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THE THOMAS-FERMI MODEL OF THE ATOM WITH QUANTUM AND EXCHANGE CORRECTIONS

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Quantum and exchange corrections to the energy and the chemical potential of the Thomas-Fermi atom are derived and numerical calculations of thermodynamical functions for a cold atom are presented. The extrapolation of the model into the region of normal densities is considered. The calculations are compared with the experimental data.

1. INTRODUCTION

ONE of the models used for the description of the behavior of matter at high temperatures and pressures is the statistical Thomas-Fermi model of the atom (abbreviated TF model),[1,2] which is the quasi-classical approximation to the method of the self-consistent field. The inclusion of exchange effects in the Thomas-Fermi-Dirac (TFD model)[1,3] represents a refinement of this approximation. However, the TFD model is not consistent, since here the exchange effects are computed exactly within a quasi-classical framework, i.e., one considers the exchange effects of all orders, but neglects the quantum corrections. The more rigorous treatment of the quantum effects with the help of the Weizsäcker equation[4,5] involves considerable methodological difficulties and leads to arduous numerical calculations.

The TF model with quantum and exchange corrections (abbreviated TFC model) has been considered by a number of authors.[5-8] In the present paper we calculate corrections to the potential, the energy, and the chemical potential of the atom within the framework of this model and present the numerical results of these calculations for the compressed atom at zero absolute temperature.

2. THE ATOM AT ARBITRARY TEMPERATURES

The operator corresponding to the single particle density matrix for a nondegenerate Fermi gas has the form

$$\hat{\rho}(\mathbf{r}, \hat{\mathbf{p}}) = 2(2\pi\hbar)^{-3}[1 + \exp\{(\hat{H} - \mu)/kT\}]^{-1}, \tag{1}$$

where $\hat{H}$ is the Hamiltonian of the electron in the Hartree-Fock field. The magnitude of the chemical potential μ is determined by the total energy of the system, which, according to the self-consistent field approximation, is equal to

$$E = \int \hat{H}\hat{\rho}\, d\mathbf{p}\, d\mathbf{r} - \frac{e^2}{2}\int \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)|\mathbf{r}_1 - \mathbf{r}_2|^{-1} d\mathbf{r}_1 d\mathbf{r}_2. \tag{2}$$

Kirzhnits[5] has shown that expression (1) satisfies the system of TFD equations written in operator form

$$\Delta\varphi(\mathbf{r}) = -4\pi Ze\delta(\mathbf{r}) + 4\pi e\int \hat{\rho}(\hat{H})\, d\mathbf{p},$$

$$\hat{H} = \hat{\mathbf{p}}^2/2m - e\varphi(\mathbf{r}) - 2\pi\hbar^2 e^2 \int \hat{\rho}(\hat{H}')|\mathbf{p} - \mathbf{p}'|^{-2} d\mathbf{p}'. \tag{3}$$

The zeroth approximation to this system is, of course, the TF equation.* Using the rules for the computation of a function of a sum of noncommuting arguments, we can expand Eqs. (1) to (3) in powers of n^2 (see references 5 to 7) and obtain corrections of arbitrary order to the equations of the TF model.

We shall denote the quantum and exchange corrections of first order by the symbols δ_1 and δ_2, respectively. We introduce the dimensionless potential function of the TF model and the quantum and exchange corrections to it:†

$$\xi(\mathbf{r}) = [e\varphi(\mathbf{r}) + \mu]/kT,$$

$$\begin{aligned}\delta_i\xi(\mathbf{r}) &= [e\delta_i\varphi + \delta_i\mu]/kT\\ &= (e/3\pi\sqrt{2a_0kT})[I'_{1/2}(\xi)\delta_{1i} + u_i(\mathbf{r})].\end{aligned} \tag{4}$$

The corrections to the potential satisfy the following equation and boundary conditions:[8]

$$\begin{gathered}\Delta u_i(\mathbf{r}) - \sqrt{32kT/\pi^2e^2a_0^3}\, I'_{1/2}(\xi)\, u_i(\mathbf{r}) = \sqrt{32kT/\pi^2e^2a_0^3}\, \Psi'_i(\xi),\\ (ru_i)_{r=0} = 0, \qquad (du_i/dr)_{r=r_0} = 0.\end{gathered} \tag{5}$$

Here we use the following notation for the Dirac functions and their combinations:

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*Not the TFD equation, since the exchange term in the Hamiltonian is itself a correction of order $\hbar^2$.

†Here δ_{1i} is the Kronecker symbol, which separates out the quantum correction.

$$I_k(\xi) = \int_0^\infty \frac{x^k dx}{1 + \exp(x - \xi)},$$

$$\Psi_1(\xi) = I_{3/2}(\xi)\, I'_{1/2}(\xi), \quad \Psi_2(\xi) = 6\int_{-\infty}^{\xi} [I'_{1/2}(x)]^2 dx.$$

Since we assume that the potential vanishes at the boundary of the atom in any approximation, it follows from (4) that the corrections to the chemical potential of the atom and to the potential of the self-consistent field have the form

$$\delta_i\mu = \frac{e}{3\pi}\sqrt{kT/2a_0}\,\{I'_{1/2}(\xi(r_0))\,\delta_{1i} + u_i(r_0)\}, \tag{6}$$

$$e\delta_i\varphi(r) = \frac{e}{3\pi}\sqrt{kT/2a_0}\,\{I'_{1/2}(\xi(r))\,\delta_{1i} + u_i(r)\} - \delta_i\mu. \tag{7}$$

The calculation of the correction to the energy leads to a divergent volume integral: as is known, one cannot compute the quantum correction of Weizsäcker with the help of the quasi-classical electron density. However, the divergence is related to the region near the nucleus which is not affected by the external conditions (temperature and pressure). The divergent terms therefore cancel out in the calculation of the difference of the energies of the atom under different external conditions. The remaining finite expression represents the correction to the energy of excitation of the atom and has the following form:

$$\delta_i E = \frac{e}{3\pi}\sqrt{\frac{kT}{2a_0}}\,Zu_i(0) + \frac{1}{3\pi^3}\left(\frac{kT}{ea_0}\right)^2 \int_V \left[\frac{1}{2}u_i I_{1/2}(\xi) + \Psi_i(\xi)\right] d\mathbf{r} + C(Z), \tag{8}$$

where C(Z) is chosen such that the energy of the unexcited atom is zero. This still leaves the correction to the binding energy of the atom undetermined.

In the region where the electron density is nearly uniform we can obtain[8] explicit expressions for the thermodynamical quantities in terms of the boundary conditions. Denoting the correction due to the non-uniformity by the symbol δ_n, we find for the energy of the uniform distribution and the correction to it:

$$E_0 = ZkT I_{3/2}(\xi_0)/I_{1/2}(\xi_0), \quad \delta_n E = -3\sqrt[3]{36\pi}Z^2e^2/10V^{1/3},$$

$$\delta_i E = -(Ze/3\pi)\sqrt{kT/2a_0}\left[\frac{3}{2}\Psi'_i(\xi_0)/I'_{1/2}(\xi_0) - \Psi_i(\xi_0)/I_{1/2}(\xi_0)\right], \tag{9}$$

where ξ_0 is determined by the equation

$$Z/V = (2kT/e^2a_0)^{3/2} I_{1/2}(\xi_0)/2\pi^2. \tag{9a}$$

3. THE COLD ATOM

For the description of the compressed atom at zero absolute temperature we go to the limit $T \to 0$ in Eqs. (5) to (8) (for $\mu > 0$), using the asymptotic Dirac functions:

$$I_k(\xi) \to \xi^{k+1}/(k+1), \quad \Psi_1(\xi) \to \frac{2}{3}\xi^2,$$
$$\Psi_2(\xi) \to 3\xi^2 \text{ for } \xi \to +\infty. \tag{10}$$

Since the asymptotic functions Ψ_i of (10) differ only by numerical factors, the quantum and exchange corrections also differ only by the numerical factor $9/2$ at absolute zero. For simplicity we shall consider in the following only the sum of the quantum and exchange corrections of first order.

For a complete description of the TFC model we must use the equations of the TF model[1,2] and the expression for the corrections to the pressure.[8] For convenience of calculation we make the following change of coordinates:

$$x = r/r_0, \quad \Phi(x)/x = \xi(r)/\xi(r_0),$$
$$\psi(x)/x = u_i(r)/u_i(r_0) \tag{11}$$

and go to the limit as above. The equations and boundary conditions for the dimensionless potential then take the form

$$\Phi''(x) = \alpha\Phi^{3/2}(x)/\sqrt{x}, \quad \Phi(1) = \Phi'(1) = 1,$$
$$\Phi(0) \equiv \Phi_0 = Ze^2/r_0\mu,$$
$$\psi''(x) - \frac{3}{2}\alpha\sqrt{\Phi(x)/x}\,\psi(x) = \beta\psi(x),$$
$$\psi(1) = \psi'(1) = 1, \quad \psi(0) = 0, \tag{12}$$

where

$$\alpha = r_0^2\mu^{1/2}/e(\varkappa a_0)^{3/2},$$

$$\beta = 11\alpha\sqrt{\mu/kT}/[u_1(r_0) + u_2(r_0)], \quad \varkappa = (9\pi^2/128)^{1/3}.$$

Transforming expression (8) with the help of equations analogous to the virial theorem in the TF model, we obtain the following expressions for the thermodynamical quantities and the corrections to them:

$$ZV = \frac{4\pi(\varkappa a_0)^3}{3}\alpha^2\Phi_0, \qquad \frac{\mu}{Z^{4/3}} = \frac{e^2}{\varkappa a_0}(\alpha\Phi_0^2)^{-2/3},$$

$$\frac{P}{Z^{10/3}} = \frac{e^2}{10\pi(\varkappa a_0)^4}(\alpha\Phi_0^2)^{-5/3},$$

$$\frac{E}{Z^{7/3}} = \frac{e^2}{\varkappa a_0}\left[C_\infty + \frac{\alpha^{1/3}}{\Phi_0^{7/3}}\left(\frac{2}{35} + \frac{3}{7}\frac{\Phi_0\Phi'_0}{\alpha}\right)\right],$$

$$\frac{\delta\mu}{Z^{2/3}} = \frac{e^2}{16\varkappa^2 a_0}(\alpha\Phi_0^2)^{-1/3}\left[1 + \frac{11\alpha}{\beta}\right],$$

$$\frac{\delta P}{Z^{8/3}} = \frac{11e^2}{64\pi\varkappa^5 a_0^4}(\alpha\Phi_0^2)^{-4/3}\left[\frac{1}{2} + \frac{\alpha}{\beta}\right],$$

$$\frac{\delta E}{Z^{5/3}} = -\frac{11e^2}{32\varkappa^2 a_0}\left[\delta C_\infty + \frac{\alpha^{2/3}}{\Phi_0^{5/3}}\int_0^1 \Phi^2(x)\,dx\right], \tag{13}$$

where C_∞ and δC_∞ are chosen such that the energy and its correction become zero for an infinite atom. The potential and its correction are obtained from the formulas

ZV, Å^3	$Z^{-10/3}P$, dyne/cm^2	$-Z^{-8/3}\delta P$, dyne/cm^2	$Z^{-7/3}E$, erg/atom	$-Z^{-5/3}\delta E$, erg/atom	$Z^{-4/3}\mu$, erg/atom	$-Z^{-2/3}\delta\mu$, erg/atom
.21078 (—3)	.30412 (20)	.55306 (18)	.93547 (—8)	.33829 (—9)	.16304 (—7)	.40323 (—9)
.16483 (—2)	.95892 (18)	.35577 (17)	.22487	.16484	.40907 (—8)	.20328
.62812	.99762 (17)	.59598 (16)	.86759 (—9)	.10162	.16545	.13021
.24391 (—1)	.98523 (16)	.96937 (15)	.31962	.60883 (—10)	.65539 (—9)	.82860 (—10)
.10168 (0)	.83186 (15)	.14178	.10592	.34219	.24384	.51432
.26456	.15396	.38603 (14)	.48388 (—10)	.22544	.12418	.37294
.41652	.68308 (14)	.20691	.32843	.18279	.89717 (—10)	.31984
.12101 (1)	.97281 (13)	.46674 (13)	.12584	.10759	.41143	.22194
.23973	.26900	.17537	.65214 (—11)	.74094 (—11)	.24603	.17472
.47555	.71642 (12)	.64075 (12)	.32458	.49412	.14493	.13671
.96270	.17573	.21958	.15111	.31355	.82608 (—11)	.10536
.13114 (2)	.93461 (11)	.13558	.10637	.25350	.64171	.93704 (—11)
.18739	.44521	.76876 (11)	.70018 (—12)	.19622	.47699	.81629
.26012	·22241	.45150	.47082	.15345	.36136	.71718
.35927	.11094	.26452	.31471	.11924	.27360	.62966
.50824	.51816 (10)	.14712	.20138	.89897 (—12)	.20178	.54579
.71602	.24067	.81334 (10)	.12772	.67196	.14848	.47232
.10150 (3)	.10857	.43883	.79167 (—13)	.49348	.10798	.40623
.14862	.44678 (9)	.22005	.46147	.34716	.75705 (—12)	.34310
.20701	.20338	.11914	.28453	.25264	.55259	.29519
.28687	.92408 (8)	.63314 (9)	.17445	.18273	.40306	.25373
.41240	.37795	.31923	.99690 (—14)	.12582	.28188	.21358
.61577	.13804	.14472	.52758	.82059 (—13)	.18841	.17576
.81519	.67390 (7)	.82305 (8)	.33418	.60277	.14142	.15292
.11248 (4)	.29238	.42611	.19569	.41916	.10127	.12997
.15950	.11650	.20604	.10808	.27959	.70084 (—13)	.10859
.22919	.44137 (6)	.95619 (7)	.05754	.18152	.47534	.89791 (—12)
.31529	.18559	.48144	.03266	.12297	.33613	.75746
.42552	.81345 (5)	.25034	.01901	.84621 (—14)	.24167	.64401
.86918	.10973	.51008 (6)	.00505	.33762	.10845	.43378
.16984 (5)	.16014 (4)	.11035	.00140	.13790	.50220 (—14)	.29640
.39330	.13569 (3)	.15450 (5)	.00026	.04310	.18711	.18164
.23448 (6)	.60040 (0)	.20455 (3)	.00001	.00321	.21402 (—15)	.61776 (—13)
.90408	.88368 (—2)	.70377 (1)	.00000	.00041	.39591 (—16)	.26638
.44188 (7)	.56275 (—4)	.12372 (0)	.00000	.00004	.52385 (—17)	·97086 (—14)

The numbers in the table represent decimal fractions to be multiplied by the power of ten indicated in parentheses)

$$e\varphi(r) = \mu\left[\Phi(x)/x - 1\right],$$

$$e\delta\varphi(r) = Z^{-2/3}\mu\left[\delta\Phi(x)/x - \delta\Phi(1)\right],$$

$$\delta\Phi(x) = \frac{(\alpha\Phi_0^2)^{1/3}}{16\varkappa}\left[\sqrt{x\Phi(x)} + \frac{11\alpha}{\beta}\psi(x)\right]. \qquad (14)$$

Expanding (12) in a power series in the parameter α, we find the asymptotic expressions for the case of high compression:

$$\Phi(x) = x + \alpha\left(\tfrac{1}{6}x^3 - \tfrac{1}{2}x + \tfrac{1}{3}\right) + O(\alpha^2),$$

$$\Phi_0 = \tfrac{1}{3}\alpha + \tfrac{1}{20}\alpha^2 + O(\alpha^3), \qquad \psi(x) = x + O(\alpha^2),$$

$$\alpha = \left(r_0\sqrt[3]{3Z}/\varkappa a_0\right)\left(1 - r_0\sqrt[3]{3Z}/20\varkappa a_0 + \ldots\right),$$

$$\beta = -\frac{3}{2}\alpha\left(1 - \frac{1}{20}\alpha\right) + O(\alpha^3). \qquad (15)$$

The asymptotic values of the thermodynamic quantities will not be quoted here; they are easy to obtain by substituting (15) in (13).

4. SOLUTION OF THE EQUATIONS

It is known that the TF equation has a universal form. If we take ZV and $Z^{-4/3}T$ for the unknown variables and $Z^{-10/3}P$, $Z^{-7/3}E$, and $Z^{-4/3}\mu$ for the functions of these variables, the equations do not contain Z in any other fashion than the one indicated. If we further introduce the functions $Z^{-8/3}\delta P$, $Z^{-5/3}\delta E$, and $Z^{-2/3}\delta\mu$ this universality is extended to the equations for the corrections of first order. This circumstance greatly facilitates the numerical calculations, since any solution of the TFC equations can be used for all elements; we recall that the TFD equation or the Weizsäcker equation have to be solved separately for each element.

The numerical integration of (12) was performed on the computer "Strela." The computations were carried up to values of the compression for which the relations (15) are applicable with an accuracy of 10^{-3} to 10^{-4}. The calculations for very rarefied matter (up to $r_0 Z^{1/3} \approx 100$ A) led to the following values for the constants C_∞ and δC_∞:

$$C_\infty = 0.6806018678, \quad \delta C_\infty = -0.615434693.$$

The calculated thermodynamical quantities are given in the table.* The tables listing the shapes of the potentials for the various values of the radius of the atom are omitted for lack of space.

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*Our values for the charge of the electron and the Bohr radius, e = 4.80286 × 10^{-10} cgs esu and a_0 = 0.529172 A, are somewhat different from those used by Latter.[2]

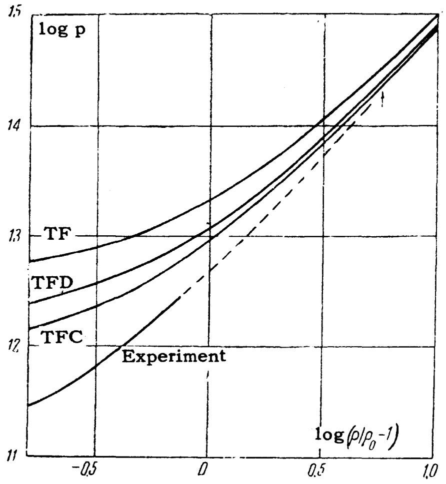

FIG. 1

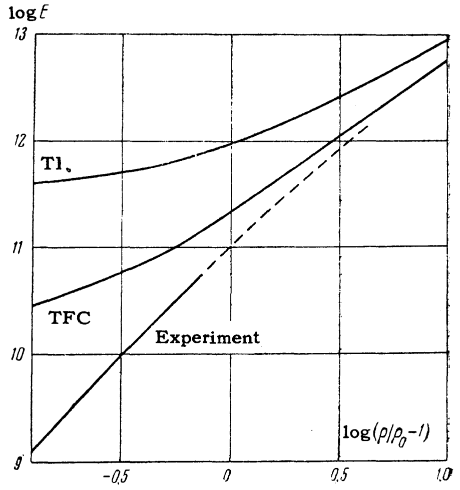

FIG. 2

5. DISCUSSION OF THE RESULTS

Let us compare the results of our calculations with the experimental data of Al'tshuler et al.[9] on the compressibility of iron. Figures 1 and 2 show the theoretical and experimental curves for the pressure and the energy* (P is in dyne/cm^2 and E in erg/g). It is seen that the TFC model reproduces the experimental curves better than the TF and TFD models. The Weizsäcker model gives much lower pressures;† this is due to the fact that the coefficient of the correction term used by Gombas is ten times too large (see reference 5). The dotted curves represent the extrapolation of the experimental curves into the region where the correction to the pressure calculated by the TF model amounts to 30% (arrow in Fig. 1). These extrapolated curves, which go over into the curves of the TFC model, apparently describe (with an accuracy of 10 to 15%) the compressibility of iron at pressures which have not yet been attained by experiment.*

In the region of normal densities where it is impossible to neglect the shell structure of the atom and where the approximation of spherical cells and the self-consistent field method become inaccurate, the TFC model is, in general, not applicable. However, in contrast to the TF model, the TFC model does describe qualitatively some properties of solid matter, so that the discussion below has some significance.

The corrections to the thermodynamical quantities are negative and go to zero more slowly for $V \to \infty$ than the uncorrected quantities. Therefore the corrected pressure becomes zero for some finite density $\rho_0(Z)$. By virtue of the thermodynamical relation $P = -(\partial E/\partial V)_{T=0}$ the energy has a minimum for this density;† the value of this mini-

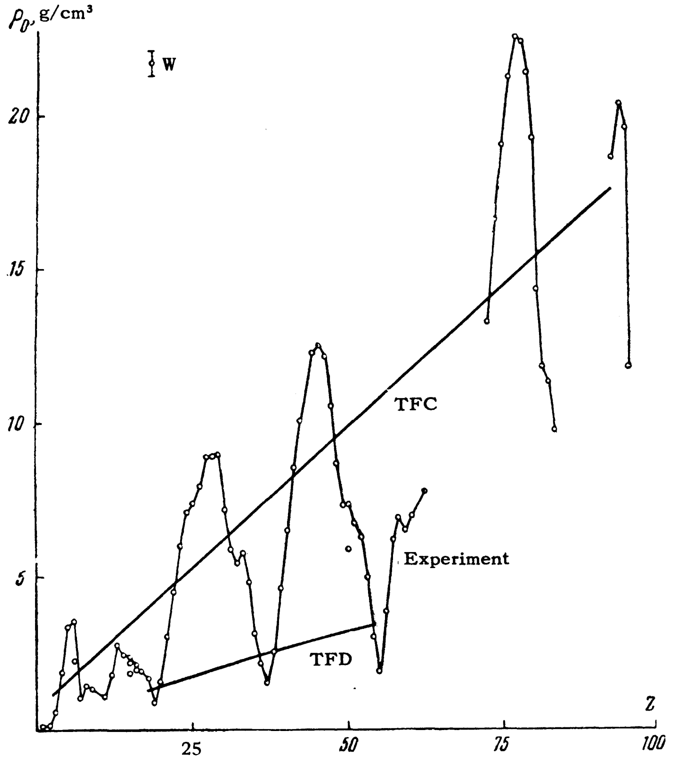

FIG. 3

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*The energy in the TFC model was reckoned from the minimum (see below), which is equal to –5.488 ev/atom relative to the energy of the cold infinite atom.

†The corresponding curves are not shown in Figs. 1 and 2, since the points obtained by Gombas[4] lie beyond the limits of the graphs.

*It was pointed out by Ya. B. Zel'dovich that the occurrence of a phase transition in the unknown region may complicate the picture.

†Since the dependence of the corrections on Z is different from that of the uncorrected quantities, the binding energy and the density of the uncompressed matter are obtained separately for each element from the data of the table.

mum gives the binding energy of solid matter in our model.

Figure 3 shows the experimental and theoretical dependence of the density of the uncompressed matter on the charge of the nucleus. The TFC model, in which the dependence of the physical quantities on Z is monotonic, is not adequate for the explanation of the behavior of the experimental curves. It does, however, describe the average dependence of the density on the charge better than the TFD model. The reasons for the sharp disagreement between experiment and the results of the Weizsäcker model (point W in the figure) were discussed earlier.

In conclusion we note that the numerical calculations of Kompaneets and Pavlovskiĭ,[6] who obtained the correction to the potential for the infinite cold atom, are not sufficiently accurate for distances from the nucleus larger than $rZ^{1/3} = 2$ A. Furthermore, reference 6 contains a printing error: the quantity shown in the figure is not $y(x)$, as indicated in the paper, but $y(x)/8(6\pi)^{2/3}$.

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