The Hückel Model of Alternant Systems Having Dichromatic Symmetry

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Abstract   This paper describes an elementary utilization of color symmetry in molecular orbital theory. It is shown that the Hückel matrix of an alternant system having dichromatic symmetry can be written in a particular form enabling us to treat the eigenvalue problem of the system by working with that of a half-size reduced system. Fundamental features of dichromatically symmetric systems are elucidated concerning delocalization energies, bond orders, and so on. A few remarks are made on reduction for planar alternants and on closed expressions of eigensolutions.

1. Introduction

The concept of alternant symmetry has established already in the early days of molecular orbital theory (Coulson and Rushbrooke, 1940). The coloration of sites with two colors for alternant systems is rather popular in molecular orbital theory but, somehow, color symmetry (Loeb, 1971) does not seem to have been utilized so far, at least explicitly. This paper describes an elementary utilization of color symmetry in molecular orbital theory.

A conjugated system of π-electrons is termed an alternant system, or simply an alternant, if the two-color coloration of its sites is possible. As distinct from this, an alternant is termed dichromatically symmetric if there exists at least one symmetry operation after exchange of colors at every site of the alternant. Let us refer to the symmetry operation used for attaining the color symmetry as a recovering operation, or a recovering for brevity. Figure 1 will suffice to see what is dichromatic symmetry. Naturally, for an alternant to be dichromatically symmetric, it is necessary that it has at least one symmetry operation and that the number of its black sites is identical with that of white.

Possible recoverings for an alternant having dichromatic symmetry necessarily include at least one of two-fold symmetry operations such as reflection, inversion, and two-fold axis rotation. It should be noted that such recoverings provide a one-to-one correspondence between each black site and each white. If a $2k$-fold axis rotation exists as a recovering, then a two-fold axis rotation necessarily does. It is obvious that no k-fold rotation for odd k is possible as a recovering because of alternancy.

Color exchange and recovering

Dichromatically symmetric systems
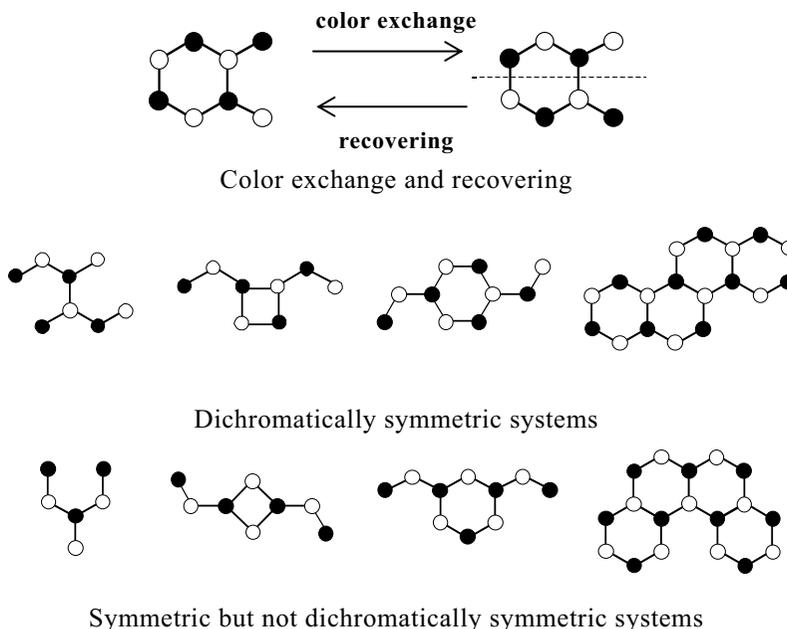

Symmetric but not dichromatically symmetric systems

Figure 1.　Dichromatic symmetry

2.　The Hückel matrix and its eigensolution

As usual, in place of the original Hückel matrix H, using a standard coulomb integral α and a standard resonance integral β, we adopt the adjacency matrix

$$A = (H - \alpha I)/\beta \tag{1}$$

as the Hückel matrix. The Hückel model of alternants postulates an identical coulomb integral α for all sites but does not require an identical resonance integral for all bonds. The resonance integral β_{rs} for bond rs is replaced by b_{rs}, devided by β. If all resonance integrals of an alternant are assumed to equal β, the Hückel matrix becomes a pure adjacency matrix. Otherwise, it is a weighted adjacency matrix.

Consider a dichromatically symmetric alternant of m black and m white sites. Taking a two-fold symmetry recovering, we can label the black sites from ●1 to ●m and the white sites from ○1 to ○m so as to make ●r and ○r correspond to each other by the recovering. Then, in the Hückel matrix A of the alternant, the components for (●r, ○s), (●s, ○r), (○r, ●s), and (○s, ●r) become equivalent. Numbering site ●r with r and site ○r with $r+m$, we can write A in the form

$$A = \begin{pmatrix} 0 & B \\ B & 0 \end{pmatrix} \tag{2}$$

with a half-size real-symmetric submatrix B. Note that essentially different recoverings yield essentially different B's.

Since B is real-symmetric, we can regard it as the Hückel matrix of an m-site system with new numbering from 1 to m. The system can be derived easily from the graph of the original alternant by folding ●r to ○r or ○r to ●r for each r. If the original graph has edges of weight b_{rs} between ●r and ○s (and necessarily between ●s and ○r), then folding gives edge rs of weight b_{rs}. For an edge of weight b_{rr} between ●r and ○r, the resulting graph has a loop on site r, which is interpreted as the coulomb integral variance b_{rr}. When A is supposed to be a pure adjacency matrix, the site of weight 1 of the reduced system is symbolized as D for convenience. Process of folding is illustrated in Figure 2, which exemplifies "different B's by different recoverings" at a time. See section 4.1 as to general results of reduction for planar alternants.

Let J be the set of integers from 1 to m. Denote the j-th eigenvector of B by v_j and its eigenvalue by μ_j, that is,

$$Bv_j = \mu_j v_j \qquad (j \in J). \tag{3}$$

We can assume the m eigenvectors $\{v_j\}$ to form a complete orthonormal set because of the real-symmetricity of B. Then, the $2m$ orthonormalized eigenvectors $\{w_i\}$ of A
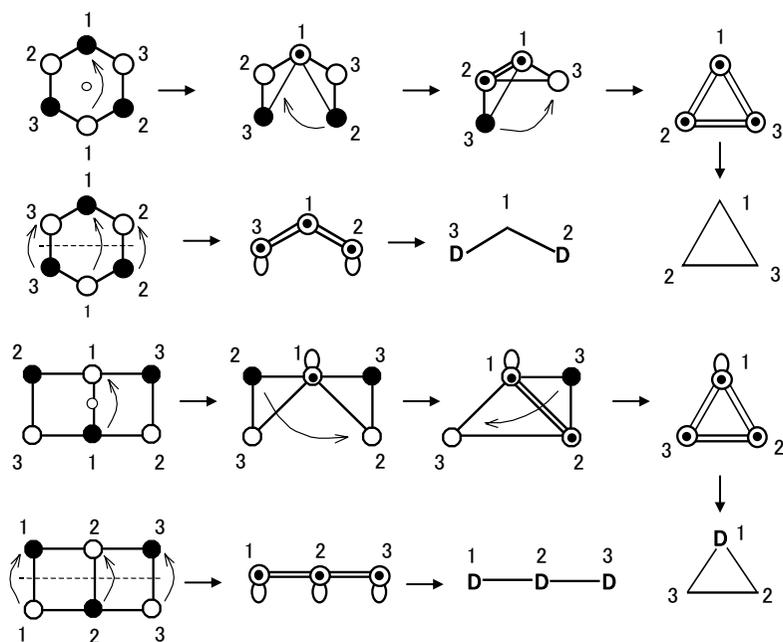

Figure 2.   Reduction by folding

can be labelled suitably with $i = \pm 1, \cdots, \pm m$ to be given by

$$w_{\pm j} = \frac{1}{\sqrt{2}} \begin{pmatrix} v_j \\ \pm v_j \end{pmatrix} \qquad (j \in J) \tag{4}$$

with its eigenvalue

$$\lambda_{\pm j} = \pm \mu_j \qquad (j \in J). \tag{5}$$

Naturally, $\{w_i\}$ forms a complete set.

The eigensolution of B leads us immediately to that of A. Reversely, if we know the eigensolution of A through any other way, then that of B can be obtained by ckecking the alternant symmetry parity of eigenvectors. It will be suitable to refer to an original alternant having dichromatic symmetry as a parent (system) and to its half-size reduced system as its child (system). Child systems are rather hardly alternant.

Consider two different child systems of a parent, denoting their Hückel matrices B and B'. Since the two matrices must result from different numberings of sites of the same color, there exist two permutation matrices S and T fulfilling

$$B' = S^T B T = T^T B S. \tag{6}$$

Thus it holds that

$$B'^2 = S^T B^2 S = T^T B^2 T, \tag{7}$$

which means that B^2 and B'^2 do not differ essentially. They provide an idential set of eigenvalues.

3. Fundamental features

3.1 Delocalization energies

In the Hückel model, eigenvectors belonging to positive, zero, and negative eigenvalues are traditionally called occupied, nonbonding, and unoccupied orbitals, respectively. Let J_+, J_0, and J_- be the subsets of J, respectively, corresponding to occupied, nonbonding, and unoccupied orbitals of B and let f_+, f_0, and f_- be the number of elements of J_+, J_0, and J_-, respectively. The f_+ occupied and the f_- unoccupied orbitals of B lead to $f_+ + f_-$ occupied orbitals of A with eigenvalues μ_j's $(j \in J_+)$ and $-\mu_j$'s $(j \in J_-)$ and, as well, lead to $f_+ + f_-$ unoccupied with μ_j's $(j \in J_-)$ and $-\mu_j$'s $(j \in J_+)$. The f_0 nonbonding orbitals of B give rise to f_0 pairs of nonbonding orbitals of A. A system devoid of nonbonding orbitals is termed regular. Obviously, if a child system is regular, so is its parent and *vice versa*. Using the trace Γ of B, we

have

$$\sum_{j \in J_+} \mu_j = \sum_{j \in J_-} \left| \mu_j \right| + \Gamma, \tag{8}$$

which may give a little information about the eigenvalue distribution of B. Still, in general, no detailed knowledge is available for "smaller-larger" estimation between μ_j's for $j \in J_+$ and $-\mu_j$'s for $j \in J_-$ without solving the eigenvalue problem.

In the $2m$-electron ground state of A, the $f_+ + f_-$ occupied orbitals are doubly occupied literally and, if $f_+ + f_- < m$, the eigenspace spanned by the $2f_0$ nonbonding orbitals is half-filled. Since no nonbonding orbitals contribute, the delocalization energy E (in the unit of β) for the $2m$-electron ground state is expressed as

$$E = 2 \sum_{j \in J} \left| \mu_j \right|, \tag{9}$$

which can be rewritten as

$$E = 2\widetilde{E} \tag{10}$$

with

$$\widetilde{E} = 2 \sum_{j \in J_+} \mu_j - \Gamma \tag{11}$$

the delocalization energy for the $2f_+$-electron ground state of B.

3.2 Bond orders

Let us refer to the electron density-bond order matrix as the p-density matrix for brevity. It is readily found that the partial p-density matrix of A is given by

$$\rho_{\pm j} = \frac{1}{2} \begin{pmatrix} \widetilde{\rho}_j & \pm \widetilde{\rho}_j \\ \pm \widetilde{\rho}_j & \widetilde{\rho}_j \end{pmatrix} \qquad (j \in J) \tag{12}$$

with that of B

$$\widetilde{\rho}_j = v_j v_j^T \qquad (j \in J). \tag{13}$$

Assume that the $2m$-electron ground state of A makes each of nonbonding orbitals w_{+j} and w_{-j} for $j \in J_0$ singly occupied if $f_0 \neq 0$. By virtue of the completeness

$$\sum_{j \in J} \widetilde{\rho}_j = I, \tag{14}$$

the p-density matrix Q for the state can be written as

$$Q = \begin{pmatrix} I & \widetilde{P} \\ \widetilde{P} & I \end{pmatrix} \tag{15}$$

with

$$\widetilde{P} = \sum_{j\in J_+}\widetilde{\rho}_j - \sum_{j\in J_-}\widetilde{\rho}_j . \tag{16}$$

The result for the two diagonal blocks is solely due to alternancy and, as is well-known, common to alternants (Coulson and Rushbrooke, 1940).

To see what the off-diagonal block $\widetilde{P}$ implies, using the completeness of $\{\widetilde{\rho}_j\}$ again, we rewrite it as

$$\widetilde{P} = \widetilde{Q} - I \tag{17}$$

with

$$\widetilde{Q} = 2\sum_{j=J_+}\rho_j + \sum_{j\in J_0}\rho_j , \tag{18}$$

which is just the p-density matrix for the $2f_++f_0$-electron ground state of B. In general, since charge densities in this state of B are not necessarily unity, we cannot regard $\widetilde{P}$ genuinely as the bond order matrix for the state. The bond order matrix P for the $2m$-electron ground state of A has the neat relation

$$P = \begin{pmatrix} 0 & \widetilde{P} \\ \widetilde{P} & 0 \end{pmatrix} \tag{19}$$

with the "quasi" bond order matrix $\widetilde{P}$ for the $2f_++f_0$-electron ground state of B.

The case of $f_0 \neq 0$ has a concise way to the result above. Let F be the Hückel matrix of a general regular system having f occupied orbitals. Then, it is easily proved that the p-density matrix Q' for the $2f$-electron ground state is expressed as

$$Q' = I + F(F^2)^{-1/2} . \tag{20}$$

Substituting A for F and Q for Q', we have (Hall, 1955)

$$\widetilde{P} = B(B^2)^{-1/2} , \tag{21}$$

while trivial substitution gives

$$\widetilde{Q} = I + B(B^2)^{-1/2} . \tag{22}$$

It is thus obvious that $\widetilde{P}$ is the quasi bond order matrix for the $2f_+$-electron ground state of B.

3.3 Ruedenberg bond orders and resonance delocalizabilities

Ruedenberg bond order (Ruedenberg, 1954; Ham and Ruedenberg, 1958) is a useful bond order quantity for regular alternants, regarded as true resonance-theoretic bond order in stead of the primitive bond order in resonance theory (Isihara, 1996). The Ruedenberg bond order ν_{rs} between sites r and s is defined as the (r, s) component of the inverse of the Hückel matrix. It follows from

$$A^{-1} = \begin{pmatrix} 0 & B^{-1} \\ B^{-1} & 0 \end{pmatrix} \tag{23}$$

that all of $\nu_{\bullet r \bigcirc s}$, $\nu_{\bigcirc s \bullet r}$, $\nu_{\bullet s \bigcirc r}$, and $\nu_{\bigcirc r \bullet s}$ are equal to $(B^{-1})_{rs}$; $\nu_{\bullet r \bigcirc r}$ and $\nu_{\bigcirc r \bullet r}$ to $(B^{-1})_{rr}$. However, because no child system must be an alternant with traceless B, we cannot immediately read $(B^{-1})_{rs}$ as the Ruedenberg bond order between sites r and s in the child system.

Resonance delocalizability is a practical index of reactivity for regular alternants. It requires to solve no eigenvalue problem, being an excellent substitue for superdelocalizability (Isihara, 2001). Since we have

$$A^{-2} = \begin{pmatrix} B^{-2} & 0 \\ 0 & B^{-2} \end{pmatrix}, \tag{24}$$

the resonance delocalizability on site r, defined as r-th diagonal component of A^{-2}, is simply that of B^{-2}. This quantity may be interpreted as the resonance delocalizability on site r of the child system. Still, we have to extend the concept of resonance delocalizability relevantly to nonalternant systems. Note that B^{-2} as well as B^{2} remains essentially identical for all child systems of a parent.

3.4 Characteristic polynomials

A few methods are known for decomposition of larger symmetrical systems into smaller subsystems to factorize the characteristic polynomial of the larger. As for the decomposition of systems with two-fold symmetry, we have mirror plane fragmentation (McClelland, 1974, 1982) and two-fold rotation factorization (D'Amato, 1979). Folding by dichromatic symmetry works sufficiently in place of these, as far as dichromatically symmetric alternants are concerned. Let $D(X)$ be the characteristic polynomial of a parent system and let $C(X)$ be that of its child. If we know

$$C(X) = \sum_{k=0}^{m} c_k X^{m-k} \qquad (c_0 = 1), \tag{25}$$

then the relationship

$$D(X) = (-1)^m C(X)C(-X) \tag{26}$$

immediately provides a factorized form of $D(X)$.

It is obvious that $D(X)$ is a polynomial of X^2. If we have interest in the coefficients of $D(X)$ in

$$D(X) = \sum_{k=0}^{m} d_{2k} X^{2m-2k} \qquad (d_0 = 1), \tag{27}$$

it will suffice to use

$$d_{2k} = \sum_{i} (-1)^i c_i c_{2k-i}, \tag{28}$$

where i runs from $\max(0, 2k-m)$ to $\min(2k, m)$. In particular, the tail coefficient d_{2m} is simply $(-1)^m c_m^2$. If the parent system contains no $4n$-membered ring and if its Hückel matrix is nonweighted, the absolute value of the tail coefficient gives the square of the number K of Kekulé structures and, therefore, K is obtainable as the absolute value of the tail coefficient of the child.

4. Parent and child systems

4.1   Reduction for planar alternants

When a parent system is planar, we may take reflection and/or inversion into account as a recovering. It will be appropriate to present general results of reduction for this exclusively frequent case.

Reflection works quite plainly as a recovering. No site is on the plane of reflection for dichromatic symmetry and, normally (see below), only bonds between equivalent sites of different colors can cross the plane of reflection in a parent system. Thus, its child has as many D's as the parent has bonds crossing the plane of reflection. See (a) in Figure 3.

Dichromatic symmetry allows no site on the center of inversion. A parent system having inversion as a recovering can be devided into two equivalent connected parts each of which contains either ●r or ○r for every r. If ●r of one part has a bond with ○s of the other, then ●s of the part does ○r of the other. The two bonds are converted into the bond between sites r and s in its child. If we have a bond between ●r and ○r (if the center of inversion is on a bond) in the parent, the bond is converted into D in the child. See (b) in Figure 3.

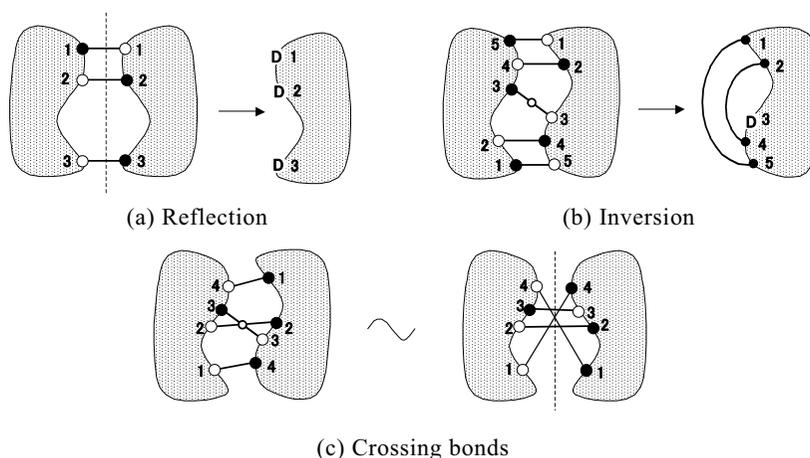(a) Reflection   (b) Inversion

(c) Crossing bonds

Figure 3.　Reduction for planar alternants

We suppose that no bonds cross with each other in the above. This supposition is, however, not inevitable from a graph-theoretical point of view. If we exclude the supposition, it becomes superficial to distinguish between reflection and inversion. Only the two-fold symmetric one-to-one correspondence between sites of different colors remains essential. The situation is illustrated by (c) in Figure 3.

4.2　Closed expressions of eigensolutions

The most interesting fact resulting from the present utilization of dichromatic symmetry is that it connects different systems through simple and exact relation of eigenvalues and eigenvectors. Remarkable connection exits also between child systems of a parent, as already mentioned.

In particular, if a closed expression of an eigensolution is known for either a parent or a child system, that of the other follows directly. This must be a very important aspect, because closed expressions are often fruitful and the possibility of obtaining closed expressions is one of the greatest advantages of the Hückel model. Table 1 shows several examples related to the closed expressions of linear and cyclic polyenes (Hückel, 1932; Lennard-Jones, 1937), linear polyacenes (Coulson, 1947) and linear square lattices (Nagao, Nishikawa, and Aono, 1993).

5.　Concluding remarks

So many conjugated systems are not only alternant but also dichromatically symmetric, so that introducing the concept of dichromatic symmetry seems to be

Table 1

From one closed expression to another

parent	child		parent	child
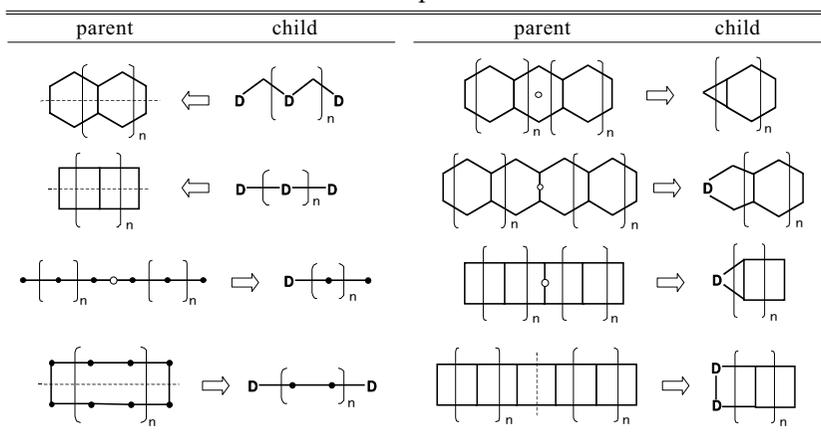
never futile. Although the present utilization is quite elementary, it provides a lucid perspective of applications. The author would like to regard this paper rather as an encouragement to further investigations of utilizing color symmetry in molecular orbital theory.

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