Statistical model of matter, corrected in the neighborhood of nuclei

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A systematic quantum-mechanical method is developed for correcting the Thomas–Fermi model at short distances from the nucleus, where the semiclassical approximation is invalid. The proposed approach covers both degenerate and high-temperature systems and makes it possible to eliminate the defects of the Thomas–Fermi model associated with proximity to nuclei, namely, divergence of the quantum corrections to the energy values at the point $r=0$ and the disagreement with the results of perturbation theory in the region of superhigh pressures and/or temperatures. Specific applications are to the theory of the equation of state of matter with high energy density. © *1995 American Institute of Physics.* [S1063-7761(95)00510-9]

1. INTRODUCTION

In the theory of electron–nucleus systems with high energy density, one traditionally uses the Thomas–Fermi statistical model,[1–3] which is distinguished by its elegance and simplicity of the calculations. In particular, this model possesses the property of self-similarity, which makes it possible to describe matter with different values of the charge $Z\gg 1$ of the nucleus in a unified manner. The Thomas–Fermi model is usually combined with replacement of the solution of the multi-center problem (matter) by consideration of a single-center neutral cell with radius R equal to half the mean separation between the nuclei of the matter, $R\sim(Z/n_e)^{1/3}$ (n_e is the electron concentration), with corresponding boundary conditions.

The region of applicability of the Thomas–Fermi model is determined by the condition for quasiclassical motion of the electron in the self-consistent field $U(r)$:

$$\xi=dp_\mu^{-1}/dr\ll 1. \tag{1}$$

where $p_\mu=\sqrt{2(\mu-U)}^{1/2}(\mu\geqslant U)$, $p_\mu=0(\mu<U)$ is the Fermi momentum, and μ is the chemical potential. Here and in what follows, we use atomic units. For $\xi<1$, the results can be improved if we take into account the quantum (gradient) and shell corrections to the Thomas–Fermi model.[4,5]

In an isolated atom ($R=\infty$), the condition (1) is satisfied at distances $1/Z<r<1$, i.e., it is violated in the neighborhood of the nucleus and at large distances. For atoms of strongly compressed and/or heated matter, this condition is also satisfied in their peripheral part, where the electron distribution is nearly uniform. This explains the success of the Thomas–Fermi model in the description of extreme states of matter. However, in a small region of radius r_0 adjoining the nucleus, the condition (1) is violated under all external conditions. To determine the value of r_0 in the general case, we use the fact that the field $U(r)$ in the neighborhood of the nucleus, $r<r_0$, is practically identical to the Coulomb field:

$$U(r)\simeq -Z/r,\quad r<r_0. \tag{2}$$

This enables us, using the condition $\xi=1$ at $r=r_0$, to find readily $r_0=Z^{-1}$ and $r_0=\sqrt{Z}|\mu|^{-3/4}$, respectively, in the regions

$$|\mu|<Z^2, \tag{3a}$$

$$|\mu|>Z^2. \tag{3b}$$

It can be seen from this that in the case of "cold" (temperature $T=0$) compressed matter the ratio of the radius r_0 to the cell radius R in the region (3a) increases with increasing compression as $\mu^{1/2}$, reaches values $Z^{-1/3}\ll 1$ for $\mu\sim Z^2$, and then decreases as $\mu^{-1/4}$ (see Fig. 1a) in the region (3b). In contrast, in the case of a constant-density plasma (on an isochor) an increase in the temperature (increase in the absolute value of the chemical potential) does not change the ratio $r_0/R\sim(n/Z^4)^{1/3}\ll 1$ in the region (3a), but in the region (3b) the ratio decreases as $\sim|\mu|^{-3/4}$ (see Fig. 1b).

The answer to the important question of whether the electrons on the scale r_0 are affected by an external perturbation is determined by the ratio $|\mu|r_0/Z$, the value of which is less than (or greater than) unity in the region (3a) [or (3b)]. It follows from this that in the region (3b) the failure of the condition (1) near a nucleus must affect the value of the pressure and the specific heat.

This violation of the condition (1) leads to the following defects of the Thomas–Fermi model:

1) the integrated energy values calculated with it differ appreciably from the exact values, and the quantum corrections to these values are expressed in terms of integrals over the volume that diverge at the point $r=0$;

2) even if this last difficulty can be avoided by considering only the change in the energy values as a result of compression and/or heating,[6,7] in the region (3b) the results of perturbation theory with respect to the interaction, which is valid here, are not reproduced.[5,8]

In the literature, various methods for eliminating these defects of the Thomas–Fermi model have been described.[9–13] One of them consists of treating the lowest quantum correction on an equal footing with the remaining

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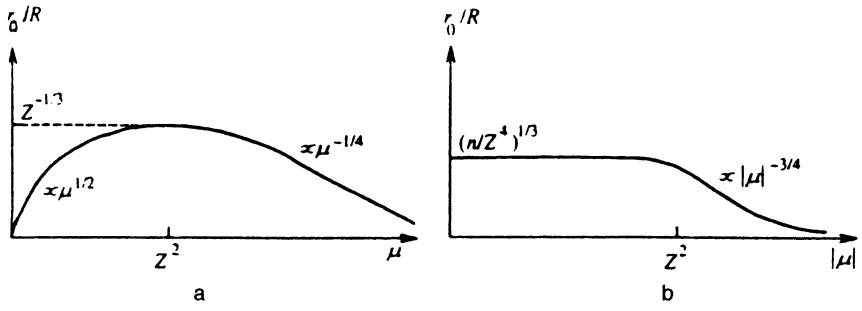

FIG. 1. Ratio of the radius r_0 of the region of nonsemiclassical behavior in the neighborhood of the nuclei to the mean separation $2R$ between nuclei of the matter as a function of the chemical potential μ: a—on the zero isotherm $T=0$; b—on the isochor $n_e=$const.

terms of the energy functional (in particular the exchange energy) in the variational method; this makes the extremal (the density) a regular function of r.[11] Such an approach, which is known as the quantum statistical model,[14–16] leads to an Euler–Lagrange equation in which the contribution of the quantum corrections of the higher orders is replaced by the nonlinear contribution of the lower correction. A second method consists of an artificial "truncation" of the energy distribution of the levels at its lower limit using a specially chosen quantity.[10] Finally, a third approach, a development of which is the approach adopted in this paper, is based on the expression (2) and on the fact that for the Coulomb field the exact solution of the problem is known. In particular, this makes it possible, using the exact spectrum, to "cut off" the divergences of the quantum corrections to the energy at r_0 by replacing them with the Scott correction:[9,12,13]

$$E_{Sc}=Z^2/2. \tag{4}$$

However, none of the methods we have described satisfies the complete set of requirements, namely, the elimination of the defects of the Thomas–Fermi model described above, the ability to deal with all types of extreme states (heavy atoms, compressed and hot matter), a consistently quantum-mechanical derivation, and retention of the simplicity and self-similarity inherent in the Thomas–Fermi model. The aim of the presence paper is to propose a general method for correcting the Thomas–Fermi model at short distances from a nucleus so as to fulfill all these requirements. A brief description of the approach and preliminary results have been published in Refs. 17 and 18.

To conclude this section, we note that from the methodological point of view the correction of the Thomas–Fermi model in the neighborhood of a nucleus is intended to complete the many years of work on the improvement of this model and extend the domain of its applicability. The remaining efforts, concerned with methods of describing the exchange, correlation, and shell effects, have been fairly well developed and are described in the literature.

2. THE METHOD OF THE APPROACH

To solve the problem we have posed for an arbitrary integrated physical quantity A, it is convenient to operate with the difference δA of the values of this quantity corresponding to the Hartree approximation and the approximation of the Thomas–Fermi model (near a nucleus, the exchange and correlation corrections are relatively small and can be considered independently). Namely, this difference, which is the total sum of the quantum (gradient) and shell corrections of all orders, becomes small when the condition (1) is satisfied and is very sensitive to its violation. In what follows, except in Sec. 7, we shall consider only the part of δA that corresponds to the total sum of the quantum (gradient) corrections, i.e., we remove from it the shell corrections. When the condition (1) is satisfied, the sum of the quantum corrections in which we are interested reduces to the quantum correction of the lowest (second) order $\delta_2 A$, which is a quantity integrated over space and for which, in particular, the defects listed in the Introduction are characteristic.

The problem is to correct this quantity, i.e., to go from $\delta_2 A$ to a quantity δA^c corrected in the neighborhood of a nucleus. The density that occurs in the latter expression must be equal to the density in the first for $r>r_0$ and to the exact solution of the Coulomb problem for $r<r_0$ [see (2)]. The simplest and most transparent way of making such a transition, which was proposed by one of the present authors in Ref. 19, is as follows. Besides the original problem, one solves an auxiliary problem (the quantities relating to it will be identified below by the addition of a tilde), in which the electrons are assumed to interact only with the nucleus and not with each other, so that Eq. (2) will hold in the complete space. The chemical potential $\tilde{\mu}$ of this system is assumed to be equal to the chemical potential μ of the original problem in the Thomas–Fermi approximation.

We now show that representation of the required quantity δA^c in the form of the combination

$$\delta A^c=\delta_2 A-\delta_2\tilde{A}+\delta\tilde{A} \tag{5}$$

satisfies the imposed conditions. Indeed, for $r<r_0$, when Eq. (2) holds, the densities of the first two terms on the right-hand side of (5) must cancel, and the result is identical to the exact solution of the Coulomb problem. In contrast, at distances $r>r_0$, where the motion is semiclassical in accordance with the definition of r_0, the densities of the last two terms of (5) cancel, and the result reduces to the density of the original quantity $\delta_2 A$. Note that the integrals over space that arise in (5) are taken over the volume of the cell for the original problem, while for the auxiliary problem they can be taken over the whole of space.

The described method is suitable both for a "cold" system ($T=0$) and for a nonzero temperature. In the second

case, it must be borne in mind that although for $T>n_e$ the quantum corrections become small compared with the correlation corrections and it would appear that their consideration becomes largely meaningless the existence of the region near the nucleus in which the behavior is not semiclassical has the consequence that the revised quantum correction is by no means small, as will be shown below, and must definitely be taken into account.

3. GENERAL RELATIONS

In this paper, we restrict consideration to energies, understanding by A the free energy $\mathscr{F}$ (at $T=0$, simply the energy $\mathscr{E}$). Therefore, in what follows we shall deal with the quantities $\delta\mathscr{F}$, $\delta\mathscr{E}$, etc., in which the corresponding differences (see Sec. 2) are taken at the same values of the temperature $T\equiv\beta^{-1}$, the volume V, and the total number N of particles. As is well known,[20] such differences are equal to the corresponding differences for the thermodynamic potential Ω corresponding to the same values of T, V, and μ and are denoted below by the symbol $\bar{\delta}$. Thus, we have[5]

$$\delta\mathscr{F}=\bar{\delta}\ \Omega=-\int_{-\infty}^{\mu}d\mu'\,\bar{\delta}N(\mu'). \tag{6}$$

Here μ is the chemical potential in the Thomas–Fermi approximation, and $N(\mu)$ is related by

$$N(\mu)=2\int_{-\infty}^{\infty}d\mu'\rho(\mu')\Phi(3(\mu'-\mu)),$$

$$\Phi(x)=\frac{1}{1+\exp x}, \tag{7}$$

to the level density of the system:

$$\rho(\mu')=\mathrm{Tr}\ \delta(\mu'-\hat{H})=-\frac{1}{\pi}\,\mathrm{Im\ Tr}\,\hat{G}(\mu'). \tag{8}$$

Here $\hat{H}=\hat{\mathbf{p}}^2/2+U(\mathbf{x})$ is the single-particle Hamiltonian, and

$$G(\mathbf{x},\mathbf{x}'|\mu')=\hat{G}(\mu')\delta(\mathbf{x}-\mathbf{x}'),\quad \hat{G}(\mu')=(\mu'-\hat{H}+i\delta)^{-1} \tag{9}$$

is the retarded Green's function of an electron in the self-consistent field. Taking the trace with respect to the system of plane waves $\exp(i\mathbf{px})$ and bearing in mind that the Thomas–Fermi model corresponds to neglect of the commutators of the terms of the Hamiltonian $\hat{H}$ (Ref. 21), we have

$$\bar{\delta}\rho(\mu')=\rho(\mu')-\rho_{TF}(\mu')=\int d\mathbf{x}d^3p\left[\delta\left(\mu'-\frac{1}{2}(\hat{\mathbf{p}}-i\nabla)^2/2-U\right)-\delta\left(\mu'-\frac{p^2}{2}-U\right)\right], \tag{10}$$

where $d^3p=d\mathbf{p}/(2\pi)^3$, the gradient acts only on U, and

$$\rho_{TF}(\mu')=\frac{1}{2\pi^2}\int d\mathbf{x}p_{\mu'}(\mathbf{x}). \tag{11}$$

At zero temperature ($\beta\to\infty$), the expressions (6) and (7) give

$$\delta\mathscr{F}=\delta\mathscr{E}=-2\int_{-\infty}^{\mu}d\mu'(\mu-\mu')\bar{\delta}\rho(\mu'). \tag{12}$$

The same expressions lead to a relationship between the corrections $\delta\mathscr{F}$ and $\delta\mathscr{E}$:

$$\delta\mathscr{F}=\hat{B}\,\delta\mathscr{E}\equiv-\int_{-\infty}^{\infty}d\mu'\,\frac{\partial\Phi(\beta(\mu'-\mu))}{\partial\mu'}\,\bar{\delta}\mathscr{E}(\mu'), \tag{13}$$

and this relationship makes it possible to carry out the most laborious part of the calculations in the low-temperature limit and go over to finite values of β only in the final stage. The operation $\hat{B}$ introduced in (13) leads to the results

$$\hat{B}1=1,\quad \hat{B}p_{\mu'}^n=\left(\frac{2}{3}\right)^{n/2}I'_{n/2}\left(\frac{\beta p_\mu^2}{2}\right),$$

where

$$I_\nu(x)=\int_0^\infty dy y^\nu\frac{1}{e^{y-x}+1}$$

is the Fermi–Dirac function, which satisfies the recursion relation

$$I'_\nu=\nu I_{\nu-1}\quad(\nu>0)$$

and has the asymptotic behavior

$$I_\nu\to\begin{cases}x^{\nu+1}/(\nu+1), & x\to\infty,\\ \Gamma(\nu+1)e^{x}, & x\to-\infty.\end{cases}$$

Note that in the expression (12) it is possible to transform to integration over $\mu'\geqslant\mu$ by using the sum rules[17]

$$\int_{-\infty}^{\infty}d\mu'\,\bar{\delta}\rho(\mu')=0,\quad \int_{-\infty}^{\infty}d\mu'\mu'\,\bar{\delta}\rho(\mu')=\frac{Z^2}{8}, \tag{14}$$

which are obtained by accurate consideration of the contribution of the Coulomb singularity in the region of large μ'. Like anomalies in quantum field theory, the nonvanishing right-hand side of the second relation (14) (although it vanishes formally as a result of the substitution of (10)) is associated with precisely this contribution.

4. QUANTUM CORRECTIONS OF LOWEST ORDER

In this section, we shall determine for the original and the auxiliary problem the quantities $\delta_2\mathscr{E}$ and $\delta_2\bar{\mathscr{E}}$, the difference of which occurs in the expression (5). We emphasize that in what follows it is necessary to distinguish μ, the chemical potential in the Thomas–Fermi model, from μ', the independent argument, with respect to which integration will later be performed in the transition to nonzero temperatures. Using the standard method[21] and expanding (10) to second order in the gradients, we obtain

$$\bar{\delta}_2\rho(\mu')=\frac{1}{192\pi^2}\frac{\partial^2}{\partial\mu'^2}\int d\mathbf{x}\left[4p_{\mu'}\Delta p_{\mu'}^2+\frac{(\nabla p_{\mu'}^2)^2}{p_{\mu'}}\right],$$

substitution of which in (12) gives the well-known relation

$$\bar{\delta}_2\mathscr{E}(\mu')=-\frac{1}{96\pi^2}\int d\mathbf{x}\left[4p_{\mu'}\Delta p_{\mu'}^2+\frac{(\nabla p_{\mu'}^2)^2}{p_{\mu'}}\right]. \tag{15}$$

Further, using the equation

$$\frac{(\nabla p_{\mu'}^2)^2}{2p_{\mu'}}=\nabla(p_{\mu'}\nabla p_{\mu'}^2)-p_{\mu'}\Delta p_{\mu'}^2, \tag{16}$$

we can readily reduce the expression (15) to the form

$$\bar{\delta}_2\mathscr{K}(\mu')=-\frac{1}{48\pi^2}\int d\mathbf{x}p_{\mu'}\Delta p_{\mu'}^2+\mathscr{K}_\Sigma(\mu'), \qquad (17)$$

where $\mathscr{K}_\Sigma$, which is generated by the term with the divergence in (16), is a sum of surface integrals over the outer surface of a cell of radius R and over a surface of infinitesimal radius surrounding the point $r=0$. The first of these integrals is equal to zero for a neutral cell, while the second integral is infinite (inf_1) on account of the singularity of (2) at the point $r=0$. Further, we take into account the Thomas–Fermi equation

$$\Delta p_{\mu'}^2=-2\Delta U=8\pi n_{TF}(\mathbf{x},\mu)-8\pi Z\delta(\mathbf{x}). \qquad (18)$$

Here in the first term on the right-hand side

$$n_{TF}(\mathbf{x},\mu)=\frac{\sqrt{2T^3}}{\pi^2}I_{1/2}\left(\frac{\beta p_\mu^2}{2}\right)$$

is the electron charge density in the Thomas–Fermi model. The second term in (18) contains the charge density of a point nucleus, which is one further source of infinities (inf_2). Thus, we can write $\bar{\delta}_2\mathscr{E}(\mu')$ in the form

$$\bar{\delta}_2\mathscr{E}(\mu')=-\frac{1}{6\pi}\int d\mathbf{x}p_{\mu'}n_{TF}(\mathbf{x},\mu)+\mathrm{inf}_1+\mathrm{inf}_2. \qquad (19)$$

The appearance of the infinities inf_1 and inf_2 corresponds to the difficulty 1 (see the Introduction).

For the auxiliary problem, the same relations (15) and (16) hold. At the same time, by virtue of (2) the surface integral around the point $r=0$ is exactly equal to the analogous integral for the original problem inf_1 (see above). Because of the absence of the interelectron interaction, the Thomas–Fermi equation now has the form

$$\Delta\tilde{p}_{\mu'}^2=-8\pi Z\delta(\mathbf{x}). \qquad (20)$$

Therefore, the second source of the infinities—the right-hand side of (20)—also leads to the same expression for inf_2 that was obtained for the original system. Therefore, the difference $\bar{\delta}_2\mathscr{E}(\mu')-\bar{\delta}_2\tilde{\mathscr{E}}(\mu')$ in (5) will be a finite quantity, i.e., it will be free of difficulty 1. However, because of the slow decrease of the Coulomb potential, the integral over the outer surface, which will be infinite in the case of the auxiliary problem, will have a nonzero value for $\mu'>0$. With allowance for this contribution, the lowest quantum correction for the auxiliary problem has the form

$$\bar{\delta}_2\tilde{\mathscr{E}}(\mu')=\mathrm{inf}_1+\mathrm{inf}_2+\frac{Z}{6\pi}\sqrt{2\mu'}\,\theta(\mu'). \qquad (21)$$

where $\theta(x)=0$ $(x<0)$, $\theta(x)=1$ $(x>0)$.

5. EXACT SOLUTION OF THE AUXILIARY PROBLEM

In accordance with the expression (5), it remains for us to find the exact expression for the difference $\delta\tilde{\mathscr{E}}(\mu')$. As was emphasized at the beginning of Sec. 2, from this quantity it is necessary to remove the shell corrections that arise when μ' crosses the discrete energy levels. Accordingly, we begin by considering the region of bound states: $\mu<0$. The level density of the discrete spectrum has the obvious form

$$\tilde{\rho}(\mu')=\sum_{n=1}^{\infty}n^2\delta(\mu'-E_n),\quad E_n=-\frac{Z^2}{2n^2}, \qquad (22)$$

where n is the principal quantum number, and n^2 is the degeneracy of the level. Using for the calculation of the sum the well-known Poisson formula

$$\sum_{n=1}^{\infty}f_n=\sum_{k=-\infty}^{\infty}\int_{1-\varepsilon}^{\infty}f(n)\cos(2\pi kn),\quad 0<\varepsilon<1,$$

which follows from the equation

$$\sum_{k=-\infty}^{\infty}\cos(2\pi kn)=\sum_{m=-\infty}^{\infty}\delta(n-m), \qquad (23)$$

separating the term with $k=0$, and extending the integration over n to zero, we obtain

$$\tilde{\rho}(\mu')=\left\{\int_0^{\infty}dn+\left[\int_0^{\infty}dn\sum_{k=0}-\int_0^{1-\varepsilon}dn\sum_k\right]\cos(2\pi kn)\right\}n^2\delta(\mu'-E_n). \qquad (24)$$

Here the first term in curly brackets corresponds to the Thomas–Fermi model and the second corresponds to the shell effects,[22] while the third term can be written in the form

$$-\int_0^{1-\varepsilon}dn\,\delta(n)\delta(\mu'-E_n)n^2, \qquad (25)$$

and, since both sides of (23) are even in n, the function $\delta(n)$ is symmetric about the point $n=0$. Subtracting the first and second terms from (24) in accordance with what we said above and substituting the remainder in (12), we find in accordance with (4)

$$\bar{\delta}\tilde{\mathscr{E}}(\mu')=E_{Sc},\quad \mu'<0. \qquad (26)$$

We make three remarks. First, from the condition that the spectrum is bounded below [$\tilde{\rho}(\mu')=0$ for $\mu'<-Z^2/2$] it follows that the Scott correction can be represented in the form

$$E_{Sc}=-\tilde{\mathscr{E}}_{TF}(\mu')-\tilde{\mathscr{E}}_{sh}(\mu'),\quad (\mu'<-Z^2/2),$$

where $\tilde{\mathscr{E}}_{TF}(\mu')=Z^3/\sqrt{2|\mu'|}$ is the energy in the Thomas–Fermi model, and $\tilde{\mathscr{E}}_{sh}(\mu')$, is the shell correction[23] for the auxiliary problem. It is also clear that this relation is valid not only for the auxiliary problem but also for all the electron–nucleus systems that we consider, since the region $\mu'<-Z^2/2$ corresponds to strongly bound electrons, for which the condition (2) holds. Therefore, in the general case

$$E_{Sc}=-\mathscr{K}_{TF}(\mu')-\mathscr{K}_{sh}(\mu'),\quad \mu'<-Z^2/2. \qquad (27)$$

Second, since the Scott correction can be expressed in terms of $\delta(n)$ [see (25)], it can be regarded as a cancellation of the unphysical state with $n=0$ and $E_0=-\infty$ taken into account redundantly in the Thomas–Fermi model and in the shell correction [see (27)]. Third, as is clear, for example, from the problem of an isolated atom, where $\xi^2\sim Z^{-2/3}$ [see (1)], the Scott correction to the energy is nonanalytic with respect to this parameter since it has the order $\sqrt{\xi^2}$ relative to the prin-

TABLE I. The function $f(\sigma)$ and its derivative $f'(\sigma)$.

σ	$f(\sigma)$	$f'(\sigma)$	σ	$f(\sigma)$	$f'(\sigma)$
20.00	5.9539 + 00	3.3041 − 01	2.00	2.4061 − 01	2.3446 − 01
10.00	2.6724 + 00	3.2411 − 01	1.25	8.6927 − 02	1.6734 − 01
6.67	1.6038 + 00	3.1566 − 01	1.00	4.9305 − 02	1.3117 − 01
5.00	1.0850 + 00	3.0575 − 01	0.80	2.6439 − 02	9.6192 − 02
4.00	7.8422 − 01	2.9482 − 01	0.50	6.2255 − 03	3.9823 − 02
3.33	5.9136 − 01	2.8321 − 01	0.40	3.0653 − 03	2.4411 − 02
2.50	3.6444 − 01	2.5895 − 01	0.20	3.4553 − 04	5.4036 − 03

cipal term in the Thomas–Fermi model ($\sim Z^{7/3}$). Therefore, in the power-law expansion of this quantity in even powers of ξ infinities arise (difficulty 1; see the Introduction).

We turn to consideration of the case $\mu>0$. It is clear, in the first place, that the contribution of the region $\mu'<0$ to the integral (12) is, as before, determined by the expression (26). With regard to the contribution of the region $0<\mu'<\mu$, in which there are no shell effects, it is expressed in accordance with (8)–(12) in terms of the exact Coulomb Green's function[24]

$$G(\mathbf{x},\mathbf{x}'|\mu)=\frac{ik}{2\pi}\int_1^\infty ds e^{i\alpha}J_0(\gamma), \tag{28}$$

where

$$k=\sqrt{2\mu},\quad \alpha=k(r+r')s+\lambda,$$
$$\gamma=k\sqrt{2(rr'+\mathbf{x}\mathbf{x}')(s^2-1)},$$
$$r=|\mathbf{x}|,\quad r'=|\mathbf{x}'|,\quad \lambda=\frac{Z}{k}\ln\frac{s+1}{s-1}.$$

For the free Green's function ($Z=0$), the exact value is equal to the semiclassical value, from which we obtain the equation

$$\frac{2k}{\pi}\int_0^\infty dr r^2\left[1+\cos(2kr)\int_1^\infty ds J_0(2kr\sqrt{s^2-1})\right]=0.$$

Accordingly, we can write $\delta\tilde{\rho}$ in the form

$$\frac{2k}{\pi}\int_0^\infty dr r^2\left\{2\int_1^\infty ds\,\sin\frac{\lambda}{2}\sin\left(2krs+\frac{\lambda}{2}\right)J_0(2kr\sqrt{s^2-1})-\sqrt{1+\frac{2Z}{k^2r}}+1\right\}.$$

Cumbersome but in principle simple calculations[1)] give

$$\delta\tilde{\rho}(\mu')=\frac{1}{96\pi Z^2\sigma^3}\left(1+3\sigma^2\frac{\partial^3}{\partial\sigma^3}A\right),\quad \sigma=\frac{\sqrt{2\mu'}}{2Z},$$
$$A=\int_0^\infty\frac{dx}{x^3}\sin x\left[\coth(x\sigma)-\frac{1}{x\sigma}\right]. \tag{29}$$

Substitution of (29) in (12) leads to the final expression

$$\delta\tilde{\varepsilon}=E_{Sc}+\left[\frac{Z}{6\pi}\sqrt{2\mu'}+\frac{Z^2}{\pi}f(\sigma)\right]\theta(\mu'), \tag{30}$$

where

$$f(\sigma)=\left(1-\sigma\frac{\partial}{\partial\sigma}\right)A(\sigma).$$

For $\sigma\ll 1$, the condition of semiclassical behavior (1) is satisfied for the Coulomb problem, and for $\sigma\gg 1$ perturbation theory with respect to the Coulomb interaction is valid. For the function $f(\sigma)$ in (30), we have the following expansions. The series in powers of σ has the form

$$f(\sigma)=\sum_{n=2}^\infty\frac{2^{2n}|B_{2n}|\sigma^{2n-1}}{(2n-3)(2n-1)2n}$$

(B_n are the Bernoulli numbers) and it begins with the small (for small σ) term

$$f(\sigma)=\frac{2}{45}\sigma^3+O(\sigma^5). \tag{31}$$

In the opposite case ($\sigma\gg 1$)

$$f(\sigma)=\frac{\sigma}{3}-\frac{\pi}{4}-\frac{1}{3\sigma}\ln\left(\frac{\gamma}{2\sigma}\right)+\frac{4}{9\sigma}+\sum_{n=2}^\infty\frac{(-1)^n\zeta(2n-1)\sigma^{1-2n}}{2(2n-2)(4n^2-1)}$$

($\ln\gamma=C$ is Euler's constant, ζ is the Riemann zeta function), and the corresponding asymptotic behavior is

$$f(\sigma)=\frac{\sigma}{3}-\frac{\pi}{4}+O\left(\frac{1}{\sigma}\right). \tag{32}$$

In the general case, introducing the mean value

$$\langle a(y)\rangle_n=\frac{n}{y^n}\int_0^y dx x^{n-1}a(x),$$

we can express $f(\sigma)$ in terms of the gamma function of imaginary argument:

$$f(\sigma)=\mathrm{Im}\langle\ln\Gamma(i\sigma')\rangle_2-\frac{2\sigma'}{3}\times\left(\ln\sigma'-\frac{4}{3}\right)+\frac{1}{6\sigma'}+\frac{\pi}{4},\quad \sigma'=\frac{1}{2\sigma}.$$

The results of numerical calculation of the function $f(\sigma)$ and its derivative are given in Table I and in Fig. 2.

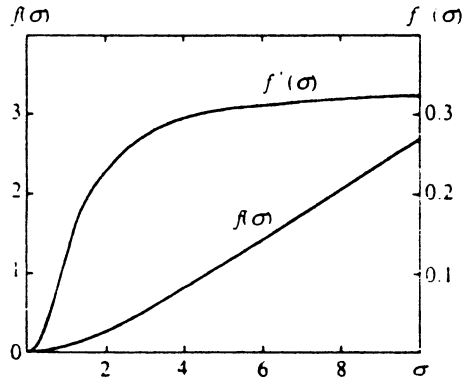

FIG. 2. The function $f(\sigma)$ and its derivative $f'(\sigma)$.

6. REVISED QUANTUM CORRECTION: ZERO TEMPERATURE

To obtain expressions for the revised quantum correction, it remains to substitute the results (17), (19), (21), and (30) obtained in Secs. 4 and 5 in the expression (5), understanding by A the free energy $\mathscr{F}$. If we use (13), this substitution gives

$$\delta_2\mathscr{F}^c = E_{Sc} + \mathscr{F}_{qu} - \frac{Z^2}{\pi}\int_0^\infty d\mu' f(\sigma)\frac{\partial\Phi(\beta(\mu'-\mu))}{\partial\mu'}. \tag{33}$$

The second term on the right-hand side of (33) is the finite part of the lowest quantum correction to the free energy:

$$\mathscr{F}_{qu} = -\frac{\pi}{6}\int d\mathbf{x} n_{TF}\frac{\partial n_{TF}}{\partial\mu}. \tag{34}$$

The general case of finite temperatures will be considered in more detail below in Sec. 7; here we restrict ourselves to calculating the revised quantum correction to the equation of state of the matter at zero temperature. In this case, the electron density in the Thomas–Fermi model is

$$n_{TF}(\mathbf{x},\mu) = p_\mu^3(\mathbf{x})/3\pi^2,$$

$\partial\Phi/\partial\mu' = -\delta(\mu'-\mu)$, and from (33) we obtain

$$\delta_2\mathscr{E}^c = -\frac{1}{18\pi^3}\int d\mathbf{x} p_\mu^4 + E_{Sc} + \frac{Z^2}{\pi} f\left(\frac{\sqrt{2\mu}}{2Z}\right)\theta(\mu). \tag{35}$$

The first term on the right-hand side (the finite part of the quantum correction to the energy) is 2/9 of the exchange correction.[21] For an isolated atom, the chemical potential μ in the Thomas–Fermi model is equal to zero, from which, adding to (35) the principal term of the Thomas–Fermi model and the exchange correction, we obtain the well-known three-term expression

$$\mathscr{E}_0 = -0.7687Z^{7/3} + Z^2/2 - 0.2699Z^{5/3}, \tag{36}$$

which for $Z>4$ describes, to an accuracy of fractions of a percent, the energy of the electron shell of an atom in accordance with the Hartree–Fock model.[12,26]

A positive chemical potential in the Thomas–Fermi model corresponds to compressed matter with $\sigma>0$, and the final term in (25) gives a nonzero contribution. We first investigate the role of this term in the region $n_e>Z^2$, where the electron distribution can be assumed to be homogeneous,[5] in accordance with which

$$p_\mu = (3\pi^2 n_e)^{1/3}, \quad \mu = \frac{p_\mu^2}{2}, \quad \sigma = \frac{p_\mu}{2Z}.$$

For $Z^2<n_e<Z^3$, when we are within the region (3a), we have $\sigma\ll 1$, and the final term in (35) is negligibly small [see (31)]. Then for the revised quantum correction to the energy per cell of volume Z/n_e, we obtain the expression

$$\delta_2\mathscr{E}^c = -\frac{Z(3\pi^2 n_e)^{1/3}}{6\pi} + \frac{Z^2}{2}, \quad Z^2<n_e<Z^3, \tag{37}$$

the principal term of which in the considered region is given, as in the case of an atom, by Scott's expression (4). Since for $n_e<Z^2$ the value of σ is even smaller than in the region of homogeneity, the expression (35) without the final term can be used for $n_e<Z^3$, i.e., in the complete region (3a).

The situation is different in the region (3b), in which $n_e>Z^3$ and $\sigma>1$ hold. The asymptotic form (32) gives for the final term in (35) an expression that exactly compensates the first term in (35), and all that remains is the Scott correction, which is relatively small in the region in question. Thus, we have shown that the second-order quantum correction, which before revision destroys the agreement with perturbation theory in the region (3b), vanishes after the revision in this region. Thus, difficulty 2 (see the Introduction) is eliminated (so far, only in the case $T=0$).

Of real physical interest is the correction to the pressure $P=-\partial\mathscr{E}/\partial V$, where $\mathscr{E}$ is the energy per cell, the corrections to which are given by the expressions (35) and (37). In the region of homogeneity ($n_e>Z^2$), the unrevised quantum correction to the pressure has the form

$$\delta_2 P = \frac{n_e^2}{Z}\frac{\partial\delta_2\mathscr{E}}{\partial n_e} = \frac{8Z^2}{9\pi^2}\sigma^4\frac{\partial\delta_2\mathscr{E}}{\partial\sigma} = \frac{1}{18}\left(\frac{3}{\pi}\right)^{1/3} n_e^{4/3}, \tag{38}$$

while the revised correction is

$$\delta_2 P^c = \delta_2 P[1-3f'(\sigma)]. \tag{39}$$

In the region (3b), the quantities in the brackets in (39) cancel in accordance with perturbation theory. Figure 3 shows the relative deviation from the Thomas–Fermi model of the results of calculating the pressure of aluminum as a function of the compression in accordance with the different models in the homogeneity region transitional between (3a) and (3b). It can be seen that there is fairly good quantitative agreement of the results of the theory presented above and the complete quantum-mechanical calculation by the augmented-plane-wave method.[27]

7. THE CASE OF FINITE TEMPERATURES

To calculate the correction to the free energy at finite temperatures, it is necessary to use the general expressions (33) and (34). We first consider the case of a Boltzmann plasma at superhigh temperatures ($\beta Z^2\sim 1$) corresponding to the region bounded between (3a) and (3b),[2)] where the electron distribution is practically homogeneous and the chemical potential is negative and large in absolute magnitude:

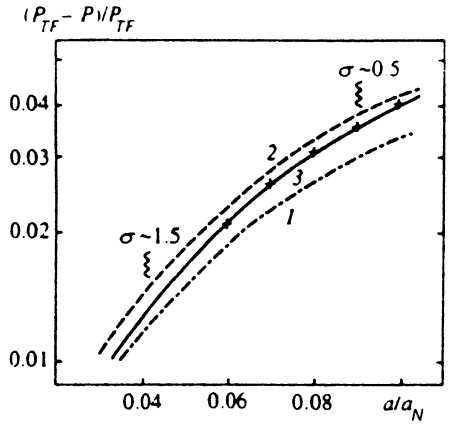

FIG. 3. Comparison of different models of the equation of state of aluminum: *1*—Thomas–Fermi model with exchange correction (perturbation theory); *2*—Thomas–Fermi model with exchange correction and unrevised quantum correction (38); *3*—Thomas–Fermi model with exchange correction and revised quantum correction (39); the plus signs correspond to the augmented-plane-wave method (Ref. 27). Here a/a_N is the reduced lattice constant, $a_N=7.65288$, $\sigma=\sqrt{2\mu}/2Z$.

$\mu<0$, $\beta\mu\gg1$. In this case, (34) gives for the second term in (33) $\mathscr{F}_{qu}=-\pi\beta Zn_e/6$, the finite part of the unrevised quantum correction, which here is 1/3 of the exchange energy $\mathscr{F}_{ex}$. With regard to the third term in (33), its value depends on the value of the product βZ^2, which for a homogeneous plasma is equal to $\pi n_e/36Z$ and $\pi\beta Zn_e/6$, respectively, in the regions $\beta Z^2\gg1$ (3a) and $\beta Z^2\ll1$ (3b). In the first of them, the third term in (33) is negligibly small, and in the second it is compensated by $\mathscr{F}_{qu}$, and there remains only the Scott correction:

$$\delta_2\mathscr{F}^{c}=\begin{cases}E_{Sc}-\pi\beta Zn/6, & \beta Z^2\gg1,\\ E_{Sc}, & \beta Z^2\ll1.\end{cases}\tag{40}$$

It is obvious that also in the complete region (3a), and not only for a homogeneous plasma, the final term in (33) can be ignored, and the revision of the correction to the free energy (and, accordingly, to the internal energy) reduces to replacement of the divergences of the Scott correction and has no effect on the response functions—the pressure and specific heat. Therefore, in this region the unrevised results (see, for example, the tables in Ref. 7) do not require revision. In the intermediate region between (3a) and (3b) the quantum correction $\mathscr{F}_{qu}$ "dies out" in accordance with (33), and not only the corrections to the energy quantities but also the corrections to the pressure and the specific heat differ from the uncorrected values. At the same time, it is found, in particular, that $E_{Sc}=Z^2/2$ is large compared with the exchange energy $-\pi\beta Zn/2$ by a factor VT, and its presence in the region (3b) [see (40)] contradicts the result of perturbation theory:

$$\mathscr{F}_{PT}=Z(\mu-T)-\frac{9}{10}\frac{Z^2}{R}+\mathscr{F}_{ex}.\tag{41}$$

In addition, in the analysis of the principal term in the Thomas–Fermi model the term $\tilde{\mathscr{F}}_{TF}$, which is an additional term compared with the first two terms of (41), stands out in the region (3b) considered. This term is the contribution of short distances $r<r_0$, in which the Coulomb interaction of the electrons with a nucleus is large, and perturbation theory is locally invalid. The discrepancies noted above correspond to the difficulty 2 at high temperatures.

As was shown in Refs. 22 and 28, this problem can be solved by introducing into the statistical model the shell correction

$$\mathscr{F}_{sh}=-\int_{-\infty}^{\infty}d\mu'\,\mathscr{E}_{sh}\frac{\partial\Phi(\beta(\mu'-\mu))}{\partial\mu'}.\tag{42}$$

Then the free energy in the corrected Thomas–Fermi model is made up of the principal term, the exchange term, the shell correction, and the revised quantum correction:

$$\mathscr{F}_{\text{stat}}=\mathscr{F}_{TF}+\mathscr{F}_{ex}+\mathscr{F}_{sh}+\delta_2\mathscr{F}^{c}.\tag{43}$$

We note here that at zero temperature the role of the shell effects is small for the cases considered above of an isolated atom[26,29] and strongly compressed matter, and the introduction of $\mathscr{F}_{sh}$ does not affect the results presented in Sec. 6.

Comparing (43) and (40) with (41), we find that in the region (3b) the following three-term combination is "redundant":

$$\tilde{\mathscr{F}}_{TF}+E_{Sc}+\mathscr{F}_{sh}=\hat{B}(\mathscr{E}_{TF}+E_{Sc}+\mathscr{E}_{sh}).\tag{44}$$

We have here used the operation $\hat{B}$ introduced in (13), which in the integral over μ' contains the bell-shaped function $\partial\Phi(\beta(\mu'-\mu))/\partial\mu'$ with extremum at the point μ and exponential decrease on both sides of this point. Since $|\mu|\gg Z^2$ holds in the region (3b) in which we are interested, the real region of integration over μ' satisfies the condition $\mu'<-Z^2/2$. Hence, bearing in mind the relation (27) in Sec. 5, we obtain cancellation of the terms in (44) to the accuracy of the integrands, and this means that the results of the statistical model (43) agree with the results of perturbation theory (41).

Note that the use of the approach (43) with shell correction in the region (3a), where the shell structure of the ions persists, leads to very good agreement with the results of Saha's model.[18,22,30]

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[1)]Introducing in the integrand of the integral over r a regularizing exponential $\exp(-2kr\eta)$, in which η is later made to tend to zero, we find that the integral over r of the final terms in the curly brackets reduces to Macdonald functions, while the integral of the first term can be calculated by means of the tabulated expression of Ref. 25.

[2)]To logarithmic accuracy in this region, $|\mu|\sim\beta^{-1}=T$.

[1] L. H. Thomas, Proc. Cambridge Philos. Soc. **23**, 542 (1926).
[2] E. Fermi, Rend. Accad. Linc. **6**, 602 (1927).
[3] R. Feynman, N. Metropolis, and E. Teller, Phys. Rev. **75**, 1561 (1949).
[4] D. A. Kirzhnits, Zh. Éksp. Teor. Fiz. **32**, 115 (1957) [Sov. Phys. JETP **5**, 139 (1957)].
[5] D. A. Kirzhnits, Yu. E. Lozovik, and G. V. Shpatakovskaya, Usp. Fiz. Nauk **117**, 3 (1975) [Sov. Phys. Usp. **18**, 649 (1975)].
[6] N. N. Kalitkin, Zh. Éksp. Teor. Fiz. **38**, 1534 (1960) [Sov. Phys. JETP **11**, 1106 (1960)].
[7] N. N. Kalitkin and L. V. Kuz'mina, "Tables of thermodynamic functions of matter at high energy concentrations," Preprint No. 35 [in Russian] (Institute of Problems of Mechanics, USSR Academy of Sciences, Moscow, 1975).
[8] I. L. Iosilevskiĭ and V. K. Gryaznov, Teplofiz. Vys. Temp. **19**, 1121 (1981).
[9] J. M. C. Scott, Philos. Mag. **43**, 859 (1952).

[10]E. S. Fradkin, Zh. Éksp. Teor. Fiz. **36**, 1533 (1959) [Sov. Phys. JETP **9**, 1087 (1959)].
[11]D. A. Kirzhnits, Tr. Fiz. Inst. Akad. Nauk SSSR **16**, 3 (1961).
[12]G. I. Plindov and I. K. Dmitrieva, Phys. Lett. A **64**, 348 (1978).
[13]J. Schwinger, Phys. Rev. A **22**, 1827 (1980).
[14]N. N. Kalitkin and L. V. Kuz'mina, Fiz. Tverd. Tela (Leningrad) **13**, 2314 (1971) [Sov. Phys. Solid State **13**, 1938 (1972)]; Fiz. Plazmy **2**, 858 (1976) [Sov. J. Plasma Phys. **2**, 478 (1976)]; N. N. Kalitkin, Doctoral Dissertation [in Russian] (Institute of Problems of Mechanics, USSR Academy of Sciences, Moscow, 1974).
[15]F. Perrot, Phys. Rev. A **20**, 586 (1979).
[16]R. M. More, Phys. Rev. A **19**, 1234 (1979).
[17]D. A. Kirzhnits and G. V. Shpatakovskaya, Pis'ma Zh. Eksp. Teor. Fiz. **59**, 446 (1994) [JETP Lett. **59**, 467 (1994)].
[18]D. A. Kirzhnits and G. V. Shpatakovskaya, Phys. Lett. A **198**, 94 (1995).
[19]G. V. Shpatakovskaya, *Diploma Thesis* [in Russian] (Moscow State University, Moscow, 1970).
[20]L. D. Landau and E. M. Lifshitz, *Statistical Physics*, 2nd ed. (Pergamon Press, Oxford, 1969) [Russ. original Nauka, Moscow, 1964].
[21]D. A. Kirzhnits, *Field-Theoretical Methods in Many-Body Systems* (Pergamon Press, Oxford, 1967) [Russ. original Atomizdat, Moscow, 1963].
[22]E. A. Kuz'menkov and G. V. Shpatakovskaya, Int. J. Thermophys. **13**, 315 (1992).
[23]G. V. Shpatakovskaya, in *Proceedings Nineteenth AIRAPT Conference on High Pressure Science and Technology* (Colorado, 1993), p. 159.
[24]L. Hostler, J. Math. Phys. **5**, 591 (1964).
[25]I. S. Gradshteyn and I. M. Ryzhik, *Table of Integrals, Series, and Products* (Academic Press, New York, 1965) [Russ. original Fizmatgiz, Moscow, 1962].
[26]B. G. Englert, *Semiclassical Theory of Atoms*, Vol. 300, Lecture Notes in Physics (Springer, Berlin, 1988).
[27]A. K. McMahan and M. Ross, *High Pressure Science and Technology*, Vol. 2 (Plenum, New York, 1979).
[28]G. V. Shpatakovskaya, Preprint No. 160 [in Russian] (Institute of Problems of Mechanics, USSR Academy of Sciences, Moscow, 1988).
[29]B. G. Englert and J. Schwinger, Phys. Rev. A **32**, 26 (1985).
[30]E. A. Kuz'minkov and G. V. Shpatakovskaya, Teplofiz. Vys. Temp. **27**, 677 (1989).

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