

## Equations of State of Elements Based on the Generalized Fermi-Thomas Theory\*

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The Fermi-Thomas model has been used to derive the equation of state of matter at high pressures and at various temperatures. Calculations have been carried out both without and with the exchange terms. Discussion of similarity transformations lead to the virial theorem and to correlation of solutions for different  $Z$  values.

### I. INTRODUCTION

THE Fermi-Thomas statistical model of the atom has been used by several investigators<sup>1</sup> for approximate calculations of potential fields and charge densities in metals as a function of lattice spacing. The method has also served as a starting point for the study of the behavior of matter under extremely high pressures as found, for example, in stars.

In its original form, the theory makes several simplifying assumptions: the effect of exchange forces is not taken into account, and the temperature of electrons and nuclei is taken as zero degrees absolute,  $T=0$ . With these simplifications, a set of universal potential functions may be found, applicable to all atomic numbers,  $Z$ , by a simple change in scale of linear dimensions.

Dirac<sup>2</sup> has extended the theory to include the effects of exchange forces. However, the solutions of the modified equation do not lend themselves to the above mentioned similarity transformation and it is necessary to obtain separate solutions for each  $Z$ .

Marshak and Bethe<sup>3</sup> have carried through a perturbation treatment of the simple Fermi-Thomas equation to include temperatures corresponding to several electron volts.

In the following, we present first a set of solutions for the simple Fermi-Thomas equation without exchange forces and for  $T=0$ . Although these numerical solutions are known, they have been calculated again because they are the unperturbed solutions in subsequent perturbation calculations. Hence, rather precise values are needed. A set of solutions was given for the case with exchange effects, but with  $T=0$  as before, for several  $Z$  values

by Slater and Krutter and by Jensen. To make more accurate interpolation possible we have obtained further solutions for  $Z=6$  and 92. The various solutions for a given  $Z$  correspond to a series of atomic volumes. The value of the potential at the boundary is simply related to the pressure. Consequently a pressure-volume (or -density) relation can be obtained for that element. These new solutions with previously calculated ones<sup>4</sup> permit rather reliable interpolation for  $P-v$  relations corresponding to any  $Z$  value. A set of numerical solutions is also given for the perturbation problem corresponding to non-zero temperatures. Finally solutions are given for the case of very high temperatures where the perturbation treatment is no longer valid and the complete equation must be considered.

### II. SIMPLE FERMI-THOMAS METHOD

We consider first the simple Fermi-Thomas equation without exchange effects and for temperature,  $T=0$ ,

$$d^2\phi/dx^2 = \phi^{3/2}/x^{3/2}. \quad (1)$$

This equation is derived with the assumption that at each point in coordinate space there exists a relation between the electron density  $\rho_e$  and the potential  $V$ , namely

$$\rho_e = 8\pi/3h^3 [2m(E - eV)]^{3/2}, \quad (1a)$$

where  $m$  is the electronic mass and  $E$  the total energy. This relation is in turn obtained from the postulate that the electron wave functions in a small volume element behave like plane waves and that the electrons satisfy the Pauli exclusion principle. Spherical symmetry is assumed;  $x$  is the distance from the nucleus measured in units of

$$\mu = a_0(9\pi^2/128Z)^{1/3} = 0.88534a_0/Z^{1/3}, \quad (1b)$$

where  $a_0$  is the Bohr radius for hydrogen.  $\phi$  is essentially the potential multiplied by  $r = \mu x$ ; more precisely

$$Ze^2\phi = (E_0 - eV)r, \quad (2)$$

where  $E_0$  is the maximum total energy.

<sup>4</sup> H. Jensen, G. Meyer-Gossler and H. Röhde, *Zeits. f. Physik* **110**, 277 (1938); see also, J. C. Slater and H. M. Krutter, reference 1.

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<sup>1</sup> J. C. Slater and H. M. Krutter, *Phys. Rev.* **47**, 559 (1935); H. Jensen, *Zeits. f. Physik* **111**, 373 (1938) and additional references given there.

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

<sup>3</sup> R. E. Marshak and H. A. Bethe, *Ap. J.* **91**, 239 (1940).

TABLE I. Coefficients of the series solution for the Fermi-Thomas equation.  $a_2$  is the initial slope. See Eq. (4).

$a_3 = \frac{4}{3}$
$a_4 = 0$
$a_5 = \frac{2}{5}a_2$
$a_6 = \frac{1}{3}$
$a_7 = \frac{3}{70}a_2^2$
$a_8 = \frac{2}{15}a_2$
$a_9 = \frac{2}{27} - \frac{1}{252}a_2^3$
$a_{10} = \frac{1}{175}a_2^2$
$a_{11} = \frac{31}{1485}a_2 + \frac{1}{1056}a_2^4$

The boundary conditions may be written

$$\phi(0) = 1 \quad (3)$$

and at the surface of the atom, since the potential gradient is zero,

$$d\phi/dx = \phi/x. \quad (3a)$$

In an actual crystal, the solutions of spherical symmetry are, of course, not strictly valid. It is more appropriate to surround each nucleus with a polyhedron containing an average number of electrons sufficient to neutralize the nuclear charge.

In many cases, the polyhedron may be replaced in good approximation by a sphere. Then condition (3a) is valid on the surface of this sphere and the radius  $R (= \mu x_0)$  is defined as the atomic radius. It is to be noted that use of this procedure need not be restricted to crystals of pure elements.

$\phi$  may be expanded about the origin in a semi-convergent power series of the form

$$\phi = 1 + a_2x + a_3x^{\frac{1}{2}} + a_4x^2 + \dots \quad (4)$$

Once a value is selected for the initial slope, i.e.,  $a_2$ , the remaining coefficients are determined. Expressions for the first few coefficients in terms of  $a_2$  are given in Table I. For a particular value of  $a_2$ ,  $\phi$  approaches the  $x$ -axis asymptotically. This solution corresponds to the free atom. For numerically smaller initial slopes, solutions are obtained for atoms of finite radius. Numerically greater initial slopes yield solutions for ions.

For the numerical integration it is convenient to introduce a change of independent variable,

$$x = w^2/2.$$

This, in effect, makes the interval for each step of the numerical integration conveniently small near

the origin where  $\phi$  changes appreciably, and automatically increases the interval farther out where the function changes more slowly. To initiate the numerical integration routine, the series given by (4) is rewritten in terms of  $w$ ; it is evaluated at two points  $w=0.88$  and  $w=0.92$ , hence the derivative is obtained at  $w=0.90$ . This procedure is more accurate than the evaluation of the derivative from the differentiation of the series. Intervals are taken as  $\Delta w=0.04$ . The error in each step is  $<0.00002_5$  in  $\phi$ .

In Table II, numerical solutions are given corresponding to eight values of the initial slope.  $\phi$  is given at intervals  $\Delta w=0.08$ . These values are frequent enough for most purposes; if values for intermediate  $w$  values are desired, quadratic interpolation is adequate.

In Table III the values of  $a_2$  are given corresponding to these solutions together with values for the atomic radius  $x_0$  and for  $\phi(x_0)$ . The last two solutions, in which  $\phi$  reaches zero, correspond to ions.

Finally one can obtain a pressure-volume relation based on this model with the aid of the following virial theorem,<sup>5</sup>

$$\left(\frac{3}{2}\right)Pv = \text{kinetic energy} + \left(\frac{1}{2}\right)(\text{potential energy}), \quad (5)$$

where  $P$  is pressure (dynes/cm<sup>2</sup>) and

$$v = (4\pi/3)(\mu x_0)^3 \text{ cm}^3,$$

the volume. One can easily show that

$$Pv = (e/15)(Z^2e^2/\mu)x_0^{1/2}\phi^{5/2}(x_0). \quad (6)$$

Thus, having chosen a  $Z$  value, one can substitute values for  $x_0$  and  $\phi(x_0)$  from Table III and obtain a series of points on a  $P-v$  diagram in this approximation. We shall return to a more complete discussion of equations of state after we have discussed the effects of exchange.

### III. FERMI-THOMAS-DIRAC EQUATION

Dirac<sup>2</sup> has introduced modifications to the original Fermi-Thomas theory to include effects of exchange. Instead of Eq. (1) we have now to consider

$$d^2\psi/dx^2 = x(\epsilon + \psi^{\frac{1}{2}}/x^{\frac{1}{2}})^3. \quad (7)$$

$x$  has the same meaning as before,

$$\epsilon = (3/32\pi^2)^{\frac{1}{2}}Z^{-\frac{1}{2}} = 0.211873Z^{-\frac{1}{2}}.$$

The potential without exchange effects, denoted by  $V_0$ , is connected with  $\psi$  by the relation

$$eV_0 = E_0 + 2me^4/h^2 - Ze^2\psi/\mu x.$$

Equation (7) is obtained by including in the expression for the average potential energy of an

<sup>5</sup> This is to be discussed in Section VI.



TABLE III. Summary of the numerical integrations for the Fermi-Thomas equation (without exchange effects and for  $T=0$ ).  $a_2$  is the initial slope,  $x_0$  is the radius of the atom,  $\phi(x_0)$  is the boundary value of the  $\phi$  function.

$-a_2$	$x_0$	$\phi(x_0)$
1.58806	7.385 <sub>1</sub>	0.0979 <sub>9</sub>
1.58842	8.588 <sub>0</sub>	0.0739 <sub>8</sub>
1.58856	9.565 <sub>1</sub>	0.0599 <sub>0</sub>
1.58865	10.803 <sub>8</sub>	0.0470 <sub>1</sub>
1.58870	11.963 <sub>4</sub>	0.0381 <sub>3</sub>
1.58874	15.869 <sub>8</sub>	0.0208 <sub>8</sub>
1.58884*	10.935 <sub>8</sub>	0
1.58876*	16.982 <sub>4</sub>	0

\* Ions.

electron an exchange term equal to  $2e^2p_0/h$ , where  $p_0$  is the maximum momentum for the coordinate point under consideration. The electron density is now connected to the electrostatic potential by the relation<sup>6</sup>

$$\rho_e = \frac{8\pi}{3h^3} \left\{ \frac{2e^2m}{h} + \left[ \frac{4e^4m^2}{h^2} + 2m(E_0 - eV_0) \right]^{1/2} \right\}^3.$$

In order to get the numerical integration of Eq. (7) started,  $\psi$  is first expanded into a semiconvergent power series about the origin. The form of this series is identical with that of Eq. (4). For convenience, we list the corresponding coefficients up to  $a_9$  in Table IV. Again we introduce a change in independent variable  $x = w^2/2$  and use the same numerical integration procedure beginning at  $w = 0.92$ .

Slater and Krutter<sup>1</sup> have carried through numerical integrations for  $Z=3, 11, 29$  and Jensen<sup>7</sup> for  $Z=18, 36, 54$ . We have obtained a family of six solutions for  $Z=6$  and of ten for  $Z=92$ . The initial slopes and boundary values are shown in Tables V

TABLE IV. Coefficients of the series solution for the Fermi-Thomas-Dirac equation.  $a_2$  is the initial slope and

$$\epsilon = (3/32\pi^2)^{1/3} Z^{-2/3} = 0.211873Z^{-2/3}.$$

$a_3 = \frac{4}{3}$
$a_4 = \frac{3}{2}\epsilon$
$a_5 = \frac{2}{5}a_2 + \frac{4}{5}\epsilon^2$
$a_6 = \frac{1}{3} + \frac{a_2\epsilon}{2} + \frac{\epsilon^3}{6}$
$a_7 = \frac{6}{35}a_2\epsilon^2 + \frac{3}{70}a_2^2 + \frac{5}{7}\epsilon$
$a_8 = \frac{2}{15}a_2 + \frac{77}{120}\epsilon^2$
$a_9 = \frac{2}{27} - \frac{1}{252}a_2^3 + \frac{11}{35}a_2\epsilon - \frac{1}{42}a_2^2\epsilon^2 + \frac{10}{63}\epsilon^3 + \frac{16}{105}\epsilon^4$

<sup>6</sup> See J. C. Slater and H. M. Krutter, reference 1.

and VI for  $Z=6$  and 92, respectively. Values for the two sets of  $\psi$  functions are listed in Tables VII and VIII at intervals of  $\Delta w = 0.08$ . Here again quadratic interpolation is adequate to obtain  $\psi$  for intermediate  $w$ -values.

From these results one may obtain a relation between pressure and density (or volume) for various elements at  $T=0$ . The pressure depends only on the minimum of the potential,  $Ze\psi/r$ , which is attained at the boundary of the atom. On that boundary no average force acts on the electrons, and the pressure is the same as would be caused by a density of free electrons equal to the electron density at the boundary. This electron density is in turn determined by the potential at the boundary, and one obtains for the pressure the formula

$$P = \frac{Ze^2}{10\pi\mu^4} \left( \left( \frac{\psi(x_0)}{x_0} \right)^{1/2} + \epsilon \right)^5 \left\{ 1 - \frac{5\epsilon/4}{(\psi(x_0)/x_0)^{1/2} + \epsilon} \right\}. \quad (8)$$

The relation just obtained is in effect a dependence of the pressure on the atomic volume since the value of  $\psi/x$  depends exclusively on the atomic radius and hence on the atomic volume.

In this way the pressure-density relationship is applicable to materials composed of several kinds of elements. The volume at a given pressure is obtained by adding the atomic volumes appropriate for that pressure.

In order to express pressure-density relationships for various  $Z$  values in a form which permits convenient interpolation for intermediate  $Z$  values, we follow Jensen<sup>7</sup> and express the pressure in units of the pressure  $\bar{P}$  resulting from a uniform distribution of all the electrons of the material throughout the total available volume,<sup>7a</sup> i.e.,

$$P = \bar{P} f^{5/3},$$

where

$$f(\xi) = \frac{x_0^3}{3} \left( \left( \frac{\psi(x_0)}{x_0} \right)^{1/2} + \epsilon \right)^3 \left\{ 1 - \frac{5\epsilon/4}{(\psi(x_0)/x_0)^{1/2} + \epsilon} \right\}^{3/5} \quad (9)$$

where

$$\xi = Z^{-1/3} a_0 \left( \frac{3Z}{4\pi\mu x_0} \right)^{1/3} = \frac{0.701}{x_0}$$

is the variable against which we plot the function  $f$ .

In Fig. 1 we have compiled the values given by Jensen for  $Z=18, 36, 54$ ; rewritten data of Slater and Krutter in this form; and added the new calculations for  $Z=6, 92$ . In this way we have obtained sufficient data, so that satisfactory interpolation for any  $Z$  value is possible. Finally we have graphed our numerical values for the case without exchange.

<sup>7</sup> See H. Jensen, reference 1, Eqs. (4a, b, c) and (5).

<sup>7a</sup> Explicitly,  $\bar{P} = 2/5(3/8\pi)^{2/3}(h^2/2m)(\bar{\rho})^{5/3}$ , where  $\bar{\rho}$  is the uniform density of electrons.

TABLE V. Summary of the numerical results (with exchange effects) for carbon. The initial slope  $a_2$ , and the boundary values are given.\*

$-a_2$	$x_0$	$\psi(x_0)$
1.6740	3.2617	0.23194
1.6800	3.7153	0.16946
1.6840	4.3784	0.10816
1.6858	5.1678	0.06124
1.6863	5.7291	0.03942
1.6867	7.0084	0.01079

\*  $x_0(\rho=2.28) = 6.28$ .

The pressure-density relations so derived are valid only at rather high pressures at which the detailed influence of the outer shell structure of the atoms has been obliterated. This usually happens at pressures exceeding ten megabars.

IV. PERTURBATION TREATMENT OF TEMPERATURE EFFECTS

If the value of the temperature is low compared to the maximum kinetic energy of electrons near the boundary between atoms, i.e., if

$$kT \ll (Ze^2/\mu)[\phi(x_0)/x_0], \quad (10)$$

the influence of the temperature can be treated by perturbation methods. The influence of this perturbation on the Fermi-Thomas distribution will now be discussed and in this discussion we shall disregard the effects of exchange. It has been shown by Ashkin<sup>3</sup> that the influence of the temperature perturbation and of exchange effects are very nearly additive.

Marshak and Bethe<sup>3</sup> have shown that the perturbation from temperature can be taken into account by modifying Eq. (1a), which connects the electron density and the electrostatic potential. The modified expression

$$\frac{d\Phi}{dx} = \frac{\Phi^3}{x^3} \left[ 1 + \frac{\pi^2 k^2 T^2}{8(E - eV)} \right], \quad (11)$$

where  $E$  is the Fermi energy and  $k$  is the Boltzmann constant. This leads to the corresponding differential equation for the potential

$$\frac{d^2\Phi}{dx^2} = \frac{\Phi^3}{x^3} \left[ 1 + \frac{\zeta T^2 x^2}{\Phi^2} \right], \quad (12)$$

where  $(Ze^2\Phi/\mu x) = E - eV$  analogous to Eq. (2),  $\zeta = \pi^2 k^2 \mu^2 / 8Z^2 e^4$ , and  $\mu$  is given by Eq. (1b). The boundary conditions are  $\Phi(0) = 1$  and  $d\Phi/dx = \Phi/x$ . The solution of this equation can be written

$$\Phi = \phi + \zeta T^2 \phi_1,$$

where  $\phi$  is the unperturbed solution obtained in

\* J. Ashkin, unpublished report.

TABLE VI. Results of the numerical integration of the Fermi-Thomas-Dirac equation for uranium.\*

$-a_2$	$x_0$	$\psi(x_0)$
1.60394	6.5139	0.10164
1.60444	7.4877	0.07495
1.60484	10.2143	0.03507
1.60488	11.3326	0.02623
1.60490	12.4037	0.01991
1.60491	13.3862	0.01551
1.60491 <sub>5</sub>	14.2941	0.01228
1.60492	15.6084	0.00871
1.60492 <sub>4</sub>	19.4301	0.00286
1.60500*, **		0

\*  $x_0(\rho=19.0) = 16.47$ .

\*\* Ion.

Section II and  $\phi_1$  satisfies the differential equation

$$\frac{d^2\phi_1}{dx^2} = \frac{3\phi^{\frac{1}{2}}\phi_1}{2x^{\frac{1}{2}}} + \frac{x^{\frac{1}{2}}}{\phi^{\frac{3}{2}}}. \quad (13)$$

Expanding  $\phi_1 = \sum C_n x^{n/2}$  and using the series expansion for  $\phi$  given by Eq. (4), one finds, taking  $C_2 = 0$ , that

$$\begin{aligned} C_3 = C_4 = C_5 = C_6 = 0, \\ C_7 = (4/35); \quad C_8 = 0; \quad C_9 = -(4/63)a_2; \\ C_{10} = -(13/525); \quad C_{11} = 0, \end{aligned}$$

where  $a_2$  is the initial slope of  $\phi$ . Here again it is

TABLE VII. Solutions of the Fermi-Thomas-Dirac equation for carbon. It is to be noted that the more convenient independent variable  $w$  is used here.

	Case 1 $-a_2 = 1.6740$	Case 2 1.6800	Case 3 1.6840	Case 4 1.6858	Case 5 1.6863	Case 6 1.6867
$w$	$\psi$	$\psi$	$\psi$	$\psi$	$\psi$	$\psi$
0.92	0.62232	0.61957	0.61774	0.61691	0.61668	0.61650
1.00	0.58007	0.57676	0.57455	0.57356	0.57328	0.57306
1.08	0.53924	0.53528	0.53264	0.53145	0.53112	0.53086
1.16	0.50013	0.49543	0.49230	0.49089	0.49049	0.49018
1.24	0.46300	0.45744	0.45373	0.45206	0.45160	0.45123
1.32	0.42803	0.42146	0.41709	0.41513	0.41458	0.41414
1.40	0.39534	0.38763	0.38249	0.38018	0.37954	0.37903
1.48	0.36507	0.35602	0.34999	0.34728	0.34653	0.34593
1.56	0.33727	0.32667	0.31962	0.31644	0.31556	0.31486
1.64	0.31201	0.29962	0.29137	0.28766	0.28663	0.28581
1.72	0.28935	0.27487	0.26524	0.26091	0.25970	0.25874
1.80	0.26933	0.25242	0.24118	0.23613	0.23472	0.23361
1.88	0.25202	0.23228	0.21916	0.21327	0.21162	0.21033
1.96	0.23747	0.21442	0.19913	0.19227	0.19033	0.18884
2.04	0.22578	0.19888	0.18104	0.17304	0.17078	0.16905
2.12	0.21707	0.18565	0.16484	0.15552	0.15288	0.15087
2.20	0.21150	0.17477	0.15050	0.13964	0.13656	0.13422
2.28	0.20927	0.16630	0.13797	0.12532	0.12172	0.11901
2.36	0.21067	0.16034	0.12725	0.11251	0.10831	0.10514
2.44	0.21605	0.15701	0.11833	0.10113	0.09623	0.09254
2.52	0.22589	0.15649	0.11121	0.09114	0.08542	0.08112
2.60	0.24080	0.15903	0.10595	0.08250	0.07582	0.07081
2.68	0.26156	0.16494	0.10261	0.07518	0.06738	0.06153
2.76	0.28920	0.17465	0.10129	0.06917	0.06005	0.05321
2.84		0.18870	0.10214	0.06447	0.05378	0.04579
2.92			0.10536	0.06109	0.04857	0.03920
3.00			0.11123	0.05909	0.04438	0.03340
3.08			0.12011	0.05853	0.04123	0.02833
3.16			0.13247	0.05953	0.03914	0.02396
3.24			0.14892	0.06224	0.03814	0.02024
3.32				0.06688	0.03831	0.01714
3.40					0.03975	0.01465
3.48					0.04261	0.01275
3.56						0.01143
3.64						0.01072
3.72						0.01063
3.80						0.01123
3.88						0.01259
3.96						
4.04						
4.12						
4.20						

TABLE VIII. Solutions of the Fermi-Thomas-Dirac equation for uranium.

$w$	Case 1 $-a_1=1.60394$ ψ	Case 2 1.60444 ψ	Case 3 1.60484 ψ	Case 4 1.60488 ψ	Case 5 1.60490 ψ	Case 6 1.60491 ψ	Case 7 1.604915 ψ	Case 8 1.60492 ψ	Case 9 1.604924 ψ	Case 10 1.60500 ψ
0.92	0.64210	0.64187	0.64169	0.64167	0.64166	0.64166	0.64165	0.64165	0.64165	0.64161
1.00	0.60189	0.60161	0.60139	0.60137	0.60136	0.60135	0.60135	0.60135	0.60134	0.60130
1.08	0.56284	0.56251	0.56225	0.56222	0.56221	0.56220	0.56220	0.56220	0.56219	0.56214
1.16	0.52521	0.52482	0.52451	0.52448	0.52446	0.52445	0.52445	0.52444	0.52444	0.52438
1.24	0.48917	0.48871	0.48834	0.48830	0.48828	0.48828	0.48827	0.48827	0.48826	0.48819
1.32	0.45485	0.45431	0.45387	0.45383	0.45381	0.45380	0.45379	0.45378	0.45378	0.45370
1.40	0.42232	0.42169	0.42118	0.42113	0.42110	0.42109	0.42108	0.42108	0.42107	0.42097
1.48	0.39164	0.39089	0.39030	0.39024	0.39021	0.39019	0.39018	0.39018	0.39017	0.39009
1.56	0.36279	0.36192	0.36123	0.36116	0.36113	0.36111	0.36110	0.36109	0.36109	0.36095
1.64	0.33578	0.33477	0.33396	0.33388	0.33384	0.33382	0.33381	0.33380	0.33380	0.33364
1.72	0.31057	0.30939	0.30846	0.30836	0.30832	0.30829	0.30828	0.30827	0.30826	0.30808
1.80	0.28710	0.28574	0.28465	0.28455	0.28449	0.28447	0.28445	0.28444	0.28443	0.28422
1.88	0.26532	0.26375	0.26249	0.26237	0.26231	0.26228	0.26226	0.26225	0.26223	0.26199
1.96	0.24517	0.24336	0.24190	0.24176	0.24169	0.24165	0.24163	0.24161	0.24160	0.24132
2.04	0.22658	0.22448	0.22280	0.22264	0.22255	0.22251	0.22249	0.22247	0.22245	0.22213
2.12	0.20947	0.20705	0.20511	0.20492	0.20483	0.20478	0.20475	0.20473	0.20471	0.20434
2.20	0.19378	0.19099	0.18875	0.18853	0.18842	0.18837	0.18834	0.18831	0.18829	0.18786
2.28	0.17946	0.17621	0.17364	0.17339	0.17326	0.17320	0.17316	0.17313	0.17311	0.17262
2.36	0.16637	0.16266	0.15970	0.15941	0.15926	0.15919	0.15915	0.15912	0.15909	0.15852
2.44	0.15452	0.15026	0.14686	0.14652	0.14635	0.14627	0.14622	0.14618	0.14615	0.14550
2.52	0.14384	0.13894	0.13503	0.13464	0.13445	0.13436	0.13430	0.13426	0.13422	0.13347
2.60	0.13427	0.12864	0.12416	0.12371	0.12349	0.12338	0.12332	0.12327	0.12323	0.12237
2.68	0.12577	0.11931	0.11417	0.11366	0.11340	0.11328	0.11321	0.11315	0.11310	0.11212
2.76	0.11831	0.11089	0.10500	0.10442	0.10413	0.10398	0.10390	0.10384	0.10378	0.10265
2.84	0.11185	0.10335	0.09660	0.09593	0.09560	0.09543	0.09534	0.09527	0.09520	0.09391
2.92	0.10637	0.09663	0.08891	0.08815	0.08776	0.08757	0.08747	0.08738	0.08731	0.08583
3.00	0.10187	0.09072	0.08188	0.08101	0.08057	0.08035	0.08023	0.08014	0.08003	0.07836
3.08	0.09834	0.08557	0.07547	0.07447	0.07397	0.07372	0.07359	0.07347	0.07337	0.07145
3.16	0.09579	0.08117	0.06963	0.06849	0.06792	0.06764	0.06748	0.06735	0.06724	0.06504
3.24	0.09424	0.07750	0.06432	0.06302	0.06238	0.06205	0.06187	0.06173	0.06160	0.05910
3.32	0.09373	0.07456	0.05952	0.05804	0.05730	0.05693	0.05673	0.05656	0.05642	0.05357
3.40	0.09430	0.07235	0.05519	0.05350	0.05266	0.05224	0.05201	0.05182	0.05165	0.04841
3.48	0.09603	0.07088	0.05130	0.04938	0.04842	0.04794	0.04768	0.04747	0.04725	0.04359
3.56	0.09900	0.07017	0.04783	0.04564	0.04456	0.04401	0.04371	0.04347	0.04325	0.03907
3.64	0.10332	0.07024	0.04476	0.04227	0.04104	0.04042	0.04008	0.03981	0.03959	0.03480
3.72		0.07114	0.04207	0.03925	0.03785	0.03714	0.03676	0.03644	0.03615	0.03077
3.80		0.07293	0.03975	0.03655	0.03496	0.03416	0.03372	0.03336	0.03305	0.02694
3.88		0.07567	0.03779	0.03415	0.03235	0.03144	0.03095	0.03054	0.03018	0.02326
3.96			0.03619	0.03205	0.03001	0.02898	0.02842	0.02796	0.02755	0.02073
4.04			0.03493	0.03024	0.02792	0.02676	0.02612	0.02560	0.02514	0.01829
4.12			0.03402	0.02870	0.02607	0.02475	0.02403	0.02344	0.02292	0.01623
4.20			0.03347	0.02742	0.02445	0.02296	0.02214	0.02148	0.02092	0.01462
4.28			0.03328	0.02642	0.02305	0.02136	0.02044	0.01969	0.01907	0.01333
4.36			0.03347	0.02568	0.02186	0.01995	0.01891	0.01806	0.01738	0.01203
4.44			0.03406	0.02521	0.02088	0.01873	0.01755	0.01659	0.01574	
4.52			0.03507	0.02502	0.02012	0.01768	0.01634	0.01526	0.01440	
4.60				0.02511	0.01955	0.01680	0.01529	0.01407	0.01318	
4.68				0.02551	0.01920	0.01608	0.01438	0.01301	0.01205	
4.76				0.02622	0.01907	0.01554	0.01361	0.01206	0.01106	
4.84				0.02728	0.01916	0.01516	0.01298	0.01124	0.00967	
4.92					0.01948	0.01495	0.01249	0.01052	0.00871	
5.00					0.02005	0.01492	0.01214	0.00991	0.00791	
5.08						0.01507	0.01192	0.00941	0.00721	
5.16						0.01541	0.01185	0.00901	0.00671	
5.24						0.01596	0.01193	0.00872	0.00589	
5.32							0.01216	0.00853	0.00534	
5.40							0.01255	0.00845	0.00485	
5.48								0.00848	0.00442	
5.56								0.00862	0.00404	
5.64								0.00889	0.00371	
5.72									0.00344	
5.80									0.00321	
5.88									0.00304	
5.96									0.00291	
6.04									0.00283	
6.12									0.00280	
6.20									0.00282	
6.28									0.00290	

convenient to make the change of independent variable  $x=w^2/2$ . The series solution for the perturbation function was evaluated at  $w=0.48$  and was extended by a numerical procedure similar to those used above.

Three numerical solutions for  $\phi_1$  were obtained. They are obtained by substituting three different  $\phi$  functions from Part II into Eq. (13). These  $\phi$  functions may be characterized by their initial slopes  $a_2=1.58856, 1.58865, \text{ and } 1.58874$  (see Tables II and III). In Table IX numerical solutions are given corresponding to these three cases for the range of  $w$  that is of interest. The derivatives are also given as they are needed to satisfy the boundary conditions.

With these solutions, a series of points on a  $P-v-T$  diagram may be obtained in the following manner. For a given  $Z$ , one assumes a temperature  $T$  and determines  $x_0$ , and hence atomic volume (or density), from the boundary condition  $d\Phi/dx = \Phi/x$ . The pressure may be obtained either by the approximate expression obtained by Marshak and Bethe or by using tables of the complete expression worked out by MacDougall and Stoner.<sup>9</sup> Specifically they tabulate

$$I_{3/2}(\eta) = \int_0^\infty x^{3/2} dx / (e^{x-\eta} + 1).$$

The expression for the pressure in dynes/cm<sup>2</sup> is<sup>10</sup>

$$P = \frac{8\pi}{3h^3} (2m)^{3/2} (kT)^{5/2} I_{3/2}(\eta),$$

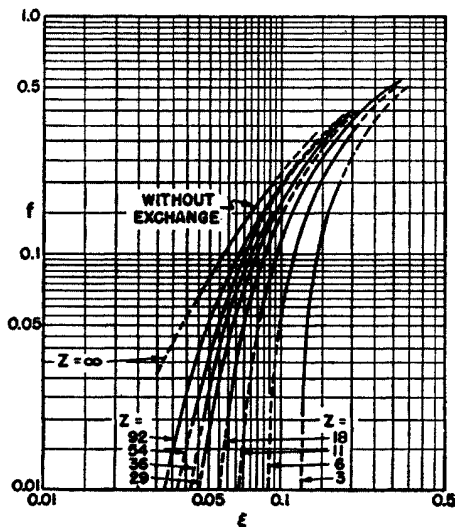


FIG. 1. A representation of the numerical solutions of the Fermi-Thomas-Dirac equation in a form that permits interpolation for intermediate  $Z$  values.  $f$  is related to pressure and  $\xi^3$  is proportional to density (see Eq. (9)).

<sup>9</sup> J. MacDougall and E. C. Stoner, Phil. Trans. Roy. Soc. 237, 67 (1938).

<sup>10</sup> In the next section, this expression is discussed in more detail.

TABLE IX. Solutions of the temperature-perturbation equation. The unperturbed solutions associated with them may be identified by the given values of  $a_2$ . Only the interesting region is tabulated.

$(a_2=1.58856)$		$(a_2=1.58865)$		$(a_2=1.58874)$			
$w$	$\phi_1$	$\frac{d\phi_1}{dw}$	$\phi_1$	$\frac{d\phi_1}{dw}$	$w$	$\phi_1$	$\frac{d\phi_1}{dw}$
2.60	19.211		19.223		3.60	310.28	
2.64		68.757		68.833	3.64		829.73
2.68	24.712		24.730		3.68	376.66	
2.72		86.027		86.139	3.72		987.60
2.76	31.594		31.621		3.76	455.67	
2.80		107.07		107.24	3.80		1171.9
2.84	40.160		40.200		3.84	549.42	
2.88		132.61		132.84	3.88		1386.6
2.92	50.768		50.827		3.92	660.35	
2.96		163.45		163.79	3.96		1636.0
3.00	63.844		63.931		4.00	791.23	
3.04		200.55		201.04	4.04		1925.0
3.08	79.888		80.014		4.08	945.23	
3.12		245.00		245.69	4.12		2259.0
3.16	99.488		99.669		4.16	1126.0	
3.20		298.06		299.03	4.20		2644.3
3.24	123.33		123.59		4.24	1337.5	
3.28		361.16		362.51	4.28		3087.6
3.32	152.22		152.59		4.32	1584.5	
3.36		435.94		437.79	4.36		3596.6
3.40	187.10		187.61		4.40	1872.2	
3.44		524.25		526.77	4.44		4179.9
3.48	229.04		229.76		4.48	2206.6	
3.52		628.24		631.62	4.52		4847.1
3.56	279.30		280.29		4.56	2594.4	
3.60		750.30		754.77	4.60		5608.7
3.64	339.33		340.67		4.64	3043.1	
3.68		893.18		899.00	4.68		6476.7
3.72	410.79		412.59		4.72	3561.2	
3.76		1060.0		1067.4	4.76		7464.3
3.80	495.59		497.98		4.80	4158.4	
3.84		1254.4		1263.7	4.84		8586.4
3.88	595.94		599.08		4.88	4845.3	
3.92		1480.5		1491.7	4.92		9859.8
3.96	714.38		718.41		4.96	5634.1	
4.00		1743.0		1756.1	5.00		11303.0
4.04	853.82		858.90		5.04	6538.3	
4.08		2047.6		2062.1	5.08		12938.0
4.12	1017.6		1023.9		5.12	7573.4	
4.16		2401.0		2415.7	5.16		14789.0
4.20	1209.7		1217.1		5.20	8756.5	
4.24		2811.1		2823.8	5.24		16884.0
4.28	1434.6		1443.0		5.28	10107.0	
4.32		3287.5		3294.4	5.32		19256.0
4.36	1697.6		1706.6		5.36	11648.0	
4.40		3842.0		3837.0	5.40		21942.0
4.44	2005.0		2013.5		5.44	13403.0	
4.48		4489.1		4462.8	5.48		24987.0
4.52	2364.1		2370.6		5.52	15402.0	
4.56					5.56		28443.0
4.60			2785.4		5.60	17678.0	
4.64					5.64		32375.0
4.68			3267.1		5.68	20268.0	
4.72					5.72		36856.0
					5.76	23216.0	
					5.80		41977.0
					5.84		

where

$$\eta = \pi \frac{\Phi(x_0)}{x_0} / (2T(2\xi)^{3/2}).$$

V. EXACT TREATMENT OF TEMPERATURE EFFECTS

For the case of high temperatures the perturbation treatment given in the preceding section is not very accurate. In this section the effects of temperature will be taken into account exactly. Inasmuch as the effects of exchange for this range of temperature are relatively unimportant, we consider only the approximation in which they are neglected.

The effect of temperature is to alter the charge distribution of electrons in the atom. The number of states available to an electron of momentum  $p$  at position  $r$  is  $2[4\pi p^2 dp][4\pi r^2 dr]/h^3$ . The basis of

the simple Fermi-Thomas model at  $T=0$  is to consider that all of the states up to the maximum available momentum are occupied and that the rest are empty. If the temperature is raised, the statistical analysis of Fermi and Dirac tells us that the probability that a state of momentum  $p$ , and hence of energy,  $p^2/2m - eV$ , is filled is

$$1/[\exp[(p^2/2m - eV)/kT] + \eta] + 1,$$

where  $k$  is Boltzmann's constant and  $\eta$  is a constant which is determined by the condition that the total number of electrons is given. Therefore the density of electrons is

$$-\rho_e = \int_0^\infty \frac{2 \cdot 4\pi p^2 dp / h^3}{\exp[(p^2/2m - eV/kT) + \eta] + 1}. \quad (14)$$

Substituting this expression for the charge density into Poisson's equation we obtain

$$\frac{1}{r} \frac{d^2 V}{dr^2} = \frac{16\pi^2}{h^3} \cdot e((2mkT)^{\frac{1}{2}})^3 I_{\frac{3}{2}}\left(\frac{eV}{kT} - \eta\right), \quad (15)$$

where the function  $I_{\frac{3}{2}}(\eta)$  is defined by

$$I_n(\eta) = \int_0^\infty \frac{y^n dy}{\exp(y - \eta) + 1} \quad (15a)$$

and arises for  $n = \frac{1}{2}$  from Eq. (14) if one replaces  $p^2/2mkT$  by  $y$ . It is Eq. (15) that we solve numerically.

The equation can be simplified by a change of variables. Let  $s = r/c$  where

$$c = \left( \frac{h^3}{32\pi^2 e^2 m (2mkT)^{\frac{1}{2}}} \right)^{\frac{1}{2}} = \frac{1.602 \times 10^{-9} \text{ cm}}{T_{kv}^{\frac{1}{2}}}, \quad (16)$$

where  $T_{kv}$  is the temperature measured in kilovolts. The constant  $\eta$  in Eq. (15) can be removed by a change in the zero of potential  $V$ . Setting

$$\beta/s = (eV/kT) - \eta,$$

Eq. (15) becomes

$$d^2\beta/ds^2 = s I_{\frac{3}{2}}(\beta/s). \quad (17)$$

The boundary condition is

$$d\beta/ds = \beta/s \text{ at } s = b, \quad (18)$$

where  $a = cb$  is the atomic radius. At the origin, since  $V$  is to vary as  $Ze/r$ ,  $\beta$  must approach a constant value

$$\alpha = Ze^2/kTc = 0.0899Z/T_{kv}^{\frac{1}{2}}. \quad (19)$$

Because of the singular behavior of  $I_{\frac{3}{2}}(\beta/s)$  as  $s \rightarrow 0$  (it varies as  $s^{-\frac{1}{2}}$ ) numerical integration from the origin is laborious. To avoid this difficulty, another procedure was used. Setting  $s = w^2/2$ , Eq. (17)

becomes,

$$(d/dw)(1/w)(d\beta/dw) = 2w^3 I_{\frac{3}{2}}(2\beta/w^2). \quad (20)$$

The equation was integrated from the outside ( $w^2 = 2a/c$ ) inwards (to  $w=0$ ) and no difficulties arise as the origin is approached. The limiting value of  $\beta$  as  $w \rightarrow 0$ , i.e.,  $\alpha$  is easily determined. The solution is started by choosing, arbitrarily, a value of  $b$ , and of  $\beta$  at  $s=b$  and using Eq. (18) or its equivalent  $(d\beta/dw) = 2\beta/w$  to get the initial value of the derivative of  $\beta$ . It is only after the solution is complete and the value of  $\alpha$  is determined that the temperature (from Eq. (19)) and the density (from  $a = bc$  where  $c$  is given by Eq. (16)) can be evaluated. That these turn out to be in an interesting region requires judicious choice of the initial values of  $b$  and  $\beta$ , but this is not a real difficulty.

The numerical procedure is similar to that described earlier. The values of  $I_{\frac{3}{2}}(2\beta/w^2)$  are obtained with the help of tables of the function  $I_{\frac{3}{2}}(y)$  given by MacDougall and Stoner.<sup>9</sup> The interval  $g$  is so chosen that the error in  $2\beta$  per step which is approximately

$$\frac{g}{6} \left[ \frac{d}{dw} w^3 I_{\frac{3}{2}}\left(\frac{2\beta}{w^2}\right) + \frac{w}{2} \frac{d^2}{dx^2} \left(\frac{2\beta}{w^2}\right) \right]$$

is kept below 0.0001. This usually means that for large  $w$ , the interval  $g$  can be 0.05 but as the origin is approached it is frequently necessary (below  $w=1.4$ ) to reduce it to 0.025.

The values of  $\beta$  as a function of  $w$  for various cases are given in Table X.

After the potential distribution  $V$  is known, we can calculate at a given temperature and density values for the internal energy and pressure. The internal energy  $E_{\text{tot}}$  is the sum of two terms, the potential energy,  $E_{\text{pot}}$ , and the kinetic energy,  $E_{\text{kin}}$ . We shall calculate these quantities in turn.

In calculating the potential energy we must be careful to avoid adding the (infinite) self-energy of the nucleus. We find, if  $\delta$  is some very small radius,

$$E_{\text{pot}} = \frac{e}{2} \int_{\delta}^a \rho_e V \cdot 4\pi r^2 dr + \frac{1}{2} Z [V - (Ze/r)]_{r=\delta}. \quad (21)$$

The first term is the energy of the atomic electrons, being their charge density times the potential in which they find themselves, and the second term is the energy of the nucleus of charge  $Ze$  because of its interaction with the electrons, the potential of this interaction being  $V - Ze/r$ , i.e., the total potential less that due to the nucleus itself. (The factor  $\frac{1}{2}$  arises in the usual manner because calculating this way we count each interaction twice.) If for  $\rho_e$ , the expression given by Eq. (14) is used, the lower limit of the integral can be put equal to zero. For  $[V - (Ze/r)]$  at small  $r$ , we can write its equal,



TABLE X. Solutions of the temperature dependent Fermi-Thomas equation.

	Case 1*	Case 2	Case 3	Case 4	Case 5	Case 6	Case 7	Case 8	Case 9	Case 10	Case 11
$\alpha$	$\beta$	$\beta$	$\beta$	$\beta$	$\beta$	$\beta$	$\beta$	$\beta$	$\beta$	$\beta$	$\beta$
0.00	7.2021	3.9774	9.8160	6.8602	3.7659	6.8918	0.31208	5.8808	2.3570	5.2326	30.3768
0.10	7.1183	3.9324	9.6912	6.7770	3.7162	6.8136	0.27857	5.8127	2.3156	5.1661	29.8494
0.2	6.8914	3.8071	9.3559	6.5510	3.5762	6.6016	0.17822	5.6268	2.1961	4.9820	28.4774
0.3	6.5549	3.6156	8.8631	6.2118	3.3584	6.2874	0.01115	5.3472	2.0044	4.7006	26.5480
0.4	6.1386	3.3698	8.2594	5.7872	3.0736	5.8992	-0.2227	4.9964	1.7452	4.3415	24.2840
0.5	5.6676	3.0800	7.5832	5.3002	2.7302	5.4604	-0.5232	4.5922	1.4217	3.9179	21.8776
0.6	5.1615	2.7536	6.8648	4.7679	2.3338	4.9902	-0.8908	4.1492	1.0351	3.4402	19.4648
0.7	4.6352	2.3960	6.1256	4.2025	1.8872	4.5024	-1.3250	3.6773	0.5849	2.9148	17.1384
0.8	4.0985	2.0100	5.3798	3.6112	1.3906	4.0074	-1.8262	3.1828	0.0694	2.3438	14.9551
0.9	3.5572	1.5959	4.6348	2.9964	0.8419	3.5111	-2.3940	2.6684	-0.5130	1.7262	12.9442
1.0	3.0132	1.1527	3.8924	2.3567	0.2377	3.0162	-3.0288	2.1336	-1.1631	1.0576	11.1144
1.1	2.4655	0.6782	3.1494	1.6876	-0.4248	2.5229	-3.7302	1.5756	-1.8812	0.3328	9.4598
1.2		0.1702	2.3992	0.9828	-1.1481	2.0294	-4.4986	0.9902	-2.6674	-0.4530	7.9651
1.3		-0.3731	1.6328	0.2357	-1.9324	1.5328	-5.3336	0.3731	-3.5216	-1.3036	6.6084
1.4		-0.9528	0.8413	-0.5584	-2.7782	1.0224	-6.2360	-0.2804	-4.4440	-2.2194	5.3642
1.5		-1.5695	0.0167	-1.4046	-3.6856	0.5028	-7.2046	-0.9731	-5.4346	-3.2014	4.2054
1.6		-2.2234	-0.8466	-2.3030	-4.6548	-0.02762	-8.2400	-1.7048	-6.4933	-4.2498	3.1051
1.7		-2.9145	-1.7552	-3.2548	-5.6857	-0.5698	-9.3422	-2.4766	-7.6201	-5.3648	2.0387
1.8		-3.6426	-2.7084	-4.2602	-6.7783	-1.1237	-10.5110	-3.2886	-8.8150	-6.5464	0.9857
1.9		-4.4076	-3.7076	-5.3198	-7.9326	-1.6887	-11.7466	-4.1410	-10.0780	-7.7947	-0.06935
2.0		-5.2088	-4.7536	-6.4337	-9.1486	-2.2636	-13.0490	-5.0338	-11.4090	-9.1097	-1.1370
2.1		-6.0459	-5.8467	-7.6018	-10.4262	-2.8470	-14.4180	-5.9666	-12.8081	-10.4914	-2.2246
2.2		-6.9182	-6.9870	-8.8241	-11.7654	-3.4365	-15.8536	-6.9392	-14.2751	-11.9396	-3.3389
2.3		-7.8252	-8.1746	-10.1005	-13.1660	-4.0298	-17.3558	-7.9511	-15.8100	-13.4546	-4.4842
2.4		-8.7664	-9.4093	-11.4308	-14.6280	-4.6236	-18.9247	-9.0018	-17.4129	-15.0360	-5.6582
2.5		-9.7405	-10.6908	-12.8150	-16.1512	-5.2146	-20.5601	-10.0908	-19.0836	-16.6840	-6.8620
2.6		-10.7467	-12.0190	-14.2528	-17.7356	-5.7986	-22.2620	-11.2172	-20.8222	-18.3984	-8.0961
2.7		-11.7839	-13.3935	-15.7438	-19.3812	-6.3704	-24.0304	-12.3805	-22.6284	-20.1790	-9.3604
2.8		-12.8509	-14.8138	-17.2880	-21.0876	-6.9243	-25.8652	-13.5797	-24.5024	-22.0260	-10.6544
2.9		-13.9464	-16.2794	-18.8850	-22.8547	-7.4536	-27.7663	-14.8140	-26.4439	-23.9391	-11.9776
3.0		-15.0684	-17.7898	-20.5345	-24.6825		-29.7337	-16.0822	-28.4530	-25.9182	-13.3291
3.1		-16.2162	-19.3445	-22.2361	-26.5708		-31.7673	-17.3833	-30.5295	-27.9634	-14.7079
3.2		-17.3877	-20.9428	-23.9894	-28.5192		-33.8670	-18.7161	-32.6734	-30.0743	-16.1128
3.3		-18.5807	-22.5840	-25.7940	-30.5278		-36.0328	-20.0790	-34.8846	-32.2509	-17.5422
3.4		-19.7930	-24.2673	-27.6496	-32.5962		-38.2644	-21.4706	-37.1629	-34.4930	-18.9946
3.5		-21.0222	-25.9919	-29.5554	-34.7242		-40.5619	-22.8893	-39.5082	-36.8006	-20.4682
3.6		-22.2654	-27.7568	-31.5112	-36.9116		-42.9250	-24.3332	-41.9206	-39.1734	-21.9610
3.7		-22.8912; 3.65)	-29.5612	-33.5162	-39.1580		-45.3538	-25.8002	-44.3996	-41.6112	-23.4706
3.8			-31.4037	-35.5698	-41.4632		-47.8480	-27.2881	-46.9453	-44.1140	-24.9946
3.9			-33.2834	-37.6715	-43.8269		-50.4074	-28.7945	-49.5575	-46.6813	-26.5302
4.0			-35.1988	-39.8204	-46.2487		-53.0320	-30.3166	-52.2360	-49.3131	-28.0744
4.1			-37.1488	-42.0158	-48.7283		-55.7214	(-31.0828; 4.05)	-54.9806	-52.0092	-29.6236
4.2			-39.1317	-44.2569	-51.2653		-58.4756		-57.7912	-54.7692	-31.1740
4.3			-41.1459	-46.5428	-53.8592		-61.2944		-60.6676	-57.5928	-32.7216
4.4			-43.1897	-48.8725	-56.5097				-63.6094	-60.4800	(-33.4928; 4.35)
4.5			-45.2612	-51.2450	-59.2162				-66.6165	-63.4368	
4.6			-47.3582	-53.6592	-61.9782				-69.6886	-66.4564	
4.7			-49.4786	-56.1189	-64.7952				-72.8255	-69.5388	
4.8			-51.6200	-58.6128	-67.6666				-76.0268	-72.6834	
4.9				-61.1446	-70.5918				-79.2924	-75.8899	
5.0				-63.7128	-73.5701				-82.6218	-79.1578	
5.1				-66.3158	-76.6008				-86.0146	-82.4868	
5.2				-68.9520	-79.6831				-89.4706	-85.8764	
5.3					-82.8162				-92.9893	-89.3262	
5.4					-85.9994				-96.5704	-92.8355	
5.5					-89.2316				-100.2132	-96.4039	
5.6					-92.5120				-103.9176	-100.0308	
5.7									-107.6830	-103.7156	
5.8									-111.5086	-107.4576	
5.9									-115.3942	-111.2563	
6.0									(-117.3593; 5.95)	-115.1108	
6.1										-119.0205	
6.2										-122.9845	
6.3										-127.0020	
6.4										-131.0720	

\* The first part of this integration was based on Eq. (17); it was completed in the form given by Eq. (20). Only the latter is given.

$[d(Vr)/dr]_{r=0}$ . Changing then to the coordinates  $\beta$  and  $s$ , we find

$$E_{\text{pot}} = -ZkT \int_0^{(2\beta)^{1/2}} (\beta - \frac{1}{4}) w^3 I_{3/2}(2\beta/w^2) dw. \quad (22)$$

The integral is obtained numerically from the data of the solution.

The kinetic energy of each electron of momentum  $p$  is  $p^2/2m$ . Multiplying by the density of electrons and integrating over all space, we find for the

kinetic energy of all electrons

$$E_{\text{kin}} = \int_0^a 4\pi r^2 dr \int_0^\infty \frac{p^2/2m \cdot 2 \cdot 4\pi p^2 dp/h^3}{\left[ \exp\left(\frac{p^2/2m - eV}{kT} + \eta\right) + 1 \right]}. \quad (23)$$

This expression can be simplified by a rather long sequence of operations. If one integrates by parts first by  $r$ , and then again by  $p$ , and then uses Eq. (14) to replace one of the integrals on  $p$  one can

TABLE XI. Summary of the numerical results for the temperature dependent Fermi-Thomas equation (see Table X). Various thermodynamics quantities are evaluated corresponding to these solutions for the case of iron.

Case	$\beta_b$	$b$	$\alpha$	$E_{\text{pot}}/kTZ$	$E_{\text{kin}}/kTZ$	$Pv/kTZ$	$U/kTZ$	$\frac{1}{\gamma-1}$	$\gamma$	For Fe <sub>56</sub>				
										$T_{\text{kv}} = (0.428\alpha)^{-4/3}$	$\frac{a = 1.602 \times 10^{-9}b}{T_{\text{kv}}^{1/4}}$	$v = \frac{4\pi}{3}a^3$	$\rho$ g/cm <sup>3</sup>	$P$ megabars
1	-13.5000	5.4000	7.2021	-13.5750	7.5715	0.5227	1.2210	2.336	1.428	0.2231	1.259A	8.353A <sup>3</sup>	11.874	581.5
2	-22.8914	6.6612	3.9774	-5.4520	3.780 <sub>2</sub>	0.7028	1.6014	2.278	1.439	0.4926	1.274	8.659	11.455	1665.
3	-51.6200	11.5200	9.8160	-20.2006	10.882	0.5210	1.5976	3.066	1.326	0.1476	2.977	110.54	0.8974	28.97
4	-68.9520	13.5200	6.8602	-11.6576	6.799 <sub>2</sub>	0.6470	1.9122	2.924	1.342	0.2381	3.101	124.91	0.7644	51.40
5	-92.5120	15.6800	3.7659	-4.2351	3.360 <sub>0</sub>	0.8283	2.1681	2.618	1.382	0.5297	2.944	106.88	0.9280	170.9
6	-7.4536	4.2050	6.8918	-13.0006	7.2902	0.5266	1.1017	2.092	1.578	0.2366	0.966	3.774	26.28	1375.
7	-61.2944	9.2450	0.3121	-0.0676	0.7742	0.5936	0.8165	1.654	1.605	14.660	0.757	1.816	54.62	1.66 × 10 <sup>5</sup>
8	-31.0828	8.2012	5.8808	-9.6867	5.7792	0.6239	1.6059	2.574	1.389	0.2923	1.787	23.893	4.154	3.179
9	-117.3593	17.7012	2.3570	-1.7505	2.2511	0.9172	2.1298	2.322	1.431	0.9892	2.844	96.30	1.030	392.4
10	-131.0720	20.4800	5.2326	-7.0961	4.7536	0.8037	2.3760	2.956	1.338	0.3416	4.292	331.04	0.2996	34.54
11	-33.4928	9.4612	30.3768	-97.300	49.0072	0.2380	0.7632	3.207	1.313	0.0326	3.567	189.52	0.5235	1.703

show finally that

$$E_{\text{kin}} = \frac{16\pi^2}{h^3 m} \times \frac{a^3}{3} \int_0^x \frac{p^4 dp}{\left[ \exp\left(\frac{p^2/2m - eV_a}{kT} + \eta\right) + 1 \right]} - \frac{1}{2} E_{\text{pot}}, \quad (24)$$

where  $V_a$  is the value of the potential at the surface of the atom  $r=a$ . The integral is, of course, proportional to  $I_{3/2}[(eV_a/kT) - \eta]$  (see Eq. (15a)).

We next compute the pressure. Since there is no field at  $r=a$ , all of the momentum carried across this surface (which in one second per cm<sup>2</sup> is  $P$ , the pressure) must be carried by electrons crossing this surface. This is the reason why computing the pressure at  $r=a$  is particularly simple. At this point pressure simply appears as the pressure of a free electron gas. One obtains

$$P = \int_0^\infty \frac{\frac{1}{3} p \cdot (p/m) \cdot 4\pi p^2 dp / h^3}{\left[ \exp\left[\frac{p^2/2m - eV_a/kT}{kT} + \eta\right] + 1 \right]}. \quad (25)$$

The value of  $Pv$  per atom where  $v = (4/3)\pi a^3$  is the atomic volume, is therefore

$$Pv = \frac{32\pi^2 a^3}{9h^3} (2mkT)^{3/2} (kT) I_{3/2} \left( \frac{eV}{kT} - \eta \right) = \frac{2}{9} (ZkT) \cdot \frac{b^3}{\alpha} I_{3/2} \left( \frac{\beta_b}{b} \right), \quad (26)$$

where  $\beta_b$  is the value of  $\beta$  on the boundary  $s=b$ . Comparison of Eqs. (24) and (25) shows that we can express the kinetic energy as

$$E_{\text{kin}} = \frac{3}{2} Pv - \frac{1}{2} E_{\text{pot}}. \quad (27)$$

This equation will be obtained more directly by consideration of similarity transformation in Section VI.

The total energy per atom is therefore most conveniently calculated from

$$E_{\text{tot}} = \frac{3}{2} Pv + \frac{1}{2} E_{\text{pot}},$$

where  $Pv$  is computed from Eq. (26) and the potential energy  $E_{\text{pot}}$  from Eq. (22).

Actually the total energy is not interesting. What we should like to know is the excess of this energy over what the energy would be if the material were at zero temperature and pressure. That is, to find the net internal energy  $U$  we must subtract from  $E_{\text{tot}}$  the energy of a single atom at zero temperature and pressure. This energy is given by<sup>11</sup>

$$(3/7)(Z^2 e^2 / \mu) \phi'(0),$$

where  $\mu$  is given by Eq. (1b) and  $\phi'(0)$  has been calculated to be  $-1.58875$  (see Section II). In terms of our present quantities,

$$Z^2 e^2 / \mu = kTZ(2\alpha^2/3)^{3/2},$$

so we have

$$U = E_{\text{tot}} + (kTZ)0.6809(2\alpha^2/3)^{3/2}. \quad (28)$$

In this way  $Pv$  and  $U$  have been calculated for the various conditions for which the differential equation was solved. The conditions  $\beta_b$  and  $b$  are given in the first two columns of Table XI. The value of  $\alpha$  which results is given in the third column. In the next four columns the potential, kinetic,  $Pv$  and net internal energy are given in units of  $kTZ$  so that they are applicable for any  $Z$ . The ratio of the net internal energy to  $Pv$ , which we have called  $1/(\gamma-1)$  is given, as well as the value of  $\gamma$  to which this corresponds. The ratio is written in this form in analogy to the perfect gas formulae but it is not to be assumed that in our case  $\gamma$  is actually the ratio of specific heats, nor the exponent in the isentropic equation  $Pv^\gamma = \text{constant}$ . We define  $\gamma$  only through the equation  $U = Pv/(\gamma-1)$ .

The above quantities are independent of the value of  $Z$ . But to obtain actual numerical values

<sup>11</sup> See Slater and Krutter, reference 1, and Section VI.

for the temperature, atomic volume, density, and pressure one must assume a definite substance.

The numerical values for these quantities for  $\text{Fe}_{56}$  (unit of density is  $1 \text{ g/cm}^3$ ) are given in columns 10 to 14 of Table XI. For any other atom of atomic number  $Z$ , atomic weight  $A$ , these values should be multiplied by various factors:

- (i) temperature  $T$  by  $(Z/26)^{4/3}$
- (ii) atomic volume  $v$  by  $(26/Z)$
- (iii) density  $\rho$  by  $(Z/26)(A/56)$
- (iv) pressure  $P$  by  $(Z/26)^{10/3}$ .

The above calculations from the Fermi-Thomas model can be scaled, as was indicated, to apply to a substance with arbitrary  $Z$ . For any definite  $Z$  there is, however, an effect it is worth while to take into account. To the internal energy per atom,  $\text{Fe}$ , one should add  $3kT/2$  to account for the kinetic energy of motion of the nuclei. For the same reason,  $kT$  should be added to  $Pv$  to account for the extra pressure developed by this motion.

## VI. SIMILARITY CONSIDERATIONS

We shall summarize in this section a few simple relations which apply to the electron distributions obtained above.

The first of these relations is the virial theorem, connecting pressure  $P$ , volume  $v$ , with kinetic energy  $E_{\text{kin}}$  and potential energy  $E_{\text{pot}}$

$$\frac{3}{2}Pv = \frac{1}{2}E_{\text{pot}} + E_{\text{kin}}. \quad (29)$$

We shall show below that in the Fermi-Thomas approximation this virial theorem is exactly satisfied. This fact has indeed been proved in the literature for some special cases.<sup>12</sup> The proof given here is more general.

We consider first a similarity transformation in which all charges (including the elementary charge  $e$ ) are changed by the factor  $(1+\epsilon)$ , all distances by the factor  $(1+\rho)$  and all energies by  $(1+\eta)$ . The quantities  $\epsilon$ ,  $\rho$ ,  $\eta$  are assumed small compared to unity. The quantum of action  $h$  and the electron mass  $m$  are assumed to be unchanged.

From the expression for potential energy, the following relation obtains

$$1+\eta = (1+\epsilon)^2/(1+\rho) \quad \text{or} \quad \eta = 2\epsilon - \rho.$$

The deBroglie wave-length  $\lambda$ , as all lengths, must change as  $(1+\rho)$ ; thus momenta change as  $1/(1+\rho)$  and kinetic energies as  $1/(1+\rho)^2$ . However, these energies, like potential energies, must change as  $(1+\eta)$ , hence we obtain

$$\eta = -2\rho \quad (30)$$

and with the above relation

$$2\epsilon = -\rho. \quad (31)$$

Equations (30) and (31) give the change in potential distribution and in energy due to a change of the charges.

If  $T \neq 0$ , the two similar systems to be compared must be such that the temperature should change proportionally to the energy of an electron. Hence, the entropy which changes as the heat transfer divided by temperature will remain unaltered.

We shall now treat the effect of the change of charges by a perturbation treatment. Consider first the effect of the change in all charges by the factor  $(1+\epsilon)$ , without altering the electron distribution. This we can consider accomplished with the aid of imaginary rigid and infinitely thin walls which subdivide the system and which prevent any change in electron densities. (It is consistent with the assumptions of the Fermi-Thomas model to localize sharply electrons even though their momentum distribution is given. Introduction of such walls is therefore permissible.) Thus densities and hence kinetic energies will remain unaltered and the change of total energy will be given by the change in potential energy, namely,  $2\epsilon E_{\text{pot}}$ .

As a second step we now permit the imaginary walls to readjust themselves, but we shall keep in this step the total volume unchanged. The compression and dilatation of the volume elements will introduce temperature changes which we allow to be equalized by heat conduction. Since any energy conducted away from one element must go into another, the total energy change by conduction is zero. The work done by the motion of the walls does not vanish exactly. However, the displacement of the walls is proportional to the electron density differences; since the pressure differences are also infinitesimal, the actual work performed is quadratically small. Thus the energy change introduced by changing the charge distribution remains, to the first order,  $2\epsilon E_{\text{pot}}$ . We also observe that the entropy change due to heat conduction described above is infinitesimal to second order, since both the amount of heat conducted and the temperature differences are infinitesimals of the first order.

In order to arrive at the same configuration reached by the similarity transformation, the volume must now be readjusted. This is done by a volume increase  $(1+\rho)^3$ . In this process, the entropy will be kept constant. At the same time, however, the energy of the system will decrease by an amount equal to the pressure multiplied by the volume change, i.e., by  $P(3\rho v)$ . Thus the total energy change is  $2\epsilon E_{\text{pot}} - 3\rho Pv$ . Equating this with  $\eta$  times the original total energy we obtain

$$2\epsilon E_{\text{pot}} - 3\rho Pv = \eta(E_{\text{pot}} + E_{\text{kin}}).$$

Using Eqs. (30) and (31) to express  $\eta$  and  $\rho$  in terms of  $\epsilon$  we finally have

$$2\epsilon E_{\text{pot}} + 6\epsilon Pv = 4\epsilon(E_{\text{pot}} + E_{\text{kin}})$$

<sup>12</sup> V. Fock, Physik. Zeits. Sowjetunion 1, 747 (1932).

or

$$E_{\text{pot}} + 2E_{\text{kin}} = 3Pv. \quad (29)$$

The reasoning which has just been described can be applied equally to calculations with or without exchange effects. The reason is that the exchange energy, as all other potential energies, is proportional to  $e^2/r$ . The characteristic distance entering into the exchange energy happens to be the deBroglie wave-length of the fastest electron.

It is well known that the virial theorem is exactly valid for a quantum mechanical system (as well as for a classical system) when the exact equations of motion of the electrons and nuclei are taken into account. The above simple argument merely shows that the virial theorem is not invalidated by the simplifying assumptions introduced in the Fermi-Thomas method.

It is of interest to study a second similarity transformation which consists of increasing the nuclear charge and simultaneously increasing the number of electrons so that the system remains neutral. This similarity transformation describes correlations between solutions for various nuclear charges; it also leads to a further relation between the various forms of energy in the Fermi-Thomas model. The procedure to be described and the relations following from it hold only for the case where exchange forces are neglected.

It is to be noted that in this similarity transformation  $\lambda$  does not change like other lengths. In fact, the Fermi-Thomas equation remains unchanged, but we do not retain the detailed microscopic relations from which it is derived. The transformation consists of the following changes:

$$Z \rightarrow Z(1+\zeta), \quad r \rightarrow r(1+\rho), \quad \bar{E} \rightarrow \bar{E}(1+\eta).$$

Here  $\bar{E}$  represents any form of energy per electron, and also stands for the temperature  $T$ . At the same time electron densities are changed by the factor  $(1+\nu)$ .

We shall consider

$$\zeta, \rho, \eta, \nu \ll 1.$$

It follows directly from the charge balance that

$$(1+\nu)(1+\rho)^3 = 1+\zeta \quad (32)$$

or

$$\nu + 3\rho = \zeta.$$

Since the potential energy of an electron must change as  $(1+\eta)$ , we have

$$(1+\zeta/1+\rho) = 1+\eta$$

or

$$\zeta - \rho = \eta. \quad (33)$$

Since the kinetic energy is proportional to the two-thirds power of the electron density, for  $T=0$ , we are lead to postulate

$$(1+\nu)^{\frac{2}{3}} = 1+\eta$$

or

$$\frac{2}{3}\nu = \eta. \quad (34)$$

If we assume that the temperature  $T$  has changed by the factor  $(1+\eta)$ , it is easily seen that the kinetic energy per electron will transform as  $(1+\eta)$ .

Eliminating  $\nu$  from Eqs. (32), (33), (34), we obtain

$$\rho = -\frac{1}{3}\zeta, \quad \eta = (4/3)\zeta.$$

If we now continue to apply such similarity transformations until there is a finite change of the nuclear charge and of the other quantities involved, we find that solutions of the Fermi-Thomas equation for different  $Z$  values are correlated by the statements that the radius changes proportionally to  $Z^{-1}$ ; energy per electron  $\bar{E}$  and temperature both change as  $Z^{4/3}$ . For the case  $T=0$ , these statements follow directly from the well-known form of the Fermi-Thomas equation. We should also note that the total energy per atom changes as  $Z^{7/3}$ . Thus in an infinitesimal similarity transformation the total energy per atom is multiplied by  $1+7\zeta/3$ .

We shall now treat the same problem by a perturbation method in the following steps.

(i) First we shall multiply the nuclear charge of a single nucleus by  $(1+\zeta)$  and apply a perturbation calculation. In this step we shall keep the number of electrons, the volume, and the temperature unchanged. Due to the complete shielding of a nucleus by its electrons, assumed throughout this paper, the interaction of nuclei with each other and with electrons of other atoms need not be considered. Thus one obtains a change in energy  $\zeta E_{e,N}$ , where  $E_{e,N}$  is the electrostatic interaction energy of electrons of an atom with its nucleus.

(ii) Second we add  $\zeta Z$  electrons to re-establish the charge balance. This addition gives the energy  $-\zeta Z E_w$ , where  $E_w$  is the work function of the solid, i.e., the energy needed to extract an electron from the solid. If one wants to apply this argument to an isolated ion, then  $E_w$  must be replaced by the ionization energy of the outermost electron.

(iii) As a third step the solid is expanded. This expansion gives rise to a change in energy of  $-3\rho P v$ , where  $v$  is the atomic volume.

(iv) As a final step the temperature is raised by  $\eta T$  which gives the added energy  $\eta T C_v$ , where  $C_v$  is the specific heat per atom at constant volume.

The sum of these energy contributions is equal to the total energy change  $(7\zeta/3)(E_{\text{pot}} + E_{\text{kin}})$  obtained from the infinitesimal similarity transformation. We have, therefore,

$$(7/3)\zeta(E_{\text{pot}} + E_{\text{kin}}) = \zeta E_{e,N} - \zeta Z E_w - 3\rho P v + \eta T C_v.$$

Using the relations between  $\eta$ ,  $\zeta$ ,  $\rho$  we obtain

$$(7/3)(E_{\text{pot}} + E_{\text{kin}}) = E_{e,N} - Z E_w + P v + (4/3) T C_v.$$

Using the virial theorem and introducing the relation

$$E_{\text{pot}} = E_{e,e} + E_{e,N}$$

where  $E_{e,e}$  is the potential energy due to the interaction of electrons within an atom, we get

$$(5/2)Pv + (7/6)E_{e,e} + (1/6)E_{e,N} = -ZE_w + (4/3)TC_v.$$

In the special case of  $T=0$  and of isolated atoms, this relation becomes particularly simple. In fact

in this case  $P=0$  and the ionization energy  $E_w$  is also set to zero, so that

$$E_{e,N} = -7E_{e,e}.$$

This relation had been derived by Fermi for the Fermi-Thomas equation.

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On the Wave Equation with Small Quantum Numbers

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The determination of the *Eigenwerte*, and the normalization of the *Eigenfunktionen* of the one-dimensional wave equation, with a potential energy that has a single minimum, is customarily based on the use of the so-called phase integral and W.K.B. formulas. These formulas are asymptotic in character. As they have usually been applied, they accordingly lead to conclusions which can be regarded as established only when the respective quantum numbers are sufficiently large. This restriction has been both unfortunate and puzzling. For on the one hand, the cases of small or moderate quantum numbers are often peculiarly interesting while, on the other hand, the phase integral formulas have been found by trial, at least in a variety of simple cases, to give surprisingly good results even in the lower quantum number range.

It is shown in this paper how the asymptotic method should be applied when small or moderate quantum numbers are in question. In the case of the *Eigenwerte*, the characteristic equation appropriate to the lower range is derived, and a

comparison of this new equation with the familiar one based on the phase integral is made. It is thus theoretically established that under certain very liberal conditions upon the potential energy the older method does give good approximations. In the special case of the harmonic oscillator the two equations are, in fact, identical. For the normalization of the *Eigenfunktionen* a method which has been used in principle by W. H. Furry is applied. It is, however, framed in a manner appropriate to the smaller quantum number range. Formulas are given for the normalized *Eigenfunktionen* over the several intervals of the variable, over the critical interval which includes the minimum of the potential energy and the turning points, as well as over the intervals remote from the turning points.

In the special case of the harmonic oscillator, the method here used gives certain exact—not merely asymptotic—results. These, therefore, supply a basis for the appraisal of the corresponding results that are obtainable by other means.

1. INTRODUCTION

THE subject of this discussion is the one-dimensional wave equation

$$(d^2u/dx^2) + \lambda^2 \{E - V(x)\}u = 0, \quad (1.1)$$

in which

$$\lambda^2 = 8\pi^2m^2/\hbar^2,$$

and in which  $V(x)$ , the potential energy, is defined over the entire  $x$  axis and has a single minimum say at a point  $x_0$ . The characteristic values  $E_n$  (*Eigenwerte*) are the values of  $E$  for which this equation admits of a solution that is bounded for all  $x$ . A solution  $u_n$  corresponding to such a characteristic value is a characteristic solution (*Eigenfunktion*) and is said to be normalized when its constant factors—which are not determined by the equation—are so adjusted that

$$\int_{-\infty}^{\infty} u_n^2 dx = 1. \quad (1.2)$$

A familiar procedure for the determination of the *Eigenwerte* is based upon the phase integral and W.K.B. methods. Elementary analytical forms are used in this to represent the solutions of the differential equation asymptotically with respect to  $\lambda$ , in intervals which lie on opposite sides of, and are sufficiently remote from, the turning points. To account for the Stokes' phenomenon, "connection formulas" are invoked to identify the forms which represent one and the same solution in different intervals. From the fact that two such forms differently arrived at, but valid in the same interval, must be equivalent, the characteristic equation, whose roots are the *Eigenwerte*, is deduced. Quantitatively, the procedure is in brief the following.

For values of  $E$  that are larger than  $V(x_0)$  but which are nevertheless exceeded by  $V(x)$  for some positive and some negative  $x$ , the equation

$$E - V(x) = 0$$