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Electronic Structures of the Hückel Ring and the Möbius Ring

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The electronic structures of the Hückel- and Möbius type species are investigated in the Hückel approximation. The Green's function approach is employed to evaluate the total energy, the charge density and the bond order of various series. The results are successfully expressed in analytical forms, which displays the Hückel $4m+2$ and the Möbius $4m$ rules very clearly.

In studying the electronic structure of conjugated hydrocarbons, the π electron approximation employing the Hückel method is still useful. Even if the recent ab initio method enables us to reproduce a specified observation in a reasonable accuracy, when the extended system is in question, the overall behavior is apt to be lost in the jungle of numerals. In this respect, the Hückel method, which is called in physics the tight-binding approximation combined with the band-calculation, is frequently tried, especially by experimental chemists. However the results are almost always given by numerals. So if we are not careful when looking at these numerals, it is difficult to deduce a general and concrete conclusion.

As will be seen in the following, if we limit ourselves to the simple (which does not mean small) system in the Hückel approximation, the Green's function method gives results in an analytical expression.[1)] Then we can at once recognize the general trend of the object in question. We want to develop such an approach not only on the Hückel system but also on the Möbius system; the latter is rarely found as an actual molecule, but it suggests interesting concepts in studying chemical reactivity and perhaps in exploiting new materials.

Green's Function

In order to orient ourselves, we begin by reviewing the important points to obtain the Green's function given in the preceding work.[2)] Corresponding to the Schrödinger equation

$$(z-H)\varphi = 0, \tag{1}$$

the Green's operator is defined by

$$(z-H)G(z) = 1. \tag{2}$$

Keeping in mind the conjugated hydrocarbons, we set the Hamiltonian in the Hückel approximation as $H=\alpha+v$, where v is the coupling term between adjacent sites, and α is the atomic energy which is put to be zero as an energy standard. Moreover we assume that the basis set is orthonormal. Then the Green's function of the single atom is given as

$$G_1(a) = \frac{1}{z}, \tag{3}$$

where the suffix 1 infers the number of sites is 1, and the argument a indicates the head of series. Next, the Green's function for the head of the two sites system $a-b$ in Fig. 1a is obtained as an infinite series:

$$\begin{aligned} G_2(a) &= G_1(a) + G_1(a)vG_1(b)vG_1(a) \\ &\quad + G_1(a)vG_1(b)vG_1(a)vG_1(b)vG_1(a) + \cdots \\ &= \left[G_1(a)^{-1} - vG_1(b)v\right]^{-1} \\ &= \frac{z}{z^2 - v^2}. \end{aligned} \tag{4}$$

The denominator is a determinant:

$$z^2 - v^2 = \begin{vmatrix} z & v \\ v & z \end{vmatrix}. \tag{5}$$

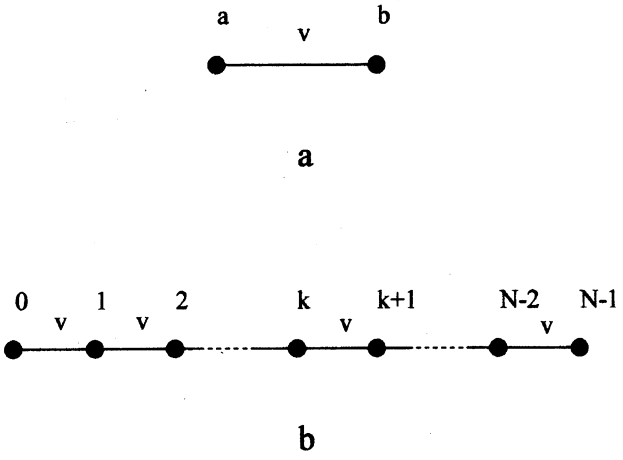

Fig. 1. Schematic diagrams of linear chain molecules. Where v (<0) is the coupling term between adjacent sites. a: Two sites system, b: N sites system.

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Namely, to estimate the infinite series Eq. 4 is equivalent to the eigenvalue problem.

The off-diagonal term $G_2(a,b)$ in Fig. 1a is given by

$$\begin{aligned} G_2(a,b) &= G_2(a)vG_1(b) \\ &= \frac{v}{z^2 - v^2}. \end{aligned} \tag{6}$$

The above relation is generalized as: The off-diagonal term $G_N(a,k)$ in Fig. 1b is

$$\begin{aligned} G_N(a,k) &= G_N(a)vG_N(b,k[a]) \\ &= G_N(a)vG_{N-1}(a,k-1), \end{aligned} \tag{7}$$

where $G_N(b,k[a])$ is a fictitious Green's function of the N site system if it were not for the a site, and its real feature is given in the next line. This is the fundamental rule for composing a compound Green's function from the simple ones.

Now we give the compact analytical forms to the above Green's function in term of trigonometrical functions. Let us put

$$v = 1, \tag{8}$$

$$z = 2\cos\theta. \tag{9}$$

Note that θ is a complex similar to z. Then it is apparent that

$$G_1(a) = \frac{1}{2\cos\theta} = \frac{\sin\theta}{\sin 2\theta}, \tag{10}$$

$$G_2(a) = \frac{\sin 2\theta}{\sin 3\theta}, \tag{11}$$

$$\begin{aligned} G_2(a,b) &= G_2(a)vG_1(a) \\ &= \frac{\sin\theta}{\sin 3\theta}. \end{aligned} \tag{12}$$

Then one can conjecture that

$$L_N^H(0) = \frac{\sin N\theta}{\sin(N+1)\theta}, \tag{13}$$

$$L_N^H(k) = \frac{\sin(N-k)\theta \sin(k+1)\theta}{\sin(N+1)\theta \sin\theta}, \tag{14}$$

$$L_N^H(k,l) = \frac{\sin(N-l)\theta \sin(k+1)\theta}{\sin(N+1)\theta \sin\theta}, \tag{15}$$

where the Green's function of Hückel linear chain shown in Fig. 1b denoted by L_N^{H}. The verification of Eqs. 13, 14, and 15 are given in the preceding work.[1)]

In obtaining the Green's function of the ring molecule, we should be a little careful. Let us consider the Hückel ring shown in Fig. 2a. In this case, the diagonal element of the Green's function, $R_N^H(0)$, is obtained as

$$\begin{aligned} R_N^H(0) &= \Big[R_1^H(0)^{-1} - vR_N^H(1[0])v - vR_N^H(N-1[0])v \\ &\quad -vR_N^H(1,N-1[0])v - vR_N^H(N-1,1[0]v)\Big]^{-1} \\ &= \Big[L_1^H(0)^{-1} - vL_{N-1}^H(0)v - vL_{N-1}^H(N-2)v \\ &\quad -vL_{N-1}^H(0,N-2)v - vL_{N-1}^H(N-2,0)v\Big]^{-1} \\ &= \left[\frac{\sin 2\theta}{\sin\theta} - 2\frac{\sin(N-1)\theta}{\sin N\theta} - 2\frac{\sin\theta}{\sin N\theta}\right]^{-1} \\ &= \frac{-\cos\frac{N\theta}{2}}{2\sin\frac{N\theta}{2}\sin\theta}, \end{aligned} \tag{16}$$

where, in passing through from the second equality to the third, use was made of the relations Eqs. 8 and 9. It is noted that, in the first equality, the fourth term arises from the route: 0→1→⋯→$N-1$→0, and the fifth term from the reverse route: 0→$N-1$→⋯→1→0; other terms can be understood from the previous explanation. The off-diagonal element, $R_N^H(0,k)$, is similarly obtained as

$$\begin{aligned} R_N^H(0,k) &= R_N^H(0)vR_N^H(1,k[0]) + R_N^H(0)vR_N^H(N-1,k[0]) \\ &= R_N^H(0)vL_{N-1}^H(0,k-1) + R_N^H(0)vL_{N-1}^H(0,N-k-1) \\ &= -\frac{\sin(N-k)\theta + \sin k\theta}{4\sin^2\frac{N\theta}{2}\sin\theta} \\ &= -\frac{\cos\frac{N-2k}{2}\theta}{2\sin\frac{N\theta}{2}\sin\theta}. \end{aligned} \tag{17}$$

In this case, the first term in the first equality is due to the normal route and the second term is due to the reverse route. It should be stressed that such an analysis is never found in the usual molecular orbital theory.

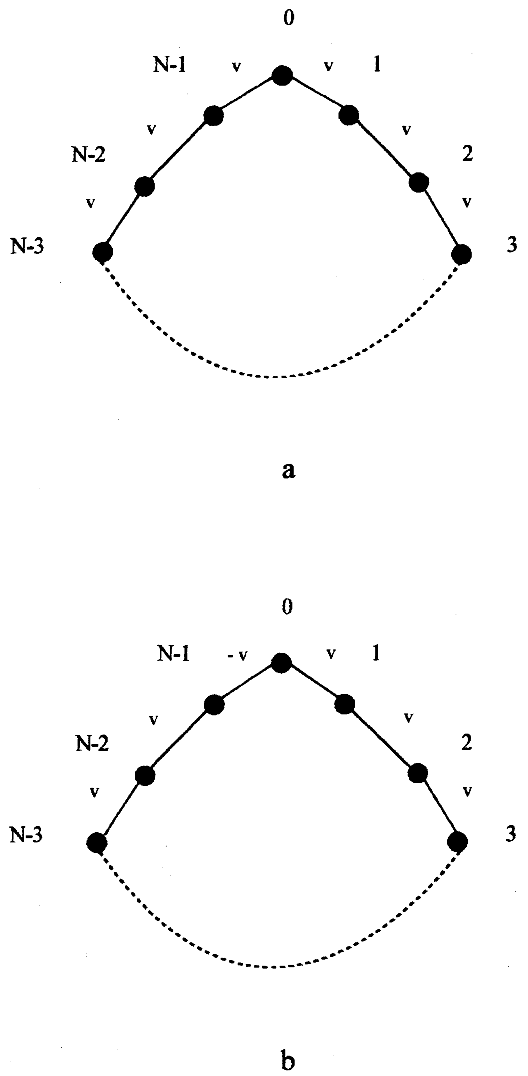

Fig. 2. Schematic diagrams of ring molecules. Where $v(<0)$ is the coupling term between adjacent sites. a: The Hückel ring, b: the Möbius ring.

Now we turn to the Möbius case. We suppose that, in the Möbius chain with N sites, each site rotates gradually, and the final one rotates from the beginning one through an angle $(N-1)\pi/N$. This implies that, if the chain makes a ring by connecting head and tail, the coupling term between them has the reverse sign to other adjacent ones. In the chain or the ring of N members, the rotation angle, ρ_N, of the n-th basis set, f_n, is

$$n\rho_N = \frac{n\pi}{N}, \quad n = 0,1,2,\cdots,N-1. \tag{18}$$

Then the n-th basis becomes, assuming its absolute strength is unity,

$$f_n = \cos n\rho_N + \sin n\rho_N. \tag{19}$$

The interaction between the n-th and $(n+1)$-th bases is

$$\begin{aligned} v_n &= v_0\{\cos(n+1)\rho_N \cos n\rho_N + \sin(n+1)\rho_N \sin n\rho_N\} \\ &= v_0 \cos \rho_N \\ &= v_N, \end{aligned} \tag{20}$$

where v_0 is the coupling term in the Hückel chain without rotation, and we note that v_N does not depend on the site position but on the chain length, N. Hereafter, it is noted simply as v for the given N. The Green's functions which are denoted as L_N^M for the Möbius chains are the same to the Hückel ones except for the coupling constant (v_N=1 now).

$$L_N^M(k) = \frac{\sin(N-k)\theta \sin(k+1)\theta}{\sin(N+1)\theta \sin\theta}, \tag{21}$$

$$L_N^M(k,l) = \frac{\sin(N-l)\theta \sin(k+1)\theta}{\sin(N+1)\theta \sin\theta}. \tag{22}$$

The case of a ring is interesting. Coming back to Eqs. 16 and 17, we find that the effects arising from the cyclic routes have the opposite sign, due to the opposite sign of coupling constant between the 0-th site and the $(N-1)$-th site. Thus the diagonal element, $R_N^M(0)$, in Fig. 2b is obtained as

$$\begin{aligned} R_N^M(0) &= \Big[R_1^M(0)^{-1} - vR_N^M(1[0])v - (-v)R_N^M(N-1[0])(-v) \\ &\quad -vR_N^M(1,N-1[0])(-v) - (-v)R_N^M(N-1,1[0]v)\Big]^{-1} \\ &= \Big[L_1^M(0)^{-1} - vL_{N-1}^M(0)v - vL_{N-1}^M(N-2)v \\ &\quad +vL_{N-1}^M(0,N-2)v + vL_{N-1}^M(N-2,0)v\Big]^{-1} \\ &= \left[\frac{\sin 2\theta}{\sin\theta} - 2\frac{\sin(N-1)\theta}{\sin N\theta} + 2\frac{\sin\theta}{\sin N\theta}\right]^{-1} \\ &= \frac{\sin\frac{N\theta}{2}}{2\cos\frac{N\theta}{2}\sin\theta}. \end{aligned} \tag{23}$$

The off-diagonal element, $R_N^M(0,k)$, is similarly obtained as

$$\begin{aligned} R_N^M(0,k) &= R_N^M(0)vR_N^M(1,k[0]) + R_N^M(0)(-v)R_N^M(N-1,k[0]) \\ &= R_N^M(0)vL_{N-1}^M(0,k-1) - R_N^M(0)vL_{N-1}^M(0,N-k-1) \\ &= \frac{\sin(N-k)\theta - \sin k\theta}{4\cos^2\frac{N\theta}{2}\sin\theta} \\ &= \frac{\sin\frac{N-2k}{2}\theta}{2\cos\frac{N\theta}{2}\sin\theta}. \end{aligned} \tag{24}$$

Comparing Eq. 17 with Eq. 24, we can clearly understand that in the Hückel ring, the reverse route works additively to the normal route, while in the Möbius ring, it works destructively. This interference phenomenon arises from the wave nature of the Green's functions characteristic to the quantum effect, and results in the change of phase.

Hückel versus Möbius

Once we obtain the Green's functions of the system under consideration, almost all the physical quantities can be estimated.

Total Energy. The ground state energy, E_N, is obtained from the diagonal elements of the Green's function, since they are essentially the particle densities at sites.

$$E_N = Tr\frac{1}{2\pi i}\int_c \mathrm{d}z\, zG_N(z), \tag{25}$$

where $G_N(z)$ is of course z dependent, Tr means $\Sigma_{\text{site,spin}}$, and the integration contour, c, is the so-called Coulson contour shown in Fig. 3.

In the present treatment, we restrict ourselves to the case that the number of sites is equal to the number of electrons, or the case where molecules are neutral. However, if we investigate the chemical reactivity problem, the negative or the positive ion especially of the odd-membered species is interesting.

From now on we are concerned with rings. The ground state energy of the Hückel N-membered ring, E_N^H, is obtained as

$$\begin{aligned} E_N^H &= N\frac{1}{4\pi i}\int_c \mathrm{d}\theta(-)2\sin\theta\, 2\cos\theta \frac{-\cos\frac{N\theta}{2}}{2\sin\frac{N\theta}{2}\sin\theta} \\ &= \frac{N}{4\pi i}\int_c \mathrm{d}\theta \frac{\cos\frac{N\theta}{2}\cos\theta}{\sin\frac{N\theta}{2}} \\ &= 2\sum_r \cos\theta_r, \end{aligned} \tag{26}$$

where the change of variable, z=2cos θ, causes the additional multiplicative factor, 1/2, since the integration contour

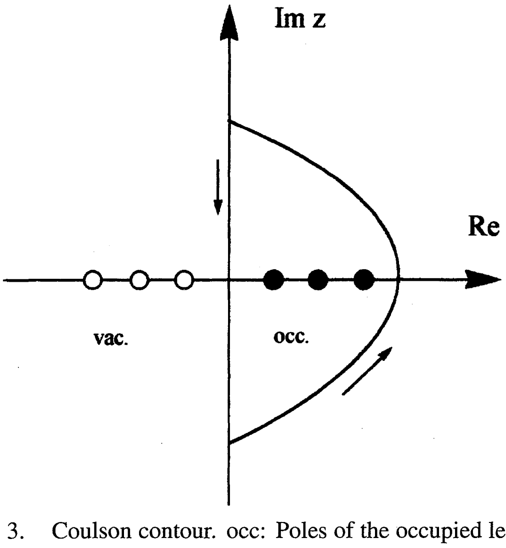

Fig. 3. Coulson contour. occ: Poles of the occupied levels, vac: poles of the unoccupied levels.

in z space goes round the poles twice, compared to once in θ space. The poles in θ space are determined as

$$\sin\frac{N\theta_r}{2}=0. \tag{27}$$

Namely,

$$\theta_r=\frac{2\pi r}{N},\quad r=0,\pm1,\pm2,\cdots. \tag{28}$$

The calculated details are given in Table 1.

Similarly the ground state energy of the Möbius N-membered ring, E_N^M, is obtained as

$$\begin{aligned}E_N^M&=N\frac{1}{4\pi i}\int_c \mathrm{d}\theta(-)2\sin\theta\, 2\cos\theta\frac{\sin\frac{N\theta}{2}}{2\cos\frac{N\theta}{2}\sin\theta}\\&=-\frac{N}{4\pi i}\int_c \mathrm{d}\theta\frac{\sin\frac{N\theta}{2}\cos\theta}{\cos\frac{N\theta}{2}}\\&=2\sum_r\cos\theta_r.\end{aligned} \tag{29}$$

The poles in Eq. 29 are determined as

$$\cos\frac{N\theta_r}{2}=0. \tag{30}$$

Namely

$$\theta_r=\frac{\pi}{N}(2r-1),\quad r=0,\pm1,\pm2,\cdots. \tag{31}$$

Details are given in Table 2.

When we compared Tables 1 and 2, we can clearly understand the contrast between the Hückel rings and Möbius rings. The series: $4m$, $4m+2$, $4m+1$, $4m-1$ of the Hückel rings just corresponds to the series: $4m+2$, $4m$, $4m-1$, $4m+1$ of the Möbius rings, respectively. The correspondence between other chemical properties of both must be expected as above. Moreover, the atomic localizing energy has shown the famous Hückel $4m+2$ rule and the Möbius $4m$ rule in analytical form. The calculated details of the atomic localizing energy are given in an appendix.

Charge Density. This is given by a simple integration of the diagonal part of the Green's function. In the ring, every site is equivalent with every other one, so that the charge density is denoted as $q_N(0)$.

$$q_N(0)=\frac{1}{2\pi i}\int_c \mathrm{d}z\, G_N(0), \tag{32}$$

where we assume the spin sum is implicitly carried out.

From this equation, we can calculate the charge density of the Hückel N-membered ring, $q_N^H(0)$, as follows:

$$\begin{aligned}q_N^H(0)&=\frac{1}{4\pi i}\int_c \mathrm{d}\theta(-)2\sin\theta\frac{-\cos\frac{N\theta}{2}}{2\sin\frac{N\theta}{2}\sin\theta}\\&=\frac{1}{4\pi i}\int_c \mathrm{d}\theta\frac{\cos\frac{N\theta}{2}}{2\sin\frac{N\theta}{2}}\\&=\frac{1}{N}\sum_{\text{poles,spin}}\\&=1.\end{aligned} \tag{33}$$

Similarly the charge density of the Möbius N-membered ring, $q_N^M(0)$, is obtained as

$$\begin{aligned}q_N^M(0)&=\frac{1}{4\pi i}\int_c \mathrm{d}\theta(-)2\sin\theta\frac{\sin\frac{N\theta}{2}}{2\cos\frac{N\theta}{2}\sin\theta}\\&=-\frac{1}{4\pi i}\int_c \mathrm{d}\theta\frac{\sin\frac{N\theta}{2}}{2\cos\frac{N\theta}{2}}\\&=\frac{1}{N}\sum_{\text{poles,spin}}\\&=1.\end{aligned} \tag{34}$$

The poles we must count in Eqs. 33 and 34 are already given in Tables 1 and 2, respectively. These results are quite simple as expected and are not interesting.

Bond Order. In comparison with the charge density at each site, which is not so important a physical quantity

Table 1. Ground State Energies (E_N^H) and Atom Localizing Energies (E_L^H) of the Hückel Rings; Poles, $\theta_r=\frac{2\pi r}{N}$

N	Poles (Doubly occupied)	Poles (Singly occupied)	E_N^H	E_L^H
$4m$	$r=0,\pm1,\cdots,\pm\left(\frac{N}{4}-1\right)$	$r=\pm\frac{N}{4}$	$2\left(\cot\frac{\pi}{2N}-\tan\frac{\pi}{2N}\right)$	$2\left(1-\tan\frac{\pi}{2N}\right)$
$4m+2$	$r=0,\pm1,\cdots,\pm\left(\frac{N-2}{4}\right)$	—	$2\left(\cot\frac{\pi}{2N}+\tan\frac{\pi}{2N}\right)$	$2\left(1+\tan\frac{\pi}{2N}\right)$
$4m+1$	$r=0,\pm1,\cdots,\pm\left(\frac{N-5}{4}\right),\frac{N-1}{4}$	$r=-\left(\frac{N-1}{4}\right)$	$2\left(\operatorname{cosec}\frac{\pi}{2N}-\sin\frac{\pi}{2N}\right)$	$2\left(1-\sin\frac{\pi}{2N}\right)$
$4m-1$	$r=0,\pm1,\cdots,\pm\left(\frac{N-3}{4}\right)$	$r=\frac{N+1}{4}$	$2\left(\operatorname{cosec}\frac{\pi}{2N}-\sin\frac{\pi}{2N}\right)$	$2\left(1-\sin\frac{\pi}{2N}\right)$

Table 2. Ground State Energies (E_N^M) and Atom Localizing Energies (E_L^M) of the Möbius Rings; Poles, $\theta_r=\frac{\pi}{N}(2r-1)$

N	Poles (Doubly occupied)	Poles (Singly occupied)	E_N^M	E_L^M
$4m$	$r=0,\pm1,\cdots,\pm\left(\frac{N-4}{4}\right),\frac{N}{4}$	—	$2\left(\cot\frac{\pi}{2N}+\tan\frac{\pi}{2N}\right)$	$2\left(1+\tan\frac{\pi}{2N}\right)$
$4m+2$	$r=0,\pm1,\cdots,\pm\left(\frac{N-6}{4}\right),\frac{N-2}{4}$	$r=\frac{N+2}{4},-\left(\frac{N-2}{4}\right)$	$2\left(\cot\frac{\pi}{2N}-\tan\frac{\pi}{2N}\right)$	$2\left(1-\tan\frac{\pi}{2N}\right)$
$4m+1$	$r=0,\pm1,\cdots,\pm\left(\frac{N-5}{4}\right),\frac{N-1}{4}$	$r=\frac{N+3}{4}$	$2\left(\operatorname{cosec}\frac{\pi}{2N}-\sin\frac{\pi}{2N}\right)$	$2\left(1-\sin\frac{\pi}{2N}\right)$
$4m-1$	$r=0,\pm1,\cdots,\pm\left(\frac{N-3}{4}\right)$	$r=\frac{N+1}{4}$	$2\left(\operatorname{cosec}\frac{\pi}{2N}-\sin\frac{\pi}{2N}\right)$	$2\left(1-\sin\frac{\pi}{2N}\right)$

in the present case, the bond order is crucial to investigate the chemical properties. Our theory of chemical reactivity[3,4] states that, to the first order of an external perturbation, the bond order which is obtained by taking into account all of the electrons is responsible in the ground state, on the other hand in the radiation field, the partial bond order of the lowest vacant level minus that of the highest occupied level is responsible. This is not an assumption, but a theoretically verified conclusion.[5] If a higher order treatment more than first order approximation is required, it is necessary to use the polarizability.[2,6]

The bond order, $q_N(k,l)$, is obtained from the off-diagonal element of the Green's function:

$$q_N(k,l) = \frac{1}{2\pi i}\int_c \mathrm{d}z\, G_N(k,l), \tag{35}$$

where the contour, c, encloses poles appropriate to the case in question.

Let us begin the case of the Hückel ring. In order to keep the interference effect which is previously mentioned, we would use the third equation rather than the last equation in Eq. 17. Accordingly, the bond order of the Hückel N-membered ring, $q_N^H(0,k)$, is obtained as

$$\begin{aligned} q_N^H(0,k) &= \frac{1}{4\pi i}\int_c \mathrm{d}\theta(-)2\sin\theta \frac{(-)\{\sin(N-k)\theta+\sin k\theta\}}{4\sin^2\frac{N\theta}{2}\sin\theta} \\ &= \frac{1}{4\pi i}\int_c \mathrm{d}\theta \frac{\sin(N-k)\theta+\sin k\theta}{2\sin^2\frac{N\theta}{2}} \\ &= \frac{1}{N^2}\{(N-k)+k\}\sum_r \cos\frac{2\pi kr}{N}. \end{aligned} \tag{36}$$

In obtaining this results, we have used the relation

$$\frac{1}{2\pi i}\int_c \mathrm{d}z \frac{f(z)}{(z-a)^2} = f'(a), \tag{37}$$

where the prime infers the differentiation with respect to z, and of course $f(z)$ is regular on and inside the contour.

In the case of the Möbius N-membered ring, the bond order, $q_N^M(0,k)$, is similarly obtained as

$$\begin{aligned} q_N^M(0,k) &= \frac{1}{4\pi i}\int_c \mathrm{d}\theta(-)2\sin\theta \frac{\sin(N-k)\theta-\sin k\theta}{4\cos^2\frac{N\theta}{2}\sin\theta} \\ &= \frac{-1}{4\pi i}\int_c \mathrm{d}\theta \frac{\sin(N-k)\theta-\sin k\theta}{2\cos^2\frac{N\theta}{2}} \\ &= \frac{1}{N^2}\{(N-k)+k\}\sum_r \cos(2r-1). \end{aligned} \tag{38}$$

In cases of both the Hückel and the Möbius, we have the same expression. However the differences between them arise from the poles for various cases which will be discussed in the following. It should be noted that in the factor, $\{(N-k)+k\}/N^2$, the first term arises from the normal route, $0\rightarrow1\rightarrow2\rightarrow\cdots\rightarrow k$, while the second term arises from reverse route, $0\rightarrow N-1\rightarrow N-2\rightarrow k$. Such a classification has been never achieved in the usual molecular orbital theoretical treatment. For the sake of simplicity, this factor is written as $1/N$ in the following.

From Eq. 38, we have the bond order of the Hückel N-membered ring, $q_N^H(0,k)$. The poles taken into account are already shown in Table 1. The spin sum is also carried out. In the following, we have shown the cases where N is $4m$, $4m+2$, $4m+1$, and $4m-1$.

$(i)\, N=4m$

$$\begin{aligned} q_N^H(0,k) &= \frac{1}{N}\left(2[0]+4\sum_{r=1}^{\frac{N-4}{4}}+2\left[\frac{N}{4}\right]\right)\cos\frac{2\pi k}{N}r \\ &= \frac{2}{N}\sin\frac{k\pi}{2}\cot\frac{k\pi}{N}, \end{aligned} \tag{39}$$

where, for example, $[N/4]$ denotes the term with $r=N/4$. In the course of this calculation, the following relation is useful.

$$\sum_{r=1}^{n}\cos xr = \frac{\cos\frac{(n+1)x}{2}\sin\frac{nx}{2}}{\sin\frac{x}{2}}. \tag{40}$$

$(ii)\, N=4m+2$

$$\begin{aligned} q_N^H(0,k) &= \frac{1}{N}\left(2[0]+4\sum_{r=1}^{\frac{N-2}{4}}\right)\cos\frac{2\pi k}{N}r \\ &= \frac{2}{N}\sin\frac{k\pi}{2}\mathrm{cosec}\frac{k\pi}{N}. \end{aligned} \tag{41}$$

$(iii)\, N=4m+1$

$$\begin{aligned} q_N^H(0,k) &= \frac{1}{N}\left(2[0]+4\sum_{r=1}^{\frac{N-5}{4}}+2\left[\frac{N-1}{4}\right]+\left[\frac{-(N-1)}{4}\right]\right)\cos\frac{2\pi k}{N}r \\ &= \frac{1}{N}\left(\sin\frac{k\pi}{2}\cot\frac{k\pi}{2N}\cos\frac{k\pi}{2N}+\cos\frac{k\pi}{2}\tan\frac{k\pi}{2N}\sin\frac{k\pi}{2N}\right), \end{aligned} \tag{42}$$

where it is noted that the $(N-1)/4$-th level is doubly occupied and $-(N-1)/4$-th level is singly occupied.

$(iv)\, N=4m-1$

$$\begin{aligned} q_N^H(0,k) &= \frac{1}{N}\left(2[0]+4\sum_{r=1}^{\frac{N-3}{4}}+\left[\frac{N+1}{4}\right]\right)\cos\frac{2\pi k}{N}r \\ &= \frac{1}{N}\left(\sin\frac{k\pi}{2}\cot\frac{k\pi}{2N}\cos\frac{k\pi}{2N}-\cos\frac{k\pi}{2}\tan\frac{k\pi}{2N}\sin\frac{k\pi}{2N}\right). \end{aligned} \tag{43}$$

Similarly, we can obtain the bond order of the Möbius N-membered ring, $q_N^M(0,k)$, as follows:

$(i)\, N=4m$

$$\begin{aligned} q_N^M(0,k) &= \frac{4}{N}\sum_{r=1}^{\frac{N}{4}}\cos\frac{k\pi}{N}(2r-1) \\ &= \frac{2}{N}\sin\frac{k\pi}{2}\mathrm{cosec}\frac{k\pi}{N}. \end{aligned} \tag{44}$$

In order to obtain Eq. 44 we have a useful relation

$$\sum_{r=1}^{n}\cos x(2r-1) = \frac{\sin 2nx}{2\sin x}. \tag{45}$$

The poles taken into account are shown in Table 2.

$(ii)\, N=4m+2$[7]

$$q_N^M(0,k) = \frac{1}{N}\left(4\sum_{r=1}^{\frac{N-2}{4}}+\left[\frac{N+2}{4}\right]+\frac{-[N-2]}{4}\right)\cos\frac{k\pi}{N}(2r-1)$$

$$= \frac{2}{N} \sin \frac{k\pi}{2} \cot \frac{k\pi}{N}. \tag{46}$$

$(iii) N = 4m + 1$

$$q_N^M(0,k) = \frac{1}{N}\left(4\sum_{r=1}^{\frac{N-1}{4}} + \left[\frac{N+3}{4}\right]\right) \cos \frac{k\pi}{N}(2r-1)$$

$$= \frac{1}{N}\left(\sin \frac{k\pi}{2} \cot \frac{k\pi}{2N} \cos \frac{k\pi}{2N} - \cos \frac{k\pi}{2} \tan \frac{k\pi}{2N} \sin \frac{k\pi}{2N}\right). \tag{47}$$

$(iv) N = 4m - 1$

$$q_N^M(0,k) = \frac{1}{N}\left(4\sum_{r=1}^{\frac{N-3}{4}} +2\left[\frac{-(N-3)}{4}\right] + \left[\frac{N+1}{4}\right]\right) \cos \frac{k\pi}{N}(2r-1)$$

$$= \frac{1}{N}\left(\sin \frac{k\pi}{2} \cot \frac{k\pi}{2N} \cos \frac{k\pi}{2N} + \cos \frac{k\pi}{2} \tan \frac{k\pi}{2N} \sin \frac{k\pi}{2N}\right). \tag{48}$$

Discussion

The famous rule that the $4m+2$ electron system is stable in the Hückel ring while the $4m$ electron system is stable in the Möbius ring is clearly shown in an analytical expression. Furthermore the analytical expressions give beautiful contrast. Namely, not only in energy but also in orbital properties, the expressions of the Hückel ring just correspond to those of the Möbius ring. Somebody may criticize that a one-electron approximation lacking in electron–electron interactions is not reliable. Zimmerman[8] has investigated this problem by employing the SCF method including the electron–electron interactions plus some configuration interactions between the degenerate levels and he has concluded that the rules deduced from the one-electron approximation need not change up to this approximation. In general, the electron–electron interaction or the configuration interaction changes to a considerable extent the absolute values of level energies and sometimes changes even the order of levels. However the qualitative behavior of electrons described by wave functions is hardly affected. The latter is crucial to the difficulty of chemical reactivity.[3–5]

When one constructs the molecular orbital theory by the linear combination of atomic orbital, the basis set or the set of atomic orbitals is first set up. The basis set is to be realized as a device to write the Hamiltonian matrix rather than a device to evaluate the object numerically in a good approximation. Thus, if we get the Hamiltonian matrix, all of the information of the object under consideration can be deduced from this matrix in a given approximation. The eigenvectors obtained through the eigenvalue problem of this energy matrix give the so-called LCAO coefficients, which are the probability amplitudes of finding the electron on the atomic orbitals in each one-particle level. In quantum chemistry the word, molecular orbital, is used as a combination of the basis set and the LCAO coefficients. However the essential part of the molecular orbital should be LCAO coefficients. If a chemical reactivity is in question, we must strictly distinguish the basis set and the LCAO coefficients. For example, let us consider the problem of the ring formation from the chain with six sites. The bond order between the head and the tail, q_{05}, is equal to 0.301 whether this chain rotates or not.[1] In this case the positive sign of q_{05} is important. Therefore, the negative coupling between the head and the tail in this chain is favorable for the ring formation. Thus the dis-rotatory motion is favorable for this case. If the dis-rotatory motion of them follows, the Hückel ring or benzene molecule will be made. The case that the rotation angle between the head and the tail is over π will be discussed in the following. The motions of the ring formation are shown in Fig. 4. Next, we consider the chain which is composed with eight sites. In this case, the bond order, q_{07}, is equal to -0.229. The story is similar to the previous one. In this case, we conclude that

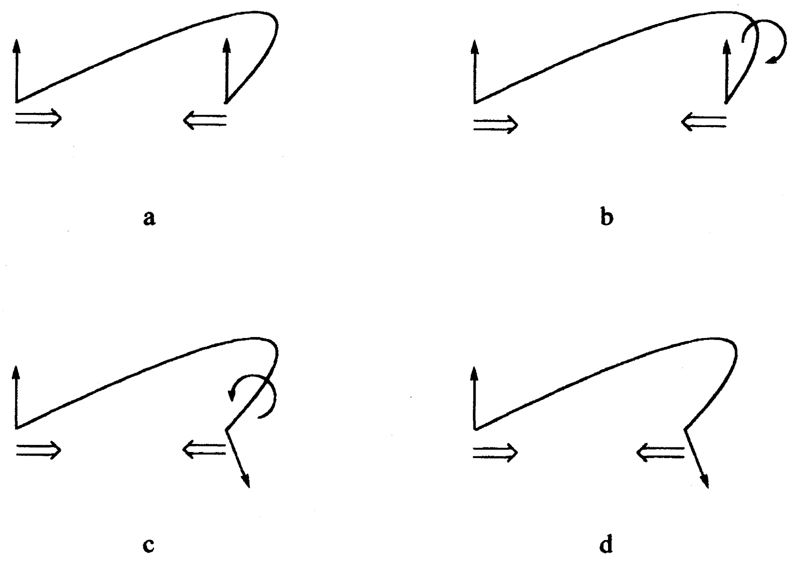

Fig. 4. Schematic diagrams of the motion of the ring formation. The arrows at both ends stand for the basis functions, 2pπ, together with the phases. a: The dis-rotatory motion of the Hückel chain, b: the con-rotatory motion of the Hückel chain, c: the dis-rotatory motion of the Möbius chain, d: the con-rotatory motion of the Möbius chain.

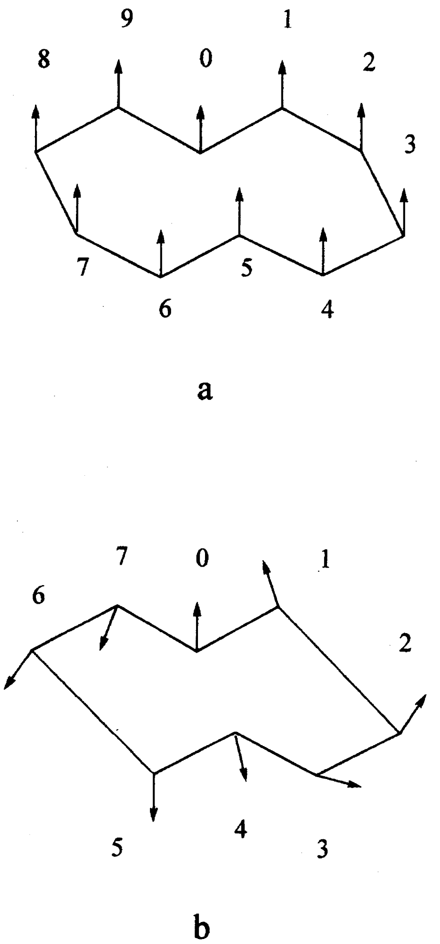

Fig. 5. The Hückel ten membered ring and the Möbius eight membered ring. The arrows stand for the basis functions, $2p\pi$, together with the phases.

the Möbius ring will be made. The reason is that the conrotatory motion makes the coupling between the head and the tail positive.

Now let us consider the Hückel ten-membered ring (see Fig. 5a). The bond order, $q_{05}=0.200$, suggests that the naphtalene molecule will be promising just as it is. Similarly, in the case of the Möbius eight-membered ring (see Fig. 5b), we may expect the central bond as in the naphthalene from the bond order $q_{04}=0.271$. However, in this case, the chain twist makes the coupling, v_{04}, small. Thus the naphthalene-like species or the pentalene will not be likely.

Up to now the Möbius type compounds are not really found. However it is very useful to imagine these fictitious species, in investigating the thermo- and photo-chemical reactivities.[3,4,6] We believe that the present work has shown some clearcut fundamental concepts in the Hückel–Möbius problem.

Appendix

According to Polansky,[9] we can define the atomic localizing energy, E_L, as follows:

$$E_L \equiv E_N^R - \left(E_1^L + E_{N-1}^L\right) \tag{A1}$$

where E_N^R is the total energy of the ring with N sites and E_{N-1}^L is the total energy of the chain with $N-1$ sites.

The substitution of Eq. 14 or Eq. 21 into Eq. 25 yields

$$E_N^L = \begin{cases} 2\left[\operatorname{cosec}\dfrac{\pi}{2(N+1)} - 1\right], & N=\text{even}, \quad \text{(A2)} \\ 2\left[\cot\dfrac{\pi}{2(N+1)} - 1\right], & N=\text{odd}. \quad \text{(A3)} \end{cases}$$

Moreover we can assume that

$$E_1^L = 0, \tag{A4}$$

since the Coulomb integral is put to be zero as an energy standard.

Substituting Eqs. A3 and A4 into Eq. A1, we have the atomic localizing energy of the Hückel ring with $N=4m+2$ sites, $E_L^H(4m+2)$.

$$\begin{aligned} E_L^H(4m+2) &= 2\left(\cot\frac{\pi}{2N} + \tan\frac{\pi}{2N}\right) - 2\left(\cot\frac{\pi}{2N} - 1\right) \\ &= 2\left(1 + \tan\frac{\pi}{2N}\right). \end{aligned} \tag{A5}$$

Similarly $E_L^H(4m)$ is obtained as

$$E_L^H(4m) = 2\left(1 - \tan\frac{\pi}{2N}\right). \tag{A6}$$

Comparing Eqs. A5 and A6, we can conclude that the $4m+2$ membered Hückel ring is more stable than the $4m$ membered Hückel ring.

The atomic localizing energies of the other cases can be obtained in similar ways.

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