
Electrodynamical and Quantum-Chemical Approaches to Modeling the Electrochemical and Catalytic Processes on Metals, Metal Alloys, and Semiconductors

A. V. GLUSHKOV,^{1,2} P. A. KONDRATENKO,³ YA. I. LEPIKH,¹
A. P. FEDCHUK,¹ L. LOVETT,⁴ A. A. SVINARENKO¹

¹Odessa State University, P. O. Box 24a, Odessa-9, 65009, Ukraine

²Russian Academy of Sciences, Troitsk, Moscow 142090, Russia

³National Aviation University, Kiev 03680, Ukraine

⁴UK National Academy of Sciences and Bookdata Co., London SW1Y 5AG, United Kingdom

Received 2 December 2008; accepted 27 April 2009

Published online 23 June 2009 in Wiley InterScience (www.interscience.wiley.com).

DOI 10.1002/qua.22338

ABSTRACT: A problem of the catalytic activity definition for metals, binary metallic alloys, and semiconductor materials is considered within new quantum mechanical and electrodynamics approach in the electron theory of catalysis. The quantitative link between the electron structure parameters of the materials and their catalytic activity on example of simple model reactions of the following type are found: $\text{H} = \text{H}^+ + e$, $\text{O}_2 + e^- = \text{O}_2^-$. © 2009 Wiley Periodicals, Inc. Int J Quantum Chem 109: 3473–3481, 2009

Key words: electron theory of catalysis; quantum-mechanical approach; electrodynamical model; metals and alloys; semiconductors

Correspondence to: A. V. Glushkov; e-mail: glushkov@paco.net

Contract grant sponsors: Russian Academy of Sciences (Troitsk, Moscow, Russia), Christian-Albrechts-University of Kiel and University of Dresden (Germany), University of Zurich and Geneva (DFT grant, Switzerland), State Foundation of the Fundamental Investigations (Kiev, Ukraine).

Introduction

A study of catalytic activity for metals, metallic alloys, and semiconductors is of 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. [1–8]. It is known [2, 3, 8–10] that the components' concentration 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 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 articles (see [1–25]).

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 chemisorption and provide the radical mechanism of the heterogeneous reactions. But, naturally it does not mean that nonradical 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, 15]. There is a great number of articles (see [1–9]), 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 [8, 11, 12]. 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 computationally 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 [9, 10, 13]). Above cited approaches are separately mentioned in a group of articles [16–22], which are devoted to simple homogeneous model models by Lang-Kohn, Bardeen, Theophilou, Vannimenus-Budd, Norskov-Lundqvist-Hjelmberg et al. and based on the conception of the Kohn-Sham density functional theory (a detailed review of the corresponding models and results is given in Refs. [8, 10]).

At present time, there is a great number of experimental articles (see Refs. [1–10]), 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. It is now clear that the 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 the main aim of the electron theory of catalysis. Naturally here one could mention the pioneering articles in the field of electron theory of catalysis by Hauffe et al. (Germany), Boudart, Voltz, Taylor et al. (USA), Germain, Claudel et al. (France), Piszarshevsky, Wolkenstein, Lyashenko, Terenin, Lidorenko (USSR) et al. (see reviews in [1, 2, 5, 7, 9, 13]). 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.

In this article, we consider a problem of catalytic activity definition for metals, binary metallic alloys, and semiconductor materials and propose a new approach to electronic theory of catalysis, which is based on using the electro-dynamical and quantum-mechanical models [9, 24, 25]. We found the electron structure parameters of the studied materials, which define their catalytic activity on example of a simple model reactions of the following type: $H = H^+ + e^-(A)$, $O_2 + e^- = O_2^-$. It should be noted that the level (A) often plays the role of limiting factor in the hydration reactions.

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 that 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 chemisorption. A semiconductor in the catalytic process has a role not only as an inert layer (where the chemical reaction runs) but as an active participant of the process too. Moreover, it can be 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 semicon-

ductor changes its catalytic properties [5, 7]. Moreover, now it is a well established 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 chemisorption 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_v^F . The direct link between the values E_F^s and E_v^F can be obtained from the condition of the electric neutrality of crystal:

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

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 $x \geq 0$). Further one could write as follows:

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

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_v^F :

$$\int_0^\infty \rho(x)dx = R(T; E_F^s; E_v^F). \quad (3)$$

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 electro-dynamical and quantum-mechanical models in the electron theory of catalysis for metals, metal alloys, and semiconductors.

Electrodynamical and Quantum-Mechanical Approaches for Metals and Metallic Alloys

It is well known [8, 26, 27] 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:

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

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:

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

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; $v_i(E_F) = N_i(E_F) a_B^2$, $N_i(E_F)$ is a density of states on the Fermi surface in "i" band. The corresponding expression for ε_{dd} is as follows:

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

Here the matrix element \dot{I}_{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:

$$\varepsilon_{ds} = [2m_s k_d e^2 f_c / \pi \pi^2 k^2] \{1 + [4(k_d)^2 - k^2] \ln|(2k_d + k)/(2k_d - k)| / 4k_d k\}. \quad (8)$$

where m_s is the effective mass of electron in the conductivity band; k_d, f_c are the numeral parameters [10, 13]. 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:

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

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

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

where

$$\alpha = [\pi^{-1} 12 (k_F^s)^2]^{-1/4} \{v_s(E_F) + (k_F^d / k_F^s) v_d(E_F) + f_c (k_F^d / k_F^s)^2 v_s(E_F)\}^{1/4},$$

$$R = 2q_F^s r, a = (k_F^s)^{-1}$$

Further the key idea is as follows. We find the numerical solution of the Schrödinger 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 $\zeta^{-1} = \alpha/a$ [10, 13, 28]. Such a problem for the potential (10) has been considered in details by Bonch-Bruevich and Glasko, Marinov and Popov and reconsidered by Lidorenko et al. (look the reviews in [10, 13, 28, 29]). In Figure 1, the corresponding parameters α and a for a number of metals are presented [10, 13]. The spectrum is continual, if $\zeta < 0.362$ and the corresponding material is a catalyst for the hydrogen ionization reaction in accordance to [13].

If $\zeta > \zeta_0$, the spectrum is discrete (metal or metal alloy does not demonstrate catalytic activity for cited reaction). In Refs. [10, 13], such an approach has been successfully applied to study the catalytic properties of the metals in relation to reaction of the hydrogen ionization and obtained excellent agreement with the known experimental data [1, 6, 7].

Let us consider further more interesting case of the binary metallic alloys and present the corresponding model. In the binary metallic alloy the

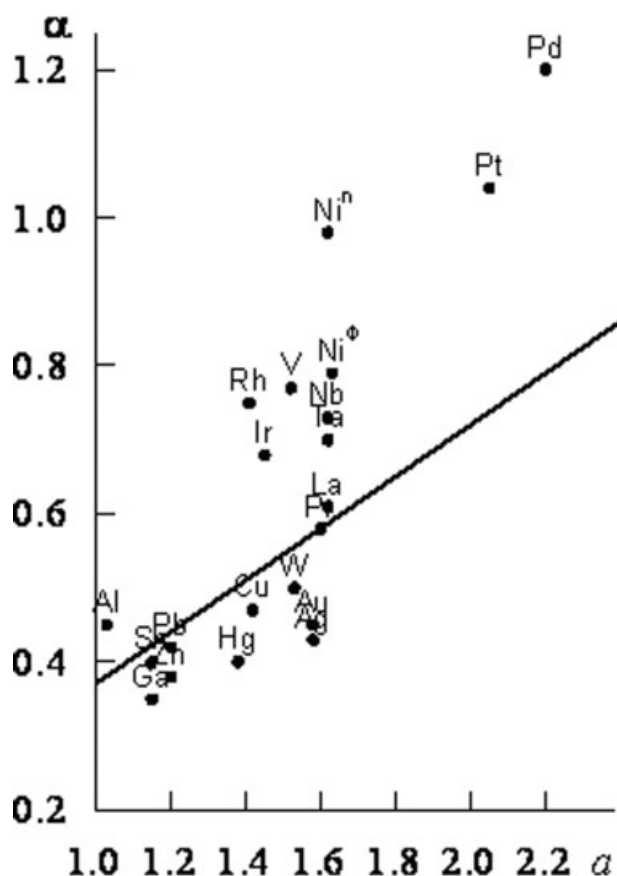


FIGURE 1. A diagram of parameters α , a for a number of metals.

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 [8, 9]. 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 is the electron gas characteristic parameter. Let us remind that $(qr_s)^{-3} \sim 0.01-0.05$ 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 [8]:

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

Elementary solution of Eq. (7) with the boundary conditions:

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

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

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

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

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

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 Figure 2 a dependence of the Fermi level shift ΔE_F in the alloy Ni-Cu upon the Cu

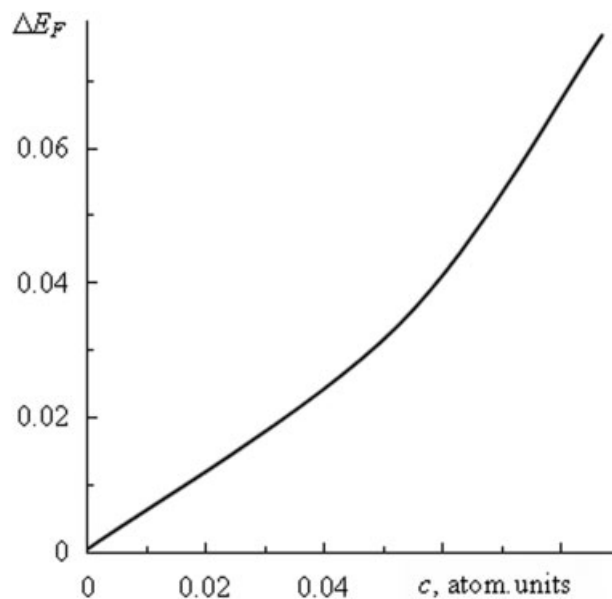


FIGURE 2. A dependence of the Fermi level shift ΔE_F in the alloy Ni-Cu upon Cu concentration c (in atomic units).

concentration \bar{n} (in atomic units) is presented and calculated according to Eq. (13).

The numerical 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 good agreement with the experimental data [1, 6, 7].

Let us now establish a link between the metallic alloys electron structure parameters and their catalytic activity for the oxygen electrorestoring reaction. We solve again the Schrödinger equation for system "oxygen molecule-electron" in the potential field $\Phi(r)$. If the negative ion O_2^- (the experimental value of electron bound energy to oxygen molecule 0.44 eV) has the bound state for given values of (6)–(9), then the material under examination is a good catalyst for the indicated reaction. Naturally, solution of the corresponding Schrödinger equation in a case of diatomic molecules is complicated. Usually one could use the two-center approximation [30]. The potential Φ could be written in the coordinates (r_a, r_b) as follows:

$$\Phi(r) = -\frac{e^2 a}{2r_a} e^{-2\alpha q r_a} \cos(2\alpha q r_a) - \frac{e^2 a}{2r_b} e^{-2\alpha q r_b} \cos(2\alpha q r_b) \quad (14)$$

The solution of the Schrödinger equation for oxygen in the potential field Φ is a well known two-centers problem of quantum mechanics. It is naturally solved in the elliptic coordinates: $\mu = (r_a + r_b)/R_{ab}$, $\eta = (r_a - r_b)/R_{ab}$ (R_{ab} is a distance between nuclei) [30]. The variables' separation in the Schrödinger equation and transition to three 1D differential equations is possible using the approximation [31]: $1/2R_{ab}(\mu + \eta) \approx 1/2R_{ab}\mu$. Then the potential (10) has the form:

$$\begin{aligned} \Phi(\mu, \eta) &= -2\mu a \exp \\ &\times [-\alpha q r_{ab} \mu] \cos[\alpha q r_{ab} \mu] / [R_{ab}(\mu^2 - \eta^2)] \\ &= g(\mu) / (\mu^2 - \eta^2). \end{aligned}$$

The Schrödinger equation is reduced to the following differential equations system [32]:

$$\begin{aligned} \{d/d\mu(\mu^2 - 1)d/d\mu - [\lambda_{ml} + m^2/(\mu^2 - 1) + \mu^2 c^2 \\ + R_{ab}g(\mu)/2\} T_{nlm} = 0 \quad (15) \end{aligned}$$

$$\begin{aligned} \{d/d\eta(-\eta^2 + 1)d/d\eta + [\lambda_{ml} + \eta^2 c^2 m^2(1 - \eta^2)]\} S_{lm} \\ = 0, \{d^2/d\varphi^2 + m^2\} \Sigma_m = 0 \end{aligned}$$

Wave function can be represented as follows: $\Psi_{nlm} = T_{nlm}(\mu)S_{lm}(\eta)\Sigma_m(\varphi)$. The one-electron energy $E = -2c^2/R_{ab}^2$ is dependent upon the main quantum number and also the symmetry of quantum numbers l, m ; λ_{ml} is a coupling constant. The usual molecular orbitals (MO) are related to the orbitals-solutions (MOS) of the Eqs. (15) as follows [33, 34]:

$$\begin{aligned} (\text{MO}) - (\text{MOS}) &= 1\sigma_g - 1s\sigma; 1\sigma_u - 2p\sigma; 2\sigma_g \\ &- 2s\sigma; 2\sigma_u - 3p\sigma; 3\sigma_g - 3d\sigma; 1\pi_u - 2p\pi; 1\pi_g \\ &- 3d\pi; 3\sigma_u - 4p\sigma. \end{aligned}$$

The ground configuration of the oxygen molecule: $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 1\pi_g^2$. Our task is to calculate the bond energy $E(1\pi_g)$. A standard approach to numerical solution of the task is based on the Numerov method and matrix technique of the Newton-Rafson (see for example [33–36]). In our opinion, more effective is another approach, which is proposed in Refs. [31–33] and based on the differential equations method and operator perturbation theory. On the basis of the latter we have carried out an estimate of the catalytic properties for metallic alloy Ni-Cu in relation to the oxygen electrorestoring reaction. In a case of the small content of Cu [$c(\text{Cu}) = 20\%$; $c(\text{Ni}) = 80\%$; $E(1\pi_g) = 1.3$ eV] the compound Ni-Cu is an effective catalyst. But, with a change of compounds components' concentration, the situation is changing into opposite side. Catalytic activity of material decreases if $c(\text{Cu}) = 50\%$, $c(\text{Ni}) = 50\%$ [$E(1\pi_g) = 1.1$ eV]. These facts correlate well with the experimental data [6, 7]. If $c(\text{Cu}) = 90\%$, $c(\text{Ni}) = 10\%$ [$E(1\pi_g) = 1.5$ eV], the catalytic activity is quite high again.

Electrodynamical and Quantum-Mechanical Model for Semiconductors

Now, let us at first formulate a new (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. To describe the electronic structure of semiconductor let us use the known Resta model [37] in the Thomas–Fermi theory for semiconductors (see [8]). We consider the model semiconductor as the electron gas with nonperturbed 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:

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

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:

$$V(r) = -Ze^2/r\{C_1 \exp(qr) + C_2 \exp(-qr)\} + A, \quad r < R \quad (16)$$

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

$$V(r) = -\{Ze^2/r\}\{\text{sh}[q(R-r)]/\text{sh}[qR] - Ze/\varepsilon(0)R\}, \quad r < R \quad (17)$$

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

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

If $\varepsilon(0) \gg 1$, 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 4.8–6.1 Å) [7]. The Schrödinger equation solution with potential (17) allows to define the corresponding energy spectrum in dependence upon the parameters $\varepsilon(0)$, k_F (Å_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 po-

tential of the Debye type) approximation is well known in a theory of plasma and considered in many articles (see [26–29, 38]). However, the potential (17) 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 $\zeta < \zeta_0$ 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 [39]. In their turn this means that 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, 7]. We believe that the simplified model for semiconductors may be naturally improved, but the key idea remains the same.

Conclusions

We have presented a new approach to estimate the catalytic activity of the metallic and semiconductor materials in the electron theory of catalysis, which is based on the combined quantum-mechanical and electro-dynamical 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 semiquantitative one in more degree and surely cannot provide a full quantitative description of the catalysis properties for any substances in relation to any reactions. Moreover, it would be very useful to link the elaborating approach with recent theory of the catalysis on the metals and semiconductors (not only by means of the Eqs. (3) and (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. It is self-understood that the corresponding potentials should be modified in a case of the nanocluster films (semiconductor heterostructures and superlattices; the Stark effect in nanocluster films). In this essence earlier developed quantum-mechanical models (see [27–29, 38, 40–45]) can be easily and naturally combined with the presented approach.

ACKNOWLEDGMENTS

The authors are very much thankful to Professors A. Wang (Chair), E. Brändas, and J. Maruani (Co-Chairs) for invitation to make contributions on the Sixth Congress of the International Society for Theoretical Chemical Physics (Vancouver, Canada). The useful comments of Professors W. Kohn, C. Roothaan, S. Wilson, I. Kaplan, A. Theophilou, and S. Malinovskaya are very much acknowledged. The authors would like to thank the referees for very useful comments.

References

- (a) Waite, R. E.; Bockris, J.; Conway, B. E. *Modern Aspects of Electrochemistry*, Vol. 21; Plenum Press: New York, 1993; (b) Paunovic, M., Ed. *Fundamentals of Electrochemical Deposition*, The Electrochemical Society Series; Wiley: New York, 2006.
- (a) Thomas, J. M.; Thomas, W. J. *Principles and Practice of Heterogeneous Catalysis*; Wiley-VCH: New York, 1996; (b) Richards, R. *Surface and Nanomolecular Catalysis*; CRC: New York, 2006.
- (a) Fornasiero, P.; Montini, T.; Graziani, M.; Zilio, S.; Succi, M. *Catalysis Today* 2008, 137, 475; (b) Ma, Z.; Yin, H.; Overbury, S. H.; Dai, S. *Catal Lett* 2008, 126, 20.
- Albonetti, S.; Bonelli, R.; Mengou, J. E.; Femoni, C.; Tiozzo, C.; Zacchini, S.; Trifirò, F. *Catal Today* 2008, 137, 483.
- (a) Austin, S. *Material Solid State Batteries*; World Scientific: Singapore, 1996; (b) Kiselev, V. F.; Krylov, O. V., Eds. *Electronic Phenomena in Adsorption and Catalysis on Semiconductors and Dielectrics*, Springer Series in Surface Sciences, Vol. 7; Springer: Berlin, 1987.
- Royter, V. A. *Catalytic Properties of Substances*; Nauka: Moscow, 1968.
- (a) Wolkenstein, F. F. *Electron Processes on Surface of Semiconductors Under Chemosorption*; Nauka: Moscow, 1991; (b) Meylikhov, E. Z.; Lazarev, S. D. *Electrophysical Properties of Semiconductors*; Nauka: Moscow, 1987.
- Lundqvist, S.; March, N. *Theory of Inhomogeneous Electron Gas*; Plenum Press: New York, 1983; Chapter 5.
- (a) Glushkov, A. V. *Electrochemistry* 1991, 27, 131; (b) Glushkov, A. V. *Electrochemistry* 1993, 29, 369.
- (a) Schwab, G.-M. *Surf Sci* 1969, 13, 198; (b) Aubry, S. *J Phys Condens Matter* 2007, 19, 255204.
- (a) Wilson, S. *Handbook on Molecular Physics and Quantum Chemistry*; Wiley: Chichester, 2007; 650 p; (b) Glushkov, A. V. *Relativistic Quantum Theory. Quantum Mechanics of Atomic Systems*; Astroprint: Odessa, 2008; 900 p.
- Slater, J. C. *The self-Consistent Field Method for Molecules and Solids: Quantum Theory of Molecules and Solids*; McGraw-Hill: New York, 1974.
- Lidorenko, I. S.; Izmistiev, A. A.; Medvedev, I. G.; Muchnik, G. F. *Dokl Akad Nauk USSR* 1975, 223, 639.
- (a) Hohenberg, P.; Kohn, W. *Phys Rev B* 1964, 136, 864; (b) Kohn, W.; Sham, L. J. *Phys Rev A* 1965, 140, 1131.
- Maruani, J.; Lefebvre, R.; Brändas, E., Eds. *Advanced Topics in Theoretical Chemical Physics, Progress in Theoretical Chemistry and Physics*, Vol. 12; Springer: Berlin, 2004.
- Gidopoulos, N. I.; Wilson, S., Eds. *The Fundamentals of Electron Density, Density Matrix and Density Functional Theory in Atoms, Molecules and the Solid State, Progress in Theoretical Chemistry and Physics*, Vol. 14; Springer: Berlin, 2004.
- (a) Bardeen, J. *Surf Sci* 1964, 2, 381; (b) Lang, N. D.; Kohn, W. *Phys Rev B* 1973, 7, 3541.
- (a) Theophilou, A. K. *J Phys F* 1972, 2, 1124; (b) Vannimenus, J.; Budd, H. F. *Solid State Commun* 1975, 10, 1157.
- (a) Lundqvist, B. I.; Nørskov, J. K.; Hjelmberg, H. *Surf Sci* 1979, 80, 441; (b) Gunnarsson, O.; Nørskov, J. K.; Hjelmberg, H. *Phys Scripta* 1980, 22, 165.
- (a) Piccinin, S.; Stampfl, C.; Scheffler, M. *Phys Rev B* 2008, 77, 075426; (b) Li, W.-X.; Stampfl, C.; Scheffler, M. *Phys Rev Lett* 2003, 90, 256102; (c) Stampfl, C.; Kreuzer, J. J.; Payne, S. H.; Scheffler, M. *Appl Phys A* 1999, 69, 471.
- Gracia, L.; González-Navarrete, P.; Calatayud, M.; Andrés, J. *Catal Today* 2008, 139, 214.
- (a) Föhlisch, A.; Nyberg, M.; Hasselström, J.; Karis, O.; Pettersson, L. G. M.; Nilsson, A. *Phys Rev Lett* 2002, 89, 276102; (b) Wallinder, D.; Hultquist, G.; Tvenen, B.; Hörlund, E. *Corr*

- Sci 2001, 43, 1267; (c) Wallinder, D.; Hörlund, E.; Hultquist, G. *J Electrochem Soc* 2002, 149, B393.
23. Glushkov, A. V.; Fedchuk, A. P.; Khetselius, O. Y. In: Proceedings of European Science Foundation REHE School and Workshop; Karwowski, J., Ed.; Torun University Publication: Torun, Poland, 1998; p 11.
 24. Glushkov, A. V. In: Proceedings of 220th National Meeting of American Chemical Society: Catalysis and Plasma Technologies; ACS Publication: Washington, 2000; p 221.
 25. Glushkov, A. V. In: Proceedings of 12th International Congress on Catalysis, Granada, Spain, 2000, Th31.
 26. Pines, D.; Nozières, F. *Theory of Quantum Liquids*; Benjamin: New York, 1966.
 27. Maradulin, A.; Lozovik, Yu. E., Eds. *Two-Dimensional Electron Systems*; North-Holland: Amsterdam, 1986.
 28. (a) Bonch-Bruevich, V. L.; Glasko, V. B. *Sov Phys Dokl* 1959, 4, 147; (b) Kar, S.; Ho, Y.-K. *Int J Quantum Chem* 2006, 106, 814; (c) Ghoshal, A.; Ho, Y.-K. *J Phys B At Mol Opt Phys* 2009, 42, 075002.
 29. Kraeft, W.-D.; Kremp, D.; Ebeling, W.; Ropke, G. *Quantum Statistics of Charged Particle Systems*; Akad.-Verlag: Berlin, 1986.
 30. Komarov, I. V.; Ponomarev, L. I.; Slavyanov, S. Yu. *Spheroidal and Coulomb Spheroidal Functions*; North-Holland: Amsterdam, 1982.
 31. (a) Glushkov, A. V. *Russ J Phys Chem* 1990, 64, 3100; (b) Glushkov, A. V. *Russ J Phys Chem* 1991, 65, 2970; (c) Glushkov, A. V. *Russ J Phys Chem* 1992, 66, 589; (d) Glushkov, A. V. *Russ J Phys Chem* 1992, 66, 1516.
 32. (a) Glushkov, A. V. *Opt Spectr* 1991, 71, 395; (b) Glushkov, A. V. *Opt Spectr* 1992, 72, 55; (c) Glushkov, A. V. *Opt Spectr* 1994, 77, 5; (d) Glushkov, A. V. *Opt Spectr* 1996, 80, 60.
 33. (a) Glushkov, A. V. *Russ J Struct Chem* 1990, 31, 3; (b) Glushkov, A. V. *Russ J Struct Chem* 1993, 34, 3; (c) Glushkov, A. V. *Russ J Struct Chem* 1993, 34, 13.
 34. Miller, K. J.; Green, A. E. *J Chem Phys* 1974, 60, 2617.
 35. Bates, D. R.; Ledsham, K.; Stewart, A. L. *Phil R Trans* 1953, A246, 215.
 36. (a) Aubert, M.; Bessis, M.; Bessis, G. *Phys Rev A* 1974, 10, 51; (b) Aubert, M.; Bessis, M.; Bessis, G. *Phys Rev A* 1974, 10, 61.
 37. Resta, R. *Phys Rev B* 1977, 16, 2717.
 38. (a) Glushkov, A. V.; Ivanov, L. N. *Phys Lett A* 1992, 170, 33; (b) Glushkov, A. V.; Ivanov, L. N. *J Phys B: At Mol Opt Phys* 1993, 26, L379.
 39. Mott, N. F. *Metal-Insulator Transitions*; Taylor & Francis: London, 1974.
 40. Glushkov, A. V.; Ambrosov, S. V.; Ignatenko, A. V.; Korchevsky, D. A. *Int J Quantum Chem* 2004, 99, 936.
 41. (a) Glushkov, A. V.; Malinovskaya, S. V. In: *New Projects and New Lines of Research in Nuclear Physics*; Fazio, G.; Hanappe, F., Eds.; World Scientific: Singapore, 2003; p 242; (b) Glushkov, A. V.; Rusov, V. D.; Ambrosov, S. V.; Loboda, A. V. In: *New Projects and New Lines of Research in Nuclear Physics*; Fazio, G.; Hanappe, F., Eds.; World Scientific: Singapore, 2003; p 146.
 42. (a) Glushkov, A. V. *Low Energy Antiproton Phys* 2005, 796, 206; (b) Glushkov, A. V.; Loboda, A. V.; Gurnitskaya, E. P.; Svinarenko, A. A. *Phys Scripta* 2009, T134, 305001.
 43. (a) Glushkov, A. V.; Malinovskaya, S. V.; Svinarenko, A. A.; Chernyakova, Yu. G. *Int J Quantum Chem* 2004, 99, 879; (b) Glushkov, A. V.; Ambrosov, S. V.; Loboda, A. V.; Gurnitskaya, E. P.; Prepelitsa, G. P. *Int J Quantum Chem* 2005, 104, 562.
 44. (a) Glushkov, A. V.; Khetselius, O. Yu.; Malinovskaya, S. V. *Eur Phys J* 2008, 160, 195; (b) Glushkov, A. V.; Khetselius, O. Yu.; Malinovskaya, S. V. *Mol Phys* 2008, 106, 1257.
 45. Glushkov, A. V.; Khetselius, O. Yu.; Loboda, A. V.; Svinarenko, A. A. In *Frontiers in Quantum Systems in Chemistry and Physics, Progress in Theoretical Chemistry and Physics*; Wilson, S.; Grout, P. J.; Maruani, J.; Delgado-Barrio, G.; Piecuch, P., Eds.; Springer: Berlin, 2008; Vol. 18, p 523.