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The Hypervirial Condition upon Coulson-Longuet-Higgins Polarizabilities in the Hückel Model

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This paper describes a fundamental condition upon Coulson-Longuet-Higgins polarizabilities in the Hückel model. The condition, named the hypervirial condition upon polarizabilities, consists of linear equations to be fulfilled by polarizabilities, being derivable from the hypervirial condition upon site electron densities and bond orders. The hypervirial condition upon polarizabilities can lead us to various simple relationships between polarizabilities, aided by the two auxiliary conditions stemming from the conservation of the number of electrons and from the Hellmann-Feynman theorem. The relationships, being characteristic of a system, will be useful for considering the reactivity of the system within the Hückel model. Several examples for typical systems are given to illustrate how the hypervirial and the auxiliary conditions work practically.

In the previous paper,[1] the author has derived the hypervirial condition upon p-densities[2] in the Hückel model and has set forth the significance of the condition with illustrative applications. The present paper, following the previous one, describes the hypervirial condition upon Coulson-Longuet-Higgins polarizabilities[3–6] (called merely polarizabilities below) in the Hückel model. From now on, the hypervirial conditions upon p-densities and upon polarizabilities are abbreviated to the pHVC and the πHVC, respectively.

The πHVC can lead us to various simple relationships between polarizabilities, aided by the two auxiliary conditions stemming from the conservation of the number of electrons and from the Hellmann-Feynman theorem. The relationships, being characteristic of a system, will be useful for considering the reactivity of the system within the Hückel model. The πHVC must have wide applicability as the pHVC.

We have the four sections below: The first section, deriving the πHVC from the pHVC after preparation of basic definitions, gives some general remarks on the πHVC. The second is a brief account of the symmetry condition and the intrinsic πHVC nontrivial under the symmetry condition. The third concerns the two auxiliary conditions and the last includes several examples illustrating how the πHVC and the auxiliary conditions work practically.

The Hypervirial Condition upon Polarizabilities

Let us consider the Hückel model of an electronic system of m sites. Denote the set $\{1, \cdots, m\}$ of the sites by M and the set of the up- and the down-spin states by Ω. Assume that the Hückel matrix B is real symmetric and that the Hückel model Hamiltonian $H(B)$ depends parametrically on the components $\{b_{rs}\}$ of B under the $m(m-1)/2$ constraints

$$b_{rs}=b_{sr} \qquad (r<s\in M). \tag{1}$$

Using the annihilators $\{a_{r\mu}\}$ and the creators $\{a^\dagger_{r\mu}\}$ for the $2m$ one-electron quantum states $\{r\mu\}$, we can write $H(B)$ explicitly as

$$H(B)=\sum_{r,s\in M} b_{rs}\rho_{rs} \tag{2}$$

with

$$\rho_{rs}=\sum_{\mu\in\Omega}(a^\dagger_{r\mu}a_{s\mu}+a^\dagger_{s\mu}a_{r\mu})/2. \tag{3}$$

For each normalized eigenstate $|B\rangle$ of $H(B)$ we have the matrix $P(B)$ of p-densities

$$p_{rs}(B)=\langle B|\rho_{rs}|B\rangle \qquad (r,s\in M). \tag{4}$$

Polarizabilities $\{\pi^{tu}_{rs}(B)\}$ are defined as[4]

$$\pi^{tu}_{rs}(B)=\frac{\partial}{\partial b_{tu}}p_{rs}(B) \qquad (r,s,t,u\in M), \tag{5}$$

which have the following inherent symmetry for interchange of subscripts.

$$\pi^{tu}_{rs}(B)=\pi^{tu}_{sr}(B)=\pi^{ut}_{rs}(B)=\pi^{ut}_{sr}(B) \tag{6}$$

and

$$\begin{cases}\pi^{tu}_{rs}(B)=\pi^{rs}_{tu}(B) & (r=s,\ t=u \text{ or } r\neq s,\ t\neq u)\\ \pi^{tu}_{rr}(B)=2\pi^{rr}_{tu}(B) & (t\neq u).\end{cases} \tag{7}$$

Let $\Pi^{tu}(B)$ be the matrix having $\pi^{tu}_{rs}(B)$ as r,s-component;

$$\Pi^{tu}(B)=\frac{\partial}{\partial b_{tu}}P(B) \qquad (t,u\in M), \tag{8}$$

which is real symmetric as well as $P(B)$.

Now, the pHVC for the Hamiltonian $H(B)$ can be written in the matrix form as[1]

$$[B, P(B)]=0. \tag{9}$$

Differentiating this with respect to b_{tu}, we obtain the πHVC

$$[B, \Pi^{tu}(B)]=\Phi^{tu}(B) \qquad (t\leqq u\in M), \tag{10}$$

where $\Phi^{tu}(B)$ is the real antisymmetric matrix having the components $\{\phi^{tu}_{rs}(B)\}$ expressible in general form as

$$\begin{aligned}\phi^{tu}_{rs}(B)=(&\delta_{st}p_{ru}(B)-\delta_{rt}p_{su}(B)\\ &+\delta_{su}p_{rt}(B)-\delta_{ru}p_{st}(B))/(1+\delta_{tu}).\end{aligned} \tag{11}$$

Each of the components is actually quite simple even if nonvanishing. The matrix $\Phi^{tu}(B)$ is invariant for interchange of subscripts tu as well as $\Pi^{tu}(B)$.

What is to be kept in mind is that the πHVC is formally common to all the eigenstates of $H(B)$ without regard to the number of electrons as the pHVC is. Say, supposing the one-electron eigenstate, we can regard polarizabilities and p-densities in the πHVC as being due to one Hückel orbital. We can suppose not only ground but also excited states. Now assume that a system in $|B\rangle$ is perturbed with the change of b_{tu} that alters B to B'. Then, the electron distribution in the system is so rearranged as to fit $|B'\rangle$. What the πHVC means here is that the rearrangement occurs keeping some detailed balance, and that the detailed balance is of the same character for all the eigenstates of $H(B)$.

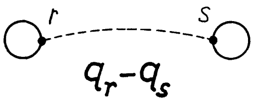
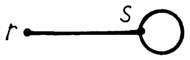
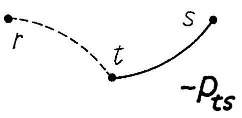
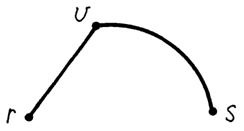
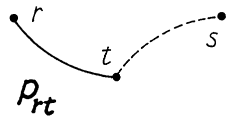
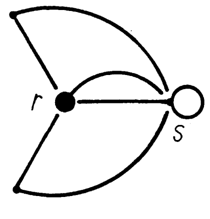
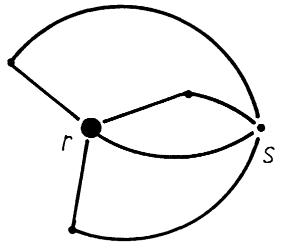
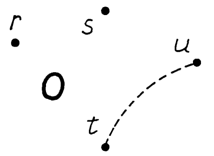
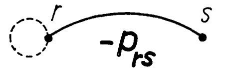
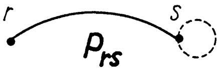
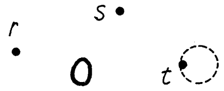
So far, the Hückel matrix B remains parametric, specified only by its dimension m the number of sites. Actually, we are almost always interested in the effect of small changes of b_{tu} at certain standard "values" $\{\beta_{rs}\}$ of $\{b_{rs}\}$. Let B_0 be the Hückel matrix having the components $\{\beta_{rs}\}$ and let us omit the argument symbol (B) after the substitution of B_0. In what follows, the πHVC at $B=B_0$

$$[B_0, \Pi^{tu}] = \Phi^{tu} \qquad (t \leqq u \in M) \tag{12}$$

is considered exclusively, where B_0 reflects the structural and the symmetry features of the system. The terms "the simple Hückel model" and "the semisimple Hückel model" 7) are operative with regard to B_0. Thus, the simple Hückel model has the πHVC of the form

$$[J, \Pi^{tu}] = \Phi^{tu} \qquad (t \leqq u \in M) \tag{13}$$

Table 1. Dictionary of the Diagrammatic Representation of πHVRs in the Semisimple Hückel Model a)

Term	Diagram	Term	Diagram
$\alpha_r\pi^{tu}_{rs}$ b)		ϕ^{rs}_{rs}	
$\beta_{rs}\pi^{tu}_{ss}$ c)		ϕ^{rt}_{rs}, ϕ^{tr}_{rs} ($t\neq s$)	
$\beta_{rv}\pi^{tu}_{vs}$ ($v\neq r,s$)		ϕ^{st}_{rs}, ϕ^{ts}_{rs} ($t\neq r$)	
ψ^{tu}_{rs}	 	ϕ^{tu}_{rs} ($t\neq r,s$; $u\neq r,s$)	
		ϕ^{rr}_{rs} d)	
		ϕ^{ss}_{rs}	
		ϕ^{tt}_{rs} ($t\neq r,s$)	

a) The symbols α_r and q_r are used instead of β_{rr} and p_{rr}, respectively. b) This term is ignorable in the simple Hückel model, canceling the corresponding term in ψ^{tu}_{sr}. c) This term appears only for adjacent rs, sharing the factor β_{rs} with the corresponding term in ψ^{tu}_{sr}. d) These three are really special cases of the above.

with the adjacency matrix J.[8] Here, Π^{tu} stands for $\beta\Pi^{tu}$ with β the sole resonance integral between adjacent sites.

The πHVC consists of linear equations to be fulfilled by polarizabilities, which can be written as

$$\psi^{tu}_{rs} - \psi^{tu}_{sr} = \phi^{tu}_{rs} \qquad (r<s,\ t\leqq u\in M) \tag{14}$$

with

$$\psi^{tu}_{rs} = \sum_{v\in M} \beta_{rv}\pi^{tu}_{vs}. \tag{15}$$

The case of $r\geqq s$ is excluded because of the antisymmetry. Each of the equations, specified by upper tu and lower rs subscripts, is called the πHVR (hypervirial relationship between polarizabilities) for $[rs]tu$. In particular, for the simple Hückel model, we can put

$$\psi^{tu}_{rs} = \sum_{v\in C_r} \pi^{tu}_{vs}, \tag{16}$$

using the set C_r of the sites adjacent to r and rewriting $\beta\pi^{tu}_{rs}$ as π^{tu}_{rs}. Exceptional cases aside, no πHVR contains many terms in the simple Hückel model even if m becomes large. The situation is similar in the semisimple Hückel model.

We can represent πHVRs with simple diagrams on structural formulas in the semisimple Hückel model. The diagrammatic representation is especially useful for writing out πHVRs for individual systems. Table 1 is an adequate dictionary of the diagrammatic representation of πHVRs, doubling as a list of the concrete expressions of ϕ^{tu}_{rs}'s. Note that the representation of ψ^{tu}_{rs} is not affected by upper subscripts.

The Symmetry Condition and the Intrinsic πHVC

Let G be the permutation group on M that consists of all the permutations $\{x\}$ keeping B_0 invariant in the sense that[1]

$$\beta_{xrxs} = \beta_{rs} \qquad (r,s\in M). \tag{17}$$

Then, we have the permutational symmetry condition

$$\pi^{xtxu}_{xrxs} = \pi^{tu}_{rs} \qquad (r,s,t,u\in M) \tag{18}$$

for faithful states.[9] Confine ourselves to faithful states whenever the permutational symmetry is taken into account. Incorporating the inherent symmetry into the permutational symmetry condition, we have the symmetry condition.

Let us refer to the πHVR remaining nontrivial under the symmetry condition as the intrinsic πHVR. All the intrinsic πHVRs together constitute the intrinsic πHVC. As to how to draw out intrinsic πHVRs, the situation being similar to that for intrinsic pHVRs[1] (hypervirial relationships between p-densities), details are omitted here. The crucial point peculiar to intrinsic πHVRs is that the value of b_{tu} for the perturbed position tu[10] should be regarded tentatively as being off β_{tu}, and that the tentative perturbed symmetry should be considered for each tu individually.

Let G^{tu} be the subgroup of G that consists of all the permutations $\{x\}$ satisfying $x(tu)=tu$ or $x(tu)=ut$. In many cases, G^{tu} is a tiny group of order one or two, even if the order of G is large. The following guidelines will suffice to draw out intrinsic πHVRs practically. The last one is determinative.

(1) The πHVR for $[x(rs)]tu$ is identical with that for $[rs]x^{-1}(tu)$ for any $x\in G$.

(2) The πHVR for $[r's']tu$ is identical with that for $[rs]tu$ if there exists $x\in G^{tu}$ satisfying $r's'=x(rs)$.

(3) The πHVR for $[rs]tu$ is intrinsic unless there exists $x\in G^{tu}$ satisfying $sr=x(rs)$.

Apart from exceptional cases, all the intrinsic pHVRs of a system are necessarily independent.[1,11] In contrast to this, it is possible for some intrinsic πHVRs to be mutually dependent. When a system has intrinsic pHVRs, it is also possible for some intrinsic πHVRs to contain the intrinsic pHVRs implicitly. Then, reversely, the intrinsic pHVRs make the intrinsic πHVRs mutually dependent.

The symmetry condition classifies polarizabilities into sets of equivalent polarizabilities. Taking one polarizability from each set as a representative, we have the symmetry-independent representatives, which are abbreviated to the SIRs below. When we treat a lot of equations for polarizabilities simultaneously, it is helpful or rather necessary to translate the equation containing arbitrary polarizabilities into that containing only SIRs.

The Auxiliary Conditions

The analysis with the πHVC is facilitated by using the following two auxiliary conditions,[12] particularly when a system does not have many sites. Both conditions are also formally common to all the eigenstates of $H(B)$ without regard to the number of electrons.

The Number Conservation Condition. The number n of electrons can be constant for the change of b_{tu}. Hence, differentiating the number condition

$$\mathrm{Tr}(P(B)) = n \tag{19}$$

with respect to b_{tu} and substituting B_0 for B, we have the number consevation condition

$$\mathrm{Tr}(\Pi^{tu}) = 0 \qquad (t\leqq u\in M), \tag{20}$$

each constituent of which is referred to as the NCR (number conservation relationship) for tu. The NCR for $x(tu)$ is identical with that for tu for any $x\in G$.

The number conservation condition makes πHVRs for $[rs]tt$'s for arbitrary rs and all t's mutually dependent, since we have

$$\sum_{t\in M}[B_0, \Pi^{tt}] = 0 \tag{21}$$

as well as

$$\sum_{t\in M}\Phi^{tt} = 0. \tag{22}$$

The intrinsic πHVC is, therefore, not always independent of the number conservation condition.

The Polarizability Sum Condition. It follows from the Hellmann–Feynman theorem[13)] immediately that

$$\left(\frac{\partial}{\partial b_{tu}}\langle B|\right)H(B)|B\rangle+\langle B|H(B)\left(\frac{\partial}{\partial b_{tu}}|B\rangle\right)=0 \quad (t\leqq u\in M). \tag{23}$$

Using the expression

$$\pi_{rs}^{tu}(B)=\left(\frac{\partial}{\partial b_{tu}}\langle B|\right)\rho_{rs}|B\rangle+\langle B|\rho_{rs}\left(\frac{\partial}{\partial b_{tu}}|B\rangle\right) \tag{24}$$

and substituting B_0 for B, we obtain the polarizability sum condition[14)]

$$\mathrm{Tr}(B_0 \Pi^{tu})=0 \qquad (t\leqq u\in M), \tag{25}$$

each constituent of which is referred to as the PSR (polarizability sum relationship) for tu. The PSR for $x(tu)$ is identical with that for tu for any $x\in$G. Since

$$\sum_{t\in M}\mathrm{Tr}(B_0 \Pi^{tt})=0 \tag{26}$$

holds, PSRs for tt's become mutually dependent under the number conservation condition.

By using the polarizability sum condition it is readily found that

$$\sum_{t\leqq u\in M}\beta_{tu}[B_0, \Pi^{tu}]=0, \tag{27}$$

while we obtain

$$\sum_{t\leqq u\in M}\beta_{tu}\Phi^{tu}=[P, B_0]. \tag{28}$$

That is, πHVRs for $[rs]tu$'s for arbitrary rs and all $t\leqq u$'s[15)] together yield the pHVR for rs. This brings on the case that some intrinsic πHVRs become mutually dependent under the polarizability sum condition and the intrinsic pHVC.

To write out PSRs practically, it is preferable to arrange the terms as

$$\sum_{r\in M}\beta_{rr}\pi_{rr}^{tu}+2\sum_{r<s\in M}\beta_{rs}\pi_{rs}^{tu}=0 \qquad (t\leqq u\in M), \tag{29}$$

which is reduced for the simple Hückel model to

$$\sum_{r<s\in M}{}' \pi_{rs}^{tu}=0 \qquad (t\leqq u\in M). \tag{30}$$

Here, the prime means that the summation is restricted to adjacent sites.

It remains still possible for other additional dependence to occur in intrinsic πHVRs. However, it seems quite knotty to analyze the situation exhaustively to ascertain a fully systematic way of extracting only independent equations from all the conditions. Fortunately, this annoying point for completeness causes no serious difficulties actually.

Illustrative Examples

To treat typical systems with the πHVC and the auxiliary conditions will be the best way of understanding the nature of the conditions. Throughout this section, π_{rs}^{tu} is used for $\beta\pi_{rs}^{tu}$, being dimensionless and opposite to the original one in sign with β negative. See Fig. 1 for the numbering of sites and the notation for p-densities.

The Symmetric Two-Site System. This system provides the simplest example of the intrinsic πHVC. Let us choose π_{11}^{11}, π_{22}^{11}, π_{12}^{11}, and π_{12}^{12} as the SIRs. Even if b_{12} becomes off β, the two sites remain equivalent; if b_{11} becomes off α, the symmetry vanishes. Hence,

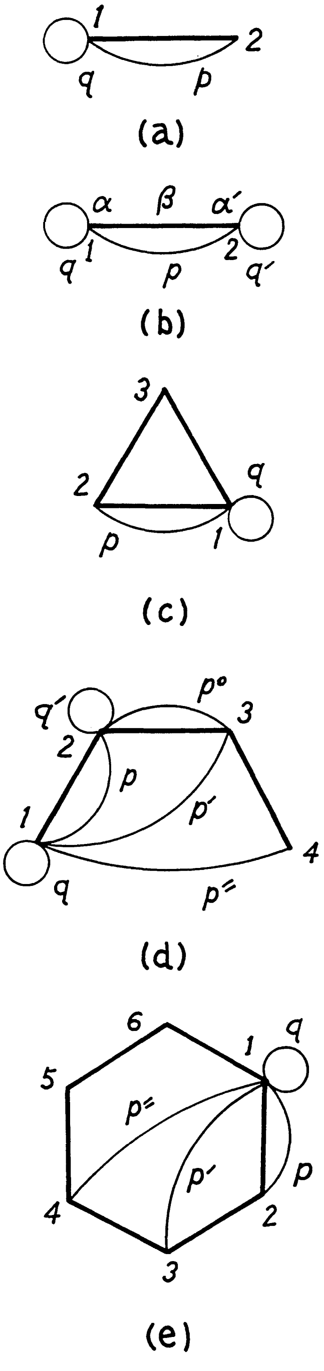


Fig. 1. The notation and the numbering of sites in the examples: (a) The symmetric two-site system, (b) The asymmetric two-site system, (c) The three-site ring, (d) The four-site linear chain, (e) The six-site ring.

only the πHVR for [12]11

$$\pi_{22}^{11}-\pi_{11}^{11}=-p \tag{31}$$

is intrinsic. From this and the NCR for 11

$$\pi_{11}^{11}+\pi_{22}^{11}=0 \tag{32}$$

it follows that

$$\pi_{11}^{11}=-\pi_{22}^{11}=p/2. \tag{33}$$

The PSRs for 11 and 12 are, in themselves,

$$\pi_{12}^{11}=\pi_{12}^{12}=0. \tag{34}$$

We have positive π_{11}^{11}, as expected, for the ground state of less than four electrons. Yet, if p is negative or zero, so is π_{11}^{11}, which is really the case for excited states.

The Asymmetric Two-Site System. This system can exemplifies the relation between the conditions concisely. Choose π_{11}^{11}, π_{22}^{11}, π_{12}^{11}, π_{22}^{22}, π_{12}^{22}, and π_{12}^{12} as the SIRs. Under the NCRs for 11, 22, and 12

$$\pi_{11}^{11}+\pi_{22}^{11}=0, \tag{35}$$

$$\pi_{22}^{11}+\pi_{22}^{22}=0, \tag{36}$$

and

$$\pi_{12}^{11}+\pi_{12}^{22}=0, \tag{37}$$

the PSRs for 11 and 22 become dependent on each other, leading to

$$\lambda\pi_{11}^{11}+\pi_{12}^{11}=0 \tag{38}$$

with

$$\lambda=(\alpha-\alpha')/2\beta. \tag{39}$$

The PSR for 12 is written, by using the NCR for 12, as

$$2\lambda\pi_{12}^{11}+\pi_{12}^{12}=0. \tag{40}$$

These five equations suffice to express all the SIRs in terms of π_{11}^{11}. The π_{11}^{11}-expression

$$\begin{cases}\pi_{22}^{22}=-\pi_{22}^{11}=\pi_{11}^{11}\\ \pi_{12}^{11}=-\pi_{12}^{22}=-\lambda\pi_{11}^{11}\\ \pi_{12}^{12}=2\lambda^{2}\pi_{11}^{11}\end{cases} \tag{41}$$

is instructive in itself showing the sign and the order of each SIR.

The intrinsic πHVC consists of three πHVRs. The NCRs make the πHVRs for [12]11 and [12]22 dependent on each other. Using the π_{11}^{11}-expression in the πHVR for [12]11

$$2\lambda\pi_{12}^{11}+\pi_{22}^{11}-\pi_{11}^{11}=-p, \tag{42}$$

we find

$$\pi_{11}^{11}=p/2(1+\lambda^{2}), \tag{43}$$

which enables us to express the other SIRs in terms of p and λ.16) On the other hand, the πHVR for [12]12

$$2\lambda\pi_{12}^{12}+2\pi_{12}^{22}-2\pi_{12}^{11}=q-q' \tag{44}$$

results in the intrinsic pHVR1)

$$2\lambda p=q-q'. \tag{45}$$

With this presupposed, the πHVR for [12]12 is no longer independent of the others.

The Three-Site Ring. Next, take the smallest ring in the simple Hückel model, the simplest nonalternant system. This system has the five independent equations connecting the six SIRs π_{11}^{11}, π_{22}^{11}, π_{12}^{11}, π_{23}^{11}, π_{12}^{12}, and π_{23}^{12}. Let us, therefore, find the π_{11}^{11}-expression of the SIRs. From the auxiliary conditions, we have

$$\pi_{22}^{11}=-\pi_{11}^{11}/2, \tag{46}$$

$$\pi_{12}^{11}=-\pi_{23}^{11}/2, \tag{47}$$

and

$$\pi_{23}^{12}=-\pi_{12}^{12}/2, \tag{48}$$

which are substituted into the πHVRs

$$\pi_{22}^{11}+\pi_{23}^{11}-\pi_{11}^{11}-\pi_{12}^{11}=-p \tag{49}$$

and

$$2\pi_{12}^{11}+\pi_{12}^{12}-2\pi_{23}^{11}-\pi_{23}^{12}=p \tag{50}$$

to yield

$$\pi_{23}^{11}=\pi_{11}^{11}-2p/3 \tag{51}$$

and

$$\pi_{12}^{12}=2(\pi_{11}^{11}-p/3). \tag{52}$$

Note that this system has the degeneracy causing nonfaithful states, to which the above relationships are inapplicable. The one- and the two-electron ground states, necessarily faithful, have $\pi_{11}^{11}=4p/9$ and $p=n/3$, which leads to, say,

$$\pi_{23}^{11}-\pi_{12}^{11}=-n/9 \tag{53}$$

and

$$\pi_{12}^{12}-\pi_{23}^{12}=n/9. \tag{54}$$

No explanation will be necessary as to what these mean.

The Four-Site Linear Chain. The number of the SIRs amounts to thirty-one for the four-site linear chain even in the simple Hückel model. The auxiliary conditions give seven independent equations. The number of the intrinsic πHVRs that remain independent of one another and of the auxiliary conditions is twenty-one under the intrinsic pHVC

$$\begin{cases}p'=q'-q\\ p''=p^{\circ}-p.\end{cases} \tag{55}$$

Fortunately, the thirty-one SIRs are seperated into three sets in entering twenty-eight equations because of the alternant symmetry and the number of SIRs of each set is one more than that of equations for the set. All the SIRs of each set are, hence, expressible in terms of one SIR of the set. Because each equations contains, at most, only four SIRs, it is never intractable to work out the equations in spite of the largeness of the number of SIRs.

The twelve SIRs π_{11}^{11}, π_{22}^{11}, π_{33}^{11}, π_{44}^{11}, π_{22}^{22}, π_{33}^{22}, π_{13}^{11}, π_{24}^{11}, π_{13}^{22}, π_{24}^{22}, π_{13}^{13}, and π_{24}^{13} concern the three NCRs for 11, 22, and 13

$$\pi_{11}^{11}+\pi_{22}^{11}+\pi_{33}^{11}+\pi_{44}^{11}=0, \tag{56}$$

$$\pi_{22}^{11}+\pi_{22}^{22}+\pi_{33}^{22}+\pi_{33}^{11}=0, \tag{57}$$

and

$$\pi_{13}^{11}+\pi_{13}^{22}+\pi_{24}^{22}+\pi_{24}^{11}=0, \tag{58}$$

and the eight πHVRs for [12]11, [12]33, [12]13, [23]11, [23]22, [14]11, [14]22, and [14]13

$$\pi_{22}^{11}-\pi_{11}^{11}-\pi_{13}^{11}=-p, \tag{59}$$

$$\pi_{33}^{22}-\pi_{33}^{11}-\pi_{24}^{22}=0, \tag{60}$$

$$2\pi_{13}^{22}-2\pi_{13}^{11}-\pi_{13}^{13}=-p^{\circ}, \tag{61}$$

$$\pi_{33}^{11}+\pi_{13}^{11}-\pi_{22}^{11}-\pi_{24}^{11}=0, \tag{62}$$

$$\pi_{33}^{22}+\pi_{13}^{22}-\pi_{22}^{22}-\pi_{24}^{22}=-p^{\circ}, \tag{63}$$

$$\pi_{24}^{11}-\pi_{13}^{11}=-p'', \tag{64}$$

$$\pi_{24}^{22}-\pi_{13}^{22}=0, \tag{65}$$

and

$$\pi_{24}^{13}-\pi_{13}^{13}=-p. \tag{66}$$

The last three may be suggestive by themselves. Expressing the SIRs in terms of π_{11}^{11}, we obtain the result summarized in Table 2. We can reconstruct arbitrary relationships between the SIRs using only π_{11}^{11}, p, and p°, at most. For the four-electron ground state, an easy, direct estimation[5] gives $\pi_{11}^{11}=0.626$, $p=0.894$, and $p^{\circ}=0.447$, which is enough to estimate the other SIRs.

On the other hand, the seven SIRs π_{12}^{12}, π_{23}^{23}, π_{23}^{12}, π_{34}^{12}, π_{14}^{12}, π_{14}^{23}, and π_{14}^{14} concern the three PSRs for 12, 23, and 14

$$\pi_{12}^{12}+\pi_{23}^{12}+\pi_{34}^{12}=0, \tag{67}$$

$$2\pi_{23}^{12}+\pi_{23}^{23}=0, \tag{68}$$

and

$$2\pi_{24}^{12}+\pi_{14}^{23}=0, \tag{69}$$

and the three πHVRs for [13]12, [13]23, and [13]14

$$\pi_{23}^{12}-\pi_{12}^{12}-\pi_{14}^{12}=-p^{\circ}, \tag{70}$$

$$\pi_{23}^{23}-\pi_{23}^{12}-\pi_{14}^{23}=p, \tag{71}$$

and

$$\pi_{14}^{23}-\pi_{14}^{12}-\pi_{14}^{14}=-p, \tag{72}$$

which suffice to express the SIRs in terms of π_{12}^{12}. The result is summarized in Table 3. For the four-electron ground state, we can use $\pi_{12}^{12}=0.089$ to estimate the other SIRs. As to the remaining twelve SIRs and eleven equations, the description is omitted for brevity.

Table 2. The π_{11}^{11}-Expression of Some SIRs of the Four-Site Linear Chain in the Simple Hückel Model[a)]

tu	rs	c_1	c_p	$c_{p^{\circ}}$
22	22	1	−1/2	1/2
11	22	−1	0	1/2
11	33	−1	1	−1/2
11	44	1	−1	0
22	33	1	−1/2	−1/2
11	13	−2	1	1/2
11	24	−2	3/2	0
22	13,24	2	−3/2	0
13	13	8	−5	0
13	24	8	−6	0

a) $\pi_{rs}^{tu}=c_1\pi_{11}^{11}+c_p p+c_{p^{\circ}}p^{\circ}$.

It must be relevant to mention here the general features of the πHVC for alternant systems. Define the indicator σ_r of the attribute of site r as

$$\sigma_r=\begin{cases}1 & (r\text{ starred})\\ -1 & (r\text{ unstarred})\end{cases} \tag{73}$$

and classify polarizabilities of an alternant system into three sets as

$$\pi_{rs}^{tu}=\begin{cases}{}^1\pi_{rs}^{tu} & (\sigma_r\sigma_s=\sigma_t\sigma_u=1)\\ {}^2\pi_{rs}^{tu} & (\sigma_r\sigma_s=\sigma_t\sigma_u=-1)\\ {}^3\pi_{rs}^{tu} & (\sigma_r\sigma_s\sigma_t\sigma_u=-1).\end{cases} \tag{74}$$

Then, the πHVRs can be classified also into three sets;

$$\sum_{v\in C_r}\beta_{rv}{}^i\pi_{vs}^{tu}-\sum_{v\in C_s}\beta_{sv}{}^i\pi_{vr}^{tu}={}^i\phi_{rs}^{tu} \qquad (i=1,2,3) \tag{75}$$

with

$$\phi_{rs}^{tu}=\begin{cases}{}^1\phi_{rs}^{tu} & (\sigma_r\sigma_s=-1;\ \sigma_t\sigma_u=1)\\ {}^2\phi_{rs}^{tu} & (\sigma_r\sigma_s=1;\ \sigma_t\sigma_u=-1)\\ {}^3\phi_{rs}^{tu} & (\sigma_r\sigma_s=\sigma_t\sigma_u).\end{cases} \tag{76}$$

The NCRs and the PSRs are classified as

$$\sum_{r\in M}{}^i\pi_{rr}^{tu}=0 \qquad (i=1,3) \tag{77}$$

and

$$\sum_{r<s\in M}{}' \beta_{rs}{}^i\pi_{rs}^{tu}=0 \qquad (i=2,3). \tag{78}$$

In particular, for the m-electron ground state of the m-site alternant system ${}^3\phi_{rs}^{tu}$'s are all vanishing and the equations for $i=3$ give nothing more than

$${}^3\pi_{rs}^{tu}=0 \tag{79}$$

a natural consequence of the fact that no perturbation at the site pair of different attributes violates the alternant symmetry.[17)]

The Six-Site Ring. The last example is the simple Hückel model of the six-site ring, which has no intrin-

Table 3. The π_{12}^{12}-Expression of Some SIRs of the Four-Site Linear Chain in the Simple Hückel Model[a)]

tu	rs	c_{12}	c_p	$c_{p^{\circ}}$
23	23	4	2	−4
12	23	−2	−1	2
12	34	1	1	−2
23	14	6	2	−6
12	14	−3	−1	3
14	14	9	4	−9

a) $\pi_{rs}^{tu}=c_{12}\pi_{12}^{12}+c_p p+c_{p^{\circ}}p^{\circ}$.

sic *p*HVR. The intrinsic πHVC gives seventeen independent equations under the auxiliary conditions consisting of seven independent equations. The thirty SIRs enter twenty-four equations, separated into three sets. We have ten, eight, and six equations, respectively, for twelve, ten, and eight SIRs. Hence, all the SIRs of each set are expressible in terms of relevantly chosen two SIRs of the set.

The description here is, however, confined to the derivation of a few relationships between atom-atom polarizabilities. Substituting the πHVR for [14]11

$$\pi^{11}_{24}-\pi^{11}_{13}=-p''/2 \tag{80}$$

into that for [12]33

$$\pi^{11}_{22}+\pi^{11}_{24}-\pi^{11}_{33}-\pi^{11}_{13}=0, \tag{81}$$

we obtain

$$\pi^{11}_{22}-\pi^{11}_{33}=p''/2. \tag{82}$$

From the πHVRs for [12]11, [12]44, and [14]22

$$\pi^{11}_{22}+\pi^{11}_{26}-\pi^{11}_{11}-\pi^{11}_{13}=-p, \tag{83}$$

$$\pi^{11}_{33}+\pi^{11}_{35}-\pi^{11}_{44}-\pi^{11}_{24}=0, \tag{84}$$

and

$$\pi^{11}_{13}+\pi^{11}_{35}-\pi^{11}_{26}-\pi^{11}_{24}=0, \tag{85}$$

it follows that

$$\pi^{11}_{11}-\pi^{11}_{22}+\pi^{11}_{33}-\pi^{11}_{44}=p, \tag{86}$$

which leads to

$$\pi^{11}_{11}-\pi^{11}_{44}=p+p''/2. \tag{87}$$

Further, using the NCR for 11

$$\pi^{11}_{11}+2\pi^{11}_{22}+2\pi^{11}_{33}+\pi^{11}_{44}=0, \tag{88}$$

we attain the π^{11}_{11}-expression

$$\begin{cases} \pi^{11}_{22}=-\pi^{11}_{11}/2+p/4+3p''/8 \\ \pi^{11}_{33}=-\pi^{11}_{11}/2+p/4-p''/8 \\ \pi^{11}_{44}=\pi^{11}_{11}-p-p''/2. \end{cases} \tag{89}$$

Note that these relationships are valid for any faithful states without regard to the number of electrons. For the six-electron ground state, although the values of all the atom-atom polarizabilities are already known,5) the above relationships remain eloquent of how simply but delicately the polarizabilities are interrelated.

As the above treatment shows, we can often attain the result of significance only by working out some equations in the πHVC and the other conditions. This is an important advantage from an applicational point of view.

References

1) M. Isihara, *Bull. Chem. Soc. Jpn.*, **62**, 2284 (1989).

2) Site electron densities and bond orders are called generically *p*-densities, for convenience' sake. Ref. 11 of Ref. 1 includes the reason for the name.

3) The term "polarizability" has been used peculiarly in the Hückel model since Coulson and Longuet-Higgins' papers. The term has another meaning in the theory of dielectrics and it is prevalent to use the term fixedly for that meaning. Some authors prefer "mutability" to "polarizability." Still, we seem to have no decisive alternative at present.

4) C. A. Coulson and H. C. Longuet-Higgins, *Proc. R. Soc. London, Ser. A*, **191**, 39 (1947), the inceptive paper on polarizabilities in the Hückel model.

5) C. A. Coulson and H. C. Longuet-Higgins, *Proc. R. Soc. London, Ser. A*, **192**, 16 (1947); **193**, 447 (1948), which include the first basic applications of polarizabilities.

6) S. Aono and K. Nishikawa, *Bull. Chem. Soc. Jpn.*, **58**, 288 (1985), where polarizabilities are treated in a propagator formalism.

7) For the definition of these terms, see Ref. 1.

8) For the adjacency matrix, see, for example, Refs. 4 and 15 of Ref. 1.

9) The faithful eigenstate was introduced in Ref. 1, associated with the degeneracy, for which P.-O. Löwdin, *J. Chem. Phys.*, **21**, 496 (1953) may be suggestive.

10) Even if β_{tu} is zero, we should not ignore the change of b_{tu}. The perturbed position can be the site pair *tu* of vanishing β_{tu}.

11) The term "independent" is often used to mean "linearly independent" for short; so is "dependent."

12) Though Coulson and Longuet-Higgins have touched upon both conditions (Ref. 4), they have regarded the conditions only as such as checking tools for numerical calculation.

13) For example, S. T. Epstein, "The Hellmann-Feynman Theorem," in "The Force Concept in Chemistry," ed by B. M. Deb, Van Nostrand Reinhold, New York (1981).

14) This derivation is a little more transparent than Coulson and Longuet-Higgins' one.

15) The simple Hückel model allows us to replace "all $t\leqq u$" with "all adjacent $t<u$" here.

16) This does not mean that the dependence of the polarizabilities on λ is fully resolved, because *p* itself dependes on λ.

17) Obviously, π^{tu}_{rr} are zero for adjacent *tu*'s, but ${}^{1}\pi^{tu}_{rr}$ does not vanish, in general.