REVIEWS OF TOPICAL PROBLEMS

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Semiclassical model of the structure of matter

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Abstract. The modern semiclassical method developed over the past few decades and used for describing the properties of the electronic subsystems of matter is reviewed, and its application to quantum physics problems is illustrated. The method involves the Thomas – Fermi statistical model and allows an extension by including additive corrections that take the shell structure of the electronic spectrum and other physical effects into account. Applying the method to the study of matter and finite systems allowed the following, inter alia: (1) an analysis of the total electron energy oscillations as a function of the number of particles in a 1D quantum dot; (2) a description of spatial oscillations of the electron of the stepwise temperature dependence of

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Received 27 May 2011, revised 15 July 2011 Uspekhi Fizicheskikh Nauk **182** (5) 457–494 (2012) DOI: 10.3367/UFNr.0182.201205a.0457 Translated by M Sapozhnikov; edited by A M Semikhatov the ionicity and ionization energy in a Boltzmann plasma; (4) an evaluation of free ion ionization potentials; (5) an interpretation and evaluation of the difference in the patterns of oscillations in the mass spectra of metal clusters.

To the memory of David Abramovich Kirzhnits

1. Introduction

More than 35 years have elapsed since the publication of review [1] describing the application of the semiclassical method based on the statistical Thomas–Fermi (TF) model for calculating the characteristics of many-electron systems. This method has been improved since then, and its field of applications has been extended, in particular, to include nanoobjects. Finite systems like clusters, quantum dots, nanoconductors, fullerenes, and similar electron–ion complexes are convenient for semiclassical physical studies because they contain a sufficiently large number of particles and reveal quantum properties.

The aim of this review is to present the modern semiclassical method and a number of problems solved using this method. A semiclassical method for describing the local and integral characteristics of atoms and ions, metal clusters, and quantum dots is considered, the efficiency of the method for calculating the equation of state of plasma is demonstrated, and a qualitative and quantitative semiclassical analysis of results obtained by more complicated quantum mechanical methods is performed.

The review content does not overlap, in fact, with that of well-known monograph [2], in which a somewhat different approach was used and the problems of nuclear and mesoscopic physics were mainly addressed.

The density functional method [3] in the Kohn–Sham representation, being the most efficient method for studying the properties of a system of interacting fermions in an external field, requires the solution of Hartree-type equations for the wave functions and the spectrum of quasiparticle states. As the number N_e of particles in the system increases, the difficulties encountered in solving this problem considerably increase, whereas the conditions of applicability of the TF model improve. This model, as was already shown by Dirac [4], corresponds to the leading term in the expansion of the characteristics of the system in the semiclassical behavior parameter

$$\xi = \frac{1}{2\pi} \left| \frac{d\lambda}{d\mathbf{r}} \right| = \hbar \left| \frac{\nabla \mathbf{p}}{p^2} \right| \ll 1.$$
(1.1)

Here, $\lambda(\mathbf{r})$ is the particle wavelength, $\mathbf{p}(\mathbf{r})$ is the characteristic momentum of the particle, and \mathbf{r} is its radius vector. In the one-dimensional case, the semiclassical behavior parameter is inversely proportional to the number of particles ($\xi \propto N_e^{-1}$); in the two-dimensional case, it is inversely proportional to the square root of the number of particles ($\xi \propto N_e^{-1/2}$), and in the three-dimensional case, to the cubic root ($\xi \propto N_e^{-1/3}$). Hence, the larger the number of particles in the system is, the more justified the use of the semiclassical approximation, i.e., the smaller the corrections to the TF model characterizing the difference between its results and quantum mechanical results.

The TF model was initially proposed to describe a manyelectron system at zero [5, 6] and finite [7] temperatures, assuming the local validity of expressions for the ideal gas of fermions in an external field. In this case, the Poisson equation with the corresponding boundary conditions closes the ideal-gas relation between the density n_e and potential V:

$$\Delta V(\mathbf{r}) = 4\pi n_{\rm e}(\mathbf{r}), \ n_{\rm e}(\mathbf{r}) = \frac{\sqrt{2}}{\pi^2} \ T^{3/2} I_{1/2} \left(\frac{\mu - V(\mathbf{r})}{T}\right), \ (1.2)$$

leading to the TF equation for the self-consistent potential $V(\mathbf{r})$. Here, $I_{1/2}(x)$ is the Fermi–Dirac function (see Appendix A), μ is the chemical potential, and T is the temperature. This model allows calculating various characteristics of free atoms and ions [8–18]; it is widely used in problems of the physics of matter at high energy densities and in problems of solid-state (see, e.g., [19–21]), nuclear, and molecular physics.

The TF model is very simple and physically transparent; however, it neglects many important physical effects: correlation (corr), exchange (ex), gradient (qu), shell (sh), and oscillation (osc). The presence of a small parameter ξ in a many-particle system ($N_e \ge 1$) allows a physically reasonable improvement of the model by adding independent corrections caused by the effects listed above, which leads to the expression

$$n_{\rm e} \simeq n_{\rm TF} + \delta n_{\rm corr} + \delta n_{\rm ex} + \delta n_{\rm qu} + \delta n_{\rm sh} + \delta n_{\rm osc} \tag{1.3}$$

for the number density of particles in the semiclassical approximation.

Another important expression derived in [1] gives a relation between small corrections to the density and the free energy of a system of particles: ¹

$$\Delta F = -\int_{-\infty}^{\mu_{\rm TF}} \mathrm{d}\mu' \int \delta n_{\rm e}(\mathbf{r},\mu';T) \,\mathrm{d}\mathbf{r} \,. \tag{1.4}$$

Thus, calculations in the consistent semiclassical approximation are reduced to the determination of corrections to the density in the right-hand side of (1.3). Based on the TF model, with the expression for the density correction caused by one effect or another and using expression (1.4), we can construct the semiclassical thermodynamics of a system of fermions, taking all important physical effects into account. In many cases, semiclassical results obtained by this method are virtually identical to the results obtained with the help of more complicated models and provide a clear interpretation of the observed dependences. The efficiency of the semiclassical approach for solving problems in quantum physics is demonstrated in this review.

Correlation effects are not a subject of our special investigation. We note, however, that the semiclassical study [24] of nonlocality sources showed that the use of the local density approximation for the correlation correction can be substantiated at zero temperature only for high densities, and this approximation is certainly inapplicable at high temperatures. In practice, the dependence of the correlation energy on the density in inhomogeneous systems is obtained by approximating the results of numerical calculations, these dependences being different in different ranges of parameters (see, e.g., [25–33]).

Exchange effects describe the influence of the Pauli principle on the interaction of particles. They reduce the Coulomb repulsion and do not violate the concept of the independence of particles, which is inherent in the self-consistent field approximation. The corresponding free-energy correction can be written in form (1.4),

$$\Delta F_{\rm ex} = -\pi \int_{-\infty}^{\mu} d\mu' \int d\mathbf{r} \left(\frac{\partial n_{\rm e}}{\partial \mu'}\right)^2. \tag{1.5}$$

Hereafter, $\mu = \mu_{\text{TF}}$. The lower, second-order quantum gradient correction

$$\Delta F_{\rm qu} = -\frac{\pi}{6} \int n_{\rm e} \, \frac{\partial n_{\rm e}}{\partial \mu} \, \mathrm{d}\mathbf{r} \tag{1.6}$$

has the same order of smallness in the semiclassical behavior parameter as the exchange correction has [34]. Their combined contribution is taken into account in the TF model with quantum and exchange corrections (TFCs) [1, 35–37], which is widely used in the physics of matter with high energy densities [38]. The disadvantages of the TFC model, such as its inconsistency with the perturbation theory in the high-compression and high-temperature limits and the divergence of gradient corrections to energies at the localization sites of nuclei, can be eliminated by accurately taking the vicinity of nuclei into account [39–43]. This leads to a modified form of the known Scott correction [44–47].

We recall that semiclassical physics involves the characteristics of the classical motion of a particle in the correspond-

¹ It is shown in the density functional theory [22, 23] (see Section 5.2) that this relation has a more general character.

ing potential. In particular, the semiclassical Green's function $G(\mathbf{r}, \mathbf{r}', \varepsilon)$, which is equal to the distribution function of particles in the phase space at coinciding points, is the sum of the contributions of possible trajectories of the classical motion of a particle with energy ε between points \mathbf{r} and \mathbf{r}' . The leading contribution, the Thomas–Fermi term, is given by the shortest trajectory connecting points \mathbf{r} and \mathbf{r}' [1, 48]. Trajectories with reflection from turning points with an incomplete cycle are responsible for spatial density oscillations—oscillation (interference) effects, while completely cyclic closed trajectories are responsible for shell effects (due to the discreteness of the spectrum of bound states).

The shell structure of one-particle spectra of atoms and ions is manifested, for example, in the nonmonotonic dependence of the properties of elements on the atomic number in the periodic table, in oscillations in the radial electron density distribution in atoms, and in stepwise temperature dependences of the ionization degree and ionization energy of plasma. Traditional statistical models give regular monotonic functions of the parameters, reflecting only their average behavior. This disadvantage of the statistical approach seemed insurmountable, and it was asserted repeatedly in the literature that these irregularities can be described only in the framework of an exact quantum mechanical treatment.

However, it was already shown in [48, 49] (see also [1]) that the shell and oscillation effects can be described by separating the leading terms in the semiclassical behavior parameter in the derived nonanalytic dependences of physical quantities. The development of this idea for studying shell effects in the thermodynamics of matter with high energy concentration resulted in the generalization of the theory of shell effects to the case of finite temperatures. The dependence of the shell correction on the compression ratio of matter was also considered in [50–53] and, in particular, the prediction in [49] (see also [1]) of the increasing role of shell effects during cold compression, which attracted great interest at that time, was explained theoretically.

Shell effects have been considered by different methods in a number of papers [12, 13, 54, 55] for free atoms.

The theory of oscillation effects and a semiclassical description of the spatial distribution of the electron density in electron–ion systems was developed in [56–58] based on the principles proposed in [48].

The semiclassical studies of many-electron systems are often performed in the central symmetry approximation, which amounts to considering matter in the Wigner-Seitz spherical cell approximation [59], free atoms and ions, and spherical clusters and nuclei. It turns out that the central selfconsistent attraction potential V(r) in these systems can belong to one of two types: (i) the cluster (nuclear) potential finite at the center or (ii) the atomic (ion) potential having a Coulomb singularity at the center. The description of the gradient, shell, and oscillation effects essentially depends on the type of the potential in the problem under study. Notably, the application of the semiclassical approximation to problems with a Coulomb singularity involves additional difficulties due to violation of the semiclassical behavior at the system center [39-43]. Also, considerable differences exist in the shape of one-particle spectra [60] and possible classical mechanical trajectories [61, 62].

Semiclassical methods, as pointed out above, have been also successfully used to describe the properties of finite systems [63]: nuclei, clusters, nanoconductors, and quantum dots. Of great interest are atomic (in particular, metal) clusters representing complexes containing from a few to several tens of thousands atoms [64, 65]. The study of such clusters allows investigating the evolution of matter in passing from atomic scales to the solid-state scale. Shell effects in nuclei and clusters and their relation to classical periodic trajectories were studied, for example, in [58, 61–70].

One of the problems of the physics of atomic clusters is how to explain oscillations observed in experimental mass spectra: the dependence of the number of *N*-atomic clusters on *N*. More specifically, it is known that the characteristic feature of the mass spectrum of sodium clusters is the existence of 'magic' numbers: the number of clusters with such numbers noticeably exceeds the number of neighboring clusters. As *N* increases, the amplitudes of these deviations decrease, then they increase again, and so on, i.e., oscillations with beats occur. These effects decay with increasing the temperature. The mass spectra of metal aluminum clusters look quite different. These differences have been described quantitatively and explained by semiclassical methods [23, 61, 62].

We note that along with the consistent semiclassical additive approach in (1.3) and (1.4), another semiclassical model, the so-called extended TF (ETF) model, is used in the literature. In this model, for example, the kinetic energy K[n] in the energy functional at zero temperature,

$$E[n] = K[n] + \int \left[V_{\text{ext}}(\mathbf{r}) + \frac{1}{2} V_{\text{int}}(\mathbf{r}) \right] n(\mathbf{r}) \, \mathrm{d}\mathbf{r} + E_{\text{xc}}[n], \quad (1.7)$$
$$\int n(\mathbf{r}) \, \mathrm{d}\mathbf{r} = N_{\text{e}}, \quad (1.8)$$

for a system of $N_{\rm e}$ electrons with the interaction potential $V_{\rm int}(\mathbf{r})$ in the external field $V_{\rm ext}(\mathbf{r})$ is described by an expression that in addition to the ideal-gas term includes the lower, second-order gradient correction, and sometimes the next, fourth-order correction. In this case, the exchange and correlation (xc) terms can also be included in the total energy functional. An extremum of the functional then gives the equation for the density in which gradient, exchange, and correlation corrections are self-consistently taken into account.

Although the ETF model cannot be substantiated theoretically, it describes the density distribution better than the TF model does, and is widely used for calculating the smooth, averaged behavior of various characteristics of fermion systems in nuclear physics [71] and the physics of metal clusters [66], as well as for describing the properties of compressed [72] and heated [25] matter. Shell and oscillation effects are neglected in this model.

The review has the following structure:

In Section 2, a consistent semiclassical method [58] with the use of additive corrections (1.3) and (1.4) is demonstrated with the example of describing the properties of a one-dimensional quantum dot.

In Section 3, different semiclassical models are used for calculating averaged local and integral characteristics of free atoms and ions, and bulk and hollow atomic clusters.

In Section 4, the features of one-particle spectra are analyzed for the two types of central potentials typical for atom–ion and nuclear–cluster systems. A semiclassical method is proposed for describing spatial density oscillations in these two systems.

In Section 5, the use of the TF model and different corrections to it for calculating the equation of state for the

electron component of the Boltzmann plasma is discussed and the form of gradient corrections in systems of different dimensions is considered.

In Section 6, the semiclassical model of the equation of state taking shell effects into account is generalized to the case of degenerate matter, and a self-similar wide-range equation of state for the electron component of matter with high energy density is proposed.

Section 7 is devoted to the semiclassical description of shell effects in characteristics of metal clusters.

In what follows, unless stated otherwise, atomic units are used: $\hbar = m_e = e = 1$, mass $[m] = 9.11 \times 10^{-28}$ g, length $[L] = a_0 = 5.29 \times 10^{-9}$ cm, density $[n] = 6.75 \times 10^{24}$ cm⁻³, mass density $[\rho] = 11.2$ g cm⁻³, pressure [P] = 294.18 Mbar, energy and temperature [E] = [T] = 27.21 eV.

2. Semiclassical model of a one-dimensional quantum dot

In this section, the application of the semiclassical additive correction method is demonstrated in a simple one-dimensional case. Expressions for gradient, shell, and oscillation corrections to the density and energy are obtained using an expansion in the semiclassical behavior parameter, and it is also shown that the TF model with these corrections not only gives the results coinciding with those obtained by the more complicated and time-consuming density functional method but also allows separating the contribution from each physical effect and analyzing its dependence on the parameters of the problem.

The one-dimensional example is taken from [73]. A system of charged particles (one-dimensional quantum dot) is considered. The motion of particles is restricted from two sides along the x axis by an external confining potential $V_{\text{ext}}(x)$ and is homogeneous in transverse directions y and z.

A physical example of such a system in a rough approximation is the system of mobile electrons in graphene, where the free motion of electrons is possible only in two dimensions, while motion in the perpendicular direction is quantized [74–76].

In [73], a one-dimensional quantum dot is described by three different methods: the Thomas–Fermi, Strutinsky [2, 77], and density functional method in the Kohn–Sham approximation. The method for calculating corrections to the local and integral characteristics of this system in the TF model (see Sections 2.2 and 2.3) and a comparison with the results of the density functional method (Section 2.4) are considered in more detail in our paper [58].

2.1 One-dimensional quantum dot

in the Thomas–Fermi model

The distribution function in the phase space in the onedimensional TF model has the form $f(x,p) = \theta(p_{\mu}^2(x) - p^2)$. Its integration over p (followed by division by the volume 2π of one state) gives the relation between the density and Fermi momentum $n_{\rm e}(x) = p_{\mu}(x)/\pi$, neglecting the spin. Here, $p_{\mu}(x) = \sqrt{2(\mu - V(x))}$, $V(x) = V_{\rm int}(x) + V_{\rm ext}(x)$ is the selfconsistent potential, $V_{\rm int}(x)$ is the interaction potential of particles, satisfying the Poisson equation $V''_{\rm int}(x) = -4\pi e^2 n_{\rm e}(x)$, the Fermi energy μ is determined from the condition of normalization to the number of particles $N_{\rm e}$, and the interaction parameter e used in Section 2 is measured in electron charge units. It then follows that the electron density distribution $n_{\rm e}(x)$ satisfies the equation [73]

$$\frac{\pi^2}{2} \left[n_{\rm e}^2(x) \right]'' - 4\pi e^2 n_{\rm e}(x) + V_{\rm ext}''(x) = 0 \,. \tag{2.1}$$

The kinetic energy density in the same approximation is determined by the integral of $(p^2/2)f(x,p)$ over the momentum p, and the total electron energy is

$$E_{\rm TF} = \int_{-\infty}^{\infty} n_{\rm e}(x) \left[\frac{\pi^2 n_{\rm e}^2(x)}{6} + V_{\rm ext}(x) + \frac{1}{2} V_{\rm int}(x) \right] \mathrm{d}x \,.$$
(2.2)

The authors of [73] studied a particular system with the confining potential $V_{\text{ext}}(x) = gx^4$ (assuming in calculations that g = 0.5) and boundary conditions $n'_{\text{e}}(0) = 0$, $n_{\text{e}}(x = \pm \infty) = 0$. It can be shown that Eqn (2.1) with such a biquadratic potential has a similarity property with respect to the number of electrons N_{e} [58]:

$$x_{N_{e}} = x_{1} N_{e}^{1/3}, \quad n_{e}^{(N_{e})}(x_{N_{e}}) = n_{e}^{(1)}(x_{1}) N_{e}^{2/3},$$

$$\mu_{N_{e}} = \mu_{1} N_{e}^{4/3}, \quad E_{N_{e}} = E_{1} N_{e}^{7/3}.$$
 (2.3)

It follows from the solution of TF equation (2.1) with $N_e = 1$ and e = 1 that the self-consistent potential V(x) has the form of a symmetric double well separated by a barrier, the Fermi energy μ being located near the 'hump' of this barrier (Fig. 1). In the conduction theory of a quantum dot [78], a change in the total electron energy under the addition of one electron to the system, i.e., the chemical potential, and also the derivative of this quantity with respect to the number of particles, play an important role. At zero temperature, the chemical potential coincides with the Fermi energy μ , and similarity property (2.3) allows performing the corresponding differentiation analytically:

$$\mu_{N_{\rm e}} = \frac{\partial E_{N_{\rm e}}}{\partial N_{\rm e}} = \frac{7}{3} E_1 N_{\rm e}^{4/3}, \quad \chi_{N_{\rm e}} = \frac{\partial \mu_{N_{\rm e}}}{\partial N_{\rm e}} = \frac{4}{3} \mu_1 N_{\rm e}^{1/3}. \quad (2.4)$$

Relations (2.3) and (2.4) give the corresponding dependences for the total electron energy *E* and χ in the TF model: $E_1 = 3\mu_1/7, \chi_1 = 4\mu_1/3.$



Figure 1. Self-consistent potential V(x) = V(-x) in a one-dimensional quantum dot with $V_{\text{ext}}(x) = x^4/2$. Calculation by the TF model for the charge e = 1 and the number of electrons $N_e = 1$ (solid curve). Dotted straight lines are the Fermi energy μ and the energy level ε ; $X_{\varepsilon}^{1}, X_{\varepsilon}^{r}$, and X_{μ} are the corresponding turning points.

2.2 Density corrections

To obtain corrections (1.3) to the TF density, we express the electron density in terms of one-particle wave functions as $n_e(x) = \sum_n |\psi_n(x)|^2$ (the spin is neglected, as in [73]). To determine the spectrum of one-particle energies $\varepsilon(n)$, we use the quantization condition²

$$S_{\varepsilon}^{0} = \int_{X_{\varepsilon}^{1}}^{X_{\varepsilon}^{\mathrm{r}}} \mathrm{d}x p_{\varepsilon}(x) = \hbar(\pi n + \alpha_{\varepsilon}^{1} + \alpha_{\varepsilon}^{\mathrm{r}}), \qquad (2.5)$$

while for the wave functions, we use the semiclassical approximation, taking the next terms of the expansion in the semiclassical behavior parameter into account [79, 80]. In (2.5), X_{ε}^{1} and X_{ε}^{T} are the left and right turning points and α_{ε}^{1} are phases upon reflection from these turning points, which depend on the potential behavior in their vicinity (for the linear behavior, $\alpha = \pi/4$).

Using the Poisson formula to pass from the sum to an integral,

$$\sum_{n=a}^{b} f_n = \sum_{s=-\infty}^{\infty} \int_{a-\epsilon_1}^{b+\epsilon_2} dn f(n) \cos(2\pi sn), \quad \epsilon_1, \, \epsilon_2 < 1, \quad (2.6)$$

expressing the quantum number n in terms of the action according to quantization condition (2.5), and retaining, along with the leading TF term, a few next-order terms in the semiclassical behavior parameter, we obtain

$$n_{e}(x) \equiv n(x,\mu) \simeq \frac{1}{\pi\hbar} \left\{ \int_{V(x)}^{\mu} \frac{d\varepsilon}{p_{\varepsilon}(x)} + 2\sum_{s=1}^{\infty} \int_{V(x)}^{\mu} \frac{d\varepsilon}{p_{\varepsilon}(x)} \cos\left[s\left(\frac{2S_{\varepsilon}^{0}}{\hbar} - 2\alpha^{1} - 2\alpha^{r}\right)\right] + \sum_{s=-\infty}^{\infty} \int_{V(x)}^{\mu} \frac{d\varepsilon}{p_{\varepsilon}(x)} \cos\left(\frac{2S_{\varepsilon}(x)}{\hbar} - 2\alpha^{1}\right) \\ \times \cos\left[s\left(\frac{2S_{\varepsilon}^{0}}{\hbar} - 2\alpha^{1} - 2\alpha^{r}\right)\right] - 2\hbar^{2} \int_{V(x)}^{\mu} \frac{d\varepsilon}{p_{\varepsilon}(x)} \sigma_{3}(\varepsilon, x) \right\} \\ = n_{\text{TF}}(x) + \delta n_{\text{sh}}(x) + \delta n_{\text{osc}}(x) + \delta_{2}n_{\text{qu}}(x), \qquad (2.7)$$

$$\sigma_3(\varepsilon, x) = \frac{V''}{8p_{\varepsilon}^4(x)} + \frac{5(V')^2}{16p_{\varepsilon}^6(x)} \,.$$
(2.8)

The first term in curly brackets in (2.7) is equal to the density in the TF model, the second term describes the influence of the discreteness of the electron spectrum resulting in shell effects, the third term reflects the wave properties of electrons leading to oscillation effects, and the fourth term, representing the second-order quantum gradient correction, describes the contribution due to the inhomogeneity of the potential.

Direct integration with respect to energy in the fourth term gives the gradient correction to the density [80]:

$$\delta_2 n_{\rm qu}(x) = \frac{1}{8\pi p_{\mu}^5(x)} \left[\left(V' \right)^2 + \frac{2}{3} p_{\mu}^2(x) V''(x) \right].$$
(2.9)

Using similarity property (2.3) and separating the dependence on the number of particles in (2.9),

$$\delta_2 n_{\rm qu}(x;N) = N_{\rm e}^{-4/3} \delta_2 n_{\rm qu}(x;1) \,,$$

² In (2.5), as in (2.7) below, the dependence on \hbar and, correspondingly, on the semiclassical behavior parameter ξ is manifest.

we see that the gradient correction has the second order of smallness $(\xi^2 \propto N_e^{-2})$ compared to the density in the TF model.

By integrating the third term in (2.7) by parts, we retain the leading term in the semiclassical behavior parameter outside the integral and take into account that $S^0_{\mu}/\pi\hbar = N_e$ is an integer. As a result, we obtain the oscillation correction to the density:

$$\delta n_{\rm osc}(x) \simeq -\frac{\cos\left[2S_{\mu}(x)\right]}{2p_{\mu}(x) t_{\mu}^{0} \sin\left(\pi t_{\mu}(x)/t_{\mu}^{0}\right)}, \qquad (2.10)$$

where $\mu = \mu_{\text{TF}}$, $t_{\mu}(x) = dS_{\mu}(x)/d\mu$ is the classical time of the electron motion with the energy $\varepsilon = \mu$ from the left turning point $X_{\varepsilon}^{1} = -X_{\mu}$ to the point *x*, and $t_{\mu}^{0} = t_{\mu}(X_{\mu})$, where X_{μ} is the right turning point (Fig. 1). The range of applicability of the obtained expression excludes the vicinities of the turning points.

Although the dependence of the oscillation correction on the number of particles is more complicated, it can also be calculated using similarity property (2.3). Considering the amplitude (A) and phase (ϕ) factors separately,

$$\begin{split} &\delta n_{\rm osc}(x;N_{\rm e}) = A(x;N_{\rm e})\,\cos\left[\phi(x;N_{\rm e})\right],\\ &A(x;N_{\rm e}) = A(x;1)\,N_{\rm e}^{-1/3},\;\phi(x;N_{\rm e}) = \phi(x;1)\,N_{\rm e}\,, \end{split}$$

we see that the oscillation effects have the first order of smallness in ξ compared to the result obtained in the TF model, and their contribution to the density is greater than that of gradient effects.

2.3 Quantization condition and energy corrections

To calculate the shell correction, it is necessary to have the quantization condition valid in the entire spectral region, in particular, near the hump of the barrier. This condition differs from standard Bohr–Sommerfeld expression (2.5) with $\alpha^1 = \alpha^r = \pi/4$. The correct result

$$S_{\varepsilon}^{0} = (2n+1) \pi + \gamma_{\varepsilon}^{\pm}, \ S_{\varepsilon}^{0} = S_{\varepsilon}(-X_{\varepsilon}, X_{\varepsilon}) = 2S_{\varepsilon}(0, X_{\varepsilon}),$$
(2.11)

$$\begin{split} \gamma_{\varepsilon}^{\pm} &= \frac{d_{\varepsilon}^{2}}{2} \left(1 - \ln \frac{|d_{\varepsilon}^{2}|}{2} \right) + \arg \Gamma \left(\frac{1 + \mathrm{i} d_{\varepsilon}^{2}}{2} \right) \\ &\pm \left[\frac{\pi}{4} + \arctan \left(\tanh \frac{\pi d_{\varepsilon}^{2}}{4} \right) \right], \end{split}$$

is obtained by using the known exact solution of the Schrödinger equation with a potential near the hump in the form

$$V(x) = V(0) - \frac{|V''(0)|}{2} x^2, \ V''(0) = -4\pi e^2 n(0).$$

In quantization condition (2.11), S_{ε}^{0} is the classical action for electron motion with the energy ε above the hump between the two turning points $-X_{\varepsilon}$ and $+X_{\varepsilon}$, and the quantity

$$d_{\varepsilon}^{2} = \frac{p_{\varepsilon}^{2}(0)}{\sqrt{4\pi e^{2}n(0)}}$$
(2.12)

characterizes the closeness of the energy ε to the hump of the potential V(0) ($\varepsilon = \mu$ in Fig. 1). The sign of d_{ε}^2 , which coincides with the sign of the squared momentum $p_{\varepsilon}^2(0)$, can be respectively positive or negative in the regions of classically



Figure 2. Phases γ_{μ}^{\pm}/π from quantization condition (2.11) (solid curves) and their derivatives $d\gamma_{\mu}^{\pm}/d(d^2)$ (dashed curves) as functions of parameter d^2 .

allowed or forbidden motion of the particle. Above, we considered the case of classically allowed motion, where the energy level is located above the top of the potential hump: $\varepsilon > V(0), d_{\varepsilon}^2 > 0$. In the case $\varepsilon < V(0), d_{\varepsilon}^2 < 0$, which is also shown in Fig. 1, the action in (2.11) has the form $S_{\varepsilon}^0 = 2S_{\varepsilon}(X_{\varepsilon}^1, X_{\varepsilon}^n)$.

The phases γ^{\pm} depend on the energy via the parameter d_{ϵ}^2 in (2.12) (Fig. 2). It is because of this dependence that quantization condition (2.11) continuously connects the two limit cases: a transparent barrier in which the particle moves high above the hump $(d^2 \rightarrow \infty, \gamma^{\pm}/\pi \rightarrow \pm 1/2)$ and an impenetrable barrier in which the particle is confined in one of the two lower wells $(d^2 \rightarrow -\infty, \gamma^{\pm} \rightarrow 0)$; in the latter case, a doubly degenerate level exists. The number of states in the TF model with the shell correction turns out to be a step-like function of the chemical potential

$$N(\mu) = \frac{S_{\mu}^{0}}{\pi} + \frac{1}{\pi} \sum_{s=1}^{\infty} \frac{(-1)^{s}}{s} \left\{ \sin \left[s(S_{\mu}^{0} - \gamma_{\mu}^{+}) \right] + \sin \left[s(S_{\mu}^{0} - \gamma_{\mu}^{-}) \right] \right\}.$$
(2.13)

This reflects the fact that when the chemical potential intersects an energy level, the number of states changes discretely by unity.

To study the contribution of the effects under consideration to the energy, we use expression (1.4) at zero temperature. Due to the averaging via double integration, the role of oscillation effects is negligible, and the gradient and shell terms are dominant.

The expression for the gradient correction to the energy is obtained by the direct integration of (2.9) over the energy μ' . Replacing the momentum by the density and using Thomas– Fermi equation (2.1) and similarity relations (2.3), we obtain

$$\delta_2 E_{qu}(N_e) = -\frac{1}{12} \int \left[\frac{(n')^2}{2n} + n'' \right] dx$$

= $\frac{1}{2\pi} \left[\int_0^{X_{\mu}} \frac{x^2 dx}{p_{\mu}(x)} - \frac{2}{3} e^2 X_{\mu} \right] = \delta_2 E_{qu}(1) N_e^{1/3}.$ (2.14)

The shell correction to the energy

$$\delta E_{\rm sh} = \frac{1}{\pi} \sum_{s=1}^{\infty} \frac{(-1)^s}{s^2} \\ \times \left\{ \frac{\cos\left[s(S^0_{\mu} - \gamma^+_{\mu})\right]}{t^0_{\mu} - \partial \gamma^+_{\mu}/\partial \mu} + \frac{\cos\left[s(S^0_{\mu} - \gamma^-_{\mu})\right]}{t^0_{\mu} - \partial \gamma^-_{\mu}/\partial \mu} \right\}; \quad (2.15)$$

is obtained by integrating the second term in (2.13) by parts over energy and keeping the leading nonintegral term.

The phases γ_{μ}^{\pm} in (2.11) and their derivatives

$$\frac{\partial \gamma_{\mu}^{\pm}}{\partial \mu} = \frac{m}{\sqrt{4\pi e^2 n(0)}}$$

$$\times \left[\operatorname{Re} \psi \left(\frac{1 + \mathrm{i} d_{\mu}^2}{2} \right) - \ln \frac{|d_{\mu}^2|}{2} \pm \frac{\pi}{2 \cosh \left(\pi d_{\mu}^2 / 2 \right)} \right] \quad (2.16)$$

determine the result of interference in the addition of the two sums in (2.15). In (2.16), $\psi(z) = d \ln \Gamma(z)/dz$ is the Euler psi function. The logarithmic divergence of derivatives (2.16) at $d_{\mu}^2 = 0$, as shown in Section 2.4, strongly affects the amplitude of shell oscillations.

2.4 Calculation results

We use the approach considered above for calculating the characteristics of a 1D quantum dot with $N_e \ge 4$ by comparing our results with calculations performed in [73], where, apart from the TF model, the Kohn–Sham density functional method [3] and Strutinsky method [2, 77] were used.

Figure 3a presents the results of calculations of the electron density in the TF model, taking oscillation correction (2.10) into account or neglecting it for the number of electrons $N_e = 5$ and 20, in comparison with calculations in



Figure 3. (a) Distribution of the electron density n(x) in a one-dimensional quantum dot. Calculations with the TF model with the oscillation correction (2.10) neglected (dashed curves) and taken into account (solid curves) are compared with the calculations in [73] by the density functional method (dotted curves). The interaction parameter is e = 1, the number of electrons is $N_e = 5$ (lower curves) and $N_e = 20$ (upper curves). (b) Quantum correction δE_{qu} (2.14) to the total electron energy (thick curve) and its sum with shell correction δE_{sh} (2.15) (thin curve) as a function of the number N_e of electrons in a one-dimensional quantum dot with the interaction parameter e = 1. Black dots show the difference between the total electron energy calculated by the density functional method and by the TF model [73].

the Kohn–Sham model. The TF model gives the smooth component of the density distribution, while considering the oscillation correction allows describing spatial density oscillations quite accurately. Analytic expressions that we obtained for a quantum dot with the number of particles $N_e \ge 10$ only very weakly deviate from the results of the density functional method [73] everywhere except a small vicinity of turning points; this deviation is indiscernible in Fig. 3a.

The quantum gradient correction to the total electron energy calculated by expression (2.14) in the range $4 \le N_e \le 40$ is presented in Fig. 3b. Figure 3b also shows the sum of gradient and shell (2.15) corrections compared with the difference between the exact total energy calculated in the Kohn–Sham model and in the TF model, taken from [73]. This difference coincides with the principal Strutinsky correction calculated in [73] by solving the Schrödinger equation.

Below, based on the analysis of shell correction (2.15), we explain the dependence of the period and amplitude of oscillations on the interaction parameter *e* obtained for the Strutinsky correction in calculations [73] for $e \leq 1.5$.

Figure 4 shows shell correction (2.15) calculated as a function of the number of electrons in a quantum dot for several values of the charge *e*. The dependences $d_{\mu}^2(N_e)$ are also presented in this figure. We can see that as the interaction parameter of particles *e* increases, the amplitude of energy oscillations increases and remains constant for increasing N_e . The same increase in the oscillation amplitude and its constant value in the range $N_e = 2-20$ were obtained in numerical calculations [73] by the density functional method for the charge e = 1.5. The semiclassical method can explain this behavior. It follows from (2.15) that it is determined by the phases γ_{μ}^{\pm} in (2.11) and their derivatives $d\gamma_{\mu}^{\pm}/d(d^2)$ in (2.16), which depend on the value of d_{μ}^2 in (2.12), characterizing the closeness of the Fermi energy of the system to the central maximum of the self-consistent potential V(0) (Fig. 1). As *e* increases, $d_{\mu}^2(e)$ rapidly tends to zero, i.e., to the region of



Figure 4. Shell correction $\delta E_{\rm sh}$ (2.15) (solid curves) and parameter d_{μ}^2 (2.12) (dotted straight lines) as functions of the number of electrons $N_{\rm e}$ in the quantum dot for different electron charges *e*.

the logarithmic singularity of derivatives (2.16) (Fig. 2), which causes a considerable change in the form of shell oscillations upon increasing the parameter *e*.

Thus, the semiclassical additive correction method gave results coinciding with those obtained by the density functional method and allowed analyzing the relative contributions of gradient and shell effects and explaining the dependence of the oscillating part of the total energy on the number of particles and the interaction parameter.

3. Averaged description of spherically symmetric electron systems

In this section, spherically symmetric electron systems are considered mainly at zero temperature. The use of the TF model and its different modifications with the quantum, exchange, and correlation corrections taken into account additively (TFC) and self-consistently (ETF) allows describing the averaged behavior of the local and integral characteristics in atoms, ions, and bulk and hollow clusters quite accurately.

3.1 Free ion in the Thomas–Fermi model. Ionization potentials and partition functions

The composition and thermodynamic properties of plasma are often calculated using the chemical model [81], which leads to Saha equations for the concentration of particles (electrons, atoms, and ions with different charges). The parameters of these equations are the ionization potentials and partition functions of ions, which can be calculated if the excitation spectra of the corresponding ions are known. The ionization potentials and excitation energies of ions are usually determined from experimental spectroscopic data or, if these data are not available, from quantum mechanical calculations (see, e.g., [82] and [83]). We show that the TF model can be used for this purpose.

The problem of describing a free positive ion with a charge $z = Z - N_e \ge 0$ (where Z is the nucleus charge) in the TF model was consider by Sommerfeld in 1933 [8, 9, 79]. In this case, the electron density distribution $n_e(r)$ is described by relations

$$n_{\rm e}(r) = (3\pi^2)^{-1} \left[2(\mu_z - V_z(r)) \right]^{3/2},$$

$$\mu_z - V_z(r) = \frac{Z\varphi_z(x)}{R_z x},$$
(3.1)

where the function $\varphi_z(x)$ satisfies the TF equation

$$\sqrt{x}\varphi_z''(x) = A\varphi_z^{3/2}(x), \ \varphi_z(0) = 1, \ \varphi_z(1) = 0, \ \varphi_z'(1) = \frac{z}{Z}.$$

Here, $x = r/R_z$, R_z is the ion radius, $A = 8\sqrt{2ZR_z^3/3\pi}$, $\mu_z = -z/R_z$ is the Fermi energy (chemical potential), and $V_z(r)$ is the potential energy of an electron in the self-consistent field. At distances exceeding the ion radius $(r \ge R_z)$, the electron density is zero and $V_z(r) = -z/r$.

The ionization energy E_z of an ion in the TF model [8, 9] and the quantum-exchange correction to it [14–16] are expressed in terms of the function $\varphi_z(x)$ as

$$E_z^{\rm TF} = \frac{8\sqrt{2R_z}}{5\pi} Z^{5/2} \int_0^1 \frac{\varphi_z^{5/2}(x)}{\sqrt{x}} \, \mathrm{d}x \,,$$

$$\delta E_z^{\rm qu-ex} = \frac{44R_z}{9\pi^2} Z^2 \int_0^1 \varphi_z^2(x) \, \mathrm{d}x \,,$$

(3.2)

0



Figure 5. Ionization potentials of free aluminum (a) and iron (b) ions calculated by the TF (solid curves) and TFC (dashed curves) models compared with the experimental data in [82] (triangles).

and the ionization potentials are calculated as differences between the ionization energies of neighboring ions: $I_z = E_z - E_{z+1}, z \ge 0$ (I_{z+1} is the ionization potential of the z ion).

Figure 5 shows the ionization potentials of aluminum and iron ions calculated in the TF and TFC models in comparison with empirical data [82]. We can see that the TF model, especially with the quantum-exchange correction, describes the averaged behavior of ionization potentials well (the larger Z, the better), but does not describe shell effects.

In [14–16], the ionization potentials of ions calculated in the TFC model were approximated by analytic expressions, which allows readily estimating the ionization potential of any ion for any element. The corresponding approximations were obtained using the relation between the ionization and chemical potentials of an ion:

$$I_z = I(N_e) = -\mu \left(N_e - \frac{1}{2} \right) = -\mu \left(z + \frac{1}{2} \right).$$
 (3.3)

We present these dependences of the chemical potential of the ion on its charge z and the degree of ionization

$$\begin{split} \mu &= z/Z = 1 - N_{e}/Z; \\ \mu_{TFC} &= \mu_{TF} + \delta \mu_{qu-ex} , \\ \mu_{TF}(0 \leqslant \alpha \leqslant 0.12) = -0.1103 \, z^{4/3} [1 - 0.9102 \alpha^{\sigma/3}]^{-1} , \\ \sigma &= 0.5(\sqrt{73} - 7) , \\ \mu_{TF}(0.12 \leqslant \alpha \leqslant 1) = -\frac{0.2438 \, z^{4/3}}{(1 - \alpha)^{2/3}} \\ &\times \left[1 + 0.5651 \alpha - 0.1059 \, (1 - \alpha)^{2} - \frac{0.2097 \, (1 - \alpha)^{3}}{1 + 2.8285 \, \alpha} \right] \\ \delta \mu_{qu-ex} &= -0.2153 \left(\frac{z^{2}}{1 - \alpha} \right)^{1/3} \\ &\times \left[1 + 0.3398 \alpha - \frac{0.3444 \, (1 - \alpha)^{2}}{1 + 2.7807 \alpha} \right]. \end{split}$$

The TF model of a free ion described above can also be used, as was shown in [17, 18], to estimate the partition functions of ions, which are also required for calculations of the plasma composition in the chemical model [81]. The partition function of an ion in plasma at a temperature T can be written as

$$Q_{z} = g_{0}^{(z)} + 2\sum_{n,l} (2l+1) \exp\left[-\frac{\varepsilon_{nl} - \mu_{z}}{T}\right] \theta(\varepsilon_{nl} - \mu_{z}) \omega(\varepsilon_{nl}),$$
(3.4)

where the excitation levels ε_{nl} are referenced to the Fermi energy μ_z , *n* and *l* are the principal and orbital quantum numbers, $\omega(\varepsilon)$ is the cut-off form factor that allows restricting the number of excitation levels included in the sum based on one consideration or another, and $g_0^{(z)}$ is the statistical weight of the ground state.

Using characteristics obtained in the TF model, we can perform analytic summation in expression (3.4) with the mean-radius cut-off criterion. The mean radius R is determined from the plasma density $\rho = 11.2(M/v)$ g cm⁻³ as $R = (3v/4\pi)^{1/3}$, where M is the atomic mass of the element. In [18], different cut-off methods are also considered: a cut-off with respect to the plasma temperature T and the Planck– Brillouin–Larkin approximation.

Figure 6, schematically showing the characteristics of a free ion with charge z and plasma parameters T and R, explains the corresponding algorithm. In the case of the mean-radius cut-off criterion, the spectrum of bound excited states is restricted by the value -z/R (for the temperature cut-off criterion, by -T) from above and by μ_z from below. Obviously, the mean radius should then exceed the ion radius, $R \ge R_z$ (for the temperature cut-off criterion, $R_T \ge R_z$); otherwise, the ions cannot be treated as free ions and the free-ion TF model described above cannot be used for them.

We determine the excitation spectrum ε_{nl} by using the Bohr–Sommerfeld quantization condition and take the simplest step function $\omega(\varepsilon_{nl}) = \theta(-z/R - \varepsilon_{nl})$ as the cut-off function. Replacing sums in (3.4) with integrals over the energy and orbital momentum, we obtain a semiclassical expression for the partition function (see the details in [17]):

$$Q_{z}^{(R)}(v,T) \simeq g_{0}^{(z)} + \frac{\sqrt{2}}{\pi^{2}} T^{3/2} \int_{v} d\mathbf{r} \exp\left(\frac{\mu_{z} - \tilde{\mu}_{z}}{T}\right)$$

$$\times \left(\frac{\sqrt{\pi}}{2} \exp\left(u_{1}\right) \left[\Phi(\sqrt{u_{2}}) - \Phi(\sqrt{u_{1}})\right] + \sqrt{u_{1}} - \sqrt{u_{2}} \exp\left(du\right)\right),$$
(3.5)



Figure 6. Characteristics of a free *z*th ion in the TF model (the potential electron energy V(r) in a self-consistent field, the ion radius R_z , and the Fermi energy μ_z) and plasma parameters (the temperature *T* and the mean atomic radius *R*). R_T is the 'temperature' radius.

$$du = u_1 - u_2, \quad u_1 = \frac{\tilde{\mu}_z - V_z(r)}{T},$$
$$u_2 = \frac{-z/R - V_z(r)}{T}, \quad \tilde{\mu}_z = \max\left(\mu_z, -\frac{z}{r}\right)$$

where $\Phi(x)$ is the probability integral.

The low-density and low-temperature limits of function (3.5) have the respective forms

$$\begin{aligned} Q_z(R \to \infty, T) &\approx \frac{1}{3\sqrt{2}} \left(zR \right)^{3/2} \exp\left(\frac{\mu_z}{T}\right), \\ Q_z(R, T \to 0) &\approx g_0^{(z)} + \frac{4\sqrt{2z}}{\pi} TR_z^{5/2} \int_0^1 \mathrm{d}x x^{3/2} \sqrt{\varphi_z(x)} \,. \end{aligned}$$

The expression for partition function (3.5) can be analytically differentiated with respect to the thermodynamic parameters v and T. The corresponding derivatives are

$$v \frac{\partial Q_{z}^{(R)}}{\partial v} = \frac{\sqrt{2T}}{3\pi^{2}} \frac{z}{R} \exp\left(\frac{\mu_{z} + z/R}{T}\right) \int_{v} d\mathbf{r} \sqrt{u_{2}},$$

$$T^{2} \frac{\partial \ln Q_{z}^{(R)}}{\partial T}$$

$$= \frac{\sqrt{2}}{\pi^{2}} \frac{T^{3/2}}{Q_{z}^{(R)}} \int_{v} d\mathbf{r} \exp\left(\frac{\mu_{z} - \tilde{\mu}_{z}}{T}\right) \left(\frac{\sqrt{\pi}}{2} U_{z}(r) \exp\left(u_{1}\right)\right)$$

$$\times \left[\Phi(\sqrt{u_{2}}) - \Phi(\sqrt{u_{1}})\right] \tilde{\mu}_{z} \sqrt{u_{1}} + \frac{z}{R} \sqrt{u_{2}} \exp\left(du\right)$$

$$+ \left(\frac{3}{2} T - \mu_{z}\right) \frac{Q_{z}^{(R)} - g_{0}^{(z)}}{Q_{z}^{(R)}}.$$
(3.6)

It can be easily verified that the mean excitation energy

$$\langle \varepsilon_z^{\text{ex}} \rangle = \frac{1}{Q_z^{(R)}} \sum_s g_s^{(z)} (\varepsilon_s^{(z)} - \varepsilon_0^{(z)})$$

$$\times \exp\left[-\frac{\varepsilon_s^{(z)} - \varepsilon_0^{(z)}}{T}\right] \theta\left(-\frac{z}{R} - \varepsilon_s^{(z)}\right)$$

$$(3.7)$$

in this case exactly coincides with (3.6)



Figure 7. Dependence of the mean excitation energy of an ion on its charge z in aluminum plasma in the case of the average-radius cut-off criterion. The plasma density is $\rho = 10^{-2}$ g cm⁻³ and the temperature is T = 5 eV (solid curve and triangles) and T = 10 eV (dashed curve and dots). The curves are calculated by (3.6), symbols are calculated from empirical data [81].

Figure 7 presents mean excitation energies (3.7) for all aluminum ions in dense plasma at two temperatures calculated by expression (3.6) and compared with calculations [81] based on empirical data. Figure 8 shows the partition functions of ions calculated by expression (3.5) with $g_0^{(z)} = 2$ for aluminum and iron plasmas with various densities and temperatures compared with the calculations in [81] from empirical excitation spectra. We can see that theoretical expressions (3.5) and (3.6) correctly describe the averaged dependences of the partition functions of ions on the plasma temperature and density, but do not describe the dependence of shell oscillations on the ion charge *z*.

3.2 Extended Thomas–Fermi model

The disadvantage of the TF model for free atoms and ions is the incorrect behavior of the electron density at small distances from the nucleus and at the periphery because the semiclassical approximation is valid at distances $1/Z \le r \le 1$ [79]. In this section, we consider a more complicated alternative semiclassical EFT model in which these disadvantages are absent.

The ETF model has been widely used [25, 34, 6, 72, 84, 85] to describe the averaged characteristics of a variety of many-electron systems, despite the theoretical invalidity of simultaneously taking the leading and correction semiclassical terms into account. In particular, in a variant of this model that we used in [86, 87], expression (1.7) for the total electron energy, along with the principal ideal-gas (Thomas–Fermi) term, contains quantum, exchange, and correlation corrections, which were obtained assuming the smallness of the corresponding effects (in this section, $n \equiv n_{\rm e}(\mathbf{r})$):

$$E[n] = \int d\mathbf{r} \left\{ k(n) + n \left[V_{\text{ext}}(\mathbf{r}) + \frac{1}{2} V_{\text{int}}(\mathbf{r}) \right] + \epsilon_{\text{ex}}(n) + \epsilon_{\text{corr}}(n) \right\}.$$
(3.8)

Here, k(n) is the kinetic energy density in which the secondorder quantum correction to the TF model is taken into



Figure 8. Partition functions of ions in (a) aluminum and (b) iron plasma for the mean-radius cut-off criterion. Aluminum: T=25 eV; $\rho=10^{-2} \text{ gm}^{-3}$ (solid curve and triangles), $\rho=10^{-5} \text{ g cm}^{-3}$ (dashed curve and dots). Iron: $\rho=10^{-5} \text{ g cm}^{-3}$; T=5 eV (solid curve and triangles), T=10 eV (dashed curve and black dots), T=25 eV (dash-and-dot curve and rhombs). The curves are calculated by TF model (18), symbols are calculated from empirical data [81].

account [1],

$$k(n) = k_{\rm TF}(n) + \delta_2 k(n) = \frac{3}{10} (3\pi^2)^{2/3} n^{5/3} - \frac{1}{72} \frac{(\nabla n)^2}{n},$$
(3.9)

 $V_{\text{int}}(\mathbf{r}) = \int d\mathbf{r}' n(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'|$ is the Coulomb electron interaction potential,

$$\epsilon_{\text{ex}}(n) = -\frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3} n^{4/3}, \quad V_{\text{ex}} = -\left(\frac{3}{\pi}\right)^{1/3} n^{1/3},$$

$$\epsilon_{\text{corr}}(n) = -0.033n \left[(1+X^3) \ln(1+X^{-1}) + \frac{X}{2} - X^2 - \frac{1}{3} \right],$$

$$V_{\text{corr}} = -0.033 \ln(1+X^{-1})$$

are the exchange and correlation [26] energy densities and corresponding potentials, $X=r_s/11.4$, and $r_s=(3/4\pi n)^{1/3}$ is the electron radius.

The extremum of functional (3.8) with normalization condition (1.8) gives an equation for the density in the ETF model

$$\frac{1}{2} \left(3\pi^2 n\right)^{2/3} + \frac{1}{72} \left(\frac{\nabla n}{n}\right)^2 - \frac{1}{36} \frac{\Delta n}{n} + V(\mathbf{r}) - \mu = 0, \ (3.10)$$

with the total potential

$$V(\mathbf{r}) = V_{\text{int}}(\mathbf{r}) + V_{\text{ext}}(\mathbf{r}) + V_{\text{ex}}(\mathbf{r}) + V_{\text{corr}}(\mathbf{r})$$

including the interaction, external, exchange, and correlation potentials. Elimination of all the correction terms from (3.8) leads to a relation between the density and the potential in the TF model.

We use Eqn (3.10) to calculate the electron density distributions in atoms and various atomic clusters [86, 87]. For spherically symmetric systems considered here, only the form of the external potential $V_{\text{ext}}(r)$ changes in Eqn (3.10). These potentials for an atom and a bulk atomic cluster are

$$V_{\text{ext}}^{(\text{at})}(r) = -\frac{Z}{r},$$

$$V_{\text{ext}}^{(\text{cl})}(r) = \begin{cases} -\frac{N_{\text{e}}}{2R} \left[3 - \left(\frac{r}{R}\right)^2 \right], & r \leq R, \\ -\frac{N_{\text{e}}}{R}, & r > R. \end{cases}$$
(3.11)

Here, the so-called jelly cluster model is used, in which ions are assumed to be homogeneously distributed within a volume with the radius $R = r_s N_e^{1/3}$, where r_s is the electron Wigner–Seitz radius of the condensed phase of the element, $N_e = wN_i$ is the number of electrons, N_i is the number of ions (atoms) in the cluster, and w is the valence of atoms. For a hollow cluster in which the ion charge is homogeneously distributed over a spherical shell with the radius R and an atom with a valence w_0 is located at the center of the cavity, the external potential produced by the ions has the form

$$V_{\text{ext}}^{(\text{holcl})}(r) = -\frac{w_0}{r} - \begin{cases} \frac{N_{\text{e}} - w_0}{R} , & r \leq R \\ \frac{N_{\text{e}} - w_0}{r} , & r > R \end{cases}$$

In this case, w_0 valence electrons of the central atom are included in the number N_e of electrons. The value $w_0 = 0$ corresponds to an 'empty' hollow cluster. Such clusters were used in the literature for simulating C₆₀ and LaC₆₀ fullerenes [88].

Taking the spherical symmetry into account and passing from the radius to the dimensionless variable x = r/L(L) is the characteristic size of the system) and from the density to the function $v(x) = x\sqrt{n}$, we obtain a nonlinear integro-differential equation for this function and the chemical potential, which was solved in [86, 87] by the Newton method using finite differences.

We first consider the results of such calculations for atoms. Figure 9a shows the distributions of the radial electron density $D(r) = 4\pi r^2 n_e(r)$ in neon (Z = 10) and mercury (Z = 80) atoms calculated in the ETF model. To compare these results with those obtained in the TF model, the reduced quantities $D(r) Z^{-4/3}$ and $\sqrt{rZ^{1/3}}$ are plotted on the axes. The corresponding dependence in the TF model is universal and independent of Z. We can see from the figure that the results of the ETF model in the middle part of the



Figure 9. (a) Distribution of the radial electron density $D(r) = 4\pi r^2 n_e(r)$ in a free atom. The curve corresponds to the TF model, symbols correspond to the ETF model: Z = 10 (dots), and Z = 80 (triangles). (b) Distributions of the radial electron density in two hollow clusters with the number of ions in the shell $N_i = 60$ for equilibrium radii. 'Empty' cluster with $w_0 = 0$ (solid curve), cluster with the central valence atom $w_0 = 3$ (dotted curve).

atom approach this universal curve upon increasing the atomic number Z; the results of taking the corrections into account additively and self-consistently coincide where these corrections are small. This illustrates well the condition $Z \ge 1$ of the applicability of the semiclassical description of an atom.

Another condition, r > 1/Z, is related to the inapplicability of the semiclassical approximation in the region of small distances from the Coulomb center, where corrections are not small, and therefore, notably, the density at zero in the TF model diverges: $n_{\rm TF}(r) \sim r^{-3/2}$ and hence the radial density has the dependence $D_{\rm TF}(r \rightarrow 0) \sim \sqrt{r}$. This region requires a special study, which is performed in Section 6.2.

In the ETF model, as in the quantum statistical model [72], the electron density at zero is constant and the radial density depends on the radius quadratically: $D_{\text{ETF}}(r \rightarrow 0) \sim r^2$. At the periphery of an atom, a difference also exists between the exponentially decreasing dependence of the radial density in the ETF model and the slowly decreasing power-like dependence on the radius in the TF model. Our analysis thus shows that the advantage of taking the corrections into account self-consistently rather than additively is related to a new class of solutions obtained for the density, which are finite at zero for systems with a Coulomb singularity and behave more correctly at the periphery of the system.

We now consider the results of our calculations for hollow clusters that simulate fullerenes C_{60} and LaC_{60} . Figure 9b shows the radial electron-density distributions for two hollow clusters with the number of ions in the shell $N_i = 60$ calculated in the ETF model for the corresponding equilibrium values of the cluster radius R_0 . The 'empty' hollow cluster ($w_0 = 0$) simulates C₆₀, while the hollow cluster with a trivalent atom at the center ($w_0 = 3$) simulates LaC₆₀.

To determine the equilibrium radius R_0 , the dependence of the total energy $E = E_e + E_i$ of the cluster on its radius is studied to find its minimum. In the jelly model used here, the energy of ions uniformly distributed over the sphere is $E_i = 0.5 N_e^2/R$. This gives a root dependence of the calculated equilibrium radius on the number of particles, $R_0 = \alpha N_e^{1/2}$, with the coefficient $\alpha = 3.743$ [86]. The use of this expression for fullerenes gives too large a value $R_0 = 29$, which is explained by a strong overstating of the ion energy in replacing the real arrangement of ions by a spherical shell. If the ion energy $E_i = 0.4311 N_e^2/R$ is used, which corresponds to the real arrangement of the C_{60} molecule ions at the vertices of a truncated icosahedron with the radius R, then a much smaller equilibrium radius $R_0 = 5$ is obtained, which is closer to the experimental radius $R_0^{(exp)} = 6.75$ for the C_{60} fullerene.

We note that a hollow cluster in the TF model, as shown in [88], does not give a finite equilibrium radius R_0 at all when the ion energy is described by the expression of the jelly model, whereas the use of the ion energy corresponding to the real arrangement of ions gives the radius $R_0 = 7.36$.

The ETF model, like the TF model, can be a basis for the calculation of the contribution of oscillation and shell effects not taken into account in it. The corresponding theorem is formulated within the density functional theory in Section 5.2, while spatial density oscillations in an atom and a bulk atomic cluster are calculated in the ETF model with the oscillation correction in Section 4.3 (Figs 13 and 14).

4. Dependence of the system properties on the potential type

In spherically symmetric many-electron systems, two types of self-consistent potentials should be distinguished: potentials with the Coulomb singularity and potentials finite at the center. Many properties of the electron system, in particular, the form of one-particle spectra and spatial oscillations of the electron density, substantially differ for these two types of potentials.

4.1 Potentials in spherically symmetric many-electron systems

Self-consistent attraction potentials in the electron systems under study can belong to two types, depending on the form of the external potential. The interacting electrons in an atom, ion, and atomic cell are located in the external field of the nucleus, which has a Coulomb singularity at zero (Fig. 6).

Valence electrons in a metal cluster are often considered to be located in the external field of the ion core. The ion lattice can be replaced in some range of parameters by a uniformly distributed positive charge. Such a replacement leads to the jelly model, which describes many properties of clusters well, although it oversimplifies the real system. The corresponding self-consistent potential at zero is finite and has the zero derivative, being similar to the model potential used in nuclear physics (schematically shown in Fig. 10). Of course, such a potential is not a first-principle potential like the Coulomb potential.

In considering quantum effects, it is important to distinguish these two types of potentials, because they determine some features of the properties of the correspond-



Figure 10. Qualitative spatial dependences of the potential fermion energy in a nucleus and a metal cluster according to different models: a harmonic oscillator (1), the Woods–Saxon potential (2), and a rectangular well (3).

ing systems. The presence of these features casts some doubt on the validity of using pseudopotentials in some cases where a Coulomb singularity of the potential is replaced by a 'ledge', i.e., a passage to a different type of potential is performed.

In this section, we demonstrate these differences with the example of a semiclassical analysis of one-particle spectra. It turns out that some conclusions about their structure can be made based only on the type of the self-consistent potential.

Energy levels in a central potential depend on two quantum numbers: the orbital number l and the principal number n (or the radial number n_r), and are determined in the semiclassical approximation from the Bohr–Sommerfeld quantization condition

$$S_{\varepsilon\lambda} = \int_{R'_{\varepsilon\lambda}}^{R_{\varepsilon\lambda}} \mathrm{d}r \, p_{\varepsilon\lambda}(r) = \pi \left(n_{\mathrm{r}} + \frac{1}{2} \right), \tag{4.1}$$

where $S_{\varepsilon\lambda}$ and $p_{\varepsilon\lambda}(r) = \sqrt{p_{\varepsilon}^2(r) - \lambda^2/r^2}$ are the radial action and the radial momentum of an electron with the energy ε and orbital momentum $\lambda = l + 1/2$, $p_{\varepsilon}^2(r) = 2[\varepsilon - V(r)]$, the integration region is restricted by turning points $R_{\varepsilon\lambda}$ and $R'_{\varepsilon\lambda}$, and n_r is the number of nodes of the radial wave function.

We introduce the function $v_{\varepsilon}(\lambda)$ related to the radial action by the expression

$$u_{arepsilon}(\lambda) = rac{S_{arepsilon\lambda}}{\pi} \quad ext{for} \quad \lambda > 0 \,, \quad v_{arepsilon}(0) = rac{1}{\pi} \int_{0}^{R_{arepsilon0}} \, \mathrm{d}r \, p_{arepsilon0}(r) \,.$$

As a function of the continuous argument λ , $v_{\varepsilon}(\lambda)$ monotonically decreases from $v_{\varepsilon}(0)$ to $v_{\varepsilon}(\lambda_{\varepsilon}) = 0$, where λ_{ε} is the maximum orbital momentum for the energy ε . Figures 11 and 12 show the corresponding functions and their derivatives for atoms and metal clusters for the energy equal to the Fermi energy. In the (v, λ) plane, all the intersections of coordinates v and λ with half-integer values located below the curve $v_{\mu}(\lambda)$ correspond to occupied states at zero temperature, as follows from Bohr–Sommerfeld quantization condition (4.1).

The study of the dependence of $v_{\varepsilon}(\lambda)$ on λ for small λ ,

$$v_{\varepsilon}(\lambda) = v_{\varepsilon}(0) + v_{\varepsilon}'(0) \lambda + \frac{1}{2} v_{\varepsilon}''(0) \lambda^{2} + \dots$$
(4.2)

(the prime denotes differentiation with respect to λ), shows that in the spherical harmonic oscillator, with $V(r) = -V_0 + \omega^2 r^2/2$, and in a Coulomb field, with V(r) = -Z/r,



Figure 11. Dependences $v_{\mu}(\lambda)$ (a) and $v'_{\mu}(\lambda)$ (b) for sodium clusters (rigid potential) for different numbers of particles calculated using the Woods–Saxon potential [23].

 $v_{\varepsilon}(\lambda)$ is linear in λ :

$$v_{\varepsilon}(\lambda) = v_{\varepsilon}(0) + v_{\varepsilon}'(0) \lambda, \quad v_{\varepsilon}'(0) = -\frac{1}{\gamma}.$$
(4.3)

Here, $\gamma = 1$ and 2 respectively for the Coulomb potential and harmonic oscillator.

Using relation (4.3) and quantization condition (4.1), we can easily calculate energy levels in these 'main' potentials. Quantization condition (4.1) for a harmonic oscillator with l = 0 has the form

$$2v_{\varepsilon}(0) = n' + \frac{1}{2}, \qquad (4.4)$$

because a particle can pass through the center in this case. For $l \neq 0$, according to (4.3) and (4.1), we have

$$v_{\varepsilon}(\lambda) = v_{\varepsilon}(0) - \frac{\lambda}{2} = n_{\mathrm{r}} + \frac{1}{2}, \quad n_{\mathrm{r}} = 0, 1, 2, \dots$$

Substituting $v_{\varepsilon}(0)$ from expression (4.4) and introducing the notation n' = n + 1, we obtain the relation

$$\frac{n-l}{2} = n_{\rm r} \,, \tag{4.5}$$

which gives the condition that the principal, n (n = 0, 1, ...), and orbital, l, quantum numbers have the same parity, as well as the equality $2v_{\varepsilon}(0) = n + 3/2$. Calculating the integral of $v_{\varepsilon}(0) = (V_0 - |\varepsilon|)/2\omega$, we obtain the known expression $\varepsilon_{nl} = -V_0 + \omega(n + 3/2)$ for the spectrum.

Quantization condition (4.1) for the Coulomb potential, with (4.3) taken into account, becomes $v_{\varepsilon}(\lambda) = v_{\varepsilon}(0) - l - 1/2 = n_{\rm r} + 1/2$, $n_{\rm r} = 0, 1, 2, ...$, where $v_{\varepsilon}(0) = Z/\sqrt{2|\varepsilon|}$. This gives $\varepsilon_{nl} = -Z^2/2(n_{\rm r} + l + 1)^2 = -Z^2/2n^2$, where $n = n_{\rm r} + l + 1 = 1, 2, ...$

We have shown in [48] that for monotonic attraction potentials that are finite at zero, the derivative $v'_{\varepsilon}(0)$ in (4.2) is equal to -1/2, as in the case of an oscillator. We combine such potentials into the group of 'harmonic'-type potentials.



Figure 12. Dependences $v_{\mu}(\lambda)$ (a) and $v'_{\mu}(\lambda)$ (b) for atoms with different atomic numbers calculated in the ETF model [86, 87].

The examples of harmonic-type potentials are self-consistent potentials in metal clusters in the jelly model and their analogs used in nuclear physics.

Similarly, we can distinguish a group of Coulomb-type potentials in which screened potentials have a Coulomb singularity at zero, $V(r) \rightarrow -Z/r$ as $r \rightarrow 0$, and for which, as is shown in [48], $v_{\varepsilon}'(0) = -1$. In particular, this group includes intra-atomic potentials.³

The value of the second derivative $v_{\varepsilon}''(0)$ in (4.2) characterizes the degree of influence of anharmonicity or screening and leads to the lift of the degeneracy in the orbital momentum *l*, which is present in the spectra of the main potentials.

In the case of an anharmonic potential, the s-level ε_{n0} is also determined from a quantization condition of type (4.4). We estimate the deviation of a level with a nonzero *l* from the s-level. In the expansion of $v_{\varepsilon}(\lambda)$ in the left-hand side of quantization condition (4.1) in the energy and orbital momentum near this level,

$$v_{\varepsilon}(\lambda) \cong v_{\varepsilon_{n0}}(0) + v_{\varepsilon_{n0}}'(0) \lambda + \frac{1}{2} v_{\varepsilon_{n0}}''(0) \lambda^2 + \frac{t_{\varepsilon_{n0}}}{\pi} \left(\varepsilon - \varepsilon_{n0}\right),$$
(4.6)

the notation $t_{\varepsilon} = \partial S_{\varepsilon}/\partial \varepsilon$ for the classical time and expression (4.2) are used. With relation (4.5), the right-hand side of quantization condition (4.1) can be rewritten as $n/2 + 3/4 - \lambda/2$, which gives the relation

$$\varepsilon_{nl} = \varepsilon_{n0} - \Delta \varepsilon_n \, \frac{1}{2} \, v_{\varepsilon_{n0}}''(0) \, \lambda^2 \,, \tag{4.7}$$

where, in the semiclassical approximation, $\Delta \varepsilon_n = \pi / t_{\varepsilon_{n0}}$ is the mean difference between the energies of s-levels for shells with quantum numbers *n* and $n \pm 1$.

Similar calculations for 'Coulomb'-type potentials lead to the same result. Expression (4.7) yields a quantitative criterion of the lift of degeneracy in the anharmonic or screened potential and shows that the corresponding splitting quadratically depends on the orbital momentum, with the sign of the deviation from the s-level dependent on the sign of the derivative $v_{\tilde{e}_{r0}}^{"}(0)$. For the positive sign, the energy levels decrease with increasing *l*, while for the negative sign, they increase. In atoms, the latter case is realized, while in metal clusters both variants are possible.⁴

4.2 One-particle spectra of atoms and ions

We find the range of energies and orbital momenta where quadratic dependence (4.7) in one-particle spectra of atomic and ion systems occurs (the specific features of spectra of atomic metal clusters are considered in Section 7).

The screening of the Coulomb potential in atoms and ions leads to a shift of the deepest energy levels by a constant corresponding to the potential of the electron cloud at zero, and $v_{\varepsilon}''(0) = 0$ in this energy region; the spectrum is therefore similar to the Coulomb spectrum up to a shift in this constant. For shell levels with higher *n*, the screening becomes more substantial, which is quantitatively reflected by the value $v_{\varepsilon}''(0) < 0$.

An analysis of the energy levels calculated in the nonrelativistic Hartree–Fock model for mercury and radon atoms [89] confirms a dependence close to (4.7) even for not small orbital momentum values $l = 1, 2, 3.^5$ The coefficients $a_{nl} = -(\varepsilon_{nl} - \varepsilon_{n0})/(l + 1/2)^2$ presented in Table 1 are almost constant for shells with different *n* under study. This means that quadratic dependence (4.2) (and, correspondingly, a linear dependence for the derivative $v'_{\varepsilon}(0)$) is valid in a broad range of values of ε and λ , i.e., the equality

$$v_{\varepsilon}(\lambda) = v_{\varepsilon}(0) - \lambda + \frac{1}{2} v_{\varepsilon}''(0) \lambda^2$$
(4.8)

is satisfied with good accuracy for internal energy levels in an atom. Figure 12b confirms the linear dependence of the

³ An example from the second group, a potential in a free atom in the TF model, was analyzed in detail in [12, 13], where the exceptional case $\varepsilon = 0$ was identified, for which the value of the derivative $v'_{\varepsilon}(0)$ also depends on the rate of the potential decrease at infinity.

⁴ Figure 11 shows only one of the possible variants: the calculation for sodium clusters with a 'rigid' potential (see Sections 7.3 and 7.4 below).

⁵ For such heavy elements, relativistic effects are substantial and should be taken into account using the relativistic correction to one-particle energies $\Delta \varepsilon_{nj} = -(Z_n^2 \alpha^2/2n^3)[1/(j+1/2)-3/4n]$, where $Z_n = Z - 2n^3/3 - n/3$, $\alpha = 1/137$, and $j = l \pm 1/2$ [90].

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Table 1. The coefficients $a_{nl} = -(\varepsilon_{nl} - \varepsilon_{n0})/(l + 1/2)^2$ in mercury (Z = 80) and radon (Z = 88) atoms calculated from the one-particle energy level spectrum in the nonrelativistic Hartree–Fock model [91].

nl	$-a_{nl}$ (Hg)	$-a_{nl}$ (Ra)
3p	3.911	4.489
3d	4.000	4.592
4p	1.733	2.044
4d	1.760	2.096
4f	1.682	2.033

derivative $v'_{\mu}(\lambda)$ in a rather broad range of $\lambda \ge 0$, even for the energy equal to the Fermi energy.

We note that the function $v_{\varepsilon}(\lambda)$ and its derivatives for a free atom were studied in detail in the TF model in [12, 13]. The expansion in λ was performed in these papers in the vicinity of another limit $\lambda = \lambda_{\varepsilon}$:

$$v_{\varepsilon}(\lambda) = v_{\varepsilon}'(\lambda_{\varepsilon})(\lambda - \lambda_{\varepsilon}) + \frac{1}{2} v_{\varepsilon}''(\lambda_{\varepsilon})(\lambda - \lambda_{\varepsilon})^{2}.$$
(4.9)

It was shown that the derivative $v'_{e=\mu}(\lambda Z^{-1/3})$ in a free atom at the Fermi energy is independent of the atomic number and changes from $v'_{\mu}(0) = -1$ to $v'_{\mu}(\lambda_{\mu}) = -1.93768.^{6}$

To proceed, it is necessary to compare the smoothness of the dependences of one-particle spectra of atoms and ions on the quantum numbers n and l. It follows from spectroscopic data (see, e.g., [82]) that for inner occupied shells and the outer shell with regular filling (elements of main groups), the dependence on l is smooth enough inside each nth shell, whereas these shells with different n do not overlap and are separated by sufficiently large energy gaps. Such a picture is well demonstrated by the empirical curves of ionization potentials of aluminum and iron ions (Fig. 5). In the case of intermediate and heavy elements, this is also true for deep occupied shells. We use spectra of this shape in this energy region in Section 5.4 in calculations of the 'high-temperature' shell correction.

4.3 Spatial density oscillations in an atom and a metal cluster

As is shown in Section 3, the TF model and its TFC and ETF modifications describe the averaged electron density distribution well but do not reflect its spatial oscillations. To describe these oscillations by the additive semiclassical method, it is necessary to introduce the oscillation correction into the model. This correction is derived using the general formula for the electron density $n_e(r)$ in a spherically symmetric system in the ground state — the equation for the semiclassical radial wave function $\Re_n(r)$,

$$n_{\rm e}(r) = \frac{1}{2\pi} \sum_{n,l} (2l+1) |\Re_{nl}(r)|^2 \theta(\mu - \varepsilon_{nl}) ,$$

$$|\Re_{nl}^{\rm (sc)}(r)|^2 = \frac{1}{\pi} \frac{\partial \varepsilon_{nl}}{\partial n} \frac{1 + \sin [2S_{nl}(r)]}{r^2 p_{nl}(r)} ,$$
(4.10)

Bohr–Sommerfeld quantization condition (4.1), and Poisson formula (2.6) for passing from sums over quantum numbers to integrals (see the details in [57, 87]). As a result, the

oscillation correction is obtained in the form

$$\delta n_{\rm osc}(r) = \frac{1}{2\pi^2 r^2} \int_{U(r)}^{\mu} d\varepsilon \int_{0}^{p_{\varepsilon}^2(r)r^2} d\lambda^2$$
$$\times \sum_{k,s}^{\prime} (-1)^{k+s} \frac{\sin\left[2S_{\varepsilon\lambda}(r) + 2kS_{\varepsilon\lambda}^0 + 2\pi s\lambda\right]}{p_{\varepsilon\lambda}(r)} .$$
(4.11)

Here, the prime on the sum means the absence of the term with k = s = 0, equal to the TF density, while the superscript 0, as above, indicates the total integral between turning points.

The energy integral can be estimated using the completeness property [80], taking into account that integration by parts⁷ allows separating the term at the upper limit $\varepsilon = \mu$; this is the leading term in the parameter of semiclassical behavior. After the change of variables $y = p_{\mu\lambda}(r)/p_{\mu}(r)$, we obtain

$$\delta n_{\rm osc}(r) \simeq -\frac{p_{\mu}(r)}{2\pi^2} \int_0^1 dy \sum_{k,s}' \frac{(-1)^{k+s}}{t_{\mu y}(r) + kt_{\mu y}^0} \\ \times \cos\left[2S_{\mu y}(r) + 2kS_{\mu y}^0 + 2\pi sp_{\mu}(r) r\sqrt{1-y^2}\right], \quad (4.12)$$

where $t_{\mu y}(r) = \partial S_{\mu y}(r)/\partial \mu$ is the classical time. The oscillation correction has the same form (4.12) if the 'additional' quantities $\tilde{S}_{\mu y}(r) = S^0_{\mu y} - S_{\mu y}(r)$ and $\tilde{t}_{\mu y}(r) = t^0_{\mu y} - -t_{\mu y}(r)$ are used instead of $S_{\mu y}(r)$ and $t_{\mu y}(r)$. Such a representation should be used for atoms.

After simple calculations, we obtain the following expressions for the oscillation correction $\delta D_{\rm osc}(r) = 4\pi r^2 \delta n_{\rm osc}(r)$ to the radial density:

(i) For an atom (and an electron system with a Coulombtype potential),

$$\delta D_{\rm osc}(r) \simeq \frac{\sin \left\{ 2\tilde{S}_{\mu}(r) + \tilde{\alpha} \left[(2n+1) \,\pi - 2S_{\mu}^{0} \right] \right\}}{p_{\mu}(r) \, t_{\mu}^{0} \, \tilde{\delta}_{\mu}(r) \, \sin \left(\pi \tilde{\alpha} \right)} \,, \quad (4.13)$$

where

$$\begin{split} \tilde{S}_{\mu}(r) &= \int_{0}^{r} dr' p_{\mu}(r') \,, \quad S_{\mu}^{0} = \tilde{S}_{\mu}(R_{\mu}) \,, \\ n &\leq \frac{S_{\mu}^{0}}{\pi} \leqslant n+1 \,, \quad \tilde{\alpha} = \frac{\tilde{t}_{\mu}(r)}{t_{\mu}^{0}} \,, \\ \tilde{t}_{\mu}(r) &= \int_{0}^{r} \frac{dr'}{p_{\mu}(r')} \,, \quad t_{\mu}^{0} = \tilde{t}_{\mu}(R_{\mu}) \,, \\ \tilde{\delta}_{\mu}(r) &= \int_{0}^{r} \frac{dr'}{r'^{2}} \left[\frac{1}{p_{\mu}(r')} - \frac{1}{\sqrt{2Z/r'}} \right] - \sqrt{\frac{2}{Zr}} \,. \end{split}$$

In the case of a free atom in the TF model, the radius R_{μ} is infinite, $t_{\mu}^{0} = \infty$, and Eqn (4.13) coincides with the expression obtained in [48].

(ii) For a metal cluster (and an electron system with a harmonic-type potential),

$$\delta D_{\rm osc}(r) \simeq -\frac{\sin\left[2S_{\mu}(r) + \alpha(n\pi - 2S_{\mu}^{0})\right]}{2p_{\mu}(r) t_{\mu}^{0} \delta_{\mu}(r) \sin(0.5\pi\alpha)},\tag{4.14}$$

⁷ In the semiclassical approximation, only the rapidly changing function sin [...] should be differentiated and integrated.

⁶ The value of the derivative at $v'_{\mu}(\lambda)$ at the boundary point λ_{μ} can be expressed in terms of derivatives of the self-consistent potential at the point r_0 of the maximum of the function $p_{\mu}(r) r [12]: v'_{\mu}(\lambda_{\mu}) = -\sqrt{2} \lambda_{\mu}/\omega r_0$, $\omega^2 = \left[p_{\mu}^2(r) r^2\right]''_{r_0}, \lambda_{\mu} = p_{\mu}(r_0) r_0$.

where

$$n - \frac{1}{2} \leqslant \frac{2S_{\mu}^{0}}{\pi} \leqslant n + \frac{1}{2}, \quad \alpha = \frac{t_{\mu}(r)}{t_{\mu}^{0}}$$
$$\delta_{\mu}(r) = \int_{r}^{R_{\mu}} \frac{\mathrm{d}r'}{r'^{2}p_{\mu}(r')}$$

and integrals over r' in the expressions for $S_{\mu}(r)$ and $t_{\mu}(r)$ are also taken from r to the right turning point R_{μ} , $S_{\mu}^{0} = S_{\mu}(0)$, $t_{\mu}^{0} = t_{\mu}(0)$.

The range of applicability of expressions (4.13) and (4.14) is determined by the validity of the assumptions made in their derivation. Integration by parts and restriction to the term outside the integral gives a correct estimate of the integral if the derivative of the argument of the oscillating function with respect to y in (4.12) is sufficiently large. In our case, this derivative at the upper limit is a product proportional to $p_{\mu}^2(r) \, \tilde{\delta}_{\mu}(r)$. The points where each of the factors vanishes determine the regions in which the estimate described above is invalid.

For an atom, two such points exist: $r = R_{\mu}$ and $r = r_1$ ($\tilde{\delta}_{\mu}(r_1) = 0$). For $r = r_1 < R_{\mu}$, the point $\lambda = 0$ in the integral over λ in the term with k = 0 and s = 1 is a stationaryphase point, and therefore the method used above cannot be applied and the vicinity of this point must be considered separately.⁸ The corresponding integral can be calculated by the saddle-point method [39].

Figure 13 shows the electron density at the middle part of the mercury atom calculated in the ETF model (without the exchange and correlation terms) with oscillation correction (4.13) and without it, in comparison with the quantum mechanical Hartree calculation [91]. In the range of its applicability, the oscillation correction well describes oscillations related to the electrons grouped in the K, L, and M shells.

Analyzing the range of applicability of expression (4.14), we see that the vicinity of the turning point $r = R_{\mu}$ is excluded for a cluster. Figure 14 shows that expression (4.14) based on the ETF potential describes the electron density oscillations in an atomic cluster quite accurately.



Figure 13. Distribution of the radial electron density $D(r) = 4\pi r^2 n_c(r)$ in the middle part of the mercury atom calculated by neglecting exchangecorrelation terms. Dashed curve: the ETF model, thick curve: the Hartree model [91], thin curve: the ETF model with oscillation correction (4.13).

⁸ To estimate r_1 , we note that in the case of a free atom, the analytic Tietz approximation [92] $V(r) = -Z/r(1 + r/r_1)^2$ for the potential in the TF model contains precisely this quantity, $r_1 = (4.5/Z)^{1/3}$.



Figure 14. Relative distribution of the electron density $n_e(r)/n_i$ in an Na₅₈ cluster. Dashed curve: the ETF model, solid curve: the ETF model with oscillation correction (4.14), triangles: the Kohn–Sham method (data from review [64]; the dotted line is the ion distribution.

4.4 Electron density distribution in the atomic cell of compressed matter

We use the semiclassical approximation to describe the electron density distribution in the volume v of a compressed atomic cell, in particular, near the nucleus for different degrees of cold compression [39, 56].

We note that the knowledge of the electron density at the nucleus localization site is important in and of itself because it is used, for example, in nuclear physics for calculating the excitation probability of a nucleus in the K-electron capture [93]. Many properties of atoms also depend on the behavior of the electron density near the nucleus. These include the fine and hyperfine structures of atomic levels and the isotope shift of energy levels [79]. These properties are of interest not only at normal temperatures and pressures but also under extremal conditions occurring in stellar matter, where the temperature and compression are high. Under such conditions, the mean atomic characteristics are described well by the TF model.

We first estimate the electron density at the center of an atom. Because of the dependence $\Re_{nl}(r \sim 0) \propto r^l$ for exact wave functions, only the s-states make a contribution [see (4.10)]. At distances $r \leq r_0 \sim 1/Z$, the exact solution of the radial equation with the Coulomb potential at l = 0 is expressed in terms of the Whittaker functions:

$$\Re(r) = \frac{a_{\varepsilon}}{r} M_{Z/\sqrt{2|\varepsilon|}, 1/2} \left(2\sqrt{2|\varepsilon|}r \right), \quad \Re(0) = 2a_{\varepsilon} \sqrt{2|\varepsilon|}.$$
(4.15)

A comparison of the asymptotic form of (4.15) for large *r* with the corresponding semiclassical function gives the quantization condition for s-states $S_{\varepsilon 0} = \pi n$ and the normalization coefficient $|a_{\varepsilon_n}|^2$ expressed in terms of the semiclassical normalization factor $|c_n|^2 = 2/t_{\varepsilon}^0 = 2\pi^{-1} d\varepsilon/dn$. As a result, Eqn (4.10) becomes

$$n_{e}(0,v) = \frac{1}{2\pi} \sum_{\varepsilon_{n} \leqslant \mu} |\Re_{n0}|^{2} = Z \sum_{\varepsilon_{n} \leqslant \mu} |c_{n}|^{2}$$
$$= \frac{2Z}{\pi} \sum_{n} \frac{\mathrm{d}\varepsilon_{n}}{\mathrm{d}n} \theta [\mu(v) - \varepsilon_{n}].$$
(4.16)

We assume that compression affects only energy levels $\varepsilon_n > \varepsilon_{n_0}$, and therefore $\varepsilon_n(v) - \mu(v) = \varepsilon_n(\infty) - \mu(\infty)$ at $n \le n_0$. We divide the sum over *n* into two parts with $n \le n_0$ and $n > n_0$, supplement the first part with the sum with $n > n_0$, in which summation is performed over the levels of a

free atom, and subtract the same sum. Then the supplemented sum gives the electron density $n_e(0, \infty)$ at zero for a free atom, and we can pass from summation over *n* to integration in the other two sums. As a result, the difference of the electron densities at zero for a compressed cell of a volume *v* and a free atom is expressed through the difference of the corresponding Fermi energies:

$$n_{\rm e}(0,v) - n_{\rm e}(0,\infty) = \frac{2Z}{\pi} \left[\mu(v) - \mu(\infty) \right].$$
(4.17)

To calculate the electron density at the center of a free atom, we use the TF model with the Fermi energy $\mu(\infty)=0$, $V_{\rm TF}(r)=-Z\varphi(x)/r$, $x=brZ^{1/3}$, b=0.885, and $\varphi'(0)=-1.588$ [79]. The quantization condition for the s-states and expression (4.16) give two relations:

$$Z^{1/3}\sigma(\epsilon_n) = \pi n , \ n_{\rm e}(0,\infty) = 2Z^2 \sum_n \tau^{-1}(\epsilon_n), \ \varepsilon_n = \epsilon_n Z^{4/3} ,$$
(4.18)

containing the universal, Z-independent functions

$$\begin{aligned} \sigma(\epsilon) &= Z^{-1/3} S_{\varepsilon 0} = \sqrt{2b} \int_0^{X_{\epsilon}} \mathrm{d}x \sqrt{\frac{\varphi(x)}{x} - \epsilon} \,, \\ \tau(\epsilon) &= Z \, t_{\varepsilon 0} = \frac{b^{3/2}}{\sqrt{2}} \int_0^{X_{\epsilon}} \frac{\mathrm{d}x}{\sqrt{\varphi(x)/x - \epsilon}} \,. \end{aligned}$$

Eliminating ϵ from the dependences $\sigma(\epsilon)$ and $\tau(\epsilon)$, we obtain the function $\tau^{-1}(\sigma)$ shown in Fig. 15.

Thus, the algorithm for calculating $n_e(0, \infty)$ is as follows: first, the value of σ_n is determined for each *n* from the first expression in (4.18), then $\tau^{-1}(\sigma_n)$ is found, and summation over *n* is performed according to the second expression in (4.18). The results of calculations performed by this method for argon and mercury are presented in Table 2 and compared with calculations by the Hartree method [91].

The last column in Table 2 presents the electron density at zero calculated by the simple formula

$$n_{\rm e}(0,\infty) = \frac{Z^3 e^2}{\pi^2} \left(1.125 - 1.794 Z^{-2/3}\right),\tag{4.19}$$



Figure 15. The function $\tau^{-1}(\sigma)$ for a free hydrogen atom (Z = 1) in the TF model.

Z n _e	Hartree [91]	(4.18)	(4.19)
18	$3.83 imes 10^3$	3.83×10^3	$3.79 imes 10^3$
80	3.72×10^5	3.69×10^{5}	3.95×10^5

which is obtained assuming that an electron in the s-state moves in the effective potential $V_{l=0}(r) = V(r) + 1/(8r^2)$ with the centrifugal repulsive part. Then the region near the nucleus is classically forbidden, and the semiclassical wave function to the left of the left turning point decreases exponentially. Its square at zero is expressed through the semiclassical normalization factor as $|\Re_{n0}^{(sc)}(0)|^2 = Ze^2 |c_n|^2$. This gives the result

$$n_{\rm e}^{\rm (sc)}(0) = \frac{Ze^2}{\pi^2} \left(\left. \frac{\mathrm{d}\varepsilon_n}{\mathrm{d}n} \right|_{n=1} + \sum_{n=2}^{\varepsilon_n \leqslant \mu} \frac{\mathrm{d}\varepsilon_n}{\mathrm{d}n} \right) \tag{4.20}$$

for the density, which is $e^2/2\pi = 1.18$ times larger than that following from (4.16). We replace the sum in (4.20) by an integral, assuming that energy levels with n = 1, 2 are hydrogen-like, i.e., $\varepsilon_n = -Z^2/2n^2 - Z^{4/3}\varphi'(0)/b$. The substitution of the values of all quantities in the TF model leads to expression (4.19). For argon and mercury, this expression gives the respective error of the density calculation at zero equal to 1% and 6%.

Analysis shows that for $r \leq 1/Z$, we can approximately calculate the density by the expression

$$n_{\rm e}(r) = n_{\rm e}^{\rm (sc)}(0) \exp\left(-2Zr\right),$$
 (4.21)

while for distances r > 1/Z, the expressions in the TF model with oscillation correction (4.13) are valid. Figure 16 shows the radial electron densities at zero for compressed aluminum calculated in the TF model and by the method described above [39]. Figure 16 also presents the electron density distribution in a compressed aluminum crystal calculated in the model of attached plane waves (APWs) [94]. We can see from the figure that the results of our TF calculations of the electron density in the region of small distances $r \leq 1/Z$ and for $r \geq 1/Z$ smoothly join and agree well with precise APW calculations for a compressed aluminum crystal.

5. Thermodynamics of the electron component of plasma in the semiclassical approximation

In this section, we demonstrate the use of the TF model with the exchange, gradient, and shell corrections taken into account additively for calculating thermodynamic characteristics of a high-temperature plasma. The results of the TF model with these corrections for a weakly nonideal Boltzmann plasma agree well with the results of the Saha–Reiser model describing the plasma composition in the average-ion approximation. This agreement allows estimating the ionization potentials of ions theoretically, taking shell effects into account.

We preliminarily discuss the general form of corrections to the free energy using the density functional theory and present expressions for gradient corrections of different



Figure 16. Distribution of the radial electron density in an aluminum atom calculated using various models for different compression degrees. The radii of atomic cells from bottom up are R = 3, 1.8, 0.6, 0.3, and 0.18. Solid curves: the APW model [94], dashed-dotted curves: the TF model, dashed curves: the TF model with oscillation correction (4.13), triangles: expression (4.21).

orders for the density and energy in systems with different dimensions at zero and finite temperatures.

5.1 Semiclassical equation of state of the plasma in the Thomas–Fermi model

The semiclassical TF model of the equation of state of electrons, which is commonly used in the cell approximation [59], accounts for the spatial inhomogeneity, the interaction of electrons with the nucleus and between electrons, and the exchange, correlation, and degeneracy effects within a spherical Wigner–Seitz cell. The volume v and radius R of the cell in atomic units are determined from the mean density of matter: $v = 4\pi R^3/3 = 11.2M/\rho$ [g cm⁻³]. Because all matter is represented by a set of identical, independent, electrically neutral cells, which do not interact with each other, the calculation of thermodynamic properties of the electron properties in the cell. The contribution of ions to the equation of state is taken into account separately.

We present a set of formulas of the TF model for electrons in a neutral, spherical Wigner–Seitz cell with the nucleus charge $Z = N_e$. The free energy, internal energy, and pressure are described by the respective expressions

$$F_{\rm TF} = \frac{\sqrt{2}}{\pi^2} T^{5/2} v \Big[2I_{3/2} \big[\eta(1) \big] \\ + \int_0^1 \Big\{ 3\eta(x) I_{1/2} \big[\eta(x) \big] - 8I_{3/2} \big[\eta(x) \big] \Big\} x^2 \, \mathrm{d}x \Big], \quad (5.1)$$

$$E_{\rm TF} = \frac{\sqrt{2}}{\pi^2} T^{5/2} v \Big[2I_{3/2} \big[\eta(1) \big] - 3 \int_0^1 I_{3/2} \big[\eta(x) \big] x^2 \, \mathrm{d}x \Big],$$

$$P_{\rm TF} = \frac{2\sqrt{2}}{3\pi^2} T^{5/2} I_{3/2} \big[\eta(1) \big],$$
(5.2)

where the function

$$\eta\left(x = \frac{r}{R}\right) = \tilde{\eta}(r) = \frac{\mu - V(r)}{T} = \frac{Z}{RT} \frac{\varphi(x)}{x}$$

satisfies the Poisson equation with the boundary conditions at the cell center and the boundary *R*:

$$\begin{split} \Delta \tilde{\eta}(r) &= \frac{4\sqrt{2T}}{\pi} I_{1/2} \big[\tilde{\eta}(r) \big] \,, \quad r \tilde{\eta}(r) |_{r=0} = Z, \\ \frac{\mathrm{d} \tilde{\eta}(r)}{\mathrm{d} r} \bigg|_{r=R} &= 0 \,, \quad V(R) = 0 \,, \end{split}$$

while the electron density distribution inside the cell is described by expression (1.2).⁹

The TF model has the similarity property with respect to the atomic number Z. For example, the temperature, volume, chemical potential, pressure, and energy in the TF model have the following dependences on Z:

$$T^{(Z)} = Z^{4/3}T^{(1)}, \quad v^{(Z)} = Z^{-1}v^{(1)}, \quad \mu^{(Z)} = Z^{4/3}\mu^{(1)},$$
$$P^{(Z)} = Z^{10/3}P^{(1)}, \quad E^{(Z)} = Z^{7/3}E^{(1)}.$$
(5.3)

The semiclassical behavior condition is satisfied for matter with a high energy concentration, which provides the theoretically substantiated possibility of using the TF model in conjunction with the cell model for describing the thermodynamics of condensed matter at high pressures, $P \ge 1$. This model has always been used in the wide-range equations of state to describe the region of cold, strongly compressed matter [96, 97].

The semiclassical behavior parameter is also small at high temperatures $T \ge 1$ corresponding to the binding energy of outer-shell electrons and realized in a weakly nonideal Boltzmann plasma. However, the validity of the TF model for calculating the thermodynamic characteristics of high-temperature plasma [98] was critically evaluated in [99]. First, a comparison with the reference Saha model showed the absence of the correct high-temperature ideal-gas limit of the plasma ionization energy and noticeable deviations of the oscillating character in the degree of ionization and ionization energy. Second, the use of the cell approximation restricts the correlation radius by a half of the mean distance between ions, which does not allow obtaining the results in the Debye approximation for pressure in the case of a weakly nonideal plasma.

We show in Section 5.4 that the first group of these disadvantages is removed by introducing the shell and Scott (Sc) corrections. This also provides the correct ideal-gas limit for the ionization energy of the system, which is equal to the total electron binding energy in an atom, allowing the use of the improved TF model in the cell approximation for calculating the composition and equation of state of the ideal, not fully ionized plasma [52].

The passage to the non-cell modification of the TF model [100] gives the correct Debye asymptotic expressions, i.e., removes the second disadvantage pointed out above; however, this modification considerably complicates the model, and we therefore restrict ourselves here to the cell approximation. We note that the Debye asymptotic form can also be

⁹ A method for calculating the second derivatives of the free energy in the TF model was recently presented in [95].

obtained in the cell approximation, but with the ion Debye radius $D_i = (vT/4\pi z_{eff}^2)^{1/2}$. As is shown in paper [101], the ion Debye asymptotic form can be obtained by including the average-charge (z_{eff}) ion contribution to the free energy of the cell in the one-component plasma model, for example, in the approximation [102]

$$F_{\rm i} = -T \ln \left[ev \left(\frac{M T}{2\pi} \right)^{3/2} \right] + 0.9 \frac{z_{\rm eff}^2}{R} - \frac{z_{\rm eff}^2}{3} \left[D_{\rm i}^p + \left(\frac{10R}{27} \right)^p \right]^{-1/p}, \quad p = \frac{10}{7}.$$
 (5.4)

5.2 Density and thermodynamic corrections

We generalize expression (1.4) for the correction to the free energy at a small change in the density for a many-particle system of fermions in the density functional theory.

We consider a system of $N_{\rm e}$ interacting electrons in an external field $V_{\rm ext}(\mathbf{r})$ at temperature *T*. According to the Hohenberg–Kohn–Mermin [3] theory, the electron density functional $n(\mathbf{r})$ of the form

$$F[n] = K[n] + \int n(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) \,\mathrm{d}\mathbf{r} + \frac{1}{2} \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \,\mathrm{d}\mathbf{r} \,\mathrm{d}\mathbf{r}' + F_{\text{xc}}[n],$$
(5.5)

where K[n] and $F_{xc}[n]$ are the kinetic and exchange-correlation energy functionals, reaches a minimum, equal to the free energy F_e of the system, when its functional argument $n(\mathbf{r})$ coincides with the real equilibrium electron density $n_e(\mathbf{r})$ in the chosen external field $V_{ext}(\mathbf{r})$. The extremum condition for the functional F[n] for a fixed number of particles leads to the Euler–Lagrange equation

$$\frac{\delta K}{\delta n} = \mu - V(\mathbf{r}), \quad V(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, \mathrm{d}\mathbf{r}' + \frac{\delta F_{\text{xc}}}{\delta n},$$
(5.6)

where μ is a Lagrange multiplier — the chemical potential of the system.

Because the exact form of the functionals K[n] and $F_{xc}[n]$ is not known, various approximations are used. In this connection, the following is useful.

We assume that we know the solution $n_0(\mathbf{r})$, μ_0 , $V_0(\mathbf{r})$ of problems (5.5) and (5.6) with the approximate functional $F_0[n]$ and the small correction $\delta n(\mathbf{r}, \mu, T)$ to the electron density caused by some effect neglected in $F_0[n]$. Then, up to the terms quadratic in $\delta n(\mathbf{r}, \mu, T)$, the corresponding correction ΔF to the free energy $F_0[n]$ has a form [22, 23] similar to (1.4):¹⁰

$$\Delta F = -\int_{-\infty}^{\mu_0} \mathrm{d}\mu \int \delta n(\mathbf{r},\mu,T) \,\mathrm{d}\mathbf{r} = -\int_{-\infty}^{\mu_0} \Delta N(\mu,T) \,\mathrm{d}\mu \,. \tag{5.7}$$

The separation of the explicit temperature dependence allows expressing the free-energy correction in terms of corrections to the energy and the number of states at zero temperature:

$$\Delta F = -\int_{-\infty}^{\infty} \frac{\partial f((\mu - \mu_0)/T)}{\partial \mu} \Delta E(\mu, 0) \, \mathrm{d}\mu$$
$$= -\int_{-\infty}^{\mu_0} \frac{\pi \hat{k}_{\mu}}{\sinh(\pi \hat{k}_{\mu})} \, \Delta N(\mu, 0) \, \mathrm{d}\mu \,. \tag{5.8}$$

Here, the operator $\hat{k}_{\mu} = -iT\partial/\partial\mu$ is used and ΔN and ΔE are corrections to the number of states and energy due to the effect under study, neglecting the explicit temperature dependence, which are expressed in terms of the correction $\delta g(\mu)$ to the level density:

$$\Delta N(\mu, 0) = \int \delta n(\mathbf{r}, \mu, 0) \, \mathrm{d}\mathbf{r} = \int_{-\infty}^{\mu} \delta g(\mu') \, \mathrm{d}\mu',$$

$$\Delta E(\mu, 0) = \int_{-\infty}^{\mu} (\mu - \mu') \, \delta g(\mu') \, \mathrm{d}\mu'.$$
(5.9)

The temperature dependence in (5.8) enters implicitly through the potential $V_0(\mathbf{r})$, from which the corrections ΔE , δn , and δg are calculated.

We also discuss the procedure of a thermodynamically consistent derivation of expressions for pressure and internal energy corrections in the cell TF model based on (1.4) (see the details in [39, 51]), i.e., in the case where the density correction can be expressed only in terms of the characteristics obtained in the TF model.

The volume derivative of (5.7) is given by

$$\Delta P = -\frac{\partial \Delta F}{\partial v} = \frac{\partial \mu_{\rm TF}}{\partial v} \int \delta n(r, \mu_{\rm TF}) \, \mathrm{d}\mathbf{r} + \int_{-\infty}^{\mu_{\rm TF}} \mathrm{d}\mu' \int \frac{\partial \delta n(r, \mu')}{\partial v} \, \mathrm{d}\mathbf{r} + \int_{-\infty}^{\mu_{\rm TF}} \delta n(R, \mu') \, \mathrm{d}\mu'. \tag{5.10}$$

We use in calculations that the correction $\delta n(r, \mu')$ depends on the volume only through the potential $V_{\text{TF}}(r)$, which everywhere enters in the combination $\mu' - V_{\text{TF}}(r)$, and that the total change in the density $\delta n_{\text{tot}}(r)$ satisfies the normalization condition

$$\delta n_{\text{tot}}(r) = \frac{\partial n_{\text{TF}}(r)}{\partial \mu_{\text{TF}}} \left[\delta \mu - \delta V(r) \right] + \delta n(r), \quad \int \delta n_{\text{tot}}(r) \, \mathrm{d}\mathbf{r} = 0 \,.$$
(5.11)

Also using the Poisson equation and boundary conditions for the potential correction and differentiating the normalization condition in the TF model, we obtain the pressure correction

$$\Delta P = n_{\rm TF}(R)\,\delta\mu + \int_{-\infty}^{\mu_{\rm TF}} \delta n(R,\mu')\,\mathrm{d}\mu'\,. \tag{5.12}$$

The expression for the internal energy correction

$$\Delta E = \Delta F - T \frac{\partial \Delta F}{\partial T} = \Delta F$$

+
$$\int \left[\frac{3}{2} n_{\rm TF}(r) - \frac{\partial n_{\rm TF}(r)}{\partial \mu_{\rm TF}} \left(\mu_{\rm TF} - V_{\rm TF}(r)\right)\right] (\delta \mu - \delta V(r)) \, \mathrm{d}\mathbf{r}$$
(5.13)

is derived similarly using the explicit and implicit (through the potential $V_{\text{TF}}(r)$) temperature dependences of $n_{\text{TF}}(r)$ and $\delta n(r, \mu')$, the Poisson equation for the potential in the TF model and for the potential correction, and the Green's formula and the independence of the normalization condition from temperature.

¹⁰ The Strutinsky energy correction [71, 77, 103] describing the shell effect in a nucleus at zero temperature has a similar form in the treatment in [2]. But expression (5.7) can be used for calculating not only shell corrections but also any small corrections due to effects neglected in the original model.

5.3 Gradient corrections to the Thomas–Fermi model in systems of various dimensions

We consider the form of quantum gradient corrections in onedimensional, two-dimensional, and three-dimensional systems and discuss the possibility of their use for semiclassical calculations of the density and total energy of fermions.

Expressions for gradient corrections to the density can be obtained in the general case by the operator method [35, 104],¹¹ and in the case of separable variables, also from quantum corrections to the wave function [80].

The operator method is based on the first terms in the expansion of the distribution function [1], which give a second-order correction to the density and contain derivatives of the delta function:

$$f(\mathbf{r}, \mathbf{p}) = \theta(p_{\mu}^{2} - p^{2}) + \frac{1}{2} [\Delta p_{\mu}^{2} + 2i\mathbf{p}\nabla p_{\mu}^{2}] \,\delta'(p_{\mu}^{2} - p^{2}) + \frac{1}{3} [(\nabla p_{\mu}^{2})^{2} - 2(\mathbf{p}\nabla)^{2} p_{\mu}^{2}] \,\delta''(p_{\mu}^{2} - p^{2}) - \frac{(\mathbf{p}\nabla p_{\mu}^{2})^{2}}{2} \,\delta'''(p_{\mu}^{2} - p^{2}) + \dots$$
(5.14)

Table 3 presents second-order corrections to the spatial distribution density of fermions, $\delta_2 n_e(\mathbf{r})$, and to their total energy density, $\delta_2 \epsilon(\mathbf{r})$, for systems of dimension *D*, obtained from expressions (5.14), (5.7), and $n_e(\mathbf{r}) = 2 \int f(\mathbf{r}, \mathbf{p}) d^D p$, with $d^D p = d\mathbf{p}/(2\pi)^D$.

We can see from the table that the dependences of the correction on the density (Fermi momentum) in the onedimensional and three-dimensional cases are similar, but have different numerical coefficients. The terms with the Laplacian transform after spatial integration into surface integrals that are equal to zero for neutral systems, but they cause a divergence of the correction at zero in systems with a Coulomb singularity (see Section 6.2).

The second- and fourth-order gradient corrections to the kinetic energy density at finite temperatures for D = 3, expressed in terms of the electron density, are given by

$$\delta K_2(n_{\rm e},T) = -\frac{\pi^2 \sqrt{2}}{24T^{3/2}} \frac{\mathrm{d} \left[I_{-1/2}^{-1}(y) \right]}{\mathrm{d} y} \left(\nabla n_{\rm e} \right)^2 \tag{5.15}$$

and [106]

$$\delta K_4(n_e, T) = -\frac{\sqrt{2T}}{288\pi^2} I'_{1/2}(y) \left[\left(J_2^2 - \frac{3}{5} J_3 \right) (\Delta y)^2 + \frac{1}{4} \left(J_3^2 - \frac{1}{5} J_5 \right) (\nabla y)^4 + \left(J_2 J_3 - \frac{2}{5} J_4 \right) (\nabla y)^2 \Delta y \right].$$
(5.16)

The relation of y to the density n_e in expressions (5.15) and (5.16) is $n_e = \sqrt{2}T^{3/2}I_{1/2}(y)/\pi^2$. In (5.16), $J_k = I_{1/2}^{(k)}(y)/I_{1/2}'(y)$, where $I'_{1/2}(y)$ and $I_{1/2}^{(k)}(y)$ are the first and kth derivatives of the Fermi–Dirac function $I_{1/2}(y)$.

At zero temperature [35, 104],

$$\delta K_4(n_e, 0) = -\frac{n_e^{1/3}}{540(3\pi^2)^{2/3}} \times \left[\frac{1}{3}\left(\frac{\nabla n_e}{n_e}\right)^4 - \frac{9}{8}\left(\frac{\nabla n_e}{n_e}\right)^2 \frac{\Delta n_e}{n_e} + \left(\frac{\Delta n_e}{n_e}\right)^2\right].$$
 (5.17)

¹¹ The fourth-order gradient correction at zero temperature was obtained in these papers, long before paper [105] cited in [2]. **Table 3.** Second-order gradient corrections to the distribution density $\delta_2 n_e(\mathbf{r})$ and to the total electron energy density $\delta_2 \epsilon(\mathbf{r})$ in systems of dimension *D* at zero temperature.

D	$\delta_2 n_{\rm e}(\mathbf{r})$	$\delta_2 \epsilon(\mathbf{r})$
1	$\frac{1}{16\pi p_{\mu}^{5}} \left[\left(\nabla p_{\mu}^{2} \right)^{2} - \frac{4}{3} p_{\mu}^{2} \Delta p_{\mu}^{2} \right]$	$-\frac{\left(\nabla n\right)^2}{12n}-\frac{\Delta n}{6}$
2	$\frac{1}{12\pi} \Delta p_{\mu}^{2} \delta(p_{\mu}^{2}) + \frac{1}{24\pi} (\nabla p_{\mu}^{2})^{2} \delta'(p_{\mu}^{2})$	$-\frac{\pi(\nabla n)^2}{12}\delta(n)-\frac{\Delta n}{6}$
3	$-\frac{1}{96\pi^2 p_{\mu}^3} \left[(\nabla p_{\mu}^2)^2 - 4 p_{\mu}^2 \Delta p_{\mu}^2 \right]$	$\frac{\left(\nabla n\right)^2}{72n} - \frac{\Delta n}{12}$

For the two-dimensional system, as follows from Table 3, gradient corrections of all orders to the electron density are identically zero everywhere except at the system boundary. This is explained by the fact that in integrating distribution function (5.14) over momenta, the integrands are products of power-like functions and derivatives of delta functions, with the order of the derivatives always greater than the integer power.

The absence of quantum corrections of the standard form in the two-dimensional system, similar to corrections in the cases D = 1, 3, does not allow theoretical substantiation of taking them into account in a number of papers, for example, [107, 108]. The correct description of averaged characteristics obtained in these papers is probably explained by the inclusion of higher-order derivatives into the density equation: the higher their order is, the smoother the solution turns out to be. This also explains the successful inclusion of the fourth-order correction in [66, 69, 84], although this cannot be theoretically substantiated either, because accounting for this correction requires the simultaneous consideration of quantum corrections to the exchange energy, while this problem has not yet been solved.

5.4 Shell corrections at high temperatures

We use the TF model in the cell approximation to describe the thermodynamic properties of a Boltzmann plasma and show how shell effects can be taken into account based on this model [39, 40, 50, 51]. We emphasize that these effects are related to the temperature (thermal) ionization of bound electrons. We call the corresponding shell corrections the temperature corrections. The decay of temperature shell effects under compression and the effects caused by the redistribution of electrons under cold compression formulated in [1, 49] are considered separately in Section 6.

It was shown in Section 5.2 that the final result for corrections to pressure (5.12) and energy (5.13) contains corrections $\delta\mu$ and $\delta V(r)$ to the chemical and self-consistent potentials, and they can be determined by solving the corresponding Poisson equations. Such a solution for shell corrections at high temperatures showed that the main role of shell effects amounts to a shift of the chemical potential [39]; in other words, the integral contribution of terms with the correction $\delta V(r)$ is much smaller than that of terms with the correction $\delta\mu$. In addition, the second term in expression (5.12) for the shell correction to pressure and the first term in expression (5.13) for the energy correction are negligibly small at high temperatures. As a result, all the shell corrections to pressure and internal energy can be approximately expressed in terms of the correction to the chemical potential, which is calculated from the characteristics of the TF model,

$$\Delta E_{\rm sh} = \left[\frac{3}{2} Z - \int \frac{\partial n_{\rm TF}(r)}{\partial \mu} \left(\mu_{\rm TF} - V_{\rm TF}(r)\right) d\mathbf{r}\right] \delta \mu_{\rm sh},$$

$$\Delta P_{\rm sh} = n_{\rm TF}(R) \,\delta \mu_{\rm sh},$$

(5.18)

$$\delta\mu_{\rm sh} = -\Delta N_{\rm sh}(\,\mu_{\rm TF}) \left\{ \int \frac{\partial n_{\rm TF}(r)}{\partial \mu} \, \mathrm{d}\mathbf{r} \right\}^{-1}.$$
(5.19)

The correction $\Delta N_{\rm sh}(\mu, T)$ to the number of states must therefore be calculated. Because this requires knowing the spectrum of one-particle states, we use the results obtained in Section 4.1, where the features of energy spectra were considered for the two types of central attraction potentials [60].

In the semiclassical approximation, the one-particle energy levels ε_{nl} in the self-consistent central potential $V_{\text{TF}}(r)$ of an atomic cell are determined from quantization condition (4.1) with $n_{\text{r}} = n - l - 1$. The leading contribution to the number of states with $\mu < \mu_{\text{TF}}$ for a Boltzmann plasma $(\mu_{\text{TF}} < 0, |\mu_{\text{TF}}|/T \ge 1)$ gives the discrete spectrum

$$N(\mu, T) = 2\sum_{n,l} (2l+1) f\left(\frac{\varepsilon_{nl} - \mu}{T}\right).$$
 (5.20)

The difference between (5.20) and the number of states in the TF model,

$$\Delta N(\mu, T) = N(\mu, T) - N_{\rm TF}(\mu, T), \qquad (5.21)$$

must contain the shell correction, but can also include other corrections, as we show below.

To pass from sums over quantum numbers *n* and *l* in (5.20) to integrals, we use Poisson formula (2.6) and change the variables $n \rightarrow \varepsilon$ in the obtained integral over *n*:

$$\int_{1-\epsilon} \dots \, \mathrm{d}n = \int_{\tilde{\varepsilon}_{10}}^{\infty} \dots \frac{\partial n(\varepsilon, l)}{\partial \varepsilon} \, \mathrm{d}\varepsilon \, .$$

We consider the lower limit in the integral over energy ε . Obviously, the exact value of the lowest energy level for n = 1is $\varepsilon_{10} = -Z^2/2 + C$, where C = const. A value $\epsilon < 1$, required to avoid the restriction on the integration interval of the delta function in the Poisson formula, shifts this energy down to $\tilde{\varepsilon}_{10}$, while still preserving its finite value. We rewrite (5.20), adding and subtracting the integration region from $-\infty$ to $\tilde{\varepsilon}_{10}$ in the energy integral,

$$N(\mu, T) = 2\sum_{k,s} \left\{ \int_{-\infty}^{\infty} - \int_{-\infty}^{\tilde{\varepsilon}_{10}} \right\} f\left(\frac{\varepsilon - \mu}{T}\right)(\dots) \, \mathrm{d}\varepsilon \,.\,(5.22)$$

Here and hereafter, we use the notation

$$(\ldots) = \int_{-\epsilon'} (2l+1) \frac{\partial n(\varepsilon,l)}{\partial \varepsilon} \cos \left[2\pi \left(kn(\varepsilon,l) + sl \right) \right] \mathrm{d}l.$$

Separating the term in the sum with k = s = 0 in the first integral in the right-hand side of (5.22) and differentiating quantization condition (4.1) to determine the derivative $\partial n(\varepsilon, \lambda)/\partial \varepsilon$, we can easily see that this term is exactly equal to the number of states in the TF model. Hence, the sought correction (5.21) is equal to (5.22) without this term, and is the

sum of two integrals

$$\Delta N(\mu, T) = 2 \left\{ \int_{-\infty}^{\infty} \sum_{k,s}^{\prime} - \int_{-\infty}^{\tilde{\epsilon}_{10}} \sum_{k,s} \right\} f\left(\frac{\varepsilon - \mu}{T}\right)(\ldots) d\varepsilon$$
$$= \Delta N_{\rm sh} + \Delta N_{\rm Sc} \,. \tag{5.23}$$

The energy spectrum of one-particle states in the TF model extends from $-\infty$ to $+\infty$; therefore, the first integral describes the difference between the TF model and the model taking the discreteness of the spectrum of bound states in this energy range into account. We take it as the definition of the shell correction to the number of states.

To elucidate the nature of the second integral, we substitute the total correction (5.23) in expression (5.7) for the correction to the free energy and obtain two terms:

$$\Delta F = -2 \int_{-\infty}^{\mu_{\rm TF}} \left\{ \int_{-\infty}^{\infty} \sum_{k,s}^{\prime} - \int_{-\infty}^{\tilde{\varepsilon}_{10}} \sum_{k,s} \right\}$$
$$\times f\left(\frac{\varepsilon - \mu^{\prime}}{T}\right)(\ldots) \,\mathrm{d}\varepsilon \,\mathrm{d}\mu^{\prime} = \Delta F_{\rm sh} + E_{\rm Sc} \,. \tag{5.24}$$

The first term is equal to the shell correction to the free energy in our definition, while the second term is the so-called Scott correction $E_{Sc} = Z^2/2$ [44–47]. This correction is calculated by returning to the variable *n*, converting the sums of cosines into delta functions, and taking the Coulomb type of the spectrum in this energy region into account, $\varepsilon_{nl} = -Z^2/2n^2 + C$. The principal quantum number n = 0 corresponds to the energy $\varepsilon_{nl} = -\infty$. Hence, the Scott correction compensates for the partially accounted for nonphysical state with n = 0 in expressions for the free energy in the TF model and for the shell correction to it.

In the high-temperature case considered above, the Scott correction is a constant, independent of temperature and density. In Section 6.2, we present a more general derivation of the expression for this correction and show that it depends on the density in the limit of strongly compressed cold matter, while its physical meaning is related to the problem of the inapplicability of the semiclassical approximation near the nucleus (the Coulomb center).

We return to the discussion of the 'high-temperature' shell correction. To calculate it, we integrate the energy integral in the first term in (5.23) by parts. The term outside the integral is zero, and we therefore have

$$\Delta N_{\rm sh}(\mu, T) = -\sum_{k,s}^{\prime} \frac{(-1)^s}{\pi k} \int_{-\infty}^{\infty} \frac{\mathrm{d}f\left((\varepsilon - \mu)/T\right)}{\mathrm{d}\varepsilon}$$
$$\times \int_{0}^{\lambda_{\varepsilon}^2} \sin\left[2\pi(kn_{\varepsilon\lambda} + s\lambda)\right] \mathrm{d}\lambda^2 \,\mathrm{d}\varepsilon. \tag{5.25}$$

Taking the dependence of the derivative of the function $f((\varepsilon - \mu)/T)$ into account, we can see that the leading contribution to the energy integral is made by the vicinity of the point $\varepsilon = \mu \le \mu_{\text{TF}}$. For high temperatures and low densities, this corresponds to the energy region of deep shells. The spectra of these shells were considered in Section 4.2 (also see Fig. 5). In this case, the sum over *l* can be replaced by the integral, resulting in the consideration of only the term with s = 0 in the sum over *s*. The discreteness of *n* is taken into account via the sum over $k \neq 0$.

In a more general case, for energies in the spectrum at which the occupation of a new *n*th shell begins when the (n-1)th shell is incomplete, the quantum numbers *n* and *l* are

equivalent, and this situation can be successfully described only if the corresponding interference is taken into account, i.e., both sums in (5.25) are completely preserved. Such an approach was used, for example, to calculate the shell correction to the electron binding energy in a free atom [12, 13]. However, in the general case, the problem of separating the oscillating dependence from a double infinite sum of the obtained Fresnel integrals is rather complicated, and the approach loses the simplicity inherent in the TF method. Instead of (5.25), we can then write the simplified expression

$$\Delta N_{\rm sh}(\mu, T) = -\sum_{k=1}^{\infty} \frac{2}{\pi k} \int_{-\infty}^{\infty} \frac{\mathrm{d}f((\varepsilon - \mu)/T)}{\mathrm{d}\varepsilon} \\ \times \int_{0}^{\lambda_{\varepsilon}^{2}} \sin\left(2\pi k[v_{\varepsilon\lambda} + \lambda]\right) \mathrm{d}\lambda^{2} \,\mathrm{d}\varepsilon, \qquad (5.26)$$

where the quantization condition $S_{\varepsilon\lambda} = \pi v_{\varepsilon\lambda} = \pi [n_{\varepsilon\lambda} - \lambda]$ is used for Coulomb potentials.

Another variant of the derivation of similar relations is based on the form of the squared modulus of the radial wave function in the lowest semiclassical approximation and the corresponding electron density (4.10). Applying the Poisson formula and restricting ourselves to the term s = 0 in the sum over *s*, we use (4.10) to obtain the shell correction to the density

$$\Delta n_{\rm sh}(r) = \frac{1}{2\pi^2 r^2} \sum_{k}^{\prime} \int_{-V(r)}^{\infty} f\left(\frac{\varepsilon - \mu}{T}\right) \\ \times \int_{0}^{\lambda_{\varepsilon}^2} \frac{\cos\left(2\pi k [v_{\varepsilon\lambda} + \lambda]\right)}{p_{\varepsilon\lambda}(r)} \, \mathrm{d}\lambda^2 \, \mathrm{d}\varepsilon \,.$$
(5.27)

Integrating by parts in the energy integral and taking into account that $\cos (2\pi k [v_{\epsilon\lambda} + \lambda])$ is a rapidly oscillating function, we can segregate the leading term in the semiclassical behavior parameter, containing, as in (5.25), the derivative of $f(\epsilon)$ in the integrand.

It was shown in Section 4.2 that the dependence of $v(\varepsilon, \lambda)$ on λ is quadratic in a rather broad spectral range and is linear down to the deepest energy levels. If the quadratic dependence of $v(\varepsilon, \lambda)$ on λ is valid in the entire range $0 \le \lambda \le \lambda_{\mu}$, then the equality

$$S_{\mu} = \pi \lambda_{\mu} + \frac{1}{2} \, \delta_{\mu}^{0} \lambda_{\mu}^{2}, \quad \delta_{\mu}^{0} = -\pi v_{\mu}''(0)$$
(5.28)

must be satisfied, which relates the action S_{μ} at the zero momentum to the maximum orbital momentum λ_{μ} .

Figure 17 demonstrates the temperature range where the linear dependence is applicable and shows the region of applicability of quadratic formulas (4.8) and (5.28). In the linear dependence range, where the potential coincides with the Coulomb potential up to a constant, it follows from (5.26) that

$$\Delta N_{\rm sh}(\mu, T) = 4\lambda_{\mu}^{2} t_{\mu} T \sum_{k=1}^{\infty} \frac{\sin(2kS_{\mu})}{\sinh(2\pi k t_{\mu} T)} \,.$$
(5.29)

Integrating (5.27) over the cell volume, we obtain the expression

$$\Delta N_{\rm sh}(\mu, T) = 8T \left[\int_0^{R_{\mu}} p_{\mu}(r) r^2 \, \mathrm{d}r \right] \sum_{k=1}^{\infty} \frac{\sin\left(2kS_{\mu}\right)}{\sinh\left(2\pi kt_{\mu}T\right)} \,,$$
(5.30)



Figure 17. Radial action S_{μ} (solid curve) of an electron with energy equal to the chemical potential in comparison with the linear $\pi \lambda_{\mu}$ (dashed curve) and quadratic $\pi \lambda_{\mu} + 0.5 \delta_{\mu}^{0} \lambda_{\mu}^{2}$ (dashed-dotted curve) functions of the orbital moment λ_{μ} at different temperatures in iron plasma with density $\rho = 10^{-4} \text{ g cm}^{-3}$.

which differs in its form from (5.29). However, the relations

$$S_{\mu} = \frac{\pi Z}{\sqrt{2|\mu|}}, \quad t_{\mu} = \frac{\partial S_{\mu}}{\partial \mu} = \frac{\pi Z}{(2|\mu|)^{3/2}},$$

$$\pi \lambda_{\mu} = S_{\mu}, \quad \frac{\partial(\pi \lambda_{\mu})}{\partial \mu} = t_{\mu}$$

(5.31)

are valid for the Coulomb potential, and it can be easily shown that expressions (5.29) and (5.30) are identical.

We analyze the high-temperature asymptotic form of the shell correction. The sum $\sum_{k} [\sin(ak)/\sinh(bk)]$ in (5.29) and (5.30) can be calculated analytically under the conditions $a < 1.6\pi$, a/b > 10 by replacing it with an integral using the Euler formula. In this case of very high temperatures, the shell correction to the number of states is given by

$$\Delta N_{\rm sh}(\mu, T) = \lambda_{\mu}^{2} \left(\tanh \frac{S_{\mu}}{2t_{\mu}T} - \frac{2S_{\mu}}{\pi} \right) \rightarrow \frac{Z^{2}}{2|\mu|},$$

$$\mu = -T \ln \left[\frac{v}{Z\sqrt{2}} \left(\frac{T}{\pi} \right)^{3/2} \right].$$
(5.32)

It follows from (5.32) that the shell correction in the hightemperature limit has the first order in the semiclassical behavior parameter [see (5.3)]: $\Delta N_{\rm sh}/Z \sim Z^{-1/3}$, similarly to the Scott correction.

The inclusion of both these corrections (shell and Scott) in the TFC model not only leads to the correct value of the ionization energy limit for Boltzmann plasma at very high temperatures but also describes the step-like temperature dependences of the degree of ionization and ionization energy for the ideal plasma. This is illustrated well in Fig. 18, which presents the results of calculations of the thermal and caloric equations of states for high-temperature iron plasma in the TF model, with or without the shell and Scott corrections, in comparison with calculations using the semiempirical Saha–Reiser model [109]. The good agreement between semiclassical results and the results obtained in this



Figure 18. High-temperature part of the dependence of (a) the number of ionized electrons *z* and (b) the ionization energy Q = E - 3Pv/2 on temperature in iron plasma with the ion density $n_i = 10^{18}$ cm⁻³ calculated using different models: curve *I* with white dots: the TFC model, curve *2*: the Saha–Raizer model [109], curve *3* with crosses: the TFC model [109] taking the shell and Scott corrections into account, tringles are calculations by the modified Hartree–Fock–Slater model [110].

model underlies the 'hot' method for estimating ionization potentials of free ions, which is considered in Section 5.5.

Expression (5.26) can also be integrated analytically in a more general case of not very high temperatures, at which quadratic dependences (4.8) and (5.28) are valid. As a result, the compact expression

$$\Delta N_{\rm sh}(\mu, T) = \frac{2}{\pi \delta_{\mu}^{0}} \sum_{k=1}^{\infty} \left[\frac{k X_{\lambda}}{\sinh(k X_{\lambda})} \cos(2\pi k \lambda_{\mu}) - \frac{k X_{S}}{\sinh(k X_{S})} \cos(2k S_{\mu}) \right] \frac{1}{k^{2}}, \qquad (5.33)$$

$$X_S = 2\pi t_\mu T, \quad X_\lambda = 2\pi \, rac{\partial \pi \lambda_\mu}{\partial \mu} \, T$$

is obtained, which contains only the characteristics of electron motion with the energy equal to the chemical potential μ of the system with zero (the s-state) and maximal orbital moments λ_{μ} corresponding to linear trajectories (with reflection from the center) and circular trajectories. As $\delta_{\mu}^{0} \rightarrow 0$, expression (5.33) transforms into (5.29).

Shell correction (5.33) depends on the semiclassical behavior parameter nonanalytically, as $\cos(a/\xi)$, and the oscillation amplitude at low temperatures has the same order ξ^2 as the quantum-exchange correction. At very high temperatures, the shell correction, as shown above, becomes a first-order correction (~ ξ).

5.5 'Hot' method for estimating the ionization potentials of ions

The number of ionized electrons in a statistical model is determined in terms of the electron density at the boundary of an atomic cell and, in view of the asymptotic form of the Fermi–Dirac function for the Boltzmann plasma, is given by

$$z = n_{\rm e}(R) v = \frac{T^{3/2}}{\sqrt{2\pi^3}} \exp\left(\frac{\mu}{T}\right) v.$$
 (5.34)

A comparison of this expression with the corresponding formula in the Saha–Reiser model [109] for the classical plasma in the average-ion approximation gives the relation

$$\mu_z = -I_z \,, \tag{5.35}$$

between the chemical and ionization potentials. We note that the values $\mu = \mu_{z+1/2}$ shifted by 1/2 in z should be used in (5.34), which agrees with similar relations for ions with different charges at zero temperature (see Section 3.1).

The calculation of the chemical potential in the refined TF (RTF) model

$$\mu_{\rm RTF}(T) = \mu_{\rm TF} + \delta \mu_{\rm qu-ex} + \delta \mu_{\rm sh}$$

and of the corresponding quantity $z_{RTF}(T)$ via (5.34), after elimination of the temperature dependence, allows determining the function $\mu_{RTF}(z_{RTF})$. Using relation (5.35) between potentials and taking the shift into account, we can then calculate the corresponding ionization potentials. The results of such calculations are presented in Fig. 19 for aluminum and uranium ions. We can see from this figure that the introduction of the shell correction into the statistical model allows reproducing shell oscillations in the dependence of the ionization potentials of ions on their charge quite accurately.

The above method for calculating ionization potentials in terms of the chemical potential is called the 'hot' method, in contrast to the known 'cold' method for calculating the ionization potentials of ions in the TF [8, 9] and TFC [14–16] models, which was considered in Section 3.1.

6. Wide-range equation of state of matter

In this section, the semiclassical equation of state for the electron component of matter is generalized to the case of degenerate matter. A consistent quantum mechanical correction of the statistical TF model in the vicinity of nuclei gives an everywhere finite expression for the lowest quantum correction to the free energy and an expression for the modified Scott correction. In an limit of strongly compressed



Figure 19. Ionization potentials of free (a) aluminum and (b) uranium ions as functions of the charge in the 'hot' semiclassical model (solid curve). Symbols are empirical data [82] for aluminum and quantum mechanical calculations for uranium.

matter, these corrections provide an agreement between the results of the statistical model and the perturbation theory.

The refined TF model obtained by incorporating the corrections described above retains the self-similarity property. Hence, the data tabulated for hydrogen allow calculating the thermodynamic characteristics of matter with high energy density in the applicability range of the ionization equilibrium model and the TFC model, as well as in the intermediate range between them.

6.1 Generalized quantization condition

It was shown in Section 5 that to calculate the shell correction, it is necessary to know the classical characteristics (momentum, action, time, and the maximal orbital momentum) of an electron with the energy equal to the chemical potential μ_{TF} in the self-consistent potential $V_{\text{TF}}(r)$.

The chemical potential of electrons in the Boltzmann plasma is negative (the potential at the boundary of an atomic cell is set equal to zero, $V_{\text{TF}}(R) = 0$) and the electron energy is located in the region of the discrete spectrum of strongly bound states and is determined by Bohr–Sommerfeld quantization condition (4.1). As the temperature of the electron system decreases or its density increases, the chemical potential of the system falls into the region of bound states in the band spectrum.

If the discrete energy levels of bound electrons did not broaden with compression, forming energy bands, passing to a continuum spectrum would result in drastic features in the thermodynamic characteristics, including phase transitions, as predicted in [1, 49]. The presence of the intermediate band region between discrete and continuum spectra considerably levels these effects. In what follows, we describe the intermediate band region using the model quantization condition.

The problem of calculating the band spectrum $\varepsilon_{nlm}(\kappa)$ of a compressed crystal was first formulated in Gandelman's papers (see [111] and the references therein). In these pioneering papers, a crystal was considered in the Wigner–Seitz cell approximation and conditions for the Bloch wave functions and their derivatives at the boundaries of the cell were written taking the crystal periodicity into account.

The model quantization condition

$$\begin{split} \tilde{S}_{\varepsilon l} &= \pi \left(n - l - \frac{1}{2} \right) - (-1)^{l} \arcsin \left[\tan \Delta_{\varepsilon l} \cos \left(\pi \frac{\kappa}{\kappa_{0}} \right) \right], \\ (6.1) \\ \tilde{S}_{\varepsilon l} &= S_{\varepsilon l} + \frac{d_{\varepsilon l}^{2}}{4} \ln \frac{|d_{\varepsilon l}^{2}|}{2e} + \frac{1}{2} \arg \Gamma \left(\frac{1 - i d_{\varepsilon l}^{2}}{2} \right), \\ \Delta_{\varepsilon l} &= \frac{\pi}{8} + \frac{1}{2} \arctan \left[\tanh \frac{\pi d_{\varepsilon}^{2}}{4} \right], \\ d_{\varepsilon l}^{2} &= \frac{p_{\varepsilon l}^{2}(R) R^{2}}{\beta_{l}^{1/2}} - \frac{(l + 1/2)^{2}}{\beta_{l}^{3/2}}, \ \beta_{l} = 4\pi n_{c}(R) R^{4} - 3(l + 1/2)^{2}, \\ \kappa_{0} R &= 2.418, \quad 0 \leq \kappa \leq \kappa_{0}, \end{split}$$

was constructed using the same method for the description of matter as in [111, 112] and the solution for a one-dimensional crystal (see Appendix B). Quantization condition (6.1) describes the discrete, band, and continuum spectra. Not aspiring to a high quantitative accuracy in the description of the band spectrum, this condition correctly reflects all the features of the spectrum and has the following properties:

(i) For a strong coupling, it transforms into Bohr– Sommerfeld quantization condition (4.1) with an exponentially small level-band width;

(ii) for sufficiently high energies, this condition describes the continuum spectrum;

(iii) for small quasimomenta κ , the energy $\varepsilon_{nl}(\kappa)$ quadratically depends on κ as $\varepsilon_{nl}(\kappa) = \varepsilon_{nl}(0) + \alpha_{nl}\kappa^2$.

Figure 20 illustrates the qualitative agreement of the electronic spectra calculated by (6.1) with these spectra calculated using the band Gandelman model [111].

To describe shell effects taking the band structure of the spectra into account, we represent the number of states, unlike in (5.22), in the form

$$N(\mu,T) = \frac{2}{\kappa_0} \int_0^{\kappa_0} \sum_{n,l} (2l+1) f\left(\frac{\varepsilon_{nl}(\kappa) - \mu}{T}\right) \mathrm{d}\kappa \,. \tag{6.2}$$

Here, we assume for simplicity that the band occupation with respect to the quasimomentum corresponds to the onedimensional case. Because the spectrum strongly depends on the orbital momentum parity, the sums over even and odd *l*



Figure 20. Electronic spectrum of iron for the compression degree $\sigma = 4.3$ at T = 0. Calculations of $\varepsilon_{nlm}(\kappa)$ in the band Gandelman model [111]: dashed curves; calculation of $\varepsilon_{nl}(\kappa)$ by expression (6.1): solid curves.

are considered separately. Using the Poisson formula for the sum over n, after simple transformations (see the details in [39]), we obtain the expression

$$N(\mu, T) = 2 \sum_{k=-\infty}^{\infty} \sum_{l} (2l+1)$$

 $\times \int f\left(\frac{\varepsilon_{nl} - \mu}{T}\right) \cos\left[2k\left(\tilde{S}_{\varepsilon l} + \pi(l+1/2)\right)\right] \Psi_k(\varphi_{\varepsilon l}) \,\mathrm{d}n\,,\,(6.3)$
 $\Psi_0(\varphi) = 1\,,$
 $\Psi_{k>0}(\varphi) = \frac{(-1)^k}{2} \left[P_k(2\varphi^2 - 1) - P_{k-1}(2\varphi^2 - 1)\right],$

where $\varphi_{\epsilon l} = \tan \Delta_{\epsilon l}$ and $P_k(x)$ is the Legendre polynomial of order k. The formula for the number of states with the band structure of the spectrum neglected, i.e., according the Bohr– Sommerfeld quantization condition (4.1), differs from (6.3) only by the absence of the factor $\Psi_k(\varphi_{\epsilon l})$, which accounts for the influence of the broadening of levels to bands under compression.

The value of Δ_{el} changes from zero in the discrete spectrum region to $\pi/4$ in the continuum spectrum region (Fig. 21). Because $\Psi_k(\varphi \to 0) \to 1$ and $\Psi_k(\varphi \to 1) \to 0$, the maximum contribution to the shell correction is made by the discrete spectrum. The continuum spectrum does not make



Figure 21. Dependences of the functions $\Delta_{\varepsilon 0}$ (dashed-dotted curve), $\varphi_{\varepsilon 0} = \tan \Delta_{\varepsilon 0}$ (dashed curve), and $\partial \Delta_{\varepsilon 0} / \partial \varepsilon$ (solid curve) for the s-state.

any contribution to the shell correction, and an intermediate energy region $(-\sqrt{\pi n_e(R)} < \varepsilon < \sqrt{\pi n_e(R)}$ for l = 0) exists between these two regions in which the role of shell effects gradually decreases. In [1, 49], the width of this region was set equal to zero, i.e., it was assumed that the discrete and continuum spectra are separated by a sharp boundary. Under this assumption, the function $\Psi_{k>0}(\varphi_{\varepsilon})$ has the shape of the step-like Heaviside function, whose derivative is the delta function, and all the dependences in the model constructed in this way turn out to be very sharp. This disadvantage of the model in [49] can be eliminated using generalized quantization conditions (6.1).

We also note semiclassical calculations [113, 114] in which the influence of the discreteness of spectra on thermodynamic quantities was studied taking the band broadening into account in the model proposed in [115]. In that case, the parameter of the problem was the boundary ε_0 of the spectrum above which the continuum spectrum was assumed. The advantage of our approach is the absence of such a parameter and the physical clarity of expressions obtained.

Separating the Thomas–Fermi term from expression (6.3), passing to the energy integral, and integrating by parts, we write the shell correction to the number of states as the sum of two terms:

$$\Delta N_{\rm sh}^{\mu} + \Delta N_{\rm sh}^{0} = -\frac{2}{\pi} \sum_{k=1}^{\infty} \frac{1}{k} \int_{-\infty}^{\infty} d\varepsilon \int \sin\left[2k(\tilde{S}_{\varepsilon\lambda} + \pi\lambda)\right] \\ \times \left[\Psi_k \frac{\partial f}{\partial \varepsilon} + f \frac{\partial \Psi_k}{\partial \varepsilon}\right] d\lambda^2.$$
(6.4)

Here, as in Section 5.4, the sum over l is replaced by an integral. As a result, the first term gives an expression for the 'temperature' shell correction:

 $\Delta N^{\mu}_{
m sh}$

$$= \frac{2}{\pi \delta_{\mu}} \sum_{k=1}^{\infty} \left[\frac{k X_{\lambda}}{\sinh(k X_{\lambda})} \cos(2\pi k \lambda_{\mu}) - \frac{k X_S}{\sinh(k X_S)} \cos(2k S_{\mu}) \right] \\ \times \frac{\Psi_k(\varphi_{\mu 0})}{k^2} , \qquad (6.5)$$

which coincides with (5.33) in the Boltzmann plasma region, where $\Psi_k(\varphi_{\mu 0}) = 1$. This function tends to zero when the chemical potential is in the region of positive energies, and therefore describes the decay of temperature oscillations typical for a nondegenerate plasma in passing to degenerate matter. The superscript $\mu \ln \Delta N_{\rm sh}^{\mu}$ means that all the quantities entering (6.5) are calculated for the energy equal to the chemical potential.

An analysis of the second term in (6.4), taking the form of the derivative $\partial \Delta_{\varepsilon 0}/\partial \varepsilon$ into account (Fig. 2), together with the expansion of the integrand at the extremum $\varepsilon = 0$, leads to the expression

$$\Delta N_{\rm sh}^{0} = \frac{f(-\mu/T)}{2\delta_0} \sum_{k=1}^{\infty} \left[\frac{\cos\left(2kS_0\right)}{\cosh\left(kX_S^0\right)} - \frac{\cos\left(2\pi k\lambda_0\right)}{\cosh\left(kX_\lambda^0\right)} \right] \\ \times \frac{\partial \Psi_k(\varphi_{00})}{\partial A_0} \frac{1}{k^2} , \qquad (6.6)$$

$$X_{\mathcal{S}}^{0} = 2 \,\tilde{t}_{0} \sqrt{\pi n_{\mathrm{e}}(R)} \,, \quad X_{\lambda}^{0} = 2 \frac{\partial(\pi \lambda_{\varepsilon})}{\partial \varepsilon} \bigg|_{\varepsilon=0} \sqrt{\pi n_{\mathrm{e}}(R)} \,,$$

where the superscript 0 indicates that the momentum, action, motion time, and maximal orbital moment of an electron are calculated for zero energy. For the Boltzmann plasma, the value of (6.6) is exponentially small because of the factor $f(-\mu/T)$. In the opposite limit case of degenerate matter, $f(-\mu/T) \rightarrow 1$ and (6.6) describes oscillations due to the extrusion of the discrete shell to the continuum spectrum. Numerical estimates give values of X_S^0 and X_λ^0 certainly greater than unity, which corresponds to a very small oscillating addition ($\leq 1\%$) to all thermodynamic quantities in the TF model at T = 0. This is also confirmed by calculations in the cell Hartree–Fock–Slater model [110].

We note that although the role of shell effects in the equation of state of strongly compressed matter, predicted in [1, 49], proved to be grossly overestimated, these papers stimulated interest in more accurate calculations of the equation of state of matter in the entire compression range. For example, the calculations in [94, 116–119] revealed weak pressure oscillations with respect to the results of the statistical model (Fig. 22), which the authors explained by a redistribution of electrons among bands under compression.

It follows that 'temperature' shell effects in plasma caused by the successive thermal ionization of inner electron shells are most important; the characteristic oscillations of Hugoniot curves with respect to results of the TFC model are related precisely to them (see Fig. 25). These conclusions agree with the investigations in [113, 114].

6.2 Correction of the statistical model of matter in the vicinity of nuclei

The violation of semiclassical behavior condition (1.1) in the vicinity of nuclei leads to a number of consequences. First, the integral energy characteristics in the TF model are greatly overestimated; second, the volume integrals through which gradient (quantum) corrections to these quantities are expressed diverge at r = 0; and, third, in regions of superhigh compressions or temperatures with the chemical potential $|\mu| > Z^2$, the results differ from those obtained in the perturbation theory, which is valid in these regions [1, 99].

We show how these disadvantages of the semiclassical model can be eliminated by correcting the expression for the lower-order quantum gradient correction $\delta_2 A$ to any physical



Figure 22. Dependence of the relative pressure on the relative size of a crystal cell. Comparison of pressures in compressed aluminum calculated using the APW, TFC, and TFD models at T = 0 [94].

quantity A [41–43]. For this purpose, the correction to the level density in the TF model is calculated:

$$\delta g(\mu') = \frac{1}{(2\pi)^3} \int \left[\delta \left(\mu' - \frac{1}{2} \left(\hat{\mathbf{p}} - \mathbf{i} \nabla \right)^2 + V(\mathbf{r}) \right) - \delta \left(\mu' - \frac{p^2}{2} + V(\mathbf{r}) \right) \right] d\mathbf{r} d\mathbf{p}, \qquad (6.7)$$

which is involved, in particular, in expression (5.9). Here, $\hat{\mathbf{p}}$ is the momentum operator and the gradient acts only on $V(\mathbf{r})$.

We next use the fact that in a small vicinity of the nucleus $r < r_0$, where semiclassical behavior condition (1.1) is violated, the potential $V(\mathbf{r})$ virtually coincides with the Coulomb potential. Along with the initial problem, we then solve an auxiliary Coulomb problem (with the relevant quantities indicated by a tilde), assuming that electrons interact only with the nucleus. The corrected quantity

$$\delta A^{\,c} = \delta_2 A - \delta_2 \tilde{A} + \delta \tilde{A} \tag{6.8}$$

is then finite everywhere and is equal to the exact solution of the Coulomb problem for $r < r_0$ and to the original value $\delta_2 A$ at distances $r > r_0$, where the semiclassical approximation is valid by the definition of r_0 .

Next, the standard method for expanding a function of the sum of operators is used [35]. The expansion in gradients in (6.7) through the second order and the use of (5.9) give the lowest quantum correction to the energy in the original problem:

$$\Delta_2 E(\mu') = -\frac{1}{6\pi} \int p_{\mu'} n_{\rm TF}(\mathbf{r},\mu') \,\mathrm{d}\mathbf{r} + \inf_1 + \inf_2 \,, \qquad (6.9)$$

where n_{TF} is the electron density in the TF model, the infinite quantity inf₁ is a diverging integral over a surface of an infinitely small radius surrounding the point r = 0, and the divergence inf₂ is related to the density of the point-like nuclear charge entering the TF equation.

For the auxiliary Coulomb problem, the expression

$$\Delta_2 \tilde{E}(\mu') = \inf_1 + \inf_2 + \frac{Z}{6\pi} \sqrt{2\mu'} \,\theta\left(\mu'\right) \tag{6.10}$$

is similarly obtained with the same infinite quantities \inf_1 and \inf_2 . Here, $\theta(x)$ is the step-like Heaviside function.

The exact solution of the auxiliary problem is considered separately for continuum and discrete spectra. In the discrete spectrum region ($\mu < 0$), the obvious expression

$$\tilde{g}(\mu') = \sum_{n=1}^{\infty} n^2 \,\delta(\mu' - E_n), \quad E_n = -\frac{Z^2}{2n^2}, \quad \mu' < 0.$$
(6.11)

for the density of levels is used. Calculating the sum by the Poisson formula, separating the term with k = 0, and extending the integration over *n* to zero, we rewrite (6.11) as the sum of three integrals:

$$\tilde{g}(\mu') = \left\{ \int_0^\infty 1 + \left[\int_0^\infty \sum_{k \neq 0} - \int_0^{1-\epsilon} \sum_k \right] \cos(2\pi k n) \right\}$$
$$\times n^2 \delta(\mu' - E_n) \,\mathrm{d}n \,. \tag{6.12}$$

To obtain the total contribution of gradient terms, we should remove the Thomas–Fermi term (the first integral) and the shell correction (the second integral) from exact expression (6.12). The substitution of the third integral in (5.9) gives the contribution to the Scott correction for the discrete spectrum, coinciding with the result obtained in Section 5.4:

$$\Delta \tilde{E}(\mu') = E_{\rm Sc} = \frac{Z^2}{2} , \quad \mu' < 0 .$$
 (6.13)

It follows from the boundedness of the spectrum from below $(g(\mu') = \tilde{g}(\mu') = 0$ for $\mu' < -Z^2/2)$ for both the original and auxiliary problems that the Scott correction can be written in the form

$$E_{\rm Sc} = -E_{\rm TF}(\mu') - E_{\rm sh}(\mu'), \quad \mu' < -\frac{Z^2}{2}. \tag{6.14}$$

In the case $\mu > 0$, where integral (5.9) also contains the continuum-spectrum region, the contribution of the region $\mu' < 0$ is still determined by expression (6.13). The contribution of the region $0 < \mu' < \mu$, in which shell effects are absent, can be expressed in terms of the exact Coulomb Green's function [120], which is related to the density of levels as $g(\mu') = -\text{Im Tr } \hat{G}(\mu')/\pi$. As a result, we obtain the final expression for the correction in the entire range of values of μ' (see the details in [41, 42]):

$$\Delta \tilde{E}(\mu') = E_{\rm Sc} + \left[\frac{Z}{6\pi}\sqrt{2\mu'} + \frac{Z^2}{\pi}\phi\left(\frac{\sqrt{2\mu'}}{2Z}\right)\right]\theta(\mu'). \quad (6.15)$$

The behavior of the function $\phi(x)$ and its derivative $\phi'(x)$ was analyzed in [22, 42]. The asymptotic expressions of this function in the limit case $x \ll 1$, where the semiclassical behavior condition is satisfied, and for $x \ge 1$, where the

perturbation theory is valid, are

$$\phi(x) = \frac{2}{45} x^3 + O(x^5), \quad x \le 1;$$

$$\phi(x) = \frac{x}{3} - \frac{\pi}{4} + O\left(\frac{1}{x}\right), \quad x \ge 1.$$

Assuming that A is the free energy F and substituting (6.9), (6.10), and (6.15) in (6.8), we obtain the final expression for the improved gradient (quantum) correction,

$$\Delta F^{c} = E_{Sc} - \frac{\pi}{6} \int n_{TF} \frac{\partial n_{TF}}{\partial \mu} d\mathbf{r} - \frac{Z^{2}}{\pi} \int_{0}^{\infty} \phi\left(\frac{\sqrt{2\mu'}}{2Z}\right) \frac{\partial f((\mu' - \mu)/T)}{\partial \mu'} d\mu', \qquad (6.16)$$

where the second term in the right-hand side is the commonly used finite part of the lowest quantum correction to free energy (1.6).

It is easy to show that expression (6.16) is free of the disadvantages inherent in the original model. The improved quantum correction to the energy at zero temperature has the form

$$\Delta E^{c} = E_{Sc} - \frac{1}{18\pi^{3}} \int p_{\mu}^{4} d\mathbf{x} + \frac{Z^{2}}{\pi} \phi\left(\frac{\sqrt{2\mu}}{2Z}\right) \theta(\mu) \,. \quad (6.17)$$

The chemical potential for an isolated atom in the TF model is zero, the last term being absent in this case. Adding the TF term and exchange correction to (6.17), we obtain the known trinomial expression

$$E_0 = -0.7687 Z^{7/3} + \frac{Z^2}{2} - 0.2699 Z^{5/3}, \qquad (6.18)$$

which describes the energy of the electron atomic shell in the Hartree–Fock model for Z > 4 with an accuracy of a few fractions of a percent [10, 121]. This example demonstrates the elimination of the first and second disadvantages of the initial model.

We now consider cold, strongly compressed matter in the region $\mu > Z^2$, where the results of the noncorrected TFC model and the perturbation theory, corresponding here to the Thomas–Fermi–Dirac (TFD) model, are inconsistent. Of real physical interest is the pressure correction, its improved expression having the form

$$\Delta P^{c} = \Delta_{2} P \left[1 - 3\phi' \left(\frac{\sqrt{2\mu}}{2Z} \right) \right].$$
(6.19)

In the region under study, the quantity in square brackets tends to zero in accordance with the perturbation theory. Figure 23 compares different models of the equation of state of aluminum in the region of superhigh compressions. We can see that the results of the theory considered here and of the complete quantum mechanical calculation by the method of augmented plane waves (APWs) are in good quantitative agreement [94]. We also note that result (6.19) becomes closer to the results of the perturbation theory as the compression increases and to the original model as the compression decreases.

In the region of very high temperatures, the perturbation theory (PT) should also be valid, according to which the free energy of electrons [see (1.2)], taking the exchange interaction



Figure 23. Relative deviation of the aluminum pressure from the TF model calculated in different models as a function of the reduced lattice constant a/a_N under compression in the intermediate region $\sigma = \sqrt{2\mu}/2Z \sim 1$. Dotted curve: the TF model with the exchange correction (perturbation theory), dashed curve: the TF model with the exchange and uncorrected quantum corrections, solid curve: RTF, the TF model with exchange and corrected quantum corrections (6.19), symbols: the APW method [94], $a_N = 7.65288$.

into account, has the form

$$F_{\rm PT} = Z(\mu - T) + \Delta F_{\rm ex} \,. \tag{6.20}$$

In Section 5.4, we already considered the limit hightemperature case and showed that the semiclassical model, taking the Scott and shell corrections into account, describes the ideal Boltzmann plasma well. We now prove this in a more general case.

We consider the improved semiclassical expression for the free energy containing the Thomas–Fermi term, the exchange, corrected quantum, and shell corrections:

$$F_{\rm RTF} = F_{\rm TF} + \Delta F_{\rm ex} + \Delta F^{\rm c} + F_{\rm sh} \,. \tag{6.21}$$

A comparison of (6.20) with (6.21) in the region under consideration ($\mu < -Z^2/2$) shows that the combination of terms

$$E_{\rm Sc} + F_{\rm TF} + F_{\rm sh} , \qquad (6.22)$$

is 'redundant'. Taking into account expressions (5.8) and (6.14), we obtain the mutual compensation of terms in (6.22) at the level of integrands, which means that the results of the refined TF model and perturbation theory (6.20) completely coincide. This is well illustrated in Fig. 18, which presents calculations of the thermal and caloric equations of states of high-temperature iron plasma by using various semiclassical models compared with calculations in the semiempirical Saha–Reiser model.

6.3 Self-similar matter equation of state

The investigation described above forms the basis for constructing the wide-range semiclassical equation of state of the electron component of matter with high energy density, which correctly describes the ideal Boltzmann plasma and degenerate matter, and in the intermediate region represents a reasonable physical interpolation taking the effects of nonideality, degeneracy, band broadening, etc., into account.

The free energy of electrons in this refined cell TF model is written as the sum of Thomas–Fermi term (5.1), exchange (1.5), corrected quantum gradient (6.16), and shell corrections according to (6.21). Expressions for the pressure and internal energy can be written similarly, with the shell corrections to these quantities calculated in accordance with (5.18) and (5.19).

An attractive feature of the statistical TF method is its self-similarity with respect to the atomic number Z. It is sufficient to perform calculations for hydrogen; the corresponding recalculation for any other substance then amounts to scale transformations in accordance with to (5.3). The quantum-exchange correction in the TFC model also has this property. For example, pressure and energy corrections have factors $Z^{8/3}$ and $Z^{5/3}$ in a representation similar to (5.3). The detailed tables [37] of thermodynamic quantities calculated from the TFC model for hydrogen are based on this property.

For the shell correction, the dependences are not so simple; however, they can also be calculated using the self-similarity property because all the quantities entering shell corrections (5.18), (5.19), and (6.5) to the thermodynamic functions are calculated using the TF model [122]:

$$S_{\mu}^{(Z)} = Z^{1/3} S_{\mu}^{(1)}, \quad t_{\mu}^{(Z)} = Z^{-1} t_{\mu}^{(1)},$$

$$\lambda_{\mu}^{(Z)} = Z^{1/3} \lambda_{\mu}^{(1)}, \quad \delta_{\mu}^{(Z)} = Z^{-1/3} \delta_{\mu}^{(1)},$$

$$\left(\frac{\partial \lambda_{\mu}}{\partial \mu}\right)^{(Z)} = Z^{-1} \left(\frac{\partial \lambda_{\mu}}{\partial \mu}\right)^{(1)},$$

$$\left(\int \frac{\partial n_{\rm TF}}{\partial \mu} \, d\mathbf{r}\right)^{(Z)} = Z^{1/3} \left(\int \frac{\partial n_{\rm TF}}{\partial \mu} \, d\mathbf{r}\right)^{(1)},$$

$$\left(\int \frac{\partial n_{\rm TF}}{\partial \mu} \left(\mu_{\rm TF} - V_{\rm TF}(r)\right) d\mathbf{r}\right)^{(Z)}$$

$$= Z \left(\int \frac{\partial n_{\rm TF}}{\partial \mu} \left(\mu_{\rm TF} - V_{\rm TF}(r)\right) d\mathbf{r}\right)^{(1)}.$$
(6.23)

We discuss the applicability range of the proposed equation of state of matter in more detail. We recall that in the cell approximation, the contribution of thermal oscillations of the ion component is considered separately. This contribution is described in different parts of the phase diagram via different models, such as the Mie–Grüneisen model, ideal gas, one-component plasma, neutral and rigid and soft sphere charges, etc. (see, e.g., [110]).

Because the detailed description of the ion subsystem is beyond the scope of our consideration, we here discuss the electron–electron and electron–ion interactions. They are taken into account in the equation of state by the electron contributions to pressure and internal energy in the semiclassical model in the framework of a self-consistent field in the cell approximation. The interaction between electrons is then described up to correlation effects. Their smallness signifies the smallness of the corresponding parameter equal to the ratio of the mean energy of the Coulomb interaction of a pair of particles to their mean kinetic energy,

$$\delta_0 \sim \frac{n_{\rm e}^{1/3}}{p_{\mu}^2} \sim \frac{n_{\rm e}^{1/3}}{T} \ll 1.$$
 (6.24)

This condition coincides with the applicability condition of the cell approximation.

As regards the interaction of electrons with nuclei, the interaction of electrons with their nucleus in a cell is described quite completely, while the interaction with other cells is determined by boundary conditions valid for condensed matter. The inaccuracy of this approximation for a disordered system such as plasma is not so great, as can be seen from the correct description of the ideal-gas limit by cell models: the proposed semiclassical model and the quantum mechanical Hartree–Fock–Slater model (HFSM) [110].

The semiclassical behavior parameter ξ in the Boltzmann plasma region is

$$\xi = \frac{\sqrt{n_e}}{p_\mu^2} \sim \frac{\sqrt{n_e}}{T} , \qquad (6.25)$$

and the condition of its smallness $n_e \ll T^2$ is weaker than condition (6.24), which can therefore be regarded as a theoretical substantiation of the applicability condition for statistical models of plasma. For degenerate matter, the



Figure 24. Phase diagram for aluminum. Parameter (6.24) on curve *I* is $\delta_0 = 1$, semiclassical behavior parameter (6.25), (6.26) on curve 2 is $\xi = 1$. On degeneracy line 3, the temperature $T \sim n_e^{2/3}$; 4 is the curve of equal ion and electron contributions. Curve 5 is the boundary of the applicability range of the Saha model, and curve 6 is the region of parameters of the normal Hugoniot curve. The dashed curves correspond to the plasma nonideality parameter $\gamma = 0.1$ and $\gamma = 1$, and C is a critical point on the spinodal.

semiclassical behavior condition has the form

$$\xi \sim n_{\rm e}^{-1/6} \ll 1$$
. (6.26)

The corresponding curves are presented in the (ρ, T) phase diagram for aluminum in Fig. 24. The theoretically substantiated applicability range of semiclassical models in the cell approximation is the region above curve 1 and to the right of curve 2. Degeneracy line 3 restricts the applicability of the TFC model from above in temperature; in the region below line 4, the ion contribution to thermodynamic characteristics dominates over the electron contribution. The analysis shows that the semiclassical model gives a good description of the equation of state of matter for a more than 10-fold cold compression or (and) temperatures exceeding several tens of electronvolts; this model therefore describes an extreme state of matter with high energy density. Under these conditions, the role of the ion component is small, which is confirmed by precision calculations [94, 116-119] performed in the entire compression range. In addition, the Wigner-Seitz cell approximation used here cannot describe structural phase transitions at lower pressures. Nevertheless, the actual applicability range of the semiclassical model for plasma proves to be broader that that predicted theoretically (from T > 10 eV for gas densities up to T > 30 eV at the normal density), possibly because of an interplay of numerical factors.

That the semiclassical equation of state of matter can be correct only at such high parameters is also explained by the inversely proportional dependence of the semiclassical behavior parameter in the three-dimensional case on the cubic root of the number of particles ($\xi \sim N_e^{-1/3}$), as mentioned above. Because $N_e = Z \leq 100$, this means that matter cannot be treated in full measure as multiparticle. In this sense, the situation is more advantageous in atomic clusters, where the number of particles can exceed a few hundred or even thousand (see Section 7).

Figure 25 [52] shows normal Hugoniot curves for aluminum and molybdenum calculated in the RTF model and compared with TFC calculations and experimental data. The equation of state of ions was calculated using the onecomponent plasma model [134]. Figure 25 illustrates the role of temperature shell effects well.

Thus, the RTF model proposed for matter with a very high energy density already covers the regions in which the ionization equilibrium model (Boltzmann plasma) and the TFC model (condensed matter) are commonly used, as well as the intermediate region in which different methods for sewing these two models together are used in the literature (see, e.g., [97, 135]). In addition, the RTF model has the similarity property with respect to the atomic number, which allows using tabulated hydrogen data for calculations for any substances.

The semiclassical equation of state for the electron component is used in [53] to construct a wide-range semiempirical equation of state of matter. To properly describe the low-temperature region, the corrected RTF model is used in which the theoretical zero isotherm is replaced by a semiempirical isotherm and the ion component is described using the modified Mie–Grüneisen model. Compact tables for hydrogen are also presented, which are necessary for calculations of Thomas–Fermi and correction (quantum-exchange and shell) thermodynamic quantities, the procedure of calculations with the tables is described,



Figure 25. Normal Hugoniot curves of (a) aluminum and (b) molybdenum calculated in the RFT model [52] (solid curves) in comparison with TFC calculations (dashed curves) and experimental data [123–133] (symbols). The equation of state of ions is calculated in the one-component plasma model [134].

and the normal Hugoniot curves are calculated for some metals.

7. Shell effects in metal clusters

In this section, the semiclassical model is used to describe metal clusters. The relative role of different classical trajectories in the formation of oscillations observed in the mass spectra of clusters is analyzed. The conditions for the appearance of different types of trajectories are determined depending on the temperature, cluster size, and shape and rigidity of the potential. The proposed approach is especially efficient for large clusters, in which self-consistent calculations by the density functional method are very timeconsuming and their results are difficult to interpret.

The obtained analytic expressions were used to describe the experimental mass spectra for sodium and aluminum clusters and to explain their difference.

7.1 Mass spectra of metal clusters

Theoretical studies of metal clusters are often based on the spherical jelly model mentioned in Section 3.2, which assumes that ions are homogeneously distributed in a cluster volume with the radius $R = r_s N_e^{1/3}$. This model is used for self-consistent calculations (see, e.g., [136], where sodium clusters were studied by the density functional method in the Kohn–Sham representation). One of the results of such calculations is the reproduction of two characteristic types of periodicity in the oscillating part of the electron energy $\Delta E_{\rm sh}$ as a function of the cluster size observed in experiments: oscillations with a small period accompanied by beats with a period an order of magnitude greater. Similar results were also obtained in calculations in [137] using the phenomenological Woods–Saxon potential and in [138] for various metals with potentials close to self-consistent potentials.

For small clusters with N < 100, the interpretation of numerical calculations meets no difficulty: the cusps of the minima of the electron shell energy correspond to clusters in which the shell with the maximum orbital momentum $l = l_{\text{max}}$ is completely occupied. But this property is violated for N > 100, and the nature of such specific oscillations has already been discussed in the literature for a few decades.

The theory developed in fundamental paper [139] explains the beats of the electronic level density in a potential of a spherical cavity by a superposition of contributions from closed periodic classical electron trajectories. It was shown in [139] that these effects can be approximately described using only triangular and square orbits. This theory has been successfully used in nuclear physics to describe the shell structure of atomic nuclei [68].

The detailed numerical calculations in [138] for clusters with more complex potentials also reproduce similar oscillations with beats. It was found that electronic energy levels $\varepsilon(n_r, l)$ with high angular momenta are grouped into supershells with pseudoquantum numbers $Kn_r + l$: $\varepsilon(n_r, l) \simeq$ $\varepsilon(n_r + 1, l - K)$, where n_r is the radial quantum number and K = 2, 3, 4,

It was found (see, e.g., [140]) that a correspondence can be established between quantum supershells and classical trajectories. The integer K characterizing a supershell is equal to the ratio of the frequencies of the radial and angular motions for the corresponding closed orbit. For K = 2, the pseudoquantum number coincides with the principal quantum number and characterizes the location of one-electron levels in small clusters. The corresponding classical motion of an electron occurs along a linear orbit passing through the point r = 0. As the number N of atoms in the cluster increases, supershells with K = 3 and then with K = 4 appear, corresponding to triangular and square orbits.

Thus, the scrupulous analysis of time-consuming calculations performed in the above-mentioned papers suggests that, first, the expansion in classical trajectories is equivalent to the expansion in supershells and, second, the result obtained in [139] for a spherical cavity is also valid for a spherical cluster potential of a more general form. The second assumption was partially confirmed in [141] for the Woods–Saxon potential by expanding in the parameter a/R (where *a* is the surface width) near the known result [139].

Just the use of the semiclassical method of separating shell effects allowed obtaining the expansion in trajectories and studying the origin of supershells and their appearance for potentials in the general form [23, 61, 62]. We follow these papers in Sections 7.2 and 7.3.

Oscillations in the mass spectra of metal clusters can be not only a manifestation of the shell structure of electronic spectra but also a consequence of the arrangement of ions in lattice sites [142]. Experiments have shown that the form of oscillations in the mass spectra of large aluminum Al_N [143, 144] and sodium Na_N [145] clusters is substantially different. While sodium clusters reveal oscillations with beats, aluminum clusters with N > 250 exhibit sinusoidal oscillations at a frequency approximately twice that for sodium. The spectra of smaller Al_N clusters are quite intricate and have no distinct period.

In [146], an attempt was made to explain experimental results in the framework of a spherical jelly model using the semiclassical theory [137, 147–149]. It was assumed that in the soft potential of Al_N clusters in the range 250 < N < 900, only one trajectory of a five-point star shape makes the main contribution. This considerably differs from the situation in the rigid potential of Na_N clusters, in which a triangular trajectory and a square trajectory close in frequency dominate (the interference of their contributions leads to oscillations with beats). According to this theory, the triangular trajectory and then the square trajectory should appear in larger clusters (this is confirmed by the calculation of the density of states for $N_e = 4940$ in a self-consistent model [143]), which should result in a change in the oscillation frequency.

An alternative to this explanation is given by the results in [144], where the mass spectra of 'cold' (T = 100 K) Al_N clusters were experimentally studied and analyzed in a very broad range of the number of atoms (250 < N < 10,000). The analysis of the spectra showed that the maxima of oscillations numbered successively with the index k (k > 25) in the entire range under study appeared with a constant frequency and corresponded to the dependence $N \simeq 0.0104k^3$, which is explained well by the arrangement of ions into an octahedral lattice. In this case, the cluster is not a sphere but an octahedron, and the occupation of the shell corresponds to the formation of one of its facets. Obviously, in this case, the spherical jelly model, in which ions are assumed homogeneously distributed within the sphere volume, should not give correct results.

The assumption about the leading contribution of the five-point star shell in aluminum was refuted by the authors of [150] based on the quantum mechanical calculation of the density of states in the Woods–Saxon potential for the number of electrons $N_e = 1000$.

Nevertheless, the positions of maxima observed in [143] for T = 295 K and 250 < N < 430 agree well with the results of self-consistent calculations [143] in the jelly model, while a comparison of the mass spectra for Al_N with N < 250 for T = 110 K and 295 K reveals a noticeable influence of temperature on these spectra, which was attributed to the melting of the crystal lattice with increasing temperature and the manifestation of the electron shell structure.

It therefore seems that the contribution of the Al ion lattice to oscillations of the mass spectrum at low temperatures dominates, and the spherical jelly model is inapplicable in this region, while the role of the crystal lattice decreases with increasing the temperature, and the application of the jelly model becomes more substantiated. We can assume that the electron structure should be manifested in 'hot' clusters during lattice melting, and the lattice melting point can be experimentally determined by the characteristic change in the mass spectrum in the region $N \sim 1000$.

In paper [23], which we follow in Section 7.4, the dependence of the oscillating part of the free energy of electrons in an aluminum cluster on its size and temperature was studied in the jelly model in the semiclassical approximation, and the assumption about the decisive role of the five-point star orbit in the oscillations of Al_N spectra for $T \simeq 300$ K in the experimentally established range [146] of the number of atoms was confirmed.

7.2 Shell correction to the number of states

Shell effects in clusters [23, 61, 62] are described by the same semiclassical method that was previously successfully used in problems of atomic [1, 13] and plasma [51, 52] physics (see also Sections 2, 4–6).

We assume that the chemical μ and self-consistent V(r) potentials of the electron system in a cluster, neglecting shell effects, are known. These potentials are approximated below by the Woods–Saxon potential ¹²

$$V_0(r) = -V_0 \left[1 + \exp\left(\frac{r-R}{a}\right) \right]^{-1}, \quad R = r_{\rm s} N_{\rm e}^{1/3}, \quad (7.1)$$

with the parameters for aluminum ($V_0 = 0.5319$, a = 2.7, $r_s = r_s^b = 2.07$, $\mu_0 = -0.1053$) and sodium ($V_0 = 0.22$, a = 1.4, $r_s = r_s^b = 3.93$, $\mu_0 = -0.1015$) clusters as in [146]. Here, r_s^b is the electron radius in a solid. An extremely rigid potential is approximated by a 'rectangular well':

$$V_{0}(r) = \begin{cases} -2\varepsilon_{\rm F}, & r \leq R, \\ 0, & r > R, \end{cases} \quad R = r_{\rm s} N_{\rm e}^{1/3},$$

$$\varepsilon_{\rm F} = \frac{1}{2r_{\rm s}^{2}} \left(\frac{9\pi}{4}\right)^{2/3}, \quad \mu_{0} = -\varepsilon_{\rm F}.$$
(7.2)

We study the contribution of shell effects in clusters at high temperatures using correction (5.8) to the free energy containing correction (5.9) to the number of states $\Delta N(\mu) \equiv \Delta N(\mu, 0) = N(\mu, 0) - N_0(\mu, 0)$ without the explicit temperature dependence,

$$N(\mu, 0) = 2 \sum_{n_{\rm r}, l} (2l+1) \,\theta(\,\mu - \varepsilon_{n_{\rm r}l}) \,. \tag{7.3}$$

Here, energy levels ε_{n_rl} are determined from quantization condition (4.1) with n_r from (4.5). Simple transformations similar to those presented in Section 5.4 with the use of Poisson formula (2.6) for replacing sums over quantum numbers ε_{n_rl} by integrals allow rewriting expression (5.21) for the shell correction, after integration with respect to energy in the form¹³

$$\Delta N_{\rm sh}(\mu) = \frac{2}{\pi} \sum_{k,s=-\infty}^{\infty} \frac{(-1)^{k+s}}{k} \int_0^{\lambda_{\mu}} \sin\left(2\pi \left[kv_{\mu}(\lambda) + s\lambda\right]\right) \lambda \, \mathrm{d}\lambda \,.$$
(7.4)

¹² The difference between potential (7.1) and the self-consistent potential is discussed in [137].

¹³ Expression (7.4) was used for calculating the shell correction to the number of states for a free atom in the TF model in [12, 13], and for systems with the cylindrical symmetry in [151, 152].

Here, the prime on the summation symbol denotes the omission of the term with k = s = 0, which corresponds in the expression for $N(\mu, 0)$ to the averaged nonoscillating dependence $N_0(\mu, 0)$.

It follows from (7.4) that shell oscillations are completely determined by the radial action function $S_{\mu\lambda} = \pi v_{\mu}(\lambda)$ for the motion of an electron with the energy μ and orbital momentum λ in the spherically symmetric potential V(r). The corresponding curves for different numbers of atoms in sodium clusters are presented in Fig. 11a.

In the general case, the leading contributions to integrals (7.4) are made by integration limits and stationary-phase points $\overline{\lambda}_i$, which are determined from the relation

$$v_{\mu}'(\bar{\lambda}_j) = \frac{\partial v_{\mu}(\lambda)}{\partial \lambda} \Big|_{\bar{\lambda}_j} = -\frac{s_j}{k_j}, \quad 0 \leq \bar{\lambda}_j \leq \lambda_{\mu}, \quad j = 0, 1, 2, \dots.$$
(7.5)

Condition (7.5) separates the leading terms k_j and s_j (where *j* labels the stationary-phase points) in sums over *k* and *s* and leads to substantially different results for cluster and atomic potentials.

The derivative in (7.5) is always negative (Figs 11b and 12b) and its modulus is equal to the ratio of frequencies of the angular and radial motion of a particle with the energy μ and orbital momentum $\bar{\lambda}_j$. The requirement that this ratio be a ratio of integers is the condition of the closure of the trajectory and periodicity of this motion [153]. We note that the motion with the maximum possible orbital momentum λ_{μ} is also virtually closed. In this case, the two turning points of the radial motion merge into one, and the particle moves along a circular orbit of the radius $R_{\mu\lambda_{\mu}}$.

For clusters of any size, $v'_{\mu}(0) = -1/2$. This means that the point $\lambda = 0$, i.e., the lower integration limit, is also a stationary-phase point, because it satisfies condition (7.5) for $k_0 = 2s_0$. The trajectory with $\bar{\lambda}_0 = 0$ for a cluster potential corresponds to a linear orbit passing through the center.

Shell effects also contain a contribution from the upper integration limit, i.e., the circular trajectory with the maximum orbital momentum λ_{μ} , the role of the circular orbit being dominant over that of the linear orbit due to the small number of particles in the s-states.

In the case of small clusters with $N_{\rm e} < 100$, the solutions of Eqn (7.5) with small k and s are absent in the possible range of λ (Fig. 11b), and shell effects are determined only by trajectories with $\lambda = 0$, λ_{μ} considered above. This agrees with the interpretation of numerical calculations: the minima of the electron shell energy correspond to clusters in which the shell with the maximum orbital momentum is completely filled.

The sum of contributions from other stationary-phase points — solutions of Eqn (7.5) — is given by

$$\Delta N_{\rm sh}(\mu) = \frac{4}{\pi} \sum_{j \neq 0} \sum_{k_j} \frac{(-1)^{k_j + s_j} \bar{\lambda}_j}{\sqrt{\left|v_{\mu}''(\bar{\lambda}_j)\right|} k_j^{3/2}} \\ \times \sin\left[2\pi \left(k_j v_{\mu}(\bar{\lambda}_j) + s_j \bar{\lambda}_j\right) + \frac{\sigma_j \pi}{4}\right],$$
(7.6)

where s_j and k_j are related by (7.5), $v''_{\mu}(\bar{\lambda}_j) = \partial^2 v_{\mu}(\lambda)/\partial \lambda^2|_{\bar{\lambda}_j}$, and $\sigma_j = \text{sign}\left[v''_{\mu}(\bar{\lambda}_j)\right]$.

For a fixed stationary-phase point $\bar{\lambda}_j$, the leading contribution to the sums in (7.6) is made by terms with the lowest values of $k_j = \bar{k}_j$ and $s_j = \bar{s}_j$, giving the ratio \bar{s}_j/\bar{k}_j in (7.5). We call the corresponding minimal-length trajectory the *j*th orbit. Then the quantity $\pi v_{\mu}(\bar{\lambda}_j)$ is the radial action for the motion of an electron with the energy μ and orbital momentum $\bar{\lambda}_j$ along the *j*th orbit between turning points. Multiplying the numerator and denominator in the ratio \bar{s}_j/\bar{k}_j by an integer m = 1, 2, 3, ..., we obtain trajectories with *m* periods of motion along the *j*th orbit. This allows rewriting expression (7.6) in the form

$$\Delta N_{\rm sh}(\mu) = \frac{4}{\pi} \sum_{j \neq 0} \frac{\overline{\lambda}_j}{\sqrt{\left|v_{\mu}''(\overline{\lambda}_j)\right|} \overline{k}_j^{3/2}} \sum_{m=1}^{\infty} \frac{(-1)^{m(k_j + \overline{s}_j)}}{m^{3/2}}$$
$$\times \sin\left[2\pi m \left(\overline{k}_j v_{\mu}(\overline{\lambda}_j) + \overline{s}_j \overline{\lambda}_j\right) + \frac{\sigma_j \pi}{4}\right]. \tag{7.7}$$

Differentiating (7.7) with respect to μ , we obtain an expression for the shell correction to the density of levels,

$$\delta g_{\rm sh}(\mu) = \frac{8}{\pi} \sum_{j \neq 0} \frac{\bar{\lambda}_j \, \tilde{t}_\mu(\bar{\lambda}_j)}{\sqrt{\bar{k}_j |v_\mu''(\bar{\lambda}_j)|}} \sum_{m=1}^{\infty} \frac{(-1)^{m(k_j + \bar{s}_j)}}{\sqrt{m}} \\ \times \cos\left[2\pi m (\bar{k}_j v_\mu(\bar{\lambda}_j) + \bar{s}_j \bar{\lambda}_j) + \frac{\sigma_j \pi}{4}\right], \tag{7.8}$$

where $\tilde{t}_{\mu}(\bar{\lambda}_j) = t_{\mu}(\bar{\lambda}_j) - v'_{\mu}(\bar{\lambda}_j) \partial(\pi \bar{\lambda}_j) \partial \mu$ and $t_{\mu}(\bar{\lambda}_j) = \partial[\pi v_{\mu}(\lambda)] / \partial \mu|_{\bar{\lambda}_j}$ is the motion time of a particle with the energy μ and orbital momentum $\bar{\lambda}_j$ between turning points, i.e., half the radial period for the *j*th orbit. Expression (7.8) coincides with the result obtained in [154] for spherically symmetric systems by a different method.

The integration of (7.7) with respect to μ , taking (5.8) into account, gives an expression for the shell correction to the free energy,

$$\Delta F_{\rm sh}(\mu) = \sum_{j \neq 0} \frac{4\bar{\lambda}_j T}{\sqrt{|\nu_{\mu}''(\bar{\lambda}_j)|} \bar{k}_j^{3/2}} \sum_{m=1}^{\infty} \frac{(-1)^{m(k_j + \bar{s}_j)}}{m^{3/2} \sinh[X_m^j(T)]} \\ \times \cos\left[2\pi m \big(\bar{k}_j \nu_{\mu}(\bar{\lambda}_j) + \bar{s}_j \bar{\lambda}_j\big) + \frac{\sigma_j \pi}{4}\right].$$
(7.9)

Here, the notation $X_m^j(T) = mT 2\pi k_j \tilde{t}_\mu(\bar{\lambda}_j) = mT/T_j$ is used, where T_j is the characteristic temperature determining the decay of the contribution of the *j*th orbit with increasing temperature.

The contribution of trajectories with j = 0, $\bar{\lambda}_0 = 0$ is not included in expressions (7.6)–(7.9). This contribution should be considered separately because the point $\lambda = 0$, being a stationary-phase point, is also the lower integration limit and, in addition, the integrand vanishes at this point. The term with $j = j_{\mu}$, where $\bar{\lambda}_j = \lambda_{\mu}$ is the upper integration limit, should also be considered separately. As a result, we obtain the sum of these terms:

$$\Delta N_{\rm sh}^{j=0,j_{\mu}}(\mu) = -\frac{1}{\pi^2 v_{\mu}''(0)} \sum_{m=1}^{\infty} (-1)^m \frac{\cos\left[4\pi m v_{\mu}(0)\right]}{m^2} + \frac{2\lambda_{\mu}}{\pi \sqrt{\left|v_{\mu}''(\lambda_{\mu})\right|} \bar{k}_{\mu}^{3/2}} \sum_{m=1}^{\infty} \frac{(-1)^{m(\bar{k}_{\mu}+\bar{s}_{\mu})}}{m^{3/2}} \times \sin\left(2\pi m \bar{s}_{\mu} \lambda_{\mu} + \frac{\sigma_{\mu} \pi}{4}\right).$$
(7.10)

The notation $\bar{k}_{\mu} = \bar{k}_{j_{\mu}}, \bar{s}_{\mu} = \bar{s}_{j_{\mu}}, \bar{s}_{\mu} = v'_{\mu} \bar{k}_{\mu}$ is used here.

The calculation of the sum entering (7.8)–(7.10) essentially depends on the rigidity of the cluster potential. In Section 7.3, we consider clusters with a rigid potential (Na_N) and in Section 7.4, clusters with a soft potential (Al_N).

7.3 Rigid potential

As is shown in Section 7.2, the shell correction is the sum of contributions from closed trajectories *j* determined by condition (7.5). We note that not all the trajectories make the same contribution to quantities (7.6) and (7.9), which are of interest to us. Because of the presence of terms $\bar{k}_j^{3/2}$, Eqn (7.6), and $\bar{k}_j^{5/2}$ [see (7.9) for T = 0] in the denominator, the trajectories with minimal values of \bar{k}_j make the leading contribution to sums (7.6) and (7.9).

Figure 11 demonstrates the behavior of the function $v_{\mu}(\lambda)$ and its derivative for sodium clusters, which is typical for a rigid potential. We can see that the derivative $v'_{\mu}(\lambda)$ for sodium clusters of all sizes monotonically increases from the value -1/2. This means that rational fractions \bar{s}_j/\bar{k}_j satisfying condition (7.5) must lie in the range

$$-\nu'_{\mu}(\lambda_{\mu}) \leqslant \frac{\bar{s}_j}{\bar{k}_j} \leqslant \frac{1}{2} , \qquad (7.11)$$

which gives the conditions $\bar{s}_i \ge 1$, $\bar{k}_i \ge 2$.

Fractions with the least value $\bar{s}_j = 1$ and $\bar{k}_j = 2, 3, 4, ...,$ i.e., fractions like

$$\begin{aligned} -\frac{\bar{s}_j}{\bar{k}_j} &= \frac{\partial v_\mu(\lambda)}{\partial \lambda} \Big|_{\bar{\lambda}_j} \\ &= -\frac{1}{2+j}, \quad j = 0, 1, ..., j_{\max}, \quad j_{\max} = \left[\frac{1}{v'_\mu} - 2\right], \ (7.12) \end{aligned}$$

correspond to the linear, triangular, square, etc., on orbits.

For $\bar{s}_j \ge 2$, the smallest corresponding numbers are $\bar{k}_j = 2\bar{s}_j + 1$. In this case, the values of \bar{s}_j/\bar{k}_j lie between 2/5 and 1/2 and correspond to orbits with the $(2\bar{s}_j + 1)$ -point star shape.

The horizontal straight lines $v'_{\mu}(\lambda) = -1/(2+j)$, j = 1, 2, ... are plotted in Fig. 11b. According to (7.12), the intersection points of the derivative curve with these lines determine the stationary-phase points $\bar{\lambda}_j$. We can see from the figure that in the case of a rigid sodium potential for $N_e = 100$, a contribution from the triangular orbit (j = 1) exists, whereas for the cluster with $N_e = 1000$, contributions from the square (j = 2) and pentagonal (j = 3) trajectories are also present. The contribution to (7.9) from the five-point star orbit corresponding to $\bar{s}_j = 2$, $\bar{k}_j = 5$ proves to be insignificant against their background because of the factor $\bar{\lambda}_j/\bar{k}_j^{5/2}$.

Hence, in this case, the sum over the leading trajectories in the expression for the free energy correction has the form

$$\Delta F_{\rm sh}(\mu) = \sum_{j=1}^{j_{\rm max}} \frac{4\bar{\lambda}_j T}{\sqrt{\left|\nu_{\mu}''(\bar{\lambda}_j)\right| (j+2)^{3/2}}} \sum_{m=1}^{\infty} \frac{(-1)^{m(j+1)}}{m^{3/2}\sinh(mT/T_j)} \\ \times \cos\left[2\pi m \left((j+2)\nu_{\mu}(\bar{\lambda}_j) + \bar{\lambda}_j\right) + \frac{\pi}{4}\right],$$
(7.13)

where

$$\frac{1}{T_j} = 2\pi (2+j) \,\tilde{t}_\mu(\bar{\lambda}_j) = 2\pi \left[(2+j) \,t_\mu(\bar{\lambda}_j) + \frac{\partial(\pi\bar{\lambda}_j)}{\partial\mu} \right] (7.14)$$



Figure 26. (a) Oscillating part of energy (7.13) for T = 0 as a function of the cluster size *N* for sodium with potential (7.1) in Fermi energy units. The different number of *j*-trajectories is taken into account. (b) The oscillating part of the free energy as a function of the cluster size *N* for sodium with 'rectangular well' potential (7.2) at different temperatures.

and it is taken into account that we always have $v''_{\mu} > 0$ for a rigid potential.

The terms in the sum over i in (7.13) are contributions from supershells with quantum numbers $n_i = Kn_r + l$, K = 2 + i, where an essential point is given by quantization at the energy level equal to the chemical potential μ of the system. Figure 26a demonstrates the results of analysis [23] based on (7.13) of the relative role of supershells (trajectories) with different *j* in the formation of beats at zero temperature in sodium clusters with Woods-Saxon potential (7.1) and schematically shows the corresponding trajectories. We can see that including trajectories with j > 4 does not change the form of oscillations, i.e., they make no contribution in this range of cluster sizes. The results of calculations in [23] are in good agreement with quantum mechanical calculations [137] for potential (7.1). In particular, the magic numbers $N_{\rm e}$ corresponding to the positions of minima can be calculated up to the third significant digit, and the beat period, the curve shape, and the fine-structure details are reproduced well.

At a temperature exceeding the characteristic temperature T_j , the contribution of the corresponding orbit becomes negligibly small. The role of temperature in the reduction of free-energy oscillations is demonstrated in Fig. 26b, which shows the results of calculations by expression (7.13) for two

finite temperatures, compared with zero temperature for the 'rectangular well' potential in (7.2). These results are in good agreement with reference calculations [136]. We can see from Fig. 26b that supershells (trajectories) with a large number *j* 'evaporate' more rapidly. The analysis of the dependences of characteristic temperatures (7.14) on the cluster size shows that although the slowest temperature decay corresponds to the trajectory with j = 0, the contribution of the corresponding shell is insignificant, and the decay of the supershell with j = 1 plays a key role. We note that this differs from the estimate of T_0 often used in the literature by analogy with a harmonic oscillator.

7.4 Soft potential

The difference between rigid and soft potentials is well illustrated in Fig. 27 [62], showing the dependences $v'_{\mu}(\lambda)$ for sodium and aluminum clusters for different numbers N_e of electrons. In the case of the rigid potential in sodium clusters studied in Section 7.3, the triangular and square trajectories, already appearing in small clusters, make the leading contribution. The contribution of star-shaped trajectories is negligibly small. In the case of aluminum, the situation is quite different. Because of the weak dependence of the derivative on λ in a soft potential, the triangular orbit appears only in very large clusters for $N_e \approx 3000$, while for smaller clusters, for example, for $N_e = 1000$, the five-point star orbit dominates.

A comparison of expressions (7.8) and (7.9) shows, however, that the domination of this orbit in the correction to the density of levels (7.8) is not so obvious as in free-energy correction (7.9): according to our calculations, the oscillation amplitudes for five-point and seven-point stars differ in (7.8) only by a factor of 1.36, whereas in (7.9), the contribution of the five-point star is 3.3 times larger that that of the sevenpoint star. For this reason, it was difficult to distinguish a definite period in numerical calculations [150] of only the density of levels as a function of μ' for a fixed number of particles $N_e = 1000$. In our opinion, the negative conclusion about the possible role of the five-point star trajectory made in [150] is explained by this fact.



Figure 27. Dependences of the derivative $v'_{\mu}(\lambda)$ of the radial action on the orbital momentum $\lambda = l + 1/2$ for the rigid (sodium: solid curves) and soft (aluminum: heavy dashed curves) variants of Woods–Saxon potential (7.1) for different numbers $N_{\rm e}$ of electrons in a cluster. The shape of symbols corresponds to the trajectory shape.

We can see from expression (7.1) and Fig. 27 that the size N_e^j of aluminum clusters at which new stationary-phase points $\bar{\lambda}_j$ appear can be estimated from the condition $v'_{\mu}(\lambda_{\mu}; N_e^j) = -\bar{s}_j/\bar{k}_j$. For this, it is sufficient to know the dependence of $v'_{\mu}(\lambda_{\mu})$ on the cluster size N_e . The analysis of this dependence performed in [62] for different parameters r_s and *a* showed that a decrease in r_s is equivalent to an increase in *a*, i.e., to the softening of the potential. The weak dependence of r_s on N_e found in self-consistent model calculations [137] should result in a very weak increase in the oscillation period with increasing N_e and a gradual passage from curves with large r_s to a curve with the smaller Wigner–Seitz electron radius $r_s^b = 2.07$, corresponding to the bulk characteristic of the metal.

The shell correction to the total electron energy was calculated in [62] for Al_N by expression (7.9) at T = 0 with potential (7.1) for a constant $r_s = 2.17 > r_s^b$. Figure 28 presents the results of these calculations, together with signal oscillations measured for the mass spectra of aluminum [146]. We can see that the contribution of five-point-star trajectories becomes dominant for $N_e > 750$ ($N_e^{1/3} > 9.1$), whereas the contribution of other star trajectories considered here is negligible. The argument of the cosine for the five-point-star trajectory linearly depends on $N_e^{1/3}$,

$$5v_{\mu}(\bar{\lambda}_{\star}) + 2\bar{\lambda}_{\star} = -2.75317 + 3.1487 N_{\rm e}^{1/3} \,, \tag{7.15}$$

which determines the periodic dependence on this variable. It is easy to see that the curves presented in Fig. 28 are in good agreement in their structure and period for $N_e > 750$. We also note the similar behavior of the chaotic part of the calculated and experimental spectra for $N_e < 750$, which, in our opinion, is formed by the contributions of star trajectories with $\bar{s}_j/\bar{k}_j = 3/7, 4/9, 5/11, 6/13$, and 6/13. The triangular trajectory and, correspondingly, the reconstruction of spectra should appear for $N_e^{1/3} \ge 14$, N > 900, i.e., outside the range of cluster sizes studied experimentally in [146].

Estimates [23] of the temperature decay of contributions from five-point-star and triangular trajectories show that the temperature factor for T = 300 K weakly differs from unity. Hence, if the lattice melts at T = 300 K, oscillations related to electron shells should be manifested almost in full measure.



Figure 28. (a) Dependence of the shell correction to the total electron energy on the aluminum cluster size $N_e = 3N$ according to (7.9) at zero temperature. The cosine-like curve is the contribution of the five-point star trajectory [see (7.15)]. Parameters are a = 2.7 and r = 2.17 (7.1). (b) Ion signal (IS) oscillations in the mass spectrum of aluminum clusters [146].

8. Conclusions

We have presented the modern semiclassical method for describing systems of many interacting fermions. The method is based on a refinement of the well-known, simple but comparatively rough Thomas–Fermi statistical model widely used in atomic and molecular physics, high-energydensity physics, nuclear physics, finite system physics, and so on. The introduction of additive corrections removed many disadvantages of the initial TF model, thereby extending the scope of its applications and the number of objects and properties described by the method without losing its simplicity and universality.

The correction of the TF model in the vicinity of Coulomb centers (nuclei of matter or individual atoms and molecules) removed theoretical difficulties inherent in the semiclassical model and completed its development. It was shown that these difficulties are related in part to another disadvantage of the TF statistical model and its modifications with the additive and self-consistent consideration of quantum and exchange corrections: the neglect of the shell structure of atoms and molecules. These difficulties can be eliminated only by considering all the quantum effects together.

Taking the refined quantum correction and exchange, correlation, and shell corrections into account, the refined model based on the TF model has been constructed; this model describes the thermodynamics of a weakly nonideal plasma well without the use of any experimental data, is consistent with the Saha–Reiser model at high temperatures, and transforms into the TFC model for degenerate matter. Thus, the RTF model covers a large region of the phase diagram corresponding to matter with high energy density and replaces the traditionally used combination of the ionization equilibrium model (for plasma) and the TFC model (for degenerate matter), with ambiguous interpolation between them.

We note that the RFT model retains the important selfsimilarity property with respect to the atomic number inherent in the TF model, while tabulated data available for hydrogen allow obtaining results for any substance, which considerably simplifies large-scale numerical calculations.

We have also shown that many properties of a spherically symmetric many-electron system are determined by the type of the self-consistent potential, which is either finite at the center, as in atomic clusters and nuclei, or has the Coulomb singularity, as in atoms and ions. These two types of potentials considerably differ, in particular, in the shape of one-particle spectra and possible forms of classical trajectories. This fact poses a question about the correctness of using pseudopotentials in which the Coulomb singularity of the potential is replaced by a 'ledge'. When quantum effects are taken into account, such a passage to a different type of potential can lead to erroneous results.

The semiclassical method was used for studying the local and integral characteristics of a variety of many-electron systems, such as one-dimensional quantum dots, atoms, ions, hollow and bulk atomic clusters, high-energy-density matter, and metal clusters. In particular, the intricate dependence of total-electron-energy oscillations on the number of particles and the interaction parameter in a one-dimensional quantum dot was explained, the reason for differences between the mass spectra of aluminum and sodium clusters was elucidated, an algorithm was proposed for estimating the ionization potentials of free ions, and the wide-range equation of state of highenergy-density matter was constructed. The high efficiency and clarity of the rather simple and universal semiclassical RTF model for describing the properties of matter and finite systems have thus been demonstrated.

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9. Appendices

Appendix A

The monotonically increasing Fermi-Dirac functions

$$I_{\nu}(y) = \int_{0}^{\infty} \frac{x^{\nu}}{1 + \exp(x - y)} \, \mathrm{d}x$$

satisfy the recurrence relation $I'_{\nu} = \nu I_{\nu-1}$ and have the asymptotic forms

$$\frac{y^{\nu+1}}{\nu+1} \quad \text{as} \quad y \to \infty, \quad \Gamma(\nu+1) \exp y \quad \text{as} \quad y \to -\infty.$$

Approximating relations between some frequently used Fermi–Dirac functions and the function $I_{1/2}$ are given by the Kalitkin formulas [102]

$$\begin{split} I_{3/2} &= \frac{3}{2} z \left(1 + 0.795z + 0.104z^{7/3} \right)^{2/7}, \\ I_{1/2}' &= \frac{1}{2} I_{-1/2} = z \left(1 + 1.452z + 0.623z^{7/3} \right)^{-2/7}, \\ I_0 &= \frac{2}{\sqrt{\pi}} z \left(1 + 1.28z + 0.351z^{7/3} \right)^{-1/7}, \end{split}$$

where $z = I_{1/2}(y) = \pi^2 n/(\sqrt{2}T^{3/2})$ and $I_0(y) = \ln(1 + \exp y)$ is the zeroth-order Fermi–Dirac function expressed in terms of elementary functions.

Appendix **B**

We consider the semiclassical spectrum of particles in a onedimensional periodic potential U(x) with period 2*R* satisfying the conditions U(R) = U(-R) = 0, U'(R) = U'(-R) = 0. Taking Bloch relations into account, the spectrum is determined from the solution of the Schrödinger equation in one cell $-R \le x \le R$ with the boundary conditions

$$\psi(R) = \exp(2ikR)\psi(-R), \quad \psi'(R) = \exp(2ikR)\psi'(-R).$$
(B.1)

The traditional semiclassical approximation is inapplicable at r = R near the 'hump' of the potential $(|\varepsilon| \sim 0)$ because the classical momentum of the particle $|p_{\varepsilon}(R)| = \sqrt{2|\varepsilon|}$ becomes small. We wish to obtain the quantization condition describing this region correctly by using the explicit form of the potential U(x) in the vicinity of the cell boundary r = R:

$$U(x) = -\gamma (R - x)^2, \quad \gamma > 0.$$

The solution of the Schrödinger equation with this potential is expressed in terms of parabolic cylinder functions. By matching the asymptotic forms of these functions with the semiclassical solution and using conditions (B.1) (see the details in [39, 112]), we obtain the quantization condition valid in the entire energy region:

$$\cos S_{\varepsilon} = \sin \left(\delta_{\varepsilon} \right) \, \cos \left(2kR \right),$$

where

$$\begin{split} \delta_{\varepsilon} &= \frac{\pi}{4} - \arctan\left(\tanh\frac{\pi d^2}{4}\right), \\ \tilde{S}_{\varepsilon} &= S_{\varepsilon} - \frac{d^2}{2}\ln\frac{|d^2|}{2e} + \arg\Gamma\left(\frac{1 + \mathrm{i}d^2}{2}\right), \\ d^2 &\equiv d_{\varepsilon}^2 = -\sqrt{\frac{2}{\gamma}}\varepsilon\,, \end{split}$$

and $\Gamma(z)$ is the gamma function of complex argument.

As the energy ε changes from $-\infty$ to $+\infty$, the value of δ_{ε} changes from 0 to $\pi/2$, characterizing the energy band in the spectrum of a one-dimensional crystal, the main change in δ_{ε} occurring for $|d^2| \leq 1$. This region is intermediate between the discrete and continuum spectra. The strong-coupling approximation corresponds to energies with $d^2 > 1$ when the value of δ_{ε} is proportional to the tunnel exponential, and the spectrum consists of discrete narrow bands (levels). The continuum spectrum corresponds to energies with $d^2 < -1$, where $\delta_{\varepsilon} = \pi/2$.

References

- Kirzhnits D A, Lozovik Yu E, Shpatakovskaya G V Usp. Fiz. Nauk 117 3 (1975) [Sov. Phys. Usp. 18 649 (1975)]
- 2. Brack M, Bhaduri R K Semiclassical Physics (Reading, Mass.: Addison-Wesley, 1997)
- 3. Lundqvist S, March N H (Eds) *Theory of the Inhomogeneous Electron Gas* (New York: Plenum Press, 1983)
- 4. Dirac P A M Proc. Cambr. Philos. Soc. 26 376 (1930)
- 5. Thomas L H Proc. Cambr. Philos. Soc. 23 542 (1927)
- 6. Fermi E Rend. Accad. Naz. Lincei 6 602 (1927)
- 7. Feynman R P, Metropolis N, Teller E Phys. Rev. 75 1561 (1949)
- 8. Sommerfeld A Z. Phys. 80 415 (1933)
- Gombás P Die statistische Theorie des Atoms und ihre Anwendungen (Wein: Springer-Verlag, 1949) [Translated into Russian (Moscow: IL, 1951)]
- 10. Schwinger J Phys. Rev. A 22 1827 (1980)
- Englert B-G, Schwinger J Phys. Rev. A 29 2331 (1984); Phys. Rev. A 29 2339 (1984)
- 12. Englert B-G, Schwinger J Phys. Rev. A 32 26 (1985)
- 13. Englert B-G Semiclassical Theory of Atoms (Berlin: Springer, 1988)
- 14. Dmitrieva I K, Plindov G I Phys. Lett. A 55 3 (1975)
- 15. Plindov G I, Dmitrieva I K J. Physique 38 1061 (1977)
- 16. Dmitrieva I K, Plindov G I J. Physique 45 85 (1984)
- 17. Shpatakovaskaya G V Pis'ma Zh. Eksp. Teor. Fiz. **86** 11 (2007) [JETP Lett. **86** 9 (2007)]
- Shpatakovskaya G V Fiz. Plazmy 34 275 (2008) [Plasma Phys. Rep. 34 245 (2008)]
- Gergel' V A, Suris R A Zh. Eksp. Teor. Fiz. 84 719 (1983) [Sov. Phys. JETP 57 415 (1983)]
- Gergel' V A, Shpatakovskaya G V Zh. Eksp. Teor. Fiz. 102 640 (1992) [Sov. Phys. JETP 75 342 (1992)]
- Gergel' V A, Shpatakovskaya G V Fiz. Tekh. Poluprovodn. 27 923 (1993) [Semiconductors 27 500 (1993)]
- 22. Kirzhnits D A, Shpatakovskaya G V Zh. Eksp. Teor. Fiz. 108 1238 (1995) [JETP 81 679 (1995)]
- 23. Shpatakovaskaya G V Zh. Eksp. Teor. Fiz. 118 87 (2000) [JETP 91 76 (2000)]
- Kirzhnits D A, Ivanov O V Zh. Eksp. Teor. Fiz. 104 3150 (1993) [JETP 77 488 (1993)]
- 25. Perrot F, Dharma-wardana M W C Phys. Rev. A 30 2619 (1984)
- 26. Hedin L, Lundqvist B I J. Phys. C 4 2064 (1971)
- 27. Hubbard J Proc. R. Soc. Lond. A 243 336 (1958)
- 28. Singwi K S et al. Phys. Rev. B 1 1044 (1970)

- 29. Vashishta P, Singwi K S Phys. Rev. B 6 875 (1972)
- 30. Von Barth U, Hedin L J. Phys. C 5 1629 (1972)
- 31. Vosko S H, Wilk L, Nusair M Can. J. Phys. 58 1200 (1980)
- 32. Wang Y, Perdew J P Phys. Rev. B 44 13298 (1991)
- 33. Perdew J P et al. Phys. Rev. B 46 6671 (1992)
- 34. Kirzhnits D A Zh. Eksp. Teor. Fiz. **32** 115 (1957) [Sov. Phys. JETP **5** 64 (1957)]
- Kirzhnits D A Polevye Metody Teorii Mnogikh Chastits (Field Theoretical Methods in Many-Body Systems) (Moscow: Atomizdat, 1963) [Translated into English (Oxford: Pergamon Press, 1967)]
- Kalitkin N N Zh. Eksp. Teor. Fiz. 38 1534 (1957) [Sov. Phys. JETP 11 1106 (1960)]
- Kalitkin N N, Kuz'mina L V, Preprint No. 35 (Moscow: Institute of Applied Mathematics of the USSR Academy of Sciences, 1975)]
- Fortov V E Ekstremal'nye Sostoyaniya Veshchestva (Extreme States of Matter) (Moscow: Fizmatlit, 2010) [Translated into English: Extreme States of Matter on Earth and in the Universe (Berlin: Springer, 2011)]
- Shpatakovskaya G V, Dissertation, Doctor of Physics and Mathematics (Moscow: LPI, 1992)]
- 40. Shpatakovskaya GV, in Proc. XIX AIRAPT Conf. on High Pressure Science and Technology, Colorado, 1994, p. 159
- Kirzhnits D A, Shpatakovskaya G V Pis'ma Zh. Eksp. Teor. Fiz. 59 446 (1994) [JETP Lett. 59 467 (1994)]
- 42. Kirzhnits D A, Shpatakovskaya G V Phys. Lett. A 198 94 (1995)
- Kirzhnits D A, Shpatakovskaya G V Teor. Mat. Fiz. 109 124 (1996) [Theor. Math. Phys. 109 1342 (1996)]
- 44. Scott J M C Philos. Mag. 43 859 (1952)
- 45. Fradkin E S *Zh. Eksp. Teor. Fiz.* **35** 1533 (1959) [*Sov. Phys. JETP* **9** 1087 (1959)]
- 46. Lieb E H Phys. Lett. A 70 444 (1979)
- 47. Siedentop H, Weikard R, Müller A M K Invent. Math. 97 159 (1989)
- Kirzhnits D A, Shpatakovskaya G V Zh. Eksp. Teor. Fiz. 62 2082 (1972) [Sov. Phys. JETP 35 1088 (1972)]
- Kirzhnits D A, Shpatakovskaya G V Zh. Eksp. Teor. Fiz. 66 1828 (1974) [Sov. Phys. JETP 39 899 (1974)]
- Shpatakovskaya G V, Preprint No. 67 (Moscow: Institute of Applied Mathematics of the USSR Academy of Sciences, 1983)]
- Spatakovskaya G V Teplofiz. Vys. Temp. 23 42 (1985) [High. Temp. 23 40 (1985)]
- 52. Shpatakovskaya G V, Kuz'menkov E A Int. J. Thermophys. 13 315 (1992)
- 53. Kirzhnits D A, Shpatakovskaya G V, Preprint No. 33 (Moscow: LPI, 1998)]
- Garanin S F Izv. Vyssh. Uchebn. Zaved. Fiz. (2) 81 (1984) [Sov. Phys. J. 27 156 (1984)]
- Magomedov K M Dokl. Akad. Nauk SSSR 62 2082 (1985) [Sov. Phys. Dokl. 20 1046 (1985)]
- Shpatakovskaya G V, Preprint No. 66 (Moscow: Institute of Applied Mathematics of the USSR Academy of Sciences, 1981)]
- 57. Shpatakovskaya G V Zh. Eksp. Teor. Fiz. **125** 518 (2004) [JETP **98** 455 (2004)]
- Shpatakovskaya G V Zh. Eksp. Teor. Fiz. 129 533 (2006) [JETP 102 466 (2006)]
- Shpatakovskaya G V, in *Entsiklopediya Nizkotemperaturnoi Plazmy* (Encyclopedia of Low-Temperature Plasma) Introductory Vol. 1 (Ed. V E Fortov) (Moscow: Nauka, 2000) p. 313
- Shpatakovskaya G V Pis'ma Zh. Eksp. Teor. Fiz. 73 306 (2001) [JETP Lett. 73 268 (2001)]
- Shpatakovskaya G V Pis'ma Zh. Eksp. Teor. Fiz. 70 333 (1999) [JETP Lett. 70 334 (1999)]; cond-mat/0001116
- Shpatakovskaya G V Pis'ma Zh. Eksp. Teor. Fiz. 72 394 (2000) [JETP Lett. 72 269 (2000)]
- 63. Brack M Adv. Solid State Phys. 41 459 (2001)
- 64. Brack M Rev. Mod. Phys. 65 677 (1993)
- 65. de Heer W A Rev. Mod. Phys. 65 611 (1993)
- 66. Yannouleas C, Landman U Phys. Rev. B 48 8376 (1993)
- 67. Strutinsky V M Nucleonika 20 679 (1975)
- 68. Strutinsky V M et al. Z. Phys. A 283 269 (1977)
- 69. Yannouleas C, Landman U J. Phys. Chem. B 101 5780 (1997)
- Yannouleas C, Bogachek E N, Landman U Phys. Rev. B 57 4872 (1998)
- 71. Strutinsky V M Nucl. Phys. A 95 420 (1967)

- Kalitkin N N, Kuz'mina L V Fiz. Tverd. Tela 13 2314 (1971) [Sov. Phys. Solid State 13 1938 (1972)]
- 73. Ullmo D et al. Phys. Rev. B 63 125339 (2001)
- 74. Novoselov K S et al. Science 306 666 (2004)
- 75. Novoselov K S et al. Nature 384 197 (1996)
- Castro Neto A H et al. *Rev. Mod. Phys.* 81 109 (2009); arXiv:0709.1163
- 77. Strutinsky V M Nucl. Phys. A 122 1 (1968)
- 78. Beenakker C W J Phys. Rev. B 44 1646 (1991)
- Landau L D, Lifshitz E M Kvantovaya Mekhanika. Nerelyativistskaya Teoriya (Quantum Mechanics. Non-Relativistic Theory) (Moscow: Fizmatlit, 1989) [Translated into English (Oxford: Pergamon Press, 1977)]
- Baz' A I, Zel'dovich Ya B, Perelomov A M Rasseyanie, Reaktsii i Raspady v Nerelyativistskoi Kvantovoi Mekhanike (Scattering, Reactions and Decay in Nonrelativistic Quantum Mechanics) (Moscow: Nauka, 1971) [Translated into English (Jerusalem: Israel Program for Scientific Translations, 1969)]
- Gryaznov V K, in *Entsiklopediya Nizkotemperaturnoi Plazmy* (Encyclopedia of Low-Temperature Plasma) Introductory Vol. 1 (Ed. V E Fortov) (Moscow: Nauka, 2000) p. 299
- Moore C E Atomic Energy Levels as Derived from the Analyses of Optical Spectra (Washington: U.S. Dept. of Commerce, National Bureau of Standards, 1949)
- 83. Carlson T A et al. Atom. Data Nucl. Data Tabl. 2 63 (1970)
- 84. Brack M, Quentin P Nucl. Phys. A 361 35 (1981)
- 85. Membrado M, Pacheco A F, Saudo J Phys. Rev. B 41 5643 (1990)
- Karpov V Ya, Shpatakovskaya G V Elektr. Zh. "Issledovano v Rossii" 5 2118 (2002); http://zhurnsl.ape.relarn.ru/articles/2002/ 191.pdf
- Shpatakovskaya G V, in *Fizika Ekstremal'nykh Sostoyanii Veshchestva*—2004 (Physics of the Extreme States of Matter 2004) (Eds V E Fortov et al.) (Chernogolovka: Inst. Probl. Khim. Fiz. Ross. Akad. Nauk, 2004) p. 9
- 88. Clougherty D P, Zhu X Phys. Rev. A 56 632 (1997)
- 89. Mann J B Atom. Data Nucl. Data Tabl. 12 1 (1973)
- 90. Parker G W Phys. Rev. A 33 799 (1986)
- 91. Hartree D R, Hartree W Proc. R. Soc. Lond. A 149 210 (1935)
- 92. Tietz T J. Chem. Phys. 22 2094 (1954)
- Akhiezer A I, Berestetskii V B Kvantovaya Elektrodinamika (Quantum Electrodynamics) (Moscow: Gostekhizdat, 1953) [Translated into English (New York: Interscience Publ., 1965)]
- McMahan A K, Ross M, in *High Pressure Science and Technology*. *Proc. of the 7th Intern. AIRAPT Conf., Le Creusot, France, July 30 – August 3, 1979* Vol. 2 (Eds B Vodar, Ph Marteau) (New York: Pergamon Press, 1980)
- 95. Shemyakin O P et al. J. Phys. A Math. Theor. 43 335003 (2010)
- Altshuler L V, in Shock Compression of Condensed Matter 1991. Proc. of the American Physical Society Topical Conf., Williamsburg, Virginia, June 17–20, 1991 (Eds S C Schmidt et al.) (Amsterdam: Elsevier, 1992)
- 97. Young D A et al. Phys. Lett. A 108 157 (1985)
- Gorbacheva G F, El'yashevich M A, Romanov G S Teplofiz. Vys. Temp. 13 61 (1975)
- 99. Iosilevskii I L, Gryaznov V K Teplofiz. Vys. Temp. 19 1121 (1981)
- 100. Stewart J C, Pyatt K D (Jr.) Astrophys. J. 144 1203 (1966)
- 101. Shpatakovskaya G V, in *Fizika Ekstremal'nykh Sostoyanii Veshchestva*—2005 (Physics of the Extreme States of Matter 2005) (Eds V E Fortov et al.) (Chernogolovka: Inst. Probl. Khim. Fiz. Ross. Akad. Nauk, 2005) p. 120
- Kalitkin N N, Ritus I V, Preprint No. 26 (Moscow: Institute of Applied Mathematics of the USSR Academy of Sciences, 1977)]
- 103. Strutinski V M Yad. Fiz. 3 614 (1966) [Sov. J. Nucl. Phys. 3 449 (1966)]
- 104. Kirzhnits D A Zh. Eksp. Teor. Fiz. 34 1625 (1958) [Sov Phys. JETP 7 1116 (1958)]
- 105. Hodges C H Can. J. Phys. 51 1428 (1973)
- 106. Polischuk A Ya Solid State Commun. 61 193 (1987)
- 107. Puente A, Casas M, Serra L Physica E 8 387 (2000)
- 108. Serra L, Puente A Eur. Phys. J. D 14 77 (2001)
- 109. Zel'dovich Ya B, Raizer Yu P Fizika Udarnykh Voln i Vysokotemperaturnykh Gidrodinamicheskikh Yavlenii (Physics of Shock Waves and High-Temperature Hydrodynamic Phenomena) (Moscow:

Nauka, 1966) [Transated into English (Mineola, N.Y.: Dover Publ., 2002)]

- 110. Nikiforov A F, Novikov V G, Uvarov V B Kvantovo-Statisticheskie Modeli Vysokotemperaturnoi Plazmy (Quantum-Statistical Models of Hot Dense Matter) (Moscow: Fizmatlit, 2000) [Translated into English (Basel: Birkhäuser Verlag, 2005)]
- 111. Voropinov A I, Gandel'man G M, Podval'nyi V G Usp. Fiz. Nauk 100 193 (1970) [Phys. Usp. 13 56 (1970)]
- 112. Shpatakovskaya G V, Preprint No. 28 (Moscow: Institute of Applied Mathematics of the USSR Academy of Sciences, 1985)]
- 113. Sin'ko G V Chisl. Metody Mekh. Splosh. Sredy 10 124 (1979)
- 114. Sin'ko G V Chisl. Metody Mekh. Splosh. Sredy **12** 121 (1981)
- 115. Rozsnyai B F Phys. Rev. A 5 1137 (1972)
- 116. Zittel W, Meyer-ter-Vehn J, Kübler J *Physica B*+C **139-140** 364 (1986)
- 117. McMahan A K *Physica B*+C **139-140** 31 (1986)
- 118. Meyer-ter-Vehn J, Zittel W Phys. Rev. B 37 8674 (1988)
- 119. Chernov S V Teplofiz. Vys. Temp. 26 264 (1988)
- 120. Hostler L J. Math. Phys. 5 591 (1964)
- 121. Plindov G I, I K Dmitrieva I K Phys. Lett. A 64 348 (1978)
- 122. Shpatakovskaya G V, Preprint No. 160 (Moscow: Institute of Applied Mathematics of the USSR Academy of Sciences, 1988)]
- 123. Bushman A V et al. Pis'ma Zh. Eksp. Teor. Fiz. 39 341 (1984) [JETP Lett. 39 411 (1984)]
- 124. Ragan C E (III) Phys. Rev. A 25 3360 (1982)
- 125. Ragan C E (III) Phys. Rev. A 29 1391 (1984)
- Nellis W J et al., in Shock Waves in Condensed Matter 1983. Proc. of the American Physical Society Topical Conf., Santa Fe, New Mexico, July 18-21, 1983 (Amsterdam: North-Holland, 1983)
- 127. Al'tshuler L B et al. Zh. Eksp. Teor. Fiz. 72 317 (1977) [Sov. Phys. JETP 45 167 (1977)]
- 128. Kormer S B et al. Zh. Eksp. Teor. Fiz. 42 686 (1962) [Sov. Phys. JETP 15 477 (1962)]
- 129. Simonenko V A et al. Zh. Eksp. Teor. Fiz. 88 1452 (1985) [Sov. Phys. JETP 61 869 (1985)]
- Avrorin E N et al. Pis'ma Zh. Eksp. Teor. Fiz. 43 241 (1986) [JETP Lett. 43 308 (1986)]
- 131. Marsh S P (Ed.) *LASL Shock Hugoniot Data* (Berkeley: Univ. California Press, 1980)
- 132. Krupnikov K K et al. *Dokl. Akad. Nauk SSSR* **148** 1302 (1963) [*Sov. Phys. Dokl.* **8** 205 (1963)]
- 133. Ragan C E (III), Silbert M G, Diven B C J. Appl. Phys. 48 2860 (1977)
- 134. Kopyshev V P Chisl. Metody Mekh. Splosh. Sredy 8 54 (1977)
- 135. Trainor K S J. Appl. Phys. 54 2372 (1983)
- 136. Genzken O, Brack M Phys. Rev. Lett. 67 3286 (1991)
- 137. Nishioka H, Hansen K, Mottelson B R Phys. Rev. B 42 9377 (1990)
- 138. Clemenger K Phys. Rev. B 44 12991 (1991)
- 139. Balian R, Bloch C Ann. Physics 69 76 (1972)
- Björnholm S, in Nuclear Physics Concepts in the Study of Atomic Cluster Physics (Eds R Schmidt, H O Lutz, R Dreizler) (Berlin: Springer, 1992) p. 26
- 141. Koch E Phys. Rev. B 58 2329 (1998); cond-mat/9803309
- 142. Martin T P et al. Chem. Phys. Lett. 172 209 (1990)
- 143. Persson J L et al. Chem. Phys. Lett. 186 215 (1991)
- 144. Martin T P, Näher U, Schaber H Chem. Phys. Lett. 199 470 (1992)
- 145. Pedersen J et al. *Nature* **353** 733 (1991)
- 146. Lermé J et al. Phys. Rev. Lett. 68 2818 (1992)
- 147. Gutzwiller M C J. Math. Phys. 8 1979 (1967)
- 148. Gutzwiller M C J. Math. Phys. 10 1004 (1969)
- 149. Gutzwiller M C J. Math. Phys. 12 343 (1971)
- Mansikka-aho J, Manninen M, Nishioka H Phys. Rev. B 48 1837 (1993)
- Bogachek É N, Gogadze G A Zh. Eksp. Teor. Fiz. 63 1839 (1972) [Sov. Phys. JETP 36 973 (1973)]
- 152. Yannouleas C, Bogachek E N, Landman U Phys. Rev. B 57 4872 (1998)
- Landau L D, Lifshitz E M Mekhanika (Mechanics) (Moscow: Fizmatgiz, 1958) [Translated into English (Oxford: Pergamon Press, 1976)]
- 154. Creagh S C, Littlejohn R G J. Phys. A Math. Gen. 25 1643 (1992)