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Electron states and adiabatic potential of the hydrogen bond

ЛЬВІВ

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Електронні стани та адіабатичні потенціали водневого зв'язку

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Анотація. Вивчаються властивості водневого зв'язку на прикладі найпростішого об'єкту, що містить водневий зв'язок, - іонного комплексу $O-H-O$. Отримано електронний енергетичний спектр комплекса $O-H-O$. Досліджується формування двомінімумного адіабатичного потенціалу для протона в залежності від довжини водневого зв'язку R_{OO}, відстані R_{OH}, числа електронів N на комплексі. Отримано карти електронної густини і розподілу електронного заряду вздовж осі комплекса. Досліджено також зміну густини електронного заряду і заселеностей атомних орбіталей вихідного базису в залежності від зміщення протона вздовж водневого зв'язку.

Electron states and adiabatic potential of the hydrogen bond

I.V.Stasyuk, Yu.V.Sizonenko, R.Ya.Stetsiv

Abstract. The properties of the hydrogen bond are investigated on the basis of the simplest object with hydrogen bond, the ionic complex $O-H-O$. The electron energy spectrum of the $O-H-O$ complex is obtained. The formation of the two-minima adiabatic proton potential as a function of the hydrogen bond length R_{OO}, R_{OH} distance, electron number N in complex is investigated. The electron density graphs and distribution of the electron charge along the complex axis are obtained. Also we investigate the change of the electron charge density and the occupancy of the atomic orbitals of the initial basis connected with proton shifts along the hydrogen bond.

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1. Introduction

There are many papers devoted to the investigation of the hydrogen bond systems including review papers sheding some light on the nature of the hydrogen bond [1-5]. The main subjects are the study of the electron structure, optimum geometry, investigation of the adiabatic potentials for the proton, vibrational spectra, proton transfer. Nevertheless, the problem of the formation of adiabatic potential for the proton needs a more detailed study. For example the role of the Coulomb components of the interaction between excessive charges, which appear during the displacement of ions and electron redistribution, are not sufficiently studied. In the paper [6] the authors propose new model in which a strong coupling between the protons and distorsion of the structural units, connected by the hydrogen bonds (for example, PO_4 tetrahedrons in KH_2PO_4 crystal) is assumed and the interaction between protons is disregarded. It is supposed there that the distorsion of tetrahedron is proportional to its electric dipole moment. One should try to extend such models, as not only dipole moment on the edge structure units changes with the proton motions along hydrogen bond, but the charge value is changed also.

The problem of the formation of the locally anharmonic lattice potentials using model approach was considered in [7]. In the present paper this problem is solved on the basis of quantum chemical calculations.

We consider ionic complex $O-H-O$ (in further reffered to $A-B-A'$). The Hamiltonian of such complex has a following form:

$$H(\vec{r},R)=\sum_i(-\frac{\hbar^2}{2m}\Delta_i)+\sum_{i<j}\frac{e^2}{|\vec{r}_i-\vec{r}_j|}+\sum_{i,n}U(\vec{r}_i-\vec{R}_n)+$$
$$+\sum_n(-\frac{\hbar^2}{2M_n}\Delta_n)+{\sum_{m,n}}'W(\vec{R}_m-\vec{R}_n), \qquad (1)$$

where $\vec{r}_i$, $\vec{R}_m$ - electron and ion coordinates.

The first three terms form the electron part of the Hamiltonian; the last two describe the ionic subsystem;

$$U(\vec{r}_i-\vec{R}_n)=\frac{e^2Z_{el}}{|\vec{r}_i-\vec{R}_n|} \qquad (2)$$
$$W(\vec{R}_m-\vec{R}_n)=\frac{e^2Z_{ion}}{|\vec{R}_m-\vec{R}_n|},$$

here Z_{el} and Z_{ion} are the effective ion charges (excluding valence electrons) used for the description of the interaction between them and other electrons or ions respectively.

In the present paper we calculate the electron spectrum of the $O-H-O$ cluster. The formation of the adiabatic proton potential as a function of the hydrogen bond length R_{OO}, R_{OH} distance, electron number in cluster N is investigated. The electron density pictures and distribution of electron charge along complex axis is obtained. We investigate also the change of the electron charge density with proton shift along the bond.

2. Initial basis of electon wavefunctions and its orthogonalization.

In our model approach we take into consideration the minimum basis of electron wavefunctions consisting of the three valence atomic orbitals. The 2p-functions of oxygen ions ($\{\psi_a(\vec{r}-\vec{R}_a)\}$, $\{\psi_{a'}(\vec{r}-\vec{R}_{a'})\}$), directed along the hydrogen bond and 1s-function of the hydrogen atom ($\{\psi_b(\vec{r}-\vec{R}_b)\}$) are taken into account.

They are the solutions of the corresponding Schrodinger equations

$$\left[\sum_i(-\frac{\hbar^2}{2m}\Delta_i)+U(\vec{r}_i-\vec{R}_s)\right]\psi_s(\vec{r}_i)=E_s\psi_s(\vec{r}_i), \qquad (3)$$

(here $s=a,b,a'$).

At first the orthogonalization of functions ψ_a and $\psi_{a'}$ is performed:

$$\tilde{\psi_a}=N_1(\psi_a+\psi_{a'}) \quad N_1=\frac{1}{\sqrt{2(1+S_{aa'})}} \qquad (4)$$
$$\tilde{\psi_{a'}}=N_2(\psi_a-\psi_{a'}) \quad N_2=\frac{1}{\sqrt{2(1-S_{aa'})}}$$

Here $S_{aa'}=\int\psi_a^*(\vec{r})\psi_{a'}(\vec{r})d\vec{r}$ - overlap integral of initial atomic function.

The transformation of vector 45^o rotation type is used for symmetrization of the new basis.

$$\varphi_a(\vec{r})=\frac{1}{\sqrt{2}}(\tilde{\psi_a}+\tilde{\psi_{a'}})=\xi\psi(\vec{r}-\vec{R}_a)+\eta\psi(\vec{r}-\vec{R}_{a'}) \qquad (5)$$
$$\varphi_{a'}(\vec{r})=\frac{1}{\sqrt{2}}(\tilde{\psi_a}-\tilde{\psi_{a'}})=\eta\psi(\vec{r}-\vec{R}_a)+\xi\psi(\vec{r}-\vec{R}_{a'})$$

Here

$$\xi = \frac{1}{2\sqrt{(1+S_{aa'})}} + \frac{1}{\sqrt{2(1-S_{aa'})}}$$
$$\eta = \frac{1}{2\sqrt{(1+S_{aa'})}} - \frac{1}{\sqrt{2(1-S_{aa'})}} \qquad (6)$$

Orthogonizing the third function to the first and the second ones gives:

$$\varphi_b = \rho\psi_b(\vec{r}-\vec{R}_b) + \xi_a\varphi_a + \xi_{a'}\varphi_{a'} = \qquad (7)$$
$$\rho\psi(\vec{r}-\vec{R}_b) + (\xi_a\xi + \xi_{a'}\eta)\psi(\vec{r}-\vec{R}_a) + (\xi_{a'}\xi + \xi_a\eta)\psi(\vec{r}-\vec{R}_{a'})$$

Here the following notations are introduced:

$$\rho = \sqrt{\frac{1-S_{aa'}^2}{1-S_{aa'}^2-S_{ba}^2-S_{ba'}^2+S_{ba}S_{ba'}S_{aa'}}};$$
$$\xi_a = -(S_{ba}\xi + S_{ba'}\eta)\rho; \qquad (8)$$
$$\xi_{a'} = -(S_{ba}\eta + S_{ba'}\xi)\rho,$$

The functions $\{\ \varphi_a, \varphi_b, \varphi'_a\ \}$ form a orthogonalized and normalized basis of states.

3. Electron spectra and electron density distribution for $O-H-O$ cluster.

Electron part of the Hamiltonian (1) in secondary quantization representation on $\{\varphi_l(\vec{r})\}$ basis has the following form:

$$H_{el}(R) = \epsilon_1\sum_\sigma c^\dagger_{a\sigma}c_{a\sigma} + \epsilon_3\sum_\sigma c^\dagger_{a'\sigma}c_{a'\sigma} + \epsilon_2\sum_\sigma c^\dagger_{b\sigma}c_{b\sigma} +$$
$$+t_{ab}\sum_\sigma(c^\dagger_{a\sigma}c_{b\sigma} + c^\dagger_{b\sigma}c_{a\sigma}) + t_{a'b}\sum_\sigma(c^\dagger_{a'\sigma}c_{b\sigma} + c^\dagger_{b\sigma}c_{a'\sigma}) +$$
$$+t_{aa'}\sum_\sigma(c^\dagger_{a\sigma}c_{a'\sigma} + c^\dagger_{a'\sigma}c_{a\sigma}) +$$
$$U(n_{a\uparrow}n_{a\downarrow} + n_{a'\uparrow}n_{a'\downarrow}) + U'(n_{b\uparrow}n_{b\downarrow}) +$$

$$+\Phi\sum_\sigma n_{a-\sigma}(c^\dagger_{a\sigma}c_{b\sigma} + c^\dagger_{b\sigma}c_{a\sigma}) + \Phi_1\sum_\sigma n_{b-\sigma}(c^\dagger_{a\sigma}c_{b\sigma} + c^\dagger_{b\sigma}c_{a\sigma}) +$$
$$+\Phi'\sum_\sigma n_{a'-\sigma}(c^\dagger_{a'\sigma}c_{b\sigma} + c^\dagger_{b\sigma}c_{a'\sigma}) +$$
$$\Phi'_1\sum_\sigma n_{b-\sigma}(c^\dagger_{a'\sigma}c_{b\sigma} + c^\dagger_{b\sigma}c_{a'\sigma}) +$$
$$+\Phi_a\sum_\sigma(n_{a-\sigma} + n_{a'-\sigma})(c^\dagger_{a\sigma}c_{a'\sigma} + c^\dagger_{a'\sigma}c_{a\sigma}) +$$
$$+K\sum_{\sigma\sigma'}n_{a\sigma}n_{b\sigma'} + K'\sum_{\sigma\sigma'}n_{a'\sigma}n_{b\sigma'} + V\sum_{\sigma\sigma'}n_{a\sigma}n_{a'\sigma'} + \qquad (9)$$
$$+(Q/2)\sum_\sigma(c^\dagger_{a\sigma}c^\dagger_{a-\sigma}c_{b-\sigma}c_{b\sigma} + c^\dagger_{b\sigma}c^\dagger_{b-\sigma}c_{a-\sigma}c_{a\sigma}) -$$
$$-Q\sum_{\sigma\sigma'}c^\dagger_{b\sigma}c^\dagger_{b\sigma'}c_{a\sigma'}c_{a\sigma} +$$
$$+(Q'/2)\sum_\sigma(c^\dagger_{a'\sigma}c^\dagger_{a'-\sigma}c_{b-\sigma}c_{b\sigma} + c^\dagger_{b\sigma}c^\dagger_{b-\sigma}c_{a'-\sigma}c_{a'\sigma}) -$$
$$-Q'\sum_{\sigma\sigma'}c^\dagger_{b\sigma}c^\dagger_{b\sigma'}c_{a'\sigma'}c_{a'\sigma} +$$
$$+(Q_a/2)\sum_\sigma(c^\dagger_{a\sigma}c^\dagger_{a-\sigma}c_{a'-\sigma}c_{a'\sigma} + c^\dagger_{a'\sigma}c^\dagger_{a'-\sigma}c_{a-\sigma}c_{a\sigma}) -$$
$$-Q_a\sum_{\sigma\sigma'}c^\dagger_{a'\sigma}c^\dagger_{a'\sigma'}c_{a\sigma'}c_{a\sigma} +$$
$$+L_1\sum_{\sigma\sigma'}(c^\dagger_{a\sigma}c^\dagger_{a'\sigma'}c_{b\sigma'}c_{a\sigma} + c^\dagger_{a\sigma}c^\dagger_{b\sigma'}c_{a'\sigma'}c_{a\sigma}) +$$
$$+L'_1\sum_{\sigma\sigma'}(c^\dagger_{a'\sigma}c^\dagger_{a\sigma'}c_{b\sigma'}c_{a'\sigma} + c^\dagger_{a'\sigma}c^\dagger_{b\sigma'}c_{a\sigma'}c_{a'\sigma}) +$$
$$+L_2\sum_{\sigma\sigma'}(c^\dagger_{b\sigma}c^\dagger_{a'\sigma'}c_{a\sigma'}c_{b\sigma} + c^\dagger_{b\sigma}c^\dagger_{a\sigma'}c_{a'\sigma'}c_{b\sigma}) +$$
$$+L_3\sum_\sigma(c^\dagger_{a\sigma}c^\dagger_{a-\sigma}c_{b-\sigma}c_{a'\sigma} + c^\dagger_{a'\sigma}c^\dagger_{b-\sigma}c_{a-\sigma}c_{a\sigma}) +$$
$$+L_3\sum_{\sigma\sigma'}(c^\dagger_{a'\sigma}c^\dagger_{a\sigma'}c_{b\sigma'}c_{a\sigma} + c^\dagger_{a\sigma}c^\dagger_{b\sigma'}c_{a\sigma'}c_{a'\sigma}) +$$
$$+L'_3\sum_\sigma(c^\dagger_{a'\sigma}c^\dagger_{a'-\sigma}c_{b-\sigma}c_{a\sigma} + c^\dagger_{a\sigma}c^\dagger_{b-\sigma}c_{a'-\sigma}c_{a'\sigma}) +$$
$$+L'_3\sum_{\sigma\sigma'}(c^\dagger_{a\sigma}c^\dagger_{a'\sigma'}c_{b\sigma'}c_{a'\sigma} + c^\dagger_{a'\sigma}c^\dagger_{b\sigma'}c_{a'\sigma'}c_{a\sigma}) +$$

$$+L_4\sum_{\sigma}(c^{\dagger}_{b\sigma}c^{\dagger}_{b-\sigma}c_{a-\sigma}c_{a'\sigma}+c^{\dagger}_{a'\sigma}c^{\dagger}_{a-\sigma}c_{b-\sigma}c_{b\sigma})+$$
$$+L_4\sum_{\sigma\sigma'}(c^{\dagger}_{a'\sigma}c^{\dagger}_{b\sigma'}c_{a\sigma'}c_{b\sigma}+c^{\dagger}_{b\sigma}c^{\dagger}_{a\sigma'}c_{b\sigma'}c_{a'\sigma}).$$

Here the notations are used

$$t_{ij}=<i|-\frac{\hbar^2}{2m}\Delta+\sum_m U(\vec{r}-\vec{R}_m)|j>=$$
$$=\int\varphi_i^*(\vec{r})(-\frac{\hbar^2}{2m}\Delta+\sum_m U(\vec{r}-\vec{R}_m))\varphi_j(\vec{r})d\vec{r};$$
$$<ij|...|kl>\equiv\langle ij|\frac{e^2}{|\vec{r}_1-\vec{r}_2|}|kl\rangle=$$
$$\int\varphi_i^*(\vec{r_1})\varphi_j^*(\vec{r_2})\frac{e^2}{|\vec{r}_1-\vec{r}_2|}\varphi_k(\vec{r_1})\varphi_l(\vec{r_2})d\vec{r}_1d\vec{r}_2$$
$$U=<aa|...|aa>;\quad U'=<bb|...|bb>;$$
$$\Phi=<aa|...|ab>;\quad \Phi_1=<bb|...|ba>;$$
$$\Phi'=<a'a'|...|a'b>;\quad \Phi'_1=<bb|...|ba'>;\qquad(10)$$
$$\Phi_a=<aa'|...|aa>=<a'a'|...|a'a>;$$
$$K=<ab|...|ab>;\quad K'=<a'b|...|a'b>;\quad V=<aa'|...|aa'>;$$
$$Q=<aa|...|bb>;\quad Q'=<a'a'|...|bb>;\quad Q_a=<aa|...|a'a'>;$$
$$L_1=<aa'|...|ab>;\quad L'_1=<a'a|...|a'b>;\quad L_2=<ba'|...|ba>;$$
$$L_3=<aa|...|a'b>;\quad L'_3=<a'a'|...|ab>;\quad L_4=<bb|...|aa'>;$$
$$\epsilon_1=t_{aa};\quad \epsilon_2=t_{bb};\quad \epsilon_3=t_{a'a'};\quad t=t_{ab};\quad t'=t_{a'b}.$$

Let us go to the basis of electron states in occupation number representation $|n_{a\uparrow}n_{a\downarrow}n_{b\uparrow}n_{b\downarrow}n_{a'\uparrow}n_{a'\downarrow}>$, which includes 64 states:

	$\|p>$		$\|p>$		$\|p>$
$\|000000>$	$\|1>$	$\|111000>$	$\|23>$	$\|111001>$	$\|45>$
$\|100000>$	$\|2>$	$\|110100>$	$\|24>$	$\|110110>$	$\|46>$
$\|010000>$	$\|3>$	$\|110010>$	$\|25>$	$\|110101>$	$\|47>$
$\|001000>$	$\|4>$	$\|110001>$	$\|26>$	$\|110011>$	$\|48>$
$\|000100>$	$\|5>$	$\|101100>$	$\|27>$	$\|101110>$	$\|49>$
$\|000010>$	$\|6>$	$\|101010>$	$\|28>$	$\|101101>$	$\|50>$
$\|000001>$	$\|7>$	$\|101001>$	$\|29>$	$\|101011>$	$\|51>$
$\|110000>$	$\|8>$	$\|100110>$	$\|30>$	$\|100111>$	$\|52>$
$\|101000>$	$\|9>$	$\|100101>$	$\|31>$	$\|011110>$	$\|53>$
$\|100100>$	$\|10>$	$\|100011>$	$\|32>$	$\|011101>$	$\|54>$
$\|100010>$	$\|11>$	$\|011100>$	$\|33>$	$\|011011>$	$\|55>$
$\|100001>$	$\|12>$	$\|011010>$	$\|34>$	$\|010111>$	$\|56>$
$\|011000>$	$\|13>$	$\|011001>$	$\|35>$	$\|001111>$	$\|57>$
$\|010100>$	$\|14>$	$\|010110>$	$\|36>$	$\|111110>$	$\|58>$
$\|010010>$	$\|15>$	$\|010101>$	$\|37>$	$\|111101>$	$\|59>$
$\|010001>$	$\|16>$	$\|010011>$	$\|38>$	$\|111011>$	$\|60>$
$\|001100>$	$\|17>$	$\|001110>$	$\|39>$	$\|110111>$	$\|61>$
$\|001010>$	$\|18>$	$\|001101>$	$\|40>$	$\|101111>$	$\|62>$
$\|001001>$	$\|19>$	$\|001011>$	$\|41>$	$\|011111>$	$\|63>$
$\|000110>$	$\|20>$	$\|000111>$	$\|42>$	$\|111111>$	$\|64>$
$\|000101>$	$\|21>$	$\|111100>$	$\|43>$		
$\|000011>$	$\|22>$	$\|111010>$	$\|44>$		

(11)

Hamiltonian (9) matrix on this basis is easier presentable using Hubbard operators X^{pq} acting as $X^{pq}|r>=\delta_{qr}|p>$. The transition to X-representation may be performed using the formulae for electron creation operators written on this basis:

$$c^{\dagger}_{a,\uparrow}=X^{2,1}+X^{12,7}+X^{11,6}+X^{32,22}+X^{10,5}+X^{31,21}+X^{30,20}+$$
$$+X^{52,42}+X^{9,4}+X^{29,19}+X^{28,18}+X^{51,41}+X^{27,17}+X^{50,40}+$$
$$+X^{49,39}+X^{62,57}+X^{8,3}+X^{26,16}+X^{25,15}+X^{48,38}+X^{24,14}+$$
$$+X^{47,37}+X^{46,36}+X^{61,56}+X^{23,13}+X^{45,35}+X^{44,34}+X^{60,55}+$$
$$+X^{43,33}+X^{59,54}+X^{58,53}+X^{64,63}$$
$$c^{\dagger}_{a,\downarrow}=X^{3,1}+X^{16,7}+X^{15,6}+X^{38,22}+X^{14,5}+X^{37,21}+X^{36,20}+$$
$$+X^{56,42}+X^{13,4}+X^{35,19}+X^{34,18}+X^{55,41}+X^{33,17}+X^{54,40}+$$
$$+X^{53,39}+X^{63,57}+X^{8,2}-X^{26,12}-X^{25,11}-X^{48,32}-X^{24,10}-$$

$$-X^{47,31}-X^{46,30}-X^{61,52}+X^{23,9}-X^{45,29}-X^{44,28}-X^{60,51}-$$
$$-X^{43,27}-X^{59,50}-X^{58,49}-X^{64,62}$$
$$c^{\dagger}_{b,\uparrow}=X^{4,1}+X^{19,7}+X^{18,6}+X^{41,22}+X^{17,5}+X^{40,21}+X^{39,20}+$$
$$+X^{57,42}-X^{13,3}-X^{35,16}-X^{34,15}-X^{55,38}-X^{33,14}-X^{54,37}-$$
$$-X^{53,36}-X^{63,56}-X^{9,2}-X^{29,12}-X^{28,11}-X^{51,32}-X^{27,10}-$$
$$-X^{50,31}-X^{49,30}-X^{62,52}+X^{23,8}+X^{45,26}+X^{44,25}+X^{60,48}+$$
$$+X^{43,24}+X^{59,47}+X^{58,46}+X^{64,61} \qquad (12)$$
$$c^{\dagger}_{b,\downarrow}=X^{5,1}+X^{21,7}+X^{20,6}+X^{42,22}-X^{17,4}-X^{40,19}-X^{39,18}-$$
$$-X^{57,41}-X^{14,3}-X^{37,16}-X^{36,15}-X^{56,38}+X^{33,13}+X^{54,35}+$$
$$+X^{53,34}+X^{63,55}-X^{10,2}-X^{31,12}-X^{30,11}-X^{52,32}+X^{27,9}+$$
$$+X^{50,29}+X^{49,28}+X^{62,51}+X^{24,8}+X^{47,26}+X^{46,25}+X^{61,48}-$$
$$-X^{43,23}-X^{59,45}-X^{58,44}-X^{64,60}$$
$$c^{\dagger}_{a',\uparrow}=X^{6,1}+X^{22,7}-X^{20,5}-X^{42,21}-X^{18,4}-X^{41,19}+X^{39,17}+$$
$$+X^{57,40}-X^{15,3}-X^{38,16}+X^{36,14}+X^{56,37}+X^{34,13}+X^{55,35}-$$
$$-X^{53,33}-X^{63,54}-X^{11,2}-X^{32,12}+X^{30,10}+X^{52,31}+X^{28,9}+$$
$$+X^{51,29}-X^{49,27}-X^{62,50}+X^{25,8}+X^{48,26}-X^{46,24}-X^{61,47}-$$
$$-X^{44,23}-X^{60,45}+X^{58,43}+X^{64,59}$$
$$c^{\dagger}_{a',\downarrow}=X^{7,1}-X^{22,6}-X^{21,5}+X^{42,20}-X^{19,4}+X^{41,18}+X^{40,17}-$$
$$-X^{57,39}-X^{16,3}+X^{38,15}+X^{37,14}-X^{56,36}+X^{35,13}-X^{55,34}-$$
$$-X^{54,33}+X^{63,53}-X^{12,2}+X^{32,11}+X^{31,10}-X^{52,30}+X^{29,9}-$$
$$-X^{51,28}-X^{50,27}+X^{62,49}+X^{26,8}-X^{48,25}-X^{47,24}+X^{61,46}-$$
$$-X^{45,23}+X^{60,44}+X^{59,43}-X^{64,58}$$

As a result, Hamiltonian will possess the following form: $H_{el}(R)=\sum_{pq}H_{pq}(R)X^{pq}$.

In present paper cases $N=3$,$N=4$,$N=5$ are analyzed.

Matrix $H_{ij}(R)$ on this basis consists of independed blocks each of them corresponding to different number of electrons N. Using adopted conceptions of valency, the most probable number of electrons on such cluster $O-H-O$ (in its three valent states that compose initial basis and organise hydrogen bond) is four (N=4, see examples in fig. 1).

The realization of other values of N also is possible when electron transfer between ions participating in forming of different hydrogen bonds takes place.

For $N=4$ case the corresponding basis of states includes 15 states. Matrix $H_{ij}(R)$ of (15x15) size consists of three blocks: (3x3) - summary

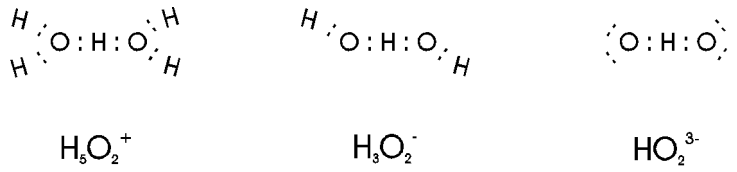

Figure 1. Chemical bonds in H_nO_2 clusters

spin projection $S^z=+1$; (3x3) - summary spin projection $S^z=-1$; (9x9) - summary spin projection $S^z=0$. The most energetically advantageous case $S^z=0$ is realised on states

$$\begin{array}{lll} |43>=|111100> & |48>=|110011> & |53>=|011110> \\ |45>=|111001> & |50>=|101101> & |55>=|011011> \\ |46>=|110110> & |52>=|100111> & |57>=|001111> \end{array} \qquad (13)$$

For $N=3$ case matrix $H_{ij}(R)$ of (15x15) size consists of four blocks: (1x1) - summary spin projection $S^z=-3/2$; (1x1) - summary spin projection $S^z=+3/2$; (9x9) - summary spin projection $S^z=+1/2$; (9x9) - summary spin projection $S^z=-1/2$. Cases with opposite spin are equivalent. $S^z=1/2$ case is realised on the states

$$\begin{array}{lll} |23>=|111000> & |29>=|101100> & |34>=|011010> \\ |25>=|110010> & |30>=|100110> & |39>=|001110> \\ |27>=|110110> & |32>=|100011> & |41>=|001011> \end{array} \qquad (14)$$

For $N=5$ case matrix $H_{ij}(R)$ of (15x15) size consists of two blocks: (3x3) - summary spin projection $S^z=+1/2$; (3x3) - summary spin projection $S^z=-1/2$. $S^z=1/2$ case is realised on the states

$$\begin{array}{l} |58>=|111110> \\ |60>=|111011> \\ |62>=|101111> \end{array} \qquad (15)$$

The components of matrix $H_{ij}(R)$ blocks corresponding to the states (13), (14), (15) are given in Appendix 1.

Matrix elements $H_{ij}(R)$ are formed by the matrix elements (10) on the orthogonalized basis of functions $\varphi_l(\vec{r})$, which in turn are liniar combinations of corresponding matrix elements built on the initial basis of atomic functions $\psi_m(\vec{r})$. Analytical expressions obtained for some of them are given in Appendix 2. General scheme of calculations is described and formulae for evaluation of exchange integrals are also presented there. For the rest of the matrix elements numerical evaluation was performed (including evaluation of 3-center integrals) on the basis of atomic functions $\psi_m(\vec{r})$.

For the numerical calculations the methods of Monte-Carlo type for multi-dimensional integrals are used. Error of evaluation was no more then 4%.

Matrix of the Hamiltonian, obtained as a result of orthogonalization, was diagonalized, its eigenvalues λ_i and eigenvectors were found.

Eigenvalues of Hamiltonian of electron subsystem (where ion-electron and electron-electron interactions were considered) were added by the enegry of ion-ion interaction (excluding oxygen-oxygen interaction), the result spectrum for the given values of distance R_{OO} is presented as a dependence on the R_{OH} distance (see fig. 2).

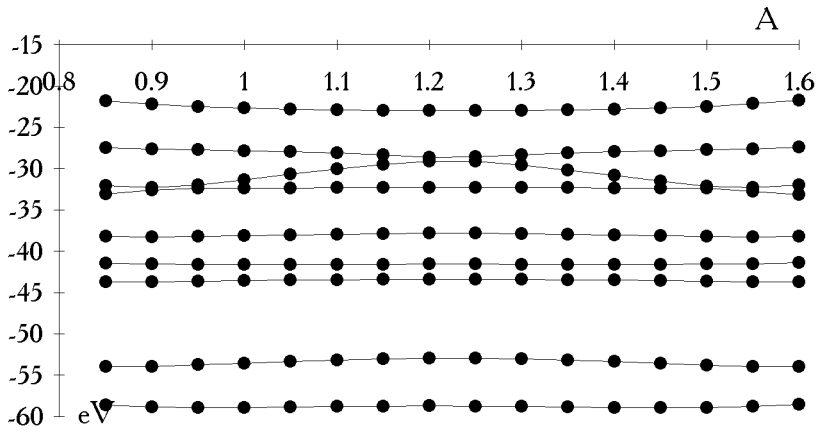

Figure 2. Dependence of the energy spectrum of system (eV) on R_{OH} distance (A) at the following values of parameters: $N = 4$, $R_{OO} = 2.44$, $Z_{el} = 1.5$, $Z_{ion} = 2.5$.

The lowest level from this spectrum is presented on fig. 3. It is shown, that at bond length smaller then some critical value, we have a potential with one central minimum, which at the increasing of the complex length

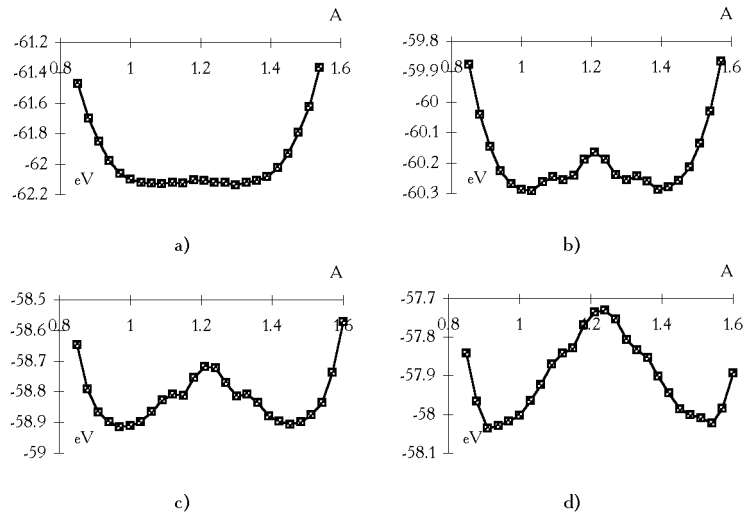

Figure 3. Lowest level of energy spectrum of system (proton adiabatic potential) as a function of R_{OH} distance at $N = 4$ ($Z_{el} = 1.5, Z_{ion} = 2.5$) at different values of bond lenght: a) $R_{OO} = 2.38A$ c) $R_{OO} = 2.44A$ b) $R_{OO} = 2.42A$ d) $R_{OO} = 2.46A$

transforms into double-well potential. This fact show us the existance of two equlibrium states of system, different in the shift of the central ion in opposite directions along complex axis. At some values of effective charges Z_{el} and Z_{ion} we can obtain parameters of proton potential on hydrogen bond known from experiments. Optimum Z values are different for different number of electrons on cluster $O - H - O'$. The results of calculations are especially sensitive to the difference $\Delta Z = Z_{ion} - Z_{el}$. Optimum values for model parameters are $2.0 \leq \alpha \leq 2.1$; $\Delta Z = 1.0$ ($N = 4$); $\Delta Z = 0.3$ ($N = 3$); $\Delta Z = 2.0$ ($N = 5$), howewer $Z_{el} > 1$. For the given values of effective parameters critical value of hydrogen bond length is $R^{cr}_{OO} = 2.38A$ which is in accordance with known from literature data (see [5]). As one can see from fig. 3-5 values of effective parameters optimal for the case $N = 4$ are insufficient for the cases $N = 3$ and $N = 5$ as R^{cr}_{OO} value does not correspond to the known data and are 2.68A and 2.14A correspondingly. At increasing of the hydrogen bond length the height of the potential barrier increases also as well as δ value - distance between positions of minima of the proton potential on bond.

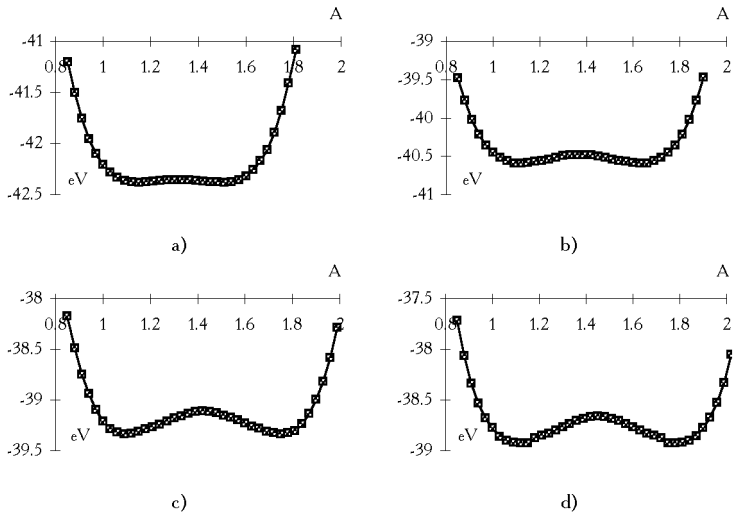

Figure 4. Lowest level of energy spectrum of system (proton adiabatic potential) as a function of R_{OH} distance at $N = 3$ ($Z_{el} = 1.5, Z_{ion} = 2.5$) at different values of bond lenght: a) $R_{OO} = 2.65A$ c) $R_{OO} = 2.85A$ b) $R_{OO} = 2.75A$ d) $R_{OO} = 2.9A$

Using eigenvectors of Hamiltonian, corresponding, in particular, to the lowest eigenvalue λ_{min}, the distribution of the electron density was obtained. The states of basis of diagonalized Hamiltonian are linearly expressed by the states of previos basis

$$|\tilde{i}>=\sum_j \alpha_{ij}|j> \tag{16}$$

then electron density of states should be

$$\tilde{\rho}_i(\vec{r}) = \sum_j \alpha_{ij}^2 \rho_j(\vec{r}) \tag{17}$$

The density of the initial state $\rho_j(\vec{r})$, built on the basis of atomic wavefunctions $\{\varphi_1(\vec{r}), \varphi_2(\vec{r}), \varphi_3(\vec{r})\}$ can be expressed as

$$\rho_j(\vec{r}) = \sum_i^3 n_i(j)|\varphi_i(\vec{r})|^2 \tag{18}$$

here $n_i(j)$ - number of electrons at ion i in state j. For the $N = 4$ case

density distribution is presented at fig. 6a and 6b (for the proton located in one of the pots and in the middle of the bond correspondingly).

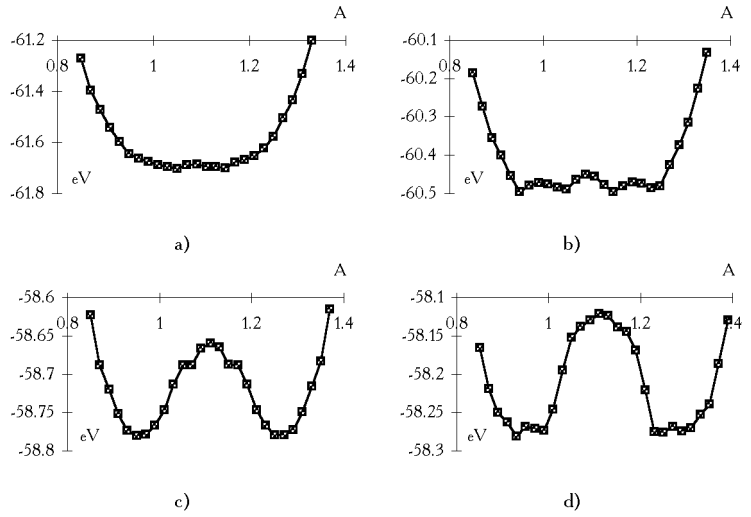

Figure 5. Lowest level of energy spectrum of system (proton adiabatic potential) as a function of R_{OH} distance at $N = 5$ ($Z_{el} = 1.5, Z_{ion} = 2.5$) at different values of bond lenght: a) $R_{OO} = 2.17A$ c) $R_{OO} = 2.22A$ b) $R_{OO} = 2.19A$ d) $R_{OO} = 2.23A$

Howewer, more informational is the distribution of electron density along the complex axis as the result of integration of the space distribution over the planes, perpendicular to the complex axis. (see fig. 7a and 7b). The difference between curves showes us redistribution of the electron density with proton shifts from the central position.

On the basis of the electron density distribution in space the atomic orbitals occupations were calculated using the method of minimal squares. If $f(x)$ - obtained earlier electron distribution; $F(x) = \sum_i n_i \psi_i^2(x)$ - some helper function (coefficients n_i are occupations), then n_i are found from the condition of minimum of the $\sigma^2 = \int (f(x) - F(x))\psi_i^2(x)$. Solving the equation $\frac{\partial \sigma^2}{\partial n_i} = 0$ we obtain orbital occupations (see fig. 8) as dependences on the R_{OH} distance.

A lot of papers were devoted to the calculation of electron spectrum and adiabatic potential of the proton on bond (see [1-5]) for different structures with hydrogen bonds. Our goal was to concentrate more on the investigation of the electron density change caused by the ion shifts,

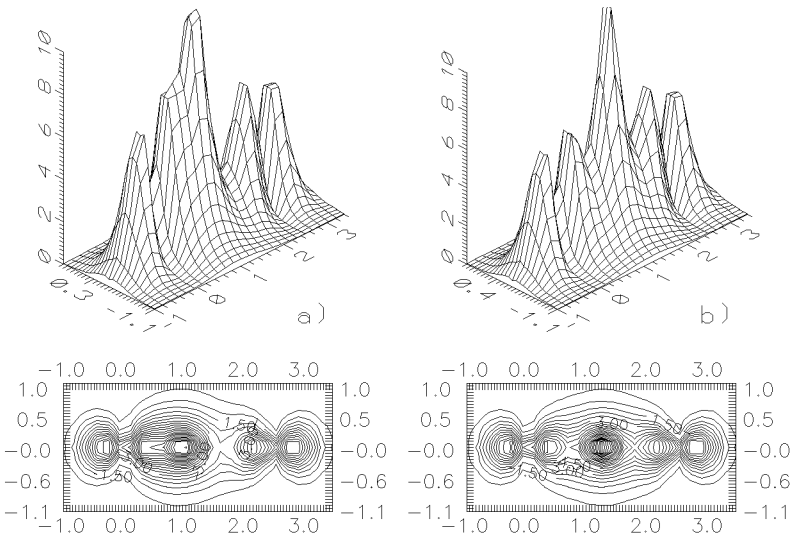

Figure 6. Electron density distribution in the plane parallel to complex axis at different positions of proton: a) in the left pot of the effective potential; b) in the middle of the bond. $N = 4$, $Z_{el} = 1.5$, $Z_{ion} = 2.5$, $R = 2.44A$

in particular, hydrogen motion on bond. Similar calculations for the cluster with few hydrogen bonds allow us to investigate correlations between electron density change and proton-proton short-range interactions. Describing system with hydrogen bonds using different models one should take into account short-range proton-proton interactions. Until now such short-range correlations were postulated and their nature was not studied. The role of electron subsystem there is evidently especial as it can determine the actual proton-proton interaction. Thats why the study of electron density change with proton shifts is important. We obtained that proton shifts on bond is accompanied by increasing of the summary electron density at the regions where the proton is moved to (see fig. 6-7); howewer, the occupancy of the $2p$-orbitals of the corresponding oxygen ion is decreased. Occupancy of $1s$-orbitals of hydrogen ion changes weakly and possesses maximum at the location of proton in the middle of the bond (see fig.8).

More detailed study of the electron density change in system with hydrogen bonds connected with ion shifts will give an oppotunity to formulate more real models for description of such objects.

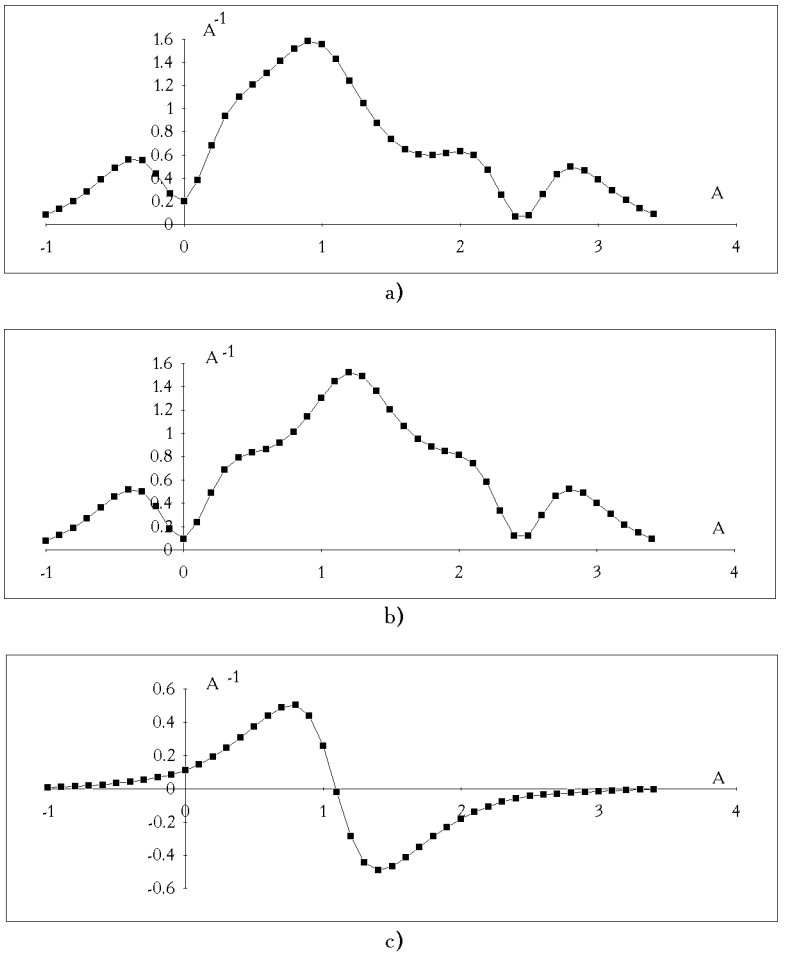

Figure 7. Linear electron density distribution along complex axis at different positions of proton: a) in the left pot of the effective potential; b) in the middle of the bond; c) change of electron density with proton shifts from the central position (over value of R_{OH} distance). $N = 4$, $Z_{el} = 1.5$, $Z_{ion} = 2.5$, $R = 2.44A$

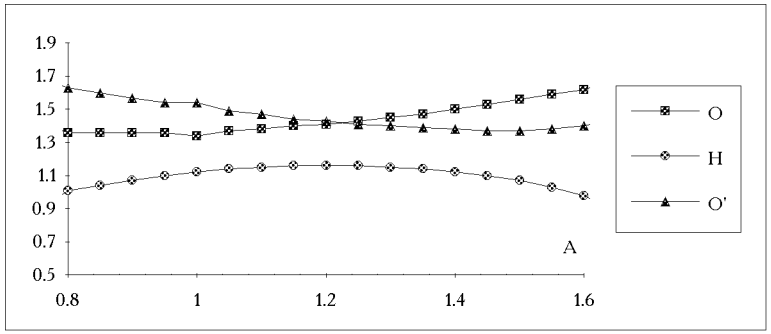

Figure 8. Orbital occupation versa R_{OH} distance ($N = 4$, $Z_{el} = 1.5$, $Z_{ion} = 2.5$, $R = 2.44A$)

Acknowledgements

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References

1. Reviews in Computational Chemistry. / Eds. K.B.Lipkowitz, D.B.Boyd, VCH, New York, 1991./ Scheiner S. Calculating the Properties of Hydrogen Bonds by ab Initio Methods, vol.2. ch.6, pp. 165-218.
2. Aggregation Processes in Solution. / Eds. E.Wyn-Jones and J.Gorally, Elsevier, Amsterdam, 1983. / Scheiner S. Molecular Orbital Treatment of Hydrogen-Bonded Systems, p. 462-508.
3. The Hydrogen Bond. Recent Developments in Theory and Experiments. / Eds. P.Schuster, G.Zundel and Sandorfy, North-Holland, Amsterdam, 1976.
4. Structure and Dynamics of WeaklyBound Molecular Complexes. / Ed. A.Weber, Reidel, Dordrecht, 1987.
5. Proton Transfer in Hydrogen-Bonded Systems. / Ed. T.Bountic, Plenum Press, New York, 1992. / Scheiner S. Extraction of the principles of proton transfer by ab inition methods. p. 29-47.

6. Sugimoto H., Ikeda S. Isotope effects in hydrogen-bonded crystal KH_2PO_4. // Phys.Rev.Lett., vol.67, N10, pp.1306-1309.
7. Stasyuk I.V., Sizonenko Yu.V. Effective local anharmonic potentials in solids. A model approach. // Condensed Matter Physics, 1995, iss.5, pp. 161-191.
8. Gombas P. Theorie and losungsmethoden des mehrtielchenproblems der wellenmechanic. Basel, 1950
9. Slater J. Quantum theory of molecules and solids. Volume 1. Electronic structure of molecules. - Mc. Grawhill Book Company, Inc. New York - San Francisko - Toronto - London, 1963.
10. Flygare W.H. Molecular structure and dynamics. v.1, v.2 - Moskow, Myr, 1982 - 872p.
11. Bersuker I.B. Electronic structure and properties of coordinational units. L.: Chemistry, 1986 - 287p.
12. Batsanov S.S., Zviagina P.A. Overlap integrals and problem of effective charges. - Novosibirsk: Nauka, 1966 - v.I. - 385p.

Appendix 1. Matrix blocks corresponding to the examined cases.

Case N=3:

$$
\begin{aligned}
H(23,23) &= 2\epsilon_1 + \epsilon_2 + 2K - Q + U \\
H(23,25) &= 2L_1 - L_3 + t' \\
H(23,27) &= -\Phi - \Phi_1 - t \\
H(23,29) &= -L_2 - \Phi_a - t_{aa'} \\
H(23,30) &= L_4 \\
H(23,32) &= -L_3' \\
H(23,34) &= L_2 - L_4 + \Phi_a + t_{aa'} \\
H(23,39) &= -L_3 \\
H(23,41) &= Q_a \\
H(25,23) &= 2L_1 - L_3 + t' \\
H(25,25) &= 2\epsilon_1 + \epsilon_3 - Q_a + U + 2V \\
H(25,27) &= -L_4 \\
H(25,29) &= -L_3' \\
H(25,30) &= L_1' + \Phi + t \\
H(25,32) &= -2\Phi_a - t_{aa'} \\
H(25,34) &= -L_1' + L_3' - \Phi - t
\end{aligned}
$$

$$H(25,39) = Q$$
$$H(25,41) = -L_3$$
$$H(27,23) = -\Phi - \Phi_1 - t$$
$$H(27,25) = -L_4$$
$$H(27,27) = \epsilon_1 + 2\epsilon_2 + 2K - Q + U'$$
$$H(27,29) = L_1 + \Phi_1' + t'$$
$$H(27,30) = -L_1 + L_3 - \Phi_1' - t'$$
$$H(27,32) = Q'$$
$$H(27,34) = -L_3$$
$$H(27,39) = 2L_2 - L_4 + t_{aa'}$$
$$H(27,41) = -L_3'$$
$$H(29,23) = -L_2 - \Phi_a - t_{aa'}$$
$$H(29,25) = -L_3'$$
$$H(29,27) = L_1 + \Phi_1' + t'$$
$$H(29,29) = \epsilon_1 + \epsilon_2 + \epsilon_3 + K + K' - Q + V$$
$$H(29,30) = -Q'$$
$$H(29,32) = L_1 - L_3 + \Phi' + t'$$
$$H(29,34) = -Q_a$$
$$H(29,39) = L_3'$$
$$H(29,41) = -L_2 + L_4 - \Phi_a - t_{aa'}$$
$$H(30,23) = L_4$$
$$H(30,25) = L_1' + \Phi + t$$
$$H(30,27) = -L_1 + L_3 - \Phi_1' - t'$$
$$H(30,29) = -Q'$$
$$H(30,30) = \epsilon_1 + \epsilon_2 + \epsilon_3 + K + K' - Q_a + V$$
$$H(30,32) = -L_1 - \Phi' - t'$$
$$H(30,34) = -Q$$
$$H(30,39) = L_1' - L_3' + \Phi_1 + t$$
$$H(30,41) = -L_4$$
$$H(32,23) = -L_3'$$
$$H(32,25) = -2\Phi_a - t_{aa'}$$
$$H(32,27) = Q'$$
$$H(32,29) = L_1 - L_3 + \Phi' + t'$$

$$H(32,30) = -L_1 - \Phi' - t'$$
$$H(32,32) = \epsilon_1 + 2\epsilon_3 - Q_a + U + 2V$$
$$H(32,34) = L_3$$
$$H(32,39) = -L_4$$
$$H(32,41) = 2L_1' - L_3' + t$$
$$H(34,23) = L_2 - L_4 + \Phi_a + t_{aa'}$$
$$H(34,25) = -L_1' + L_3' - \Phi - t$$
$$H(34,27) = -L_3$$
$$H(34,29) = -Q_a$$
$$H(34,30) = -Q$$
$$H(34,32) = L_3$$
$$H(34,34) = \epsilon_1 + \epsilon_2 + \epsilon_3 + K + K' - Q' + V$$
$$H(34,39) = -L_1' - \Phi_1 - t$$
$$H(34,41) = L_2 + \Phi_a + t_{aa'}$$
$$H(39,23) = -L_3$$
$$H(39,25) = Q$$
$$H(39,27) = 2L_2 - L_4 + t_{aa'}$$
$$H(39,29) = L_3'$$
$$H(39,30) = L_1' - L_3' + \Phi_1 + t$$
$$H(39,32) = -L_4$$
$$H(39,34) = -L_1' - \Phi_1 - t$$
$$H(39,39) = 2\epsilon_2 + \epsilon_3 + 2K' - Q' + U'$$
$$H(39,41) = -\Phi' - \Phi_1' - t'$$
$$H(41,23) = Q_a$$
$$H(41,25) = -L_3$$
$$H(41,27) = -L_3'$$
$$H(41,29) = -L_2 + L_4 - \Phi_a - t_{aa'}$$
$$H(41,30) = -L_4$$
$$H(41,32) = 2L_1' - L_3' + t$$
$$H(41,34) = L_2 + \Phi_a + t_{aa'}$$
$$H(41,39) = -\Phi' - \Phi_1' - t'$$
$$H(41,41) = \epsilon_2 + 2\epsilon_3 + 2K' - Q' + U$$

Case N=4:

$$H(43,43) = 2\epsilon_1 + 2\epsilon_2 + 4K - 2Q + U + U'$$
$$H(43,45) = 2L_1 - L_3 + \Phi_1' + t'$$
$$H(43,46) = -2L_1 + L_3 - \Phi_1' - t'$$
$$H(43,48) = Q'$$
$$H(43,50) = 2L_2 - L_4 + \Phi_a + t_{aa'}$$
$$H(43,52) = -L_3'$$
$$H(43,53) = -2L_2 + L_4 - \Phi_a - t_{aa'}$$
$$H(43,55) = L_3'$$
$$H(43,57) = Q_a$$
$$H(45,43) = 2L_1 - L_3 + \Phi_1' + t'$$
$$H(45,45) = 2\epsilon_1 + \epsilon_2 + \epsilon_3 + 2K + K' - Q - Q_a + U + 2V$$
$$H(45,46) = -Q'$$
$$H(45,48) = 2L_1 - L_3 + \Phi' + t'$$
$$H(45,50) = -L_1' + L_3' - \Phi - \Phi_1 - t$$
$$H(45,52) = L_4$$
$$H(45,53) = -L_3'$$
$$H(45,55) = L_2 - L_4 + 2\Phi_a + t_{aa'}$$
$$H(45,57) = -L_3$$
$$H(46,43) = -2L_1 + L_3 - \Phi_1' - t'$$
$$H(46,45) = -Q'$$
$$H(46,46) = 2\epsilon_1 + \epsilon_2 + \epsilon_3 + 2K + K' - Q - Q_a + U + 2V$$
$$H(46,48) = -2L_1 + L_3 - \Phi' - t'$$
$$H(46,50) = -L_3'$$
$$H(46,52) = L_2 - L_4 + 2\Phi_a + t_{aa'}$$
$$H(46,53) = -L_1' + L_3' - \Phi - \Phi_1 - t$$
$$H(46,55) = L_4$$
$$H(46,57) = L_3$$
$$H(48,43) = Q'$$
$$H(48,45) = 2L_1 - L_3 + \Phi' + t'$$
$$H(48,46) = -2L_1 + L_3 - \Phi' - t'$$
$$H(48,48) = 2\epsilon_1 + 2\epsilon_3 - 2Q_a + 2U + 4V$$
$$H(48,50) = -L_4$$

$$H(48,52) = 2L_1' - L_3' + \Phi + t$$
$$H(48,53) = L_4$$
$$H(48,55) = -2L_1' + L_3' - \Phi - t$$
$$H(48,57) = Q$$
$$H(50,43) = 2L_2 - L_4 + \Phi_a + t_{aa'}$$
$$H(50,45) = -L_1' + L_3' - \Phi - \Phi_1 - t$$
$$H(50,46) = -L_3'$$
$$H(50,48) = -L_4$$
$$H(50,50) = \epsilon_1 + 2\epsilon_2 + \epsilon_3 + 2K + 2K' - Q - Q' + U' + V$$
$$H(50,52) = -L_1 + L_3 - \Phi' - \Phi_1' - t'$$
$$H(50,53) = -Q_a$$
$$H(50,55) = -L_3$$
$$H(50,57) = 2L_2 - L_4 + \Phi_a + t_{aa'}$$
$$H(52,43) = -L_3'$$
$$H(52,45) = L_4$$
$$H(52,46) = L_2 - L_4 + 2\Phi_a + t_{aa'}$$
$$H(52,48) = 2L_1' - L_3' + \Phi + t$$
$$H(52,50) = -L_1 + L_3 - \Phi' - \Phi_1' - t'$$
$$H(52,52) = \epsilon_1 + \epsilon_2 + 2\epsilon_3 + K + 2K' - Q_a - Q' + U + 2V$$
$$H(52,53) = -L_3$$
$$H(52,55) = -Q$$
$$H(52,57) = 2L_1' - L_3' + \Phi_1 + t$$
$$H(53,43) = -2L_2 + L_4 - \Phi_a - t_{aa'}$$
$$H(53,45) = -L_3'$$
$$H(53,46) = -L_1' + L_3' - \Phi - \Phi_1 - t$$
$$H(53,48) = L_4$$
$$H(53,50) = -Q_a$$
$$H(53,52) = -L_3$$
$$H(53,53) = \epsilon_1 + 2\epsilon_2 + \epsilon_3 + 2K + 2K' - Q - Q' + U' + V$$
$$H(53,55) = -L_1 + L_3 - \Phi' - \Phi_1' - t'$$
$$H(53,57) = -2L_2 + L_4 - \Phi_a - t_{aa'}$$
$$H(55,43) = L_3'$$
$$H(55,45) = L_2 - L_4 + 2\Phi_a + t_{aa'}$$

$$H(55,46) = L_4$$
$$H(55,48) = -2L_1' + L_3' - \Phi - t$$
$$H(55,50) = -L_3$$
$$H(55,52) = -Q$$
$$H(55,53) = -L_1 + L_3 - \Phi' - \Phi_1' - t'$$
$$H(55,55) = \epsilon_1 + \epsilon_2 + 2\epsilon_3 + K + 2K' - Q_a - Q' + U + 2V$$
$$H(55,57) = -2L_1' + L_3' - \Phi_1 - t$$
$$H(57,43) = Q_a$$
$$H(57,45) = -L_3$$
$$H(57,46) = L_3$$
$$H(57,48) = Q$$
$$H(57,50) = 2L_2 - L_4 + \Phi_a + t_{aa'}$$
$$H(57,52) = 2L_1' - L_3' + \Phi_1 + t$$
$$H(57,53) = -2L_2 + L_4 - \Phi_a - t_{aa'}$$
$$H(57,55) = -2L_1' + L_3' - \Phi_1 - t$$
$$H(57,57) = 2\epsilon_2 + 2\epsilon_3 + 4K' - 2Q' + U + U'$$

Case N=5:

$$H(58,58) = 2\epsilon_1 + 2\epsilon_2 + \epsilon_3 + 4K + 2K' - \\ -2Q - Q_a - Q' + U + U' + 2V$$
$$H(58,60) = -2L_1 + L_3 - \Phi' - \Phi_1' - t'$$
$$H(58,62) = -2L_2 + L_4 - 2\Phi_a - t_{aa'}$$
$$H(60,58) = -2L_1 + L_3 - \Phi' - \Phi_1' - t'$$
$$H(60,60) = 2\epsilon_1 + \epsilon_2 + 2\epsilon_3 + 2K + 2K' - \\ -Q - 2Q_a - Q' + 2U + 4V$$
$$H(60,62) = -2L_1' + L_3' - \Phi - \Phi_1 - t$$
$$H(62,58) = -2L_2 + L_4 - 2\Phi_a - t_{aa'}$$
$$H(62,60) = -2L_1' + L_3' - \Phi - \Phi_1 - t$$
$$H(62,62) = \epsilon_1 + 2\epsilon_2 + 2\epsilon_3 + 2K + 4K' - \\ -Q - Q_a - 2Q' + U + U' + 2V$$

Appendix 2. Some integrals used in the electron spectra of $O-H-O'$ cluster calculations.

1. We have obtained analytical expressions for some integrals used for the calculations of the $O-H-O'$ cluster electron spectra. The atomic orbitals were chosen in the form of Slater functions:

$$\psi = R_{nl}(r) \cdot Y_{lm}(\theta, \varphi) \tag{19}$$

Radial part of the function has the following form:

$$R_{nl}(\vec{r}) = A_{n,l}(\alpha) r^{n^*-1} e^{-\alpha \frac{r}{a_0}} \tag{20}$$

where the normalized factor $A_{n,l}(\alpha)$ is equal:

$$[A_{n,l}(\alpha)]^2 = \int_0^\infty dr r^{-2n^*} e^{-2\alpha \frac{r}{a_0}}, \alpha = \frac{z^*}{n^*} \tag{21}$$

n^* – effective quantum number (for $1s, 2p$ – functions $n^* = n$), z^* – effective nuclear charge, a_0 – the first Bohr orbital radius. Generally the values α (or z^*) are the variational parameters but one can use the values for them obtained for this atom in another compounds (see Appendix 3).

We have calculated the two centre integrals using spheroidal coordinates [8,9]

$$\lambda = \frac{r_a + r_b}{R}, \mu = \frac{r_a - r_b}{R}, \varphi = \varphi_a = \varphi_b \tag{22}$$

Element of volume in this coordinates is:

$$dV = \frac{R^3}{8}(\lambda^2 - \mu^2) d\lambda d\mu d\varphi$$

there are the boundris of integration:

$$1 \le \lambda \le \infty, -1 \le \mu \le 1, 0 \le \varphi \le 2\pi$$

Here r_a i r_b means the electron distance from two center a and b, R is the distance between centers.

We present the analytical expressions obtained for some molecular integrals, which are not mentioned in literature, for example in [8,9]:

$$\int \psi_A(\vec{r}) \frac{e^2}{r_A} \psi_B(\vec{r}) d\vec{r} = \frac{1}{4} \cdot \frac{e^2}{a_0} \alpha_H \alpha_0^2 \sqrt{\frac{1}{3}\alpha_H \alpha_0} \left(\frac{R}{a_0}\right)^3 \times \\ \times \frac{1}{p} e^{-p} \cdot \frac{4}{\gamma} \left\{ \frac{1}{p} \left(1 + \frac{1}{p}\right) \sinh\gamma + \frac{1}{\gamma} \left(\cosh\gamma - \frac{1}{\gamma}\sinh\gamma\right) \right\} \tag{23}$$

$$\int \psi_A(\vec{r})\frac{e^2}{r_B}\psi_B(\vec{r})d\vec{r} = \frac{1}{4}\cdot\frac{e^2}{a_0}\alpha_H\alpha_0^2\sqrt{\frac{1}{3}\alpha_H\alpha_0}\left(\frac{R}{a_0}\right)^3\times$$
$$\times\left\{e^{\gamma}+\left(\frac{1}{p}-\frac{1}{\gamma}\right)\sinh\gamma\right\} \qquad (24)$$

Here $\psi_A(\vec{r})$ – $2p$ – oxygen orbital, directed along the line connected the centres ($2P_\sigma$), $\psi_B(\vec{r})$ – $1s$ hydrogen orbital.

Here:

$$p=\frac{\alpha_b+\alpha_A}{2}\cdot\frac{R}{a_0}, \gamma=\frac{\alpha_b-\alpha_A}{2}\cdot\frac{R}{a_0} \qquad (25)$$

The following expression is obtained for the Coulomb integral

$$\int \psi_A^2(r_1)\frac{e^2}{|\vec{r}_1-\vec{r}_2|}\cdot\psi_B^2(\vec{r}_2)d\vec{r}_1d\vec{r}_2 =$$
$$=\frac{1}{2}\cdot\frac{e^2}{R}\left\{2+\frac{6}{g^2}-\left(2g^3+6g^2+11g+14+\frac{12}{g}+\frac{6}{g^2}\right)e^{-2g}\right\}-$$
$$-\frac{1}{8}(g)^5\cdot\frac{1}{u}\cdot\frac{e^2}{R}\cdot\frac{2}{s}e^{-u}\left(\left\{\left(3+\frac{5}{u}+\frac{6}{u^2}+\frac{6}{u^3}\right)\cdot\right.\right.$$
$$\cdot\left(\sinh s-\frac{2}{s}\cosh s+\frac{2\sinh s}{s^2}\right)-$$
$$-\left(3+\frac{4}{u}+\frac{4}{u^2}\right)\left(-\cosh s+\frac{1}{s}\sinh s\right)+\left(1+\frac{1}{u}\right)\sinh s- \qquad (26)$$
$$\left.-\left(1+\frac{2}{u}+\frac{4}{u^2}\right)\left(-\cosh s+\frac{3}{s}\sinh s-\frac{6}{s^2}\cosh s+\frac{6}{s^3}\sinh s\right)\right\}+$$
$$+\frac{1}{2}\cdot\rho\cdot\left\{\left(1+\frac{2}{u}+\frac{2}{u^2}\right)\sinh s-\right.$$
$$-2\left(1+\frac{3}{u}+\frac{6}{u^2}+\frac{6}{u^3}\right)\left(-\cosh s+\frac{1}{s}\sinh s\right)+$$
$$+\left(\frac{4}{u}+\frac{12}{u^2}+\frac{24}{u^3}+\frac{24}{u^4}\right)\cdot\left(\sinh s-\frac{2}{s}\cosh s+\frac{2}{s^2}\sinh s\right)+$$
$$+2\left(1+\frac{1}{u}\right)\left(-\cosh s+\frac{3}{s}\sinh s-\frac{6}{s^2}\cosh s+\frac{6}{s^3}\sinh s\right)-$$
$$-\left(1+\frac{2}{u}+\frac{2}{u^2}\right)\cdot$$
$$\left.\left.\cdot\left(\sinh s-\frac{4}{s}\cosh s+\frac{12}{s^2}\sinh s-\frac{24}{s^3}\cosh s+\frac{24}{s^4}\sinh s\right)\right\}\right).$$
$$u=2p, s=2\gamma, g=\alpha_O\frac{R}{a_0}, \rho=\alpha_H\frac{R}{a_0}$$

We have obtained the energy of the Coulomb repulsion between two electrons in $1s$-state of the hydrogen atom:

$$\int \psi_B^2(\vec{r}_1)\frac{e^2}{r_{12}}\psi_B^2(\vec{r}_2)d\vec{r}_1d\vec{r}_2=\frac{5}{8}\cdot\frac{e^2}{a_0}\mu_H, \qquad (27)$$

which concide with the known in the literature expression for the Helium atom [8]. In the case of the Coulomb repulsion between two electrons in $2p$-state of the oxygen atom we have:

$$\int \psi_A^2(\vec{r}_1)\frac{e^2}{r_{12}}\psi_A^2(\vec{r}_2)d\vec{r}_1d\vec{r}_2=\frac{501}{1280}\cdot\frac{e^2}{a_0}\mu_0, \qquad (28)$$

Here $|\vec{r}_1-\vec{r}_2|=r_{12}$.

Below we present the formula, obtained for one of the hybrid integrals:

$$\int \psi_B^2(\vec{r}_1)\frac{e^2}{r_{12}}\psi_A(\vec{r}_2)\psi_B(\vec{r}_2)d\vec{r}_1d\vec{r}_2 =$$
$$=\frac{1}{4}\frac{e^2}{a_0}(\mu_H)^{3/2}(\mu_0)^{5/2}\left(\frac{R}{a_0}\right)^3\cdot\left(\frac{4}{\gamma}\cdot\frac{1}{p}e^{-p}\right.$$
$$\left\{\left(1+\frac{1}{p}\right)\cdot\left(\sinh\gamma-\frac{1}{\gamma}\cosh\gamma+\frac{1}{\gamma^2}\sinh\gamma\right)-\right.$$
$$\left.\left(1+\frac{1}{p_1}+\frac{1}{p_1^2}\right)\left(-\cosh\gamma_1+\frac{1}{\gamma_1}\sinh\gamma_1\right)\right\}- \qquad (29)$$
$$-\frac{4}{\gamma_1}\cdot\frac{1}{p_1}e^{-p_1}\left\{\left(1+\frac{1}{p_1}\right)\left(\sinh\gamma_1-\frac{\cosh\gamma_1}{\gamma_1}+\frac{\sinh\gamma_1}{\gamma_1^2}\right)-\right.$$
$$\left.\left(1+\frac{1}{p_1}+\frac{1}{p_1^2}\right)\left(-\cosh\gamma_1+\frac{\sinh\gamma_1}{\gamma_1}\right)\right\}-$$
$$\frac{\mu_H}{2}\frac{R}{a_0}\frac{4}{\gamma_1}\frac{1}{p_1}e^{-p_1}\left\{\left(\frac{1}{p_1}+\frac{1}{\gamma_1}\right)e^{\gamma_1}+\left(\frac{1}{p_1^2}+\frac{1}{\gamma_1^2}\right)\sinh\gamma_1-\right.$$
$$-3\left(\frac{1}{p_1^2}+\frac{1}{p_1^3}\right)\left(-\cosh\gamma_1+\frac{1}{\gamma_1}\sinh\gamma_1\right)+$$
$$\left.+3\left(1+\frac{1}{p_1}\right)\left(-\frac{1}{\gamma_1^2}\cosh\gamma_1+\frac{1}{\gamma_1^3}\sinh\gamma_1\right)\right\}\Big),$$

where

$$p_1=\frac{3\mu_H+\mu_0}{2}\cdot\frac{R}{a_0}; \gamma_1=\frac{3\mu_H-\mu_0}{2}\cdot\frac{R}{a_0}$$

2. One can obtain the analytical expression for the exchange integral

$$\tilde{Q} = \int \psi_A^*(\vec{r}_1)\psi_B^*(\vec{r}_2) \cdot \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}\psi_B(\vec{r}_1)\psi_A(\vec{r}_2)d\vec{r}_1 d\vec{r}_2 \qquad (30)$$

only in the case of hydrogen molecula, or in the case where $\psi_A(\vec{r}_1)$ and $\psi_B(\vec{r}_2)$ are the same nS functions, which are centered at A i B points. In the other cases one can obtain the analytical expression for the exchange integral only in the form of the infinite series. The authors propose the general scheme of the calculation and formula in the form of infinity series, obtained for the exchange integrals in the case, when electron functions $\psi(\vec{r})$ are S-type functions n_1S and P-type functions directed along the line connecting atoms (n_2P_σ); n_1, n_2 - the principal quantum numbers.

We have used the expansion into a series in the spheroidal coordinates of the $\frac{1}{|\vec{r}_1-\vec{r}_2|}$ function [9]:

$$\frac{1}{|\vec{r}_1 - \vec{r}_2|} = \frac{2}{R}\sum_{k=0}^{\infty}\sum_{m=-k}^{k}(-1)^m(2k+1)\left[\frac{(k-|m|)!}{(k+|m|)!}\right]^2 P_k^{|m|}[\lambda(a)] *$$
$$*Q_k^{|m|}[\lambda(b)]P_k^{|m|}(\mu_1)P_k^{|m|}(\mu_2)e^{im(\varphi_1-\varphi_2)} \qquad (31)$$

Here $\lambda_1, \mu_1, \varphi_1$ i $\lambda_2, \mu_2, \varphi_2$ – spheroidal coordinates of the two electrons, $\lambda(a)$ – is the minimum and $\lambda(b)$ – is the maximum from λ_1 and λ_2, $Q_k^{|m|}$ – Legendre functions of the second type.

$$Q_k^{|m|}(x) = (1-x^2)^{\frac{|m|}{2}}\frac{d^{|m|}}{dx^m}Q_k(x)$$
$$Q_k(x) = \frac{1}{2}P_k(x)\ln\frac{x+1}{x-1} - \frac{1\cdot 3....(2k-1)}{k!}\cdot \qquad (32)$$
$$\cdot\left\{x^{k-1} + x^{k-3}\left[\frac{1}{3} - \frac{k(k-1)}{2(2k-1)}\right] + \right.$$
$$\left. + x^{k-5}\cdot\left[\frac{1}{5} - \frac{1}{3}\frac{k(k-1)}{2(2k-1)} + \frac{k(k-1)(k-2)(k-3)}{2\cdot 4(2k-1)(2k-3)}\right] + ...\right\}$$

A series continues to the last positive power of x

Quantum numbers m_1 and m_2 are equal zero for n_1S and $n_2P\sigma$ – functions therefore only components $m = 0$ from the sum over m in (31) give contribution to $\tilde{Q}$ (30), which will be:

$$\frac{2}{R}\sum_{k=0}^{\infty}(2k+1)P_k[\lambda(a)]Q_k[\lambda(b)]P_k(\mu_1)P_k(\mu_2)$$

Then we go to the spheroidal coordinats in integrand for $\tilde{Q}$ (30). Let us consider the part of the integrand (without $\frac{1}{r_{12}}$) depending on one variable $\psi_A(\vec{r}_1)\psi_B(\vec{r}_1)d\vec{r}_1$. After transition to spheroidal coordinates we obtain:

$$\psi_A(\vec{r}_1)\psi_B(\vec{r}_1)d\vec{r}_1 = \beta M_1(\lambda_1, \mu_1,) \qquad (33)$$

where $M_1(\lambda_1, \mu_1)$ is a polinomial in spheroidal coordinates.

Coefficient β does not involve the variable of integration and is equal to the product of normalized factors of functions ψ_A and ψ_B; also it includes multiplyer $2\pi(\frac{R}{2})^{n_1+n_2+1}$. The coefficient β is equal $\beta = 2(\frac{\alpha_H}{a_0})^{3/2}(\frac{\alpha_0}{a_0})^{5/2}(\frac{R}{2})^4$ in the case when $\psi_A = 2\rho_\sigma(0)$, $\psi_B = 1S(H)$. Let us consider the underintegral expression in λ_1, μ_1 variables for k-term of series. The expression (33) is multiplied by the Legendre polinomial $P_k(\mu_1)$:

$$\beta M_1(\lambda_1, \mu_1) * P_k(\mu_1) = \beta M_2^k(\lambda_1, \mu_1) \qquad (34)$$

Now, the variable μ_1 is involved in the M_2^k polynomial. The integration of the $M_2^k(\lambda_1, \mu_1)$ polinom over the μ_1 variable is not complicated:

$$\int_{-1}^{1}\mu_1^n e^{-\gamma\mu_1}d\mu_1 = F(n,\gamma,1) - F(n,\gamma,-1) \qquad (35)$$

where

$$F(n,\alpha,r) \equiv \int r^n e^{-\alpha r}dr = -\frac{n!}{\alpha^{n+1}}e^{-\alpha r}\sum_{s=0}^{n}\frac{(\alpha r)^s}{s!} \qquad (36)$$

Denote

$$\beta\int_{-1}^{1}M_2^k(\lambda_1, \mu_1)d\mu_1 = \beta M_3^k(\lambda_1) \qquad (37)$$

Obtained polinomial in the variable λ_1 (37) is multiplied further by the Legendre function of λ_1 variable, from (31) series. Denote

$$\beta M_3^k(\lambda_1)\cdot P_k(\lambda_1) = \beta\sum_i A_i^k\lambda_i^{m_i} \qquad (38)$$

In the integrand for $\tilde{Q}$ the following components also are presented:

$$\beta M_3^k(\lambda_1) * f_k(\lambda_1) = \beta\sum_j C_j^k\lambda_i^{m_j} \qquad (39)$$

We write (see 32)

$$Q_k(x) = \frac{1}{2}P_k(x)\ln\frac{x+1}{x-1} - f_k(x) \qquad (40)$$

We have obtained the general formula for the exchange integral (30)

$$\tilde{Q} = \frac{e^2}{R}\beta^2 \sum_{k=0}^{\infty}(2k+1)\sum_i\sum_j \left(A_i^k A_j^k \cdot \right.$$
$$\{F(m_i,p,1)\cdot F(m_j,p,1)\,[c+\ln p] -$$
$$-\,[F(m_i,p,-1)F(m_j,p,1)+F(m_i,p,1)F(m_j,p,-1)]\times$$
$$\times E_i(-2p)+F(m_i,p,-1)F(m_j,p,-1)*E_i(-4p)+$$
$$+F(m_i,p,1)\cdot\frac{m_j!}{p^{m_j+1}}e^{-p}\sum_{s=1}^{m_j}\frac{p^s}{s!}\sum_{k'=0}^{s-1}C_s^{k'}\frac{(s-k'-1)!}{p^{s-k'}}\times$$
$$\times\left(1-\frac{1}{2^{s-k'}}-(-1)^{k'}\sum_{l=0}^{s-k'-1}\frac{(2p)^l}{l!}\right)-F(m_i,p,-1)\cdot \qquad (41)$$
$$\cdot\frac{m_j!}{p^{m_j+1}}e^{p}\sum_{s=1}^{m_j}\frac{p^s}{s!}\sum_{k'=0}^{s-1}(-1)^{k'}C_s^{k'}\cdot F(s-k'-1,2p,2)+$$
$$+\frac{m_i!}{p^{m_i+1}}\sum_{s=1}^{m_i}\frac{p^s}{s!}\sum_{k'=0}^{s-1}C_s^{k'}\frac{(s-k'-1)!}{p^{s-k'}}\times$$
$$\left.\times\sum_{l=0}^{s-k'-1}\frac{p^l}{l!}\sum_{l_1=0}^{l}C_l^{l_1}F(m_j+l-l_1,2p,1)\cdot[(-1)^{l_1}-(-1)^{k'}]\right\}+$$
$$+2A_i^kC_j^k\left\{-\frac{m_i!}{p^{m_i+1}}\sum_{s=0}^{m_i}\frac{p^s}{s!}F(n_j+s,2p,1)-\right.$$
$$\left.-F(m_i,p,1)\cdot F(n_j,p,1)+\frac{n_j!}{p^{n_j+1}}\sum_{l=0}^{n_j}\frac{p^l}{l!}F(m_i+l,2p,1)\right. \qquad (42)$$

$E_i(x)$ is the exponential integral

$$E_i(-x) = -\int_x^{\infty}\frac{e^{-t}}{t}dt,\ \text{where } x>0.$$

c is the Eyler constant

$$c = \int_0^1\frac{1-e^{-t}}{t}dt - \int_1^{\infty}\frac{e^{-t}}{t}dt = 0.577216$$

$C_s^k = \dfrac{s!}{k!(s-k)!}$ – coefficient from the Newton binomial

Let us consider the example of the described scheme realization in the calculation of the exchange integrals for the hydrogen molecula. We have

$$M_1 = \lambda_1^2-\mu_1^2,\ \beta=\frac{1}{4}(\alpha\frac{R}{a_0})^3,\ \alpha=1 \qquad (43)$$

The integration over the variable μ_1 is produces only two nonzero terms of a series (31) $k=0$ and $k=2$. We have for $k=0$:

$$M_2^{(0)}(\lambda_1,\mu_1) = M_1(\lambda_1,\mu_1) \qquad (44)$$

In accordance with (37) $M_3^{(0)}(\lambda_1) = 2\lambda_1^2-2/3$ and $A_1^{(0)}=2$, $m_1=2$; $A_2^{(0)}=-2/3$, $m_2=0$.

We have for $k=2$:

$$M_2^{(2)}(\lambda_1,\mu_1) = P_2(\mu_1)(\lambda_1^2-\mu_1^2) \qquad (45)$$
$$M_3^{(2)}(\lambda_1) = -4/5$$
$$\sum_i A_i^{(2)}\lambda_i^{m_i} = -\frac{4}{5}P_2(\lambda_1) = -\frac{2}{15}(2\lambda_1^2-1),$$

therefore $A_1^{(2)}=-2/5$, $m_1=2$; $A_2^{(2)}=2/15$, $m_2=0$.

Also $\sum_j C_j^{(2)}\lambda_1^{n_j} = M_3^{(2)}(\lambda_1)f_2(\lambda_1) = -(2/5)\lambda_1$ and $C_1^{(2)}=-2/5$, $n_1=1$.

One can obtain the known formula for the exchange integral of the hydrogen molecule [9] using the expression (41) and using the obtained above nonzero coefficients A_i, C_j.

Appendix 3. Effective parameters of the Slater type atomic orbitals.

It was obtained on the basis of the great amount of results of the electron structure calculations of the molecules and clusters, that the behaviour of the certain atom in the some class of compounds is the similar, and the calculations of the spectra of these compounds or moleculas in them give us the similar values of the effective parameters (which were taken as a variational parameters). There are determined the rules of the calculations of the effective parameters of the Slater type atomic orbitals on the basis of this results [10,11,12]. We used the modified Slater-Engus rules int the calculations of the effective parameters Z^* and n^* [12]. In

accordance to them we have for $n \leq 3$, $n^* = n$ and for the hydrogen and oxygen atom:

$\psi_{1s}^{(H)}$: $Z^* = 1$, $n^* = 1$, $\alpha(1S_H) = 1.0$

$\psi_{2p}^{(O)}$: $Z^* = 4.55$, $n^* = 2$, $\alpha(2P_O) = 2.275$

One can take into account the ionic state of the oxygen atomin the compounds, for example for O^{-1} and $O^{-1.5}$ we have

$\psi_{2p}^{(O^{-1})}$: $Z^* = 4.2$, $n^* = 2$, $\alpha(2P_{O^{-1}}) = 2.1$

$\psi_{2p}^{(O^{-1.5})}$: $Z^* = 4.025$, $n^* = 2$, $\alpha(2P_{O^{-1.5}}) = 2.012$

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