

a difference is quite small,⁴⁷ if one takes into account the assumption made, the inherent accuracy of semiempirical methods, and especially the dramatic and constant decrease of the ΔE value following the application of greatly refined, and hence more trustworthy theoretical, calculations to the unsubstituted phenylium ion. It is difficult to assess, at the present time, whether mechanism 6, based on 1,2 hydride shifts, would be consistent with the results of higher level theoretical methods, as those recently applied to $C_6H_5^+$. In any event, the discrepancy, if any, should not be nearly as serious as with earlier semiempirical results.

As to the relative stability of tolyl ions, the order deduced from the MINDO/3 approach, i.e., para < meta < ortho, is not consistent with the experimental evidence from this study, pointing to an increase of the product deriving from **1c** and to a simultaneous decrease of the product from **1a** at low MeOH pressures.

On the other hand, the energy barrier of process 7, e.g., **1c** \rightarrow **4** calculated at the MINDO/3 level, was 25 kcal mol⁻¹, considerably lower than of process 6, e.g., **1b** \rightarrow **1c**, namely 38.9 kcal mol⁻¹. Consequently, excited tolyl ions **1b** were predicted to collapse directly to **4**, without being trapped as **1c**.²⁶ This view is at variance with the experimental results of this study, that provides positive evidence against occurrence of isomerization 7 of tolyl ions which instead appear capable of significant interconversion.

Independent evidence supports the view that the activation energy of process 7 exceeds the barrier calculated at the MINDO/3 level. In fact, tolyl ions formed in the mass spectrometer via the reaction of H_3^+ ions with *p*-fluorotoluene, whose exothermicity (-57 kcal mol⁻¹) is much larger than the calculated barrier, fail to isomerize into benzyl cations, despite the relatively low H_2 pressure (≤ 1 torr) and the high temperature (160 °C) prevailing in the ion source.²²

Comparison with Mass Spectrometric Results. Once the differences existing in the time scale and the excitation mechanism typical of the two experimental approaches are taken into account, the results from the application of the decay technique to gaseous tolyl ions support, in general, the conclusions of pertinent mass spectrometric studies.

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In fact, species tentatively identified as tolyl ions with use of indirect structural criteria based on the nature of their neutral precursors, or by diagnostic techniques such as collisional activation (CA), have been obtained in a state of high purity (>90%) by electron impact^{15,17,18,48} or by chemical ionization^{18,22,49} mass spectrometry.

These species appear to survive as long as 10⁻⁵ s without rearrangement to the benzyl or tropylium structure,¹⁸ despite the excitation energy from their formation processes. In this connection, the present study provides "hard" confirmatory evidence, based on the actual isolation of structurally diagnostic products, for the occurrence of tolyl ions as distinct species in the dilute gas state. The different rate of processes 6 and 7, deduced from the decay experiments, is also consistent with the mass spectrometric evidence. First, the low rate of (7) explains the surprising stability of tolyl ions with respect to isomerization to benzyl, or tropylium cations, noted in mass spectrometric studies.^{17,18} Furthermore, process 6, observed in the present study even at "high" pressures (6 to 100 torr), is expected to be much more efficient at the excitation levels and the low pressures typical of mass spectrometry, thus causing complete equilibration of tolyl ions **1** with sufficient internal energy to the most stable ortho isomer **1c** well before structural assay by CA. This could explain the observation that tolyl ions, irrespective of their precursor and therefore, presumably, of their initial isomeric composition, exhibit nearly identical CA spectra, which, however, are different from those of benzyl or tropylium ions, excluding rearrangement of **1** into either of these common structures.

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Registry No. **1a**, 61837-10-3; **1b**, 61837-09-0; **1c**, 53272-68-7; **2a**, 37145-50-9; **2b**, 92014-29-4; MeF, 593-53-3; Me₂F⁺, 64710-12-9; MeOH, 67-56-1; CH₃Ph-ring-³H_x, 92077-38-8; *o*-MeC₆H₄OMe-ring-³H_x, 92014-30-7; *m*-MeC₆H₄OMe-ring-³H_x, 92014-31-8; *p*-MeC₆H₄OMe-ring-³H_x, 92014-32-9; *p*-cresol, 106-44-5.

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Hückel Rules and Electron Correlation[†]

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Abstract: The possible effects of electron correlation on Hückel-type rules for cyclic π -electron systems are considered. General exact results are developed for a wide variety of models, including a range of degrees of electron correlation, for homo- or heteroannulenes or various distorted cycles, either of Hückel or Möbius type. The theoremtic results confirm some general qualitative points of the Hückel-type rules and provide checks on approximate solutions to these various models.

1. History and Introduction

Cyclic π -electron systems and their special (often "aromatic") features have long been of much interest. Hückel's¹ celebrated $4n + 2$ rule provided a key step toward elucidating these features. As such, it has been acclaimed²⁻⁴ one of the most fundamental rules of chemistry and has found⁵⁻⁷ wide applicability among (organic) chemists. The original rule states that the planar

monocyclic systems containing $(4n + 2)$ π -electrons are expected to exhibit aromatic stability. A later amendment states that the

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Table I. The Hückel-Möbius Rule

	$N_e = 4n + 2$	$N_e = 4n$
Hückel	aromatic	antiaromatic
Möbius	antiaromatic	aromatic

corresponding $4n$ π -electron systems should be^{8,9} unstable and exhibit antiaromatic properties. Extensive experimental work, especially in the areas of annulene, bridged-annulene, and heteroannulene chemistry, abundantly confirm^{2,3,5-9} the general validity of the Hückel model.

Even before Hückel's work, the special features of benzene (the most common and stable $4n + 2$ cycle) had been widely recognized. For instance, the rule of six indicated¹⁰ that cyclic structures containing six "benzene-like valencies" (i.e., six planar π -electrons) should show unusual stability (in both thermodynamic and kinetic senses). Thiele's synthesis¹¹ of cyclopentadienyl anion in 1900 provided an early test of the rule. A valence-bond-like view of aromaticity in terms of "aromatic sextets" was presented by Armitt and Robinson¹² in the 1920s and then developed by Clar.

Hückel's treatment¹ also drew the attention of many theoreticians. In addition to chemical properties as an index to aromaticity, they advocated as indexes various other physical properties, including thermodynamic stability,^{1,13,14} bond lengths,^{3,14} magnetic properties,¹⁵ and symmetry.¹⁶ It was argued that as n increases both $(4n + 2)$ and $4n$ π -systems (annulenes) converge to a mean nonaromaticity, and this was experimentally confirmed.⁵ The relations of Hückel-type rules to many cases of the Woodward-Hoffmann rules were elucidated.^{17,18} Extensions to planar

polycyclic conjugated hydrocarbons,^{3,19} as well as to²⁰ inorganic systems and three-dimensional frameworks, were suggested.

Another extension by Mason and Zimmerman²¹ was made for application to cyclic arrays including the possibility of phase dislocations between adjacent orbitals. That is, they allowed for the possibility of negative overlap (and positive resonance integrals) between adjacent orbitals. Such systems were partitioned^{21,22} into two types: Hückel systems with an even number of sign changes and Möbius systems with an odd number. The earlier Hückel rule was then argued to apply exclusively to Hückel systems, while for Möbius systems the role of $(4n + 2)$ - and $4n$ -electron systems was interchanged. Thus the overall Hückel-Möbius rule is as summarized in Table I. All these various rules, including the possibility of special characteristics for $(4n \pm 1)$ π -electron systems, have been²³ termed *modulo 4 rules*.

A further crucial theoretical point concerns the extension of Hückel's argument beyond the simple (Hückel) model he used. The closely parallel results²⁴ for the free-electron model are unsurprising, since this model is nothing but a "continuum analogue" of Hückel's discrete model. The ready extension of Hückel's argument to Hartree-Fock solutions^{3,25,26} of better models (e.g., the Pariser-Parr-Pople (PPP) model) is also unsurprising. The central question concerns the possible effects of "electron correlation". There are, of course, brute force configuration interaction computations for various improved models. These²⁷⁻²⁹ make individual (valuable but piecemeal) tests of different aspects of the rule and often seem to verify the rules' predictions. In fact, an apparently successful interpretation of the results from a number of such calculations has been made²⁹ to predict ground-state spin multiplicities based upon the manner of localization of near nonbonding molecular (or natural) orbitals. In another view toward general statements, there have been some approximate treatments of valence-bond (VB) models^{30,31} and of PPP mod-

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els.³²⁻³⁴ There are some exact results³⁵ for the VB model (with nearest-neighbor interactions and covalent structures only). Exact results for "better" models, including correlation, are quite rare; one exception³⁶ relates energies of certain Möbius and Hückel annulenes.

Here we develop some general exact results simultaneously applicable to all the above-identified models, as well as others, generally including electron correlation, over a whole range of parametrizations, for homo- or heteroannulenes or various distorted cycles, either of Hückel or Möbius type. With such a general class of models the theorematic consequences are somewhat weaker than for the usual Hückel rules, but much of the general "flavor" is found to be preserved. On the other hand, these theorematic results fall short of dealing with the full (nonrelativistic, fixed-nucleus) coordinate-space Hamiltonian in the Schrödinger picture, but the general class of models dealt with here is widely believed to include "very reasonable" effective Hamiltonians. Most of the present results proceed via the Frobenius-Perron theorem,³⁷ much as implicitly used by Lieb and Mattis³⁸ to establish some exact results for linear chain systems.

A general descriptive discussion of the various models included and results obtained is found in section 7, which is designed to be easily read without necessarily going through the more precise formalities and proofs in the intervening sections. Section 2 defines a class of models in a concise second-quantized framework, and section 3 gives symmetries that at least some of these models exhibit. Formal theorems for this class of models are developed in section 4, where an advantage of second quantization is seen in keeping track of crucial phases. Section 5 establishes some additional results involving point-group or "particle-hole" symmetries. Section 6 shows how the theorems extend to an even wider class of models.

2. π -Electron Models

The models are defined on the space spanned by $(2p_z)$ π -orbitals, one to each atom of the π -network. (The electrons not occupying these π -orbitals often are viewed as being "frozen" in lower-lying doubly occupied σ -orbitals.) Operations in this space are conveniently expressed in terms of Fermion creation and annihilation operators, $a^+_{i\sigma}$ and $a_{i\sigma}$, for $\chi_{i\sigma}$, a spin- σ orbital on atom i . That is, $a^+_{i\sigma}$ acting on a (normalized) Slater determinant gives a new (normalized) Slater determinant differing from the old only in having an additional electron in the orbital $\chi_{i\sigma}$; the operator $a_{i\sigma}$ accomplishes the "reverse" process. As a consequence of the Pauli exclusion principle, these operators satisfy the Fermion anticommutation relations

$$a^+_{i\sigma} a^+_{j\sigma} = -a^+_{j\sigma} a^+_{i\sigma} \quad (2.1)$$

$$a_{i\sigma} a_{j\sigma} = -a_{j\sigma} a_{i\sigma}$$

$$a^+_{i\sigma} a_{j\tau} = \delta_{ij} \delta_{\sigma\tau} - a_{j\tau} a^+_{i\sigma}$$

Also of importance are the number operators

$$\hat{n}_i \equiv a^+_{i\alpha} a_{i\alpha} + a^+_{i\beta} a_{i\beta} \quad (2.2)$$

which when applied to a configuration with the π -orbital occupancy of site i fixed (at 0, 1, or 2) give the same configuration back multiplied by this occupancy value (0, 1, or 2).

The model Hamiltonians which we consider are of the general form

$$\mathcal{H} = \sum_{i=1}^N \sum_{\sigma} (t_{i,i+1} a^+_{i\sigma} a_{i+1\sigma} + t_{i+1,i} a^+_{i+1\sigma} a_{i\sigma}) + \sum_{i=1}^N J_{i,i+1} a^+_{i\alpha} a^+_{i+1\beta} a_{i\beta} a_{i+1\alpha} + V(\hat{n}_1, \hat{n}_2, \dots, \hat{n}_N) \quad (2.3)$$

where we have presumed N sites, with the site index $N+1$ being interpreted as equivalent to site index 1. That the potential V is a real function only of the number operators (2.2) is equivalent to saying that V is spin independent and "local" (on the atomic basis). The t and J terms in \mathcal{H} are, respectively, the kinetic energy and exchange terms. They account for the graph-theoretic (or chemical-structure theoretic) nature of the model in that the parameters t_{ij} and J_{ij} are taken to be nonzero only between nearest-neighbor sites in the cycle. The Hermiticity of \mathcal{H} implies that $J_{ij} = J_{ji}$ is real and that $t^*_{ij} = t_{ji}$. We restrict our attention to Hamiltonians for which

$$J_{i,i+1} \leq 0 \quad i = 1 \text{ to } N \quad (2.4)$$

and for which the t_{ij} are real with

$$t_{i,i+1} < 0 \quad i = 1 \text{ to } N-1 \quad (2.5)$$

The sign of (2.4) is that appropriate for VB-type models, while the sign of (2.5) is appropriate for PPP-type models of ordinary planar π -networks (with the usual phase convention for orbitals). Finally, if $t_{1,N} \neq 0$, we assume it to be real and denote its sign by

$$s \equiv \text{sign}(t_{1,N}) = \text{sign}(t_{N,1}) \quad (2.6)$$

If $s = -1$, the cycle is said to be *Hückel*, whereas if $s = +1$, the cycle is said to be *Möbius*.

3. Symmetries

All the Hamiltonians \mathcal{H} of the previous section are "spin free" and consequently commute with spin-space operations. Thus, the total spin S^2 and z -component of spin S_z operators, which commute with one another, provide exact quantum numbers, S and M_S , for the eigenstates of \mathcal{H} .

A reflection symmetry occurs when $t_{ij} = t_{-j,-i}$ and $J_{ij} = J_{-j,-i}$ where $-k \cong N - k + 1$ identifies the site to which site k is carried by the reflection $\hat{\sigma}_0$. The action of $\hat{\sigma}_0$ on the π -orbitals may be defined via

$$\hat{\sigma}_0 a^+_{k\sigma} \hat{\sigma}_0^{-1} = a^+_{-k\sigma} \quad (3.1)$$

whence we see that $\hat{\sigma}_0$ commutes with the kinetic energy term of \mathcal{H} . With the presumption that V also is invariant under $\hat{\sigma}_0$ we see that $\hat{\sigma}_0$ provides quantum numbers of the eigenstates to \mathcal{H} .

A cyclic type of point-group symmetry occurs when the $J_{i,i+1}$ are all equal and the nonzero t_{ij} are all equal in magnitude; in particular, $t_{j,j+1} = t_{j+1,j}$ are all negative except possibly for $t_{1,N} = t_{N,1}$, which has sign s . The action of a (perhaps "twisted") rotation \hat{C} by $2\pi/N$ in the clockwise direction is defined via

$$\begin{aligned} \hat{C} a^+_{k\sigma} \hat{C}^{-1} &= a^+_{k+1\sigma} & k = 1 \text{ to } N-1 \\ &= -s a^+_{1\sigma} & k = N \end{aligned} \quad (3.2)$$

Then \hat{C} transforms \hat{n}_i to $+\hat{n}_{i+1}$, and with the presumption that $V(\hat{n}_1, \dots, \hat{n}_N)$ is invariant under such permutations of its arguments, it is seen that \hat{C} commutes with \mathcal{H} . Thus, the group generated by \hat{C} provides irreducible representation labels for the eigenstates of \mathcal{H} . If both $\hat{\sigma}_0$ and \hat{C} commute with \mathcal{H} , then the associated larger group C_{Nv} (or its double group²⁶ if $s = +1$) provides labels.

Finally, there is³⁹ the so-called "particle-hole symmetry" operator

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$$K \equiv \prod_{j=1}^N \prod_{\sigma} \{i^j a_{j\sigma}^+ + (-i)^j a_{j\sigma}\} \quad (3.3)$$

This is readily verified to be unitary and to interchange creation and annihilation operators

$$K a_{j\sigma} K^\dagger = a_{j\sigma}^+ \text{ and } K a_{j\sigma}^+ K^\dagger = a_{j\sigma} \quad (3.4)$$

Then K carries N_e -electron spaces to $(2N - N_e)$ -electron spaces, and the Hamiltonian \mathcal{H} of (2.3) is transformed to a Hamiltonian which is the same except that $t_{1,N} = t_{N,1}$ is replaced by $(-1)^N t_{1,N}$ and the arguments \hat{n}_i of V are changed to $1 - \hat{n}_i$. Thus, K does not ordinarily commute with \mathcal{H} , but this transformation will still have interesting consequences.

4. Basic Theorems

The results we establish here are based upon developments³⁷ originally due to Frobenius and Perron. We use (without proof) their theorem:

Theorem 1—Suppose that on a particular basis a Hermitian operator \mathcal{H} has all off-diagonal matrix elements nonpositive. Further, suppose that the matrix representation of \mathcal{H} is not block diagonalizable by any simultaneous permutation of rows and columns. Then the minimum eigenvalue is nondegenerate, and the associated eigenvector has all positive coefficients.

The particular basis we employ for the π -electron space is expressed in terms of sets A and B of sites to which α - and β -spins can be assigned. Each choice for A and B identifies a basis ket

$$|A, B\rangle \equiv \prod_{i \in A} a_{i\alpha}^+ \prod_{j \in B} a_{j\beta}^+ |0\rangle \quad (4.1)$$

where $|0\rangle$ is the "vacuum" ket and the products are chosen to be ordered (from small to large indexes). These basis kets may be ordered simply as Slater determinants, with atomic orbitals $\chi_{i\alpha}$, $i \in A$, in the first rows of the determinant and $\chi_{j\beta}$, $j \in B$, in the last rows. The ordering of the orbitals is crucial since it affects the phases of the basis kets and hence the signs of the matrix elements in theorem 1. Note that (4.1) exhibits an S_z quantum number $M_s = (|A| - |B|)/2$, where $|A|$ and $|B|$ are the orders of sets A and B .

The Frobenius–Perron theorem applies to the models of section 2 when represented on the atomic configuration basis of (4.1). The only off-diagonal matrix elements arise from the kinetic-energy and exchange operators. Consider the application of any one of the electron-hopping operators

$$a_{i\sigma}^+ a_{i+1\sigma} \text{ or } a_{i+1\sigma} a_{i\sigma} \quad (4.2)$$

for $i = 1$ to $N - 1$, to any one of the basis kets of (4.1). Because of (2.1) the operators of (4.2) commute with any $a_{j\sigma}^+$, except for $j = i + 1$ or $j = i$, and application of (4.2) gives back either 0 or ± 1 times another basis ket, with a single spin- σ electron shifted by a single site (from $i + 1$ to i or from i to $i + 1$). Thus, with the condition of (2.5), the nonzero off-diagonal elements of the ("noncyclic") portion of the kinetic energy operator excluding the $t_{1,N}$ and $t_{N,1}$ terms are negative. Since the exchange terms may be viewed as products of electron-hopping terms (4.2), it is seen that the noncyclic portion of the exchange operator also gives only negative off-diagonal matrix elements. Moreover, any basis ket of (4.1) can be transformed into any other with the same number of α - and β -spins by an application of a sequence of electron-hopping terms as in (4.2) with $i = 1$ to $N - 1$. Hence, in a space with a given total spin component M_s , the \mathcal{H} matrix (with $t_{i,i+1} \neq 0$ for $i = 1$ to $N - 1$) cannot be block diagonalized via a permutation of rows and columns. Thus, within an M_s space the hypothesis conditions of theorem 1 are met except possibly for those involving the signs of the $t_{1,N} = t_{N,1}$ and $J_{1,N} = J_{N,1}$ matrix elements.

If these last sign conditions are presumed to hold, then theorem 1 applies. In such a case the eigenstate $\Psi(M_s)$ of lowest energy $E(M_s)$ in an M_s space must be nondegenerate and so also be of pure spin symmetry. Since a basis ket with the maximum number of doubly occupied sites has total spin $S = |M_s|$ and since theorem 1 implies that such kets are included in the expansion of $\Psi(M_s)$,

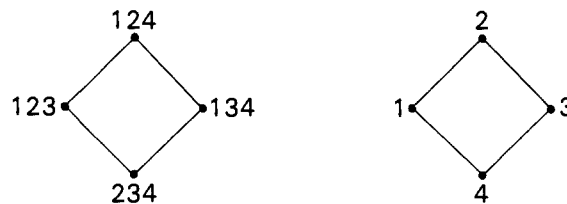


Figure 1. The A and B graphs for cyclobutadiene configurations with $N = 4$ electrons and total z -component of spin $M_s = 1$. Graph A (on the left) indicates which arrangements of the three spin-up electrons are connected by the Hamiltonian, while graph B (on the right) concerns the arrangements of the single spin-down electron.

it must be that $\Psi(M_s)$ also has this same spin. Finally, this M_s space contains states corresponding to eigenstates of every possible spin $S' > M_s$; thus, $E(S') > E(S)$ for $S' > S$. The presumption of this paragraph may be verified in several different cases.

Clearly in the noncyclic case the presumption applies:

Theorem 2—If $t_{1,N} = J_{1,N} = 0$, then

$$S' > S \Rightarrow E(S') > E(S)$$

This has been previously proved by Lieb and Mattis³⁸ when all the J 's are zero.

In the cyclic case consider the application of $a_{N\alpha}^+ a_{1\alpha}$ to a basis ket as in (9). This gives a nonzero result only in the case that the α -spin orbital on site 1 is initially occupied and that on site N is initially unoccupied; then the result is obtained from the initial basis ket just by replacing $a_{1\alpha}^+$ in its definition by $a_{N\alpha}^+$. Next the anticommution of the $a_{N\alpha}^+$ through the $|A| - 1$ other occupied α -spin orbitals leads to a basis ket multiplied by $(-1)^{|A|-1}$. Thus, $t_{N,1} a_{N\alpha}^+ a_{1\alpha}$ and $t_{1,N} a_{1\alpha}^+ a_{N\alpha}$ also, when applied to a basis ket can only give back other basis kets with coefficients of sign $(s)(-1)^{|A|-1}$. The corresponding sign for the β -spin term is $(s)(-1)^{|B|-1}$. For the exchange term, viewed as a product of α - and β -type hopping terms as in (4.2) with $i = N$, the sign is $(-1)(-1)^{|A|-1} (-1)^{|B|-1}$; this sign is negative if and only if the total number of electrons

$$N_e \equiv |A| + |B| \quad (4.3)$$

is even. Theorem 1 applies when all three signs are negative, so that we have the following:⁴⁰

Theorem 3—Suppose either that $N_e = 4n + 2$ with $s = -1$ or that $N_e = 4n$ with $s = +1$. Then, for even spin S

$$S' > S \Rightarrow E(S') > E(S)$$

Theorem 4—Suppose either that $N_e = 4n$ with $s = -1$ or that $N_e = 4n + 2$ with $s = +1$. Then, for odd spin S

$$S' > S \Rightarrow E(S') > E(S)$$

Some aspects of the proofs for theorems 2–4 can be further elucidated in terms of graphs. These proofs depend critically on the manner in which the t terms of \mathcal{H} carry the basic configurations $|AB\rangle$ of (4.1) into one another. Now this can be represented in terms of two graphs, one for the (spin-up) A part and one for the (spin-down) B part of the configurations. The A graph has vertices corresponding to the different allowed A configurations (i.e., to the different assignments of spin-up electrons to sites); further, this graph has edges corresponding to pairs of A configurations which are interchangeable by a single application of one of the t terms of the Hamiltonian. Figure 1 illustrates the A and B graphs for the $M_s = +1$ space of (neutral) cyclobutadiene. Figure 2 applies for the $M_s = 0$ space, where the A and B graphs

(40) A first-quantized spin-free approach to cyclic systems may be taken, much as done by Lieb and Mattis³⁸ for the linear chain case. In place of spins one deals with "partitions" labeling irreducible representations of the symmetric group, and these partitions are partially ordered by a relation termed "pouring" by Lieb and Mattis. It results that for Hückel ($s = -1$) systems if λ is a partition with only odd-length columns, then the lowest energy state of symmetry λ has energy less than that of any state with a symmetry "pourable" into λ . For Möbius systems a parallel statement holds involving partitions λ with only even-length columns. If specialized to Pauli-allowed states (for spin $1/2$ Fermions) these statements reduce to those proved in section 4.

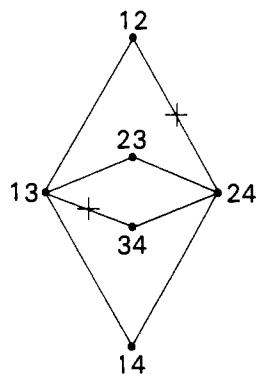


Figure 2. Either the *A* and *B* graphs for cyclobutadiene configurations with $N = 4$ electrons and total z -component of spin $M_s = 0$.

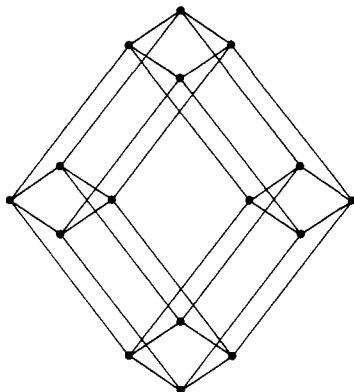


Figure 3. The product graph $A \times B$ for the two cyclobutadiene configuration graphs of Figure 1.

are identical (even up to vertex labels). In Figure 2 we have placed a + sign on two of the edges corresponding to t -matrix elements of the "wrong" sign (i.e., positive sign when the sign of the t parameter is included).

Such (signed) *A* and *B* graph pairs are in close correspondence with the \mathcal{H} matrix on the corresponding M_s basis of states (4.1). For a pair of graphs *A* and *B*, one may define a *product* graph $A \times B$ such that, first, $A \times B$ has vertices which correspond to pairs (a, b) of vertices a from *A* and b from *B*, and second, $A \times B$ has an edge between two vertices (a, b) and (a', b') if either $a = a'$ while b is adjacent to b' in *B* or else $b = b'$ while a is adjacent to a' in *A*. For instance, the product of the *A* and *B* graphs of Figure 1 is shown in Figure 3. Such $A \times B$ product graphs have adjacency matrices whose off-diagonal nonzero matrix elements are in one-to-one correspondence with those of the \mathcal{H} matrix; if the edges are signed as indicated above, then even the signs of these off-diagonal \mathcal{H} matrix elements are given. Now the condition for the application of the Frobenius–Perron theorem 1 is that all the edges of the product graph have a negative sign, this in turn being equivalent to the condition that all the edges of the component *A* and *B* graphs have a negative sign. Clearly this condition is met for the $M_s = 1$ cyclobutadiene case of Figure 1. But for the $M_s = 0$ case of Figure 2 the condition is not met, nor is it possible to do so by any change of phases of the basis states. (To see this it is useful, first, to note that changing the sign of a basis configuration simply amounts to changing the signs of all the edges incident on the corresponding graph vertex, and second, to note that a "Möbius twist" in a single cycle cannot be eliminated, such as is the case in the 12, 13, 14, 24 cycle of Figure 2 with the twist between 24 and 12.) Thus, one way to state the conditions for application of the Frobenius–Perron theorem here is that all the cycles of the *A* and *B* graphs be of "Hückel type" (i.e., all the edges are of the "correct" sign).

Finally, we note that these proof techniques seem only rarely to be directly applicable to other chemical π -network "topologies". One such (rare) case is that of trimethylenemethane, for which it can be proved that the (neutral, $N_e = 4$) ground state is of spin

0 or 1, while the two- and six-electron ground states are spin 0.

5. Additional Symmetry Theorems

First we consider cases where the reflection $\hat{\sigma}_0$ of (3.1) commutes with \mathcal{H} and where we have identified a lowest energy state $\Psi(S)$ which is nondegenerate within the $M_s = S$ subspace. Since $\hat{\sigma}_0\Psi(S) \neq 0$ is of the same energy as $\Psi(S)$, it follows that $\hat{\sigma}_0\Psi(S)$ must differ from $\Psi(S)$ by no more than a phase. When $\hat{\sigma}_0$ is applied to one of the basis kets in (4.1), the resultant merely has each occupied orbital index n replaced by $-n \equiv N - n + 1$. That is, the occupied orbital indexes are in reverse order but may be restored to standard numerical order by anticommuting the various occupied $a^+_{k\sigma}$ about. Explicitly, a reverse-ordered product $a^+_{j_1\sigma} a^+_{j_2\sigma} \dots a^+_{j_{|A|}\sigma}$ may be brought to standard order, first, by moving $a^+_{j_1\sigma}$ to the right through the $|A| - 1$ other creation operators, thereby introducing a phase $(-1)^{|A|-1}$, second, by moving $a^+_{j_2\sigma}$ to the right through the remaining $|A| - 2$ misordered creation operators, thereby introducing a phase $(-1)^{|A|-2}$, etc. The phase associated with correctly reordering the α -spins is $(-1)^{|A|(|A|-1)/2}$ and that for the β -spin is $(-1)^{|B|(|B|-1)/2}$. The overall phase involves -1 raised to a power, which can be taken as

$$\begin{aligned} & [|A|(|A|-1)/2] - [|B|(|B|-1)/2] = \\ & \frac{1}{2}(|A| + |B| + 1)(|A| - |B|) = (N_e + 1)S \quad (5.1) \end{aligned}$$

Because all the basis kets with $M_s = S$ occur with positive expansion coefficients in $\Psi(S)$ (for the cases we consider), it follows that

$$\hat{\sigma}_0\Psi(S) = (-1)^{(N_e+1)S}\Psi(S) \quad (5.2)$$

Recalling the various cases associated with theorems 2–4 we then find the following:

Theorem 2'—Suppose $[\hat{\sigma}_0, \mathcal{H}] = 0$ and the hypothesis of theorem 2 holds. Then, for even N_e , the lowest state $\Psi(S)$ of spin S is symmetric or antisymmetric with respect to $\hat{\sigma}_0$ as S is even or odd; for odd N_e , $\Psi(S)$ is symmetric or antisymmetric as $N_e = 4n - 1$ or $N_e = 4n + 1$.

Theorem 3'—Suppose $[\hat{\sigma}_0, \mathcal{H}] = 0$ and the hypothesis of theorem 3 holds. Then, the lowest-energy state $\Psi(S)$ for any even S is symmetric with respect to $\hat{\sigma}_0$.

Theorem 4'—Suppose $[\hat{\sigma}_0, \mathcal{H}] = 0$ and the hypothesis of theorem 4 holds. Then, the lowest energy state $\Psi(S)$ for any odd S is antisymmetric with respect to $\hat{\sigma}_0$.

Now consider cases where the rotation \hat{C} commutes with \mathcal{H} and where we have identified $\Psi(S)$ to be nondegenerate. Then, $\hat{C}\Psi(S)$ differs from $\Psi(S)$ by no more than a phase. When \hat{C} is applied to one of the basis kets of (4.1), the resultant has each occupied orbital index i replaced by $i + 1$; in addition, \hat{C} introduces a factor $-s$ for each $a^+_{N\sigma}$ converted to $a^+_{1\sigma}$. All the resultant $a^+_{j\sigma}$ obtained are in the standard numerical order except for any $a^+_{1\sigma}$, which gave a factor $-s$. To place $a^+_{1\sigma}$ in the correct (first) position entails anticommuting it through all the other creation operators of the same σ . Thus, if $a^+_{1\sigma}$ occurs in the resultant, a factor $-s(-1)^{|A|-1}$ arises; for $a^+_{1\beta}$, the factor is $-s(-1)^{|B|-1}$. But for the conditions of the different theorems 3 or 4, these phases are positive.

Theorem 3''—Suppose $[\hat{C}, \mathcal{H}] = 0$ and the hypothesis of theorem 3 holds. Then, the lowest energy state $\Psi(S)$ for any even spin S is symmetric with respect to \hat{C} .

Theorem 4''—Suppose $[\hat{C}, \mathcal{H}] = 0$ and the hypothesis of theorem 4 holds. Then, $\Psi(S)$ for any odd spin is symmetric with respect to \hat{C} .

Finally, there are some theorems which give interrelations between the eigenvalues for certain corresponding Hamiltonians. Define the Hamiltonian \mathcal{H}^- correspondent to \mathcal{H} to be equal except for the $t_{1,N} = t_{N,1}$ terms which simply have opposite signs (in \mathcal{H}^- and \mathcal{H}). The first theorem is as follows:

Theorem 5—Let V have cyclic symmetry, let V be no more than quadratic in the \hat{n}_i , and let N be odd. Then the N_e -electron eigenvalue spectrum of \mathcal{H} is the same, up to a uniform shift, as the $(2N - N_e)$ -electron eigenvalue spectrum of \mathcal{H}^- .

The first step toward the proof involves noting that the first two conditions imply

$$V(1 - \hat{n}_1, 1 - \hat{n}_2, \dots, 1 - \hat{n}_N) = V(\hat{n}_1, \dots, \hat{n}_N) + c_1 \sum_{i=1}^N \hat{n}_i + c_2 \quad (5.3)$$

where c_1 and c_2 are constants dependent on the details of V . Next, from the results following (3.4) we have, when N is odd,

$$K\mathcal{H}K^{-1} = \mathcal{H}^- + c_1 \sum_{i=1}^N \hat{n}_i + c_2 \quad (5.4)$$

This along with the fact that the particle-hole (K) transformation interchanges N_e^- and $(2N - N_e^-)$ -electron spaces thus establishes the theorem. Independently Harris³⁶ has proved the same result (without allowance either for $J_{ij} \neq 0$ or for the extensions of section 6). The more well-known result,³⁹ with the $J_{i,i+1} = 0$, for even N (i.e., alternant) cycles does not actually interrelate \mathcal{H} and \mathcal{H}^- . Rather, this result says, extended to $J_{i,i+1} < 0$, the following:

Theorem 6'—Let $[\hat{C}, V] = 0$, let V be no more than quadratic in the \hat{n}_i , and let N be even. Then, the N_e^- and $(2N - N_e^-)$ -electron eigenvalue spectra of \mathcal{H} are the same, up to a uniform shift.

The proof is much the same as for theorem 5, with \mathcal{H} replacing \mathcal{H}^- on the right-hand side of (5.4).

Our final theorem is the following:

Theorem 7—Let \mathcal{H} have either $s = -1$ be $N_e = 4n + 2$ or $s = +1$ with $N_e = 4N$. Then, the ground-state energy of \mathcal{H} is less than that of \mathcal{H}^- .

Here all the nonzero off-diagonal matrix elements of \mathcal{H} on the $M_s = 0$ basis of (4.1) have already been noted to be negative. The correspondent Hamiltonian \mathcal{H}^- will have all these matrix elements of the same magnitude but with some of them positive. Now \mathcal{H}^- has a ground state with a normalized $M_s = 0$ component

$$|\Psi^-\rangle \equiv \sum_{AB} c(A,B) |AB\rangle \quad (5.5)$$

Then the state

$$|\Psi^+\rangle \equiv \sum_{AB} |c(A,B)| |AB\rangle \quad (5.6)$$

is normalized too. Consider the expectation value

$$\langle \Psi^+ | \mathcal{H} | \Psi^+ \rangle = \sum_{AB, A'B'} |c(A,B)| |c(A',B')| \langle AB | \mathcal{H} | A'B' \rangle \quad (5.7)$$

which by the Rayleigh–Ritz variational principle must be an upper bound to the ground-state energy of \mathcal{H} . The diagonal (i.e., $A = A', B = B'$) terms in (5.7) are the same as those that appear on similarly expanding $\langle \Psi^- | \mathcal{H}^- | \Psi^- \rangle$. However, the off-diagonal terms in (5.7) sometimes differ in phase from the corresponding terms in $\langle \Psi^- | \mathcal{H}^- | \Psi^- \rangle$, the terms in (5.7) always being negative. Consequently (5.7) gives a lower upper bound to the ground-state energy of \mathcal{H}^- , and the theorem is established.

6. Extensions

There are several extensions of the models of section 2. The first extension allows²² phases for the $t_{i,i+1} = t_{i+1,i}$ subject only to the constraint

$$\text{sign} \left(\prod_{i=1}^N t_{i,i+1} \right) = (-1)^{N-1} s \quad (6.1)$$

Then readjustment of the phases of the atomic orbitals $\chi_{i\sigma}$ and associated operators $a_{i\sigma}^+, a_{i\sigma}$ brings the kinetic energy operator to the form presumed in section 2. Thus, the theorems of sections 4 and 5 still apply.

A second type of extension allows the t_{ij} parameters to be replaced by operators \hat{t}_{ij} which are functions of the number operators \hat{n}_k such that the eigenvalues of $\hat{t}_{i,i+1} = \hat{t}_{i+1,i}^+$ are negative, except possibly in the case of $\hat{t}_{1,N} = \hat{t}_{N,1}^+$. Of particular interest are operators of the form

$$\hat{t}_{ij} = \sum_{m,n=0}^2 t_{ij}^{(m,n)} P_i^{(m)} P_j^{(n)} \quad (6.2)$$

where the $P_k^{(p)}$ are projection operators onto configurations with site occupancy $p = 0, 1$, and 2 on site k ,

$$\begin{aligned} P_k^{(0)} &= \frac{1}{2}(\hat{n}_k)^2 - \frac{3}{2}\hat{n}_k + 1 \\ P_k^{(1)} &= -(\hat{n}_k)^2 + 2\hat{n}_k \\ P_k^{(2)} &= \frac{1}{2}(\hat{n}_k)^2 - \frac{1}{2}\hat{n}_k \end{aligned} \quad (6.3)$$

The $t_{ij}^{(m,n)}$ are scalars which are 0 if i and j are not neighbors and⁴¹

$$\begin{aligned} t_{i,i+1}^{(m,n)} &< 0 \quad i = 1 \text{ to } N-1 \\ \text{sign}\{t_{1,N}^{(m,n)}\} &= s \end{aligned} \quad (6.4)$$

Such a choice as (6.2) allows (perhaps quite reasonably)⁴² the electron-transfer parameters to depend upon the valence state of the atomic configurations involved. Because of the construction of (6.2) with (6.4), the off-diagonal matrix elements of the kinetic energy operator have the same signs as previously, and all the conclusions of sections 4 and 5 still apply. Similar extensions of the nonzero J_{ij} to operators \hat{J}_{ij} could also be made without spoiling the conclusions.

A third sort of extension yields one-dimensional Hamiltonians in the Schrödinger picture (both with cyclic boundary conditions and without). To see this, consider the case when all the $J_{ij} = 0$ and the $t_{i,i+1}$ are all equal and negative. Then rewrite \mathcal{H} of (2.3) in a "first-quantized" manner as

$$\mathcal{H} = t \sum_{i=1}^N \sum_{n=1}^{N_e} \{ |\chi_i(n)\rangle \langle \chi_{i+1}(n)| - 2 + |\chi_{i+1}(n)\rangle \langle \chi_i(n)| \} + V' \quad (6.5)$$

where the introduction of the constant in the t sum may be counterbalanced by a constant of the opposing sign in V' , which is a function of the $|\chi_i(n)\rangle \langle \chi_i(n)|$. Now $\sum_{i=1}^N |\chi_i(n)\rangle \langle \chi_{i-1}(n)|$ can be viewed simply as a "translation" operator moving electron n a distance, say $\delta = L/N$, from one site to the next, so that

$$\sum_{i=1}^N |\chi_i(n)\rangle \langle \chi_{i-1}(n)| \cong \exp\left(\delta \frac{\partial}{\partial x_n}\right) \quad (6.6)$$

where the equivalence (denoted by \cong) here is understood to be for the restriction of the continuous space translation operator to our discrete space. Then taking the $\delta \rightarrow 0$ (or $N \rightarrow \infty$, $L = \text{fixed}$) limit with t presumed to scale as $1/\delta^2$, say $-\hbar^2/2m\delta^2$, we find a Schrödinger Hamiltonian

$$\mathcal{H} \rightarrow -\frac{\hbar^2}{2m} \sum_{n=1}^{N_e} \frac{\partial^2}{\partial x_n^2} + V'(x_1, \dots, x_{N_e}) \quad (6.7)$$

Here V' is a "local" potential in the usual sense. The so-called "sites" labeled by i are not to be interpreted as locating atoms here but rather as identifying positions around a ring. The presence of $t_{1,N} = t_{N,1} \neq 0$ (with $s = -1$) merely leads to cyclic boundary conditions (matching $x = L$ to $x = 0$). It should perhaps also be noted that the present limiting procedure modifies some of the theorems of sections 4 and 5 in that strict nondegeneracies are no longer excluded (without additional conditions on V').

7. Discussion

The implications of our theorems for the ground-state symmetries of a cyclic system are summarized in Table II. Of course the point-group symmetry statements apply only in the cases where the molecular model exhibits that symmetry. The spin symmetry results are from theorems 3 and 4 (which also provide additional results for higher spins). The ambiguity in ground-state spin for the $(N_e = 4n)$ -electron Hückel cycle and $(N_e = 4n + 2)$ -electron Möbius cycle is not a deficiency in our proof; the occurrence of $S = 0$ or $S = 1$ in these cases depends upon further details of the models. (For example, PPP models for symmetric Hückel cycles with $N_e = 4$ give ground-state spins $S = 0$ for $N = 4$ sites and $S = 1$ for $N = 5$ sites.) The point-group results, which are given not in parentheses, follow from theorems 2', 3', 2'', and 3''. The

(41) Of course, $\hat{t}_{ij}^{(m,n)} a_{i\sigma}^+ a_{j\sigma} = 0$ if $m = 0$ or $n = 2$, so that our condition in (5.4) is without content for this case.

Table II. Summary of Results

model type	$N_e = 4n + 2$		$N_e = 4n$		property being characterized
Hückel ($s = -1$)	$S = 0$ $+$ $+$ more than the Möbius case below		$S = 0$ (\mp) $(-)$	or $S = 1$ $-$ $+$	spin reflection cyclic } symmetries } stability
Möbius ($s = +1$)	$S = 0$ (\pm) $(-)$	or $S = 1$ $-$ $+$	$S = 0$ $+$ $+$ more than the Hückel case above		spin reflection cyclic } symmetries } stability

point-group results in parentheses are not generally proved, for our whole class of models. But for the cyclic homocentric case with π -electrons and π -centers equal in number, these results are found both for various approximate treatments³¹⁻³⁵ of fairly general models and for exact results on Hückel, free-electron, or VB³⁶ models. That is, the $S = 1$ results seem to apply for ions of the cyclic annulenes in either the $s = -1$, $N_e = 4n$ case or the $s = +1$, $N_e = 4n + 2$ case. Otherwise, $S = 0$ seems to be the typical occurrence. The stability results are from theorem 7.

There is an evident similarity in form between Tables II and I. The similarity is made somewhat more pronounced if we note that $S > 0$ and/or a point-group antisymmetry implies⁴³ an open-shell situation, which presumably is more reactive than a closed-shell situation. Further, when the number N of sites is odd, theorem 5 implies a close correspondence between (the eigenvalue spectrum associated to) diagonal boxes in these tables. However, there is a significant difference in the foundations between Tables I and II in that the conclusions of Table I are usually argued from simple Hückel theory, whereas Table II has here been argued to apply for a wide variety of models including electron correlation, over a wide range of conditions and parameterizations.

Some of the special models to which our theorems apply are (i) the Hückel model, for which $J_{ij} = 0$ and V is linear in the \hat{n}_i , (ii) the free-electron model, as in the third extension of section 6, with V being a one-electron operator, (iii) the simple valence-bond model with the $t_{ij}^{(m,n)}$ which mix different degrees of

ionicity taken to the limit of 0, (iv) the Pariser-Parr-Pople-type models with any parameterization, where $J_{ij} = 0$ and V is (no more than) quadratic in the \hat{n}_i , (v) the free-electron model extended to include electron-electron interaction in V' as in (6.7), and (vi) the extended valence-bond model including interactions between states of different ionicities.

We have termed the last model an extended valence-bond (VB) model rather than an extended Pariser-Parr-Pople (PPP) model simply because of the sign of the J_{ij} . Commonly the various parameters of the PPP model are interpreted⁴⁴ as simple integrals over Löwdin orthogonalized atomic orbitals, in which case the exchange integrals take the sign opposite to that of the J_{ij} here. In contrast for VB models the "exchange parameters" are properly interpreted⁴⁵ in a different fashion and take the sign considered here. Further we note that, although the J_{ij} are set to 0 in the extended free-electron Hamiltonian \mathcal{H} , the model still does include "exchange" in the ordinary sense, as can be seen on considering matrix elements of \mathcal{H} over Slater determinants.

In conclusion it is seen that a number of qualitative points the common Hückel-type rules make are independent of a great variety of decorations that are reasonably appended to the simple Hückel model. The present theorems just provide broader justification for Hückel-type rules. Also they provide checks for approximate solutions to the considered models.

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