A Convenient Method for the Calculation of the π-Electronic Structures of Aromatic Derivatives

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Theoretical investigations about the π-electronic structures of the aromatic derivatives based on the LCAO MO method have been carried out by many authors[1]. According to the results obtained by them, the molecular properties have been well correlated with their π-electronic structures, if the parameters appearing in the method have been properly chosen. But the actual calculation of the π-electronic structure of the molecule by means of the MO method is in general rather laborious. Therefore, it will be very convenient if one can find the method by which the calculation is simplified. In this paper we shall provide a convenient method using the set of vacant orbitals for the calculation and apply this method to the calculation of the molecular diagrams of the benzene hydroxy derivatives. In later discussions, we shall refer to this method as the "VO method" (vacant orbital method).

Method

The method is based on the framework of LCAO MO approximation, neglecting the differential overlap. When the molecule contains $2p\pi$ atomic orbitals (AO) in number of n, the molecular orbitals (MO), φ_i, are expressed by the linear combination of these AO's as follows:

$$\varphi_i = \sum_{\mu}^{n} \phi_\mu c_\mu \qquad (1)$$

where ϕ_μ is the μ-th $2p\pi$AO and c_μ is the coefficient to be determined by the variational method. When the following matrix notations which are the same as in Roothaan's paper[2] are used

$$\boldsymbol{\Phi} = (\varphi_1\varphi_2\cdots\cdots\varphi_n)$$

$$\boldsymbol{\phi} = (\phi_1\phi_2\cdots\cdots\phi_n)$$

$$\mathbf{C} = \begin{vmatrix} c_{11} & c_{12} \cdots\cdots & c_{1n} \\ c_{21} & c_{22} \cdots\cdots & c_{2n} \\ \vdots & \vdots & \vdots \\ c_{\mu 1} & c_{\mu 2} \cdots\cdots & c_{\mu n} \\ \vdots & \vdots & \vdots \\ c_{n1} & c_{n2} \cdots\cdots & c_{nn} \end{vmatrix}$$

we may write then for Eq. 1

$$\boldsymbol{\Phi} = \boldsymbol{\phi}\mathbf{C}$$

If we multiply the right-hand side by $\boldsymbol{\Phi}^*$ and the left-hand side by $\boldsymbol{\phi}^*\mathbf{C}^*$, then the following relation may be obtained,

$$\mathbf{C}^*\mathbf{C} = \mathbf{E}$$

$$\text{or} \qquad \sum_{\mu}^{n} c_{\mu i}^{*} c_{\mu i} = 1 = \sum_{\mu}^{occ} c_{\mu i}^{*} c_{\mu i} + \sum_{\mu}^{vac} c_{\mu i}^{*} c_{\mu i}$$

$$\sum_{\mu}^{n} c_{\mu i}^{*} c_{\nu i} = 0 = \sum_{i}^{occ} c_{\mu i}^{*} c_{\nu i} + \sum^{vac} c_{\mu i}^{*} c_{\nu i} \qquad (2)$$

where $\sum_{i}^{occ}$ and $\sum_{i}^{vac}$ mean the summation over the set of occupied orbitals and that of vacant orbitals, respectively. According to the definitions, the charge density q_μ and the bond order $p_{\mu\nu}$ may be written as,

$$2\sum_{i}^{occ} c_{\mu i}^{*} c_{\mu i} = q_\mu$$

$$2\sum_{i}^{occ} c_{\mu i}^{*} c_{\nu i} = p_{\mu\nu}$$

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[1] See, e.g., B. Pullman and A. Pullman, "Les Theories Electroniques de la Chimie Organique", Masson et Cie, Paris (1952).

[2] C. C. J. Roothaan, *Rev. Modern Phys.*, **23**, 69 (1951).

It is convenient to introduce q^v_μ and $p^v_{\mu\nu}$ as the corresponding quantities for the set of vacant orbitals, that is,

$$2\sum_i^{vac} c^*_{\mu i} c_{\mu i} = q^v_\mu$$

$$2\sum_i^{vac} c^*_{\mu i} c_{\nu i} = p^v_{\mu\nu}$$

Using these quantities, Eq. 2 can be rewritten as

$$(q_\mu - 1) = -(q^v_\mu - 1)$$

$$p_{\mu\nu} = -p^v_{\mu\nu} \qquad (3)$$

$(q_\mu - 1)$ represents the net charge at the position of the μ-th carbon atom belonging to the parent hydrocarbon system. As seen in Eq. 3, the set of vacant orbitals may become a mirror image of that of occupied orbitals. For the case of substituents which have only the lone pair orbitals, such as OH, NH_2, Cl, etc., the net charge must be expressed by $(q_\mu - 2)$ instead of $(q_\mu - 1)$. Therefore, in this case $-q^v_\mu$ may directly measure the net charge at the substituent. Using the relation 3, the calculation of the molecular diagram of the aromatic derivative may be considerably simplified, because

(1) the number of vacant orbitals is always less than that of occupied orbitals, and

(2) the vacant orbital and their energies differ only slightly from those of the reference system, since the large differences in orbital energies between the occupied and the vacant orbitals in the reference system may restrict the deformation of the vacant orbitals by conjugation to small extent. Here, we call the system in which the interactions between the parent hydrocarbon system and the substituents do not take place, as the reference system.

Pople's method for the LCAO SCF MO calculation tells us that the matrix elements of the Hartree-Fock Hamiltonian can be expressed by q_μ's, $p_{\mu\nu}$'s and the fundamental atomic integrals. Therefore, the SCF calculation based on his method may substantially expedited by the use of VO method, because

(1) the calculations of q_μ's and $p_{\mu\nu}$'s are easily carried out, and

(2) the rapid convergence to the SCF MO's may be expected, since the vacant orbitals may differ only slightly from those of the reference system. When the square of the coefficient of the carbon atom to be bonded with the substituent in the lowest vacant orbital (frontier orbital) of the parent hydrocarbon system has considerably large value, the deformation for the lowest vacant orbital by conjugation may be greater than for others. Thus, in this case the frontier orbital will make the greatest contribution to the mirror image relations. Actually, it is well known[3] in many cases that the frontier orbital theory provides satisfactory information for the discussion of chemical reactions.

Next, we shall show a mirror image relation of orbital energies. The energy, ε_i, of the φ_i is determined by the solution of the secular determinant of n-th degree, that is,

$$\det|H_{\mu\nu} - \delta_{\mu\nu}\varepsilon| = 0$$

where $H_{\mu\nu}$ is the matrix element of the Hamiltonian, which is expressed by

$$H_{\mu\nu} = \int \phi^*_\mu H \phi_\nu \, dv$$

where H is the (effective or Hartree-Fock) Hamiltonian operator. According to the algebraic theory, the total sum of roots is equal to the negative value of the coefficient of ε^{n-1} term in the development of the secular determinant in terms of ε, that is,

$$\sum_i^n \varepsilon_i = \sum_\mu^n H_{\mu\mu} = \sum_i^{occ} \varepsilon_i + \sum_i^{vac} \varepsilon_i \qquad (4)$$

From this equation we obtain

$$2\sum_i^{occ} \varepsilon_i - \sum_\mu^n H_{\mu\mu} = -(2\sum_i^{vac} \varepsilon_i - \sum_\mu^n H_{\mu\mu}) \qquad (5)$$

For many purposes, only the extra delocalization energy, $\Delta\varepsilon$, arising from the delocalization of the $2p\pi$ electrons by substitution may be important. $\Delta\varepsilon$ is defined as follows:

$$\Delta\varepsilon = 2(\sum_i^{occ} \varepsilon_i - \sum_i^{occ} \varepsilon^0_i) \qquad (6)$$

where ε^0_i is the orbital energy in the reference system. Similar relation to Eqs. 4 and 5 may also be obtained for the case of reference system, that is,

$$\sum_i^n \varepsilon^0_i = \sum_\mu^n H^0_{\mu\mu} = \sum_i^{occ} \varepsilon^0_i + \sum_i^{vac} \varepsilon^0_i$$

$$2\sum_i^{occ} \varepsilon^0_i - \sum_\mu^n H^0_{\mu\mu} = -(2\sum_i^{vac} \varepsilon^0_i - \sum_\mu^n H^0_{\mu\mu}) \qquad (7)$$

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[3] K. Fukui, T. Yonezawa and H. Shingu, *J. Chem. Phys.*, **20**, 722 (1952); K. Fukui, T. Yonezawa, C. Nagata and H. Shingu, ibid., **22**, 1433 (1954); K. Fukui, T. Yonezawa and C. Nagata, This Bulletin, **27**, 423 (1954).

TABLE I. MO'S AND MO ENERGIES

Orbital energy in β	MO
	Benzene
−2	$\varphi_1{}^v=1/\sqrt{6}\,(\phi_1-\phi_2+\phi_3-\phi_4+\phi_5-\phi_6)$
−1	$\varphi_2{}^v=1/\sqrt{12}\,(2\phi_1-\phi_2-\phi_3+2\phi_4-\phi_5-\phi_6)$
−1	$\varphi_3{}^v=1/\sqrt{4}\,(\phi_2-\phi_3+\phi_5-\phi_6)$
	Catechol
−2.0497	$\varphi_1{}^v=0.3978(\phi_1-\phi_4)-0.4365(\phi_2-\phi_3)-0.3790(\phi_6-\phi_5)+0.0861(\phi_7-\phi_8)$
−1.0897	$\varphi_2{}^v=0.0462(\phi_1-\phi_4)+0.4651(\phi_2-\phi_3)-0.5155(\phi_6-\phi_5)-0.1256(\phi_7-\phi_8)$
−1.0346	$\varphi_3{}^v=0.5663(\phi_1+\phi_4)-0.3076(\phi_2+\phi_3)-0.2783(\phi_6+\phi_5)+0.0849(\phi_7+\phi_8)$
	Resorcinol
−2.0480	$\varphi_1{}^v=0.4125\phi_1-0.4224(\phi_2+\phi_6)+0.3943(\phi_3+\phi_5)-0.3850\phi_4+0.0833(\phi_7+\phi_8)$
−1.0987	$\varphi_2{}^v=0.5129(\phi_2-\phi_6)-0.4668(\phi_3-\phi_5)-0.1381(\phi_7-\phi_8)$
−1.0313	$\varphi_3{}^v=0.5258\phi_1-0.2711(\phi_2+\phi_6)-0.3389(\phi_3+\phi_5)+0.5791\phi_4+0.0752(\phi_7+\phi_8)$
	Hydroquinone
−2.0475	$\varphi_1{}^v=0.4180(\phi_1-\phi_4)-0.3990(\phi_2-\phi_3-\phi_5+\phi_6)-0.0826(\phi_7-\phi_8)$
−1.1269	$\varphi_2{}^v=0.5748(\phi_1+\phi_4)-0.2702(\phi_2+\phi_3+\phi_5+\phi_6)-0.1532(\phi_7+\phi_8)$
−1.0000	$\varphi_3{}^v=0.5000(\phi_2-\phi_3+\phi_5-\phi_6)$
	Phloroglucinol
−2.0698	$\varphi_1{}^v=0.4111(\phi_1+\phi_3+\phi_5)-0.3973(\phi_4+\phi_2+\phi_6)-0.0806(\phi_7+\phi_8+\phi_9)$
−1.0987	$\varphi_2{}^v=0.2961(2\phi_1-\phi_3-\phi_5)+0.2695(2\phi_4-\phi_2-\phi_6)-0.0797(2\phi_7-\phi_8-\phi_9)$
−1.0987	$\varphi_3{}^v=0.5129(\phi_3-\phi_5)-0.4668(\phi_2-\phi_6)-0.1381(\phi_8-\phi_9)$
	2, 3, 5, 6-Tetrahydroxybenzene
−2.0923	$\varphi_1{}^v=0.3909(\phi_1-\phi_4)-0.4090(\phi_2-\phi_3-\phi_5+\phi_6)+0.0797(\phi_7-\phi_8-\phi_9+\phi_{10})$
−1.1827	$\varphi_2{}^v=0.4838(\phi_2-\phi_3+\phi_5-\phi_6)-0.1261(\phi_7-\phi_8+\phi_9-\phi_{10})$
−1.0664	$\varphi_3{}^v=0.5571(\phi_1+\phi_4)-0.2971(\phi_2+\phi_3+\phi_5+\phi_6)+0.0810(\phi_7+\phi_8+\phi_9+\phi_{10})$

We may now define $\varDelta\varepsilon^v$ as follows:

$$\varDelta\varepsilon^v=2\Big(\sum_i^{vac}\varepsilon_i-\sum_i^{vac}\varepsilon_i^0\Big) \tag{8}$$

Then the following expression may be derived from above equations,

$$\varDelta\varepsilon-\sum_i^n(H_{\mu\mu}-H_{\mu\mu}^0)=-\Big[\varDelta\varepsilon^v-\sum_\mu^n(H_{\mu\mu}-H_{\mu\mu}^0)\Big] \tag{9}$$

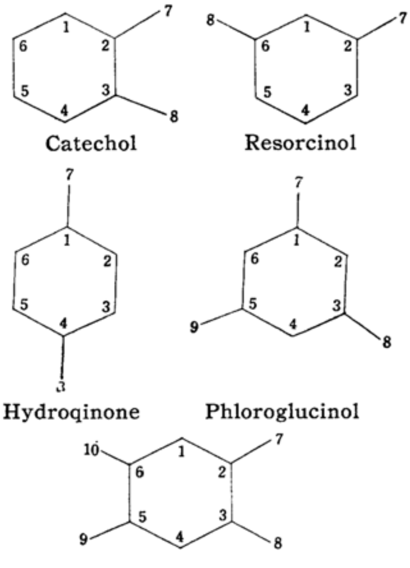
When $H_{\mu\mu}=H_{\mu\mu}^0$, which is the case in the simple LCAO MO treatment neglecting the inductive effect, Eq. 9 becomes

$$\varDelta\varepsilon=-\varDelta\varepsilon^v$$

Thus the mirror image relation of orbital energies is established.

Calculation of the Molecular Diagrams

We shall apply VO method to the calculation of the molecular diagrams of benzene hydroxy derivatives. The method is based on the framework of simple LCAO AO method neglecting the inductive effect. The parameters used are the same as those of phenol[4]. All the hydroxy derivatives have only three vacant orbitals, since the reference systems have



Catechol Resorcinol

Hydroqinone Phloroglucinol

2, 3, 5, 6-Tetrahydroxy benzene

Fig. 1. Numbering of atoms.

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[4] K. Nishimoto and R. Fujishiro, This Bulletin, **31**, 1036 (1958).

only three vacant orbitals, respectively. Therefore, the calculation based on the VO method is an easier task than that employing the set of occupied orbitals. The numbering of atoms is shown in Fig. 1. The calculated vacant MO's, ϕ_i^v, and their energies are collected in Table I, with those of a benzene molecule. Comparison of ϕ_1^v's of hydroxy derivatives with that of benzene indicates that the former are polarized regularly along the direction toward the substituent; but their magnitudes are rather small. On the other hand, the frontier orbitals, φ_2^v and φ_3^v, seem to reflect roughly the characters of the ground states of the molecules. The molecular diagrams calculated are given in Fig. 2. When we try to plot the magnitude of the charge migration, Δe, from the substituents into the benzene ring, against the extra delocalization energy, $\Delta\varepsilon$, a linear relationship is obtained as shown in Fig. 3.

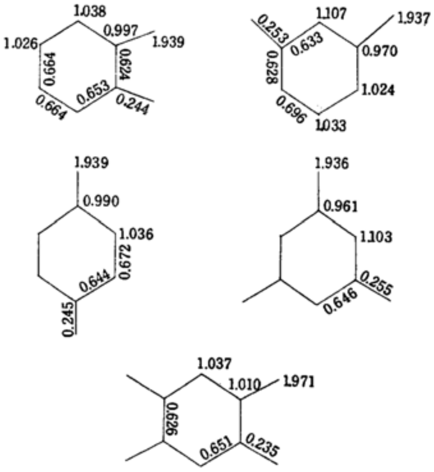

Fig. 2. Molecular diagrams.

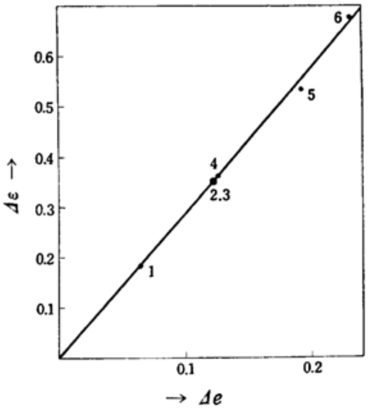

Fig. 3. Relation between $\Delta\varepsilon$ and Δe for benzene hydroxy derivatives.

1. Phenol
2. Catechol
3. Hydroquinone
4. Resorcinol
5. Phloroglucinol
6. 2, 3, 5, 6-Tetrahydroxy benzene

Summary

It was shown that the set of vacant orbitals of the conjugated system would be a mirror image of that of occupied orbitals. Using this relation the calculations of the π-electronic structures of the aromatic derivatives are considerably simplified. As an example, the molecular diagrams of the benzene hydroxy derivatives were calculated.

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