

Electrodynamical and Quantum Chemical Modelling of Electrochemical and Catalytic Processes on Metals and Semiconductors: A Review

A.V. Glushkov, A.A. Svinarenko, O.Yu. Khetselius,
Yu.V. Dubrovskaya, A.S. Kvasikova, A.A. Kuznetsova
and E.L. Ponomarenko

Abstract The advanced quantum-mechanical and electrodynamical approaches in the electron theory of catalysis have been generalized to determine quantitatively the catalytic activity for metals, binary metallic alloys and semiconductor materials. The solutions of some model tasks associated with stabilization of ionic states of atomic hydrogen and molecular oxygen in effective electron gas are given. Within the approach the quantitative correlation between the electron structure parameters of the materials and their catalytic activity is found on example of simple model reactions.

Keywords Electron theory of catalysis · Quantum and electrodynamics models · Metals and binary metallic alloys · Semiconductor materials

1 Introduction

At present time a great interest attracts studying an electrochemical and catalytic activity properties of the different materials, including a development of advanced chemical industry technologies, search and construction of the electrochemical solid-state energy sources, etc. [1–13]. A great number of the attempts to develop a quantitative theory of electron catalysis for the metal-like and semiconductor systems including the description of processes on electrodes' surfaces of the electrochemical solid-state energy sources have been undertaken (see [1–8]). One could mention quite good understanding of a mechanism of heterogeneous catalytic process under obligatorily treating intermediate stages, namely, stages of adsorption and desorption [1, 2]. Naturally, any heterogeneous reaction can be treated as the

A.V. Glushkov (✉) · A.A. Svinarenko · O.Yu. Khetselius · Yu.V. Dubrovskaya ·
A.S. Kvasikova · A.A. Kuznetsova · E.L. Ponomarenko
Odessa State Environmental University, L'vovskaya str., 15, Odessa-9 65016, Ukraine
e-mail: glushkovav@gmail.com; dirac13@mail.ru

process based on a radical mechanism. The matter is in the fact that the radicals and ion-radicals appear on the surface under chemisorption and provide the corresponding mechanism of these reactions. It is important to note that the reaction path through one-electron charged intermediates (ion-radicals) is not the main mechanism in a heterogeneous catalysis. Nevertheless, it can be possible in some special cases. The detailed review of different approaches to adsorption and catalysis, including the key aspects of different conceptual models (such as the density functional method, ab initio quantum chemistry methods) are presented in [9–26]. The cited methods allowed to get very useful information about the electrochemical and catalytic activity properties of the different materials, nevertheless, different fundamental physical and chemical aspects of the problem remain up to known degree veiled [1–15]. In this chapter we present an advanced quantum-mechanical and electro-dynamical approach to description of the catalytic activity for metals, binary metallic alloys and semiconductor materials. Within the approach the quantitative correlation between the electron structure parameters of the materials and their catalytic activity is found on example of simple model reactions.

2 Electro-dynamical and Quantum-Mechanical Models for Metals, Alloys and Semiconductors

It is well known that the catalytic properties of different metallic and semiconductor materials are linked with the electronic processes inside and on the surface of the materials. The Fermi level position determines the adsorption and catalytic activity of the surface in relation to molecules of the given kind under other equal conditions. The chemisorption ability of the surface, a degree of its charging, a reactive ability of the chemisorbed particles etc. are dependent upon the Fermi level position on the surface of crystal (speech is about distance between the Fermi level and the conductivity band bottom: E_F^s). The position of the Fermi level inside the crystal can be defined as E_F^v . The corresponding expression linking the values E_F^s and E_F^v is as follows:

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

where ρ is a density of the volume charge in the plane, σ is a density of the surface charge. The value of σ can be expressed as function of a pressure P , temperature T : $\sigma = \sigma(P, T, E_F)$ [2, 6, 7]. The second item in (1) is the function of E_F^s and E_F^v :

$$\int_0^{\infty} \rho(x) dx = R(T; E_F^s; E_F^v) \quad (2)$$

The relationship between E_F^s and E_F^v (defining the correlation between the surface and bulky properties of the material) can be written as follows:

$$\sigma(P, T; E_F^s) + R(T; E_F^s; E_F^v) = 0 \quad (3)$$

or

$$E_F^s = f(P, T; E_F^v) \quad (4)$$

Let us further to consider in details the electrodynamical approach to structure of a metallic system. Within the simple approximation [9] with using a set of isotropic s-d energy bands, one could write the next obvious formula for a static dielectric permeability:

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

In Eq. (5) $\varepsilon(ij)$ means the contribution into ε due to the i-j transitions. If one accept here the approximation of the free electrons, then it is easily to write the expression for ε_{ss} component:

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

$$\nu_i(E_F) = N_i(E_F)a_B^2 e$$

Here the following notations are used: a_B is the Bohr radius, $k = q \cdot a_B$, q is the wave number, $q_F = (3\pi^2 z_i / \Omega)^{1/3}$; z_i is a number of electrons in “i” band; $N_i(E_F)$ is a density of states on the Fermi surface in “i” band.

This corresponding ε_{ds} contribution can be represented as follows:

$$\varepsilon_{ds} = [2m_s k_d e^2 f_c / \pi \pi^2 k^2] \left\{ 1 + \left[4(k_d)^2 - k^2 \right] \ln \left| (2k_d + k)/2k_d - k \right| / 4k_d k \right\}. \quad (7)$$

where m_s is the effective mass of electron in the conductivity band; k_d, f_c are the numeral parameters [7, 8, 11]. At last, the corresponding formula for ε_{dd} looks as:

$$\varepsilon_{dd} = 2\pi\nu_d(E_F)k^{-2} |M_{dd}|^2 \left\{ 1 + \left[4(k_F^d)^2 - k^2 \right] \ln \left| (2k_F^d + k)/2k_F^d - k \right| / 4k_F^d k \right\} \quad (8)$$

where M_{dd} is the matrix element, determined by the superposition of the wave functions for d electrons.

The next key step is in supposing that we can work using the spherical symmetry and the crystal potential is fully screened by the conductivity electrons. Then one could introduce an effective potential, which imitates an influence of the metallic field on the hydrogen atom (for example, for process of the following type: $H = H^+ + e^-$). This effective potential can be determined in the following form:

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

or after substitution of (5) to (7) resulted in the expression:

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

where

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

$$R = 2q_F^s r, \quad (11)$$

$$a = (k_F^s)^{-1}$$

According to Ref. [8, 23] further key idea in the following. One could find the numerical solution of the Schrödinger equation for the hydrogen atom in a field $\Phi(r)$ and obtain a spectrum of states, which could be continual or discrete in dependence upon the parameter $\zeta^{-1} = \alpha/a$ [8]. The spectrum is continual, if $\zeta < \zeta_0$ ($\zeta_0 = 0,362$) and the corresponding material is a catalyst for the hydrogen ionization reaction. If $\zeta > \zeta_0$, the spectrum is discrete (metal or alloy does not demonstrate catalytic activity for cited reaction). In Refs. [8, 23–25] such an approach was successfully applied to studying the metal catalytic properties in relation to reaction of the H ionization and obtained excellent agreement with experiment [2, 5–7]. In Ref. [8] there are listed the corresponding parameters α and a for a number of metals.

The analogous consideration can be performed for the binary metallic alloy. Obviously, one should take into account a dependence of the Fermi level position E_F as well as the state density $\nu(E_F)$, accompanied with the structure parameters α and a upon the change of the admixture concentration c [8, 9]. It is easily to suppose that the admixture's atoms volume has the spherical form and a radius R_c is linked with the concentration as:

$$(qR_c)^{-3} = (qr_s)^{-3} c, \quad (12)$$

where r_s —the electron gas parameter.

Further one could write the standard Poisson equation [8] for the screened potential $V(r)$ near an admixture:

$$\Delta V(r) = q^2 \{V(r) - \Delta E_F\} \quad (13)$$

which has the with the elementary solution of the following type:

$$V(r, R_c) - \Delta E_F = [-Z_\nu e/r] \{qR_c ch[q(R_c - r)] + sh[q(R_c - r)]\} / [qR_c ch(qR_c) + sh(qR_c)] \quad (14)$$

Here Z_ν is a difference of the components valences. Finally, the value $\nu(E_F)$ for the binary metallic alloy can be expressed as follows [8]:

$$\nu(E_F) = \nu(E_F) + \Delta\nu(E_F). \quad (15)$$

The Fermi level position and respectively the metallic alloy catalytic activity is quantitatively dependent upon the components concentration.

In Refs. [8, 25] there are presented the concrete examples of the modeling the catalytic activity of metallic alloy in relation of the H ionization reaction for different metallic alloys. For example, the corresponding estimates show 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 experiment [1, 6, 7].

The similar approach can be generalized to find a link between the alloy structure parameters and their catalytic activity for oxygen electro-restoring reaction. One should again to solve the Schrödinger equation for system “O₂-electron” in the potential $\Phi(r)$. If the negative ion system has the bound state for given values of (6)–(9), then the studied material is a good catalyst for the reaction. In order to solve the Schrödinger equation in a case of diatomic molecule it is necessary to use the two-centre approximation [27–32]. In the standard elliptic coordinates: $\mu = (r_a + r_b)/R_{ab}$, $\eta = (r_a - r_b)/R_{ab}$ (R_{ab} is a distance between nuclei) the variables’ in the corresponding Schrödinger equation are separated if one use the formula: $1/2R_{ab}(\mu + \eta) \approx 1/2 R_{ab}\mu$. Then the potential (10) in the molecular approximation can be written as follows:

$$\Phi(\mu, \eta) = -2\mu\alpha \exp[-\alpha q_F R_{ab}\mu] \cos[\alpha q_F R_{ab}\mu] / [R_{ab}(\mu^2 - \eta^2)] = g(\mu)/(\mu^2 - \eta^2). \quad (16)$$

Further one can write the corresponding Schrödinger equation which is reduced to the differential equations system [8, 28]:

$$\begin{aligned} \{d/d\mu(\mu^2 - 1)d/d\mu - [\lambda_{ml} + m^2/(\mu^2 - 1) + \mu^2 c^2 + R_{ab}g(\mu)/2]\} T_{nlm} &= 0, \\ \{d/d\eta(-\eta^2 + 1)d/d\eta + [\lambda_{ml} + \eta^2 c^2 m^2(1 - \eta^2)]\} S_{lm} &= 0, \\ \{d^2/d\varphi^2 + m^2\} \Sigma_m &= 0. \end{aligned} \quad (17)$$

where $\Psi_{nlm} = T_{nlm}(\mu) S_{lm}(\eta) \Sigma_m(\varphi)$ is a wave function; $E = -2c^2/R_{ab}^2$ is one-electron energy, λ_{ml} is a coupling constant. In order to fine the numerical

solution of the Eqs. (17) one could use the standard approaches such as the Numerov method or matrix technique of the Newton-Rafson etc. (see [27–32]).

In Refs. [8, 25] the authors has presented the results of application of the described model to estimating the catalytic properties for the alloy *Ni-Cu* in relation to the oxygen electro-restoring 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. With changing c , 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 to 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.

In order to generalize the above presented approach on a case of description of the catalytic processes on semiconductors and determine a link between their electron structure parameters and the catalytic activity in the relation to model H ionization reaction one could use the known Resta model in the Thomas-Fermi theory [33, 34]. The master Poisson equation has the standard form:

$$V(r) = q\{V(r) - A\}, \quad (18)$$

where $q = 4k_F/\pi a_B$ and A is a constant. Beyond the radius R the point charge Z_e potential is equal to:

$$V(R) = -Ze^2/[\varepsilon(0)r], r > R, \quad (19)$$

where $\varepsilon(0)$ is a static dielectric permeability. The general solution with taking into account for the corresponding continuity and boundary conditions looks as:

$$V(r) = -\{Ze^2/r\}\{sh[q(R-r)]/sh[qR] - Ze/\varepsilon(0)R, r < R \quad (20)$$

The link between the screening parameter and $\varepsilon(0)$ is determined by the relationship: $\varepsilon(0) = sh[qR]/qR$. Let us note that 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 4.8–6.1 Å) [7, 35]. The next step is the numerical solution of the Schrödinger equation with the potential (20), which allows to determine the corresponding energy spectrum in dependence upon $\varepsilon(0)$, k_F (E_F) and then to find a link between the semiconductors structure parameters and their catalytic activity likely above described approach. In ref. [8, 24] there are presented the concrete estimates of the catalytic activity for the *CuO*, *ZnO* semiconductors in the hydrogen ionization (oxidation) reaction. The general conclusion is that the *CuO* and *ZnO* semiconductors are good catalysts for the hydrogen ionization reaction. This fact is in a good agreement with the known experimental data [6, 7].

In conclusion of this section we present a brief generalization of the model to the case of the influence of an external electric field. To determine the corresponding spectrum of the quasi-bound states one needs to carry out the diagonalization of the energy matrix, calculated between states with the same main quantum number (e.g.

[36–39]). Let us note that the corresponding Hamiltonian can be written in the cylindrical coordinates (ρ, z) , namely:

$$H\psi(\rho, z) = E\psi(\rho, z) \quad (21)$$

$$H = -1/2(\partial^2/\partial\rho^2 + 1/\rho\partial/\partial\rho + \partial^2/\partial z^2 - 1/\left[(z + R/2)^2 + \rho^2\right]^{1/2} - 1/\left[(z - R/2)^2 + \rho^2\right]^{1/2} - Fz + V(\rho, z)$$

Here F denotes an electric field strength; V is an effective potential (of the type (16), (20)). To solve the Eq. (21) one should use the finite differences method (look [40]). The eigen-values of the Hamiltonian can be computed by means of the inverse iterations method. The corresponding system of inhomogeneous equations can be solved by the Thomas method. However, to date any of the similar theoretical model application are missing.

3 Conclusions

We have presented an advanced quantum-mechanical and electrodynamical approaches in the electron theory of catalysis to determine quantitatively the catalytic activity for metals, binary metallic alloys and semiconductor materials. The solutions of some model tasks associated with stabilization of ionic states of atomic hydrogen and molecular oxygen in effective electron gas are given. Within the approach the quantitative correlation between the electron structure parameters of the materials and their catalytic activity is found on example of simple model reactions. Surely, the catalytic activity properties of different materials are directly connected with the corresponding electronic processes inside and on the surface of the materials. Naturally, to carry out more advanced approach one should take into account a whole number of the additional important factors (for example the electrolyte influence, surface effects, the electrodes potential, electron concentration in the surface layer etc. [1–10]). A great interest attracts the establishment of correlation between the presented approach and recent theories of the catalysis on the metals and semiconductors. In conclusion let us underline that the presented approach ideas can be quite easily generalized in order to take into consideration a whole number of such additional physical and chemical factors such as a direct electric, magnetic or laser field effect on the catalytic processes and governing by these processes, search and approbation of new classes of nanocluster catalysts and so on [38, 39, 41, 42].

Acknowledgements Authors are thankful to Prof. E. Brändas, J. Maruani, A. Tadjer, R. Pavlov for the invitation to present an invited report at the workshop QSCP-XX (Bulgaria, 2015). The help in editing the manuscript by Mr. Heike Rossel and Ms. Heena Naveen (Springer) is very much appreciated.

References

1. Waite RE, Bockris J, Conway BE (1993) *Modern aspects of electrochemistry*, vol 21. Plenum Press, N-Y.; Paunovic M (ed) (2006) *Fundamentals of electrochemical deposition, the electrochemical society series*. John Wiley & Sons, Inc., N.-Y.
2. Thomas JM, Thomas WJ (1996) *Principles and practice of heterogeneous catalysis*. Wiley-VCH, N.-Y.; Richards R (2006) *Surface and nanomolecular catalysis*. CRC Press, N.-Y.
3. Fornasiero P, Montini T, Graziani M, Zilio S, Succi M (2008) *Catal Today* 137:475–482; Ma Z, Yin H, Overbury SH, Dai S (2008) *Catal Lett* 126:20–30
4. Albonetti S, Bonelli R, Mengou JE, Femoni C, Tiozzo C, Zacchini S, Trifirò F (2008) *Catal Today* 137:483–488; Baddeley CJ, Kyriakou G (eds) (2016) *Surface science for heterogeneous catalysis, a special issue in Honour of Richard Lambert*, *Surf Sci* 646:1–360 (Elsevier)
5. Austin S (1996) *Material solid state batteries*. World Scientific, Singapore; Kiselev VF, Krylov OV (eds) (1987) *Electronic phenomena in adsorption and catalysis on semiconductors and dielectrics*. Springer series in surface science, vol 7. Springer, Berlin
6. Royter VA (1968) *Catalytic properties of substances*. Moscow, Nauka Publisher
7. Wolkenstein FF (1991) *Electron Processes on surface of semiconductors under chemisorption*. Nauka Publisher, Mosco; Meylikhov EZ, Lazarev SD (1987) *Electrophysical properties of semiconductors*. Nauka Publisher, Moscow
8. Glushkov AV (1991) *Electrochemistry* 27:131–135; *ibid.* (1993) 29:369–376; Glushkov AV, Kondratenko PA, Lepikh YI, Fedchuk AP, Svinarenko AA, Lovett L (2009) *Int J Quantum Chem* 109:3473–3481
9. Lundqvist S, March N (1983) *Theory of Inhomogeneous electron gas*. Plenum Press, N.-Y., Ch. 5
10. Schwab G-M (1969) *Surface Sci* 13:198–200; Aubry S (2007) *J Phys Condens Matter* 19:255204
11. Wilson S (2007) *Handbook on molecular physics and quantum chemistry*. Wiley, Chichester, 650 p; Glushkov AV (2008) *Relativistic quantum theory. quantum mechanics of atomic systems*. Astroprint, Odessa, 900 p
12. Slater JC (1974) *The self-consistent field method for molecules and solids: quantum theory of molecules and solids*. McGraw-Hill, N.-Y.
13. Lidorenko IS, Izmetiev AA, Medvedev IG, Muchnik GF (1975) *Dokl Akad Nauk USSR* 223:639–642
14. Hohenberg P, Kohn W (1964) *Phys Rev B* 136:864–878; Kohn W, Sham LJ (1965) *Phys Rev A* 140:1131–1145
15. Maruani J, Lefebvre R, Brändas E (eds) (2004) *Advanced topics in theoretical chemical physics, progress in theoretical chemistry and physics*, vol 12. Springer, Berlin
16. Gidopoulos NI, Wilson S (eds) (2004) *The fundamentals of electron density, density matrix and density functional theory in atoms, molecules and the solid state, series: progress in theoretical chemistry and physics*, vol 14. Springer, Berlin
17. Bardeen J (1964) *Surf Sci* 2:381–394; Lang ND, Kohn W (1973) *Phys Rev B* 7:3541–3552
18. Theophilou AK (1972) *J Phys F* 2:1124–1132; Vannimenus J, Budd HF (1975) *Solid State Commun* 10:1157–1168
19. Lundqvist BI, Norskov JK, Hjelmberg H (1979) *Surf Sci* 80:441–448; Gunnarsson O, Norskov JK, Hjelmberg H (1980) *Phys Scr* 22:165–178
20. Piccinin S, Stampfl C, Scheffler M (2008) *Phys Rev B* 77:075426; Li W-X, Stampfl C, Scheffler M (2003) *Phys Rev Lett* 90:256102; Stampfl C, Kreuzer JJ, Payne SH, Scheffler M (1999) *Appl Phys A* 69:471–480
21. Gracia L, González-Navarrete P, Calatayud M, Andrés J (2008) *Catal Today* 139:214–220; Schwab G-M (1969) *Surf Sci* 13:198–200

22. Föhlisch A, Nyberg M, Hasselström J, Karis O, Pettersson LGM, Nilsson A (2002) *Phys Rev Lett* 89:276102; Wallinder D, Hultquist G, Tvenen B, Hörlund E (2001) *Corr Sci* 43: 1267–1282; Wallinder D, Hörlund E, Hultquist G (2002) *J Electrochem Soc* 149:B393
23. Glushkov AV, Fedchuk AP, Khetselius OY (1998) In: Karwowski J (ed) *Proceedings of the European science foundation REHE school and workshop on “Spin-Orbit Coupling in Chemical Reactions”*. Torun University Publisher, Torun, Poland, pp 11–12
24. Glushkov AV (2000) In: *Proceedings of the 220th national meeting of american chemical society: catalysis and plasma technologies*. ACS Publisher, Washington, USA, pp 221–224
25. Glushkov AV (2000) In: *Proceedings of the 12th international congress on catalysis*. Granada, Spain, Th31
26. Kraeft W-D, Kremp D, Ebeling W, Ropke G (1986) *Quantum statistics of charged particle systems*. Akad.-Verlag, Berlin
27. Bonch-Bruevich VL, Glasko VB (1959) *Sov Phys Dokl* 4:147–150; Kar S, Ho Y-K (2006) *Int J Quantum Chem* 106:814–820; Ghoshal A, Ho Y-K (2009) *J Phys B At Mol Opt Phys* 42:075002
28. Komarov IV, Ponomarev LI, Slavyanov SY (1982) *Spheroidal and coulomb spheroidal functions*. North-Holland, Amsterdam
29. Glushkov AV *Russ J Phys Chem* 64:3100–3106 (1990); *ibid.* (1991) 65:2970–2978; *ibid.* (1992) 66:589–596; *ibid.* (1992) 66:1516–1524
30. Glushkov AV (1991) *Opt Spectr* 71:395–398; *Ibid* 72:55–61 (1992); *ibid.* (1994) 77:5–10; *ibid.* (1996) 80:60–67
31. Glushkov AV (1990) *Russ J Struct Chem* 31:3–8; *ibid.* (1993) 34:3–12; *ibid.* (1993) 34:13–24
32. Miller KJ, Green AE (1974) *J Chem Phys* 60:2617–2624
33. Resta R (1977) *Phys Rev B* 16:2717–2726
34. Mott NF (1974) *Metal-insulator transitions*. Taylor & Francis, London
35. Glushkov AV, Malinovskaya SV (2003) In: Fazio G, Hanappe F (eds) *New projects and new lines of research in nuclear physics*. World Scientific, Singapore, pp 242–280; Glushkov AV, Rusov VD, Ambrosov SV, Loboda AV *ibid.* pp 146–160
36. Glushkov AV, Khetselius OY, Malinovskaya SV (2008) *Eur Phys J ST* 160:195–204; Glushkov AV, Khetselius OY, Malinovskaya SV (2008) *Mol Phys (UK)* 106:1257–1260
37. Glushkov AV, Khetselius OY, Loboda AV, Svinarenko AA (2008) *Frontiers in quantum systems in chemistry and physics, progress in theoretical chemistry and physics*. In: Wilson S, Grout PJ, Maruani J, Delgado-Barrio G, Piecuch P(eds), vol 18. Springer, Berlin, pp 523–540
38. Glushkov AV, Ivanov LN (1992) *Phys Lett A* 170:33–37; (1993) *J Phys B At Mol Opt Phys* 26:L379–389
39. Glushkov AV, Ambrosov SV, Ignatenko AV, Korchevsky DA (2004) *Int J Quantum Chem* 99:936–939
40. Glushkov AV (2005) *Atom in an electromagnetic field*. TEC, Odessa
41. Glushkov AV (2005) *Low Energy Antiproton Phys*, AIP Serie, 796:206–210; Glushkov AV, Loboda AV, Gurnitskaya EP, Svinarenko AA (2009) *Phys Scr T135:014022*; Khetselius OY (2009) *Phys Scr T135:014023*
42. Glushkov AV, Malinovskaya SV, Svinarenko AA, Chernyakova YG (2004) *Int J Quantum Chem* 99:879–896; Glushkov AV, Ambrosov SV, Loboda AV, Gurnitskaya EP, Prepelitsa GP (2005) *Int J Quantum Chem* 104:562–569