

Statistical model of matter

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This review is devoted to the development of the statistical model of matter over the last twenty years. The ranges of applicability of the model for electron-nuclear systems (atoms, solids, plasmas) are considered. Effects lying beyond the scope of statistical model (exchange, correlation, quantum and shell effects) are analyzed. The relative roles of the effects enumerated are estimated in different regions of temperature and pressure. The possibility of taking these effects into account as small corrections in the region of applicability of the statistical model is demonstrated. Here a procedure for expanding the physical quantities in series in the small parameters characterizing the corresponding effects is used. Allowance for the corrections considerably extends the possibilities of the statistical model in the study of the structure of matter and makes it possible to obtain new qualitative and quantitative results. It is found, e.g., that allowance for shell effects in the thermodynamics of highly-compressed matter leads to the existence of first-order phase transitions associated with the "squeezing-out" of discrete shells into the continuous spectrum. The refinement of the statistical model at short distances from the nucleus, and other applications to atomic physics, are discussed. The application of the statistical model to the description of the dynamical properties of matter is also considered. In particular, the problem of the collective oscillations of the electron cloud of an atom is treated and the results of a numerical calculation of the corresponding frequencies and widths are given. The method of the density functional is briefly described.

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I. INTRODUCTION

The statistical model of matter (the Thomas-Fermi method or model—the TFM for short) forms the basis of a special approximate approach which is widely used to describe the properties of matter in its hierarchy of different levels (the atomic nucleus, atom, molecule, solid, etc.). Applications of the TFM to the theory of the extremal states of matter that arise under the action of high pressures, high temperatures or strong external fields have achieved particular development. The corresponding fields of physics and related sciences (astrophysics, quantum chemistry and a number of applied disciplines) constitute the field of application of the TFM. The popularity of the TFM is connected with its simplicity, clarity and universality. The latter means that the result of a calculation by the TFM pertains immediately to all the chemical elements: the change from one element to another is effected by a simple transformation of scale. These features of the TFM make it an extremely convenient instrument for qualitative, and in many cases quantitative, analysis. They arise, of course, as a consequence of the approximate nature of the TFM, which is able to give an exact description of reality only in particular limiting situations. Namely, for the TFM to be applicable as a quantitative theory it is necessary that the density or temperature of the substance have a sufficiently high value.

It is not surprising, therefore, that in the course of the almost half-century history of the TFM attempts have continually been made to improve it, with the purpose of extending the range of applicability of the model while preserving its achievements. In the twenty years

that have passed since the publication of the well-known book by Gombás^[1] considerable progress has been achieved in this direction. An account of the corresponding range of questions forms the principal content of this article (Chaps. II, III, V). Additional information can be found in the monographs and reviews^[1-8], and also in the original articles cited below.

Another line of development of the TFM that has already reached a certain degree of completion pertains to the description of the dynamical properties of matter—the response of a nonuniform system to external perturbations varying in time, the characteristics of the normal (collective) oscillations, etc. An account of these questions is given in Chaps. IV and V (see also the monographs and reviews^[1,5,9,10] and the literature cited below). Finally, in recent years a new approach to the theory of condensed media—the density-functional method, which borders closely upon the TFM—has been developing rapidly. The theory of this method is briefly described in Sec. 15, where the corresponding bibliography is also indicated.

In this review we describe the theory of the TFM as applied to ordinary electron-nuclear systems (atoms, solids, plasmas), without touching at all upon applications of the TFM to the theory of the atomic nucleus. The latter problem lies outside the scope of our account, both physically and methodologically (cf.^[5,11-13]). As is usual, the electronic component of matter for a given state of the nuclei serves as the object to which the TFM is applied. In conditions of applicability of the TFM, phonon effects can, to a considerable extent, be described independently (cf., in this connection,^[7,14]).

The results of the development of the TFM show that the statistical model of matter is, in its modern form, an effective method in the theory of the structure of matter, having well-defined and fairly broad limits of applicability. The possibilities of this method are still far from completely opened up. However, it is now already clear that in a number of problems the TFM can successfully replace traditional numerical quantum-mechanical calculations, as it has over the latter the undoubted advantage that belongs to any analytical approach. It is indisputable that the range of such problems will be widened still further in the future development of the TFM.

We dedicate this article to the memory of Aleksandr Solomonovich Kompaneets, our teacher in two generations, who did much to develop the statistical model and extend its range of applications.

II. THOMAS-FERMI MODEL AND ITS LIMITS OF APPLICABILITY

1. Thomas-Fermi model (general information)

The TFM was proposed originally by Thomas^[15] and Fermi^[16] to describe the electron cloud of a heavy atom, which is characterized by a comparatively uniform electron-density distribution.

The TFM is based on the well-known relations of quantum statistics¹⁾

$$a) n = \frac{p_F^3}{3\pi^2}, \quad b) \mu = \frac{p_F^2}{2},$$

where n is the particle-number density, and p_F and μ are the momentum and energy at the boundary of the Fermi distribution. These relations refer to an ideal, uniform, degenerate electron gas. If the gas is weakly nonuniform, it is natural to retain (a) as a local relation²⁾

$$n(x) = \frac{p_F^3(x)}{3\pi^2}, \quad (1.1)$$

and add to the right-hand side of (b) the potential energy

$$U(x) = \int dx' \frac{n(x')}{|x-x'|} + U_e(x) \quad (1.2)$$

of an electron in the field of the other electrons and the external sources (the nuclei):

$$\mu = \frac{p_F^2(x)}{2} + U(x). \quad (1.3)$$

Taking into account the Poisson equation corresponding to (1.2):

$$-\Delta U = \frac{\Delta p_F^3}{2} = 4\pi n + \text{external source} \quad (1.4)$$

it is easy to arrive at a nonlinear differential equation (the Thomas-Fermi equation) for p_F^2 or U . By solving this with the appropriate boundary conditions it is possible to obtain a full description of the "cold" electron system.

The local characteristics of the system are described by the distribution function

¹⁾Here and below we use atomic units: $e = \hbar = m = k = 1$.

²⁾The statement that the properties of a weakly nonuniform system at a given point in space coincide with the properties of the uniform system with the same local value of the density is called the "principle of quasi-uniformity." We shall discuss its limits of applicability below, in Sections 3, 5 and 6.

$$f(x, p) = \theta(p_F^2(x) - p^2), \quad (1.5)$$

where $\theta(x) = 1$ ($x > 0$), $\theta(x) = 0$ ($x < 0$). In particular, the densities in coordinate and momentum space are given by the formulas ($d^3p \equiv dp/(8\pi^3)$)

$$n(x) = 2 \int d^3p f(x, p), \quad n(p) = 2 \int dx f(x, p) \quad (1.6)$$

(the first of these leads to (1.1)). The thermodynamic properties of the system are described by the expression for its energy ($E = E_K + E_e + E_i$), where

$$E_K = \frac{1}{40\pi^2} \int dx p_F^5(x) = \frac{3(3\pi^2)^{2/3}}{10} \int dx n^{5/3}(x), \quad (1.7)$$

$$E_e = \int dx n(x) U_e(x), \quad E_i = \frac{1}{2} \int dx dx' \frac{n(x)n(x')}{|x-x'|}.$$

To generalize the TFM to the case of finite temperatures it is necessary to replace (1.5) by the corresponding quantum-statistical expression

$$f(x, p) = \left[\exp\left(\frac{p^2 - p_F^2(x)}{2T}\right) + 1 \right]^{-1}. \quad (1.8)$$

Then (1.6) gives

$$n(x) = \frac{\sqrt{2}}{\pi^2} T^{3/2} I_{1/2}(\lambda(x)), \quad (1.9)$$

where I_n is the special Fermi-Dirac function, whose properties are given in Appendix 1, and $\lambda \equiv p_F^2/2T$. The expression (1.9) replaces (1.1); as regards (1.2)–(1.4), these equalities remain valid but by μ we now mean the chemical potential of the "hot" system. Having available the solution of the Thomas-Fermi equation for $T \neq 0$, and the expression for the free energy:

$$F = \frac{\sqrt{2}}{\pi^2} T^{5/2} \int dx \left(\lambda I_{1/2}(\lambda) - \frac{2}{3} I_{3/2}(\lambda) \right) + E_e + E_i, \quad (1.10)$$

we can obtain a complete thermodynamic description of the "hot" system. In particular, the chemical potential and pressure are obtained from (1.10) by differentiation with respect to the number of particles and the volume of the system, respectively.

This calculation is substantially simplified if $U|_S = 0$ at the boundary of the system. In this case,

$$\mu = \frac{1}{2} p_F^2, \quad P = \frac{2\sqrt{2}}{3\pi^2} T^{5/2} I_{3/2}\left(\frac{\mu}{T}\right). \quad (1.11)$$

The expression for the pressure P can be regarded as the result of applying the principle of quasi-uniformity and the virial theorem ($P = \frac{2}{3} E_K/V$) at points where the electron gas is locally ideal. This is precisely the situation in the widely used model of spherical Wigner-Seitz cells (cf., e.g.,^[1,5]). In this model a substance is divided into an assembly of spherical cells, each of which contains one nucleus and is electrically neutral as a whole; the latter condition determines the radius R of the cell:

$$\int_R dx n(x) = Z$$

and the behavior of $U(x)$ (cf. (1.2)) near the boundary of the cell:

$$U(x) \sim (R - r)^2. \quad (1.12)$$

Use of the cell model makes it possible to go over from a many-center problem to a spherically symmetric single-center problem, and this makes it very much simpler to solve the Thomas-Fermi equation.

An explicit solution of a many-center problem is possible only in that region of high pressures or temperatures in which the TFM differs little from the model of an ideal uniform gas^[5] (in the following we

shall call this region the region of uniformity); the limits of this region are indicated below in Sec. 2. In the zeroth approximation (the ideal gas) the relations (1.9)–(1.11) give

$$n = \frac{\sqrt{2}}{\pi^2} T^{3/2} I_{1/2}(\lambda), \quad F = \frac{\sqrt{2}}{\pi^2} VT^{5/2} \left(\lambda I_{1/2}(\lambda) - \frac{2}{3} I_{3/2}(\lambda) \right),$$

$$P = \frac{2\sqrt{2}}{3\pi^2} T^{5/2} I_{3/2}(\lambda), \quad \lambda = \frac{\mu}{T} = \frac{p_F^2}{2T}. \quad (1.13)$$

In the next approximation, which takes into account the small effects of the Coulomb interaction,

$$\delta p_F^2(x) = 2\delta\mu - 2n \int \frac{dx'}{|x-x'|} - 2U_e(x),$$

$$\delta F = -\frac{n^2}{2} \int \frac{dx dx'}{|x-x'|} + n \int dx U_e(x) + E_0,$$

where E_0 is the energy of the Coulomb interaction of the external sources with each other. Taking into account the electrical neutrality of the system over scales $\sim (Z/n)^{1/3}$, we have

$$\delta F = -\alpha Z^{2/3} n^{4/3} V, \quad (1.14)$$

where α is the analog of the Madelung constant and depends on the concrete structure of the short-range order in the system; in the cell model, $\alpha = (9/10)(4\pi/3)^{1/3}$. Correspondingly,

$$\delta\mu = -\frac{4}{3} \alpha Z^{2/3} n^{1/3}, \quad \delta P = -\frac{\alpha}{3} Z^{2/3} n^{4/3}. \quad (1.15)$$

The TFM can also be easily generalized to the relativistic case. However, the corresponding effects would be appreciable only under conditions (near the nuclei, at ultra-high pressures or temperatures) such that the TFM is either completely inapplicable or differs little from the ideal-gas model.

The TFM possesses the important property of self-similarity: the atomic number Z appears in any physical relation only in the form of the combinations

$$xZ^{1/3}, \quad \omega Z^{-1}, \quad pZ^{-2/3}, \quad EZ^{-4/3}, \quad TZ^{-4/3}, \quad PZ^{-10/3}, \quad nZ^{-2}, \quad (1.16)$$

where x is the length, ω the frequency, p the momentum, E the energy (free energy) per particle, T the temperature, P the pressure and n the density. The universality property of the TFM, which we mentioned in the Introduction, is connected with precisely this property.

The derivation of the TFM was based on the assumption of a small degree of nonuniformity of the system. Below we shall need a quantitative measure of this quantity. For this we use a characteristic "nonuniformity length" L over which the characteristics of the system change noticeably. In the region of applicability of the TFM this quantity can be found directly from Eq. (1.4) by omitting the term with the external sources³⁾ and replacing Δ by $1/L^2$:

$$L \sim \frac{p_F}{\sqrt{n}} \sim r_D. \quad (1.17)$$

This quantity coincides with the Debye radius $r_D \sim v/\omega$ for the electron subsystem, where v is the characteristic velocity and ω is the characteristic (plasma) frequency.

³⁾In the region where the TFM leads to nontrivial results (to the left of curve 3 in the Fig. 1 given below), the quantity L is less than the average distance between the nuclei. Therefore, the nuclei do not participate in the screening and their contribution to (1.4) need not be taken into account.

2. Limits of applicability of the TFM (correlation effects)

From the semi-intuitive derivation of the TFM given above it is difficult to understand how this model can be written into the general scheme of quantum mechanics and statistics. The answer to this question was given by Dirac^[17], who showed that the "cold" TFM is the semi-classical limit with respect to the Hartree self-consistent field equations in quantum mechanics; the "hot" TFM was found to be the analogous quantum-statistical limit.

Accordingly, the approximate character of the TFM has a twofold nature. Beyond the scope of the model there remain, firstly, correlation effects, reflecting the inexactness of the Hartree method and associated with the deviation of the true interaction from the self-consistent (averaged) interaction. Secondly, in the TFM, quantum-mechanical effects corresponding to the approximate character of the semi-classical description itself are not taken into account. In this and the following subsections we consider a theory of the effects enumerated that enables us to find the limits of applicability of the TFM in its original form and to generalize the model beyond the corresponding limits.

We begin by considering correlation effects, which, in turn, are divided into two classes. These are, first of all, the effects of statistical correlation (exchange effects), which describe the effect of the Pauli principle on the interaction of the particles. Under otherwise equal conditions, electrons with parallel spins are kept at a greater distance apart than electrons in a singlet state, and the range of this correlation coincides with the de Broglie wavelength $\lambda \sim 1/p_F$ of the electron. The corresponding weakening of the Coulomb repulsion, which is equivalent to an additional effective attraction between the particles, is of the order of magnitude of $(\lambda/L)^2 U \sim n/p_F^2$ (cf. (1.4), (1.17)). The ratio of this quantity to the mean kinetic energy p_F^2 of the electron gives the dimensionless parameter

$$\delta_{\text{exch}} \sim \frac{n}{p_F^2}, \quad (2.1)$$

which determines the relative contribution of exchange effects. They do not violate the independent-particle picture characteristic of the Hartree method, but lead only to a certain modification of the self-consistent potential (the Hartree-Fock method).

A generalization of the TFM, the Thomas-Fermi-Dirac model^[1,17], which arises when the semi-classical limit is taken in the framework of the Hartree-Fock method and takes into account exchange effects of all orders in the parameter (2.1), has been frequently discussed and used in the literature. However, we shall see below that the quantum-mechanical effects are characterized by the same parameter (cf. (3.1)). It is clear, therefore, that the use of this model constitutes an inadmissible excess of accuracy. The only consistent approach is to take the exchange and quantum-mechanical effects into account simultaneously and commensurately⁴⁾.

The second class of correlation effects (these are called dynamical-correlation effects or, simply, correlation effects) reflect the inexactness of the independent-particle picture itself, i.e., the impossibility of

⁴⁾This important conclusion, which invalidates the results of a number of papers on applications of the TFM, is due to Kompaneets (cf. [18]).

speaking of the state of an individual electron in an effective average field of the other particles (because of their influence on each other, which lies outside the scope of the self-consistent description). Being dynamical in nature, correlation effects are characterized by the perturbation-theory dimensionless parameter

$$\delta_0 \sim \frac{n^{1/3}}{p_F^2} \quad (2.2)$$

equal to the ratio of the mean Coulomb-interaction energy of a pair of particles to their mean kinetic energy. Therefore, the relative contribution of these effects should be determined by a certain positive power of the parameter (2.2):

$$\delta_{\text{cor}} \sim \delta_0^\nu \quad (2.3)$$

The dynamical effects of first order in δ_0 are already taken into account in the framework of the Hartree method (e.g., the Hartree equations in the case of a uniform system correspond exactly to the zeroth and first order in the perturbation-theory parameter (2.2)^[5]). Therefore, for the exponent ν in (2.3) we might expect the value 2. However, the long-range character of the Coulomb forces complicates the situation: the higher orders of perturbation theory contain infrared (corresponding to large distances) divergences. A more accurate calculation, reducing in essence to taking the Debye screening into account, leads to the result that the divergences are "cut off" at distances of the order of r_D (cf. (1.17)), or, in dimensionless variables, at the value $r_D n^{1/3} \sim \delta_0^{-1/2}$. The result is that the exponent ν decreases to a value less than 2 (but greater than unity).

This value depends on the degree of degeneracy of the electron gas, i.e., on the size of the parameter $n^{2/3}/T$ (see curve 1, corresponding to $n^{2/3} \sim T$, in Fig. 1). In the regime of degeneracy

$$n^{2/3} \gg T, \quad p_F \sim n^{1/3}, \quad \delta_0 \sim n^{-1/3} \quad (2.4)$$

the infrared divergence is found to be strongly suppressed because of the Pauli principle, which decreases the phase volume for virtual transitions^[5]; the divergence turns out to be logarithmic, at most, and so $\nu = 2$. Correspondingly, (2.1) and (2.3) give

$$\delta_{\text{exch}} \sim n^{-1/3}, \quad \delta_{\text{cor}} \sim n^{-2/3} \quad (2.5)$$

As already mentioned, the contribution of the quantum-mechanical effects is determined by the same parameter (2.1). Therefore, the region of applicability of the TFM in the "cold" case is given by the inequality

$$n \gg 1. \quad (2.6)$$

The curve 2 in Fig. 1 delimits the region of applicability of the TFM; its upper part corresponds to $n \sim 1$. We emphasize that, by virtue of (2.5), in the degeneracy regime the exchange and quantum-mechanical effects, while being relatively small, play a dominant role compared with the correlation effects.

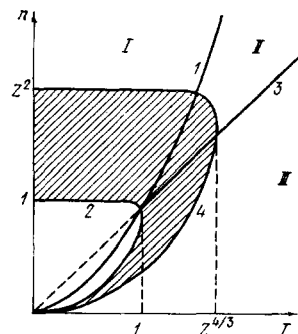
For a classical electron gas

$$n^{2/3} \ll T, \quad p_F \sim T^{1/2}, \quad \delta_0 \sim \frac{n^{1/3}}{T} \quad (2.7)$$

the infrared divergence turns out to be of the linear type, as in the usual Debye-Hückel theory (cf. Sec. 5 below) and $\nu = 3/2$. Hence,

$$\delta_{\text{exch}} \sim \frac{n}{T^2}, \quad \delta_{\text{cor}} \sim \frac{n^{1/2}}{T^{3/2}} \quad (2.8)$$

FIG. 1. Limits of applicability of the TFM. 1—degeneracy curve, 2—boundary of applicability of the TFM, 3—curve along which the exchange, quantum-mechanical and correlation effects are equal, 4—boundary of the uniformity regime. I—region in which exchange and quantum-mechanical effects dominate for a degenerate gas, II—the same for a Boltzmann gas, III—region in which correlation effects are dominant. The region in which the use of the TFM is justified is shaded.



The region of applicability of the TFM corresponds to the inequality

$$n \ll T^3 \quad (2.9)$$

and is bounded by the lower part of curve 2. From the estimates given (cf. (2.8)) it follows that for $n \ll T$ correlation effects are dominant while for $n \gg T$ exchange and quantum-mechanical effects are dominant; the curve $n \sim T$ is shown in Fig. 1 (curve 3).

As can be seen from (2.3), for the TFM to be applicable it is necessary in all cases that the interaction energy of a pair of electrons be small compared with their kinetic energy. This does not yet imply, however, that the TFM is close to the ideal-gas model: in a nonuniform system (and real matter is such a system), the electrons interact with the nuclei and also with a large number of their partners situated in the sphere of radius equal to the effective range of the Coulomb forces. For $Z \gg 1$ these interactions are far from small, even in the region of applicability of the TFM. For example, the characteristic parameter δ_Z determining the interaction of the electrons with the nuclei is obtained from (2.2) by multiplying it by Z and replacing n by the number density n/Z of the nuclei:

$$\delta_Z \sim Z^{2/3} \delta_0 \quad (2.10)$$

The same estimate is obtained for the collective inter-electronic interaction. The curve $\delta_Z \sim 1$ (curve 4 in Fig. 1) delimits the region in which the TFM is indeed close to the ideal-gas model; this region has already been considered in the preceding Subsection and has been called the uniformity regime. The region in which application of the TFM is justified and leads, at the same time, to nontrivial results is shaded in Fig. 1.⁹⁾

3. Limits of applicability of the TFM (quantum-mechanical effects)

When the conditions (2.6), (2.9) are fulfilled we can go over from the many-particle Schrödinger equation to the Hartree self-consistent field equations. To obtain the TFM it is necessary to take one further step, i.e., to go over to the semi-classical approximation. With this step is associated an extra source of inexactness of the TFM.

The applicability of the semi-classical description is determined by the dimensionless parameter $\xi \sim \pi/L \sim 1/p_F L$. The relative contribution of the quantum-

⁹⁾See, however, Sec. 14.

mechanical effects is characterized by the square of this parameter⁶⁾

$$\delta_{qu} \sim \xi^2 \sim \frac{n}{p_F^2} \sim \delta_{exch}. \quad (3.1)$$

That this quantity coincides with (2.1) is not accidental: both the range of exchange correlations and the distances over which the wave nature of a particle is manifested are of the order of the de Broglie wavelength.

If the parameter (3.1) is sufficiently small we can expand the Hartree-approximation expressions for the physical quantities in this parameter. The zeroth term of such an expansion corresponds to the TFM, and the other terms describe the quantum-mechanical effects. It turns out that these effects too are divided into two classes. Effects describable by terms of the expansion that are powers of the parameter (3.1) belong to the first class; these are called quantum effects. They describe the "diffuseness" of the Bohr orbits, associated with the uncertainty principle. On a more formal plane, the quantum effects reflect the violation of the local character of the relationship between the density and potential (cf. (1.1), (1.11)), which is unavoidable because of the finite value of the particle wavelength. The situation reduces to the appearance, in the right-hand side of the relations indicated, of gradients of the potential that are of higher order the higher is the expansion term being considered. Therefore, quantum effects play the role of corrections for the nonuniformity and establish the limits of applicability of the quasi-uniformity principle used in the derivation of the TFM (cf. Sec. 1).

It is found, however, that the change-over from the Hartree approximation to the TFM entails not only neglect of quantum effects. From a study of the simplest exactly-soluble models (noninteracting particles in a uniform or oscillator field)⁷⁾ it has been elucidated^[19] that the expressions for physical quantities in the Hartree method are nonanalytic functions of ξ at the point $\xi = 0$. It was found that the nonanalytic corrections to the power series in ξ are such (trigonometric and more complicated periodic functions of $1/\xi$) that their contribution to the Taylor series in ξ is equal to zero. However, this series is asymptotic in character and is far from conveying the behavior of the quantity being expanded.

The above has an entirely general character, and applies to the case of an arbitrary self-consistent field in which there is at least one turning point for the classical motion of the particle. We shall consider the simplest case of a one-dimensional "cold" system. The semi-classical wavefunction of the particle has the form

$$\psi_n = c_n p_n^{-1/2} \sin \left(S_n + \frac{\pi}{4} \right), \quad (3.2)$$

where c_n is the normalization constant and S_n and p_n are the classical action and momentum. Substituting (3.2) into the expression $n = 2 \sum_{E_n < \mu} |\psi_n|^2$ gives

$$n = \sum_{E_n < \mu} |c_n|^2 p_n^{-1} (1 + \sin 2S_n). \quad (3.3)$$

After replacement of the summation by integration the

first term leads to the TFM, and the second gives the nonanalytic dependence (see Sec. 7 below)

$$\sin(2S_\mu + \text{const}), \quad S_\mu \sim \frac{1}{\xi} \quad (3.4)$$

(in the usual units the argument of (3.4) has the form $(2S_\mu/\hbar) + \text{const}$). Expressions corresponding to the TFM and the lowest-order quantum effects have been established in many papers by precisely this method of direct summation over the levels. However, since the pioneering work of Brillouin on the WKB method, the rapidly oscillating terms have simply been discarded.

The effects under discussion, which are called shell (oscillation) effects, have a simple and clear physical meaning. The action function in (3.4) determines the energy spectrum of the system by the Bohr-Sommerfeld quantization rule $S_n = \pi(n + 1/2)$. Therefore, the shell effects describe those irregularities (oscillations) of physical quantities that are associated with the discreteness of the energy spectrum and that arise when an energy level crosses the Fermi energy μ . Such effects include, e.g., the well-known de Haas-van Alphen effect (oscillations of the magnetic susceptibility of an electron gas on variation of the magnetic field, because of the Landau quantization). Another example, about which more will be said below, in Subsection 14, is the nonmonotonic dependence of the properties of matter on its composition, as expressed by Mendeleev's periodic law. The TFM, because of its inherent universality property, cannot, in principle, describe this dependence.

We note that, unlike the quantum effects, shell effects are sharply reduced by averaging the physical quantities over the external parameters of the problem or over the atomic number. The well-known fact that the TFM quite often gives a satisfactory description of the averaged characteristics of matter without reflecting the details of its behavior is connected with precisely this circumstance.

We emphasize that shell effects are already described in the lowest semi-classical approximation for the wavefunction, and this approximation thus contains substantially more information about the system than does the TFM. On the other hand, it might appear from the form of formula (3.3) that the contribution of the shell effects is of order unity with respect to the TFM itself. Actually, however, the result of the summation in the second, rapidly oscillating term of (3.3) leads to the appearance of additional positive powers of the parameter ξ . It turns out that, in a real three-dimensional case, leaving aside the oscillatory dependence, the contribution of the shell effects is determined by the parameter (3.1) and is essentially the same as for the quantum effects (see Sec. 7).

Returning to the quantum effects, we cannot fail to notice that their contribution is always significant in regions $r < Z^{-1}$, i.e., near the nucleus, and $r > 1$ (on the periphery of an isolated atom). Correspondingly, in quantities for which these regions play an important role, this contribution can turn out to be considerably greater than would follow from the estimate (3.1). Thus, e.g., application of the TFM to the calculation of the total energy of a heavy atom, for which, according to (2.5) and (3.1),

$$\delta_{exch} \sim \delta_{qu} \sim Z^{-2/3}, \quad \delta_{cor} \sim Z^{-4/3}, \quad (3.5)$$

will actually lead to a substantially greater error. We shall return to this question in Chap. V.

⁶⁾The condition that the physical quantities be real leads to the result that they can be expanded in series containing only even powers of ξ .

⁷⁾The analysis performed in [20] also lies, essentially within this class of problems.

III. EFFECTS BEYOND THE SCOPE OF THE THOMAS-FERMI MODEL

4. Exchange effects

The preceding chapter contained a general qualitative treatment of the effects limiting the applicability of the TFM. We proceed now to a systematic account of the quantitative theory of the effects. First of all we shall give several useful general relations (for their derivation see Appendix 2).

The effects under discussion lead to violation of the simple relationship, characteristic of the TFM, between the density and potential, and to the appearance in the right-hand sides of (1.1) and (1.11) of an additional term:

$$n \rightarrow n(p_F) + n'. \quad (4.1)$$

The quantity n' is assumed to be relatively small, and therefore interference between the different effects is absent; a separate term in n' corresponds to each of them. The correction to p_F associated with n' is determined by the equation

$$(\Delta - \kappa^2(x)) \delta p_F = 8\pi n'. \quad (4.2)$$

where $\kappa = (4\pi \partial n / \partial \mu)^{1/2}$ is the inverse Debye radius of the electron subsystem. The corrections to the chemical potential, potential energy and density are given, respectively, by the expressions⁸⁾

$$\delta \mu = \frac{\delta p_F(\infty)}{2}, \quad \delta U = \frac{1}{2} [\delta p_F(\infty) - \delta p_F(x)], \quad \delta n = \frac{\Delta \delta p_F}{8\pi}. \quad (4.3)$$

The correction to the free energy is determined by the simple formula

$$\delta F = - \int_{-\infty}^{\mu} \delta \mu \int dx n'. \quad (4.4)$$

The quantity δp_F^2 does not appear in this, and, therefore, to derive the thermodynamics there is no need to solve the complicated equation (4.2). The correction to the pressure can be written in the form

$$\delta P = \frac{N \delta \mu - \delta F}{V}. \quad (4.5)$$

(for other representations of δP see^[5,21]).

We shall begin by treating the exchange effects. The study of these as applied to the "cold" TFM was begun by Dirac^[17]; for the generalization to the case of arbitrary temperatures, see^[21,22]. As already pointed out in Sec. 2, exchange effects consist in the appearance of an additional effective attraction between the electrons, associated with the Pauli principle. If in a volume V there are two free electrons with parallel spins and momenta \mathbf{p} and \mathbf{p}' , the exchange attraction corresponds to a potential energy $-4\pi/(V|\mathbf{p} - \mathbf{p}'|^2)$ (the Fourier transform of the Coulomb interaction). In the general case when the electrons are described by a distribution function $f(\mathbf{x}, \mathbf{p})$, there arises an exchange of "potential"

$$-A(\mathbf{x}, \mathbf{p}) = -4\pi \int d^3 p' \frac{f(\mathbf{x}, \mathbf{p}')}{|\mathbf{p} - \mathbf{p}'|^2}. \quad (4.6)$$

supplementing U in the single-particle Hamiltonian.

The exchange correction to the distribution function is equal to

$$f'(\mathbf{x}, \mathbf{p}) = \frac{\partial f(\mathbf{x}, \mathbf{p})}{\partial \mu} A(\mathbf{x}, \mathbf{p}),$$

and, when (4.6) is taken into account, the correction to the density has the form

$$n' = 2 \int d^3 p f' = \frac{\partial C}{\partial \mu},$$

where

$$C(\mathbf{x}) = \int d^3 p f(\mathbf{x}, \mathbf{p}) A(\mathbf{x}, \mathbf{p}) = \frac{2T^2}{\pi^3} \int_{-\infty}^{\lambda} d\lambda (I_{1/2}(\lambda))^2, \quad \lambda = \frac{p_F}{2T} \quad (4.7)$$

(for the calculation of this integral, see Appendix 3). Hence,

$$n' = \frac{2T}{\pi^3} (I'_{1/2}(\lambda))^2. \quad (4.8)$$

The correction to the free energy is found from (4.4):

$$\delta F = - \frac{2T^2}{\pi^3} \int dx \int_{-\infty}^{\lambda} d\lambda (I_{1/2}(\lambda))^2; \quad (4.9)$$

In the case of low temperatures,

$$n' = \frac{p_F}{\pi^3} \quad (4.10)$$

and

$$\delta E = - \frac{1}{4\pi^3} \int dx p_F = - \frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \int dx n^{4/3}. \quad (4.11)$$

An exact solution of the problem in explicit form is possible in the regime of uniformity of the electron gas (Secs. 1 and 2), in which (4.2), (4.5) give⁹⁾

$$\delta \mu = \frac{\delta p_F}{2} = - \frac{\sqrt{2T}}{\pi} I_{1/2}(\lambda), \quad \delta P = - \frac{2T^2}{\pi^3} \int_{-\infty}^{\lambda} d\lambda I_{1/2}(\lambda) I'_{1/2}(\lambda). \quad (4.12)$$

In the limits of low and high temperatures, respectively, we have

$$\delta P = - \frac{(3\pi^2)^{1/3}}{4\pi} n^{4/3}, \quad \delta P = - \frac{T^2 n^2}{\pi^3}. \quad (4.13)$$

We note that the exchange effects violate the self-similarity characterizing the TFM: when expressed in the variables (1.16), the exchange corrections have a factor $Z^{-2/3}$ left over.

5. Correlation effects

We turn now to a consideration of correlation effects, which reflect the inexact character of the idea of the self-consistent field that lies at the basis of the Hartree method. We shall concentrate on the simplest case of the classical electron gas; this case is, at the same time, the most important one, since it is precisely for this case that correlation effects are the "sticking point" of the TFM (region III in Fig. 1).

We note immediately that, although the relations given below outwardly resemble the formulas of the well-known Debye-Hückel theory (cf., e.g.,^[23]), the latter theory is inapplicable in the region of pressures and temperatures of interest to us (not too far from the outer boundary of the shaded region in Fig. 1). This

⁸⁾The argument "∞" corresponds to a point lying outside the (neutral) system.

⁹⁾To avoid confusion we point out that the quantity δp_F^2 in (4.2) has the meaning of a correction to the potential energy and not to the Fermi momentum (cf. [5]).

theory applies to a weakly nonideal plasma, in which the Coulomb interaction between the nuclei is relatively small, and can be used only in the region $n \gg T^3/Z^5$, which, for $Z \gg 1$, lies substantially below the above-mentioned boundary. Our treatment applies to conditions when the electron gas is nonideal and nonuniform, and the nuclei form a given distribution and do not participate in the Debye-screening process (see the end of Sec. 1).

Correlations in a classical gas (cf.^[24] and Appendix 4) are conveniently described by means of the n -particle distribution function with respect to the coordinates¹⁰⁾, which, in the case of small correlations, has the following form:

$$f_n(x_1, \dots, x_n) = f_1(x_1) \dots f_1(x_n) \left[1 + \frac{1}{2} \sum_{i,j=1}^n v(x_i, x_j) \right], \quad (5.1)$$

where the single-particle function f_1 is connected with the density by the relation

$$n(x) = n f_1(x), \quad n = N/V, \quad (5.2)$$

and the correlator v satisfies the equation

$$\left(\Delta - \frac{4\pi n(x)}{T} \right) v(x, x') = \frac{4\pi}{T} \delta(x - x'). \quad (5.3)$$

The result of the straightforward calculations has the form

$$n'(x) = \sqrt{\pi} \left(\frac{n(x)}{T} \right)^{3/2}, \quad (5.4)$$

where, according to (1.11),

$$n(x) = \frac{1}{4} \left(\frac{2T}{\pi} \right)^{3/2} \exp \left(\frac{p_k^2}{2T} \right).$$

The correction to the free energy is

$$\delta F = -\frac{2}{3} \sqrt{\frac{\pi}{T}} \int dx n^{3/2}(x). \quad (5.5)$$

Correlation effects also violate the self-similarity of the TFM; in the variables (1.16) a spare factor Z^{-1} is associated with them.

In the uniformity regime of an electron gas,

$$\delta\mu = -\sqrt{\frac{\pi n}{T}}, \quad \delta P = -\frac{1}{3} \sqrt{\frac{\pi n^3}{T}}. \quad (5.6)$$

Using the virial theorem, we can show that (5.6) are particular cases of the more general relations

$$\delta\mu = \frac{3}{2} \frac{\delta F}{N}, \quad \delta P = \frac{1}{2} \frac{\delta F}{V}, \quad (5.7)$$

which are valid outside the uniformity regime as well.

The expression (5.5) can be regarded as the result of applying the principle of quasi-uniformity to a Debye plasma of electrons in a background of "inert" positive charge (cf. the Debye-Hückel theory). It is important to stress that this is possible only for a classical gas: in the case of partial or complete degeneracy we cannot use the above principle to calculate correlation effects. The point is that these effects display anomalous sensitivity to the nonuniformity of the system^[25,5],

In fact, for the principle of quasi-uniformity to be applicable it is necessary that the nonuniformity length L (cf. Sec. 1) be large compared with all the characteristic quantities with the dimensions of length for the given problem. In the framework of the TFM there is only one such quantity—the mean distance $n^{-1/3}$ between the particles. In the conditions we are considering, the parameter $L n^{1/3} \sim \xi^{-1}$ is indeed large compared with unity and it is legitimate to use the principle of quasi-uniformity. However, when we turn to the correlation effects a further characteristic length (the Debye radius r_D), associated with dynamical effects, appears in the problem. According to (1.17), this quantity coincides in order of magnitude with L , and this excludes the possibility of using the principle of quasi-uniformity. In the case of a classical gas, however, the dependence of the physical quantities on the ratio r_D/L disappears and the simple answer given above is obtained.

As regards the case of partial or complete degeneracy, a solution to the problem of calculating the correlation effects has still not been found. The results cited at various times, which were derived on the basis of the principle of quasi-uniformity, can be regarded as qualitative at best. This pertains, in particular, to the well-known formula of Gell-Mann and Brueckner^[26], derived for a strictly uniform system,

$$\delta E \sim -V n \ln n,$$

which has been applied frequently to real systems by replacing n by $n(x)$, and V by an integral over the volume. Additional information on correlation effects in a "cold" system can be found below, in Sec. IV.

6. Quantum effects

In this section we consider effects reflecting the inexactness of the semi-classical approximation to the equations of the Hartree method and corresponding to the first term of the expansion of physical quantities in a power series in the semi-classicality parameter (3.1). The first attempt to describe these effects was due to Weizsäcker^[27]. However, the inadequacy of his method led to an overestimate (by a factor of 9, as was shown later) for the coefficient in his formula¹¹⁾. That this coefficient was too large was noted by a number of authors on the basis of empirical arguments, before a quantitative theory of the quantum effects was established. Such a theory was proposed almost simultaneously¹²⁾ by several authors^[18,28,30] (cf. also^[31]), who used different methods for the expansion in powers of the semi-classicality parameter. Below we shall use the most direct route for this purpose (cf. also^[5]).

Here and below we shall start from the expression for the single-particle Green function of an electron in the self-consistent field:

$$G(x, x', \epsilon) = \int d^3 p G(x, p, \epsilon) e^{ip(x-x')} = \sum_n \frac{\psi_n^*(x') \psi_n(x)}{\epsilon - \epsilon_n + i\delta}, \quad (6.1)$$

where ψ_n and ϵ_n are the wavefunction and energy of the particle in the Hartree method. The Green function satisfies the equation

¹¹⁾However, Weizsäcker's formula becomes valid in the opposite limiting case of large ξ ,^[28] when it leads to the usual Schrödinger equation (see Sec. 11 below).

¹²⁾The first publication with an account of the theory of the quantum effects is due to Kompaneets and his student Pavlovskii^[18].

¹⁰⁾The distribution with respect to the momenta has the trivial Maxwellian form.

$$\left(\varepsilon - \frac{p^2}{2} - U(\mathbf{x})\right) G(\mathbf{x}, \mathbf{x}', \varepsilon) = \delta(\mathbf{x} - \mathbf{x}') \quad (6.2)$$

and leads to the expressions for the distribution function and density:

$$f(\mathbf{x}, \mathbf{p}) = \frac{i}{\pi} \int_{-\infty}^{\mu} d\varepsilon (G(\mathbf{x}, \mathbf{p}, \varepsilon) - G^*(\mathbf{x}, -\mathbf{p}, \varepsilon)),$$

$$n(\mathbf{x}) = -\frac{2}{\pi} \int_{-\infty}^{\mu} d\varepsilon \operatorname{Im} G(\mathbf{x}, \mathbf{x}, \varepsilon). \quad (6.3)$$

The relations given pertain to a "cold" system. For $T \neq 0$ it is sufficient to make the replacement

$$\int_{-\infty}^{\mu} d\varepsilon (\dots) \rightarrow \int_{-\infty}^{\infty} d\varepsilon f(\varepsilon) (\dots), \quad f(\varepsilon) = \left[\exp\left(\frac{\varepsilon - \mu}{T}\right) + 1 \right]^{-1}. \quad (6.4)$$

It has already been noted, in Sec. 3, that the quantum effects correspond to expanding in increasing powers of the gradient of the potential. Confining ourselves to treating the lowest-order quantum correction, which corresponds to the second power of the gradient, we can represent the quantity $G(\mathbf{x}, \mathbf{p}, \varepsilon)$ in (6.1) in its only possible form:

$$G = G_0 + A(\mathbf{p}\nabla) p\hbar + B[(\mathbf{p}\nabla) p\hbar]^2 + C(\nabla p\hbar)^2 + D(\mathbf{p}\nabla)^2 p\hbar + E\Delta p\hbar,$$

where $G_0 = 2/[2(\varepsilon - U) - p^2 + i\delta]$. Substitution into Eq. (6.2) gives explicit expressions for the coefficients A, \dots, E . As a result we obtain the following expressions for the "cold" quantum corrections to the distribution function:

$$f'(\mathbf{x}, \mathbf{p}) = \frac{1}{2} (\Delta p\hbar + 2i\mathbf{p}\nabla p\hbar) \delta'(p\hbar - p^2) + \frac{1}{3} [(\nabla p\hbar)^2 - 2(\mathbf{p}\nabla)^2 p\hbar] \delta''(p\hbar - p^2) - \frac{1}{2} (\mathbf{p}\nabla p\hbar)^2 \delta'''(p\hbar - p^2),$$

and to the density:

$$n' = -\frac{1}{96\pi^2 p\hbar^2} [(\nabla p\hbar)^2 - 4p\hbar \Delta p\hbar]. \quad (6.5)$$

From this the correction to the energy is

$$\delta E = -\frac{1}{96\pi^2} \int \frac{d\mathbf{x}}{p\hbar} [(\nabla p\hbar)^2 + 4p\hbar \Delta p\hbar]. \quad (6.6)$$

By means of (1.1) we can rewrite it in the form

$$\delta E = \frac{1}{72} \int d\mathbf{x} \left[\frac{(\nabla n)^2}{n} - 6 \Delta n \right]. \quad (6.6a)$$

For a regular function $n(\mathbf{x})$ the last term in this expression drops out and the Weizsäcker formula is obtained, but with a coefficient nine times smaller.

At finite temperatures the relations (6.5) and (6.6) are replaced by the following relations ($\lambda = p\hbar^2/2T$):

$$n' = \frac{\sqrt{2T}}{24\pi^2} [I'_{1/2}(\lambda) (\nabla\lambda)^2 + 2I_{1/2}(\lambda) \Delta\lambda], \quad (6.7)$$

$$\delta F = -\frac{\sqrt{2T^3}}{24\pi^2} \int d\mathbf{x} [I'_{1/2}(\lambda) (\nabla\lambda)^2 + 2I_{1/2}(\lambda) \Delta\lambda]. \quad (6.8)$$

Using the identity

$$\Delta I_{1/2} = I_{1/2} \Delta\lambda + I'_{1/2} (\nabla\lambda)^2$$

and the Thomas-Fermi equation (cf. (1.4), (1.11))

$$\Delta\lambda = \frac{4\sqrt{2T}}{\pi} I_{1/2}(\lambda) + \text{external source}$$

it is not difficult to bring (6.8) to the form

$$\delta F = -\frac{T^2}{3\pi^2} \int d\mathbf{x} I_{1/2}(\lambda) I_{1/2}(\lambda) + \dots;$$

here, \dots denote terms¹³⁾ that are nonzero only at the

¹³⁾Actually, these terms diverge, and this is connected simply with the inapplicability of the semi-classical description at short distances from the nucleus (cf. Sec. 3).

positions of the nuclei. Inasmuch as these terms do not change with change of volume of the system, they drop out from the expression for the quantum correction to the pressure:

$$\delta P = -\frac{\partial}{\partial V} \delta F = \frac{T^2}{3\pi^2} \frac{\partial}{\partial V} \int d\mathbf{x} I_{1/2} I_{1/2}. \quad (6.9)$$

We shall compare this quantity with the exchange correction to the pressure, which, according to (4.9), is equal to

$$\delta_{\text{exch}} P = \frac{2T^2}{\pi^3} \frac{\partial}{\partial V} \int d\mathbf{x} \int_{-\infty}^{\lambda} d\lambda (I_{1/2})^2. \quad (6.10)$$

Using the asymptotic forms of the Fermi-Dirac functions (see Appendix 1), it is easy to see that the ratio of (6.9) to (6.10) is 2/9 for a degenerate electron gas and 1/3 for a classical electron gas^[5,21]. This is a further argument against the Thomas-Fermi-Dirac model (cf. Sec. 2).

In the regime of uniformity of an electron gas it is not difficult, using the formulas of Sec. 4, to arrive at the expressions

$$\delta\mu = -\frac{1}{3\pi} \sqrt{\frac{T}{2}} \left(I_{1/2} \div \frac{I'_{1/2} I'_{1/2}}{I_{1/2}} \right), \quad \delta P = -\frac{T^2}{3\pi^2} \frac{I'_{1/2} I'_{1/2}}{I_{1/2}}. \quad (6.11)$$

Comparing with (4.1), we can check that the numerical relationships indicated above are fulfilled.

It seems at first glance that the expressions (6.11) are valid for any, arbitrarily large, values of the density or temperature, lying beyond the boundaries of the shaded region in Fig. 1. At the same time, there is no doubt that perturbation theory, which gives the expressions (1.13), (1.15), (4.12) and (5.7) but does not contain the quantum corrections (6.11), becomes valid at sufficiently high values of the density or temperature. To resolve this paradox and determine the boundaries of applicability of (6.11) on the high-pressure or high-temperature side, we must bear in mind that in the Coulomb field of the nucleus the semi-classical description is applicable only when the condition $Z/p\hbar \gg 1$ is fulfilled. Therefore, it is meaningful to expand in the parameter (3.1) only when the conditions

$$n \ll Z^3, \quad T \ll Z^2, \quad (6.12)$$

referring to the degenerate and classical regimes, respectively, are fulfilled. This is the condition for the formulas (6.11) to be applicable.

With the opposite inequalities to (6.12), when $Z/p\hbar \ll 1$, on the other hand, perturbation theory becomes applicable in the Coulomb field and the quantum effects disappear. Actually, therefore, (6.11) ought to be multiplied by a certain function of $Z/p\hbar$ that tends to zero at small values of the argument and to unity at large values. We shall not give its explicit expression (it is represented by a combination of Whittaker functions) in view of the small magnitude of the quantum effects in the region under consideration.

7. Shell effects

As already pointed out in Sec. 3, the shell effects reflect the irregularities of physical quantities due to the discrete energy spectrum; however, these effects can appear in the case of the continuous spectrum also, as a result of interference of de Broglie waves. In the semi-classical regime ($\xi \ll 1$) the shell effects are described by expression that are periodic functions of $1/\xi$. The first important stride in the theory of shell

effects was made by Kohn and Sham^{[32]14)}. However, in this paper, as in later papers^[33] also, only the one-dimensional case was considered, and the smallness of the semi-classicality parameter was not used throughout (e.g., hypergeometric functions appeared in the answer in place of trigonometric functions). A theory encompassing the three-dimensional case and taking the necessary account of the smallness of the parameter ξ was constructed in^[34-36], which we follow below.

A direct way of constructing such a theory has already been noted, in essence, in Sec. 3, and consists in the explicit calculation of the irregular terms of (3.3) by changing from the summation to an integration with the help of the Poisson formula (see Appendix 5). Confining ourselves in this Subsection to the case $T = 0$, we shall represent the shell correction to the density in the form

$$n' = n'_1 + n'_2 + n'_3, \quad (7.1)$$

The quantity n'_1 arises from the first term of (3.3) as the correction in the replacement of the sum by an integral, and describes the irregularities that appear when the individual energy levels cross the Fermi level. The second term of (7.1) corresponds to the second term of (3.3) and it was precisely this term that we discussed in Sec. 3; it describes not only "energy" shell oscillations but also spatial shell oscillations. Finally the quantity n'_3 takes its origin from the factor $|c_n|^2$ in (3.3), and, being a normalizing term, satisfies the equality

$$\int dx (n'_2 + n'_3) = 0. \quad (7.2)$$

The shell oscillations of thermodynamics quantities are determined, according to (4.4) and (7.2), entirely by the term n'_1 . If, however, we are interested in the shell oscillations of the density itself, only the term n'_2 is important for these. For a fixed value of μ , the other terms of (7.1) can be separated out from n' and carried over into the term $\delta p_F^2 \kappa^2 / 8\pi$ (see Appendix 2).

We first give the complete solution of the problem for the one-dimensional case, considering a finite motion with turning points R and R' . We introduce the notation

$$S = \int_R^x dx p_F, \quad \tau = \int_R^x \frac{dx}{p_F}$$

for the action function and time of motion on the Fermi boundary (the same symbols with the subscript 0 correspond to integration from R to R'). In addition, we introduce the periodic function

$$[f(S_0)]^* = f(S_0) \quad (-\pi/2 < S_0 < \pi/2)$$

with a periodic continuation outside this region; the discontinuities of this function, as is clear from the quantization condition, correspond exactly to coincidence of an energy level with the Fermi boundary. In this notation (cf. Appendix 5),

$$n'_1 = -\frac{2}{\pi p_F \tau_0} [S_0]^*, \quad \int_R^{R'} dx n'_1 = -\frac{2}{\pi} [S_0]^*. \quad (7.3)$$

¹⁴⁾We are not concerned here with papers on shell effects in the atomic nucleus, where the situation is much simpler because of the constancy of the density over its volume. In essence, many of the results of [37], in which, moreover, there are a number of important qualitative arguments (cf. also [38, 39]), also apply to systems of this type.

In combination with the expression $n = 2p_F / \pi$ (the one-dimensional TFM), this leads to the result that the total number of particles changes by two as each energy level passes through. Furthermore,

$$n'_2 = -\frac{\text{cosec}(\pi\tau/\tau_0)}{p_F \tau_0} \cos\left(2S - 2\frac{\tau}{\tau_0} [S_0]^*\right). \quad (7.4)$$

On going over to semi-infinite motion ($R' \rightarrow \infty$), $\tau_0 \rightarrow \infty$ and

$$n'_1 = 0, \quad n'_2 = -\frac{1}{\pi p_F \tau} \cos(2S). \quad (7.5)$$

The three-dimensional spherically symmetric problem (cf. Appendix 5), in which there is in addition a summation over the orbital quantum number, leading to partial smoothing of the oscillations (e.g., in place of the discontinuities of the function n'_1 itself, discontinuities only of its derivative appear), is solved analogously. We introduce the notation¹⁵⁾

$$S = \int_R^r dr \sqrt{p_F^2 - \frac{1}{4r^2}} \approx \int_0^r dr p_F + \frac{\pi}{2}, \quad \tau = \int_0^r \frac{dr}{p_F}, \quad \delta = \int_0^r \frac{dr}{r^2 p_F}$$

for the action function, time of motion and derivative of the angle of rotation with respect to the angular momentum in the state with zero orbital angular momentum. Then the three-dimensional analogs of (7.3) and (7.5) take the form

$$\int dx n'_1 = -\frac{2}{\pi \delta_0} [S_0]^*, \quad (7.6)$$

$$n'_2 = -\frac{1}{4\pi^2 r^2 p_F \tau \delta} \sin\left(2 \int_0^r dr p_F\right) \quad (7.7)$$

(for more-general relations see^[34, 36]).

There is also another method for describing shell effects, which is more transparent physically and is applicable in the general case of nonseparable variables. It is based on an analysis of the semi-classical Green function (cf. (6.1), (6.2)), which, in the one-dimensional case, has the form

$$G(x, x', e) = -\frac{i}{\sqrt{p_e(x) p_e(x')}} \sum_j \exp\left[i \left(\int_{\Gamma_j} ds |p_e| - \frac{\pi}{2} n_j \right)\right], \quad p_e = \sqrt{2(e - U)}; \quad (7.8)$$

here Γ_j is the trajectory of the classical motion from x to x' ; there exists, generally speaking, a whole set of such trajectories, of which one ($j = 0$) joins these points directly, as it were, and the others join them by varying numbers of reflections at the turning points. The number of such reflections is equal to n_j , and the last term in the phase of (7.8) corresponds to the change of phase in the reflections.

The density is expressed in terms of the Green function at coincident points (cf. (6.3)). The trajectory with $j = 0$ then degenerates to a point, and the corresponding term of (7.8) loses its oscillatory character and leads to the TFM result. The remaining terms of (7.8) are responsible for the shell effects. In the case of semi-infinite motion (Fig. 2a) there are two terms ($j = 0, 1$), with $n_0 = 0$ and $n_1 = 1$, in the sum (7.8). For finite motion, however, the number of terms is infinite. These include, first of all, terms corresponding to a complete cycle (n_j is an even number); the sum over such cyclic trajectories (Fig. 2c) forms the term n'_1 . In addition,

¹⁵⁾In the case (to which the formulas cited pertain) when attractive Coulomb forces act at the coordinate origin, $R = 0$ and the symbol f means that the quantity $\int_0^f dr r^{-3/2} \sqrt{2Z}$ is subtracted from the integral.

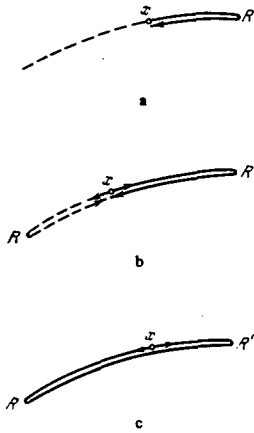


FIG. 2. Trajectories corresponding to shell effects. a) infinite motion in one direction, b) finite motion-semicyclic trajectory, c) finite motion-cyclic trajectory.

there are "semi-cyclic" trajectories (Fig. 2b), for which n_j is an odd number; the sum over such trajectories gives the term n'_2 describing spatial oscillations of the density. Thus, the latter arise as a result of interference of the incident wave and the wave reflected at the turning point (a standing de Broglie wave). Substitution of (7.8) into (6.3) does indeed lead to the results obtained above by a different method.

In the three-dimensional case the qualitative picture remains as before, although the corresponding expressions are appreciably more complicated. We note, first of all, that for the semi-cyclic trajectories it is necessary to take linear trajectories, on which the particle returns from the turning point along the same path as in its motion to this point. This corresponds to a true turning point, at which all components of the momentum vanish (the distinct character of an s-wave is connected with precisely this; cf. above). Furthermore, the Coulomb center of attraction, which, because of the well-known quantum-mechanical effects, does not allow particles to pass through itself, must be counted as one of the turning points¹⁶⁾. However, the inapplicability of the semi-classical description at this point leads to the result that the phase change in the reflection is opposite in sign to the usual phase change; one can verify this by using the exact expression for the Green function in a Coulomb field^[40] and matching it with the semi-classical expression in the same way as is done in the case of an ordinary turning point^[36].

In conclusion, we note that shell effects violate the self-similarity of the TFM in a substantially more radical way than do the other effects. After the change to the variables (1.16) there remains a complicated irregular dependence on Z , which corresponds to the actual oscillations of the physical quantities with variation of the composition of the substance.

8. Shell effects (thermodynamics)

It remains for us to consider shell effects at nonzero temperatures, and also their contribution to thermodynamic quantities. We note immediately that, in a "hot" system, a number of factors leading to smoothing of the oscillations appear. Our formulation of the problem (cf. the Introduction) makes it possible to take the chief

¹⁶⁾This is the reason why, in a problem with a Coulomb potential, the region of the continuous spectrum, where there are no true turning points, also makes a contribution to the spatial oscillations of the density.

of these into account, namely, the smearing-out of the distribution of electrons over the levels¹⁷⁾. It is found that in the region of interest to us (the sectors I and II, where the quantum-mechanical effects are dominant, in Fig. 1) this smoothing is described simply by a temperature-dependent coefficient:

$$\begin{aligned} n'_2(T) &= k_n n'_2(0), \\ \delta F(T) &= k_F \delta F(0) \equiv k_F \delta E. \end{aligned} \quad (8.1)$$

More precisely, in the right-hand sides of (8.1) are expressions calculated from the formulas of Sec. 7, but with potential U and chemical potential μ adjusted to the actual temperature of the system. For U this stipulation becomes superfluous in the uniformity regime, in which the potential does not depend on the temperature and (in the cell model-cf. Sec. 1) is equal to

$$U = -\frac{Z}{r} \left(1 + \frac{r}{2R}\right) \left(1 - \frac{r}{R}\right)^2. \quad (8.2)$$

In the region of pressures and temperatures under consideration, matter is "metallized"; accordingly, at any temperature the electrons occupy parts of both the continuous and the discrete spectrum (Fig. 3). The boundary separating these parts corresponds, according to (1.12), to the energy value

$$\bar{\mu} = 0; \quad (8.3)$$

in reality, it is somewhat lower because of the smearing-out of the levels into bands and because of their overlap. However, when the condition for semi-classicality at the level $\bar{\mu}$, which has the form $(Z/n)^{1/3} U^{1/2} \gg 1$ or

$$n \ll Z^4, \quad (8.4)$$

is fulfilled, these effects are small and, to logarithmic accuracy, do not affect the results (for more detail, see^[35]).

The shell corrections to the density are found from (6.4) (cf. also^[39]):

$$n'(T, \mu) = \int_{-\infty}^{\infty} d\varepsilon \frac{f(\mu - \varepsilon) \partial n'(\varepsilon)}{\partial \varepsilon}. \quad (8.5)$$

Using (7.7), we find

$$k_n = \frac{2\pi\tau T}{\text{sh}(2\pi\tau T)} \quad (8.6)$$

(see Appendix 6). Since $\tau \sim Z^{1/3} n^{-2/3}$, the density oscillations become exponentially small for $T > n^{2/3} Z^{-1/3}$ (in the case of relatively weakly compressed matter—for $T > Z$). But if the temperature is less than the above value, the coefficient (8.6) is close to unity and the dependence of $n'(0, \mu)$ (cf. (8.1)). With increasing temperature the chemical potential becomes negative

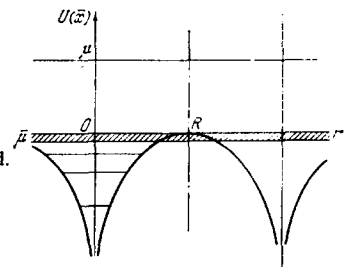


FIG. 3. Scheme of the levels of highly compressed matter. The region of overlap of bands is shaded.

¹⁷⁾Another factor—the thermal vibrations of the nuclei—becomes appreciable at ultra-high temperatures.

and increases in magnitude. Therefore, as T increases, the oscillations corresponding to deeper and deeper shells, for which the potential energy becomes comparable with the quantity $|\mu|$, disappear. These conclusions are confirmed by a comparison with the results of an exact calculation by the Hartree-Fock method (cf. [99]).

The corrections to the free energy are determined by the quantity n'_i , which is nonzero only in the region of the discrete spectrum (cf. (7.5) and (7.7)). Therefore, using (8.5), it is necessary to put the upper limit equal to $\bar{\mu} = 0$ (cf. (8.3)). Analogously, taking (6.3) into account, it is easy to see that the expression for $n'(0, \epsilon)$ is itself equal to $n'(0, \bar{\mu})$ for $\epsilon > \bar{\mu}$. Substitution of (8.5) into (4.4) gives

$$\delta F(T) = -T \ln(e^{\mu/T} + 1) \int dx n'_i(0) - \int_{-\infty}^0 d\epsilon f(\mu - \epsilon) \int dx n'_i(0).$$

Integrating the second term by parts, it is easy to see that it makes a relative contribution of the order of $1/\mu\tau_0$ (degenerate case) and $1/T\tau_0$ (classical case). When we take into account that $\tau_0 \sim n^{-1/2}$, these parameters are found to be small throughout the region of applicability of the TFM. Therefore, the problem reduces to the first term of δF . In particular, for $T = 0$ (7.6) gives

$$\delta E = -\mu_0 \int dx n'_i(0) = \frac{2}{\pi} \frac{\mu_0}{\delta_0} [S_0^*], \quad (8.7)$$

where μ_0 is the "cold" chemical potential and the other quantities in (8.7) are referred to the boundary $\bar{\mu}$. Hence,

$$k_F = \frac{1}{\mu_0} T \ln \left[\exp \left(\frac{\mu}{T} \right) + 1 \right]. \quad (8.8)$$

This coefficient also falls off with temperature, but substantially more slowly than (8.6): it can be seen from (1.13) that (8.8) decreases in a power-law fashion, becoming negligibly small only when $T \gg \mu_0$.

The physical nature of the shell oscillations of the free energy consists in the fact that, on variation of the density of matter or its composition, energy levels are "squeezed out" of the discrete spectrum into the continuous spectrum, or vice versa, whenever the value of the action in (8.7) becomes equal to an odd multiple of $\pi/2$ (see Fig. 3)¹⁸⁾. It is this which leads to the irregularities in the behavior of the physical quantities. Leaving a more detailed discussion of these questions to Chap. V, we give here explicit expression valid in the uniformity regime and pertaining to the case $T = 0$.

In place of the density we shall use the cell volume $v = Z/n$ and denote $\mathcal{P} = 5P/(3\pi^2)^{2/3}$. Then, taking (8.2) into account, we have

$$S_0 = kZ^{1/2}v^{1/6} - \frac{\pi}{2}, \quad k = 3 \left(\frac{3}{4\pi} \right)^{1/6} \ln \frac{1 + \sqrt{3}}{\sqrt{2}} \approx 1.56. \quad (8.9)$$

Analogously (cf. Sec. 7 and [351]),

$$\delta_0 = \frac{(36\pi)^{1/6}}{36} \ln(Z^3 v) Z^{-1/2} v^{-1/6}.$$

Hence, for the shell correction to the energy we have

$$\delta E = 36 \left(\frac{9\pi}{4} \right)^{1/6} \frac{Z^{7/6} v^{-1/2}}{\ln(Z^3 v)} [S_0^*], \quad (8.10)$$

this quantity, like (8.7), refers to the volume of one cell.

¹⁸⁾The shell effects disappear after all the energy levels have moved out into the continuous spectrum; this corresponds to $n > Z^4$ (cf. (8.4)). We take this opportunity to point out an error made in [5], where the value $n > Z^3$ was given.

It is important to note that, in reality, (8.10) corresponds to a situation that is unstable near the points of irregularity

$$v_n = Z^{-3} \left(\frac{\pi n}{k} \right)^6 \quad (n = 1, 2, \dots), \quad (8.11)$$

This can be seen from the expression for the shell correction to the pressure:

$$\delta P = -12 \left(\frac{9\pi}{4} \right)^{1/6} k \frac{Z^{5/3} v^{4/3}}{\ln(Z^3 v)} [S_0^*] \quad (8.12)$$

(cf. the dashed lines in Fig. 4), which is obtained from (8.10) by differentiating its last, most rapidly-varying factor with respect to the volume. It is well known that, because of the negative value of the bulk modulus, such a state is unstable and rearranges, as a result of which the pattern depicted in Fig. 4 by the thick solid curve arises. This corresponds to a first-order phase transition between a phase in which the n -th level lies in the discrete spectrum and another phase in which the n -th level lies in the continuous spectrum. The pattern of oscillations of the volume on variation of the pressure or atomic number is depicted by Fig. 4 (rotated through 90°) and Fig. 5. The corresponding analytic expression has the form

$$\delta v/v = -36 \left(\frac{9\pi}{4} \right)^{1/6} \times \frac{kZ^{1/3} [S_0^*]}{(3\pi^2)^{2/3} \mathcal{P}^{1/3} \ln(Z^{2/3} \mathcal{P})}, \quad (8.13)$$

where

$$S_0 = \frac{kZ^{2/3}}{\mathcal{P}^{1/3}} - \frac{\pi}{2}$$

and the points of irregularity (phase-transition points) are

$$\mathcal{P}_n = Z^{2/3} \left(\frac{k}{\pi n} \right)^{1/3}, \quad Z_n = \mathcal{P}^{3/2} \left(\frac{\pi n}{k} \right)^{3/2}. \quad (8.14)$$

The large value of the numerical coefficient in (8.13) is worth special mention, and makes the shell oscillations entirely noticeable even under conditions when they are essentially small.

The shell effects in quantities obtained from the pressure by differentiating it further with respect to the volume are particularly clearly manifested. Thus, the modulus of elasticity (Fig. 6) is found to be always equal to zero in the region of coexistence of the phases, while the Grüneisen constant for the electronic component, corresponding to a further differentiation with respect to the volume, even becomes negative. We shall continue the discussion of the shell effects in Chap. V.

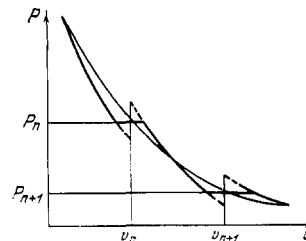


FIG. 4

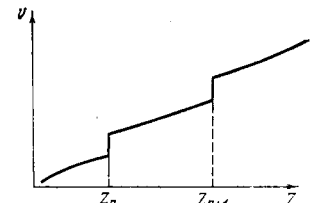


FIG. 5

FIG. 4. Dependence of the pressure on the volume (shell effects).

FIG. 5. Dependence of the atomic volume on the atomic number (shell effects).

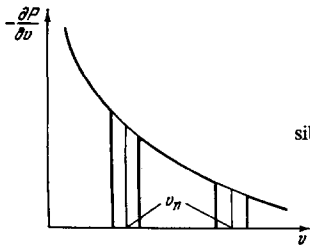


FIG. 6. Dependence of the compressibility on the volume (shell effects).

IV. DYNAMICAL GENERALIZATION OF THE THOMAS-FERMI MODEL

9. Response function of a nonuniform electron system

The TFM theory described in the preceding chapters only enables us to describe the static properties of a system. Amongst these, in particular, is the static response function $\epsilon(\mathbf{x}, \mathbf{x}', 0)$:

$$\int d\mathbf{x}' \epsilon(\mathbf{x}, \mathbf{x}', 0) \delta U(\mathbf{x}) = \delta U_e(\mathbf{x}), \quad (9.1)$$

relating the variations of the total (δU) and external (δU_e) potentials¹⁹⁾. This function coincides with the longitudinal part of the static dielectric permittivity of the system. In the framework of the TFM it is easily calculated using (1.2):

$$\epsilon(\mathbf{x}, \mathbf{x}', 0) = \delta(\mathbf{x} - \mathbf{x}') + \frac{\kappa^2(\mathbf{x}')}{4\pi|\mathbf{x} - \mathbf{x}'|}, \quad (9.2)$$

where $\kappa = \sqrt{4\pi\partial n/\partial \mu}$ is the inverse Debye radius (cf. (4.2)). In the case of a uniform system, (9.2) describes the usual Debye screening.

A still more important characteristic of the system is the dynamical response function $\epsilon(\mathbf{x}, \mathbf{x}', \omega)$, defined by the same relation (9.1) but with replacement of the static variations $\delta U(\mathbf{x})$, $\delta U_e(\mathbf{x})$ by the temporal Fourier components $\delta U(\mathbf{x}, t)_\omega$, $\delta U_e(\mathbf{x}, t)_\omega$ of the dynamical variations. Such a function is capable of describing practically all the dynamical characteristics of a system encountered in applications. Amongst these characteristics, above all, are the results of the action of different external agents on the system. For example, the photo-absorption cross section has the form^[9] $\sigma(\omega) = 2\pi^2 g(\omega)/137$, where the spectral density of the oscillator strengths

$$g(\omega) = -\frac{\omega}{2\pi^2} \text{Im} \int d\mathbf{x} d\mathbf{x}' \epsilon^{-1}(\mathbf{x}, \mathbf{x}', \omega), \quad (9.3)$$

where ϵ^{-1} is the "inverse matrix":

$$\int d\mathbf{x}'' \epsilon(\mathbf{x}, \mathbf{x}'', \omega) \epsilon^{-1}(\mathbf{x}'', \mathbf{x}', \omega) = \delta(\mathbf{x} - \mathbf{x}'). \quad (9.4)$$

The response function enables us to find the frequencies and damping constants of the normal oscillations of the system as the real and imaginary parts of the eigenvalues of Eq. (9.1) without the right-hand side:

$$\int d\mathbf{x}' \epsilon(\mathbf{x}, \mathbf{x}', \omega) \delta U(\mathbf{x}')_\omega = 0. \quad (9.5)$$

In addition, the effective interaction between the electrons, the correlation energy of the system, and so on, can be expressed in terms of the function ϵ .

¹⁹⁾A nonuniform system is characterized by one further response function ("charge-charge"), which differs from (9.1) by the replacement of δU , δU_e by δn , δn_e (n_e is the density of external charge) and is connected with ϵ by the relation $-\Delta_\lambda \int d\mathbf{x}'' \epsilon(\mathbf{x}, \mathbf{x}'', \omega)/4\pi|\mathbf{x} - \mathbf{x}''|$ (sic).

There exists a simple relationship between the response function and the polarization operator Π :

$$\epsilon(\mathbf{x}, \mathbf{x}', \omega) = \delta(\mathbf{x} - \mathbf{x}') - \int d\mathbf{x}'' \frac{\Pi(\mathbf{x}', \mathbf{x}'', \omega)}{|\mathbf{x} - \mathbf{x}''|}, \quad (9.6)$$

Π relates the variations of the density and potential:

$$\delta n(\mathbf{x})_\omega = \delta n_e(\mathbf{x})_\omega + \int d\mathbf{x}' \Pi(\mathbf{x}, \mathbf{x}', \omega) \delta U(\mathbf{x}')_\omega. \quad (9.6a)$$

Combining (9.6) with (9.1), it is easy to arrive at the Poisson equation

$$\Delta \delta U(\mathbf{x})_\omega + 4\pi \int d\mathbf{x}' \Pi(\mathbf{x}, \mathbf{x}', \omega) \delta U(\mathbf{x}')_\omega = -4\pi \delta n_e(\mathbf{x})_\omega, \quad (9.7)$$

which replaces (9.1).

If the dynamical parameter δ_0 is small (cf. Sec. 2), the polarization operator is described by a closed loop (particle-hole) in lowest order of perturbation theory (the random-phase of high-density approximation; cf., e.g.,^[6]). In the case of a uniform system we can arrive at a simple result, which is particularly transparent in the t -representation, in which (9.1) has the form

$$\int d\mathbf{x}' \int dt' \epsilon(\mathbf{x}, \mathbf{x}', t - t') \delta U(\mathbf{x}', t') = \delta U_e(\mathbf{x}, t).$$

Namely, for zero temperature,

$$\epsilon(\mathbf{x}, \mathbf{x}', t) = \delta(\mathbf{x} - \mathbf{x}') \delta(t) + \frac{\theta(-t)\theta(\eta)}{\pi^2 t^2}, \quad \eta \equiv \frac{(\mathbf{x} - \mathbf{x}')^2}{t^2} - p_F^2; \quad (9.8)$$

here the causality property ($t < 0$) and the retardation property ($t > |\mathbf{x} - \mathbf{x}'|/p_F$) are manifested explicitly. For $T \neq 0$ it is necessary to replace $\theta(\eta)$ by $[\exp(\eta/T) + 1]^{-1}$.

Attempts to generalize (9.2) and (9.8) to the nonuniform dynamical case have been undertaken in various directions. The principle of quasi-uniformity (cf., e.g.,^[41]), which reduces to substituting the quantity $p_F^2(\mathbf{x})$ in place of p_F^2 in (9.8), has been used quite often for this purpose. However, as was emphasized in Sec. 5, as applied to correlation effects (and a dynamical response is, in essence, such an effect) this principle is invalid. Another approach—use of the hydrodynamic (acoustic) equations of motion in combination with the TFM^[1,10,42,43]—is justified only in the long-wavelength limit and is unable to describe damping (absorption) effects without invoking additional information. Finally, the use of the high-frequency expression for the response function, known from the sum rules, has also been suggested^[44]. However, because of the divergence of the series in ω^{-2} obtained, it is not possible to extend this approach into the region of frequency of real interest for most problems^[45].

A response-function theory that makes adequate use of the characteristic smallness of a number of parameters in the TFM has been proposed in^[46] (cf. also^[5,9]). The inequality $\delta_0 \ll 1$ enables us to take the polarization operator in its simplest form (cf. above), and the condition $\xi^2 \ll 1$ gives the possibility of passing to the semi-classical limit^[20]. In the case of a cold system (the case $T \neq 0$ is discussed below), the above two parameters coincide and the accuracy of the results obtained is determined by their magnitude; for a heavy atom, the latter is $Z^{-2/3}$. The simplest approach leading to a correct answer consists in using the classical collisionless kinetic equation with a self-consistent field^[47,38,9].

²⁰⁾Being interested only in the linear response, we can take the semi-classicality in the spatial sense only, without worrying about restrictions on the frequencies (for a more complicated case, cf., e.g.,^[46]).

As a result of such a calculation it is found (cf. Appendix 7) that the answer is expressed in terms of the classical trajectory (and law of motion of) $\mathbf{x}(t)$ of an electron in the self-consistent field determined by the TFM, i.e., in terms of the solution of the equation

$$\ddot{\mathbf{x}} = \frac{\nabla p_F^2}{2} \quad (9.9)$$

with the initial conditions (\mathbf{n} is an arbitrary unit vector)

$$\mathbf{x}(0) = \mathbf{x}, \quad \dot{\mathbf{x}}(0) = p_F(\mathbf{x}) \mathbf{n} \quad (9.10)$$

We shall give expressions for the polarization operator in several forms (the bar denotes averaging over the directions of \mathbf{n}).

In the t -representation,

$$\Pi(\mathbf{x}, \mathbf{x}', t) = \theta(-t) \frac{d}{dt} \overline{\delta(\mathbf{x}(t) - \mathbf{x}') \frac{p_F(\mathbf{x})}{\pi^2}}, \quad (9.11)$$

In the ω -representation,

$$\Pi(\mathbf{x}, \mathbf{x}', \omega) = -\frac{p_F(\mathbf{x})}{\pi^2} \left[\delta(\mathbf{x} - \mathbf{x}') + i\omega \int_{-\infty}^0 dt e^{-i\omega t} \overline{\delta(\mathbf{x}(t) - \mathbf{x}')} \right], \quad (9.12)$$

and in a representation of the Kramers-Kronig type, in which the causality property is explicitly reflected,

$$\Pi(\mathbf{x}, \mathbf{x}', \omega) = \frac{p_F(\mathbf{x})}{\pi^2} \int_0^{\infty} \frac{d\omega' \omega'^2}{(\omega + i\delta)^2 - \omega'^2} \overline{\delta(\mathbf{x}(t) - \mathbf{x}')}_{|\omega'}. \quad (9.13)$$

An expression for the response function itself can be found from this by means of (9.6). The expressions obtained lead to explicit generalizations of (9.2) and (9.8). We note that replacement of the actual trajectory of the particle in the field of the TFM by a trajectory of rectilinear uniform motion with the initial conditions (9.10) would correspond to the quasi-uniformity approach. Correspondingly, the inapplicability of the principle of quasi-uniformity is manifested in the radical difference between these trajectories (cf. Sec. 13 below).

To conclude this Section we point out the self-similarity properties of the response function^[49]. The self-similarity of the quantity p_F^2 leads to the result that, after change to the variables (1.16), the explicit dependence on Z drops out of the solution of Eq. (9.9) and out of the expression for the response function itself. Accordingly, $\epsilon(\omega) = \epsilon(\omega/Z)$, the proper frequencies are found to be proportional to Z , and the oscillator-strength density $g(\omega) = Zf(\omega/Z)$.

10. Collective oscillations of a nonuniform system

One of the important applications of response functions is in the calculation of the proper frequencies and damping constants of the oscillations of a nonuniform electron system. We are concerned with oscillations associated with the presence of the Coulomb restoring force, the long range of which causes a large number of particles to oscillate simultaneously. Therefore, such oscillations are called collective oscillations.

To describe them we can start from Eq. (9.5), or, equivalently, from Eq. (9.7) without the right-hand side:

$$\Delta \delta U(\mathbf{x})_{\omega} + 4\pi \int d\mathbf{x}' \Pi(\mathbf{x}, \mathbf{x}', \omega) \delta U(\mathbf{x}')_{\omega} = 0. \quad (10.1)$$

When solved with the appropriate boundary condition, it gives information on the spectrum and damping of the proper frequencies, on the form of the normal oscillations, and so on. Equation (10.1) can be brought to a form suitable for numerical calculations by simplifying the expression for its kernel.

This expression (cf. (9.12)) contains three integrations—over the time t and over the direction angles of the vector \mathbf{n} , i.e., over θ and φ . All these integrations can be removed by using the presence of the δ -function in the integrand. We need only keep in mind that the equation $\mathbf{x}(t) = \mathbf{x}'$ ($\mathbf{x}(0) = \mathbf{x}$) has, generally speaking, a whole set of solutions, which we shall label by the subscript j ; this corresponds to the presence of several trajectories joining the points \mathbf{x} and \mathbf{x}' . To each such trajectory correspond its own functions $t_j^0(\mathbf{x}, \mathbf{x}')$, $\theta_j^0(\mathbf{x}, \mathbf{x}')$, $\varphi_j^0(\mathbf{x}, \mathbf{x}')$, having the meaning, respectively, of the time of motion from \mathbf{x} to \mathbf{x}' and the direction angles of the initial velocity. Introducing the Jacobian $D_j = D(\mathbf{x}(t))/D(t, \cos \theta, \varphi) |_{t_j^0, \theta_j^0, \varphi_j^0}$, we have

$$\Pi(\mathbf{x}, \mathbf{x}', \omega) = -\frac{p_F(\mathbf{x})}{\pi^2} \left[\delta(\mathbf{x} - \mathbf{x}') + \frac{i\omega}{4\pi} \sum_j \frac{e^{i\omega t_j^0}}{|D_j|} \right]. \quad (10.2)$$

The kernel (10.2) of Eq. (10.1) has a nonzero imaginary part describing the damping of the collective oscillation. It is essential to emphasize^[46] that in a nonuniform system the damping constant is a quantity of the same order as the proper frequency, in the region of applicability of the TFM. Therefore, the question of the very existence of a collective level, which reduces to the question of the relative magnitude of these parameters, requires a numerical calculation to resolve it. Only in the case when such a calculation leads to a damping constant that is numerically small compared with the frequency can we speak of a real collective degree of freedom of the system.

The statement that the damping constant and frequency are of the same order stems from the following simple arguments. As is well-known from the theory of collective oscillations in a uniform system (cf., e.g.,^[47]), in the random-phase approximation under consideration the damping is rigorously equal to zero, if the wave-vector of the oscillation does not exceed a certain critical value. This happens because, under such conditions, the only mode of decay of the oscillation^[21]—into a ‘particle-hole’ pair—is forbidden by the energy and momentum conservation laws. In a nonuniform system the momentum ceases to be a good quantum number, or, which is the same thing, scattering by an inhomogeneity produces an uncertainty in the momentum of the order of $1/L$, where L is the characteristic non-uniformity length (cf. Sec. 1).

For this reason, the decay channel under consideration becomes open, and the corresponding damping is determined by an inverse power of L . The ratio of the damping to the frequency should be expressed in terms of the dimensionless combinations $1/Ln^{1/3}$ and r_D/L . In the region of applicability of the TFM the first of these is indeed small, but the second is always of order unity (cf. (1.17)). From this the statement under discussion follows.

The situation in the important case of periodic motion of the particle (with period T) is particularly visualizable. In this case, as can be shown, the Jacobian does not depend on the index j , and the quantity $t_j^0 > 0$ is equal to $t^0 + jT$ for motion from \mathbf{x} to \mathbf{x}' in one direction, and equal to $T - t^0 + jT$ for motion in the opposite direction, in a closed cycle; $j = 0 - \infty$. Substitution into (10.2) gives

²¹⁾Here and below, we neglect the extremely small radiative damping.

$$\text{Im } \Pi(x, x', \omega) \sim \text{Im } \delta\left(\text{ctg } \frac{\omega T}{2}\right) = \sum_n \delta\left(\omega - \frac{2\pi n}{T}\right) \quad (n=1, 2, \dots), \quad (10.3)$$

where we have used the rule ($\omega \rightarrow \omega + i\delta$) for going "causally" round the pole (cf. (9.13)). The physical meaning of (10.3) is that the damping of the collective oscillation is connected with a resonance of frequency ω , with the semi-classical particle-excitation frequency $2\pi n/T$. It is this which corresponds to the decay of the collective oscillation into a "particle-hole" pair, which is the analog of Landau damping in the case of a nonuniform system. In accordance with what has been said above, only the δ -function of the energy-conservation law appears in the expression (10.3). This leads to a significant (in the literal sense) magnitude for the damping, proportional, like the frequency itself (cf. the end of Sec. 9), to Z .

The arguments and formulas expounded in this Subsection (like the relations (9.11)–(9.13)) apply directly to the case of zero temperature only. The generalization to the case $T \neq 0$ is effected by means of the simple formula

$$\Pi(T) = \int_{-\infty}^{\infty} d\mu' f(\mu - \mu') \frac{d}{d\mu'} \Pi(0), \quad (10.4)$$

analogous to (8.5) (cf. Appendix 7).

In conclusion, we shall discuss the question of the absorption of light by the system when collective oscillations are present in it. Introducing the quantity

$$u(x, \omega) = \int dx' e^{-i(x, x', \omega)},$$

we can rewrite the oscillator-strength density in the form $g(\omega) = -(\omega/2\pi^2) \text{Im} \int dx u$, and obtain for u the equation (cf. (9.4))

$$\int dx' e^{i(x, x', \omega)} u(x', \omega) = 1. \quad (10.5)$$

This is an inhomogeneous equation corresponding to the homogeneous equation (9.5) that determines the spectrum and damping of the collective oscillations. It follows from this, already, that to each collective level with sufficiently small damping there corresponds a peak in the oscillator-strength density, positioned at the same frequency.

Applications of the theory described in this Section to the problem of the collective oscillations of the electron cloud of a heavy atom are considered below, in Sec. 13.

V. APPLICATIONS TO THE PHYSICS OF THE ATOM AND THE PHYSICS OF EXTREMAL STATES OF MATTER

11. Refinement of the TFM at short distances from the nucleus

In this chapter we shall consider a number of applications of the TFM, in its improved form, to different problems in atomic physics and the physics of extremal states of matter. It is important to emphasize from the outset that the theory described in the preceding Sections is far from being directly applicable to all such problems. There are a number of important quantities whose calculation requires preliminary modification of this theory. However, the situation does not involve a radical change of the theory, but only, in essence, a different interpretation of the expressions obtained in Chap. III.

These expressions, corresponding to the exchange, correlation, quantum and shell effects, were obtained under the assumption that their contribution to physical quantities was relatively small. Essentially, we were concerned with the first term of the expansion in the appropriate parameter δ . As always in such cases, the small size of the first term of the expansion makes it possible to discard all the other terms. The corresponding conditions, expressed in terms of the density and temperature, are contained in the diagram of Fig. 1.

However, fulfillment of these conditions does not yet guarantee the applicability of the theory of Chap. III to all the physical characteristics of a substance. The point is that, as already noted at the end of Sec. 3, the TFM is essentially inapplicable in the region near the nucleus (and on the periphery of an isolated atom). In this region the quantum effects are so substantial that this invalidates not only the TFM itself, but also its generalizations²²⁾. Therefore, those physical quantities for which this region is important (the total energy, the polarizability of the neutral atom, etc.) should be described in a special way.

Having chiefly in mind the region near the nucleus (and, correspondingly, the quantum effects), we shall discuss two ways of modifying the TFM. The first consists in treating the quantum correction and the zeroth term corresponding to the TFM on an equal footing^[4, 29, 50]. Expansions in the parameter δ_{qu} are not performed in this case. Now the process of successive approximations consists in treating the TFM itself in the first stage, treating the TFM and, on an equal footing, the first quantum correction in the next stage, treating the same plus the quantum correction of second order in δ_{qu} in the third stage, and so on, without making any additional assumption at each stage. Such an approach (which is sometimes called the quantum-statistical model, or QSM for short) is found to be highly effective. The process of successive approximations converges rapidly, and a sufficiently good description is already achieved at the second stage. In any case, the corresponding result is an immeasurably better starting point for subsequent improvements (if there is any need for these) than the TFM itself.

In the case of zero temperature the program of the QSM can be realized by considering the minimum of the functional $E(n) = E - \int dx n$, where E is the sum of the expressions (1.7) and (6.6a). One may proceed either by a direct variational method^[29, 41], or by solving the Euler-Lagrange equation^[50]

$$[\zeta \Delta + p^2(x)] \psi = (3\pi^2)^{2/3} \psi^{7/3}, \quad (11.1)$$

where $\psi^2 \equiv n$ and $\zeta = 1/9$. Eq. (11.1) resembles the Schrödinger equation, differing from it by the nonlinear term²³⁾ and also by the quantity ζ (in the Schrödinger equation, $\zeta = 1$ and the factor-of-nine difference between (6.6a) and the Weizsäcker formula is connected with this; cf. Sec. 6).

²²⁾This is manifested, e.g., in the divergence at short distances of the quantum correction to the energy (cf. Sec. 6).

²³⁾Additional nonlinearity would appear if the exchange term (4.13) were included. This would reduce to adding the term $-2(3/\pi)^{1/3} \psi^{5/3}$ to the right-hand side of (11.1) and would imply a return to the Thomas-Fermi-Dirac model, but with parallel allowance for the quantum effects.

The success of the QSM program is connected with the following simple circumstance. The inapplicability of the TFM at short distances is manifested in the fact that it leads to incorrect behavior of the density in this region: as can be seen from (1.11), for $\xi = 0$ the density is singular at zero: $\psi \sim r^{-3/4}$, $n \sim r^{-3/2}$, while in an exact quantum-mechanical treatment the density is described by a regular function. It turns out that the behavior of the density is already radically improved in the second stage of the QSM: as can be seen from (11.1), its solution at zero has the form $n \sim 1 - (Zr/\xi)$. Therefore, the subsequent stages of the QSM lead only to insignificant quantitative refinements of the result.

Another way of refining the TFM at short distances from the nucleus is based on the fact that in this region the potential created by the electrons is practically constant and can be put equal to a constant C . At the same time, the problem with the potential $U' = -Z/r + C$ can be solved in explicit form. From this, without any additional assumptions, we can arrive at the following expression for the distribution function:

$$f = f_1 - f_2 + f_3; \quad (11.2)$$

here f_1 is the exact quantum-mechanical expression for f for the potential U' , and can be expressed in terms of Whittaker functions^[40]; $f_2 = \theta[2(\mu - U') - p^2]$ is the semi-classical expression for the same potential; $f_3 = \theta[2(\mu - U) - p^2]$ is the usual TFM result. At short distances, where the potential is close to U' , only the first term remains, while in the region of relatively large distances, where the motion becomes semi-classical, the TFM expression is regained (cf.^[51]).

There also exist other methods of refining the TFM at short distances. We shall mention only the paper^[52], in which the introduction of a special lower "cutoff" of the electron-energy spectrum, leading to a sharp decrease in density in the vicinity of the nucleus, was proposed. However, up to now, the most highly-developed and effective method is the QSM method.

12. Applications to the physics of the atom

In this section we consider only those applications which illustrate the results of Chap. III. Applications pertaining to the material of Chap. IV have been carried over into the next section. Here and below we consider a neutral isolated atom with a sufficiently large value of Z . Corresponding to this, in the framework of the TFM, are the quantities

$$\mu = 0, \quad p_F^2(\mathbf{x}) = \frac{2Z}{r(1+\xi)^2}, \quad \xi = \frac{r}{\alpha}, \quad \alpha = \left(\frac{9}{2Z}\right)^{1/3}, \quad (12.1)$$

where for p_F^2 we have used the approximate expression of^[53], which will be applied below.

We begin with the question of the total energy of the electron cloud of an atom. The TFM gives for this quantity the expression $E(Z) = -0.769Z^{7/3}$, which is considerably greater in magnitude than the results of experiment and of quantum-mechanical calculations. This happens because of the inapplicability of the semi-classical description at short distances from the nucleus (cf. Sec. 11). In addition, the formula given does not reflect the weak, but perfectly observable, oscillations of the function $E(Z)$ that are associated with shell effects. Figure 7, borrowed from^[54], shows the results of calculating the energy of an atom by the TFM, by the Thomas-Fermi-Dirac model, by the QSM (with inclu-

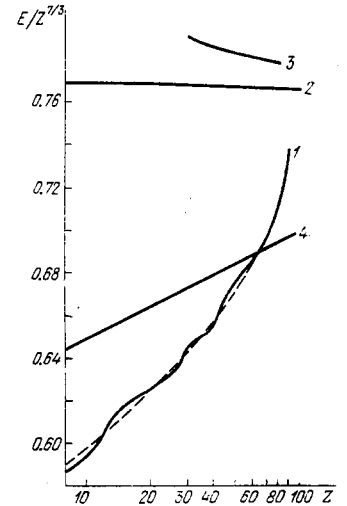


FIG. 7. Energy of the electron cloud of an atom. 1—from the Hartree model^[92], 2—from the TFM, 3—from the Thomas-Fermi-Dirac model, 4—from the QSM.

sion of an exchange correction), and by the Hartree-Fock method. It can be seen that allowance for quantum effects considerably improves the result: e.g., for $Z \sim 20-30$ the disagreement with the results of the quantum-mechanical calculation falls from $\sim 25\%$ to $\sim 5\%$. The second method discussed in Sec. 11^[51] leads to similar results.

The shell contribution to the energy of the atom can be estimated by means of (4.4) and (7.6) (since $\mu_0 = 0$, we cannot use formula (8.7) in the present case). The principal role in the integral (4.4) is played by small values of μ and, correspondingly, large values of r , where the semi-classical description is inapplicable. Therefore, we can only count on obtaining qualitative results. The first of these is an explanation of the extremely small amplitude of the oscillations: its relative magnitude $\delta E/E$ is substantially smaller than the parametric estimate $\delta_{qu} \sim Z^{-2/3}$. The explanation lies precisely in the unsuitability of the semi-classical method for describing the oscillations under consideration. In the region of importance for these oscillations, i.e., the region of the outer shells of the atom, where the charge of the nucleus is practically completely screened, the amplitude of the oscillations does not depend on Z . Correspondingly,

$$\frac{\delta E}{E} \sim Z^{-1/3}, \quad (12.2)$$

which is in agreement with the curve of Fig. 7.

The second result concerns the type of oscillations. Substituting (7.6) into (4.4), it is easy to see that the oscillations of the energy are smoothed compared with the oscillations of the density. Namely,^[24]

$$\delta E \sim \left[S_0^2 - \frac{\pi^2}{4} S_0 \right]^*, \quad (12.3)$$

which corresponds to wave-like behavior with a discontinuous second derivative, rather than with a discontinuous first derivative as in δn . This also agrees qualitatively with Fig. 7. The points of discontinuity correspond to the "magic" values $Z_{mag} = \dots 19, 37, 55, \dots$ (the alkali metals), at which a level with quantum numbers n and $l = 0$ emerges into the continuous spec-

²⁴⁾Formula (12.3) is obtained by iteration in μ of the oscillating factor in (7.6), to which we ought to add the further term $-\pi^2/12$ (cf. Appendix 5).

trum, and $S_0 = \pi(n - \frac{1}{2})$ for $E = 0$. It can be seen from (12.3) that the nodes of the oscillations are located both at the values Z_{mag} and in the intervals between them. This property corresponds qualitatively to Fig. 7, in which the nodes correspond to $Z \approx 21, 29, 37, 53, 59, \dots$

We turn now to the description of the density distribution in the core of the atom (for $Z^{-1} \ll r \ll 1$). In this region the quantum effects are small, while the shell effects are quite noticeable because of the large numerical coefficient in formula (7.7). Use of this formula and (12.7) gives²⁵⁾

$$\delta n \sim \sin \left(\sqrt{8Z\alpha} \arccos \frac{\alpha-r}{\alpha+r} \right) \quad (12.4)$$

(for simplicity, the non-oscillating factor has been omitted) and leads to good (about 5%) agreement with the quantum-mechanical calculations for atoms of average and large atomic number (Fig. 8)^[34]. What is measured directly in experiment is not the density, but the atomic form factor $F(q) = \int dx n(x) e^{-iq \cdot x}$, where q is the momentum transfer in scattering of fast electrons or photons. Substituting (7.7), using (9.1) and proceeding by the method of stationary phase, it is possible to arrive at the expression^[55]

$$\delta F(q) \sim \cos [1.82Z^{1/3}(\pi - x)], \quad (12.5)$$

where $x = q/1.1Z^{2/3}$. The inclusion of this correction appreciably improves the behavior of the function $F(q)$ (Fig. 9).

The next quantity with which we shall be concerned is the potential p_F^2 of the atom. With quantum effects taken into account, it was calculated in the paper by Kompaneets and Pavlovskii^[18]. These results were used to calculate the polarizability and magnetic susceptibility of the atom and it was found that, in comparison with the TFM, the theoretical results come appreciably closer to the experimental data. Thus, according to the author of^[56], the above quantities for xenon have (in certain units) the experimental values 4.10 and 4.39, respectively, the values 24.8 and 113.0 in the TFM, and the values 4.06 and 45.7 when quantum effects are taken into account. The behavior of p_F^2 with shell effects taken into account has recently been obtained^[57]; it is shown in Fig. 10.

In the literature there are also data on the distribution of the partial electron density corresponding to a given value of l (see Appendix 5). We shall not discuss this topic (cf. ^[1]).

We may state that, on the whole, the generalized TFM, incorporating quantum, exchange and shell effects, gives a considerably better description of the properties of a heavy atom than does the standard TFM. The contrary statement in^[58] is based on the factual errors pointed out in^[56].

13. Collective oscillations of the electron cloud of an atom

Amongst the nonuniform systems that have collective levels as well as single-particle levels in the excitation spectrum is the electron cloud of a heavy atom. Such levels correspond to the classical oscillations of a

²⁵⁾In the given case the quantities n' and δn coincide: because of the rapid oscillation of n' the first term in the left-hand side of (4.2) is much larger than the second (cf. (4.3)).

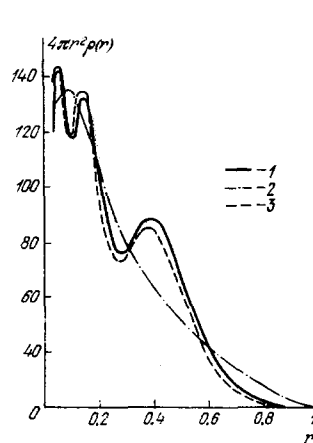


FIG. 8

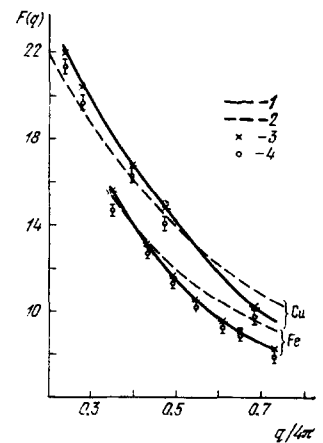
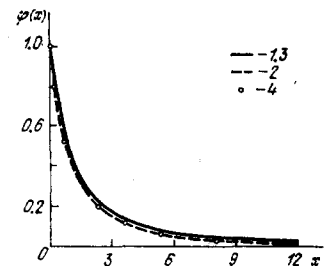


FIG. 9

FIG. 8. Radial electron density in the mercury atom. 1—from the Hartree model^[93], 2—from the TFM, 3—from the TFM with shell corrections.

FIG. 9. Atomic form factor for iron and copper. 1—from the Hartree-Fock model^[94], 2—from the Thomas-Fermi-Dirac model^[95], 3—the same with a shell correction, 4—experiment^[96].

FIG. 10. The atomic potential ($\varphi(x) = (r/Z)p_F^2$, $r = 0.885Z^{-1/3}x$). 1—from the Hartree-Fock model, 2—from the TFM, 3—from the TFM with a shell correction, 4—from the QSM^[59].



charged liquid drop, to which a sufficiently heavy atom can be likened²⁶⁾. As has been discussed in detail in the review^[9], the collective levels of an atom might manifest themselves as peaks in the cross-sections for scattering of photons or electrons by the atom; in addition, such levels might lead to those features of atomic processes that are characteristic of the "Bohr" picture (the absence of correlations between the initial and final states, and so on).

The question of the existence of collective levels in atoms was raised a long time ago^[42,43]. However, up to the most recent times (cf. ^[59,60]), two points of cardinal importance for the answer to this question have remained unclarified. The first pertains to the magnitude of the Landau damping, which, as was noted in Sec. 10, is not strictly small in relation to the frequency of the oscillations. Therefore, only a numerical calculation in the framework of a consistent theoretical scheme could lead to a small damping, and thereby to an affirmative answer to the question of the real existence of collective degrees of freedom in the atomic cloud.

The second point is connected with the question of the spatial localization of the collective excitation. If we supplement Eq. (10.1) by the natural (at first sight) boundary condition

²⁶⁾We are concerned with "truly collective" levels, having specific quantum numbers, and not with collective effects in single-particle transitions (concerning the latter, cf. ^[61]).

$$\delta n|_{r \rightarrow \infty} = 0 \quad (13.1)$$

(together with the condition $\delta n < \infty$ or $r\delta U = 0$ at $r = 0$), then, as it turns out, a continuous spectrum of excitation energies $\omega \geq 0$ is obtained. The hydrodynamic approach (cf. Sec. 10 and^[10]) also leads to the same result when (13.1) is used. The point is that the density distribution in the TFM falls off relatively slowly at large distances and there are always excitations that correspond to density "spikes" at large distances from the nucleus and have arbitrary (including arbitrarily small) energies.

The result obtained not only raises doubts concerning the inapplicability of the TFM at large distances from the nucleus, but, moreover, corresponds to an incorrect formulation of the problem. The energy $\omega \sim Z$ of a collective level (cf. Sec. 9) is considerably greater than the ionization energy of the outer electrons ($\omega \sim 1$), and so this level, strictly speaking, lies in the continuous spectrum: a collective excitation that originally arose in the core of the atom will sooner or later transfer its energy to the outer electrons of the atom and thereby cease to exist. Therefore, the boundary condition (13.1), being referred to an infinitely distant point, describes not the collective excitation itself but its decay products, which do indeed correspond to the continuous spectrum.

A correct formulation of the problem is as follows. A collective excitation originally arises in the core of the atom (for $r < R \sim Z^{-1/3}$), i.e., in the region of applicability of the TFM, where we can use the relation of Sec. 10. Whether the excitation is indeed localized in the region under consideration can be judged by replacing (13.1) by the condition

$$\delta n|_R = 0, \quad (13.2)$$

varying R within certain limits, and noting the appearance of a plateau in the dependence of the frequency ω and damping Γ on R . The values of the functions $\omega(R)$ and $\Gamma(R)$ corresponding to this plateau can be identified with the frequency and damping constant of the collective level, and for $\Gamma \ll \omega$ we may speak of the level as a real level of excitation of the atom. Subsequently this level will be damped, both as a result of mechanisms operating in the region of its original localization (Landau damping and radiative decay), and as a result of transfer of excitation energy to the outer shells (cf. above). Strictly, the Landau damping $\Gamma \sim Z$ is the most important (it will be determined by a numerical calculation); the radiative damping and the damping associated with the outer shells are certainly small compared with ω , although they can become comparable with the Landau damping because of the anomalous numerical smallness of the latter (see below).

The verification of the correctness of the picture we have drawn and the determination of the parameters of the collective excitations are carried out by means of Eqs. (10.1) and (10.2) and the boundary condition (13.2). Newton's equation (9.9) is first solved analytically in the field (12.1). Its solutions are closed self-intersecting trajectories (Fig. 11), describable in polar coordinates by the equation $r/\alpha + \alpha/r = \Delta + 1 + (\Delta - 1)\cos\theta$, where $\Delta = (Z\alpha/M^2) - 1$; M is the angular momentum of the particle. The motion turns out to be periodic with period $T = \pi(\Delta + 1)(3\Delta - 1)\alpha^2/M$ (cf. Sec. 10).²⁷⁾

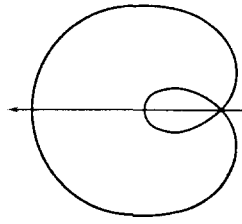


FIG. 11.

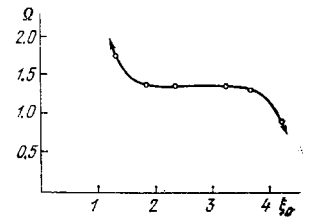
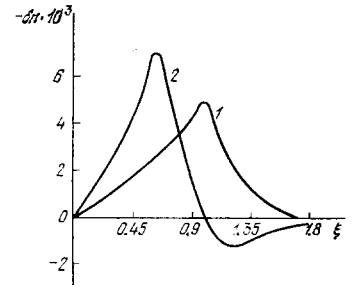


FIG. 12.

FIG. 11. Trajectory of a particle in the field of an atom.
FIG. 12. Dependence of the frequency of a collective oscillation on the radius of the region of localization ($\Omega = 3\omega/\sqrt{2Z}$, $\xi_0 = R/\alpha$).

FIG. 13. Perturbations of the radial density for collective levels ($\xi = r/\alpha$).



The numerical calculation was carried out by the completed-vector method of^[62] and led to two dipolar ($\delta U \sim \cos\theta$) levels with relatively small width (cf.^[59]). The curves $\omega(R)$ and $\Gamma(R)$ do indeed have clear plateaux (the curve for the $\omega(R)$ of one of the levels is shown in Fig. 12), to which correspond the values (in electronvolts)

$$\begin{aligned} \omega_1 &= 13.7Z, & \omega_2 &= 36.0Z, \\ \Gamma_1 &= 3 \cdot 10^{-3}Z, & \Gamma_2 &= 10^{-4}Z. \end{aligned} \quad (13.3)$$

Figure 13 shows the radial parts $\delta n(r)$ of the change in density on excitation. It can be seen that the lowest collective level corresponds, in the first approximation, to a displacement of the cloud, as a whole, relative to the nucleus (this picture was discussed a long time ago by E. L. Feinberg). However, the cloud is, in fact, slightly deformed, while remaining unmoved near the nucleus and at the periphery of the atom.

By means of the relations given in Subsection 10, the oscillator-strength density has also been calculated^[60]. As it should, the function $g(\omega)$ has sharp peaks corresponding to (13.3). The areas within the peaks, which have the meaning of the oscillator strengths of the collective levels, are of the order of 0.1Z for the lower level and three orders of magnitude smaller for the upper level. Thus, the collective levels exhaust a considerable proportion of the sum rule $\int d\omega g(\omega) = Z$ and should make an appreciable contribution to optical transitions.

To conclude this section we shall touch briefly upon the question of the correlation energy of a heavy atom^[49]. In the framework of the quasi-uniformity ap-

²⁷⁾The fact that the period coincides with the characteristic time $1/Z$ of a collective oscillation implies that the motion of the particle differs strongly from the rectilinear and uniform motion corresponding to the quasi-uniformity approach (cf. Sec. 9).

proach we would obtain a dependence of δE on Z of the form $\delta E \sim Z \ln Z$ (cf. Sec. 5). However, the true expression turns out to be different. Using the general expression, valid in the random phase approximation,

$$\delta E = -\frac{i}{4\pi} \int_{-\infty}^{\infty} d\omega \text{Sp} (\ln \hat{\epsilon}(\omega) + \hat{\epsilon}(\omega) - 1), \quad (13.4)$$

where $\epsilon(\mathbf{x}, \mathbf{x}', \omega)$ is regarded as a matrix with indices \mathbf{x} and \mathbf{x}' , and taking the self-similarity of $\hat{\epsilon} = \hat{\epsilon}(\omega/Z)$ into account (cf. Sec. 9), it is easy to see that the convergent integral in (13.4) gives the dependence $\delta E \sim Z$ (cf. (3.5)). This is a further indication of the inapplicability of the quasi-uniformity principle to the atom.

14. Applications to the physics of the extremal states of matter

The most important and widely-used applications of the TFM to the physics of extremal states of matter pertain to the thermodynamics. Here, primarily, we must single out the problem of the equation of state of matter, i.e., the dependence between the pressure, density, temperature and chemical composition of matter. It is the equation of state that we shall be concerned with in this section, although in the papers cited below there are also data on other thermodynamic characteristics.

The application of the TFM and its generalizations to the derivation of the equation of state of matter is realized, as a rule, in the framework of the Wigner-Seitz cell model (cf. Sec. 1). Without dwelling on the details (cf. [1, 5, 81]), we point out that the most complete data on the equation of state in the TFM are contained in the [63] (cold matter) and [64] (hot matter) by Latter [63]. A considerable part of these data, which refer to a wide range of pressures and temperatures, is incorrect because of the inapplicability of the TFM itself; this conclusion is also confirmed by direct comparison with the available experimental data [65].

Refinement of the TFM by the inclusion of the effects considered in Chap. III makes it possible to distinguish the reliable part of these data and obtain an improved equation of state of matter, valid in a wider range of pressures and temperatures. In Chap. III general expressions ((4.13), (5.6), (6.11)) were given for the corresponding corrections to the equation of state, together with their explicit form in the uniformity regime [28] (shell effects in the equation of state are considered below).

In the region of not very high temperatures (cf. Fig. 1), the principal contribution to the equation of state is made by the exchange and quantum effects. The first have been investigated in most complete form in [22]. However, the results are invalidated to a considerable extent by the fact that the quantum effects were not taken into account at all. As was explained in Sec. 6, numerically the latter makes the same contribution (to within a coefficient $\approx 1/3$).

A quantitative theory of the quantum effects in the equation of state of matter was constructed in [21], and a numerical solution of the problem for cold matter is contained in [68], from which we borrow Fig. 14. It can

[28] Cf. also, in this connection, [66, 67].

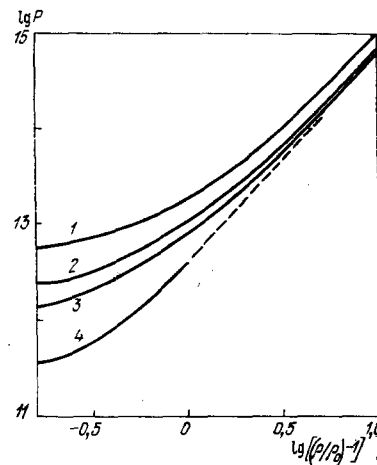


FIG. 14. Equation of state of iron (ρ_0 is the normal density). 1—from the TFM, 2—from the Thomas-Fermi-Dirac model, 3—from the TFM with exchange and quantum corrections, 4—experiment [65].

be seen from this figure that the quantum and exchange corrections do indeed make the TFM result come closer to the experimental data [29]. The results of [70], which, like [68], refer to the cold compression of iron, lead to an analogous conclusion. In [71] the equation of state with quantum effects taken into account was compared with experiment in the high-temperature region and convergence of the data was again noted.

Although the TFM, even when refined by allowance for quantum and other effects, is not directly applicable in the low-pressure region, it leads to reasonable results for the atomic volumes (or densities) of uncompressed matter [54, 68]. In this connection, we recall that at zero pressure the TFM itself leads to an infinite radius for the atom [72]. In the framework of the Thomas-Fermi-Dirac model, or when quantum effects are taken into account, the situation is changed: uncompressed matter acquires a finite density. Although these models are not capable of describing the shell oscillations of the atomic volume, they convey the behavior of this quantity averaged over the periodic table. The best results are given by the quantum-statistical model (cf. Sec. 11). The above is illustrated by Fig. 15a, borrowed from [54]. The empirical curve in this figure reflects the atomic-volume oscillations associated with shell effects. The peaks correspond to the alkali metals, for which an electron with a given value of the principal quantum number and $l = 0$ first appears in the atom. The descending parts of the curve correspond to close-packed structures; a description of these parts can be found in [73]. As Z increases the curves pass through a minimum and the ascending parts correspond to structures that are not close-packed. This is the reason why the atomic volume of a Group-0 element, for which we might expect the lowest value, in fact differs little from the atomic volume of the alkali metal that follows it. This is connected with the fact that a crystal of a Group-0 element belongs to the class of loosely-packed

[29] The papers [68, 69] contain a complete thermodynamic description in the framework of the TFM with quantum and exchange effects taken into account. The paper [101] contains detailed tables of thermodynamic quantities calculated from the TFM with quantum and exchange corrections taken into account.

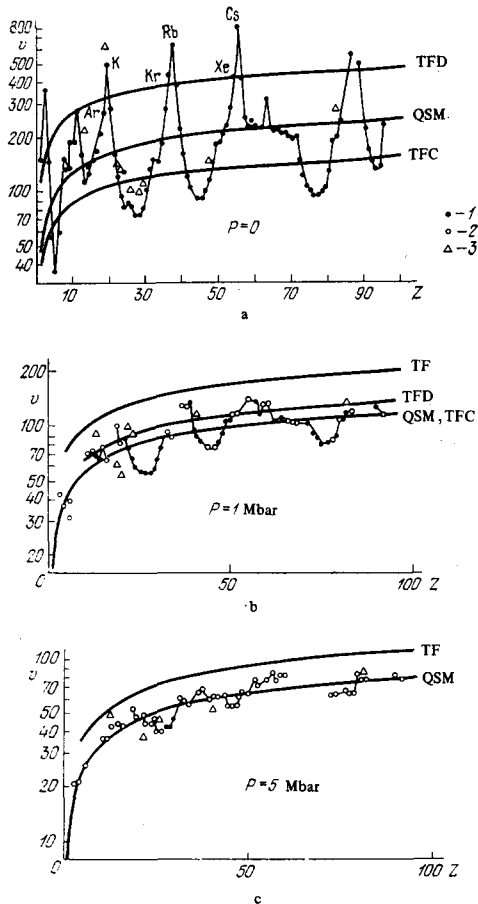


FIG. 15. Curves of the atomic volumes $V(a, e)$. 1—experiment [65,97], 2—interpolation formulas [67], 3—quantum-mechanical calculation [98] (TFC—TF model with quantum and exchange corrections, TFD—Thomas-Fermi-Dirac model, QSM—quantum-statistical model).

van der Waals structures. Therefore, the curve under consideration is characterized by a discontinuity not of the function itself, but of its derivative.

The question of how the shell effects behave with increasing pressure is of considerable interest. The conventional point of view is that they decrease with increasing pressure, becoming negligibly small for $P > 1$ (in the usual units this corresponds to 300 Mbar). At higher pressures the properties of matter become universal, and the dependence of its characteristics on the atomic number becomes smooth and monotonic. At first sight, the empirical curves shown in Figs. 15b and 15c [54,65] justify this point of view.

However, the results of Sec. 8 show that, in fact, the situation with the shell effects is more complicated. Oscillations associated with discontinuity of the derivative of the function $v(Z)$ (cf. Fig. 15) are indeed "washed out" at a pressure of order 1, but at higher pressures sharper oscillations, associated with discontinuity of the function $v(Z)$ itself, appear in their place. Physically, this corresponds to the fact that even the structures corresponding to the ascending parts of Fig. 15a become close-packed with increasing pressure; because of this, the minima of the curve $v(Z)$ disappear and a discontinuity in the atomic volume arises between a Group-0 element and the neighboring alkali metal. The discontinuity points themselves remain the same as

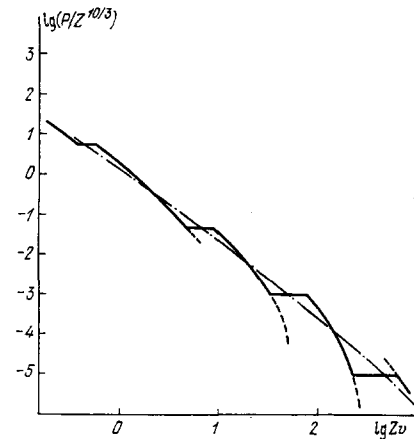


FIG. 16. Equation of state with allowance for shell effects ($Z = 100$).

at zero pressure, so long as we are far from the limits of the uniformity regime ($n \ll Z^2$). However, at higher pressures the "magic" values of Z begin to move in the direction of higher Z , as can be seen from formula (8.14).³⁰⁾ This happens because, on account of the influence of the neighboring cells, the character of the occupation of the levels becomes less and less hydrogen-like. Only when $n > Z^4$ do the shell oscillations completely disappear, because all the levels have crossed into the continuous spectrum. As was shown with regard to the uniformity regime in Sec. 8, in the language of the function $v(P)$ (the equation of state) the shell effects are manifested in the appearance of a series of first-order phase transitions, corresponding to the "squeezing out" of deep levels of the atoms into the continuous spectrum. Of course, such transitions will also occur outside the uniformity regime. This is illustrated by Fig. 16, borrowed from [74] (cf. also [35]). Such phase transitions will occur, e.g., inside "white-dwarf" stars, and are manifested in the form of discontinuities in the density distribution, and in the appearance of singularities on the mass-radius curve. Moreover, as was noted by A. S. Kompaneets, the latent heat of the phase transition could turn out to be an appreciable factor in the evolution of stars.

To conclude this section we shall touch briefly upon one further extremal factor—a high-intensity external magnetic field, confining ourselves to treating its influence on the structure of a many-electron atom (cf. [75-78]). In a strong field³¹⁾ $H \gg Z^{4/3}$, all the electrons occupy the lowest Landau level and have spin opposite in direction to the external field. So long as $Z^3 \gg H \gg Z^{4/3}$, the atom remains spherically symmetric, but its radius decreases like $Z^{1/5} H^{-2/5}$ with increase of the field. At still higher fields $H \gg Z^3$, the atom is elongated in the direction of the field, and it becomes favorable for the system of atoms to form a distinctive polymeric structure.

Being interested in this problem from the point of view of the TFM, we should consider lower field values $1 \ll H \ll Z^{4/3}$, for which the semi-classicality condition is fulfilled with respect to the field: $r_H p_F \gg 1$, where $r_H = p_F / H$ is the Larmor radius. Under these conditions the action of the field reduces to flipping the elec-

³⁰⁾Cf. also [91].

³¹⁾The field is measured in units $m^2 e^3 c / \hbar^3 = 10^9$ gauss.

tron spins, and we are dealing with the atomic analog of Pauli paramagnetism. The electron-density distribution is now characterized by two functions: $n_+ = [-2(U + H)]^{3/2}/6\pi^2$ for $r < r_+$ and $n_+ = 0$ for $r > r_+$ ($U(r_+) + H = 0$) for a spin parallel to the field, and $n_- = (-2U)^{3/2}/6\pi^2$ for a spin antiparallel to the field. The actual potential U is determined by the Thomas-Fermi equation

$$\Delta U = -4\pi(n_+ + n_-).$$

Referring to^[75] for the details, we point out that the total spin S of the atom increases with the field in accordance with the law $S = Zf(HZ^{-4/3})$, where f is a certain universal function. The effects considered are important in the conditions obtaining on the surface of a pulsar^[79].

15. The density-functional method

The expression (cf. (1.7) for the energy in the TFM at $T = 0$ can be represented in the form of an explicit density functional

$$E\{n\} = E_k\{n\} + E_e\{n\} + E_i\{n\}, \quad (15.1)$$

$$E_k\{n\} \sim \int dx n^{5/3}(x). \quad (15.2)$$

The minimum of the functional $E - \mu \int dx n$ with respect to n leads to the Thomas-Fermi equation and determines the ground-state energy of the system and the corresponding density distribution.

As is easily seen, when we go beyond the framework of the TFM and take into account the corresponding corrections we continue to deal with the functional (15.1) (cf. (4.11), (6.6a)) but the form of the functional (15.2) becomes more complicated. In particular, allowance for quantum effects leads to the result that, in place of a quasi-uniform functional, we obtain a functional depending on derivatives of n . It is not surprising, therefore, that the following statement is valid: in the exact formulation of the many-body problem (the many-particle Schrödinger equation), the energy of the system is expressed in the form of the functional (15.1) with a unique universal functional E_k of a general form, and the minimum of the functional $E - \mu \int dx n$ gives the energy and density-distribution in the ground state of the system. This statement was substantiated by perturbation theory by March and Murray^[80] and proved as a rigorous theorem by Hohenberg and Kohn^[81].³² In effect, we have already used it in Appendix 2.

On this statement is based a new method, called the density-functional method, for treating a number of problems in the theory of solids. With its help, problems in the theory of surface phenomena^[82,83,100], the theory of magnetic phenomena^[84], and many others, have been solved successfully. The range of application of the method is so wide and varied that to give an account of it would require a special review article. Therefore, we shall confine ourselves below to a few general remarks.

Decisive for the success of the density-functional method is the possibility of choosing a sufficiently valid and, at the same time, not too complicated expression for $E_k\{n\}$. In practice, the following variants are used:

a) The quasi-uniform expression

$$E_k\{n\} = E_k^0\{n\} + \delta E_{\text{exch}}\{n\} + \delta E_{\text{cor}}\{n\}, \quad (15.3)$$

where E_k^0 is the quantity (15.2), δE_{exch} is the exchange correction (4.11) and δE_{cor} is the correlation correction. The problem of calculating this is extremely complicated (cf. Sec. 5), and is bypassed by considering, for want of anything better, the quasi-uniform generalization of the Gell-Mann-Brueckner expression or of more complicated interpolation expressions^[29,88,89]. If we omit the correlation energy, the expression (15.3) corresponds to the Thomas-Fermi-Dirac model (cf. Sec. 2).

b) An expression including the density gradient:

$$E_k\{n\} = E_k^0 + \delta E_{\text{exch}} + \delta E_{\text{cor}} + \frac{1}{72} \int dx \frac{(\nabla n)^2}{n}, \quad (15.4)$$

where the last term corresponds to the quantum correction (6.6a). If we omit the correlation energy, we arrive at the quantum-statistical model (cf. Sec. 11). The expression (15.4) gives appreciably better results than (15.3), e.g., in the problem of the work function of electrons in a metal.

c) An expression describing small changes of density:

$$E_k\{n\} = E_k\{n_0\} + \int dx dx' K(x - x') \delta n(x) \delta n(x'), \quad (15.5)$$

where $\delta n = n - n_0$, $E_k\{n_0\}$ is the functional (15.3) for a constant argument n_0 , and the Fourier component of the kernel is $K(q) = (2\pi/q^2)[\epsilon(0, q) - 1]^{-1}$, where $\epsilon(\omega, q)$ is the dielectric permittivity of the system. This expression is valid if the density changes themselves are small, without restrictions on their rate of change in space^[81,89].

Summarizing, it must be said that, by its nature, the density-functional method, being equivalent to an exact solution of the many-body problem, is much broader than the TFM. However, the practical realization of this method is not essentially different from the TFM with the appropriate corrections treated on an equal footing with the zeroth term (Sec. 11). Only if other functionals (besides the variant (c)) differing essentially from the TFM appear in the future will be fully justified in speaking of the density-functional method as an independent method in many-body theory.

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APPENDIX

1. FERMI-DIRAC FUNCTIONS

From the definition of the Fermi-Dirac functions

$$I_n(x) = \int_0^\infty dy \frac{y^n}{\exp(y-x)+1}$$

it follows that they increase monotonically with increasing argument, have the asymptotic forms

$$x^{n+1}/(n+1) \quad (x \rightarrow \infty), \quad \Gamma(n+1) e^x \quad (x \rightarrow -\infty)$$

and satisfy the recurrence relation $I_n' = nI_{n-1}$. For tables of these functions for integer and half-integer n , see in^[90].

³²This proof has been generalized to the case $T \neq 0$ [85], to systems with uncompensated spin [84,86,87], to relativistic systems [87], etc.

2. CORRECTIONS TO THE THOMAS-FERMI MODEL

To derive (4.2) we take into account that the argument p_F^2 in the first term of (4.1) itself contains a correction δp_F^2 associated with n' . Therefore, the total change in density is equal to $\delta n = n' + \delta p_F^2 \kappa^2 / 8\pi$, in which, according to (1.3),

$$\frac{\delta p_F^2(x)}{2} = \delta\mu - \int dx' \frac{\delta n(x')}{|x-x'|}.$$

From this, (4.2), and also (4.3), follow. The solution of (4.2) should then have no singularities of the type $1/r$, either at finite x or at infinity.

The derivation of (4.4) (for particular cases of this relation, see in^[5,35]) is based on the condition $\delta F / \delta n = \mu$ for the minimum of the quantity $F - \mu \int dx n$. The functional $\Psi = F - E_e - E_i$ (cf. (1.7)) serves as the potential with respect to $p_F^2/2 \equiv \eta$: $\delta \Psi / \delta n = \eta$. Changing to the new argument η , we arrive at the functional

$$\Phi = \Psi - \int dx n \eta = F - \mu \int dx n + E_i,$$

which serves as the potential with respect to n : $\delta \Phi / \delta \eta = -n$. Analogously, (4.1) can be written as $\Phi \rightarrow \Phi + \Phi'$, with $\delta \Phi' / \delta \eta = -n'$. Considering a total variation of Φ , it is easy to see that $\Phi' = \delta F$. Therefore, $\delta(\delta F) / \delta \eta = -n'$. Understanding by $\delta \eta$ the variation of the chemical potential, and integrating over it, we arrive at (4.4).

3. CALCULATION OF THE EXCHANGE INTEGRAL

The integral

$$C = 4\pi \int d^3 p d^3 p' \frac{f(x, p) f(x, p')}{|p-p'|^2}$$

after integration over the angles is brought to the form $T^2 \kappa(\lambda) / 2\pi^3$, where

$$\kappa = \int_0^\infty \frac{dx}{\exp(x-\lambda)+1} \ln \left| \frac{\sqrt{x} + \sqrt{y}}{\sqrt{x} - \sqrt{y}} \right|;$$

making the replacement $x, y \rightarrow x + \lambda, y + \lambda$ and differentiating with respect to λ , we have $\kappa' = (I_{-1/2})^2$. From this, expression (4.7) is obtained.

4. CORRELATIONS IN A CLASSICAL COULOMB GAS

For the calculation we use the Bogolyubov method, leading to a system of coupled equations for the distribution functions:

$$\begin{aligned} & [V_i - \nabla \lambda(x_i)] f_n(x_1, \dots, x_n) \\ & + \frac{n}{T} \int dx_{n+1} \nabla \frac{1}{|x_i - x_{n+1}|} [f_{n+1}(x_1, \dots, x_{n+1}) - f_1(x_{n+1}) f_n(x_1, \dots, x_n)] \\ & = -\frac{1}{T} \sum_{j=1}^n \nabla \frac{1}{|x_i - x_j|} f_n(x_1, \dots, x_n). \end{aligned}$$

Their right-hand sides can be regarded as a perturbation. Substitution of (5.1) leads to an equation for the correlator:

$$\nabla v(x, x') + \frac{n}{T} \int dx'' \nabla \frac{1}{|x-x''|} f_1(x'') v(x', x'') = -\frac{1}{T} \nabla \frac{1}{|x-x'|}, \quad (*)$$

which is easily reduced to (5.3). On the other hand, putting $f_1 = (n(x)/n)(1 + \varphi)$, we find for φ the equation

$$\nabla \varphi(x) = -\frac{1}{T} \int dx'' \nabla \frac{1}{|x-x''|} n(x'') v(x, x').$$

Comparing this with the equation (*) gives

$$\nabla \varphi(x) = \lim_{x' \rightarrow x} \nabla \left(v(x, x') + \frac{1}{T|x-x'|} \right).$$

But for small $|x - x'|$ the solution of Eq. (5.3) has the form

$$v(x, x') \approx -\frac{1}{T|x-x'|} \exp \left[-|x-x'| \kappa \left(\frac{x+x'}{2} \right) \right],$$

whence $\varphi = \kappa / 2T$. Using (5.2), from this it is easy to arrive at (5.4). We also point out the relation

$$\delta p_F^2(x) = 2T \int dx' v(x, x') n'(x'),$$

which follows from comparison of (5.3) and (4.2).

5. SHELL EFFECTS

a) One-dimensional case

The expression (3.3) has (when higher-order effects are neglected) the following expanded form:

$$n = 2 \sum_{n=0}^N Q_n / (p n^0), \text{ where}$$

$$Q_n = 1 + \sin(2S_n) - \frac{1}{\tau_0} \int_{R'}^R \frac{dx}{p_n(x)} \sin(2S_n(x)).$$

The terms Q_n correspond directly to the terms of the right-hand side of (7.1), and the property (7.2) is directly discernible.

We use the Poisson summation formula

$$\sum_a^b f(n) = \sum_{k=-\infty}^{\infty} \int_{a-\epsilon'}^{b+\epsilon'} dn f(n) \cos(2\pi kn),$$

where $0 < \epsilon, \epsilon' < 1$.³³⁾ We proceed to the energy integration, taking into account the formula $\partial E / \partial n = \pi / \tau_0$, which follows from the quantization rule extended to noninteger n . Hence,

$$n(x) = \frac{2}{\pi} \sum_{k=-\infty}^{\infty} (-1)^k \int_{E_0}^x \frac{dE}{p_E(x)} Q_E(x) \cos(2kS_0E).$$

We consider first the contribution of the first term of Q . In the sum the $k = 0$ term, which corresponds simply to replacement of the sum by an integral, is of the form $2p_F / \pi$ and coincides exactly with the TFM result. Correspondingly, the terms with $k \neq 0$ give n'_i . Integrating by parts and keeping the integrated term at the upper limit (which is the leading term in the parameter ξ), we have

$$n'_i = \frac{2}{\pi p_F \tau_0} \sum_{k=1}^{\infty} \frac{(-1)^k}{k} \sin(2kS_0),$$

which leads directly to (7.3). Analogously, the second term of Q gives

$$n'_i = -\frac{1}{\pi p_F} \sum_{k=1}^{\infty} \frac{(-1)^k}{\tau + k\tau_0} \cos(2S + 2kS_0),$$

whence (7.4) is obtained.

b) Three-dimensional case

We start from the expression

$$n = \frac{1}{2\pi r^2} \sum_{nr, l} \frac{(2l+1)}{p_{\nu} \tau_{0\nu}} Q_{\nu},$$

where Q has the same structure as in the one-dimensional case, $\nu = (n_r, l)$ and $p_{\nu} = \sqrt{2(E_{\nu} - U) - [(l + 1/2)]^2 / r^2}$. Using the quantization rule $S_{0\nu} = \pi(n_r + 1/2)$, we have

³³⁾The Poisson formula follows from the relation $\sum_{n=-\infty}^{\infty} \delta(n-m) = \sum_{k=-\infty}^{\infty} \cos(2\pi km)$. The quantity ϵ is chosen from the condition $S_0 = \pi(N + \epsilon - 1/2)$, and the quantity ϵ' is put equal to $1/2$. Then the energy E_0 can be identified with the minimum of the potential U , inasmuch as E_0 corresponds to the condition $S_0 E_0 = 0$, or $p_{E_0} = 0$.

$$n = \frac{1}{2\pi^2 r^2} \sum_{k, s=-\infty}^{\infty} (-1)^{k+s} \int_0^{\lambda_{\text{max}}} d\lambda^2 \int_{E_0}^{\mu} \frac{dE}{pE} Q_E \cos(2kS_{0E} - 2\pi s\lambda),$$

where $\lambda = l + 1/2$. When the Poisson formula is applied to the summation over l the quantity ϵ is chosen from the condition $S(l_{\text{max}} + \epsilon) = 0$ (l_{max} is the largest possible angular momentum), and $\epsilon' = 1/2$.

The first term of Q for $k = s = 0$ gives the TFM result

$$\frac{1}{2\pi^2 r^2} \int_0^{\lambda_{\text{max}}} d\lambda^2 \int_{E_0}^{\mu} \frac{dE}{pE} = \frac{p_F^3}{3\pi^2},$$

and for the other values of k and s (and for the second term of Q) the answer depends on the behavior of the potential for small r . For an attractive Coulomb field we have, for small λ ,

$$S_0(\lambda) = S_0(0) + \pi\lambda - \frac{\lambda^2 \delta}{2} + \dots, \quad S_0(0) = \int_0^{R'} dr p_F.$$

The main contribution to n'_1 is given by the term with $k = s$, for which the terms linear in λ in the argument of the cosine vanish. Integrating by parts and keeping the integrated terms at $E = \mu$ and $\lambda = 0$, we obtain

$$n'_1 = -\frac{1}{2\pi^2 r^2 p_F \tau_0 \delta_0} \sum_{k=1}^{\infty} \frac{\cos(2kS_0(0))}{k^2}.$$

From this it is not difficult to arrive at the formula (7.6). Proceeding analogously with the second term of Q , and keeping the term with $k = 0$, $s = 1$ as $\tau_0 \rightarrow \infty$, we obtain the expression (7.7).

We note that, by changing to an integral only for the sum over n_r , it is easy to find the partial density $n_1(r)$ with a given value of 1 . If μ coincides with the boundary of the continuous spectrum ($\tau_0 \rightarrow \infty$), then

$$n_1 = \frac{2l+1}{2\pi r^2} \left(p_F - \frac{1}{2p_F \tau} \cos 2S \right).$$

6. TEMPERATURE SMOOTHING OF THE DENSITY OSCILLATIONS

The relation (8.5) can be written in the form

$$n'(T, \mu) = I(k) n'(0, \mu), \quad I(k) = ik \int_{-\infty}^{\infty} \frac{dx e^{ikx}}{e^x + 1},$$

where $k = -iT\partial/\partial\mu$. The integral I is found to be equal to

$$I(k) = 1 - 2k \int_0^{\infty} \frac{dx \sin(kx)}{e^x + 1} = \frac{\pi k}{\text{sh}(\pi k)}.$$

Taking derivatives only of the rapidly varying sine in the differentiation of (7.7), we have $k^2 = 4T^2 T^2$. This then leads to the formula (8.6).

7. CALCULATION OF THE POLARIZATION OPERATOR

The classical kinetic equation for $T = 0$ has the form

$$\left(\frac{\partial}{\partial t} + \mathbf{p}\nabla - \nabla U \nabla_{\mathbf{p}} \right) \delta f(\mathbf{x}, \mathbf{p}, t) = \nabla_{\mathbf{p}} f \nabla \delta U,$$

where f is the unperturbed distribution function (1.5) and δf is its variation, with

$$\delta n(\mathbf{x})_{\omega} = 2 \int d^3 p \delta f(\mathbf{x}, \mathbf{p}, \omega), \quad (*)$$

In the Lagrangian picture the initial equation has the form

$$\frac{d}{dt'} \delta f(\mathbf{x}(t'-t), \mathbf{p}(t'-t), t') = A(\mathbf{x}(t'-t), \mathbf{p}(t'-t), t'),$$

where $\mathbf{p}(t) = \dot{\mathbf{x}}(t)$, $\mathbf{x}(0) = \mathbf{x}$, $\mathbf{p}(0) = \mathbf{p}$, and the right-hand side of the equation is denoted by A . Hence, taking the causality principle into account,

$$\delta f(\mathbf{x}, \mathbf{p}, t) = \int_{-\infty}^0 dt' A(\mathbf{x}(t'), \mathbf{p}(t'), t+t').$$

The right-hand side of this equality can be represented in the form

$$-2\delta(p_F^2(\mathbf{x}) - p^2) \int dx' \int_{-\infty}^0 dt' \frac{d}{dt'} [\delta(\mathbf{x}(t') - \mathbf{x}') \delta U(\mathbf{x}', t+t')]$$

when the relations $p_F^2(\mathbf{x}(t)) - p^2(t) = p_F^2(\mathbf{x}) - p^2$ and $(\mathbf{p}(t) \cdot \nabla) F(\mathbf{x}(t)) = \dot{\mathbf{F}}$ are taken into account. Substitution of the expressions obtained into the equation (*) and comparison with (9.6a) indeed lead to (9.11) and (9.12). For $T \neq 0$, using (1.8) it is not difficult to arrive at the relation (10.4).

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