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A. P. FEDCHUK, A. V. GLUSHKOV, YA. I. LEPIKH

I. I. Mechnikov Odessa National University,
Odessa State Environmental University

COMBINED ELECTRODYNAMICAL AND QUANTUM — CHEMICAL APPROACHES TO MODELLING THE CATALYTIC ACTIVITY OF METALS, METAL ALLOYS AND SEMICONDUCTORS

The catalytic activity estimating of the metals, binary metallic alloys and semiconductor materials is considered within the combined quantum mechanical and electrodynamics approach in the electron theory of catalysis.

INTRODUCTION

A study of catalytic activity for metals, metallic alloys and semiconductors is of a great importance for different practical applications, for example, during the elaboration of electrochemical solid-state energy sources, planning the efficacy of semiconductor sensors and naturally developing advanced chemical industry technologies etc [1–19]. It is known [2,3,8–10], that the components concentration's change in metallic alloys could result in drastic variation of catalytic activity as well as of electrochemical properties. The same effect is characteristic for semiconductors when some impurities are introduced inside the pure material. Generally speaking catalysis on semiconductors is more widespread phenomenon that it seems at first sight. Really, a majority of metals is usually covered by semiconductor film [5,7]. In the contact with pure surface the oxygen, hydrogen and nitrogen are quickly absorbed by a surface even under low temperatures. The attempts of comprehensive quantitative description of the metal-like systems (metallic alloys, heavily doped semiconductors) electronic structure including the description of processes on electrodes' surfaces of the electrochemical solid-state energy sources and naturally electrochemical and catalytic processes have been undertaken in a number of papers (see refs.in [1–26]).

Naturally a mechanism of heterogeneous catalytic process can be understood under obligatorily treating intermediate stages, namely, stages of adsorption and desorption [1,2]. Generally speaking, as any chemical process, the heterogeneous catalytic process has the electron mechanism in the end. Any heterogeneous reaction can be interpreted as the process based on radical mechanism. Radicals and ion-radicals appear on the surface under chemosorption and provide the radical mechanism of the heterogeneous reactions. But, naturally it doesn't mean that non-radical mechanisms are excluded. The catalytic reaction path through one-electron charged intermediates (ion-radicals) is not the main mechanism in heterogeneous catalysis but, of course, is possible in some special cases. As example, above the cited approaches to adsorption and catalysis one could mention a group of the conceptual models which are based on using the density functional formalism [14–16]. There is a great number of papers (see [1–5, 16–19,26]), where the catalysis and electrochemical problems are considered within *ab initio* quantum chemistry methods. Using these methods allowed to get very useful information about processes considered, however, some quite important moments of the physical and chemical nature of these processes often remain up to known degree veiled. Besides, one could mention well known calculation difficulties of description of the catalysis processes within *ab initio* quantum chemistry methods [1–5,8–13]. Simplification of the corresponding calculation schemes leads to a loss of the quantitative accuracy for phenomenon description and, generally saying, to qualitatively invalid conclusions in many cases. Naturally, a great interest attracts a development of more physical and calculationally economical model approaches to a catalysis problem. In this sense, as alternative, one could indicate more simplified (from the calculation point of view), but quite effective electrodynamical and quantum-chemical modeling models for description of the catalytic processes (see [8–10, 20–22]). Above cited approaches it should be separately mentioned a group of papers, which are devoted to simple homogeneous phone models by Lang-Kohn, Bardeen, Theophilou, Vannimenus-Budd, Norskov-Lundqvist-Hjelmberg et al and base on an conception of the Kohn-Sham density functional theory (look a detailed review of the corresponding models and results in refs.[1–5,15–19,26]).

At present time there is a great number of experimental papers (see refs. [1–3,5–7]), where it has been shown that the electronic processes in metallic and semiconductor materials provide their electric, optical and magnetic properties and simultaneously the catalytic ones. Though now it is clear that activation of reagents in heterogeneous catalysis is associated, as a common rule, with surface adsorption but not with deep penetration into the solid matrix. Nevertheless, there is a certain parallelism between electronic and catalytic properties of the material. To find a link between these two groups of properties is a main aim of the electron theory of catalysis. Naturally here one could mention the pioneering papers in a field of electron theory of catalysis by Hauffe et al (Germany), Boudart, Voltz, Taylor et al (USA), Germain , Claudel et al (France), Pisarzhevsky, Wolkenstein, Lyashenko, Terenin, Lidorenko (USSR) et al (see reviews [1–

10,26]). On the one hand, the electron theory of catalysis is based on the modern theory of chemical bond, but on the other hand its fundament is modern theory of solids. It is well known that the theory of chemical bond has to do with the transformations of molecules on the surface and the theory of solids treats the processes inside material. The theory of chemisorption and heterogeneous catalysis has to do with the transformations of the surface molecules each connecting the crystal and forming a united system. As a rule, the electron theory of catalysis like other modern variants of the catalysis theory are not alternative and do not compete with each other. As a matter of fact, these theories describe different aspects of the process and surely differ only by the conceptual approach to the problem. Here we consider a problem of catalytic activity definition for metals, binary metallic alloys and semiconductor materials and present the basises of a new approach to electronic theory of catalysis, which is based on using the electrodynamical and quantum-mechanical models [8–10, 20–22].

1. LINK BETWEEN THE FERMI LEVEL POSITIONS ON SURFACE AND INSIDE THE MATERIAL

Now it is obvious that the catalytic properties of metals and semiconductors are directly connected with electronic processes which occur inside and on the surface of the materials and provide these properties in the end. The role of catalyst results in generation of the surface radicals, which are arisen due to the free valences of catalyst on the surface and forming during reaction. Naturally the free valences on the surface exhaust very slowly as the valences supply on the surface from the volume. Appearance of the radical or ion-radical forms is connected with a role of the crystal lattice free electrons and holes during chemosorption. Say, a semiconductor in the catalytic process has a role not only inert layer (where the chemical reaction runs) but as an active e participant of the process too. More over it can by one of the components in the intermediate stages of the reaction. In any case, the catalytic properties of semiconductor are defined by their nature and electron structure and a mechanism of the catalytic action is in definite degree inside the material too. One could mention that introduction of the impurities inside the semiconductor changes its catalytic properties [5,7]. More over, now it is well established a certain correlation between the material electroconductivity, the output work (forbidden band width in the energy spectrum of semiconductor) and its catalytic properties (the adsorption ability of material too). An effect of the light (laser radiation) on semiconductor leads to internal photoelectric effect and changing its adsorption and catalytic activity. One could note that the Fermi level position defines the adsorption and catalytic activity of the surface in relation to molecules of the given kind under other equal conditions. Naturally, the Fermi level position on the surface is dependent upon its position inside the crystal. Surely there is a direct link between the surface and bulk properties of materials. The factors, which shift the Fermi level inside, say, in the semiconductor, influence on its surface properties too. Naturally, special case is a case of the large density of the surface states.

The chemosorption ability of the surface, a degree of its charging, a reactive ability of the chemisorbed particles etc are directly defined by the Fermi level position on the surface of crystal (say, a distance between the Fermi level and the conductivity band bottom: E_F^s). Let us denote the position of the Fermi level inside the crystal as E_F^v . The direct link between the values E_F^s and E_F^v can be obtained from the condition of the electric neutrality of crystal:

$$\sigma + \int_0^\infty \rho(x)dx = 0\,, \qquad (1)$$

where σ is a density of the surface charge and ρ is a density of the volume charge in the plane, say x (the material occupies the semispace x>0). Further one could write as follows:

$$\sigma = \sigma(P,T;E_F^s)\,, \qquad (2)$$

where P is a pressure, T is a temperature. Naturally, if all surface charge is provided only by the chemisorbed particles (say, the same kind), then the expression for σ has more complicated form (see refs. [2,5,7]). The second item in Eq. (1) is the function of E_F^s and E_F^v :

$$\int_0^\infty \rho(x)dx = R(T;E_F^s;E_F^v)\,. \qquad (3)$$

In result one can write the obvious relationship, which gives a direct link between E_F^s and E_F^v :

$$\sigma(P,T;E_F^s) + R(T;E_F^s;E_F^v) = 0 \text{ or } E_F^s = f(P;T;E_F^v) \quad (4)$$

This equation establishes correlation between the surface and bulky properties of the material (semiconductor etc.). Let us further to introduce new advanced electrodynamical and quantum-mechanical models in the electron theory of catalysis for metals, metal alloys and semiconductors.

2. ELECTRODYNAMICAL AND QUANTUM-MECHANICAL APPROACHES FOR METALS AND METALLIC ALLOYS

It is well known [23,24] that the electron structure of a metallic system in the simple approximation can be approximated by a set of isotropic s-d energy bands. The static dielectric permeability is represented as follows:

$$\varepsilon = 1 + \varepsilon_{ss} + \varepsilon_{dd} + \varepsilon_{sd} + \varepsilon_{ds}\,, \qquad (5)$$

where ε *(ij)* describes the contribution into ε due to the i-j transitions. In approximation of the free electrons the expression for ε_{ss} looks as:

$$\varepsilon_{ss} = 2\pi\nu_s(E_F)k^{-2}\{1 + [4(k_F^s)^2 - -k^2]\ln\left|(2k_F^s + k)/2k_F^s - k)\right|/4k_F^s k\}. \qquad (6)$$

where $k=q\cdot a_B$, q is the wave number, a_B is the Bohr radius, $q_F = (3\pi^2 z_i/\Omega)^{1/3}$; z_i is a number of electrons in "i" band; $\nu_i(E_F) = N_i(E_F)a_B^2 e$, $N_i(E_F)$ is a density of states on the Fermi surface in "i" band. The corresponding expression for ε_{dd} is as follows:

$$\varepsilon_{dd} = 2\pi\nu_d(E_F)k^{-2}\left|M_{dd}\right|^2\{1+[4(k_F^d)^2 - -k^2]\ln\left|(2k_F^d+k)/2k_F^d-k)\right|/4k_F^dk\} \quad (7)$$

Here the matrix element M_{dd} is defined by the superposition of the wave functions for d electrons. The contribution ε *(ds)* is important only for systems containing the precious metals. This contribution is defined as follows:

$$\mathring{a}_{ds} = [2m_sk_de^2f_c/\eth h^2k^2]\times$$
$$\times\{1+[4(k_d)^2-k^2]\ln\left|(2k_d+k)/2k_d-k)\right|/4k_dk\}. \quad (8)$$

where m_s is the effective mass of electron in the conductivity band; k_d, f_c are the numeral parameters [23,24]. Usually the contribution ε_{ds} in Eq. (5) for transition metals is about several percents. The effective potential, which imitates an effect of metallic potential field on the hydrogen atom (for process $H=H^+ + e^-$) is defined as follows:

$$\ddot{O}(r) = -\frac{2e^2}{\pi r}\int_0^\infty \frac{\sin kr}{k\varepsilon(k)}dk \quad (9)$$

Further it is supposed that a problem considered has the spherical symmetry and crystal potential is fully screened by the conductivity electrons. Substitution of (5) to (9) leads to the expression:

$$\Phi\,(r) = -(e^2a/r)\exp[-\alpha R]\cos[\alpha R] \quad (10)$$

where

$$\alpha = [\pi^{-1}12(k_F^s)^2]^{-1/4}\times$$
$$\times\{\nu_s(E_F)+(k_F^d/k_F^s)\nu_d(E_F)+f_c(k_F^d/k_F^s)^2\nu_s(E_F)\}^{1/4},$$
$$R = 2q_F^sr\ ,\ a = (k_F^s)^{-1}$$

Further the key idea is as follows. We find the numerical solution of the Schrodinger equation for the hydrogen atom in a field $\Phi(r)$ and obtain the corresponding spectrum of states, which could be continual or discrete in dependence upon the critical parameter $\zeta^{-1} = \alpha/a$ [8–10]. Such a problem for the potential (10) has been in details considered by Bonch-Bruevich and Glasko, Marinov and Popov and reconsidered by Lidorenko etal (look the reviews in [8–10,23,25,26]). In fig.1 the corresponding parameters α and a for a number of metals are presented [8]. The spectrum is continual, if $\zeta<0{,}362$ and the corresponding material is a catalyst for the hydrogen ionization [27,28] reaction.

If $\zeta>\zeta o$, the spectrum is discrete (metal or metal alloy does not demonstrate catalytic activity for cited reaction). In refs. [9,10] such an approach has been successfully applied to studying the catalytic properties of the metals in relation to reaction of the hydrogen ionization and obtained a good agreement with the known experimental data [1,5–7].

Let us consider further more interesting case of the binary metallic alloys and present the corresponding model. In the binary metallic alloy the Fermi level position E_F as well as the corresponding state density $\nu(E_F)$, accompanied with electronic structure parameters α and a are changing under change of the admixture concentration c. To define the cited changing it is quite correct to use the Thomas-Fermi approach [23]. We suppose that the admixture's atoms volume has the spherical form. The radius R_c is connected with concentration by the formula:

$$(qR_c)^{-3} = (qr_s)^{-3}c\ ,$$

where r_s — the electron gas characteristic parameter. Let us remind that $(qr_s)^{-3}$~0.01–0.05 for the typical metals. For screened potential $V(r)$ near the admixture (if $|\Delta E_F - V| < E_F$), the corresponding Poisson equation looks as:

$$\Delta V(r) = q^2\{V(r) - \Delta E_F\} \quad (11)$$

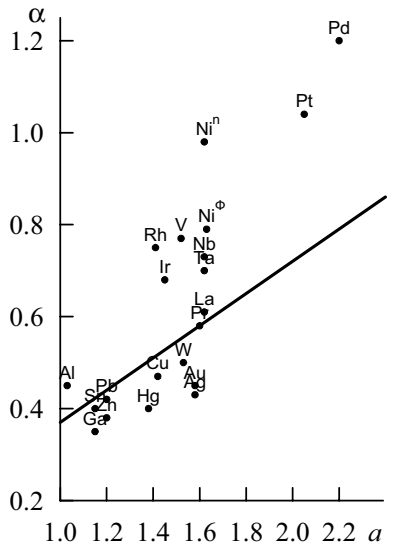

Fig.1. A diagram of parameters α, a for a number of metals

Elementary solution of equation (7) with the boundary conditions:

$$(dV/dr)_{Rc}=0\ ,\ V(R_c)=0,\ V\to -Z_v e/r\ ,\ r\to 0$$

(here Z_v is a difference of the components valences) is defined as:

$$V(r,R_c) - \Delta E_F = [-Z_v e/r]\{qR_c ch[q(R_c-r)] + +sh[q(R_c-r)]\}/[qR_c ch(qR_c)+sh(qR_c)] \quad (12)$$

Second boundary condition provides the expression for Fermi level shift in dependence upon the concentration c:

$$\Delta E_F = Z_v e^2 q/[qR_c ch(qR_c)+sh(qR_c)]\ . \quad (13)$$

So, for the binary metallic alloy, the value $\nu(E_F)$ is substituted by the value $\nu(E_F)=\nu(E_F)+\Delta\nu(E_F)$ [9]. In fact the parameters, which define the catalytic activity for metallic compounds, are directly dependent upon the components concentration. As example of the models application for definition of the catalytic activity of metallic alloy in relation of the hydrogen ionization reaction let us consider the alloy Ni-Cu. In fig.2 a dependence of the Fermi level shift ΔE_F in the alloy Ni-Cu upon the Cu concentration c (in atomic units) is presented and calculated according to Eq. (13).

The estimate shows that the alloy Ni-Cu with a small concentration of Cu (till 16%) is a good catalyst for the hydrogen ionization reaction, however situation is changed in the opposite direction with a growth of ζ. This is in acceptable agreement with the experimental data [1,5–7].

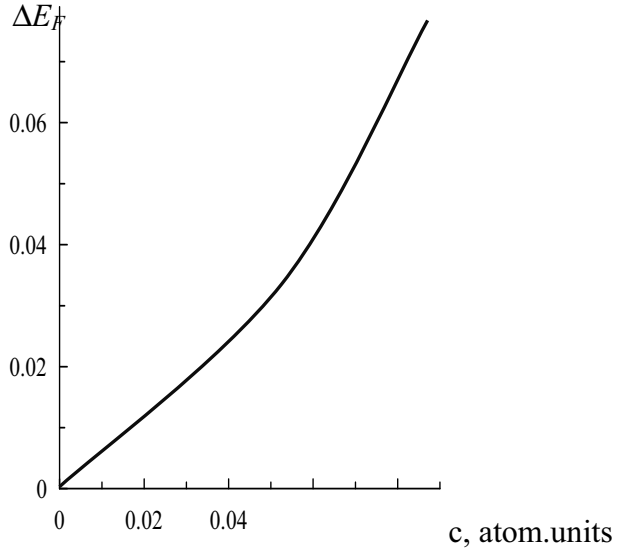

Fig. 2. A dependence of the Fermi level shift ΔE_F in the alloy Ni-Cu upon Cu concentration c (in atomic units) [9]

3. ELECTRODYNAMICAL AND QUANTUM-MECHANICAL MODEL FOR SEMICONDUCTOR

Now, we consider similar to above described one approach to description of catalytic processes on semiconductors and determine a connection between the semiconductors electron structure parameters and their catalytic activity in the relation to simple model reaction of the $H = H^+ + e$ type. Above proposed model is transformed through the following way. In order to describe the electronic structure of semiconductor let us use the known Resta model [39] in the Thomas-Fermi theory for semiconductors (see [8]). We consider the model semiconductor as the electron gas with non-perturbed density n_0. The corresponding Poisson equation is as follows:

$$V(r) = q\,\{V(r) - A\},$$

where $q = 4k_F / \pi a_B$ and A is a constant. Let us suppose that there is the finite screening radius R near the probing charge Z_e and $n(R) = n_0$. Then a constant A is equal $V(R)$. Beyond the radius R the point charge Z_e potential is equal to:

$$V(R) = -Ze^2 / [\varepsilon(0)\, r],\ r > R,$$

where $\varepsilon(0)$ is a static dielectric permeability. Independent solution for the Poisson equation have the following form: $Ze^2 \exp[qr]/r$. So, the general expression for potential energy is:

$$V(r) = -Ze^2 / r\,\{C_1 \exp(-qr) + C_2 \exp(qr)\} + A,\ r < R \qquad (14)$$

Taking into account the continuity condition, boundary condition ($V(r) \to 0,\ r \to 0$), the expression for V (r) looks as follows:

$$V(r) = -\{Ze^2 / r\}\{\mathrm{sh}[q(R-r)] / \mathrm{sh}[qR] - Ze / \varepsilon(0)R,\ r < R \qquad (15)$$

The continuity condition for electric field under $r = R$ allows to define a link between the screening parameter and $\varepsilon(0)$ as:

$$\varepsilon(0) = \mathrm{sh}[qR]/qR.$$

If $\varepsilon(0) > 1$, R is equal to finite value comparable with distance to the nearest atoms (for example, for NiO, CuO, ZnO, ZnS, ZnTe semiconductors this value is 4.8–6.1E) [6]. The Schrodinger equation solution with potential (15) allows to define the corresponding energy spectrum in dependence upon the parameters $\varepsilon(0)$, k_F (E_F) and then to find a link between the semiconductors electron structure parameters and their catalytic activity likely above described approach. Let us note here that a problem of definition of the hydrogen atom state energies in the static screened potential (in particular, the potential of the Debye type) approximation is well known in a theory of plasma and considered in many papers (see [23–26]). However, the potential (15) in this task is firstly considered by us. As an example of the approach application, we have carried out an estimate of the catalytic activity for the CuO, ZnO semiconductors in the hydrogen ionization (oxidation) reaction. Our estimate (the considered case for semiconductors is corresponding to the numerical estimate $\zeta < \zeta o$ for metals) shows that the ground level of the hydrogen atom in a case of the CuO and ZnO semiconductors is in a continuum, i.e. the known Mott effect has a place here [30]. In their turn this means that the the CuO and ZnO semiconductors are good catalysts for the hydrogen ionization reaction. This is in an excellent agreement with the known experimental data [1,5–7]. We believe that the simplified model for semiconductors may be naturally improved, but the key idea remains the same.

CONCLUSIONS

We presented the combined approach to estimating the catalytic activity of the metallic and semiconductor materials in the electron theory of catalysis, which is based on the combined quantum-mechanical and electrodynamical models. We have shown that even in the zeroth approximation very useful information about catalytic activity of the studied materials for some model reactions can be obtained within quite simple and physically reasonable approach. The catalytic properties of the semiconductor and metallic materials are directly connected with electronic processes which occur inside and on the surface of the materials and provide these properties in the end. In fact, our approach can be considered as an effective zeroth approximation in the electron theory of catalysis. It can also provide an evaluation of the charge exchange processes on a surface and, in such a way, could be used for the semiconductor sensors efficiency prediction for the given type reactions. Naturally, some additional factors such as the electrolyte influence, surface effects, the electrodes potential, the electrolyte type, electron concentration in the surface layer and many others [1–10] should be taken into account. Let us underline that very important and positive feature of the approach is clear quantitative physical correlation

between the electron structure parameters for metallic and semiconductor materials and their catalytic properties. On the other hand, naturally, the presented approach is the semi-quantitative one in more degree and surely can not provide a full quantitative description of the catalysis properties for any substances in relation to any reactions. More over it would be very useful further to link the elaborating approach with recent theory of the catalysis on the metals and semiconductors (not only by means of the eq. (3,4) and similar sufficiently complicated relationships) in order to provide more consistent, combined quantitative description of the complicated reactions on metals, metallic alloys, semiconductors. In any case we believe that the presented conception can be very useful in dealing with new challenges in the modern theory of catalysis, connected with direct electric or laser field effect on the catalytic processes on the surface of metallic and semiconductor materials (by means of the photoeffect, the Szilard-Chalmers type effects etc) and governing by these processes, carrying out new biocatalysts and studying related topics, searching new classes of the nanocluster catalysts) etc (see refs. in [31,32]). It is self-understood that the corresponding potentials should be modified in a case of the nano-cluster films (semiconductor heterostructures and superlattices; the Stark effect in nanocluster films). In this essence earlier developed quantum-mechanical methods (see [27,28]) can be easily and naturally combined with the presented approach.

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A. P. Fedchuk, A. V. Glushkov, Ya.I. Lepikh

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Abstract.
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Key words: catalytic properties, metals, binary metallic alloys, semiconductors

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А. П. Федчук, А. В. Глушков, Я. И. Лепих

ЭЛЕКТРОДИНАМИЧЕСКИЙ И КВАНТОВОХИМИЧЕСКИЙ ПОДХОД К МОДЕЛИРОВАНИЮ КАТАЛИТИЧЕСКОЙ АКТИВНОСТИ МЕТАЛЛОВ, СПЛАВОВ

И ПОЛУПРОВОДНИКОВ

Резюме.
Изложен комбинированный электродинамический и квантово-химический подход в электронной теории катализа к моделированию электрохимических свойств и каталитической активности металлов, металлических сплавов и полупроводниковых материалов.
Ключевые слова: квантово-химический подход, каталитические свойства, металлы, металлические сплавы, полупроводники

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О. П. Федчук, О. В. Глушков, Я. І. Лепіх

ЕЛЕКТРОДИНАМІЧНИЙ І КВАНТОВОХІМІЧНИЙ ПІДХІД ДО МОДЕЛЮВАННЯ КАТАЛІТИЧНОЇ АКТИВНОСТІ МЕТАЛІВ, СПЛАВІВ І НАПІВПРОВІДНИКІВ

Резюме.
Викладено комбінований електродинамічний та квантово-хімічний підхід в електронній теорії каталізу до моделювання електрохімічних властивостей та каталітичної активності металів, металічних сплавів і напівпровідникових матеріалів.
Ключові слова: квантово-хімічний підхід, каталітичні властивості, метали, металічні сплави, напівпровідники