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100 years of work function

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This paper traces early inquires on the nature of the work function (*WF*). Much attention was paid to the papers published by Einstein (1905), Richardson (1901), Jentzsch (1908), Debye (1910), Schottky (1914) and Langmuir (1916). Those authors assumed that the image force, introduced already by Thomson for macroscopic bodies, may be the main reason for the barrier at the metal surface. The formula derived by Schottky (1914) is still used for calculation of the lowering of the surface barrier in presence of an external electric field. In further development of surface physics, however, much emphasis was paid to the role of a dipole layer. However, at the end of 20th century the idea of the image potential as the main contribution to *WF* was restored by Brodie (1995) and subsequently improved by Halas and Durakiewicz (1998). In these theories a distance *d* from which the image force can be integrated is found from the uncertainty principle and from the length of spontaneous metallic plasma polarization, respectively. The last approach has appeared to be very useful in calculation of *WF* of conducting compounds and ionization potentials of metallic clusters.

Key words: *cluster; cold emission; ionization potential; photoeffect; surface ionization; thermionic emission; work function*

1. Introduction

The term "work function" (*WF*) was coined about 1923 for the work expressed in eV which is necessary to get electron out of metal. Prior to that time it was defined as *the work necessary to get electron out of metal*, or *work done when electron escapes from a metal*. Over the last 100 years this fundamental property of a surface has been examined nearly for all elements and for many conducting compounds or alloys. It is related to the ionization energy of atoms, but it is less strictly defined than ionization energy because it strongly depends on the presence of impurities at surface and *WF* appears to be face-dependent, if single crystals are investigated. Table 1 contains *WF* for polycrystalline elements along with ionization energies and the values of electron affinity (which is discussed in Sect. 4). This paper contains a brief review of the *WF* significance in understanding various phenomena and the nature of *WF* itself.

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Table 1. The periodic table of elements[*]

$_{1}$H 13.598 0.7542																	$_{2}$He 24.58 −0.22
$_{3}$Li 5.39 2.9 0.6182	$_{4}$Be 9.32 4.98 −0.19											$_{5}$B 8.30 4.45 0.227	$_{6}$C 11.26 5.0 1.2629	$_{7}$N 14.54 −0.07	$_{8}$O 13.61 1.462	$_{9}$F 17.42 3.399	$_{10}$Ne 21.56 −0.3
$_{11}$Na 5.14 2.75 0.5479	$_{12}$Mg 7.64 3.66 −0.22											$_{13}$Al 5.98 4.28 0.442	$_{14}$Si 8.15 4.85 1.385	$_{15}$P 10.55 0.7464	$_{16}$S 10.36 2.077	$_{17}$Cl 13.01 3.615	$_{18}$Ar 15.76 −0.36
$_{19}$K 4.34 2.30 0.5015	$_{20}$Ca 6.11 2.87 0.0215	$_{21}$Sc 6.56 3.4 0.189	$_{22}$Ti 6.83 4.33 0.080	$_{23}$V 6.74 4.3 0.526	$_{24}$Cr 6.76 4.5 0.667	$_{25}$Mn 7.43 4.1 <0.005	$_{26}$Fe 7.90 4.5 0.164	$_{27}$Co 7.86 5.0 0.662	$_{28}$Ni 7.63 5.15 1.157	$_{29}$Cu 7.72 4.51 1.228	$_{30}$Zn 9.39 4.33 0.093	$_{31}$Ga 6.00 4.15 0.31	$_{32}$Ge 7.89 5.0 1.23	$_{33}$As 9.81 4.77 0.81	$_{34}$Se 9.75 5.9 2.0208	$_{35}$Br 11.84 3.364	$_{36}$Kr 14.00 <0
$_{37}$Rb 4.18 2.16 0.4859	$_{38}$Sr 5.69 2.59 0.11	$_{39}$Y 6.38 3.1 0.308	$_{40}$Zr 6.95 4.05 0.427	$_{41}$Nb 6.88 4.3 0.894	$_{42}$Mo 7.18 4.6 0.747	$_{43}$Tc 7.28 4.9 0.55	$_{44}$Ru 7.36 4.71 1.05	$_{45}$Rh 7.46 4.98 1.138	$_{46}$Pd 8.343 5.12 0.558	$_{47}$Ag 7.57 4.26 1.303	$_{48}$Cd 8.99 4.22 0.260	$_{49}$In 5.78 4.12 0.30	$_{50}$Sn 7.34 4.42 1.15	$_{51}$Sb 8.64 4.55 1.07	$_{52}$Te 9.01 4.95 1.9708	$_{53}$I 10.45 3.059	$_{54}$Xe 12.13 <0
$_{55}$Cs 3.893 2.14 0.4716	$_{56}$Ba 5.21 2.7 0.17	$_{57}$La 5.57 2.96 0.518	$_{72}$Hf 7.00 3.9 ≥0.1	$_{73}$Ta 7.89 4.25 0.323	$_{74}$W 7.98 4.55 0.816	$_{75}$Re 7.87 4.87 0.12	$_{76}$Os 8.70 4.83 1.12	$_{77}$Ir 9.0 5.27 1.566	$_{78}$Pt 8.96 5.65 2.128	$_{79}$Au 9.22 5.1 2.309	$_{80}$Hg 10.43 4.49 0.186	$_{81}$Tl 6.11 3.84 0.3	$_{82}$Pb 7.41 4.25 0.364	$_{83}$Bi 7.29 4.22 0.946	$_{84}$Po 8.43 5.0 1.9	$_{85}$At 9.64 2.8	$_{86}$Rn 10.74 <0
$_{87}$Fr 3.98 2.1	$_{88}$Ra 5.28 2.8 0.17	$_{89}$Ac 5.17 3.2															

$_{58}$Ce 5.466 2.97 0.518	$_{59}$Pr 5.42 2.96 ≥0.1	$_{60}$Nd 5.49 3.2 ≥0.05	$_{61}$Pm 5.54 3.1	$_{62}$Sm 5.6 2.85 ≥0.05	$_{63}$Eu 5.67 2.5 ≥0.05	$_{64}$Gd 6.14 3.17 ≥0.1	$_{65}$Tb 5.85 3.15 ≥0.1	$_{66}$Dy 5.93 3.25 0.15	$_{67}$Ho 6.02 3.22 <0.005	$_{68}$Er 6.10 3.25 <0.005	$_{69}$Tm 6.18 3.1 0.035	$_{90}$Yb 6.25 3.0 0.010
$_{90}$Th 6.08 3.4 >0.05	$_{91}$Pa 5.89 3.7 >0.05	$_{92}$U 6.05 3.63 >0.05	$_{93}$Np 6.19 3.9	$_{94}$Pu 6.06 3.6 ≥0.05	$_{95}$Am 6.00 3.7	$_{96}$Cm 6.02 3.9	$_{97}$Bk 6.23 3.8	$_{98}$Cf 6.30 4.0	$_{99}$Es 6.42 3.3	$_{100}$Fm	$_{101}$Md	$_{102}$No

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[*] The numbers under the symbols of elements are the ionization energies (upper rows), work functions (middle rows) and electron affinities (lower rows), given in eV/atom.

2. Einstein's heuristic paper

In 1895 Heinrich Hertz observed that ultraviolet light from the sparks of the generator of the radio waves he had recently discovered, falling on the negative electrode of his radio wave detector, induced the flow of electricity in the gap between the electrodes. He discovered the photoelectric effect. Lenard made improved measurements and he demonstrated by determination of their charge-to-mass ratio that the ejected particles are identical with the electrons.

In 1905, 26 year old Albert Einstein wrote within a few months five papers which changed the foundations of physics and our understanding of the Universe. The first paper of this series, written in May 1905, Einstein calls in a letter to his friend Conrad Habicht *very revolutionary* [1]. The paper deals with radiation and the energy properties of light. It was the objective of his paper to fill the gap, which existed at the beginning of XX century, between wave theory of light and statistical description of gas molecules. He considered Planck's quanta as particles of energy:

$$E = \frac{R}{N}\beta\nu \tag{1}$$

Equation (1) is equivalent to $E = h\nu$ introduced later by Millikan, since $R/N = k$ is the Boltzmann constant, and β is the second radiation constant in the Planck formula for the energy density of black-body radiation:

$$\rho_\nu = \frac{\alpha\nu^3}{\mathrm{e}^{\beta\nu/T} - 1} \tag{2}$$

Therefore $\beta\nu/T = h\nu/kT$ from which it follows that $h = k\beta$ or $h = (R/N)\beta$.

After the derivation of entropy of radiation, Einstein subsequently considered the following three phenomena in which light was transformed and converted to energy of various forms: (i) photoluminescence, (ii) photoeffect, and (iii) gas ionization by ultraviolet light.

In (i), he derives the Stokes rule on the basis of energy conservation to light quanta:

$$\frac{R}{N}\beta\nu_2 \le \frac{R}{N}\beta\nu_1 \tag{3}$$

where ν_1 is the frequency of primary beam and ν_2 is the frequency of the light to which the primary beam is converted. The Stokes rule, i.e. $\nu_2 \le \nu_1$ follows directly from Eq. (3).

The photoeffect was already investigated experimentally by Lenard in 1902 [2]. Einstein considers this effect as generation of electrons from a cathode by its irradiation by light quanta. He assumed that *on every electron leaving a solid has to be done a characteristic work P, therefore the kinetic energy of such electron is*

$$\frac{R}{N}\beta\nu - P \tag{4}$$

In this statement we recognize both the definition of electronic work function and the conservation energy principle. Using Lenard's experimental data, Einstein estimated P value for Zn as 4.3 eV. Later on the Einstein's photoelectric equation (4) for maximum energy of emitted electron was rewritten to the following form [3]:

$$\frac{1}{2}mv^2 = h\nu - P \tag{5}$$

From this equation Millikan determined the Planck constant, h, with much greater accuracy than it was possible to calculate it from the Planck radiation law (Table 2).

Table 2. The evolution of Planck constant

Author	h [J·s]
Einstein (1905)	$6.74\cdot10^{-34}$
Millikan (1914)	$6.58\cdot10^{-34}$
Today	$6.626\cdot10^{-34}$

In (iii), Einstein considers the action of ultraviolet light on gas molecules, and introduces *the work for ionization of one mole of a gas, J* and writes the following condition for the frequency of light:

$$R\beta\nu \geq J \tag{6}$$

Then using Lenard's maximum wavelength of light which is capable to ionize the air he estimated an average ionization energy of air molecule as ca. 10 eV, which is in fairly good agreement with determined by mass spectrometry the appearance potential of O_2^+, (12.3±0.3) V [4] which is the lowest among the air constituents.

In summary of Einstein revolutionary article on the quantum nature of light, let us emphasize that the introduced quanta can be converted to other quanta and can do real work. He defined *works* which later on were called as *work function* and *ionization energy*.

3. *WF* in thermionic emission

Somewhat earlier than Einstein's consideration of the photoeffect, the work function was defined by Richardson in his paper *On negative radiation from hot platinum* [5]. The thermionic emission was studied by various researchers in the last decade of 19th century, but Richardson first published in 1901 a quantitative interpretation of this phenomenon as the release of free-electron gas (*corpuscles*) existing in any conducting material. Starting from the Maxwell–Boltzmann distribution of electron velocity, he found the following law for the saturation current density (j_s) which can be measured at sufficiently high potential of anode vs. hot cathode (120 V in his experiments):

$$j_s = ne\sqrt{\frac{kT}{2\pi m}}\mathrm{e}^{-\Phi/kT} \tag{7}$$

where Φ is defined by himself as *the work done by a corpuscle in passing through the surface layer*, T is the absolute temperature, k is Boltzmann constant (in his paper it was denoted as *R being the gas constant for a single corpuscle*), n is the total number of corpuscles per unit volume and m is its mass.

From his law, by plotting $\ln j_s$ vs. $1/T$, Richardson could determine both Φ and n for platinum: $\Phi = 4.1$ eV and $n = (1.0–2.0)\cdot 10^{21}$ cm^{-3}. He used, after Thomson, $6.0\cdot 10^{-16}$ C for the elementary charge, and $1.204\cdot 10^{-11}$ cgs units for the m/k ratio.

Richardson interprets Φ/e as *the discontinuity in the potential at the surface of the metal.* Though from his paper follows the electric nature of *WF*, neither he nor Einstein did explain the origin of the postulated electric barrier which appears at the metal surface.

Richardson's law was derived about three decades later using the Fermi–Dirac distribution, see eg. textbook by Max Born [6]:

$$j_s = \frac{4\pi emk^2}{h^3}T^2\mathrm{e}^{-\Phi/kT} \tag{8}$$

where the universal constant $4\pi emk^2/h^3 = 120$ A·cm^{-2}·K^{-1} is expressed in terms of defined above physical constants e, m, k and h (Planck constant) which appear in the Fermi–Dirac distribution.

An entirely different derivation of the equations for electron emission from metals was published by Dushman in 1923 [7]. He considered electron emission from a metal as thermodynamically equivalent to the evaporation of atoms from a monoatomic solid. He derived identical temperature dependence as Eq. (8) but with the constant

$$\frac{2\pi emk^2}{h^3} = 60\ \mathrm{A\cdot cm^{-2}\cdot K^{-2}} \tag{9}$$

which differs by the factor two, because Dushman could not consider the statistical weight of the spin of free electrons (Uhlenbeck and Goudsmit derived the electron spin in 1926). The values reported in Dushman's paper for the thermionic emission constant varied from 60.2 to 38.4 A·cm^{-2}·K^{-1}. Later studies by numerous researches yield highly scattered results, but for pure metals with high melting point the emission constant is about 60 A·cm^{-2}·K^{-1}, which does not mean that only about 50% of the surface emits electrons if we consider that *WF* is variable (patchy) in the atomic scale.

4. Other phenomena

Simultaneously with the early investigations of the photoeffect and thermionic emission, the following phenomena were studied experimentally and considered theoretically, in which *WF* plays a great role. Below we briefly discuss these phenomena.

When electrons are emitted from incandescent metals there is an *absorption of thermal energy*, the absorbed power P is related to Φ as follows:

$$Pe = j\Phi \tag{10}$$

where j is the emission current, Φ is the work function and e is elementary charge. Note that Φ/e is the height of electric barrier at metal surface. From the heat absorption accompanying electron emission, Richardson and Cooke determined Φ values for several metals, which agree fairly well with those obtained from the Richardson law. Equation (7) was supplemented by Richardson with a small term of the average kinetic energy of emitted electrons which is $2kT$ and not $3/2kT$, hence

$$Pe = j(\Phi + 2kT) \tag{10a}$$

Davisson and Germer derived $\Phi = 4.52$ eV for tungsten from their calorimetric determinations using Eq. (10a), whereas their direct measurement of the emission as a function of temperature yields 4.48 eV [8].

The contact potential difference between a pair of metals, e.g. copper and zinc, was studied by Lord Kelvin in 1898 in the paper entitled *Contact electricity of metals* [9]. However the origin of the contact electricity was finally understood a decade later due to a great effort of Richardson, Debye and Langmuir. Making this long story as short as possible, I will recall a sharp distinction between potential difference and electromotive force (EMF) made by Langmuir in his seminal paper [10]: *The potential difference is equal to dW/de, i.e. work per unit charge when the charge becomes infinitesimal. In contrast, the EMF is defined as W/e, where W is the work done when an electron (charge e) moves from one place to another. Thus EMF is that which tends to cause current (actual electrons and ions) to flow.*

Langmuir shows that at the surface of a metal EMF = Φ/e (tending to make electrons flow into the metal), but there is no potential difference between metal and a remote point in vacuum. However, at the contact of two metals there is a potential difference which appears equal to $(\Phi_1 - \Phi_2)/e$, but there is no EMF (at identical temperature of both metals). A little EMF is observed when one junction is maintained at different temperature than the other. This effect is a measure of the temperature coefficient of the potential difference.

It should be emphasized here that the accurate method devised by Lord Kelvin becomes later on a very important method of *WF* determination, in which the contact potential difference is measured between an investigated sample and an electrode with known Φ. This electrode is made in form of a tip, and this way of *WF* determination is known as Kelvin probe method. The method is very useful in surface science until today.

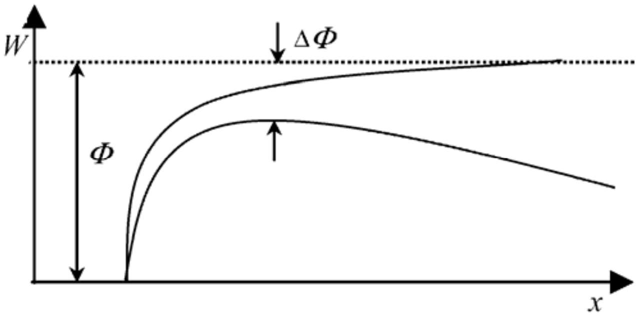

Fig. 1. Explanation of the Schottky effect

The *WF* is also connected with ionizing potentials of metal atoms but this relationship was poorly understood for a long time. This matter will be explained below in discussion of the ionization potential of metal clusters.

The Schottky effect is the effect of stronger electric fields applied to draw electrons emitted by hot cathodes and also by illuminated photocathodes. This effect of lowering the electric barrier at the surface was predicted theoretically by Schottky in 1923 [13]. He assumed that without external field an electron outside of a metal surface experiences the electrostatic image force, which was introduced previously by Thomson (i.e., Kelvin) for explanation of attraction of charged balls by a grounded metal plane. Considering the potential energy of an electron at distance x, we have

$$W_{\text{image}} = \int_x^{\infty} \frac{e^2}{4\pi\varepsilon_0 (2x)^2} dx = -\frac{e^2}{16\pi\varepsilon_0 x} \tag{11}$$

where ε_0 is the electric permittivity of free space. When a field strength E is applied the total potential energy near the surface is

$$W = \Phi - \frac{e^2}{16\pi\varepsilon_o x} - eEx \tag{12}$$

This function is plotted in Fig. 1. The maximum value of W is lowered by

$$\Delta\Phi = e\sqrt{\frac{eE}{4\pi\varepsilon_0}} \tag{13}$$

The Schottky formula was very well confirmed experimentally for moderately strong fields at which the barrier is very thick and no tunnelling of electrons occurs. In the case of thermionic emission, a test was made by Bruyne in 1928, and in the photoeffect case by Lawrence and Linford in 1930. These researchers have found *that outside the film of potassium on a thin layer of oxygen on tungsten the field followed closely the Schottky image law in the range* 1.5×10^{-6}*–*10^{-5} *cm from the surface* [14].

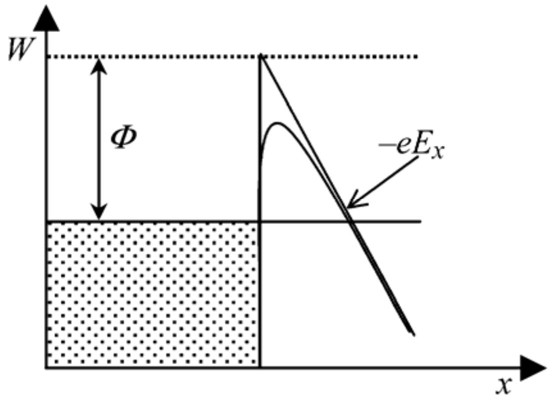

Fig. 2. A simplified plot of electron energy barrier at high electric fields E at the metal surface used by Fowler and Nordheim

Cold emission and STM. It was observed in the beginning of 20th century by a number of workers that electrons can be drawn from a cold cathode to which strong electric fields (~10^7 V·cm^{-1}) were applied. In 1928, Millikan and Lauritsen showed that the emission current density depends on the electric field according to the empirical formula

$$j = aE^2 \exp\left(-\frac{b}{E}\right) \tag{14}$$

where a and b are constants to be fitted for a particular material.

Electron emission under strong electric field at metal surface was theoretically described as the quantum-mechanical tunneling of electrons through a thin barrier by Fowler and Nordheim [11]. For the barrier shown in Fig. 2, they demonstrated that Eq. (14) holds with the following emission constants:

$$a = \frac{e}{2\pi h}\left(\frac{E_F}{\Phi}\right)^{1/2}\left(\Phi + E_F\right)^{-1}, \qquad b = \frac{8\pi\sqrt{2m}}{3h}\Phi^{3/2} \tag{15}$$

where E_F is the Fermi energy, Φ is work function, h is Planck constant, m is mass of electron. It is seen from Eq. (15) that *WF* is strongly related to the cold emission constants. Nowadays the formulae (14) and (15) are the basis of the scanning tunneling microscopy (STM). The tip of a STM may also be considered as the tool for *WF* examination in the atomic scale (cf. ref. [12]).

Surface ionization is a phenomenon of positive or negative ion emission from hot solid or liquid surfaces. The use of hot surfaces for ion production requires much lower temperatures than thermal ionization proceeding in the volume of a hot gas. The first observation of positive ion currents emitted from hot Pt were made by Richardson in 1906 and he noticed a similar exponential dependence vs. $1/T$ as in the case of electron emission. In 1923, surface ionization of Cs atoms was investigated on heated tungsten wire by Kingdon and Langmuir [15].

In order to understand why hot surface with *WF* = Φ enhances the production of positive ions, consider the equivalent 3-step process: (i) evaporation of a neutral atom, (ii) its ionization in vacuum to ion and electron and (iii) return of this electron to the surface. The first step (i) requires little work in comparison to step (ii) where ionization energy *EI*, is needed. However in step (iii) the *WF* is returned to the surface. Hence practically only work equal to *EI* – Φ is needed in surface ionization, whilst as much as *EI* is needed in the thermal ionization in volume of a gas containing metal vapours. Conclusion: for high efficiency of positive ion emission one has to use a surface with high *WF*, eg. oxidized tungsten.

The case of negative ion emission, is equivalent to: (i) evaporation of a neutral atom, (ii) evaporation of electron and (iii) formation of negative ion, at which process the energy equal to the electron affinity (*EA*) is released. Assuming that *EA* is totally returned to the surface, we see that practically work Φ – *EA* is needed for negative ion formation. Hence for their efficient production one has to apply a low *WF* surface, eg. covered by Cs atoms or alkali earth oxides.

4. The nature of *WF*

Richardson in his pioneering study understood *WF* as the height of an electric barrier which keeps electrons within the metal volume. In 1912, he considered the existence of a double layer at a surface and the work against the attraction of its image in the conductor. Richardson explained why this work is not infinite, as in the ordinary electrostatics: This is *because the volume density of the electrification in the ultimate atoms of positive and negative electricity is finite* [16].

The earlier attempts to apply the Thomson formula for the potential energy of electron at distance x

$$W = -\frac{e^2}{16\pi\varepsilon_0 x} \tag{16}$$

can be found in papers by Jentzsch [17] and Debye [18], however these authors, similarly to Schottky [13], did not succeed in derivation of the potential energy at distances comparable to the size of atoms. This subject was considered in detail by Langmuir in 1916 [10], but he also could not find any method for calculation the critical distance x_0 from which the substitution to Eq. (16) leads to the proper value of *WF*. Instead he and also Dushman [7] calculated x_0 from known Φ and they found that x_0 runs from 1.58 Å (tungsten) to 3.19 Å (calcium). The intriguing question why work must be done against the image force in the region outside x_0 was attacked by Langmuir again in 1933. He concluded that in the region from metal interior to x_0 the forces acting on electrons are balanced by *electron pressure and the force due to po-*

tential gradient [19]. This explanation, however, did not lead him to a method of calculation of x_0 and *WF*. It should be noted that the formula for electron energy at a distance x proposed by Seitz [20]

$$W(x) = -\frac{e^2}{16\pi\varepsilon_o x + \dfrac{e^2}{\Phi}}, \qquad 0 \le x < \infty \tag{17}$$

and other similar formulae, which appeared later on, are useless in *WF* calculation because Φ has to be known for $W(x)$ calculation.

In 1936, Bardeen in his quantum-mechanical calculation first considered the exchange and correlation forces acting on electron close to the surface. Unfortunately, the quantum-mechanical calculation methods following Bardeen's idea did not lead to a formula for *WF* calculation.

With the advent of high speed computers sophisticated algorithms were developed to compute electronic properties of crystalline solid by solving the Schrödinger equation. These *ab-initio* methods succeeded in calculation of bulk electron energy distribution, but the surface properties were weakly predicted until early 70's of XX century. The most successful calculations of *WF* and surface energy for simple metals (Li, Na, K, Rb, Cs, Al, Pb, Zn and Mg) on the basis of uniform-positive-background model (latter called *jellium* model) were published by Lang and Kohn [21] in 1971. They obtained Φ values for simple metals which agree with experimental data within 5–10%. However, for noble metals the computed *WF* are 15–30% too low. It is important for understanding the nature of *WF* that they calculated

$$\Phi = \Delta\Phi - \bar{u} \tag{18}$$

where $\Delta\Phi$ is the change in electrostatic potential across the surface dipole layer created by the spilling out of electrons, and $\bar{u}$ is the chemical potential of the electrons in the bulk metal relative to the mean electrostatic potential there (Fig. 3). Equation (18) includes all many-body effects, in particular, the work against the image force.

The original *jellium* model, which totally ignored the discrete ionic structure, leads to a lack of mechanical equilibrium, hence it was "stabilized" by adding extra parameter to account properly the bulk metal properties, and the modified parameter accounting for atomic corrugation at the exposed crystal face. Good results with stabilized *jellium* model for simple metals were obtained recently by Kiejna [22].

Another important *ab-initio* study was published by Skriver and Rosengaard [23] in 1992. They implemented an efficient self-consistent Green's-function technique and calculated *WF* and surface energy for simple and transition metals. Their results for most of transition metals are, however, generally too high when compared with experiment, see comment by Durakiewicz et al. [24]. Moreover, the nature of electronic work function is lost in complex and approximate calculations.

An entirely different approach was proposed by Brodie [25] in 1995. He returned to the electrostatic image potential energy (see Eq. (11)) but the integration is done from a minimum distance *d* at which the image force starts to act. This distance is incidentally equal to x_0 in early works, e.g. in Dushman and Langmuir papers. However Brodie derived a simple formula from the Heisenberg uncertainty principle.

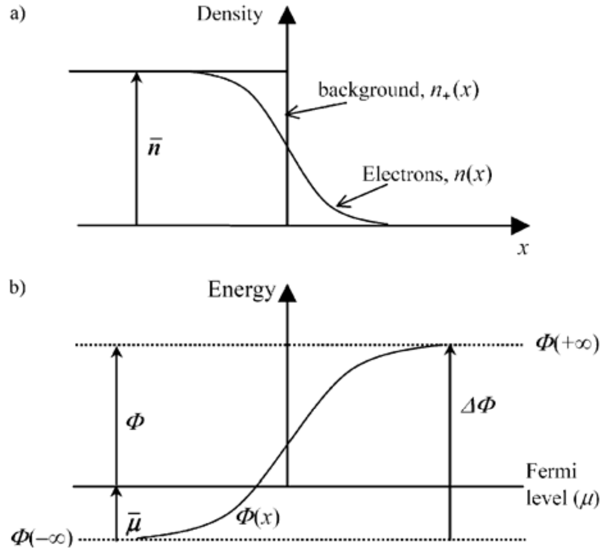

Fig. 3. Distribution of positive and negative charge densities in the jellium model (a) and plot of the potential energy of a free electron at the metal surface in jellium model (b)

He argues as follows: *There is a region bounded by a surface spaced d from the classical metal surface that an electron inside the metal can transverse by converting its kinetic energy to potential energy without doing any work. At d the kinetic energy of electron is zero and it is assumed that at this point the classical image force begins to act. The work function is then the energy that has to be given to an electron to take it from d where it has zero kinetic energy to a field-free region far enough away from the metal surface for the image force to be zero.* […] *Inside the metal, quantum theory is required to determine the highest kinetic energy an electron may have at 0 K as it approaches the classical metal surface (namely, the Fermi energy* E_F*). Beyond d, classical mechanics is adequate to determine the work function. Between the classical metal surface and the d surface, the momentum changes from* $(2E_F/m^*)^{1/2}$ *to zero, where* m^* *is the effective mass of the electron inside the metal as it approaches the surface. We identify the distance d with the Heisenberg uncertainty distance associated with this change in momentum, as appears to be required by continuous decoherence from quantum to classical states.*

Brodie's novel approach to *WF* calculation without use of the *ab-initio* methods was substantially improved by Halas and Durakiewicz [26], who applied the metallic plasma model for calculation of the *d* value. Their method become very effective not only in calculation *WF* of elements, but also for conducting compounds as hydrides [27], borides and alkali and alkaline earth metal oxides [28].

In order to introduce this method, let us recall the basic formulae from plasma physics such as these for the length of spontaneous polarization and the screening length. Necessary modifications of these formulae will be made to make them applicable to the plasma constituted of free electrons and ions in a metal lattice.

Locally, plasma can spontaneously polarize itself, which means that electrons are somewhat shifted against ions. The polarization requires energy which in the case of gaseous plasma is taken from thermal energy, i.e. average kinetic energy per degree of translational motion, $(1/2)kT$. In the case of free electrons such polarization can be produced mainly at the expense of Fermi kinetic energy E_F because even at melting point of a crystal, the thermal energy is small in comparison to E_F.

Hence, the polarization length in the case of metal may be calculated by replacing $(1/2)kT$ by E_F in the classical formula of plasma physics, which leads to the following formula:

$$d = \sqrt{\frac{2\varepsilon_0 E_F}{ne^2}} \tag{19}$$

where ε_0 is the electric permittivity of free space, n is average density of free electrons in the metal lattice, and e is the elementary charge.

The work function is calculated from Eq. (11) in which x is substituted by d given by Eq. (19) being divided by the common scaling factor α. Before doing this, let us rewrite formula (11) in a more convenient form:

$$\Phi = \frac{\alpha}{2}\frac{e^2}{8\pi\varepsilon_0 a_0}\frac{a_0}{d} = \frac{\alpha Ry}{2\dfrac{d}{a_0}} \tag{20}$$

where a_0 is Bohr radius (0.52918 Å) and Ry is the atomic unit of energy (13.6058 eV). The d value is conveniently calculated using Eq. (19) in which free electron density n is replaced by density parameter r_s, defined as follows:

$$\frac{1}{n} = \frac{4}{3}\pi r_s^3 \tag{21}$$

Now, Eq. (19) can be rewritten in the following way:

$$d = \sqrt{\frac{2\varepsilon_0 EF}{e^2}\cdot\frac{4\pi r_s^3}{3}} = \sqrt{E_F\left(\frac{e^2}{8\pi\varepsilon_0 a_0}\right)^{-1}\frac{r_s^3}{3a_0}} = \frac{a_0}{\sqrt{3}}\left(\frac{E_F}{Ry}\right)^{1/2}\left(\frac{r_s}{a_0}\right)^{3/2} \tag{22}$$

When this formula is substituted to Eq. (21), one obtains:

$$\Phi = \frac{\alpha\sqrt{3}}{2}Ry\left(\frac{E_F}{Ry}\right)^{-1/2}\left(\frac{r_s}{a_0}\right)^{-3/2} \tag{23}$$

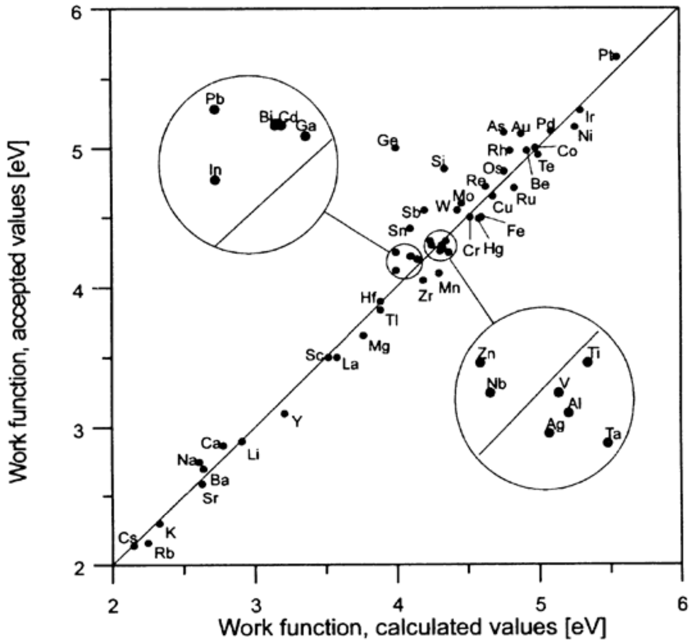

Fig. 4. Measured *WF* values vs. calculated by the metallic plasma model

For practical calculations, Eq. (23) may be rewritten in the following form:

$$\Phi = \frac{11.783\alpha}{\left(r_s[\text{a.u.}]\right)^{3/2}\left(E_F[Ry]\right)^{1/2}} = \frac{43.46\alpha}{\left(r_s[\text{a.u.}]\right)^{3/2}\left(E_F[\text{eV}]\right)^{1/2}} \quad [\text{eV}] \qquad (24)$$

where r_s is expressed in units of the Bohr radius. One can see that work function is expressed by the density parameter r_s, and the Fermi energy E_f. The scaling factor α was assumed to be equal to unity for all elements except the alkali metals, Ca, Sr, Ba, Ra and Tl for which it was assumed to be equal 0.86. So far the α factor is treated as only an empirical constant which most likely may be derived theoretically. In Figure 4, measured *WF* values vs. those calculated by this method are shown.

6. Ionization potential (*IP*) and *WF*

The relation between *IP* and *WF* is conceptually very simple and it is shown in Fig. 5, where *a* represents a single atom of metal vapour with its barrier for a valence electron, while *b* represents a solid constituted from a few atoms. The ground state of the atom is split into a band of states which are filled to the maximum level, called the Fermi level. For no field in the space around the atom and the solid, the potential energy at infinity in both cases is the same and it may be assumed as zero. This simple picture leads, however, to many-body calculation for a single atom but with a number of electrons and to yet more difficult calculation in the case of a solid. At the beginning of 21th century, there is no hope that a simple relationship between *IP* and *WF* will be found by the *ab-initio* methods.

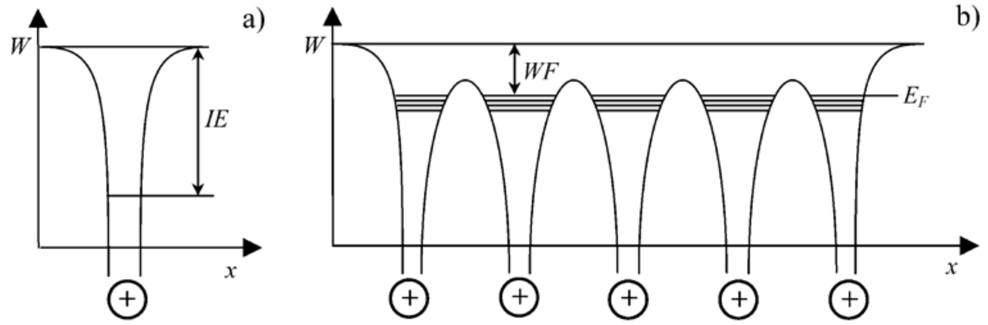

Fig. 5. Plot of potential energy of the valence electron as a function of distance from the positive ion core and its ground level (a), as well as plot of potential energy across a metal where the valence electrons occupy the conduction band up to the Fermi level E_F (b)

In order to solve this problem in a simplified way, consider a neutral spherical ball of a metal cluster consisting a large number N of atoms and then we will reduce $N \rightarrow 1$. Hence *IP* of the cluster will turn in to *IP* of single atom (of metal vapour). The *IP* of clusters were calculated for a long time very roughly without the metallic plasma model. Serious errors in derivation of the asymptotic formula (for cluster radius, $R \gg$ atom radius, r) in the literature was corrected by the author of this paper [29]. The "exact" formula derived in the framework of the metallic plasma model for *IP* of a cluster is:

$$IP = \Phi\left[\left(1+\frac{x}{2}\right)^{-1} + 2x\frac{1+2x}{(1+x)^2}\right] \tag{25}$$

where Φ is the *WF* of a macroscopic piece of metal, $x = d/R$, d is the distance from which the image force starts to act (see the preceding section), and R is the cluster radius.

It follows from the image potential formula (11) that d may be expressed by Φ:

$$d = \frac{e^2}{16\pi\varepsilon_0\Phi} \tag{26}$$

Substituting Eq. (26) and $R = r$ into Eq. (25), we obtain the relationship between *IP* of a metal vapour and metal *WF*. Table 1 convinces us that $WF \approx 0.5IP$ which also follows from Eq. (25) applied to $N = 1$. Better agreement is obtained for transition metals if we consider that the number of free electrons per atom gradually increases with N, when $N \to 1$. Therefore we should substitute into Eq. (26) not real *WF*, but modified Φ value for a reduced number z.

7. Conclusion

It seems that the semi-empirical approach in *WF* calculation, which was developed about 100 years after it was defined by Richardson and Einstein, provides a good basis for understanding the origin of *WF* and its relationship with *IP* of metallic clusters and atoms. So far the plasma model gives the best prediction of *WF* for metals and some important conducting compounds.

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Table 1. The periodic table of elements*

$_{1}$H 13.598 0.7542																	$_{2}$He 24.58 −0.22
$_{3}$Li 5.39 2.9 0.6182	$_{4}$Be 9.32 4.98 −0.19											$_{5}$B 8.30 4.45 0.227	$_{6}$C 11.26 5.0 1.2629	$_{7}$N 14.54 −0.07	$_{8}$O 13.61 1.462	$_{9}$F 17.42 3.399	$_{10}$Ne 21.56 −0.3
$_{11}$Na 5.14 2.75 0.5479	$_{12}$Mg 7.64 3.66 −0.22											$_{13}$Al 5.98 4.28 0.442	$_{14}$Si 8.15 4.85 1.385	$_{15}$P 10.55 0.7464	$_{16}$S 10.36 2.077	$_{17}$Cl 13.01 3.615	$_{18}$Ar 15.76 −0.36
$_{19}$K 4.34 2.30 0.5015	$_{20}$Ca 6.11 2.87 0.0215	$_{21}$Sc 6.56 3.4 0.189	$_{22}$Ti 6.83 4.33 0.080	$_{23}$V 6.74 4.3 0.526	$_{24}$Cr 6.76 4.5 0.667	$_{25}$Mn 7.43 4.1 <0.005	$_{26}$Fe 7.90 4.5 0.164	$_{27}$Co 7.86 5.0 0.662	$_{28}$Ni 7.63 5.15 1.157	$_{29}$Cu 7.72 4.51 1.228	$_{30}$Zn 9.39 4.33 0.093	$_{31}$Ga 6.00 4.15 0.31	$_{32}$Ge 7.89 5.0 1.23	$_{33}$As 9.81 4.77 0.81	$_{34}$Se 9.75 5.9 2.0208	$_{35}$Br 11.84 3.364	$_{36}$Kr 14.00 <0
$_{37}$Rb 4.18 2.16 0.4859	$_{38}$Sr 5.69 2.59 0.11	$_{39}$Y 6.38 3.1 0.308	$_{40}$Zr 6.95 4.05 0.427	$_{41}$Nb 6.88 4.3 0.894	$_{42}$Mo 7.18 4.6 0.747	$_{43}$Tc 7.28 4.9 0.55	$_{44}$Ru 7.36 4.71 1.05	$_{45}$Rh 7.46 4.98 1.138	$_{46}$Pd 8.343 5.12 0.558	$_{47}$Ag 7.57 4.26 1.303	$_{48}$Cd 8.99 4.22 0.260	$_{49}$In 5.78 4.12 0.30	$_{50}$Sn 7.34 4.42 1.15	$_{51}$Sb 8.64 4.55 1.07	$_{52}$Te 9.01 4.95 1.9708	$_{53}$I 10.45 3.059	$_{54}$Xe 12.13 <0
$_{55}$Cs 3.893 2.14 0.4716	$_{56}$Ba 5.21 2.7 0.17	$_{57}$La 5.57 2.96 0.518	$_{72}$Hf 7.00 3.9 ≥0.1	$_{73}$Ta 7.89 4.25 0.323	$_{74}$W 7.98 4.55 0.816	$_{75}$Re 7.87 4.87 0.12	$_{76}$Os 8.70 4.83 1.12	$_{77}$Ir 9.0 5.27 1.566	$_{78}$Pt 8.96 5.65 2.128	$_{79}$Au 9.22 5.1 2.309	$_{80}$Hg 10.43 4.49 0.186	$_{81}$Tl 6.11 3.84 0.3	$_{82}$Pb 7.41 4.25 0.364	$_{83}$Bi 7.29 4.22 0.946	$_{84}$Po 8.43 5.0 1.9	$_{85}$At 9.64 2.8	$_{86}$Rn 10.74 <0
$_{87}$Fr 3.98 2.1	$_{88}$Ra 5.28 2.8 0.17	$_{89}$Ac 5.17 3.2															

$_{58}$Ce 5.466 2.97 0.518	$_{59}$Pr 5.42 2.96 ≥0.1	$_{60}$Nd 5.49 3.2 ≥0.05	$_{61}$Pm 5.54 3.1	$_{62}$Sm 5.6 2.85 ≥0.05	$_{63}$Eu 5.67 2.5 ≥0.05	$_{64}$Gd 6.14 3.17 ≥0.1	$_{65}$Tb 5.85 3.15 ≥0.1	$_{66}$Dy 5.93 3.25 0.15	$_{67}$Ho 6.02 3.22 <0.005	$_{68}$Er 6.10 3.25 <0.005	$_{69}$Tm 6.18 3.1 0.035	$_{90}$Yb 6.25 3.0 0.010	$_{71}$Lu 5.43 3.3 ≥0.1
$_{90}$Th 6.08 3.4 >0.05	$_{91}$Pa 5.89 3.7 >0.05	$_{92}$U 6.05 3.63 >0.05	$_{93}$Np 6.19 3.9	$_{94}$Pu 6.06 3.6 ≥0.05	$_{95}$Am 6.00 3.7	$_{96}$Cm 6.02 3.9	$_{97}$Bk 6.23 3.8	$_{98}$Cf 6.30 4.0	$_{99}$Es 6.42 3.3	$_{100}$Fm	$_{101}$Md	$_{102}$No	$_{103}$Lr

*The numbers under the symbols of elements are the ionization energies (upper rows), work functions (middle rows) and work functions (lower rows), given in eV/atom.