

## Semi-infinite jellium: Step potential model

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The semi-infinite jellium using the step potential model of surface potential is studied. The barrier height is found from the condition of the minimum of the surface energy. It is shown that this minimum is caused by the Coulomb interaction between electrons. The surface energy is positive in the entire domain of the Wigner-Seitz radius of metals, and it is in sufficiently good agreement with experimental data. The one-particle distribution function of electrons and the distance from the surface potential to the dividing plane within this model are calculated. Influence of the Coulomb interaction between electrons on these calculated characteristics is studied.

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### I. INTRODUCTION

In Ref. [1], using the method of functional integration, the quantum-statistical theory of simple semibounded metal within the framework of the semi-infinite jellium is built. The advantage of this theory is taking into account of the Coulomb interaction between electrons in the semibounded system. In particular, using the infinite barrier model of the surface potential, the one-particle distribution function of electrons and the surface energy are calculated. This model potential is the simplest, but it obtained an important result—the surface energy of the semi-infinite jellium is positive in the entire area of the Wigner-Seitz radius ( $r_s$ ) of metals. Conversely, the usage of the density-functional theory, which today is the most popular, leads to the well-known problem of the surface energy negative values at high concentrations of electrons. An overview of papers that focus on the study of the surface energy is in Ref. [1].

This paper is a continuation of Ref. [1], the difference is in the way of modeling the surface potential, namely, in using the step potential model for the surface potential. This model was used in Ref. [2] to calculate the surface energy of a noninteracting electron system as a function of the height of the potential barrier. The height of the potential barrier was chosen arbitrarily. In contrast to Ref. [2] we take into account the Coulomb interaction between electrons. This leads to the appearance of the minimum of the surface energy from which the height of the potential barrier is found. The calculated values of the surface energy are somewhat lower than obtained in Ref. [1] for the infinite barrier model. These values are in sufficiently good agreement with experimental data for simple metals.

A variational calculation of the surface energy without taking the correlation energy into account was performed in Ref. [3]. The minimization procedure yielded magnitudes of the surface energy, which are very similar to those obtained by Lang and Kohn [4], i.e., the surface energy continues to be negative for large values of the electron concentration.

In Ref. [5], jellium-metal surface energies were obtained by application of the Vannimenus-Budd theorem [6], which

is derived from the density-functional formalism, by the determination of the individual components of the energy within the local exchange-correlation approximation, and by variational calculation of the surface energy for the step model within the local-density approximation. The obtained results are close to results of Lang and Kohn [4] for medium and low densities. For high densities, calculations via the Vannimenus-Budd theorem gave positive but very small values of the surface energy, calculations in the local-density approximation gave slightly larger values than results of Lang and Kohn [4], but negative near  $r_s = 2a_B$ .

Influence of the Coulomb interaction between electrons on the one-particle distribution function of electrons and the distance from the surface potential to the dividing plane is studied. It is shown that the Coulomb interaction leads to an increase of this distance and to its nonlinear behavior with respect to the Wigner-Seitz radius (whereas one for the noninteracting system is a linear function), and leads to an increase of the period of damped oscillations of this distribution function in the bulk. It is found out that the one-particle distribution function of electrons more slowly goes down to zero out of the positive charge in comparison with the one-particle distribution function for the infinitely high potential barrier. It is shown that if the potential barrier height tends to infinity, the obtained results coincide with the results of Ref. [1].

### II. MODEL

As in Ref. [1], we consider a semibounded metal within the framework of the semi-infinite jellium, i.e., a system of  $N$  electrons is located in the volume  $V = SL$  ( $S, L \rightarrow \infty$ ) in the field of the surface potential  $V_{\text{surf}}(z)$ ,  $z \in [-L/2, +L/2]$ . The dividing plane is at  $z = 0$ . In this work, in contrast to Ref. [1], the surface potential is modeled by the step potential of the height  $W = \frac{\hbar^2 s^2}{2m} = \tilde{W}\mu$  (where  $\mu = \frac{\hbar^2 K_F^2}{2m}$  is the chemical potential of the system taking into account the Coulomb interaction between electrons,  $K_F$  is the magnitude of the Fermi wave vector,  $m$  is the electron mass), which is placed at the point  $z = d$ , i.e.,

$$V_{\text{surf}}(z) = \begin{cases} W, & z > d, \\ 0, & z < d, \end{cases} \quad (1)$$

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and allows an analytical solution of the one-dimensional stationary Schrödinger equation,

$$\left[ -\frac{\hbar^2}{2m} \frac{d^2}{dz^2} + V_{\text{surf}}(z) \right] \varphi_\alpha(z) = \varepsilon_\alpha \varphi_\alpha(z).$$

Such solution, which satisfies the boundary conditions,

$$\varphi_\alpha(-L/2) = 0, \quad \varphi_\alpha(+L/2) = 0, \quad L \rightarrow \infty,$$

the conditions of continuity and smoothness,

$$\begin{aligned} \varphi_\alpha(z < d)|_{z=d} &= \varphi_\alpha(z > d)|_{z=d}, \\ \varphi'_\alpha(z < d)|_{z=d} &= \varphi'_\alpha(z > d)|_{z=d} \end{aligned}$$

is

$$\begin{aligned} \varepsilon_\alpha &= \frac{\hbar^2 \alpha^2}{2m}, \\ \varphi_\alpha(z) &= C(\alpha) \begin{cases} \sin[\alpha(d-z) + \gamma(\alpha)], & z \leq d, \\ \frac{\alpha}{s} e^{-\varkappa(\alpha)(z-d)}, & z > d, \end{cases} \end{aligned} \quad (2)$$

where

$$\begin{aligned} \gamma(\alpha) &= \arcsin \frac{\alpha}{s}, \\ \varkappa(\alpha) &= \left( \frac{d\gamma(\alpha)}{d\alpha} \right)^{-1} = \sqrt{s^2 - \alpha^2}, \quad \alpha \leq s, \end{aligned}$$

and quantum numbers  $\alpha$  satisfy the algebraic transcendental equation,

$$\alpha \left( \frac{L}{2} + d \right) + \gamma(\alpha) = \pi n, \quad n = 1, 2, 3, \dots$$

From the normalization condition for the wave functions,

$$\int_{-\frac{L}{2}}^{+\infty} |\varphi_\alpha(z)|^2 dz = 1, \quad (3)$$

it follows that

$$C(\alpha) = \frac{2}{\sqrt{L + 2(d + \frac{1}{\varkappa(\alpha)})}} = \frac{2}{\sqrt{L + 2(d + \frac{d\gamma(\alpha)}{d\alpha})}}.$$

Note that the electron states  $\varepsilon_\alpha > W$  are not written out, because only the states  $\varepsilon_\alpha \leq \mu$  are really interesting for us, and for physically interesting problems the chemical potential of electrons is less than the barrier height,  $\mu \leq W$ .

The step potential (1) has the parameter  $d$ , which determines the position of the potential barrier, and is determined by the condition of electroneutrality. It is necessary to calculate the one-particle distribution function of electrons.

### III. ONE-PARTICLE DISTRIBUTION FUNCTION OF ELECTRONS

Let us calculate the one-particle distribution function of electrons for the step potential model (1) in the case of low temperatures

$$\begin{aligned} F_1^0(z) &= \frac{1}{\bar{n}S} \sum_{\mathbf{k}_\parallel, \alpha} |\varphi_\alpha(z)|^2 n_\alpha(\mathbf{k}_\parallel) \\ &= \frac{1}{\bar{n}S} \sum_{\mathbf{k}_\parallel, \alpha} |\varphi_\alpha(z)|^2 \theta(\mathcal{K}_F^2 - k_\parallel^2 - \alpha^2), \end{aligned} \quad (4)$$

where  $n_\alpha(\mathbf{k}_\parallel)$  is the Fermi-Dirac distribution,  $\mathbf{k}_\parallel$  is the two-dimensional wave vector of the electron in the plane parallel to the dividing plane,  $\bar{n}$  is the electron concentration, and  $\theta(x)$  is the Heaviside step function.

Transition from the sums to the integrals according to rules [1],

$$\sum_{\mathbf{k}_\parallel} f(k_\parallel) = \frac{2S}{(2\pi)^2} \int_{-\infty}^{+\infty} d\mathbf{k}_\parallel f(k_\parallel) = \frac{S}{\pi} \int_0^\infty dk_\parallel k_\parallel f(k_\parallel), \quad (5)$$

$$\begin{aligned} \sum_\alpha f(\alpha) &= \int_0^\infty d\alpha \left\{ \frac{L}{2\pi} \left[ 1 + \frac{2}{L} \left( d + \frac{d\gamma(\alpha)}{d\alpha} \right) \right] - \frac{1}{2} \delta(\alpha) \right\} f(\alpha) \\ &= \int_0^\infty d\alpha \left( \frac{2}{\pi |C(\alpha)|^2} - \frac{1}{2} \delta(\alpha) \right) f(\alpha), \end{aligned} \quad (6)$$

(here  $\delta(\alpha)$  is the Dirac  $\delta$  function) and integration with respect to the variable  $k_\parallel$  lead to

$$\begin{aligned} F_1^0(z) &= \frac{3}{\mathcal{K}_F^3} \int_0^{\mathcal{K}_F} d\alpha (\mathcal{K}_F^2 - \alpha^2) \\ &\quad \times \begin{cases} \sin^2[\alpha(d-z) + \gamma(\alpha)], & z \leq d, \\ \frac{\alpha^2}{s^2} e^{-2\varkappa(\alpha)(z-d)}, & z > d. \end{cases} \end{aligned} \quad (7)$$

Integration with respect to the variable  $\alpha$  must be performed numerically.

If in Eq. (7) the barrier height tends to infinity, this equation takes the well-known form [1]

$$\begin{aligned} F_1^0(z) &= \left\{ 1 + \frac{3 \cos[2\mathcal{K}_F(d-z)]}{[2\mathcal{K}_F(d-z)]^2} - \frac{3 \sin[2\mathcal{K}_F(d-z)]}{[2\mathcal{K}_F(d-z)]^3} \right\} \\ &\quad \times \theta(d-z), \end{aligned}$$

which is the one-particle distribution function of electrons in the case of infinite potential barrier model.

In Fig. 1, the one-particle distribution function of electrons (7) as a function of the electron coordinate normal is presented for the following values of Wigner-Seitz radius:  $r_s = 2a_B$  and  $r_s = 6a_B$ , and different values of the barrier height parameter. The solid line represents the one-particle distribution function of electrons, which depends on the chemical potential of interacting electrons. The dashed line represents the one-particle distribution function of electrons without the Coulomb interaction. The positive charge is located in the domain  $z \leq 0$ . It can be concluded: (i) taking into account the Coulomb interaction leads to an increase of the period of damping oscillations of the one-particle distribution function around its value in the bulk of the metal, which equals to unity; and (ii) increasing of the barrier height leads to more rapid damping of the one-particle distribution function near the dividing plane.

The parameter  $d$  is determined by the condition of electroneutrality, which for the one-particle function has the form

$$\lim_{L \rightarrow \infty} \int_{-\frac{L}{2}}^{+\infty} [F_1^0(z) - \theta(-z)] dz = 0.$$

Substituting Eq. (4) into this condition, we get

$$\lim_{L \rightarrow \infty} \left[ \frac{1}{\bar{n}S} \sum_{\mathbf{k}_\parallel, \alpha} |\varphi_\alpha(z)|^2 \theta(\mathcal{K}_F^2 - k_\parallel^2 - \alpha^2) - \frac{L}{2} \right] = 0.$$

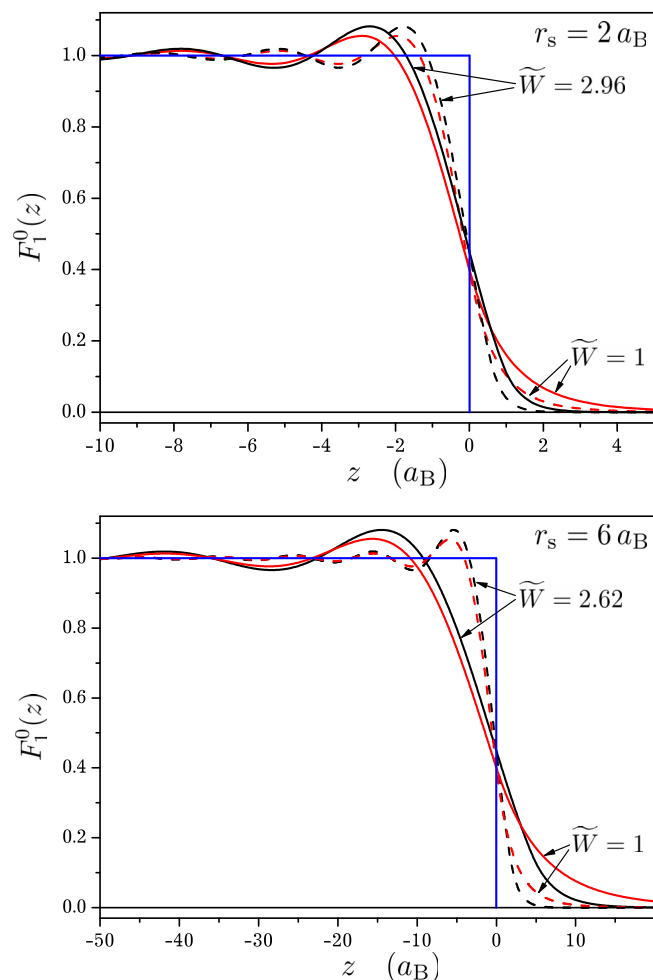


FIG. 1. The one-particle distribution function of electrons as a function of the electron coordinate normal to the dividing plane at  $r_s = 2a_B$  (top) and  $r_s = 6a_B$  (bottom) for different values of the barrier height parameter (the solid line is for interacting electrons whereas the dashed line is for noninteracting electrons).

By using the normalization condition (3), the rules of transition from the sums to integrals (5), (6), and  $\bar{n} = \mathcal{K}_F^3/(3\pi^2)$ , we obtain the equation for the parameter  $d$ ,

$$\lim_{L \rightarrow \infty} \left[ \frac{L}{2} + d + \frac{3}{2\mathcal{K}_F^3} \int_0^{\mathcal{K}_F} d\alpha (\mathcal{K}_F^2 - \alpha^2) \frac{d\gamma(\alpha)}{d\alpha} - \frac{3\pi}{8\mathcal{K}_F} - \frac{L}{2} \right] = 0.$$

From this equation we find the parameter  $d$ ,

$$d = \frac{3\pi}{8\mathcal{K}_F} - \frac{3}{2\mathcal{K}_F^3} \int_0^{\mathcal{K}_F} d\alpha (\mathcal{K}_F^2 - \alpha^2) \frac{d\gamma(\alpha)}{d\alpha}.$$

Integrating this equation by parts, we get

$$d = \frac{3\pi}{8\mathcal{K}_F} - \frac{3}{\mathcal{K}_F^3} \int_0^{\mathcal{K}_F} d\alpha \alpha \gamma(\alpha). \quad (8)$$

Taking into account that  $\gamma(\alpha) = \arcsin \frac{\alpha}{s}$ , we get

$$d = \frac{3\pi}{8\mathcal{K}_F} - \frac{3}{4\mathcal{K}_F} \left( \sqrt{\tilde{W} - 1} + (2 - \tilde{W}) \arcsin \frac{1}{\sqrt{\tilde{W}}} \right). \quad (9)$$

Note that, in Eq. (9), if we put the magnitude of the Fermi wave vector  $\mathcal{K}_F^0$  of noninteracting electrons,

$$\mathcal{K}_F^0 = \left( \frac{9\pi}{4} \right)^{1/3} \frac{1}{r_s}, \quad (10)$$

instead of the magnitude of the Fermi wave vector  $\mathcal{K}_F$  of interacting electrons, we get the well-known equation for noninteracting electrons [7–9].

It should be noted that increase of the barrier height leads to an increase of the distance  $d$ , and

$$\lim_{W \rightarrow \infty} d = d_{\text{IBM}} = \frac{3\pi}{8\mathcal{K}_F},$$

that is the distance from the dividing plane to the infinite barrier model [1].

In Fig. 2, the parameter  $d$  (9) as a function of the Wigner-Seitz radius  $r_s$  is given for different values of the barrier height parameter of the step potential. The solid line represents the parameter  $d$  for interacting system, the dashed line, for noninteracting system. This parameter is the distance from the surface potential to the dividing plane. We see that taking into account the Coulomb interaction between electrons leads to an increase of this distance and its nonlinear dependence on  $r_s$ , whereas the parameter  $d$  for the noninteracting system is a linear function of  $r_s$ . In the case of noninteracting electrons, this distance increases linearly with increasing of Wigner-Seitz radius, because the average distance between the electrons increases, and electrons can travel farther into the region  $z \geq 0$ . The Coulomb repulsion between the electrons leads to an additional increase in the average distance between the electrons. Therefore, electrons can travel even farther into the region  $z \geq 0$ , this distance as a function of Wigner-Seitz radius increases faster than linearly.

In Fig. 3, the difference between locations of the infinite potential barrier and the step potential,  $d_{\text{IBM}} - d$ , as a function of the barrier height parameter  $W$  is given for different values of the Wigner-Seitz radius  $r_s$ . For the barrier height  $W$ , which

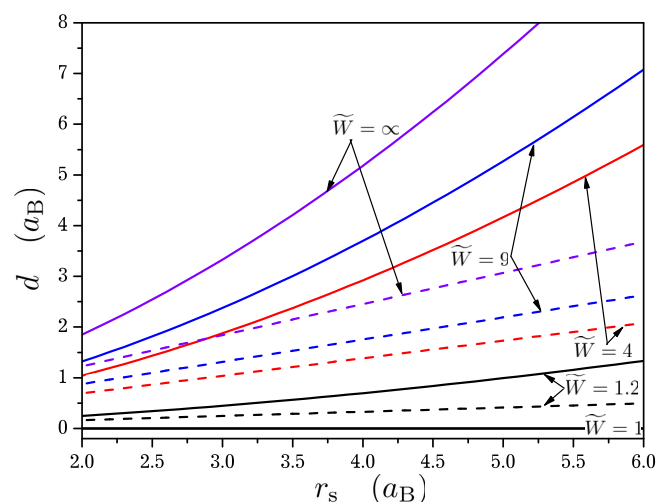


FIG. 2. The parameter  $d$  as a function of the Wigner-Seitz radius at different values of the barrier height parameter (the solid line is for interacting electrons whereas the dashed line is for noninteracting electrons).

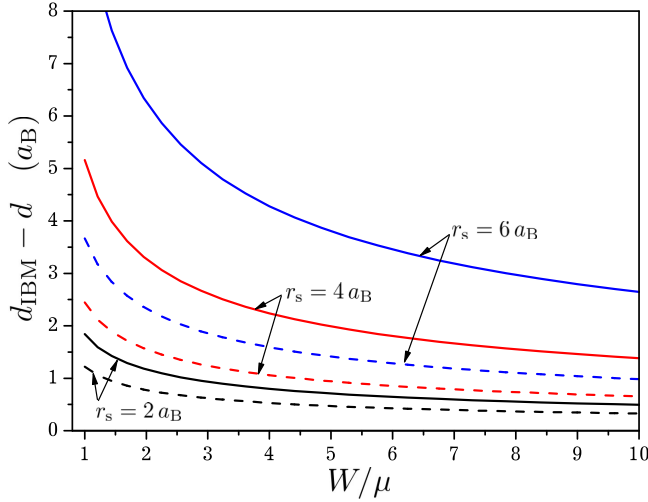


FIG. 3. The difference between locations of the infinite potential barrier and the step potential as a function of the barrier height parameter  $W$  is given for different values of the Wigner-Seitz radius  $r_s$  (the solid line is for interacting electrons whereas the dashed line is for noninteracting electrons).

is equal to the chemical potential  $\mu$ , this difference is equal to  $d_{IBM}$ . The conclusion from the curves is that a decrease of the barrier height  $W$  leads to an increase of the effective linear size of the semibounded metal. It is similar to one of the results of Ref. [10], where it was shown that the main influence of the soft-wall boundary condition consists in the increase of the effective radius of the wire relative to the hard-wall condition. Moreover, Fig. 3 shows that taking into account the Coulomb interaction between electrons leads to intensification of this effect.

#### IV. INTERNAL ENERGY

The internal energy of the system can be obtained from the thermodynamic potential  $\Omega$  and the Gibbs-Helmholtz equation generalized for the case of variable number of particles,

$$U = \Omega - \theta \frac{\partial \Omega}{\partial \theta} - \mu \frac{\partial \Omega}{\partial \mu}.$$

In the case of low temperatures ( $\theta \rightarrow 0$ ), the second term of the right-hand side of this equation vanishes and we get

$$U = \Omega + \mu \langle N \rangle, \quad (11)$$

where we have used the relation

$$\langle N \rangle = - \frac{\partial \Omega}{\partial \mu}$$

is the average number operator of electrons.

The general expressions for  $\Omega$  and  $\langle N \rangle$  are obtained by us in Ref. [1]. Substituting this expressions in Eq. (11), the internal energy  $U$  can be represented as

$$U = U_0 + \Delta U_1 + \Delta U_2, \quad (12)$$

where

$$U_0 = \Omega_0 + \mu \sum_{\mathbf{k}_{||}, \alpha} n_{\alpha}(\mathbf{k}_{||})$$

is the internal energy of the noninteracting system (the calculations of  $\Omega_0$  and  $U_0$  are done in Appendix A) though it indirectly takes into account the Coulomb interaction between electrons via the chemical potential  $\mu$  of interacting electrons.

$$\begin{aligned} \Delta U_1 &= \frac{1}{2S} \sum_{\mathbf{q} \neq 0} \sum_{\mathbf{k}_{||}, \alpha} \int_{-\frac{L}{2}}^{+\infty} dz |\varphi_{\alpha}(z)|^2 \left\{ n_{\alpha}(\mathbf{k}_{||}) \int_0^1 d\lambda [g(\mathbf{q}, z, z, \lambda) \right. \\ &\quad \left. - v(\mathbf{q}, 0)] - \mu \frac{\partial n_{\alpha}(\mathbf{k}_{||})}{\partial \mu} [g(\mathbf{q}, z, z, 1) - v(\mathbf{q}, 0)] \right\}, \\ \Delta U_2 &= \frac{1}{2S} \sum_{\mathbf{q} \neq 0} \sum_{\mathbf{k}_{||}, \alpha_1, \alpha_2} \int_{-\frac{L}{2}}^{+\infty} dz_1 \int_{-\frac{L}{2}}^{+\infty} dz_2 \varphi_{\alpha_1}^*(z_1) \varphi_{\alpha_2}(z_1) \varphi_{\alpha_2}^*(z_2) \\ &\quad \times \varphi_{\alpha_1}(z_2) \left[ \mu \frac{\partial (n_{\alpha_1}(\mathbf{k}_{||}) n_{\alpha_2}(\mathbf{k}_{||} - \mathbf{q}))}{\partial \mu} g(\mathbf{q}, z_1, z_2, 1) \right. \\ &\quad \left. - n_{\alpha_1}(\mathbf{k}_{||}) n_{\alpha_2}(\mathbf{k}_{||} - \mathbf{q}) \int_0^1 d\lambda g(\mathbf{q}, z_1, z_2, \lambda) \right], \end{aligned}$$

where  $v(\mathbf{q}, z) = \frac{2\pi e^2}{q} e^{-q|z|}$  is the two-dimensional Fourier transform of the Coulomb interaction,  $g(\mathbf{q}, v, z_1, z_2, \lambda)$  is the effective interelectron interaction potential in  $(\mathbf{q}, z)$  representation, which depends on the parameter  $\lambda$  and is a solution of the integral equation [1].

The calculation of the sums of the Fermi-Dirac distribution over the wave vector in a plane parallel to the dividing plane  $\mathbf{k}_{||}$  at low temperature yields

$$\begin{aligned} \sum_{\mathbf{k}_{||}} n_{\alpha}(\mathbf{k}_{||}) &= \frac{S}{2\pi} (\mathcal{K}_F^2 - \alpha^2) \theta(\mathcal{K}_F - \alpha), \\ \sum_{\mathbf{k}_{||}} \frac{\partial n_{\alpha}(\mathbf{k}_{||})}{\partial \mu} &= \frac{S}{2\pi} \frac{2m}{\hbar^2} \theta(\mathcal{K}_F - \alpha), \\ \sum_{\mathbf{k}_{||}} n_{\alpha_1}(\mathbf{k}_{||}) n_{\alpha_2}(\mathbf{k}_{||} - \mathbf{q}) &= \frac{2S}{(2\pi)^2} \tilde{J}(q, \alpha_1, \alpha_2), \\ \sum_{\mathbf{k}_{||}} \frac{\partial (n_{\alpha_1}(\mathbf{k}_{||}) n_{\alpha_2}(\mathbf{k}_{||} - \mathbf{q}))}{\partial \mu} &= \frac{2S}{(2\pi)^2} \frac{4m}{\hbar^2} I(q, \alpha_1, \alpha_2), \end{aligned}$$

where expressions for the functions  $\tilde{J}(q, \alpha_1, \alpha_2)$  and  $I(q, \alpha_1, \alpha_2)$  are given in Ref. [1].

The calculated results for the integrals of products of the wave functions and the effective potential are given in Appendix B.

#### V. SURFACE ENERGY

Since the main aim of this work is to calculate of the free surface energy  $\sigma$ , then it is necessary to single out the surface contribution  $U_{\text{surf}}$  (it is proportional to the area of the dividing plane  $S$ ) from the internal energy (12). Then the surface contribution to the internal energy per unit area of the dividing plane will be a required free surface energy, i.e.,

$$\begin{aligned} \sigma &= \frac{U_{\text{surf}}}{S} = \frac{U_{0, \text{surf}} + \Delta U_{1, \text{surf}} + \Delta U_{2, \text{surf}}}{S} \\ &= \sigma_0 + \Delta \sigma_1 + \Delta \sigma_2, \end{aligned} \quad (13)$$

where  $U_{0,\text{surf}}$  is the surface contribution to the internal energy of the noninteracting system [the calculation of  $U_{0,\text{surf}}$  is done in Appendix A, see Eq. (A3)],

$$\sigma_0 = \frac{U_{0,\text{surf}}}{S} = \frac{\hbar^2 \mathcal{K}_F^4}{160\pi m} \left\{ 1 + \frac{1}{2\pi} \left[ (15\tilde{W} - 14)\sqrt{\tilde{W} - 1} - (15\tilde{W}^2 - 24\tilde{W} + 8) \arcsin \frac{1}{\sqrt{\tilde{W}}} \right] \right\} \quad (14)$$

is the surface energy of noninteracting system,

$$\begin{aligned} \Delta\sigma_1 &= \frac{\Delta U_{1,\text{surf}}}{S} = \frac{1}{2\pi^2} a_B^3 \int_0^\infty dq q \int_0^{\mathcal{K}_F} d\alpha \\ &\times \left[ (\mathcal{K}_F^2 - \alpha^2) \int_0^1 d\lambda \Delta G(q, \alpha, \lambda) - \mathcal{K}_F^2 \Delta G(q, \alpha, 1) \right] \frac{e^2}{a_B^3}, \\ \Delta\sigma_2 &= \frac{\Delta U_{2,\text{surf}}}{S} \\ &= \frac{2}{\pi^4} a_B^3 \int_0^\infty dq q \int_0^{\mathcal{K}_F} d\alpha_1 \int_0^{\mathcal{K}_F} d\alpha_2 \left[ \mathcal{K}_F^2 I(q, \alpha_1, \alpha_2) G(q, \alpha, 1) \right. \\ &\quad \left. - \frac{1}{2} \tilde{J}(q, \alpha_1, \alpha_2) \int_0^1 d\lambda G(q, \alpha, \lambda) \right] \frac{e^2}{a_B^3}, \end{aligned}$$

where the transitions from the sums to the integrals are performed according to Eq. (6). Expressions for functions  $\Delta G(q, \alpha, \lambda)$  and  $G(q, \alpha, \lambda)$  are given in Appendix B [see Eqs. (B3) and (B4) respectively].

Note that, if in Eq. (14) we put the magnitude of the Fermi wave vector  $\mathcal{K}_F^0$  of noninteracting electrons Eq. (10), instead of the magnitude of the Fermi wave vector  $\mathcal{K}_F$  of interacting electrons, we get the well-known equation (14) for the surface energy of noninteracting system [7–9].

In Fig. 4, the dependence of the surface energy  $\sigma$  on the barrier height parameter  $W$  is presented for different values of the Wigner-Seitz radius. The solid line is for interacting electrons [see Eq. (13)] whereas the dashed line is for noninteracting electrons [see Eq. (14)]. It can be concluded that if the barrier height of the step potential increases, the surface energy tends to the value, which is obtained for the infinite barrier model [1]. If the barrier height narrows down to the chemical potential, the surface energy of noninteracting system increases. It is clear, because in this case the average distance between the electrons increases, electrons can travel even farther into the region  $z \geq 0$ , and therefore the surface energy increases. Taking into account the Coulomb interaction between electrons leads to a significant increase in the surface energy, its dependence on the barrier height parameter  $W$  is no longer monotonic, and the surface energy as a function of the parameter  $W$  has a minimum. Since a system always tends to the lowest-energy state, the minimum of the surface energy can be seen as self-consistent condition for the barrier height of the step potential (the values of the parameter  $W$  are presented in Table I for different values of the Wigner-Seitz radius). The received values of the parameter  $W/\mu$  are significantly greater than those obtained by Mahan without taking the correlation energy into account [3], namely for  $r_s = 5a_B$  the minimum of the surface energy occurs at 1.3, for  $r_s \geq 3a_B$  minimization occurs just exactly 1, and the corresponding values of the

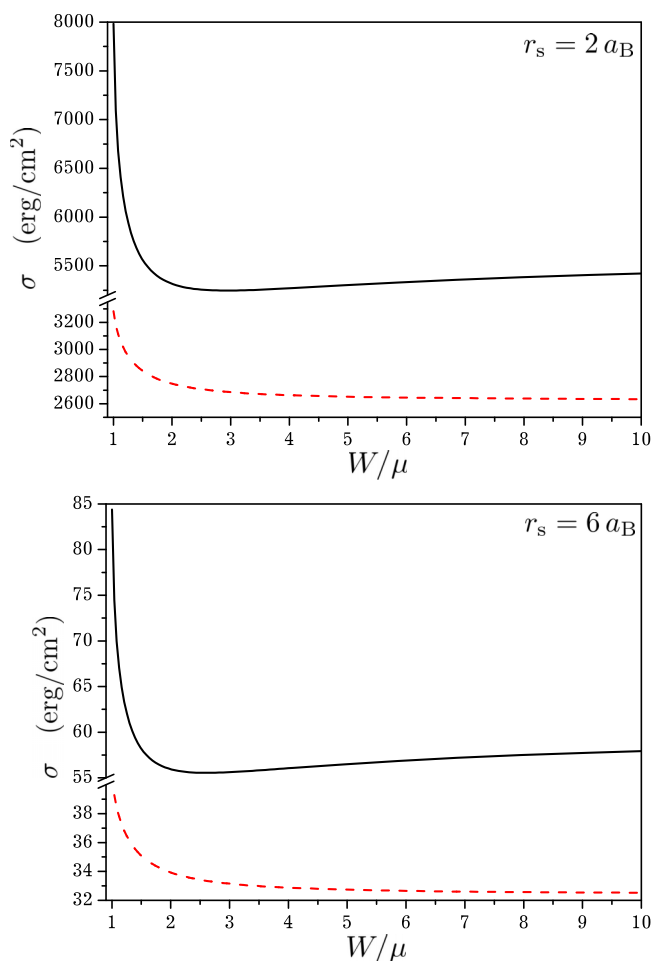


FIG. 4. The surface energy as a function of the barrier height parameter  $W$  at  $r_s = 2a_B$  (top) and  $r_s = 6a_B$  (bottom) (the solid line is for interacting electrons whereas the dashed line is for noninteracting electrons).

surface energy are negative for large values of the electron concentration.

In Fig. 5, the dependence of the surface energy  $\sigma$  on the Wigner-Seitz radius  $r_s$  is presented. The solid line is the surface energy calculated for the values of the barrier height parameter  $W$  fulfilled the condition for minimum of the surface energy. The dashed line is the surface energy for the infinite barrier model [1], the dash-dotted line is the well-known result of Lang and Kohn [4], and the dots are experimental data for some metals according to Ref. [11].

The results given in this figure show that the calculated values of the surface energy for the step potential model is positive in the entire domain of the Wigner-Seitz  $r_s$ , these values are lower than the values of the surface energy for the

TABLE I. The values of the surface energy minimum and its coordinates.

$r_s, a_B$	2	3	4	5	6
$W/\mu$	2.96	2.76	2.69	2.66	2.62
$\sigma, \text{erg/cm}^2$	5246	1067	322	123	55

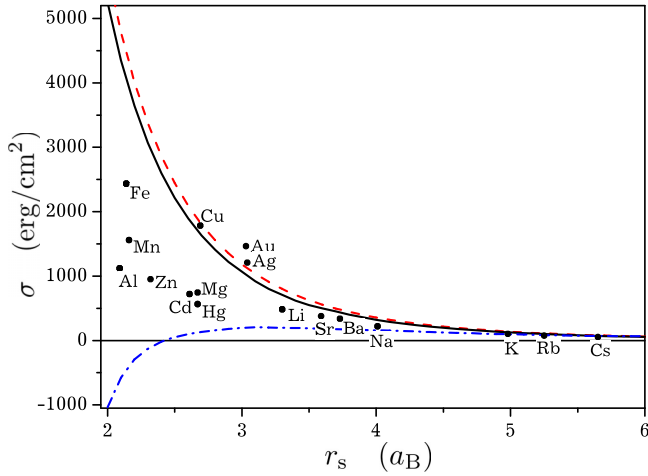


FIG. 5. The surface energy as a function of the Wigner-Seitz radius (the solid line is for the height of the potential barrier, which fulfills the condition for minimum of the surface energy; the dashed line is for the infinite barrier model [1]; the dash-dotted line is the result of Lang and Kohn [4], whereas the dots are experimental data [11]).

infinite barrier model, and in the domain  $r_s > 5a_B$ , the values of the surface energy for finite and infinite barrier model are in good agreement with the well-known result of Lang and Kohn [4]. In addition, for such a simple model of semibounded metal, which is the semi-infinite jellium, the calculated values of the surface energy are in sufficiently good agreement with experimental data for simple metals (Li, Na, K, Rb, Cs, Sr, Ba), which are satisfactorily described by the semi-infinite jellium. The reason of this is domination of the electronic structure of simple metal, and the ionic cores are of secondary importance (see, e.g., Ref. [12]). Obviously, incorporation of the discreteness of the ionic subsystem is necessary for better agreement with experimental data for other metals.

## VI. CONCLUSIONS

By using the step potential model for the surface potential, the one-particle distribution function of electrons, the distance from the surface potential to the dividing plane, and the surface energy of the semibounded metal within the framework of the semi-infinite jellium are calculated and studied at low temperatures.

It is found that taking into account the Coulomb interaction between electrons leads to an increase in the period of damped oscillations around its average value in the bulk of the metal, and increasing of the barrier height of the step potential leads to more rapid damping of the one-particle distribution function near the dividing plane.

The Coulomb interaction also leads to an increase in the distance between the dividing plane and the surface potential, and its nonlinear dependence on the Wigner-Seitz radius, whereas this distance for the noninteracting system is a linear function. The Coulomb repulsion between the electrons leads to an additional increase of the average distance between the electrons. Therefore, electrons can travel even farther into the

region  $z \geq 0$ , this distance as a function of Wigner-Seitz radius increases faster than linearly.

The Coulomb interaction causes a significant increase in the surface energy, its dependence on the barrier height of the step potential is no longer monotonic; whereas, the surface energy of the noninteracting system is a monotonically decreasing function. There is the minimum of the surface energy at some value of the barrier height. The condition of this minimum is used as a self-consistent condition for the barrier height at different values of the Wigner-Seitz radius. The obtained values of the barrier height of the step potential decrease with increasing of the Wigner-Seitz radius. Using these values, the surface energy is calculated as a function of the Wigner-Seitz radius, and it is lower than the surface energy for the infinite barrier model of the surface potential Ref. [1].

In contrast to the surface energy calculated by Lang and Kohn, the surface energy of semibounded metal within the framework of the semi-infinite jellium calculated by us is positive in the entire area of the Wigner-Seitz radius, and it is in sufficiently good agreement with experimental data for  $s$ -electron-type metals (Li, Na, K, Rb, Cs, Sr, Ba), and for some transition metals (Ag, Cu). Experimental data for other transition metals disagree with the values of the surface energy calculated by us. This is not surprising because jellium is one of the simplest models of metal, which satisfactorily describes simple metals (see, e.g., Ref. [12]).

## APPENDIX A: THERMODYNAMICAL POTENTIAL AND INTERNAL ENERGY OF NONINTERACTING SYSTEM

Let us calculate the thermodynamical potential of noninteracting system,

$$\Omega_0 = -\frac{1}{\beta} \sum_{\mathbf{k}_{||}, \alpha} \ln[1 + e^{\beta(\mu - E_\alpha(\mathbf{k}_{||}))}],$$

where  $E_\alpha(\mathbf{k}_{||})$  is the energy of the electron in the state  $(\mathbf{k}_{||}, \alpha)$ . Since here  $\mu$  is the chemical potential of interacting electron system, the Coulomb interaction in this expression is taken into account indirectly via chemical potential.

To perform summation with respect to  $\mathbf{k}_{||}$  and  $\alpha$ , we use

$$\rho(E) = \frac{SL}{2} \frac{\sqrt{2}m^{3/2}}{\pi^2 \hbar^3} \sqrt{E} + S \left[ \frac{\sqrt{2}m^{3/2}d}{\pi^2 \hbar^3} \sqrt{E} + \frac{m}{\pi^2 \hbar^2} \gamma \left( \frac{\sqrt{2mE}}{\hbar} \right) - \frac{m}{4\pi \hbar^2} \right],$$

which coincides with the density of states for the infinite barrier model Ref. [1] if the barrier height  $W$  tends to infinity.

At low temperatures ( $\beta \rightarrow \infty$ ), the thermodynamical potential of noninteracting system has the form

$$\Omega_0 = \Omega_{0,\text{bulk}} + \Omega_{0,\text{surf}}, \quad (\text{A1})$$

where

$$\begin{aligned} \Omega_{0,\text{bulk}} &= -\frac{SL}{2} \frac{4\sqrt{2}m^{3/2}}{15\pi^2 \hbar^3} \mu^{5/2} \\ &= -\frac{SL}{2} \frac{\hbar^2}{15m\pi^2} \mathcal{K}_F^5 \end{aligned}$$

is the extensive contribution to the thermodynamical potential of noninteracting system (it is proportional to the volume of the system  $SL$ ), which is dependent on the magnitude of the Fermi wave vector  $\mathcal{K}_F$  of interacting system of electrons,

$$\begin{aligned}\Omega_{0,\text{surf}} &= -S \left[ \frac{4\sqrt{2}m^{3/2}d}{15\pi^2\hbar^3} \mu^{5/2} \right. \\ &\quad \left. + \frac{m}{\pi^2\hbar^2} \int_0^\mu dE (\mu - E) \gamma \left( \frac{\sqrt{2mE}}{\hbar} \right) - \frac{m}{8\pi\hbar^2} \mu^2 \right] \\ &= S \frac{\hbar^2 \mathcal{K}_F^4}{m\pi^2} \left[ \frac{\pi}{32} - \frac{d\mathcal{K}_F}{15} \right. \\ &\quad \left. - \frac{1}{2\mathcal{K}_F^4} \int_0^{\mathcal{K}_F} d\alpha \alpha (\mathcal{K}_F^2 - \alpha^2) \gamma(\alpha) \right] \quad (\text{A2})\end{aligned}$$

is the surface contribution (it is proportional to the area of the dividing plane  $S$ ). Taking into account Eq. (8) for the parameter  $d$ , we get that

$$\Omega_{0,\text{surf}} = S \frac{\hbar^2 \mathcal{K}_F^4}{160\pi m} \left[ 1 + \frac{80}{\pi \mathcal{K}_F^4} \int_0^{\mathcal{K}_F} d\alpha \alpha \left( \alpha^2 - \frac{3}{5} \mathcal{K}_F^2 \right) \gamma(\alpha) \right].$$

Using Eqs. (A1)–(A2), the average of the number operator of electrons without taking into account the Coulomb interaction between electrons can be represented as

$$\langle N \rangle_0 = -\frac{\partial \Omega_0}{\partial \mu} = N_{0,\text{bulk}} + N_{0,\text{surf}},$$

where

$$N_{0,\text{bulk}} = -\frac{\partial \Omega_{0,\text{bulk}}}{\partial \mu} = \frac{SL}{2} \frac{\mathcal{K}_F^3}{3\pi^2},$$

$$\begin{aligned}N_{0,\text{surf}} &= -\frac{\partial \Omega_{0,\text{surf}}}{\partial \mu} = S \left[ \frac{2\sqrt{2}m^{3/2}d}{3\pi^2\hbar^3} \mu^{3/2} + \frac{m}{\pi^2\hbar^2} \int_0^\mu dE \gamma \left( \frac{\sqrt{2mE}}{\hbar} \right) - \frac{m}{4\pi\hbar^2} \mu \right] \\ &= S \frac{\mathcal{K}_F^2}{\pi^2} \left[ \frac{\mathcal{K}_F d}{3} - \frac{\pi}{8} + \frac{1}{\mathcal{K}_F^2} \int_0^{\mathcal{K}_F} d\alpha \alpha \gamma(\alpha) \right].\end{aligned}$$

Taking into account Eq. (8) for the parameter  $d$ , we get that

$$N_{0,\text{surf}} = 0.$$

At low temperatures, the internal energy of noninteracting system can be represented as

$$U_0 = \Omega_0 + \mu \langle N \rangle_0 = U_{0,\text{bulk}} + U_{0,\text{surf}},$$

where

$$\begin{aligned}U_{0,\text{bulk}} &= \Omega_{0,\text{bulk}} + \mu N_{0,\text{bulk}} = \frac{SL}{2} \frac{\hbar^2 \mathcal{K}_F^2}{10\pi^2 m}, \\ U_{0,\text{surf}} &= \Omega_{0,\text{surf}} + \mu N_{0,\text{surf}} = \Omega_{0,\text{surf}} \\ &= S \frac{\hbar^2 \mathcal{K}_F^4}{160\pi m} \left[ 1 + \frac{80}{\pi \mathcal{K}_F^4} \int_0^{\mathcal{K}_F} d\alpha \alpha \left( \alpha^2 - \frac{3}{5} \mathcal{K}_F^2 \right) \gamma(\alpha) \right].\end{aligned}$$

Taking into account that  $\gamma(\alpha) = \arcsin \frac{\alpha}{s}$ , we get

$$\begin{aligned}U_{0,\text{surf}} &= S \frac{\hbar^2 \mathcal{K}_F^4}{160\pi m} \left\{ 1 + \frac{1}{2\pi} \left[ (15\tilde{W} - 14)\sqrt{\tilde{W} - 1} \right. \right. \\ &\quad \left. \left. - (15\tilde{W}^2 - 24\tilde{W} + 8) \arcsin \frac{1}{\sqrt{\tilde{W}}} \right] \right\}. \quad (\text{A3})\end{aligned}$$

## APPENDIX B: CALCULATION OF INTEGRALS WITH EFFECTIVE INTERELECTRON INTERACTION

In this Appendix the results of calculation of the integrals

$$\int_{-\frac{1}{2}}^{+\infty} dz |\varphi_\alpha(z)|^2 [g(\mathbf{q}, z, z, \lambda) - \nu(\mathbf{q}, 0)], \quad (\text{B1})$$

and

$$\int_{-\frac{1}{2}}^{+\infty} dz_1 \int_{-\frac{1}{2}}^{+\infty} dz_2 \varphi_{\alpha_1}^*(z_1) \varphi_{\alpha_2}(z_1) \varphi_{\alpha_2}^*(z_2) \varphi_{\alpha_1}(z_2) g(\mathbf{q}, z_1, z_2, \lambda) \quad (\text{B2})$$

are given. Here  $\varphi_\alpha(z)$  are the wave function (2) of electrons in the field of the step potential, which is located at the point  $z = d$ ;  $g(\mathbf{q}, z_1, z_2, \lambda)$  is the effective interelectron interaction, which is obtained using the technique of Ref. [13]. This potential depends on the module of the vector  $\mathbf{q}$ :

$$\begin{aligned}g(\mathbf{q}, z_1 \leq d, z_2 \leq d, \lambda) &= \frac{2\pi e^2}{Q_1(\lambda)} \left[ e^{-Q_1(\lambda)|z_1 - z_2|} + \frac{Q_1(\lambda) - Q_2(\lambda)}{Q_1(\lambda) + Q_2(\lambda)} e^{Q_1(\lambda)(z_1 + z_2 - 2d)} \right], \\ g(\mathbf{q}, z_1 \geq d, z_2 \geq d, \lambda) &= \frac{2\pi e^2}{Q_2(\lambda)} \left[ e^{-Q_2(\lambda)|z_1 - z_2|} - \frac{Q_1(\lambda) - Q_2(\lambda)}{Q_1(\lambda) + Q_2(\lambda)} e^{-Q_2(\lambda)(z_1 + z_2 - 2d)} \right], \\ g(\mathbf{q}, z_1 \geq d, z_2 \leq d, \lambda) &= \frac{4\pi e^2}{Q_1(\lambda) + Q_2(\lambda)} e^{Q_1(\lambda)(z_2 - d) - Q_2(\lambda)(z_1 - d)}, \\ g(\mathbf{q}, z_1 \leq d, z_2 \geq d, \lambda) &= \frac{4\pi e^2}{Q_1(\lambda) + Q_2(\lambda)} e^{Q_1(\lambda)(z_1 - d) - Q_2(\lambda)(z_2 - d)},\end{aligned}$$

where

$$Q_1(\lambda) = \sqrt{q^2 + \lambda x_{\text{TF}}^2 \left[ L\left(\frac{q}{2\mathcal{K}_F}\right) - \Delta\left(\frac{q}{2\mathcal{K}_F}\right) \right]}, \quad Q_2(\lambda) = \sqrt{q^2 + \lambda x_{\text{TF}}^2 \Delta\left(\frac{q}{2\mathcal{K}_F}\right)}, \quad L(x) = \frac{1}{2} + \frac{1-x^2}{4x} \ln \left| \frac{1+x}{1-x} \right|,$$

$$\Delta(x) = \frac{2}{\tilde{s}^2} \int_0^1 d\xi \xi \sqrt{\tilde{s}^2 - \xi^2} \left[ 1 - \sqrt{1 - \frac{1-\xi^2}{x^2}} \theta\left(1 - \frac{1-\xi^2}{x^2}\right) \right], \quad \tilde{s} = \frac{s}{\mathcal{K}_F}.$$

Note that the integrals (B1) and (B2) are equal to zero for  $\alpha = 0$ , because in this case the wave functions (2) are equal to zero.

After integration, Eq. (B1) for  $\alpha \neq 0$  has the form

$$\int_{-\frac{L}{2}}^{+\infty} dz |\varphi_\alpha(z)|^2 [g(q, z, z, \lambda) - v(q, 0)] = 2\pi e^2 |C(\alpha)|^2 \frac{L}{4} \left( \frac{1}{Q_1(\lambda)} - \frac{1}{q} \right) + 2\pi e^2 |C(\alpha)|^2 \Delta G(q, \alpha, \lambda),$$

where

$$\begin{aligned} \Delta G(q, \alpha, \lambda) &= \left( \frac{d}{2} + \frac{\sin[2\gamma(\alpha)]}{4\alpha} \right) \left( \frac{1}{Q_1(\lambda)} - \frac{1}{q} \right) + \frac{1}{2\kappa(\alpha)} \left( \frac{\alpha}{s} \right)^2 \left( \frac{1}{Q_2(\lambda)} - \frac{1}{q} \right) \\ &+ \frac{1}{4Q_1(\lambda)} \frac{Q_1(\lambda) - Q_2(\lambda)}{Q_1(\lambda) + Q_2(\lambda)} \left( \frac{1}{Q_1(\lambda)} - \frac{Q_1(\lambda) \cos[2\gamma(\alpha)] - \alpha \sin[2\gamma(\alpha)]}{Q_1^2(\lambda) + \alpha^2} \right) \\ &- \frac{1}{2Q_2(\lambda)} \left( \frac{\alpha}{s} \right)^2 \frac{Q_1(\lambda) - Q_2(\lambda)}{Q_1(\lambda) + Q_2(\lambda)} \frac{1}{Q_2(\lambda) + \kappa(\alpha)}. \end{aligned} \tag{B3}$$

After integration, Eq. (B2) for  $\alpha_1 \neq 0$  and  $\alpha_2 \neq 0$  has the form

$$\begin{aligned} &\int_{-\frac{L}{2}}^{+\infty} dz_1 \int_{-\frac{L}{2}}^{+\infty} dz_2 \varphi_{\alpha_1}^*(z_1) \varphi_{\alpha_2}(z_1) \varphi_{\alpha_2}^*(z_2) \varphi_{\alpha_1}(z_2) g(q, z_1, z_2, \lambda) \\ &= 2\pi e^2 |C(\alpha_1)|^2 |C(\alpha_2)|^2 \frac{L}{4} \frac{Q_1^2(\lambda) + \alpha_1^2 + \alpha_2^2}{(Q_1^2(\lambda) + \alpha_1^2 + \alpha_2^2)^2 - 4\alpha_1^2 \alpha_2^2} + 2\pi e^2 |C(\alpha_1)|^2 |C(\alpha_2)|^2 G(q, \alpha_1, \alpha_2, \lambda), \end{aligned}$$

where

$$\begin{aligned} G(q, \alpha_1, \alpha_2, \lambda) &= \frac{1}{4} [f_1(\alpha_1, \alpha_2, \lambda) + f_1(\alpha_1, -\alpha_2, \lambda)] + \frac{1}{4Q_1(\lambda)} \frac{Q_1(\lambda) - Q_2(\lambda)}{Q_1(\lambda) + Q_2(\lambda)} [f_2(\alpha_1, \alpha_2, \lambda) - f_2(\alpha_1, -\alpha_2, \lambda)]^2 \\ &+ \frac{(\alpha_1 \alpha_2)^2}{s^4} \frac{1}{Q_2(\lambda)} \left( \frac{1}{(\kappa(\alpha_1) + \kappa(\alpha_2))(Q_2(\lambda) + \kappa(\alpha_1) + \kappa(\alpha_2))} - \frac{Q_1(\lambda) - Q_2(\lambda)}{Q_1(\lambda) + Q_2(\lambda)} \frac{1}{(Q_2(\lambda) + \kappa(\alpha_1) + \kappa(\alpha_2))^2} \right) \\ &+ \frac{\alpha_1 \alpha_2}{s^2} \frac{2}{Q_1(\lambda) + Q_2(\lambda)} \frac{1}{Q_2(\lambda) + \kappa(\alpha_1) + \kappa(\alpha_2)} [f_2(\alpha_1, \alpha_2, \lambda) - f_2(\alpha_1, -\alpha_2, \lambda)], \\ f_1(\alpha_1, \alpha_2, \lambda) &= \frac{1}{Q_1^2(\lambda) + (\alpha_1 - \alpha_2)^2} \left[ d - \frac{\sin[2(\gamma(\alpha_1) - \gamma(\alpha_2))]}{2(\alpha_1 - \alpha_2)} + \frac{\sin[2\gamma(\alpha_1)]}{2\alpha_1} + \frac{\sin[2\gamma(\alpha_2)]}{2\alpha_2} + \frac{Q_1(\lambda)}{Q_1^2(\lambda) + (\alpha_1 + \alpha_2)^2} \right. \\ &- \frac{Q_1^2(\lambda)[1 + \cos^2[\gamma(\alpha_1) - \gamma(\alpha_2)]] - (\alpha_1 - \alpha_2)^2 \sin^2[\gamma(\alpha_1) - \gamma(\alpha_2)]}{Q_1(\lambda)(Q_1^2(\lambda) + (\alpha_1 - \alpha_2)^2)} \\ &+ \frac{Q_1(\lambda) \cos[\gamma(\alpha_1) - \gamma(\alpha_2)] + (\alpha_1 - \alpha_2) \sin[\gamma(\alpha_1) - \gamma(\alpha_2)]}{Q_1(\lambda)(Q_1^2(\lambda) + (\alpha_1 + \alpha_2)^2)} \\ &\left. \times (Q_1(\lambda) \cos[\gamma(\alpha_1) + \gamma(\alpha_2)] - (\alpha_1 + \alpha_2) \sin[\gamma(\alpha_1) + \gamma(\alpha_2)]) \right], \\ f_2(\alpha_1, \alpha_2, \lambda) &= \frac{Q_1(\lambda) \cos[\gamma(\alpha_1) - \gamma(\alpha_2)] - (\alpha_1 - \alpha_2) \sin[\gamma(\alpha_1) - \gamma(\alpha_2)]}{Q_1^2(\lambda) + (\alpha_1 - \alpha_2)^2}. \end{aligned} \tag{B4}$$

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