

# 琉球大学学術リポジトリ

## $\pi$ 電子分子軌道計算における $2p \pi$ -Slater型原子軌道の実効電荷について

メタデータ	言語: 出版者: 琉球大学文理学部 公開日: 2011-11-25 キーワード (Ja): キーワード (En): 作成者: Yara, Asao, Igei, Ryokan, 屋良, 朝夫, 伊芸, 諒寛 メールアドレス: 所属:
URL	<a href="http://hdl.handle.net/20.500.12000/22448">http://hdl.handle.net/20.500.12000/22448</a>

## On Effective Charges of $2p\pi$ -Slater type Atomic Orbitals

### In $\pi$ -Electron Molecular Orbital Calculations

Ryokan IGEI and Asao YARA

We computed the orbital energy difference between the lowest empty and the highest filled SCF LCAO molecular orbitals in benzene for various effective charge values of the basic  $2p\pi$ -Slater type carbon atomic orbital, and compared the results with the value estimated by Mulliken and Roothaan through the experimental data of the benzene absorption spectra.

We obtained the optimum value, 1.94, for effective charge of the basic  $2p\pi$ -Slater type atomic orbital, which makes our computation value agree with the value, 0.404 a. u., estimated by Roothaan and Mulliken.

#### 1. Introduction

The LCAO MO methods are still useful approximation procedures available in examining the behavior of  $\pi$  electrons in organic conjugated molecules. In the nonempirical LCAO MO method,  $2p\pi$ -Slater type atomic orbitals are frequently used as basic atomic orbitals. And optimum effective charge values for atomic orbitals in isolated atoms are conventionally adopted as effective charge values of the basic  $2p\pi$ -Slater type orbitals. For instance, Parr, Craig and Ross employed the  $2p\pi$ -Slater type atomic orbitals with Zener's effective charge value 3.18 in calculating the lower excited electronic levels of benzene and obtained the reliable result (by including the configuration interaction).

However, we thought it was worthwhile to examine if there were optimum effective charge values for the basic  $2p\pi$ -Slater type atomic orbitals, which constitute molecular orbitals. Indeed,  $\sigma$  and  $\pi$  electrons come from identical atomic orbitals in isolated atoms, but in molecules they behave in different manner. Once they participate in the formation of bonds,  $\sigma$  electrons occupy localized molecular orbitals on bonds and give much contribution to the binding energy, but  $\pi$  electrons occupy delocalized molecular orbitals over the whole molecule and give less contribution to the binding energy than  $\sigma$  electrons. Furthermore,  $\pi$  molecular orbitals extend to broader area than  $\sigma$  molecular orbitals about bond axis. It may, therefore, be reasonable to think that  $\sigma$  electrons shield nuclear charges more intensively in conjugated molecules than in isolated atoms. And by taking the more intensive shielding effect of  $\sigma$  electrons into consideration, it becomes reasonable to adopt as the basic atomic orbitals the  $2p\pi$ -Slater type atomic orbitals with smaller effective charge values than optimum values in isolated atoms.

From the foregoing point of view, we attempted to search for an optimum

effective charge value for the  $2p\pi$ -Slater type carbon atomic orbital in treating  $\pi$  electrons in benzene with the non-empirical LCAO MO method. We computed the orbital energy difference between the lowest empty and the highest filled SCF LCAO molecular orbitals in benzene for various effective charge values of the  $2p\pi$ -Slater type carbon atomic orbital, and compared the result with the value estimated by Mulliken and Roothaan through the experimental data of the benzene absorption spectra.<sup>(2)</sup>

## 2. SCF equation of coefficient vectors

The system we treat is six  $\pi$  electrons in a benzene molecule. The total hamiltonian operator  $H$  is defined by

$$\bar{H} = \sum_{\mu=1}^6 H^{\mu} + \frac{1}{2} e^2 \sum_{\mu \neq \nu} \frac{1}{r^{\mu\nu}} \quad (1)$$

where  $H^{\mu}$  is the one electron hamiltonian operator for the  $\mu$ th  $\pi$  electron moving in the potential field which are produced by nuclei, inner shell electrons and  $\sigma$  electrons, and  $r^{\mu\nu}$  is the distance between the  $\mu$ th and the  $\nu$ th  $\pi$  electron.  $\pi$  molecular orbitals are represented by a linear combination of  $2p\pi$ -Slater type atomic orbitals  $\chi_p$  centered on the carbon atoms ;

$$\varphi_i = \sum_{p=1}^6 \chi_p C_{pi} \quad i = 1, 2, 3, \dots, 6 \quad (2)$$

The atomic orbitals  $\chi_p$ 's are assumed to be normalized and orthogonalized each other, that is,

$$\int \chi_p \chi_q dv = \delta_{pq} \quad p, q = 1, 2, 3, \dots, 6 \quad (3)$$

The superscript  $\mu$  stands for the coordinates of the  $\mu$ th electron, the subscripts  $i, j, \dots$  label the different molecular orbitals and the subscripts  $p, q, \dots$  are used to distinguish the atomic orbitals. The total wave function is built up as antisymmetrized product of the molecular spin orbitals  $\varphi_i\alpha$ 's and  $\varphi_i\beta$ 's which are products of the molecular orbital function  $\varphi_i$  and the spin eigen function  $\alpha$  or  $\beta$ .

Under these conditions, the self-consistent equation for determining the coefficients  $C_{pi}$ 's in the molecular orbitals  $\varphi_i$ 's occupied by  $\pi$  electrons in the ground state was given by Roothaan.<sup>3)</sup> Let us introduce the following row and column vectors to write the equation in the matrix form :

$$\begin{aligned} \mathbf{x} &= (\chi_1, \chi_2, \dots, \chi_6), & \mathbf{C}_i^+ &= (C_{1i}, C_{2i}, \dots, C_{6i}) \\ \mathbf{C}_i &= \begin{pmatrix} C_{1i} \\ C_{2i} \\ \vdots \\ C_{6i} \end{pmatrix} & \mathbf{x}^+ &= \begin{pmatrix} \chi_1 \\ \chi_2 \\ \vdots \\ \chi_6 \end{pmatrix} \end{aligned} \quad (4)$$

Using these vectors, the matrices  $\mathbf{H}$ ,  $\mathbf{S}$ ,  $\mathbf{J}$  and  $\mathbf{K}$  are defined by

$$\mathbf{H} = \int \mathbf{x}^+ \mathbf{H} \mathbf{x} dv$$

$$\mathbf{S} = \int \mathbf{x}^+ \mathbf{x} dv \quad (5)$$

$$\mathbf{J}_j = \int \frac{\mathbf{x}^+(1) \mathbf{c}_j^+ \mathbf{x}^+(2) \mathbf{x}(2) \mathbf{c}_j \mathbf{x}(1) dv^1 dv^2}{r^{12}}$$

$$\mathbf{K}_j = \int \frac{\mathbf{x}^+(1) \mathbf{c}_j^+ \mathbf{x}^+(2) \mathbf{x}(2) \mathbf{x}(1) \mathbf{c}_j dv^1 dv^2}{r^{12}}$$

These matrices correspond to the one electron hamiltonian operator and the overlap, Coulomb and exchange integrals respectively.

Then the matrix  $\mathbf{F}$  corresponding to the Fock's operator given by

$$\mathbf{F} = \mathbf{H} + \sum_{j=1}^3 (2 \mathbf{J}_j - \mathbf{K}_j) \quad (6)$$

and the coefficient vector  $\mathbf{C}_j$ , representing the molecular orbital  $\varphi_j$ , must satisfy the following self-consistent field equation,

$$(\mathbf{F} - \varepsilon_j \mathbf{S}) \mathbf{C}_j = \mathbf{0} \quad (7)$$

where  $\varepsilon_j$  is the orbital energy of the molecular orbital  $\varphi_j$  ( $= \sum_p x_p C_{pj}$ ).

### 3. Derivation of orbital energy difference.

In benzene, the SCF LCAO molecular orbitals of  $\pi$  electrons can be obtained without performing the self-consistent calculation, for they are easily determined by using the high degree of symmetry of the molecule. They are shown here, with real coefficients,

$$\begin{aligned} \varphi_1 &= \frac{1}{\sqrt{6}} (\chi_1 + \chi_2 + \chi_3 + \chi_4 + \chi_5 + \chi_6) \\ \varphi_2 &= \frac{1}{\sqrt{12}} (2\chi_1 + \chi_2 - \chi_3 - 2\chi_4 - \chi_5 + \chi_6) \\ \varphi_3 &= \frac{1}{\sqrt{4}} (\chi_2 + \chi_3 - \chi_5 - \chi_6) \\ \varphi_4 &= \frac{1}{\sqrt{4}} (\chi_2 - \chi_3 + \chi_5 - \chi_6) \\ \varphi_5 &= \frac{1}{\sqrt{12}} (2\chi_1 - \chi_2 - \chi_3 + 2\chi_4 - \chi_5 - \chi_6) \\ \varphi_6 &= \frac{1}{\sqrt{6}} (\chi_1 - \chi_2 + \chi_3 - \chi_4 + \chi_5 - \chi_6) \end{aligned} \quad (8)$$

where  $\chi_p$  is the atomic orbital centered on the  $p$ th atom and the carbon atom numbers are indicated in Fig. 1.

Concerning the orbital energies,  $\varepsilon_1 < \varepsilon_2 = \varepsilon_3 < \varepsilon_4 = \varepsilon_5 < \varepsilon_6$ . (9)

In the ground state, the lower three molecular orbitals  $\varphi_1$ ,  $\varphi_2$  and  $\varphi_3$  are occupied by six electrons.

From the equation (8), the coefficient vectors become

$$\mathbf{C}_1 = \frac{1}{\sqrt{6}} \begin{pmatrix} 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \end{pmatrix} \quad \mathbf{C}_2 = \frac{1}{\sqrt{12}} \begin{pmatrix} 2 \\ 1 \\ -1 \\ -2 \\ -1 \\ 1 \end{pmatrix} \quad \mathbf{C}_3 = \frac{1}{2} \begin{pmatrix} 0 \\ 1 \\ 1 \\ 0 \\ -1 \\ -1 \end{pmatrix} \quad (10)$$

$$\mathbf{C}_4 = \frac{1}{2} \begin{pmatrix} 0 \\ 1 \\ -1 \\ 0 \\ 1 \\ -1 \end{pmatrix} \quad \mathbf{C}_5 = \frac{1}{\sqrt{12}} \begin{pmatrix} 2 \\ -1 \\ -1 \\ 2 \\ -1 \\ -1 \end{pmatrix} \quad \mathbf{C}_6 = \frac{1}{\sqrt{6}} \begin{pmatrix} 1 \\ -1 \\ 1 \\ -1 \\ 1 \\ -1 \end{pmatrix}$$

The Fock's equation (7), the self-consistent field equation for the coefficient vector  $\mathbf{C}_j$ , is written explicitly in the matrix form,

$$\begin{pmatrix} F_{11} - \epsilon_j & F_{12} & F_{13} & \dots & F_{16} \\ F_{21} & F_{22} - \epsilon_j & F_{23} & \dots & F_{26} \\ F_{31} & F_{32} & F_{33} - \epsilon_j & \dots & F_{36} \\ \dots & \dots & \dots & \dots & \dots \\ F_{61} & F_{62} & F_{63} & \dots & F_{66} - \epsilon_j \end{pmatrix} \begin{pmatrix} C_{1j} \\ C_{2j} \\ C_{3j} \\ \dots \\ C_{6j} \end{pmatrix} = 0 \quad (11)$$

Let us take for example, the second row component equation of (11).

$$F_{21} C_{1j} + (F_{22} - \epsilon_j) C_{2j} + F_{23} C_{3j} + F_{24} C_{4j} + F_{25} C_{5j} + F_{26} C_{6j} = 0 \quad (12)$$

Putting  $j=2$  and  $j=4$  in this equation, we can get two equations and take their difference. And then the resulting equation becomes

$$F_{12} - F_{14} = \frac{1}{2} (\epsilon_2 - \epsilon_4) \quad (13)$$

where the following relations are used,

$$\begin{aligned} F_{22} &= F_{44} \\ F_{12} &= F_{21} = F_{23} = F_{43} = F_{45} \\ F_{24} &= F_{42} = F_{46} = F_{26} \\ F_{14} &= F_{41} = F_{25} \end{aligned} \quad (14)$$

Even if we start with any other component equation of (11), instead of taking the equation (12), the same procedure leads to the same result as (13).

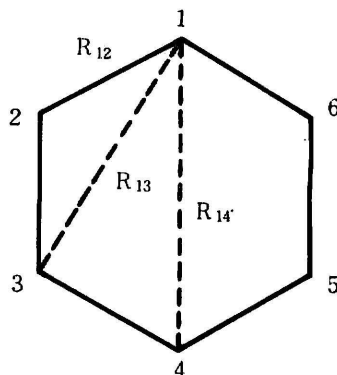


Fig. 1. The carbon atom numbers.

#### 4. Calculation and Result

Roothaan and Mulliken estimated the mean value of excitation energies of the lower six excited electronic levels at  $5.5\text{eV} = 0.404 \text{ a.u.}$  through the experimental data of benzene absorption spectra. These lower six excited levels correspond to electron configurations which arise when one electron transfers from one of the highest filled orbitals ( $\varphi_2$  and  $\varphi_3$ ) to one of the lowest empty molecular orbitals ( $\varphi_4$  and  $\varphi_5$ ). And so the foregoing mean excitation energy value,  $5.5 \text{ eV}$ , may be regarded as the value representing the orbital energy difference between these molecular orbitals, for example,  $\epsilon_4 - \epsilon_2$ . Therefore, we computed the values of  $F_{12} - F_{14}$  for various values of effective charge of the basic  $2p\pi$ -Slater type atomic orbital.

In computing  $F_{12} - F_{14}$ , the one electron hamiltonian operator  $H$  is assumed to be

$$H = -\frac{\hbar^2}{2m} \nabla^2 - \sum_{p=1}^6 \frac{Ze^2}{r_p} \tag{15}$$

where  $Z$  is the carbon nuclear charge shielded by  $\sigma$  and inner shell electrons, and  $r_p$  is the distance between the electron and the  $p$ th carbon atom center. We look upon the  $Z$  in (15) as just the same one as the effective charge of the basic Slater type atomic orbital ;

$$\chi = \left(\frac{Z^3}{32\pi}\right)^{1/2} \cos \theta \exp\left(-\frac{Zr}{2}\right) \tag{16}$$

For the distance,  $R_{12}$  (shown in Fig. 1), between adjacent carbon atoms, the observed value, 1.39 Å (= 2.627 a. u.) is adopted.

Thus, we have  $R_{13} = 4,550$  a.u.,  $R_{14} = 5,253$  a. u.

We utilized the Roothaan's lists in computing numerical values of molecular integrals. But three and four center integrals were evaluated by using Mulliken's approximation, in which  $\chi_p(r) \chi_q(r)$  ( $q \neq p$ ) is replaced as follows :

$$\chi_p \chi_q = \frac{1}{2} \left( \int \chi_p \chi_q dv \right) \{ \chi_p \chi_p + \chi_q \chi_q \} \tag{17}$$

where the integrals  $\int \chi_p \chi_q dv$  are calculated straightforwardly, neglecting the assumption of orthogonalization condition for  $\chi_p$ 's.

Our results are given in Table 1. We obtained the optimum value 1.94 for effective charge of the basic  $2p\pi$ -Slater type atomic orbital, which makes our computation value for  $\epsilon_4 - \epsilon_2$  agree with the value, 0.404 a. u., estimated by Roothaan and Mulliken.

$Z$ ; Effective charge value of atomic orbital.

$\epsilon_4 - \epsilon_2$ ; Orbital energy difference between the lowest empty and the highest occupied molecular orbitals.

Estimated value by Roothaan and Mulliken 0.404 a. u.

1 a. u. = 27.205 e. v.

Table 1.

$Z$	$\frac{1}{2} (\epsilon_4 - \epsilon_2)$ in a. u.	$Z$	$\frac{1}{2} (\epsilon_4 - \epsilon_2)$ in a. u.
1.	-0.250	1.90	0.172
2.	0.248	1.93	0.195
3.	0.763	1.95	0.210
4.	0.742	1.97	0.225
5.	0.575	2.	0.248
6.	0.371		

## 5. Discussion

The optimum effective charge value, 1.94, which we obtained, is fairly smaller

than Zener's value, 3.18, which is conventionally used for  $2p\pi$ -Slater type carbon atomic orbitals.

There are some faults in our treatment, namely :

- (1). The Fock's equation (12) for coefficient vectors is obtained on the assumption that the basic atomic orbitals  $\chi_p$ 's are orthogonalized each other. Therefore, the smaller the effective value  $Z$  is, the worse the approximation of our treatment becomes. And this is the case in the vicinity of the optimum  $Z$  value, 1.94, which we obtained.
- (2). In addition, evaluations of three and four center molecular integrals give rise to some numerical errors.

Though there are such faults, the results obtained lead us to conclude that  $\sigma$  electrons shield nuclear charges more intensively in conjugated molecules than in isolated atoms. And this conclusion seems to support the situation of conventional  $\pi$  electron theories, in which  $\pi$  electrons are treated almost independently of  $\sigma$  electron system and  $\sigma$  electrons are regarded only a part of potential sources.

On the contrary, there are some phenomena, for which it is convenient to consider that  $\pi$  electrons are sensitive to the behavior of  $\sigma$  electron system. For instance, enzymes, such as trypsin and chymotrypsin, hydrolyse specific peptide bonds (right side bonds of lysine residues etc.) in protein, and then  $\pi$  electrons on a peptide bond seem to play some roles. In our treatment in which we reflect the shielding effect of  $\sigma$  electrons on effective charge values of basic atomic orbitals, we should reflect variations of  $\sigma$  electron polarizations on a peptide bond, which are caused by substitutions of adjacent residues, on effective charge values of  $2p\pi$ -Slater type atomic orbitals which constitute  $\pi$  molecular orbitals. Therefore, the smaller the atomic orbital effective charge values are, the more sensitive  $\pi$  electrons become to the behavior of underlying  $\sigma$  electrons.

We have now two statements which apparently contradict each other :

- (A).  $\pi$  electrons are treated almost independently of  $\sigma$  electron system.
- (B). The behavior of  $\pi$  electrons should be sensitive to the variations of  $\sigma$  electron distribution on peptide bonds.

In order to explain consistently the statements (A) and (B), it is convenient to adopt smaller effective charge values for  $2p\pi$ -Slater type atomic orbitals which constitute  $\pi$  molecular orbitals than optimum values for atomic orbitals in isolated atoms.

#### References :

1. R. G. Parr, D. P. Craig and I. G. Ross, J. Chem. Phys., 18 1561 (1950)
2. K. Higashi and H. Baba, Quantum Organic Chemistry, p. 195. (Asakura Publishing Company, Tokyo, (1964))
3. C. C. J. Roothaan, Rev. Mod. Phys. 23 69(1951)
4. C. C. J. Roothaan, J. Chem. Phys. 19 1445 (1951)

## 要 約

ベンゼン  $\pi$  電子系の SCF LCAO 分子軌道について、その最低空軌道と最高充満軌道間の軌道エネルギーの差を基礎関数としてとる所の  $2p\pi$ -Slater 型の炭素原子軌道の実効荷電のいろいろな値に対して計算した。

そして、その結果を、ベンゼンの吸収スペクトル資料に基づいて Mulliken と Roothaan により推定された値と比較した。

我々の計算値を、Mulliken と Roothaan による推定値と一致せしめるためには、基礎の  $2p\pi$ -Slater 型原子軌道の実効荷電として、1.94 という値が適するという結果を得た。