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Simple Relationships between Coulson–Longuet–Higgins Polarizabilities in Linear Chains

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This paper describes general consequences of the hypervirial condition upon Coulson–Longuet–Higgins polarizabilities in the simple Hückel model of linear chains. The condition is put into the form of a tractable formula by introducing the modified polarizability; many simple relationships between polarizabilities are obtained through the formula. The relationships are often instructive conceptually, reflecting some characteristics of the Hückel model of linear chains, besides being helpful for numerical estimation of polarizabilities.

Coulson–Longuet–Higgins polarizabilities, called mutabilities below,1) are one of the most useful and informative quantities for consideration of reactivity in the Hückel model. Nowadays, we have no practical difficulty in computing mutabilities for individual systems, but relationships between mutabilities seem to remain almost latent. They will be scarcely revealed by individual numerical calculations.

In the previous paper2) the author has derived the hypervirial condition upon mutabilities, setting forth its significance and usefulness with several examples. We have no systematization, however, for deriving interpretable relationships from a set of the linear equations for mutabilities consequent on the condition.

The present paper analyzes the hypervirial condition upon mutabilities in the simple Hückel model3) of linear chains in a general, systematic way similar to the one used previously for deriving a theorem on p-densities.4,5) The modified mutability is introduced to put the condition into the form of a tractable formula. The formula is ready to yield various relationships between mutabilities, being named the hypervirial formula. It is utilized in practice to obtain many simple relationships between mutabilities. The relationships are often instructive conceptually, reflecting some characteristics of the Hückel model of linear chains, besides being helpful for numerical estimation of mutabilities.

We have four sections below: The first gives the hypervirial formula with the basic notation. The second and the third concern the relationships between two mutabilities for particular positions. The last describes a general way of expressing mutabilities in terms of mutabilities for identical or adjacent site pairs with p-densities.

The following mathematical symbols are used: 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, respectively; understand the set as empty if $z_l < z_s$. The indicator $\chi^z_{[z_s,z_l]}$ takes unity if z belongs to $[z_s, z_l]$, vanishing otherwise. The symbol $[z]$ means the largest integer not more than z. Throughout this paper, z_+ and z_- are short for $z+1$ and $z-1$, respectively.

The Hypervirial Formula

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. Let p_{rs} be the p-density for site pair rs and let π^{tu}_{rs} be the mutability for rs by tu in unit of the resonance integral.6) The identical site pair rr and the adjacent site pair rr_+ are referred to as the primary site pair generically for convenience' sake.

This system has the symmetry represented by the permutation group that consists of the identity and the permutation x acting on the site index as

$$xr = m - r + 1 \qquad (r \in M). \tag{1}$$

Every stationary state is faithful; the p-density and the mutability always fulfil the permutational symmetry beside the inherent symmetry for interchange of subscripts.2,7)

The hypervirial condition upon mutabilities in this system gives a set of the linear equations (the hypervirial relationships)2)

$$\pi^{tu}_{r_+s} + \pi^{tu}_{r_-s} - \pi^{tu}_{rs_-} - \pi^{tu}_{rs_+} = \phi^{tu}_{rs} \qquad (r < s \in M)\,(t \leqq u \in M), \tag{2}$$

where the second and the fourth terms are understood as absent for $r=1$ and $s=m$, respectively, and we have

$$\phi^{tu}_{rs} = (\tilde{\phi}^{tu}_{rs} + \tilde{\phi}^{ut}_{rs})/(1 + \delta_{tu}) \tag{3}$$

with

$$\tilde{\phi}^{tu}_{rs} = \delta_{st}p_{ru} - \delta_{rt}p_{su}. \tag{4}$$

Bear it in mind that the form of the equations is common to all the stationary states without regard to the number of electrons.2) Say, we can apply the equations to "separate" mutabilities and p-densities.8) The m-electron ground state is called the normal state distinctively in this paper.

From now on, when no confusion is expected, the specification of ranges of subscripts will be omitted fully or partially. Let C be $[1, c]$ with

$$c=[(m+1)/2], \tag{5}$$

denote $[f, xf]$ $(f\in C)$ by $M(f)$, and define the modified mutability $\eta^{tu}_{rs}(f)$ as[9]

$$\eta^{tu}_{rs}(f)=\begin{cases}\pi^{tu}_{rs} & (r=f \text{ or } s=xf)\\ \pi^{tu}_{rs}-\pi^{tu}_{r-f,s+f} & \text{otherwise}\end{cases}\qquad (r\leqq s\in M(f)). \tag{6}$$

Then, the hypervirial relationships can be rewritten as

$$\eta^{tu}_{r_+s_+}(1)-\eta^{tu}_{rs}(1)=\phi^{tu}_{rs_+}\qquad (r\leqq s\leqq m_-), \tag{7}$$

from which we obtain

$$\eta^{tu}_{r+z,s+z}(1)-\eta^{tu}_{rs}(1)=\sum_{y=0}^{z_-}\phi_{r+y,s_++y}\qquad (r\leqq s<s+z\leqq m) \tag{8}$$

by successive applications. On the other hand, immediately from the definition, there follows

$$\eta^{tu}_{rs}(f)=\sum_{k=0}^{f_-}\eta^{tu}_{r-k,s+k}(1)\qquad (r\leqq s\in M(f)), \tag{9}$$

so that we attain "the hypervirial formula"

$$\eta^{tu}_{r+z,s+z}(f)-\eta^{tu}_{rs}(f)=F^{tu}_{rs}(f:z)\quad (r\leqq s<s+z\in M(f)) \tag{10}$$

with

$$F^{tu}_{rs}(f:z)=\sum_{k=0}^{f_-}\sum_{y=0}^{z_-}\phi^{tu}_{r-k+y,s_++k+y}. \tag{11}$$

Note that the symmetry for interchange of upper and lower subscripts is necessarily lost in modified mutabilities.

We can give an expression to $F^{tu}_{rs}(f:z)$ in the single summation form as

$$F^{tu}_{rs}(f:z)=(\tilde{F}^{tu}_{rs}(f:z)+\tilde{F}^{ut}_{rs}(f:z))/(1+\delta_{tu}) \tag{12}$$

with

$$\tilde{F}^{tu}_{rs}(f:z)=\left(\sum_{y=g^t_1}^{h^t_1}-\sum_{y=g^t_2}^{h^t_2}\right)p_{r+s_+-t+2y,u}, \tag{13}$$

where g^t_1, h^t_1, g^t_2, and h^t_2 are independent of u, given in terms of t, r, s_+, z_-, and f_- as

$$g^t_1=\begin{cases}0 & (t\in[s_+, s_++f_-])\\ t-s_+-f_- & (t\in[s_++f_-, s_++z_-+f_-]),\end{cases} \tag{14}$$

$$h^t_1=\begin{cases}t-s_+ & (t\in[s_+, s_++z_-])\\ z_- & (t\in[s_++z_-, s_++z_-+f_-]),\end{cases} \tag{15}$$

$$g^t_2=\begin{cases}0 & (t\in[r-f_-, r])\\ t-r & (t\in[r, r+z_-]),\end{cases} \tag{16}$$

and

$$h^t_2=\begin{cases}t-r+f_- & (t\in[r-f_-, r+z_--f_-])\\ z_- & (t\in[r+z_--f_-, r+z_-]).\end{cases} \tag{17}$$

Understand each summation as absent if t lies out of the specified range. It is often profitable to put the p-densities appearing in the expression into p-densities for primary site pairs. Let bvi be the triple index corresponding to the site pair index rs $(r\leqq s)$,[4]

$$b=\begin{cases}0 & (s-r \text{ even})\\ 1 & (s-r \text{ odd}),\end{cases} \tag{18}$$

$$v=[(r+s)/2], \tag{19}$$

and

$$i=[(s-r)/2], \tag{20}$$

and use "the reduction formula"[4]

$$p_{rs}=p_{v,v+b}-p_{i,i+b}\qquad (s-r\geqq 2) \tag{21}$$

as the need arises.

Relationships between π^{tu}_{1s} and $\pi^{tu}_{xs,m}$

Substituting $f=1$, $r=1$, and $z=m-s$ into the hypervirial formula, we obtain the difference

$$\pi^{tu}_{xs,m}-\pi^{tu}_{1s}=F^{tu}_{1s}(1:m-s)\qquad (s\in[1, m_-]), \tag{22}$$

where the right hand side can be calculated with

$$\tilde{F}^{tu}_{1s}(1:m-s)=\chi^t_{[s_+,m]}p_{t-s,u}-\chi^t_{[1,m-s]}p_{t+s,u}. \tag{23}$$

Namely, the difference is a function of few p-densities. Let us examine some typical cases subsequently.

First, take a few cases of $u=t$. We can assume t to lie in C. Setting $s=1$, we find the simple relationship

$$\pi^{tt}_{mm}-\pi^{tt}_{11}=\begin{cases}-p_{12} & (t=1)\\ p_{t_-t}-p_{tt_+} & (t\in[2, c])\end{cases} \tag{24}$$

between the atom–atom mutabilities concerning the end site. In particular, since π^{11}_{mm} becomes vanishing as m tends to infinity,[10] there follows

$$\pi^{11}_{11}\rightarrow p_{12}\qquad (m\rightarrow\infty). \tag{25}$$

If s is set at m_-, we have

$$\pi^{tt}_{2m}-\pi^{tt}_{1m_-}=\begin{cases}-p_{1m} & (t=1)\\ 0 & (t\in[2, c]).\end{cases} \tag{26}$$

Aside from $t=1$, this exemplifies an "insensitivity"

$$\pi^{xtxt}_{1s}=\pi^{tt}_{1s}\qquad (t\in[xs, s])\ (s\in[c_+, m]) \tag{27}$$

of the mutability for distant $1s$ to the position of the internal perturbed site.

Next, set u at t_+. We can assume t to belong to $[1, l]$, which is denoted by L below, with

$$l=[m/2]. \tag{28}$$

By the aid of the reduction formula, the $s=1$ case gives

$$\pi^{tt_+}_{mm}-\pi^{tt_+}_{11}=2(p_{tt}-p_{t_+t_+}) \qquad (t\in L). \tag{29}$$

Such a relationship is trivial for the normal state because of the alternant symmetry,[2] but remains meaningful for other stationary states. The $s=2$ case gives

$$\pi^{tt_+}_{m_-m}-\pi^{tt_+}_{12}=2(p_{t_-t}-p_{t_+,t+2}) \qquad (t\in[2, l])\ (m\geqq 4) \tag{30}$$

and rather peculiarly

$$\pi^{12}_{m_-m}-\pi^{12}_{12}=\begin{cases}-p_{23} & (m=3)\\ p_{12}-2p_{23} & (m\geqq 4),\end{cases} \tag{31}$$

connecting the bond-bond mutabilities concerning the end bond with one another. We have

$$\pi^{12}_{12}\to 2p_{23}-p_{12} \qquad (m\to\infty) \tag{32}$$

as the limit of long chains.[10]

Relationships between π^{tu}_{rs} and $\pi^{tu}_{x(rs)}$

Unless xt coincides with u, π^{tu}_{rs} and $\pi^{tu}_{x(rs)}$ differ in general except the case of $xr=s$. The difference can be a quantity of interest, representing a basic feature of the system. We can assume $xr>s$ beside $r\leqq s$ without loss of generality. Substituting $f=r$ and $z=xr-s$ into the hypervirial formula, we have

$$\pi^{tu}_{x(rs)}-\pi^{tu}_{rs}=F^{tu}_{rs}(r:xr-s) \qquad (r\leqq s;\ xr>s), \tag{33}$$

which contains the result in the preceding section as the particular case of $r=1$. Use

$$g^t_1=\begin{cases}0 & (t\in[s_+, s+r])\\ t-r-s & (t\in[s+r, m]),\end{cases} \tag{34}$$

$$h^t_1=\begin{cases}t_--s & (t\in[s_+, m_+-r])\\ m-r-s & (t\in[m_+-r, m]),\end{cases} \tag{35}$$

$$g^t_2=\begin{cases}0 & (t\in[1, r])\\ t-r & (t\in[r, m-s]),\end{cases} \tag{36}$$

and

$$h^t_2=\begin{cases}t_- & (t\in[1, m_+-r-s])\\ m-r-s & (t\in[m_+-r-s, m-s])\end{cases} \tag{37}$$

for calculating $\tilde{F}^{tu}_{rs}(r:xr-s)$, which contains no first summation for $t\leqq s$ and no second for $t\geqq xs$.

Let us deal with exemplary cases, preparing the symbol S^h_g for the sum of the adjacent bond orders included between site g and site h;

$$S^h_g=\sum_{y=g}^{h_-}p_{yy_+} \qquad (g<h\in M). \tag{38}$$

Understand S^h_g to vanish unless $g<h$. Now, set t at r with $s=r$ and $u=t$. Then, we find the relationship

$$\pi^{rr}_{x(rr)}-\pi^{rr}_{rr}=\begin{cases}S^r_1-S^{2r}_r & (r\in[1, \tau])\\ S^{m_+-2r}_1-S^{m_+-r}_r & (r\in[\tau_+, c])\end{cases} \tag{39}$$

with

$$\tau=[(m+1)/3]. \tag{40}$$

This is helpful for estimating the difference between the changes in electron densities on two equivalent sites caused by a small change in the coulomb integral of either. For the long chain in the normal state, the asymptotic form[11]

$$p_{yy_+}\simeq\frac{2}{\pi}\left(1-\frac{(-1)^y}{2y+1}\right) \qquad (y\in C)\ (1\ll m) \tag{41}$$

leads us to

$$\pi^{rr}_{x(rr)}-\pi^{rr}_{rr}\simeq-\frac{2}{\pi}(K^r_1-K^{2r}_{r_+}) \qquad (r\ll m) \tag{42}$$

with

$$K^k_g=\sum_{y=g}^{k}\frac{(-1)^{y-1}}{2y-1} \qquad (g\leqq k) \tag{43}$$

for the site near the end. When the site is far from the end, that is, when $xr-r$ is small enough, we have

$$\pi^{rr}_{x(rr)}-\pi^{rr}_{rr}\simeq-\frac{2}{\pi}K^{xr-r}_1 \qquad (xr-r\ll m), \tag{44}$$

which is consistent with the asymptotic estimation[12]

$$\pi^{tt}_{rr}\simeq\frac{2}{\pi}\left(\frac{\pi}{4}-K^{|r-t|}_1\right) \qquad (|r-t|\ll r) \tag{45}$$

of mutabilities for sites in the middle of the long chain. Here, understand $K^{|r-t|}_1$ as vanishing if $r=t$.

Next, assume m to be even and set r at c, again with $s=r$ and $u=t$. Then, we have

$$\pi^{tt}_{c_+c_+}-\pi^{tt}_{cc}=-p_{t,\,m_+-t} \qquad (t\in C)\ (m\text{ even}), \tag{46}$$

which includes the characteristic relationships

$$\pi^{cc}_{c_+c_+}-\pi^{cc}_{cc}=-p_{cc_+} \qquad (m\text{ even}) \tag{47}$$

and

$$\pi^{11}_{c_+c_+}-\pi^{11}_{cc}=-p_{1m} \qquad (m\text{ even}) \tag{48}$$

as particular cases. The analytic expression[4)]

$$p_{t,m_+-t}=-\frac{(-1)^c}{m_+}\left(1-(-1)^t\sec\frac{t\pi}{m_+}\right)\qquad (m\text{ even})\qquad (49)$$

is available for the normal state.

The analogous result can be obtained for the bond–bond mutabilities concerning two equivalent bonds. Set $s=r_+$ and $u=t_+$. The $t=r$ case gives

$$\pi^{rr_+}_{x(rr_+)}-\pi^{rr_+}_{rr_+}=\begin{cases}2(S^r_1-S^{2r+1}_{r_+})+p_{rr_+} & (r\in[1,\tau'])\\ 2(S^{m-2r}_1-S^{m-r}_{r_+})-p_{rr_+} & (r\in[\tau'_+,l])\end{cases}\qquad (50)$$

with

$$\tau'=[(m-1)/3].\qquad (51)$$

For the long chain in the normal state, when the bond rr_+ lies near the end, there follows

$$\pi^{rr_+}_{x(rr_+)}-\pi^{rr_+}_{rr_+}\simeq-\frac{2}{\pi}(1+2K^r_2+K^{r_+}_{r_+}-2K^{2r+1}_{r+2})\qquad (r\ll m).\ (52)$$

For the bond far from the end, we have

$$\pi^{rr_+}_{x(rr_+)}-\pi^{rr_+}_{rr_+}\simeq-\frac{2}{\pi}(1+2K_2^{x(r_+)-r})\qquad (x(r_+)-r\ll m)\quad (53)$$

consistently with the asymptotic estimation[13)]

$$\pi^{tt_+}_{rr_+}\simeq\frac{4}{\pi}\left(\frac{\pi}{4}-K_1^{|r-t|}-\frac{1}{2}\delta_{rt}\right)\qquad (|r-t|\ll r)\qquad (54)$$

of mutabilities for bonds in the middle of the long chain. With m odd, the $r=c_-$ case gives

$$\pi^{tt_+}_{cc_+}-\pi^{tt_+}_{c_-c}=(\delta_{tc_-}-2)p_{t,m-t}\qquad (t\in L)\ (m\text{ odd}),\qquad (55)$$

where we can use

$$p_{t,m-t}=\frac{(-1)^c}{m_+}\left(\tan\frac{\pi}{2m_+}-(-1)^t\tan\frac{(2t+1)\pi}{2m_+}\right)\qquad (m\text{ odd})\qquad (56)$$

for the normal state.[4)]

Expression in Terms of Mutabilities for Primary Site Pairs

Set r at f in the hypervirial formula and replace z and $s+z+f$ newly with r and s, respectively. It follows that

$$\pi^{tu}_{rs}=\pi^{tu}_{r+f,s-f}-\pi^{tu}_{f,s-r-f}-F^{tu}_{f,s-r-f}(f:r)\qquad (s-r\geqq 2).\qquad (57)$$

Here, note that the two mutabilities in the right hand side have the closer site pairs than the mutability in the left hand side by $2f$. Hence, in particular, let bvi be the triple index corresponding to rs and set $f=i$. Then, putting

$$U^{tu}_{rs}=F^{tu}_{i,i+b}(i:r)\qquad (58)$$

for clarity, we obtain

$$\pi^{tu}_{rs}=\pi^{tu}_{v,v+b}-\pi^{tu}_{i,i+b}-U^{tu}_{rs}\qquad (s-r\geqq 2).\qquad (59)$$

Thus, any mutability for distant site pairs can be put into mutabilities for primary site pairs with p-densities.

It will be useful to draw an expression of U^{tu}_{rs} from the general expression. Putting

$$U^{tu}_{rs}=(\tilde{U}^{tu}_{rs}+\tilde{U}^{ut}_{rs})/(1+\delta_{tu}),\qquad (60)$$

we have

$$\tilde{U}^{tu}_{rs}=\left(\sum_{y=g^t_1}^{h^t_1}-\sum_{y=g^t_2}^{h^t_2}\right)p_{s_+-r-t+2y,u}\qquad (61)$$

with

$$g^t_1=\begin{cases}0 & (t\in[s-v_-,s-r])\\ t+r-s & (t\in[s-r,s_-]),\end{cases}\qquad (62)$$

$$h^t_1=\begin{cases}t-s+v_- & (t\in[s-v_-,s-i])\\ r_- & (t\in[s-i,s_-]),\end{cases}\qquad (63)$$

$$g^t_2=\begin{cases}0 & (t\in[1,i])\\ t-i & (t\in[i,v_-]),\end{cases}\qquad (64)$$

and

$$h^t_2=\begin{cases}t-1 & (t\in[1,r])\\ r_- & (t\in[r,v_-]).\end{cases}\qquad (65)$$

The first summation is absent for $t\leqq s-v$ or $t\geqq s$ and the second is absent for $t\geqq v$.

Let us utilize the above result for reducing the atom-bond mutability π^{tt}_{rs} to atom–atom mutabilities, assuming $s-r$ to be even beside $r<s$. We have $b=0$ and $i\geqq 1$ in the triple index. If $t<v$, then $xt>xv$ holds for $\pi^{x(tt)}_{x(rs)}$. Hence, we can suppose $t\geqq v$, which makes the second summation always absent. Since the first summation is also absent for $t\geqq s$, we have

$$\pi^{tt}_{rs}=\pi^{tt}_{vv}-\pi^{tt}_{ii}\qquad (t\in[s,m]).\qquad (66)$$

For t lying in the rest, it follows that

$$\pi^{tt}_{rs}=\pi^{tt}_{vv}-\pi^{tt}_{ii}+\begin{cases}S^{t-i}_{t-v}-S^v_i & (t\leqq 2i)\\ S^i_{t-v}-S^v_{t-i} & (t\geqq 2i)\end{cases}\qquad (t\in[v,s_-]),\quad (67)$$

where the lower subscript $t-v$ should be read as 1 if $t=v$. For example, setting $i=1$ and utilizing the symmetry, we have

$$\pi^{tt}_{v_-v_+}=\pi^{tt}_{vv}+\begin{cases}-\pi^{tt}_{mm} & (t\in[1,v_-])\\ -\pi^{tt}_{11}-\delta_{tv}p_{v_-v} & (t\in[v,m])\end{cases}\qquad (v\in M(2)).\quad (68)$$

For the long chain in the normal state, again for example, we have

$$\pi^{vv}_{v-i,v+i} \simeq -\pi^{vv}_{ii} + \frac{2}{\pi}\left(\frac{\pi}{4} - K^i_1\right) \qquad (i \ll v) \qquad (69)$$

for the site v far from the end, using the asymptotic value 1/2 of the self-mutability for such sites as well as the asymptotic form of bond orders.

Now, consider the expression of the mutability π^{tu}_{rs} in terms of the mutabilities having primary site pairs in both upper and lower subscripts. Assume $t \leqq u$ and let awj be the triple index corresponding to tu. If i or j is zero, the foregoing result is sufficient. Hence, suppose both i and j to be positive. Noting

$$\pi^{tu}_{y,y+b} = (2-b)\pi^{y,y+b}_{tu} \qquad (y = v,\, i), \qquad (70)$$

we obtain

$$\pi^{tu}_{rs} = (2-b)(\pi^{v,v+b}_{w,w+a} - \pi^{v,v+b}_{j,j+a} - \pi^{i,i+b}_{w,w+a} + \pi^{i,i+b}_{j,j+a}) - W^{tu}_{rs} \qquad (71)$$

with

$$W^{tu}_{rs} = (2-b)(U^{v,v+b}_{tu} - U^{i,i+b}_{tu}) + U^{tu}_{rs}. \qquad (72)$$

It is never difficult to write out W^{tu}_{rs}; a small personal computer suffices to do it with a simple program.

As an example, let us take the self-mutability π^{1s}_{1s} ($s \geqq 3$). We have $v = w = [s_+/2]$ and $i = j = v_-$. The expression

$$\widetilde{U}^{tu}_{1s} = (\chi^t_{[s-i,s_-]} - \chi^t_{[1,i]})p_{s-t,u} \qquad (73)$$

is useful for calculating W^{1s}_{1s}. The resultant leads us to

$$\pi^{1s}_{1s} - p_{s\_s} = \begin{cases} 2(\pi^{vv}_{vv} - 2\pi^{vv}_{v_-v_-} + \pi^{v_-v_-}_{v_-v_-} - 2p_{v_-v}) & (s \text{ odd}) \\ \pi^{vv_+}_{vv_+} - 2\pi^{vv_+}_{v_-v} + \pi^{v_-v}_{v_-v} - p_{v_-v} - p_{vv_+} & (s \text{ even}). \end{cases} \qquad (74)$$

Turn to the long chain in the normal state and assume s to be large with $m-s$ small enough. Since v_-, v, and v_+ lie in the middle of the chain, all the terms in the right hand side can be estimated asymptotically. They cancel out completely and the exchange of p_{s_s} for $p_{x(s\_s)}$ results in

$$\pi^{1s}_{1s} \simeq \frac{2}{\pi}\left(1 + \frac{(-1)^{m-s}}{2(m-s)+3}\right) \qquad (m-s \ll m), \qquad (75)$$

which gives the large value $8/3\pi$ to the self-mutability for the end site pair $1m$.

There is ample room for application: The relationships obtained in this paper as well as the hypervirial formula itself will be fruitful in various concrete problems. It can be helpful to incorporate analytic or asymptotic expressions available for some types of mutabilities and p-densities.[4,11-14] Auxiliary conditions, say, the two sum rules for mutabilities,[2] can be utilized as the case may be.

References

1) Derivatives of electron densities and bond orders with respect to components of the Hückel matrix were named polarizabilities by Coulson and Longuet-Higgins; C. A. Coulson and H. C. Longuet-Higgins, *Proc. R. Soc. London, Ser. A,* **191**, 39 (1947). The term "polarizability" is, however, prevalently used for another meaning in the theory of dielectrics. No descisive alternative seems to be present, but it will be better to use the term "mutability" proposed by Lennard-Jones, at least, for shortness' sake; J. Lennard-Jones, *ibid.,* **207**, 75 (1951).

2) M. Isihara, *Bull. Chem. Soc. Jpn.,* **64**, 559 (1991).

3) The simple Hückel model assumes a sole coulomb integral for all the sites and a sole resonance integral for all the adjacent site pairs.

4) M. Isihara, *Bull. Chem. Soc. Jpn.,* **64**, 2284 (1991).

5) Electron densities and bond orders are generically called p-densities (Ref. 11 in Ref. 7).

6) The present mutability is opposite to the original one in sign with the resonance integral negative.

7) M. Isihara, *Bull. Chem. Soc. Jpn.,* **62**, 2284 (1990).

8) P.-O. Löwdin, *J. Chem. Phys.,* **21**, 496 (1953) includes a systematic description of the "separate" quantities. The "partial" bond order first appeared in Ref. 11.

9) The present f differs by 1 from the f used to define the modified p-density in the previous note (Ref. 4).

10) As expected from the definition, π^{11}_{mm} vanishes in the long chain limit, provided that the stationary state under consideration is well defined in the limit. For the normal state, which exemplifies the situation of convergence, see Ref. 12. The same holds for $\pi^{12}_{m_-m}$ and, for the normal state, see Ref. 13.

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