

# The Electron-Pair Origin of Antiaromaticity: Spectroscopic Manifestations

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*Received 5 February 1998; revised 13 May 1998; accepted 27 May 1998*

**ABSTRACT:** It is shown that the antiaromatic character of certain conjugated cyclic hydrocarbons is due to the presence of an even number of distinct electron pairs in the system (such as, but not necessarily  $\pi$  electrons). In these systems, the ground state is constructed from an out-of-phase combination of two valence bond (VB) structures, and its equilibrium geometry is necessarily distorted along the coordinate that interchanges these structures. If a new symmetry element appears during the transition between the two structures, the ground electronic state at the symmetric point transforms as one of the nontotally symmetric irreducible representations of the point group. The conjugate excited state, formed from the in-phase combination of the same two structures, transforms as the totally symmetric representation of the group and is strongly bound. Its structure is similar to that of the ground state at the symmetric point, and the energy separation between the two states is small compared to that of conjugated cyclic hydrocarbons having an odd number of distinct electron pairs. Motion along the "Kekulé-type" vibrational mode on the excited-state potential surface is very similar to motion along the reaction coordinate connecting the two distorted structures on the ground-state surface. It is characterized by a significantly higher vibrational frequency compared to frequencies of similar modes in ground-state molecules. These qualitative predictions are supported by quantum chemical calculations on cyclobutadiene, cyclooctatetraene, and pentalene. © 1999 John Wiley & Sons, Inc. *Int J Quant Chem* 71: 133–145, 1999

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Contract grant sponsor: Israel Science Foundation.

## Introduction

We have recently discussed the frequency exaltation phenomenon of the Kekulé vibrational mode upon excitation of aromatic molecules from the ground  $A_{1g}$  (or  $A_g$ ) state to the  $1^1B_{2u}$  (or  $1^1B_u$ ) state [1–3]. It was shown that this phenomenon is a natural result of the fact that these two states may be described as arising from the in-phase and out-of-phase combinations of the two Kekulé structures, respectively. This was taken as experimental evidence that the  $\pi$  structure of aromatic molecules is distortive and that the special stability of these system is due to the sigma structure. The two states were termed twin states, to denote their common parentage. It was later realized that twin states are found in other cyclic systems and that the frequency exaltation phenomenon is not limited to aromatic systems [4]. These properties are a direct consequence of the fact that two states are required to properly account for the properties of the ground state of these systems. Feynmann et al. used the special case of benzene as a model for a two-state system and discussed its properties, including the resulting forbiddingness of an electric dipole electronic transition between the two twins [5].

In this work, we extend the twin-state concept to a discussion of the properties of antiaromatic systems. In spite of their widespread usage, the concepts of aromaticity and antiaromaticity have escaped a precise definition. Some workers offer a definition based on magnetic properties [6a]: Compounds that exhibit significant exalted magnetic susceptibility are aromatic, while those with exalted paramagnetic susceptibility may be antiaromatic. As summarized in a recent monograph [6b], "nobody has been able to produce a physically sound explanation to this (aromaticity or antiaromaticity) effect." Abundant experimental evidence exists for the special stability of cyclic conjugated hydrocarbons having  $4n + 2$   $\pi$  electrons, while the preparation of such systems with  $4n$   $\pi$  electrons was always very difficult. We shall refer to these systems as odd and even, respectively, denoting the number of  $\pi$ -electron pairs that can be formed in these systems. It is also well known that once formed the even-parity systems are invariably found to be distorted in their ground state, showing pronounced bond-length alternation,

while the odd-parity systems tend to have a symmetric ground state. It will be shown that the twin-state concept holds for all monocyclic molecular systems having alternating double bonds. In all of them, the excited state is strongly bound and the Kekulé mode has a very high frequency. Due to symmetry considerations, the ground state is found to be formed by the in-phase combination of the two Kekulé structures for odd-parity systems and by the out-of-phase combination for even-parity systems. The symmetric ground-state structure is always subject to distortive forces, tending to distort the molecule along the coordinate that exchanges the two Kekulé structures. In even-parity systems, these forces always dominate, accounting for their antiaromatic character. Aromatic molecules are odd-parity systems in which these forces are overcompensated by a resonance stabilization. In other odd systems, the symmetric form is found to be a transition state.

Our model is based on a single premise—the tendency of electrons to pair in chemical systems. This is the celebrated G. N. Lewis hypothesis [7], which was later supported by extensive quantum mechanical arguments. It is the underlying theorem of both MO and valence-bond (VB) approximations, explaining the success of these two methods, when employed at the appropriate level, to reproduce the aromatic and antiaromatic properties. The model uses extensively VB terminology, based on the method developed by Pauling and Wheland [8, 9]. It is well known that classical VB theory cannot account for antiaromaticity, for instance, in accounting for Hückel's  $4n + 2$  versus  $4n$  rules. The theory was extended by Oosterhoff and coworkers [10] and further developed by Klein [11] and Malrieu and Maynau [12]. A succinct account was given by Kuwajima [13], but there is still a lack of a clear physical picture of the nature of aromaticity and antiaromaticity.

## The Model

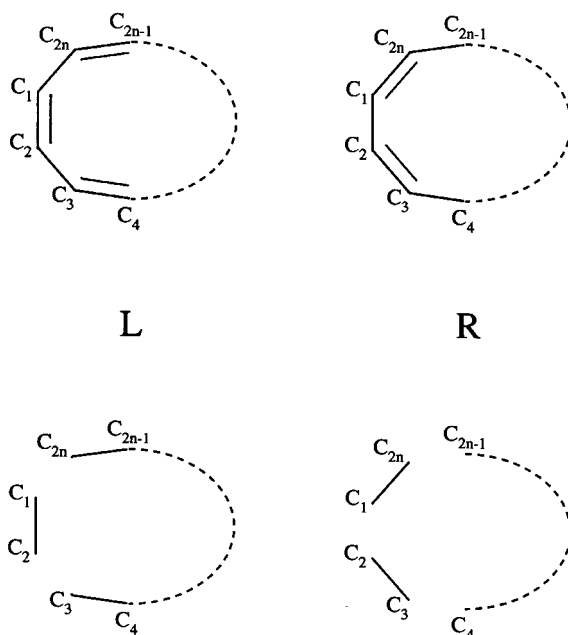
We consider a hydrocarbon consisting of one ring (or more, see below) of the general formula  $C_{2n}H_{2n}$  ( $n \geq 2$ ). The basic assumption of the model is that the system will tend to form as many valence electron pairs between the atoms as possible. In the present case, this assumption leads to the formation of  $\sigma$  bonds between one carbon atom and one hydrogen atom and between adja-

cent carbon atoms. These bonds account for the one  $1s$  hydrogen electron and three of the four carbon  $2s^2 2p^2$  electrons. The  $2n$  remaining electrons can form  $\pi$  bonds between neighboring carbon atoms or longer bonds between nonadjacent atoms. The latter option leads to higher-energy systems and is rejected. As seen from Figure 1, there are two ways of pairing the  $\pi$  electrons: Starting with, say,  $C_1$ , a  $C_1C_2$  bond may be formed, and going clockwise, bonds  $C_3C_4$ ,  $C_5C_6$ , etc., up to  $C_{2n-1}C_{2n}$ . Alternatively, going counterclockwise from  $C_1$ , the  $C_1C_n$  bond is formed, etc., concluding with the  $C_2C_3$  bond. These two options may be written in VB language as the "Kekulé" structures **Ia** and **Ib** shown for cyclobutadiene (CB), **IIa** and **IIb** shown for cyclooctatetraene (COT), and **IIIa** and **IIIb** for pentalene (see Scheme 1). (The model applies also to polycyclic systems, such as pentalene, as long as only two electron pairing arrangements are possible\*).

Sigma bonds around the cycle are also electron pairs. In the absence of  $\pi$  electrons, they are all equivalent, but after the introduction of the  $\pi$  electrons, the  $\sigma$  bonds split, in principle, into two distinguishable groups: those carrying also  $\pi$  electrons and those that do not. All arguments related to electron-pair systems apply to these bonds as well.

The task is now to calculate the structure and energy of the of the system in its lowest electronic state. Since the two electron-pairing arrangements are equivalent, the desired system is likely to be constructed from a linear combination of the two. It is convenient to use VB terminology at this stage, following the classical work of Pauling, and

\* Polycyclic systems for which more than two electron-pairing arrangements are slightly more complicated but can be analyzed by an analogous procedure.

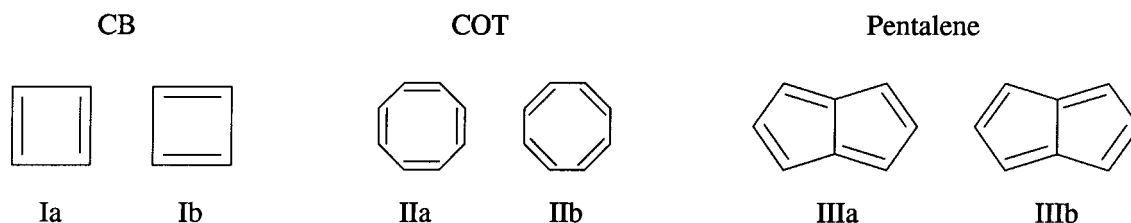


**FIGURE 1.** A diagrammatic representation of a cyclic  $C_{2n}H_{2n}$  hydrocarbon with alternating bond lengths. The lower scheme shows the spin-pairing pattern for the two possible Kekulé structures.

as elaborated at length by Eyring et al. [14]. Let the clockwise arrangement be described by a VB function  $|L\rangle$  and the counterclockwise one as  $|R\rangle$ .

The  $|L\rangle$  and  $|R\rangle$  wave functions are written in the standard fashion:

$$L = \sum_p \varepsilon_p P1(1)2(2) \cdots 2n(2n) \cdot [\alpha(1)\beta(2) - \beta(1)\alpha(2)][\alpha(3)\beta(4) - \beta(3)\alpha(4)] \cdots [\alpha(2n-1)\beta(2n) - \beta(2n-1)\alpha(2n)] \quad (1)$$



**SCHEME 1.**

$$R = \sum_p \varepsilon_p P1(1)2(2) \cdots 2n(2n) \cdot$$

$$[\alpha(1)\beta(2n) - \beta(1)\alpha(2n)][\alpha(2n-1)\beta(2n-2)$$

$$- \beta(2n-1)\alpha(2n-2)] \cdots$$

$$[\alpha(3)\beta(2) - \beta(3)\alpha(2)], \quad (2)$$

where the summation is over all  $2n!$  permutations  $P$  each with parity  $\varepsilon_p$ . We use a short-hand notation:

$$L = (\bar{1}2 - \bar{1}2)(\bar{3}4 - \bar{3}4) \cdots (2n - \bar{1}2n - \bar{2}n - \bar{1}2n), \quad (3)$$

with  $L$  containing a normalization factor and all permutations over the atomic orbital wave functions  $i$  ( $1 = 1, 2, \dots, 2n$ ). Likewise, the other Kekulé wave function,  $|R\rangle$ , has the form

$$R = (\bar{1}2n - \bar{1}2n)(2n - \bar{1}2n - \bar{2}$$

$$- \bar{2}n - \bar{1}2n - \bar{2}) \cdots (\bar{3}2 - \bar{3}2). \quad (3')$$

The actual wave function of the system is constructed from the combination of the two VB structures  $L$  and  $R$ . Two combinations are possible: an in-phase one  $L + R$ , and an out-of-phase one  $L - R$ . Their energies are given by

$$E^\pm = \frac{H_{LL} + H_{RR} \pm 2H_{LR}}{2 \pm 2S_{LR}}. \quad (4)$$

According to Eq. (4), if  $H_{LR} < 0$ , the ground state will be the in-phase combination, and the out-of-phase one, an excited state. On the other hand, if  $H_{LR} > 0$ , the ground state will be the out-of-phase combination, while the in-phase one, which transforms as the totally symmetric irreducible representation (irrep) of the point group, is an excited state. *This conclusion is far reaching, since it means that the electronic wave function of the ground state is nonsymmetric in this case, in contrast with common chemical intuition.* We show that when an even number of electron pairs is involved, *this is indeed the case, so that the ground state is not stable as a symmetric species. In fact, the symmetric species is a transition state, and the stable structure of the molecule is distorted.*

To show this, we have to evaluate the matrix element  $H_{LR} = \langle L|H|R \rangle$ . We begin by writing out the orbital part of the  $L$  wave function explicitly:

$$L = (\bar{1}2 - \bar{1}2)(\bar{3}4 - \bar{3}4) \cdots$$

$$(2n - \bar{1}2n - \bar{2}n - \bar{1}2n)$$

$$= \{ \bar{1}2\bar{3}4 \cdots 2n - \bar{1}2n - \bar{1}2\bar{3}4 \cdots 2n - \bar{1}2n$$

$$- \bar{1}2\bar{3}4 \cdots 2n - \bar{1}2n + \cdots$$

$$(-1)^n \bar{1}2\bar{3}4 \cdots \bar{2}n - \bar{1}2n \}. \quad (5)$$

The sign of the last term depends on the parity of the system. It is noted that in the first and last terms (in fact, determinants) the spin-orbit functions alternate, while in *all* others, there are two pairs of adjacent atoms with the same spin functions. We denote the determinants in which the spin functions alternate as the alternant spin functions (ASF), as they turn out to be important reference terms.

Next, we transform the VB function  $R$  [Eq. (3')] to a form similar to  $L$  by making  $n - 1$  transpositions of the form  $(2n, 2)$ ,  $(2n - 1, 3)$ , etc. Each transposition multiplies the function by  $-1$ , obtaining

$$R = (-1)^{n-1} \{ \bar{1}2\bar{3}4 \cdots 2n - \bar{1}2n - \bar{1}2\bar{3}4 \cdots$$

$$2n - \bar{1}2n - \bar{1}2\bar{3}4\bar{5}6 \cdots 2n - \bar{1}2n + \cdots$$

$$+ (-1)^n \bar{1}2\bar{3}4 \cdots \bar{2}n - \bar{1}2n \}$$

$$= (-1)^{n-1} \{ \bar{1}2\bar{3}4 \cdots 2n - \bar{1}2n \} + \cdots$$

$$+ (-1)^{2n-1} \{ \bar{1}2\bar{3}4 \cdots \bar{2}n - \bar{1}2n \}. \quad (6)$$

It is evident that the only determinants that appear in both  $L$  and  $R$  are the ASFs.

The cross term  $\langle L|H|R \rangle$  in Eq. (4) can now be evaluated. This term may be written as (omitting the normalization constant)

$$H_{LR, CL} = (-1)^{n-1} 2 \{ Q + K_{12} + K_{23} + \cdots$$

$$K_{ii+1} + \cdots K_{2n1}$$

$$+ \text{higher exchange integrals} \}, \quad (7)$$

where the Coulomb integral  $Q = \langle 1 \bar{2} 3 \bar{4} \cdots 2n - 1 \bar{2}n | H | 1 \bar{2} 3 \bar{4} \cdots 2n - 1 \bar{2}n \rangle$  and  $K_{ij}$  are exchange integrals containing terms such as  $\langle i, i+1 | g | i+1, i \rangle + 2S_{i, i+1} \langle i | h | i+1 \rangle$  [15]. The second term, representing the attractive interaction between two nuclei and the electronic overlap charge between them, is the dominant one and completely outweighs the first repulsive term.  $K_{i, i+1}$  therefore has the same sign as has the Coulomb integral  $Q$ . (For details of the derivation, see the treatment given by Eyring et al. for the special cases of four- and six-electron systems [14, Chap. 13]).

In Eq. (7),  $H_{LR,CL}$  is the cross term obtained by classic VB theory [8], in which only contributions from electron pairwise transposition permutations were considered. In particular, higher permutations, including the cyclic ones, were neglected. Bonding in these systems is due mainly to the exchange integrals  $K_{i,i+1}$  between orbitals in the same cycle [15]. Pauling [8] showed that the most important contributions are due to neighboring orbitals, justifying the neglect of the smaller terms in Eq. (7). His article did not explicitly mention the contribution of the cyclic permutations, although they are also due to neighboring orbitals.

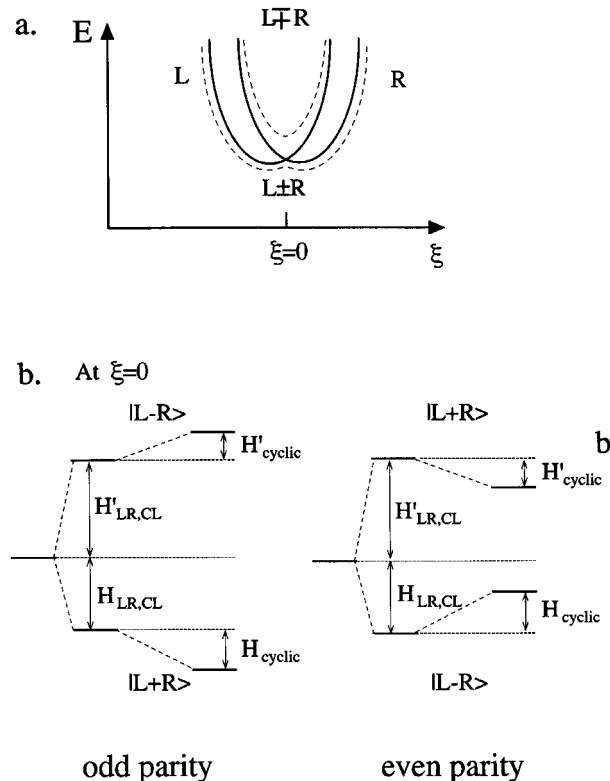
Because of the orthogonality of the spin functions, and since we assume no spin-orbit coupling, only the first and last terms in Eqs. (5) and (6) will contribute to the Coulomb integral in  $H_{LR,CL}$ . The Coulomb integrals together with the exchange ones between neighbors,  $K_{i,i+1}$ , are larger than all other terms and determine which will be the ground state. The sign of their contributions is determined as follows:

- When  $n$  is odd, the first ASF in both  $L$  and  $R$  is positive, while the second is negative. The two resulting Coulomb integrals are equal, contributing together  $2Q$ .
- When  $n$  is even, the two terms in  $L$  have equal signs, as in  $R$ , but the sign in  $R$  is opposite to that in  $L$ . Therefore, the total contribution to the energy is  $-2Q$ .

Since  $Q$  is negative, and  $H_{LR,CL}$  for the ground state must carry a negative sign, it follows that the ground state for the odd-parity case is the in-phase combination, while for the even-parity case, the out-of-phase combination is the ground state.

This is the classical VB picture, using only pairwise electron transpositions in the permutations, in which the spins of the two electrons of every bond are paired sometimes termed “the perfect pairing approximation” [15]. Figure 2 shows a schematic representation of the different contributions to the in-phase and out-of-phase combinations. It should be noted that the energies of the twin excited states shown in Figure 2 can also be calculated from Eq. (7). Their destabilization with respect to the  $H_{LL} + H_{RR}$  reference due to the cross term will be larger than the stabilization of the ground state, due to the different contributions of the overlap integral in the denominator of Eq. (4).

### Schematic twin state diagram



**FIGURE 2.** The twin state model: (a) The avoided crossing of two Kekulé curves leads to the formation of two electronic states from the in-phase and out-of-phase combinations.  $\xi$  is the coordinate that exchanges the two original structure, which would have crossed at  $\xi = 0$ . (b) The effect of the two main exchange integrals on the energies of the twin states at  $\xi = 0$  for (left) odd-parity systems and (right) even-parity system. The main splitting is due to the transposition permutations, leading to  $H_{LR,CL}$ , the classical VB term. In odd-parity systems, the cyclic permutation term,  $H_{cyclic}$ , acts in harmony with the classical term and increases the gap between the ground and excited states. In the even-parity systems, it acts to decrease the gap. See text for details.

Oosterhoff and coworkers [10] were the first to note the important contribution due to the cyclic permutations. Two such permutations are possible (clockwise and anticlockwise). It is readily verified that their contribution to the stabilization of the in-phase combination bears the same sign as that due to the pairwise transposition permutations, whereas for the out-of-phase combination, their contribution has an opposite sign. This is shown schematically in Figure 2(b).

It is concluded that the even and odd cyclic systems differ fundamentally from each other. We suggest that this difference is the basic origin for the characterization of aromaticity and propose a practical definition of an antiaromatic system: It has a ground state which may be constructed from the out-of-phase combination of two bond-alternating even-parity cyclic VB structures (even parity Kekulé structures). It will usually transform as one of the nontotally symmetric irreducible representations (irreps) of the relevant point group. This result, which was previously obtained [16, 17] for the special cases of cyclobutadiene and cyclooctatetraene, is seen here to be of a general nature. The in-phase combination transforms as the totally symmetric irrep, but is an excited state. Thus, antiaromatic molecules always have a nonsymmetric ground state and, as we show in the next section, are necessarily distorted from the fully symmetric geometry. The case of more than two VB structures can be treated in a similar way but will be deferred to a later publication.

### Distortive Nature of the Ground State in Even-parity Systems

From Figure 2(a), it is evident that when  $H_{LR}$  is small the system at  $\xi = 0$  is unstable and will tend to distort to either  $|L\rangle$  or  $|R\rangle$ . This can be readily seen by considering motion along the coordinate  $\xi$  that exchanges the two basic VB functions (we denote this coordinate "the reaction coordinate" in the following). As the system moves along the reaction coordinate, it is assumed that the wave function may be expressed as a linear combination:

$$\Psi^+(\xi) = C_L(\xi)|L\rangle + C_R(\xi)|R\rangle \quad (8)$$

By symmetry, at  $\xi = 0$ ,  $C_L(\xi) = C_R(\xi)$ , so that apart from a normalization factor,  $\Psi^+(\xi = 0) = |L\rangle + |R\rangle$ . We define the state represented by the function

$$\Psi^-(\xi = 0) = |L\rangle - |R\rangle \quad (9)$$

as the twin state of  $\Psi^+(\xi = 0)$ . At  $\xi = 0$ , the system may have an additional symmetry element, so that the resulting two combinations  $\Psi^+(\xi)$  and  $\Psi^-(\xi)$  belong to two different symmetry species.  $\Psi^+(\xi)$  always transforms as the totally symmetric representation, while the out-of-phase combination transforms as some other representation of the

point group. It is clear from the construction of Figure 2 and the discussion following Eqs. (4)–(6), that the ground state near  $\xi = 0$  is distortive if we consider only the transposition permutations. The physical reason for that is clear—from the crossing point, any infinitesimal motion to the right leads to the stable  $R$  configuration, and to the left, to the  $L$  one. Above the crossing point, the trend is reversed—a small distortion to the right goes up the  $L$  wall in the wrong direction. Therefore, a strong restoring force in the  $\xi = 0$  direction results, leading to a deep minimum at the symmetric configuration.

Why, then, are aromatic molecules found to have a symmetric structure in the ground state? The key to the answer is in the cyclic permutations. The cross term  $H_{LR}$ , which consists of the usual Coulomb- and transposition-type exchange integrals ( $Q$  and  $K_{ij}$ , respectively), contains also the cyclic exchange integrals  $K_{\text{cyclic}}$ ,

$$\begin{aligned} H_{LR} &= (-1)^{n-1} 2\{Q + K_{12} + K_{23} + \cdots \\ &\quad + K_{2n-12n} + K_{\text{cyclic}}\} \\ &= H_{LR,CL} + (-1)^{n-1} 2K_{\text{cyclic}}, \end{aligned} \quad (10)$$

where  $H_{LR,CL}$  is the classical contribution of the VB theory to the cross term.  $K_{\text{cyclic}}$  consists of terms such as  $S_{12}S_{23}S_{34} \cdots h_{ij} \cdots S_{2n1}$ . Using the usual assumption that the  $h_{ij}$  term is proportional to the overlap integral  $S_{ij}$  (with opposite sign), we write  $K_{\text{cyclic}}$  as

$$K_{\text{cyclic}} = \text{const} \cdot S_{12}S_{23}S_{34} \cdots S_{2n1}. \quad (11)$$

Motion along the Kekulé mode leads to changes in neighboring bond lengths—alternate small increases  $\Delta X_{\text{inc}}$  and decreases  $\Delta X_{\text{dec}}$ , leading to corresponding changes in the overlap integrals—half of them increase (by  $\Delta S_{\text{inc}}$ ) and the other half decrease (by  $\Delta S_{\text{dec}}$ ). The overall energy change  $\Delta K_{\text{cyclic}}$  is proportional to  $(\Delta S_{\text{inc}})^n \cdot (-\Delta S_{\text{dec}})^n$ , so that whether the system is stabilized or destabilized by this motion is determined by the parity: In the case of an odd number of electron pairs  $n$ , this motion leads invariably to an overall negative contribution, while with  $n$  even,  $\Delta K_{\text{cyclic}}$  is positive. Taking into account the  $(-1)^{n-1}$  term in Eq. (8), both contributions are seen to carry a negative sign. The overall effect of the cyclic terms on the energy change due to the Kekulé distortion is determined by considering Eq. (4). If the ground state is in-phase combination  $L + R$ , the term will

stabilize the system. If the ground state is the out-of-phase combination  $L - R$ , it will destabilize it [recall the minus sign in Eq. (4)]. Thus, the cyclic term operates in harmony with the classical term for the antiaromatic systems and counteracts it in aromatic systems. It has the opposite effect on the stabilization of the excited state (Figure 3).

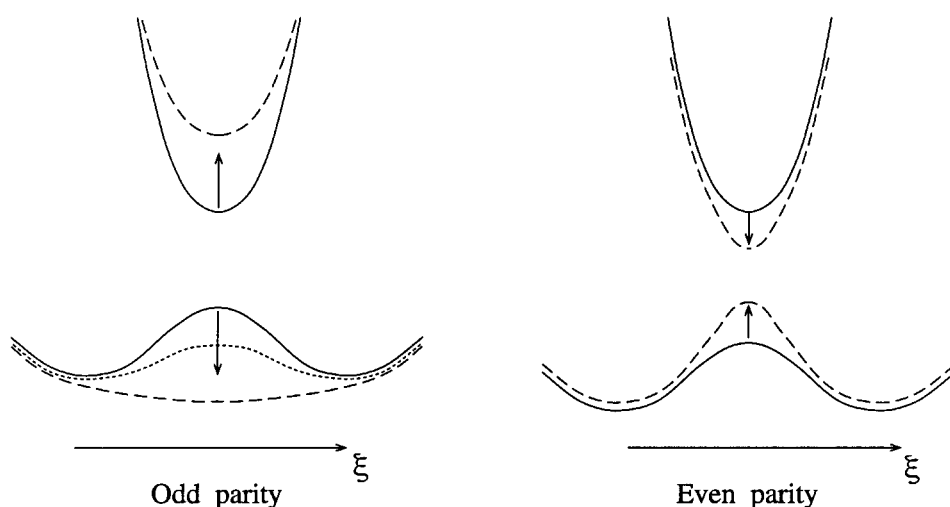
Taking into account the two possibilities for the ground state, we qualitatively summarize in Table I the influence of small distortion along the Kekulé mode near  $\xi = 0$  on the different terms contributing to the energy. In practice, the restoring force in the excited state is always larger than that of the ground state. This is because the curvature of the repulsive potentials in the excited state is much larger than near the minimum in the ground state. This was shown to be the case for the odd number of electron pairs (aromatic molecules [1, 3]) and, as seen here, is expected to be even more pronounced for twin states in which the ground state is a transition state: *The force constant of the mode interchanging the two original VB structures is expected to be much larger than "normally" expected for the CC stretch.* Assuming that the reduced mass of the molecule for this mode does not change much between the two states, we expect the frequency

associated with this mode to be considerably exalted.

According to Table I, odd-parity systems need not have a stable minimum at the symmetric geometry. This seemingly surprising result appears at first sight to be in contradiction to the well-known stability of aromatic systems. However, it turns out that this situation holds for many systems ("aromatic" transition states are quite common in concerted reactions) and was recently demonstrated computationally for the case of semibullvalene isomerization [4].

## Computational Examples

Several VB calculations were made on antiaromatic systems [16, 17]. The two Kekulé structures of the highest symmetry forms of CB and of COT were found to be the dominant configurations in the ground state, in line with the basic postulate of this article. It was noted that while in benzene the two Kekulé forms participate with coefficients of the same sign, in CB and COT, the coefficients are of opposite signs. This was considered as indicating the property of the particular systems under



**FIGURE 3.** The effect of motion along the Kekulé structures interchanging coordinate  $\xi$  on the energy of the ground and excited states. Unperturbed curves are shown as solid lines. For even-parity systems, this motion increases the distortion of the ground state from the symmetric form and acts to stabilize the excited state. In the case of odd-parity systems, this motion always stabilizes the ground state and destabilizes the excited state. Two possible outcomes are shown for the ground state: strong stabilization, leading to a minimum in the symmetric geometry (long dashed line), or small stabilization, retaining the distortive character of the ground state. The curvature of the excited-state potential curve is reduced, but is usually larger than that of the ground state, leading to frequency exaltation.

**TABLE I**  
**Stabilization effect of motion along the Kekulé mode away from the symmetric geometry due to different components of the exchange integral of  $H_{LR}$  in cyclic systems containing an even number of electrons.**

Parity <sup>a</sup>	State <sup>b</sup>	$\Delta K_{LR,CL}$ <sup>c</sup>	$\Delta K_{cyclic}$ <sup>c</sup>	$\Delta K_{global}$ <sup>c</sup>
Even	GS = $L - R$	Destabilize	Destabilize	Destabilize
Even	ES = $L + R$	Stabilize	Stabilize	Stabilize
Odd	GS = $L + R$	Destabilize	Stabilize	Varies
Odd	ES = $L - R$	Stabilize	Destabilize	Varies

<sup>a</sup> Parity: parity of electron pairs participating in the reaction.

<sup>b</sup> GS, ground state; ES, excited state.

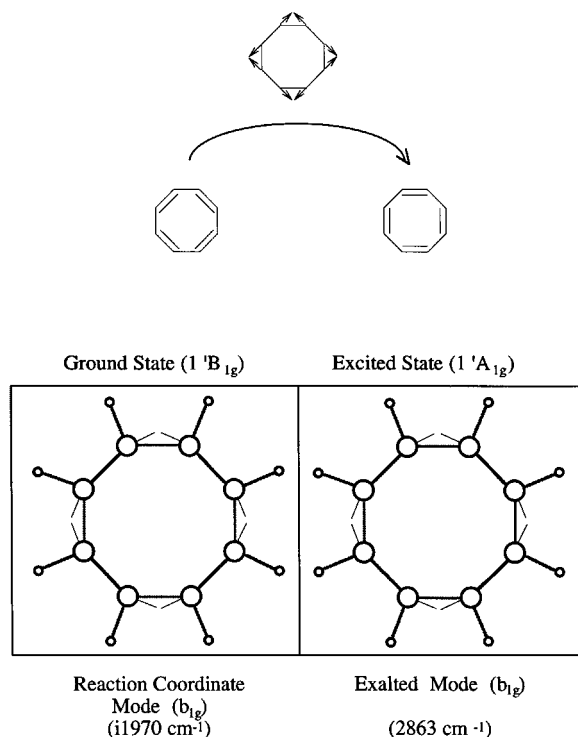
<sup>c</sup> The  $\Delta K_{LR,CL}$ ,  $\Delta K_{cyclic}$ , and  $\Delta K_{global}$  denote energy changes due to the classical exchange integral, the cyclic one, and the global change (the combination of the two), respectively.

study, not necessarily as a fundamental property of an even-parity system, as shown by the present model. Moreover, the model predicts that *all even-parity systems* must have a low-lying electronically excited state that is strongly bound, transforms as the totally symmetric irrep, and may be constructed from the in-phase combination of the two basic VB structures. This prediction was fully substantiated by quantum chemical calculations for CB, COT, and pentalene.

We have used the CAS method to calculate the properties of the ground state and the  $1^1A_g$  excited state of three prototype even-parity systems: CB, COT, and pentalene [18]. In particular, we were interested in the energy gap between the two states (at  $\xi = 0$ ) and in the vibrational mode that corresponds to the exchange of the two Kekulé structures (the Kekulé mode). In the ground state, this mode is a reaction coordinate, having an imaginary frequency. The results are compared with those obtained for two odd-parity systems—benzene, for which a stable minimum is obtained at  $\xi = 0$ , and semibullvalene, which is also a transition state. Figures 4 and 5 show the calculated forms of the Kekulé mode for COT and pentalene, respectively. The similarity to the analogous calculation for benzene [1] is obvious. It is found that these modes involve purely carbon atom motions, the hydrogen atoms being essentially motionless. The vector displacements of the atoms in the two states for a given molecule are calculated to be almost identical, as expected from the model. The unusually large frequency is also noted; it is much larger than that calculated for the analogous case of benzene, in which a frequency exaltation compared to the ground state was also found. This is in line with the arguments presented pictorially in Figure 3: The frequency of this mode is found, as

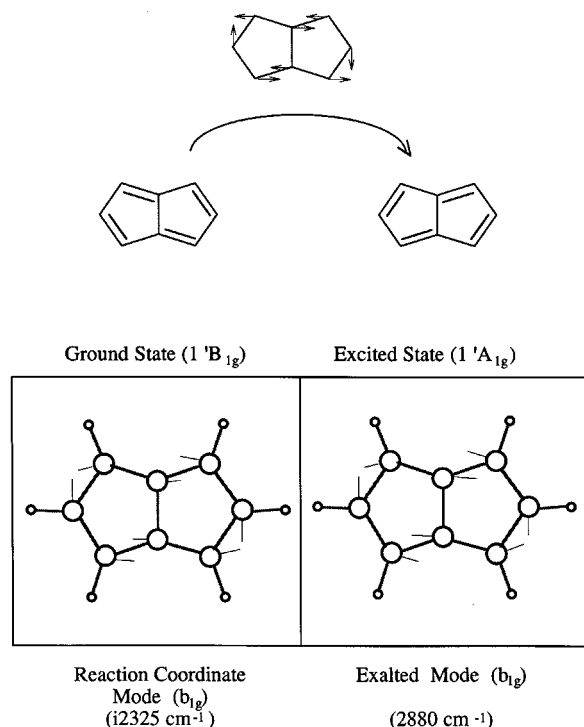
expected, to be much larger than the usual for a C=C stretch motion ( $\sim 1600\text{ cm}^{-1}$ ).

Table II lists the results for the five molecules. It is seen that the energy gap is systematically lower for the odd-parity molecules than for the even-parity ones and that the frequency of the exchanging mode is much larger for the even-parity systems



**FIGURE 4.** The calculated Kekulé mode motion for COT on the ground state (imaginary value, the motion is along the reaction coordinate) and on the excited-state potential surface. Note the very large frequency of the latter and the similarity in the atom motion vectors.





**FIGURE 5.** The calculated Kekulé mode motion for pentalene on the ground and on the excited-state potential surfaces. As in the case of COT (Fig. 4), note the very large frequency of the latter and the similarity in the atom motion vectors.

than for the odd-parity ones. For comparison with possible future experiments, we list also normalized frequencies for the excited states which were scaled by 0.87 (a value obtained from the experimental result for benzene).

**TABLE II**  
Calculated properties of some odd- and even-parity molecular system.<sup>a</sup>

Molecule <sup>b</sup>	CB	COT	Pentalene	Benzene	SB
Parity	Even	Even	Even	Odd	Odd
$\Delta E^c$ (eV)	2.4	1.5	0.82	4.86	5.16
Frequency <sup>d</sup> (cm <sup>-1</sup> )					
Ground state	i1278	i1970	i2375	1300	i555
Twin state, cal <sup>e</sup>	2098	2863	2880	1802	1642
Twin state, nor <sup>e</sup>	1825	2491	2506	1570	1429
Distortion					
Energy (eV)	0.29	0.22	0.42	—	0.57

<sup>a</sup> Calculations at the CAS(4,4) level for CB, CAS(8,8) for COT and pentalene, CAS(6,6) for benzene, all using the GAMESS program suit [18a], and HF/CIS for SB using the GAUSSIAN package [18b]. The basis set was 3-21G.

<sup>b</sup> CB, cyclobutadiene; COT, cyclooctatetraene; SB, semibullvalene.

<sup>c</sup>  $\Delta E$ , the energy gap between the ground state and its twin at the symmetric structure ( $\xi = 0$ ).

<sup>d</sup> Frequency of the mode exchanging the two Kekulé structures. Imaginary frequencies indicate a reaction coordinate.

<sup>e</sup> Cal, calculated, and nor, normalized using the scaling factor of 0.87 derived from the experimental value for benzene (1570 cm<sup>-1</sup>).

## Discussion

### GENERAL COMMENTS

The essential part of the model is the fact that electrons tend to be paired in chemical bonds. In the  $C_{2n}H_{2n}$  system, there are three C—C bonds for each carbon atom, creating an asymmetry that leads to the representation of the system by two covalent VB structures. Note that there is no special role for the  $\pi$  electrons, except for providing a “marker” that makes the two forms distinguishable. Thus, one can describe the system as containing three types of electron pairs: sigma pairs between atoms bound also by a  $\pi$  pair ( $\sigma_\pi$  electrons), sigma pairs between atoms not bound by a  $\pi$  pair ( $\sigma$  electrons), and  $\pi$  pairs ( $\pi$  electrons).

Each of the three different types has  $n$ -electron pairs, which are arranged around the ring with the same symmetry pattern. Since there are three (an odd number) of them, the total wave function will transform as each individual one. The  $L$ – $R$  out-of-phase combination of each bond type transforms as one of the nontotally symmetric irreps, and so does the out-of-phase overall one. It is common to assign the symmetry properties to the  $\pi$ -electron system alone, but, in fact, it is immaterial whether the  $\sigma$ ,  $\sigma_\pi$ , or  $\pi$  electrons are “responsible”—in fact, their roles are completely interchangeable.

It is concluded that the properties of antiaromatic molecules are essentially due to the presence of an odd number of different bond types that alternate around the ring and to the even parity of the system. The fact that it was found for conju-

gated hydrocarbons is not fundamental. Therefore, the conclusion of [19] that the antiaromaticity of cyclobutadiene arises from the  $\sigma$  frame ring strain may be correct, but is not of a basic nature. Indeed, pentalene is also antiaromatic, while ring strain is practically unimportant.

Antiaromatic molecules have often been discussed in terms of biradical structures [20, Chap. 3]. This is in line with our model: An odd number of electron pairs tends to stabilize a cyclic system. In an even-parity system, there is an "extra" pair. If the two electrons of this pair were correlated, destabilization would result. The symmetric ground-state structure is therefore unstable and could be the transition state between the two distortive structures *were the isomerization reaction a concerted one*. However, if the electrons of the "extra" pair are not correlated, destabilization is avoided, so that a biradical nature is as expected. This accounts for the calculated magnetic properties of antiaromatic molecules. In the said reaction, the system is therefore likely to develop along a nonconcerted coordinate, for instance, one that involves lengthening of a certain bond to the extent that the two electrons become uncoupled, forming a biradical.

Our approach is based largely on the avoided crossing model that was extensively used by Shaik et al. [21]. They considered mostly ground-state properties and concluded that in benzene, for instance,  $\pi$  electrons tend to distort the system along the Kekulé coordinate to one of the  $D_{3h}$  structure. According to their theory, the extra stability of benzene and other aromatic systems is due to the strong restoring force exerted by the  $\sigma$  electrons. This model is in line with the observed frequency exaltation in aromatic molecules [3]. In the present model, we show that this is a possible interpretation of the situation in an odd-parity system. However, the basic origin of the stability of the symmetric form of the six-membered ring of benzene is the stabilizing effect of the cyclic exchange integrals that more than compensates for the distortive tendency of the pairwise transposition permutations. The vastly rich aromatic chemistry is thus due to the particular combination of terms prevalent in a six-membered carbon ring with conjugated bonds.

The present model does not discriminate between forces due to the  $\pi$  or  $\sigma$  systems. It emphasizes the importance of the forces generated in the

cyclic systems due to constraints inherent to the fact that electron pairing in a ring system requires that *each* binding electron is subject to symmetry constraints on *both* sides of the atom that it originates from. The distortive tendency due to the classical exchange integrals can be interpreted as showing that  $\pi$  electrons in cyclic conjugated systems are distortive, as proposed in the model of Shaik and coworkers [21].

## COMPARISON WITH PREVIOUS VB TREATMENTS

The classical theory of resonance, considering simple VB structures, predicts strong resonance stabilization for both benzene and cyclobutadiene [8, 9, 14]. It is only when two VB structures are considered that the antiaromatic character reveals itself. The notion that an antiaromatic molecule has a nontotally symmetric wave function was derived by Craig as early as 1951 [22] for cyclobutadiene based on a molecular orbital theory (Platt's free-electron model applied to motion on a ring [23]). He found correctly that the ground state of the square form of this molecule is of  $B_{1g}$  symmetry<sup>†</sup> and the excited state of  $A_{1g}$  symmetry. Using VB arguments to illustrate his point, he showed that these two states may be faithfully represented by the in-phase and out-of-phase combinations of the two Kekulé forms. However, he stated erroneously that the ground state is the in-phase combination. As noted by Longuet-Higgins [24], there was no very obvious reason why electronic asymmetry should destroy the stability of a molecule, so the physical basis of the distortion of antiaromatic ring systems remained obscure.

Oosterhoff and coworkers considered a cyclic transition state in a concerted reaction [10], which is a linear combination of two Kekulé structures of the same nature as discussed in this work. They were the first to consider explicitly the role of the cyclic permutations, the only ones that differentiate between positive and negative atomic orbital overlap integrals. These integrals distinguish between the conrotatory and disrotatory modes of a concerted reaction and were therefore of essential interest in the Mulder-Oosterhoff theory. In the present case, we are interested only in positive overlap integrals, and, therefore, the parameter that distinguishes between an aromatic and an

<sup>†</sup> Craig denoted the ground state as a  $B_{2g}$  one; we use the presently accepted coordinate scheme, according to which the ground state is of  $B_{1g}$  symmetry.

tiaromatic system, according to the Mulder–Oosterhoff treatment, is the number of electron pairs: odd for the former, even for the latter.

An extensive discussion of the properties of cyclic systems based on the Mulder–Oosterhoff approach [10] was given by Kuwajima [13], who showed that the cyclic permutation contribution accounts for the difference between even- and odd-parity systems, explaining why the former are resonance-destabilized. He also calculated excited-state energies, finding that the gap between the ground state and the conjugate excited state was always smaller for even-parity systems than for odd-parity ones. However, he did not explicitly consider the fact that the ground state of even-parity systems is formed by the out-of-phase combination of the Kekulé structures, nor the fact the small energy gap in antiaromatic systems is a necessary result the spin pairing model, as shown in this work.

The dominant role of the cyclic permutations was stressed by Malrieu and Maynau [12], who also explicitly mentioned that the parity determines the symmetry of the ground state. Since they considered only the determinant of a single Kekulé form, rather than the in-phase and out-of-phase combinations, they regarded the ground state as being always of  $^1A_g$  symmetry. Thus, the fundamental property of antiaromatic systems as out-of-phase combinations of Kekulé structures is not apparent in their model.

A complete correct VB-based model for an antiaromatic molecule was given by Voter and Goddard [16] for the special case of cyclobutadiene. It was shown that the ground state belongs to a nontotally symmetric irrep and may be constructed by the out-of-phase combination of two Kekulé structures. The present article shows that this result is a special case and necessarily arises from the fact that an even number of electron pairs is involved.

## CONNECTION WITH MO TREATMENTS

MO-based models were frequently used to describe antiaromatic systems. The distortivity from the most symmetric form (typical of aromatic systems) was usually accounted for by invoking the pseudo Jahn–Teller effect [25, 26]. For instance, the single  $C_{4n}H_{4n}$  rings, such as cyclobutadiene (CB) and cyclooctatetraene (COT), possess, in the simple one-electron configuration picture, a pair of

degenerate nonbonding orbitals to which two electrons are assigned. In the case of hypothetical planar square CB, for instance, the highest occupied MO has an  $e_g$  symmetry and the  $(e_g)^2$  configuration splits into four nondegenerate states ( $^1B_{1g} + ^1A_{1g} + ^1B_{2g} + ^3A_{2g}$  in this case). The standard Jahn–Teller theorem does not hold in this case (in contrast with the  $CB^+$  cation case, which is genuinely degenerate and therefore distortive). The argument is that the ground  $^1B_{1g}$  state and the  $^1A_{1g}$  state are only slightly different in energy and interact by vibronic coupling along a  $b_{1g}$  stretching coordinate, which leads to the stabilization of the bond-alternating form, in agreement with experiment [25, p. 487]. Ab initio calculations support this result, but it is worth noting that a single-configuration HF calculation invariably leads to a fully symmetric ( $A_{1g}$ ) ground state. The correct symmetry requires configuration interaction, a result that has been assigned, in turn, to the biradical nature of these systems [26]. The MO argument needs to be stretched further for systems such as pentalene in which even the molecular orbitals are not degenerate in the one-configuration picture. Again, the pseudo Jahn–Teller effect is invoked to explain the experimental (and computational) finding of bond alternation in this molecule, by referring to the small energy difference between the ground and the first excited state. Since configuration interaction is required to correctly calculate the properties of ground-state antiaromatic systems, schemes such as restricted Hartree–Fock (RHF) or density functional theory (DFT), which use a single HF configuration, are bound to predict a totally symmetric ground state. This was actually recently found to be the case for CB, COT, and pentalene [27]. The fact that the ground state for the  $D_{2h}$  form of pentalene does not transform as the totally symmetric irrep seems to have caused some difficulties in the quantum chemical calculations of the properties of this system [28, 29].

In this article, we showed that the fact that even-parity ring hydrocarbons are found to be distorted in their ground state is a fundamental property, traceable to the electron-pairing nature of the chemical bond. This may be taken as the physical origin of the pseudo-Jahn–Teller treatment of the MO method. The VB picture provides a simple way for determining the distortion coordinate: It is the same coordinate as that which interchanges the two VB structures. This model also explains why a

single-determinant MO calculation can never account for the properties of antiaromatic systems: It lacks the basic ingredients necessary for the minimum possible description.

## Conclusion

A model explaining the origin of antiaromaticity has been presented. It is based on the tendency of electrons to form pairs and on the permutation properties of cyclic systems. The distortive nature of antiaromatic molecules is found to be a fundamental property of even-parity systems because the ground state is formed from the out-of-phase combination of two Kekulé structures. In contrast, ground states of aromatic systems are due to an in-phase combination of odd-parity systems. However, an in-phase combination does not ensure stabilization of a totally symmetric ground state—some are found to be distortive. The model emphasizes the importance of using the *combinations* of Kekulé structures. This provides a lucid physical explanation of the frequency exaltation phenomenon, which cannot be obtained by considering a single structure. It predicts a stronger exaltation for the antiaromatic systems than for the aromatic ones and a significantly larger energy separation between the ground and excited states due to the in- and out-of-phase combinations in odd-parity systems than in even-parity ones. These qualitative predictions are substantiated by quantum chemical calculations.

## Acknowledgments

This work was supported by the Israel Science Foundation founded by The Israel Academy of Sciences and Humanities. The Farkas Center is supported by Minerva Gesellschaft mbH, Munich. We are indebted to Professor S. Shaik for many illuminating discussions on the avoided crossing model.

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