A Further Study of Simple LCAO MO Perturbation Treatment of Conjugated Molecules

By Kenichi FUKUI, Keiji MOROKUMA, Teijiro YONEZAWA and
Chikayoshi NAGATA

(Received December 19, 1959)

The perturbation theory in the simple LCAO MO method has been studied by many authors, for instance, by Coulson and Longuet-Higgins1) and by Dewar2). Recently, by the present authors3), a new mathematical method of perturbation theory, named the method of perturbed secular determinant, has been developed and several useful equations have been derived which give the orbital energy, the electron density and the bond order of the perturbed system.

The only system involved in these works, however, was the one which suffered only one perturbation, that is, a small change of a Coulomb integral or of a resonance integral, or a weak bonding to another system. There could be seen no systematic perturbation treatment of the system which was affected by two or more perturbations, for instance, changes of two Coulomb integrals, changes of a Coulomb integral and of a resonance integral, and a weak bonding with a change of a Coulomb integral. To deal with such a system would be of practical interest in discussing the chemical reactivity, absorption spectrum, dipole moment and other electronic properties of large conjugated molecules.

In the present paper are derived several equations or relations which give the molecular orbital, its orbital energy, the electron density and the bond order of systems affected by two perturbations, and lastly they are extended to a more general case of many perturbations.

Non-degenerate System

1. Summary of Results for Single Perturbation.—In order to simplify the expression of various equations appearing in the treatment of multiple-perturbed systems, it would be convenient to summarize the results for single perturbation. The following formulae, obtained by the method of perturbed secular determinant and also by the existing method of perturbation, were given in the previous paper, though some of them not explicitly.

In this section it is assumed that the system to be treated is not degenerate in itself, nor has it any degenerate level between another system to conjugate with.

First, if the Coulomb integral, α_r, of the rth atom in a conjugated system, $\Delta(\varepsilon)$,* is increased by α_r' (Case A of Ref. 3), then, as its consequence, the jth orbital energy, ε_j, will increase by $(\delta\varepsilon_j)_r$, the separate bond order, $p_{uv}{}^j$, by $(\delta p_{uv}{}^j)_r$, the separate electron density, $p_{uu}{}^j$, by $(\delta p_{uu}{}^j)_r$, the total π electronic energy, ε, by $(\delta\varepsilon)_r$, the bond order, p_{uv}, by $(\delta p_{uv})_r$, the electron density, p_{uu}, by $(\delta p_{uu})_r$ and the jth molecular orbital, Ψ_j, by $(\delta\Psi_j)_r$, in such a way that**

$$(\delta\varepsilon_j)_r=(c_r{}^j)^2\alpha_r'+\sum_{k(\neq j)}^{\text{all}}\frac{(c_r{}^jc_r{}^k)^2}{\varepsilon_j-\varepsilon_k}(\alpha_r')^2+\cdots\cdots \tag{1}$$

$$\begin{aligned}(\delta p_{uv}{}^j)_r=&\sum_{k(\neq j)}^{\text{all}}\frac{c_r{}^jc_r{}^k(c_u{}^jc_v{}^k+c_v{}^jc_u{}^k)}{\varepsilon_j-\varepsilon_k}\alpha_r'\\&+\sum_{k(\neq j)}^{\text{all}}\frac{c_r{}^jc_r{}^k}{\varepsilon_j-\varepsilon_k}\left[\sum_{m(\neq j)}^{\text{all}}\frac{c_r{}^m\{c_r{}^jc_u{}^kc_v{}^m+c_r{}^m(c_u{}^jc_v{}^k+c_v{}^jc_u{}^k)\}}{\varepsilon_j-\varepsilon_m}\right.\\&\left.-\frac{c_r{}^j\{c_r{}^kc_u{}^jc_v{}^j+c_r{}^j(c_u{}^jc_v{}^k+c_v{}^jc_u{}^k)\}}{\varepsilon_j-\varepsilon_k}(\alpha_r')^2+\cdots\cdots\right.\qquad(u=v\text{ or }u\neq v)\end{aligned} \tag{2}$$

---

1) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.* (*London*), **A191**, 39 (1947); **A192**, 16 (1947): **A193**, 447, 456 (1948); **A195**, 188 (1948).

2) M. J. S. Dewar, *J. Am. Chem. Soc.*, **74**, 3341 (1952).

3) K. Fukui, C. Nagata, T. Yonezawa, H. Kato and K. Morokuma, *J. Chem. Phys.*, **31**, 287 (1959).

* $\Delta(\varepsilon)$ is the secular determinant of the system and will be used also to characterize a conjugated system.

** As for the nomenclature, see Ref. 3. Electron density will be looked upon as a special case ($u=v$) of bond order in the further discussion.

$$(\delta\varepsilon)_r = p_{rr}\alpha_r' + 2\sum_j^{\text{occ}}\sum_k^{\text{unocc}}\frac{(c_r^j c_r^k)^2}{\varepsilon_j-\varepsilon_k}(\alpha_r')^2+\cdots\cdots \tag{3}$$

$$\begin{aligned}(\delta p_{uv})_r = {} & 2\sum_j^{\text{occ}}\sum_k^{\text{unocc}}\frac{c_r^j c_r^k(c_u^j c_v^k + c_v^j c_u^k)}{\varepsilon_j-\varepsilon_k}\alpha_r' \\ & + 2\sum_j^{\text{occ}}\{\text{the second order term in}\,(\delta p_{uv}{}^j)_r\}+\cdots\cdots \qquad (u=v \text{ or } u\neq v)\end{aligned} \tag{4}$$

$$\begin{aligned}(\delta\Psi_j)_r = {} & \sum_{k(\neq j)}^{\text{all}}\frac{c_r^j c_r^k}{\varepsilon_j-\varepsilon_k}\alpha_r'\Psi_k - \frac{1}{2}\left\{\sum_{k(\neq j)}^{\text{all}}\frac{(c_r^j c_r^k)^2}{(\varepsilon_j-\varepsilon_k)^2}\right\}(\alpha_r')^2\Psi_j \\ & + \sum_{k(\neq j)}^{\text{all}}\frac{c_r^j c_r^k}{\varepsilon_j-\varepsilon_m}\left\{\sum_{m(\neq j)}^{\text{all}}\frac{(c_r^m)^2}{\varepsilon_j-\varepsilon_m}-\frac{(c_r^j)^2}{\varepsilon_j-\varepsilon_k}\right\}(\alpha_r')^2\Psi_k+\cdots\cdots\end{aligned} \tag{5}$$

Secondly, when the resonance integral, β_{st}, of the bond (st) in the system $\Delta(\varepsilon)$ is increased by β_{st}' (Case B of Ref. 3), increases of those quantities are written as follows:

$$(\delta\varepsilon_j)_{st} = 2c_s^j c_t^j\beta_{st}' + \sum_{k(\neq j)}^{\text{all}}\frac{(c_s^j c_t^k + c_t^j c_s^k)^2}{\varepsilon_j-\varepsilon_k}(\beta_{st}')^2+\cdots\cdots \tag{6}$$

$$\begin{aligned}(\delta p_{uv}{}^j)_{st} = {} & \sum_{k(\neq j)}^{\text{all}}\frac{(c_s^j c_t^k + c_t^j c_s^k)(c_u^j c_v^k + c_v^j c_u^k)}{\varepsilon_j-\varepsilon_k}\beta_{st}' \\ & + \sum_{k(\neq j)}^{\text{all}}\frac{(c_s^j c_t^k + c_t^j c_s^k)}{\varepsilon_j-\varepsilon_k}\left\{\sum_{m(\neq j)}^{\text{all}}\frac{(c_s^j c_t^m + c_t^j c_s^m)c_u^k c_v^m + (c_s^k c_t^m + c_t^k c_s^m)(c_u^j c_v^m + c_v^j c_u^m)}{\varepsilon_j-\varepsilon_m}\right. \\ & \left. - \frac{(c_s^j c_t^k + c_t^j c_s^k)c_u^j c_v^j + 2c_s^j c_t^j(c_u^j c_v^k + c_v^j c_u^k)}{\varepsilon_j-\varepsilon_k}\right\}(\beta_{st}')^2+\cdots\cdots \qquad (u=v \text{ or } u\neq v)\end{aligned} \tag{7}$$

$$(\delta\varepsilon)_{st} = 2p_{st}\beta_{st}' + 2\sum_j^{\text{occ}}\sum_k^{\text{unocc}}\frac{(c_s^j c_t^k + c_t^j c_s^k)^2}{\varepsilon_j-\varepsilon_k}(\beta_{st}')^2+\cdots\cdots \tag{8}$$

$$\begin{aligned}(\delta p_{uv})_{st} = {} & 2\sum_j^{\text{occ}}\sum_k^{\text{unocc}}\frac{(c_s^j c_t^k + c_t^j c_s^k)(c_u^j c_v^k + c_v^j c_u^k)}{\varepsilon_j-\varepsilon_k}\beta_{st}' \\ & + 2\sum_j^{\text{occ}}\{\text{the second order term in}\,(\delta p_{uv}{}^j)_{st}\}+\cdots\cdots \qquad (u=v \text{ or } u\neq v)\end{aligned} \tag{9}$$

$$\begin{aligned}(\delta\Psi_j)_{st} = {} & \sum_{k(\neq j)}^{\text{all}}\frac{(c_s^j c_t^k + c_t^j c_s^k)}{\varepsilon_j-\varepsilon_k}\beta_{st}'\Psi_k - \frac{1}{2}\sum_{k(\neq j)}^{\text{all}}\frac{(c_s^j c_t^k + c_t^j c_s^k)^2}{(\varepsilon_j-\varepsilon_k)^2}(\beta_{st}')^2\Psi_j \\ & + \sum_{k(\neq j)}^{\text{all}}\frac{c_s^j c_t^k + c_t^j c_s^k}{\varepsilon_j-\varepsilon_k}\left\{\sum_{m(\neq j)}^{\text{all}}\frac{c_s^k c_t^m + c_t^k c_s^m}{\varepsilon_j-\varepsilon_m}-\frac{2c_s^j c_t^j}{\varepsilon_j-\varepsilon_k}\right\}\Big](\beta_{st}')^2\Psi_k+\cdots\cdots\end{aligned} \tag{10}$$

Thirdly, when a conjugated system, $\Delta(\varepsilon)$, conjugates at the rth atom through a weak bonding, whose resonance integral is γ_r, with another conjugated system, whose secular determinant is $\Delta_1(\varepsilon)$, (Case C of Ref. 3), then the increases of molecular quantities by this perturbation are given by the following formulae. The orbital energy of the kth orbital ψ_{1k} of the system $\Delta_1(\varepsilon)$ is η_{1k} and the coefficient of the ξth atomic orbital in that molecular orbital is written as $d_\xi{}^{1k}$.

$$(\delta\varepsilon_j)_{r\xi} = \sum_k^{\text{all}}\frac{(c_r^j d_\xi{}^{1k})^2}{\varepsilon_j-\eta_{1k}}(\gamma_r)^2 + \left\{\sum_k^{\text{all}}\frac{(c_r^j d_\xi{}^{1k})^2}{\varepsilon_j-\eta_{1k}}\right\}\left[\sum_k^{\text{all}}\frac{(d_\xi{}^{1k})^2}{\varepsilon_j-\eta_{1k}}\left\{\sum_{m(\neq j)}^{\text{all}}\frac{(c_r^m)^2}{\varepsilon_j-\varepsilon_m}-\frac{(c_r^j)^2}{\varepsilon_j-\eta_{1k}}\right\}\right](\gamma_r)^4+\cdots\cdots \tag{11}$$

$$(\delta p_{uv}{}^j)_{r\xi} = \sum_k^{\text{all}}\frac{c_r^j d_\xi{}^{1k}}{\varepsilon_j-\eta_{1k}}\left\{\sum_{m(\neq j)}^{\text{all}}\frac{c_r^m d_\xi{}^{1k}(c_u^j c_v^m + c_v^j c_u^m)}{\varepsilon_j-\varepsilon_m}-\frac{c_r^j d_\xi{}^{1k} c_u^j c_v^j}{\varepsilon_j-\eta_{1k}}\right\}(\gamma_r)^2+\cdots\cdots \qquad (u=v \text{ or } u\neq v) \tag{12}$$

$$(\delta p_{r\xi}{}^j)_{r\xi} = \sum_k^{\text{all}}\frac{(c_r^j d_\xi{}^{1k})^2}{\varepsilon_j-\eta_{1k}}\gamma_r + 2\sum_k^{\text{all}}\sum_n^{\text{all}}\frac{(c_r^j d_\xi{}^{1k} d_\xi{}^{1n})^2}{(\varepsilon_j-\eta_{1k})(\varepsilon_j-\eta_{1n})}\left\{\sum_{m(\neq j)}^{\text{all}}\frac{(c_r^m)^2}{\varepsilon_j-\varepsilon_m}-\frac{(c_r^j)^2}{\varepsilon_j-\eta_{1k}}\right\}(\gamma_r)^3+\cdots \tag{12'}$$

$$(\delta p_{uv}{}^{1k})_{r\xi} = \sum_j^{\text{all}}\sum_m^{\text{all}}\frac{c_r^j c_r^m (d_\xi{}^{1k})^2 c_u^j c_v^m}{(\eta_{1k}-\varepsilon_j)(\eta_{1k}-\varepsilon_m)}(\gamma_r)^2+\cdots\cdots \qquad (u=v \text{ or } u\neq v) \tag{13}$$

$$(\delta\Psi_j)_{r\xi}=\sum_k^{\text{all}}\frac{c_r{}^j d_\xi{}^{1k}}{\varepsilon_j-\eta_{1k}}\gamma_r\psi_k-\frac{1}{2}\sum_k^{\text{all}}\frac{(c_r{}^j d_\xi{}^{1k})^2}{(\varepsilon_j-\eta_{1k})^2}(\gamma_r)^2\Psi_j+\sum_{m(\neq j)}^{\text{all}}\frac{c_r{}^j c_r{}^m}{\varepsilon_j-\varepsilon_m}\sum_k^{\text{all}}\frac{(d_\xi{}^{1k})^2}{\varepsilon_j-\eta_{1k}}(\gamma_r)^2\Psi_m+\cdots\cdots \tag{14}$$

where the atom u and the bond (uv) are in the system $\Delta(\varepsilon)$, and ξ is the position of weak conjugation in the system $\Delta_1(\varepsilon)$. Similar formulae would be obtained for the system $\Delta_1(\varepsilon)$. Thus the change of bond order and that of electron density and total π electronic energy change of the combined system are obtained as follows:

$$\begin{aligned}(\delta\varepsilon)_{r\xi}&=2\sum_j^{\text{occ}}(\delta\varepsilon_j)_{r\xi}+2\sum_k^{\text{occ}}(\delta\eta_{1k})_{r\xi}\\&=2\Big(\sum_j^{\text{occ}}\sum_k^{\text{unocc}}-\sum_j^{\text{unocc}}\sum_k^{\text{occ}}\Big)\frac{(c_r{}^j d_\xi{}^{1k})^2}{\varepsilon_j-\eta_{1k}}(\gamma_r)^2+2\sum_j^{\text{occ}}\{\text{the fourth order term in}(\delta\varepsilon_j)_{r\xi}\}\\&\quad+2\sum_k^{\text{occ}}\{\text{the fourth order term in}(\delta\eta_{1k})_{r\xi}\}+\cdots\cdots\end{aligned} \tag{15}$$

$$\begin{aligned}(\delta p_{uv})_{r\xi}&=2\sum_j^{\text{occ}}(\delta p_{uv}{}^j)_{r\xi}+2\sum_k^{\text{occ}}(\delta p_{uv}{}^{1k})_{r\xi}\\&=2\Big(\sum_k^{\text{occ}}\sum_j^{\text{unocc}}-\sum_k^{\text{unocc}}\sum_j^{\text{occ}}\Big)\Bigg[\frac{(d_\xi{}^{1k})^2}{\varepsilon_j-\eta_{1k}}\Bigg\{\frac{(c_r{}^j)^2c_u{}^jc_v{}^j}{\varepsilon_j-\eta_{1k}}\\&\quad-\sum_{m(\neq j)}^{\text{all}}\frac{c_r{}^jc_r{}^m(c_u{}^jc_v{}^m+c_v{}^jc_u{}^m)}{\varepsilon_j-\varepsilon_m}\Bigg\}\Bigg](\gamma_r)^2+\cdots\cdots\qquad(u=v\text{ or }u\neq v)\end{aligned} \tag{16}$$

$$\begin{aligned}(\delta p_{r\xi})_{r\xi}&=2\Big(\sum_j^{\text{occ}}\sum_k^{\text{unocc}}-\sum_j^{\text{unocc}}\sum_k^{\text{occ}}\Big)\frac{(c_r{}^j d_\xi{}^{1k})^2}{\varepsilon_j-\eta_{1k}}\gamma_r+2\sum_j^{\text{occ}}\{\text{the third order term in}(\delta p_{r\xi}{}^j)_{r\xi}\}\\&\quad+2\sum_k^{\text{occ}}\{\text{the third order term in}(\delta p_{r\xi}{}^{1k})_{r\xi}\}+\cdots\cdots\end{aligned} \tag{16$'$}$$

Here it was assumed that the highest occupied orbitals of the systems $\Delta(\varepsilon)$ and $\Delta_1(\varepsilon)$ are lower than the lowest unoccupied orbitals of the systems $\Delta_1(\varepsilon)$ and $\Delta(\varepsilon)$, respectively. The total charge transfer, δQ, from the system $\Delta_1(\varepsilon)$ to the system $\Delta(\varepsilon)$ is defined by

$$\delta Q=\sum_{u=1}^{n}\delta p_{uu} \tag{17}$$

where n is the number of atomic orbitals in the system $\Delta(\varepsilon)$.

For this case δQ is given by the following equation.

$$(\delta Q)_{r\xi}=2\Big(\sum_k^{\text{occ}}\sum_j^{\text{unocc}}-\sum_k^{\text{unocc}}\sum_j^{\text{occ}}\Big)\frac{(c_r{}^j d_\xi{}^{1k})^2}{(\varepsilon_j-\eta_{1k})^2}(\gamma_r)^2+\cdots\cdots \tag{18}$$

As a special case involved in the Case C, when the system $\Delta_1(\varepsilon)$ is an atom or a mesomeric group, X, Eqs. 11 to 16 and 18 become

$$(\delta\varepsilon_j)_{rX}=\frac{(c_r{}^j)^2}{\varepsilon_j-\alpha_X}(\gamma_r)^2+\frac{(c_r{}^j)^2}{\varepsilon_j-\alpha_X}\Bigg\{-\frac{(c_r{}^j)^2}{(\varepsilon_j-\alpha_X)^2}+\sum_{m(\neq j)}^{\text{all}}\frac{(c_r{}^m)^2}{(\varepsilon_j-\alpha_X)(\varepsilon_j-\varepsilon_m)}\Bigg\}(\gamma_r)^4+\cdots\cdots \tag{11-a}$$

$$(\delta\alpha_X)_{rX}=\sum_j^{\text{all}}\frac{(c_r{}^j)^2}{\alpha_X-\varepsilon_j}(\gamma_r)^2+\Bigg\{\sum_j^{\text{all}}\frac{(c_r{}^j)^2}{\alpha_X-\varepsilon_j}\Bigg\}\Bigg\{-\sum_j^{\text{all}}\frac{(c_r{}^j)^2}{(\alpha_X-\varepsilon_j)^2}\Bigg\}(\gamma_r)^4+\cdots\cdots \tag{11-b}$$

$$(\delta p_{uv}{}^j)_{rX}=\Bigg\{\sum_{m(\neq j)}^{\text{all}}\frac{c_r{}^jc_r{}^m(c_u{}^jc_v{}^m+c_v{}^jc_u{}^m)}{(\varepsilon_j-\varepsilon_m)(\varepsilon_j-\alpha_X)}-\frac{(c_r{}^j)^2c_u{}^jc_v{}^j}{(\varepsilon_j-\alpha_X)^2}\Bigg\}(\gamma_r)^2+\cdots\cdots \tag{12-a}$$

$$(\delta p_{rX}{}^j)_{rX}=\frac{(c_r{}^j)^2}{\varepsilon_j-\alpha_X}\gamma_r+\frac{2(c_r{}^j)^2}{(\varepsilon_j-\alpha_X)^2}\Bigg\{\sum_{m(\neq j)}^{\text{all}}\frac{(c_r{}^m)^2}{\varepsilon_j-\varepsilon_m}-\frac{(c_r{}^j)^2}{\varepsilon_j-\alpha_X}\Bigg\}(\gamma_r)^3+\cdots\cdots \tag{12$'$-a}$$

$$(\delta p_{uv}{}^X)_{rX}=\Bigg\{\sum_j^{\text{all}}\sum_m^{\text{all}}\frac{c_r{}^jc_r{}^mc_u{}^jc_v{}^m}{(\varepsilon_j-\alpha_X)(\varepsilon_m-\alpha_X)}\Bigg\}(\gamma_r)^2+\cdots \tag{13-a}$$

$$(\delta p_{rX}{}^X)_{rX}=\sum_j^{\text{all}}\frac{(c_r{}^j)^2}{\alpha_X-\varepsilon_j}\gamma_r-2\Bigg\{\sum_j^{\text{all}}\sum_m^{\text{all}}\frac{(c_r{}^jc_r{}^m)^2}{(\alpha_X-\varepsilon_j)^2(\alpha_X-\varepsilon_m)}\Bigg\}(\gamma_r)^3+\cdots\cdots \tag{13$'$-a}$$

$$(\delta p_{XX^j})_{rX}=\frac{(c_r{}^j)^2}{(\varepsilon_j-\alpha_X)^2}(\gamma_r)^2+\cdots\cdots \tag{12-b}$$

$$(\delta p_{XX^X})_{rX}=-\sum_j^{\text{all}}\frac{(c_r{}^j)^2}{(\alpha_X-\varepsilon_j)^2}(\gamma_r)^2+\cdots\cdots \tag{13-b}$$

$$(\delta p_{uv})_{rX}=(\nu\sum_j^{\text{all}}-2\sum_j^{\text{occ}})\left\{\frac{(c_r{}^j)^2c_u{}^jc_v{}^j}{(\varepsilon_j-\alpha_X)^2}+\sum_{m(\neq j)}^{\text{all}}\frac{c_r{}^jc_r{}^m(c_u{}^jc_v{}^m+c_v{}^jc_u{}^m)}{(\alpha_X-\varepsilon_j)(\varepsilon_j-\varepsilon_m)}\right\}(\gamma_r)^2+\cdots\cdots \tag{16-a}$$

$$(\delta p_{XX})_{rX}=(2\sum_j^{\text{occ}}-\nu\sum_j^{\text{all}})\frac{(c_v{}^j)^2}{(\alpha_X-\varepsilon_j)^2}(\gamma_r)^2+\cdots\cdots \tag{16-b}$$

$$(\delta p_{rX})_{rX}=(2\sum_j^{\text{occ}}-\nu\sum_j^{\text{all}})\frac{(c_r{}^j)^2}{\varepsilon_j-\alpha_X}\gamma_r+2\sum_j^{\text{occ}}\{\text{the third order term in}(\delta p_{rX^j})_{rX}\}$$

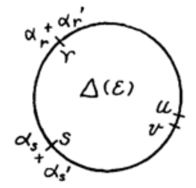
$$+\nu\{\text{the third order term in}(\delta p_{rX^X})_{rX}\}+\cdots\cdots \tag{16'-a}$$

$$(\delta Q)_{rX}=(\nu\sum_j^{\text{all}}-2\sum_j^{\text{occ}})\frac{(c_r{}^j)^2}{(\alpha_X-\varepsilon_j)^2}(\gamma_r)^2+\cdots\cdots \tag{18-a}$$

where ν is the number of electrons in the atom X. The equations corresponding to Eqs. 14 and 15 are omitted for simplicity.

In the following paragraphs some important cases of doubly perturbed systems will be treated.

2. Case I. Changes of Two Coulomb Integrals.—If two atoms, say the rth and the sth atoms, in a conjugated molecule, $\varDelta(\varepsilon)$, are replaced by two heteroatoms, the Coulomb integrals of these atoms will become $\alpha_r+\alpha_r'$ and $\alpha_s+\alpha_s'$, respectively. Then the perturbed secular determinant of the system will be written



$$D(\varepsilon)=\varDelta(\varepsilon)+\alpha_r'\varDelta_{rr}(\varepsilon)+\alpha_s'\varDelta_{ss}(\varepsilon)+\alpha_r'\alpha_s'\varDelta_{rrss}(\varepsilon) \tag{19}$$

where $\varDelta_{rr}(\varepsilon)$ and $\varDelta_{rrss}(\varepsilon)$ are the (rr) minor and the (rr, ss) minor of $\varDelta(\varepsilon)$, respectively. Regarding these changes, α_r' and α_s', as perturbations, one can easily obtain the perturbed orbital energy, of the jth molecular orbital, the perturbed bond order and the perturbed electron density by the use of the method of perturbed secular determinant, as will be briefly explained in the following.

First if one intermediately considers a system where α_s' is zero, the intermediate perturbed secular determinant is given as:

$$\square(\varepsilon)=\varDelta(\varepsilon)+\alpha_r'\varDelta_{rr}(\varepsilon) \tag{20}$$

According to the procedure utilized in the previous paper, the intermediate perturbed orbital energy, $\tilde{\varepsilon}_j$, and the intermediate perturbed separate bond order, $\tilde{p}_{uv}{}^j$, are expanded in powers of α_r':

$$\left.\begin{aligned}\tilde{\varepsilon}_j&=\sum_{m=0}^{\infty}a_r{}^{j(m)}(\alpha_r')^m\\ \tilde{p}_{uv}{}^j&=\sum_{m=0}^{\infty}a_{r,uv}{}^{j(m)}(\alpha_r')^m\end{aligned}\right\} \tag{21}$$

and the coefficients, $a_r{}^{j(m)}$ and $a_{r,uv}{}^{j(m)}$, are given by the following formulae.

$$\left.\begin{aligned}a_r{}^{j(m)}&=\frac{(-1)^m}{m!}\left[\frac{\mathrm{d}^m}{\mathrm{d}z^m}\frac{z\{\varDelta_{rr}(z)\}^{m-1}\{\varDelta'(z)\varDelta_{rr}(z)-\varDelta(z)\varDelta_{rr}'(z)\}}{\{\varDelta(z)/(z-\varepsilon_j)\}^{m+1}}\right]_{z=\varepsilon_j}\\ &\qquad\qquad (m=0,1,2,\cdots\cdots)\\ a_{r,uv}{}^{j(m)}&=\frac{(-1)^{m+1}}{m!}\left[\frac{\mathrm{d}^m}{\mathrm{d}z^m}\frac{\{\varDelta_{rr}(z)\}^m\varDelta_{ur}(z)\varDelta_{rv}(z)}{\{\varDelta(z)/(z-\varepsilon_j)\}^{m+1}}\right]_{z=\varepsilon_j}\\ &\qquad\qquad (m=0,1,2,\cdots\cdots)\end{aligned}\right\} \tag{22}$$

Directly from these formulae the following expressions are obtained

$$\left.\begin{aligned}\tilde{\varepsilon}_j&=\varepsilon_j+(\delta\varepsilon_j)_r\\ \tilde{p}_{uv}{}^j&=p_{uv}{}^j+(\delta p_{uv}{}^j)_r\end{aligned}\right\}\tag{23}$$

where $(\delta\varepsilon_j)_r$ and $(\delta p_{uv}{}^j)_r$ are given by Eqs. 1 and 2.

Then the second perturbation, α_s', is to be taken into account. The perturbed secular determinant of the system in question is expressed with the aid of the secular determinant of the intermediate system,

$$D(\varepsilon)=\square(\varepsilon)+\alpha_s'\square_{ss}(\varepsilon)\tag{24}$$

A similar procedure leads to the expansion formulae

$$\left.\begin{aligned}\varepsilon_j'&=\sum_{m=0}^{\infty}b_s{}^{j(m)}(\alpha_s')^m\\ P_{uv}{}^j&=\sum_{m=0}^{\infty}b_{s,uv}{}^{j(m)}(\alpha_s')^m\end{aligned}\right\}\tag{25}$$

where the coefficients, $b_s{}^{j(m)}$ and $b_{s,uv}{}^{j(m)}$, are the functions of α_r' and are given by

$$\left.\begin{aligned}b_s{}^{j(m)}&=\frac{(-1)^m}{m!}\left[\frac{\mathrm{d}^m}{\mathrm{d}z^m}\frac{z\{\square_{ss}(z)\}^{m-1}\{\square'(z)\square_{ss}(z)-\square(z)\square_{ss}'(z)\}}{\{\square(z)/(z-\tilde{\varepsilon}_j)\}^{m+1}}\right]_{z=\tilde{\varepsilon}_j}\\ &\qquad(m=0,1,2,\cdots\cdots)\\ b_{s,uv}{}^{j(m)}&=\frac{(-1)^{m+1}}{m!}\left[\frac{\mathrm{d}^m}{\mathrm{d}z^m}\frac{\{\square_{ss}(z)\}^m\square_{us}(z)\square_{sv}(z)}{\{\square(z)/(z-\tilde{\varepsilon}_j)\}^{m+1}}\right]_{z=\tilde{\varepsilon}_j}\\ &\qquad(m=0,1,2,\cdots\cdots)\end{aligned}\right\}\tag{26}$$

Thus we finally reach the following results for this perturbed system.

$$\varepsilon_j'=\varepsilon_j+(\delta\varepsilon_j)_r+(\delta\varepsilon_j)_s+2\sum_{k(\neq j)}^{\text{all}}\frac{c_r{}^jc_r{}^kc_s{}^jc_s{}^k}{\varepsilon_j-\varepsilon_k}\alpha_r'\alpha_s'+\cdots\cdots\tag{27}$$

$$\begin{aligned}P_{uv}{}^j=p_{uv}{}^j&+(\delta p_{uv}{}^j)_r+(\delta p_{uv}{}^j)_s\\ &+\left[\sum_{k(\neq j)}^{\text{all}}\sum_{m(\neq j)}^{\text{all}}\frac{c_r{}^jc_s{}^j(c_r{}^kc_s{}^m+c_s{}^kc_r{}^m)c_u{}^kc_v{}^m+c_r{}^mc_s{}^m(c_r{}^jc_s{}^k+c_s{}^jc_r{}^k)(c_u{}^jc_v{}^k+c_v{}^jc_u{}^k)}{(\varepsilon_j-\varepsilon_k)(\varepsilon_j-\varepsilon_m)}\right.\\ &\left.-\sum_{k(\neq j)}^{\text{all}}\frac{c_r{}^jc_s{}^j\{(c_r{}^jc_s{}^k+c_s{}^jc_r{}^k)(c_u{}^jc_v{}^k+c_v{}^jc_u{}^k)+2c_r{}^kc_s{}^kc_u{}^jc_v{}^j\}}{(\varepsilon_j-\varepsilon_k)^2}\right]\alpha_r'\alpha_s'+\cdots\cdots\end{aligned}\tag{28}$$

where $(\delta\varepsilon_j)_r$ and $(\delta p_{uv}{}^j)_r$ are the change of the orbital energy and the separate bond order (or the separate electron density) respectively, of the *j*th molecular orbital caused by the perturbation α_r', as were given in Eqs, 1 and 2.

On inspection of Eqs. 27 and 28 it is clearly seen that, as concerns the first order terms, two perturbations have no effect upon each other and, therefore, the so-called "additivity rule" comes into being. That is to say, the change of the orbital energy, the bond order or the electron density caused by two perturbations is expressed by the mathematical sum of its changes caused by each perturbation. In the second order a cross term appears, which may become comparable in magnitude with the non-cross term and cannot be neglected. Also as for the total π electronic energy, the bond order and the electron density, which are expressed by the sum of corresponding separate quantity, the circumstances are the same, as follows:

$$\varepsilon'=\varepsilon+(\delta\varepsilon)_r+(\delta\varepsilon)_s+2\sum_{j}^{\text{occ}}\sum_{k}^{\text{unocc}}\frac{c_r{}^jc_r{}^kc_s{}^jc_s{}^k}{\varepsilon_j-\varepsilon_k}\alpha_r'\alpha_s'+\cdots\cdots\tag{29}$$

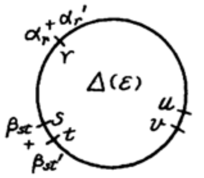
$$P_{uv}=p_{uv}+(\delta p_{uv})_r+(\delta p_{uv})_s+\sum_{j}^{\text{occ}}\{\text{cross term of the order }\alpha_r'\alpha_s'\text{ in }P_{uv}{}^j\}+\cdots\cdots\tag{30}$$

where $(\delta\varepsilon)_r$ and $(\delta p_{uv})_r$, given by Eqs. 3 and 4, are the changes of total π electronic energy and the bond order (or the electron density) respectively, caused by the perturbation α_r'. Eqs. 27 to 30 can also be derived by the existing method of perturbation.

The explicit expression of perturbed molecular orbital would be useful for some purposes. It is

$$\Psi_j'=\Psi_j+(\delta\Psi_j)_r+(\delta\Psi_j)_s-\sum_{k(\neq j)}^{\text{all}}\frac{c_r{}^jc_r{}^kc_s{}^jc_s{}^k}{(\varepsilon_j-\varepsilon_k)^2}\alpha_r'\alpha_s'\Psi_j$$
$$+\sum_{k(\neq j)}^{\text{all}}\frac{(c_r{}^jc_s{}^k+c_s{}^jc_r{}^k)}{\varepsilon_j-\varepsilon_k}\left\{\sum_{m(\neq j)}^{\text{all}}\frac{c_r{}^mc_s{}^m}{\varepsilon_j-\varepsilon_m}-\frac{c_r{}^jc_s{}^j}{\varepsilon_j-\varepsilon_k}\right\}\alpha_r'\alpha_s'\Psi_k+\cdots\cdots \tag{31}$$

where $(\delta\Psi_j)_r$ is given by Eq. 5.



3. Case II. Changes of a Coulomb Integral and a Resonance Integral.—When at the same time the Coulomb integral of the *r*th atom is increased by α_r' and the resonance integral of the bond (*st*), β_{st}, by β_{st}', then the perturbed secular determinant of the system is expressed* by

$$D(\varepsilon)=\varDelta(\varepsilon)+\alpha_r'\varDelta_{rr}(\varepsilon)+(-1)^{s+t}2\beta_{st}'\varDelta_{st}(\varepsilon)-(\beta_{st}')^2\varDelta_{sstt}(\varepsilon)$$
$$+(-1)^{s+t}\alpha_r'\beta_{st}'\varDelta_{rrst}(\varepsilon)-\alpha_r'(\beta_{st}')^2\varDelta_{rrsstt}(\varepsilon) \tag{32}$$

As well as in Case I, the following expressions of the orbital energy, the separate bond order and the separate electron density are obtained.

$$\varepsilon_j'=\varepsilon_j+(\delta\varepsilon_j)_r+(\delta\varepsilon_j)_{st}+2\sum_{k(\neq j)}^{\text{all}}\frac{c_r{}^jc_r{}^k(c_s{}^jc_t{}^k+c_t{}^jc_s{}^k)}{\varepsilon_j-\varepsilon_k}\alpha_r'\beta_{st}'+\cdots\cdots \tag{33}$$

$$P_{uv}{}^j=p_{uv}{}^j+(\delta p_{uv}{}^j)_r+(\delta p_{uv}{}^j)_{st}$$
$$+\left[\sum_{k(\neq j)}^{\text{all}}\sum_{m(\neq j)}^{\text{all}}\frac{c_r{}^jc_r{}^k(c_s{}^jc_t{}^m+c_t{}^jc_s{}^m)(c_u{}^kc_v{}^m+c_v{}^kc_u{}^m)}{(\varepsilon_j-\varepsilon_k)}\right.$$
$$\times\frac{\{c_r{}^kc_r{}^m(c_s{}^jc_t{}^m+c_t{}^jc_s{}^m)+c_r{}^mc_r{}^j(c_s{}^kc_t{}^m+c_t{}^kc_s{}^m)\}(c_u{}^jc_v{}^k+c_v{}^jc_u{}^k)}{(\varepsilon_j-\varepsilon_m)}$$
$$\left.-\sum_{k(\neq j)}^{\text{all}}\frac{2\{2c_r{}^jc_r{}^kc_s{}^jc_t{}^j+(c_r{}^j)^2(c_s{}^jc_t{}^k+c_t{}^jc_s{}^k)\}(c_u{}^jc_v{}^k+c_v{}^jc_u{}^k)c_r{}^jc_r{}^k(c_s{}^jc_t{}^k+c_t{}^jc_s{}^k)c_u{}^jc_v{}^j}{(\varepsilon_j-\varepsilon_k)^2}\right]\alpha_r'\beta_{st}'$$
$$+\cdots\cdots \tag{34}$$

where $(\delta\varepsilon_j)_r$, $(\delta\varepsilon_j)_{st}$, $(\delta p_{uv}{}^j)_r$ and $(\delta p_{uv}{}^j)_{st}$ are given by Eqs. 1, 6, 2 and 7, respectively. Also in this case a cross term between the two perturbations, both in the orbital energy and in the bond order (and the density), first arises in the second order, and therefore the additivity rule is correct in the first order. The circumtances are the same for the total energy, the bond order and the electron density.

$$\left.\begin{aligned}&\varepsilon'=\varepsilon+(\delta\varepsilon)_r+(\delta\varepsilon)_{st}+2\sum_j^{\text{occ}}\{\text{cross term of the order }\alpha_r'\beta_{st}'\text{ in }\varepsilon_j'\}+\cdots\cdots\\&P_{uv}=p_{uv}+(\delta p_{uv})_r+(\delta p_{uv})_{st}+2\sum_j^{\text{occ}}\{\text{cross term of the order }\alpha_r'\beta_{st}'\text{ in }P_{uv}{}^j\}\\&\qquad+\cdots\cdots\end{aligned}\right\} \tag{35}$$

where $(\delta\varepsilon)_{st}$ and $(\delta p_{uv})_{st}$ are given by Eqs. 8 and 9. The perturbed molecular orbital is obtained as follows:

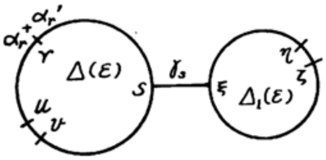
$$\Psi_j'=\Psi_j+(\delta\Psi_j)_r+(\delta\Psi_j)_{st}+\sum_{k(\neq j)}^{\text{all}}\left\{\sum_{m(\neq j)}^{\text{all}}\frac{c_r{}^kc_r{}^m(c_s{}^jc_t{}^m+c_t{}^jc_s{}^m)+c_r{}^jc_r{}^m(c_s{}^kc_t{}^m+c_t{}^kc_s{}^m)}{(\varepsilon_j-\varepsilon_k)(\varepsilon_j-\varepsilon_m)}\right.$$
$$\left.-\frac{2c_r{}^jc_r{}^kc_s{}^jc_t{}^j+(c_r{}^j)^2(c_s{}^jc_t{}^k+c_t{}^jc_s{}^k)}{(\varepsilon_j-\varepsilon_k)^2}\right\}\alpha_r'\beta_{st}'\Psi_k$$
$$-\sum_{m(\neq j)}^{\text{all}}\frac{c_r{}^jc_r{}^k(c_s{}^jc_t{}^k+c_t{}^jc_s{}^k)}{(\varepsilon_j-\varepsilon_k)^2}\alpha_r'\beta_{sr}'\Psi_k+\cdots\cdots \tag{36}$$

where $(\delta\Psi_j)_{st}$ is given by Eq. 10.

4. Case III. A Weak Bonding with a Change of a Coulomb Integral.—When a conjugated system, $\varDelta(\varepsilon)$, conjugates at the *s*th atom through a weak bonding, whose

---

* When $r=t$, though the perturbed secular determinant becomes $D(\varepsilon)=\varDelta(\varepsilon)+\alpha_r'\varDelta_{rr}(\varepsilon)+(-1)^{s+r}2\beta_{sr}'\varDelta_{sr}(\varepsilon)-(\beta_{sr}')^2\varDelta_{ssrr}(\varepsilon)$, Eqs. 33 to 36 are valid.



resonance integral is γ_s, with another conjugated system $\varDelta_1(\varepsilon)$, and at the same time the Coulomb integral of the rth atom is increased by α_r', as illustrated in the figure, then the following formulae are obtained.

$$D(\varepsilon)=\varDelta(\varepsilon)\varDelta_1(\varepsilon)+\alpha_r'\varDelta_{rr}(\varepsilon)\varDelta_1(\varepsilon)-(\gamma_s)^2\varDelta_{ss}(\varepsilon)\varDelta_{1\xi\xi}(\varepsilon)$$
$$-\alpha_r'(\gamma_s)^2\varDelta_{rrss}(\varepsilon)\varDelta_{1\xi\xi}(\varepsilon) \tag{37}$$

$$\varepsilon_j'=\varepsilon_j+(\delta\varepsilon_j)_r+(\delta\varepsilon_j)_{s\xi}+\sum_k^{\text{all}}\frac{c_r{}^jc_s{}^j(d_\xi{}^{1k})^2}{\varepsilon_j-\eta_{1k}}\left\{2\sum_{m(\neq j)}^{\text{all}}\frac{c_r{}^mc_s{}^m}{\varepsilon_j-\varepsilon_m}-\frac{c_r{}^jc_s{}^j}{\varepsilon_j-\eta_{1k}}\right\}\alpha_r'(\gamma_s)^2+\cdots\cdots \tag{38}$$

$$\eta_{1k}'=\eta_{1k}+(\delta\eta_{1k})_{s\xi}+\sum_j^{\text{all}}\frac{c_r{}^jc_s{}^j(d_\xi{}^{1k})^2}{\eta_{1k}-\varepsilon_j}\left\{2\sum_{m(\neq j)}^{\text{all}}\frac{c_r{}^mc_s{}^m}{\varepsilon_j-\varepsilon_m}-\frac{c_r{}^jc_s{}^j}{\varepsilon_j-\eta_{1k}}\right\}\alpha_r'(\gamma_s)^2+\cdots\cdots \tag{39}$$

$$P_{uv}{}^j=p_{uv}{}^j+(\delta p_{uv}{}^j)_r+(\delta p_{uv}{}^j)_{s\xi}+\{\text{cross term of the order } \alpha_r'(\gamma_s)^2\}+\cdots\cdots \tag{40}$$

$$P_{s\xi}{}^j=(\delta p_{s\xi}{}^j)_{s\xi}+\sum_k^{\text{all}}\frac{c_r{}^jc_s{}^j(d_\xi{}^{1k})^2}{\varepsilon_j-\eta_{1k}}\left\{2\sum_{m(\neq j)}^{\text{all}}\frac{c_r{}^mc_s{}^m}{\varepsilon_j-\varepsilon_m}-\frac{c_r{}^jc_s{}^j}{\varepsilon_j-\eta_{1k}}\right\}\alpha_r'\gamma_s+\cdots\cdots \tag{40'}$$

$$P_{uv}{}^{1k}=(\delta p_{uv}{}^{1k})_{s\xi}+\{\text{cross term of the order } \alpha_r'(\gamma_s)^2\}+\cdots \tag{41}$$

$$P_{\eta\zeta}{}^{1k}=p_{\eta\zeta}{}^{1k}+(\delta p_{\eta\zeta}{}^{1k})_{s\xi}+\{\text{cross term of the order } \alpha_r'(\gamma_s)^2\}+\cdots \tag{42}$$

$$P_{s\xi}{}^{1k}=(\delta p_{s\xi}{}^{1k})_{s\xi}+\sum_j^{\text{all}}\frac{c_r{}^jc_s{}^j(d_\xi{}^{1k})^2}{\eta_{1k}-\varepsilon_j}\left\{2\sum_{m(\neq j)}^{\text{all}}\frac{c_r{}^mc_s{}^m}{\varepsilon_j-\varepsilon_m}-\frac{c_r{}^jc_s{}^j}{\varepsilon_j-\eta_{1k}}\right\}\alpha_r'\gamma_s+\cdots\cdots \tag{42'}$$

$$P_{\eta\zeta}{}^j=(\delta p_{\eta\zeta}{}^j)_{s\xi}+\{\text{cross term of the order } \alpha_r'(\gamma_s)^2\}+\cdots \tag{43}$$

where ξ is the position of weak conjugation in the system $\varDelta_1(\varepsilon)$, the bond $(\eta\zeta)$ is in the system $\varDelta_1(\varepsilon)$; and $(\delta\varepsilon_j)_{s\xi}$, $(\delta p_{uv}{}^j)_{s\xi}$, $(\delta p_{s\xi}{}^j)_{s\xi}$ and $(\delta p_{uv}{}^{1k})_{s\xi}$ are given by Eqs. 11, 12, 12′ and 13, from which $(\delta\eta_{1k})_{s\xi}$, $(\delta p_{\eta\zeta}{}^j)_{s\xi}$, $(\delta p_{\eta\zeta}{}^{1k})_{s\xi}$ and $(\delta p_{s\xi}{}^{1k})_{s\xi}$ will easily be formulated. Therefore the total π electronic energy of the combined system is

$$\varepsilon'=\varepsilon+(\delta\varepsilon)_r+(\delta\varepsilon)_{s\xi}+2\Big(\sum_j^{\text{occ}}\sum_k^{\text{unocc}}-\sum_j^{\text{unocc}}\sum_k^{\text{occ}}\Big)$$
$$\times\left[\frac{c_r{}^jc_s{}^j(d_\xi{}^{1k})^2}{\varepsilon_j-\eta_{1k}}\left\{2\sum_{m(\neq j)}^{\text{all}}\frac{c_r{}^mc_s{}^m}{\varepsilon_j-\varepsilon_m}-\frac{c_r{}^jc_s{}^j}{\varepsilon_j-\eta_{1k}}\right\}\right]\alpha_r'(\gamma_s)^2+\cdots\cdots \tag{44}$$

And

$$P_{uv}=p_{uv}+(\delta p_{uv})_r+(\delta p_{uv})_{s\xi}+\{\text{cross term of the order } \alpha_r'(\gamma_s)^2\}+\cdots \tag{45}$$

$$P_{s\xi}=(\delta p_{s\xi})_{s\xi}+2\Big(\sum_j^{\text{occ}}\sum_k^{\text{unocc}}-\sum_j^{\text{unocc}}\sum_k^{\text{occ}}\Big)\left[\frac{c_r{}^jc_s{}^j(d_\xi{}^{1k})^2}{\varepsilon_j-\eta_{1k}}\left\{2\sum_{m(\neq j)}^{\text{all}}\frac{c_r{}^mc_s{}^m}{\varepsilon_j-\varepsilon_m}-\frac{c_r{}^jc_s{}^j}{\varepsilon_i-\eta_{1k}}\right\}\right]\alpha_r'\gamma_s$$
$$+\cdots\cdots \tag{45'}$$

$$P_{\eta\zeta}=p_{\eta\zeta}+(\delta p_{\eta\zeta})_{s\xi}+\{\text{cross term of the order } \alpha_r'(\gamma_s)^2\}+\cdots \tag{46}$$

$$\delta Q=(\delta Q)_{s\xi}+\{\text{cross term of the order } \alpha_r'(\gamma_s)^2\}+\cdots \tag{47}$$

where $(\delta\varepsilon)_{s\xi}$, $(\delta p_{uv})_{s\xi}$, $(\delta p_{s\xi})_{s\xi}$ and $(\delta Q)_{s\xi}$ are given by Eqs. 15, 16, 16′ and 18. $(\delta p_{\eta\zeta})_{s\xi}$ is easily written on inspection of Eq. 16. As is seen in Eqs. 45 to 47, a cross term first appears in the third order, that is, the order of $\alpha_r'(\gamma_s)^2$, and the additivity rule is valid up to the second order perturbation.

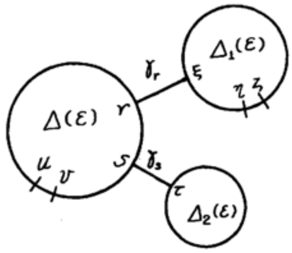
The wave functions of this perturbed system are represented by

$$\varPsi_j'=\varPsi_j+(\delta\varPsi_j)_r+(\delta\varPsi_j)_{s\xi}+\sum_k^{\text{all}}\frac{c_r{}^jd_\xi{}^{1k}}{\varepsilon_j-\eta_{1k}}\left\{\sum_{m(\neq j)}^{\text{all}}\frac{c_r{}^mc_s{}^m}{\varepsilon_j-\varepsilon_m}-\frac{c_r{}^jc_s{}^j}{\varepsilon_j-\eta_{1k}}\right\}\alpha_r'\gamma_s\psi_{1k}+\cdots\cdots \tag{48}$$

$$\psi_{1k}'=\psi_{1k}+(\delta\psi_{1k})_{s\xi}+\sum_j^{\text{all}}\frac{c_r{}^jd_\xi{}^{1k}}{\eta_{1k}-\varepsilon_j}\sum_{m(\neq j)}^{\text{all}}\frac{c_r{}^mc_s{}^m}{\eta_{1k}-\varepsilon_m}\alpha_r'\gamma_s\varPsi_j+\cdots \tag{49}$$

where $(\delta\varPsi_j)_{s\xi}$ is given by Eq. 14, from which also $(\delta\psi_{1k})_{s\xi}$ may easily be written.

5. Case IV. Weak Bondings to Two Conjugated Systems.—Here we consider a case in which a conjugated system, $\varDelta(\varepsilon)$, conjugates at the rth and the sth atoms with two other conjugated systems, $\varDelta_1(\varepsilon)$ and $\varDelta_2(\varepsilon)$, respectively, making weak bondings whose resonance integrals are γ_r and γ_s, respectively. The molecular orbital, its orbital energy and the coefficient of atomic orbital in the non-perturbed $\varDelta_1(\varepsilon)$ system are designated by ψ_{1k}, η_{1k} and $d_\mu{}^{1k}$, respectively, and in the system $\varDelta_2(\varepsilon)$ by ψ_{2k}, η_{2k} and $d_\nu{}^{2k}$. Then the following expressions are easily obtained for the perturbed combined system.



$$D(\varepsilon)=\varDelta(\varepsilon)\varDelta_1(\varepsilon)\varDelta_2(\varepsilon)-(\gamma_r)^2\varDelta_{rr}(\varepsilon)\varDelta_{1\xi\xi}(\varepsilon)\varDelta_2(\varepsilon)$$
$$-(\gamma_s)^2\varDelta_{ss}(\varepsilon)\varDelta_1(\varepsilon)\varDelta_{2\tau\tau}(\varepsilon)+(\gamma_r\gamma_s)^2\varDelta_{rrss}(\varepsilon)\varDelta_{1\xi\xi}(\varepsilon)\varDelta_{2\tau\tau}(\varepsilon) \tag{50}$$

$$\varepsilon_j{}'=\varepsilon_j+(\delta\varepsilon_j)_{r\xi}+(\delta\varepsilon_j)_{s\tau}+\sum_k^{\text{all}}\frac{c_r{}^j(d_\xi{}^{1k})^2}{\varepsilon_j-\eta_{1k}}U_{jk}(\gamma_r\gamma_s)^2+\cdots\cdots \tag{51}$$

$$U_{jk}=\sum_l^{\text{all}}\frac{c_s{}^j(d_\tau{}^{2l})^2}{\varepsilon_j-\eta_{2l}}\left\{2\sum_{m(\neq j)}^{\text{all}}\frac{c_r{}^m c_s{}^m}{\varepsilon_j-\varepsilon_m}-\frac{c_r{}^j c_s{}^j}{\varepsilon_j-\eta_{1k}}-\frac{c_r{}^j c_s{}^j}{\varepsilon_j-\eta_{2l}}\right\} \tag{51-a}$$

$$\eta_{1k}{}'=\eta_{1k}+(\delta\eta_{1k})_{r\xi}+\sum_j^{\text{all}}\frac{c_r{}^j(d_\xi{}^{1k})^2}{\eta_{1k}-\varepsilon_j}U_{jk}(\gamma_r\gamma_s)^2+\cdots\cdots \tag{52}$$

$$P_{uv}{}^j=p_{uv}{}^j+(\delta p_{uv}{}^j)_{r\xi}+(\delta p_{uv}{}^j)_{s\tau}+\{\text{cross term of the order }(\gamma_r\gamma_s)^2\}+\cdots\cdots \tag{53}$$

$$P_{r\xi}{}^j=(\delta p_{r\xi}{}^j)_{r\xi}+\sum_k^{\text{all}}\frac{c_r{}^j(d_\xi{}^{1k})^2}{\varepsilon_j-\eta_{1k}}U_{jk}\gamma_r(\gamma_s)^2+\cdots\cdots \tag{53$'$}$$

$$P_{uv}{}^{1k}=(\delta p_{uv}{}^{1k})_{r\xi}+\{\text{cross term of the order }(\gamma_r\gamma_s)^2\}+\cdots\cdots \tag{54}$$

$$P_{r\xi}{}^{1k}=(\delta p_{r\xi}{}^{1k})_{r\xi}+\sum_j^{\text{all}}\frac{c_r{}^j(d_\xi{}^{1k})^2}{\eta_{1k}-\varepsilon_j}U_{jk}\gamma_r(\gamma_s)^2+\cdots\cdots \tag{54$'$}$$

$$P_{uv}{}^{2l}=(\delta p_{uv}{}^{2l})_{s\tau}+\{\text{cross term of the order }(\gamma_r\gamma_s)^2\}+\cdots\cdots \tag{55}$$

$$P_{r\xi}{}^{2k}=\sum_k^{\text{all}}\frac{(d_\xi{}^{1k})^2}{\eta_{2l}-\eta_{1k}}\sum_j^{\text{all}}\sum_m^{\text{all}}\frac{c_r{}^j c_r{}^m c_s{}^j c_s{}^m(d_\tau{}^{2l})^2}{(\eta_{2l}-\varepsilon_j)(\eta_{2l}-\varepsilon_m)}\gamma_r(\gamma_s)^2+\cdots\cdots \tag{55$'$}$$

$$P_{\eta\zeta}{}^{1k}=p_{\eta\zeta}{}^{1k}+(\delta p_{\eta\zeta}{}^{1k})_{r\xi}+\{\text{cross term of the order }(\gamma_r\gamma_s)^2\}+\cdots\cdots \tag{56}$$

$$P_{\eta\zeta}{}^j=(\delta p_{\eta\zeta}{}^j)_{r\xi}+\{\text{cross term of the order}(\gamma_r\gamma_s)^2\}+\cdots\cdots \tag{57}$$

$$P_{\eta\zeta}{}^{2l}=\{\text{cross term of the order}(\gamma_r\gamma_s)^2\}+\cdots\cdots \tag{58}$$

where ξ and τ are the positions of the weak conjugation in the systems $\varDelta_1(\varepsilon)$ and $\varDelta_2(\varepsilon)$, respectively, and the bond (uv) or the atom u is assumed to be in the system $\varDelta(\varepsilon)$, and the bond $(\eta\zeta)$ or the atom η in the system $\varDelta_1(\varepsilon)$. Similar expressions as above may be written for the system $\varDelta_2(\varepsilon)$. Thus the total π electronic energy and the bond order of this perturbed system are given as follows:

$$\varepsilon'=2\sum_j^{\text{occ}}\varepsilon_j{}'+2\sum_k^{\text{occ}}\eta_{1k}{}'+2\sum_l^{\text{occ}}\eta_{2l}{}'$$
$$=\varepsilon+(\delta\varepsilon)_{r\xi}+(\delta\varepsilon)_{st}$$
$$+\left\{\sum_j^{\text{occ}}\Big(\sum_k^{\text{unocc}}\sum_l^{\text{unocc}}-\sum_k^{\text{occ}}\sum_l^{\text{occ}}\Big)-\sum_j^{\text{unocc}}\Big(\sum_k^{\text{occ}}\sum_l^{\text{all}}+\sum_k^{\text{all}}\sum_l^{\text{occ}}\Big)\right\}\frac{c_r{}^j c_s{}^j(d_\xi{}^{1k})^2(d_\tau{}^{2l})^2}{(\varepsilon_j-\eta_{1k})(\varepsilon_j-\eta_{2l})}$$
$$\times\left(2\sum_{m(\neq j)}^{\text{all}}\frac{c_r{}^m c_s{}^m}{\varepsilon_j-\varepsilon_m}-\frac{c_r{}^j c_s{}^j}{\varepsilon_j-\eta_{1k}}-\frac{c_r{}^j c_s{}^j}{\varepsilon_j-\eta_{2l}}\right)(\gamma_r\gamma_s)^2+\cdots\cdots \tag{59}$$

$$P_{uv}=p_{uv}+(\delta p_{uv})_{r\xi}+(\delta p_{uv})_{s\tau}+\{\text{cross term of the order }(\gamma_r\gamma_s)^2\}+\cdots\cdots \tag{60}$$

$$P_{r\xi}=(\delta p_{r\xi})_{r\xi}+\Bigg[2\Big(\sum_j^{\text{occ}}\sum_k^{\text{unocc}}-\sum_j^{\text{unocc}}\sum_k^{\text{occ}}\Big)\frac{c_r{}^j(d_\xi{}^{1k})^2}{\varepsilon_j-\eta_{1k}}U_{jk}$$
$$+2\sum_l^{\text{occ}}\sum_k^{\text{all}}\frac{(d_\xi{}^{1k})^2}{\eta_{2l}-\eta_{1k}}\sum_j^{\text{all}}\sum_m^{\text{all}}\frac{c_r{}^j c_r{}^m c_s{}^j c_s{}^m(d_\tau{}^{2l})^2}{(\eta_{2l}-\varepsilon_j)(\eta_{2l}-\varepsilon_m)}\Bigg]\gamma_r(\gamma_s)^2+\cdots \tag{60$'$}$$

$$P_{\eta\zeta}=p_{\eta\zeta}+(\delta p_{\eta\zeta})_{r\xi}+\{\text{cross term of the order } (\gamma_r\gamma_s)^2\}+\cdots\cdots \tag{61}$$

The changes of total charge involved in the systems $\varDelta(\varepsilon)$ and $\varDelta_1(\varepsilon)$ are designated as δQ and δQ_1, respectively, which are written as follows:

$$\delta Q=(\delta Q)_{r\xi}+(\delta Q)_{s\tau}+\{\text{cross term of the order } (\gamma_r\gamma_s)^2\}+\cdots\cdots \tag{62}$$

$$\delta Q_1=(\delta Q)_{r\xi}+\{\text{cross term of the order } (\gamma_r\gamma_s)^2\}+\cdots\cdots \tag{63}$$

A similar equation may be written also for the system $\varDelta_2(\varepsilon)$.

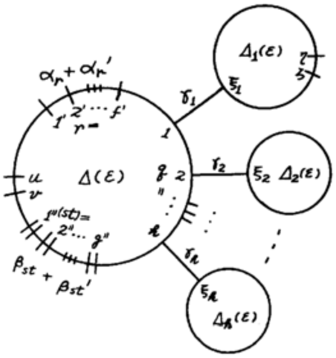
The molecular orbitals of this perturbed system are

$$\varPsi_j'=\varPsi_j+(\delta\varPsi_j)_{r\xi}+(\delta\varPsi_j)_{s\tau}+\{\text{cross term of the orders } \gamma_r(\gamma_s)^2 \text{ and } (\gamma_r)^2\gamma_s\}+\cdots\cdots \tag{64}$$

$$\psi_{1k}'=\psi_{1k}+(\delta\varPsi_{1k})_{r\xi}+\sum_j^{\text{all}}\sum_l^{\text{all}}\frac{c_r^jc_s^jd_\xi^{1k}d_\eta^{2l}}{(\eta_{1k}-\eta_{2l})(\eta_{1k}-\varepsilon_j)}\gamma_r\gamma_s\psi_{2k}+\cdots\cdots \tag{65}$$

As to special cases in which either or both of the systems $\varDelta_1(\varepsilon)$ and $\varDelta_2(\varepsilon)$ are single atoms, one may simplify the results of Cases III and IV by using Eqs. 11-a to 18-a instead of Eqs. 11 to 18 for non-cross terms and by abridging cross terms.

6. More General Case of Many Perturbations. — Perturbation treatment of systems affected by two perturbations stated above may be extended to a more general case of many perturbations. As illustrated in the figure, we consider a conjugated system, $\varDelta(\varepsilon)$, and increase the Coulomb integrals of the rth atoms in it $(r=1', 2', \cdots\cdots, f')$ by α_r' and the resonance integrals of the bonds (st) $(st=1'', 2'', \cdots\cdots, g'')$ by β_{st}', and make weak bondings, whose resonance integral is γ_q, between the qth atoms $(q=1, 2, \cdots\cdots, h)$ in the system and the ξ_qth atoms in other conjugated systems $\varDelta_q(\varepsilon)$. Here some of the r's, s's and q's may be the identical atoms.



Then the perturbed jth orbital energy of the system $\varDelta(\varepsilon)$ is

$$\begin{aligned}\varepsilon_j'=\varepsilon_j&+\sum_{r=1'}^{f'}(\delta\varepsilon_j)_r+\sum_{(st)=1''}^{g''}(\delta\varepsilon_j)_{st}+\sum_{q=1}^{h}(\delta\varepsilon_j)_{q\xi}\\&+C(\alpha^2,\alpha\beta,\beta^2)+C(\alpha^3,\alpha^2\beta,\alpha\beta^2,\beta^3,\alpha\gamma^2,\beta\gamma^2)\\&+C(\alpha^4,\alpha^3\beta,\alpha^2\beta^2,\alpha\beta^3,\beta^4,\alpha^2\gamma^2,\alpha\beta\gamma^2,\beta^2\gamma^2,\gamma^4)+\cdots\cdots\end{aligned} \tag{66}$$

where $(\delta\varepsilon_j)_r$, $(\delta\varepsilon_j)_{st}$ and $(\delta\varepsilon_j)_{q\xi}$ are energy changes caused by perturbations α_r', β_{st}' and γ_q, respectively, and are given by Eqs. 1, 6 and 11. and C means the cross term among perturbations. For instance $C(\alpha^2,\alpha\beta,\beta^2)$ consists of cross terms of orders $\alpha_1'\alpha_2', \alpha_1'\alpha_3', \cdots\cdots, \alpha_2'\alpha_3', \cdots\cdots, \alpha_1'\beta_1', \alpha_1'\beta_2', \cdots\cdots, \alpha_2'\beta_1', \cdots\cdots, \beta_1'\beta_2', \beta_1'\beta_3', \cdots\cdots, \beta_2'\beta_3', \cdots\cdots$; and $C(\alpha^3,\alpha^2\beta, \alpha\beta^2, \beta^3, \alpha\gamma^2, \beta\gamma^2)$ of orders $(\alpha_1')^2\alpha_2', \cdots\cdots, \alpha_1'\alpha_2'\alpha_3', \cdots\cdots, (\alpha_1')^2\beta_1', \cdots\cdots, \alpha_1'\alpha_2'\beta_1', \cdots\cdots, \alpha_1'(\beta_1')^2, \cdots\cdots, \alpha_1'\beta_1'\beta_2', \cdots\cdots, (\beta_1')^2\beta_2', \cdots\cdots, \beta_1'\beta_2'\beta_3', \cdots\cdots, \alpha_1'(\gamma_1)^2, \cdots\cdots, \beta_1'(\gamma_1)^2, \cdots\cdots$. The perturbed separate bond order by this orbital of the bond (uv) in the system $\varDelta(\varepsilon)$ is

$$\begin{aligned}P_{uv}^j=p_{uv}^j&+\sum_{r=1'}^{f'}(\delta p_{uv}^j)_r+\sum_{(st)=1''}^{g''}(\delta p_{uv}^j)_{st}+\sum_{q=1}^{h}(\delta p_{uv}^j)_{q\xi}\\&+C(\alpha^2,\alpha\beta,\beta^2)+C(\alpha^3,\alpha^2\beta,\alpha\beta^2,\beta^3,\alpha\gamma^2,\beta\gamma^2)\\&+C(\alpha^4,\alpha^3\beta,\alpha^2\beta^2,\alpha\beta^3,\beta^4,\alpha^2\gamma^2,\alpha\beta\gamma^2,\beta^2\gamma^2,\gamma^4)+\cdots\cdots\end{aligned} \tag{67}$$

where $(\delta p_{uv}^j)_r$, $(\delta p_{uv}^j)_{st}$ and $(\delta p_{uv}^j)_{q\xi}$ are the changes caused by α_r', β_{st}' and γ_q, respectively, and are given by Eqs. 2, 7 and 12. The perturbed separate bond order by this orbital of the bond $(\eta\zeta)$ in another system, say, the system $\varDelta_1(\varepsilon)$, is

$$\begin{aligned}P_{\eta\zeta}^j=(\delta p_{\eta\zeta}^j)_{1\xi}&+C\{\alpha(\gamma_1)^2,\beta(\gamma_1)^2\}\\&+C\{\alpha^2(\gamma_1)^2,\alpha\beta(\gamma_1)^2,\beta^2(\gamma_1)^2,\gamma^2(\gamma_1)^2\}+\cdots\cdots\end{aligned} \tag{68}$$

The perturbed kth orbital energy of a system, say, the system $\varDelta_1(\varepsilon)$, is

$$\eta_{1k}'=\eta_{1k}+(\delta\eta_{1k})_{1\xi}+C\{\alpha(\gamma_1)^2,\ \beta(\gamma)_1)^2\}$$
$$+C\{\alpha^2(\gamma_1)^2,\ \alpha\beta(\gamma_1)^2,\ \beta^2(\gamma_1)^2,\ \gamma^2(\gamma_1)^2\}+\cdots\cdots \tag{69}$$

The perturbed separate bond orders by this orbital of bonds $(\eta\zeta)$ and (uv) are

$$P_{\eta\zeta}{}^{1k}=p_{\eta\zeta}{}^{1k}+(\delta p_{\eta\zeta}{}^{1k})_{1\xi}+C\{\alpha(\gamma_1)^2,\ \beta(\gamma_1)^2\}$$
$$+C\{\alpha^2(\gamma_1)^2,\ \alpha\beta(\gamma_1)^2,\ \beta^2(\gamma_1)^2,\ \gamma^2(\gamma_1)^2\}+\cdots\cdots \tag{70}$$

$$P_{uv}{}^{1k}=(\delta p_{uv}{}^{1k})_{1\xi}+C\{\alpha(\gamma_1)^2,\ \beta(\gamma_1)^2\}$$
$$+C\{\alpha^2(\gamma_1)^2,\ \alpha\beta(\gamma_1)^2,\ \beta^2(\gamma_1)^2,\ \gamma^2(\gamma_1)^2\}+\cdots\cdots \tag{71}$$

Also this bond order by this orbital of the bond $(\mu\nu)$, which is located in another system, say, the system $\varDelta_h(\varepsilon)$, is given by

$$P_{\mu\nu}{}^{1k}=C\{(\gamma_1)^2(\gamma_h)^2\}+\cdots\cdots \tag{72}$$

The perturbed separate bond order of the bond which is made anew by perturbation between conjugated systems, say, the bond $(1\xi_1)$ between the systems $\varDelta(\varepsilon)$ and $\varDelta_1(\varepsilon)$, may be written as

$$P_{1\xi}{}^{j}=(\delta p_{1\xi}{}^{j})_{1\xi}+C\{\alpha\gamma_1,\ \beta\gamma_1\}+C\{\alpha^2\gamma_1,\ \alpha\beta\gamma_1,\ \beta^2\gamma_1,\ \gamma^2\gamma_1\}$$
$$+C\{\alpha^3\gamma_1,\ \alpha^2\beta\gamma_1,\ \alpha\beta^2\gamma_1,\ \beta^3\gamma_1,\ \alpha\gamma^2\gamma_1,\ \beta\gamma^2\gamma_1,\ \alpha(\gamma_1)^3,\ \beta(\gamma_1)^3\}+\cdots\cdots \tag{73}$$

$$P_{1\xi}{}^{1k}=(\delta p_{1\xi}{}^{1k})_{1\xi}+C\{\alpha\gamma_1,\ \beta\gamma_1\}+C\{\alpha^2\gamma_1,\ a\beta\gamma_1,\ \beta^2\gamma_1,\ \gamma^2\gamma_1\}$$
$$+C\{\alpha^3\gamma_1,\ \alpha^2\beta\gamma_1,\ \alpha\beta^2\gamma_1,\ \beta^3\gamma_1,\ \alpha\gamma^2\gamma_1,\ \beta\gamma^2\gamma_1,\ \alpha(\gamma_1)^3,\ \beta(\gamma_1)^3\}+\cdots\cdots \tag{74}$$

$$P_{1\xi}{}^{ql}=C\{(\gamma_q)^2\gamma_1\}+C\{\alpha(\gamma_q)^2\gamma_1,\ \beta(\gamma_q)^2\gamma_1\}+\cdots\cdots \qquad (q=2,3,\cdots\cdots,h) \tag{75}$$

As for the total π electronic energy an equation similar to Eq. 66, as for the total bond order (and the electron density) one similar to Eq. 67, and as for the total bond order of a newly formed bond one similar to Eq. 75 may be obtained.

Thus it has become clear to what order of perturbation terms the additivity rule applies, and what kinds of terms appear in several molecular quantities. If it is necessary, one could formulate cross terms in reference to the results of two perturbations.

Degenerate System

In the previous section it was assumed that no molecular orbital is degenerate with any other molecular orbital in the same molecule, not with molecular orbitals in any other system to be subjected to conjugation.

Even if some levels in the non-perturbed systems are degenerate, so far as they are chosen mutually orthogonal, the perturbed orbital energy and the perturbed separate bond order (and electron density) corresponding to non-degenerate orbitals are not affected at all, that is, equations derived in the preceding section, giving separate quantities, are valid also in this case.

As for degenerate levels, on the other hand, the sum of the perturbed orbital energies or of the perturbed bond orders over all the degenerate levels is easily obtained by taking a limit of the corresponding sum which is derived as if they were not degenerate. For instance, in Case I, when the lth and the $(l+1)$th levels are degenerate,

$$\varepsilon_l'+\varepsilon_{l+1}'=\lim_{\varepsilon_{l+1}\to\varepsilon_l}[\varepsilon_l{}',{}_{\text{nondeg}}+\varepsilon_{l+1}{}',{}_{\text{nondeg}}]$$
$$=2\varepsilon_l+[\delta(\varepsilon_l+\varepsilon_{l+1})]_r+[\delta(\varepsilon_l+\varepsilon_{l+1})]_s$$
$$+2\sum_{\substack{k\\(\neq l,l+1)}}^{\text{all}}\frac{c_r{}^k c_s{}^k(c_r{}^l c_s{}^l+c_r{}^{l+1}c_s{}^{l+1})}{\varepsilon_l-\varepsilon_k}(\alpha_r{}'\alpha_s{}')+\cdots\cdots \tag{76}$$

where

$$[\delta(\varepsilon_l+\varepsilon_{l+1})]_r=[(c_r{}^l)^2+(c_r{}^{l+1})^2]\,\alpha_r{}'$$
$$+\sum_{\substack{k\\(\neq l,l+1)}}^{\text{all}}\frac{(c_r{}^k)^2[(c_r{}^l)^2+(c_r{}^{l+1})^2]}{\varepsilon_l-\varepsilon_k}(\alpha_r{}')^2+\cdots\cdots \tag{77}$$

and $\varepsilon_l{}',{}_{\text{nondeg}}$ is given by Eq. 27, which is derived for non-degenerate system. Explicit formulae for other various degenerate cases are omitted here for the sake of brevity, but one might write them down without difficulty according to the above principle. The total π electronic energy and the bond order (or the electron density) being represented as the sums of orbital energies and separate orders (or densities) over the occupied orbitals, it is concluded that, even in the degenerate cases, if all the degenerate levels are occupied, the degeneracy does not affect the additivity rule, though concrete formulae involved may differ from the case of no degeneracy.

Discussion

By the results obtained in the preceding sections the additivity rule concerning multiple perturbations and its limits of use have been clarified.

When a hetero-substitution of an atom in a conjugated system causes changes of the Coulomb integral of the atom and of the resonance integrals between neighboring atoms, their effects as a whole may be additively estimated in the first order perturbation treatment. When introduction of a conjugable group into a conjugated system at its certain atom gives rise simultaneously to a change of the Coulomb integral of the atom, the additivity rule applies to the first order terms.

Further, for the introduction of many substituents and hetero-substitutions, the additivity of these effects are materialized, and various examples are seen in experiments. The additivity of shift of absorption sprctra would be explained by the additivity in the orbital energy. The vector additivity of dipole moment would be understood as the additivity in the electron density or in the amount of charge transfer. Aono and Higuchi[4] interpreted the additivity of hyperfine splitting in the electron spin resonance spectrum of substituted semiquinones in terms of the additivity in the unpaired electron density.

Speaking of reactivity indices, i. g. the frontier electron density, $P_{uu}{}^{f}$, localization energy, ε'(localized state)$-\varepsilon'$(non-localized state), total π electron density, P_{uu}, free valence, $\sqrt{3}-\sum_{v}{}' P_{uv}$, and most other indices, the additivity rule is applicable to a certain order of perturbation terms. Superdelocalizability is also proved to fulfil the additivity rule.

If one practically evaluates the cross terms appearing in the formulae, one would be able to discuss the deviation from the additivity rule, which is also often realized in experiments.

The authors are much indebted to Mr. Shigeyuki Aono for his helpful suggestions.

Faculty of Engineering
Kyoto University
Sakyo-ku, Kyoto

---

4) S. Aono, J. Higuchi, *Busseiron Kenkyu*, 7, 197 (1960).