Atomic Structure Oscillation Effects

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An expression for the oscillation corrections to the Thomas-Fermi model is obtained within the framework of the quasiclassical approximation. This expression makes it possible to describe not only the averaged characteristics of a physical system, but also the irregularities connected with the shell structure. As applied to a heavy atom, the spatial oscillations of the electron density are described with an approximate accuracy 5%.

1. INTRODUCTION

IT is well known that the radial density of the electrons in the atom depends on the distance to the nucleus in a nonmonotimic oscillatory) manner, with maxima corresponding to the filled shells of the atom. Such a behavior of the density is well described by the self-consistent field method; the corresponding numerical calculations, however, are complicated and must be performed separately for each value of the nuclear charge and of the number of electrons in the atom. We shall show here that the density oscillations of an atom that is not too light are described by simple closed formulas.

More generally, the results of this paper constitute further improvement of the Thomas-Fermi model, whereby it is possible to obtain not only the averaged physical quantities but also more subtle details of their behavior.

Our approach is based on the condition that the motion of the electrons in a self-consistent field $U(x)$ is quasiclassical

$$\xi = \hbar / p_F L \ll 1; \tag{1}$$

here $p_F(x) = \sqrt{2m(\mu - U(x))}$, is the limiting momentum, m is the electron mass, μ is the chemical potential, and L is a characteristic length over which $U(x)$ and $p_F(x)$ vary in a noticeable manner. Inside a heavy atom we have $p_F \sim Z^{2/3}\hbar/a_0$, $L \sim Z^{-1/3}a_0$ and $\xi \sim Z^{-1/3}$, where a_0 is the Bohr radius and Z is the number of electrons in the atom.

In the lowest-order approximation in ξ, corresponding to the Thomas-Fermi model, the expression for the density is well known:

$$\rho(x) = p_F^3(x) / 3\pi^2\hbar^3. \tag{2}$$

It describes relatively well the averaged distribution of the density, but does not account for the oscillations of this quantity. We can take into account also the next higher terms in the expansion in ξ (see, for example[1]):

$$\Delta\rho_{qu}(x) = -\frac{1}{96\pi^2 p_F^3(x)\hbar}[(\nabla p_F^2)^2 - 4p_F^2\Delta p_F^2]. \tag{2a}$$

These so-called quantum corrections, while improving the agreement with experiment in several respects, do not change the monotonic behavior of the density, owing to the good convergence of the series in ξ. It might be therefore be assumed, as was indeed suggested frequently, that the density oscillations can be described only within the framework of an exact quantum-mechanical analysis.

However, an investigation of models that admit of exact solution (homogeneous field, oscillator) has shown[2,3] that the density cannot be regarded as an analytic function of ξ. Consequently, the power series in ξ does not account for all the singularities of the behavior of the expanded function. It turned out that the asymptotic form of the density as $\xi \to 0$ consists of two parts. The first and regular part can be represented by a series in powers of ξ and reduces to the expressions (2) and (2a) and to higher-order quantum corrections. The second and oscillating part takes the form of a combination of terms of the type $\sin(\alpha(x)/\xi + \beta(x))$, accompanied by series in powers of ξ. Owing to the dependence of the functions α and β on x, this second part, henceforth designated ρ_{osc}, oscillates when either ξ or the coordinates vary.

It is therefore clear that when condition (1) is satisfied there is no need for an exact quantum-mechanical calculation in order to describe the density oscillations. It suffices to separate the quantity ρ_{osc} from the asymptotic expression for the density, and retain in this case only the principle part of ρ_{osc} with respect to the parameter ξ.

It is important that the quantity of interest to us can be obtained in the usual quasiclassical approximation[1)]. Indeed, squaring the expression for the quasiclassical wave function $\psi \sim \sin(\hbar^{-1}S_0 + \delta)$ (S_0 is the classical action for the motion up to the turning point and δ is a numerical phase shift) and summing over the filled levels, we can easily obtain both the regular and the oscillating parts of the density. This is precisely the method used sometimes (see[6]) to obtain the irregular part; unfortunately, the oscillating terms were simply discarded in this case.

The method of direct summation over the levels, which is considered in Sec. 2, turns out, however, not

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[1)]This simple fact, pointed out earlier by one of the authors (see G. V. Shpatakovskaya's diploma thesis, Moscow State University, 1969), has apparently remained unnoticed. It is precisely for this reason that a general functional approach, with a quadratic approximation of U(x), had to be used in[4] to describe density oscillations in an arbitrary field. This approximation, for which there is in fact no need, actually does not go outside the framework of the models mentioned above and is certainly unsuitable for use in the case of the atom (see Sec. 4). The possibility of deriving the shell effects in a quasiclassical approach is mentioned by Balian and Bloch in one of their recent papers[5] devoted to a systematic study of the quasiclassical situation.

to be very convenient when applied to arbitrary potentials U(x). In Sec. 3 we present a more general and actually simpler Green's function method, and solve incidentally the problem of determining the quasiclassical Green's function. The results are compared with those of the exact quantum-mechanical calculation in Sec. 4.

2. DIRECT SUMMATION METHOD

We start from the usual expression for the particle-number density at zero temperature:

$$\rho(x)=2\sum_{\epsilon_n\leqslant\mu}|\psi_n(x)|^2; \tag{3}$$

here $\psi_n(x)$ is the solution of the equation $(\hat{H}-\epsilon_n)\psi_n=0$, $\hat{H}=\hat{p}^2/2m+U(x)$, the factor 2 corresponds to the two spin directions, and the small exchange and correlation effects are disregarded.

A. One-dimensional Motion[2)]

In the quasiclassical approximation, the wave function in the allowed region is given by[7]

$$\psi_n(x)=\frac{c_n}{\sqrt{p_n(x)}}\sin\left(\frac{1}{\hbar}\sigma_n(x)+\frac{\pi}{4}\right);$$

We use here the notation

$$\sigma_n(x)=\int_x^{R_n}p_0(x')\,dx',\quad \sigma_n^{(0)}=\int_{R_n'}^{R_n}p_n(x')\,dx',$$

$$\tau_n(x)=m\int_x^{R_n}\frac{dx'}{p_n(x')},\quad \tau_n^{\,0}=m\int_{R_n'}^{R_n}\frac{dx'}{p_n(x')},$$

where $p_n=[2m(\epsilon_n-U(x))]^{1/2}$, and R_n and R_n' are the turning points.

Assuming the motion to be finite, we write down the Bohr-Sommerfeld quantization condition

$$2\sigma_n^{\,0}=2\pi\hbar(n+1/2) \tag{4}$$

and the normalization condition[8]

$$|c_n|^2\tau_n^{\,0}/2m=1.$$

The particle-number density in this approximation is $\rho=\rho_{reg}+\rho_{osc}$, where

$$\rho_{reg}(x)=2\sum_n[p_n(x)\tau_n^{\,0}]^{-1}, \tag{5}$$

$$\rho_{osc}(x)=2\sum_n[p_n(x)\tau_n^{\,0}]^{-1}\sin\frac{2}{\hbar}\sigma_n(x). \tag{6}$$

Using the Poisson formula to change from summation over the levels to integration, and integrating by parts (see Appendix I), we find that in the lowest approximation in ξ the quantity ρ_{reg} is represented in the form of a sum of two terms. The first of them

$$\rho_{reg}^{(1)}(x)=2p_F(x)/\pi\hbar \tag{5a}$$

corresponds to the Thomas-Fermi model, and the second $\rho_{reg}^{(2)}$, the expression for which we do not present, is a reflection of the step-like character of the dependence of the density on the Fermi energy.

The oscillatory part of the density takes the form

$$\rho_{osc}(x)=-[p_F(x)\tau^0]^{-1}\operatorname{ctg}\left(\pi\frac{\tau(x)}{\tau^0}\right)\cos\frac{2}{\hbar}\sigma(x). \tag{6a}$$

If the motion is infinite to the left, then

$$\rho_{osc}(x)=-\frac{1}{\pi}[p_F(x)\tau(x)]^{-1}\cos\frac{2}{\hbar}\sigma(x). \tag{6b}$$

In formulas (6a) and (6b), the quantities $\sigma(x)$, σ^0, $\tau(x)$ and τ^0 without a subscript pertain to the Fermi energy, that is, they correspond to the substitution $p_n(x)\to p_F(x)$.

B. Three-dimensional Motion

For the spherically-symmetrical case we have

$$\rho(r)=\frac{1}{2\pi}\sum_{n,l}(2l+1)R_{nl}^2, \tag{3a}$$

where in the quasiclassical approximation[3)]

$$R_{nl}(r)=\frac{c_{nl}}{r\sqrt{p_{nl}(r)}}\sin\left(\frac{1}{\hbar}\sigma_{nl}(r)+\frac{\pi}{4}\right),$$

$$p_{nl}(r)=[2m(\varepsilon_{nl}-U(r)-\hbar^2(l+1/2)^2/2mr^2)]^{1/2},$$
$$2\sigma_{nl}^{\,0}=2\pi\hbar(n+1/2).$$

The summation region in (3a) is $n_1l\geq 0$, $\epsilon_{nl}\leq\mu$. We introduce the notation

$$\sigma_{nl}(r)=\int_r^{R_{nl}}p_{nl}(r')\,dr',\quad \sigma_{nl}^{\,0}=\int_{R_{nl}'}^{R_{nl}}p_{nl}(r')\,dr',$$

$$\tau_{nl}(r)=m\int_r^{R_{nl}}dr'/p_{nl}(r'),\quad \tau_{nl}^{\,0}=m\int_{R_{nl}'}^{R_{nl}}dr'/p_{nl}(r'),$$

$$\delta_{nl}(r)=\int_r^{R_{nl}}dr'/r'^2p_{nl}(r'),\quad \delta_{nl}^{\,0}=\int_{R_{nl}'}^{R_{nl}}dr'/r'^2p_{nl}(r').$$

As before, the corresponding quantities without subscripts pertain to the Fermi boundary.

We are interested only in the oscillatory part of the density. Applying Poisson's formula twice, we change from summation over n and l to integration. Just as in the one-dimensional case, we integrate by parts and confine ourselves to the lowest approximation in ξ. As a result we obtain (see Appendix II), for the case of repulsion at small distances, the oscillatory part of the density in the form

$$\rho_{osc}(r)=-\frac{\sin(2\sigma(r)/\hbar)}{4\pi r^2\hbar p_F(r)}\frac{\operatorname{ctg}(\pi\tau(r)/\tau^0)-\operatorname{ctg}(\pi\delta(r)/\delta^0)}{\tau^0\delta(r)-\tau(r)\delta^0}. \tag{7}$$

In the case of attraction, if the particle motion near the point r = 0 can be regarded as quasiclassical, we have

$$\rho_{osc}(r)=-\frac{\sin(2\sigma(r)/\hbar)}{8\pi r^2\hbar p_F(r)}\frac{\operatorname{ctg}(\pi\tau(r)/2\tau^0)-\operatorname{ctg}(\pi\delta(r)/2\delta^0)}{\tau^0\delta(r)-\tau(r)\delta^0}. \tag{7a}$$

In this and in the succeeding formulas, the integrals τ^0 and δ^0 have R′ = 0 as the lower limit. δ^0 stands for the "regularized" expression corresponding to discarding in the integral

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[2)]This simple example explains the idea of the calculations used later in the realistic three-dimensional case.

[3)]The expression given for p_{nl} corresponds to replacement of $l(l+1)$ by $(l+1/2)^2$, a procedure justified for potentials with oscillatory or Coulomb behavior at zero. The effectiveness of this replacement for other potential is doubtful[9].

$$\int_{R'_{F\lambda}}^{R_{F\lambda}} dr'/r'^2\sqrt{p_F^2-\lambda^2/r'^2}$$

the term of the type $1/\lambda$ as $\lambda \to 0$.

If the attraction potential is of the Coulomb type at short distances, then

$$\rho_{\text{осц}}(r) = -\frac{\sin(2\sigma(r)/\hbar)}{4\pi r^2\hbar p_F(r)}\frac{\operatorname{cosec}(\pi\tau(r)/\tau^0)-\operatorname{cosec}(\pi\delta(r)/\delta^0)}{\tau^0\delta(r)-\tau(r)\delta^0}. \quad (7b)$$

Expression (7), (7a), and (7b) show that in the three-dimensional case the oscillatory increment to the density has the same order of magnitude with respect to ξ as the quantum correction (2a).

3. GREEN'S FUNCTION METHOD

In this section we calculate the oscillatory part of the density by another method based on the use of the Green's function. This method makes it possible to consider potentials of general form and makes the physical meaning of the expression obtained above more lucid.

A. Quasiclassical Green's Function

The expression for the density (3) can be easily written in the form

$$\rho(\mathbf{x}) = -\frac{2}{\pi}\int_{-\infty}^{\mu} d\varepsilon\, \operatorname{Im} G(\mathbf{x},\mathbf{x}',\varepsilon), \quad (8)$$

where we have introduced the retarded Green's function of a particle in a given field

$$G(\mathbf{x},\mathbf{x}',\varepsilon) = \sum_n \frac{\psi_n^*(\mathbf{x}')\psi_n(\mathbf{x})}{\varepsilon-\varepsilon_n+i\eta}, \quad (9)$$

satisfying the equation

$$(\varepsilon-\hat{H})G(\mathbf{x},\mathbf{x}',\varepsilon) = \delta(\mathbf{x}-\mathbf{x}'). \quad (10)$$

For the excited states of the system (particularly, at non-zero temperature), it is necessary to replace $\int_{-\infty}^{\mu} d\epsilon \ldots$ in (8) by $\int_{-\infty}^{\mu} d\epsilon n(\epsilon)\ldots$, where $n(\epsilon)$ are the occupation numbers.

In the quasiclassical approximation, the Green's function can be represented in the form

$$G(\mathbf{x},\mathbf{x}',\varepsilon) = K\exp\left(\frac{i}{\hbar}S_0+S_1\right), \quad (11)$$

where $S_{0,1}$ are functions that are real in the classically allowed region (the forbidden region is not considered), and the non-exponential dependence of G on $\hbar$ is accounted for in the coefficient K. When $\mathbf{x}' \neq \mathbf{x}$, substitution of (13) in (12) yields the well-known equations for $S_{0,1}$:

$$(\nabla S_0)^2 = 2m(\varepsilon-U(\mathbf{x})) \equiv p^2(\mathbf{x}), \quad (12)$$

$$\nabla S_0\cdot\nabla S_1 = -{}^1/_2\Delta S_0. \quad (12a)$$

It turns out that these equations have in the general case several admissible solutions and accordingly (11) can be modified as follows:

$$G = \sum_j K_{(j)}\exp\left(\frac{i}{\hbar}S_0^{(j)}+S_1^{(j)}\right). \quad (11a)$$

The ambiguity of the system (12) and (12a) lies in the fact that a particle with a given energy ϵ can move along several trajectories between the points $\mathbf{x}$ and $\mathbf{x}'$. One of them connects these points, so to speak, "directly," and is characterized by an arc length between the points in question that vanishes as $\mathbf{x}' \to \mathbf{x}$. The corresponding term in (11a) has a singularity in this limit, and the values of $S_{0,1}$ and K must be chosen for it in such a way that it satisfies Eq. (10) with the right-hand side. This term and the corresponding trajectory will be called regular. The remaining trajectories differ in that the particle experiences one or several reflections from the turning point on moving from $\mathbf{x}$ to $\mathbf{x}'$. Accordingly, as $\mathbf{x}' \to \mathbf{x}$ we deal with closed trajectory loops of finite length. In this limit, the corresponding terms in (11a) have no singularities and satisfy Eq. (12) without the right-hand side in all of space. These terms and the corresponding trajectories will be called oscillatory.

The meaning of these designations becomes clear when we consider the solution of Eq. (12)

$$S_0^{(j)} = \int_{\Gamma_j} ds\,|p(\mathbf{x})|, \quad (13)$$

where Γ_j is the arc of the classical particle trajectory between the points $\mathbf{x}$ and $\mathbf{x}'$, and ds is the element of this arc. The sign in the right-hand side of (13) corresponds to a diverging wave, and reflects the retarded character of the Green's function. The integration constant in (13) is chosen such that S_0 on the irregular trajectory vanishes as $\mathbf{x}' \to \mathbf{x}$. This is necessary to prevent an additional phase factor from appearing in the right-hand side of (10).

On the other hand, it is seen from a comparison of (11a) and (8) that the source of the density oscillations is the non-zero value of the classical action S_0 at coinciding points. It is therefore clear that the regular term in the sum (11a) has no bearing on the density oscillations and is responsible for the regular part of the latter. At the same time, the oscillatory term in (11a) corresponds to nonzero values of $S_0(x, x)$, which indeed lead to density oscillations.

It turns out, however, that not any closed loop of the trajectory leads actually to density oscillations. One cannot choose as such a loop a closed trajectory of periodic motion as a whole, for which, according to the quantization rules,

$$S_0 = 2\pi\hbar(n+\beta), \quad (14)$$

where n is an integer and β a certain numerical phase. Substitution of (14) in (11a) leads to vanishing of the oscillatory dependence on ξ and on the coordinates[4)].

The oscillatory effects are connected with linear degenerate trajectories; Fig. 1a shows such a trajectory for finite motion, and Fig. 1b for infinite motion. Such trajectories exist always if the field and energy of the particle are such that there is at least one turning point (the total momentum at this point is equal to zero). In fact, let us imagine the surface that serves as the geometric locus of the turning points. We place

[4)]Strictly speaking, at arbitrary values of ϵ, the rules (14) do not hold, since they are intended precisely for the determination of the admissible values of ϵ. As will be shown below, however, the principal part of the integral (8) corresponds to $\epsilon=\mu$, and the chemical potential μ coincides with the energy of the highest occupied level.

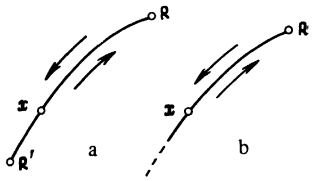

FIG. 1

one particle at each such point and allow them to "fall freely" in the given field. Obviously, the corresponding trajectories fill the entire classically allowed region. One of them, in particular, will pass through the given point $\mathbf{x}$ with a momentum $\mathbf{p}$. It is perfectly clear that the particle that started its motion from the point $\mathbf{x}$ with momentum $-\mathbf{p}$ will move along the trajectory in question to the turning point and will return along the same trajectory. It is just such a closed degenerate loop which we must identify with the contour Γ_j in the oscillatory terms. Obviously, the corresponding quantity $S_0^{(j)}$ no longer satisfies the rules (14) in this case and can be arbitrary. It is precisely such trajectories which lead to density oscillations, which can be interpreted as the result of interference between the incident wave and that reflected from the turning point.

The statements made in the preceding paragraph with respect to the contour Γ pertain verbatim only to the case of infinite motion, when there is only one turning point $\mathbf{R}$ on the trajectory ($\mathbf{p}(\mathbf{R}) = 0$) and there is only one contour $\Gamma(\mathbf{x} - \mathbf{R} - \mathbf{x})$ (see Fig. 1b). If the particle motion is finite, then the situation is more complicated. In this case there are two turning points $\mathbf{R}$ and $\mathbf{R}'$, and accordingly two contours $\Gamma_1(\mathbf{x} - \mathbf{R} - \mathbf{x})$ and $\Gamma_2(\mathbf{x} - \mathbf{R} - \mathbf{x})$ (see Fig. 1a). In addition, we can add to each of them an arbitrary number (for concreteness, k) of total circuits over the entire closed trajectory; such circuits will be designated by the symbol C. Summing all the foregoing, we can write symbolically

$$\Gamma_j = \begin{cases} 2(\mathbf{x}-\mathbf{R}) & \text{infinite motion} \\ \left.\begin{matrix} 2(\mathbf{x}-\mathbf{R})+kC \\ -2(\mathbf{x}-\mathbf{R})+(k+1)C \end{matrix}\right\} & \text{finite motion} \end{cases} \tag{15}$$

Let us return to (11a), and separate from it the regular term, which we shall label with the index $j = 0$. As already mentioned the quantities $K^{(0)}$ and $S_1^{(0)}$ can be determined from the right-hand sides of (10); this will be done later on. As to these quantities with $j \neq 0$, they can be calculated in the following manner. Assume that we have a single expression for the function S_1, in the form of an explicit functional of the contour Γ and satisfying the correct boundary conditions on the regular trajectory. The question then reduces to a determination of the coefficients $K^{(j)}$. Let us trace the motion of the particle along the trajectory Γ_j. From the elasticity of the reflection it is clear that $|K^{(j)}| = |K^{(0)}|$, and the phase shift of the coefficient $K^{(j)}$ is determined in the usual quasiclassical manner and is equal to $-\pi n_j/2$, where n_j is the number of reflections from the simple turning points and characterizes the trajectory Γ_j. Thus, dividing (11a) into a regular part and an oscillatory part, we can write

$$G_{\text{reg}} = K^{(0)} \exp\left(\frac{i}{\hbar}\int_{\Gamma_0} ds|p(\mathbf{x})| + S_1^{(0)}\right), \tag{16}$$

$$G_{\text{osc}} = K^{(0)} \sum_{j\neq 0} \exp\left(\frac{i}{\hbar}\int_{\Gamma_j} ds|p(\mathbf{x})| + S_1^{(j)} - i\frac{\pi}{2}n_j\right). \tag{16a}$$

Returning to (15), we have

$$n_j = \begin{cases} 1 & \text{(infinite motion)} \\ 2k+1 & \text{(finite motion)} \end{cases} \tag{15a}$$

We proceed now to determine $S_1^{(0)}$ and $k^{(0)}$. We begin with the simplest one-dimensional case, for which we have on the regular trajectory, in accordance with (13) $S^{(0)} \to p(x')|x - x'|$ as $x' \to x$. Substitution in (10) leads to the relation $K^{(0)} \exp S_0^{(1)} \to -im/\hbar p(x)$. We can put

$$S_1^{(0)}(x, x) = -\ln p(x), \qquad K^{(0)} = -im/\hbar.$$

The general solution of (12a) is

$$S_1(x, x') = -\tfrac{1}{2}\ln(p(x)p(x'))$$

and the oscillatory part of the Green's function can be written in the form

$$G_{\text{osc}}(x, x', \varepsilon) = -\frac{im}{\hbar[p(x)p(x')]^{1/2}} - \sum_{j\neq 0}\exp\left(\frac{i}{\hbar}\int_{\Gamma_j}|p(x)|ds - i\frac{\pi}{2}n_j\right). \tag{17}$$

The situation is more complicated in the three-dimensional case, when it is difficult to obtain an explicit solution of (12a). In this case the δ-function in the right-hand side of (10) can be obtained only if on the regular trajectory

$$\exp S_1^{(0)} \to 1/|\mathbf{x} - \mathbf{x}'| \quad \text{as} \quad \mathbf{x}' \to \mathbf{x}.$$

More accurately, in this limit $K^{(0)} \exp S_1^{(0)}$ should tend to $-m/2\pi\hbar^2|\mathbf{x} - \mathbf{x}'|$. We choose

$$S_1^{(0)} \to -\ln|\mathbf{x} - \mathbf{x}'|, \qquad K^{(0)} = -m/2\pi\hbar^2.$$

Such a behavior of the function $S_1^{(0)}$ is indeed in full correspondence with Eq. (12a), as can be easily verified by recognizing that $S_0 \to p(\mathbf{x})|\mathbf{x} - \mathbf{x}'|$ as $\mathbf{x}' \to \mathbf{x}$. The obtained form of the function S_1 on the regular trajectory suggests the general form of this function

$$\exp S_1(\mathbf{x}, \mathbf{x}') = A(\mathbf{x}, \mathbf{x}') \Big/ \int_{\Gamma} ds\, B, \tag{18}$$

where $A(\mathbf{x}, \mathbf{x}) = B(\mathbf{x})$. We shall confirm this result below and obtain the explicit form of the functions A and B for a radially-symmetrical field. Using (18), we easily arrive at the following expression for the oscillatory part of the Green's function in the three-dimensional case.

$$G_{\text{osc}}(\mathbf{x}, \mathbf{x}', \varepsilon) = -\frac{m}{2\pi\hbar^2}A(\mathbf{x}, \mathbf{x}')\sum_j\left(\int_{\Gamma_j} ds\, B\right)^{-1}\exp\left(\frac{i}{\hbar}\int_{\Gamma_j}|p|ds - i\frac{\pi}{2}n_j\right). \tag{19}$$

The meaning of the summation with respect to j is determined by relations (15), but at this stage we shall not carry out the summation in explicit form.

B. Oscillatory Part of the Density

Using the obtained expression for the oscillatory part of the Green's function and formula (8), we can obtain the oscillatory part of the density of interest to us. First, we can get rid of the integration with respect to ϵ in (8) by separating the principal part of ρ_{osc} with respect to the parameter ξ. To this end, we

multiply and divide each term in (17) and (19) by the quantity

$$T_j = \frac{\partial S_0^{(j)}}{\partial \varepsilon} = m\int_{\Gamma_j} \frac{ds}{p(\mathbf{x})}, \tag{20}$$

which has the meaning of the time of motion along the trajectory between the points x and x′. Then, integrating by parts and retaining only the term outside the integral sign, referred to $\epsilon = \mu$, we obtain the sought principal part of the expression in question.

We begin with a case of one-dimensional motion. Performing the required operations, we obtain

$$\rho_{osc}(x) = \frac{2}{\pi p_F(x)} \sum_j \left[\int_{\Gamma_j} \frac{dx'}{p_F}\right]^{-1} \sin\left(\frac{1}{\hbar}\int_{\Gamma_j} p_F\, dx' - \frac{\pi}{2} n_j\right). \tag{21}$$

The situation is simplest for infinite motion bounded by a turning point R, say from the right. In this case (21) with allowance for (15a) leads to formula (6b). On the other hand, in the case of finite motion it is necessary to sum in (21) over k (15a). Assuming that μ coincides with the energy of the higher occupied level, we arrive at (6a).

We now proceed to the three-dimensional case, which is of direct physical interest. We consider the most important case of a radially symmetrical field U(r). It is easily seen that the linear degenerate trajectories are radial straight lines in our case. It is also clear that the problem has axial symmetry with respect to such a trajectory. Therefore, when solving (12a) it is convenient to use cylindrical coordinates, denoting by z the distance along the trajectory from the center and by ρ the polar radius. It is obvious that the functions U and p_F depends only on the combination $\sqrt{z^2 + \rho^2}$.

Proceeding to the solution of (12a) (see[10]), we recognize that on the trajectory itself, i.e., at $\rho = 0$, we have $\partial S_0/\partial\rho = 0$. Therefore, in particular,

$$\frac{1}{\rho}\frac{\partial S_0}{\partial \rho} = \frac{\partial^2 S_0}{\partial \rho^2}; \qquad \frac{\partial S_0}{\partial z} = p_F(z),$$

and Eq. (12a) assumes on the trajectory the form

$$\frac{\partial S_1}{\partial z} = -\frac{\alpha}{p_F} - \frac{1}{2}\frac{\partial}{\partial z}\ln p_F, \tag{22}$$

where $\alpha = (\partial^2 S_0/\partial\rho^2)_{\rho=0}$. On the other hand, differentiating Eq. (12), which takes the form

$$\left(\frac{\partial S_0}{\partial z}\right)^2 + \left(\frac{\partial S_0}{\partial \rho}\right)^2 = p_F^2(\sqrt{z^2+\rho^2}),$$

with respect to z and ρ, we obtain at $\rho = 0$ the expression $\partial^2 S_0/\partial z^2 = \partial p_F/\partial z$ and

$$\frac{\partial \alpha}{\partial z} + \frac{1}{p_F}\alpha^2 = \frac{1}{z}\frac{\partial p_F}{\partial z}. \tag{23}$$

Equation (23) is a Riccati equation and its solution is

$$\alpha = \frac{p_F}{z} + 1\Big/ z^2\left(\int \frac{dz'}{z'^2 p_F} + \text{const}\right). \tag{23a}$$

Substitution of this expression in (22) and solution of the resultant equation yields, after returning to the variable r[5)]

$$\exp S_1 = \left[rr'\sqrt{p_F(r)\,p_F(r')}\int_{\Gamma_j} \frac{ds}{r'^2 p_F}\right]^{-1}. \tag{24}$$

We have thus confirmed relation (11) with

$$A = 1/rr'\sqrt{p_F(r)\,p_F(r')},\quad B = 1/r^2 p_F(r).$$

Calculating further the value of ρ_{osc}, in a manner similar to that used for one-dimensional motion, and using (24), we get

$$\rho_{osc}(r) = -\frac{1}{\pi^2\hbar r^2 p_F}\sum_j{}' \left(\int_{\Gamma_j}\frac{ds}{r'^2 p_F}\int_{\Gamma_j}\frac{ds}{p_F}\right)^{-1}\cos\left(\frac{1}{\hbar}\int_{\Gamma_j} p_F\, ds - \frac{\pi}{2}n_j\right) \tag{25}$$

In the case of infinite motion (external problem), we have

$$\rho_{osc}(r) = -\frac{1}{4\pi^2\hbar r^2 p_F}\left[\int_R^r \frac{dr'}{r'^2 p_F}\int_R^r \frac{dr'}{p_F}\right]^{-1}\sin\left(\frac{2}{\hbar}\int_R^r p_F\, dr'\right). \tag{26}$$

For finite motion we obtain formulas (7) and (7a).

More accurately speaking, we arrive directly only at formula (7), which corresponds to repulsion at short distances. In the case of attraction and in the absence of a singularity of U(r) at short distances (this corresponds, for example, to an oscillator potential), the particle passes freely through the center and the lower turning point should be taken to mean the point with Z = −R. We then arrive at formula (7a). On the other hand, if the potential has the character of Coulomb attraction at r = 0, then the quantum effects at small r are significant and make it impossible for the particle to pass through the center. In this case the role of R′ is played by the point r = 0. It is not, however, a real turning point, for by considering the quasiclassical limit of the exact Coulomb Green's function[11] we find that when the particle is reflected from this point the phase shifts by $+\pi/2$, and therefore the sign factor in (15a) is different (for finite $n_j = 1$), and accordingly the formula for ρ_{osc} takes the form (7b).

4. COMPARISON WITH THE RESULTS OF THE EXACT QUANTUM-MECHANICAL CALCULATION

The formulas obtained above can be compared with expressions obtained from quantum-mechanical calculations. In the one-dimensional case, for a linear or an oscillator potential, the expressions for the oscillation correction to the density is obtained in full accordance with the results of[2-4].

From among the three-dimensional spherically-symmetrical problems, we have considered the model of a neutral atom with the interaction between electrons turned off. The results of the calculation by formula (7b) was compared with the expression obtained by summing the exact Coulomb functions. Figure 2 shows that these expressions agree sufficiently well, whereas Troshin's formula[4] gives even an incorrect period for the oscillations.

Of direct physical interest is the oscillation of electron density in a heavy atom. In the Tietz approximation[12], for an atomic potential

$$p_F(r) = \sqrt{\frac{2Z}{r}}\Big/\left(1+\frac{r}{a}\right), \qquad a = (4.5)^{1/3}Z^{-1/3}, \qquad \mu = 0,$$

we calculated the irregular and oscillatory parts of the electron density for mercury, Z = 80, and for argon, Z = 18. In this approximation we obtain from (26)[6)]

[5)]The constant in formula (23a) is chosen such as to eliminate the divergence of the integral (if the divergence exists).

[6)]We have left out here the correction that must be introduced in the density to account for the change of p_F itself as a result of the oscillatory effects. This correction is of the order of ξ^2 relative to ρ_{osc}.

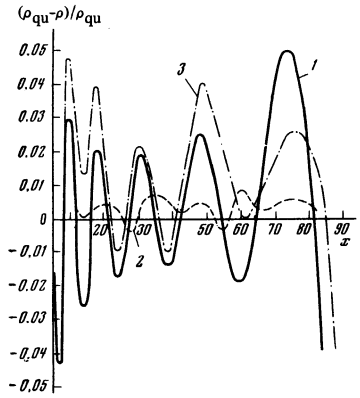

FIG. 2. Relative difference between the quantum-mechanical electron density ρ_{qu} and the Thomas-Fermi density (1), the density with the oscillatory correction (2), and the density with Troshin's correction [4] (3) for the model of an ideal electron gas in a Coulomb field.

$$\rho_{osc}(r)=\frac{3a\sqrt{2Z}(a+r)}{4\pi\sqrt{r}(a-r)(a+0{,}6r)}\sin\left[2\sqrt{2Za}\arccos\frac{a-r}{a+r}\right]. \quad (27)$$

This formula is not valid in the vicinity of the point r = a (a = 0.383 for Z = 80 and a = 0.629 for Z = 18). The point is that the regularized part of the integral

$$\int_0^a \frac{dr'}{r'^2 p_F}$$

is equal to zero and we have no right to integrate by parts in the integral with respect to λ (see Appendix II). This integral was therefore calculated near the point r = a with a computer. The results of the calculations are shown in Figs. 3 and 4 together with the data obtained by the Hartree method[13,14]. Formula (27) describes sufficiently well the density oscillations and can be used in calculations where there is no need for high accuracy.

The authors thank V. L. Ginzburg and the participants of the seminar under his direction for a discussion of the work and also V. G. Nosov for acquainting them with his paper on oscillatory effects in the atomic nucleus prior to publication.

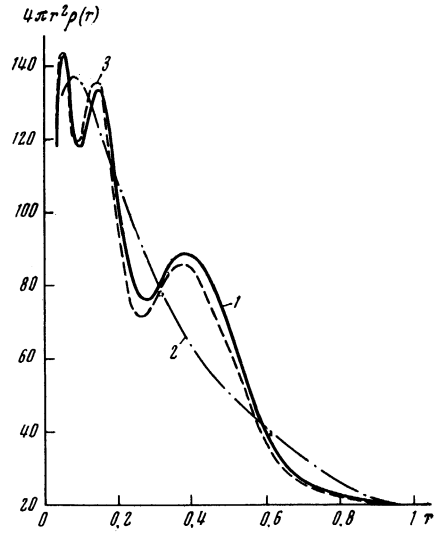

FIG. 3. Radial electron density for the mercury atom: 1—Hartree, 2—Thomas-Fermi, 3—Thomas-Fermi with quantum and oscillator corrections.

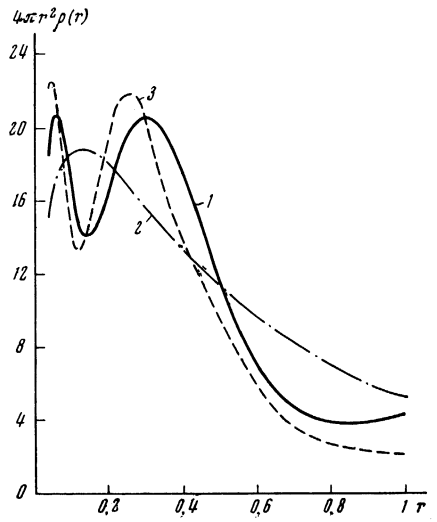

FIG. 4. The same as in Fig. 3, but for the argon atom.

APPENDIX I

As usual in a theory of oscillatory effects, we use the Poisson formula

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

and change over in (6) and (7) to integration with respect to n:

$$\rho_{reg}(x)=2m\sum_{k=-\infty}^{\infty}\int_{-\delta}^{N+\delta}\frac{dn}{p_n\tau_n^0}\cos 2\pi kn, \quad (I.1)$$

$$\rho_{osc}(x)=2m\sum_{k=-\infty}^{\infty}\int_{-\delta}^{N+\delta}\frac{dn}{p_n\tau_n^0}\sin\left(\frac{2}{\hbar}\sigma_n(x)\right)\cos 2\pi kn, \quad (I.2)$$

where $0<\delta<1$. We extend the quantization condition (5) to include non-integer n, and after differentiating this condition with respect to n we obtain

$$[\tau_n^0]^{-1}=(\pi\hbar)^{-1}d\varepsilon/dn.$$

This equation enables us to change over to integration with respect to the energy in (I.1) and (I.2). In particular, this yields (5a) directly.

Successive integration by parts in the integrals with the trigonometric functions enables us to expand them in powers of ξ. Confining ourselves to the first term of such an expansion, we obtain $\rho_{reg}^{(2)}$ from (I.1) and formula (6a) from (I.2).

APPENDIX II

We start from the expression

$$\rho(r)=\frac{m}{2\pi r^2}\sum_{n,l}\frac{2l+1}{p_{nl}\tau_{nl}^0}\left(1+\sin\frac{2}{\hbar}\sigma_{nl}(r)\right) \quad (II.1)$$

and separate its oscillatory part. Summing by the Poisson method, we replace the sum $\sum_{n,l}\ldots$ by the integral

$$\int_{n_0-\Delta}^{N+\Delta}dn\int_{-1/2}dl\ldots$$

We put $\lambda \equiv \hbar(1 + \frac{1}{2})$, taking into account the fact that

$$[\tau_{nl}^0]^{-1} = (\pi\hbar)^{-1}\partial\varepsilon_{nl}/\partial n$$

and change from integration with respect to n to integration with respect to ϵ. As a result we get

$$\rho_{osc}(r) = \frac{m}{2\pi^2 r^2\hbar^3}\sum_{k=-\infty}^{\infty}(-1)^k\int_0^{p_F^2 r^2} d\lambda^2 \cos\left(\frac{2\pi k\lambda}{\hbar}\right) I(\lambda), \qquad \text{(II.2)}$$

where

$$I(\lambda) = \sum_{s=-\infty}^{\infty}(-1)^s \int_{U+\lambda^2/2mr^2}^{\mu} \frac{d\varepsilon}{p_{\varepsilon\lambda}} \sin\frac{2}{\hbar}(\sigma_{\varepsilon\lambda}(r) + s\sigma_{\varepsilon\lambda}^0). \qquad \text{(II.3)}$$

We integrate in (II.3) by parts and confine ourselves to the first term

$$I(\lambda) = -\frac{\hbar}{2mp_{F\lambda}}\sum_{s=-\infty}^{\infty}(-1)^s \frac{\cos[2(\sigma_{F\lambda}(r) + s\sigma_{F\lambda}^0)/\hbar]}{\tau_{F\lambda}(r) + s\tau_{F\lambda}^0}; \qquad \text{(II.4)}$$

Here $p_{F\lambda} = [p_F^2 - \lambda^2/r^2]^{1/2}$.

We substitute (II.4) in (II.2):

$$\rho_{osc}(r) = -\frac{1}{4\pi^2 r^2\hbar^2}\sum_{k,s=-\infty}^{\infty}(-1)^{k+s}\int_0^{p_F^2 r^2} d\lambda^2 \qquad \text{(II.5)}$$

$$\times \frac{\cos[2(\sigma_{F\lambda}(r) + s\sigma_{F\lambda}^0 + \pi k\lambda)/\hbar]}{p_{F\lambda}(\tau_{F\lambda}(r) + s\tau_{F\lambda}^0)}.$$

We integrate by parts (II.5) with respect to λ^2, leaving those terms which are outside the integral sign and are referred to $\lambda = 0$. This gives rise to the characteristic quantities

$$\frac{d}{d\lambda^2}\frac{2}{\hbar}\sigma_{F\lambda}(r) = -\frac{1}{\hbar}\delta_{F\lambda}(r), \qquad \text{(II.6)}$$

$$\frac{d}{d\lambda^2}\frac{2\pi k\lambda}{\hbar} = \frac{\pi k}{\hbar\lambda}, \qquad \text{(II.7)}$$

$$\frac{d}{d\lambda^2}\frac{2s}{\hbar}\sigma_{F\lambda}^0 = -\frac{s}{\hbar}\int_{R'_{F\lambda}}^{R_{F\lambda}}\frac{dr'}{r'^2 p_{F\lambda}}, \qquad \text{(II.8)}$$

the combination of which appears in the denominator of (II.5). It is easy to see that the terms containing (II.7) in the denominator are not equal to zero at $\lambda = 0$ only if the divergence of (II.7) is compensated for by the divergence of the integral in (II.8). On the other hand, the behavior of this integral as $\lambda \to 0$ depends essentially on the form of the potential at small distances.

We consider three important cases.

1) Repulsion at short distances. The integral (II.8) is finite as $\lambda \to 0$ and is equal to

$$-\frac{s}{\hbar}\int_{R'}^{R}\frac{dr'}{r'^2 p_F} = -\frac{s}{\hbar}\delta^0.$$

There is no compensation in this case, and all that remain in (II.5) are terms with k = 0. The remaining summation with respect to s leads to the formula (7).

2) Attraction at small distances and $p_F(0)$ is finite. In this case

$$\lim_{\lambda\to 0}\int_{R'_{F\lambda}}^{R_{F\lambda}}\frac{dr'}{r'^2 p_{F\lambda}} = \lim_{\lambda\to 0}\frac{\pi}{2\lambda} + \delta^0;$$

here and below (in case 3)) the quantity δ^0 denotes the finite part of the initial integral. Compensation of the divergences in the denominator is possible at s = 2k. As a result of the summation we arrive at (7a).

3) Attraction of Coulomb type at short distances. Near the point r = 0 we have $p_F^2(r) \sim 1/r$ and

$$\lim_{\lambda\to 0}\int_{R'_{F\lambda}}^{R_{F\lambda}}\frac{dr'}{r'^2 p_{F\lambda}} = \lim_{\lambda\to 0}\frac{\pi}{\lambda} + \delta^0.$$

Compensation occurs at s = k. The corresponding summation leads to the formula (7b).

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