

Bond-Alternating Hückel–Möbius and Related, Twisted Linear, Cyclic and Helical Systems—Their Molecular Orbitals, Energies and Phase Correlation Upon Dissociation

Ying-Nan Chiu*

Department of Chemistry, The Catholic University of America, Washington, DC 20064, U.S.A.
and Chemical Kinetics Division, National Bureau of Standards, Washington, DC 20234, U.S.A.

Cyclic group formalism and screw symmetry operation are used to clarify and generalize the definition of Hückel and Möbius systems. It is shown that the Möbius ring system has half-integral pseudo-angular momentum similar to that of spin space, and that applications of Möbius electronics to chemical reactions have been based on truncated single-circle Möbius rings which have unique beginning and end (Sect. 2). This concept is illustrated by application to the [1, 7] antarafacial hydrogen shift (Appendix A and Figs. A1–A3). Definition of a Hückel versus Möbius ring system for in-plane and out-of-plane π , δ and ϕ orbitals as well as the appropriate relative angle of twists are given (Sect. 2 and Table 1). Using the concept of the compatibility of the twist (screw) angle and rotation around a ring, we also derive the proper phase coherence and energy correlation between a parent cyclic (Hückel or Möbius) molecule and its dissociated linear fragments (Sect. 4). The concept of parentage in diabatic fragmentation is discussed.

For *finite*, open, helical chain molecules, an exact periodic boundary condition based on the compatibility of twist angle and number of turns in a helical ring parent molecule is applied to derive their analytic wave functions (Sect. 5 and Table 2). For *bond-alternating* “linear” and cyclic Hückel and Möbius systems we also derive the explicit LCAO-MO wavefunctions, energies, their degeneracies and their exact corresponding quantum members for even and odd atom systems at highest bonding and lowest antibonding levels (Sect. 3,

* Work done while on IPA leave.

Figs. 1–3). The corresponding wavefunctions and energies for uniform-bond systems are given for comparison and for completeness (Sect. 3).

Key words: Conjugate systems – Bond alternation – Hückel systems – Möbius molecular orbitals – Helical molecules – Twisted molecules – Symmetry correlation.

1. Introduction

Orbital theory of pericyclic reactions [1, 2, 3] of Hückel [4] and Möbius [5, 6, 7] systems has received a great deal of attention. There have been many applications of the Möbius concept in such hydrocarbon reactions, particularly by Zimmerman [6, 7] but there has been less work on the abstract geometric nature of the Möbius ring *per se* since the earlier work of Heilbronner [5]. A key to the orbital correlation theory for pericyclic reactions of Woodward and Hoffmann is the knowledge of orbital energies, symmetries, and the relative phases of LCAO-MO wavefunctions at reaction sites. The wavefunctions and energies of uniform-bond cyclic or open-chain Hückel systems (of parallel π -orbitals) are relatively well-known [8, 9]. For alternating-bond [9, 10] Hückel systems, however, even the classic works [11, 12, 13, 14] did not explicitly give the normalized wavefunctions for the linear open chains in analytical form (in fact, general treatment of the 4 N -atom cyclic chain also appears to be missing). In the case of Möbius systems neither the alternating-bond (cyclic and “linear”) nor the uniform-bond “linear” daughter system from Möbius parent has been treated. While the twisting of orbitals (from parallel) is natural and self-evident in a Möbius system, the twisting in a Hückel molecular system in a linear chain or in a helical situation is in principle possible (such as in the case of skewed dienes [15, 16]). Yet no systematic treatment has been given. The early treatment of helices is mainly based on infinite linear systems for which the Born-von Karman cyclic boundary condition applies. No general account was taken of *finite* systems. In the above mentioned systems, even where work is available, there appears to be insufficient detailed account of the following: one to one correspondence of which quantum number for which energy level that corresponds to which LCAO molecular orbital. This is important especially in the case of degenerate levels, and in the case of even vs. odd number of atoms and bonds. The clear delineation of which is the highest occupied and which is the lowest empty orbital is also of paramount importance in frontier-orbital reaction theory [19]. In addition, while the existing work on hydrocarbons provides many interesting examples of π (and σ) systems, in view of the discovery of quadruple (and higher multiple) bonds [20, 21] and in view of the interest in transition metal chain systems [22, 23, 24a], we should extend to conjugate systems involving δ -orbitals (Hückel or Möbius chain beyond the $P_\pi - d_\pi$ of Craig [24b]). It is the purpose of this work to re-examine the basic principle behind the solutions, energies and wavefunction for these systems and to derive general and comprehensive formulas and energy level diagrams for those not available in literature.

2. Geometric View of Hückel and Möbius Systems

We still apply cyclic boundary conditions and use cyclic group formalism [25–26]. But to the usual rotation of angle θ around the circle, C_θ , we add a rotation operation C_χ for twist of angle χ (from being parallel to the first atomic orbital ϕ_0) making it resemble a screw motion in the space group. Thus, we generate the Bloch wavefunction ψ_j for N atoms around a ring from a projection operator as follows: (C_χ and C_θ commute)

$$\psi_j = \frac{1}{\sqrt{N}} \sum_{k=0}^{N-1} e^{(2\pi i/\lambda)X_k} C_\chi^k C_\theta^k \phi_0 \quad (1)$$

where λ is the wavelength of the periodic electron wave. X_k measures the length of the “arc” from the initial atom ϕ_0 to ϕ_k . It is defined as

$$\begin{aligned} X_k &= Rk\theta && \text{(uniform bonds)} \\ X_{2k} &= Rk(\theta_1 + \theta_2) && \text{(for an even atom, alternating bonds)} \\ X_{2k-1} &= Rk(\theta_1 + \theta_2) - R\theta_2 && \text{(for an odd atom, alternating bonds)} \end{aligned} \quad (2)$$

where the bond between $\phi_0\phi_1$ has θ_1 and β_1 and the next bond between ϕ_1 and ϕ_2 has θ_2 and β_2 . R is the average radius of the ring (see illustration A-1 in Appendix). The radian angle θ subtended by the arc formed with two neighboring atoms is proportional to the bond length between them—viz. $\theta_1/\theta_2 = l_1/l_2 \equiv \gamma$, for the alternating neighboring bonds. Application of the usual Hückel (+ sign) or Möbius (– sign) cyclic boundary condition,

$$e^{(2\pi i/\lambda)RN\theta} = \pm e^{2i\pi j} \quad (3)$$

then yields the LCAO-MO for uniform bonds as

$$\psi_j = \sum_{k=0}^{N-1} C_k \phi_k = \frac{1}{\sqrt{N}} \sum_{k=0}^{N-1} e^{(2\pi i j/N)k} \phi_k \quad \text{(Hückel)} \quad (4a)$$

or

$$= \frac{1}{\sqrt{N}} \sum_{k=0}^{N-1} e^{[2\pi i(j+\frac{1}{2})/N]k} \phi_k \quad \text{(Möbius)}. \quad (4b)$$

These wavefunctions have the same form as those used by Heilbronner [5] and Zimmerman [3, 6] except that we now generalize the twists in the orbitals. Note that we have used the coefficients to define the system’s boundary conditions (3). Subsequently we will show that the twists must be compatible with the coefficients to yield stationary waves for the *idealized* Hückel and Möbius systems.

This is the same type of wavefunction that can be obtained from cyclic group projection operators [27], and j in Eq. (4a) is recognized as a pseudo-orbital angular momentum around the cyclic ring. In Eq. (4b) we have purposely displayed $(j+1/2)$ for Möbius system as the half-integral pseudo-angular momentum, corresponding to the angular momentum of a spin space.

Because of this common origin, the form of the wavefunctions for both systems is similar. If the twist of orbitals is not present the cyclic Möbius system is a (non-existing) component of the cyclic Hückel system. This component self-destructs because of destructive interference of the wave around the single Hückel circle (ring), a property of the half-integral (rather than integral) angular momentum. It, however, will survive under two conditions: (1) when the orbital twists $\phi_k = \phi_k^0 \cos \Lambda\chi$ also gives a half-integral angular momentum which adds to the half-integral angular momentum in the Möbius coefficient to give an integral value; (2) when the orbitals have no twist but there is a true Möbius ring which should have two "circles" corresponding to $\theta = 4\pi$ rotation instead of the 2π rotation here. This is similar to a spin space [28, 29] requiring 4π rotation to return to the original point. We want to stress here that the minus sign imposed as Möbius condition in Eq. (3) is but an expedient way to "truncate" a true Möbius strip confining it to one of its two original faces, and that *all of the Möbius system used in chemistry have been truncated* single-circle incomplete Möbius strips. As illustration, suppose we take a strip of paper initially having two sides, to construct a Möbius ring. When we traverse 2π (one circle) angle around the ring, we travel only one side of the paper. It is after we have traversed 4π (2 circles) around the ring, we would have travelled both sides of the paper and return to the original starting point. Only this complete Möbius ring has no beginning and no end and has true translational symmetry which permits us to shift along the ring at will. But, for the truncated single-circle Möbius systems in chemistry, there is a distinct beginning point (at ϕ_0) and a distinct end point at ϕ_{N-1} where interaction sign changes as it progresses to $\phi_N = -\phi_0$. As a result, in the LCAO molecular orbital, the real coefficients of atomic orbitals for a (truncated) Möbius system cannot be arbitrarily shifted without causing possible change in the nature and energy of the M.O. Only if one has a complete two-circle Möbius ring (with $2N$ atoms) the one-unit shift (or any integral atomic shift) will produce exactly the same real wavefunction with the same energy. However, when the coefficients are fixed with correct reference to the interaction sign change and proper twists are present, the *second Möbius circle is redundant*.

Returning to the usual Hückel and (truncated) Möbius system, if the complete cycle is 2π then each rotation C_θ corresponds to $2\pi/N$ angle. However, the constraint here is that there are two rotations C_θ and C_χ instead of one and they must be compatible: namely as repeated C_θ rotations traverse the N atoms and arrived at the 2π end point, the N repeated twists of C_χ must also produce, at this end point, the desired Hückel condition ("plus" sign in Eq. (3), meaning that the last orbital ϕ_N is identical to the first orbital ϕ_0) or to the Möbius condition ("minus" sign in Eq. (3), meaning that the last stop yields an orbital ϕ_N which is of the opposite sign to the first orbital ϕ_0). For a π -atomic orbital with angular momentum $\Lambda = 1$, twists of π , 3π or $(2I+1)\pi$ would give rise to a sign change (negative sign, Möbius condition) and hence $\chi = \pi/N$, $3\pi/N$ and $(2I+1)\pi/N$, where I is an integer. A twist of 3π corresponds to a super-Möbius strip constructed by twisting the paper three half turns instead of the usual half turn (π). These are for idealized geometrical models. Chemical adaptations in

Table 1. Angle of twist χ for atomic orbitals in a N -atomic ring system

Ring system \ Atomic orbitals	$\Lambda = 0$ $nl\sigma$	$\Lambda = 1$ $nl\pi$	$\Lambda = 2$ $nl\delta$	$\Lambda = 3$ $nl\phi$
Hückel	0	$0, \frac{2\pi}{N}, \frac{4\pi}{N}, \dots$	$0, \frac{\pi}{N}, \frac{2\pi}{N}, \dots$	$0, \frac{2\pi}{N}, \frac{4\pi}{N}, \dots$
		$\frac{2I\pi}{N}$	$\frac{I\pi}{N}$	$\frac{2I\pi}{3N}$
Möbius	—	$\frac{\pi}{N}, \frac{3\pi}{N}, \dots$	$\frac{\pi}{2N}, \frac{3\pi}{2N}, \dots$	$\frac{\pi}{N}, \frac{3\pi}{N}, \dots$
		$\frac{(2I+1)\pi}{N}$	$\frac{(2I+1)\pi}{2N}$	$\frac{(2I+1)\pi}{3N}$

literature may draw analogy only to the change of sign of resonance integrals similar to that due to twisted orbitals.

In general, for an atomic orbital with electron azimuthal angle ϕ_e and angular momentum Λ ,

$$C_x^N e^{i\Lambda\phi_e} = e^{i\Lambda(\phi_e + N\chi)} = \pm e^{i\Lambda\phi_e}$$

where the plus sign again means Hückel and the minus sign means Möbius condition. From the above, the angle of twist χ that is compatible with these conditions for σ , π , δ , and ϕ bonding atomic orbitals can be derived and they are shown in Table 1. Only when the Hückel and Möbius twists are combined respectively with Hückel and Möbius coefficients [4a, 4b], will there be stationary waves with *integral* angular momentum in three-dimensional real space, e.g. for π orbitals,

Hückel

$$\begin{aligned} \psi_j &= \frac{1}{\sqrt{N}} \sum_{k=0}^{N-1} e^{(2\pi ij/N)k} \phi_k^0 \cos \frac{2\pi k}{N} \\ &= \frac{1}{2} \frac{1}{\sqrt{N}} \sum_{k=0}^{N-1} [e^{(2\pi i/N)(j+1)k} + e^{(2\pi i/N)(j-1)k}] \phi_k^0 \end{aligned}$$

$$J = j + 1, j - 1 = \text{integers}$$

Möbius

$$\begin{aligned} \psi_j &= \frac{1}{\sqrt{N}} \sum_{k=0}^{N-1} e^{(2\pi i(j+\frac{1}{2})/N)k} \phi_k^0 \cos \frac{\pi k}{N} \\ &= \frac{1}{2} \frac{1}{\sqrt{N}} \sum_{k=0}^{N-1} [e^{(2\pi i/N)(j+1)k} + e^{(2\pi i/N)jk}] \phi_k^0 \end{aligned}$$

$$J = j + 1, j = \text{integers}$$

where ϕ_k^0 is the orbital without a twist.

The azimuthal angular momentum Λ can be quantized (1) with respect to the local (at each atomic site) axis perpendicular to the plane of the ring. Thus the orbitals are in-plane orbitals and the twists are in-plane twists, for example, see Zimmerman's treatment of cyclopropane [6] or (2) with respect to the back bone of the ring namely with respect to the tangent to the curve at each atomic site, thus the orbitals are out-of-plane orbitals and the twists are out-of-plane twists. See for example skewed cyclobutadiene.

The out-of-plane twists are strictly speaking applicable only to a smooth ring with infinite number of atoms or to a straight linear chain. For finite number of atoms, it applies only to special cases where there is equal orbital interaction between any pair of the twisted nearest-neighbor atoms. Namely the resonance integral β between the nearest neighbours must be the same (except for a sign change in the Möbius case, between the first and last atom) so that cyclic boundary condition is valid and the usual solution of the symmetric secular determinant obtains. In this case $\beta = \beta^0 \cos \Lambda\chi$ where β^0 is the resonance integral for parallel orbitals and Λ is the azimuthal angular momentum of the twisted orbital.

Thus, in our definition of the Möbius system we can take a homologous series of Walsh model of ("planar") cycloalkanes (with N carbon atoms around the ring) and consider the in-plane " π " orbital (in contrast to the sp^2 hybrid σ orbital). Then the angle of twist for successive in-plane π -orbitals is by geometry $\chi = (N - 2)\pi/N$. Based on this and referring to Table 1, cyclopropane ($\chi = 60^\circ = \pi/N$) is Möbius [6], cyclobutane ($\chi = 90^\circ = 2\pi/N$) is Hückel, cyclopentane ($\chi = 108^\circ = 3\pi/N$) is Möbius, cyclohexane ($\chi = 120^\circ = 4\pi/6$) is Hückel, cycloheptane ($\chi = 5\pi/7 = 5\pi/N$) is Möbius and cyclooctane ($\chi = 135^\circ = 6\pi/N$) is Hückel. But the angle of twist for the in-plane $sp^2\sigma$ is always $2\pi/N$ and the system is always Hückel (see Table 1).

An abstract example of out-of-plane twist is provided by the four ($N = 4$) π orbitals in allene [3, 6,7].

The above geometrical definition of the Hückel and Möbius system has allowed us to make generalization to orbitals of different angular momentum (Table 1) and to other twisted and helical systems, etc. (see below). Our geometrical definition can be related to Mason's [30] and Zimmerman's [6, 7] definition if we make use of the property of the secular determinant which is used for the solution of LCAO-MO.

3. Bond-Alternating Cyclic and "Linear" Hückel and Möbius Systems

In treating bond-alternating systems we make sure that (1) the orbital phase difference between two neighboring atoms (one with even, one with odd numbering) is explicitly expressed in terms of the ratio between the known bond lengths: $\gamma = l_1/l_2 (= \theta_1/\theta_2)$. (2) The wavefunction of the alternating system reduces to that of uniform system when $\gamma = 1$ or $l_1 = l_2$. (3) The energy which is expressed in terms of the different resonance integrals β_1 and β_2 will also reduce to that of uniform systems when $\beta_1 = \beta_2 = \beta$. (4) Each level of the alternating system goes

over to the corresponding level of the uniform system. This we do by properly labelling each level with its unique quantum number. (5) The difference in energy pattern between even and odd atom systems is definitively worked out, especially at the highest bonding, lowest anti-bonding and the non-bonding levels.

For a ring of bond-alternating system with $2n$ atoms, the Hückel (+ sign) and Möbius (– sign) cyclic boundary condition similar to Eq. (3) is

$$e^{(2\pi i/\lambda)Rn(\theta_1+\theta_2)} = \pm e^{2\pi ij} \quad (5)$$

From this and the ratio $\gamma = \theta_1/\theta_2$ and Eqs. (1)–(2), we get the wavefunction and energy for a cyclic Hückel system with alternating bonds and with $2n$ atoms as follows: (where n may be even n_e or odd n_o).

$$\psi_j = \frac{1}{\sqrt{2n}} \left[\sum_{k=1}^n e^{(2\pi ij/n)(k-1/(1+\gamma))} \phi_{2k-1} + \sum_{k=0}^{n-1} e^{(2\pi ij/n)k} \phi_{2k} \right], \quad (6a)$$

$$E_j = \alpha \pm \left[\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos \frac{4\pi j}{2n} \right]^{1/2}, \quad (6b)$$

where the minus sign applies to

$$j = 0, 1, 2 \dots \left(\frac{n_e}{2} - 1 \right), \left(\frac{n_o - 1}{2} \right); \left(\frac{3n_o + 1}{2} \right), \left(\frac{3n_e + 1}{2} \right), \dots (2n - 1),$$

the plus sign applies to

$$j = \left(\frac{n_o + 1}{2} \right), \left(\frac{n_e + 1}{2} \right) \dots (n - 1), n; (n + 1), \dots \left(\frac{3n_e - 1}{2} \right), \left(\frac{3n_o - 1}{2} \right);$$

and where for

$$j = \frac{n_e}{2}, \quad E = \alpha - |\beta_1 - \beta_2|;$$

$$j = \frac{3n_e}{2}, \quad E = \alpha + |\beta_1 - \beta_2|.$$

The energy levels, their degeneracies and exact correspondence with wavefunctions are shown on Fig. 1. The energy pattern, for the uniform-bond [8–14] Hückel systems are available for comparison. The angles of twist given in Table 1 applies to the above Hückel system. Whereas only bond-alternating *cyclic* systems with even number of atoms are susceptible to this cyclic group treatment, the corresponding bond-alternating *linear* Hückel systems can have *even or odd* atoms. The general wavefunction and energy for the linear N -atom Hückel system with alternating bonds are derived as follows:

$$\psi_j = \sqrt{\frac{2}{N+1}} \left[\sum_{k=1}^{(N_e/2), ((N_o+1)/2)} \sin \frac{2\pi j}{n+1} \left(k - \frac{1}{1+\gamma} \right) \phi_{2k-1} + \sum_{k=1}^{(N_e/2), ((N_o-1)/2)} \sin \frac{2\pi j}{N+1} k \phi_{2k} \right] \quad (7a)$$

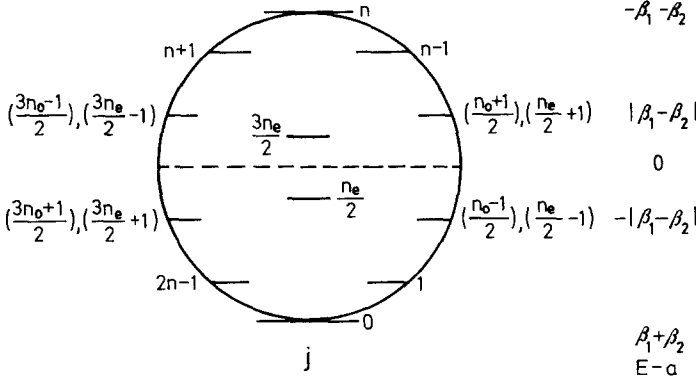


Fig. 1. Energy levels and corresponding quantum numbers of Cyclic Hückel system with even number ($2n$) atoms and *alternating bonds*, $N_e = \text{even}$, $N_o = \text{odd}$. The energy levels are symmetric with respect to the $E - \alpha = 0$ (dotted) line. (Eq. 6)

$$E = \alpha \pm \left[\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos \frac{2\pi j}{N+1} \right]^{1/2} \tag{7b}$$

where the minus sign applies to

$$j = 1, 2, \dots, \left(\frac{N_e}{2} \right), \left(\frac{N_o-1}{2} \right),$$

the plus sign applies to

$$j = \left(\frac{N_e}{2} + 1 \right), \left(\frac{N_o+3}{2} \right), \dots, N,$$

and where for

$$j = \frac{N_o+1}{2}, \quad E = \alpha.$$

The twist angles that apply to this linear Hückel system are those for the parent (see sect. below) cyclic Hückel system with $2N + 2$ atoms (in Table 1 replace N by $2N + 2$).

The energy pattern is similar to that of the uniform-bond system but the splitting between the highest bonding and lowest anti-bonding orbitals is larger for the alternating system.

For bond-alternating cyclic Möbius system with $2n$ atoms we obtained the wavefunction and energy as follows:

$$\psi_j = \frac{1}{\sqrt{2n}} \left[\sum_{k=1}^n e^{[\pi i(2j+1)/n](k-1/(1+\gamma))} \phi_{2k-1} + \sum_{k=0}^{n-1} e^{[\pi i(2j+1)/n]k} \phi_{2k} \right], \tag{8a}$$

$$E_j = \alpha \pm \left[\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos \frac{2\pi(2j+1)}{2n} \right]^{1/2}, \tag{8b}$$

where the minus sign applies to

$$j = 0, 1, 2 \cdots \left(\frac{n_e}{2} - 1\right), \left(\frac{n_0 - 3}{2}\right); \left(\frac{3n_0 + 1}{2}\right), \left(\frac{3n_e}{2}\right) \cdots (2n - 1),$$

the plus sign applies to

$$j = \left(\frac{n_e}{2}\right), \left(\frac{n_0 + 1}{2}\right) \cdots (n - 1); n \cdots \left(\frac{3n_0 - 3}{2}\right), \left(\frac{3n_e}{2} - 1\right),$$

and where for

$$j = \frac{n_0 - 1}{2}, \quad E = \alpha - |\beta_1 - \beta_2|,$$

$$j = \frac{3n_0 - 1}{2}, \quad E = \alpha + |\beta_1 - \beta_2|.$$

The energy levels, degeneracies and their exact correspondence with the wavefunctions are shown in Fig. 2. The energy patterns for the uniform-bond Möbius system [5] are available.

The angles of twist given in Table 1 apply to the above Möbius systems. Whereas linear N -atomic Hückel system can always be obtained from the $(2N + 2)$ parent cyclic Hückel system, linear N -atomic Möbius system cannot be obtained from the corresponding parent Möbius system because the wavefunction will not vanish properly beyond the end of the linear chain. It can be obtained however from the $(N + 1)$ parent Möbius system. But it turns out to be a partial fiction because it has incomplete number of energy levels. The reason is that in a $(2N + 2)$ parent cyclic Hückel system, the exponential wavefunctions of Eq. (4a) naturally combine to give $(N + 2)$ cosine functions and N sine functions. The sine function $\sin [2\pi j / (2N + 2)]k$ vanishes properly beyond the chain at $k = 0$ and $k = N + 1$ and are chosen naturally as the linear wavefunctions. On the other

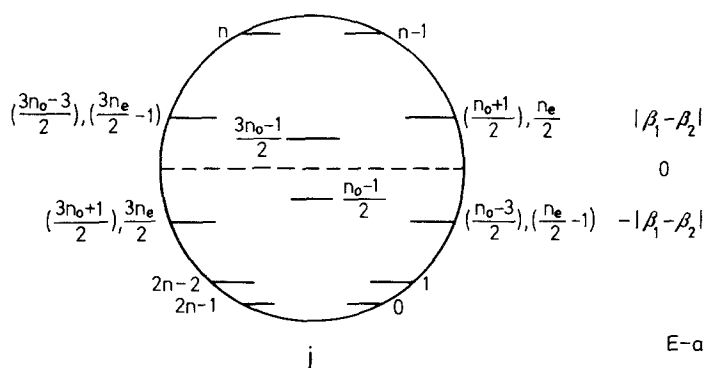


Fig. 2. Energy levels and corresponding quantum numbers of Cyclic Möbius system with even number $(2n)$ of atoms and *alternating bonds*. The energy levels are symmetric with respect to the $E - \alpha = 0$ (dotted) line. (Eq. 8)

hand the cyclic Möbius exponential functions of Eq. (4b) combine to give half cosine functions and half sine functions (for even number of atoms, for odd number of atoms there is one more cosine). The sine function does not vanish at the desired boundary, simply because the sine function $\sin [2\pi(j+1/2)/(2N+2)]k$ is not zero at $k=N+1$. It vanishes only at $k=2N+2$ hence the choice of parent cyclic chain that is one unit larger than the linear chain (of size $2N+1$). Because the bond-alternating Möbius cyclic has even number of atoms (odd-number not amenable to cyclic group treatment) we can take it to be $N_0+1=2n$ when N_0 is odd. And the N_0 -chain wavefunction and energy for bond-alternative "linear" Möbius system are as follows:

$$\psi_j = \sqrt{\frac{2}{N_0+1}} \left[\sum_{k=1}^{(N_0+1)/2} \sin \frac{2\pi(2j+1)}{N_0+1} \left(k - \frac{1}{1+\gamma} \right) \phi_{2k-1} + \sum_{k=0}^{(N_0-1)/2} \sin \frac{2\pi(2j+1)}{N_0+1} k \phi_{2k} \right], \quad (9a)$$

$$E = \alpha \pm \left[\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos \frac{2\pi(2j+1)}{N_0+1} \right]^{1/2} \quad (9b)$$

where the minus sign applies to

$$j = 0, 1, \dots, \frac{(N_0-5)}{4}, \frac{(N_0-3)}{4},$$

the plus sign applies to

$$j = \left(\frac{N_0+1}{4} \right), \left(\frac{N_0+3}{4} \right), \dots, \left(\frac{N_0-1}{2} \right) (\text{max}),$$

and where for

$$j = \frac{N_0-1}{4}, \quad E = \alpha.$$

The twist angles for this linear system are those for the N_0+1 parent Möbius cyclic system (in Table 1 set N to N_0+1). The energy pattern is given in Fig. 3.

The above formula reduce to those for uniform-bond N_0 -chain "linear" Möbius system as follows:

$$\psi_j = \sqrt{\frac{2}{N_0+1}} \sum_{k=1}^{N_0} \sin \frac{\pi(2j+1)}{N_0+1} k \phi_k, \quad (10a)$$

$$E = \alpha + 2\beta \cos \frac{\pi(2j+1)}{N_0+1} \quad (10b)$$

$$j = 0, 1, 2, \dots, \frac{N_0-1}{2} (\text{max}).$$

The maximum total number of energy levels is $(N_0+1)/2$ which is half of the number in the (N_0+1) parent cyclic Möbius system. This number is far less than

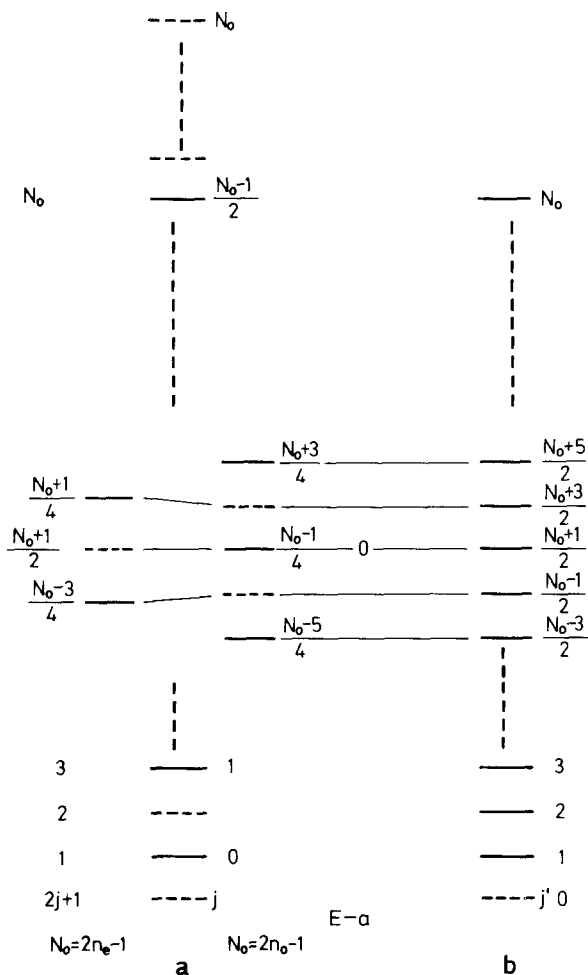


Fig. 3. Comparison of bond-alternating and uniform “linear” Möbius system (6a) with corresponding linear Hückel system (6b), both of N_0 atoms. The Möbius energy (Eq. (9)–(10)) is seen to have missing levels and the maximum number of Möbius levels $(N_0 + 1)/2$ is short of the required N_0 levels and therefore is incomplete. This linear Möbius system is split off from an even-atom $N_0 + 1 = 2N$ Cyclic Möbius parent. (Odd-atom Cyclic Möbius parent with alternating-bond is not amenable to such treatment by cyclic (periodic) boundary condition.) The Hückel energy from $(2N_0 + 2)$ parent is taken to be $E = \alpha + 2\beta \cos \pi j' / (N_0 + 1)$, (compare Eq. (10))

the expected N_0 levels for the N_0 -atom “linear” Möbius system and hence the “linear” Möbius system is *incomplete*. Since the boundary condition at both ends is the same for a linear system regardless of its twist and regardless of whether we call it Möbius or Hückel, we see that the above solutions, Eqs. (9)–(10) are incomplete in another sense—that it contains only selected levels of a linear system. This will be clear when we compare the “linear” Möbius system of Eq. (10) with the linear Hückel system. The latter can be obtained from $2N + 2$ parent rather than the $(N + 1)$ parent. From (Eq. 7) when $\gamma = 1$, the Hückel

linear system is

$$\psi_j = \left(\frac{2}{N+1} \right)^{1/2} \sum_{k=1}^N \sin \left(\frac{\pi j k}{N+1} \right) \phi_k.$$

Comparison shows (see Fig. 3) that the “linear” Möbius system is part of the more general Hückel linear system. It contains only wavefunctions with odd $j'(=2j+1)$ which are necessarily only those selected waves that when joined together to form the parent (N_0+1) circle will have destructive interference if extended over the *same* single circle—a condition for the truncated Möbius system (see Appendix A). This brings up the question of the parentage of linear systems in the next section. Parentage is pertinent when we want to know the kind of wavefunction to which the parent system will correlate at the instant of dissociation into fragments—from a $(N+1)$ atom parent to a N -atom fragment and from $(2N+2)$ to N etc.

4. Twisted Linear Hückel–Möbius Systems and their Parentage—Orbital Phase Coherence Upon Dissociation

In the treatment of finite, linear open chain of atoms, an important concern is to make sure that the wavefunction vanishes at both ends of the open chain. This we accomplish in the usual way for linear Hückel system with uniform or alternating bonds, by adding $N+2$ phantom atoms to the N -atom chain to complete a ring. The cyclic boundary condition is then applied to the resulting $2N+2$ ring.

The choice of $(2N+2)$ cyclic parent for a linear N -chain is a natural and convenient approximation for LCAO-MO as discussed previously.

However, other parent molecules can also contain N sine functions. And as long as the sine waves vanish beyond the boundary of the N -chain, they are acceptable approximations if the end effects are not severe. For example a $(2N+1)$ parent cyclic Hückel system (see Fig. 2) will have N doubly-degenerate energy levels yielding N cosine and N sine wavefunctions. The sine wavefunctions will vanish at atom 0 and at the fractional atom position $(N+1/2)$. When the phases are symmetrized with respect to the two chain ends, the waves vanish at fractional atom positions $1/4$ and $N+3/4$ and they are reasonable approximations to the linear wavefunction of the N -atom chain at the instant of fragmentation from the $(2N+1)$ parent circle. This is because when rejoined to form the parent it will have the *correct phase coherence to mesh with the rest*. Of course the angle of twist must vary with cyclic parent size in order to be compatible with the cyclic boundary condition. The most general formula for the linear N -chain phase-symmetrized (instantaneous) wavefunction and energy derived from given parents with given twist angles are as follows:

twist

$$\chi = 0, \frac{\pi}{AN+B} \quad \text{for } \pi \text{ and } \phi \text{ orbitals,}$$

$$\chi = 0, \frac{\pi}{2(AN+B)} \text{ for } \delta \text{ orbitals.}$$

From parent Hückel circle $2(AN+B)$;

$$\psi_j = \sum_{k=1}^N \sin \frac{\pi j}{AN+B} \left(k - \frac{1}{2} + \frac{B}{2A} \right) \phi_k, \quad (11a)$$

$$E_j = \alpha + 2\beta \cos \frac{\pi j}{AN+B}, \quad (11b)$$

where $j = \text{integers} = \dots j'A = \max \{ [2(AN+B)]_{\text{even}} - 2 \} / 2$ or $\max \{ [2(AN+B)]_{\text{odd}} - 1 \} / 2$.

j' is an integer and β is the resonance integral corrected for the twist. For π orbital $\beta = \beta_{\pi}^0 \cos \chi$, for δ orbital $\beta = \beta_{\delta}^0 \cos 2\chi$ and for ϕ orbital $\beta = \beta_{\phi}^0 \cos 3\chi$. From parent Hückel circle $4(AN+B)$

$$\psi_j = \sum_{k=1}^N \sin \frac{\pi j}{2(AN+B)} \left(k - \frac{1}{2} + \frac{B}{2A} \right) \phi_k, \quad (12a)$$

$$E = \alpha + 2\beta \cos \frac{\pi j}{2(AN+B)}, \quad (12b)$$

where $j = \text{integers} = 2j'A = \dots \max \{ [4(AN+B)]_{\text{even}} - 2 \} / 2$ or $\max \{ [4(AN+B)]_{\text{odd}} - 1 \} / 2$.

A, B may be fractional numbers but $-1 < B/A \leq 1$ must be true to insure that the wave does not vanish at more than one extra atom beyond the end of the chain. (This latter would obligate us to include this extra atom in LCAO-treatment).

The wavefunctions vanish at fractional atomic positions $k = 1/2 - B/(2A)$ and $k = N + 1/2 + B/(2A)$.

As was alluded to previously, the parent molecule dictates not only the instantaneous phase of the daughter fragment but also the energy levels of the fragment. For example, for the same twist of $2\pi/(N+1)$, the smaller cyclic parent ($N+1$) gives linear-system energies that are larger (quantum number $2j$ vs. j) than those from the larger cyclic parent ($2N+2$). This is in parallel to the fact that smaller systems have larger quantum. At the same time while the smaller parent gives insufficient sine wavefunctions and only selected (excited) energies, the larger parent will allow for all of the sine functions and a complete set of energies (for the linear fragment).

Fragments can also be dissociated from Möbius parents. The general formula for the linear N -chain phase-symmetrized (instantaneous), wavefunction and energy derived from given parents with given twist angles are obtained as follows. These were referred to previously (Sect. 3) as "linear" Möbius systems (Eqs. (9)-(10)).

twist

$$\begin{aligned}\chi &= \frac{\pi}{AN+B} \quad \text{for } \pi \text{ and } \phi \text{ orbitals,} \\ &= \frac{\pi}{2(AN+B)} \quad \text{for } \delta \text{ orbitals.}\end{aligned}$$

From parent Möbius cycle $(AN+B)$

$$\psi_j = \sum_{k=1}^N \sin \frac{\pi(2j+1)}{AN+B} \left(k - \frac{1}{2} + \frac{B}{2A} \right) \phi_k, \quad (13a)$$

$$E = \alpha + 2\beta \cos \frac{\pi(2j+1)}{AN+B}, \quad (13b)$$

where $j = \text{integers} = (j'A - 1)/2 = 0, 1, 2, \dots, \max \left\{ \left[\frac{(AN+B)_{\text{even}}}{2} \right] - 1 \right\},$
or $\max \left[\frac{(AN+B)_{\text{odd}} - 3}{2} \right].$

$j' = \text{odd integers}$ and A is also odd.

From parent Möbius circle $3(AN+B)$,

$$\psi_j = \sum_{k=1}^N \sin \frac{\pi(2j+1)}{3(AN+B)} \left(k - \frac{1}{2} + \frac{B}{2A} \right) \phi_k \quad (14a)$$

$$E = \alpha + 2\beta \cos \frac{\pi(2j+1)}{3(AN+B)} \quad (14b)$$

where $j = \text{integers} = (3j'A - 1)/2 = 1, 4, 7, \dots, \max \left\{ \frac{[3(AN+B)]_{\text{even}}}{2} - 1 \right\},$
or $\max \left\{ \frac{[3(AN+B)]_{\text{odd}} - 3}{2} \right\}.$

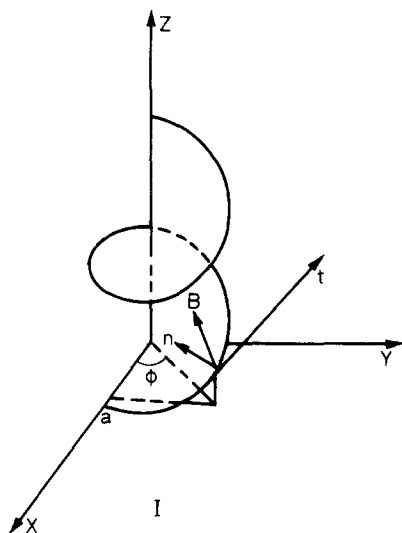
As alluded to previously there is no linear Möbius system *per se*, only linear systems derived from Möbius parent with appropriate twist and with insufficient and selected energy levels and special phase coherence factor. Namely, when rejoined into a Möbius parent, they will have the correct phase.

The phase factors tell where the electron wave has vanishing nodes. When combined with the correlation to selected energy levels of the fragmentation product, they may be of interest in the diabatic dissociation of (Hückel or Möbius) circlic system. For example, a five-member Hückel ring may be dissociated into N and N' fragments, with $N = 2$ and $N' = 3$ or $N = 4$ and $N' = 1$. At the instant of dissociation the phase and π electron (only) energy of fragment $N = 2$ (the ethylenic fragment) may be obtained from the parent according to $5 = 2N + 1$. Those for the allylic fragment $N' = 3$ may be obtained from the parent according to $5 = 2N' - 1$. This may be compared with the final adiabatically equilibrated

fragment for ethylene (from $2N + 2 = 6$, six-member cyclic parent) and allyl (from $2N' + 2 = 8$, eight-member cyclic parent).

5. Finite Open-Chain Helical Systems

While strictly speaking the Born–Von Karman cyclic boundary condition [18] may be applied only in *infinite* systems, it has nevertheless been applied to *finite* helical polymers in the past. From the treatment of last Section, it is seen that unless the twists and turns of a linear chain dovetail smoothly into Hückel or Möbius condition in a parent circle, none of these cyclic (periodic) conditions is strictly applicable.



In this Section we shall derive, for finite helices, a few requirements for these cyclic conditions. We consider a right circular helix (I) wound around the Z axis. We describe a point on the helical curve as follows: [31–33]

$$\begin{aligned} X &= a \cos \phi \\ Y &= a \sin \phi \\ Z &= b(\phi - \pi t) \end{aligned} \tag{15}$$

where the azimuthal angle ϕ measures from the starting point on the X axis and t is the number of turns. The pitch at the end of one turn or at $\phi = 2\pi$ is $b\pi$. The mutually perpendicular, tangent (\vec{t}), normal (\vec{n}) and binormal (\vec{B}) to the curve at a given point are

$$\vec{t} = (-a \sin \phi, a \cos \phi, b) / \sqrt{a^2 + b^2} \tag{16a}$$

$$\vec{n} = (-\cos \phi, -\sin \phi, 0) \tag{16b}$$

$$\vec{B} = (b \sin \phi, -b \cos \phi, a) / \sqrt{a^2 + b^2}. \tag{16c}$$

A π -atomic orbital parallel to the tangent is similar to the in-plane π orbital for a Walsh-model cycloalkane (Sect. 2). The normal is always pointed past the Z axis. The binormal may be taken for convenience as the axis for perpendicular orbitals similar to those off-plane orbitals. (A "off-plane" π orbital simply points along \vec{B} direction). If this helix is made up of N atoms completing t (may be fractional) turns, then the azimuthal angle between two successive atoms should be $\phi = 2\pi t/(N-1)$. At the first atom ($\phi = 0$) the binormal vector (or the "off-plane" π -orbital) is

$$\vec{B}_1 = (0, -b, a)/\sqrt{a^2 + b^2}.$$

At the second atom, the binormal vector has the form of (16c). The angle between these two binormals is the twist angle χ_0 between the two "off-plane" atomic orbitals and may be approximated for large N and smooth helix from the scalar product of these two vectors. Viz.

$$\begin{aligned} \cos \chi_0 &\equiv \frac{1}{a^2 + b^2} (a^2 + b^2 \cos \phi) \\ &= \frac{1}{a^2 + b^2} \left(a^2 + b^2 \cos \frac{2t\pi}{N-1} \right). \end{aligned} \quad (17a)$$

Similarly for "in-plane" type orbital along the tangent of curve, the twist angle is defined by:

$$\begin{aligned} \cos \chi_i &\equiv \frac{1}{a^2 + b^2} (a^2 \cos \phi + b^2) \\ &= \frac{1}{a^2 + b^2} \left(a^2 \cos \frac{2t\pi}{N-1} + b^2 \right). \end{aligned} \quad (17b)$$

Here χ is a dihedral angle defined only between two successive atomic orbitals and strictly speaking is valid only when the two centers are assumed very close. However, after a complete integral turn ($t = \text{integer} = n$) of the helix $\phi = 2\pi t = 2\pi n$, it is seen that Eq. (17) gives $\cos \chi = 1$ or $\chi = 2\pi$, returning all twisted orbitals to the original as expected. The same result obtains if the orbital is taken to be along an arbitrary vector $P\vec{i} + q\vec{j} + s\vec{k}$ provided $p^2 + q^2 + s^2 = 1$. Eq. (17) is the basic condition governing the relationship between the size, the (fractional) number of turns of the finite helix, its radius and its pitch. However this condition is not enough if we are to apply cyclic boundary condition to the cyclic parent molecule of this finite helical chain. This parent molecule must have *integral* number of turns for the twist and turns of the helix to dove-tail into a closed smooth ring. For the Hückel and Möbius condition we take the parent size as $2(AN+B)$ and $(AN+B)$ respectively and get the twist angles (χ^h for Hückel and χ^m for Möbius) as follows:

$$\begin{aligned} 2(AN+B) \frac{2t\pi}{N-1} &= 2\pi n \quad (\text{Hückel}) \\ \chi^h &= \frac{2I\pi}{2(AN+B)} \end{aligned} \quad (18a)$$

$$(AN + B) \frac{2t\pi}{N-1} = 2\pi n' \quad (\text{Möbius})$$

$$\chi^m = \frac{(2I+1)\pi}{(AN+B)}$$
(18b)

where I , n and n' are integers, and the Hückel and Möbius conditions are from Table 1, (the χ 's in Eq. (18) are for π and ϕ orbitals for δ orbitals reduce the angle by half).

For both conditions Eqs. (17) and (18) to hold and be compatible we combine them to solve for the necessary ratio of a/b as related to other (somewhat adjustable) parameters A and B :

“off-plane” orbital (along binormal)

(Hückel)

$$\frac{a^2}{b^2} = \frac{\sin \left[\frac{t}{N-1} + \frac{I}{2(AN+B)} \right] \pi \sin \left[\frac{t}{N-1} - \frac{I}{2(AN+B)} \right] \pi}{\sin^2 \frac{I\pi}{2(AN+B)}},$$
(19a)

(Möbius)

$$\frac{a^2}{b^2} = \frac{\sin \left[\frac{2t}{N-1} + \frac{2I+1}{AN+B} \right] \frac{\pi}{2} \sin \left[\frac{2t}{N-1} - \frac{2I+1}{AN+B} \right] \frac{\pi}{2}}{\sin^2 \frac{(2I+1)\pi}{2(AN+B)}}.$$
(19b)

For “in-plane” orbital (along tangent) the role of a and b is interchanged and the ratio is the inverse of those of “off-plane” orbitals. Eq. (19) above is for π and ϕ orbitals for δ orbitals read $2(AN+B)$ for every $(AN+B)$.

The wavefunction of the linear chain may then be obtained from the cyclic parent according to equations similar to Eqs. (11) and (13).

Examples for Eq. (19) for some finite systems with various a/b ratios are given in Table 2 where the analytic form of wavefunctions and energies are also given. In principle, for a finite chain of molecules one can solve in numerical form the energies and LCAO wavefunctions [34–38], even including electronic interactions in SCF treatment, and other sophisticated approximations [36]. Therefore the conditions and wavefunctions derived here are more meaningful as a guide to dissociation of a finite helical chain from a parent cyclic molecule (as a guide to energy and phase correlation). The theoretical treatment (Eqs. (18)–(19) defines the relationship between the helix parameters of parent and fragments. Qualitative understanding of the orbital phases is also possible given a/b ratios approximating the values of the theoretical model. As is seen from Table 2 the most natural dissociation giving a complete set of ground energy levels for a linear fragment is from a $(2N+2)$ cyclic parent in Hückel case. Dissociation from Möbius $(N+1)$ parent or $(3N+3)$ parent either gives insufficient number

Table 2. Helical parameters and LCAO-MO wavefunctions of finite helical chain derived from cyclic parent molecules¹

Twist angle χ	Orbital	Helix size	No. turns	a/b	Cyclic parent size	LCAO-MO,		Vanishing end points $k =$	Energy ² $E - \alpha =$	Quantum numbers
						Wavefunction of open helical chain $\psi =$	Wavefunction of open helical chain $\psi =$			
$2\pi/8$	π, ϕ	3	1	2.414	8, Hückel	$\sqrt{\frac{1}{2}} \sum_{k=1}^3 \sin \frac{\pi j k}{4} \phi_k$	$\sqrt{\frac{1}{2}} \sum_{k=1}^3 \sin \frac{\pi j k}{4} \phi_k$	$k = 0, 4$	$2\beta \cos \frac{\pi j}{4}$	$j = 1, 2, 3$
$2\pi/8$	π, ϕ	3	$\frac{1}{2}$	1.554	8, Hückel	$\sqrt{\frac{1}{2}} \sum_{k=1}^3 \sin \frac{\pi j k}{4} \phi_k$	$\sqrt{\frac{1}{2}} \sum_{k=1}^3 \sin \frac{\pi j k}{4} \phi_k$	$k = 0, 4$	$2\beta \cos \frac{\pi j}{4}$	$j = 1, 2, 3$
$2\pi/16$	δ	3	1	5.027	8, Hückel	$\sqrt{\frac{1}{2}} \sum_{k=1}^3 \sin \frac{\pi j k}{4} \phi_k$	$\sqrt{\frac{1}{2}} \sum_{k=1}^3 \sin \frac{\pi j k}{4} \phi_k$	$k = 0, 4$	$2\beta \cos \frac{\pi j}{4}$	$j = 1, 2, 3$
$2\pi/16$	δ	3	$\frac{1}{2}$	3.483	8, Hückel	$\sqrt{\frac{1}{2}} \sum_{k=1}^3 \sin \frac{\pi j k}{4} \phi_k$	$\sqrt{\frac{1}{2}} \sum_{k=1}^3 \sin \frac{\pi j k}{4} \phi_k$	$k = 0, 4$	$2\beta \cos \frac{\pi j}{4}$	$j = 1, 2, 3$
$2\pi/12$	π, ϕ	5	1	2.542	12, Hückel	$\sqrt{\frac{1}{3}} \sum_{k=1}^5 \sin \frac{\pi j k}{6} \phi_k$	$\sqrt{\frac{1}{3}} \sum_{k=1}^5 \sin \frac{\pi j k}{6} \phi_k$	$k = 0, 6$	$2\beta \cos \frac{\pi j}{6}$	$j = 1, 2, 3, 4, 5$
$2\pi/24$	δ	5	1	5.324	12, Hückel	$\sqrt{\frac{1}{3}} \sum_{k=1}^5 \sin \frac{\pi j k}{6} \phi_k$	$\sqrt{\frac{1}{3}} \sum_{k=1}^5 \sin \frac{\pi j k}{6} \phi_k$	$k = 0, 6$	$2\beta \cos \frac{\pi j}{6}$	$j = 1, 2, 3, 4, 5$
$\pi/4$	π, ϕ	3	1	2.414	4, Möbius	$\sqrt{\frac{1}{2}} \sum_{k=1}^3 \sin \frac{\pi(2j+1)}{4} k \phi_k$	$\sqrt{\frac{1}{2}} \sum_{k=1}^3 \sin \frac{\pi(2j+1)}{4} k \phi_k$	$k = 0, 4$	$2\beta \cos \frac{\pi(2j+1)}{4}$	$j = 0, 1$ (incomplete)
$\pi/4$	π, ϕ	3	$\frac{1}{2}$	1.554	4, Möbius	$\sqrt{\frac{1}{2}} \sum_{k=1}^3 \sin \frac{\pi(2j+1)}{4} k \phi_k$	$\sqrt{\frac{1}{2}} \sum_{k=1}^3 \sin \frac{\pi(2j+1)}{4} k \phi_k$	$k = 0, 4$	$2\beta \cos \frac{\pi(2j+1)}{4}$	$j = 0, 1$ (incomplete)

$\pi/8$	δ	3	1	5.027	4, Möbius	$\sqrt{\frac{1}{2}} \sum_{k=1}^3 \sin \frac{\pi(2j+1)}{4} k\phi_k$	$k=0, 4$	$2\beta \cos \frac{\pi(2j+1)}{4}$	$j=0, 1$ (incomplete)
$\pi/8$	δ	3	$\frac{1}{2}$	3.483	4, Möbius	$\sqrt{\frac{1}{2}} \sum_{k=1}^3 \sin \frac{\pi(2j+1)}{4} k\phi_k$	$k=0, 4$	$2\beta \cos \frac{\pi(2j+1)}{4}$	$j=0, 1$ (incomplete)
$\pi/15$	π, ϕ	4	1	8.226	15, Möbius	$\sqrt{\frac{2}{5}} \sum_{k=1}^4 \sin \frac{\pi(2j+1)}{15} k\phi_k$	$k=0, 5$	$2, \beta \cos \frac{\pi(2j+1)}{15}$	$j=1, 4$ (incomplete)
$\pi/30$	δ	4	1	16.518	15, Möbius	$\sqrt{\frac{2}{5}} \sum_{k=1}^4 \sin \frac{\pi(2j+1)}{15} k\phi_k$	$k=0, 5$	$2, \beta \cos \frac{\pi(2j+1)}{15}$	$j=1, 4$ (incomplete)
$\pi/16$	π, ϕ	6	1	5.912	16^3 , Möbius	$\sqrt{\frac{2}{7}} \sum_{k=1}^6 \sin \frac{\pi(2j+1)}{16} \left(k - \frac{5}{6}\right) \phi_k$	$k = \frac{5}{6}, \frac{37}{6}$	$2\beta \cos \frac{\pi(2j+1)}{16}$	$j=1, 4, 7$ (incomplete, excited)
$\pi/32$	δ	6	1	11.937	16^3 , Möbius	$\sqrt{\frac{2}{7}} \sum_{k=1}^6 \sin \frac{\pi(2j+1)}{16} \left(k - \frac{5}{6}\right) \phi_k$	$k = \frac{5}{6}, \frac{37}{6}$	$2\beta \cos \frac{\pi(2j+1)}{16}$	$j=1, 4, 7$ (incomplete, excited)

¹ The a/b ratio is given for off-plane orbitals (along binormal). The a/b ratio is the inverse of those given if the orbitals are in-plane (along tangent).

² For off-plane π -orbitals $\beta = \beta_\pi^0 \cos \chi$, for δ , $3 = \beta_\delta^0 \cos 2\chi$, for ϕ , $\beta = \beta_\phi^0 \cos 3\chi$.

³ Approximation. For perfect dovetailing, 15-member ring parent ($\chi = \pi/15$ or $\pi/30$ respectively) is needed.

of energy levels or excited energies. It may be mentioned that although the justifications of periodic boundary condition have been given in the past [39–40], these are concerned with the longitudinal symmetry along the backbone of the helix. Only Power and Thirunamachandran [32] has considered the transverse motions of a free electron so far, and they were not concerned with the twist of orbitals along the backbone of the helix.

Acknowledgment. The writer wishes to thank Drs. Wing Tsang and John T. Herron for making possible his stay at the Chemical Kinetics Division, National Bureau of Standards where this work was done. He had enjoyed discussions with Drs. Morris Krauss, William Sanders and Gerald Zon. Dr. Krauss in particular served as a proving ground for the writer's ideas and called the writer's attention to aspects of electronic theory of chemical reactions that are worth further thought and study. In addition Dr. Krauss read the manuscript and suggested improvements in presentation and in content. The writer is grateful and delighted to receive, near the completion of the manuscript a preprint from Professor Howard Zimmerman on "Möbius and Hückel system in the SCF and CI approximation" (published in *Tetrahedron*) [7b] and is gratified to note that Professor Zimmerman in a different way also shows the common origin of the Hückel and Möbius system. Professors Zimmerman and Heilbronner both gave extensive and useful comments which help improve the paper considerably. The writer surmises that Professor Heilbronner had previously thought about some of these points in the paper himself. Acknowledgment is gratefully made to colleagues at the Chemical Kinetics Division, NBS for this hospitality—Dr. Robert E. Huie especially for sharing his office and Dr. Wing Tsang for his understanding of the working habits (and hours) of some theoreticians!

Appendix A

Planar Bond-Alternating Möbius Cyclo-octatetraene and [1, 7] Antarafacial Hydrogen Migration.

As discussed in Sect. 2 the chemical system Möbius Cyclooctatetraene ($N = 2n = 8$) is the truncated system from a true Möbius ring of $N = 16$. For this truncated system with alternating bonds the (complex) wavefunction and energy from Sect.

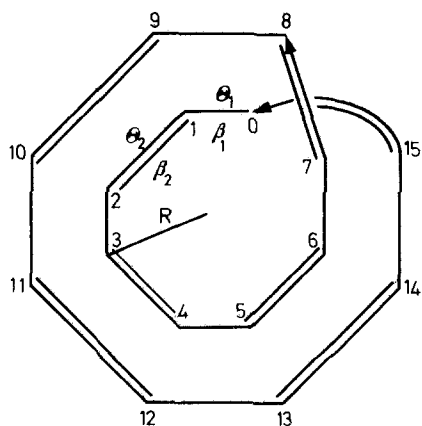


Fig. A-1. Schematic representation of a "double-circle" Möbius ring of sixteen atoms, and the representation of a planar bond-alternating cyclooctatetraene by a truncated Möbius system (from atom no. 0 to no. 7 and back to no. 0). R is the average radius of the ring (see (Eqs. (2)–(3))

3 are as follows

$$\psi_j = \frac{1}{\sqrt{8}} \left[\sum_{k=1}^4 e^{[\pi i(2j+1)/4](k-1/(1+\gamma))} \phi_{2k-1} + \sum_{k=0}^3 e^{[\pi i(2j+1)/4]k} \phi_{2k} \right],$$

$$E = \alpha \pm \left[\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos \frac{2\pi(2j+1)}{8} \right]^{1/2},$$
(A-1)

where the $-$ sign applies to $j = 0, 1, 6, 7$ and the sign $+$ applies to $j = 2, 3, 4, 5$, with two-fold degeneracy between j and $(7-j)$ levels. The ratio of bond length [9] is $\gamma = \theta_1/\theta_2 = 1.455/1.365 = 1.0659$ and $1/(1+\gamma) = 0.484$. The energy levels and numbering convention are given in Fig. A-1. The real wavefunctions in terms of cosine (ψ^c) and sine (ψ^s) functions can be obtained by linear combination of the two degenerate complex wavefunctions. The extension to the true “double-circle” Möbius ring system is straightforward by making use the symmetry property of sine/cosine functions. Thus,

$$\psi_{j,7-j}^c = N_{\frac{1}{2}}(\psi_j + \psi_{7-j})$$

$$= N_c \left[\sum_{k=1}^4 \cos \frac{\pi(2j+1)}{4}(k-0.484)\phi_{2k-1} + \sum_{k=0}^3 \cos \frac{\pi(2j+1)}{4}k\phi_{2k} \right]$$

$$- N_c \left[\sum_{k=1}^4 \cos \frac{\pi(2j+1)}{4}(k-0.484)\phi_{2k+7} + \sum_{k=0}^3 \cos \frac{\pi(2j+1)}{4}k\phi_{2k+8} \right],$$
(A-3)

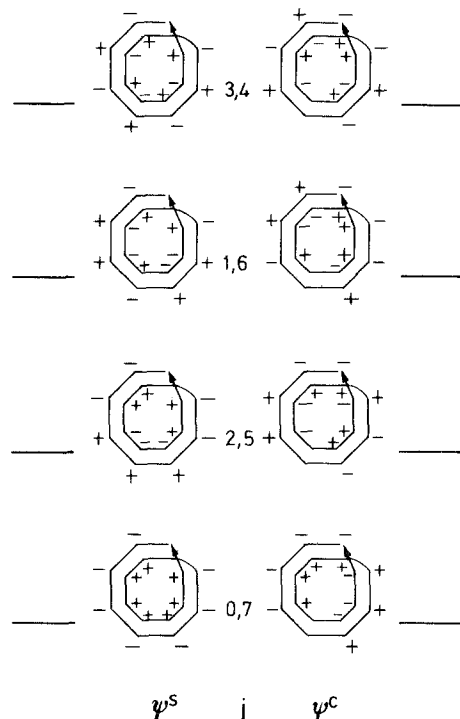


Fig. A-2. Energy levels and LCAO-MO phases of a truncated Möbius system (planar cyclooctatetraene) and its theoretical extension into a “double-circle” complete Möbius ring

$$\begin{aligned}
 \psi_{i,7-j}^s &= N \frac{1}{2i} (\psi_j - \psi_{7-j}) \\
 &= N_s \left[\sum_{k=1}^4 \sin \frac{\pi(2j+1)}{4} (k-0.484) \phi_{2k-1} + \sum_{k=0}^3 \sin \frac{\pi(2j+1)}{4} h \phi_{2k} \right] \\
 &\quad - N_s \left[\sum_{k=1}^4 \sin \frac{\pi(2j+1)}{4} (k-0.484) \phi_{2k+7} + \sum_{k=0}^3 \sin \frac{\pi(2j+1)}{4} k \phi_{2k+8} \right],
 \end{aligned}
 \tag{A-4}$$

Where the second brackets in Eqs. (A-3) and (A-4) indicate the extension into the "second" Möbius circle and also clearly shows that a shift of atomic number

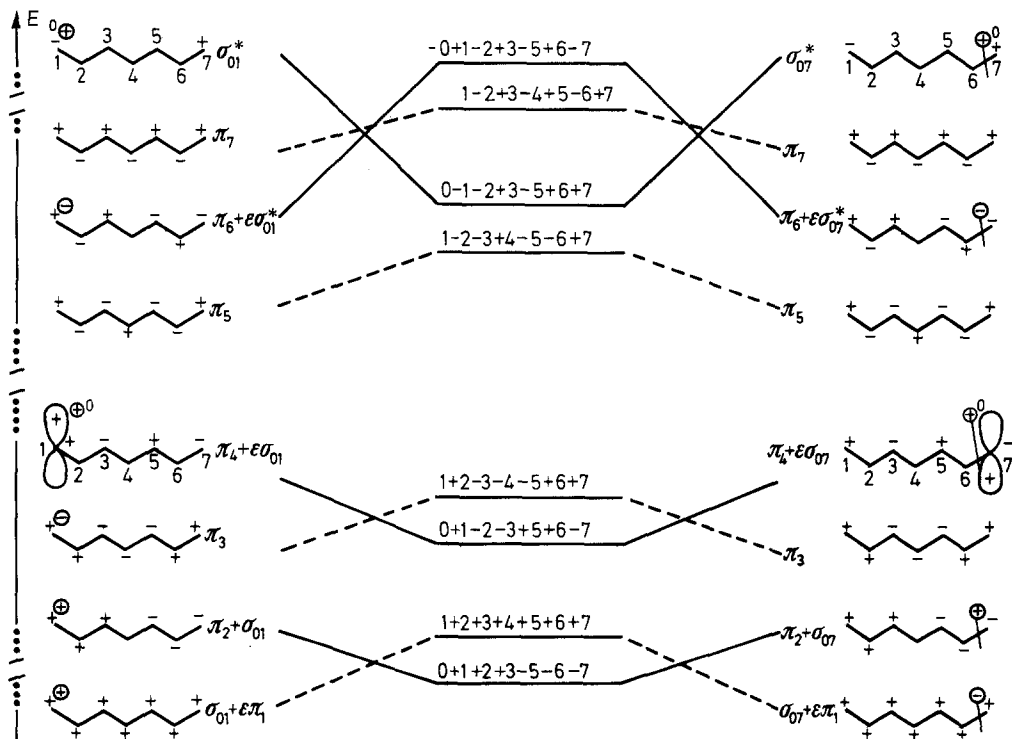


Fig. A-3. Correlation diagram for [1, 7] antarafacial hydrogen migration. The hydrogen assumes the ϕ_0 position. The truncated Möbius energy levels are split in a way assuming the $H\sigma$ bond is more stable than the C—C π -bond. (The phase relationship however is the same as Fig. A-2.) ϵ stands for a small mixing coefficient. The influence of σ antibonding is largest in the top " σ^* " orbital but less on the π_6 orbital

This way of representing the reacting molecules is a *departure from the usual way of separating π and σ system*. We combine one hydrogen and a 7-carbon skeleton to get eight energy levels with due fidelity to their respective original phases. The dotted lines indicate the only possible instantaneous diabatic correlation of the phase of the parent Möbius system with the fragment (heptatriene) when the hydrogen is split off. (The wavefunction having a vanishing node at the hydrogen atom, see Sect. IV). Note the large breaks in energy (indicated by dotted line) between lowest (σ) and the highest (σ^*) levels with their respective neighbors. (Not drawn to scale)

by 8 units changes the sign of the coefficient—provided the “second” Möbius circle is not truncated away. If the orbitals have the Möbius twist of $\pi/8$ a shift of atomic numbering by 8 also changes the sign of the orbitals and the extension to the second circle gives redundant results. The extension is not needed for the problem here nor in other chemical applications of Zimmerman [3, 6, 7]. An example where extension is needed is in the author’s study of internal rotation of ethane (C_2H_6) using six-fold instead of three-fold symmetry [41].

The relative phases of the orbitals (up to the complete Möbius double-circle ring) corresponding to these coefficients in (A-3, 4) are given in Fig. A-2.

To apply the “truncated” Möbius ring to chemical systems it is imperative to match the numbering convention with appropriate atomic interaction, i.e. the interaction-sign changes between the first (ϕ_0 here) and the last (ϕ_{N-1} here) atom, the latter atom is the one linked to the next (double) circle. For [1, 7] antarafacial hydrogen shift in C_7H_{10} we take the H -atom to be ϕ_0 which has positive interaction (upper face) with ϕ_1 , the first $P\pi$ orbital of the C_7H_9 conjugate chain. The interaction of ϕ_0 with ϕ_7 the last $P\pi$ -orbital is taken to be negative (lower face). Figure A-3 shows that bonding orbitals correlates to bonding orbitals and the reaction is allowed by the orbital following method of Zimmerman [3]. However we stress here that because of the lack of three-fold or higher symmetry, there is *no longer two-fold degeneracy in the energy levels*—even if the H -atom in the transition state is situated (two-fold) symmetrically with respect to the two end carbon atoms. Furthermore the numbering of the atoms is inflexible, it cannot be shifted (Sect. 2). As a result the wavefunctions dictate correlation from orbital with large σ to the orbital with large σ similarly for π to π . A similar application of the Möbius concept and molecular orbital following method of Zimmerman to the triplet-singlet rearrangement of cyclopropylidene to allene was also given by the author [42].

References

1. Woodward, R. B., Hoffmann, R.: The conservation of orbital symmetry. Weinheim: Verlag Chemie, 1970
2. Marchand, A. P., Lehr, R. E., eds.: Pericyclic reactions, Vol. I. New York: Academic Press, 1977
3. Zimmerman, H. E.: in *Org. Chem.* **35**, Pericyclic reactions I, pp.53–107, A. P. Marchand and R. E. Lehr, eds. New York: Academic Press, 1977
4. Hückel, E.: *Z. Physik* **70**, 204 (1931); **76**, 628 (1932)
5. Heilbronner, E.: *Tetrahedron Letters* **29**, 1923 (1964)
6. Zimmerman, H. E.: *Accounts. Chem. Research* **4**, 272 (1971)
7. (a) Zimmerman, H. E.: *Quantum mechanics for organic chemists*, pp. 37–41. New York: Academic Press, 1975; (b) Zimmerman, H. E.: *Tetrahedron* **38** 753 (1982), and references therein
8. (a) Roberts, J. D.: *Molecular orbital calculation*. New York: W. A. Benjamin, 1961; (b) Streitwieser, A.: *Molecular orbital theory for organic chemists*. New York: John Wiley, 1961; (c) Dewar, M. J. S.: *The molecular orbital theory of organic chemistry*. New York: McGraw-Hill, 1969
9. Salem, L.: *The molecular orbital theory of conjugated systems*, pp. 110–126; pp. 498–450; pp. 516–518. New York: W. A. Benjamin, 1966

10. Shustorovich, E. M.: *Zhurn. Strukt. Khimii* **6**, 123 (1965) English translation p. 107
11. Coulson, C. A.: *Proc. Roy. Soc. (London)* **A164**, 383 (1938); **A169**, 413 (1939)
12. Lennard-Jones, J. E.: *Proc. Roy. Soc. (London)* **A158**, 280 (1937); Lennard-Jones, J. E., Turkevich, J.: *Proc. Roy. Soc. (London)* **A158**, 297 (1937)
13. Longuet-Higgins, H. C., Salem, L.: *Proc. Roy. Soc. (London)* **A251**, 172 (1959); *Proc. Roy. Soc. (London)* **A257**, 445 (1960)
14. Dewar, M. J. S., Hashmall, J. A.: *J. Chem. Phys.* **49**, 492 (1968)
15. Moscovitz, A., Charney, E., Weiss, U., Ziffer, H.: *J. Am. Chem. Soc.* **83**, 4661 (1961)
16. Crabbe, P.: *Optical rotatory dispersion and circular dichroism in organic chemistry*, p. 244, San Francisco: Holden Day, 1965
17. Tinoco, I., Jr., Woody, R. W.: *J. Chem. Phys.* **32**, 461 (1960); **40**, 160 (1964)
18. Tinkham, M.: *Group theory and quantum mechanics*. New York: McGraw-Hill, 1964
19. Fukui, K.: *Molecular orbitals in chemistry, physics and biology*, Ed. Lowdin, P. O., Pullman, B., pp. 513, New York: Academic Press, 1964; Fleming, I.: *Frontier orbitals and organic chemical reactions*. New York: John Wiley, 1978
20. Cotton, F. A.: *Inorg. Chem.* **4**, 334 (1965); *Accounts. Chem. Res.* **2**, 240 (1969); **11**, 225 (1978)
21. For reviews see Templeton, J. L.: *Prog. in Inorg. Chem.* **26**, 211 (1979); Cotton, F. A.: *J. Mol. Structure* **59**, 97 (1980); Cotton, F. A.: *Reactivity of metal-metal bond*, Chisholm, M. H. ed., *A.C.S. Symposium* 155 (1981) pp. 1-16
22. Day, P.: *Physics and chemistry of low dimensional solids*, Alcacer, L. editor. NATO Advanced Study Institute (D. Reidel Pub. Co., Dordrecht Holland 1979) pp. 305-320; H. J. Keller *Ibid*, pp. 321-331
23. Poeppelmeier, K. R., Corbett, J. D.: *Inorg. Chem.* **16**, 1107 (1977); *J. Am. Chem. Soc.* **100**, 5039 (1978)
24. (a) Chiu, Y. N., Wang, F. E.: Charge-overlap study of multiple metal-metal bonding and conjugation in linear chains of transition-metal atoms (accepted for publication *Inorg. Chem.*, **21**, 4264 (1982)); (b) Craig, D. P.: *J. Chem. Soc.* 997 (1959) and discussions by Zimmerman in Ref. 7(b)
25. Borden, W. T.: *Modern molecular orbital theory for organic chemists*, p. 122 ff. New Jersey: Prentice Hall Inc., 1975
26. Hochstrasser, R. M.: *Molecular aspects of symmetry*. New York: W. A. Benjamin, 1966
27. Daudel, R., Lefebvre, R., Moser, C.: *Quantum chemistry - methods and applications*. New York: Interscience Publishers, 1959
28. (a) Brink, D. M., Satchler, G. R.: *Angular momentum*, p. 22, Oxford: Clarendon Press, 1968; (b) Professor Heilbronner pointed out that in 1964 Professor H. Primas also recognized the Möbius system's analogy to spin space.
29. (a) Chiu, Y. N.: *J. Chem. Phys.* **45**, 2969 (1966); *Phys. Rev.* **20**, 32 (1979); (b) The Möbius coupling is an implicit coupling of two half-integral angular momenta. In the definition of a magnetic multipole (Ref. 28(a), 29(a)), spin S is treated as a vector with *integral* angular momentum of one. It would be interesting to explore the magnetic property of the Möbius coupling from $J = 0$ ("pseudo monopole") and up.
30. Mason, S. F.: *Nature* **205**, 495 (1965)
31. Coxeter, H. S. M.: *Introduction to geometry*, p. 323 ff. New York: John Wiley, 1969
32. (a) Craig, D. P., Power, E. Z., Thirunamachandran, T.: *Proc. Roy. Soc. (London)* **A322**, 165 (1971); (b) Power, E. A., Thirunamachandran, T.: *Proc. Roy. Soc. (London)* **A313**, 403 (1969)
33. Brown, S., Chiu, Y. N.: *Transverse electron motion and optical rotation in a fat helix of non-integral turns* (to be published)
34. Coulson, C. A., Streitwieser, A., Jr.: *Dictionary of π -electron calculations*. San Francisco: W. H. Freeman and Company, 1965
35. Heilbronner, E., Straub: *Hückel molecular orbitals*. New York: Springer-Verlag, 1966
36. Parr, R. G.: *Quantum theory of molecular electronic structure*. New York: W. A. Benjamin, 1969
37. Pople, J. A., Beveridge, D. L.: *Approximate molecular orbital theory*. New York: McGraw-Hill, 1970
38. Mulliken, R. S., Ermler, W. C.: *Polyatomic molecules*. New York: Academic Press, 1981
39. Loxsom, F. M.: *J. Chem. Phys.* **51**, 4899 (1969)

40. Rhodes, W.: *J. Chem. Phys.* **53**, 3650 (1970)
41. Chiu, Y. N.: Application of Hückel-Möbius concept to torsional vibration and internal rotation of molecules (to be published)
42. Chiu, Y. N.: Triplet-to-singlet cyclopropylidene-allene rearrangement - A molecular example of spin angular momentum coupling in orthogonal π -systems (*J. Am. Chem. Soc.*, Dec. 1982)

Received August 9, 1982