The Effective π-Electron Hamiltonian for the Excited State. The Effect of Σ-Π Interaction*

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The effective π-electron Hamiltonian for the excited molecule has been derived from the singly excited configuration interaction method (SECI) considering Σ-Π interaction. In this paper, the zero-differential overlap (ZDO) approximation has been employed. Then, in SECI scheme, π-π* and σ-σ* configurations interact through the exchange type MO-integrals over π- and σ-MO's. As the result, only the excited singlet states are modified by Σ-Π interaction. So that the triplet states remain unchanged by this type of interaction.

When the ZDO approximation is employed, the effective electron interaction over AO's, $\tilde{\gamma}_{\mu\nu}$, can be derived. It is found that $\tilde{\gamma}_{\mu\nu}$'s are represented approximately in terms of topological matrix, so named 'bond index matrix'.

Semiempirical LCAO-SCF-MO method for the π-electron systems, namely P-P-P method,[1] has been succeeded for both the ground and excited states. However, there are still some problems left behind. For the calculations of the excitation energies, there is no good formula of the electron repulsion integrals for both the triplet and singlet states. It is generally known that Nishimoto-Mataga approximation[2] gives good results for the calculation of the excited singlet states but not good for the triplet states. On the other hand, Ohno-Klopman[3] and P-P[4] approximations calculate the satisfactory energy separation between the first singlet state and triplet state, but not good for the excited singlet states. These problems seem to be mainly caused by the difference in the Σ-Π interaction at the singlet and triplet states and also that in the electron correlation between each state. In this paper, we treat only the former problem. Concerning the Σ-Π interaction, there are some approaches based on MO techniques,[5] one approach is the MO-CI method considering all valence electrons, such as CNDO approximation.[6] However, CNDO method is suitable for the calculations of the ground state properties, but not appropriate for the excited state. In order to improve this point, Bene and Jaffe introduced a σ-π separation parameter and obtained good results of n-π* and π-π* excitation energies.[7] Recently, Lipari and Duke modified CNDO/2 by introducing empirical formula for the electron repulsion integrals and using different bonding parameters.[8]

In this paper, we analyze the Σ-Π interaction explicitly from the standpoint of the π-electron approximation. We also derive the effective π-electron interaction at the excited state considering its effect and derive the effective electron repulsion integrals, $\tilde{\gamma}_{\mu\nu}$.

Theoretical

The Effective π-Electron Hamiltonian for the Excited State. We are concerning with a closed system in the ground state and assume that the Hartree-Fock orbitals are already obtained. We use the following notation; i, j, k, l,···for the occupied molecular orbitals and α, β, γ, δ,···for the unoccupied ones.

Singly excited configuration interaction (SECI) method is our starting point.[9] The excited state is expressed as follows;

$$\Phi = \sum_{i\alpha} C_{i\alpha} |{}^{\alpha}_{i}>, \tag{1}$$

where, $|{}^{\alpha}_{i}>$ represents the singly excited configuration associated with the excitation of an electron from i to α $C_{i\alpha}$'s are coefficients to be determined by the variation method. The variation of the expectation value of the total Hamiltonian $\boldsymbol{H}$ leads to the following seqular equation,

$$[\boldsymbol{H} - \boldsymbol{E\Gamma}]\boldsymbol{C} = 0, \tag{2}$$

where, $\boldsymbol{H}$ is Hamiltonian matrix represented by singly excited configurations. $\boldsymbol{C}$ is the coefficient vector. For the Simplicity, we use the ZDO approximation in this paper. Then configurations $|{}^{\pi}_{\pi}>$ and $|{}^{\sigma}_{\sigma}>$ do not interact with $|{}^{\sigma}_{\pi}>$ or $|{}^{\pi}_{\sigma}>$. So that the matrix can be divided into two mutually independent groups; one is made from $|{}^{\pi}_{\pi}>$ and $|{}^{\sigma}_{\sigma}>$ and another is made from $|{}^{\sigma}_{\pi}>$ and $|{}^{\pi}_{\sigma}>$. As we are interested in the π-π* excited state, hereafter we treat only the former group. In order to get the effective π-electron Hamiltonian for the excited state, we divide the configurations into two subgroups. One is a subgroup containing $|{}^{\pi}_{\pi}>$ and another is one containing $|{}^{\sigma}_{\sigma}>$. Then Eq. 2 is written as follows;

$$[\boldsymbol{H}^{\Pi\Pi} - \boldsymbol{E\Gamma}]\boldsymbol{C}^{\Pi} + \boldsymbol{H}^{\Pi\Sigma}\boldsymbol{C}^{\Sigma} = 0, \tag{3-a}$$

$$\boldsymbol{H}^{\Sigma\Pi}\boldsymbol{C}^{\Pi} + [\boldsymbol{H}^{\Sigma\Sigma} - \boldsymbol{E\Gamma}]\boldsymbol{C}^{\Sigma} = 0, \tag{3-b}$$

where, $\boldsymbol{H}^{\Pi\Pi}$, $\boldsymbol{H}^{\Sigma\Sigma}$, and $\boldsymbol{H}^{\Sigma\Pi}$ mean the submatrices with elements $<{}^{\pi}_{\pi}|\boldsymbol{H}|{}^{\pi}_{\pi}>$, $<{}^{\sigma}_{\sigma}|\boldsymbol{H}|{}^{\sigma}_{\sigma}>$ and $<{}^{\sigma}_{\sigma}|\boldsymbol{H}|{}^{\pi}_{\pi}>$, respectively. $\boldsymbol{C}^{\Pi}$ and $\boldsymbol{C}^{\Sigma}$ are coefficient vectors corresponding to π-π* and σ-σ* subspaces, respectively. If the matrix $[\boldsymbol{H}^{\Sigma\Sigma} - \boldsymbol{E\Gamma}]^{-1}$ has no singularities at π-π* excitation energies, $\boldsymbol{C}^{\Sigma}$ can be given as follows from Eq. 3-b,

$$\boldsymbol{C}^{\Sigma} = -[\boldsymbol{H}^{\Sigma\Sigma} - \boldsymbol{E\Gamma}]^{-1}\boldsymbol{H}^{\Sigma\Pi}\boldsymbol{C}^{\Pi}. \tag{4}$$

Substituting this equation into Eq. 3-a, we obtain the equation containing only $\boldsymbol{C}^{\Pi}$ explicitly.

$$[\boldsymbol{H}^{\Pi\Pi} - \boldsymbol{H}^{\Pi\Sigma}(\boldsymbol{H}^{\Sigma\Sigma} - \boldsymbol{E\Gamma})^{-1}\boldsymbol{H}^{\Sigma\Pi} - \boldsymbol{E\Gamma}]\boldsymbol{C}^{\Pi} = 0, \tag{5}$$

or;

$$|\boldsymbol{H}^{\Pi\Pi} - \boldsymbol{H}^{\Pi\Sigma}(\boldsymbol{H}^{\Sigma\Sigma} - \boldsymbol{E\Gamma})^{-1}\boldsymbol{H}^{\Sigma\Pi} - \boldsymbol{E\Gamma}| = 0. \tag{6}$$

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When we write,

$$\tilde{\boldsymbol{H}}^{\Pi\Pi} = \boldsymbol{H}^{\Pi\Pi} - \boldsymbol{H}^{\Pi\Sigma}[\boldsymbol{H}^{\Sigma\Sigma} - \boldsymbol{EI}]^{-1}\boldsymbol{H}^{\Sigma\Pi}, \tag{7}$$

then, the eigenvalue problem to be solved becomes as follows;

$$|\tilde{\boldsymbol{H}}^{\Pi\Pi} - \boldsymbol{EI}| = 0. \tag{8}$$

Thus, $\tilde{\boldsymbol{H}}^{\Pi\Pi}$ represents the matrix associated with the effective π-electron Hamiltonian of the excited state, $\tilde{\boldsymbol{H}}(\pi)$. And $\tilde{\boldsymbol{H}}(\pi)$ can be expressed in the operator form, referring to the partitioning technique proposed by Löwdin,[10]

$$\tilde{\boldsymbol{H}}(\pi) = \boldsymbol{H} - \boldsymbol{VP}\frac{1}{\boldsymbol{H}-\boldsymbol{E}}\boldsymbol{PV}. \tag{9}$$

Where, $\tilde{\boldsymbol{H}}(\pi)$ is defined only in the subspace spanned by π-π* configurations and V means the operator associated with the electron repulsions. As we use the Hartree-Fock basis, Σ-Π interaction appears through the electron repulsions. $\boldsymbol{P}$ in Eq. 9 represents the projection operator defined by Eq. 10, which picks up σ-σ* configurations.

$$\boldsymbol{P} = \sum_{\sigma\sigma^*} |{}^{\sigma^*}_{\sigma}><{}^{\sigma^*}_{\sigma}|. \tag{10}$$

Thus the matrix elements associated with $\tilde{\boldsymbol{H}}(\pi)$ coincide with Eq. 7. Referring to Eq. 9, the effective π-electron interaction $\tilde{\boldsymbol{V}}(\pi)$ can be defined as follows;

$$\tilde{\boldsymbol{V}}(\pi) = \boldsymbol{V} - \boldsymbol{VP}\frac{1}{\boldsymbol{H}-\boldsymbol{E}}\boldsymbol{PV}. \tag{11-a}$$

$$\tilde{\boldsymbol{V}}(\pi) = \sum_{\xi\eta}\tilde{v}_{\xi\eta} \tag{11-b}$$

$$\boldsymbol{V}(\pi) = \sum_{\xi\eta} v_{\xi\eta}, \tag{11-c}$$

$v_{\xi\eta}$ means potential between ξ and η electrons and $\tilde{v}_{\xi\eta}$ is corresponding modified potential which is not given in the explicit form.

As σ-MO may be considered to be approximately localized in the particular bond, the off-diagonal matrix elements of $\boldsymbol{H}^{\Sigma\Sigma}$ in Eq. 5 may be negligibly small. So, the matrix element, $<{}^{\alpha}_{i}|\tilde{\boldsymbol{H}}|{}^{\beta}_{j}>$, becomes as follows;

For the singlet state,

$$\langle {}^{\alpha}_{i}|\tilde{\boldsymbol{H}}|{}^{\beta}_{j}\rangle = (\varepsilon_\alpha - \varepsilon_i)\delta_{ij}\delta_{\alpha\beta} - V_{i\alpha j\beta} + 2V_{ij\alpha\beta} - 4\sum_{k\gamma} V_{ik\alpha\gamma}V_{kj\gamma\beta}\, e_{k\gamma}, \tag{12-a}$$

$$e_{k\gamma} = [(\boldsymbol{H}^{\Sigma\Sigma} - \boldsymbol{EI})^{-1}]_{k\gamma,k\gamma}.$$

For the triplet state,

$$\langle {}^{\alpha}_{i}|\tilde{\boldsymbol{H}}|{}^{\beta}_{j}\rangle = (\varepsilon_\alpha - \varepsilon_i)\delta_{ij}\delta_{\alpha\beta} - V_{i\alpha j\beta}, \tag{12-b}$$

$$V_{i\alpha j\beta} = \iint i^*(1)\alpha^*(2)\; v_{12}\, j(1)\beta(2)\; d\tau_1 d\tau_2.$$

Where, i, j, α, and β are used for the π-MO's and k, l, γ, and δ are for the σ-MO's. Comparing Eqs.12-a and 12-b, it is seen that π-π* configurations interact with σ-σ* ones only in the excited singlet state, but not in the triplet state.[11] The matrix elements of the effective interaction of the excited singlet state can be divided into two parts,

Exchange type interaction

$$\tilde{V}_{ij\alpha\beta} = V_{ij\alpha\beta} - \frac{1}{2}\sum_{k\gamma} 4V_{ik\alpha\gamma}V_{kj\gamma\beta}\, e_{k\gamma}. \tag{13-a}$$

Coulomb type interaction

$$\tilde{V}_{i\alpha j\beta} = V_{i\alpha j\beta} \tag{13-b}$$

From Eqs. 13-a and 13-b, it is seen that only the exchange type interaction between π-electrons is modified by Σ-Π interaction. From the standpoint of the π-electron approximation, it means that π-electron excitation makes σ-field polarize and π-electrons in the excited state interact each other through the polarized σ-field, in addition to direct coulomb potential. Such kind of interaction appears only on exchange interaction between π-electrons. So that only the exchange type integrals over MO's are modified.

In the present study, $\boldsymbol{E}$ in the inverse matrix is treated as a parameter so that the calculated excitation energies agree with those of experiments.

Using the LCAO approximation as,

$$\phi = \sum_{t} d_{it}\phi_t,$$

the effective π-electron repulsion integral, $\tilde{\gamma}_{\mu\nu}$, can be written as,

$$\tilde{\gamma}_{\mu\nu} = \gamma_{\mu\nu} + \frac{1}{2}\sum_{rs}\gamma_{\mu r}\Pi_{rs}\gamma_{s\nu}, \tag{15}$$

where,

$$\Pi_{rs} = -4\sum_{k\gamma} d_{kr}d_{\gamma r}d_{ks}d_{\gamma s}e_{k\gamma}, \tag{16}$$

$\tilde{\gamma}_{\mu\nu}$ and $\gamma_{\mu\nu}$ are defined as follows,

$$\tilde{\gamma}_{\mu\nu} = \iint \phi^*_\mu(1)\phi^*_\nu(2)\; \tilde{v}_{12}\phi_\nu(1)\phi_\mu(2)\; d\tau_1 d\tau_2,$$

$$\gamma_{\mu\nu} = \iint \phi^*_\mu(1)\phi^*_\nu(2)\; v_{12}\phi_\nu(1)\phi_\mu(2)\; d\tau_1 d\tau_2,$$

where, μ and ν are used for the π-AO's and r and s for the σ-AO's. Π_{rs} represents the mutual polarizability associated with σ-electrons. Therefore, the second term of Eq.15 indicates the effect of the polarized σ-field on the π-electron-electron interaction. It is interesting to note that the formula of $\tilde{\gamma}_{\mu\nu}$ is similar to that of Little's which was derived by the RPA method.[12]

An Improvement of P-P-P Method Including σ-Electrons as the Field. Following the result mentioned above, P-P-P method can be improved from the standpoint of Σ-Π interaction, including the σ-electron as the field.

Employing the avaraged energy parameter $1/\bar{e}$ instead of $e_{k\gamma}$ in Eq.16, $\tilde{\gamma}_{\mu\nu}$ of Eq. 15 can be written as follows;

$$\tilde{\gamma}_{\mu\nu} = \gamma_{\mu\nu} + \Delta_{\mu\nu}, \tag{17-a}$$

$$\Delta_{\mu\nu} = \frac{1}{2\bar{e}}\sum_{r}\sum_{s}\gamma_{\mu r}Q_{rs}\gamma_{s\nu}, \tag{17-b}$$

$$Q_{rs} = -4\sum_{k\gamma} d_{kr}d_{\gamma r}d_{ks}d_{\gamma s}. \tag{17-c}$$

It is convenient to divide the correction term, $\Delta_{\mu\nu}$, into two terms,

$$\Delta_{\mu\nu} = \Delta^1_{\mu\nu} + \Delta^2_{\mu\nu}.$$

When r and s belong to the same atom A, the contribution is collected into the term $\Delta^1_{\mu\nu}$. On the other hand, if r and s belong to the different atoms, respectively, we collect the contribution into the term $\Delta^2_{\mu\nu}$. Using the bond order P_{rs} and the virtual bond order P^*_{rs} defined by

$$P_{rs} = 2\sum_{k}^{\text{occ.}} d_{kr}d_{ks}, \tag{18-a}$$

$$P^{*}_{rs} = 2\sum_{r}^{\text{unocc.}} d_{\gamma r}d_{\gamma s} = 2\delta_{rs} - P_{rs}. \tag{18-b}$$

$\Delta^{1}_{\mu\nu}$ and $\Delta^{2}_{\mu\nu}$ can be written as follows;

$$\Delta^{1}_{\mu\nu} = \frac{-1}{2\tilde{e}}\sum_{A}[\sum_{r}^{A}\gamma_{\mu r}(2P_{rr}-P^{2}_{rr})\gamma_{r\nu} - \sum_{\substack{r\\(r\neq s)}}^{A}\sum_{s}^{A}\gamma_{\mu r}P^{2}_{rs}\gamma_{s\nu}], \tag{19}$$

$$\Delta^{2}_{\mu\nu} = \frac{1}{2\tilde{e}}\sum_{B}\sum_{C}\sum_{r}^{B}\sum_{s}^{C}\gamma_{\mu r}P^{2}_{rs}\gamma_{s\nu}. \tag{20}$$

When CNDO scheme is adopted, the electron repulsion integrals, $\gamma_{\mu\nu}$'s depend only on the nature of atoms A, B, and C. Therefore, after the summation over r and s for each atom, Eqs. 19 and 20 become as follows:

$$\Delta^{1}_{\mu\nu} = \frac{-1}{2\tilde{e}}\sum_{A}\gamma_{\mu A}[\sum_{\substack{r,s\\(s\neq r)}}^{A}(2P_{rr}-P^{2}_{rr}-P^{2}_{rs})]\gamma_{A\nu}, \tag{21}$$

$$\Delta^{2}_{\mu\nu} = \frac{1}{2\tilde{e}}\sum_{B}\sum_{C}\gamma_{\mu B}(\sum_{r}^{B}\sum_{s}^{C}P^{2}_{rs})\gamma_{C\nu}. \tag{22}$$

The terms, $\sum(2P_{rr}-P^{2}_{rr}-P^{2}_{rs})$ in Eq. 21 and $\sum_{rs}(P^{2}_{rs})$ in Eq. 22 correspond to the bond index proposed by Wiberg.[13] These terms are easily understood by the concept of hybrid orbitals. The hibrid orbital, X^{A}_{h}, is constructed from the adequate unitary transformation of the basis AO's, ϕ_{p}'s, which are s, p_x, p_y, and p_z; $X^{A}_{h}=\sum_{p}d_{hp}\phi_{p}$. Where, X^{A}_{h} means a hybrid orbital of the atom A. The bonding orbital ϕ and antibonding orbital ϕ^{*} associated with nonpolar σ-bond between atoms A and B can be approximately written in terms of the hybrid orbitals X^{A}_{h} and $X^{B}_{h'}$;

$$\phi = \frac{1}{\sqrt{2}}(X^{A}_{h}+X^{B}_{h'}), \qquad \phi^{*} = \frac{1}{\sqrt{2}}(X^{A}_{h}-X^{B}_{h'}).$$

A lone pair orbital of the atom A can be approximately written as $\phi=X^{A}_{h}$. The values of Eqs. 21 and 22 are invariant to the unitary transformation, so that we can express approximately,

$$\sum_{rs}^{A}(2P_{rr}-P^{2}_{rr}-P^{2}_{rs}) = \sum_{h}^{A}(2P_{hh}-P^{2}_{hh}), \tag{23}$$

$$\sum_{r}^{B}\sum_{s}^{C}(P^{2}_{rs}) = \sum_{h}^{B}\sum_{h'}^{C}(P^{2}_{hh'}). \tag{24}$$

When X_h and $X_{h'}$, belong to the same atom, P_{hh} is equal to 1.0, except for the lone pair orbital. If X_h represents a lone pair orbital, P_{hh} becomes 2.0. If there exists a nonpolar σ-bond between B and C, $P_{hh'}$ becomes 1.0. Otherwise, $P_{hh'}$ is equal to zero. Therefore, the following simple relations are visualized.

$$\sum_{\substack{r,s\\(s\neq r)}}^{A}(2P_{rr}-P^{2}_{rr}-P^{2}_{rs}) = \boxed{\begin{array}{l}\text{Number of valence}\\ \text{electrons of the}\\ \text{atom A}\end{array}} - \boxed{\begin{array}{l}\text{Number of lone}\\ \text{pair electrons of}\\ \text{the atom A}\end{array}} - \boxed{\begin{array}{l}\text{Number of}\\ \pi\text{-electrons of}\\ \text{the atom A}\end{array}} \tag{25}$$

$$= N_A\ [\text{Number of } \sigma\text{-bond of the atom A}]$$

$$\sum_{r}^{B}\sum_{s}^{C}(P^{2}_{rs}) = \begin{cases}1 & \begin{pmatrix}\text{If there exists } \sigma\text{-bond between atoms}\\ \text{B and C}\end{pmatrix}\\ 0 & \text{(Otherwise)}\end{cases}$$

$$B = \begin{pmatrix} -1 & 0 & 0 & 0 & 1 & 0\\ 0 & -1 & 0 & 0 & 1 & 0\\ 0 & 0 & -1 & 0 & 0 & 1\\ 0 & 0 & 0 & -1 & 0 & 1\\ 1 & 1 & 0 & 0 & -3 & 1\\ 0 & 0 & 1 & 1 & 1 & -3 \end{pmatrix}$$

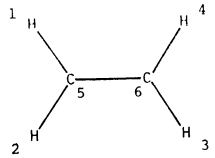

Fig. 1. The bond index matrix for ethylene and the numbering of the atoms.

Combining Eqs.21 and 22, the following relation is obtained.

$$\Delta_{\mu\nu} = \frac{1}{2\tilde{e}}[\sum_{A}(-N_A)\gamma_{\mu A}\gamma_{A\nu} + \sum_{B-C}^{\text{Bond}}\gamma_{\mu B}\gamma_{C\nu}], \tag{27}$$

where, the summation, $\sum_{B-C}^{\text{bond}}$, runs over all the σ-bonding atomic pairs.

Using Eq. 27, the effective electron repulsion integrals given by Eq. 15 can be rewritten by the matrix representation introducing a new matrix $\boldsymbol{B}$, as follows;

$$\tilde{\boldsymbol{\gamma}}^{\Pi} = \boldsymbol{\gamma}^{\Pi} + \boldsymbol{\Delta}^{\Pi}, \tag{28-a}$$

$$\boldsymbol{\Delta}^{\Pi} = \frac{1}{2\tilde{e}}\boldsymbol{\gamma}^{\Pi\Sigma}\boldsymbol{B}\boldsymbol{\gamma}^{\Sigma\Pi}, \tag{28-b}$$

$$\boldsymbol{\gamma}^{\Pi\Sigma} = (\boldsymbol{\gamma}^{\Sigma\Pi})^{+}. \tag{28-c}$$

$\tilde{\boldsymbol{\gamma}}^{\Pi}$, $\boldsymbol{\gamma}^{\Pi}$, and $\boldsymbol{\Delta}^{\Pi}$ are $N\times N$ square matrices and $\boldsymbol{\gamma}^{\Sigma\Pi}$, $N\times M$ rectangular matrix and $\boldsymbol{B}$, $M\times M$ square matrix. Here N and M are number of π-AO's and that of atoms, respectively. The value of the diagonal term of the matrix $\boldsymbol{B}$ is equal to $(-N_A)$. The value of the off-diagonal term is equal to $P_{hh'}$, namely 0 or 1. This matrix is named bond index matrix and is easily made from the structural formula of the molecule. As an example, $\boldsymbol{B}$ matrix of ethylene is shown in Fig. 1. This matrix reflects bonding relations of atoms in the molecule. So that the correction terms, $\Delta_{\mu\nu}$, depend on the topological nature of the molecule.

From these results we conclude that the most important effect of Σ-Π interaction on the π-electron-electron interactions depends on the topology and conformation of the molecule. Using Eqs. 28-a and 28-b, we can take into account the effect of σ-electrons explicitly in the π-electron approximation.

Calculational Procedure. π-π^{*} Excitation energies are calculated, considering Σ-Π interaction by the method mentioned above. According to the present theory, all valence electrons are taken into account, however, only the SCF-MO-CI calculation based on P-P-P scheme is needed, because σ-electrons are treated as it forms a field.

The calculational procedure is summarized as follows. First of all, we carry out the usual P-P-P calculation for the ground state. Secondly, we evaluate the effective $\tilde{\gamma}_{\mu\nu}$, using Eq. 28-a and an appropriate bare $\gamma_{\mu\nu}$. Lastly, we perform the SECI calculation, in which we use $\tilde{\gamma}_{\mu\nu}$ instead of $\gamma_{\mu\nu}$, only in the evaluation of the exchange type integrals over MO's in CI matrix elements.

In the present calculation, Ohno-Klopman formula[3] is applied for the standard (or bare) electron repulsion integrals,

$$\gamma_{\mu\nu} = \frac{14.40}{\sqrt{(R_{\mu\nu}^2 + a_{\mu\nu}^2)}} \text{(eV)},$$

where $R_{\mu\nu}$ is the interatomic distance between μth and νth atoms.

One center repulsion integrals, $\gamma_{\mu\mu}$, are evaluated by the approximation suggested by Pariser and Parr,[14]

$$\gamma_{\mu\mu} = I_\mu - A_\mu,$$

where A_μ and I_μ are the valence state electron affinity and the valence state ionization potential of the μth atom, respectively. These values are found in the work of Hinze and Jaffé.[15] Two center core integrals $\beta_{\mu\nu}$ are approximated by the formula given by Nishimoto and Forster,[16]

$$\beta_{\mu\nu} = A_0 + A_1 P_{\mu\nu}$$

where, $P_{\mu\nu}$'s are bond order which depend on each iteration. Standard values of parameters for A_0 and A_1 are summarized by Younkin *et al.*[17]

In order to estimate the correction term $\Delta_{\mu\nu}$ in Eq. 27, the electron repulsion integrals between π and σ AO's are required, which does not come out in the usual π-electron theory. For the calculation of these integrals we employ the same approximations as used for the π-electrons, namely, Pariser-Parr prescription for the one center electron repulsion integrals and Ohno-Klopman formula for the two center ones. Iwata[18] have pointed out that Pariser-Parr approximation for the one center electron repulsion integral includes Σ-Π interaction. Therefore, in this paper, we did not apply the present method to one center electron repulsion integrals.

We use 13.0 eV as the value of the averaged energy parameter $\tilde{e}$ to reproduce the lower excitation energies of benzene. We consider whether the approximation $\tilde{e}$ and the value of 13.0 eV are reasonable or not by the following manner: The mutual polarizability of σ-cores, Π_{rs}, is written by the atomic suffix as follows,

$$\Pi_{AB} = \sum_r^A \sum_s^B \Pi_{rs},$$

and Π_{AB} is related to the matrix element of the bond index matrix B_{AB} by

$$\Pi_{AB} = \frac{1}{2\tilde{e}} B_{AB}.$$

In Tables 1 and 2, the calculated values of Π_{AB} and $(B_{AB}/2\tilde{e})$ are listed, respectively. The atom-atom mutual polarizabilities associated with σ-electrons of ethylene are calculated by CNDO/2. From these Tables, it is found that the present approximation is reasonable and the parametrized value, 13.0 eV, is also admittable in spite of the drastic approximation was introduced. There are small discrepancies among the values in these Tables, which are caused by the approximation of averaging e_{kr} and neglecting the off-diagonal terms of the inverse matrix in Eq. 7.

Results and Discussion

In Tables 3—6, the calculated excitation energies of polyacenes are summarized. As seen from these Tables, the agreement between calculations and experiments is satisfactory.

Table 1. Atom-atom mutual polarizability (Π_{AB})[a] associated with σ-electrons calculated by CNDO/2; ethylene molecule

B \ A	1	2	3	4	5	6
1	−0.099	−0.006	0.016	0.012	0.092	−0.008
2		−0.099	0.012	0.016	0.092	−0.008
3			−0.099	−0.006	−0.008	0.092
4				−0.099	−0.008	0.092
5					−0.231	0.069
6						−0.231

a) Numbering of atoms is shown in Fig. 1.

Table 2. The values of the bond index matrix (B_{AB}) of ethylene divided by the energy parameter 13.0 eV

B \ A	1[a]	2	3	4	5	6
1	−0.077	0	0	0	0.077	0
2		−0.077	0	0	0.077	0
3			−0.077	0	0	0.077
4				−0.077	0	0.077
5					−0.231	0.077
6						−0.231

a) Numbering of atoms is shown in Fig. 1.

Table 3. Benzene. Excitation energies (eV) and oscillator strength (in parenthese)

	Nishimoto-Mataga[e]	Ohno[f]	This calc.	Exptl
$^3B_{1u}$	3.08	3.95	3.95	3.66[a]
$^3E_{1u}$	3.99	4.46	4.46	4.59[a]
$^1B_{2u}$	4.89 (0)	4.96 (0)	4.96 (0)	4.9[b] (0)
$^1B_{1u}$	6.18 (0)	4.96 (0)	6.05 (0)	6.07[c] (0.1)
$^1E_{1u}$	7.00 (2.36)	7.38 (2.44)	7.00 (2.40)	6.95[c]

a) Ref. 22. b) Ref. 19. c) Ref. 20. e) Nishimoto-Mataga formula was used for $\gamma_{\mu\nu}$. f) Ohno-Klopman formula was used for $\gamma_{\mu\nu}$.

Table 4. Naphthalene. Excitation energies (eV) and oscillator strength (in parenthese)

	Nishimoto-Mataga	Ohno	This calc.	Exptl
$^3B_{2u}$	2.04	2.36	2.36	2.64[a]
$^3B_{3u}$	3.03	3.38	3.38	3.82[a]
$^1B_{3u}$	4.03 (0)	4.03 (0)	4.03 (0)	3.97[b] (0.002)
$^1B_{2u}$	4.42 (0.20)	3.92 (0.08)	4.68 (0.23)	4.51[b] (0.18)
$^1B_{2u}$	5.46 (0)	5.26 (0)	5.67 (0)	
$^1B_{3u}$	5.58 (1.96)	6.10 (2.16)	5.80 (2.00)	5.63[b] (1.70)

a) Ref. 22. b) Ref. 21.

Table 5. Anthracene. Excitation energies (eV) and oscillator strength (in parenthese)

	Nishimoto-Mataga	Ohno	This calc.	Exptl
$^3B_{2u}$	0.99	1.75	1.75	1.82[a]
$^3B_{3u}$	1.98	2.69	2.69	3.22[a]
$^1B_{3u}$	3.39 (0)	3.51 (0)	3.51 (0)	
$^1B_{2u}$	3.41 (0.26)	3.33 (0.18)	3.79 (0.30)	3.34[b] (0.1)
$^1B_{3u}$	4.76 (2.60)	5.33 (2.96)	5.11 (2.72)	4.83[b] (2.5)
$^1B_{2u}$	5.69 (0.10)	5.77 (0.38)	6.13 (0.72)	5.61[b] (0.3)

a) Ref. 22. b) Ref. 21.

Table 6. Naphthacene. Excitation energies (eV) and oscillator strength (in paraenthese)

	Nishimoto-Mataga	Ohno	This calc.	Exptl
$^3B_{2u}$	0.86	1.43	1.43	1.28[a]
$^3B_{3u}$	2.00	2.60	2.60	2.57[a]
$^1B_{2u}$	2.89 (0.29)	3.04 (0.29)	3.25 (0.40)	2.63[a]
$^1B_{3u}$	3.28 (0)	3.49 (0)	3.49 (0)	
$^1B_{3u}$	4.41 (3.30)	4.97 (3.73)	4.81 (3.49)	4.51[a]
$^1B_{2u}$	4.82 (0.05)	4.75 (0.03)	5.14 (0.07)	

a) Ref. 22.

Table 7. Correction terms ($\Delta_{\mu\nu}$)[a] of naphthalene (eV)

μ \ ν	2	3	4	5	6	7	8	9	10
1	−0.89	−0.04	0.07	0.34	0.40	0.27	−0.33	−1.22	−0.26
2		−0.83	−0.04	0.40	0.47	0.44	0.27	−0.21	−0.02
9									−1.43

a) Numbering is shown in Fig. 2.

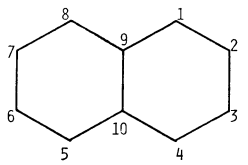

Fig. 2. The numbering of the atoms of naphthalene.

It is seen from Table 3, $^1B_{2u}$ excited state of benzene is unchanged by the Σ-Π interaction. The $^1B_{2u}$ excited state is much improved compared to that of Ohno's.

It is also found from Tables 4—6 that Σ-Π interaction has an effect of increasing the excitation energies of $^1B_{2u}$($^1B_{1u}$ in benzene) states which are polarized to the direction of molecular short axis. On the other hand, the excitation energies of $^1B_{3u}$($^1B_{2u}$ in benzene) states which are polarized to the direction of molecular long axis, remain unchanged or slightly decrease. These very interesting effect of Σ-Π interaction can be understood from the point of view of the polarization of the σ-framework caused by π-π^* excitation. It should be noted that the calculated excitation energies of the singlet state by the present method are similar to the Nishimoto-Mataga's.

In Table 7, the correction terms, $\Delta_{\mu\nu}$, of naphthalene are given. From this Table, it is found that the magnitude of $\Delta_{\mu\nu}$ depends considerably on the interatomic distance and also on the relative atomic sites in the molecule. Moreover, it can be generally said that the correction is larger at the inner part than at the outer part in the molecule.

We will apply the present theory to linear polyenes, aromatic derivatives, heterocycles and interaction of two aromatic systems connected by aliphatic chain in our next papers.

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