

spectra does not diverge. An idea of the magnitude of this photon diffusion coefficient can be had using $\tau=10^{-3}$, $\langle K^{-2} \rangle = 3 \times 10^{-3}$, giving an effective diffusion coefficient of 1 cm²/sec corresponding to a carrier mobility of 40 cm²/volt sec at room temperature, which is quite small compared to actual mobilities.

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Extension of the Thomas-Fermi-Dirac Statistical Theory of the Atom to Finite Temperatures

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The Thomas-Fermi theory of the atom is generalized to include the effects of temperature as well as exchange. This leads to a nonlinear integral equation for the Fermi electron-momentum distribution function, and the usual Poisson equation for the electron-density distribution. Analytical solutions of the integral equation are given for the limiting cases of near-degeneracy and complete nondegeneracy, and a numerical method of calculating solutions in the intermediate case is described. A complete discussion of the thermodynamics of the atom is given; in particular, it is shown that the Gibbs free energy is the product of the number of electrons and the electronic chemical potential (Fermi energy), despite statements which have been made to the contrary. Numerical results have verified the virial theorem for all Z , T , and atomic volumes. The ratio of the calculated energy for $T=\mathcal{P}=0$ to the experimental total ionization energy varies from 2.07 for H down to 1.33 for Al, and is presumably still closer to unity for higher- Z elements. Some numerical results are given for iron over the density range 0.1 to 10 times normal and for values of kT from 0 to 1000 ev. Pressures, energies, and entropies are lower than the corresponding values calculated without exchange by as much as 40% at $kT=10$ ev, by up to 10% at $kT=100$ ev, and by only negligible amounts at $kT=1000$ ev.

1. INTRODUCTION

THE Thomas-Fermi (TF) and Thomas-Fermi-Dirac (TFD) statistical models of the atom¹⁻³ have been extensively used as the basis for approximate calculations of the equations of state of compressed materials.⁴⁻⁶ The original Thomas-Fermi model has been extended in two directions—first by taking into account exchange effects at zero temperature²⁻⁵ and second by allowing nonzero temperatures but neglecting exchange.⁵⁻⁷

Some attempts have been made to include the effects of both exchange and elevated temperatures. Umeda

and Tomishima⁸ have done this by deriving a temperature-perturbation type of Thomas-Fermi equation⁶ in which the effects of exchange are taken into account by using an effective temperature⁹ which minimizes the Helmholtz free energy. Ashkin¹⁰ has generalized the Thomas-Fermi-Dirac theory (with exchange), obtaining equations applicable for any temperature. However, his solution, obtained by an analytical perturbation procedure, is (like Umeda and Tomishima's valid only to temperatures of a few volts (1 volt \cong 11 605.6°K). The present paper is an extension of this early work (including the perturbation solution), and also outlines a method by which accurate solutions may be calculated for arbitrarily high temperatures.

2. THEORY

A. Basic Integral Equation and Associated Differential Equation for the Charge Density

The application of the statistical theory of the atom to equation-of-state calculations is well known, but for

¹ L. H. Thomas, Proc. Cambridge Phil. Soc. **23**, 542 (1927); E. Fermi, Z. Physik **48**, 73 (1928).

² P. A. M. Dirac, Proc. Cambridge Phil. Soc. **26**, 376 (1930).

³ For general discussions see for example: L. Brillouin, *Actualités sci. et ind.* **160** (1934); P. Gombás, *Die statistische Theorie des Atoms und ihre Anwendungen* (Springer-Verlag, Wien, 1949); E. M. Corson, *Perturbation Methods in the Quantum Mechanics of n-Electron Systems* (Hafner Publishing Company, New York, 1950), Chap. IX.

⁴ J. C. Slater and H. M. Krutter, Phys. Rev. **47**, 559 (1935); H. Jensen, Z. Physik **111**, 373 (1938).

⁵ Feynman, Metropolis, and Teller, Phys. Rev. **75**, 1561 (1949).

⁶ R. E. Marshak and H. A. Bethe, Astrophys. J. **91**, 239 (1940).

⁷ J. J. Gilvarry, Phys. Rev. **96**, 934 and 944 (1954); J. J. Gilvarry and G. H. Peebles, Phys. Rev. **99**, 550 (1955); R. Latter, Phys. Rev. **99**, 1854 (1955).

⁸ K. Umeda and Y. Tomishima, J. Phys. Soc. (Japan) **8**, 360 (1953).

⁹ A. B. Lidiard, Phil. Mag. **42**, 1325 (1951).

¹⁰ J. Ashkin (unpublished).

completeness the basic arguments involved will be summarized here. An atom of a solid in the metallic state may be considered as a polyhedral cell which contains one nucleus and a number of electrons N equal to the atomic number Z . At high pressures, this cell exhibits a rather high degree of symmetry; thus the electric field at points outside the cell due to the charge within is small and drops off rapidly with increasing distance from the cell. It is therefore a good approximation to replace each polyhedral cell by a sphere of equal volume and regard the electron distribution within the cell as being exactly spherically symmetrical. This makes the electric field within a cell dependent only on the charge distribution within that cell, so that the problem of calculating properties of the solid as a whole reduces to that of finding the properties of a single atom. The volume of the solid is measured by the size of one of the spherical cells, the pressure (being uniform throughout the solid) is equal to the pressure of the electron cloud at the surface of the sphere, and the internal energy of the solid (since interatomic forces are neglected) is simply the product of the energy per atom and the total number of atoms.

For the purpose of finding the electron distribution within a spherical cell, we shall start with a wave function for the electrons of the atom which is an antisymmetrized product of one-electron wave functions. From Fock's equations for the individual wave functions $\phi_i(\mathbf{r})$, the energy of an electron in the i th state is found to be¹¹

$$\begin{aligned}
 E_i = & -\frac{\hbar^2}{2m} \int \phi_i^*(\mathbf{r}_1) \Delta \phi_i(\mathbf{r}_1) d\tau_1' + \int \phi_i^*(\mathbf{r}_1) V \phi_i(\mathbf{r}_1) d\tau_1' \\
 & + \sum_j e^2 \int \frac{|\phi_j(\mathbf{r}_2)|^2 |\phi_i(\mathbf{r}_1)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} d\tau_2' d\tau_1' \\
 & - \sum_j e^2 \int \frac{\phi_j^*(\mathbf{r}_2) \phi_i(\mathbf{r}_2) \phi_i^*(\mathbf{r}_1) \phi_j(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\tau_2' d\tau_1' \\
 = & E_{\text{kin}, i} + E_{\text{en}, i} + E_{\text{ee}, i} + E_{\text{ex}, i}. \quad (2.1)
 \end{aligned}$$

(The volume element $d\tau'$ implies summation over the electron spin as well as integration over space.) The first two terms of this expression represent, respectively, the kinetic energy and the electron-nuclear potential energy of the i th electron. It is convenient to consider the remaining two terms separately and they will be referred to as the electron-electron potential energy and the exchange energy, respectively, even though properly speaking the *sum* of the two terms constitutes the electron-electron potential energy. Considering the totality of all possible wave functions ϕ_i for the i th electron, the probability that the electron

lies in any particular one of these states will be assumed to be given by the Fermi distribution function

$$n_i = [1 + \exp \beta(E_i - \mu)]^{-1}, \quad (2.2)$$

where $\beta = 1/kT$, E_i is the energy of the i th electron as defined by Eq. (2.1) for this particular state of the atom, and μ is a constant whose value is the same for all electrons of the atom. The validity of Eq. (2.2) has been established, to a certain approximation, by a statistical-mechanical treatment of the atom from the point of view of the grand canonical ensemble.¹⁰

In order to evaluate the integrals in Eq. (2.1) we now assume, in keeping with the usual Thomas-Fermi theory, that the individual wave functions are approximately localized in position and momentum, so that we can assert of the i th electron that it lies approximately at a point \mathbf{r}_i with approximately a momentum \mathbf{p}_i . Replacing the sum over j in Eq. (2.1) by an integral over phase space, with a density of states $2/h^3$ and hence an electron density $2n/h^3$, the exchange energy of an electron in the state i is found to be²

$$E_{\text{ex}, i} = -\frac{e^2}{\pi \hbar} \int \{n(\mathbf{p}', \mathbf{r}_i) / |\mathbf{p}' - \mathbf{p}_i|^2\} d\mathbf{p}',$$

or integrating over the direction of \mathbf{p}'

$$E_{\text{ex}, i} = -\frac{2e^2}{h p_i} \int_0^\infty p' \left\{ \ln \left| \frac{p' + p_i}{p' - p_i} \right| \right\} n(\mathbf{p}', \mathbf{r}_i) d\mathbf{p}'. \quad (2.3)$$

Similarly the remaining terms of the energy are found to be

$$\begin{aligned}
 E_{\text{kin}, i} + E_{\text{en}, i} + E_{\text{ee}, i} \\
 = \frac{p_i^2}{2m} - \frac{Ze^2}{r_i} + \frac{2e^2}{h^3} \int \int \frac{n(\mathbf{p}', \mathbf{r}')}{|\mathbf{r}' - \mathbf{r}_i|} d\mathbf{p}' d\mathbf{r}'. \quad (2.4)
 \end{aligned}$$

Substituting these expressions into Eq. (2.2) we find that $n(\mathbf{p}_i, \mathbf{r}_i)$ must satisfy a rather complicated nonlinear integral equation in the two variables p_i and r_i . It is not possible to get rid of the nonlinearity. It is, however, possible to replace the equation in two variables by two separate equations in one variable each: Introducing a variable

$$\begin{aligned}
 \chi_i = \chi(r_i) = & -E_{\text{en}, i} - E_{\text{ee}, i} + \mu \\
 = & \frac{Ze^2}{r_i} - \frac{2e^2}{h^3} \int \int \frac{n(\mathbf{p}', \mathbf{r}')}{|\mathbf{r}' - \mathbf{r}_i|} d\mathbf{p}' d\mathbf{r}' + \mu, \quad (2.5)
 \end{aligned}$$

we may write

$$\begin{aligned}
 kT \ln \frac{1 - n(\mathbf{p}_i, \mathbf{r}_i)}{n(\mathbf{p}_i, \mathbf{r}_i)} = & \frac{p_i^2}{2m} - \frac{2e^2}{h p_i} \int_0^\infty p' \ln \left| \frac{p' + p_i}{p' - p_i} \right| \\
 & \times n(\mathbf{p}', \mathbf{r}_i) d\mathbf{p}' - \chi_i. \quad (2.6)
 \end{aligned}$$

¹¹ See, for example, F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), Secs. 49 ff; Eq. (2.1) follows from Seitz' Eq. (51.6) by setting $\lambda_{ij} = E_i \delta_{ij}$.

This expression shows that the function $n(p_i, r_i)$ depends on r_i only through the possible values that the potential energy χ_i can assume when r_i changes. Thus the equation can be regarded as an integral equation in *one* variable for a function n of p_i alone, the potential energy χ_i playing the role of a parameter in the equation.¹² We shall indicate this more explicitly by writing the distribution function hereafter as $n(p_i; \chi_i, T)$ instead of $n(p_i, r_i)$. Our first problem, then, will be to solve Eq. (2.6) for $n(p_i; \chi_i, T)$ as a function of p_i and the parameters χ_i and T . To find the explicit dependence (for given T) on the position coordinate r_i , it is only necessary to solve an equation of the Poisson type for χ_i . For, denoting by $G_2(\chi_i, T)$ the integral

$$\begin{aligned} G_2(\chi_i, T) &= (4\pi)^{-1} \int n(p_i; \chi_i, T) d\mathbf{p}_i \\ &= \int_0^\infty p_i^2 n(p_i; \chi_i, T) dp_i \end{aligned} \quad (2.7)$$

(which is proportional to the electron density), Eq. (2.5) can be written

$$\begin{aligned} \chi_i &= \frac{Ze^2}{r_i} - \frac{8\pi e^2}{h^3} \int \frac{G_2(\chi_i', T)}{|\mathbf{r}' - \mathbf{r}_i|} d\mathbf{r}' + \mu \\ &= \frac{Ze^2}{r_i} - \frac{32\pi^2 e^2}{h^3} \left\{ \frac{1}{r_i} \int_0^{r_i} r'^2 G_2' dr' + \int_{r_i}^\infty r' G_2' dr' \right\} + \mu, \end{aligned}$$

and taking the Laplacian of both sides,

$$\Delta\chi_i = (32\pi^2 e^2/h^3) G_2(\chi_i, T). \quad (2.8)$$

This can be regarded simply as a generalization of the original Thomas-Fermi equation for the electron distribution.

The solution of the integral equation (2.6) is especially simple in two special cases of interest. First, if exchange effects are neglected we find immediately that

$$n(p_i; \chi_i, T) = \{1 + \exp[\beta(p_i^2/2m - \chi_i)]\}^{-1},$$

and the Poisson equation to be solved is

$$\Delta\chi_i = \frac{32\pi^2 e^2}{h^3} \int_0^\infty \frac{p_i^2 dp_i}{1 + \exp[\beta(p_i^2/2m - \chi_i)]}. \quad (2.9)$$

This is the equation used by Feynman *et al.*, in their treatment of temperature effects.¹³

As the second example we take the case where the temperature is zero. Here the solution is simple even when the exchange term is retained. If $P = P(\chi_i)$ is the value of p_i for which the right-hand side of Eq. (2.6)

vanishes, then at zero temperature it follows that

$$n(p_i; \chi_i, 0) = \begin{cases} 1 & \text{for } p_i < P \\ 0 & \text{for } p_i > P. \end{cases} \quad (2.10)$$

Substituting $p_i = P$, then, we find

$$\begin{aligned} \chi_i &= \frac{P^2}{2m} - \frac{2e^2}{hP} \int_0^P p' \ln \left(\frac{P+p'}{P-p'} \right) dp' \\ &= P^2/2m - 2e^2 P/h. \end{aligned}$$

From Eq. (2.7), $G_2 = P^3/3$, and the Poisson equation is thus

$$\Delta(P^2/2m - 2e^2 P/h) = 32\pi^2 e^2 P^3/3h^3. \quad (2.11)$$

This is the equation first obtained by Dirac¹⁴ for the exchange case at zero temperature.

B. Thermodynamical Considerations

Before taking up the solution of Eq. (2.6) in the general case, we shall first discuss the thermodynamics of the atom. For the total energy per atom, we shall write

$$E = E_{\text{kin}} + E_{\text{en}} + E_{\text{ee}} + E_{\text{ex}}, \quad (2.12)$$

where

$$\begin{aligned} E_{\text{kin}} &= \sum n_i E_{\text{kin}, i}, & E_{\text{ee}} &= \frac{1}{2} \sum n_i E_{\text{ee}, i}, \\ E_{\text{en}} &= \sum n_i E_{\text{en}, i}, & E_{\text{ex}} &= \frac{1}{2} \sum n_i E_{\text{ex}, i}, \end{aligned}$$

the summations being over all energy states for each electron of the atom. It may be pointed out that the electron-electron energies are of the form [see Eq. (2.1)]

$$E_{\text{ee}, i} = \sum n_j E_{\text{ee}, ij}, \quad E_{\text{ex}, i} = \sum n_j E_{\text{ex}, ij}, \quad (2.13)$$

and thus of course depend on the occupation probabilities of electrons other than the i th electron. An expression for the entropy follows from its definition as the average value of $-k \ln P$, where P is the probability of occurrence of any particular electronic configuration. Since the probability that any particular energy state is occupied is n_i and the probability that it is not occupied is $1 - n_i$, this average is¹⁵

$$S = -k \sum \{n_i \ln n_i + (1 - n_i) \ln(1 - n_i)\} \quad (2.14)$$

or, from Eq. (2.2),

$$\begin{aligned} TS &= \sum \{n_i (E_i - \mu) - kT \ln(1 - n_i)\} \\ &= E + E_{\text{ee}} + E_{\text{ex}} - N\mu - kT \sum \ln(1 - n_i), \end{aligned} \quad (2.15)$$

where N is the total number of electrons per atom. It follows from Eqs. (2.14) and (2.10) that $S = 0$ at $T = 0$, in agreement with Nernst's postulate. The Helmholtz

¹⁴ Reference 2, Eq. (20). The exchange term in Dirac's paper is twice that of (2.11) owing to his neglecting the fact that exchange interactions occur only between electrons of parallel spin.

¹⁵ See J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley and Sons, Inc., New York, 1940), Eqs. (5.13) and (6.2).

¹² Equation (2.6) for the case of free electrons ($\chi_i = \mu$) has been derived by H. Koppe, *Z. Naturforsch.* 2a, 429 (1947).

¹³ Reference 5, Eq. (15).

free energy is then

$$A = E - TS = N\mu - E_{ee} - E_{ex} + kT \sum \ln(1 - n_i). \quad (2.16)$$

In writing these expressions for the thermodynamic functions, we have used not the most probable electronic distribution for an atom as a whole, but rather the most probable values of the occupation numbers of each of the individual states. For example, in writing

$$E_{ee} = \frac{1}{2} \sum_{ij} n_i n_j E_{ee,ij},$$

we have used in each term the product of most-probable values of n_i and n_j rather than the value of the product which corresponds to the most probable electronic state of the atom. This means that we neglect correlation effects which make the probability of finding an electron in state i depend on the presence or absence of an electron in state j [other than the dependence implicit in Eq. (2.2)]. The expressions written above are, however, consistent with the first and second laws of thermodynamics

$$dE = TdS - \mathcal{P}dV + \mu dN, \quad (2.17)$$

or

$$dA = -SdT - \mathcal{P}dV + \mu dN.$$

For, noting that $E_{kin,ij}$, $E_{ee,ij}$, etc., depend only on volume and nuclear charge, it may be seen by direct differentiation of Eqs. (2.12) and (2.14) that

$$\begin{aligned} (\partial E / \partial T)_{V,N} &= T(\partial S / \partial T)_{V,N} \\ &= \sum E_i (\partial n_i / \partial T)_{V,N}. \end{aligned} \quad (2.18)$$

Also, letting $E_{ee,ij} + E_{ex,ij} = V_{ij}$, it may be seen from Eq. (2.2) that

$$\left(\frac{\partial n_i}{\partial N} \right)_{T,V} = - \frac{n_i(1-n_i)}{kT} \left[\sum_j V_{ij} \left(\frac{\partial n_j}{\partial N} \right)_{T,V} - \left(\frac{\partial \mu}{\partial N} \right)_{T,V} \right],$$

so that differentiation of Eq. (2.16) gives

$$(\partial A / \partial N)_{T,V} = \mu, \quad (2.19)$$

showing that μ is the chemical potential of the electrons. Thus Eqs. (2.17) are satisfied provided the pressure is defined in such a way as to agree with the relations

$$\mathcal{P} = -(\partial E / \partial V)_{S,N} = -(\partial A / \partial V)_{T,N}. \quad (2.20)$$

The pressure may be calculated in two ways. The first is a consequence of the virial theorem:

$$\mathcal{P}V = \frac{2}{3}E_{kin} + \frac{1}{3}E_{en} + \frac{1}{3}E_{ee} + \frac{1}{3}E_{ex}, \quad (2.21)$$

which has been shown by Feynman *et al.*⁵ to hold for the generalized Thomas-Fermi atom.

A second expression for pressure, in terms of boundary conditions only, can be obtained from its definition as the rate of transfer of momentum across a unit area at the edge of the atom. In the case of a neutral atom, the electrostatic field at the boundary is zero, so that the only contributions to the pressure arise from the

gas kinetic pressure of the electrons and the exchange interactions. Since these interactions are of very short range—of the order of the de Broglie wavelength of the electrons—we may expect the electron density near the boundary to be essentially constant; for the only thing which could give a nonuniform density would be a nonvanishing long-range interaction. The problem is, then, to find the pressure of a uniform gas of electrons in which the Coulomb interactions have been reduced to zero (say by the presence of a uniform positive space charge) but in which the exchange interactions remain. For such a uniform gas of N electrons in a volume V , it is clear thermodynamically that (except for surface effects which we may regard as small) the free energy A can be written in the form $A = N \times a(T, V/N)$; that is, the free energy is equal to the number of electrons times the free energy per electron, the latter being a function of temperature and concentration only. The pressure is then, from Eq. (2.20)

$$\mathcal{P} = -(\partial A / \partial V)_{T,N} = -[\partial a / \partial (V/N)]_T.$$

From Eq. (2.19),

$$\begin{aligned} \mu &= \left(\frac{\partial A}{\partial N} \right)_{T,V} = a(T, V/N) - \frac{V}{N} \left[\frac{\partial a}{\partial (V/N)} \right]_T \\ &= \frac{A}{N} + \frac{\mathcal{P}V}{N}. \end{aligned} \quad (2.22)$$

Thus from Eq. (2.16)

$$\mathcal{P}V = E_{ex} - kT \sum \ln(1 - n_i),$$

since E_{ee} is zero for the electron gas under consideration. Replacing the sum by an integral over phase space with density of states $2/h^3$, the volume can be divided out because of the uniform spatial distribution of electrons, leaving

$$\mathcal{P} = (E_{ex}/\text{unit vol.}) - (2kT/h^3) \int \ln(1 - n_i) d\mathbf{p}_i. \quad (2.23)$$

For the atom this expression gives the pressure if n_i and the exchange-energy density are evaluated at the boundary. It may be noted that this formula, together with the virial theorem (2.21). For the case of zero potential energy, implies

$$\begin{aligned} &-(2kT/h^3) \int \ln(1 - n_i) d\mathbf{p}_i \\ &= \frac{2}{3}(E_{kin}/\text{unit vol.} - E_{ex}/\text{unit vol.}), \end{aligned} \quad (2.24)$$

a result which will be verified by a detailed calculation in Sec. 3 [see Eq. (3.9)].

Finally, we wish to obtain an expression for the Gibbs free energy F of the atom. For this purpose we shall need first an expression for the Helmholtz free energy A which is provided by Eq. (2.26) below. This

relation will be established by an explicit evaluation in Sec. 3 [see Eq. (3.24)] based on the important identity in Eq. (3.9). However, the same result may also be obtained by an artifice which it is instructive to consider at this point in the argument.

Imagine a hypothetical field-free atom in which at each point the electron density and momentum distribution are identical with the corresponding values in the actual atom under consideration, but in which the positive charge of the nucleus has been smeared out to make the atom everywhere locally electrically neutral (thereby reducing all Coulomb energies to zero). We shall denote quantities relating to this hypothetical atom by using primes. The momentum distribution at a point \mathbf{r} is given, analogously to Eq. (2.2), by

$$n_i' = [1 + \exp\beta(E_i' - \mu_i')]^{-1}.$$

But since by hypothesis $n_i' = n_i$, it follows that

$$\mu = \mu_i' + E_i - E_i' = \mu_i' + E_{en, i} + E_{ee, i}, \quad (2.25)$$

or, summing over all quantum states,

$$N\mu = \sum n_i \mu_i' + E_{en} + 2E_{ee}.$$

(The variation of the chemical potential μ_i' from point to point in the hypothetical atom shows that the distribution is not strictly in thermodynamic equilibrium if the electrons of one volume element are free to move into neighboring volume elements. In order to maintain thermodynamic equilibrium we therefore imagine the atom divided into small cells, each enclosed in rigid walls impervious to electrons but perfectly heat conducting.) Since an expression analogous to Eq. (2.22) holds locally throughout the hypothetical atom, it follows that

$$\sum n_i \mu_i' = \int (e' - Ts' + \mathcal{O}') dV',$$

where e' and s' represent local energy and entropy densities, and the local pressure \mathcal{O}' is given by the virial theorem (2.21) as

$$\mathcal{O}' = \frac{2}{3}e_{kin}' + \frac{1}{3}e_{ex}'.$$

Thus

$$\begin{aligned} \sum n_i \mu_i' &= (5/3)E_{kin}' + (4/3)E_{ex}' - TS' \\ &= (5/3)E_{kin} + (4/3)E_{ex} - TS, \end{aligned}$$

since $S' = S$ from Eq. (2.14). Using the virial theorem (2.21), we obtain finally

$$\begin{aligned} N\mu &= E - TS + \frac{2}{3}E_{kin} + E_{ee} + \frac{1}{3}E_{ex} \\ &= A + \mathcal{O}V + \frac{2}{3}E_{ee} - \frac{1}{3}E_{en}. \end{aligned} \quad (2.26)$$

This expression has been obtained by Brachman¹⁶ for the no-exchange case.

Since both E_{ee} and $-E_{en}$ are positive, it is evident that $N\mu \neq A + \mathcal{O}V$. However, this inequality is *not* to

¹⁶ M. K. Brachman, *J. Chem. Phys.* **22**, 1152 (1954).

be interpreted as meaning that $F \neq N\mu$ as claimed by Brachman¹⁶ and by Reiss,¹⁷ but rather is due to the fact that the definition $F = A + \mathcal{O}V$ is appropriate only in the case of homogeneous, field-free systems. For the atom under consideration, the expression (2.17) for dE is in fact an incomplete description of the possible ways in which the electronic energy E can change. Firstly, we must include the effect of the "external" field set up by the nucleus. Secondly, although total volume is an adequate variable for describing the kinetic and exchange energies (exchange interactions being strictly local in effect), volume alone is not adequate to determine the long-range electrostatic potential energies—which depend on the *shape* of the occupied volume (or more accurately on the values of the individual interparticle distances). Thus a complete expression for the change in internal energy is¹⁸

$$\begin{aligned} dE &= TdS + \mu dN + (\partial E_{kin}/\partial V)dV + (\partial E_{ex}/\partial V)dV \\ &+ \sum \frac{\partial E_{en}}{\partial r_i} dr_i + \frac{1}{2} \sum_{i,j} \frac{\partial E_{ee}}{\partial r_{ij}} dr_{ij} + \frac{\partial E_{en}}{\partial (Ze)} d(Ze), \end{aligned} \quad (2.27)$$

where the negatives of the derivatives with respect to V , r , and Ze are of the nature of pressures, forces, and potential, respectively. (More correctly, in the cases of the kinetic and exchange energies one should perhaps subdivide the volume V into a large number of subvolumes within each of which the Coulomb potential—and hence also the electron density and momentum distribution—is essentially constant. However, this would not alter the final result obtained below.) Corresponding to this expression for dE , one has the following expression for the Gibbs free energy¹⁸:

$$\begin{aligned} F &= A - (\partial E_{kin}/\partial V)V - (\partial E_{ex}/\partial V)V \\ &- \sum \frac{\partial E_{en}}{\partial r_i} r_i - \frac{1}{2} \sum_{i,j} \frac{\partial E_{ee}}{\partial r_{ij}} r_{ij} - \frac{\partial E_{en}}{\partial (Ze)} Ze. \end{aligned} \quad (2.28)$$

The second and third terms on the right are just the contribution of the kinetic and exchange energies to $\mathcal{O}V$, which from Eq. (2.21) is $\frac{2}{3}E_{kin} + \frac{1}{3}E_{ex}$. (Or alternatively, it may be noted that for constant occupation numbers n_i of the quantum states, the kinetic energy $p_i^2/2m$ of a particle in a box scales as $V^{-\frac{1}{3}}$, and the exchange energy according to Eq. (2.3) scales as p_i or as $V^{-\frac{1}{3}}$.) The remaining terms are easily evaluated, giving

$$\begin{aligned} F &= A + \frac{2}{3}E_{kin} + \frac{1}{3}E_{ex} + E_{en} + E_{ee} - E_{en} \\ &= A + \mathcal{O}V + \frac{2}{3}E_{ee} - \frac{1}{3}E_{en}, \end{aligned} \quad (2.29)$$

¹⁷ H. Reiss, *J. Chem. Phys.* **21**, 1209 (1953).

¹⁸ See, for example, R. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, Cambridge, 1956), pp. 58 ff; J. L. Finck, *Thermodynamics from the Classic and Generalized Standpoints* (Bookman Associates, New York, 1955), pp. 67 ff, 108 ff.

from Eq. (2.21). Comparison of this result with Eq. (2.26) indicates that indeed

$$F = N\mu, \quad (2.30)$$

just as for a homogeneous, field-free system.

3. CONVERSION TO REDUCED VARIABLES

Before continuing further, it is convenient to express all quantities in terms of dimensionless variables. For this purpose, we choose the following units of length, momentum, energy, and pressure¹⁹:

$$\begin{aligned} r_0 &= \frac{\hbar^2}{4\pi^2 m e^2} \left(\frac{9\pi^2}{128Z} \right)^{\frac{1}{3}} = \frac{0.468479 \times 10^{-8}}{Z^{\frac{1}{3}}} \text{ cm}, \\ p_0 &= 8me^2/\hbar = 2.53662 \times 10^{-19} \text{ g-cm/sec}, \\ \theta_0 &= p_0^2/2m = 3.53262 \times 10^{-11} \text{ ergs} = 22.0532 \text{ ev}, \end{aligned} \quad (3.1)$$

$$\begin{aligned} \mathcal{P}_0 &= 4\pi\theta_0 p_0^3/\hbar^3 = 24.9321 \times 10^{12} \text{ dynes/cm}^2 \\ &= 24.9321 \text{ megabars}, \end{aligned}$$

and also introduce the quantity

$$\epsilon = (3/32\pi^2 Z^2)^{\frac{1}{3}} = 0.21178271Z^{-\frac{2}{3}}. \quad (3.2)$$

We then let

$$\begin{aligned} x &= r_i/r_0, & p &= p_i/p_0, \\ \theta &= kT/\theta_0, & \chi &= \chi_i/\theta_0. \end{aligned} \quad (3.3)$$

In terms of these variables, Eq. (2.6) for the momentum distribution function can be written

$$n(p; \chi, \theta) = \{1 + \exp[(p^2 - I - \chi)/\theta]\}^{-1}, \quad (3.4)$$

where

$$\begin{aligned} I(p; \chi, \theta) &= -\frac{E_{\text{ex}, i}}{\theta_0} = \frac{1}{2p} \int_0^\infty p' \left\{ \ln \left| \frac{p' + p}{p' - p} \right| \right\} \\ &\quad \times n(p'; \chi, \theta) dp' \end{aligned} \quad (3.5)$$

is the exchange integral. For convenience in later use, we introduce the following momentum integrals (in dimensionless form):

$$G_1(\chi, \theta) = \int_0^\infty n(p; \chi, \theta) dp, \quad (3.6a)$$

$$G_2(\chi, \theta) = \int_0^\infty p^2 n(p; \chi, \theta) dp = p_0^{-3} G_2(\chi, T), \quad (3.6b)$$

$$G_3(\chi, \theta) = \int_0^\infty p^4 n(p; \chi, \theta) dp, \quad (3.6c)$$

$$G_4(\chi, \theta) = \int_0^\infty p^2 I(p; \chi, \theta) n(p; \chi, \theta) dp, \quad (3.6d)$$

$$G_5(\chi, \theta) = -\theta \int_0^\infty p^2 \ln(1-n) dp. \quad (3.6e)$$

¹⁹ Numerical values are based on the table of fundamental constants given by J. W. M. DuMond and E. R. Cohen, Phys. Rev. **82**, 555 (1951).

It is evident physically that $n(p; \chi, \theta)$ tends to zero as p tends to infinity, and in fact it is necessary that n tend to zero more strongly than p^{-5} in order that G_3 (which will be shown to be related to the kinetic energy density) be defined. Under the assumption that this is true, it is not difficult to show from Eq. (3.5) that

$$I(0; \chi, \theta) = G_1(\chi, \theta), \quad (3.7a)$$

and that as p tends to infinity,

$$I(p; \chi, \theta) \sim p^{-2} G_2(\chi, \theta). \quad (3.7b)$$

It follows from Eq. (3.4) that

$$n(p; \chi, \theta) \sim e^{\chi/\theta} \exp(-p^2/\theta). \quad (3.8)$$

It can then be shown with the aid of an integration by parts that

$$\begin{aligned} G_5 &= -\int_0^\infty p^3 n(p) [\partial(p^2 - I - \chi)/\partial p] dp \\ &= \frac{2}{3} G_3 + \frac{1}{3} G_4 - \frac{1}{3} \int_0^\infty \int_0^\infty \frac{p^2 p'^2 n(p) n(p')}{p'^2 - p^2} dp' dp \\ &= \frac{2}{3} G_3 + \frac{1}{3} G_4. \end{aligned} \quad (3.9)$$

It will appear later that this identity establishes Eq. (2.24), and thereby also the expression for the Helmholtz free energy A given in Eq. (2.26) or in Eq. (3.24) below.

Since the density of energy states in phase space is

$$2d\mathbf{p}d\mathbf{r}/h^3 = (8\pi p_0^3/\hbar^3) p^2 dp dx, \quad (3.10)$$

the electron density is

$$\begin{aligned} (8\pi p_0^3/\hbar^3) G_2(\chi, \theta) &= (2\mathcal{P}_0/\theta_0) G_2(\chi, \theta) \\ &= 1.41153 \times 10^{24} G_2 \text{ electrons/cc.} \end{aligned} \quad (3.11)$$

Introducing a further dimensionless variable ϕ related to χ in the following way:

$$\chi = \frac{Ze^2\phi}{\theta_0 r} - \frac{1}{16} = \frac{\phi}{(4\epsilon)^2 x} - \frac{1}{16}, \quad (3.12)$$

the Poisson equation (2.8) can be written

$$d^2\phi/dx^2 = (18/\pi^2 Z^2) x G_2 = 3(4\epsilon)^3 x G_2. \quad (3.13)$$

The problem at hand, then, is first to solve the integral equation (3.4) to obtain the momentum distribution $n(p; \chi, \theta)$ for each of a number of values of the parameter χ at each temperature θ of interest. After evaluating the integral (3.6b) to obtain the electron density as a function of χ (or of ϕ/x), the Poisson equation (3.13) can then be integrated to give ϕ (and hence the potential energy per electron) as a function of x . Solution of Eq. (3.13) is of course subject to two boundary conditions. The first of these follows immediately from Eq. (2.5):

$$\lim_{r \rightarrow 0} r \chi_i = \lim_{r \rightarrow 0} r \theta_0 \chi = Ze^2,$$

TABLE I. Electronic energies for fixed χ .

| | Kinetic energy | Exchange energy ^a | Electron-nuclear energy ^b | Electron-electron Coulomb energy ^a |
|---------------------------------------|----------------------------|---------------------------------------|---|--|
| Electron with momentum p : | $\theta_0 p^2$ | $-\theta_0 I$ | $-\frac{\theta_0}{(4\epsilon)^2 x}$ | $\mu - \theta_0 \chi + \frac{\theta_0}{(4\epsilon)^2 x}$ |
| One electron, averaged over all p : | $\theta_0 \frac{G_3}{G_2}$ | $-\theta_0 \frac{G_4}{G_2}$ | $-\frac{\theta_0}{(4\epsilon)^2 x}$ | $\mu - \theta_0 \chi + \frac{\theta_0}{(4\epsilon)^2 x}$ |
| Per electron, averaged over all p : | $\theta_0 \frac{G_3}{G_2}$ | $-\frac{\theta_0}{2} \frac{G_4}{G_2}$ | $-\frac{\theta_0}{(4\epsilon)^2 x}$ | $\frac{\mu - \theta_0 \chi}{2} + \frac{\theta_0}{2(4\epsilon)^2 x}$ |
| Per unit volume: | $2\mathcal{P}_0 G_3$ | $-\mathcal{P}_0 G_4$ | $-\frac{2\mathcal{P}_0 G_2}{(4\epsilon)^2 x}$ | $\mathcal{P}_0 G_2 \left(\frac{\mu}{\theta_0} - \chi + \frac{1}{(4\epsilon)^2 x} \right)$ |

^a In the case of electron-electron interactions, a factor $\frac{1}{2}$ is involved in passing from energy of one electron to average energy per electron or to energy per unit volume.

^b $\theta_0/(4\epsilon)^2 = Ze^2/r_0$.

or, from Eq. (3.12),

$$\phi(0) = 1. \quad (3.14)$$

Starting with an arbitrary value of the initial slope $\phi'(0)$, integration of Eq. (3.13) is carried forward to a value $x=X$ such that the total number of electrons within the sphere of radius X is equal to the desired number N .²⁰ Using Eqs. (3.11) and (3.13), this leads to the second boundary condition

$$N = 32\pi^2 (r_0 p_0 / h)^3 \int_0^X x^2 G_2 dx = Z \int_0^X x \phi'' dx, \quad (3.15)$$

or, integrating by parts:

$$\phi'(X) = \phi(X)/X + (N-Z)/ZX. \quad (3.16)$$

The boundary having been determined in this manner, the chemical potential (per electron) may be calculated from the expression for the potential energy of an electron at the surface of a spherically symmetric atom of net charge $(Z-N)e$: From Eq. (2.5),

$$\begin{aligned} \mu &= \chi_i(X) - (Z-N)e^2/r_0 X \\ &= \theta_0 \chi X + (N-Z)\theta_0/(4\epsilon)^2 ZX. \end{aligned} \quad (3.17)$$

For any given value of χ , expressions for the various energies and the entropy can be readily found from the various equations already given. For example, from Eqs. (2.14), (3.10), (3.6), and (3.9), the entropy per unit volume is

$$\begin{aligned} \frac{\Delta S/k}{\Delta V} &= \frac{8\pi p_0^3}{h^3 \theta} \left\{ \int_0^\infty p^2 (p^2 - I - \chi) n dp \right. \\ &\quad \left. - \theta \int_0^\infty p^2 \ln(1-n) dp \right\} \\ &= (2\mathcal{P}_0/\theta_0\theta) (G_3 - G_4 - \chi G_2 + G_5) \\ &= (2\mathcal{P}_0/\theta_0\theta) [(5/3)G_3 - \frac{2}{3}G_4 - \chi G_2]. \end{aligned} \quad (3.18)$$

Other results are collected in Table I.

²⁰ For most purposes N is of course numerically equal to Z .

Once a solution of the differential equation (3.13) has been obtained, giving χ as a function of x , total energies and entropy can be calculated. Noting that $\mathcal{P}_0 dV = 4\pi \mathcal{P}_0 r_0^3 x^2 dx = 9\theta_0 x^2 dx / \pi^2 Z$, and using the relations (3.13) and (3.16), the results may be written

$$E_{\text{kin}} = (18\theta_0/\pi^2 Z) \int_0^X x^2 G_3 dx, \quad (3.19)$$

$$E_{\text{ex}} = -(9\theta_0/\pi^2 Z) \int_0^X x^2 G_4 dx, \quad (3.20)$$

$$\begin{aligned} E_{\text{en}} &= -[18\theta_0/\pi^2 Z (4\epsilon)^2] \int_0^X x G_2 dx = -\theta_0 Z (4\epsilon)^{-2} \\ &\quad \times [-\phi'(0) + \phi(X)/X + (N-Z)/ZX], \end{aligned} \quad (3.21)$$

$$\begin{aligned} E_{\text{ee}} &= -(9\theta_0/\pi^2 Z) \int_0^X x^2 \chi G_2 dx + \frac{1}{2} N \mu - \frac{1}{2} E_{\text{en}} \\ &= -\frac{9\theta_0}{\pi^2 Z} \int_0^X x^2 \chi G_2 dx + \frac{1}{2} \theta_0 N \chi X \\ &\quad + \frac{\theta_0 N (N-Z)}{2(4\epsilon)^2 ZX} - \frac{1}{2} E_{\text{en}}, \end{aligned} \quad (3.22)$$

$$\begin{aligned} TS &= (18\theta_0/\pi^2 Z) \int_0^X x^2 [(5/3)G_3 - \frac{2}{3}G_4 - \chi G_2] dx \\ &= (5/3)E_{\text{kin}} + (4/3)E_{\text{ex}} + 2E_{\text{ee}} + E_{\text{en}} - N\mu, \end{aligned} \quad (3.23)$$

$$A = E - TS = -\frac{2}{3}E_{\text{kin}} - \frac{1}{3}E_{\text{ex}} - E_{\text{ee}} + N\mu, \quad (3.24)$$

$$F = N\mu. \quad (3.25)$$

Setting E_{ex} equal to zero, the expressions for TS and A reduce to those given by Brachman²¹ for the temperature-dependent Thomas-Fermi theory.

The pressure may be found either from the virial theorem (2.21):

$$\mathcal{P}V = \frac{2}{3}E_{\text{kin}} + \frac{1}{3}E_{\text{en}} + \frac{1}{3}E_{\text{ee}} + \frac{1}{3}E_{\text{ex}}, \quad (3.26)$$

or (for the case $N=Z$ only), from Eqs. (2.23) and (3.9):

$$\mathcal{P} = \mathcal{P}_0 (2G_5 - G_4)_X = \mathcal{P}_0 [(4/3)G_3 - \frac{1}{3}G_4]_X \quad (3.27)$$

(which can be seen from Table I to be just the virial theorem for a uniform electron gas in field-free space).

It should perhaps be noted that the integral equation (3.4) does not involve Z explicitly. Hence solution of this equation and evaluation of the integrals (3.6) as functions of χ and θ provide results applicable to any element. Solutions of the Poisson equation (3.13) are, however, applicable only to the value of Z for which ϵ was evaluated.

4. SOLUTION AT ABSOLUTE ZERO

At $T=0^\circ\text{K}$, most of the equations of Sec. 3 can be simplified greatly. If P_0 is the value of p at which

²¹ M. K. Brachman, Phys. Rev. 84, 1263 (1951).

$p^2 - I(p; \chi, \theta) - \chi$ vanishes, then

$$n(p; \chi, 0) = \begin{cases} 1, & p < P_0 \\ 0, & p > P_0. \end{cases} \quad (4.1)$$

The exchange integral (3.5) can in this case be easily evaluated, giving:

$$\begin{aligned} I^0(p; \chi) &= \frac{p}{2} \int_0^{P_0/p} y \ln \left| \frac{y+1}{y-1} \right| dy \\ &= P_0 \left[\frac{1}{2} + \frac{1}{4} \left(\frac{P_0}{p} - \frac{p}{P_0} \right) \ln \left| \frac{P_0+p}{P_0-p} \right| \right]. \end{aligned} \quad (4.2)$$

Thus $I^0(0; \chi) = P_0$, $I^0(P_0; \chi) = \frac{1}{2}P_0$, and $I^0(p; \chi) \sim P_0^3/3p^2$, in agreement with Eq. (3.7). From the definition of P_0 , it follows from Eq. (3.12) that

$$\chi = P_0^2 - \frac{1}{2}P_0, \quad (4.3)$$

$$P_0 = \frac{1}{4} \pm (\chi + \frac{1}{16})^{\frac{1}{2}} = \frac{1}{4} \pm (4\epsilon)^{-1}(\phi/x)^{\frac{1}{2}}. \quad (4.4)$$

Since P_0 must be non-negative for physical reasons, the + sign must be used except possibly for $0 \geq \chi \geq -\frac{1}{16}$.

The integrals (3.6) are easily evaluated with the aid of Eqs. (4.2), (3.4), and (4.3):

$$G_1^0(\chi) = P_0, \quad (4.5a)$$

$$G_2^0(\chi) = P_0^3/3, \quad (4.5b)$$

$$G_3^0(\chi) = P_0^5/5, \quad (4.5c)$$

$$G_4^0(\chi) = \frac{P_0^4}{6} + \frac{P_0^4}{4} \int_0^1 (y-y^3) \ln \left| \frac{1+y}{1-y} \right| dy = \frac{P_0^4}{4}, \quad (4.5d)$$

$$\begin{aligned} G_5^0(\chi) &= \lim_{\theta \rightarrow 0} \theta \int_0^\infty p^2 \ln \{ 1 + \exp [(-p^2 + I + \chi) / \theta] \} dp \\ &= \int_0^{P_0} p^2 (-p^2 + I + \chi) dp \\ &= 2P_0^5/15 + P_0^4/12. \end{aligned} \quad (4.5e)$$

The boundary pressure for the case $N=Z$ is, from Eq. (3.27),

$$p^0 = \varphi_0 (4P_0^5/15 - P_0^4/12)_x. \quad (4.6)$$

The differential equation (3.13) may then be written, with the aid of Eq. (4.4), in the well-known form

$$d^2\phi/dx^2 = x[\epsilon \pm (\phi/x)^{\frac{1}{2}}]^3. \quad (4.7)$$

For each solution of this equation, giving P_0 as a function of x , expressions (3.19)–(3.25) for the thermodynamic functions can be evaluated by using the expressions (4.5) for the required G_m^0 .

Plaskett²² has derived an equation differing from (4.7) in that ϵ is replaced by $\frac{3}{2}\epsilon$. This results from his use of an average exchange energy in place of the function (4.2): From Eq. (4.5), this average is $(\frac{1}{4}P_0^4)/(\frac{1}{3}P_0^3) = \frac{3}{4}P_0$, which gives in place of Eqs. (4.3) and (4.4)

$$\chi = P_0^2 - \frac{3}{4}P_0,$$

and

$$P_0 = \frac{3}{8} \pm [\chi + (9/64)]^{\frac{1}{2}}.$$

There is no need for us to make this approximation, and we shall therefore use Eq. (4.7) as it stands.

5. SOLUTION OF THE INTEGRAL EQUATION FOR LARGE POSITIVE χ

At nonzero temperatures, $n(p; \chi, \theta)$ loses its simple step-function form, and the integrals (3.6) can no longer be evaluated analytically. However, for large (positive) χ and/or small θ , the distribution function approximates a step function and one can obtain approximate analytical expressions by a perturbation treatment.

For the case $T=0$, it may be seen from Eq. (4.2) that the exchange integral is a monotonically decreasing function of p . It is reasonable to assume that this is true also in the present case, so that the exponent in Eq. (3.4),

$$H \equiv (p^2 - I - \chi) / \theta, \quad (5.1)$$

is monotonically increasing and (for fixed positive χ) has one and only one zero²³ at some value $p = P (\cong P_0)$. At this point, n equals $\frac{1}{2}$; and for the case with which we are concerned here, the value of n changes rapidly from essentially 1 through $\frac{1}{2}$ to essentially 0 in a very narrow interval about the point P . For purposes of evaluating n , we need to be able to calculate H only in this interval—within which we write

$$H = a_1x + a_2x^2 + a_3x^3 + \dots = y + b_2y^2 + b_3y^3 + \dots, \quad (5.2)$$

in terms of variables

$$x = (p - P) / P, \quad y = a_1x. \quad (5.3)$$

By comparison with Eq. (5.1) it may be seen that the term p^2/θ contributes $2P^2/\theta$ to a_1 and P^2/θ to a_2 . Thus any remaining contributions to a_1 and a_2 , and all of the coefficients a_3, a_4, \dots are due to $I(p; \chi, \theta)$. We shall assume that in the region of interest H can be approximated to sufficient accuracy by retaining only the first three terms of the series (5.2). We now develop expansions for $n = (1 + e^H)^{-1}$ and $1 - n = (1 + e^{-H})^{-1}$. Considering θ to be fixed and P variable (and large) and for brevity keeping at this point only those terms

²² J. S. Plaskett, Proc. Phys. Soc. (London) **A66**, 178 (1953), Sec. 5.

²³ W. Zimmermann, Z. Physik **132**, 1 (1952) discusses a case in which the existence of three zeros is assumed.

which prove to be most important, we obtain

$$n = \frac{e^{-y}}{1+e^{-y}} - \frac{e^{-y}}{(1+e^{-y})^2} [b_2 y^2 + b_3 y^3 + b_2 b_3 y^5] + \frac{2b_2 b_3 y^5 e^{-y}}{(1+e^{-y})^3}, \quad (5.4)$$

$$1-n = \frac{e^y}{1+e^y} + \frac{e^y}{(1+e^y)^2} [b_2 y^2 + b_3 y^3 - b_2 b_3 y^5] + \frac{2b_2 b_3 y^5 e^y}{(1+e^y)^3}. \quad (5.5)$$

The coefficients a_1, a_2, a_3 will be evaluated by equating derivatives of Eqs. (5.2) and (5.1) at $p=P$ ($x=y=0$). (This procedure does not, of course, lead to the *best* cubic approximation to H since it gives nonzero values for a_4, a_5, \dots , but this is an approximation which we must make.) Letting

$$J(p) = 2pI$$

$$= \lim_{\epsilon \rightarrow 0} \left\{ \left[\int_0^{p-\epsilon} + \int_{p+\epsilon}^{\infty} \right] p' \ln \left| \frac{p'+p}{p'-p} \right| n(p') dp' \right\}, \quad (5.6)$$

from Eq. (3.5), and

$$J^{(n)}(p) = d^{(n)}J(p)/dx^{(n)} = a_1^n d^{(n)}J(p)/dy^{(n)} \quad (5.7)$$

(where the differentiation is to be carried out under the integral signs before the limit is taken), the results are

$$\chi = P^2 - J(P)/2P, \quad (5.8)$$

$$a_1 = \theta^{-1} [3P^2 - \chi - J^{(1)}(P)/2P], \quad (5.9)$$

$$2(a_2 + a_1) = \theta^{-1} [6P^2 - J^{(2)}(P)/2P], \quad (5.10)$$

$$6(a_3 + a_2) = \theta^{-1} [6P^2 - J^{(3)}(P)/2P]. \quad (5.11)$$

In evaluating the integrals $J^{(n)}(P)$ and also the integrals (3.6) it is evident that we have to do with integrals of the form

$$\int_0^{\infty} f(p)n(p)dp = \int_0^P f(p)dp + \int_P^{\infty} f(p)ndp - \int_0^P f(p)(1-n)dp. \quad (5.12)$$

In the last two integrals, we use the expressions (5.4) and (5.5). Although these are accurate only near $p=P$ ($y=0$), they are so small elsewhere that we may use

$$\chi = P^2 - \frac{P}{2} - \frac{P}{a_1^2} \left\{ \mathcal{G}_{110} + \left[\frac{2a_2}{a_1} - 1 \right] \{ \mathcal{G}_{111} + \mathcal{G}_{110} [\frac{1}{2} - \ln(2a_1)] \} \right\}$$

then without great error throughout the entire range of the integrals—and may even replace the lower limit 0 by $-\infty$. If $F(y)$ is the form which $f(p)$ takes when the change of variable (5.3) is made, then for the sum of the last two integrals in Eq. (5.12) we may write approximately

$$\begin{aligned} & (P/a_1) \int_0^{\infty} F(y)n(y)dy - (P/a_1) \int_0^{\infty} F(-y)[1-n(-y)]dy \\ & \cong \frac{P}{a_1} \int_0^{\infty} [F(y) - F(-y)] \left[\frac{e^{-y}}{(1+e^{-y})} - \frac{b_3 y^3 e^{-y}}{(1+e^{-y})^2} \right] dy \\ & - \frac{P}{a_1} \int_0^{\infty} [F(y) + F(-y)] \frac{b_2 y^2 e^{-y}}{(1+e^{-y})^2} \\ & \quad \times \left[1 + b_3 y^3 - \frac{2b_3 y^3}{1+e^{-y}} \right] dy. \quad (5.13) \end{aligned}$$

[In the case of $J^{(n)}(P)$, the lower limit 0 must be replaced by ϵ , and a limiting process carried out after the integrals have been evaluated.] It turns out that the functions $F(y)$ encountered are mostly powers of y or $\ln y$. Thus we shall encounter integrals of the form

$$\mathcal{G}_{jkl} = \int_0^{\infty} \frac{y^j e^{-y} (\ln y)^l dy}{(1+e^{-y})^k}, \quad (5.14)$$

$$\mathcal{G}_{-jk} = \int_1^{\infty} \frac{e^{-y} dy}{y^j (1+e^{-y})^k}. \quad (5.15)$$

These integrals can be evaluated by using series expansions and the following relations obtained by partial integration (for $j \geq 1$):

$$\begin{aligned} \mathcal{G}_{j20} &= j \mathcal{G}_{(j-1)10}, \\ 2\mathcal{G}_{j30} &= j \mathcal{G}_{(j-1)20} + \mathcal{G}_{j20}, \\ \mathcal{G}_{j21} &= j \mathcal{G}_{(j-1)11} + \mathcal{G}_{(j-1)10}. \end{aligned} \quad (5.16)$$

In particular,

$$\begin{aligned} \mathcal{G}_{110} &= \pi^2/12, & \mathcal{G}_{310} &= 5.682197, \\ \mathcal{G}_{020} &= \frac{1}{2}, & \mathcal{G}_{111} &= 0.449043, \\ \mathcal{G}_{-11} &= 0.180628, & \mathcal{G}_{-31} &= 0.086391. \end{aligned} \quad (5.17)$$

Applying Eqs. (5.12)–(5.17) to Eqs. (5.8)–(5.11), we obtain after rather lengthy calculations the following results (keeping in each case only the leading terms in a $1/P$ expansion):

$$= P^2 - \frac{P}{2} - \frac{P}{a_1^2} \left\{ -0.038 + 1.721 \frac{a_2}{a_1} + 0.822 \left(1 - 2 \frac{a_2}{a_1} \right) \ln(2a_1) \right\}, \quad (5.18)$$

$$a_1 = \frac{P}{\theta} \left[2P + \frac{1}{2} \ln(2a_1) - \frac{1}{2} - \mathcal{J}_{-11} + \frac{1}{2} \int_0^1 \frac{(e^y - 1) dy}{y(e^y + 1)} + \frac{2\mathcal{J}_{110}a_3}{a_1^3} \right] = (P/\theta) \left(2P + \frac{1}{2} \ln(2a_1) - 0.437 + 1.64a_3a_1^{-3} \right), \quad (5.19)$$

$$a_2 = \frac{P}{\theta} \left[P - \frac{1}{4} \ln(2a_1) + \frac{5}{8} + \frac{1}{2} \mathcal{J}_{-11} - \frac{1}{4} \int_0^1 \frac{(e^y - 1) dy}{y(e^y + 1)} + \frac{a_2 \mathcal{J}_{020}}{2a_1} - \frac{a_3 \mathcal{J}_{110}}{a_1^3} \right] \\ = (P/\theta) \left[P - \frac{1}{4} \ln(2a_1) + 0.594 - 0.822a_3a_1^{-3} \right] \div \left(1 - \frac{1}{4} P/\theta a_1 \right), \quad (5.20)$$

$$a_3 = -\frac{Pa_1^2}{3\theta} \left[\mathcal{J}_{-31} + \frac{1}{2} \int_0^1 \frac{(1 - e^y) + \frac{1}{2} y(1 + e^y) dy}{y^3(1 + e^y)} - \frac{a_3 \mathcal{J}_{020}}{a_1^3} \right] = -(0.0355Pa_1^2/\theta) \div \left(1 - \frac{1}{6} P/\theta a_1 \right). \quad (5.21)$$

For given values of P and θ , a_1 can be found by substituting Eq. (5.21) into Eq. (5.19) and solving by iteration; a_2 , a_3 , and χ can then be calculated easily. This determines H from Eq. (5.2)—and therefore also I and n from Eq. (5.1)—as a function of P (or χ) and θ .

There remains the problem of calculating the momentum integrals G_2 , G_3 , and G_4 from Eq. (3.6). The first two of these involve only a straightforward application of Eq. (5.13), and the results are:

$$G_2 = \frac{P^3}{3} + \frac{P^3}{a_1^2} \left[4\mathcal{J}_{110} \left(1 - \frac{a_2}{a_1} \right) + \frac{8\mathcal{J}_{310}a_3}{a_1^3} \left(\frac{a_2}{a_1} - 2 \right) \right], \quad (5.22)$$

$$G_3 = \frac{P^5}{5} + \frac{P^5}{a_1^2} \left[4\mathcal{J}_{110} \left(2 - \frac{a_2}{a_1} \right) + \frac{8\mathcal{J}_{310}a_3}{a_1^3} \left(\frac{a_2}{a_1} - 4 \right) \right]. \quad (5.23)$$

In order to evaluate G_4 , we note by comparison of Eqs. (5.1) and (5.2) that, for small y ,

$$I = p^2 - \chi - \theta(y + b_2 y^2 + b_3 y^3). \quad (5.24)$$

Using this expression for $f(p)$ in the last two integrals of Eq. (5.12), we obtain

$$G_4 = \int_0^P p^2 I dp + G_3 - \frac{P^5}{5} - \chi \left(G_2 - \frac{P^3}{3} \right) - \frac{2\theta P^3}{a_1} \\ \times (\mathcal{J}_{110} - 3b_3 \mathcal{J}_{310}). \quad (5.25)$$

It may be easily seen from Eq. (3.5) that

$$\int_0^P p^2 I dp = \int_0^\infty p^2 I^0 n dp, \quad (5.26)$$

where by I^0 is meant the expression (4.2) with P_0 replaced by P . Using Eq. (5.12) once again gives [see Eq. (4.5d)]

$$\int_0^P p^2 I dp = \frac{P^4}{4} + \frac{P}{2} \left(G_2 - \frac{P^3}{3} \right) + \frac{P^4}{a_1^2} \\ \times (\mathcal{J}_{111} - \mathcal{J}_{110} \ln 2a_1). \quad (5.27)$$

With the results (5.18), (5.22), and (5.23), we obtain

finally

$$G_4 = \frac{P^4}{4} + \frac{P^4}{a_1^2} \left\{ \mathcal{J}_{110} \left(4P - \frac{2\theta a_1}{P} + 4 - \frac{4a_2}{a_1} - \ln 2a_1 \right) \right\} \\ + \frac{P^4}{a_1^2} \left\{ \mathcal{J}_{111} - \mathcal{J}_{310} \frac{a_3}{a_1^3} \left(16P - \frac{6\theta a_1}{P} \right) \right\}. \quad (5.28)$$

In the extreme limit $P \rightarrow \infty$ (for fixed θ), these results reduce [using Eq. (4.5)] to:

$$a_1 = 2P_0^2/\theta, \\ a_2 = P_0^2/\theta, \\ a_3 a_1^{-3} = -0.0178/P_0, \\ P = P_0(1 + 0.103\theta^2 P_0^{-5}), \quad (5.29)$$

$$G_2 - G_2^0 = \pi^2 \theta^2 / 24 P_0, \\ G_3 - G_3^0 = \pi^2 \theta^2 P_0 / 8, \\ G_4 - G_4^0 = \theta^2 \{ -(\pi^2/24) \ln(4P_0^2/\theta) + 0.804 \}. \quad (5.30)$$

The results (5.30) will be used in Sec. 8 as a guide in making analytic fits to results calculated as described in Sec. 7.

6. SOLUTION OF THE INTEGRAL EQUATION FOR LARGE NEGATIVE χ

When $-\chi/\theta \gg 1$, it is evident from Eq. (3.4) that $n(p; \chi, \theta) \ll 1$ for all p . It follows from Eq. (3.5) that $I(p; \chi, \theta)$ is negligible compared with $p^2 - \chi$, so that Eq. (3.4) reduces to the Maxwellian distribution

$$n(p; \chi, \theta) = e^{\chi/\theta} \exp(-p^2/\theta). \quad (6.1)$$

From Eq. (3.6), we readily obtain the asymptotic results:

$$G_1(\chi, \theta) = e^{\chi/\theta} \int_0^\infty \exp(-p^2/\theta) dp = \frac{1}{2}(\pi\theta)^{1/2} e^{\chi/\theta}, \quad (6.2a)$$

$$G_2(\chi, \theta) = e^{\chi/\theta} \int_0^\infty p^2 \exp(-p^2/\theta) dp = \frac{1}{4}(\pi\theta^3)^{1/2} e^{\chi/\theta}, \quad (6.2b)$$

$$G_3(\chi, \theta) = e^{\chi/\theta} \int_0^\infty p^4 \exp(-p^2/\theta) dp = \frac{3}{8}(\pi\theta^5)^{1/2} e^{\chi/\theta}. \quad (6.2c)$$

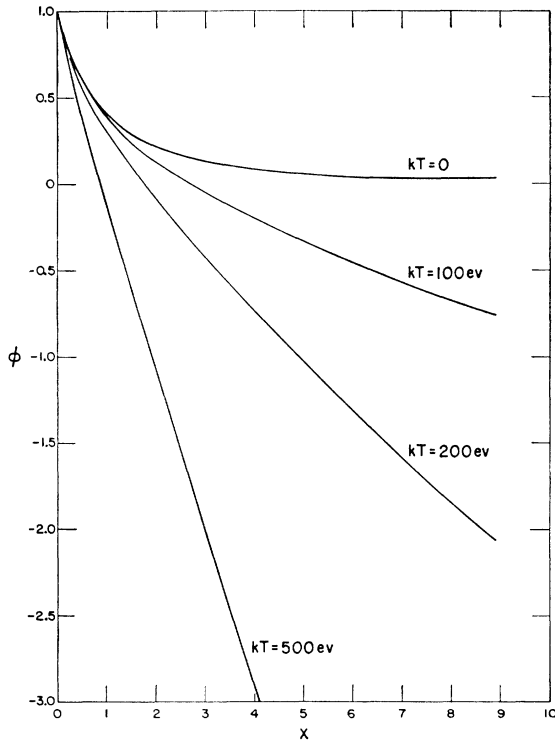


FIG. 1. The "potential" function $\phi(x)$ for iron at normal density $\rho_0 = 7.85$ g/cc. (The curve for $kT = 500$ eV extends to $\phi = -7.086$ at the atom boundary.)

With the changes of variable

$$r \cos\phi = p\theta^{-1/2}, \quad r \sin\phi = p'\theta^{-1/2},$$

we obtain from Eqs. (3.5) and (6.1)²⁴:

$$G_4(\chi, \theta) = \frac{1}{4}\theta^2 e^{2\chi/\theta} \int_0^\infty r^3 \exp(-r^2) dr \quad (6.2d)$$

$$\times \int_0^{\frac{1}{2}\pi} (\sin 2\phi) \ln |\tan(\phi + \frac{1}{4}\pi)| d\phi$$

$$= \frac{1}{4}\theta^2 e^{2\chi/\theta} \cdot \frac{1}{2} \cdot \frac{1}{2}\pi = \frac{1}{16}\pi\theta^2 e^{2\chi/\theta}.$$

7. SOLUTION OF THE INTEGRAL EQUATION FOR INTERMEDIATE χ

For the intermediate case in which $|\chi/\theta|$ is not large, neither of the previously given analytical solutions of the integral equation is adequate, and numerical methods must be used for sufficient accuracy. Such solutions have been obtained by an iterative scheme with the aid of IBM type 701 digital computers. For these purposes an integration mesh of 49 points $p_i = p_0, p_1, p_2, \dots, p_{48}$ was used. The value of p_{48} was chosen such that $n(p_{48}) \cong 10^{-8}n(0)$, and p_0 was chosen to be either zero or such that $1 - n(p_0) \cong 10^{-6}$ to 10^{-8} . Direct evalua-

²⁴ The value of the ϕ integral is given in B. de Haan, *Nouvelles Tables d'Intégrales définies* (G. E. Stechert and Company, New York, 1939), Table 309, No. 6.

tion of the exchange integral $I(p_i)$ from Eq. (3.5) by numerical quadrature [using values of $n(p_i)$ from the preceding cycle] is possible, but is complicated by the presence of the singularity in the integrand at $p' = p$. Consequently, the following analytic scheme was used.

Case I. Small χ .—In the case of (algebraically) small χ , $n(p)$ does not approximate a step function and p_0 must be chosen equal to zero. At each cycle in the iteration, $n(p_i)$ was calculated for all values of i from Eq. (3.4). For this purpose it was of course necessary to know $I(p_i)$. This was computed from Eq. (3.5) by approximating the values $n(p_i)$ from the preceding cycle with the function

$$n(p') = a_{2j} + b_{2j}p', \quad p_{2j-2} \leq p' < p_{2j}. \quad (7.1)$$

Here b_{2j} was set equal to the slope of the chord from (p_{2j-2}, n_{2j-2}) to (p_{2j}, n_{2j}) , and a_{2j} was then chosen so that the area under the line segment defined by Eq. (7.1) was equal to the area found by applying Simpson's rule to the three ordinates $n_{2j-2}, n_{2j-1}, n_{2j}$. This choice of the coefficients gives the correct value (to the accuracy of Simpson's rule) for the total area $G_1 = \int n dp$, and hence from Eq. (3.7a) the correct value of $I(0)$. Using Eq. (7.1) in Eq. (3.5), the exchange integral may be written in the form

$$I(p_i) = \frac{1}{2} \sum (a_{2j} - a_{2j+2}) p_{2j} I_1(p_{2j}/p_i) + \frac{1}{2} \sum (b_{2j} - b_{2j+2}) p_{2j}^2 I_2(p_{2j}/p_i), \quad (7.2)$$

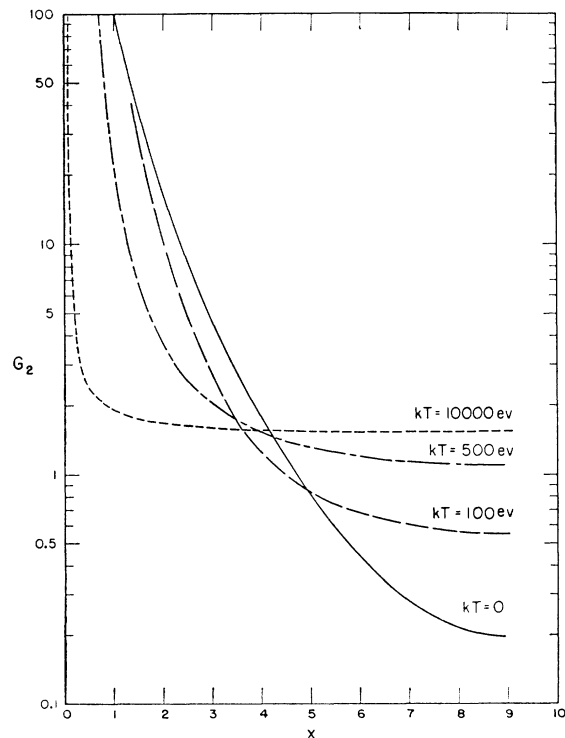


FIG. 2. Electron density as a function of radius for iron at normal density $\rho_0 = 7.85$ g/cc.

where $a_{2j}=b_{2j}=0$ for $j>24$, and the integrals

$$I_n(y) = y^{-n} \int_0^y x^n \ln \left| \frac{x+1}{x-1} \right| dx \quad (7.3)$$

are easily evaluated analytically.

Iteration was continued until all values $n(p_i)$ were essentially constant, and the G integrals (3.6) were then evaluated numerically.

Case II. Large χ .—In the case of large χ , $n(p)$ approximates more or less closely to a step function, and the calculations were modified to avoid excessive loss of significant figures by calculating

$$1-n = \{1 + \exp[-(p^2 - I - \chi)/\theta]\}^{-1} \quad \text{for } i \leq 24, \quad (7.4)$$

and

$$n = \{1 + \exp[(p^2 - I - \chi)/\theta]\}^{-1} \quad \text{for } i \geq 24.$$

The value of p_{24} could usually be taken equal to P_0 , Eq. (4.4), and the entire range of values $p_0 \rightarrow p_{48}$ was taken only such that the values calculated from Eq. (7.4) were appreciable. The straight-line approximation of Eq. (7.1) was applied to values of $n-1$ rather than n for $i \leq 24$, and the G integrals evaluated in the form of Eq. (5.12).

Calculations have been made for a number of values of χ and θ . The numerical results for large and small χ are in good agreement with the analytical results of Secs. 5 and 6, respectively, and in all cases verify the

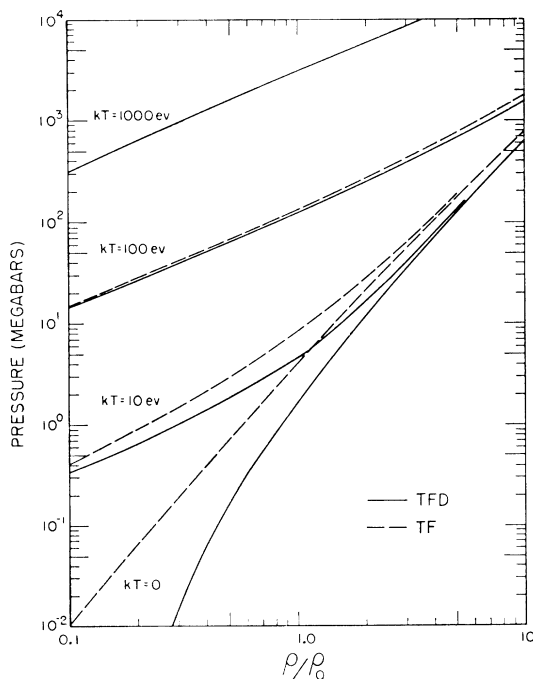


FIG. 3. Comparison of the electron pressure at the boundary of the iron atom as calculated with (TFD) and without (TF) exchange. ($\rho_0=7.85$ g/cc).

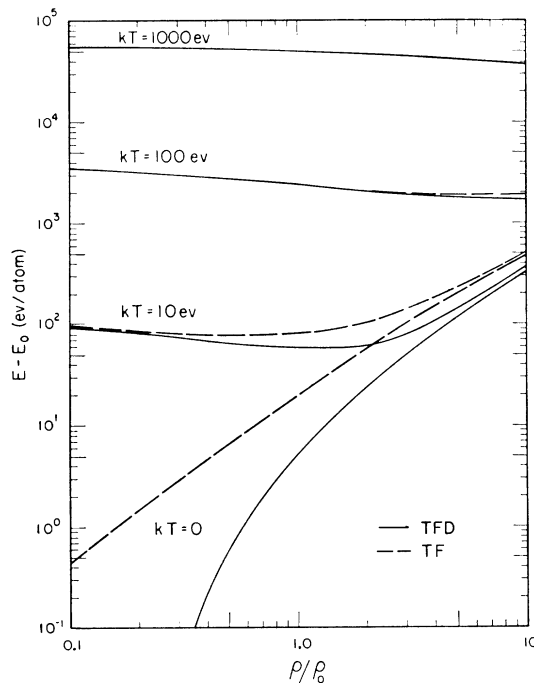


FIG. 4. Comparison of the electron energy of the iron atom relative to the energy at $T=\theta=0$ as calculated with (TFD, $E_0=-43$ 285 eV/atom) and without (TF, $E_0=-41$ 886 eV/atom) exchange. ($\rho_0=7.85$ g/cc).

relation (3.9)—which in view of Eq. (3.27) is equivalent to the virial theorem for a uniform field-free electron gas, and which is responsible for the expression (2.26) for the Helmholtz free energy A .

8. SOLUTION OF THE POISSON EQUATION

Calculation of equation-of-state data requires numerical integration of the Poisson equation (3.13), which involves the electron density G_2 . For this purpose the numerical results of Sec. 7 were fit with analytic functions of the form

$$G_2^+ = \frac{1}{3} P_0^3 + (\pi^2 \theta^2 / 24 P_0) F^+(P_0, \theta) \quad (8.1)$$

for large χ , and

$$G_2^- = \frac{1}{4} (\pi \theta^3)^{1/2} e^{\chi/\theta} F^-(\chi, \theta) \quad (8.2)$$

for small χ . The functions F^+ and F^- were chosen such as to tend asymptotically to unity, so as to agree with the results (5.30) and (6.2). For use in evaluating the thermodynamic functions (3.19)–(3.27), similar analytic fits were made for G_3 and G_4 . (In all three cases, discontinuities were avoided by making a gradual change-over from G^+ to G^- over a range of values of P_0 with the aid of an exponential weighting function.)

As with the work of previous investigators for the case $T=0$,²⁵ numerical integration of Eq. (3.13) was

²⁵ N. Metropolis and J. R. Reitz, J. Chem. Phys. **19**, 555 (1951); also reference 5.

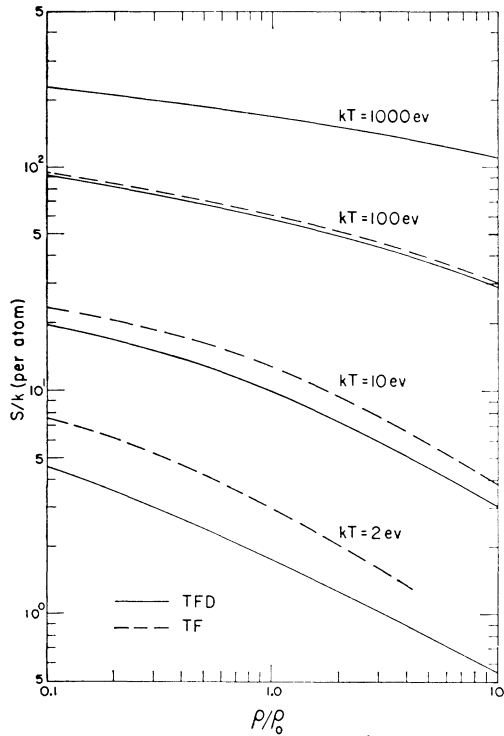


FIG. 5. Comparison of the electron entropy of the iron atom as calculated with (TFD) and without (TF) exchange. ($\rho_0 = 7.85$ g/cc).

begun with the aid of a series solution of the form

$$\phi = \sum_{i=0}^{11} a_i x^{i/2}. \quad (8.3)$$

Temperature-correction terms were added to the expressions given by Metropolis and Reitz for the a_i ; however, Eq. (8.3) was used only out to such values of x that the temperature corrections were negligible. Integration was advanced beyond these values of x by a difference method. The boundary value $x=X$ was determined from Eq. (3.16), and as a check N was calculated by numerical evaluation of the integral (3.15). The value of N thus computed usually agreed with the value used in Eq. (3.16) to five or six significant figures.

Evaluation of the necessary integrals for calculating the thermodynamic functions (3.19)–(3.26) was carried out analytically for the region in which the series solution was used, and by numerical quadrature elsewhere. The pressure was calculated from Eq. (3.27); values thus obtained (for $N=Z$) agreed with those given by the virial theorem (3.26) (except in the case of very low pressure where serious significant-figure loss was involved) usually within 0.1%—which is all that can be expected from the accuracy of the analytic fits used

for the G functions.²⁶ Graphical differentiation of calculated values of E and A in a few specific cases has given results in agreement with Eq. (2.20) within the error of the graphs. Finally, calculations made for fixed Z but several different values of N have shown that the calculated value of $(\partial A/\partial N)_{T,V}$ agrees with the value of μ found from Eq. (3.17); see Eq. (2.19).

Extensive equation-of-state calculations have been carried out for a number of different elements, using IBM Type 701 digital computers. As an example, some results for iron are given in Figs. 1 to 6. Figure 1 shows for the normal-density iron atom at several temperatures the function $\phi(x)$, which is related to the potential distribution within the atom through Eqs. (2.5), (3.3), and (3.12). Figure 2 shows for some corresponding cases the form of the electron-density function G_2 [see Eq. (3.11)]. It may be noted that for a temperature of 10 000 volts, the electron density is essentially constant throughout the volume of the atom—indicating, as one would expect, practically complete ionization. Figures 3 to 5 compare some equation-of-state results for iron with the corresponding values as

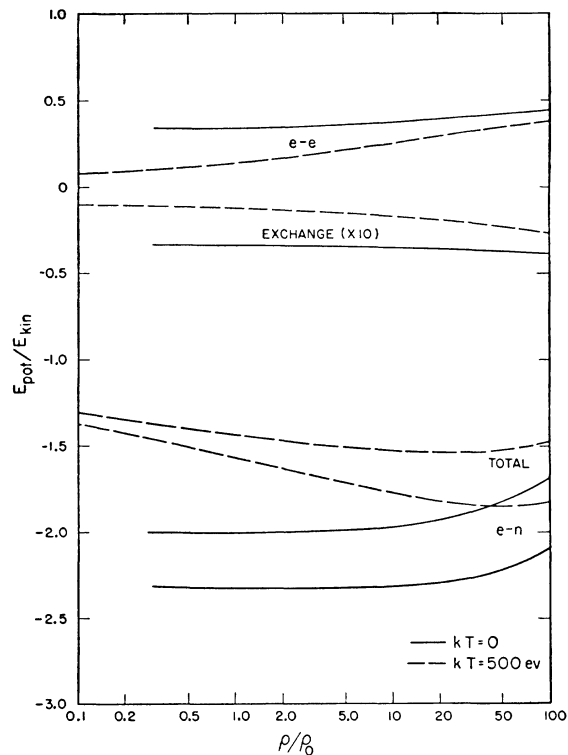


FIG. 6. The distribution of energy among the various forms of potential energy for the iron atom at temperatures of zero and 500 volts. In the case of exchange energy, $10 E_{ex}/E_{kin}$ has been plotted for greater clarity.

²⁶ In the case $T=0$ where analytic fits were not involved, the ratio of the virial-theorem to the boundary-value pressure was about 1.00028, independent of Z or the value of x to which (8.3) was used. The departure from a value unity is probably due to errors inherent in the numerical methods used.

TABLE II. Comparison of calculation with experimental total ionization energies (ev/atom).

| Z | E_{kin} | E_{ex} | E_{en} | E_{ee} | E_{calc} | E_{exp}^a | $E_{\text{calc}}/E_{\text{exp}}$ |
|-----|------------------|-----------------|-----------------|-----------------|-------------------|--------------------|----------------------------------|
| 1 | 28.07 | -8.34 | -58.65 | 10.85 | -28.07 | -13.595 | 2.065 |
| 2 | 126.7 | -23.7 | -277.4 | 47.6 | -126.7 | -78.983 | 1.604 |
| 3 | 312.4 | -44.3 | -695.4 | 115.0 | -312.4 | -203.428 | 1.536 |
| 4 | 596.3 | -69.6 | -1339.7 | 216.8 | -596.3 | -399.033 | 1.494 |
| 5 | 987.5 | -99.1 | -2231.5 | 355.6 | -987.5 | -670.790 | 1.472 |
| 6 | 1494 | -133 | -3390 | 535 | -1494 | -1029.81 | 1.451 |
| 7 | 2122 | -170 | -4830 | 755 | -2122 | -1485.64 | 1.428 |
| 8 | 2878 | -210 | -6564 | 1018 | -2878 | -2043.28 | 1.409 |
| 9 | 3768 | -254 | -8611 | 1329 | -3768 | -2715 | 1.388 |
| 12 | 7286 | -404 | -16 716 | 2548 | -7286 | -5448 | 1.337 |
| 13 | 8757 | -461 | -20 110 | 3056 | -8757 | -6600 | 1.327 |

^a Experimental values are from C. E. Moore, *Atomic Energy Levels*, U. S. National Bureau of Standards Circular No. 467 (U. S. Government Printing Office, Washington, D. C., 1952), Vol. II, p. xxviii. (The ionization potential of the final electron for $Z=9, 12,$ and 13 was estimated from that for $Z=8$).

calculated on the basis of the temperature-dependent Thomas-Fermi theory (exchange effects omitted).²⁷ It may be seen that the differences are quite large at low temperatures, become rather small at $kT=100$ ev, and are negligible for $kT \geq 1000$ ev. In Fig. 6 the partition of potential energy among the various forms is shown for iron as a function of density and temperature. At zero temperature and low density the total potential energy is equal to $-2E_{\text{kin}}$ in agreement with the virial theorem.

The calculated partition of energy among the various forms for the special case $T=\Phi=0$ is given in Table II

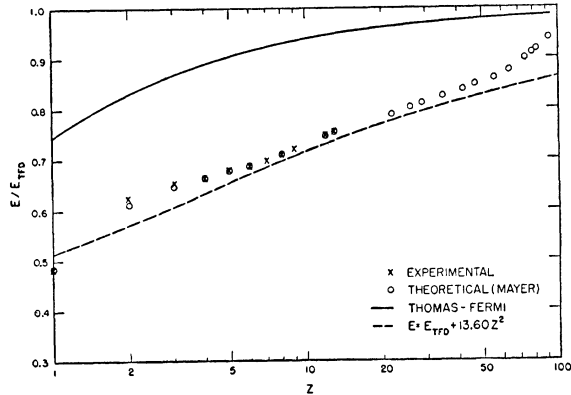


FIG. 7. Comparison of various theoretical and experimental values for the energies of the isolated zero-temperature atoms with the values calculated from the Thomas-Fermi-Dirac theory.

²⁷ R. Latter, reference 7. More accurate values than those which can be read from the graphs in this paper have been obtained directly from the author.

for low- Z elements, together with experimental total ionization energies. The agreement between calculated and experimental values is quite poor, particularly (as is to be expected) for the smallest Z . This is shown also in Fig. 7, where comparison is extended to higher Z with the aid of theoretical values calculated by Mayer using screening constants together with energy levels for an electron in a Coulomb field.²⁸ Also shown in the figure is a curve representing the Thomas-Fermi (no-exchange) values²⁷

$$E_{\text{TF}} = -20.915Z^{7/3}. \quad (8.4)$$

The large errors in the values given by the statistical theories are due primarily to the fact that these theories predict infinite electron densities at the nucleus, whereas quantum mechanics indicates the density should remain finite. The appropriate correction to the TFD energy has been calculated by Scott²⁹ to be

$$Z^2e^2/2a_0 = 13.60Z^2 \text{ ev}. \quad (8.5)$$

As shown in Fig. 7, this correction markedly improves the agreement with experiment. (The poor agreement with Mayer's values at high Z is due to the fact that Mayer included relativistic effects in his calculations.)

9. ACKNOWLEDGMENTS

The authors are indebted for numerous helpful discussions and suggestions to Dr. R. Peierls in connection with the early work and to Dr. H. L. Mayer and Dr. R. F. Christy during the later work.

²⁸ H. Mayer (private communication).

²⁹ J. M. C. Scott, *Phil. Mag.* **43**, 859 (1952).