Density Matrix in Simple LCAO MO Method

By Kenichi FUKUI, Chikayoshi NAGATA, Teijiro YONEZAWA
and Akira IMAMURA

(Received November 17, 1958)

The LCAO MO method has been applied extensively to the explanation of the facts in organic chemical reaction. That is to say, the static method by Coulson and Longuet-Higgins[1], the localization method by Wheland[2] and the frontier electron method by Fukui et al.[3-7] and many other similar methods have been used successfully to explain the reactivity of a number of conjugated molecules.

In this article, the present authors indicate that the theoretical indexes such as electron density, bond order, and various polarizabilities derived by Coulson and Longuet-Higgins[1], can be given also by a novel method which is entirely different from that of the previous authors.

Partial Density Matrix and Hamiltonian Matrix.—First, we define the following two matrices which are most fundamental in the theory. They are referred to as partial density matrix $\mathbf{D}_j$ and Hamiltonian matrix $\boldsymbol{\alpha}$, and are defined respectively as follows:

$$\mathbf{D}_j \equiv \begin{pmatrix} (C_1^j)^2 & C_1^jC_2^j & \cdots\cdots\cdots & C_1^jC_n^j \\ C_2^jC_1^j & (C_2^j)^2 & \cdots\cdots\cdots & C_2^jC_n^j \\ \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ C_n^jC_1^j & C_n^jC_2^j & \cdots\cdots\cdots & (C_n^j)^2 \end{pmatrix} \tag{1}$$

$$\boldsymbol{\alpha} \equiv \begin{pmatrix} \alpha_1 & \beta_{12} & \cdots\cdots\cdots & \beta_{1n} \\ \beta_{21} & \alpha_2 & \cdots\cdots\cdots & \beta_{2n} \\ \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ \beta_{n1} & \beta_{n2} & \cdots\cdots\cdots & \alpha_n \end{pmatrix} \tag{2}$$

$$(\beta_{rs}=\beta_{sr})$$

where C_r^j is the coefficient of atomic orbital, ϕ_r, in molecular orbital ψ_j, that is, according to the usual LCAO MO method, ψ_j is expressed as a linear combination of atomic orbitals whose number is n; $\psi_j=\sum_{r=1}^{n} C_r^j\phi_r$. α and β are the Coulomb and the resonance integral, respectively. From Eqs. 1 and 2 the following formulae are easily obtained:

$$\boldsymbol{\alpha}\mathbf{D}_j = \varepsilon_j\mathbf{D}_j \tag{3}$$

$$\boldsymbol{\alpha}\mathbf{D}_j = \mathbf{D}_j\boldsymbol{\alpha} \tag{4}$$

The partial density matrices have the following relations with each other;

$$\mathbf{D}_j=\mathbf{D}_j^2=\mathbf{D}_j^3=\cdots\cdots \tag{5}$$

$$\mathbf{D}_j\mathbf{D}_k = 0 \quad (j\neq k) \tag{6}$$

$$\mathbf{D}_j=\frac{\mathbf{D}_j\boldsymbol{\alpha}\mathbf{D}_j}{\varepsilon_j} \tag{7}$$

$$\mathbf{D}_k\boldsymbol{\alpha}\mathbf{D}_j = 0 \quad (k\neq j) \tag{8}$$

$$\sum_{j=1}^{n}\mathbf{D}_j = \mathbf{E} \tag{9}$$

where $\mathbf{E}$ is unit matrix.

Variation of $\mathbf{D}_j$ leads us to the following relations,

$$\mathbf{D}_j\cdot\delta\mathbf{D}_j+\delta\mathbf{D}_j\cdot\mathbf{D}_j=\delta\mathbf{D}_j \tag{10}$$

$$\mathbf{D}_j\cdot\delta\mathbf{D}_k+\delta\mathbf{D}_j\cdot\mathbf{D}_k=0 \quad (k\neq j) \tag{11}$$

$$\mathbf{D}_j\cdot\delta\mathbf{D}_j\cdot\mathbf{D}_j = 0 \tag{12}$$

$$\mathbf{D}_k\cdot\delta\mathbf{D}_j\cdot\mathbf{D}_k = 0 \quad (k\neq j) \tag{13}$$

$$\mathbf{D}_k\cdot\delta\mathbf{D}_j\cdot\mathbf{D}_l = 0 \quad (l\neq j,\ k\neq j) \tag{14}$$

Perturbation Theory in Density Matrix.—The perturbation theory in density matrix can be constructed in just the same way as in LCAO MO method. When the Hamiltonian matrix $\boldsymbol{\alpha}$ is subjected to perturbation by the amount of $\delta\boldsymbol{\alpha}$, $\mathbf{D}_j$ and ε_j are assumed to become $\mathbf{D}_j+\delta\mathbf{D}_j$ and $\varepsilon_j+\delta\varepsilon_j$, respectively. Then from Eq. 3, the following formulae are obtained.

$$\mathbf{D}_j\cdot\delta\varepsilon_j=\delta\boldsymbol{\alpha}\cdot\mathbf{D}_j+(\boldsymbol{\alpha}-\varepsilon_j)\delta\mathbf{D}_j \tag{15}$$

Multiplying Eq. 15 by $\mathbf{D}_k$ $(k\neq j)$ from the left-hand side, we gain the following relation,

---

[1] C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.*, **A191**, 39 (1947).

[2] G. W. Wheland, *J. Am. Chem. Soc.*, **64**, 900 (1942).

[3] K. Fukui, T. Yonezawa and H. Shingu, *J. Chem. Phys.*, **20**, 722 (1952).

[4] K. Fukui, T. Yonezawa, C. Nagata and H. Shingu, ibid., **22**, 1433 (1954).

[5] K. Fukui, T. Yonezawa and C. Nagata, This Bulletin, **27**, 423 (1954).

[6] K. Fukui, T. Yonezawa and C. Nagata, *J. Chem. Phys.*, **26**, 831 (1957).

[7] K. Fukui, T. Yonezawa and C. Nagata, ibid., **27** 1247 (1957).

$$\mathbf{D}_k\cdot\delta\mathbf{D}_j=\frac{\mathbf{D}_k\cdot\delta\boldsymbol{\alpha}\cdot\mathbf{D}_j}{\varepsilon_j-\varepsilon_k} \tag{16}$$

Similarly, from Eqs. 11 and 16,

$$\delta\mathbf{D}_j\cdot\mathbf{D}_k=\frac{\mathbf{D}_j\cdot\delta\boldsymbol{\alpha}\cdot\mathbf{D}_k}{\varepsilon_j-\varepsilon_k} \tag{17}$$

From Eqs. 16 and 17, using the idempotent nature of $\mathbf{D}_j$ we easily obtain the following formulae:

$$\mathbf{D}_k\cdot\delta\mathbf{D}_j\cdot\mathbf{D}_j=\frac{\mathbf{D}_k\cdot\delta\boldsymbol{\alpha}\cdot\mathbf{D}_j}{\varepsilon_j-\varepsilon_k}\quad(k\neq j) \tag{18}$$

$$\mathbf{D}_j\cdot\delta\mathbf{D}_j\cdot\mathbf{D}_k=\frac{\mathbf{D}_j\cdot\delta\boldsymbol{\alpha}\cdot\mathbf{D}_k}{\varepsilon_j-\varepsilon_k}\quad(k\neq j) \tag{19}$$

From Eqs. 9, 16 and 17,

$$(\mathbf{E}-\mathbf{D}_j)\delta\mathbf{D}_j=\sum_{\substack{k=1\\k\neq j}}^{n}\frac{\mathbf{D}_k\cdot\delta\boldsymbol{\alpha}\cdot\mathbf{D}_j}{\varepsilon_j-\varepsilon_k} \tag{20}$$

$$\delta\mathbf{D}_j(\mathbf{E}-\mathbf{D}_j)=\sum_{\substack{k=1\\k\neq j}}^{n}\frac{\mathbf{D}_j\cdot\delta\boldsymbol{\alpha}\cdot\mathbf{D}_k}{\varepsilon_j-\varepsilon_k} \tag{21}$$

are obtained. These formulae can be transformed to the following formulae by the aid of Eq. 10, that is

$$\delta\mathbf{D}_j\cdot\mathbf{D}_j=\sum_{\substack{k=1\\k\neq j}}^{n}\frac{\mathbf{D}_k\cdot\delta\boldsymbol{\alpha}\cdot\mathbf{D}_j}{\varepsilon_j-\varepsilon_k} \tag{22}$$

$$\mathbf{D}_j\cdot\delta\mathbf{D}_j=\sum_{\substack{k=1\\k\neq j}}^{n}\frac{\mathbf{D}_j\cdot\delta\boldsymbol{\alpha}\cdot\mathbf{D}_k}{\varepsilon_j-\varepsilon_k} \tag{23}$$

After adding Eqs. 22 and 23, we use the relation in Eq. 10, then $\delta\mathbf{D}_j$ is expressed as

$$\delta\mathbf{D}_j=\sum_{\substack{k=1\\k\neq j}}^{n}\frac{\mathbf{D}_j\cdot\delta\boldsymbol{\alpha}\cdot\mathbf{D}_k+\mathbf{D}_k\cdot\delta\boldsymbol{\alpha}\cdot\mathbf{D}_j}{\varepsilon_j-\varepsilon_k} \tag{24}$$

If Eq. 15 is multiplied by $\mathbf{D}_j$ from the left-hand side, the following equation is obtained, that is

$$\mathbf{D}_j\cdot\delta\varepsilon_j=\mathbf{D}_j\cdot\delta\boldsymbol{\alpha}\cdot\mathbf{D}_j \tag{25}$$

Taking the (r, r) element of Eq. 24, we obtain

$$\delta C_r^j=\sum_{\substack{k=1\\k\neq j}}^{n}\frac{C_r^k\sum_t\sum_u C_t^jC_u^k(\delta\boldsymbol{\alpha})_{tu}}{\varepsilon_j-\varepsilon_k} \tag{26}$$

Similarly, the (r, r) element of Eq. 25 becomes

$$\delta\varepsilon_j=\sum_t\sum_u C_t^jC_u^j(\delta\boldsymbol{\alpha})_{tu} \tag{27}$$

Now, we define the density matrix $\mathbf{Q}$ as the sum of the partial density matrices, namely,

$$\mathbf{Q}=\sum_{j=1}^{n}\nu_j\mathbf{D}_j=\begin{pmatrix} q_1 & p_{12} & \cdots\cdots & p_{1n}\\ p_{21} & q_2 & \cdots\cdots & p_{2n}\\ \cdots & \cdots & \cdots\cdots & \cdots\\ \cdots & \cdots & \cdots\cdots & \cdots\\ p_{n1} & p_{n2} & \cdots\cdots & q_n \end{pmatrix} \tag{28}$$

where q and p stand for the electron density and the bond order defined by Coulson and Longuet-Higgins and ν_j is the number of electrons in the jth molecular orbital. Then the variation of density matrix is written as

$$\delta\mathbf{Q}=\sum_{j=1}^{n}\nu_j\delta\mathbf{D}_j=\sum_{j=1}^{n}\nu_j\sum_{\substack{k=1\\k\neq j}}^{n}\frac{\mathbf{D}_j\cdot\delta\boldsymbol{\alpha}\cdot\mathbf{D}_k+\mathbf{D}_k\cdot\delta\boldsymbol{\alpha}\cdot\mathbf{D}_j}{\varepsilon_j-\varepsilon_k} \tag{29}$$

If we take the (r, r) and the (r, s) elements of Eq. 29, δq_r and δp_{rs} are obtained respectively.

$$\delta q_r=\sum_{j=1}^{n}\nu_j\sum_{\substack{k=1\\k\neq j}}^{n}\frac{2C_r^jC_r^k\sum_t\sum_u C_t^jC_u^k(\delta\boldsymbol{\alpha})_{tu}}{\varepsilon_j-\varepsilon_k} \tag{30}$$

$$\delta p_{rs}=\sum_{j=1}^{n}\nu_j\sum_{\substack{k=1\\k\neq j}}^{n}\frac{(C_r^jC_s^k+C_s^jC_r^k)\sum_t\sum_u C_t^jC_u^k(\delta\boldsymbol{\alpha})_{tu}}{\varepsilon_j-\varepsilon_k} \tag{31}$$

The total π-electron energy E is the sum of the orbital energy ε_j, that is

$$E=\sum_{j=1}^{n}\nu_j\varepsilon_j \tag{32}$$

then, from Eq. 27, is expressed as

$$\delta E=\sum_{j=1}^{n}\nu_j\delta\varepsilon_j=\sum_{j=1}^{n}\nu_j\sum_t\sum_u C_t^jC_u^j(\delta\boldsymbol{\alpha})_{tu} \tag{33}$$

Relations among Theoretical Indexes.— Differentiating $\delta\varepsilon_j$, δE, and δC_r^j with respect to α and β, we obtain the following relations:

$$\frac{\partial\varepsilon_j}{\partial\alpha_r}=(C_r^j)^2 \tag{34}$$

$$\frac{\partial\varepsilon_j}{\partial\beta_{rs}}=2C_r^jC_s^j \tag{35}$$

$$\frac{\partial E}{\partial\alpha_s}=\sum_{j=1}^{n}\nu_j(C_r^j)^2=q_r \tag{36}$$

$$\frac{\partial E}{\partial\beta_{rs}}=2\sum_{j=1}^{n}\nu_jC_r^jC_s^j=2p_{rs} \tag{37}$$

$$\frac{\partial C_r^j}{\partial\alpha_s}=C_s^j\sum_{\substack{k=1\\k\neq j}}^{n}\frac{C_r^kC_s^k}{\varepsilon_j-\varepsilon_k} \tag{38}$$

$$\frac{\partial C_r^j}{\partial\beta_{st}}=\sum_{\substack{k=1\\k\neq j}}^{n}\frac{C_r^k(C_s^jC_t^k+C_t^jC_s^k)}{\varepsilon_j-\varepsilon_k} \tag{39}$$

These equations coincide with those

derived by Coulson and Longuet-Higgins[1]. Similarly, from Eqs. 30 and 31, the following formulae are obtained and these are nothing but the polarizabilities defined by Coulson and Longuet-Higgins[1].

$$\frac{\partial q_r}{\partial \alpha_s}=\sum_{j=1}^{n}\nu_j\sum_{\substack{k=1\\k\neq j}}^{n}\frac{2C_r^jC_r^kC_s^jC_s^k}{\varepsilon_j-\varepsilon_k} \tag{40}$$

$$\frac{\partial q_r}{\partial \beta_{st}}=\sum_{j=1}^{n}\nu_j\sum_{\substack{k=1\\k\neq j}}^{n}\frac{2C_r^jC_r^k(C_s^jC_t^k+C_t^jC_s^k)}{\varepsilon_j-\varepsilon_k} \tag{41}$$

$$\frac{\partial p_{rs}}{\partial \alpha_t}=\sum_{j=1}^{n}\nu_j\sum_{\substack{k=1\\k\neq j}}^{n}\frac{C_t^jC_t^k(C_r^jC_s^k+C_s^jC_r^k)}{\varepsilon_j-\varepsilon_k} \tag{42}$$

$$\frac{\partial p_{rs}}{\partial \beta_{tu}}=\sum_{j=1}^{n}\nu_j\sum_{\substack{k=1\\k\neq j}}^{n}\frac{(C_r^jC_s^k+C_s^jC_r^k)(C_t^jC_u^k+C_u^jC_t^k)}{\varepsilon_j-\varepsilon_k} \tag{43}$$

Faculty of Engineering
Kyoto University
Sakyo-ku Kyoto