



Theory of Necessary Energy for Electron to Exit from Conductor

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Abstract

A model of a conductor consisting of a positive charge that uniformly fills a certain volume and is absent outside it, and an electron gas whose total charge is equal to a positive charge are considered. The electron density outside the conductor should tend to zero, while remaining a continuous function of coordinates. It is assumed that the electron density is proportional to some continuous function, which depends on the coordinate perpendicular to the surface of the conductor. This function depends on the parameter, which is determined from the requirement of a minimum of additional energy arising as a result of the exit of a certain number of electrons outside the conductor. The inhomogeneous density of the negative charge does not compensate for the homogeneous density of the positive charge. As a result, an electrostatic potential is created inside the conductor. Above the Fermi level, an exponential potential well is formed. Zero of this potential well is located in the centre of the conductor. Under the boundary condition that the eigenfunctions vanish at the conductor boundary, a discrete energy spectrum is obtained for an electron above the Fermi level. To go beyond the surface of a conductor, an electron from the Fermi level must receive energy no less than the lowest level of the energy spectrum of a potential well. This explains the laws of the photoelectric effect. The problem is considered for a spherical particle and a flat plate. The smoothing parameter and the minimum energy for the electron exit turn out to be different.

Keywords: Electron gas density; spherical particle; plate; exponential potential; eigenvalue problem; Macdonald function; zero level of energetically spectrum; photoelectric effect.

1. Introduction

A model of metal in the Thomas - Fermi theory describes the ion lattice as positive charged homogenous background that has a distinct form with the abrupt boundary. Then the electrostatic energy would be zero if the electron gas uniformly filled the same volume with the abrupt boundary. But the electron gas cannot have the abrupt boundary. To describe a smooth transition, it is usually assumed that where a positive background ends, a certain layer of special electronic states is formed [Ref. 1]. The energy that must be expended to remove an electron from the crystal is calculated. This energy is called the work function. It is believed that this is the work of overcoming a potential barrier that is higher than the Fermi energy. Such a description does not explain the laws of the photoelectric effect.

In the second section of this article, we propose a universal function that describes the charge density distribution of an electron gas near a surface. We use it for a spherical particle in this section. This function assumes that a certain number of electrons goes beyond the positive background and is held by an electrostatic field. The function depends on the parameter of the dimension of length, which characterizes the smoothing of the influence of sharp changes in the density of the positive charge. The value of this parameter is determined by minimizing the additional energy arising from the inhomogeneity of the charge density of the electron gas. It depends only on the average charge density of the electron gas, equal to the density of the positive charge, and coincides with the value of the screening radius obtained in the Thomas-Fermi theory. The resulting density distribution of the electron gas leads to the appearance of an exponential potential, the minimum of which is in the center of the sphere and coincides with the Fermi level.

In the third section of this article, the spectrum of electronic states in this exponential potential well is considered according to the method proposed in [Ref.2]. The energy value for the lowest level is obtained, which also depends only on the average charge density. This value is separated from the Fermi level by the forbidden band, the width of which determines the minimum energy that an electron must receive in order to leave the metal as a result of irradiation.

In the fourth section of this article, the same questions are considered for the plate. The obtained values of the smoothing parameter and the output energy differ from those obtained for the sphere.

2. Distribution of the electron gas charge density in the spherical particle

Consider a spherical metal particle with radius R . This sphere is filled with a uniform background with a charge density $e\sigma_0$, where e is an elementary charge. The total charge of the electron gas is $(-4\pi R^3 e\sigma_0/3)$. Its density should be distributed so that the total energy of the system described by the functional of this density is minimal. In, so doing it is necessary that the function describing this density distribution is differentiable everywhere. We do not know how to include this condition in the definition of the energy functional. Therefore we will minimize it by the direct variational method. From phenomenological considerations, we choose a function that describes the supposed density distribution of the electron gas and depends on some parameter. Then we calculate the energy of the system with such a distribution and find the value of the parameter that gives a minimum of this energy.

Since the system under consideration is spherically symmetric, the density of the electron gas in spherical coordinates should depend only on the radius. In the theory that takes into account quantum effects more precisely, screening leads to Friedel's density oscillations. But they are absent in the Thomas - Fermi theory, and we shall suppose that they are absent in a minimizing function. This function should assume the exit of a certain number of electrons outside the sphere to ensure differentiability on the surface of the sphere. The most pronounced change in density should be near the surface. These properties are possessed by the well-known Fermi - Dirac function, which describes the filling of energy levels by electrons of a degenerate electron gas at finite temperatures. Therefore, suppose that the density of an electron gas in a spherical particle is described by the formula:

$$\sigma_{(-)}(\rho) = \frac{\sigma_0}{1 + \exp\left(\frac{\rho - R}{\Lambda}\right)}. \quad (1)$$

Here Λ is parameter, which must be determined from condition of energy minimum. Since the nonuniform density of the negative charge does not neutralize the positive charge of the continuous background, an electric field is created in the sphere. It is directed along the radius from the center of the sphere. Each spherical layer of radius ρ increases the field strength modulus by $d|\mathbf{E}| = (e/\varepsilon_0)[\sigma_0 - \sigma_{(-)}(\rho)]d\rho$. (ε_0 is the electric constant). The field strength modulus equal to:

$$|\mathbf{E}(\rho)| = \frac{e\sigma_0}{\varepsilon_0} \int_0^\rho \left[1 - \frac{1}{1 + \exp[(\tau - R)/\Lambda]} \right] d\tau = \frac{e\sigma_0\Lambda}{\varepsilon_0} \ln \left[\frac{1 + \exp[(\rho - R)/\Lambda]}{1 + \exp(-R/\Lambda)} \right] \approx \frac{e\sigma_0\Lambda}{\varepsilon_0} \exp[(\rho - R)/\Lambda]. \quad (2)$$

The energy of this field in the particle volume:

$$\varepsilon_{\text{int}} = 2\pi\varepsilon_0 \int_0^R |\mathbf{E}|^2 \rho^2 d\rho = \frac{2\pi\Lambda^2 e^2 \sigma_0^2}{\varepsilon_0} \int_0^R \exp\left(2\frac{\rho - R}{\Lambda}\right) \rho^2 d\rho \approx \frac{\pi\Lambda^3 R^2 e^2 \sigma_0^2}{\varepsilon_0}. \quad (3)$$

This field holds electrons in the particle on the Fermi energy level. Then it is necessary to suppose that Fermi energy is zero potential energy in an electrostatic field. Therefore, the electrostatic potential:

$$\varphi(\rho) = -\int \frac{e\sigma_0\Lambda}{\varepsilon_0} \exp\left(\frac{\rho - R}{\Lambda}\right) d\rho = -\frac{e\sigma_0\Lambda^2}{\varepsilon_0} \left\{ \exp\left(\frac{\rho - R}{\Lambda}\right) - \exp\left(\frac{-R}{\Lambda}\right) \right\}. \quad (4)$$

An inhomogeneous decrease in the electron density leads to a decrease in the kinetic energy of the electron gas. From the Thomas - Fermi theory[Ref.1] it follows that in the case under consideration the kinetic energy of an electron gas is described by the formula:

$$T = \frac{12\pi}{5} \zeta_0 \sigma_0 \int_0^R \left[1 + \exp\left(\frac{\rho - R}{\Lambda}\right) \right]^{-5/3} \rho^2 d\rho, \quad (5)$$

where $\zeta_0 = (\hbar^2/2m)(3\pi^2\sigma_0)^{2/3}$ is the Fermi energy of the electron gas that has density σ_0 . Having calculated this integral approximately up to first-order terms in Λ/R , we get:

$$\Delta T = \frac{12\pi R^3}{5} \zeta_0 \sigma_0 \frac{\Lambda}{R} \left\{ -\ln(2) + \frac{1}{3} \sum_{k=1}^{\infty} \frac{1}{k} \left[\prod_{j=1}^k \frac{1}{j} \left(\frac{1}{3} - j \right) \right] \right\} \approx -0,85 \frac{12\pi}{5} \zeta_0 \sigma_0 \Lambda R^2. \quad (6)$$

The value of the parameter Λ , which leads to the smallest increase in the energy of the system, is determined by the equation:

$$\frac{d}{d\Lambda} \left(\frac{\pi (e\sigma_0)^2 \Lambda^3 R^2}{\varepsilon_0} - 0,85 \frac{12\pi}{5} \zeta_0 \sigma_0 \Lambda R^2 \right) = 0, \quad \Lambda^2 = 0,85 \frac{4 \zeta_0 \varepsilon_0}{5 e^2 \sigma_0} = 0,68 \frac{\zeta_0 \varepsilon_0}{e^2 \sigma_0}. \quad (7)$$

This result agrees well with the known value of the screening radius in the Thomas - Fermi theory $\Lambda^2 = 2\zeta_0 \varepsilon_0 / 3e^2 \sigma_0$.

3. The band gap between the Fermi level and the electron exit energy

In the previous section of this article it was shown that the exit of a certain number of electrons beyond the limits of a homogeneous positively charged background, which is necessary for smoothing the electron density distribution function, leads to the appearance of an exponential potential well, whose zero coincides with the Fermi level. At the particle boundary $\rho = R$, an increase in the electric field is replaced by a decrease, i.e., the potential well is limited by a barrier. Equality to zero on the surface of the sphere is the boundary condition for the wave functions of electrons inside the sphere. If the electron energy is higher than the top of the potential barrier, then this boundary value provides freedom for the electron to leave the sphere and pass into a state of a continuous spectrum with the corresponding energy. It is known that the smallest energy that an electron can have in a potential well (zero level) is separated from its bottom by a band gap. We shall show that in the exponential potential well the zero level is always above the top of the potential barrier.

We consider the eigenvalue problem for an electron in a spherical particle with potential energy $\{-e\varphi(\rho)\}$, where the potential is described by the formula (4). It was shown in formula (7) that parameter Λ coincides with the screening radius that obtained in the Thomas - Fermi theory. Then the potential energy is $G \exp[-(\rho - R)/\Lambda]$ where $G = 2\zeta_0/3$. We consider the angular momentum equal to zero. Then the radial equation has the form:

$$\left(\frac{d^2}{d\rho^2} + \frac{2}{\rho} \frac{d}{d\rho} \right) \psi_0(\rho) + \left\{ \tilde{E} - \tilde{G} \left[\exp\left(\frac{\rho - R}{\Lambda}\right) - \exp\left(\frac{-R}{\Lambda}\right) \right] \right\} \psi_0(\rho) = 0. \quad (8)$$

Here E is eigenvalue of energy, $\tilde{E} = (2m/\hbar^2)E$, $\tilde{G} = (2m/\hbar^2)G$. A small correction to the eigenvalue proportional to $\exp(-R/\Lambda)$ will be neglected in the future. The wave function $\psi_0(\rho)$ does not represent the true electron wave functions, but the eigenvalues E in the potential well describe the energy spectrum above the Fermi level. To calculate the energy spectrum, equation (8) must be supplemented with a boundary condition $\psi_0(R) = 0$. A solution to this problem was found in [Ref. 2]. We introduce a change of the variable:

$$\tau = \exp[(\rho - R)/2\Lambda]; \quad \tau \geq \exp(-R/2\Lambda); \quad \rho = 2\Lambda \ln(\tau) + R.$$

$$\left\{ \frac{\tau^2}{(2\Lambda)^2} \frac{d^2}{d\tau^2} + \left[\frac{\tau}{(2\Lambda)^2} + \frac{\tau}{2\Lambda^2 \ln(\tau) + \Lambda R} \right] \frac{d}{d\tau} + \tilde{E} - \tilde{G}\tau^2 \right\} \psi(\tau) = 0 \quad (9)$$

In this equation $2\Lambda^2 \ln(\tau) + \Lambda R > (2\Lambda)^2$ if $\rho > 2\Lambda$. Therefore, the second term in the square bracket can be neglected. We shall divide the resulting equation by $(\tau/2\Lambda)^2$ and get:

$$\left\{ \frac{d^2}{d\tau^2} + \frac{1}{\tau} \frac{d}{d\tau} + \frac{4\Lambda^2 \tilde{E}}{\tau^2} - 4\Lambda^2 \tilde{G} \right\} \psi_0(\tau) = 0, \quad \tau(\rho = R) = 1, \quad \psi_0(1) = 0. \quad (10)$$

The solution of this equation is the Macdonald function $K_{iv}(z)$ with imaginary index (see [Ref. 2]):

$$\psi_0(\tau) = K_{iv}(2\Lambda\sqrt{\tilde{G}\tau}), \quad v = 2\Lambda\sqrt{\tilde{E}}, \quad \psi(\tau = 1) = K_{iv}(2\Lambda\sqrt{\tilde{G}}) = 0. \quad (11)$$

If we consider the Macdonald function dependence on the modulus of the index v for a fixed value of the argument $z_0 = 2\Lambda\sqrt{\tilde{G}\tau}$ when $\tau = 1$, then it has an infinite sequence of zeros v_n and all of them are greater than the value of the argument [Ref. 3]. This means that the spectrum of eigenvalues of the single-particle problem in an exponential well in a bounded spherical region is discrete and begins above the boundary value of the potential energy. Consequently, an electron can go into a potential well only by receiving energy $\tilde{E} \geq \tilde{E}_0 > \tilde{G}$. In [Ref. 2] an equation was derived that relates the value of the index that has number n in a sequence in ascending order with a fixed value of the argument z_0 of the Macdonald function.

$$-\sqrt{\mathcal{G}_n^2 - 1} + \mathcal{G}_n \ln[\mathcal{G}_n + \sqrt{\mathcal{G}_n^2 - 1}] = \frac{\pi}{z_0} \left(n + \frac{1}{2} \right), \quad \mathcal{G}_n = \frac{v_n}{z_0} > 1. \quad (12)$$

For our task this equation has the view:

$$-\sqrt{\tilde{E}_0 - \tilde{G}} + \sqrt{\tilde{E}_0} \ln \left(\frac{\sqrt{\tilde{E}_0} + \sqrt{\tilde{E}_0 - \tilde{G}}}{\sqrt{\tilde{G}}} \right) = \frac{\pi}{4\Lambda}. \quad (13)$$

The values of Λ and \tilde{G} depend only on the charge density of a uniform background $e\sigma_0$. Suppose that there are eight electrons per unit cell of a crystal. The volume of a cubic cell is set equal $47 \cdot 10^{-30} \text{ m}^3$. Then the average density of the electron gas is $\sigma_0 = 0,17 \cdot 10^{30} \text{ m}^{-3}$. (We neglected the small change in the number of electrons in the crystal as a result of smoothing). Substituting this value in the formulas obtained above, we obtain:

$$\zeta_0 = \frac{\hbar^2}{2m} (3\pi^2 \sigma_0)^{2/3}, \quad \Lambda^2 = \frac{2\zeta_0 \varepsilon_0}{3e^2 \sigma_0} = 2,5 \cdot 10^{-21} \text{ m}^2, \quad \tilde{G} = \frac{4m\zeta_0}{3\hbar^2} = 2 \cdot 10^{20} \text{ m}^{-2}. \quad (14)$$

Using these values of the screening radius and the barrier height, one can solve equation (13) numerically. We obtain:

$$\tilde{E}_0 = 4,67 \cdot \tilde{G}, \quad E_0 = 3,11\zeta_0. \quad (15)$$

The height of the barrier G is due to the fact that at $\rho = R$ the electrostatic potential has a kink and begins to decrease rapidly. But the barrier don't determinate boundary condition (11). An electron located at the Fermi level, can go into the well only by receiving the energy of the lowest level of the well. The wave function of an electron at the zero level should have a zero value when $\rho = R$ and pass into the spherical wave function of a free particle.

This function is proportional to $\sin(kR)/R$ where $k = \sqrt{\tilde{E}_0 + (3\pi^2\sigma_0)^{2/3}}$. That is a simplified boundary condition for our model. In fact, outside the sphere, but near its surface, the potential is not constant and is described by the theories from [Ref.1]. The proposed model qualitatively explains the laws of the photoelectric effect.

We consider the possibility of the existence of states with nonzero angular momentum in a potential well. We transform the radial wave equation, replacing $\psi_l = \chi_l/\rho$, and we obtain the equation:

$$\frac{d^2}{d\rho^2} \chi_l(\rho) + \left\{ \tilde{E} - \left[\frac{l(l+1)}{\rho^2} + \tilde{G} \exp\left(\frac{\rho-R}{\Lambda}\right) \right] \right\} \chi_l(\rho) = 0, \quad \chi_l(0) = 0. \quad (16)$$

This is the one-dimensional wave equation for a particle in a bounded $\rho \leq R$ region in a potential consisting of two terms. If this potential has a sufficiently deep minimum in this region, then a bound state can exist. This minimum is determined by the equation:

$$-2 \frac{l(l+1)}{\rho^3} + \frac{G}{\Lambda} \exp\left(\frac{\rho-R}{\Lambda}\right) = 0; \quad \rho = R + \Lambda \ln \left[2 \frac{\Lambda}{G \rho^3} l(l+1) \right]. \quad (17)$$

We substitute the values of Λ and G from the formula (14) and set $l=1$. Get the equation: $\rho_1 = R - (15 \cdot 10^{-11}) \ln(\rho_1 \cdot 10^{10})$. Let's change the unknown $\rho_1 = R(1-x)$, $x < 1$. Then using the approximation $\ln(1-x) \approx -x$, we get: $x = 15 \cdot 10^{-11} \ln(R \cdot 10^{10}) / (R + 15 \cdot 10^{-11})$. Obviously, this correction is less than the accuracy of the calculations and $\rho = R$ if R has some macroscopic size, for example $R = 10^{-2}$ m. This means that in a macroscopic spherical particle there are no states with a nonzero angular momentum and energy above the Fermi level. But if $R = 6$ nm, $x = 0,1$ and then $\rho_1 = 5,4$ nm, and for nanoparticle the photoelectric effect appears at a lower energy of quanta.

4. Surface smoothing and electron exit threshold in a thin flat plate

Let's consider a thin flat plate with area L^2 and thickness $2D \ll L$. The coordinate origin is the center of the plate. The coordinate axis Z is perpendicular to the plate plane. Then we assume that the density of the electron gas has the form $\sigma_{(-)}(z) = \sigma_0 \{1 + \exp[(|z|-D)/\Lambda]\}^{-1}$ where Λ there is a parameter that must be determined in the same way as in Section 2. The plate is mirror symmetric with respect to the XY coordinate plane. Therefore, symmetrically located charged planes do not create an electric field in the space between them, but create a doubled field directed outward. We can consider the dependence on the module $|z|$. Then $d|\mathbf{E}| = 2(e/\epsilon_0)[\sigma_0 - \sigma_{(-)}(|z|)]d|z|$ and the modulus of the field strength is equal to:

$$|\mathbf{E}(|z|)| = \frac{2e\sigma_0}{\epsilon_0} \int_0^{|z|} \left[1 - \frac{1}{1 + \exp[(\tau-D)/\Lambda]} \right] d\tau \approx \frac{2e\sigma_0\Lambda}{\epsilon_0} \exp[(|z|-D)/\Lambda]. \quad (18)$$

The energy of the electric field that is created by the inhomogeneity of the electron density is:

$$\bar{\epsilon}_{int} = L^2 \epsilon_0 \int_0^D |\mathbf{E}|^2 dz = \frac{4\Lambda^2 L^2 e^2 \sigma_0^2}{\epsilon_0} \int_0^D \exp\left(2 \frac{z-D}{\Lambda}\right) dz = \frac{2\Lambda^3 L^2 e^2 \sigma_0^2}{\epsilon_0}. \quad (19)$$

From the Thomas - Fermi theory [Ref.1] the kinetic energy of an electron gas is described by the formula:

$$T = \frac{6L^2}{5} \zeta_0 \sigma_0 \int_0^D \left[1 + \exp\left(\frac{z-D}{\Lambda}\right) \right]^{-5/3} dz = \frac{6L^2 D}{5} \zeta_0 \sigma_0 - 1,26 L^2 \zeta_0 \sigma_0 \Lambda. \quad (20)$$

The increase in energy due to inhomogeneity of electron density is $\varepsilon_0^{-1} (2\Lambda^3 L^2 e^2 \sigma_0^2 - 1, 26 L^2 \zeta_0 \sigma_0 \varepsilon_0 \Lambda)$. It will be minimal, if $\Lambda^2 = 0, 21 (\zeta_0 \varepsilon_0 / e^2 \sigma_0)$. The smoothing parameter for a flat surface is appreciably smaller than for a spherical one.

The electrostatic potential in this case is:

$$\varphi(|z|) = -2 \int \frac{e \sigma_0 \Lambda}{\varepsilon_0} \exp\left\{\frac{|z|-D}{\Lambda}\right\} dz = -2 \frac{e \sigma_0 \Lambda^2}{\varepsilon_0} \left\{ \exp\left\{\frac{|z|-D}{\Lambda}\right\} - \exp\left\{\frac{-D}{\Lambda}\right\} \right\} = -0, 42 \frac{\zeta_0}{e} \left\{ \exp\left\{\frac{|z|-D}{\Lambda}\right\} - \exp\left\{\frac{-D}{\Lambda}\right\} \right\}. \quad (21)$$

The smoothing of the discontinuity in the density of the positive charge on the plate surface leads to the appearance of a mirror-symmetric exponential potential well for an electron $G \{ \exp[(|z|-D)/\Lambda] - \exp(-D/\Lambda) \}$, $G = 0, 42 \zeta_0$, the zero of which coincides with the Fermi level. The one-dimensional wave equation for an electron in this potential well has the view:

$$\frac{d^2 \psi}{dz^2} + \left[\tilde{E} + \tilde{G} \exp\left\{\frac{-D}{\Lambda}\right\} - \tilde{G} \left\{ \exp\left\{\frac{|z|-D}{\Lambda}\right\} \right\} \right] \psi(|z|) = 0, \quad \psi(|z|=D) = 0, \quad \tilde{E} = (2m/\hbar^2) E, \quad \tilde{G} = (2m/\hbar^2) G. \quad (22)$$

A small correction to the eigenvalue proportional to $\exp(-D/\Lambda)$ will be neglected in the future. We introduce the change of variable similarly to equality (9): $\tau = \exp[(|z|-D)/2\Lambda]$; $\tau \geq \exp(-D/2\Lambda)$; $|z| = 2\Lambda \ln(\tau) + D$, and divide the equation by $(\tau/2\Lambda)^2$. We shall obtain:

$$\frac{d^2 \psi}{d\tau^2} + \frac{1}{\tau} \frac{d\psi}{d\tau} + \left[\frac{4\Lambda^2 \tilde{E}}{\tau^2} - 4\Lambda^2 \tilde{G} \right] \psi(\tau) = 0, \quad \psi(\tau=1) = 0. \quad (23)$$

This equation is equivalent to equation (10), and differs only by the values of numerical coefficients in the parameters Λ^2 and \tilde{G} .

$$\Lambda^2 = 0, 21 (\zeta_0 \varepsilon_0 / e^2 \sigma_0) = 0, 79 \cdot 10^{-21} \text{ m}^2, \quad \tilde{G} = 0, 42 \cdot \frac{2m \zeta_0}{\hbar^2} = 1, 26 \cdot 10^{20} \text{ m}^{-2}, \quad E_0 = 3, 86 \zeta_0. \quad (24)$$

Therefore, the energy that must be given to the electron to exit the metal depends on the shape of the sample.

5. Conclusion

The electron density outside the conductor should tend to zero, while remaining a continuous function of coordinates. For this, it is necessary that a certain number of electrons go beyond the limits of the conductor. This phenomenon is called surface smoothing. To describe this smoothing, we assume that the electron density is proportional to the function by Fermi - Dirac, which depends on the coordinate perpendicular to the surface of the conductor. This function depends on the parameter, which is determined from the requirement of a minimum of additional energy arising as a result of smoothing. The inhomogeneous density of the negative charge does not compensate for the homogeneous density of the positive charge. As a result, an electrostatic potential is created inside the conductor. An exponential potential well is formed above the Fermi level. The zero of this potential well is in the center of the conductor. The energy spectrum in this potential well is discrete, and all eigenvalues are higher than the potential energy value on the conductor surface. To go beyond the surface of a conductor, an electron from the Fermi level must have received energy no less than the lowest level of the energy spectrum of a potential well. This explains the laws of the photoelectric effect. The problem is considered for a spherical particle and a flat plate. The smoothing parameter and the minimum energy for the electron exit turn out to be different.

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