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ELECTRODYNAMICAL AND QUANTUM - CHEMICAL MODELLING THE ELECTROCHEMICAL AND CATALYTIC PROCESSES ON METALS AND SEMICONDUCTORS: LANTHANIDE PEROVSKITES

The quantum mechanical and electrodynamical approaches are used in problem of the catalytic activity definition for metals, binary metallic alloys and semiconductor materials. There are found the quantitative link between the electron structure parameters of indicated materials and their catalytic activity on example of a simple model reactions of the following type: $H = H^+ + e$ and $O_2^- = O_2 + e^-$. It has been carried the qualitative estimate of catalytic properties for lanthanides perovskites.

INTRODUCTION

A new approach in electron theory of catalysis, based on the electrodynamical and quantum mechanical models, is being applied to study of catalytic processes on metallic and semiconductors compounds. We studied only those of the electronic structure parameters of these materials which define directly their catalytic activity in simple model reactions of the following type: $H = H^+ + e$ and $O_2^- = O_2 + e^-$. It has been found that the link between the Fermi level position dependence upon the metal alloys components concentration and their catalytic activity is quite tight. 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, etc. (c.f. [1–12] and ref. there). It is known [8–9] that the components concentration's change in metallic alloys could result in corresponding variation of catalytic activity as well as of electrochemical properties. 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 have been undertaken in a number of papers (c.f. [1–12]), in particular, within conceptual models which use the density functional formalism [2, 3]. In these models a description in the framework of electron density functional on the metals surface is produced. As a result, these models are not enough sensitive to energy value and states density on the Fermi surface. Naturally, there is a great number of papers (c.f. [1–3]), where the catalysis and hemisorption problems are considered within *ab initio* quantum chemistry methods. These calculations give 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. As alternative, the effective model approaches have been developed on the basis of the electrodynamical and quantum- chemical modeling, in particular, this approach could be represented by well known model of Lidorenko and others (c.f. [3–12]). In cited references, different versions of indicated models and different catalytic materials are considered. In this paper we consider a problem of catalytic activity definition for binary metallic alloys and heavily doped semiconductor materials. We try to find a quantitative link between the electron structure parameters of indicated materials and their catalytic activity on example of a simple model reactions of the following type: $H = H^+ + e$ (A) and $O_2^- = O_2 + e^-$ (B). It should be noted that the level (A) often plays the role of limiting factor in the hydration reactions. In paper it has been carried the qualitative estimate of catalytic properties for lanthanides perovskites too. In last years a great interest attracts studying the perovskites which represent the subgroup of oxides of the transition metals [11]. It has been shown that the rare-earth oxides of cobalt RCoO3 (R-rare-earth -element) can catalise the reaction in the gas phase. This is related to different exchanged perovdkites of the following type: $(La_{1-x}Pb_x)MnO3$ and $(Pr_{1-x}Pb_x)MnO3$. The perspective application for cited compounds is the photoelectrolise of water with the aim of obtaining oxygen and hydrogen. As anodes of photoelectrolitic cells such compounds as SrTiO3, BaTiO3 and others can be used. The biggest efficiency coefficient (10%) has been obtained in the cell with SrTiO3 of n-type under radiating by light with the photon energy which is less the forbidden zone width. In order to understand the catalytic properties of the cited compounds it is necessary to know electron characteristics of materials and mechanisms odf the adsorbtion and charge transfer processes. As the first step a qualitative estimate of catalytic properties of the cited substances is very much desirable.

SCOPE OF THE PAPER AND MODEL USED

The electron structure of metallic system in the used approximation could be approximated by a set of isotropic s-d bands [4, 5]. The static dielectric permeability is represented as follows:

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

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

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

where $k=q\,a_B$; q — wave number; a_B — Bohr radius; $q_F = (3\pi^2 z_i/\Omega)^{1/3}$; z_i – the electrons number in the "i" band; $v_i(E_F) = N_i(E_F)a^2{}_B e^e$, $N_i(E_F)$ — the state density on the Fermi surface in the 'i'.

The corresponding expression for ε_{dd} is:

$$\varepsilon_{dd} = 2\pi v_d(E_F)k^{-2}\left|M_{dd}\right|^2\left\{1+\left[4\left(k_F^d\right)^2 - k^2\right]\right.$$
$$\left.\ln\left|\left(2k_F^d + k\right)/2k_F^d - k\right|/4k_F^d k\right\}. \quad (3)$$

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 non-oxidable precious metals. This contribution is defined as follows:

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

where m_s is the effective mass of electron in the conductivity band; k_d, f_c — numeral parameters [3]. Usually the contribution ε_{ds} in (1) for transition metals is about several percents. The effective potential, which imitates an effect of metallic potential field on the inculcated hydrogen atom (for process $H = H^+ + e$) is defined as follows:

$$\Phi(r) = -\frac{2e^2}{\pi r}\int_0^\infty \frac{\sin kr}{k\varepsilon(k)}dk. \quad (5)$$

It is supposed that the problem considered has the spherical symmetry and the crystal potential is fully screened by the conductivity electrons. Substitution of (1) to (5) leads to the following expression:

$$\Phi(r) = -e^2\,a/r\exp[-\alpha R]\cos[\alpha R], \quad (6)$$

where

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

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

The numerical solution of the Schrodinger equation [13] for H atom in a field $\Phi(r)$ gives the corresponding spectrum of states, which could be continual or discrete depending on the parameter $\zeta^{-1} = \alpha/a$.The spectrum is continual, if $\zeta<\zeta o = 0{,}362$ (c.f. [4] & refs. their) and the corresponding material is a catalyst for the H ionization reaction); if $\zeta > \zeta o$, the spectrum is discrete (metal does not demonstrate catalytic activity for cited reaction). 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. It is possible to use the Thomas-Fermi approach As an approximation [14]. We suppose that the admixture's atoms volume has the spherical form. The radius R_c is connected with concentration by the formula:

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

where r_s – the electron gas characteristic parameter. For screened potential $V(r)$ near the admixture (if $|\Delta E_F^- - V| < E_F$), the corresponding Poisson equation looks as:

$$\Delta V(r) = q^2\{V(r) - \Delta E_F\} \quad (7)$$

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

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

where (Z_v — difference of the components valences) is defined as:

$$V(r, R_C) - \Delta E_F = [-Z_v e/r]\{qR_C ch[q(R_C - r)]\}/$$
$$/[qR_C ch(qR_C) + sh(qR_C)] \quad (8)$$

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

$$\Delta E_F = Z_v e^2\,q/[qR_C ch(qR_C) + sh(qR_C)] \quad (9)$$

One could see, that for the binary alloy, the value $\nu(E_F)$ is substituted by the value $\nu(E_F) = \nu(E_F) + \Delta\nu(E_F)$. The parameters, which define the catalytic activity for metallic compounds, are directly dependent upon the components concentration. Let us now establish a link between the electron structure parameters and catalytic activity for the oxygen electrorestoring reaction. We solve again the Schrodinger equation for system: oxygen molecule –electron on the potential field. If negative O_2 ion (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 indicated reaction. Potential Φ could be written with an account of the two-center (r_a, r_b) approximation as follows:

$$\Phi(r) = -e^2\,a/2ra\exp[-\alpha Ra]\cos[\alpha Ra] -$$
$$-\,e^2\,a/2rb\exp[-\alpha Rb]\cos[\alpha Rb]. \quad (10)$$

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

$$\Phi(\mu,\eta) = -2\mu\,a\exp[-\alpha q F^s R_{ab}\mu]\cos[\alpha q F^s R_{ab}\mu]/$$
$$[R_{ab}(\mu^2 - \eta^2)] = g(\mu)/(\mu^2 - \eta^2).$$

The master differential equations system has the following form:

$$\{d/d\mu\,(\mu^2 - 1)\,d/d\mu - [\lambda_{ml} + m^2/(\mu^2 - 1) +$$

$$+ \mu^2c^2 + R_{ab}g(\mu)/2\}T_{nlm} = 0 \qquad (11)$$

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

$$\{d^2/d\varphi^2 + m^2\}\Sigma_m = 0.$$

Wave function can be represented as follows:

$$\Psi_{nlm} = T_{nlm}(\mu)\,S_{lm}(\eta)\,\Sigma_m(\varphi).$$

One- electron energy $E = -2c^2/Rab^2$ is dependent upon the main quantum number and also the symmetry of quantum numbers l, m; λ_{ml} is a coupling constant. Usual molecular orbitals (MO) correspond to the orbitals-solutions (MOS) of (11) as follows:

$$(MO) - (MOS) = 1\sigma_g - 1s\sigma;\ 1\sigma_u - 2p\sigma;\ 2\sigma_g - 2s\sigma;$$

$$2\sigma_u - 3p\sigma;\ 3\sigma_g - 3d\sigma;\ 1\pi_u - 2p\pi;\ 1\pi_g - 3d\pi;\ 3\sigma_u - 4p\sigma.$$

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 is based on the Numerov method and matrix technique with using the Newton-Rafson scheme (c.f.[15-17]). A new, more effective method of the eigen-values definition and functions problem solution, which is based on the operator perturbation theory and Runge-Kutta integration procedure, was proposed in ref. [13, 12, 15–18].

MODEL TO CATALYTIC ACTIVITY OF SEMICONDUCTORS

Now, let us formulate a new effective approach to description of catalytic processes on semiconductors and determine 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 in the Thomas-Fermi theory for semiconductors (c.f. [14]). 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 solutions for the Poisson equation have the following form: $Ze^2\exp[qr]/r$. So, the general expression for potential energy is:

$$V(r) = -Ze^2/r\,\{C_1\exp(qr) +$$

$$+ C_2\exp(qr)\} + A,\ r < R. \qquad (12)$$

Taking into account the continuity condition, boundary condition ($V(r) \to 0$, $r \to 0$) and formula $A = V(R)$, the expression for V (12) looks as follows:

$$V(r) = -\{Ze^2/r\}\{sh[q(R - r)]/sh[qR] -$$

$$- Ze/\varepsilon(0)R,\ r < R. \qquad (13)$$

The continuity condition for electric field under $r = R$ allows to define a link between the screening parameter and $\varepsilon(0)$ as: $\varepsilon(0) = sh[qR]/qR$. If $\varepsilon(0) > 1$, R is equal to finite value comparable with distance to the nearest atoms for example, for Si, Ge semiconductors $R = 4{,}4$ a.u.). The Schrödinger equation solution with potential (12) allows to define the corresponding energy spectrum in dependence upon the parameters $\varepsilon(0)$, k_F and then a link between the semiconductors electron structure parameters and their catalytic activity likely above described one.

QUALITATIVE ESTIMATE FOR CATALYTIC ACTIVITY OF THE ABO3 COMPOUNDS

We are interested by a search of the most optimal and active catalyzers of the model reactions $H = H^+ + e$ and $O_2^- = O_2 + e^-$ among the compounds ABO3 (B=Fe,Ni,Co; A=La, Ce, Tb, Dy). We have applied our scheme of the electrodynamic modeling for the case of the model reaction $O_2 + e^- = O^-_2$. Calculation is resulted in solution of the Schrödinger equation (the Kohn-Sham equations system) for system: oxygen molecule – electron in the potential field of a material. If for the corresponding parameter ξ the negative ion has the bound state then the material is the catalyzer of reaction. And if the bond energy is more them the catalytic properties will be manifested in the more degree. We present the corresponding bond energies for different compounds in table 1.

Table 1

Bond energies for system $O_2 + e^-$

Compound	Bond energy, eV	Compound	Bond energy, eV
LaFeO3	1,76	TbFeO3	1,82
LaCoO3	1,75	TbCoO3	1,81
LaNiO3	1,73	TbNiO3	1,78
CeFeO3	1,67	DyFeO3	1,64
CeCoO3	1,67	DyCoO3	1,63
CeNiO3	1,65	DyNiO3	1,61

As the estimate shows, the most active catalyzers among considered materials are the compounds as follows: LaFeO3, LnCoO3, TbFeO3, TbCoO3. It is of a great interest that this is in a full correspondence with preliminary experimental studies [10,11]. It is obvious that the further studying of the electrocatalytic properties of the cited compounds requires the detailed calculation of the electron structure parameters, ab initio quantum modelling catalytic reactions, which possibly run with forming the corresponding adsorbtion complexes etc.

CONCLUSIONS

We present here the quantum mechanical and electrodynamical approaches in problem of the catalytic activity definition for metals, metallic and semiconductor materials. On its basis it has been carried the qualitative estimate of catalytic properties for lanthanides perovskites. The proposed approach could

be modified for the semiconductor surface catalytic reactions product and charge exchange processes evaluation and, in such a way, could be used for the semiconductor sensors efficacy prediction for the given reaction type. We believe that approach proposed can be improved on the way of account for the whole number of additional factors (the electrolyte influence, surface effects, electrode potential, the electrolyte type, the electron concentration in the layer and many other [8–12]).

References

1. *Glushkov A. V.* Electron theory of Catalysis on Metallic Alloys: Electrodynamical model // Electrochemistry. – 1991. — Vol. 27, N 1. — P. 131–133.
2. *Glushkov A. V.* Electron theory of Catalysis on Metals: Quantum Chemical model // Electrochemistry. — 1993. — Vol. 29, N 3. — P. 369–376.
3. *Bound* States in Catalysis: New electrodynamical & quantum chemical models in electron theory of catalysis / A. V. Glushkov, V. D. Parkhomenko, P. N. Tcybulev, M. V. Belous, A. K. Katashinsky // Uzhgorod Univ. Sci. Herald. Series. Physics. — 2000. — Vol. 8, N 2. — P. 361–365.
4. *Quantum* Chemical Modeling of Catalytic properties of Lanthanide Perovskites / A. V. Glushkov, V. D. Parkhomenko, P. N. Tcybulev, M. V. Belous, A. K. Katashinsky // Proc. European Science Foundation REHE School and Workshop on "Spin-Orbit Coupling in Chemical Reactions", Torun (Poland), 1998. – P. 12.
5. *Glushkov A. V., Fedchuk A. P., Khetselius O. Yu.* Heavy Elements, Relativistic SOC Effects in Catalysis Processes // Proc. European Science Foundation REHE School and Workshop on "Spin-Orbit Coupling in Chemical Reactions", (Poland), 1998. – P. 11.
6. *Glushkov A. V.* A new approach in Electron theory of Catalysis: Electrodynamical and QuantumChemical models.Catalysis modeling in Plasma Chemical Reactors // Proc. 220th National Meeting of American Chemical Society: Catalysis and Plasma Technologies, Washington, 2000. — P. 221–224.
7. *Glushkov A. V.* New Approach in Electron Theory of Catalysis: Electrodynamical and Quantum Mechanical Models for binary metallic alloys // Proc. 12th International Congress on Catalysis, Granada (Spain), 2000. — P. Th31.
8. *Glushkov A. V.* New Quantum Mechanical and Electrodynamical Models of the Catalytic Processes on Metallic Systems and Semiconductors // Proc. 5th European Workshop "Quantum Systems in Chemistry and Physics", Uppsala (Sweden), 2000. — P. 131.
9. *Vol'kenstein F. F.* Electron Processes on surface of semiconductors under chemosorbtion, Moscow: Nauka, 1991. — 580 p.
10. *Waite R. E., Bockris J., Conway B. E.* Modern Aspects of Electrochemistry, N-Y: Plenum Press, 1993. — Vol. 21.
11. *Austin S.* Material Solid State Batteries, Singapore: World. Sci., 1996. — 370 p.
12. *DC Strong* Field Stark Effect for Non-hydrogenic Atoms: Consistent Quantum Mechanical Approach / A. V. Glushkov, S. V. Ambrosov, A. V. Ignatenko, D. A. Korchevsky // Int. Journ. Quant. Chem. — 2004. — Vol. 99, N 5. — P. 936–939.
13. *Glushkov A. V., Ivanov L. N.* DC Strong-Field Stark-Effect: consistent quantum-mechanical approach // J. Phys. B: At. Mol. Opt. Phys. — 1993. — Vol. 26, N 16. — P. L379–389.
14. *Lundqvist S., March N.* Theory of Inhomogeneous Electron Gas, N-Y.: Plenum Press, 1993. — 480 p.
15. *Glushkov A. V.* New method for calculation of ionization potentials for molecules by Green's functions method // Journ. Phys. Chem. — 1992. — Vol. 66, N 4. — P. 589–596.
16. *Glushkov A. V.* Calculation of molecular constants of diatomic molecules in quasiparticle approximation of demsity functional // J. Phys. Chem. — 1989. — Vol. 63, N 11. — P. 3072–3074.
17. *Glushkov A. V.* Account of 2p-2h correlations in the equations of motion method for complex molecules // J. Phys. Chem. — 1990. — Vol. 64, N 11. — P. 3100–3103.
18. Electrodynamical and quantum — chemical modelling the electrochemical and catalytic processes on metals and semiconductors / A. V. Glushkov, Ya. I. Lepikh, A. P. Fedchuk, O. Yu. Khetselius // Ukr. Phys. Journ. — 2008, in print.

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ЕЛЕКТРОДИНАМІЧНЕ ТА КВАНТОВОХІМІЧНЕ МОДЕЛЮВАННЯ ЕЛЕКТРОХІМІЧНИЇХ ТА КАТАЛІТИЧНИХ ПРОЛІЦЕСІВ НА МЕТАЛАХ ТА НАПІВПРОВІДНИКАХ: ПЕРОВСКІТИ ЛАНТАНІДІВ

Викладено новий квантово- механічний й електродинамічний підхід до визначення каталітичної активності напівпровідникових та бінарних металічних матеріалів. Виявлено кількісну кореляцію параметрів електроної структури шуканих матеріалів і їх каталітичною активністю у відношенні до модельних реакцій типу: $H = H^+ + e$, $O_2^- = O_2 + e^-$. Виконано якісну оцінку каталітичних властивостей перовскитів лантанідів.

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ЭЛЕКТРОДИНАМИЧЕСКОЕ И КВАНТОВОХИМИЧЕСКОЕ МОДЕЛИРОВАНИЕ ЭЛЕКТРОХИМИЧЕСКИХ И КАТАЛИТИЧЕСКИХ ПРОЦЕССОВ НА МЕТАЛЛАХ И ПОЛУПРОВОДНИКАХ: ПЕРОВСКИТЫ ЛАНТАНИДОВ

Изложен квантово - механический и электродинамический подход к определению каталитической активности полупроводниковых и металлических материалов. Выявлена количественная корреляция параметров электронной структуры искомых материалов и их каталитической активности по отношению к модельным реакциям вида: $H = H^+ + e$, $O_2^- = O_2 + e^-$. Выполнена качественная оценка каталитических свойств перовскитов лантанидов.