SOVIET PHYSICS JETP VOLUME 35(8), NUMBER 6 JUNE, 1959

THE LIMITS OF APPLICABILITY OF THE QUASI-CLASSICAL EQUATION OF STATE OF MATTER

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Submitted to JETP editor July 17, 1958

J. Exptl. Theoret. Phys. (U.S.S.R.) **35**, 1545-1557 (December, 1958)

Quantum corrections have been found for the equation of state obtained with the aid of the Thomas-Fermi model. It is shown that, at all temperatures and densities, the lowest order quantum and exchange corrections to the pressure are negative, their ratio not exceeding $1/3$; it equals $2/9$ in the degenerate electron gas region and $1/3$ in the high-temperature region. The boundary of the region of temperatures and densities is found for which the relative contribution of the quantum correction to the pressure is small and application to the Thomas-Fermi model is feasible.

1. INTRODUCTION

THE problem of the equation of state of matter, i.e., the relation between the pressure, density and temperature, is of importance for many problems in physics and related sciences. In the derivation of this equation for condensed media, wide use is made of the Thomas-Fermi method (for brevity T-F), along with other methods. In a large number of papers setting forth the application of this method (see, for example, references 1 to 3), quantitative results are obtained relating to a wide range of densities and temperatures.

Although the T-F method is known to be approximate, the necessary analysis of the applicability of these results has not been carried out. In the literature there are only qualitative considerations of the non-applicability of the method for small compressions (in the region of low temperatures) and on the improvement of its applicability with increase in temperature. However, the quantitative problems of the limits of the regions of density and temperature in which the method is applicable with a given accuracy, and on the size of the corrections to the quasi-classical equations of state, remain essentially unresolved. The present research represents an attempt at a solution of this problem.

It should be observed that the ordinary method of applying the T-F method for the derivation of the equation of state is connected with second-order approximations. In the first place, use is made of a simplified model,[4] in which we consider isolated spherical cells that contain a motionless nucleus (of charge Z) and Z electrons. The radius of the cell corresponds to the given density; at the boundaries of the cell, the derivative of the potential is equal to zero. In this model no account is taken of many factors: pecularities connected with the crystalline structure, vibrations of the nuclei, collective interaction of the particles, etc. An analysis of these factors enters into the framework of the present research* and in what follows we shall make use of the model thus considered.

In the second place, an exact quantum mechanical solution of the problem, within the framework of this model, is replaced by an approximate consideration according to T-F method, which is the quasi-classical approximation to the Hartree-Fock method. Like the latter, the T-F method also disregards the effects of strong correlation between the particles; these effects were estimated for low temperatures in reference 5, where their contribution to the pressure is shown to be small and to be decreasing with increase in the latter.

The quantum effects that reflect the inaccuracy of the quasi-classical approximation play a much more important role; the following account is devoted to their investigation. For an uncompressed atom these effects were considered quantum mechanically in references 6 to 8.

The quantity

$$q = \hbar^2 / l^2 p_0^2, \tag{1.1}$$

where l is a characteristic length and p_0 is the

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*It can be assumed that in the really important part of the region where the Thomas-Fermi method is itself applicable, the role of these factors is not large and they can be considered independently of quantum effects (about the latter, see below).

characteristic momentum, appears as a parameter that defines the role of the quantum correction.

We use non-dimensional variables throughout the work. As the pressure $\mathcal{P}$, the numerical density of the electrons ρ, and the temperature T we use

$$\mathcal{P} = PZ^{10/3}e^2/a_0^4, \quad \rho = \nu n Z^2/a_0^3, \quad kT = \vartheta Z^{4/3}e^2/a_0, \tag{1.2}$$

where a_0 is the Bohr radius and $n = 3a_0^3/4\pi Z R^3$ is the mean density.

It is convenient to choose the potential Φ and the distance from the nucleus r in the form

$$\xi = (\mu - \Phi)/kT, \qquad x = r/R, \tag{1.3}$$

where μ is the chemical potential and R is the radius of the cell.

We proceed to estimate the parameter q. We consider two regions: I — the region of degeneracy of the electron gas ($n/\vartheta^{3/2} \gg 1$) and II — the region of high temperatures ($n/\vartheta^{3/2} \ll 1$). For p_0 we have (M is the mass of the electron)

$$p_0 \sim \hbar\rho^{1/3} \sim (\hbar/a_0) Z^{2/3} n^{1/3}, \qquad \text{I}$$

$$p_0 \sim \sqrt{MkT} \sim (\hbar/a_0) Z^{2/3} \vartheta^{1/2}. \qquad \text{II}$$

An estimate of l is more complicated; it is given by· (see Sec. 3):

$$l \sim a_0 Z^{-1/3} n^{-1/6} \quad \text{I} \qquad\qquad l \sim a_0 Z^{-1/3} (\vartheta/n)^{1/2} \quad \text{II}$$

As a result we obtain

$$\begin{aligned} q &\sim Z^{-2/3} n^{-1/3} \quad \text{I} \\ q &\sim Z^{-2/3} n/\vartheta^2 \quad \text{II} \end{aligned} \tag{1.4}$$

It then follows that the quantum corrections: (a) decrease with increasing nuclear charge Z (see references 6 and 7), (b) fall off with increasing temperature for a fixed density, and (c) at a fixed temperature, increase with increasing density in II and decrease in region I, and thus have a maximum at $n \sim \vartheta^{3/2}$. These rules are demonstrated in Fig. 3, which is drawn from the results of Sec. 7 (the dashed curve corresponds to $n \sim \vartheta^{3/2}$).

We now proceed to the problem of exchange effects, which is closely related to the foregoing. Ordinarily, exchange effects are either generally disregarded (T-F model) or are considered exactly within the framework of the classical (Thomas-Fermi-Dirac) model (see reference 3, for example). Such a manner of calculation of the exchange is, strictly speaking, inconsistent, since the quantum effects, which are not considered in this case, are commensurable with the exchange effects (reference 6). It would be more valid to limit the exchange correction to the lowest order since higher order corrections lie beyond the limits of accuracy of the model.

As the corresponding parameter of the expansion we have the quantity (see Sec. 5)

$$2MA(p_0, r)/p_0^2 \sim e^2\hbar^2\rho/p_0^2. \tag{1.5}$$

It is easy to see that this parameter is identical to q, so that the quantum and exchange corrections differ only by a numerical factor.

To conclude this section we consider the peculiarities of the Hartree-Fock approximation at temperatures differing from zero, wherein the state of the system is a mixture of pure states. In this case the concepts of the single particle approximation and the approximation in which the density matrix is multiplicative do not, strictly speaking, coincide. The multiplicative approximation usually employed (it is used in the present research) corresponds to the fact that the force field is unique for all the pure states mentioned above; self-consistency is thus produced over the entire mixed state as a whole. Self-consistency within the framework of each of the pure states separately is the more accurate (and is compatible with the single-particle description). In this case, however, the multiplicative character is destroyed and the solution of the problem is made more complicated, to say the least. The corresponding effects must be considered on a par with the usual correlations (the latter are responsible for the inapplicability of the single-particle approach).

The following notation is used in this paper: $\tilde{a}$ denotes that the quantity $a(\mathbf{r})$ is referred to the surface of the system (in particular at the point $r = R$).

2. EXPRESSION FOR THE PRESSURE IN THE HARTREE APPROXIMATION

We begin with the expression for the force acting on the system. The total momentum of the latter can be written in the form

$$G_i = \mathrm{Sp}\,(\hat{\rho}\,\hat{p}_i), \tag{2.1}$$

where $\hat{\rho}$ is the density matrix operator,[7] $\hat{\mathbf{p}} = -i\hbar\nabla$ is the momentum of the particle; the spur is taken over all variables except the spin. Differentiating (2.1) with respect to the time and taking into account

$$i\hbar\, d\hat{\rho}/dt = [\hat{H}, \hat{\rho}],$$

we get the following expression for the force:

$$dG_i/dt = -(i/\hbar)\,\mathrm{Sp}\,\{[\hat{H}, \hat{\rho}]\,\hat{p}_i\}. \tag{2.2}$$

Here,

$$\hat{H} = \hat{p}^2 / 2M + \Phi(\mathbf{r}) \qquad (2.3)$$

is the single particle Hamiltonian; $\Phi = U + B$, where U is the potential of the external field, $B(\mathbf{r}) = e^2 \int d\mathbf{r}' \rho(\mathbf{r}')/|\mathbf{r} - \mathbf{r}'|$ is the self-consistent potential of the electrons, ρ is the numerical particle density.

We compute the spur in (2.1) and (2.2) with the aid of the plane waves

$$\psi_{\mathbf{p}s}(\mathbf{r}, \sigma) = (2\pi\hbar)^{-3/2} \exp(i\mathbf{p}\cdot\mathbf{r}/\hbar)\delta_{s\sigma}.$$

We then have for the arbitrary (but diagonal in the spin variables*) operator O

$$\operatorname{Sp} \hat{O} = \sum_{s\sigma} \int d\mathbf{r} \int d\mathbf{p} \bar{\psi}_{\mathbf{p}s} \hat{O} \psi_{\mathbf{p}s} = 2(2\pi\hbar)^{-3} \int d\mathbf{r} \int d\mathbf{p} \langle \hat{O} \rangle_{\mathbf{p}}, \qquad (2.4)$$

where

$$\langle \hat{O} \rangle_{\mathbf{p}} \equiv \exp(-i\mathbf{p}\cdot\mathbf{r}/\hbar) \hat{O} \exp(i\mathbf{p}\cdot\mathbf{r}/\hbar).$$

In this notation the distribution function over the coordinates and the momentum takes the simple form[9]

$$f(\mathbf{r}, \mathbf{p}) = (2\pi\hbar)^{-3} \langle \hat{\rho} \rangle_{\mathbf{p}}.$$

In this case the density is connected to f by the relation

$$\rho(\mathbf{r}) = 2 \int f(\mathbf{r}, \mathbf{p})\, d\mathbf{p}. \qquad (2.5)$$

From (2.2) to (2.4) we have the following expression for the spatial density of the force

$$-\frac{2i}{\hbar} \int d\mathbf{p} \Big\{ -\frac{i\hbar}{M} \mathbf{p} \cdot \nabla f - \frac{\hbar^2}{2M} \Delta f$$
$$- [f(\mathbf{r}, \mathbf{p} - i\hbar\nabla) - f(\mathbf{r}, \mathbf{p})]\, \Phi(\mathbf{r}) \Big\} p_i, \qquad (2.6)$$

where the gradient in the latter term operates on Φ. Expanding this term in a series in $\hbar$ and integrating by parts, we establish the fact that it reduces to the expression $-\nabla_i \Phi \rho$. In the subsequent integration over $\mathbf{r}$, the term $-\nabla_i \beta \rho$ drops out (the internal forces) and we obtain the relation

$$dG_i / dt = -\int \rho \nabla_i U d\mathbf{r} - \int \sigma_{ik}\, dS_k. \qquad (2.7)$$

Here the first term is the exchange force, σ_{ik} is the strain tensor

$$\sigma_{ik} = (2/M) \int d\mathbf{p} p_i p_k f(\mathbf{r}, \mathbf{p}) - (i\hbar/M) \int d\mathbf{p} p_i \nabla_k f(\mathbf{r}, \mathbf{p}). \qquad (2.8)$$

Integration over the second term of (2.7) is carried out over the surface of the system; denoting the direction of the corresponding normal by $\mathbf{n}$ we obtain the desired expression for the pressure ($\mathscr{P} = n_i n_k \sigma_{ik}$)

$$\mathscr{P} = (2/M) \int d\mathbf{p} (\mathbf{n} \cdot \mathbf{p})^2 \tilde{f} - (i\hbar/M) \int d\mathbf{p} (\mathbf{n}\cdot\mathbf{p})(\mathbf{n} \cdot \nabla \tilde{f}). \qquad (2.9)$$

We recall that the tilde denotes evaluation at a point on the surface.

3. THE EQUATION OF STATE IN T-F MODEL

In the quasi-classical approximation which corresponds to the T-F model, we can discard the second term in (2.9), which vanishes with $\hbar$, and set

$$f(\mathbf{r}, \mathbf{p}) = F(E) \equiv (2\pi\hbar)^{-3} [\exp\{(E - \mu)/kT\} + 1]^{-1}, \qquad (3.1)$$

where

$$E(\mathbf{r}, \mathbf{p}) \equiv p^2/2M + \Phi(\mathbf{r}).$$

Then (2.9) gives the well-known equation[2] (non-dimensional variables are used; see Introduction):

$$P = (2\sqrt{2}/3\pi^2)\, \vartheta^{5/2} I_{3/2}(\tilde{\xi}), \qquad (3.2)$$

where*

$$I_n(x) = \int_0^\infty y^n dy / (\exp(y - x) + 1),$$

while

$$I'_n(x) = n I_{n-1}(x). \qquad (3.3)$$

To find the limiting value of ξ, we must solve the equation for the potential. We connect the latter with density by the Poisson equation

$$\Delta_x \xi(x) = \gamma \nu(x), \quad \gamma = (36\pi)^{1/2} n^{1/2} (\tilde{\xi}) \qquad (3.4)$$

The corresponding boundary conditions are

$$x\xi|_0 = \gamma/3 \quad \xi'|_1 = 0.$$

The first of these corresponds to $\Phi \rightarrow -Ze^2/r$ for $r \rightarrow 0$.

In the T-F model, substitution of (3.1) in (2.5) gives the following expression for the density:

$$\nu = (\sqrt{2}/\pi^2)\, \vartheta^{3/2} n^{-1} I_{1/2}(\xi), \qquad (3.5)$$

whence

$$\Delta_x \xi = \alpha I_{1/2}(\xi), \quad \alpha = (\sqrt{2}/\pi)(6/\pi)^{2/3} \vartheta^{1/2} n^{-2/3}. \qquad (3.6)$$

It is now expedient to transform to the integral equation

$$\xi(x) = \tilde{\xi} + \alpha \int_x^1 I_{1/2}[\xi(t)]\,(t/x - 1)\, t\,dt \qquad (3.7)$$

with the normalization condition

$$\int_0^1 I_{1/2}(\xi)\, t^2\, dt = \beta, \quad \beta = \gamma/3\alpha = (\pi^2/3\sqrt{2})\, n \vartheta^{-3/2}. \qquad (3.8)$$

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*States are considered in which the same occupation numbers apply to all levels that refer to the same energy.

*These functions were investigated and tabulated in reference 10.

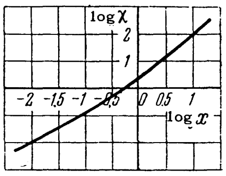

FIG. 1

The solution of the problem in the approximation under consideration is thus determined by two parameters β and α. The first of these is identical with the degeneracy parameter of a homogeneous electron gas, the second, as is evident from (3.7), is the parameter of the homogeneity of the distribution, determining the departure of $\xi(x)$ from the constant $\tilde{\xi}$.

Equation (3.7) is usually solved numerically. We limit ourselves to its analytic solution in the region in which the distribution is close to uniform. We use the iteration method, assuming α to be a small quantity. Substituting the resulting solution in (3.8), we can find the desired value of $\tilde{\xi}$. Simple calculations give*

$$\begin{gathered}\tilde{\xi} = \xi^0 - \alpha I_{1/2}/10 + \ldots, \\ P = (2\sqrt{2}/3\pi^2)\,\vartheta^{5/2}\,[I_{3/2} - (3\alpha/20) I_{1/2}^2 + \cdots].\end{gathered} \tag{3.9}$$

Here the functions I have the argument ξ^0, which is determined by the relation

$$I_{1/2}(\xi^0) = 3\beta. \tag{3.10}$$

If we can neglect corrections due to inhomogeneity, we have the following equation of state

$$P = \vartheta^{5/2}\chi(n/\vartheta^{3/2}), \tag{3.11}$$

where the function $\chi(x)$ is determined parametrically:

$$\chi = (2\sqrt{2}/3\pi^2)\, I_{3/2}(\xi^0), \qquad x = (\sqrt{2}/\pi^2)\, I_{1/2}(\xi^0).$$

Its form is shown in Fig. 1.

In the region where the electron gas is degenerate ($\beta \gg 1$ and, in accord with (3.10), $\xi^0 \to \infty$), we have $I_{1/2} = {}^2\!/_3\, \xi^{3/2}$, $I_{3/2} = {}^2\!/_5\, \xi^{5/2}$, from which we find the well-known equation[11]

$$P = {}^1\!/_5\,(3\pi^2)^{2/3}\, n^{5/3}. \tag{3.11'}$$

In the opposite limiting case of high temperatures ($\beta \ll 1$, $\xi^0 \to -\infty$)

$$I_{1/2} = (\sqrt{\pi}/2)e^{\xi}, \quad I_{3/2} = {}^3\!/_2 I_{1/2}$$

then the usual Clapeyron equation holds:

$$P = n\vartheta. \tag{3.11''}$$

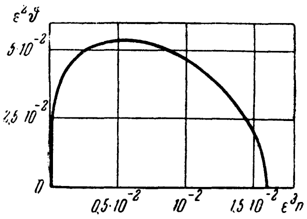

FIG. 2

The relative error in the pressure connected with neglect of non-uniformity is determined by (3.9)

$$\delta P/P = a n^{4/3}/P, \quad a = (2\pi/5)(3/4\pi)^{2/3}. \tag{3.12}$$

We now find the boundaries of the region outside of which $\delta P/P$ is less than a given quantity ϵ, while within it it is greater than ϵ. Introducing the notation $\epsilon^3 n = \sigma$, $\epsilon^2\vartheta = \tau$, we have

$$a\sigma^{4/3}/\tau^{5/2}\chi(\sigma/\tau^{3/2}) = 1. \tag{3.13}$$

for $\beta \gg 1$, this gives $\sigma = (2\pi^3)^{-1}$, for $\beta \ll 1$, $\tau = a\sigma^{1/3}$. The curve corresponding to (3.13) is shown in Fig. 2. With its help we can, for example, establish that use of Eq. (3.11′) in the degenerate case gives the correct order of magnitude of the quantities (within the framework of the T-F model), i.e., $\epsilon \sim 1$, at pressures

$$\mathcal{P} > 6\cdot10^5 Z^{10/3} \text{ atmos.}$$

In conclusion, we find the expression for the length parameter l (see Introduction). It will be the greater of the quantities

$$\xi/\nabla\xi, \quad (\xi/\Delta\xi)^{1/2}.$$

We can limit ourselves to these two quantities if we consider only the quantum correction of lowest order (see below). Estimating by Eqs. (3.7) and (3.8), we obtain

$$l \sim (\xi^0\vartheta/n^{1/3})^{1/2} R.$$

In the degenerate case $\xi^0 \sim n^{2/3}\vartheta$, at high temperatures $\xi^0 \sim 1$ (with logarithmic accuracy). We then easily obtain the estimates given in the Introduction.

4. QUANTUM CORRECTIONS TO THE PRESSURE

We now proceed to find the corrections to the equations of state necessitated by the inaccuracy of the quasi-classical approximation. For this purpose we expand (2.9) in powers of $\hbar$, limiting ourselves to terms of second order; quantum corrections of lowest order will be taken into account.

Besides consideration of the second term of (2.9), it is necessary to introduce a more accurate expression for the distribution function. We begin with the density matrix operator in the form[7]

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*It follows from (3.9) that the actual parameter of the expansion is not α but $\alpha I'_{1/2}$ (the quantities $I^2_{1/2}/I'_{1/2}$, $I_{3/2}$ are of the order of unity).

$$(2\pi\hbar)^{-3}\hat{\rho} = F(\hat{H}) \equiv (2\pi\hbar)^{-3}\left[\exp\left(\frac{\hat{H}-\mu}{kT}\right)+1\right]^{-1}, \quad (4.1)$$

where $\hat{H}$ is the Hamiltonian of (2.3). If we neglect the non-commutability of its components, we immediately return to (3.1). To obtain quantum corrections to the distribution functions, we must take into consideration the first commutators of the operators $\hat{p}^2/2M$ and Φ. A simple calculation gives:[7]

$$f(\mathbf{r}, \mathbf{p}) = F(E) - (i\hbar\mathbf{p}\nabla\Phi/2M + \hbar^2\Delta\Phi/4M)\,F''(E)$$
$$- (\hbar^2/6M)\,[(\nabla\Phi)^2 \quad (4.2)$$
$$+ (\mathbf{p}\nabla)^2\Phi/M]F'''(E) - (\hbar^2(\mathbf{p}\nabla\Phi)^2/8M^2)\,F^{\mathrm{IV}}(E) + \cdots.$$

Substituting this expression in (2.9) and considering that $\partial\Phi/\partial r = 0$ on the surface of the spherical cell, we have

$$\mathscr{P} = \frac{1}{3\pi^2 M\hbar^3}\int F(\widetilde{E})\,p^4dp$$
$$+ \frac{2\widetilde{\Phi}''}{15\pi^2M^2\hbar}\int\left\{5F''(\widetilde{E}) + \frac{p^2}{M}F'''(\widetilde{E})\right\}p^4dp.$$

It is easy to prove that the last integral on the right side vanishes identically.

Thus, in the approximation under consideration, the pressure is connected with the potential on the boundary by the same relation (3.2) as in the T-F model. This value of the potential will, however, differ from the corresponding quasi-classical value.

In what follows, the subscript zero denotes any quantity that refers to the T-F approximation. Setting $\xi = \xi_0 + \xi_1$, expanding (3.2) in ξ_1, and also taking (3.3) into account, we get the following expression for the relative quantum correction to the pressure

$$\delta_1 P/P_0 = (3I_{1/2}(\widetilde{\xi}_0)/2I_{3/2}(\widetilde{\xi}_0))\,\xi_1. \quad (4.3)$$

To find $\widetilde{\xi}_1$, we must solve the T-F equation with quantum corrections. Substituting (4.2) in (2.5), we obtain

$$\delta\nu = \frac{\sqrt{2}}{24\pi^2}(4\pi/3)^{2/3}Z^{-2/3}\vartheta^{1/2}n^{-1/3}\{I'''_{1/2}(\xi)(\nabla_x\xi)^2 + 2I''_{1/2}(\xi)\,\Delta_x\xi\}.$$

for the quantum correction to the density.

Substituting this expression in (3.4), expanding in ξ_1, and taking (3.6) into account,

$$\Delta\xi_1 - \alpha I'_{1/2}(\xi_0)\,\xi_1$$
$$= \frac{\sqrt{2}Z^{-2/3}}{6\pi\vartheta^{1/2}}\left\{I'''_{1/2}(\xi_0)(\nabla\xi_0)^2 + 2\alpha I''_{1/2}(\xi_0)\,I_{1/2}(\xi_0)\right\}. \quad (4.4)$$

A simple substitution can be suggested to simplify (4.4). Setting

$$\xi_1 = \frac{\sqrt{2}Z^{-2/3}}{6\pi\vartheta^{1/2}}(I'_{1/2}(\xi_0) + u_1),$$

we obtain

$$\Delta u_1 - \alpha I'_{1/2}(\xi_0)\,u_1 = \alpha\,[(I'_{1/2}(\xi_0))^2 + I_{1/2}(\xi_0)I''_{1/2}(\xi_0)] \quad (4.5)$$

with the boundary conditions

$$xu_1|_0 = 0, \quad u'_1|_1 = 0.$$

In this case, the quantum correction to the pressure becomes

$$\delta_1 P/P_0 = \frac{\sqrt{2}}{4\pi}\,\frac{Z^{-2/3}}{\vartheta^{1/2}}\,\frac{I_{1/2}(\widetilde{\xi}_0)}{I_{3/2}(\widetilde{\xi}_0)}\{I'_{1/2}(\widetilde{\xi}_0) + \widetilde{u}_1\}. \quad (4.6)$$

5. EXCHANGE CORRECTIONS TO THE EQUATION OF STATE

Account of exchange effects is brought about by replacing the Hamiltonian (2.3) by the expression[7]

$$\hat{H} = \hat{p}^2/2M + \Phi(\mathbf{r}) - \hat{A}, \quad (5.1)$$

where

$$\hat{A} = 4\pi e^2\hbar^2\int d\mathbf{p}'\cdot p'^{-2}\hat{\rho}(\mathbf{r}, \mathbf{p}' + \hat{\mathbf{p}}). \quad (5.2)$$

Corresponding to this, there appears in (2.6) the additional term

$$2\int d\mathbf{p}\,\{\nabla f\,(\partial A/\partial\mathbf{p}) - \nabla A\,(\partial f/\partial\mathbf{p})\}, \quad (5.3)$$

where $A(\mathbf{r}, \mathbf{p}) \equiv \langle\hat{A}\rangle_{\mathbf{p}}$. We consider only quasi-classical exchange effects [therefore (5.3) amounts to the ordinary Poisson bracket]: mixed exchange-quantum corrections are quantities of a higher border of smallness.

In the following, exchange effects are considered as small (see Introduction), so that we can replace f in (5.3) by the expression (3.1). Simple calculations give the following expression for the contribution of (5.3) to the strain tensor:

$$-\int d\mathbf{p}\,(f\partial A/\partial p_k - A\partial f/\partial p_k)p_i$$

and to the pressure

$$\delta'\mathscr{P} = -\frac{1}{3}\int d\mathbf{p}\widetilde{A}(\mathbf{r}, \mathbf{p})\widetilde{f}(\mathbf{r}, \mathbf{p}). \quad (5.4)$$

Furthermore, substitution in (3.1) of the expression $p^2/2M + \Phi - A$ for $E(\mathbf{r}, \mathbf{p})$ changes the distribution function by an amount

$$\delta f(\mathbf{r}, \mathbf{p}) = -2MA\partial f/\partial(p^2) = -A\partial f/\partial\Phi. \quad (5.5)$$

A change in pressure is also associated with this circumstance: substituting (5.5) in (2.9), we have

$$\delta''\mathscr{P} = \frac{4}{3}\int d\mathbf{p}\widetilde{A}\widetilde{f}. \quad (5.6)$$

Adding (5.4) and (5.5), we have (see Appendix I)

$$\frac{(\delta' P + \delta'' P)}{P_0} = \frac{3Z^{-2/3}}{\sqrt{2}\,\pi\vartheta^{1/2}I_{3/2}(\widetilde{\xi}_0)}\int_{-\infty}^{\widetilde{\xi}_0}(I'_{1/2}(\xi))^2d\xi. \quad (5.7)$$

Finally, exchange effects change the value of $\tilde{\xi}$ in Eq. (3.2). Denoting $\xi = \xi_0 + \xi_2$, we have

$$\delta'''P/P_0 = (3I_{1/2}(\tilde{\xi}_0)/2I_{3/2}(\tilde{\xi}_0))\tilde{\xi}_2. \qquad (5.8)$$

To find $\tilde{\xi}_2$ we solve the T-F equation with the exchange correction. Starting out from (2.5) and (5.5), we have for the exchange correction to the density

$$\delta\rho = -\frac{\partial}{\partial\Phi}\int d\mathbf{p}Af,$$

or (see Appendix I)

$$\delta\nu = \frac{2Z^{-2/3}\nu}{\pi^3 n}[I'_{1/2}(\xi)]^2. \qquad (5.9)$$

With the help of (3.4) we get

$$\Delta u_2 - \alpha I'_{1/2}(\xi_0)u_2 = 6\alpha[I'_{1/2}(\xi_0)]^2, \qquad (5.10)$$

where

$$\xi_2 = \frac{1}{3\sqrt{2\pi}}\frac{Z^{-2/3}}{\vartheta^{1/2}}u_2.$$

The boundary conditions for μ_1 and μ_2 are identical.

The total exchange correction to the pressure then has the form

$$\frac{\delta_2 P}{P_0} = \frac{\sqrt{2}}{4\pi}\frac{Z^{-2/3}}{\vartheta^{1/2}I_{3/2}(\tilde{\xi}_0)}\left\{6\int_{-\infty}^{\tilde{\xi}_0}[I'_{1/2}(\xi)]^2 d\xi + I_{1/2}(\tilde{\xi}_0)\tilde{u}_2\right\}. \qquad (5.11)$$

6. RELATION BETWEEN THE QUANTUM AND EXCHANGE CORRECTIONS

Equations (4.5), (4.6) for the quantum corrections and (5.10), (5.11) for the exchange corrections have an identical structure and can be written in the same fashion. Indeed,

$$\frac{\delta_i P}{P_0} = \frac{Z^{-2/3}}{2\sqrt{2}\pi\vartheta^{1/2}I_{3/2}(\tilde{\xi}_0)}\left\{\int_{-\infty}^{\tilde{\xi}_0}\Psi_i(\xi)\,d\xi + I_{1/2}(\tilde{\xi}_0)\tilde{u}_i\right\}, \qquad (6.1)$$

$$\Delta u_i - \alpha I'_{1/2}(\xi_0)u_i = \alpha\Psi_i(\xi_0); \quad xu_i|_0 = 0, \quad u'_i|_1 = 0, \qquad (6.2)$$

where i = 1, 2 (index 1 corresponds to the quantum, index 2 to the exchange corrections), while the functions Ψ_i have the form

$$\Psi_1 = I_{1/2}I''_{1/2} + (I'_{1/2})^2,\ \Psi_2 = 6(I'_{1/2})^2. \qquad (6.3)$$

Their ratio

$$\eta(\xi_0) = \Psi_1/\Psi_2 = {}^1/_6(1 + I_{1/2}I''_{1/2}/(I'_{1/2})^2) \qquad (6.4)$$

is a slowly-varying monotonic function.

In the region of degeneracy, where $\tilde{\xi}_0 \to \infty$, η is constant* and is equal to $^2/_9$. The same is also characteristic of the ratio of the quantum and exchange corrections:

$$\delta_1 P/\delta_2 P = 2/9. \qquad (6.5)$$

In the opposite limiting case $\xi_0 \to -\infty$, $\eta = {}^1/_3$ and

$$\delta_1 P/\delta_2 P = 1/3. \qquad (6.6)$$

It must be kept in mind that the condition $\xi_0 \to -\infty$ cannot be satisfied throughout the entire volume of the atom, since the electron gas is always degenerate close to the nucleus ($\xi_0 \sim Ze^2/rT \to \infty$). Therefore, the ratio (6.6) holds only for sufficiently large $-\tilde{\xi}_0$, where the region just mentioned plays a small role.

Going on to a consideration of the general case, we expand $\eta(\xi_0)$ in a series about the point $\tilde{\xi}_0$. Taking into consideration the boundary conditions in Eq. (3.5), we find

$$\eta(\xi_0) = \eta(\tilde{\xi}_0)(1 + C(x-1)^2 + \cdots),$$

where

$$C = \alpha I_{1/2}(\tilde{\xi}_0)\eta'(\tilde{\xi}_0)/2\eta(\tilde{\xi}_0).$$

If C is small in comparison with unity, η can be considered constant, equal to $\eta(\tilde{\xi}_0)$. In this case, in accord with (6.2),

$$\tilde{u}_1/\tilde{u}_2 = \eta(\tilde{\xi}_0). \qquad (6.7)$$

To find the regions in which C is small, we return to Eq. (3.8). Keeping in mind the monotonic character of the functions $I_{1/2}(\xi_0)$ and $\xi_0(x)$, we have

$$n/\vartheta^{3/2} > (\sqrt{2}/\pi^2)I_{1/2}(\tilde{\xi}_0).$$

Hence

$$|C| = \frac{2\sqrt{2}}{\pi}(3/4\pi)^{2/3}\vartheta^{1/2}n^{-2/3}|I_{1/2}\eta'/\eta| < 0.66\,|I_{1/2}^{2/3}\eta'/\eta|\,n^{-1/3}.$$

The function $|I_{1/2}^{2/3}\eta'/\eta|$ has a maximum equal to 1.2×10^{-3}, whence

$$n > 3\cdot 10^{-10}|C|^{-3}.$$

Even for C = 0.02, this condition reduces to $\eta > 3 \times 10^{-5}$, which corresponds to densities greater than $5 \times 10^{-4} Z^2$ g/cm^3; in this way, virtually the entire region subject to this consideration is used up. Therefore, the ratio (6.7) is valid practically everywhere. Taking this into account, we have, furthermore,

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*ξ_0 is itself an increasing function inside the atom. Therefore, if the gas is degenerate on the boundary of the cell, it is clearly degenerate inside the atom, too.

$$\frac{\delta_1 P}{P_0} - \eta(\widetilde{\xi_0})\frac{\delta_2 P}{P_0} = \frac{Z^{-2/3}}{2\sqrt{2}\pi\vartheta^{1/2} I_{3/2}(\widetilde{\xi_0})}\int\limits_{-\infty}^{\widetilde{\xi_0}} [\eta(\xi) - \eta(\widetilde{\xi_0})]\,\Psi_2(\xi)\,d\xi. \tag{6.8}$$

$\eta(\xi)$ is a monotonically decreasing function; therefore, the right hand side of (6.8) is always positive.

At the same time we can show that $\delta_1 P$ and $\delta_2 P$ are negative quantities. With this purpose we make the substitution

$$x^{-1}v_i(x) = u_i(x) + I_{1/2}^{-1}(\widetilde{\xi_0})\int\limits_{-\infty}^{\widetilde{\xi_0}} \Psi_i(\xi)\,d\xi.$$

in (6.1), (6.2). Then

$$\frac{\delta_i P}{P_0} = \frac{Z^{-2/3}\,\widetilde{I}_{1/2}}{2\sqrt{2}\pi\vartheta^{1/2}\,\widetilde{I}_{3/2}}\,\widetilde{v}_i,$$

$$v_i'' - \alpha I_{1/2}' v_i = \alpha x\Big[\Psi_i(\xi_0) + \big(I_{1/2}'(\xi_0)\,/\,I_{1/2}(\widetilde{\xi_0})\big)\int\limits_{-\infty}^{\widetilde{\xi_0}} \Psi_i d\xi\Big],$$

$$v_i|_0 = 0;\quad v_i'|_1 = v_i|_1.$$

It is shown in Appendix II that an equation of this type (under the condition that its right hand side is positive) has a solution which is a non-positive function.

It then follows that the quantum and exchange corrections to the pressure always decrease the latter:

$$\delta_1 P < 0,\quad \delta_2 P < 0. \tag{6.9}$$

In conjunction with what was said above on the sign of the right hand side of (6.8), this yields

$$0 < \delta_1 P\,/\,\delta_2 P < \eta(\widetilde{\xi_0}). \tag{6.10}$$

In this case the departure of $\delta_1 P/\delta_2 P$ from $\eta(\widetilde{\xi}_0)$ takes place only in the region in which the degeneracy parameter $\beta \sim 1$.

Thus, the ratio of the quantum correction of the lowest order to the corresponding exchange correction does not exceed one third.

7. QUANTUM AND EXCHANGE CORRECTIONS IN THE REGION OF HOMOGENEITY

We now proceed to search for the explicit expressions for the quantum and exchange corrections in the region in which the distribution is close to uniform (as in Sec. 3, this corresponds to smallness of the parameter $\alpha I_{1/2}'$). Putting (6.1) and (6.2) in integral form, we have

$$u_i(x) = \widetilde{u}_i + \alpha\int\limits_x^1 \{\Psi_i + I_{1/2}' u_i(t)\}(t/x - 1)\,t\,dt \tag{7.1}$$

with the condition

$$\int\limits_0^1 (\Psi_i + I_{1/2}' u_i)\,t^2 dt = 0. \tag{7.2}$$

Using the same method as in Sec. 3, we find as the zero approximation

$$\widetilde{u}_i = -\Psi_i\,/\,I_{1/2}'. \tag{7.3}$$

substitution of this expression (6.1) gives

$$\frac{\delta_i P}{P_0} = -\frac{Z^{-2/3}}{2\sqrt{2}\pi\vartheta^{1/2}}\,\frac{I_{1/2}^2}{I_{3/2}\;I_{1/2}'}\,\frac{d}{d\xi_0}\Big\{\int\limits_{-\infty}^{\xi^0} \Psi_i\,d\xi\,/\,I_{1/2}\Big\}. \tag{7.4}$$

We rewrite (7.4) in the form

$$-Z^{2/3}\,\delta_i P\,/\,P_0 \equiv \vartheta^{1/2}\,\Xi_i. \tag{7.5}$$

The functions Ξ, Ψ, I etc. in (7.3), (7.4) and in the formulas below refer to the argument ξ^0 which is determined by Eq. (3.10).

In the region of degeneracy we have for the quantum correction

$$-Z^{2/3}\frac{\delta_1 P}{P_0} = \frac{5}{18\pi(3\pi^2)^{1/3}}\,n^{-1/3}, \tag{7.6}$$

for $\xi_0 \to -\infty$,

$$-Z^{2/3}\,\delta_1 P\,/\,P_0 = (\pi\,/\,6)\,n\vartheta^{-2}. \tag{7.7}$$

The corresponding exchange corrections can easily be found by recalculation* (see Sec. 6). We now proceed to find the boundaries of the region outside of which the quantity $-Z^{2/3}\,\delta_i P/P_0$ is less than a given value δ_i while inside, it is greater than that value. In this way a region is defined in which the T-F model is applicable with a given accuracy $\delta Z^{-2/3}$.

Combining (7.5) and (3.10), we have

$$\delta_i^3\,n = (\sqrt{2}\,/\,\pi^2)\,I_{1/2}\Xi_i^3,\quad \delta_i^2\vartheta = \Xi_i^2, \tag{7.8}$$

While for large $n/\vartheta^{3/2}$ we have $\delta_i^3 n = (3\pi^5)^{-1}(5/18)^3$, and in the opposite case, $\delta_i^2\vartheta = (\pi\delta_i^3 n/6)^{1/2}$. The corresponding curves are plotted in Figs. 3, 4.†

Further, it is necessary to find the limits of applicability of these results. With this purpose, let us find the further terms of the expansion of $\widetilde{u}_i$ and $\delta_i P/P_0$ in series in α. In this case, the structures of Eqs. (7.1), (7.2), and (6.1) are such

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*Calculation by Eq. (7.5) shows that the minimum ratio $\delta_1 P/\delta_2 P$ is equal to 1/5 (and corresponds to $\xi^0 = 6$). We note that the temperature correction (7.6) is proportional to θ^2 for $\delta_1 P/P_0$ and to $\vartheta^2 \ln\vartheta$ for $\delta_2 P/P_0$. This pecularity of exchange effects, to which our attention was drawn by A. S. Kompaneets, is connected with the long-range character of the Coulomb forces. See also Figs. 3 and 4.

†These curves can be also used to find the values of $\delta_i P/P_0$. For this purpose, the curves must be plotted with the coordinates (n, ϑ) for different values of δ.

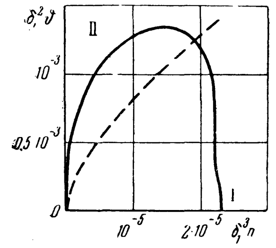

FIG. 3

that the term that is linear in α drops out of $\tilde{u}_i$ and $\delta_i P$. Therefore, the term linear in α in $\delta_i P/P_0$ is connected with the expansion of P_0. Account of inhomogeneity thus leads to the appearance in (7.4) of a factor

$$1 + (3\alpha / 20)\, I^2_{1/2} / I_{3/2},$$

and everything said in Sec. 3 on the limits of applicability of the homogenous approximation remains in force relative to $\delta_i P/P_0$.

Thus, the functions (7.8) can be used only when the corresponding curves lie inside the region of homogeneity, i.e., when they envelop the curve (3.1) (with a given value of ϵ). This takes place for sufficiently small δ_i. Thus the corrections for inhomogeneity do not change the order of magnitude of the quantities entering into (7.4) and (7.8) ($\epsilon \sim 1$) for $\delta_1 < 0.1$ and $\delta_2 < 0.5$, that is, for

$$|\delta_1 P| / P_0 < 0.1\, Z^{-2/3}, \quad |\delta_2 P| / P_0 < 0.5\, Z^{-2/3}. \qquad (7.9)$$

Thus, in the region of degeneracy, the T-F model is valid with accuracy $\delta_1 = 0.01$ at pressures

$$\mathscr{P} > 10^6 Z^{10/3} \text{ atmos.}$$

If we are interested only in the region in which the degeneracy parameter $\beta \lesssim 1$, the conditions (7.9) can be somewhat modified.

For less stringent requirements on the accuracy (larger $\delta_i P/P_0$) or larger Z, the curves under consideration lie outside the region of homogeneity. An analytic solution in this case is not possible; numerical results will be published when they are obtained. We shall abandon at this point a comparison of the results with experiment.

In conclusion, I take this opportunity to thank V. L. Ginzburg, E. L. Feinberg and E. S. Fradkin for discussions and L. V. Pariiskaia for the numerical calculations.

APPENDIX I

The integral

$$\int d\mathbf{p}\, Af = 4\pi e^2\hbar^2 \int \frac{d\mathbf{p}\, d\mathbf{p}'}{|\mathbf{p} - \mathbf{p}'|^2} f(\mathbf{r}, \mathbf{p}) f(\mathbf{r}, \mathbf{p}')$$

reduces after integration over the angles to the form

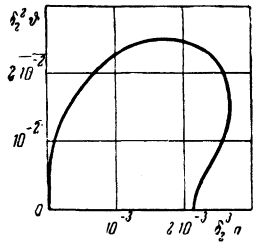

FIG. 4

$$\frac{e^2 M^2 (kT)^2}{2\pi^3\hbar^4}\,\varkappa(\xi),$$

where

$$\varkappa(\xi) = \int_0^\infty \frac{dx}{\exp(x - \xi) + 1} \int_0^\infty \frac{dy}{\exp(y - \xi) + 1} \ln\left|\frac{\sqrt{x} + \sqrt{y}}{\sqrt{x} - \sqrt{y}}\right|.$$

Making the substitution $x \to x + \xi$, $y \to y + \xi$, we have

$$\varkappa'(\xi) = \left[\int_\xi^\infty \frac{dx}{(\exp x + 1)\sqrt{x + \xi}}\right]^2 = (I_{-1/2}(\xi))^2.$$

making use of Eq. (3.3) we obtain, finally,

$$\varkappa(\xi) = 4 \int_{-\infty}^{\xi} (I'_{1/2}(x))^2 dx.$$

APPENDIX II

We shall show that the equation

$$y'' - A(x)\, y = B(x) \qquad \text{(a)}$$

with $B(x)$ a quantity of constant sign and with boundary conditions given at both ends of the interval of integration that are invariable relative to the substitution $y \to -y$, has a sign-constant solution $y(x)$, the sign of which is opposite to the sign of B.

We limit ourselves to boundary conditions of the simplest form. If they are

$$y(0) = 0, \quad y(1) = 0 \text{ or } y(0) = 0, \quad y'(1) = 0,$$

then in place of (a) we can consider the functional

$$\int_0^1 \{(y')^2/2 + Ay^2/2 + By\}\, dx, \qquad \text{(b)}$$

the minimum of which is realized by the solution of Eq. (a) [we are discussing the minimum, since the coefficient in the first term of (b) is positive].

Inasmuch as the first two terms of (b) and the boundary conditions do not change in the substitution $y \to -y$, while the latter term changes sign, the extremal of $y(x)$ belongs to the class of constant-sign functions so that $By < 0$. Actually, if the function y is constant in sign and $By > 0$, or if y changes sign inside the interval of integration, then it clearly does not achieve the minimum of (b), since the function $-|y(x)|$ (for $B > 0$) or

$|y(x)|$ (for $B < 0$) reduces to the much lower value of the functional.

In the presence of a more complicated boundary condition

$$y(0) = 0, \quad y'(1) = y(1)$$

it is necessary to make the functional more complicated, adding to the integrand the quantity $-(d/dx)(y^2/2)$ [in the opposite case, (a) and (b) will not be equivalent to each other]. The parity of this quantity relative to y is conserved by virtue of the previous discussion.

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Translated by R. T. Beyer
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