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Analytical model for the Fermi energy and the work function of thin metallic films

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Abstract

An analytical theory of size-dependent energetic characteristics of a metal film is developed in a free-electron model and a finite square potential well. A regular expansion of energetic characteristics in terms of $1/L$ is performed. The errors occurring at each step of the expansion are analyzed. This simple model allows to calculate size oscillations of the Fermi energy and the work function.

Keywords: Work function; Metallic slab; The Fermi energy; Size quantum effects; Aluminum; Sodium

1. Introduction

Different ways of an analytical approach to the problem of the density of states and the Fermi energy in a free electron model for metal films were suggested in [1,2]. Used the Euler–McLaurin summation formula allowed analytical calculations only on an assumption of an infinitely high surface barrier. On such a basis, a possibility of a contact potential difference quantization was pointed to for a metal slab [3] and an explanation of tensile force jumps in a metal contact was given [4] that were observed in experiments [5]. But calculation of the electron work function is out of the limits of this simplest model.

Detailed computations performed to date do not yield an unequivocal conclusion about size dependence of the work function of isolated films and wires and in addition, oscillations that occurred in the work function very large compared with the results of experiments [6].

In this paper, an analytical theory of size-dependent energetic characteristics of a metal slab is developed in the framework of an elementary one-particle concept without using the Euler–McLaurin formula. The simple model allows to calculate exactly size oscillations of the Fermi energy and the work function.

2. Statement of the problem

A thin slab is studied whose thickness L_z is of the order of the Fermi wavelength λ_F^0 and much

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less than the other side dimensions, $L_x \gg L_z$, $L_y \gg L_z$; so the discreteness of the electron momentum $\{p_x, p_y\}$ spectrum does not have any observable consequence. For typical metallic electron densities, λ_F^0 is about 0.5 nm.

The electron potential energy inside the slab (or the *film*) can be assumed, in first approximation, as a rectangle potential box with side lengths L_x, L_y, L_z and of constant depth U_0. Solving the Schrödinger equation for such a potential, one can obtain a set of the electron wavenumbers, $k_{xj} = 2\pi j/L_x$, $k_{ys} = 2\pi s/L_y$, where $j, s = 0, \pm 1, \pm 2, \pm 3$, and k_{zi}, $i = 1, 2, 3$, are roots of equation

$$k_{zi} L_z = -2 \arcsin(k_{zi}/k_0) + \pi i, \tag{1}$$

where $\hbar k_0 = \sqrt{2mU_0}$, m is mass of an electron. The energy eigenvalues of an electron are given by

$$E_{ijs} = \frac{\hbar^2}{2m}(k_{xj}^2 + k_{ys}^2 + k_{zi}^2).$$

It is advantageous to use dimensionless values by introducing U_0 as an energy scale and applying a length scale proportional to k_0^{-1}, such as

$$\xi_i = k_{zi}/k_0, \quad \xi_{xj} = k_{xj}/k_0, \quad \xi_{ys} = k_{ys}/k_0,$$

$$l = k_0 L_z/\pi, \quad l_x = k_0 L_x/2\pi, \quad l_y = k_0 L_y/2\pi.$$

With this scale, energy can be interpreted as square of radius vector of a state in ξ-space, $\xi_{ijs}^2 = \xi_{xj}^2 + \xi_{ys}^2 + \xi_i^2$, where $\xi_{ijs} \leqslant 1$. Eq. (1) adopt the new look

$$l\xi_i = -\frac{2}{\pi} \arcsin \xi_i + i. \tag{2}$$

3. Basic relations

Occupation of states in ξ-space by electrons starts from the point $\{0, 0, \xi_1\}$ and occurs in order of increasing radius vector, i.e., with rising of energy of states. As a result, all occupied states are contained within the space area bounded by the plane $\xi_z = \xi_1$ and by the hemisphere of radius $\xi_F = \sqrt{\varepsilon_F}$, where $\varepsilon_F \equiv E_F/U_0$ is the Fermi energy equal to the maximum energy of occupied states. They are distributed with density $\sigma = 2l_x l_y$ on circles formed by crossing the Fermi hemisphere and planes $\xi_z = \xi_i$, $i = 1, 2, \ldots, i_F$.

The number of occupied states, coinciding with the number of free electrons in the film, is given by

$$N = \sigma \sum_{i=1}^{i_F} S_i = 2l_x l_y \sum_{i=1}^{i_F} \pi(\xi_F^2 - \xi_i^2), \tag{3}$$

where summation is overoccupied circles with areas $S_i = \pi(\xi_F^2 - \xi_i^2)$ and i_F is their number. After simple transformations of Eq. (3), we obtain the formula for the Fermi energy

$$\varepsilon_F = \frac{1}{i_F}\left(\frac{\nu l}{2\pi} + \sum_{i=1}^{i_F} \xi_i^2\right), \tag{4}$$

where $\nu \equiv N/(l_x l_y l)$ is the number of occupied states per unit volume.

Using Eq. (2) we obtain an integer rising function $i_\varepsilon(\varepsilon)$ replacing ξ_i by $\sqrt{\varepsilon}$ and letting ε take any value from 0 to 1

$$i_\varepsilon = \left[l\sqrt{\varepsilon} + \frac{2}{\pi} \arcsin \sqrt{\varepsilon}\right]. \tag{5}$$

Here square brackets indicate an integer part. At the points $\varepsilon = \xi_i^2$, the magnitude of the function increases by 1 but the function is constant in intervals between these points. Substituting $\varepsilon = \varepsilon_F$ into Eq. (5) we find the number of occupied levels in the potential well

$$i_F = \left[l\sqrt{\varepsilon_F} + \frac{2}{\pi} \arcsin \sqrt{\varepsilon_F}\right]. \tag{6}$$

The average electron number density $\bar{n}$ of the sample henceforth is assumed to be independent of dimensions, and

$$\bar{n} = \frac{k_0^3}{4\pi^3} \nu. \tag{7}$$

When the depth of the well is fixed, it means that $\nu = \text{const}$.

Referring to Eq. (2) it can be easily seen that its roots are determined exclusively by the well width l. Therefore dependence on well depth in relations (4) and (6) is reflected only by the ν value. Thus, this one parameter displays both an electron number density and a well depth. Size dependence of the Fermi energy $\varepsilon_F(l)$ may be found by way of cooperative solution of Eqs. (4) and (6) under additional condition $\nu = \text{const}$.

4. The size dependence of the work function

As it has already been mentioned the minimum value of L_z corresponds to the thickness equal to the one atom diameter. To estimate minimum value of l we use $l = L_z\sqrt{2mU_0}/(\pi\hbar)$, where $L_z = 0.5$ nm (it means a single layer of atoms), and

$$U_0 = E_F^0 + W_0, \quad E_F^0 = \frac{\hbar^2}{2m}(3\pi^2\bar{n})^{2/3} \tag{8}$$

with U_0 equal to 3.50 and 15.94 eV for Cs and Al, respectively. W_0 is the work function for a semi-indefinite metal. As a result, we have $1.6 < l_{\min} < 3.5$. We assume henceforth the value $1/l$ to be small and apply an expansion in terms of $1/l$ for calculating the Fermi energy.

We write below α for $1/l$. Dependence $\xi_i(\alpha)$ is defined implicitly by Eq. (2)

$$\frac{\xi_i}{\alpha} = -\frac{2}{\pi}\arcsin \xi_i + i. \tag{9}$$

We determine $\xi_i = \xi_i(\alpha)$ in the form of an expansion in terms of α and obtain

$$\xi_i = i\alpha - \frac{2i}{\pi}\alpha^2 + \frac{4i}{\pi^2}\alpha^3 + O(\alpha^4). \tag{10}$$

As it follows from Eq. (6), $i_F = O(\alpha^{-1})$. The third term on the right-hand side of Eq. (10) does not exceed $4i_F\alpha^3/\pi^2$. The error of the approximate expression (10) is, if anything, by an order of magnitude smaller, i.e., it is of the order more or equal to α^3 for any number i. The error of ξ_i^2 is of the same order. After substituting (10) into Eq. (4) one can find that the error of the sum $\sum_{i=1}^{i_F}\xi_i^2$ has the order of smallness $i_F\alpha^3$, and the error of all the formula (4) for the Fermi energy is of the order of α^3.

Substituting (10) into Eq. (4) and omitting terms of the order more than second we obtain

$$\varepsilon_F = \frac{v}{2\pi}\frac{1}{i_F\alpha} + \left(\frac{i_F^2}{3} + \frac{i_F}{2} + \frac{1}{6}\right)\alpha^2 - \left(\frac{4i_F^2}{3\pi} + \frac{2i_F}{\pi}\right)\alpha^3 + \frac{4i_F^2}{\pi^2}\alpha^4 + O(\alpha^3). \tag{11}$$

All the range of α is broken down into intervals (α_{i+1}, α_i), $i = 2, 3, \ldots$, which corresponds to the number of occupied levels $i_F = i$. Here $\alpha_i \equiv 1/l_i$. Values of α satisfying condition $\alpha > 0.3$ are not physically reasonable (they correspond to values $l < l_{\min}$). Below we determine bounds of the intervals.

Substituting expressions (10) and (11) at $i_F = i$ into equality $\varepsilon_F = \xi_{i+1}^2$ we obtain the equation for α_{i+1}

$$\frac{8i^3}{3\pi}\alpha_{i+1}^4 - \left(\frac{2i^3}{3} + \frac{3i^2}{2}\right)\alpha_{i+1}^3 + \frac{v}{2\pi} = 0. \tag{12}$$

According to Descartes' sign rule, Eq. (12) has two real-valued positive roots. One of them is approximately equal to $\sqrt{\varepsilon_F^0}/i$, and the other is of a higher order of smallness. The left bound of the interval (α_{i+1}, α_i) is determined by the first

$$\alpha_{i+1} = \frac{1}{i}\sqrt{\varepsilon_F^0} + \frac{1}{2i^2}\sqrt{\varepsilon_F^0}\left(\frac{4}{\pi}\sqrt{\varepsilon_F^0} - 1\right). \tag{13}$$

The right bound of the interval can be found by replacing $i \to i+1$ in Eq. (13). This gives

$$\alpha_i = \frac{1}{i}\sqrt{\varepsilon_F^0} + \frac{1}{2i^2}\sqrt{\varepsilon_F^0}\left(\frac{4}{\pi}\sqrt{\varepsilon_F^0} + 1\right). \tag{14}$$

It is seen that the width of the interval reduces with increasing i as $1/i^2$: $\alpha_i - \alpha_{i+1} = \sqrt{\varepsilon_F^0}/i^2$.

The size dependence $\varepsilon_F(l)$ is represented within each interval (l_i, l_{i+1}) by a concave curve. At the bounds of the interval the derivative $d\varepsilon_F/dl$ changes by a jump whose value is equal to $-2\varepsilon_F^{0\,3/2}/i^2$ at $l = l_i$. To the left from this point the function $\varepsilon_F(l)$ rises, and to the right it diminishes. The jump of the derivative is expressed in a figure by cusps, or oscillations, with amplitude that gradually decreases.

To complete our investigation of $\varepsilon_F(l)$ we obtain an asymptotic form of this dependence at $l \to \infty$. For large l Eq. (6) can be rewritten as

$$i_F = \frac{\sqrt{\varepsilon_F^0}}{\alpha} + O(\alpha^0). \tag{15}$$

Substituting (15) into (11) and returning to usual units, we find in the limit of large L_z:

$$E_F = E_F^0 + \frac{\pi\hbar}{2}\sqrt{\frac{E_F^0}{2m}}\left(1 - \frac{8}{3\pi}\sqrt{\frac{E_F^0}{U_0}}\right)\frac{1}{L_z}. \tag{16}$$

The expression in the brackets is positive, i.e., $E_F > E_F^0$.

The size-dependent electron work function is determined by

$$W(L_z) = U_0 - E_F(L_z). \tag{17}$$

That is, W is an energetic distance from the upper occupied level of quasi-continuous spectrum to the vacuum electron level. It can be seen in Eq. (16) that $W < W_0$.

5. Results of calculations

The calculations are carried out for slabs of Al and Na with the electron number density $\bar{n} = 3/4\pi r_s^3$, corresponding to $r_s = 2.07a_0$ and $3.99a_0$, and with the work function $W_0 = 4.25$ and 2.7 eV, respectively.

The results of the calculations of the electron work function for isolated slabs of varied thickness are presented in Fig. 1. Over all the range of thickness, inequality $W < W_0$ is satisfied. The presented dependence $W(L_z)$ is in qualitative agreement with the experiment [6], with results of self-consistent calculations by the Kohn–Sham method for cylindrical nanowires of infinite length [9,11], and for slabs [10], but not with the results of calculations [7,8]. The amplitude of the largest oscillations is about 0.1–0.2 eV, and this is more reasonable than values from the papers mentioned above, because oscillations, observed in experiments, are small.

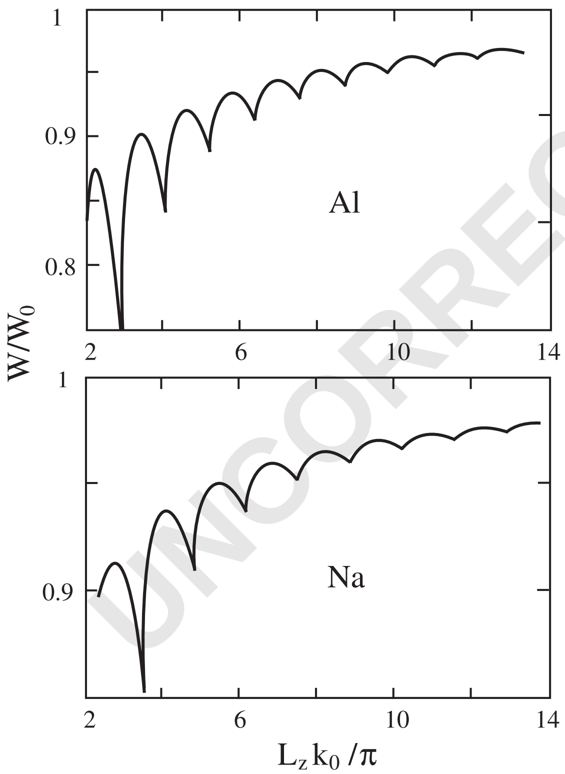

Fig. 1. The size dependence of the work function for metallic slabs.

Comparing size dependencies $W(L_z)$ for Al and Na, it is seen that all the distinctions can be explained by different values of r_s. For Al, the value of oscillations of the work function $1 - W/W_0$ is more, the period of oscillations ΔL is less than for Na, and the position of the cusps is shifted to the left. The approximate relations following from Eqs. (13)–(16), $1 - W/W_0 \sim 1/r_s L$, $\Delta L \sim r_s$, $L_i \sim i r_s$, describe well these features.

Finally, we can note that the choice of the simplified form of the potential well and a non-self-consistent approach are disadvantages of this model. It is not able to describe the surface energy.

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