

**An application of the Green Functions Method
to the solution of some electrochemical paradoxes
on metallic surfaces**

S. Romanowski

*Katedra Chemii Teoretycznej, Wydział Fizyki i Chemii,
Uniwersytet Łódzki, ul. Pomorska 149/153, 90-236 Łódź, Poland*

This paper is devoted to some paradoxes occurring in measurements on metallic surfaces. They mainly concern the great discrepancies of measured values of the electron work function onto monocrystalline surfaces, the dependence of this work function on Miller's indices of walls of crystal, some misleading in classic definition of the contact potential and the nature of specific adsorption forces which seemingly negate the electrostatic laws.

In the paper the calculated values of the work function of noble metal single crystals are presented and discussed with respect to experimental discrepancies. It is also shown that corrections introduced to work function definition by means of Green Function Method (GFM) and Extended Coherent Potential Approximation (ECPA) remove the paradoxes mentioned above. The separation of the electrode charge between a bulk and surface of the electrode by means of GFM, fully explain the nature of the specific adsorption forces.

1. INTRODUCTION

Experimental investigations on metallic surfaces have turned out to be surprising in some cases and they sometimes present big discrepancies in the measured values.

Particularly controversial problem constitutes the significant deviations of the measured values of the electron work function of the noble metal (Cu, Ag, Au) monocrystalline faces (100), (110) and (111) [1, 2]. Later on these measurements will be analysed.

The idea of "an agreement of the calculated values with experiment" commonly used as a test of the relevance of any theoretical model loses in many cases its physical meaning due to the lack of an appropriate experimental data

in comparison with the numerical calculations. Therefore, any theory which is able to produce the numerical results with the highest accuracy constitutes the only reasonable source of information of the values interested in.

In this paper some numerical results of the Green Functions Method (GFM) and Extended Coherent Potential Approximation (ECPA) are presented which are able to replace the uncertainty of experimental data and, moreover, to explain some experimental facts being seemingly in contradiction with the well established and recognized laws of physics or chemistry.

2. PARADOXES IN SOME EXPERIMENTS ON METALLIC SURFACES

The most controversial experimental results on metallic surfaces concern the electron work function and contact potential as well as the so-called the specific adsorption of ions on metallic surfaces.

They can be summarized in the following points:

1. *The great deviations of measured values of the electron work function from metal into vacuum (denoted as ϕ^{Me}) are observed for Cu, Ag and Au (100), (110) and (111) monocrystals as well as for polycrystalline Cu, presented in Table 1 [3-22].*

Such great discrepancies of the results for the monocrystalline surfaces of Cu, Au and Ag seem to be particularly surprising due to the modern technology of preparation and cleaning of the samples.

2. *Strong dependence of the measured work function of the single crystal sample with different crystallographic faces on Miller's indices of the faces takes place [1, 23].* However, it remains in contradiction with the fact that the Fermi level (denoted as E_F) of the measured sample is only one. Traditionally, the electron work function is defined as $\phi^{Me} = -E_F^{Me}$.

3. *The paradox occurs in classical definition of the contact potential applied to electrochemical problems.*

The contact potential $\Delta\phi$ between two samples of different metals (known also in electrochemistry as Volta potential) is defined as the respective difference of the work functions of these metals [24, 25] in the form

$$\Delta\phi^{MeI-MeII} = \phi^{MeI} - \phi^{MeII} = -(\varphi_{pzc}^{MeI} - \varphi_{pzc}^{MeII}) = (\varepsilon_0^{MeI} - \varepsilon_0^{MeII}) \quad (2.1)$$

where ε_0^{Me} stands for the so-called potential of zero charge (*pzc*) of metal *Me*, i.e. the potential generating the surface charge of metal $Q_s = 0$; φ_{pzc}^{Me} denotes the outer potential of the metallic phase α in *pzc* point satisfying one of the most fundamental relations of electrochemistry

Table 1. Comparison of the work function experimental data for Cu, Ag and Au (100), (110), (111) single crystals as well for polycrystalline Cu. ϕ^{av} stands for an average value of the data in appropriate column

ϕ^{Cu} [eV]		
(100)	(110)	(111)
4.59 ^{a,b} $\phi^{av} = 4.79$	4.48 ^{b,c,d} $\phi^{av} = 4.46$	4.90 ^a $\phi^{av} = 4.94$
4.65 ^c	4.45 ^c	4.94 ^{b,c}
4.77 ^f		4.98 ^e
4.83 ^e		
5.10 ^g		
Polycr. Cu: 4.352 ^h ; 4.447 ^h ; 4.448 ^h ; 4.542 ^h ; 4.651 ^h		$\phi^{av} = 4.488$
ϕ^{Ag} [eV]		
4.22±0.04 ^{j,k,l} $\phi^{av} = 4.63$	4.14±0.04 ^{j,k,l,m} $\phi^{av} = 4.33$	4.46±0.04 ^{j,kl} $\phi^{av} = 4.65$
4.62 ⁿ	4.52 ^{o,p}	4.66 ^v
4.64 ^{o,p}		4.74 ^{o,p,m}
4.72 ^v		4.75 ^v
4.76 ^s		
4.81 ^v		
ϕ^{Au} [eV]		
5.00 ^t $\phi^{av} = 5.23$	4.8 ^t $\phi^{av} = 5.10$	5.13 ^p $\phi^{av} = 5.21$
5.47 ^p	5.12±0.07 ^u	5.20 ^t
	5.37 ^p	5.30±0.05 ^u

a. Ref. [3]

b. Ref. [4]

c. Ref. [5]

d. Ref. [9]

e. Ref. [7]

f. Ref. [6]

g. Ref. [8]

h. Ref. [10]

i. Ref. [11]

j. Ref. [17]

k. Ref. [18]

l. Ref. [19]

m. Ref. [20]

n. Ref. [16]

o. Ref. [14]

p. Ref. [15]

r. Ref. [12]

s. Ref. [13]

t. Ref. [21]

u. Ref. [22]

$$\gamma^\alpha = \varphi^\alpha + \chi^\alpha \quad (2.2)$$

In eq. (2.2) γ^α is recognized as an inner potential of the metallic phase α (Galvani potential) and χ^α stands for a surface potential.

Formula (2.1) leads really to an apparent paradox. According to the definition of classical electrochemistry in *pzc* point the outer potential of the metallic phase is equal to zero, i.e. $\varphi_{pzc}^{Me} = 0$ [24]. So for two different metals Me I and Me II from one side we have $\varepsilon_0^{MeI} - \varepsilon_0^{MeII} = \phi^{MeI} - \phi^{MeII} \neq 0$ (because of the different work functions of different metals). On the other hand $(\varepsilon_0^{MeI} - \varepsilon_0^{MeII}) = -(\varphi_{pzc}^{MeI} - \varphi_{pzc}^{MeII}) = 0$.

It is worth to note once more that this paradox is caused by means of the assumption that in *pzc* the metallic phase lost its electric charge and then $\varphi_{pzc}^{Me} = 0$.

4. *The mechanism of the so-called specific adsorption of ions on metallic electrodes.*

This phenomenon was experimentally performed already at the beginning of the twenties [26, 27] and from that time it is well known that some anions (for instance halides such as Cl^- , Br^- , I^-) adsorb themselves on negative charged surfaces of the electrodes and some cations (such as Cs^+) on positively charged ones seemingly against the electrostatic laws. An explanation of this unusual phenomena was impossible for many years till the moment when the Green Functions technique was applied.

3. A BRIEF OUTLINE OF THE GREEN FUNCTIONS METHOD AND THE EXTENDED COHERENT POTENTIAL APPROXIMATION

The GFM used in the ECPA leads to numerical calculations of the most important quantities of the metallic surfaces such as: occupation numbers of an electron, work function into vacuum, surface charge of an electrode, its polarization by an external voltage and boundary conditions treated as the surface potential barrier. Such calculations for noble metals have been carried out in earlier papers [1, 2, 28, 29]. For the sake of a better understanding of this paper a brief outline of the GFM and ECPA is presented here.

The Green Functions used in this paper are called the Energetic Green Functions (EGF) being the Fourier transformates of the time-dependent retarded and advanced Green Functions (GF) exhaustively applied in sixties as the propagators of the Quantum Field Theory [30–33].

Let us now to define the local density of electronic states as the second order EGF of an electron by means of the formula [28]:

$$G_{\lambda\bar{\lambda}}(E) = \left\langle \left\langle A_{\lambda}(t) \middle| B_{\bar{\lambda}}(t) \right\rangle \right\rangle_E \quad (3.1)$$

where λ denotes the quantum state of the electron strictly defined later on and A , B are, in general, certain time-dependent operators sometimes used also for $t = 0$ as a special case. The operators in eq. (3.1) can be replaced by the chain of the appropriate operators giving the higher order GF's. A concrete form of the GF always depends on the Hamiltonian of the problem.

The Local Density of Electronic States (LDOS) can be expressed as the imaginary part of the GF [28]

$$\rho(E, \lambda) = -\frac{1}{\pi} \text{Im} G_{\lambda\lambda}(E) \quad (3.2)$$

So the important achievement of the GFM is that it provides an analytical expression for DOS if $\text{Im} G$ is assumed to be previously known. The Green Function satisfies the equation of motion which in the most general form can be written as [30]

$$E G_{\lambda\bar{\lambda}}(E) = \frac{1}{2\pi} \langle [A_{\lambda}(0), B_{\bar{\lambda}}(0)] \rangle + \left\langle \left\langle [A_{\lambda}(t), H] \middle| B_{\bar{\lambda}}(0) \right\rangle \right\rangle_E \quad (3.3)$$

where the symbols $[A, B]$ and $[A, H]_{-}$ stand for the anticommutator and the commutator, respectively, and H denotes the Hamiltonian of the considered system.

In the case of a thin metallic film, consisting of n monoatomic layers, which is a quite realistic model for a monocrystalline electrode, the electronic Hamiltonian in the second quantification representation can be used [28]

$$H_e = \sum_{\lambda\bar{\lambda}} t_{\lambda\bar{\lambda}} a_{\lambda}^{\dagger} a_{\bar{\lambda}} + \frac{1}{2} \sum_{\lambda\lambda\bar{\lambda}\bar{\lambda}} I_{\lambda\lambda\bar{\lambda}\bar{\lambda}} a_{\lambda}^{\dagger} a_{\bar{\lambda}}^{\dagger} a_{\bar{\lambda}} a_{\lambda} \quad (3.4)$$

where $\lambda = (\nu, \vec{j}_{\nu}, m, \sigma)$ is the quantum state of an electron in configuration (Wannier's) representation; $\nu = 1, \dots, n$ labels the consecutive number of a layer in a film; \vec{j}_{ν} is the position vector of an electron in layer ν ; m denotes the electronic band and $\sigma = \uparrow (\downarrow)$ is the spin orientation; a_{λ}^{\dagger} and a_{λ} are the creation and annihilation operators of an electron, respectively; and finally $t_{\lambda\bar{\lambda}}$ and $I_{\lambda\lambda\bar{\lambda}\bar{\lambda}}$ stands for hopping and Coulomb or exchange integrals.

If we apply now the equation of motion (3.3) to the Hamiltonian (3.4), making the following identification of operators as $A_{\lambda}(0) = a_{\lambda}^{\dagger}$, $B_{\bar{\lambda}}(0) = a_{\bar{\lambda}}$, and after decoupling of the fourth order GF appearing in such an equation by means of the second order GF [28] one can obtain

$$EG_{\lambda\bar{\lambda}}(E) = \frac{1}{2\pi} \delta_{\lambda\bar{\lambda}} + \sum_{\alpha} K_{\lambda\alpha} G_{\alpha\bar{\lambda}}(E) \quad (3.5)$$

where the matrix elements are taken in the Hartree-Fock approximation

$$K_{\lambda\alpha}^{HF} = t_{\lambda\alpha} + \sum_{\lambda'} (I_{\lambda\alpha\lambda'\bar{\lambda}'} - I_{\alpha\lambda\lambda'\bar{\lambda}'}) n_{\lambda'\bar{\lambda}'} \delta_{\lambda\bar{\lambda}'} \quad (3.6)$$

satisfying the set of secular equations

$$\sum_{\alpha} K_{\lambda\alpha}^{HF} \Gamma_{\alpha p}^0 = E_p^0 \Gamma_{\lambda p}^0 \quad (3.7)$$

where energy eigenvalues E_p^0 and eigenfunctions $\Gamma_{\lambda p}^0$ represent the quantum state of the electron in momentum (Bloch's) space recognized by means of an index p .

In order to simplify the calculation of the GF from eq. (3.5) the ECPA was applied [1, 2]. This method consists in the replacement of any real inhomogeneous medium (alloy, melting salt, metallic crystal with spins up and down, etc.) by means of an effective homogeneous system, described by an effective Hamiltonian, with the so-called coherent potential Θ_p .

There is a simple relation between the Green Function $G_{\lambda\lambda}(E)$ and coherent potential Θ_p which allows us to substitute $\text{Im} G_{\lambda\lambda}(E)$ by $\text{Im} \Theta_p$ [28]. Then the final formula of the LDOS can be expressed as

$$\rho(E, \lambda) = \frac{2}{\pi} \sum_p |\Gamma_{\lambda p}^0|^2 \frac{1}{B_p} \left[1 - \left(\frac{E - E_p^0}{B_p} \right)^2 \right]^{\frac{1}{2}} \quad (3.8)$$

with the value of a broadening of spectral lines of electrons in the form

$$B_p^2 = \sum_{\lambda} |\Gamma_{\lambda p}^0|^2 I_{\lambda}^2 n_{\lambda(\sigma)} n_{\lambda(-\sigma)} \quad (3.9)$$

where symbol $-\sigma$ denotes a reverse orientation of a spin with respect to σ and n_{λ} is the occupation number of an electron in a quantum state λ .

The occupation numbers are defined now as

$$n_{\lambda} = \int_{-\infty}^{+\infty} \rho(E, \lambda) f(E_F, E) dE \quad (3.10)$$

with

$$f(E_F, E) = \left[\exp\left(\frac{E - E_F}{k_B T}\right) + 1 \right]^{-1} \quad (3.11)$$

being the Fermi Distribution Function (FDF) where E_F stands for the Fermi level of a crystal; k_B is the Boltzmann's constant and T represents the temperature in K.

To find the Fermi energy E_F a mean density of states is subsequently defined

$$\bar{\rho}(E, \lambda) = \frac{1}{2nN\gamma} \sum_{\lambda} \rho(E, \lambda) \quad (3.12)$$

with N denoting the number of points of the planar Brillouin zone; γ standing for the number of electronic bands used in the calculations and also the mean number of electrons per atom is given by

$$\bar{n}_e = \frac{1}{2nN\gamma} \sum_{\lambda} n_{\lambda} \quad (3.13)$$

Now the Fermi level can be calculated as the upper limit of integration in the equation

$$\bar{n}_e = \int_{-\infty}^{E_F} \bar{\rho}(E) dE \quad \text{for } T \rightarrow 0 \quad (3.14)$$

In practice lower and upper limits of integration in (3.10) and (3.14) are both finite, chosen in such a way that, outside of this energetic limits, $\rho(E, \lambda) = 0$ everywhere.

The set of occupation numbers n_{λ} can be calculated now by means of a self-consistent procedure using eqs. (3.6) and (3.10) – (3.14) until the moment when a full convergence with assumed accuracy will be achieved in two consecutive iterations.

The quantities n_{λ} and E_F are fundamental ones for the definition and further calculations of the values reading to the solution of the paradoxes listed above.

4. AN EXPLANATION OF PARADOXES ONTO METALLIC SURFACES

In order to explain the problems listed in Section 2 it seems to be useful to consider still a role of boundary conditions and external polarizations in ECPA.

In the most cases the metallic sample is "embedded" into an external medium (vacuum, gas, another metal, electrolyte solution, electric or magnetic field, etc.) which acts with electrode surface in self-consistent way. It can be generally treated as the boundary condition of the problem.

This condition alters the surfacial matrix elements $K_{\lambda_s \lambda_s}$ in secular equation for $\lambda_s = (1, m, \sigma) = 1$; $\lambda_s = (n, m, \sigma) = n$ by means of adding new element of interaction [2, 28]

$$K_{\lambda_s \lambda_s} \rightarrow K_{\lambda_s \lambda_s} + W_{\lambda_s} = K_{11} + W_1 = K_{nn} + W_n \quad (4.1)$$

Further in the paper the symmetrical boundary conditions will be used everywhere, i.e., $W_1 = W_n = W$.

The second factor influencing significantly on the LDOS is the polarization parameter of a metal caused by and external voltage (denoted as \bar{n}_{pl}). Polarization may be defined as the change of a mean value of occupation number \bar{n}_e in electroneutral metal caused by adding to or removing from an atom the electrons by means of external voltage. It leads, in consequence, to the shift of the Fermi level of the crystal. For one-band approximation (only valence-bands 4s, 5s and 6s for Cu, Ag and Au, respectively) used in this paper, the state $\bar{n}_e = 0.5$ stands for an electroneutrality condition (two possible places of electron with spins up and down in ns^1 state), whereas $0 \leq \bar{n}_{pl} < 0.5$ and $0.5 < \bar{n}_{pl} \leq 1$ denote positive and negative charge of the metal, respectively.

Now we can define in the ECPA terminology two quantities being fundamental for the solution of the above mentioned paradoxes of metallic surfaces. These are the surface charge of the metal Q_s (mentioned earlier in comment to formula (2.1)) and corrected work function ϕ_{cor}^λ [34].

The surface charge is defined as [1, 2, 29, 34]

$$Q_s = -2eS_i \left(\sum_m n_{1,m} - \gamma \cdot \bar{n}_e \right) [\mu C \cdot cm^{-2}] \quad (4.2)$$

where e stands for the electron charge (without sign); S_i represent the number of atoms per square centimeter of a surface of the crystallographic face denoted as i . Of course, for only valence-band approximation $\gamma = 1$ in eq. (4.2).

The corrected work function has been derived [1, 34] by means of the expansion of the occupation number n_λ into Taylor's series. Taking also the boundary conditions into account, the final formula for the work function is the following:

$$\phi_{cor}^\lambda = -(E_F + \Delta E_F + E_F^\lambda) = -E_F - \Delta E_F - I_\lambda (\bar{n}_e - n_\lambda) \quad (4.3)$$

where the second term of the right-hand side of eq. (4.3) is connected with the boundary condition and is always equal to zero for vacuum. The third term in (4.3), i.e., $E_p^\lambda = I_\lambda (\bar{n}_e - n_\lambda)$, describes the surface potential barrier and is di-

rectly related to the so-called local work function which can be directly measured by means of PAX method [9].

Let us now to come back to the list of problems reported in Section 2.

All the paradoxes can be solved in the framework of GFM and ECPA in the following way:

Ad 1.

In Table 2 the calculated values of the work function ϕ_{cor}^λ have been shown for Cu, Ag and Au single crystals and compared with the same faces measured in experiment, i.e. for (100), (110) and (111) Miller's faces. The calculations for Cu have been also compared with other theoretical methods [11, 33]. It follows from a comparison between calculations and averaged values of the measured work function from Table 1 that the use of the ECPA gives better agreement with experiment than EHT (Extended Hückel Theory) [33] applied by Dempsey and Kleinman [35] and much better than Lang and Kohn's (LK) method [11]. The agreement is the best if an average experimental value of the work function was obtained from reasonable numbers of different measurements (five and six cases for Cu(100) and Ag(100) in Table 1, respectively). In other cases, particularly when only two different experimental results are available such a comparison with experiment is rather poor.

So generally one can state that GFM and ECPA reproduce quite reasonable the corrected work function ϕ_{cor}^λ for noble metal monocrystals and one can presumably expect that these calculated values are very close to the average experimental data for other metals provided that a large enough number of measurements was carried out.

Table 2. Corrected work function ϕ_{cor}^λ calculated for Cu, Ag and Au single crystals of (100), (110), (111) faces. In the case of Cu a comparison with other calculations is also shown

$\phi_{cor}^\lambda(Cu)$ [eV]					
(100)		(110)		(111)	
4.753 ^a	ECPA	4.508 ^a	ECPA	4.876 ^a	ECPA
4.406 ^b	EHT	4.410 ^b	EHT	4.379 ^b	EHT
3.794 ⁱ	LK	3.549 ⁱ	LK	3.903 ⁱ	LK
$\phi_{cor}^\lambda(Ag)$ [eV]					
4.645 ^a	ECPA	4.483 ^a	ECPA	4.761 ^a	ECPA
$\phi_{cor}^\lambda(Au)$ [eV]					
5.531 ^a	ECPA	5.423 ^a	ECPA	5.674 ^a	ECPA

a. Ref. [1], b. Ref. [33], i. Ref. [11]

Moreover, in all the calculations analysed above, the work function changes in the direction $\phi_{Me}^{(111)} > \phi_{Me}^{(100)} > \phi_{Me}^{(110)}$, (with $Me = Cu, Ag, Au$) what remains in quite good correlation with the most dense surface of (111) face when the highest surface potential barrier occurs in eq. (4.3) and the most open in the case of (110) (the smallest barrier). The same tendency appears in Lang-Kohn's results [11] in Table 2 although they remain very far from experimental data.

In fact, this tendency is only confirmed experimentally for Cu single crystals. Unfortunately, for Ag and, more particularly, for Au there are big discrepancies in the experimental data which do not allow us to analyse it.

Therefore we have shown that the problem of large deviations in the experimental data of the work function can be at least partially avoided by the use of GFM calculations. But, of course, this conclusion still demands an experimental confirmation for other metals.

Ad 2.

The paradox disappears immediately if we take the corrected work function eq. (4.3) instead of the classical one into account. We must put $\Delta E_F = 0$ in (4.3) because there are no boundary conditions influencing a crystal in a vacuum. Then it is evident that the surface barrier of the potential, i.e. $\Delta E_F^\lambda = I_\lambda (\bar{n}_e - n_\lambda)$ for a fixed state of a bulk charge ($\bar{n}_e = 0.5$ assuming that the measurements are carried out for electroneutrality conditions) depends only on n_λ distribution in the crystal. The value of the Coulomb integral I_λ is assumed to be constant for the nearest neighbours interactions in ECPA [1, 2]. For instance, $I_\lambda^{Cu} = I^{Cu} = 0.4 \text{ Ry}$ [1, 28].

In paper [28] there was calculated a distribution of an occupation number along a sample thickness. For Cu(100) and Cu(110) the shape of n_λ distribution is completely different. It means that strong anisotropy of the n_λ distribution takes place also in one sample of a single crystal with different faces. So the barrier ΔE_F^λ must be different depending on crystallographic axis of the monocrystals although the Fermi level is only one.

Ad 3.

In the light of eq. (4.3) this paradox consists in misunderstanding about an assumption $\varphi_{pzc}^{Me} = 0$.

In classical electrochemistry the *pzc* is understood as a state of compensation of a surface charge of an electrode to the zero's value $Q_s = 0$ (cf. comment follows eq. (2.1)). However, it does not mean that a metallic phase lost its electric charge in this case.

The state with $Q_s = 0$ must be treated only as a disappearance of the surface potential barrier, so then $\bar{n}_e = n_\lambda = n_1$ in eq. (4.3). But such a compensation of surface barrier can be only possible by means of an external polarization.

In the electroneutral state of a metal the surface barrier is equal to $\Delta n = I(0.5 - n_1)$ and then the polarization $\bar{n}_{pl} = -\Delta n$ is needed to compensate such a barrier. However, it leads to the bulk charge different from electroneutrality, so the metallic phase has to be charged and, in consequence, $\varphi_{pzc}^{Me} \neq 0$.

Therefore, eq. (2.1) is correct and the paradox connected with a contact potential also disappears.

Ad 4.

There are only few attempts in electrochemical literature of the last twenty years to explain the unusual phenomenon of the ionic specific adsorption. The most important theoretical papers [35–39] try to explain this process as a kind of chemisorption with covalent bonds between metal and adsorbed ions. These bonds seem to be created by means of a charge transfer from a valence band of the metal to the partially empty d-bands of halides Cl^- , Br^- , I^- . Needless to say that such an explanation takes only a final step of the process into account when desolvated ions are already chemisorbed on the metal surface.

None of the theories gives an answer for the fundamental question of what is the reason that two species (electrode surface and ions) with the same positive or negative charges attract themselves seemingly against the laws of electrostatics.

An explanation of this question has been provided by means of surface charge calculations (eq. (4.2)) as a function of boundary condition W and external polarization \bar{n}_{pl} .

Table 3, taken from [2], reports the function $Q_s = f(W, \bar{n}_{pl})$ for Cu, Ag and Au single crystals of the face (100). For other crystallographic faces the function has similar character [2].

There are two regions in Table 3, near the pzc line (from the upper left corner to the lower right one), in which the surface and bulk charges of the metal reveal the reverse signs. We can see that for $\bar{n}_{pl} = 0.3, 0.4$ $Q_s < 0$ and for $\bar{n}_{pl} = 0.6, 0.7$ $Q_s > 0$.

From the results analysed above one can conclude that a long-range Coulombic attraction between the positive bulk of the metal and an anion which is coming towards the negative crystal surface determines mainly the nature of the specific adsorption forces. Charge transfer is the final step of the process. Similar mechanism takes place in the case of the cation adsorption on positively charged electrode surface.

Table 3. Surface charge Q_s [$\mu\text{C}/\text{cm}^2$] as a function of w_1 (in Ry) and \bar{n}_{pl} calculated by means of ECPA for Ag(100) and Au(100) single crystals. The values of Q_s for Cu are taken from [1]

$W(\text{Ry})$		$\bar{n}_{pl} = 0.3$	$\bar{n}_{pl} = 0.4$	$\bar{n}_{pl} = 0.5$	$\bar{n}_{pl} = 0.6$	$\bar{n}_{pl} = 0.7$
-0.8	Cu	-27.2	-108.5	-172.5	-209.6	-22.90
	Ag	-7.3	-64.6	-107.7	-141.0	-165.4
	Au	1.8	-48.3	-88.3	-120.8	-149.9
-0.6	Cu	-1.0	-78.5	-139.4	-183.3	-213.0
	Ag	11.2	-42.8	-85.5	-121.3	-149.9
	Au	20.2	-27.9	-68.6	-103.2	-135.0
-0.4	Cu	30.8	-41.6	-99.7	-150.2	-191.0
	Ag	32.8	-18.7	-61.3	-98.9	-130.6
	Au	39.5	-6.9	-48.0	-84.1	-119.2
-0.2	Cu	65.5	1.9	-58.0	-110.2	-153.8
	Ag	54.3	8.0	-35.4	-73.6	-108.7
	Au	59.5	15.0	-25.9	-64.4	-101.8
0.0	Cu	101.3	46.6	-8.1	-63.9	-112.1
	Ag	77.1	34.5	-7.7	-46.8	-84.8
	Au	80.2	36.7	-4.3	-43.9	-83.9
+0.2	Cu	135.0	90.4	39.2	-13.6	-68.5
	Ag	100.0	51.0	20.0	-19.4	-59.7
	Au	100.6	58.5	17.9	-23.5	-65.7
+0.4	Cu	165.5	133.1	88.6	36.6	-22.5
	Ag	120.2	88.1	48.4	8.1	-34.7
	Au	119.6	80.0	39.5	-2.8	-47.3
+0.6	Cu	190.5	165.4	134.7	84.4	22.5
	Ag	138.0	111.9	77.3	35.0	-10.6
	Au	137.3	103.0	61.5	17.8	-29.6
+0.8	Cu	207.5	188.5	170.0	129.6	59.2
	Ag	152.6	132.6	104.0	61.2	12.5
	Au	151.8	123.8	84.0	38.2	11.4

So an explanation of this very strange phenomenon turned out to be very trivial. The superposition of the opposite charges on the surface and in the bulk

of the metal produces an electric field attracting ions towards the electrode. There is no contradictions in such a behaviour with respect to the classical laws of electrostatics.

In Figure 1, taken from [40], the mechanism of specific adsorption consisting of three steps is presented .

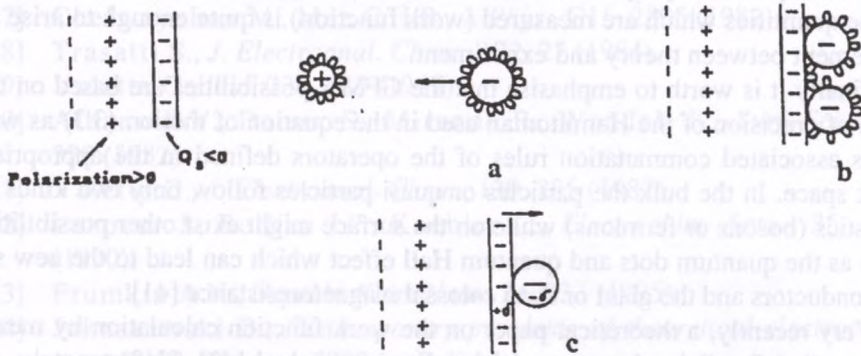


Figure 1. The three-steps mechanism of the specific absorption of anions following from the ECPA calculations

- Generation of the reverse signed charges in the bulk of metal and on the surface by means of an external polarization
- Electrostatical attraction of anions by positively charged bulk - adsorption on the surface
- Electron transfer of valence electrons from the electrode to the empty d orbitals of adsorbed anions

5. CONCLUSIONS

In this paper the possibilities of the Green Function Method and Extended Coherent Potential Approximation of the explanation of some unusual phenomena in some experiments on metallic surfaces have been reported.

In practice, this is mainly connected with the work function measurements of noble metal single crystals. In this case, when good theoretical results are achieved, it is possible to take advantage for reproducing of reasonable tendencies in the behaviour of the work function as the "vicarious experiment".

On the other hand the power of this theoretical method consists in an explanation of the effects which presumably could be never fully understood only on the basis of the experiment regardless of the technical level of the measurements. It mainly concerns the ionic specific adsorption where an experimental separation of the electrode charge between bulk and surface charge of metal is practically impossible. The only suitable experimental values are the potential of an electrode (measured with respect to certain reference electrode) and its

surface charge. As it was shown the GFM and ECPA are able to make such a separation in quite a natural way.

There are also other kinds of controversial effects which may be qualified, in fact, as artificial difficulties. For instance, the dependence of the work function of a single crystal on the Miller's indices of its face as well as the paradox of contact potential properties. In this case only the good theoretical definition of the quantities which are measured (work function) is quite enough to arise an agreement between theory and experiment.

Finally it is worth to emphasise that the GFM's possibilities are based on the level of precision of the Hamiltonian used in the equation of motion (3.3) as well as its associated commutation rules of the operators defined in the appropriate Fock space. In the bulk the particles or quasi-particles follow only two kinds of statistics (bosons or fermions) while on the surface might exist other possibilities such as the quantum dots and quantum Hall effect which can lead to the new superconductors and the giant or even colossal magnetoresistance [41].

Very recently, a theoretical paper on the work function calculation by means of so-called Brodie's plasma model has been published [42]. Unfortunately, although a good agreement of the theoretical results with experimental data (in vacuum) for many polycrystalline metals was achieved in this paper there are no boundary conditions taken into account.

Acknowledgement. The author is greatly indebted to Prof. D. Baldomir for many valuable comments and to the authorities of the University of Santiago de Compostela (Spain) for a partial financial support of the paper.

6. REFERENCES

- [1] Romanowski S., *Phys. Stat. Sol. (b)*, 145, 467 (1998).
- [2] Romanowski S., *Polish J. Chem.*, 67, 729 (1993).
- [3] Rowe J.E., Smith N.V., *Phys. Rev.*, B10, 3207 (1974).
- [4] Garland P.O., Berge S., Slagsvold B.J., *Phys. Norv.*, 7, 39 (1973); *Phys. Rev. Lett.*, 28, 738 (1972).
- [5] Samsonov G.V. (Ed.), *Svoista Elementov, Spravochnik*, vol. 1, Metallurgiya, Moskva 1976, p. 314 (in Russian).
- [6] Tibbetts G.G., Burkstrand J.M., *J. Ch. Tracy, Phys. Rev.*, B15, 3652 (1977).
- [7] Haas G.A., Thomas R.E., *J. Appl. Phys.*, 48, 48 (1977).
- [8] Stranger R.W., Mackie W., Swanson L.W., *Surf. Sci.*, 34, 225 (1973).
- [9] Wandelt K., *J. Vac. Sci. Technol.*, A2, 802 (1984).
- [10] Trasatti S., *J. Electroanal. Chem.*, 33, 351 (1971).

- [11] Lang D.N., Kohn W., *Phys. Rev.*, B3, 1215 (1971).
- [12] Farnsworth H.E., Winch R.P., *Phys. Rev.*, 58, 812 (1940).
- [13] Clarke N.E., Farnsworth H.E., *ibid.* 85, 484 (1952).
- [14] Dweydari A.W., Mee C.H.B., *Phys. Stat. Sol.*, (a), 17, 247 (1973).
- [15] Michaelson H.B., *J. Appl. Phys.*, 48, 4729 (1977).
- [16] Anderson P.A., *Phys. Rev.*, 59, 1034 (1941).
- [17] Chelwayohan M., Mee C.H.B., *J. Phys.*, C15, 2305 (1982).
- [18] Trasatti S., *J. Electroanal. Chem.*, 172, 27 (1984).
- [19] Valette G., *ibid.*, 230, 189 (1987).
- [20] Albano E.V., Daiser S., Miranda R., Wandelt K., *Surf. Sci.*, 114, 320 (1982).
- [21] Valette G., *J. Electroanal. Chem.*, 139, 285 (1982).
- [22] Lecoœur J., Bellier J.P., Koehler C., *Electrochim. Acta*, 35, 1383 (1990).
- [23] Frumkin A.N., *Uspekhi Khim Nauk*, 24, 933 (1995).
- [24] Jakuszcwski B., *Contemporary problems of theoretical electrochemistry*, PWN, Warsaw, 1970 (in Polish).
- [25] Kortüm G., *Electrochemistry*, PWN, Warsaw 1970 (Polish translation).
- [26] Stern O., *Z. Elektrochem.*, 30, 508 (1924).
- [27] Frumkin A.N., *Z. Phys. Chem.*, 103, 43 (1923), 55; 109, 34 (1924).
- [28] Wojtczak L., Romanowski S., Stasiak W., Mrygoń B., *Czech. J. Phys.*, B31, 1024 (1981).
- [29] Romanowski S., Stasiak W., Wojtczak L., *Electrochim. Acta*, 27, 511 (1982).
- [30] Zubarev D.N., *Usp. Fiz. Nauk*, 71, 71 (1960); *Sov. Phys. - Usp.*, 3, 320 (1960).
- [31] Tahir-Khelli R.A., ter Haar D., *Phys. Rev.*, 127, 88 (1962), 95; 130, 108 (1963).
- [32] Tahir-Khelli R.A., *Phys. Rev.*, 132, 689 (1963).
- [33] Mattuck R.D., *A Guide to Feynmann Diagrams*, Mc Graw - Hill, New York, 1976.
- [34] Romanowski S., Wojtczak L., *Green Functions in Electrochemistry*, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1997.
- [35] Dempsey D.G., Kleinman L., *Phys. Rev.*, B16, 5356 (1977).
- [36] Ying S.C., Smith J.R., Kohn W., *Phys. Rev.*, B11, 1485 (1975).
- [37] Bell B., Madhukar A., *ibid.*, B14, 4281 (1976).
- [38] Lorentz W., Handschuh M., *Electrochim. Acta* 25, 293 (1980).
- [39] Kuznetsov A., Reinhold J., Lorenz W., *ibid.*, 31, 928 (1986).
- [40] Romanowski S., *Polish J. Chem.*, 69, 529 (1995).

- [41] Rivas J., Sánchez R.D., Fondado A., Izco C., Garcia-Bastida A.J., Garcia-Otero J., Mira J., Baldomir D., Gonzalez A., Lado I., Lopez-Quintela M.A., Oseroff S.B., *J. Appl. Phys.*, 76, 6564 (1994).
- [42] Hałas S., Durakiewicz T., *J. Phys.: Condensed Matter*, 10, 10815 (1998).

CURRICULUM VITAE



Prof. Stanisław Romanowski. Born in Poland in 1947. Graduated from University of Łódź, Łódź, in 1970. Received his Ph. D. degree in chemistry also at Łódź University, Faculty of Mathematics, Physics and Chemistry, in 1975. Dr. Sc. degree (habilitation) received from Warsaw University in 1990. Since 1992 has been appointed on the position of Associate Professor and Head of Theoretical Chemistry Department. Full Professor position received in 1996. His main field of interest concerns the theoretical description of the various aspects of interfacial and physicochemical properties, particularly chemisorption and catalysis, in thin metallic films, metallic and molecular clusters and biological membranes mainly by means of the Green Functions Method and

Extended Coherent Potential Approximation. He published over 100 papers and took part in many conferences.

Together with professor L. Wojtczak (Solid State Physics Department, University of Łódź) he published the monograph "Green Functions in Electrochemistry" (Kluwer Academic Publishers, 1997). For scientific achievements he was awarded two times by Polish Ministry of Education and six times by the Rector of Łódź University. He cooperates with many valuable groups in the world and makes a lot of short- and long-term visits to Friedrich-Schiller University (Jena, Germany), Charles University (Prague, Czech Republic), University of Santiago de Compostela (Spain), University of Porto (Porto, Portugal), Claude-Bernard University (Lyon, France) and University of Utrecht (The Netherlands).