Expansion Formulae of Secular Determinant in Simple LCAO MO Treatment of Aromatic Hydrocarbons

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In the LCAO MO treatment of conjugated molecules, it goes without saying that the secular determinant must be known in its expanded form in order to solve it numerically. The use of secular determinant is not necessarily restricted to finding its roots. Coulson and Longuet-Higgins[1] obtained the integral formulae for electronic energy, bond order and various kinds of polarizability in which the integrands were expressed in terms of secular determinants. Also Baba[2] and the present authors[3] pointed out the importance of the coefficients in the expansion of minors of secular determinant for predicting the reactivity of alternant hydrocarbons.

In this paper, we derive several formulae which are useful for expanding the secular determinant of aromatic hydrocarbons. By using these formulae, the secular determinant can be expressed in terms of that of a smaller molecule and the laborious calculation for large molecules can be considerably simplified.

The Expansion Formulae of Secular Determinant for the Aromatic Hydrocarbon.—In the first, the types of "growth" of aromatic hydrocarbons are classified into five as shown in Fig. 1. The first, the third, and the fifth are tentatively named "even growth", and the second, and the fourth "odd growth". Then, an even molecule is formed either by an even growth of an even molecule, or otherwise by an odd growth of an odd molecule, and the formation of an odd molecule results from an odd growth of an even molecule or from an even growth of an odd molecule.

If we put the secular determinants of a molecule before and after the growth as $\Delta(\lambda)$ and $D(\lambda)$, respectively, the expansion formulae for each type are obtained as follows:

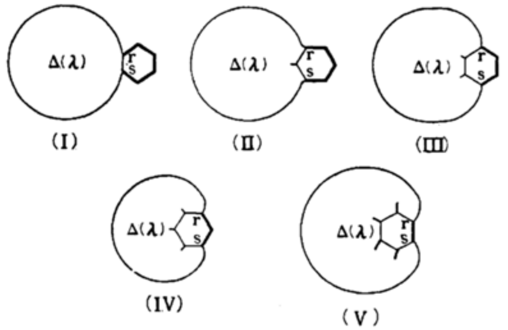

Fig. 1. The types of "growth" of aromatic hydrocarbons are shown. (I) is the first type of growth and (II) is the second type of growth and so on. The thick lines indicate the bonds formed as a result of "growth".

For the first type of growth,

$$D(\lambda)=(\lambda^4-3\lambda^2+1)\Delta(\lambda)+\lambda(\lambda^2-2)\{\Delta_{rr}(\lambda)+\Delta_{ss}(\lambda)\}+(\lambda^2-1)\Delta_{rrss}(\lambda)-2(-1)^{r+s+1}\Delta_{rs}(\lambda) \quad (1)$$

For the second type of growth,

$$D(\lambda)=-\lambda(\lambda^2-2)\Delta(\lambda)-(\lambda^2-1)\{\Delta_{rr}(\lambda)+\Delta_{ss}(\lambda)\}-\lambda\Delta_{rrss}(\lambda)+2(-1)^{r+s+1}\Delta_{rs}(\lambda) \quad (2)$$

For the third type of growth,

$$D(\lambda)=(\lambda^2-1)\Delta(\lambda)+\lambda\{\Delta_{rr}(\lambda)+\Delta_{ss}(\lambda)\}+\Delta_{rrss}(\lambda)-2(-1)^{r+s+1}\Delta_{rs}(\lambda) \quad (3)$$

For the fourth type of growth,

$$D(\lambda)=-\lambda\Delta(\lambda)-\Delta_{rr}(\lambda)-\Delta_{ss}(\lambda)+2(-1)^{r+s+1}\Delta_{rs}(\lambda) \quad (4)$$

For the fifth type of growth,

$$D(\lambda)=\Delta(\lambda)-\Delta_{rrss}(\lambda)-2(-1)^{r+s+1}\Delta_{rs}(\lambda) \quad (5)$$

Besides the above types of nuclear growth, the types of branching and bridging also exist in conjugated systems.

1) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.*, **A191**, 39 (1947).
2) H. Baba, This Bulletin, **30**, 147 (1957).
3) K. Fukui, T. Yonezawa, and C. Nagata, *J. Chem. Phys.*, **26**, 831 (1957).

They are shown in Fig. 2 and are tentatively designated as type 1, 2, ... , 9. The expansion formulae for them are given as:

For the type 1,

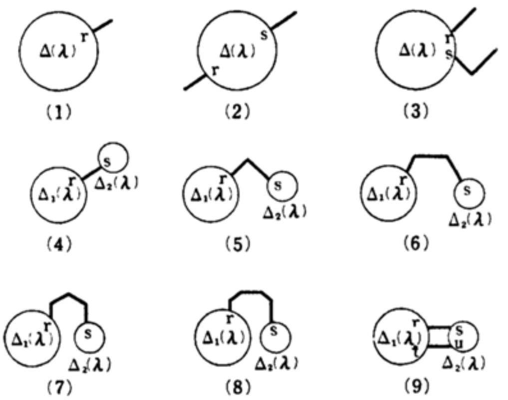

Fig. 2. The types of branching and bridging in conjugated molecules are shown. The thick lines indicate the branches {(1), (2) and (3)} and bridges {(4), (5), (6)......, (9)} respectively.

$$D(\lambda)=-\lambda\Delta(\lambda)-\Delta_{rr}(\lambda) \tag{6}$$

For the type 2,

$$D(\lambda)=\lambda^2\Delta(\lambda)+\lambda\{\Delta_{rr}(\lambda)+\Delta_{ss}(\lambda)\}+\Delta_{rrss}(\lambda) \tag{7}$$

For the type 3,

$$D(\lambda)=(\lambda^2-1)\{-\lambda\Delta(\lambda)-\Delta_{rr}(\lambda)\} -\lambda^2\Delta_{ss}(\lambda)-\lambda\Delta_{rrss}(\lambda) \tag{8}$$

For the type 4,

$$D(\lambda)=\Delta_1(\lambda)\Delta_2(\lambda)-\Delta_{1rr}(\lambda)\Delta_{2ss}(\lambda) \tag{9}$$

For the type 5,

$$D(\lambda)=-\lambda\Delta_1(\lambda)\Delta_2(\lambda)-\Delta_{1rr}(\lambda)\Delta_2(\lambda) -\Delta_{2ss}(\lambda)\Delta_1(\lambda) \tag{10}$$

For the type 6,

$$D(\lambda)=(\lambda^2-1)\Delta_1(\lambda)\Delta_2(\lambda) +\lambda\{\Delta_{1rr}(\lambda)\Delta_2(\lambda)+\Delta_{2ss}(\lambda)\Delta_1(\lambda)\} +\Delta_{1rr}(\lambda)\Delta_{2ss}(\lambda) \tag{11}$$

For the type 7,

$$D(\lambda)=-\lambda(\lambda^2-2)\Delta_1(\lambda)\Delta_2(\lambda) -(\lambda^2-1)\{\Delta_{1rr}(\lambda)\Delta_2(\lambda)+\Delta_{2ss}(\lambda)\Delta_1(\lambda)\} -\lambda\Delta_{1rr}(\lambda)\Delta_{2ss}(\lambda) \tag{12}$$

For the type 8,

$$D(\lambda)=(\lambda^4-3\lambda^2+1)\Delta_1(\lambda)\Delta_2(\lambda)+\lambda(\lambda^2-2) \times\{\Delta_{1rr}(\lambda)\Delta_2(\lambda)+\Delta_{2ss}(\lambda)\Delta_1(\lambda)\} +(\lambda^2-1)\Delta_{1rr}(\lambda)\Delta_{2ss}(\lambda) \tag{13}$$

For the type 9,

$$D(\lambda)=\Delta_1(\lambda)\Delta_2(\lambda)-\Delta_{1rr}(\lambda)\Delta_{2ss}(\lambda) -\Delta_{1tt}(\lambda)\Delta_{2uu}(\lambda)+\Delta_{1rrtt}(\lambda)\Delta_{2ssuu}(\lambda) -2(-1)^{r+t+1}\Delta_{1rt}(\lambda)(-1)^{s+u+1}\Delta_{2su}(\lambda) \tag{14}$$

where $\Delta(\lambda)$, $\Delta_1(\lambda)$ and $\Delta_2(\lambda)$ may be secular determinants of any conjugated system. $\Delta_{rr}(\lambda)$, or $\Delta_{ss}(\lambda)$ is the (r, r), or the (s, s) minor and $\Delta_{rrss}(\lambda)$ is the (rs, rs) minor of $\Delta(\lambda)$, and these are obtained by striking off the indicated rows and columns of $\Delta(\lambda)$. The equation of $\Delta_{rs}(\lambda)$ can be obtained according to the theorem proposed by Coulson and Longuet-Higgins[1].

The expansion formulae derived above, are very useful for obtaining secular equations of conjugated molecules, especially of large molecules.

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