

# An effective interionic interaction in semi-infinite metal in the presence of external electrostatic field with taking into account the local field approximation

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An effective interionic potential in semi-infinite metal, which is located in the external electrostatic field is studied. An effect of the local field correction and the applied external electric field on the effective interionic potential is investigated.

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## 1. Introduction

Due to the intensive experimental investigations of surfaces by means of scanning tunneling microscopy, scanning tunneling spectroscopy, field-ion microscopy, and their modifications [1, 2], the problem of investigating electron and ion subsystems of a metal under the action of an external electric field takes on the special actuality.

The density functional theory [3, 4] and its modifications (stabilized jellium) [5] are the first and most widely used theoretical models to describe the electron properties of simple metal surfaces (with  $s - p$  bonds). These models describe well enough the basic (one-particle) properties of inhomogeneous electron gas and do not include the impact of both ionic lattice of a metal, and the impact of many-body effects in inhomogeneous electron gas. Effect of discrete ion density on characteristics of the semi-infinite jellium by constructing a perturbation theory with pseudopotential of electron-ion interaction was made in the Refs. [3–9], which however linear response of electron density on the lattice potential did not take into account effects of heterogeneity of electron subsystem.

A method to calculate the impact of discreteness of ion subsystem on characteristics of inhomogeneous electron gas is developed in Refs. [10–12]. The basis of this method is perturbation theory with pseudopotential of electron-ion interaction taking into account the heterogeneity of electronic subsystems. In Refs. [10, 12], an effective interionic potential is calculated with the infinite square well as model of the surface potential.

In the present work, as in Refs. [10, 12], the effective interionic potential is calculated, but we take into account an external electrostatic field and use the local field correction not only in the Hubbard form [13] but also in the Ichimaru form [14]. Effects of surface of semi-infinite metal and external electrostatic field on the effective interionic potential are investigated.

## 2. Model

We consider a semi-infinite metal with ions having charges  $Z|e|$  and Cartesian coordinates  $\mathbf{R} = (\mathbf{R}_{||j}, Z_j)$ ,  $\mathbf{R}_{||j} = (X_j, Y_j)$ ,  $j = 1, 2, \dots, N_{\text{ion}}$  ( $N_{\text{ion}}$  is a number of ions,  $e$  is the charge of the electron). Ions are located in a half-space  $\Omega = \left\{ (X_j, Y_j, Z_j) : -\sqrt{S}/2 < X_j, Y_j < +\sqrt{S}/2, -L/2 < Z_j \leq Z_0 \right\}$ ,

where  $Z_0 = \text{const}$ ,  $z = Z_0$  is the division plane (surface). Electrons of a semi-infinite metal have coordinates  $\mathbf{r}_i = (\mathbf{r}_{\parallel i}, z_i)$ ,  $\mathbf{r}_{\parallel i} = (x_i, y_i)$ ,  $i = 1, 2, \dots, N$  ( $N$  is a number of electrons). We assume that the system is electroneutral, that is  $ZN_{ion} = N$ , and ions are fixed.

The semi-infinite metal is situated in the external electric field with the strength  $E$ . The field is applied perpendicular to the division surface.

As in Ref. [10], we use the semi-infinite jellium as the reference system for the study of the semi-infinite metal. Because electrons are in the external electric field, we model the surface potential  $V_{\text{surf}}(z)$  by such model potential

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

that enables to solve analytically the Schrödinger equation. The parameter  $W$  in Eq. (1) is the barrier height. Analytical solution of the Schrödinger equation with the potential model (1) is given in Ref. [15].

### 3. Effective interionic pair potential

In Refs. [10, 12], there is shown that the two-dimensional Fourier transform  $V(q|Z_1, Z_2)$  of the interionic pair potential has the form

$$V(q|Z_1, Z_2) = Z^2 \nu(q|Z_1 - Z_2) + \frac{\beta}{SL^2} \int dz \int dz' w(q|Z_1 - z) \widetilde{\mathfrak{M}}(q|z, z') w(q|z' - Z_2), \quad (2)$$

where  $w(q|z) = \int e^{i\mathbf{q}\mathbf{r}_{\parallel}} w(\sqrt{r_{\parallel}^2 + z^2}) d\mathbf{r}_{\parallel}$  is two-dimensional Fourier image of the local pseudo-potential  $w$ ,  $\beta$  is the inverse thermodynamic temperature,  $\nu(q|Z_1 - Z_2) = \frac{2\pi e^2}{q} \exp(-q|Z_1 - Z_2|)$  is the two-dimensional Fourier image of the Coulomb interaction,  $\widetilde{\mathfrak{M}}(q|z, z')$  is two-particle correlation function “density–density”, which is the solution of second order Fredholm integral equation [16],

$$\begin{aligned} \widetilde{\mathfrak{M}}(q|z_1, z_2) &= \mathfrak{M}_0(q|z_1, z_2) \\ &+ \frac{\beta}{SL^2} \int dz \int dz' \mathfrak{M}_0(q|z_1, z) [\nu(q|z - z') - \bar{\nu}(q|z - z')] \widetilde{\mathfrak{M}}(q|z', z_2), \end{aligned} \quad (3)$$

Here  $\mathfrak{M}_0(q|z_1, z)$  is the two-particle correlation function “density–density” without taking into account the Coulomb interaction between electrons [16],  $\bar{\nu}(q|z - z') = \frac{1}{L} \sum_k e^{ik(z-z')} \bar{\nu}_k(q)$ ,  $\bar{\nu}_k(q) = G_k(q) \nu_k(q)$ ,  $G_k(q)$  is a local-field correction,  $\nu_k(q) = \frac{4\pi e^2}{q^2 + k^2}$  is the three-dimensional Fourier image of the Coulomb interaction.

By using the two-dimensional Fourier transform  $V(q|Z_1, Z_2)$  (2), we can find the effective interionic pair potential in coordinate representation,

$$V(R_{\parallel}, Z_1, Z_2) = \frac{1}{2\pi} \int_0^{\infty} q J_0(qR_{\parallel}) V(q|Z_1, Z_2) dq, \quad (4)$$

where  $J_0(qR_{\parallel})$  is the Bessel function of the first kind.

### 4. Numerical results and conclusions

The numerical calculations of the effective interionic pair potential are performed for the Hartri approximation ( $G_k(q) = 0$ ), for the Ichimaru approximation [14], and the modified Hubbard approximation [13] for homogeneous electron gas,

$$G_k(q) = \frac{1}{2} \frac{q^2 + k^2}{q^2 + k^2 + \xi k_F^2}, \quad (5)$$

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where  $k_F = \sqrt{2m\mu}/\hbar$  is the magnitude of the Fermi wave vector,  $\mu$  is the chemical potential of electronic subsystem,  $m$  is the electron mass.  $\xi$  is the parameter, whose value may be the following:  $\xi = 1$  (the Hubbard approximation),  $\xi = 2$  (the Geldart and Vosko approximation),  $\xi = 1 + \frac{2}{\pi k_F a_B}$  (the Animalu approximation),  $\xi = 1 + \frac{4}{\pi k_F a_B}$  (the Sham approximation).

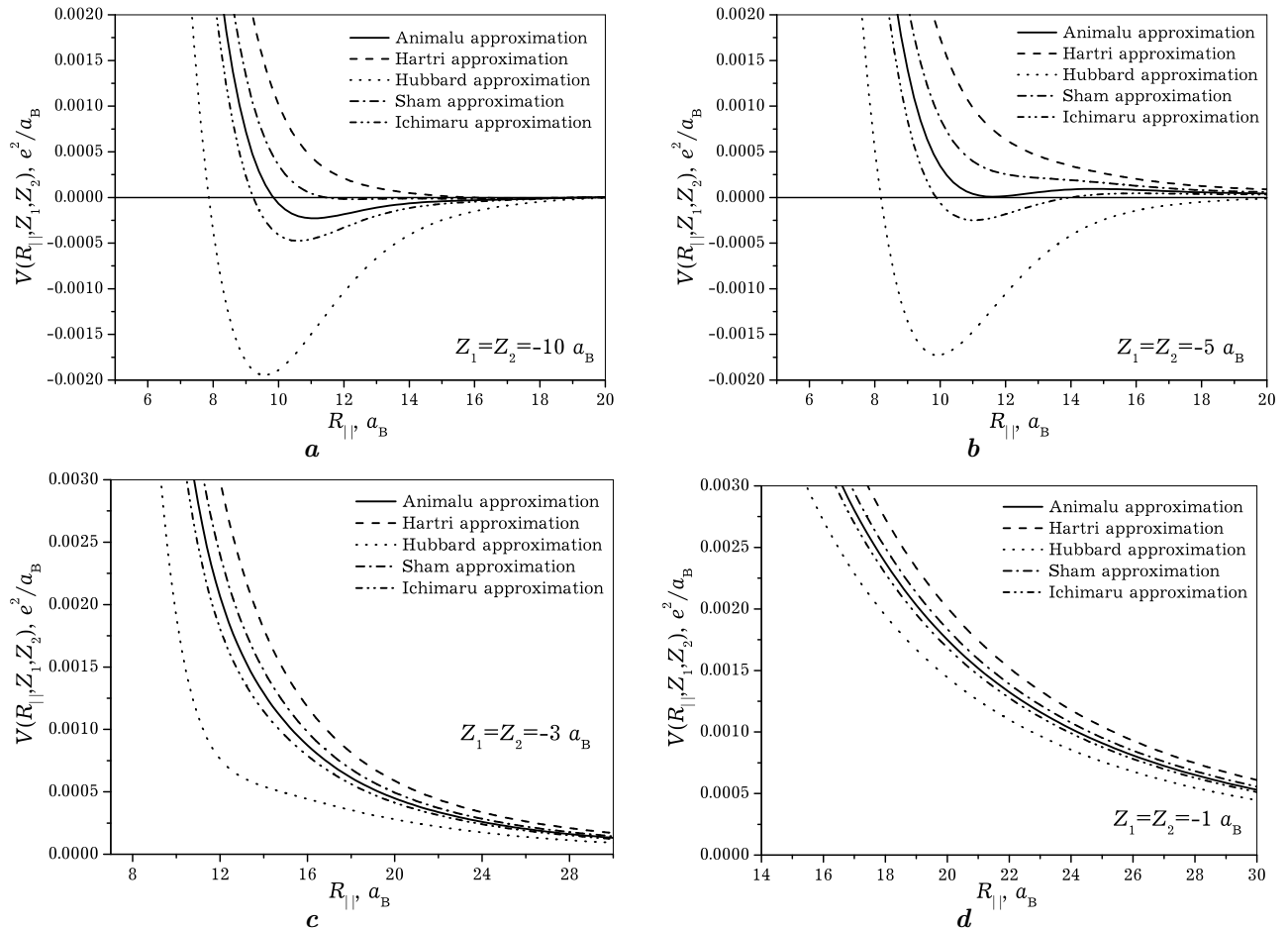
As a model of the local pseudo-potential, we use the pseudo-potential of Krasko and Gurskii (see Refs. [17, 18])

$$w(r) = -\frac{Ze^2}{r} + \frac{Ze^2}{r} \left(1 + a\frac{r}{r_c}\right) \exp\left(-\frac{r}{r_c}\right),$$

where  $a$  and  $r_c$  are parameters of the pseudo-potential. The two-dimensional Fourier image of this pseudo-potential has the form

$$w(q|z) = -\frac{2\pi Ze^2}{q} \exp(-q|z|) + 2\pi Ze^2 \left( \frac{a|z|}{1 + (qr_c)^2} + r_c \frac{1 + a + (qr_c)^2}{(1 + (qr_c)^2)^{3/2}} \right) \exp\left(-\sqrt{1 + (qr_c)^2} \frac{|z|}{r_c}\right). \quad (6)$$

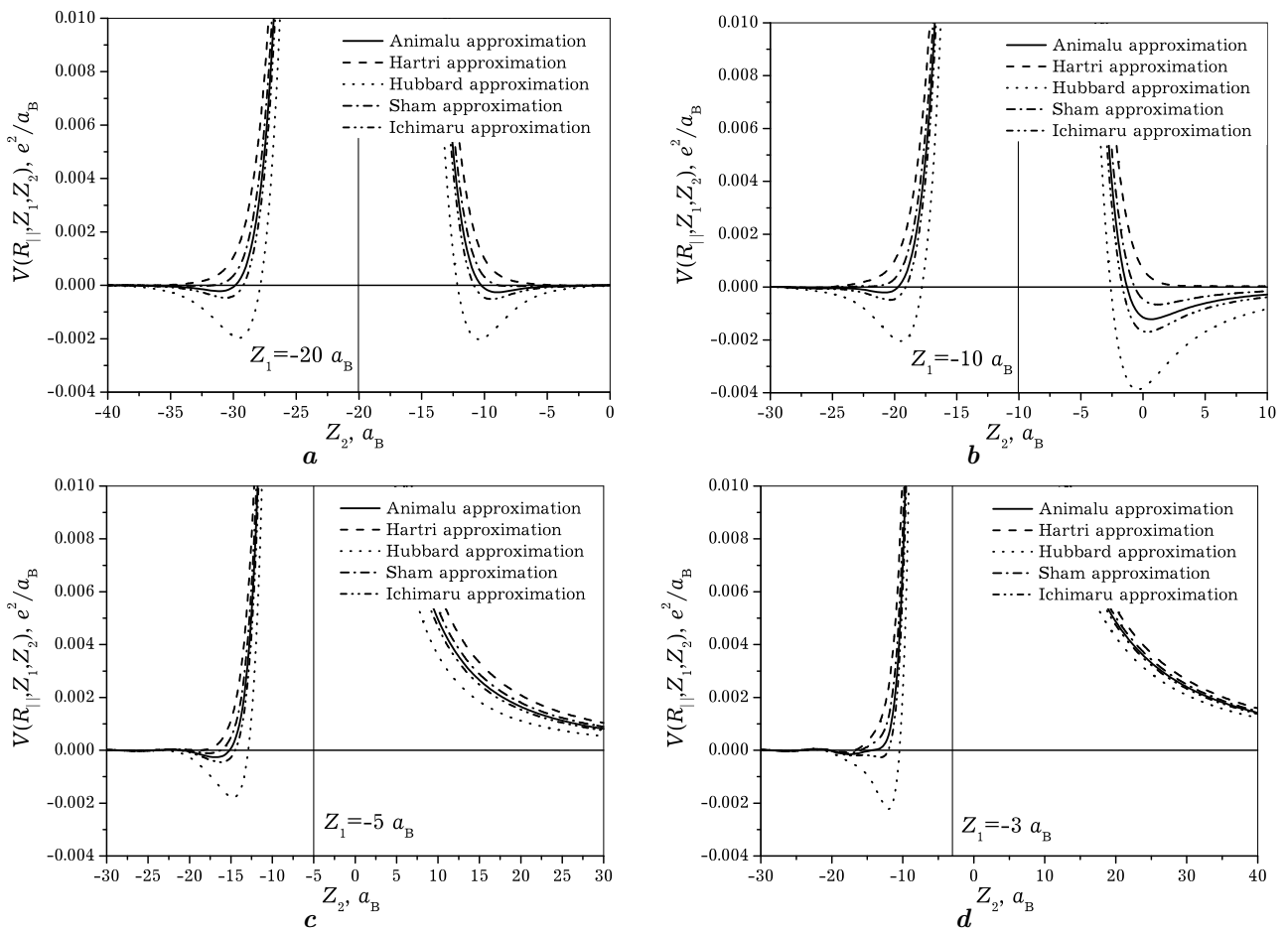
The calculation is performed for potassium (the Wigner-Seitz  $r_s = 4.86$ , the lattice period  $5.225 \text{ \AA}$  or  $9.87a_B$ ) and the following parameters  $r_c = 0.7777a_B$ ,  $a = 2.0333$ . The strength of the external electric field is  $E = 40 \text{ V/nm}$ .



**Fig. 1.** The effective interionic pair potential as a function of the distance between two ions in the division plane at  $E = 40 \text{ V/nm}$ , and the following normal to the division coordinates:  $Z_1 = Z_2 = -10 a_B$  (a);  $Z_1 = Z_2 = -5 a_B$  (b);  $Z_1 = Z_2 = -3 a_B$  (c);  $Z_1 = Z_2 = -1 a_B$  (d).

In Fig. 1, the effective interionic pair potential as a function of the distance between two ions in the division plane is presented for the same normal to the division plane coordinates ( $Z_1 = Z_2$ ). In the

case  $Z_1 = Z_2 = -10 a_B$  (see Fig. 1a), the effective interionic pair potential has the same form as one in unbounded metal, i.e. the division plane and the external electrostatic field do not affect on this potential. Using of the Hartri approximation leads to appearance of the potential well at  $R_{||} \approx 18 a_B$  with very little depth. Taking into account of the local field correction leads to shift to the left and deepening of the potential well, and the position of this potential is approximately at the lattice period for potassium. If two ions approach the division plane, the potential well decreases and shifts to the right (see Fig. 1b). This is a reason of growth of the equilibrium distance between ions in the division plane. This can lead to a restructuring of the lattice near the metal surface. With further approach of two ions to the division plane (see Fig. 1c and Fig. 1d) the potential well disappears, interaction between ions is of repulsive type. Such behavior is physically clear, because effective interionic attraction is due to screening of electrons, which are located around them. Electron density near the division is less than that in the depth of the metal. When two ions approach the division plane, number of electrons around ions becomes less, and the direct repulsion dominates attraction.

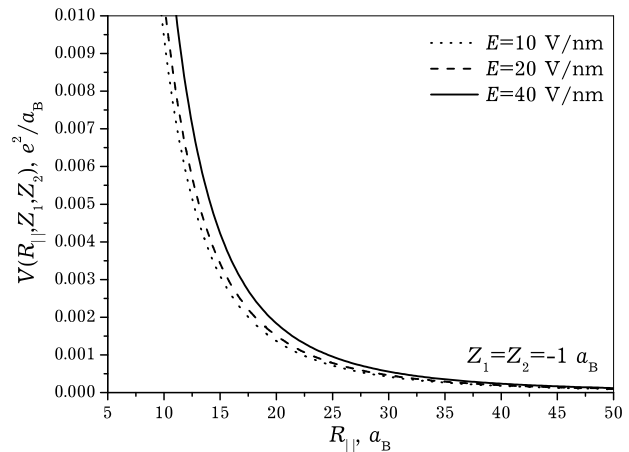


**Fig. 2.** The effective interionic pair potential as a function of the normal to the division plane coordinate of one ion at  $E = 40 \text{ V/nm}$  and the distances between two ions in the division plane is equal to zero, and the following normal to the division plane coordinates:  $Z_1 = -20 a_B$  (a);  $Z_1 = -10 a_B$  (b);  $Z_1 = -5 a_B$  (c);  $Z_1 = -3 a_B$  (d).

In Fig. 2, the effective interionic pair potential as a function of the normal to the division plane coordinate of one ion ( $Z_2$ ) (the distances between two ions in the division plane is equal to zero,  $R_{||} = 0$ ) is presented for different values of the normal to the division plane coordinates of another ion ( $Z_1$ ). In the depth of the metal (see Fig. 2a), the effective interionic pair potential is symmetric, depth of the potential well and its position are the same as in Fig. 1a, i.e. the effective interionic pair potential has a cylindrical symmetry in the depth of the metal. With approximation of ion with coordinate  $Z_2$  to the division plane, symmetry of potential wells is breaking.

At first, the depth of the potential well in the area  $Z_2 > Z_1$  increases (Fig. 2b), and with further approach to the division plane this well disappears (Fig. 2c, d). Such a behavior of the effective interionic potential is caused by the fact that the electron density is an oscillatory function of the normal to the division plane coordinate and it vanishes near the division plane. Due to this, if there are a few electrons near ions, the depth of the potential well decreases, the direct repulsion between ions increases. If there is an excess of electrons near ions, the depth of the potential well increases, the effective attraction increases. Such a behavior of the effective interionic potential causes a shift of ionic surface layers towards the normal to the division plane.

In Fig. 3, the effective interionic pair potential as a function of the distance between two ions in the division plane ( $R_{||}$ ) at  $Z_1 = Z_2 = -1 a_B$  within the Sham approximation is presented for the different strengths of the external electrostatic field. Increasing of the electrostatic field strength leads to the repulsion between ions. This is due to the shift of electrons into the metal, if the external field is applied. As a result, number of electrons near ions decreases, and the direct repulsion between ions increases.



**Fig. 3.** The effective interionic pair potential as a function of the distance between two ions in the division plane at  $Z_1 = Z_2 = -1 a_B$  within the Sham approximation for the different strengths of the external electrostatic field  $E = 10, 20, 40$  V/nm.

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## Ефективна міжйонна взаємодія в напівобмеженому металі за наявності зовнішнього електричного поля з урахуванням поправки на локальне поле

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Досліджено ефективний потенціал міжйонної взаємодії в напівобмеженому металі, який міститься у зовнішньому електростатичному полі. Досліджено вплив на ефективний потенціал міжйонної взаємодії поправки на локальне поле та напруженості прикладеного зовнішнього електростатичного поля.

**Ключові слова:** *ефективний потенціал міжйонної взаємодії, електростатичне поле, псевдопотенціал, напівобмежений метал.*

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