frac{25}{6}a_4 + \frac{40}{27}a_3{}^2 + \frac{25}{6}a_5\ln m\right)$$

$$+ m^2\left[\frac{5}{3}a_7 + 5a_6 + \frac{85}{36}a_3 a_5 + \frac{25}{6}a_3 a_4 - \frac{20}{81}a_3{}^3\right.$$

$$\left.\left. + \left(5a_7 + \frac{25}{6}a_3 a_5\right)\ln m\right]\right\}, \quad (71)$$

where the coefficients a_n are given explicitly by (68). A similar expression may be obtained for E_p.

The necessary integrals were evaluated numerically, and the various energies computed for argon. The results, expressed in units of e^2/a_0 are

$$\begin{aligned} E_k &= 703, & E_p &= -1344, & E_{np} &= -1569 \\ E_{ep} &= 225, & E_e &= -28.7, & E_c &= -1.55. \end{aligned} \quad (72)$$

We note that compared to the total energy of the atom the correlation energy is quite negligible, amounting to only some 5% of the exchange energy. It must be kept in mind, however, that the remaining energies are also affected by the correlation correction, since the density distribution differs from that of the TFD model. With the above values, the total energy of the argon atom in our model becomes $E_{tot} = -672e^2/a_0$.

VI. ATOMIC POLARIZABILITIES AND DIAMAGNETIC SUSCEPTIBILITIES

The theory of the model developed in the previous section is generally applicable to the calculation of all atomic properties which can be treated on the basis of the statistical model of the atom. As the only example
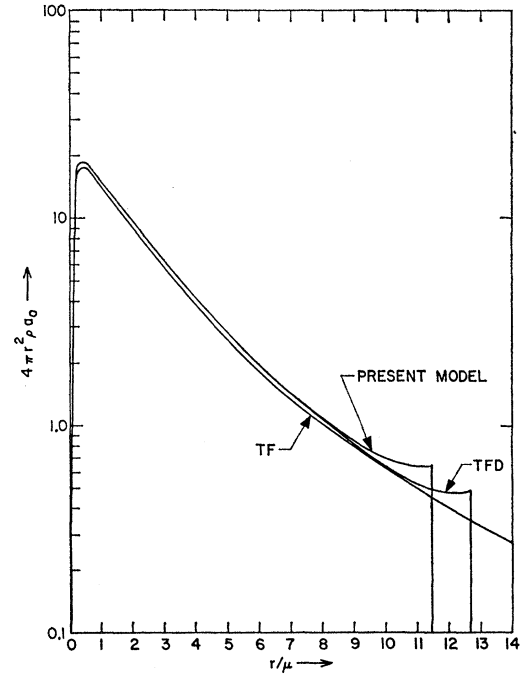

FIG. 1. Comparison of the electron density of argon, expressed as $4\pi r^2 \rho a_0$ as a function of r/μ for the TF, TFD, and present models.

we shall here consider the calculation of electric polarizabilities and diamagnetic susceptibilities of the atoms for which we have obtained solutions. Applications of the model to the calculation of equations of state and small-angle electron scattering from atoms will be presented elsewhere.

The diamagnetic susceptibility χ and polarizability α of an atom are given, respectively, by the well-known formulas[29]:

$$\chi = -N\frac{e^2}{6mc^2}\langle r^2\rangle \quad (73)$$

$$\alpha = \frac{4}{9Za_0}[\langle r^2\rangle]^2, \quad (74)$$

where N is Avogadro's number, m the mass of the electron, and $\langle r^2\rangle$ is given by

$$\langle r^2\rangle = 4\pi\int_0^R r^4\rho(r)dr. \quad (75)$$

If the expression (48) is substituted for $\rho(r)$, and r is expressed in terms of x by means of (18), we obtain

$$\langle r^2\rangle = Z\mu^2\int_0^X x^3\Psi''(x)dx. \quad (76)$$

After integrating twice by parts and using the boundary

[29] Cf., for example, Ref. 4.

conditions (25) and (27), the expression (76) for neutral atoms takes the form

$$\langle r^2 \rangle = 6Z\mu^2 \left[\int_0^X x\Psi(x)dx - \tfrac{1}{3}CX^3 \right], \qquad (77)$$

where C is given by (28). The integral occurring in (77) was evaluated numerically for each value of Z, and the value of X obtained from extrapolation to $Z-N=0$ of the X versus $(Z-N)/Z$ data. The magnetic suscepti-bilities and electric polarizabilities were then computed by means of (73) and (74). The corresponding quantities were also computed for the TF and TFD models.[30] The results are presented in Tables I and II and compared

TABLE I. Magnetic susceptibilities χ (10^{-6} cm³) for atoms of various elements.

	Ar	Cr	Kr	Xe	U
TF model	81.0	...	102.0	117.0	...
TFD model	22.1	...	35.0	45.5	...
Present model	20.88	25.96	33.00	43.61	59.25
Hartree field	20.6	...	...	...	...
Experimental	19.5	...	28.0	42.4	...

[30] The TFD model calculations were based on the potential tables given by L. H. Thomas, J. Chem. Phys. **22**, 1758 (1954).

TABLE II. Atomic polarizabilities α (10^{-24} cm³) for atoms of various elements.

	Ar	Cr	Kr	Xe	U
TF model	47.78	43.41	37.92	33.13	27.74
TFD model	2.85	...	3.60	4.02	...
Present model	2.54	2.95	3.17	3.70	4.00
Empirical	1.65	...	2.50	4.10	...

with experiment, the latter values being obtained from Ref. 4.

We see that in general our model leads to some im-provement in the agreement with experiment although the agreement is not yet quantitatively precise. From the results for argon we may observe that our model leads to much the same value for the magnetic suscepti-bility as that obtained by the much more cumbersome method of the Hartree self-consistent field.

ACKNOWLEDGMENTS

$2P \rightarrow 1S$ Transitions in Muonic Tl, Pb, and Bi*†

WILLIAM B. ROLNICK‡
Columbia University, New York, New York
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The mixing of states of a muonic atom with the nucleus in an excited state into the states with the nucleus in the ground state, for natural Tl, Pb, and Bi (due to the multipole interactions between the nucleus and the muon), is calculated. This effect fails to explain the ratio of the number of $2P_{1/2} \rightarrow 1S_{1/2}$ to $2P_{3/2} \rightarrow 1S_{1/2}$ transitions (expected to be 0.5 in the absence of mixing) as observed by Frati and Rainwater. In Bi, the calculation shows that the mixing is negligible, but the observed ratio was 0.75 ± 0.05; in Tl (where the ratio was 0.97 ± 0.09) the off-diagonal matrix elements of the Hamiltonian, required for this effect to be the sole cause of the change of ratio, differs from theory by two standard deviations. For Pb the observed ratio agrees with theory and the calculated mixing is, indeed, negligible. If we assume that some unknown effect is acting in Bi and is of the same order of magnitude in Tl, then the difference between the ratio in Tl from that in Bi is explained by the above mixing. This assumption is suggested by the fact that Tl is one proton below and Bi is one proton above a magic number closed shell (82). We suppose that this unknown effect is absent in Pb since it is a magic number nucleus (82 protons). It is proven that nonresonant effects, due to spin-independent operators, cannot affect the radiative-transition sum rules. This is applied to nonresonant hyperfine mixing and a hypothetical nuclear-Auger effect.

I. INTRODUCTION

IN recent muonic atom studies by Frati and Rain-water,[1] the relative number of $2P_{1/2} \rightarrow 1S_{1/2}$ transi-

[1] W. Frati and J. Rainwater, Phys. Rev. **128**, 2360 (1962). (Theoretical values here were calculated by K. W. Ford and J. G. Wills; their values for Bi have been corrected.)

tions to $2P_{3/2} \rightarrow 1S_{1/2}$ transitions $[W(2P \rightarrow 1S)]$ is re-ported for various atoms. The values obtained for natural Tl and Bi are well above the value which is pre-dicted by the sum rules. {Since the relative population of the $2P_{1/2}$ to $2P_{3/2}$ states measured in the $3D \rightarrow 2P$ transitions $[W(3D \rightarrow 2P)]$ was approximately $\tfrac{1}{2}$, the sum rules would have predicted that $W(2P \rightarrow 1S)$ had approximately the same value.} The mechanism in-voked to explain this is the mixing of the state $|2P_{1/2}$