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A novel approach to the work function in surface and cluster science
Nowe ujęcie pracy wyjścia w fizyce powierzchni i nauce o klasterach

ABSTRACT

In this paper we describe the entirely different point of view on the work function of curved metallic surfaces. We pointed out that in the formulae based on the classical electro-dynamics which exploits the idea of the image potential a characteristic small distance $d = \frac{1}{16} e^2 / 4\pi\varepsilon_0\varphi_\infty$, where e is elementary charge ε_0 is vacuum permeability and φ_∞ is work function of an infinite flat surface, should be considered. In the framework of this approach we obtained excellent agreement with the experimental data in estimation of work function dependence on: (1) the size of monoatomic steps, (2) surface coverage at Θ close to zero, (3) size of small metallic droplets.

1. INTRODUCTION

Wood [1] has pointed out that the work function (WF) of an isolated metallic sphere of radius R is higher by $\frac{3}{8} e^2 / 4\pi\varepsilon_0 R$ than that of a planar surface, φ_∞. His erroneous formula was discussed in numerous papers and

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monographs devoted to cluster science, see [2, 3, 4, 5] for example. Correct formula, however, has a coefficient of $\frac{1}{2}$ instead of $\frac{3}{8}$ because the electrostatic energy of a charged sphere of radius R and charge e is $\frac{1}{2}e^2/4\pi\varepsilon_0 R$ [4]. The coefficient $\frac{1}{2}$ was further confirmed by Seidl and Perdew [5] in the framework of the jellium model. Therefore, from both classical and quantum-mechanical approaches, the correct asymptotic formula for the ionization potential, *IP*, of a metallic ball is:

$$IP = \varphi_\infty + \frac{1}{2}\frac{e^2}{4\pi\varepsilon_0 R}. \tag{1}$$

It is the purpose of this paper to point out that the asymptotic formula can be used in a rather limited range due to an assumption which has been made at its derivation. The assumption was that an electron is extracted from a small distance ($d \to 0$) from the surface. The consequence of this assumption is that the radius R has to be large enough in comparison to the atomic radii. The same objection refers to spherical grounded surfaces from which we will start our considerations.

In order to extend the application of the classical electrostatic formulae down to the atomic radii we will consider a finite characteristic distance d from which integration of the image force exactly yields WF value. The WF of planar and spherical grounded surfaces (φ_∞ and φ_R, respectively) is calculated as the work done against the image force in a usual way:

$$\varphi_\infty = \frac{e^2}{16\pi\varepsilon_0 d} = \frac{3.595\,\text{eV}\cdot\overset{\text{o}}{\text{A}}}{d}, \tag{2}$$

$$\varphi_R = \frac{e^2}{16\pi\varepsilon_0 d}\frac{1}{1+\dfrac{d}{2R}} = \varphi_\infty\bigg/\left(1+\frac{d}{2R}\right). \tag{3}$$

Two proposals of the estimation of d value are given in refs. [6, 7], but here we do not need to use those estimations. The finite value of d can be

calculated simply from equation (2) and substituted to equation (3). This yields the following formula for φ_∞:

$$\varphi_R = \varphi_\infty \Bigg/ \left(1 + \frac{3.595\,\text{eV} \cdot \overset{o}{\text{Å}}}{\varphi_\infty} \frac{1}{2R} \right). \tag{4}$$

The first order approximation of this formula,

$$\varphi_R = \varphi_\infty - 3.595\,\text{eV} \cdot \overset{o}{\text{Å}} \frac{1}{2R}, \tag{5}$$

may be valid for $R \gg 1\text{Å}$. It can be rewritten in a well-known form on asymptotic equation (see e.g. [3]):

$$\varphi_R = \varphi_\infty - \frac{1}{8} \frac{e^2}{4\pi\varepsilon_0 R}. \tag{6}$$

2. WORK FUNCTION AT MONOATOMIC STEPS

By means of the accurate formula (4) we can simply explain, quantitatively or at least semiquantitatively, the variation of the local WF due to the presence of monoatomic steps and due to the presence of adsorbed atoms at coverages below one monolayer.

The local WF changes at steps of Cu(111) and Au(111) surfaces have been studied recently with scanning tunelling microscopy (STM) by Jia et al. [8, 9]. These authors have found the 1.4 ± 0.3 eV reduction of local WF at Cu-Cu monoatomic step, and 0.9 ± 0.3 eV reduction at Au-Au monoatomic step. The depth of the local WF profiles at monoatomic steps (i.e. $\varphi_\infty - \varphi_R$) can be evaluated by formula (4). The results of calculation are shown in Table 1.

It should be noted that random tracing of local WF by STM method shows large variation in their depths (± 0.3 eV). In our opinion this may be

due to tracing over various localities with respect to the top of the atom where the radius of curvature equals the atomic radius.

Table 1. The lowering of WF at monoatomic steps
Spadek wartości pracy wyjścia na jednoatomowym wyjściu

Metal	φ_∞ [eV] *	2R [Å]*	φ_R [eV]	$\varphi_\infty - \varphi_R$ [eV]
Cu(111)	4.98	2.551	3.88	1.10
Au(111)	5.31	2.878	4.30	1.02

*data from ref. [7]

3. WORK FUNCTION DEPENDENCE ON THE SURFACE COVERAGE

By means of the formula (4) we can also attack the old problem of the charge of WF of a metal surface due to adsorption of atoms with different WF. A classical example discovered by Langmuir [10] is Cs on W surface and studied in detail by Taylor and Langmuir [11]. If the coverage, Θ, of Cs atoms rises from 0 to 1 monolayer, then WF of the whole surface drops from 4.54 eV (pure W) to a value below 2.14 eV (pure Cs). The minimum value is comparable to the local WF of Cs atom calculated by formula (4):

$$\varphi_R = \frac{2.14\,\text{eV}}{1 + \dfrac{3.595}{2.14 \cdot 5.40}} = 1.63\,\text{eV} .$$

The experimentally observed minimum value is very close to this value (Fig. 1). The minimum is expected when the average spacing between Cs nuclei is of about 4R, which corresponds to the coverage Θ to be equal ca. 0.5. At this value tungsten surface is totally screened by large Cs atoms while the contribution of the neighbouring Cs atoms to WF is meaningless. The experimental value is $\Theta = 0.67$, the minimum is very broad, extending from about $\Theta = 0.5$ to $\Theta = 0.8$, see Figure 1.
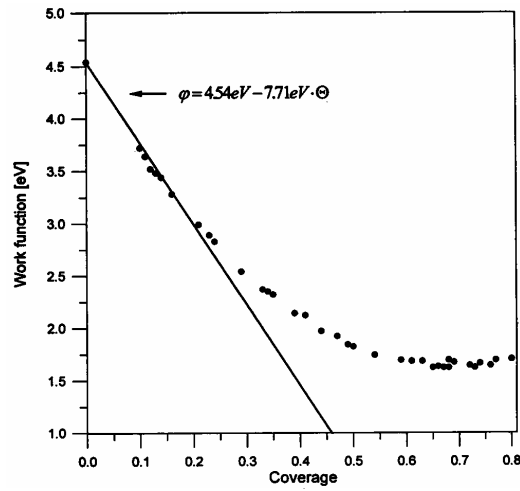
Fig. 1. A comparison of the predicted plot of φ(Θ) at Θ close
to zero with experimental data from [11]
Porównanie przewidywanego przebiegu funkcji φ(Θ) przy Θ bliskim 0
z danymi eksperymentalnymi, zawartymi w [11]

Finally we can estimate the initial slope ($\frac{d\varphi}{d\Theta}$ at $\Theta = 0$) of the φ(Θ) plot. Consider the weighted average value

$$\varphi = \varphi_R \frac{\pi(R+d)^2}{a^2} + \varphi_W \left[1 - \frac{\pi(R+d)^2}{a^2} \right], \tag{7}$$

where R radius of Cs atom, $a^2 = \pi R^2 / \Theta$ and φ_W is WF of tungsten. The above equation can be rewritten as follows:

$$\varphi = \varphi_W - (\varphi_W - \varphi_R)\left(1 + \frac{d}{R}\right)^2 \Theta, \tag{8}$$

the slope is just the coefficient at Θ, which is

$$\frac{d\varphi}{d\Theta}\bigg|_{\Theta=0} = -(4.54-1.63)\cdot \text{eV}\cdot 1.63^2 = -7.71\,\text{eV}\,.$$

The straight line with this slope fits well the experimental points (Fig. 1).

4. DERIVATION OF NONASYMPTOTIC (EXACT) FORMULAE

We will follow the classical electrodynamics formula for the force acting between isolated conducting ball of radius R charged with Q and a charge q located at distance r from the ball center [12]:

$$4\pi\varepsilon_0 F = \frac{Q+q\dfrac{R}{r}}{r^2} - \frac{q^2 Rr}{\left(r^2-R^2\right)^2}\,. \tag{9}$$

From this formula one obtains by integration the following expression for the work W of removal of the charge q from distance d to infinity:

$$W = \frac{q^2}{8\pi\varepsilon_0}\left(-2\frac{Q}{q}\frac{1}{R+d} - \frac{R}{(R+d)^2} + \frac{R}{(R+d)^2 - R^2}\right). \tag{10}$$

This formula converges to the asymptotic equation (1) for $Q=e$, $q=-e$ and $R \gg d = e^2/(16\pi\varepsilon_0\varphi_\infty)$. For practical calculations formula (10) may be rewritten in the following form:

$$W = \varphi_\infty\left[\left(1+\frac{x}{2}\right)^{-1} + 2x\frac{1+2x}{(1+x)^2}\right], \tag{11}$$

where $x = d/R$.

In the case of grounded conducting sphere the total charge of the sphere $Q+q\dfrac{R}{r}$ is zero, hence the formula for W has one term only:

$$W = \frac{q^2}{8\pi\varepsilon_0} \cdot \frac{R}{(R+d)^2 - R^2} \ .$$

(12)

Equation (12) may be identified with exact equation (3) for φ_R if $q = e$, which has the asymptotic form given by equation (6).

5. IONIZATION POTENTIAL OF SMALL METALLIC CLUSTERS

As an illustrative example of application of the exact formula (10) let us calculate the ionization potential (IP) of tantalum clusters for which experimental data are available in ref. [13]. The experimental points are plotted in Figure 2 along with theoretical curves. The W_1 line was calculated according to the exact equation (10), whilst the W_2 line according to the asymptotic formula (1) and W_3 line according to an interpolation formula given by [14]. We assumed for lines W_1 and W_2 the same relationship between the number of atoms, n, and the ball radius:
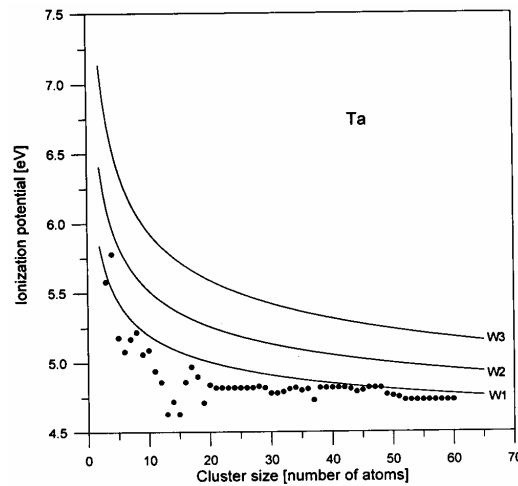

Fig. 2. IP of Ta clusters as a function of number of atoms. The experimental
data were taken from ref. [13]. See text for description of curves
Potencjał jonizacji klasterów Ta jako funkcja liczby atomów. Dane doświadczalne
pochodzą z publikacji [13]. Patrz opis krzywych w tekście

$$R = 1.81\ rn^{1/3}, \tag{13}$$

where r is the metallic radius and the numerical factor 1.81 is derived from the assumption of maximum packing density of atoms in the ball, $\left(\frac{4}{3}\pi\sqrt{2}\right)^{1/3} = 1.8094...$. It is seen in Figure 2 much better fit of calculated line according to eqn. (10) for any number of atoms in the cluster. Departures from this line may be explained by: (1) isomer formation and (2) quantum effects.

In the case of alkali metal clusters we obtained the ideal agreement of the exact curve with the experimental data when the formula (13) was replaced by :

$$R = r_s n^{1/3}. \tag{14}$$

where r_s is the Wigner-Seitz radius (see Fig. 3). This result simply means that there is no contraction of atoms in these clusters in comparison to bulk metal, unlike as in the case of transition metals the clusters of which are strongly contracted by the surface tension forces.
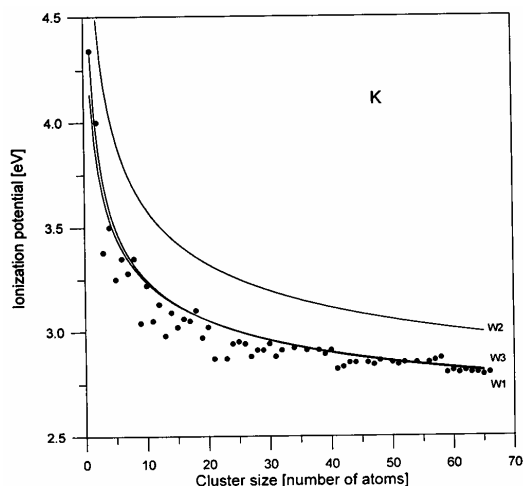

Fig. 3. IP of K clusters as a function of number of atoms. The experimental
data were taken from ref. [15]. See text for description of curves
Potencjał jonizacji klasterów K jako funkcja liczby atomów. Dane eksperymentalne
zaczerpnięto z publikacji [13]. Patrz opis krzywych w tekście

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STRESZCZENIE

W niniejszym artykule przedstawiono całkowicie nowy punkt widzenia na pracę wyjścia z zakrzywionej powierzchni metalicznej. Pracę wyjścia obliczamy jako całkę sił obrazowych, korzystając ze wzorów elektrodynamiki klasycznej, przy czym całkowanie odbywa się w granicach od wartości $d = \frac{1}{16} e^2 / 4\pi\varepsilon_0\varphi_\infty$ (gdzie e – ładunek elementarny; ε_0 – przenikalność elektryczna próżni; φ_∞ – praca wyjścia z powierzchni płaskiej) do nieskończoności. Taki sposób obliczeń dał wartości zgodne z eksperymentem w następujących sytuacjach: 1. zmiany pracy wyjścia na jednoatomowych schodkach; 2. w zależności od stopnia pokrycia powierzchni w przypadkach małych pokryć; 3. małych rozmiarów kropli metalicznej.