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The Hypervirial Condition in the Hückel Model

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This paper analyzes a fundamental aspect of the Hückel model through the hyperviral theorem. The analysis leads to the condition to be satisfied by bond orders and site electron densities as a set of linear equations. The condition, named the hypervirial condition, is common to all the eigenstates of the Hückel model Hamiltonian and brings information on a sort of detailed balance in electron distribution. The hypervirial and the symmetry conditions are related to each other, being consistent but not fully equivalent. Examination of the relation between the two conditions results in the concept of the "intrinsic" hypervirial condition that remains nontrivial with the symmetry condition fulfilled. Several examples provide various expressions obtainable from the hypervirial condition to facilitate understanding the nature of the condition. A few features of the hypervirial condition for alternant systems are mentioned.

The Hückel medel[1,2] is one of the simplest independent-particle models in the electronic structure theory of molecules and has been extensively used and investigated since the dawn of quantum chemistry.[3] The model will never lose its value in studies on molecular electronic structures particularly of conjugated systems, at least as a qualitative guide. We should regard the Hückel model as a tool of sketching out some essentials of the behavior of electrons in molecules rather than a crude approximation to real systems.

Nowadays we have no practical difficulty at all in "solving" the Hückel model numerically for individual systems except for extreme cases. With the Hückel matrix given, or usually with a pertinent set of geometrical parameters inputted, the computer immediately prints out molecular orbitals, their energies, electron densities, bond orders, and so on. This does not mean, however, that nothing remains to be explored in the world of the Hückel model. Above all, significant is to investigate the general characteristics of the model itself which might be hardly revealed through individual numerical calculations. In fact, for example, various graph-theoretical approaches[4] and the propagator formalism[5] as well as Coulson and Longuet-Higgins' formalism[6] have enriched our recognition on the Hückel model soundly.

What is intended in this paper is not to propose a novel far-reaching methodology but only to analyze a certain fundamental aspect of the Hückel model through the hypervirial theorem.[7] Still, the author believes that this must advance our understanding of the Hückel model.

We have the six sections below: the first is the preliminary section where basic definitions are introduced on the Hamiltonian, bond orders, and so on. In the second section the hypervirial condition upon bond orders and site electron densities are derived from the hypervirial theorem. The third section describes the symmetry condition in the language of permutation group theory, outlining the relation between the hypervirial and the symmetry conditions. The fourth section concerns the intrinsic hypervirial condition that remains nontrivial with the symmetry condition fulfilled. Several illustrative examples follow in the subsequent section. The last section touches upon the hypervirial condition for alternant systems.

Preliminaries

Suppose an electronic system of m sites. Denote the set $\{1,\cdots,m\}$ of the sites by M and the set $\{\uparrow,\downarrow\}$ of the one-electron spin states by Ω. The Hückel model assumes that the system has the $2m$ one-electron quantum states $\{r\mu\}$ specified by the site $r\in M$ and the spin $\mu\in\Omega$[8] and that the creators $\{a^\dagger_{r\mu}\}$ and the annihilators $\{a_{r\mu}\}$ for the one-electron quantum states $\{r\mu\}$ fulfil the canonical anticommutation relation. The Hückel model Hamiltonian H is defined with the creators and the annihilators as

$$H=\sum_{r,s\in M} b_{rs}\,(a^\dagger_{r\uparrow}a_{s\uparrow}+a^\dagger_{r\downarrow}a_{s\downarrow}), \tag{1}$$

where $\{b_{rs}\}$ are the components of what is called the Hückel matrix. Assume that the Hückel matrix B is real symmetric, which makes the model transparent without serious loss of physical contents. The matrix is almost always simplified further.

Designate the two ordered pairs of different sites $r,s\in M$ as rs and sr. Let L denote the set of all the pairs composed of different sites of M. Call the pair rs the connected pair if the sites r and s are bonded, noting that the word "bonded" is used here with regard to the site framework but not to the electronic structure considered. Denote the subset of L that consists of all the connected pairs by Y and the complementary subset by $\overline{Y}$. Let us refer to the model with the simplification

$$b_{rs}=\begin{cases}\beta_{rs} & (rs\in Y)\\ 0 & (rs\in\overline{Y})\end{cases} \tag{2}$$

as the semisimple Hückel model[9] and to the model with the more popular simplification

$$b_{rs} = \begin{cases} \alpha & (r=s) \\ \beta & (rs\in Y) \\ 0 & (rs\in \overline{Y}) \end{cases} \tag{3}$$

as the simple Hückel model.

The most informative quantities of definite physical meaning in the Hückel model are electron densities $\{q_r\}$ on sites and bond orders $\{p_{rs}\}$ between sites.[10] Let us call them p-densities generically for convenience' sake, often designating q_r as p_{rr}. Although p-densities are defined originally in terms of Hückel orbital coefficients, we can generalize the definition quite naturally. Put

$$\begin{cases} \rho_{\mu rs} = (a^{\dagger}_{r\mu}a_{s\mu} + a^{\dagger}_{s\mu}a_{r\mu})/2 \\ \zeta_{\mu rs} = -\,\mathrm{i}\,(a^{\dagger}_{r\mu}a_{s\mu} - a^{\dagger}_{s\mu}a_{r\mu})/2 \end{cases} \qquad (r,s\in M;\ \mu\in\Omega) \tag{4}$$

and define

$$\begin{cases} p_{\mu rs} = \langle|\rho_{\mu rs}|\rangle \\ z_{\mu rs} = \langle|\zeta_{\mu rs}|\rangle \end{cases} \qquad (r,s\in M;\ \mu\in\Omega) \tag{5}$$

for each eigenstate $|\rangle$ of H. We can define p-densities by

$$p_{rs} = \langle|(\rho_{\uparrow rs} + \rho_{\downarrow rs})|\rangle = p_{\uparrow rs} + p_{\downarrow rs} \qquad (r,s\in M). \tag{6}$$

The matrix P of the component $\{p_{rs}\}$ is real symmetric necessarily. Let us call the matrix the p-density matrix.[11]

Hypervirial Condition

The hypervirial theorem affirms that any eigenstate $|E\rangle$ of the Hamiltonian $\hat{H}$ of a system fulfils

$$\langle E|[\hat{H}, \hat{A}]|E\rangle = 0 \tag{7}$$

for any linear operator $\hat{A}$ of the system. Since the Hückel model has the one-body Hamiltonian conserving the spin, essential is the one-body hypervirial theorem[12]

$$\langle|[H, a^{\dagger}_{r\mu}a_{s\mu}]|\rangle = 0 \qquad (r,s\in M;\ \mu\in\Omega), \tag{8}$$

which is rewritten by calculating the commutator as

$$\sum_{t\in M}(b_{rt}\langle|a^{\dagger}_{t\mu}a_{s\mu}|\rangle - \langle|a^{\dagger}_{r\mu}a_{t\mu}|\rangle\, b_{ts}) = 0 \qquad (r,s\in M;\ \mu\in\Omega). \tag{9}$$

Thus, we find that the combination corresponding to

$$\langle|[H, \mathrm{i}\zeta_{\mu rs}]|\rangle = 0 \qquad (r<s\in M;\ \mu\in\Omega) \tag{10}$$

suffices to give the linear equations for $\{p_{\mu rs}\}$

$$\sum_{t\in M}(b_{rt}p_{\mu ts} - p_{\mu rt}b_{ts}) = 0 \qquad (r<s\in M;\ \mu\in\Omega). \tag{11}$$

Here, the case of $r>s$ is excluded because the equation for rs is essentially identical with that for sr; the case of $r=s$, giving nothing, is also excluded. By virtue of the linearity the same equations hold for $\{p_{rs}\}$. Let us refer to the equations the hypervirial relationships and shorten "hypervirial relationship" to "HVR" from now on.

We can take the other combination independent of the above one. The combination corresponding to

$$\langle|[H, \mathrm{i}\rho_{\mu rs}]|\rangle = 0 \qquad (r\leqq s\in M;\ \mu\in\Omega) \tag{12}$$

leads to the linear equations for $\{z_{\mu rs}\}$

$$\sum_{t\in M}(b_{rt}z_{\mu ts} - z_{\mu rt}b_{ts}) = 0 \qquad (r\leqq s\in M;\ \mu\in\Omega). \tag{13}$$

However, after all, these equations do not give more than the reality condition

$$z_{\mu rs} = 0 \qquad (r,s\in M;\ \mu\in\Omega), \tag{14}$$

which is a natural consequence of the reality assumption of the Hückel matrix.

To return, regarding the HVRs for p-densities as a condition imposed upon p-densities, call it the hypervirial condition, which is abbreviated as the HVC in the following. The HVC can be expressed compactly in the matrix form as[13,14]

$$[B, P] = 0. \tag{15}$$

In particular, for the simple Hückel model, we have

$$[J, P] = 0 \tag{16}$$

with the adjacency matrix J.[15,16] Bear it in mind that the HVC is common to all the eigenstates of H without regard to the number of electrons contained. Say, by supposing the one-electron eigenstate, p-densities in the HVC are read as the p-densities due to one Hückel orbital. With the number n of electrons fixed, we have the number condition

$$n = \sum_{r\in M} p_{rr} \tag{17}$$

as a condition independent of the HVC. Then, the HVC plus the number condition is common to all the n-electron eigenstates of H.

Now let n_μ denote the number of μ-spin electrons in a system. When $n_\uparrow$ and $n_\downarrow$ differ, each of the HVCs upon $\{p_{\uparrow rs}\}$ and upon $\{p_{\downarrow rs}\}$ becomes meaningful under the number conditions for n_μ's.[17] However, as long as we do not substitute numbers for n_μ's, the condition upon $\{p_{\mu rs}\}$ is identical with that upon p-densities in the form of equations. In what follows, the condition upon p-densities is treated representatively; it is enough to affix the subscript "↑" or "↓" (or "μ") to "p"

and "n" for the others.

A little arrangement of terms in HVRs is preferable, particulary for practical purposes. Putting

$$d_{rs} = b_{rs}(q_r - q_s), \tag{18}$$

$$e_{rs} = (b_{rr} - b_{ss})p_{rs}, \tag{19}$$

and

$$f_r^s = \sum_{t \neq r,s} b_{rt}p_{ts}, \tag{20}$$

we write the HVR for rs as

$$e_{rs} + f_r^s - f_s^r = d_{rs}. \tag{21}$$

The left side concerns only bond orders, while the right does site electron densities. Note that d_{rs} and e_{rs} are antisymmetric for the interchange of r and s, but that f_r^s and f_s^r differ in general. We can leave d_{rs} and e_{rs} out of account, respectively, for $b_{rs}=0$ and for $b_{rr}=b_{ss}$. Let C_r^s be the set of sites adjacent to r other than s. Note that C_s^r differs from C_r^s in general. For the semisimple Hückel model, the summation in f_r^s runs over C_r^s and the term d_{rs} vanishes unless rs is a connected pair. In particular, the simple Hückel model has the exquisitely simple HVRs independent of values of α and β;

$$\tilde{f}_r^s - \tilde{f}_s^r = \tilde{d}_{rs} \tag{22}$$

with

$$\tilde{f}_r^s = \sum_{t \in C_r^s} p_{ts} \tag{23}$$

and

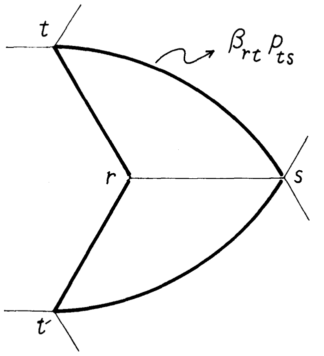
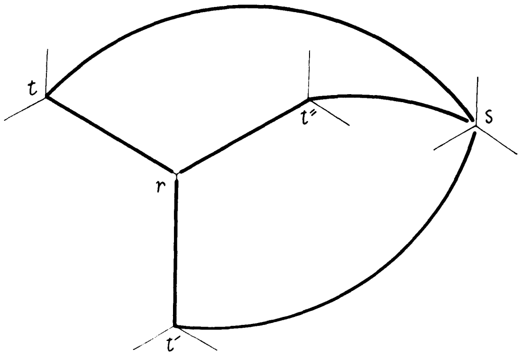
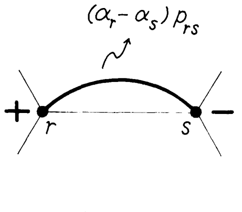
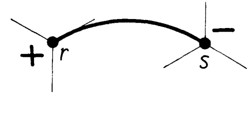
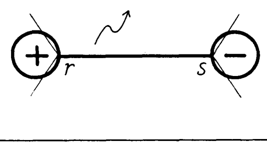
$$\tilde{d}_{rs} = \begin{cases} q_r - q_s & (rs \in Y) \\ 0 & (rs \in \bar{Y}). \end{cases} \tag{24}$$

Table 1 is an adequate dictionary for a diagrammatic representation of HVRs for the semisimple Hückel model, which can be used for the simple Hückel model with trivial translation. The diagrammatic representation will be found quite useful for writing out HVRs for individual systems. It may help us conceive the physical meaning of HVRs.

It is obvious that the HVC brings information on a sort of detailed balance in electron distribution in a system. Some portion of the balance is, however, often ascribable to the symmetry of the system. The number N_h of independent HVRs is given by

$$N_h \leqq m(m-1)/2. \tag{25}$$

Table 1. Diagrammatic Representation of HVRs for the Semisimple Hückel Model[a)]

Term	Diagram	
	For adjacent rs	For nonadjacent rs
f_r^s	 	
e_{rs}	 	
d_{rs}	 	

a) Read f_r^s as $\tilde{f}_r^s$ and d_{rs} as $\tilde{d}_{rs}$ with all β's unity for the simple Hückel model, which has no term corresponding to e_{rs}.

The equality holds only for systems of no "spatial" symmetry at all. The symmetry condition often makes some HVRs trivial, while the HVC often contains some part of the symmetry condition. Let us proceed with this problem.

Symmetry Condition

The symmetry of molecular systems is to be treated generally through the point group.[18] However, it is pertinent and rather essential for the present purpose to consider the symmetry of the Hückel matrix with permutation groups.[19] Let S_m be the symmetric group on M and designate the element consequent on the action of $x \in S_m$ on $r \in M$ simply as xr. Let G, a subgroup of S_m, be the permutation group consisting of all the permutations $\{x\}$ that keep the Hückel matrix B invariant in the sense that

$$b_{xrxs} = b_{rs} \qquad (r,s \in M). \tag{26}$$

The permutation group G carries the characteristics of the symmetry of B which fully reflects the symmetry of a system in the Hückel model.

Here, tentatively, the state $|\rangle$ is said to be faithful if it fulfils

$$\langle|\rho_{\mu xrxs}|\rangle = \langle|\rho_{\mu rs}|\rangle \quad (r,s \in M;\ \mu \in \Omega)\ (x \in G). \tag{27}$$

Any nondegenerate eigenstate of H is easily proved to be faithful. For degenerate eigenstates, however, relevant choice is required for the eigenstates to be faithful. Arbitrary configurations composed of Hückel orbitals cannot necessarily lead us to faithful states, even if they are eigenstates of H. Only faithful eigenstates are natural and satisfactory as stationary states of an entire system.[10,20] Let us confine ourselves to faithful eigenstates when the permutational symmetry is considered.

Two elements $r,s \in M$ are said to be transitive if there exists $x \in G$ satisfying $s=xr$. The transitivity is an equivalence relation and gives the classification of M

$$M = \Gamma_1 + \cdots + \Gamma_v \tag{28}$$

with $\{\Gamma_i\}$ the equivalence classes, which are called the orbits on M.[21] Let V denote the set $\{1,\cdots,v\}$ of the subscripts of the orbits. Likewise, two elements $rs,tu \in L$ are said to be transitive if there exists $x \in G$ satisfying $tu=xrxs$. We have the classification of L

$$L = \Lambda_1 + \cdots + \Lambda_w \tag{29}$$

with $\{\Lambda_i\}$ the orbits on L. Denote the set $\{1,\cdots,w\}$ of the subscripts by W. The orbit on M and that on L are often called the site orbit and the pair orbit, respectively. The number of elements contained in an orbit is conventionally called the length of the orbit. Using the concept of orbits, we can write the permutational symmetry condition as

$$\begin{cases} q_r = q_s & (r,s \in \Gamma_i) \qquad (\text{each } i \in V) \\ p_{rs} = p_{tu} & (rs,tu \in \Lambda_i) \qquad (\text{each } i \in W). \end{cases} \tag{30}$$

Note that this does not always reproduce the transpositional symmetry inherent in bond orders completely.[22] The modifier "permutational" stands for this fact. The symmetry condition is abbreviated as the SC in the following.

Let us define the subset Δ_i of L, which is said to be dual with Λ_i, as

$$\Delta_i = \{rs \mid sr \in \Lambda_i\} \qquad (i \in W). \tag{31}$$

Evidently, the subset Δ_i is a pair orbit, identical or disjoint with Λ_i. The pair orbit Λ_i is said to be selfdual if identical with Δ_i, and nonselfdual otherwise. Let w° be the number of selfdual orbits plus half the number of nonselfdual ones. Arranging the subscripts of pair orbits relevantly, we can make the w° "pseudorbits"[23]

$$\Theta_i = \Lambda_i \cup \Delta_i \qquad (i \in W^\circ = \{1,\cdots,w^\circ\}). \tag{32}$$

constitute L. The pseudorbits enable us to incorporate the transpositional symmetry into the SC;

$$\begin{cases} q_r = q_s & (r,s \in \Gamma_i) \qquad (\text{each } i \in V) \\ p_{rs} = p_{tu} & (rs,tu \in \Theta_i) \qquad (\text{each } i \in W^\circ). \end{cases} \tag{33}$$

For the number N_p of symmetry-independent p-densities, we have

$$N_p = v + w^\circ \tag{34}$$

immediately from this.

To see the general relation between the HVC and the SC, let us use the matrix notation, denoting the permutation matrix corresponding to $x \in G$ by X. The transpositional symmetry is always presupposed here; we can identify the SC with the permutational SC. What serves the purpose is the Lie–Jacobi identity

$$[[B, P], X] + [[P, X], B] + [[X, B], P] = 0 \ (x \in G), \tag{35}$$

which is reduced by the invariance of B to

$$[[B, P], X] = [[X, P], B] \qquad (x \in G), \tag{36}$$

showing the consistency of the HVC and the SC immediately. If the HVC is presupposed, we have

$$[[X, P], B] = 0 \qquad (x \in G). \tag{37}$$

Clearly, this cannot make all $[X, P]$'s for $x \in G$ vanish in general. On the other hand, with the SC presupposed, we have

$$[[B, P], X] = 0 \qquad (x\in G). \tag{38}$$

This assures that $[B, P]$ has the same permutational symmetry as B and P, but does not suffice to reproduce the HVC in general. The next section will clarify what follows upon the HVC from the presupposed SC in some detail.

Group theory is ready to provide some interesting results about the number of site orbits, that of pair orbits, lengths of them, and so on. However, let us skip the subject now, which is of rather mathematical interest. Actually, it is not difficult to check site orbits and pair orbits for a given system, usually much easier than to find the permutation group itself.

Intrinsic Hypervirial Condition

Because the SC is quite simple and much more accessible than the HVC, we suppose that the SC is fulfilled prior to the HVC in taking account of both. Let us refer to the HVR left nontrivial with the SC fulfilled as the intrinsic HVR and name the condition consisting of intrinsic HVRs the intrinsic HVC. The reason why we treat the SC using the concept of orbits is that the concept is advantageous for describing the intrinsic HVC.

For two arbitrary elements rs and $r's'$ of a pair orbit, we always have the permutation $x\in G$ that fulfils $r'=xr$ and $s'=xs$. Hence, noting

$$\sum_{t\in M} b_{rt}p_{ts} = \sum_{t\in M} b_{r'xt}p_{xts'} = \sum_{t\in M} b_{r't}p_{ts'}, \tag{39}$$

we find that the HVR for $r's'$ is identical with that for rs. Since the HVRs for rs and for sr are essentially identical, we can conclude that each pseudorbit corresponds to its HVR, whether the HVR is intrinsic or not. This neat result, mentioned in the preceding section already, is not all that follow from the presupposed SC.

Let rs be an arbitrary element of a selfdual orbit. Then, there exists the permutation $x\in G$ that fulfils $x(rs)=sr$. Since this means $xr=s$ and $xs=r$, we have

$$\sum_{t\in M} b_{rt}p_{ts} = \sum_{t\in M} b_{sxt}p_{xtr} = \sum_{t\in M} b_{st}p_{tr}, \tag{40}$$

which makes the HVR for rs trivial. Thus, the intrinsic HVC contains no HVRs for selfdual orbits. This is the most crucial result that is also fundamental for writing out intrinsic HVRs for individual systems.

To outline locations of selfdual and nonselfdual orbits in L, it is suitable to define the region L_{ij} as

$$L_{ij} = \{rs\in L \mid r\in\Gamma_i;\ s\in\Gamma_j\} \qquad (i,j\in V). \tag{41}$$

Let us refer to L_{ij} as the diagonal region if $i=j$ and as the off-diagonal region otherwise. Diagonal regions are defined for site orbits of length more than unity. We readily find that no orbit spreads over separate regions and that no orbit in off-diagonal regions is selfdual. Hence, orbits in off-diagonal regions are to correspond to intrinsic HVRs. Since orbits in the off-diagonal region L_{ji} are dual with orbits in L_{ij}, we have only to consider off-diagonal regions for $i<j$. On the other hand, orbits in diagonal regions are almost exclusively selfdual and scarcely lead to intrinsic HVRs. Roughly speaking, as the symmetry of a system becomes lower, we have more intrinsic HVRs.

Actually, it is never laborious to check whether a site pair belongs to a selfdual orbit or not; yet, as to orbits in diagonal regions, the following cases are worth noting.

(1) If the length of an orbit Γ_i is two, then L_{ii} is a selfdual orbit in itself.

(2) Let Γ_i be an orbit of length $|\Gamma_i|$ more than two. If there exists no other site orbit of the same length as $|\Gamma_i|$, then all the orbits in L_{ii} are selfdual.

(3) As a corollary of the above, if we have only one orbit on M, that is, if M itself is an orbit, then all the pair orbits are selfdual.

The proofs of these are omitted, but it will be easy to comprehend them by supposing relevant configurations of sites.

Now assume that we have more than one orbits Γ_i's of the same length more than two. Of course, it is probable for orbits in L_{ii}'s to be selfdual. However, if G is a cyclic group of order more than two, it is possible for orbits in L_{ii}'s to be nonselfdual. Then, HVRs for orbits in different L_{ii}'s are, moreover, not all independent of each other. Such a case is very exceptional and not discussed here in further detail. Instead, a typical example is shown in Fig. 1, which will be enough to understand when exceptional cases occur.

Consider the number N_p° of p-densities left independent with both of the SC and the HVC fulfilled. Put exceptional cases aside for brevity. The number of intrinsic HVRs is equal to that of pseudorbits in off-diagonal regions, so that, using the number N' of pseudorbits in diagonal regions, we have

$$N_p^\circ = v + N'. \tag{42}$$

Let N_i' denote the number of pseudorbits in the

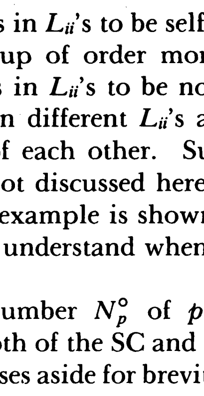


Fig. 1. Nonselfdual orbits in diagonal regions: $\Gamma_1=\{1,2,3\}$, $\Gamma_2=\{4,5,6\}$, $\Lambda_1=\{12,23,31\}$, $L_{11}=\Lambda_1+\Delta_1$, and so on.

diagonal region for an orbit Γ_i of length $|\Gamma_i|$. The obvious, rough estimate

$$N'_i \leqq |\Gamma_i| - 1 \qquad (i \in V) \tag{43}$$

leads to

$$N' = \sum_{i \in V} N'_i \leqq m - v \tag{44}$$

and gives

$$N^\circ_p \leqq m. \tag{45}$$

If $|\Gamma_1|$ is more than two and if G contains a cyclic group of order $|\Gamma_1|$, then we have the better estimate

$$N'_1 \leqq [|\Gamma_1|/2], \tag{46}$$

where $[\cdots]$ is Gauß' symbol. This can improve the estimate for N°_p considerably for systems of high symmetry.

The discussion in this section may be too crude from a mathematical point of view; there is plenty of room for refinement. Nevertheless, the results obtained here is adequate to work with the intrinsic HVC practically.

Illustrative Examples

What the HVC implies will be understood well through working on several examples. Some hints as to when and how to utilize the HVC may also be obtained. The best way for writing out HVRs for individual systems (without computers) is probably to use the diagrammatic repesentation over so-called structure formulas. Although the diagrammatic method needs neither the Hückel matrix nor the p-density matrix written explicitly, most of the following examples have expressions of the matrices for the sake of clarity, half of the off-diagonal components being often omitted to avoid useless complexity.

Simple Systems. The simplest example that has the intrinsic HVC is the asymmetric two-site system shown in Fig. 2 (a). Put

$$B = \begin{pmatrix} \alpha & \beta \\ \beta & \alpha' \end{pmatrix} \tag{47}$$

and

$$P = \begin{pmatrix} q & p \\ p & q' \end{pmatrix}. \tag{48}$$

The nonselfdual orbit $\{12\}$ corresponds to the intrinsic HVR

$$(\alpha - \alpha')p = \beta(q - q'), \tag{49}$$

which means that the bond order is proportional to the difference between the electron densities on the two sites with the proportionality constant $\beta/(\alpha-\alpha')$. If $\beta=0$, then we have $p=0$ for $\alpha' \neq \alpha$. If we put $\alpha'=\alpha$, the HVR becomes $q'=q$ for nonvanishing β. Then, the HVR is not intrinsic, contained in the SC.

The three-site chain system is another instructive simple example. Let the middle site be the third one, as shown in Fig. 2 (b). The semisimple Hückel model for the system has

$$B = \begin{pmatrix} \alpha & 0 & \beta \\ 0 & \alpha'' & \beta'' \\ \beta & \beta'' & \alpha' \end{pmatrix} \tag{50}$$

and

$$P = \begin{pmatrix} q & p' & p \\ p' & q'' & p'' \\ p & p'' & q' \end{pmatrix}. \tag{51}$$

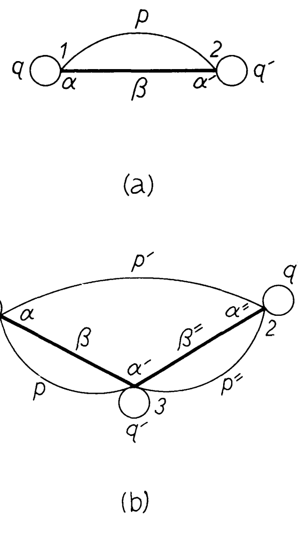
The three HVRs for the pairs 12, 13, and 23 are

$$\begin{cases} (\alpha - \alpha'')p' + \beta p'' - \beta'' p = 0 \\ (\alpha - \alpha')p - \beta'' p' = \beta(q - q') \\ (\alpha'' - \alpha')p'' - \beta p' = \beta''(q'' - q'). \end{cases} \tag{52}$$

The case of $\alpha''=\alpha$ lets the first HVR mean

$$p/\beta = p''/\beta'', \tag{53}$$

which is ready to give $p''=p$ for $\beta''=\beta$. Really, assume that $\beta''=\beta$ besides $\alpha''=\alpha$. Then, the two site orbits $\Gamma_1=\{1,2\}$ and $\Gamma_2=\{3\}$ follow immediately. The diagonal region L_{11} contains only one selfdual orbit $\Lambda_1=\{12,21\}$; the off-diagonal region L_{12} does only one nonselfdual orbit $\Lambda_2=\{13,23\}$. We have the SC that



(a)

(b)

Fig. 2. Simple systems.

$q''=q$ and $p''=p$. Intrinsic is only the HVR for A_2

$$q-((\alpha-\alpha')/\beta)p=q'-p', \tag{54}$$

which is reduced further to

$$q=q'-p' \tag{55}$$

in the simple Hückel model.

A Theorem on Invariants in Chains. It will be suitable to mention here a general theorem for chains in the simple Hückel model. Only bifurcation sites being aside, the theorem is valid for any chain part of arbitrary systems. The term "chain part" should be taken here in a broad sense; a chain part is able to have no end site or to be a part of a ring. The theorem is explained in Figs. 3 and 4.

Let K be the set of nonterminal sites $\{1,\cdots,k\}$ in a chain and q_r be the electron density on the site $r\in K$. Each site of K has two adjacent sites; let p_r denote the bond order between the two sites adjacent to r. Define the modified electron density $\tilde{q}_r$ on the site r as

$$\tilde{q}_r=q_r-p_r \qquad (r\in K). \tag{56}$$

Then, the HVC leads us to the invariance of the modified site electron density in the chain;

$$\tilde{q}_r=\tilde{q}_s \qquad (r,s\in K). \tag{57}$$

Moreover, if the chain has an end site, we have

$$\tilde{q}_r=q_0 \qquad (r\in K), \tag{58}$$

where q_0 is the electron density on the end site. Of course, this can be paraphrased into the invariance of the modified site electron density in the chain by the natural definition $\tilde{q}_0=q_0$. Thus, we can assign a unique modified site electron density to a chain.

This theorem holds for any eigenstate of H, whether faithful or not, without regard to the number of electrons or the alternant symmetry. Hence, we may regard the theorem as a generalization of Coulson-Rushbrooke's theorem,[24] as far as chain parts are concerned. Unfortunately, the bifurcation site prevents us from defining the modified electron density on the site uniquely. If we intend to sustain the invariance of the modified site electron density including bifurcation sites, it seems to be inevitable to assign a few direction-dependent modified electron densities to bifurcation sites.

We can generalize the theorem into "the invariance of the modified p-density in a chain" directly. The modified bond order between adjacent sites is definable for chains containing more than one sites apart from bifurcation sites. Here, use single letters $\{1,\cdots,\tau\}$ for nonterminal connected pairs in a chain. Denote the set by T, each pair of which has two adjacent sites. Let p_ξ be the bond order for the pair $\xi\in T$ and p'_ξ be that between the two sites adjacent to ξ. Then, it follows from the HVC that the modified bond order

$$\tilde{p}_\xi=p_\xi-p'_\xi \qquad (\xi\in T) \tag{59}$$

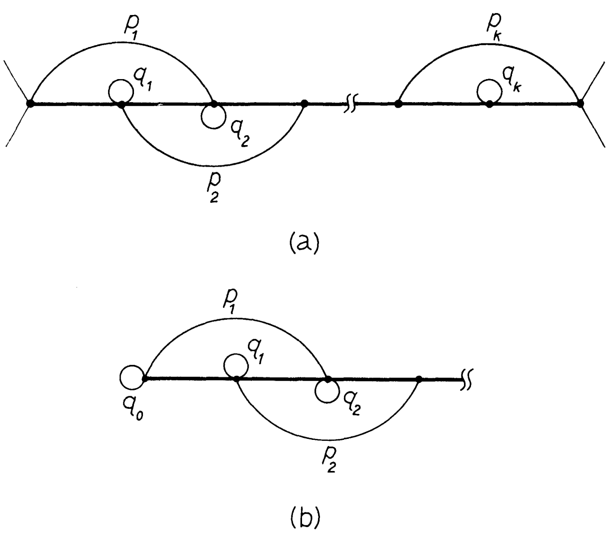
is invariant in the chain;

$$\tilde{p}_\xi=\tilde{p}_\eta \qquad (\xi,\eta\in T). \tag{60}$$

If the chain has an end connected pair, we have

$$\tilde{p}_\xi=p_0 \qquad (\xi\in T) \tag{61}$$

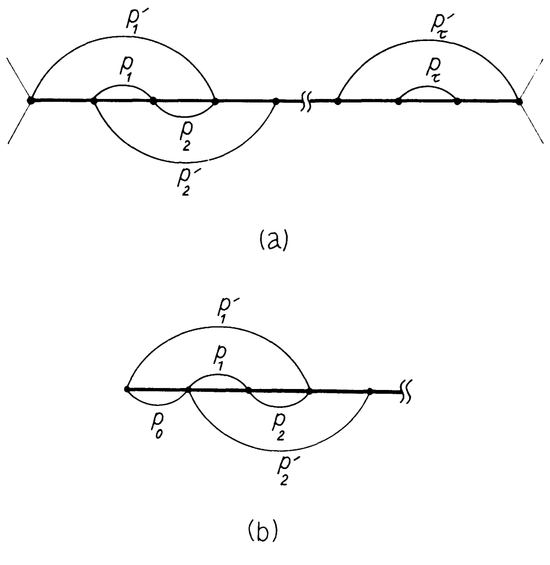
with the bond order p_0 for the end connected pair. It is



(a)

(b)

Fig. 3. The invariance of the modified site electron density in a chain: (a) $\tilde{q}_1=\tilde{q}_2=\cdots=\tilde{q}_k$ with $\tilde{q}_r=q_r-p_r$, (b) $\tilde{q}_0=\tilde{q}_1=\tilde{q}_2=\cdots$ with $\tilde{q}_0=q_0$.



(a)

(b)

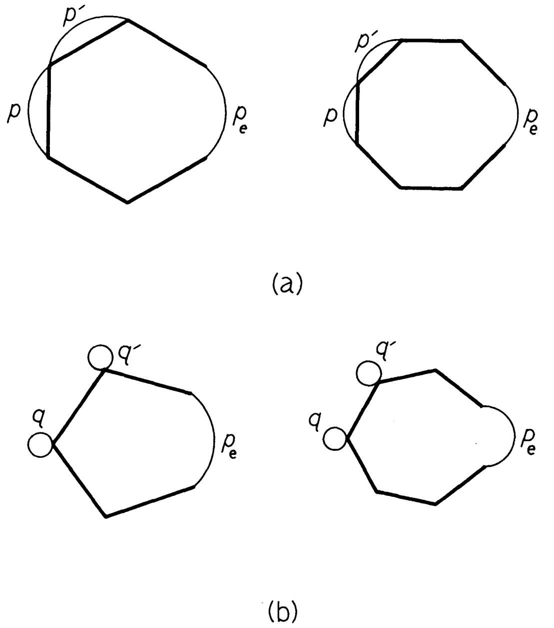
Fig. 4. The invariance of the modified bond order between adjacent sites in a chain: (a) $\tilde{p}_1=\tilde{p}_2=\cdots=\tilde{p}_\tau$ with $\tilde{p}_\xi=p_\xi-p'_\xi$, (b) $\tilde{p}_0=\tilde{p}_1=\tilde{p}_2=\cdots$ with $\tilde{p}_0=p_0$.

easy to apply the above treatment to bond orders between sites distant in a chain, with defining modified bond orders relevantly.

Consider the bond order p_e between the two end sites of a chain. Successive applications of the above theorem for modified p-densities enable us to connect p_e with other two p-densities in a simple way as follows. For even-membered chains, use the bond order p for the central connected pair and the bond order p' for the connected pair adjacent to it; for odd-membered chains, use the electron density q on the central site and the electron density q' on the site adjacent to it. Then, we have

$$\begin{cases} p_e = p - p' & \text{(even-membered)} \\ p_e = q - q' & \text{(odd-membered).} \end{cases} \tag{62}$$

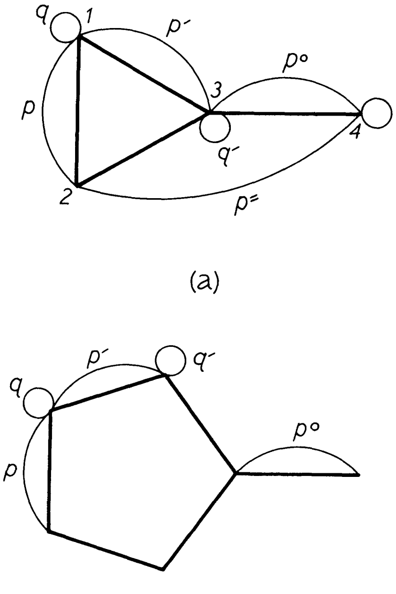
Figure 5 shows a few representatives with the notation.



(a)

(b)

Fig. 5. The bond order between the two ends of a chain: (a) $p_e=p-p'$, (b) $p_e=q-q'$.



(a)

(b)

Fig. 6. Systms of a ring with a site attached.

Systems of a Ring with a Site Attached. Let us take the simple Hückel model for the system shown in Fig. 6 (a), which is appropriate for practice-minded readers to master handling HVRs. Putting

$$B = \begin{vmatrix} \alpha & \beta & \beta & 0 \\ & \alpha & \beta & 0 \\ & & \alpha & \beta \\ & & & \alpha \end{vmatrix} \tag{63}$$

and

$$P = \begin{vmatrix} q & p & p' & p'' \\ & q & p' & p'' \\ & & q' & p^\circ \\ & & & q^\circ \end{vmatrix}, \tag{64}$$

we have the three site orbits $\Gamma_1=\{1,2\}$, $\Gamma_2=\{3\}$, and $\Gamma_3=\{4\}$. Each of the three off-diagonal regions L_{12}, L_{13}, and L_{23} is a nonselfdual orbit in itself, so that the intrinsic HVRs are

$$\begin{cases} p' - p - p'' = q - q' \\ p^\circ + p'' - p' = 0 \\ 2p'' = q' - q^\circ. \end{cases} \tag{65}$$

Now let us express p', p°, and p'' in terms of the other p-densities q, q', q°, and p. Then, we have

$$p' = p + q - (q' + q^\circ)/2, \tag{66}$$

$$p^\circ = p + q - q', \tag{67}$$

and

$$p'' = (q' - q^\circ)/2. \tag{68}$$

Further, the number condition

$$n = 2q + q' + q^\circ \tag{69}$$

can eliminate, say, q', from these. Using the "excess electron densities on sites"

$$\begin{cases} \underline{q} = q - n/4 \\ \underline{q}^\circ = q^\circ - n/4, \end{cases} \tag{70}$$

we obtain

$$p' = p + 2\underline{q}, \tag{71}$$

$$p^\circ = p + 3\underline{q} + \underline{q}^\circ, \tag{72}$$

and

$$p'' = -\underline{q} - \underline{q}^\circ. \tag{73}$$

When we take account of the number condition, the concept of excess electron densities on sites is useful in general.

Another system similar to this is shown in Fig. 6 (b) together with the notation used below. Treating the system within the simple Hückel model, we have the four site orbits $\Gamma_1=\{1,2\}$, $\Gamma_2=\{3,4\}$, $\Gamma_3=\{5\}$, and $\Gamma_4=\{6\}$. The off-diagonal region L_{12} contains two nonselfdual orbits, while each of L_{13}, L_{14}, L_{23}, L_{24}, and L_{34} is a nonselfdual orbit in itself. Thus the intrinsic HVC consists of seven HVRs expressed in terms of thirteen p-densities. Here, let us only show a few expressions for p°, without writing the HVRs explicitly. It is easy to derive

$$p^\circ = p' + q - q' \tag{74}$$

from the HVRs. As another expression, say, we have

$$p^\circ = p + 2\underline{q} + \underline{q}', \tag{75}$$

using the number condition.

Systems of a Site over a Ring. Consider the six-site system composed of a pentagonal ring and an additional site over the ring. See Fig. 7. Assuming the five-fold axis, put

$$B = \begin{pmatrix} \alpha^\circ & \beta^\circ & 0 & 0 & \beta^\circ & \beta \\ & \alpha^\circ & \beta^\circ & 0 & 0 & \beta \\ & & \alpha^\circ & \beta^\circ & 0 & \beta \\ & & & \alpha^\circ & \beta^\circ & \beta \\ & & & & \alpha^\circ & \beta \\ & & & & & \alpha' \end{pmatrix} \tag{76}$$

and

$$P = \begin{pmatrix} q^\circ & p_1^\circ & p_2^\circ & p_2^\circ & p_1^\circ & p \\ & q^\circ & p_1^\circ & p_2^\circ & p_2^\circ & p \\ & & q^\circ & p_1^\circ & p_2^\circ & p \\ & & & q^\circ & p_1^\circ & p \\ & & & & q^\circ & p \\ & & & & & q' \end{pmatrix}. \tag{77}$$

Since the site orbits are $\Gamma_1=\{1,\cdots,5\}$ and $\Gamma_2=\{6\}$, we have only one off-diagonal region L_{12}, which is a nonselfdual orbit in itself and gives one HVR. If we define α and q for the ring by

$$\alpha = \alpha^\circ + 2\beta^\circ \tag{78}$$

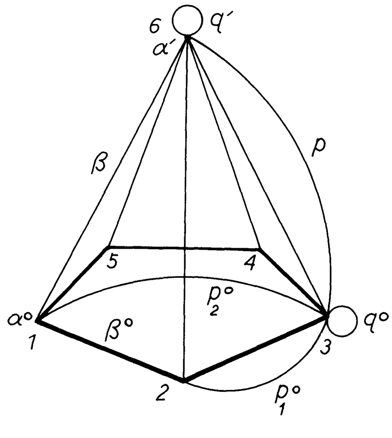
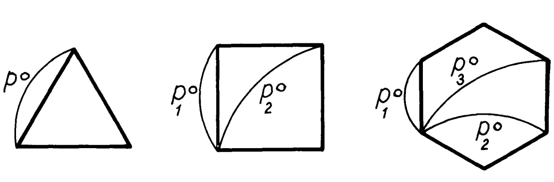


Fig. 7. A site over a pentagonal ring.



(a) (b) (c)

Fig. 8. Ξ's for polygonal rings: (a) $\Xi=2p^\circ$, (b) $\Xi=2p_1^\circ+p_2^\circ$, (c) $\Xi=2p_1^\circ+2p_2^\circ+p_3^\circ$.

and

$$q = q^\circ + \Xi \tag{79}$$

with

$$\Xi = 2p_1^\circ + 2p_2^\circ, \tag{80}$$

we can write the HVR in the same form as that for the asymmetric two-site system as

$$(\alpha - \alpha')p = \beta(q - q'). \tag{81}$$

However, there exists the qualitative difference between them that arises from the contents of α and q. Only when either $(\alpha-\alpha')$ or $(q-q')$ is negative, we have positive p under negative β. Further, for $|p|$ not to be negligible, it is necessary that $|\alpha-\alpha'|$ is comparable with or smaller than $|\beta|$. The contents of α and q are thus significant.

Even if a pentagonal ring is replaced with another polygonal ring of m° sites, we have a HVR of the same form as the above by reading Ξ as the sum of $m^\circ-1$ bond orders between one site and the others of the polygonal ring. A few Ξ's are given in Fig. 8.

Interacting Subsystems. Suppose the six-site system composed of the four- and the two-site chain subsystems interacting with each other. See Fig. 9. The system provides a simple example suggesting some applicability of the HVC to problems on reactivity. Adopting the simple Hückel model in the subsystems and assuming the reflection symmetry, we have

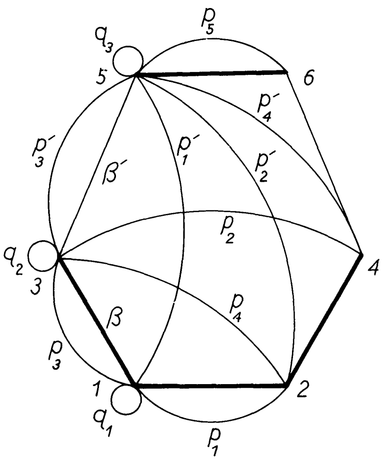


Fig. 9. Interacting four- and two-site subsystems.

$$B=\left|\begin{array}{cccccc}\alpha & \beta & \beta & 0 & 0 & 0\\ & \alpha & 0 & \beta & 0 & 0\\ & & \alpha & 0 & \beta' & 0\\ & & & \alpha & 0 & \beta'\\ & & & & \alpha & \beta\\ & & & & & \alpha\end{array}\right| \tag{82}$$

and

$$P=\left|\begin{array}{cccccc}q_1 & p_1 & p_3 & p_4 & p'_1 & p'_2\\ & q_1 & p_4 & p_3 & p'_2 & p'_1\\ & & q_2 & p_2 & p'_3 & p'_4\\ & & & q_2 & p'_4 & p'_3\\ & & & & q_3 & p_5\\ & & & & & q_3\end{array}\right| . \tag{83}$$

The site orbits are $\Gamma_1=\{1,2\}$, $\Gamma_2=\{3,4\}$, and $\Gamma_3=\{5,6\}$; each of L_{12}, L_{13}, and L_{23} contains two nonselfdual orbits. Thus, we have the six HVRs

$$\left\{\begin{array}{l}p_4-\lambda p'_1=q_1-q_2\\ p_2+p_3-p_1-\lambda p'_2=0\\ p'_3-\lambda p_3=0\\ p'_4-\lambda p_4=0\\ p'_1-p'_4=\lambda(q_2-q_3)\\ p'_2-p'_3+\lambda(p_5-p_2)=0,\end{array}\right. \tag{84}$$

where

$$\lambda=\beta'/\beta \tag{85}$$

is regarded as standing for the strength of the interaction between the subsystems. The HVRs allow us to express the four intersubsystem bond orders p'_1, p'_2, p'_3, and p'_4 in terms of six relevant intrasubsystem p-densities.

If we use the electron densities q_1, q_2, and q_3 and the intrasubsystem bond orders p_1, p_3, and p_5 between adjacent sites, then we have

$$p'_1=\lambda(1-\lambda^2)^{-1}(q_1-q_3), \tag{86}$$

$$p'_2=\lambda(1-\lambda^2)^{-1}(p_1-p_5), \tag{87}$$

$$p'_3=\lambda p_3, \tag{88}$$

and

$$p'_4=\lambda(1-\lambda^2)^{-1}q_1-\lambda q_2-\lambda^3(1-\lambda^2)^{-1}q_3. \tag{89}$$

The third equation for p'_3 is crucial. Let β be negative and p_3 be positive. If $|\beta'|$ is small, then $|p'_3|$ will be small necessarily. The sign of p'_3 is, however, opposite to that of β'. This means that $|p'_3|$ can be enlarged in "positive feedback" with $|\beta'|$. Another remarkable point is that p'_1 and p'_4 are, respectively, closely related to the inter- and intra-subsystem differences between the electron densities. This stands out in the approximate expressions

$$p'_1\simeq\lambda(q_1-q_3) \tag{90}$$

and

$$p'_4\simeq\lambda(q_1-q_2) \tag{91}$$

for the weak interaction $|\lambda|\ll 1$.

It is, of course, possible to use other intrasubsystem p-densities than the above. Say, we can rewrite p'_3 as

$$\begin{aligned}p'_3&=\lambda(1-\lambda^2)^{-1}p_1-\lambda p_2-\lambda^3(1-\lambda^2)^{-1}p_5\\ &\simeq\lambda(p_1-p_2)\end{aligned} \tag{92}$$

using p_1, p_2, and p_5.

Generally speaking, we should derive the most advisable expression from HVRs to our purpose. As far as the expression is reasonably simple, we will find its physical meaning, aside from whether or not our intuition is able to draw some image about the meaning.

The Hypervirial Condition for Alternant Systems

Many conjugated systems have the alternant symmetry, which leads to the outstanding consequences for the m-electron ground state of an m-site system, Coulson–Rushbrooke's theorem and others.[24,25] It is never futile to mention the HVC for alternant systems specially. For the assignment of starred and unstrarred sites, follow the convention.

Let $M^{\star}$ and M° be the subsets of M that consist of all the starred sites and all the unstarred sites, respectively. The Hückel matrix of the alternant symmetry has the components

$$b_{rs}=\begin{cases}\delta_{rs}\alpha & (r,s\in M^{\star}\text{ or }r,s\in M^{\odot})\\ \begin{cases}\beta_{rs} & (rs\in Y)\\ 0 & (rs\in\overline{Y})\end{cases} & \left(\begin{matrix}r\in M^{\star},\ s\in M^{\odot}\\ \text{or}\\ r\in M^{\odot},\ s\in M^{\star}\end{matrix}\right).\end{cases}\tag{93}$$

Let us use the symbols

$$p_{rs}=\begin{cases}p^{\star}_{rs} & (r,s\in M^{\star})\\ p^{\odot}_{rs} & (r,s\in M^{\odot})\\ p^{\times}_{rs} & (r\in M^{\star},s\in M^{\odot}\text{ or }r\in M^{\odot},s\in M^{\star})\end{cases}\tag{94}$$

distinctively. The set C^s_r contains only either starred or unstarred sites. Let us affix "$\star$" or "$\odot$" to C^s_r to show the attribute of the sites contained therein. It is readily found that the HVC includes the following three classes of HVRs.

$$\sum_{t\in C^s_r\odot}(\beta_{rt}p^{\times}_{ts}-p^{\times}_{rt}\beta_{ts})=0 \qquad (r<s\in M^{\star}),\tag{95}$$

$$\sum_{t\in C^s_r\star}(\beta_{rt}p^{\times}_{ts}-p^{\times}_{rt}\beta_{ts})=0 \qquad (r<s\in M^{\odot}),\tag{96}$$

and

$$\sum_{t\in C^s_r\odot}\beta_{rt}p^{\odot}_{ts}-\sum_{t\in C^s_r\star}p^{\star}_{rt}\beta_{ts}=d_{rs} \qquad (r\in M^{\star},\ s\in M^{\odot})\tag{97}$$

with

$$d_{rs}=\begin{cases}\beta_{rs}(p^{\star}_{rr}-p^{\odot}_{ss}) & (rs\in Y)\\ 0 & (rs\in\overline{Y}).\end{cases}\tag{98}$$

The primary feature is that $\{p^{\star}_{rs},\ p^{\odot}_{rs}\}$ and $\{p^{\times}_{rs}\}$ enter the HVRs separately. In particular, the first and the second classes concern only the bond orders $\{p^{\times}_{rs}\}$ without regard to any site electron density. Note that, so far, the state is not specified.

Now let us confine ourselves to the m-electron ground state. The well-known two consequences of the alternant symmetry[24,26]

$$\begin{cases}p^{\star}_{rr}=1 & (r\in M^{\star})\\ p^{\odot}_{rr}=1 & (r\in M^{\odot})\end{cases}\tag{99}$$

and

$$\begin{cases}p^{\star}_{rs}=0 & (r\neq s\in M^{\star})\\ p^{\odot}_{rs}=0 & (r\neq s\in M^{\odot})\end{cases}\tag{100}$$

are related to each other through the third class of HVRs, forming an "admissible solution" of the HVRs. Since the rest is only $\{p^{\times}_{rs}\}$, the first and the second classes of HVRs can be utilized for determining them directly with some auxiliary conditions. As a matter of fact, the main condition used by Hall in his method of determining bond orders in alternant systems is really the HVRs.[27] Although he said nothing about the hypervirial theorem there, his method is an interesting application of the HVC.[28]

References

1) E. Hückel, *Z. Phys.*, **70**, 204 (1931); **72**, 310 (1931); **76**, 628 (1932). It is surprising that the scope of this inceptive work ranges over fairly wide subjects, though the papers may be of only historical value now.

2) As a readable monograph, for example, K. Yates, "Hückel Molecular Orbital Theory," Academic Press, New York (1978). There are so many books having a pertinent description of the Hückel model that no particular recommendation is intended.

3) The Hückel orbital theory has been established gradually through a number of contribution following Hückel's work. Among others, the successive studies by Lennard-Jones, Coulson, Longuet-Higgins, Hall, and their coworkers played a leading role in analyzing the nature of the Hückel orbital and in refining Hückel's work, though only a few of their many papers are cited explicitly in this paper.

4) N. Trinajstić, "Hückel Theory and Topology," in "Semiempirical Method of Electronic Structure Calculation Part A: Techniques" ed by H. F. Schaefer III, Plenum, New York (1977), which contains a key bibliography up to 1976. In recent years, chemical applications of graph theory have developed divergingly; for example, "Mathematics and Computational Concepts in Chemistry," ed by N. Trinajstić, Ellis Horwood Ltd., Chichester, (1986) contains several reviews and topics on chemical graph theory. There are too many papers to cite separately, even if we confine ourselves to the characteristic polynomial which is a central bridge between the Hückel model and graph theory. See the review article H. Hosoya, Discrete Applied Mathematics, **19**, 239 (1988) and the references cited therein.

5) S. Aono and K. Nishikawa, *Bull. Chem. Soc. Jpn.*, **53**, 3418 (1980); S. Aono, T. Ohmae, and K. Nishikawa, *ibid.*, **54**, 1645 (1981); K. Nishikawa, M. Yamamoto, and S. Aono, *J. Chem. Phys.*, **78**, 5031 (1983). Aono and his coworkers applied their method to various problems; for example, S. Aono and K. Nishikawa, *Bull. Chem. Soc. Jpn.*, **58**, 288 (1985); T. Ohmae, K. Nishikawa, and S. Aono, *ibid.*, **58**, 294 (1985); M. Yamamoto, K. Nishikawa, and S. Aono, *ibid.*, **58**, 3176 (1985). See also J. Linderberg and Y. Öhrn, "Propagators in Quantum Chemistry," Academic Press, New York (1973), Chap. 3.

6) C. A. Coulson and H. C. Longuet-Higgins, *Proc. R. Soc. London, Ser. A*, **191**, 39 (1947); **192**, 16 (1947).

7) J. O. Hirschfelder, *J. Chem. Phys.*, **33**, 1462 (1961), in which the hypervirial theorem originated. Recently an excellent monograph on this theorem was published: F. M. Fernández and E. A. Castro, "Hypervirial Theorems," Springer-Verlag, Berlin (1987), which has a useful bibliography every chaper. S. T. Epstein, "The Variation Method in Quantum Chemistry," Academic Press, New York (1974) includes a neat description of the hypervirial theorem and several theorems related to it.

8) The word "spin" is used in place of "one-electron spin state" for brevity, which will cause no confusion.

9) Do not take the word "bonded" too literally in defining the connected pair. Then, the semisimple Hückel model is, actually, the most general Hückel model.

10) C. A. Coulson, *Proc. R. Soc. London, Ser. A*, **169**, 413 (1939) and the references cited therein.

11) Without the diagonal components, it would be proper to call this matrix the bond order matrix. Really, this matrix is a kind of density matrices, but the term "density matrix" is so variously used that it is preferable to prefix "p" the prevalent symbol for the bond order. Hence the generic name "p-density."

12) M. Isihara, *Bull. Chem. Soc. Jpn.*, **54**, 3312 (1981).

13) We can also state that the product BP is real symmetric, since both of B and P are real symmetric.

14) Hückel orbitals do not appear at all throughout the present treatment. Derivation via the orbitals is, of course, possible. However, the derivation seems to be inevitably less general in the specification of the state and to leave the physical ground of the HVC obscure.

15) The adjacency matrix is what Ruedenberg named the topological matrix; K. Ruedenberg, *J. Chem. Phys.*, **22**, 1878 (1954).

16) In some sense, we may say that the HVC in the simple Hückel model depends only on the adjacency, but this should be never misunderstood to mean that bond orders between nonadjacent sites are superfluous.

17) M. Isihara, *Bull. Chem. Soc. Jpn.*, **58**, 2472 (1985); **59**, 3963 (1986).

18) The point group is described in many books on molecular orbital theory. As a standard monograph, F. A. Cotton, "Chemical Applications of Group Theory," John Wiley & Sons, New York (1963).

19) The use of permutation groups is prevalent in constructing spin eigenfunctions for many-electron systems. As another interesting application of permutation groups in quantum chemistry, H. C. Longuet-Higgins, *Mol. Phys.*, **6**, 445 (1963).

20) G. W. Wheland, *Proc. R. Soc. London, Ser. A*, **164**, 397 (1938).

21) For the transitivity, the orbit, and other concepts related to them, consult the literature on group theory, particularly on permutation groups.

22) Say, suppose G to be the group consisting of only the identity or a cyclic group of order more than two.

23) A pseudorbit corresponds to an orbit obtained by ignoring the order in site pairs. If only the SC were considered, the nonordered pair would be used from the outset.

24) C. A. Coulson and G. S. Rushbrooke, *Proc. Camb. Phil. Soc.*, **36**, 193 (1940); H. C. Longuet-Higgins, *J. Chem. Phys.*, **18**, 265 (1950).

25) The classical studies cited in Ref. 24 were followed by various developments; for example, A. D. McLachlan, *Mol. Phys.*, **2**, 271 (1959); J. Koutecký, *J. Chem. Phys.*, **44**, 3702 (1966). See also Ref. 4.

26) Note that the state is assumed to be faithful.

27) G. G. Hall, *Proc. R. Soc. London, Ser. A*, **229**, 254 (1955); K. Ruedenberg, *J. Chem. Phys.*, **29**, 1232 (1958).

28) The HVC in the Hückel model seems to have drawn no attention somewhy, at least explicitly. The reason may include the confusion of the HVC with the reality condition or, paradoxically, the tractability of the Hückel orbital theory.