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QUANTUM-MECHANICAL CALCULATION OF ELECTRONIC STRUCTURE OF THE OZONE MOLECULE

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In work by a half-empirical method of Volfsberq-Helmholts are found a orbital energy, a molecular orbital (MO) and inhabiting of re-covering on connections of a molecule of ozone in base of sleyter functions.

In spite of the, that to the researching of ozone is devoted a lot of works [1] because of its uniqueness and many-sided applying, till today it is actually researches on studying of its structure by various methods. The elaboration on some of any its parameters will result to more effective understanding of kinetics processes occurring, as at the synthesis of ozone, and its balance in a nature.

In calculation considered two plane structures of a ozone molecule – right and isosceles triangle. Beginnings of common for all molecule the system of coordinates is at the center of weights, moreover the axis z is perpendicular to a plane of a molecule and the axis x passes through one of atoms of oxygen, which is numbered as 1st atom O_1.

It is known, that [2] in quantum- mechanical calculations of molecules it is possible to be limited only with the account valence atom orbitals (AO) of atoms, entering in compound of the given molecule and according of MO LCAO of molecular orbitals are represented as a linear combination these valence AO. Now most acceptable with physicals point of view as basic functions for molecular calculations by a method MO LCAO are considered sleyters functions [3,4].

Molecule of ozone consists from three atoms of oxygen, for each of which valence AO are 2s-, $2p_x$-, $2p_y$- and $2p_z$- sleyter functions. Thus, as basic AO we use following 12 slayter functions of atoms of oxygen:

$$\begin{aligned}&\chi_1=2s(0_1),\ \chi_2=2p_x(0_1),\ \chi_3=2p_y(0_1),\ \chi_4=2p_z(0_1);\\&\chi_5=2s(0_2),\ \chi_6=2p_x(0_2),\ \chi_7=2p_y(0_2),\ \chi_8=2p_z(0_2);\\&\chi_9=2s(0_3),\ \chi_{10}=2p_x(0_3),\ c_{11}=2p_y(0_3),\ c_{12}=2p_z(0_3);\end{aligned} \qquad (1)$$

Then MO of molecule of ozone could present as:

$$\psi_i = \sum_{q=1}^{12} c_{qi} \cdot \chi_q \qquad (2)$$

Here c_{qi}-unknown coefficients, which are defined according to a simple method of MO LCAO from the decision of system of the equations

$$\sum_q \left(H_{pq} - \varepsilon_i S_{pq}\right) c_{qi} = 0, \tag{3}$$

where the designations are entered:

$$H_{pq} = \int \chi_p^* \hat{H}_{EF} \chi_q d\mathrm{v} \tag{4}$$

$$S_{p1} = \int \chi_p^* \chi_q dv \tag{5}$$

The quantity H_{pq} represent by self of matrix elements of the effective operator of Hamilton for one electrons, moving in a molecule in some effective external field irrespective of others electrons, but the sizes S_{pq} are called as integrals re-covering between AO χ_p and χ_q.

Thus, for the decision of system of the equations (3), i.e. for define of orbital energy ε_i and according them MO ψ_i, i.e. unknown coefficient c_{qi}, entering to (2), it is necessary to know numerical meanings of matrix elements H_{pq} and integrals of re-covering S_{pq}.

However, the quantity H_{pq} could not be exact calculated and because, it is necessary estimate them by various ways, one of which is half-empirical method of Volfsberq-Helmholts (VH) [5]. According to a method VH diagonals matrix elements H_{pq} are equated to potential of ionization according of valence condition of the given atom, and the not diagonal matrix elements are defined by a ratio:

$$H_{pq} = 0{,}5kS_{pq}\left(H_{pp} + H_{qq}\right), \tag{6}$$

where the meaning of coefficient k is established from comparison with experimental data.

From above-stated follows, that for realization of quantum-mechanical calculations of molecules even by half-empirical method VH requires to find exact numerical meanings of integrals re-covering (5) in molecular system of coordinates. Let's notice, that in [6-8] in base of sleyters functions is obtained common analytical expression for integrals of re-covering in common for all molecule on system of coordinates, which is suitable at possible any combinations of quantum numbers. In computers calculations of a molecule of ozone by us used this formula for integrals of re-covering and following meanings potentials of ionization of valence condition of atom of oxygen [9]

$$\begin{aligned}(2s \mid 0 \mid 2s) &= -1{,}325536 \text{ a.u.} \\ (2p \mid 0 \mid 2p) &= -0{,}688959 \text{ a.u.}\end{aligned} \tag{7}$$

Inhabiting of re-covering (n_{AB}), i.e. measure of durability of connection between atoms A and B and effective charge q_A of atom A in a molecule are defined by the following formulas [10], accordingly:

$$n_{AB} = n_{BA} = 4\sum_i \sum_{p\in A} \sum_{q\in B} c_{pi} c_{qi} S_{pq}, \tag{8}$$

R=2.796796 a.u.; E= -9.800108 a.u. Table 1.

ε_i	-1.430337	-1.245750	-1.245750	-0.708640	-0.707700	-0.704535	-0.704535	-0.663981	-0.663981	-0.619093	-0.552903	-0.552903
AO	c_{q1}	c_{q2}	c_{q3}	c_{q4}	c_{q5}	c_{q6}	c_{q7}	c_{q8}	c_{q9}	c_{q10}	c_{q11}	c_{q12}
χ_1	0.508163	-0.877060	0.041701	0.000000	-0.112122	0.005030	-0.068654	0.000000	0.000000	-0.000000	-0.285588	-0.015216
χ_2	0.017227	-0.027481	0.001307	0.000000	-0.509548	0.027179	-0.370998	0.000000	0.000000	-0.000000	0.855111	0.045559
χ_3	0.000000	0.000000	0.000000	0.540622	0.000000	0.000000	0.000000	-0.423389	-0.733332	0.000000	0.000000	0.000000
χ_4	0.000000	-0.001104	-0.023228	0.000000	-0.000000	0.669986	0.049083	0.000000	0.000000	-0.651999	-0.022838	0.428648
χ_5	0.508163	0.402416	-0.780407	0.000000	-0.112122	-0.061970	0.029971	0.000000	0.000000	-0.000000	0.155971	-0.239718
χ_6	-0.008614	-0.024204	0.002997	0.000000	0.254774	0.420742	0.442762	0.000000	0.000000	0.564648	0.545103	-0.156145
χ_7	0.000000	0.000000	0.000000	0.540622	0.000000	0.000000	0.000000	0.846779	0.000000	0.000000	0.000000	0.000000
χ_8	0.014919	0.000586	-0.026505	0.000000	-0.441281	-0.143775	0.442646	0.000000	0.000000	0.326000	-0.224543	0.738657
χ_9	0.508163	0.474644	0.738706	0.000000	-0.112122	0.056941	0.038682	0.000000	0.000000	-0.000000	0.129617	0.254934
χ_{10}	-0.008614	-0.204379	-0.000687	0.000000	0.254774	-0.480777	0.376717	0.000000	0.000000	-0.564648	0.525425	0.213182
χ_{11}	0.000000	0.000000	0.000000	0.540622	0.000000	0.000000	0.000000	-0.423389	0.733332	0.000000	0.000000	0.000000
χ_{12}	0.014919	-0.003098	-0.026330	0.000000	0.441281	-0.077730	-0.458873	0.000000	0.000000	0.326000	0.144785	0.758334

R_{12}= R_{13}=2.759000 a.u.; R_{23}=4.699831 a.u.; φ=116.8^0; E= -9.58909 a.u. Table 2.

ε_i	-1.409429	-1.320641	-1.200740	-0.718155	-0.705092	-0.702614	-0.680247	-0.678176	-0.671747	-0.655020	-0.565571	-0.551477
AO	c_{q1}	c_{q2}	C_{q3}	c_{q4}	c_{q5}	c_{q6}	c_{q7}	c_{q8}	c_{q9}	c_{q10}	c_{q11}	c_{q12}
χ_1	-0.631613	-0.000000	0.794802	-0.000000	-0.081320	0.000000	0.000000	0.000000	-0.104954	0.000000	-0.330249	0.000000
χ_2	-0.007723	-0.000000	0.035261	-0.000000	-0.653010	0.000000	0.000000	0.000000	-0.412435	0.000000	0.685748	-0.000000
χ_3	0.000000	0.000000	0.000000	0.000000	0.000000	0.667106	-0.000000	0.000000	0.000000	-0.752391	0.000000	0.000000
χ_4	-0.000000	0.005391	-0.000000	0.530716	-0.000000	0.000000	0.000000	-0.035281	0.000000	0.000000	0.000000	0.937782
χ_5	-0.456245	0.710118	-0.552852	-0.087251	-0.052676	0.000000	0.000000	-0.001737	-0.013752	0.000000	0.145310	-0.170975
χ_6	0.006753	-0.000473	0.021507	0.355269	-0.179303	0.000000	0.000000	0.524223	0.646787	0.000000	0.245523	-0.349060
χ_7	0.000000	0.000000	0.000000	0.000000	0.000000	0.478855	0.708225	0.000000	0.000000	0.524088	0.000000	0.000000
χ_8	-0.010936	0.000761	-0.034719	-0.368799	-0.430951	0.000000	0.000000	0.480371	0.071732	0.000000	-0.591752	0.414205
χ_9	-0.456245	-0.710118	-0.552852	0.087251	-0.052676	0.000000	0.000000	0.001737	-0.013752	0.000000	0.145310	0.170975
χ_{10}	0.006753	0.000473	0.021507	-0.355269	-0.179307	0.000000	0.000000	-0.524223	0.646787	0.000000	0.245523	0.349060
χ_{11}	0.000000	0.000000	0.000000	0.000000	0.000000	0.478855	-0.708225	0.000000	0.000000	0.524088	0.000000	0.000000
χ_{12}	0.010936	0.000761	0.034719	-0.368799	0.430951	0.000000	0.000000	0.480371	-0.071732	0.000000	0.591752	0.414205

$$q_A = n_A^0 - 2\sum_i \sum_{p\in A} \left|c_{qi}\right|^2, \qquad (9)$$

where n_A^0 number of electrons in the isolated neutral atom A.

In the tables 1 and 2 the presents meanings of electronic energy E, orbital energies ε_i and coefficient c_{qi} in (2) (i.e MO), found by us in result of computers calculations by a method of VH for a molecule of ozone in case of right and isosceles triangle plane structure, accordingly.

Calculated by the formulas (8) and (9) on the base of the data of table 1 and 2 inhabiting of re-covering and effective charges in a.u. are given below:

Case right triangle:

$n_{12}=n_{13}=n_{23}=0{,}21975$

$q_1=q_2=q_3=2{,}186557$

Case isosceles triangle

$n_{12}=0{,}339801$ $q_1=3{,}251870$

$n_{13}=0{,}339801$ $q_2=1{,}658971$

$n_{23}=-0{,}020162$ $q_3=1{,}658971$

From comparison electronic energies E it is possible to make a conclusion about that as well as followed expect a isosceles triangle a plane structure of a molecule of ozone is more stable.

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OZON MOLEKULUNUN ELEKTRON STRUKTURUNUN KVANT – MEXANİKİ HESABLANMASI

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İşdə ozon molekulunun Volsberq-Helmholts yarımempirik metodu ilə sleyter funksiyalarının bazisində orbital enerjiləri, molekulyar orbitalları (MO) və rabitələrin örtülmələrin məmkunlaşması tapılmışdır.

КВАНТОВОМЕХАНИЧЕСКИЙ РАСЧЕТ ЭЛЕКТРОННОЙ СТРУКТУРЫ МОЛЕКУЛЫ ОЗОНА

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В работе полуэмпирическим методом Вольфсберга-Гельмгольца найдены орбитальные энергии, молекулярные орбитали (МО) и заселенности перекрывания на связях молекулы озона в базисе слейтеровских функций.