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Author(s)	Kamizato, Tsuneo; Yara, Asao
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**Molecular Orbital Calculation with The Extended Hückel Method for  $H_2O_2$  Molecule**

Tsuneo KAMIZATO\* and Asao YARA\*

**Summary**

We investigated the electronic structure of  $H_2O_2$  molecule using the extended Hückel method. The exchange integrals  $H_{ij}$  have been evaluated by using the Cusachs' approximation. The calculation has been carried out with the bond lengths and the O—O—H angle fixed to the experimental data and the dihedral angle used as the only parameter. The equilibrium dihedral angle, obtained as the result, almost coincide with the observed value, but the result for the electron population has come out poor.

We infer that the Cusachs type exchange integral gives fairly good result for small overlapping  $S_{ij}$  and rather poor result for large  $S_{ij}$ .

**1. Introduction**

There are many kinds of methods to calculate the electronic structure of molecules, namely the empirical simple and extended Hückel methods, various types of semi-empirical methods, non-empirical SCF LCAO methods, etc.. Recently, making use of computers, it has become possible to make fairly troublesome non-empirical SCF calculation, and some fruitful results have been obtained for small molecules.

However, there does not seem to exist satisfactory conditions enough to use such non-empirical and complex method for large molecules.. Especially macromolecules, such as enzyme proteins, nucleic acids, etc., which take an important role in biochemical reactions, we should not proceed, even if we use computer, to get any informations of electronic structures of these molecules without using the simple Hückel and extended Hückel methods which are crude one-electron approximations. Moreover if the fact, that many real chemical reactions contain  $\sigma$ -bond formations or dissociations, is taken into consideration, it is preferable to use a method which enables to give informations of not only  $\pi$ -but also  $\sigma$ -electron structures.

The extended Hückel method, which is proposed by Wolfsberg-Helmholtz,<sup>1)</sup> seems to be suitable for the purpose mentioned above, and Hoffmann<sup>2)</sup> has given some results of various hydrocarbons using this method.

Also, it suffices to obtain informations of the ground state electronic structures or perturbationally slightly transformed ones for the discussion of the usual chemical reaction processes, except special types of reactions such as photochemical reaction process, which seems to need informations for excited state structures. It is well known that the extended Hückel method, in spite of being simple one-electron approximation, is utilized for the ground state.

Furthermore, Hoffmann and Cusachs<sup>3)</sup> have suggested that it is possible to select the equilibrium atomic configuration in a molecule by calculating electronic structure with the extended Hückel method. It is certainly desirable that the method could give the atomic configuration. And, if we are able to use only empirical data of

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\* Phys Dept., Sciences & Engineering Div.

atoms but not of the molecule in performing molecular orbital calculations with the extended Hückel method, the method would be more reliable. We consider, however, that this reliability needs to be checked, so we take the simple H<sub>2</sub>O<sub>2</sub> molecule as the test case, examine the dependence of the total energy on the dihedral angle (the angle between two OOH planes), which is used as the only parameter, and attempt to calculate molecular orbital energy levels and electron populations, etc..

As the result, while the Wolfsberg-Helmholtz approximation, using the following exchange integral.

$$H_{ij} = K \cdot S_{ij} (H_{ii} + H_{jj}) / 2,$$

could not give the minimum total energy near experimental dihedral angle 111°, the Cusachs approximation<sup>4)</sup>,

$$H_{ij} = (2 - |S_{ij}|) S_{ij} (H_{ii} + H_{jj}) / 2,$$

succeeded to give rather favorable result.

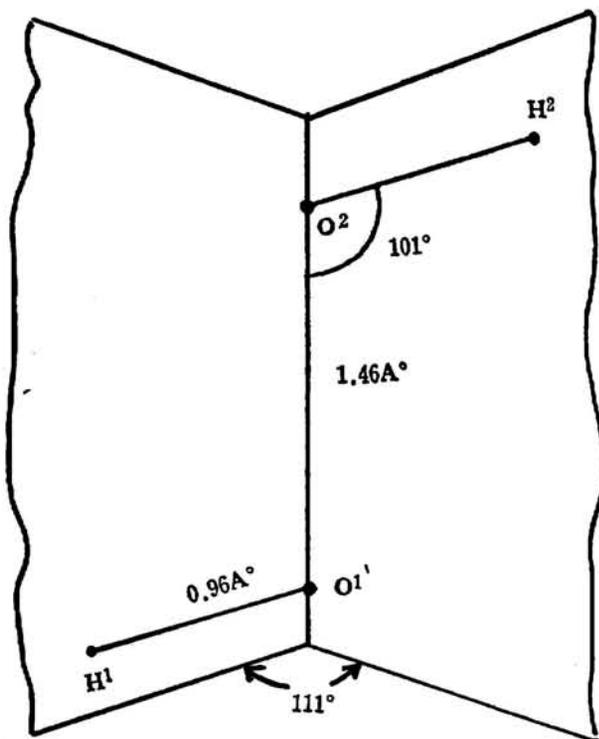


Fig. 1 The geometry of H<sub>2</sub>O<sub>2</sub>

## 2. Procedure

The geometrical structure of H<sub>2</sub>O<sub>2</sub> molecule is shown in Fig. 1. As experimental data, we have the O-O distance as R<sub>O-O</sub> = 1.46 Å, the O-H distance as R<sub>O-H</sub> = 0.96 Å, the dihedral angle as  $\theta \approx 111^\circ$ , and  $\angle \text{HOO} = 101.5^\circ$ .

The molecular orbital (MO) consists of linear combination of the atomic orbitals (AO's) and we adapt the 1s and 2s orbital for Hydrogen atom and the 2s, 2px, 2py, and 2pz orbital for oxygen atom as basic atomic orbitals. Although these AO's are the Slater type orbitals, the 2s orbital is revised for the sake of convenience in calculation,

to be orthogonal to the 1s orbital.

We take the position that two electrons occupying the 1s orbital for oxygen have no contribution to bond formation, and, therefore, the system we treat consists of 14 electrons.

The normalized molecular orbitals are expressed as follows;

$$\psi_\mu = \sum_{i=1}^{12} C_{\mu i} \chi_i, \quad (\mu = 1, 2, \dots, 12) \quad (2.1)$$

where  $\chi_i$  is the  $i$ -th atomic orbital. Molecular orbitals for the ground state are obtained by minimizing the expectation value  $\langle \psi | h | \psi \rangle$  of the one-electron

hamiltonian  $h$  for a molecular orbital  $\psi$ . Carrying out this procedure, a set of equations for coefficients  $C_i$ 's are given as follows:

$$\sum_{i=1}^{12} (H_{ij} - \epsilon S_{ij}) C_j = 0, \quad (i=1,2,\dots,12) \quad (2.2)$$

where  $S_{ij}$  is overlap integral of the  $i$ -th and  $j$ -th AO's, and

$$H_{ij} = \int x_i h x_j d\tau = \langle x_i | h | x_j \rangle \quad (2.3)$$

In order to get meaningful solutions of Eq.(2.2), the following secular equation must be solved,

$$| H_{ij} - \epsilon S_{ij} | = 0. \quad (2.4)$$

In solving the secular equation,  $H_{ii}$  and  $H_{ij}$  are empirically estimated as follows:

$$\text{coulomb integral; } H_{ii} = -I_i, \quad (2.5)$$

$$\text{exchange integral; } H_{ij} = 1/2(2 - |S_{ij}|) S_{ij} (H_{ii} + H_{jj}), \quad (2.6)$$

where  $I_i$  is the ionization potential of  $i$ -th atomic orbital in valence state, and overlap integrals  $S_{ij}$  are calculated using the formulas given by Roothaan.<sup>7</sup> Coulomb integrals for the 1s and 2s orbital of hydrogen and the 2s, 2px, 2py, and 2pz orbital of oxygen are estimated according to Hinze and Jaffe's data,<sup>5</sup> i. e.,

$$H_{O,2s} = -36.07 \text{ eV}, \quad H_{O,2p} = -18.53 \text{ eV},$$

$$H_{H,1s} = -13.60 \text{ eV}, \quad H_{H,2s} = -3.40 \text{ eV}.$$

The effective charges, which are necessary to evaluate the overlap integrals, are given by Slater's rule:<sup>8</sup>

that is,  $Z_{O,2s} = Z_{O,2p} = 4.55$ ,  $Z_{H,1s} = 1.00$ , and  $Z_{H,2s} = 1.00$

In actual calculation, by making use of the symmetry property of  $H_2O_2$  molecule, we transformed the AO's  $\{x_i\}$  to the symmetry orbitals  $\{\varphi\}$  and constructed the MO based on these  $\varphi$  is, i. e.,

$$\psi_\mu = \sum_{j=1}^{12} b_{\mu j} \varphi_j. \quad (2.7)$$

In this case, we can get two sets containing six symmetry orbitals, respectively, and the orthogonal relations hold for orbitals belonging to different set. Therefore, the secular equation with  $(12 \times 12)$  determinant breaks into two lower order secular equations with  $(6 \times 6)$  determinant, respectively; so it becomes easier to solve the secular equations.

The molecular orbital energies and the total energy for the ground state, which contains 14 electrons occupying the lowest seven molecular orbitals, have been estimated for the dihedral angle values  $0^\circ$ ,  $70^\circ$ ,  $105^\circ$ ,  $140^\circ$ , and  $175^\circ$ . But the values of  $R_{O-O}$ ,  $R_{O-H}$  and the angle between the O-O bond and the O-H bond are fixed to the experimentally observed ones in this calculation.

### 3. Result and Discussion

The dependence of the total energy on the dihedral angle is displayed in Table 1. According to the results, the equilibrium angle lies in the neighborhood of the

observed value namely, 111°.

Table 2 gives the molecular orbital energies and the coefficients of each atomic orbital, from which the molecular orbitals are constructed, for the optimum dihedral angle. The atomic orbital population calculated using values in Table 2 are as follows;

Table-1 Total energy for H<sub>2</sub> O<sub>2</sub>

Dihedral angle	-E(eV)
0°	166.57
70°	167.02
105°	167.05
140°	166.85
175°	166.65

$$N_{1S,H} = 0.588, \quad N_{2S,H} = 0.000 \quad \text{for hydrogen,}$$

and

$$\begin{aligned} N_{2P_X,O} &= 0.032, & N_{2P_Y,O} &= 0.008, \\ N_{2S,O} &= 0.628, & N_{2P_Z,O} &= 5.744 \quad \text{for oxygen.} \end{aligned}$$

Therefore, the atomic populations are 6.412 for oxygen and 0.588 for hydrogen, respectively.

In Table 3 are shown the atomic orbital bond populations for the optimum dihedral angle 105°.

We have adopted also 2s orbital of hydrogen for MO construction, which is rather unusual. The reason for doing this is because the rather expanded 2s orbital may also be expected to give effect to bring about the equilibrium dihedral angle. But the electron population of this orbital has turned out to be zero.

Therefore the 2s orbital for hydrogen could not be playing a great role in our work.

By using the Cusachs' approximation, we have obtained rather favorable results for dihedral angle and atomic population but not for the orbital and populations.

Casachs carried out calculation for H<sub>2</sub> O using his approximation with bond distance and H-O-H angle as parameters and obtained a good result for the equilibrium H-O-H angle but not for the equilibrium bond length which turned out in his work to be longer than the observed value. He did not mentioned any concerning electron population. In both our and his works the results for the equilibrium angle are fairly good. In determining the equilibrium angle, the H...H interaction can be regarded as an important factor. But the H...H distance is considerably large. Therefore overlapping of the orbitals belonging to each atom should be small. This might have contributed to the good results for the equilibrium angles.

In bond length problem the overlapping of orbitals are large and the result of Cusachs for the bond length of H-O in longer than the observed value. His rather poor result might be caused by the largeness of overlapping of the orbitals belonging to each atom. Therefore it might be said that the Cusachs' approximation tends to give good result where the overlapping of orbitals is small but rather poor result where the overlapping of orbitals is large.

Table—2 Molecular Orbital of H<sub>2</sub> O<sub>2</sub> by Extended Hückel Method

Orbital Energy (ev)	H <sub>1s</sub> <sup>1</sup>	H <sub>2s</sub> <sup>1</sup>	O <sub>2s</sub> <sup>1</sup>	O <sub>2px</sub> <sup>1</sup>	O <sub>2py</sub> <sup>1</sup>	O <sub>2pz</sub> <sup>1</sup>	H <sub>1s</sub> <sup>2</sup>	H <sub>2s</sub> <sup>2</sup>	O <sub>2s</sub> <sup>2</sup>	O <sub>2px</sub> <sup>2</sup>	O <sub>2py</sub> <sup>2</sup>	O <sub>2pz</sub> <sup>2</sup>
1 -41.532	0.2409	0.0089	0.2596	-0.0635	0.0695	0.6454	0.2409	0.0089	0.2596	-0.0635	-0.0695	-0.6454
2 -29.736	0.3060	0.0307	0.3273	-0.0784	0.0742	0.7158	-0.3060	-0.0307	-0.3273	0.0784	0.0742	0.7158
3 -20.720	0.3902	0.0251	0.3345	-0.1110	0.1228	0.6179	0.3902	0.0251	0.3345	-0.1110	-0.1228	-0.6179
4 -20.345	0.4019	0.0546	0.3778	-0.0997	0.1024	0.6872	-0.4019	-0.0546	-0.3778	0.0997	0.1024	0.6872
5 -19.802	0.4042	0.0269	0.3411	-0.1155	0.1280	0.6142	0.4042	0.0269	0.3411	-0.1155	-0.1280	-0.6142
6 -17.477	0.4460	0.0328	0.3604	-0.1293	0.1436	0.6018	0.4460	0.0328	0.3604	-0.1293	-0.1436	-0.6018
7* -17.443	0.4517	0.0693	0.4025	-0.1228	0.1175	0.6679	-0.4517	-0.0693	-0.4025	0.1228	0.1175	0.6679
8** - 8.586	0.7365	0.1935	0.5166	-0.2163	0.2102	0.4548	0.7365	-0.1935	-0.5166	0.2163	0.2102	0.4548
9*** - 2.929	-0.8581	-0.2118	-0.4062	0.2953	-0.3405	0.0891	-0.8581	-0.2118	-0.4062	0.2953	-0.3405	-0.0891

\*Highest occupied orbital, \*\*Lowest unoccupied orbital, \*\*\*Second Lowest unoccupied orbital.

Table—3 AO Bond Population for H<sub>2</sub> O<sub>2</sub>

	H <sub>1s</sub> <sup>2</sup>	H <sub>2s</sub> <sup>2</sup>	O <sub>2s</sub> <sup>1</sup>	O <sub>2px</sub> <sup>1</sup>	O <sub>2py</sub> <sup>1</sup>	O <sub>2pz</sub> <sup>1</sup>	O <sub>2s</sub> <sup>2</sup>	O <sub>2px</sub> <sup>2</sup>	O <sub>2py</sub> <sup>2</sup>	O <sub>2pz</sub> <sup>2</sup>
H <sub>1s</sub> <sup>1</sup>	0.062	0.028	-2.029	-0.234	-0.321	-0.474	-0.036	-0.006	0.011	0.046
H <sub>2s</sub> <sup>1</sup>	0.028	-0.017	0.011	-0.010	-0.013	-0.020	-0.019	0.000	-0.000	-0.005
O <sub>2s</sub> <sup>1</sup>	-0.036	-0.019	...	...	...	...	0.013	0.000	0.000	-0.034
O <sub>2px</sub> <sup>1</sup>	-0.006	0.000	...	...	...	...	0.000	0.004	0.000	0.000
O <sub>2py</sub> <sup>1</sup>	0.011	-0.000	...	...	...	...	0.000	0.000	-0.008	0.000
O <sub>2pz</sub> <sup>1</sup>	0.045	-0.005	...	...	...	...	-0.034	0.000	0.000	0.098

Our good result for the equilibrium angle and poor result for orbital and bond populations could be due to the same reason inferred above. Therefore, in order to improve approximation for exchange integral  $H_{ij}$ , it may well be to take into consideration what have been said above. In passing, we mention that Palke and Pitzer,<sup>8)</sup> using the SCF method, calculated H<sub>2</sub> O<sub>2</sub> molecule, giving reasonable result for atomic orbital population and the total energy, but 180° for the equilibrium angle.

References

- 1). M. Wolfsberg, L. Helmholz, J. chem. Phys., 20, 837 (1952).
- 2). Roald Hoffmann, J. chem. Phys., 39, 1397 (1963).
- 3). Louis Chopin Cusachs, J. chem. Phys., 43, S157 (1965).
- 4). D. G. Carroll and S. P. McGlynn, J. chem. Phys., 45, 3827 (1966).
- 5). Jurgen Hinze and H. H. Jaffe, J. American Chem. Soc., 84, 540 (1962).
- 6). J. C. Slater, Phys. Rev., 36, 57 (1930).
- 7). C. C. J. Roothaan, J. chem. Phys., 19, 116 (1951).
- 8). William E. Palke and Russell M. Pitzer, J. chem. Phys., 46, 3948(1967).