

Application of quasiparticles theory and Fourier analysis in photoelectric effect

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The interaction of electromagnetic waves with metal surface is analyzed in terms of electron waves and quasiparticles theory. Then a general relation between frequency and wavelength for excitations in condensed systems is obtained. It is shown how the work function for any metal depends on electron density and Fourier transform of potential due to a single electron. The effect of different factors on change of the work function value is considered.

Keywords: work function, quasiparticles, photoelectric effect.

1. Introduction

The existing theory of photoeffect is in principle phenomenological. The discrete nature is expressed in the postulate that the knocking out of one electron from metal surface requires one quantum of light. Both an electron and a photon are regarded as certain localized objects travelling in electron and electromagnetic radiation flux, respectively. In the photoelectric effect one particle (photon) is absorbed whereas another (electron) is emitted from the metal surface. However, in the modern theory of quantized electromagnetic and electron fields one cannot meet even a hint of the concepts of localized photon or electron. In consequence, any approach in quantum-mechanical terms suffers from some inconsistency. The essential inconsistency of the theory lies in the final description of the process, namely the evolution of electron is considered classically and electron is regarded as a particle and not a wave. This lack of consistency seems to be a fundamental feature of any quantum-mechanical measurements. A microscopic object is always observed by means of macroscopic detectors, which have all properties of classical objects. It is therefore very important to draw a boundary between the observed particle and the instrument.

In spite of that the situation in the theory of photoeffect seems to be fully satisfactory. Experiments are carried out, they are analyzed theoretically and there are no significant contradictions between theory and experiment. For example, in photoemission spectroscopy, the sample is illuminated by monochromatic light and

by measuring the energy distribution of the ejected electrons one can reconstruct the density of states. By means of two-photon photoemission one can examine both occupied and especially unoccupied surface states. If we take photon energy just below the work function we can populate the unoccupied states without having direct photoemission (pump pulse). Now the probing photon can eject the electron from the metal surface. To enhance the effect a small bias is applied between the sample and the analyzer. Experimental studies have shown that the electron emission rate can be significantly enhanced by the excitation of collective electron modes—surface plasmons [1]. Here the energy of light pulses is stored up by the surface plasmons, creating a hot electron population that has not enough time to transfer its energy to the crystal lattice but can contribute to enhance the photoemission effect. Absorbing the required number of photons to overcome the work function, the freed photoelectron is moving in vacuum in the presence of the field due to the surface plasmons. Its energy thus consists of both kinetic energy given by the Einstein multiphoton equation ($E_k = Nh\nu - W$), and energy in the external oscillating field of the surface plasmons.

In 1981, a remarkable new kind of microscope, called the scanning tunnelling microscope (STM), was invented by Binnig and Rohrer, two IBM researchers who in 1984 received the Nobel Prize. One of the key-points essential for understanding the operation of STM is the concept of work function. The work function is considered there in terms of binding energy of conduction electrons in metal. Although the conduction electrons can move about freely within the metal, actually to remove any electron from the metal surface requires some energy the exact value of which depends on the metal. The potential $V(x)$ seen by the free electrons may be approximated as a simple square well of finite depth. The quantum states of this well are filled with electrons (in accordance with Pauli principle) up to maximum filled energy level, called the Fermi level E_F , which is a work function W , below the vacuum level, see Fig. 1.

When two metal surfaces are brought near each other, some distance z apart, and a bias voltage V is applied the energy level diagram is as shown in Fig. 2. Because of the voltage difference between the two metals, the Fermi level of one of them is raised

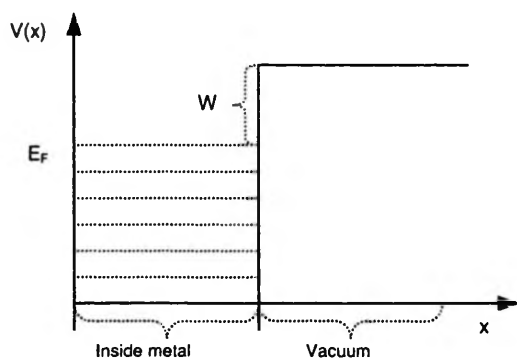


Fig. 1. Energy level diagram for electrons in a metal.

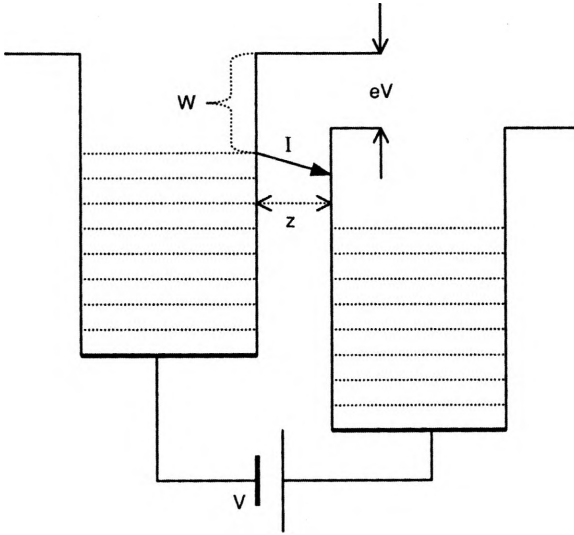


Fig. 2. Electron tunnelling between two metals.

by an energy eV with respect to the Fermi level of the other. Hence electrons near the Fermi level in the first metal are now at the same energy as unoccupied states in the second one, and in consequence they can tunnel through the potential barrier between the metals, if the barrier thickness is sufficiently small. In STM a sharp metal needle, called the tip, is brought very close to the sample and a voltage difference V is applied between them. When the tip is within about one nanometer of the surface sample electrons begin to tunnel between the tip and sample producing a tunnelling current I .

In the limit of small bias voltage and low temperature the tunnelling current is as follows:

$$I = \frac{2\pi}{\hbar} e^2 V \sum |M_{st}|^2 \delta(E_s - E_F) \delta(E_t - E_F) \tag{1}$$

where M_{st} means the tunnelling matrix element between the wave function on the tip Ψ_t and sample Ψ_s and E_F is the Fermi energy. As shown by BARDEEN [2], the tunnelling matrix element can be written as:

$$M_{st} = \frac{\hbar^2}{2m} \int (\Psi_t^* \nabla \Psi_s - \Psi_s^* \nabla \Psi_t) dS \tag{2}$$

where the integral corresponds to a surface within the barrier region between the sample and the tip. Assuming that the tip forms a locally spherical potential well with only s wave function, TERSOFF and HAMANN [3] showed that tunnelling current can be expressed in the form

$$I \propto \sum_s |\Psi_t(\mathbf{r}_0)|^2 \delta(E_s - E_F). \tag{3}$$

By definition, the summation is the local density of sample electronic states $n(\mathbf{r}_0, E)$, at the center of curvature of the tip

$$n(\mathbf{r}_0, E) = \sum_s |\Psi_s(\mathbf{r}_0)|^2 \delta(E_s - E_F). \quad (4)$$

The tunnel current is a function of the tip-sample distance z

$$I(\mathbf{r}_{\parallel}, z) \propto \exp\left(-\frac{2z}{\lambda}\right), \quad (5)$$

here subscript \parallel denotes components parallel to the surface and λ means so-called tunnelling depth. In constant current mode, the current must fulfil equation

$$dI(\mathbf{r}_{\parallel}, z) = \frac{\partial I}{\partial z} dz + \nabla_{\parallel} I d\mathbf{r}_{\parallel} = 0, \quad (6)$$

which can be solved for dz giving the corrugation of the tip. In practice, this mode is realized by keeping the current fixed and by varying the tip-sample distance accordingly. In these STM images with atomic resolution, single adatoms on a surface and single defects can be observed. However, the interpretation of atomically resolved STM images is sometimes very difficult. On the other hand, one can change the applied bias voltage and measure the alteration of the tunnelling current, which allows a local investigation of the electronic structure.

Nowadays, in order to calculate the properties of the metal surface one must in principle solve the Dirac equation for an enormous number of interacting particles. Because it is not possible to solve the equation analytically for any nontrivial system one has to find numerical schemes. Nevertheless, even in this case using the modern numerical techniques hardly leads to fully satisfactory results. Therefore one must find some methods that can simplify the mathematical model of analyzed system. One of the best simplifications used so often in metal physics is the Born–Oppenheimer approximation where one assumes fixed position of ions and in results neglects any quantum effect, which may arise from the dynamics of ions, for example electron–phonon interaction. At present, the probably most successful and most commonly used technique to solve the above mentioned problems is based on the density-functional theory of HOHENBERG and KOHN [4]. According to this theory all ground-state properties of metal are functionals of the ground-state density $n(\mathbf{r})$. Hence the ground-state total energy functional is minimal in the case of correct chosen ground-state density with respect to all densities. But now the new question arises, namely how one can find this total energy functional and how to choose the correct ground-state density. This problem has been solved partially by KOHN and SHAM [5], who assumed that this density can be presented in terms of one particle eigenfunctions of electron system placed in external potential. In such a case the energy functional $E[n]$ can be introduced as follows:

$$E[n] = T[n] + E_{\text{ext}}[n] + E_{\text{H}}[n] + E_{\text{exc}}[n] \quad (7)$$

where $T[n]$ means the kinetic energy of a non-interacting electron gas of density n , $E_{\text{ext}}[n]$ denotes the interaction with the external potential, $E_{\text{H}}[n]$ describes the classical Coulomb interaction often called the Hartree contribution, and $E_{\text{exc}}[n]$ contains exchange-correlation energy. Knowing ever of the component introduced above one can obtain the Kohn–Sham equation that has the form of a Schrödinger equation with an effective potential for some non-interacting particles. Because the exchange-correlation potential V_{exc} is connected with the exchange-correlation energy by a functional derivative

$$V_{\text{exc}}(\mathbf{r}) = \frac{\partial E_{\text{exc}}[n]}{\partial n(\mathbf{r})}. \quad (8)$$

The Kohn–Sham equation can be solved self-consistently by special iteration process [6]. Here we should point out that although the theory contains some approximations, still to obtain the electron density one must know the exchange-correlation energy. Many ways of approximating this energy have been explored [7]. Most often used is the local density approximation, and its spin dependent improvement the local spin density approximation. Lately very promising seem to be generalized gradient approximation and the random phase approximation both based on the quantum Monte Carlo simulation. All those methods and approximations show importance of problems where any attempt leading to deeper understanding should be met with approbation.

2. Excitations into a set of interacting electrons

During investigation of electron dynamics into a solid state a correctly chosen potential is a matter of great importance. At first we consider an arrangement of interacting electrons filling the whole space. The potential due to a simple electron, placed in the coordinate origin, at an arbitrary point equals $V(\mathbf{r})$. On the other hand, the potential at the same point but created by electron placed at point \mathbf{r}_i will equal respectively: $V(\mathbf{r}_i - \mathbf{r}) = V(\mathbf{r} - \mathbf{r}_i)$. Hence the total potential created by set of electrons at a given point must be exactly

$$V(\mathbf{r}) = \sum_i V(\mathbf{r} - \mathbf{r}_i). \quad (9)$$

According to Schrödinger theory the action of potential operators on wave functions resolves itself into ordinary multiplication. Thus, in this case we can write

$$\hat{V}(\mathbf{r})\Psi(\mathbf{r}) = \sum_i V(\mathbf{r} - \mathbf{r}_i)\Psi(\mathbf{r}). \quad (10)$$

However, we should realize that the electron interaction finally makes any movement of single electron impossible. Into the set of interacting electrons any movement can occur in a collective way only. So, electrons being structural units of arrangement cease to be structural dynamic units [8]. Therefore we should take into account not the wave function of a given electron but the wave function of quasiparticle [9], defined as superposition of the wave functions of all interacting electrons. Thus we can introduce a new potential operator that acts on quasiparticle wave function as follows [10]:

$$\hat{V}(\mathbf{r})\Psi(\mathbf{r}) = \sum_i V(\mathbf{r} - \mathbf{r}_i)\Psi(\mathbf{r}_i). \quad (11)$$

The addition operator on the right-hand side in the last equation seems to be very complicated but if we assume that the electron density equals n , and the volume of the cell unit in the real space corresponding to a single electron is $\Delta\mathbf{r}_i$, respectively, we can rewrite the above equation in the form

$$\hat{V}(\mathbf{r})\Psi(\mathbf{r}) = n \sum_i V(\mathbf{r} - \mathbf{r}_i)\Psi(\mathbf{r}_i)\Delta\mathbf{r}_i. \quad (12)$$

Assuming now a high electron density (that is always correct in metal, where electron gas is denser than air by more than 10^4) we obtain $\Delta\mathbf{r}_i \rightarrow 0$, and as a result we can replace the addition operation with integral, which yields

$$\hat{V}(\mathbf{r})\Psi(\mathbf{r}) = n \int V(\mathbf{r} - \mathbf{r}')\Psi(\mathbf{r}')d\mathbf{r}'. \quad (13)$$

The last relation shows that the action of the total potential operator on the quasiparticle wave function resolves itself into convolution of this function with potential created by a single electron, multiplying by electron density into given metal. In consequence, the Schrödinger equation takes the form

$$-\frac{\hbar^2}{2m}\nabla^2\Psi(\mathbf{r}, t) + n \int V(\mathbf{r} - \mathbf{r}')\Psi(\mathbf{r}')d\mathbf{r}' = i\hbar \frac{\partial}{\partial t}\Psi(\mathbf{r}, t). \quad (14)$$

Introducing now the Fourier transform of the wave function $\tilde{\Psi}(\mathbf{k}, \omega)$ and potential $\tilde{V}(\mathbf{k})$ we can pass directly to the domain of transforms, where the last equation takes the form

$$\hbar\omega = \frac{\hbar^2 k^2}{2m} + n\tilde{V}(\mathbf{k}). \quad (15)$$

Hence we can interpret the last equation as a general disperse relation for excitations into a condensed system or as a relation describing the total quasiparticle energy. The

second element on the right-hand side must correspond to the potential energy of quasiparticle. The form of potential qualifies univocally the dependence of energy on the wave vector and allows introducing a strictly physical interpretation to the Fermi sphere radius k_F [10]. At first sight it seems strange that the quasiparticle wave function does not appear in the last relation. But on the other hand, it is obvious that according to Heisenberg uncertainty principle the lack of the wave function is caused by the fact that directly from this relation we are able to calculate precisely a momentum of quasiparticle, then we must lose any information related to its spatial coordinates and contained in wave function.

Futhermore for the sake of symmetry, one can treat this relation as an equivalent of Einstein–Millikan equation where the last element (for $k = k_F$) corresponds to the work function.

In the simplest case taking into account the interaction of electrons only, the Fourier transform of potential due to a single electron equals

$$\tilde{V}(\mathbf{k}) = \frac{4\pi e^2}{k^2}. \quad (16)$$

Thus the work function takes the form

$$W = \frac{4\pi n e^2}{k_F^2}. \quad (17)$$

Of course, the above relation should be treated as the first approximation only. However, in the case of metals for which the experimental values of work function are available one can make comparison and find that the difference ranges from 2.06% (Ca) to 67.3% (Be). The average deviation for all metals mentioned above is less than 20%. By comparison with results obtained by VASILEV, *et al.* [11] where the average deviation exceeds 33% (from 1.7% (Sr) to 120% (Be)) the approximation presented seems to be satisfactory enough.

In the next step, we can take into consideration the effect of crystal lattice by using the screening potential

$$V(\mathbf{r}) = \frac{e^2}{r} \exp(-k_0 r) \quad (18)$$

where the screening effect is connected now with the crystal ions lattice effect and k_0 means the Fermi–Thomas screening parameter, for which it is easy to find the Fourier transform

$$\tilde{V}(\mathbf{k}) = \frac{4\pi e^2}{k^2 + k_0^2}. \quad (19)$$

Hence, taking into account the above we can write the work function in the form

$$W = \frac{4\pi n e^2}{k_F^2 + k_0^2}. \quad (20)$$

It follows from this approximation that the work function is equal to the Fermi energy measured from the zero level, which is the value of this energy far from the given metal [12].

The relation between the work function and electron density is not so simple as one could think looking at the last equation. We should keep in mind that both the Fermi sphere radius and the screening parameter are dependent on electron density, so the relation must be more complex. The value of Fermi–Thomas screening parameter is well known and for given a metal

$$k_0 = \frac{2e}{\hbar} \sqrt{\frac{mk_F}{\pi}} \quad (21)$$

and the Fermi sphere radius [10] is given by

$$k_F = \left(\frac{8\pi m e^2}{\hbar^2} \right)^{1/4}. \quad (22)$$

Thus, substituting the last relations to Eq. (20) we can calculate values of the work function for any metal. In general, the results obtained directly from this equation are

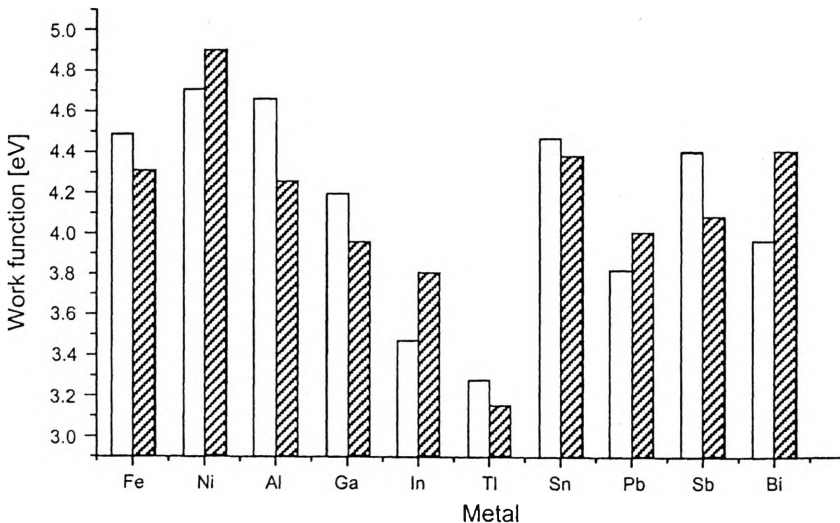


Fig. 3. Comparison of experimental (black) (after [13]) and calculated (white) values of the work function for chosen metals.

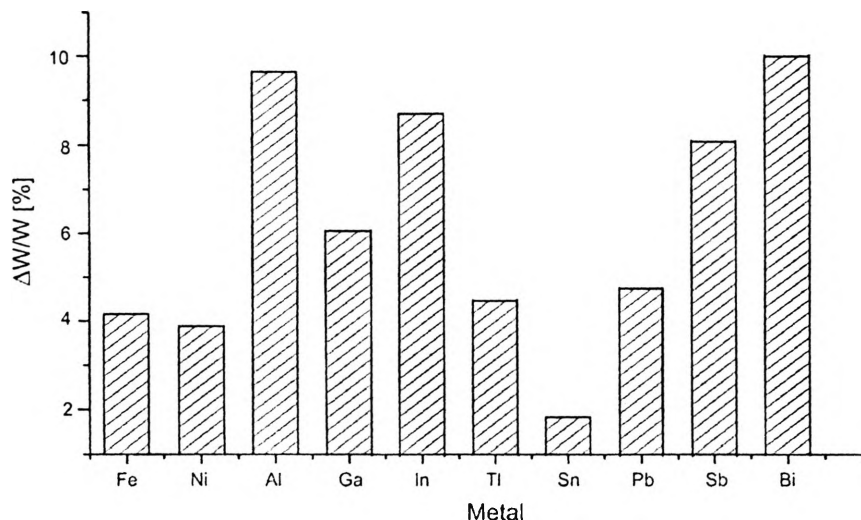


Fig. 4. Proportional rate of experimental and calculated values of the work function for chosen metals.

comparable with the available experimental values of the work function for any metal [13]. The ratio of the difference between experimental and calculated values of the work function to experimental value never exceeded 70%, which seems to be a very satisfactory result, all the more that for some metals this ratio is less than 10% (Fig. 3). For example, a satisfactory agreement with experiment can be observed for any metal from carbon and boron family. In Figure 4, in the case of Sn the ratio is less than 2%. A surprisingly good agreement has been obtained in the case of Fe and Ni, where the difference is below 4%.

Nevertheless, in the case of transition metals and light metals the difference, often of served dozen percent, seems to be definitely too big.

Looking both at equation expressing the work function and at character of those metals one can come to the conclusion that causes of divergence in both cases have to be different. As regards light metals, which have strictly definite valences and closed electronic subshells, it is difficult to suppose that inaccuracy of electron density can play a key part. We, of course, do not take local fluctuations into consideration. We can, however, suppose that mistake is caused by accepting the straightest approximation of screen radius, which we assumed to be equal the value of Thomas–Fermi screening parameter. Continuing this plot we can assume that the screening (from the crystal lattice) is in the case of alkali metals suitably weaker and introduce effective screening radius in the form $k_{\text{eff}} = \alpha k_0$, where α means the damping

Table 1. Damping coefficients for alkali metals.

Metal	Li	Na	K	Rb	Cs
α	0.84	0.58	0.36	0.31	0.32

Table 2. Average values of electron density for transition metals.

Metal	Nb	Ta	Mo	W	Mn	Re	Pt
n	5.56	11.1	6.42	12.6	16.36	13.6	6.62
\bar{n}	14.24	14.85	15.98	17.14	13.37	20.18	22.09
\bar{n}/n	2.56	1.34	2.49	1.36	0.82	1.48	3.34

coefficient. Then, accepting the experimental value of the work function as exact we can find the above mentioned coefficient for each of the light metals and check whether some logical relations occur among their values.

One can readily notice that the damping coefficient for alkali metals (see Tab. 1) decreases with increasing periodicity (which was easy to foresee because an increase in periodicity must lead to the weakening of screening the valence electrons by nuclei) and one can suppose that the discrepancy for Cs comes rather from inaccuracy of the experimental value of the work function. Analogous relation appears in the case of metals from the second periodic group.

However, as to divergence for transition metals it seems to have other causes. The transition metals have several features in common that distinguish them from others, namely variable valence and their size. The atomic radius of elements generally decreases due to increasing nuclear charge. In keeping with this trend, transition metals also generally decrease in size when one moves from the left to the right across the d -block. Here, the exceptionally weak shielding offered by the d -electrons causes these electrons to experience a greater nuclear charge and be pulled more strongly towards the nucleus. The last few elements in each row of the d -block are slightly larger than those preceding them, considering that electron–electron repulsion outweigh increasing nuclear charge as the d -orbitals are filled. Like d -electrons, electrons in f -orbitals are also ineffective at shielding nuclear charge; the increased nuclear charge in the third row transition metals causes them to be smaller than expected and virtually identical in size to the second row transition metals. For the sake of variable valence we should suppose that in the case of transition metal the difference in work function results from the inaccuracy of electron density. Therefore, we can now introduce an average electron density \bar{n} that can be calculated from Eq. (20), assuming again that the experimental values of the work function are precise. Obtained in such a way the average values of electron density for transition metals are presented in Tab. 2.

Exceptionally considerable are ratios \bar{n}/n for noble metals and mercury, however, it is difficult to forejudge whether there exists any reasonable relation between these ratios and other metal parameters because of the lack of experimental values of work function for many metals from this group.

3. Summary

The investigations of the electron collective excitations of metal surface are important for deeper understanding of the metal response to an incident electromagnetic wave.

Table 2. Continued

Metal	Hg	Cu	Ag	Au	Zn	Cd
n	8.52	8.45	5.85	5.9	13.1	9.28
\bar{n}	17.26	15.56	15.98	15.98	15.64	14.85
\bar{n}/n	2.02	1.84	2.73	2.71	1.19	1.6

Besides, these studies are basic for interpretation of all surface spectroscopy that uses electromagnetic field or charged particle. In all phenomena in which the escape of an electron from the metal surface into surrounding space or the transition of an electron from one sample to another are possible, the characteristic known as the work function is of fundamental importance. Also, from experimental point of view, the work function is considered important because its value is at present relatively simple to measure. The surface electronic property measured in STM is a local tunnelling barrier height, and shows closer relation to the concept of the local work function [14] rather than to the conventional macroscopic interpretation. Nevertheless, the concept of the work function remains a key point in the whole theory. The concept of the work function is fundamental for the photoemission spectroscopy allowing both occupied and unoccupied electron states to be find. Therefore, it is a matter of great importance to derive a relatively simple relation which would allow connecting the work function to other metal parameters, and this problem is a main theme of the present paper. For some metals the experimental values of the work function agree almost exactly with the results of calculation carried out on the basis of Eq. (20). In the case of transition metals and alkali metals the ratio DW/W_{ex} is correspondingly higher (never exceeds 60%), but this fact seems not to result from limitation of equation derived but rather comes from approximation used with reference to values of electron density and screening radius. On the other hand, these differences allow us to calculate a mean electron density \bar{n} (for some metals different from typical electron density) which should play a considerable part in explaining many metal properties. The experiments show the work function to depend not only on the nature of metal but also on its surface. For example, it may depend on the direction of the surface relative to the crystallographic axes [12] if the metal is a single crystal, on the presence of an oxide film [14], *etc.* The reference data on the work function [15] of various faces of a simple crystal metal with clean surfaces do not differ considerably from one another. However, the dependence of the work function both on the face of metal surface and on the tip-sample distance (STM) can be obtained in a simple way directly from Eq. (15) by replacing potential $V(\mathbf{r})$ with its modified form regarding size effects, but this problem is beyond the scope of the presented paper.

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