A Theorem on *p*-Densities in the Hückel Model of Linear Chains

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Synopsis. The hyperivial condition upon *p*-densities is applied to the simple Hückel model of linear chains. The invariance of the modified *p*-density is derived in fully generalized form. Any bond order between nonadjacent sites is shown expressible in terms of two electron densities or two bond orders between adjacent sites.

The author has manifested the significance and the usefulness of the hypervirial condition upon *p*-densities[1] in the Hückel model in the previous paper,[2] where he has mentioned a few consequences of the condition in the simple Hückel model[3] of linear chains as an illustrative example. In this note, the invariance of the modified electron density and that of the modified bond order between adjacent sites are fully generalized in a systematic way. The resulting theorem enables us to express any bond order between nonadjacent sites in terms of two electron densities or two bond orders between adjacent sites. In particular, for the neutral ground state, this means that an analytic expression is given to the bond order between nonadjacent sites. A few remarks are added last on the treatment of linear chain parts.

The following mathematical notation is used throughout. The symbol $[z_s,z_l]$ stands for the set of integers that contains z_s and z_l as the smallest and the largest elements, respectively; understand the set to be empty if $z_l<z_s$. The symbol $[z]$ means the largest integer not more than z.

Suppose the linear chain of m sites in the simple Hückel model. Number the sites consecutively from 1 to m and denote $[1,m]$ by M. Each stationary state has its *p*-densities $\{p_{rs}\}$ $(r,s\in M)$, which fulfil the hypervirial relationships[2]

$$p_{r+1,s}+p_{r-1,s}-p_{r,s-1}-p_{r,s+1}=0 \qquad (r<s\in M). \tag{1}$$

Here, understand the term having an improper subscript as being absent. Although the inherent symmetry

$$p_{sr}=p_{rs} \qquad (r,s\in M) \tag{2}$$

is assumed, we need not consider the symmetry of the system for the present purpose.

Introduce the index b taking the two values 0 and 1, and define p_{bvi} by

$$p_{bvi}=p_{v-i,v+b+i} \tag{3}$$

for vi of the range expressed as follows. Let M_b be $[1,m-b]$ and d_{bv} be the largest i for each $v\in M_b$;

$$d_{bv}=\begin{cases} v-1 & (v\in[1,c_b]) \\ m-b-v & (v\in[c_b+1,\,m-b]) \end{cases} \tag{4}$$

with

$$c_b=[(m-b+1)/2]. \tag{5}$$

Denoting $[0,d_{bv}]$ by D_{bv}, we have $i\in D_{bv}$ with $v\in M_b$. The other expression of the range is often useful. Let d_b be the largest of d_{bv}'s $(v\in M_b)$ given by

$$d_b=[(m-b-1)/2] \tag{6}$$

and denote $[0,d_b]$ by D_b and $[1+i,m-b-i]$ by M_{bi}. Then, we have $v\in M_{bi}$ with $i\in D_b$. Any site pair index rs $(r\leqq s\in M)$ can be transformed by

$$b=\begin{cases} 0 & (s-r \text{ even}) \\ 1 & (s-r \text{ odd}), \end{cases} \tag{7}$$

$$v=(r+s-b)/2, \tag{8}$$

and

$$i=(s-r-b)/2 \tag{9}$$

into the present triple index bvi uniquely.

Now, let us define the modified *p*-density ξ_{bvi} for each $i\in D_b$ as

$$\xi_{bvi}=\begin{cases} p_{bvi}-p_{bv,i+1} & (v\in M_{b,i+1}) \\ p_{bvi} & (v=1+i,\,m-b-i). \end{cases} \tag{10}$$

Then, the hypervirial relationships can be rewritten as

$$\xi_{bvi}=\xi_{b,v+1,i} \qquad (v,\,v+1\in M_{bi})\ (i\in D_b). \tag{11}$$

Successive applications of these lead immediately to [4]

$$\xi_{bvi}=\xi_{bwi} \qquad (v,\,w\in M_{bi})\ (i\in D_b), \tag{12}$$

which can be further generalized as shown below.

Let $D_b(f)$ be $[0,d_b-f]$ for each $f\in D_b$ and redefine the modified *p*-density $\xi_{bvi}(f)$ for each $i\in D_b(f)$ as

$$\xi_{bvi}(f)=\begin{cases} p_{bvi}-p_{bv,i+f+1} & (v\in M_{b,i+f+1}) \\ p_{bvi} & (v=1+f+i,\,m-b-f-i), \end{cases} \tag{13}$$

which contains the preceding modified p-density as the particular case of $f=0$. Because $\xi_{bvi}(f)$ can be written as

$$\xi_{bvi}(f) = \sum_{k=i}^{i+f} \xi_{bvk}, \tag{14}$$

we attain the theorem

$$\xi_{bvi}(f) = \xi_{bwi}(f) \quad (v, w \in M_{b,i+f}) \ (i \in D_b(f)) \ (f \in D_b), \tag{15}$$

namely, "The modified p-density is an invariant every fi." The theorem is ready to yield readable relationships:

(1) Let both of v and w belong to $M_{b,i+f+1}$ and rewrite $i+f+1$ as j. Then, for $i<j$, we have

$$p_{bvj} - p_{bwj} = p_{bvi} - p_{bwi} \qquad (v, w \in M_{bj}). \tag{16}$$

(2) Let v be $1+f+i$ and d_{bw} be larger than d_{bv}. Then, we have

$$p_{bwv} = p_{bwi} - p_{bvi} \qquad (i \in D_{bv}). \tag{17}$$

(3) Let v be $1+f+i$ and w be $m-b-f-i$. Then, the symmetry condition

$$p_{bvi} = p_{b,m-b+1-v,i} \qquad (v \in [1,c_b]) \tag{18}$$

follows.

Important is the $i=0$ case of the second. Arranging the letters relevantly, we find that

$$p_{bvi} = p_{bv0} - p_{bi0} \qquad (0 < i \in D_{bv}) \ (v \in M_b), \tag{19}$$

which connects bond orders between nonadjacent sites with two electron densities ($b=0$) or with two bond orders between adjacent sites ($b=1$).[5] In particular, for the m-electron ground state, using an analytic expression of the bond order between adjacent sites,[6] we obtain

$$p_{1vi} = (A_m(v) - A_m(i))/(m+1) \tag{20}$$

with

$$A_m(t) = \begin{cases} (-1)^{t-1}\mathrm{cosec}((2t+1)\pi/(2m+2)) & (m \text{ even}) \\ (-1)^{t-1}\cot((2t+1)\pi/(2m+2)) & (m \text{ odd}) \end{cases} \tag{21}$$

from the $b=1$ case. The $b=0$ case connects the two well-known consequences[7] of the alternant symmetry with each other.

The above theorem is essentially valid for any linear chain part aside from bifurcation sites. For the linear chain part having an end site, number the sites from 1 to m with the end site as 1 and the bifurcation site as m. Considering the hypervirial relationships for $r<s\in[1,m-1]$, we find that the theorem holds with the range for v and w restricted to $M_{b,i+f+1}$ plus $1+f+i$. On the other hand, for the linear chain part between bifurcation sites, number the sites from 1 to m with the bifurcation sites as 1 and m. The hypervirial relationships for $r,s\in[2,m-1]$ leave p_{1m} extraneous, so that we have

$$d_{bc_b} = c_b - 2 \qquad (c_b \text{ odd}), \tag{22}$$

which affects d_b. The range for v and w is further restricted to $M_{b,i+f}$. The expressions obtained by utilizing the property at the terminal $1+f+i$ of $M_{b,i+f}$ remain valid only if the linear chain part has an end site.

References

1) Electron densities and bond orders are called generically p-densities.

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

3) The simple Hückel model assumes a sole Coulomb integral for all sites and a sole resonance integral for all adjacent sites.

4) Putting $i=0$, we have the invariance of the modified electron density ($b=0$) and that of the modified bond order between adjacent sites ($b=1$) previously derived (Ref. 2).

5) The previous result (Ref. 2) on the bond order between the two end sites is particular cases of this.

6) C. A. Coulson and H. C. Longuet-Higgins, *Proc. R. Soc. London, Ser. A*, **193**, 447 (1948); C. A. Coulson, *Proc. R. Soc. London, Ser. A*, **169**, 413 (1939).

7) One is that all the electron densities are unity, the other being that all the bond orders between starred sites and between unstarred sites vanish.