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Molecular Orbital Resonance Theory: A Simple Model and the Generalised Hückel Rule*

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A simple approximation called MORT-1 is formulated within the framework of the MORT approach. In this approximation a Hückel Hamiltonian is assumed and only MORT Kekulé structures are retained. Matrix elements $H_{ab} = \langle K_a | H | K_b \rangle$ of the Hamiltonian operator H between Kekulé structures K_a and K_b are derived. In particular, a generalisation of a Hückel $(4m+2)$-rule is obtained. It is shown that in the case of even alternant hydrocarbons MORT Kekulé structures K_a and K_b interact with each other if and only if their superposition G_{ab} contains no $4m$-type cycle. The set $\mathbf{K}$ of all MORT Kekulé structures splits into two mutually noninteracting subsets $\mathbf{K}^+$ and $\mathbf{K}^-$. This partition formally corresponds to the Dewar and Longuet Higgins partition on »positive« and »negative« Kekulé structures. In the nonalternant case the interaction between the two subsets is due to the »cis-bridge« (nonalternant) bonds. This interaction is on the average an order of magnitude weaker then the corresponding interaction between Kekulé structures of the same parity.

INTRODUCTION

Recently a new approach to the treatment of quantum chemical problems was proposed.[1,2] This approach, called the Molecular Orbital Resonance Theory (MORT), retains the concept of the resonance from the VB method, but it treats each particular bond in the MO sense. In the present paper a simple MORT model called MORT-1 will be considered. In MORT-1 a ground state is an antisymmetrised product of spin-up and spin-down substates. These substates are linear combinations of MORT Kekulé structures, and a Hückel Hamiltonian is assumed. Finally, some consequences of the MORT-1 approach, in particular a generalisation of the well known Hückel $(4m + 2)$-rule, will be derived.

In order to formulate the MORT-1, matrix elements of one-particle operators between MORT Kekulé structures are needed. Formulation of the rules for the evalution of those matrix elements requires some new concepts and conventions. This is a rather technical part, and it will be presented at the beginning of this paper. In order to be more general, the so called »normal« resonance structures will be considered. These structures include the MORT

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Kekulé structures, and they span the complete configuration space X_n which is generated by n particles occupying $2n$ orbitals. For the sake of restricted space the proof of these rules will be given elsewhere.[3]

SPACE AND RESONANCE STRUCTURES

Let $B = \{\chi_i \mid i = 1, \ldots, N\}$ be an orthonormalised set of N real one-particle orbitals χ_i. These orbitals can be atomic orbitals (AO-s), spin atomic orbitals, molecular orbitals etc. For the sake of reference we will call orbitals χ_i, primitive orbitals (PO-s). Each subset $D_n \subset B$ of n ($n \subseteq N$) primitive orbitals $\chi_{i1}, \ldots, \chi_{in}$ defines an n-particle determinant

$$D_n = \left| \chi_{i1}, \chi_{i2}, \ldots, \chi_{in} \right| = \frac{1}{\sqrt{n!}} \sum_P (-1)^p \chi_{i1}(P1) \ldots \chi_{in}(Pn) \tag{1}$$

The set of all determinants (1) is orthonormalised and it spans the configuration interaction (CI) space X_n^N. We define resonance structures in the following way:[3]

Form bond orbitals (BO-s) as linear combinations of PO-s

$$\varphi_s = \varphi_{ij} = \frac{1}{\sqrt{2}} (\chi_i + \chi_j) \qquad \text{nonexcited BO}$$

$$\varphi_s^* = \varphi_{ij}^* = \frac{1}{\sqrt{2}} (\chi_i - \chi_j) \qquad \text{excited BO} \tag{2}$$

The term »Bond orbital« is meant to be an analogy with the usual interpretation of those orbitals when χ_i are AO-s. However, orbitals φ_s and φ_s^* do not have necessarily any direct connection with the bond picture. In particular, PO-s χ_i and χ_j can correspond to different spin states, etc.

We distinguish two types of BO-s: excited and nonexcited. An asterisk (*) denotes an excited BO. For the sake of simplicity and when there is no explicit reference to the excited and nonexcited BO-s, we will omit the asterisk in the notation of the BO.

We can now define:

Definition 1:

An n-particle resonance structure (RS) is an antisymmetrized product of n mutually disjunct BO-s, i. e.

$$S = \frac{1}{\sqrt{n!}} \sum_P (-1)^p \varphi_{s1}(P1) \varphi_{s2}(P2) \ldots \varphi_{sn}(Pn) =$$

$$= \frac{1}{\sqrt{n!}} \sum_P (-1)^p \varphi_{Ps1}(1) \varphi_{Ps2}(2) \ldots \varphi_{Psn}(n) \tag{3a}$$

Structure (3a) can be written in contracted form

$$S = |s_1, s_2, \ldots, s_n\rangle = \frac{1}{\sqrt{n!}} \sum_P (-1)^p \left| Ps1, Ps2, \ldots, Psn \right)$$

where

$$\left| s_1, s_2, \ldots, s_n \right) = \varphi_{s1}(1) \varphi_{s2}(2) \ldots \varphi_{sn}(n) \tag{3b}$$

is a simple product of BO-s. The summation in eqs. (3) is extended over all permuations P. By definition, BO-s are mutually disjunct if they have no PO in common. A resonance structure can hence be defined only if $2n \leq N$.

One can easily show that the set of all n-particle RS-s (3) spans the CI space X_n^N. Resonance structures satisfying the condition $2n = N$ will be called normal resonance structures (NRS's). For the sake of simplicity the corresponding space X_n^{2n} will be denoted by X_n. In this paper only NRS-s will be treated. This is not a serious restriction to the generality, since any quantum chemical problem formulated in the arbitrary space X_n^N can be reducted to a corresponding problem formulated in a space $X_{n'}$ through the use of »dummy« PO-s and »dummy« particles.[3,18]

There is a natural graphical representation of NRS-s. We represent each PO with a vertex and each BO with a bond connecting two vertices (PO-s). If a BO is excited, we put an arrow on the place of the PO which should be taken with a negative sign. Accordingly, the corresponding bond is oriented. In this way one can represent each NRS (see Figure 1). A graphical representation of a resonance structure is ambiguous up to the phase (—1). This ambiguity will be treated later.

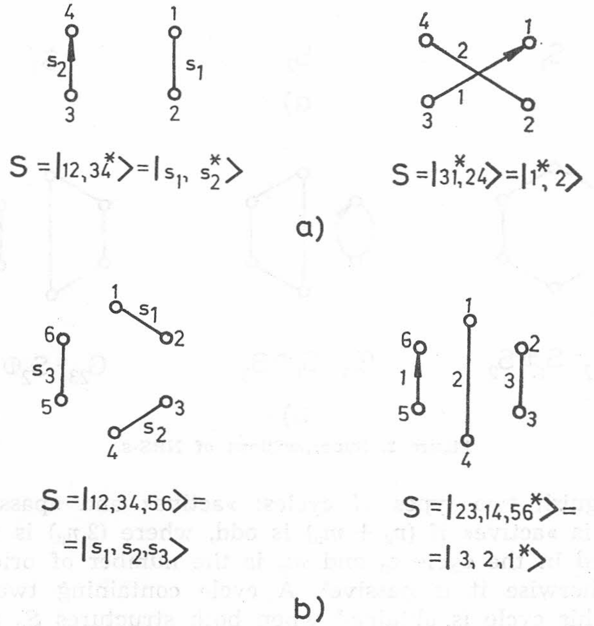


Figure 1. Graphical representation of different NRS-s. Excited BO-s are represented with oriented bonds: a) Case $n = 2$, b) Case $n = 3$.

OVERLAPS AND MATRIX ELEMENTS OF ONE-FARTICLE OPERATORS BETWEEN NRS-s

We will give here the rules for the derivation of overlaps and matrix elements of one-particle operators between arbitrary NRS-s. The proff of these rules is quite lengthy and will be given elsewhere.[3] In order to formulate these rules some additional concepts and conventions are needed.

a) Superposition of two NRS-s

We first introduce the concept of the superposition of two NRS-s. The superposition of NRS-s S_a and S_b is defined to be a graph G_{ab} such that it contains all vertices and all bonds contained in either of those two structures. If a particular bond is contained in both structures, the corresponding vertices are joined with two bonds. Bonds corresponding to excited BO-s are denoted by an arrow, i. e. they are oriented.[3] In order to represent the superposition G_{ab} of NRS-s S_a and S_b we use the notation $G_{ab} = S_a \oplus S_b$.

According to the above definition each superposition G_{ab} contains $2\,n$ bonds, either oriented or nonoriented. It is easy to show that each superposition G_{ab} consists of disjunct even cycles. These cycles contain oriented and/or nonoriented bonds. This follows from the fact that the BO-s contained in each NRS are mutually disjunct and that in addition $2n$ equals the number of all vertices.[3]

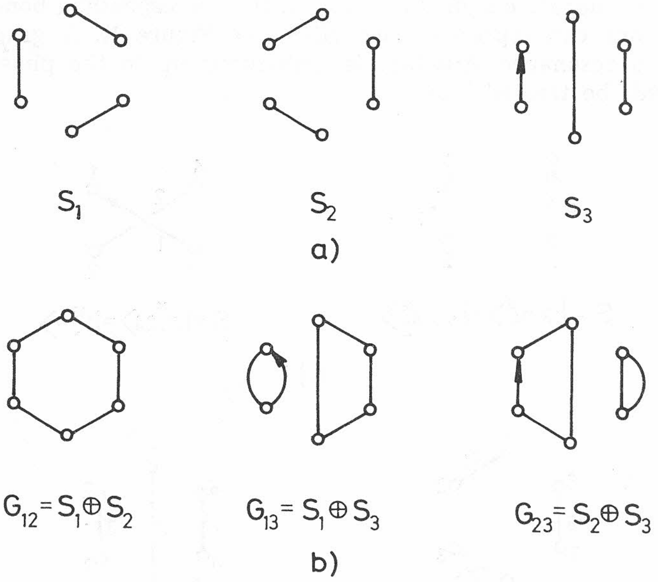


Figure 2. Superpositions of NRS-s

We distinguish two types of cycles: »active« and »passive« cycles. A cycle $c_\mu \in G_{ab}$ is »active« if $(n_\mu + m_\mu)$ is odd, where $(2\,n_\mu)$ is the number of bonds contained in the cycle c_μ and m_μ is the number of oriented bonds in this cycle. Otherwise it is passive[3]. A cycle containing two bonds has a special role. This cycle is obtained when both structures S_a and S_b contain a BO corresponding to the same bond (s). We call such a cycle a γ-cycle[3].

Examples of the superposition of different NRS-s are given in Figure 2. The superposition G_{12} contains one active cycle, the superposition G_{13} contains two passive cycles, while the superposition G_{23} contains two active cycles. Moreover, superpositions G_{13} and G_{23} contain a γ-cycle. In the former case this cycle is passive, while in the later case it is active.

There is some resemblance between the superposition G_{ab} of MORT structures and Rumer diagrams[4] which represent superpositions of VB structures. There is however more information in the MORT superposition, since it can contain oriented and nonoriented bonds, while Rumer diagrams contain only oriented bonds. In addition, each bond in G_{ab} represents a one-electron BO, while each bond in a Rumer diagram represents two electrons with paired spins.

b) *Normal Phase*

Each exchange of two BO-s in a given NRS changes a phase of this structure for the factor (-1). All matrix elements between NRS-s are hence ambiguous up to this phase. The phase between NRS- $S_a = | s_1, \ldots, s_n\rangle$ and $S_b = | p_1, \ldots, p_n\rangle$ can be fixed in the following way:[3]

1. Form the superposition $G_{ab} = S_a \oplus S_b$ and let $c_1, \ldots, c_\varrho$ be the set of all cycles contained in G_{ab}.

2. Partition the set $\{(i)\}$ of all $2\,n$ vertices into sink and source vertices in such a way that no two sinks and no two sources are adjacent to each other on G_{ab}. This partition in sink and source vertices is always possible since the superposition G_{ab} is an alternant graph. Denote sink vertices with a cross (x) (see Figure 3).

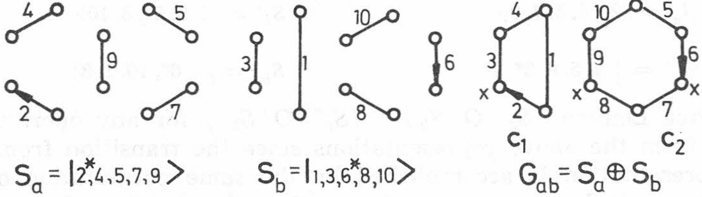


Figure 3. Illustration of the normal ordering convention

3. Fix the phase of each excited BO in such a way that it has a phase (-1) at sink and a phase $(+1)$ at the source position.

4. For eacht i $(i = 1, \ldots, n)$ bond orbitals $\varphi_{si} \in S_a$ and $\varphi_{pi} \in S_b$ should lie adjacent to each other between two sink positions on G_{ab}.

If NRS-s S_a and S_b are written in accord with the above conditions we say that they satisfy the normal ordering convention. Provided the partition on sink and source vertices is fixed, three are $n!$ different representations of NRS-s S_a and S_b satisfying the normal ordering convention. However, one can prove the following[3].

Lemma 1

The phase between NRS-s S_a and S_b does not depend on the particular representation satisfying the normal ordering convention, as long as the partition on sink and source vertices is fixed. If in the cycle $c_\mu \in G_{ab}$ the role of sink and source vertices is exchanged, this phase changes for a factor $(-1)^{n_\mu + m_\mu + 1}$, where $(2\,n_\mu)$ is the number of bonds in a cycle $c_\mu \in G_{ab}$, while m_μ is the number of oriented bonds in this cycle.

If namely the partition on sink and source vertices is not changed, then the transition from one to another representation satisfying the normal ordering convention is accomplished by some permutation P_a of the BO-s contained in the structure S_a, and some permutation P_b of the BO-s contained in the structure S_b. According to Item 4 of the normal ordering convention, these two permutations are identical. Thus the relative phase between structures S_a and S_b does not change. This proves the first part of the above Lemma. If however the role of sink and source vertices is exchanged in the cycle $c_\mu \in G_{ab}$, then all excited BO-s corresponding to this cycle change sign. This produces the factor $(-1)^{m_\mu}$. In addition, the related BO-s in respective structures do not lie any more between the two sink positions. In order to restore this condition one has to perform a cyclic permutation of n_μ BO-s which produces the additional factor $(-1)^{n_\mu+1}$. This proves the second part of this Lemma.

According to Lemma 1 the relative phase between two NRS-s is well defined as long as the partition on sink and source vertices is kept fixed. Under this provision we are justified in calling »normal« the phase between NRS-s S_a and S_b satisfying the normal ordering convention.

For example, in Figure 3 the superposition G_{ab} of NRS-s S_a and S_b contains two cycles, cycle c_1 and cycle c_2. There are many representations of those two structures consistent with the normal ordering convention. Among others are the following two

$$S_a' = |\, 2^*, 4, 5, 7, 9\rangle \qquad S_b' = |\, 1, 3, 6^*, 8, 10\rangle$$

and

$$S_a'' = |\, 7, 5, 9, 2^*, 4\rangle \qquad S_b'' = |\, 8, 6^*, 10, 1, 3\rangle$$

By the above Lemma $\langle S_a' \,|\, O \,|\, S_b' \rangle = \langle S_a'' \,|\, O \,|\, S_b'' \rangle$ for any operator O. This is obvious from the above representations since the transition from the (′) to the (″) representation is accomplished by the same permutation of BO-s in both structures. If, however, we exchange the role of sink and source vertices in, say, the cycle c_2, then the relative phase is changed by the factor $(-1)^{\mathrm{n}_2+\mathrm{m}_2+1} = (-1)^{3+1+1} = -1$.

All rules to be given subsequently for overlaps and matrix elements of different operators are derived under the assumption that the two NRS-s in question satisfy the normal ordering convention.

c) *Elementary One-particle Operators*

Each real one- particle operator can be represented as a linear combination of »elementary« one-particle operators A^{kl} $(k, l, = 1, \ldots, 2\,n)$ such that*

$$\langle \chi_i \,|\, A^{kl} \,|\, \chi_j \rangle = \delta_{ik}\,\delta_{jl} + \delta_{il}\,\delta_{jk} \tag{4}$$

i. e., in the base of PO-s χ_i all matrix elements of the operator A^{kl} vanish, except matrix element $\langle \chi_k \,|\, A^{kl} \,|\, \chi_l \rangle = \langle \chi_l \,|\, A^{kl} \,|\, \chi_k \rangle$. We will give here only the rules for the evalution of matrix elements of real elementary operators in the base of NRS-s. The real operators are by far the most important in quantum chemistry (e. g., each velocity-independent Hamiltonian is a real hermitian operator). The rules for the evaluation of matrix elements of other then real operators can also be obtained.[3]

There is a simple connection between elementary operators as defined above and creation and annihilation operators. If a_i^+ and a_i are creation and annihilation operators associated with the PO χ_i then

$$A^{kl} = a_k^+ a_l + a_l^+ a_k \tag{5}$$

Two types of elementary operators A^{kl} can be distinguished:

a) $A^{kk} = A^k$ is a vertex operator.

b) $A^{kl} = A^{lk}$ where $k \neq l$ is a bond operator. We also write $A^{kl} = A^s$ where $(s) = (k, l)$.

Relative to the given pair S_a and S_b of NRS-s one can further divide bond operators into additional subtypes:

1. Bond operator $A^s = A^{kl}$ is »internal« if vertices (k) and (l) are contained in the same cycle $c_\mu \in G_{ab}$. Otherwise it is external.
2. Bond operator $A^s = A^{kl}$ is »trans-bridge« if vertices (k) and (l) are either both sink or both source. It is »cis-bridge« if one of those vertices is sink and the other source.
3. In particular, if a bond $(s) = (k, l)$ is contained in the superposition G_{ab}, i. e., if it is contained in some cycle $c_\mu \in G_{ab}$, bond operator A^s is »normal«. This is a special case of a cis-bridge bond operator.

Some examples of different types of elementary operators are given in Figure 4.

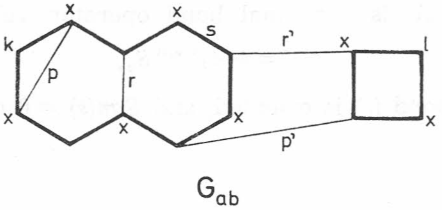


Figure 4. Different types of elementary operators. Operators A^k and A^l are vertex operators, while all other are bond operators. Further, operators A^s, A^p and A^r are internal, while operators $A^{r'}$ and $A^{p'}$ are external. Trans-bridge are operators A^p and $A^{p'}$, while cis-bridge are operators A^s, A^r and $A^{r'}$. Finally operator A^s is a normal bond operator.

d) Overlaps and Matrix Elements of Elementary Operators A^{kl} Between NRS-s

In the following Lemmas S_a and S_b are two n-particle NRS-s satisfying the normal ordering convention. G_{ab} is the superposition of those structures, and $c_1, \ldots, c_\varrho$ is the set of all cycles contained in G_{ab} (see Figure 5).

Lemma 2

Overlap $S_{ab} = \langle S_a \mid S_b \rangle$ equals

$$S_{ab} = \begin{cases} 2^{\varrho-n} & \text{if all } \varrho \text{ cycles } c_1, \ldots, c_\varrho \text{ are active} \\ 0 & \text{otherwise} \end{cases} \tag{6}$$

Lemma 3

Let A^k be a vertex operator and let vertex (k) be contained in the cycle $c_\mu \in G_{ab}$. Matrix element $A_{ab}{}^k = \langle S_a \| A^k \mid S_b \rangle$ equals zero if at least one among the cycles $c_1, \ldots, c_{\mu-1}$, $c_{\mu+1}, \ldots, c_\varrho$ is passive. Otherwise, i. e. if cycles $c_1, \ldots, c_{\mu-1}$, and $c_{\mu+1}, \ldots, c_\varrho$ are active, matrix element $A_{ab}{}^k$ equals

$$A_{ab}{}^k = 2^{\rho-n} \begin{cases} 1 & \text{if } (k) \text{ is a source vertex} \\ (-1)^{n_\mu + m_\mu + 1} & \text{if } (k) \text{ is a sink vertex} \end{cases} \tag{7}$$

where $(2\,n_\mu)$ is the number of bonds in a cycle c_μ, while m_μ is the number of oriented bonds in this cycle.

Lemma 4

Matrix element $A_{ab}{}^s = \langle S_a | A^s | S_b \rangle$ of an external operator $A^s = A^{kl}$ vanishes.

Lemma 5

Let $A^s = A^{kl}$ be an internal cis-bridge operator. Matrix element $A_{ab}{}^s = \langle S_a | A^s | S_b \rangle$ equals)

$$A_{ab}{}^s = (-1)^{n_s' + m_s' + 1}\, S_{ab} \tag{8}$$

where $(2\,n_s')$ is the number of bonds in a cycle c_s' formed by a bridge (s) over G_{ab}, while m_s' is the number of oriented bonds in this cycle (see Figure 5c).

Corollary 1

In particular, if A^s is a normal bond operator, relation (8) reduces to

$$A_{ab}{}^s = (-1)^{Sgn(s)}\, S_{ab} \tag{9}$$

where $Sgn(s) = 1$ if bond (s) is oriented, and $Sgn(s) = 0$ otherwise (see Figure 5d).

Lemma 6

Let $A^s = A^{kl}$ be a trans-bridge operator internal to the cycle $c_\mu \in G_{ab}$. Then

a) If the cycle c_μ is active and/or at least one among other $(\varrho - 1)$ cycles contained in G_{ab} is passive, then the matrix element $A_{ab}{}^s = \langle S_a | A^s | S_b \rangle$ vanishes

b) Otherwise, i. e., if the cycle c_μ is passive and at the same time all other $(\varrho - 1)$ cycles are active, matrix element $A_{ab}{}^s$ equals

$$A_{ab}{}^s = 2^{\rho-n} \begin{cases} (-1)^{n_s' + m_s'} & \text{if } (s) \text{ is a source-source bond} \\ (-1)^{n_s' + m_s' + 1} & \text{if } (s) \text{ is a sink-sink-bond} \end{cases} \tag{10}$$

where $(2\,n_s' + 1)$ is the number of bonds in a cycle c_s' formed by a bridge (s) over a cycle c_μ, while m_s' is the number of oriented bonds in this cycle (see Figure 5e).

Concerning Lemmas 2, ..., 6 some remarks are needed:

a) Comment to Lemmas 5 and 6:

Bridge (s) forms two cycles, cycle c_s' and cycle c_s'' over a cycle c_μ (see Figure 5c—f).One easily finds that the expression (8) is symmetrical with respect to the exchange of these two cycles, i. e.

$$A_{ab}{}^s = (-1)^{n_s'' + m_s'' + 1}\, S_{ab} \tag{8a}$$

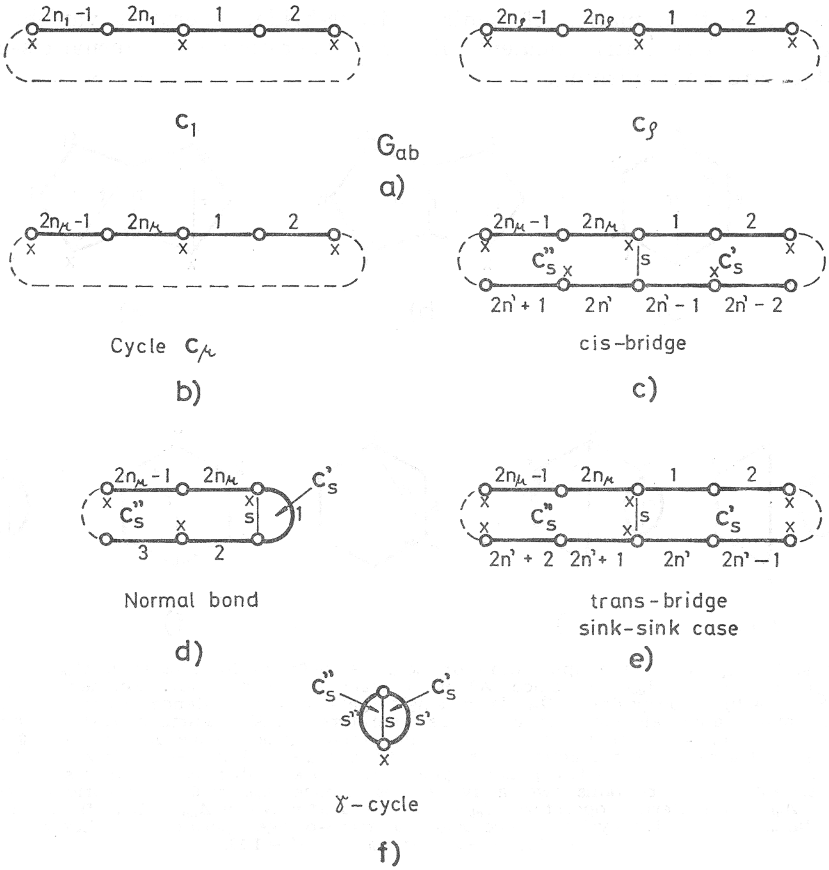


Figure 5. Overlaps and matrix elements of elementary operators A^{kl} between NRS-s. Superposition G_{ab} of n-particle resonance structures S_a and S_b contains ρ cycles $c_1, c_2, \ldots, c_\rho$. Cycle $c_\mu \in G_{ab}$ contains $(2n_\mu)$ bonds and m_μ oriented bonds. Oriented bonds are not explicitly shown. a) Superposition G_{ab}, b) Cycle $c_\mu \in G_{ab}$. See Lemmas 2 and 3, c) Cis-bridge bond. See Lemma 5, d) Normal bond. See Corollary 1, e) Trans-bridge bond. Only sink-sink case is shown. See Lemma 6, f) A γ-cycle

where (n_s'') and (m_s'') refer to a cycle c_s''. The same is true for the expression (10) concerning trans-bridge operators. Cycles c_s' and c_s'' are topologically equivalent, and if the rules for finding matrix elements were to be consistent, this symmetry requirement should be fulfilled.

b) Comment to Corollary 1

This Corollary is unambiguous whenever cycle c_μ is not a γ-cycle. If however c_μ is a γ-cycle, then there are two bonds (s') and (s'') associated with the bond operator A^s (see Figure 5f). In this case one should take $Sgn(s) = 1$ if any of those two bonds is oriented, and $Sgn(s) = 0$ otherwise.

From Lemmas 2—6 it follows that overlap S_{ab} and all matrix elements $A_{ab}{}^{kl}$ vanish if the superposition G_{ab} contains two or more passive cycles. If G_{ab} contains only one passive cycle, then only matrix elements of trans-bridges and vertex operators can be different from zero. If G_{ab} contains no passive cycle, then matrix elements of trans-bridge operators vanish, while overlap as well as matrix elements of vertex operators and internal cis-bridge operators are nonvanishing.

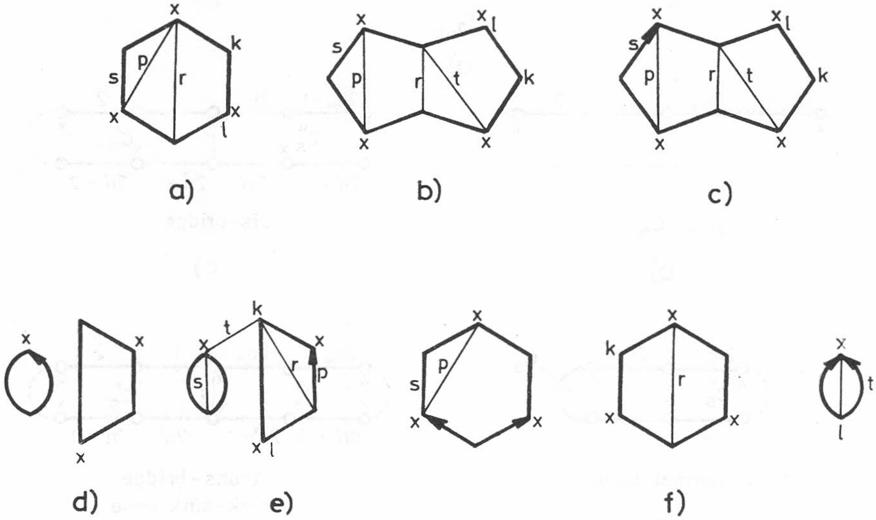


Figure 6. Examples for the application of Lemmas 2—6: a) Superposition G_{ab} is a single active cycle. Hence $A_{ab}^p = 0$, since A^p is a trans-bridge operator. Further $S_{ab} = A_{ab}^s = -A_{ab}^r = 1/4$. b) Superposition G_{ab} is a single passive cycle. Hence $S_{ab} = A_{ab}^s = A_{ab}^t = 0$ (overlap and matrix elements of cis-bridge operators vanish). Further $A_{ab}^r = A_{ab}^p = A_{ab}^k = -A_{ab}^l = 1/8$, c) Superposition G_{ab} is a single active cycle. Hence $A_{ab}^p = A_{ab}^r = 0$ (matrix elements of trans-bridge operators vanish). Further, $S_{ab} = -A_{ab}^s = -A_{ab}^t = A_{ab}^k = A_{ab}^l = 1/8$, d) Superposition G_{ab} contains two passive cycles. Overlap and all matrix elements A_{ab}^{kl} vanish, e) Superposition G_{ab} contains two active cycles. Hence $A_{ab}^r = 0$. (trans-bridge operator). Further $A_{ab}^t = 0$ (external operator), $S_{ab} = A_{ab}^s = -A_{ab}^p = A_{ab}^l = A_{ab}^k = 1/2$, f) Superposition G_{ab} contains three active cycles. Hence $A_{ab}^p = 0$ (trans-bridge operator). Further $S_{ab} = A_{ab}^s = -A_{ab}^r = -A_{ab}^t = A_{ab}^k = A_{ab}^l = 1/16$.

Some examples of the application of Lemmas 2—6 are shown in Figure 6. Using those Lemmas one is now able to find matrix elements of any real one-particle operator between arbitrary NRS-s.

MORT-1 APPROXIMATION

In order to illustrate how one can use the MORT approach, we will now formulate a very simple approximation within the MORT picture. This approximation, to be called the MORT-1 approach, is limited in scope and can be applied primarily to the ground states of conjugated hydrocarbons containing at least one Kekulé structure. In MORT-1 a Hückel Hamiltonian is assumed and only MORT Kekulé structures are retained.[1,2] Moreover, each eigenstate is spin separated, i. e., it is of the form

$$\Psi = \mathbf{A}\, \Phi_\alpha \overline{\Phi}_\beta \tag{11}$$

where **A** is an antisymmetrisation operator, while Φ_α and Φ_β are spin-up and spin-down substates, respectively. Both, Φ_α and Φ_β are linear combinations of MORT Kekulé structrues

$$\Phi_\alpha = \Sigma\, c_a K_a \qquad \Phi_\beta = \Sigma\, d_a K_a \tag{12}$$

Each MORT Kekulé structure K_a is a determinant containing mutually disjunct nonexcited BO-s φ_s

$$\varphi_s = \varphi_{ij} = \frac{1}{\sqrt{2}} (w_i + w_j) \tag{13}$$

where w_i and w_j are atomic orbitals (AO-s). These AO-s should lie adjacent to each other on the graph G of the corresponding conjugated system.

Since the Hamiltonian H is a spin independent one-particle operator, the eigenvalue equation splits into two eigenvalue equations, one for the spin-up substate Φ_α and another for the spin-down substate Φ_β. Since $n_\alpha = n_\beta$, those two eigenvalue equations are identical, and hence

$$\Phi_\alpha = \Phi_\beta = \Phi, \qquad E_\alpha = E_\beta = E \quad \text{and}$$

$$\Psi = \mathbf{A}\, \Phi \overline{\Phi} \tag{11a}$$

One can hence perform all the calculation for the substate Φ alone. The corresponding Hamiltonian is[1,2]

$$H = A - nI \tag{14}$$

where A is an adjacency operator and n is the number of particles in the state Φ. In the second quantisation formalism adjacency operator A can be written in the form

$$A = \sum_{s=(i,j)} (a_i^+ a_j + a_j^+ a_i) = \sum_{s=(i,j)} A^s \tag{15}$$

where the summation $\sum\limits_{s=(i,j)}$ is performed over all bonds (s) which are contained in the graph G of the corresponding conjugated system. This is essentially the Hückel Hamiltonian. Using eqs. (9) and (6) one obtains

$$\langle K_a \,|\, H \,|\, K_a \rangle = 0 \tag{16}$$

i. e., each Kekulé structure K_a has energy zero. Accordingly, if E is the lowest eigenvalue of the eigenvalue equation $H\,\Phi = E\,\mathbf{S}\,\Phi$, the quantity $E_R = 2\,E$ can be interpreted as the resonance energy. This is the measure of the stabilisation of the state Φ through the resonance between different Kekulé structures.

Gründler[5,6] formulated an approach which is to some extent similar to MORT-1. He represents a ground state wave function as a linear combination of the so called »Significant electron structures« (SES). Each SES structure is a closed shell configuration containing AO-s and nonexcited BO-s. Similarly as in MORT-1, the Hückel Hamiltonian is assumed. This approach follows more closely the VB picture, and the SES function Ψ_S is not spin-separated. It can be shown that the MORT-1 function Ψ is in many respects superior to the corresponding SES function Ψ_S.[7,18] For example, the function Ψ has usually lower energy then the corresponding SES function Ψ_S, and hence it should be considered to represent beter the »true« ground state.[18] Gründler however did not develop any efficient method to calculate matrix elements of the Hückel Hamiltonian between different SES structures. In the case of even conjugated systems he derived these matrix elements only in a special case of monocyclic systems and some fused bicyclic systems.[8] It should be noted that SES structures were used prior to Gründler by Malrieu et. al.[9] in the so called PCILO method. Each SES structure is in fact indentical to some PCILO zeroth order wave function.[9]

b) Resonance Between Kekulé Structures

Let us now consider matrix element $H_{ab} = \langle K_a | H | K_b \rangle$:

$$H_{ab} = \langle K_a | A | K_b \rangle - n \langle K_a | K_b \rangle \tag{17}$$

With respect to the superposition $G_{ab} = K_a \oplus K_b$, bond operators A^s contained in the adjacency operator A can be either external or internal. According to Lemma 4 matrix elements of all external operators vanish. Hence in eq. (15) one can retain only internal bond operators. Further, one can partition all internal bond operators into normal operators, proper cis-bridge operators (all cis-bridge operators except normal bond operators) and trans-bridge operators. Accordingly

$$A = A_n + A_c + A_t \tag{18}$$

where A_n contains normal bond operators, A_c contains proper cis-bridge operators, while A_t contains trans-bridge operators. Let now $c_1, c_2, \ldots, c_\varrho$ be the set of all cycles contained in G_{ab}, and let the first n_γ cycles $c_1, c_2, \ldots, c_{n\gamma}$ be γ-cycles. To each γ-cycle (containing two bonds) there correspond one normal bond operator $A^s \in A_n$. On the other hand, to each cycle $c_\mu \in G_{ab}$ containing $(2\, n_\mu)$ bonds $(2\, n_\mu > 2)$ there correspond $(2\, n_\mu)$ normal bond operators $A^s \in A_n$. According to corollary 1, and since K_a and K_b contain no excited BO, matrix element $\langle K_a | A^s | K_b \rangle$ of each normal bond operator A^s equals S_{ab}. Hence

$$\langle K_a | A_n | K_b \rangle = (2n - n_\gamma)\, S_{ab} \tag{19}$$

Consider next cis-bridge operators. According to Lemma 5 each internal cis-bridge operator A^s contributes $\langle K_a | A^s | K_b \rangle = (-1)^{n_s' + 1} S_{ab}$, where $(2\, n_s')$ is the number of bonds in a cycle c_s' formed by a bridge (s) over G_{ab}. Hence

$$\langle K_a | A_c | K_b \rangle = \sum_{\text{cis}} (-1)^{n_s' + 1} S_{ab} \tag{20}$$

where the summation is performed over all proper cis-bridges (s) which are internal to G_{ab}. As above, $(2\, n_s')$ is the number of bonds in the cycle c_s' formed by a cis-bridge (s) over G_{ab}.

Consider now trans-bridge operators. According to Lemma 6 the trans-bridge contribution can be different from zero only if the superposition G_{ab} contains exactly one passive cycle. Let this be a cycle $c_\mu \in G_{ab}$. In this case only trans-bridges over c_μ contribute to $\langle K_a | A_t | K_b \rangle$. Using eq. (10) one finds

$$\langle K_a | A_t | K_b \rangle = 2^{p-n} \left[\Sigma^0 (-1)^{n_s'} - \Sigma^* (-1)^{n_s'} \right] \tag{21}$$

where the summation Σ^0 is performed over all trans-bridges (s) connecting two source vertices on c_μ, while the summation Σ^* is performed over all trans-bridges (s) connecting two sink vertices on c_μ. In both cases $(2\, n_s' + 1)$ is the number of bonds in the cycle c_s' formed by a trans-bridge (s) over the passive cycle c_μ. Combining the above expressions one finds

$$H_{ab} = \langle K_a | H | K_b \rangle = f_{ab} \cdot S_{ab} + \langle K_a | A_t | K_b \rangle \tag{22}$$

where

$$f_{ab} = [n - n_\gamma + \sum_{\text{cis}} (-1)^{n_s'+1}] \tag{22}$$

The trans-bridge contribution vanishes if the overlap S_{ab} is different from zero, i. e., if the superposition G_{ab} contains no passive cycle. Hence, either only normal and cis-bridges, or only trans-bridges contribute to the matrix element H_{ab}. In particular, if $K_a = K_b$, the superposition G_{aa} contains only γ-cycles, there are no cis- and trans-bridges, and one obtains $H_{aa} = 0$, in accord with eq. (16).

The quantity f_{ab} can be vritten in a slightly modified form:

$$f_{ab} = \sum_\mu{}' f_{ab}{}^\mu = \sum_\mu{}' [n_\mu + \sum_{\text{cis}}^\mu (-1)^{n_s'+1}] \tag{23}$$

where the summation $\sum'_\mu$ is performed over all cycles $c_\mu \in G_{ab}$, except γ-cycles. The summation $\sum^\mu_{\text{cis}}$ is performed over all proper cis-bridges (s) internal to the cycle $c_\mu \in G_{ab}$, ($2\,n_\mu$) is the number of bonds in c_μ, and ($2\,n_s'$) is the number of bonds in either of the two cycles c_s' and c_s'' formed by the cis-bridge (s) over a cycle $c_\mu \in G_{ab}$. The quantity f_{ab} should be considered only if G_{ab} contains no passive cycle. If namely G_{ab} contains some passive cycle, then $S_{ab} = 0$, and hence in eq. (22) $f_{ab} \cdot S_{ab} = 0$. Note now that in no cycle $c_\mu \in G_{ab}$ the number of cis-bridges can exceed n_μ. This follows from the fact that no two cis-bridges can cross each other if the graph G associated with the adjacency operator A is planar (see Figure 7). Hence for each cycle c_μ

$$f_{ab}{}^\mu = n_\mu + \sum_{\text{cis}}{}' (-1)^{n_s'+1} > 0$$

i. e.,

$$f_{ab} > 0 \tag{24}$$

whenever the superposition G_{ab} contains at least one cycle c_μ which is not a γ-cycle. We will use this intequality later.

SOME CONSEQUENCES OF THE MORT-1 APPROXIMATION

Consider now a conjugated system containing only two Kekulé structures, K_a and K_b. Two cases can be distinguished, either $H_{ab} = 0$ or $H_{ab} \neq 0$. From (22) and (24) it follows that $H_{ab} = 0$ implies $S_{ab} = 0$. This means that in this case there is no extra stabilisation due to the resonance between the two Kekulé structures. If however $H_{ab} > 0$, then the state $\Phi = K_a + K_b$ is the lowest (in negative β-units) eigenstate of the eigenvalue equation $H\,\Phi = E\,\mathbf{S}\,\Phi$ with the eigenvalue

$$E_{ab} = \langle \Phi \mid H \mid \Phi \rangle \,/\, \langle \Phi \mid \Phi \rangle = H_{ab}/(1 + S_{ab}) \tag{25a}$$

Similarily, if $H_{ab} < 0$, the lowest eigenstate is the state $\Phi = K_a - K_b$ with the eigenvalue

$$E_{ab} = - H_{ab}/(1 - S_{ab}) \tag{25b}$$

The quantity E_{ab} is the measure of the stabilisation through resonance between the two Kekulé structures K_a and K_b. If the conjugated system contains more than two Kekulé structures, we will still retain this quantity as a rough

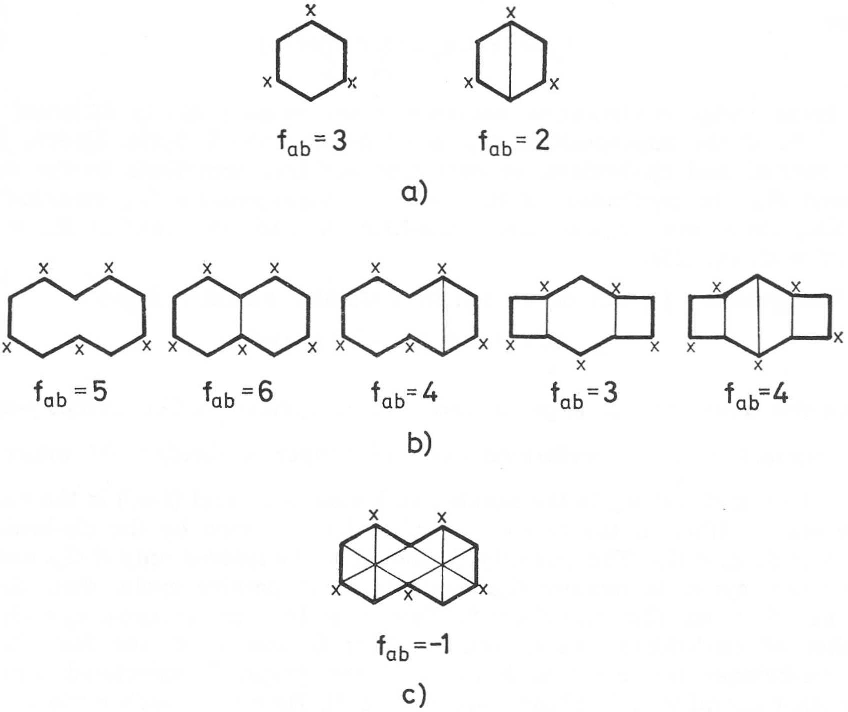


Figure 7. In a planar conjugated system $f_{ab} \geq 0$ for any two Kekulé structures K_a and K_b. $f_{ab} = 0$ if and only if G_{ab} contains only γ-cycles. Only the contribution from active cycles should be considered. a) Case $n = 3$, b) Some examples for the case $n = 5$, c) In a nonplanar conjugated system one can have $f_{ab} < 0$. Such cases are however highly artificial.

measure of the contribution to the stabilisation due to the interaction between structures K_a and K_b.

a) Alternant Hydrocarbons

Let us first consider the case of alternant hydrocarbons. By definition, the superposition of Kekulé structures K_a and K_b is a graph G_{ab} containing only those bonds which are already present in the graph G of the conjugated system. Hence in the case of alternant hydrocarbons the partition on sink and source vertices can be made to coincide with the partition on starred and nonstarred vertices. Since in the alternant system there are no bonds connecting either two starred or two nonstarred vertices, the adjacency operator A contains no trans-bridge operator, and hence

$$H_{ab} = f_{ab} \cdot S_{ab} = [n - n_{\gamma} + \sum_{\text{cis}} (-1)^{n_s' + 1}]\, S_{ab} \tag{26a}$$

and since $f_{ab} > 0$

$$E_{ab} = f_{ab} \cdot S_{ab}/(1 + S_{ab}) \tag{26b}$$

Eq. (26a) gives a general solution for a matrix element of the operator $H = A - nI$ between arbitrary MORT Kekulé structures K_a and K_b in the case of an alternant system. Eq. (26b) gives the corresponding resonance interaction between the two Kekulé structures. In particular, relations (26) can be applied to annulenes molecules. In this case there are only two Kekulé structures and no cis-bridges. One obtains[2]

$$H_{ab} = n\,S_{ab} = n\,[1 + (-1)^{n+1}]/\,2^n$$
$$E_R = 2\,E_{ab} = 2n\,[1 + (-1)^{n+1}]\,/\,[2^n + 1 + (-1)^{n+1}] \tag{27}$$

Eqs. (27) express the Hückel $(4m+2)$-rule for annulenes: If n is even, i. e. in the case of $4m$-type annulenes, $E_{ab} = 0$ and there is no resonance interaction between the two Kekulé structures. If, however, n is odd, i. e. in the case of $(4m+2)$-type annulenes, then $E_{ab} > 0$ and there is a stabilisation due to the resonance between the two Kekulé structures. This resonance stabilisation decreases with the dimension of the annulene ring.

Consider now a general alternant case. According to the eq. (26a) matrix element H_{ab} vanishes if overlap S_{ab} vanishes. From (24) the inverse follows: overlap S_{ab} vanishes if matrix element H_{ab} vanishes (unless $K_a = K_b$). According to Lemma 2 a necessary and sufficient condition for the overlap S_{ab} to vanish is that the superposition G_{ab} contains at least one passive cycle. Since K_a and K_b are Kekulé structures which by definition contain no excited BO, all passive cycles are $4m$-type cycles. Hence

Lemma 7 (alternant case)

A necessary and sufficient condition for both overlap S_{ab} and matrix element H_{ab} to vanish, is that the superposition G_{ab} contains at least one $4m$-type cycle.

The vanishing of both, the overlap and matrix element of the Hamiltonian H between the two Kekulé structures implies that there is no resonance stabilisation between those two structures. Hence

Corollary 2 (alternant case)

Resonance between Kekulé structures K_a and K_b contributes to the stabilisation if and only if the superposition G_{ab} contains no $4m$-type cycle.

A trivial example is the case of annulenes where the superposition between the two Kekulé structures is either a $4m$-type or a $(4m+2)$-type cycle. Some other examples are shown in Figure 8. Thus a naphthalene molecule (Figure 8a) has three Kekulé structures. All the superpostions G_{ab} $(a, b = 1,2,3)$ contain only $(4m+2)$-type cycles. There is a resonance stabilisation between any two of those structures, and the ground state Φ should contain all those structures. In the case of benzocyclobutadiene molecule one can also draw three Kekulé structures (Figure 8b). However, in this case superpositions G_{13} and G_{23} contain a $4m$-type cycle. Hence the structure K_3 interacts neither with the structure K_1 nor with the structure K_2. It follows that the ground state Φ contains only Kekulé structures K_1 and K_2. Due to eq. (16) we have $\Phi = K_1 + K_2$. This conclusion is different from the one reached in the VB approach where all three structures contribute to the ground state. Resonance theory hence predicts benzocyclobutadiene to be stable, contrary to experience.[10] In the MORT-1 approach the destabilisation is due to the lack of resonance between structure K_3 and the other two structures.

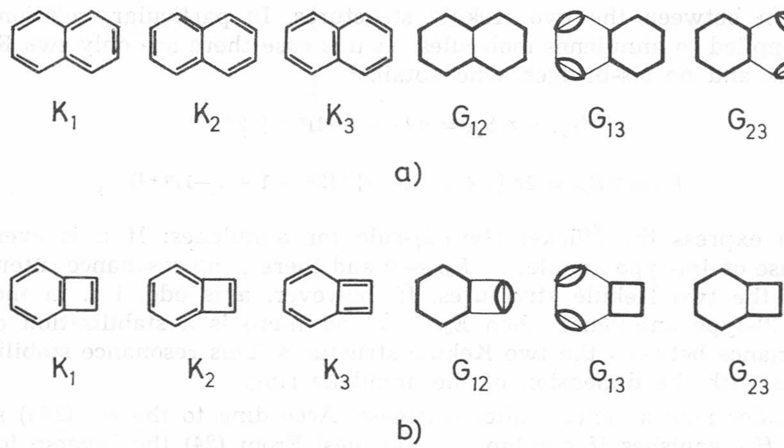


Figure 8. Illustration of Lemma 6, a) Naphthalene Kekulé structures, b) Benzocyclobutadiene Kekulé structures.

Lemma 7 and Corollary 2 allow us to decide whether the two Kekulé structures do interact with each other or not. If, however, there is an interaction between the two structures, then using relations (26) one can estimate how strong it is. One finds

$$H_{ab} = f_{ab} \cdot S_{ab} = [n - n_\gamma + \sum_{\text{cis}} (-1)^{n_s'+1}]\, 2^{\rho - n}$$

$$E_{ab} = f_{ab}/(1 + 2^{n-\rho}) \qquad (28)$$

Matrix element H_{ab} is proportional to the overlap $S_{ab} = 2^{\varrho - n}$, the factor of proportionality being f_{ab}. Similarly, resonance stabilisation E_{ab} is proportional to $S_{ab}/(1 + S_{ab}) = 1/(1 + 2^{n-\varrho})$, the factor of proportionality being again f_{ab}. There are a few interesting consequences of eq. (28):

1. Neither matrix element H_{ab} nor resonance stabilisation E_{ab} depends on γ-cycles. This follows from the fact that the summation $\sum_{\text{cis}}$ does not include γ-cycles, and that also $(n - \varrho)$ and $(n - n_\gamma)$ does not change if γ-cycles are excluded. Namely, exclusion of each γ-cycle decreases ϱ and n_γ by one, but it also decreases n by one, since each γ-cycle contributes 2 bonds to G_{ab}. Hence $(n - \varrho) = (n' - \varrho')$ and $(n - n_\gamma) = n'$, where ϱ' is the number of all cycles excluding γ-cycles, and $(2\,n')$ is the number of all bonds in G_{ab} excluding bonds contained in γ-cycles. It follows that $f_{ab} = [n' + \sum_{\text{cis}} (-1)^{n_s'+1}]$ and $S_{ab} = 2^{\varrho' - n'}$. For example, the resonance stabilisation between naphthalene structures K_1 and K_3 (Figure 8a) is the same as the resonance stabilisation between the two benzene Kekulé structures. Both, matrix elements of the Hamiltonian H and overlap are the same. One can disregard γ-cycles, i. e., this part of the two Kekulé structures in which they coincide.

2. Matrix element H_{ab} and resonance stabilisation E_{ab} rapidly decrease with the decrease of ϱ, i. e., the number of cycles in G_{ab}. This follows from the proportionality of H_{ab} and E_{ab} with $S_{ab} = 2^{\varrho - n}$ and $S_{ab}/(1 + S_{ab})$, respectively. Moreover, $S_{ab} \leq 1/4$, where $S_{ab} = 1/4$ if and only if G_{ab} contains one

benzene-like cycle, all other cycles being γ-cycles. Furthermore since $S_{ab} \leq 1/4$ we have $E_{ab} \approx H_{ab}$, and this is increasingly true with the decrease of ϱ. Thus in the case of the naphthalene molecule (Figure 8a) a resonance stabilisation between structures K_1 and K_3 is the same as a resonance stabilisation between structures K_2 and K_3 ($H_{13} = H_{23} = 3/4$, $E_{13} = E_{23} = 3/5$), and it is larger then the resonance stabilisation between structures K_1 and K_2 ($H_{12} = 3/8$, $E_{12} = 3/9$). By symmetry, structures K_1 and K_2 are suggested to be represented in the ground state Φ with the same weight. By the above comparison of matrix elements and resonance stabilisations, structure K_3 is suggested to be represented in the ground state Φ with a greater weight than the other two structures. Some other examples are shown in Figure 9.

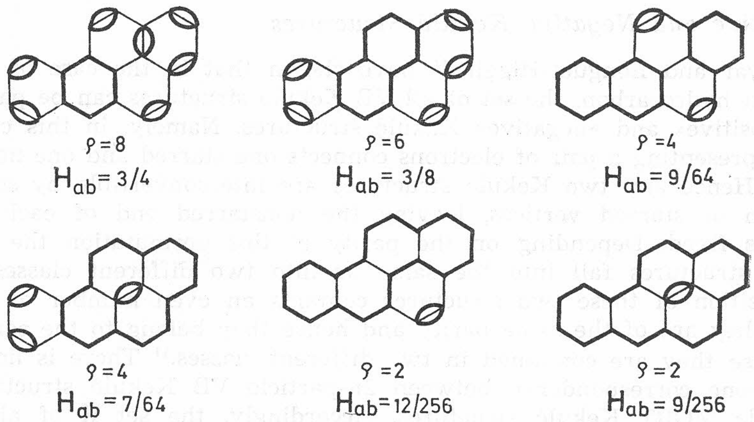


Figure 9. Decrease of the matrix element H_{ab} and resonance stabilisation E_{ab} with the decrease of the number of cycles contained in the superposition G_{ab}.

3. Each normal bond, excluding normal bonds contained in γ-cycles, contributes 1/2 to f_{ab}. Further, each proper cis-bridge bond contributes ± 1 to f_{ab}. If n_s' is odd, then $(-1)^{n_s'+1} = 1$, and the corresponding bond (s) contributes 1 to f_{ab} thus enhancing matrix element H_{ab} and the resonance stabilisation E_{ab}. If, however, n_s' is even, then $(-1)^{n_s'+1} = -1$, and the bridge (s) contributes (-1) to f_{ab} thus lowering the value of the matrix element H_{ab} and the resonance stabilisation E_{ab}. Since however ($2\,n_s'$) is the number of bonds in the cycle c_s' formed by a bridge (s) over the superposition G_{ab}, we have.

Corollary 3

Let the superposition G_{ab} contain no passive cycle. Then each internal cis-bridge contributes to a stabilisation if it forms a $(4m+2)$-type cycle over G_{ab}, and to a destabilisation if it forms a $4m$-type cycle over G_{ab}.

Here we again see how $(4m+2)$-type cycles lead to a stabilisation, while $4m$-type cycles lead to destabilisation. As shown above, if G_{ab} contains at least one $4m$-type cycle, then there is no resonance stabilisation between the two structures. But even when G_{ab} contains only $(4m+2)$-type cycles and hence $E_{ab} > 0$, each cis-brige (s) internal to G_{ab} can further stabilise or destabilise the resonance, depending on the type of cycle formed by this bridge on G_{ab}. Some examples are shown in Figure 10.

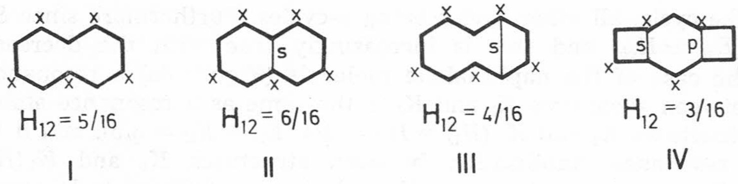


Figure 10. Effect of internal cis-bridges on stabilisation and destabilisation. Matrix element H_{12} between the two 10-annulene Kekule structures equals 5/16 (I). Matrix element between the corresponding naphthalene structures is larger ($H_{12} = 6/16$) due to a cis-bridge (*s*) forming a $(4m + 2)$-type cycle over G_{ab} (II). In the case of the compound (III) cis-bridge (*s*) forms a $4m$-type cycle, and hence H_{12} decreases ($H_{12} = 4/16$). Matrix element H_{12} further decreases if there is another cis-bridge (*p*) forming a $4m$-type cycle (compound (IV)).

b) Positive and Negative Kekulé Structures

Dewar and Longuet-Higgins[11] have shown that in the case of an even alternant hydrocarbon, the set of all VB Kekulé structures can be partitioned into »positive« and »negative« Kekulé structures. Namely, in this case each bond representing a pair of electrons connects one starred and one nonstarred vertex. Hence any two Kekulé structures are interconvertible by some permutation of starred vertices, leaving the nonstarred end of each pair of electrons fixed. Depending on the parity of this permutation the two VB Kekulé structures fall into the same or into two different classes. If the superposition of these two structures contains an even number of $4m$-type cycles, they are of the same parity and hence they belong to the same class. Otherwise they are contained in two different classes.[11] There is however a one- to-one correspondence between $2n$-particle VB Kekulé structures and n-particle MORT Kekulé structures. Accordingly, the set $\mathbf{K}$ of all MORT Kekulé structures can be partitioned into two subsets, $\mathbf{K}^{+}$ and $\mathbf{K}^{-}$. Since the superposition G_{ab} between a structure $K_a \in \mathbf{K}^{+}$ and a structure $K_b \in \mathbf{K}^{-}$ contains and odd number of $4m$-type cycles, and from Lemma 7 it follows

Corollary 4

Let $K_a \in \mathbf{K}^{+}$ and $K_b \in \mathbf{K}^{-}$. Then

$$\langle K_a \,|\, K_b \rangle = 0 \quad \text{and} \quad \langle K_a \,|\, H \,|\, K_b \rangle = 0 \tag{29}$$

There is no interaction between the two sets, and the secular equation block-diagonalises them. Accordingly, the ground state Φ is a linear combination of Kekulé structures which are either all contained in the set $\mathbf{K}^{+}$ or all contained in the set $\mathbf{K}^{-}$.

In the resonance theory the ground state is considered to be a linear combination of all Kekulé structures. Each Kekulé structure is assumed to contribute equally to the ground state, and the resonance energy depends only on the number N of Kekulé structures. The rationale behind this picture is that in the VB approach all Kekulé structures interact with each other. In the MORT picture the set of all Kekulé structures splits into two mutually noninteracting subsets. This is the fundamental difference between the two approaches. The early apparent success of the resonance theory[12] rested on the fact that only benzenoid hydrocarbons were considered. These hydrocarbons contain no $4m$-type rings, and hence all the Kekulé structures are necessarily of the same parity. This fact was recognised by various authors.[11,13,14] Dewar and Longuet-Higgins have shown that for even alternant hydrocarbons the following relation holds[11]

$$\det A = (-1)^n (N^+ - N^-) \tag{30}$$

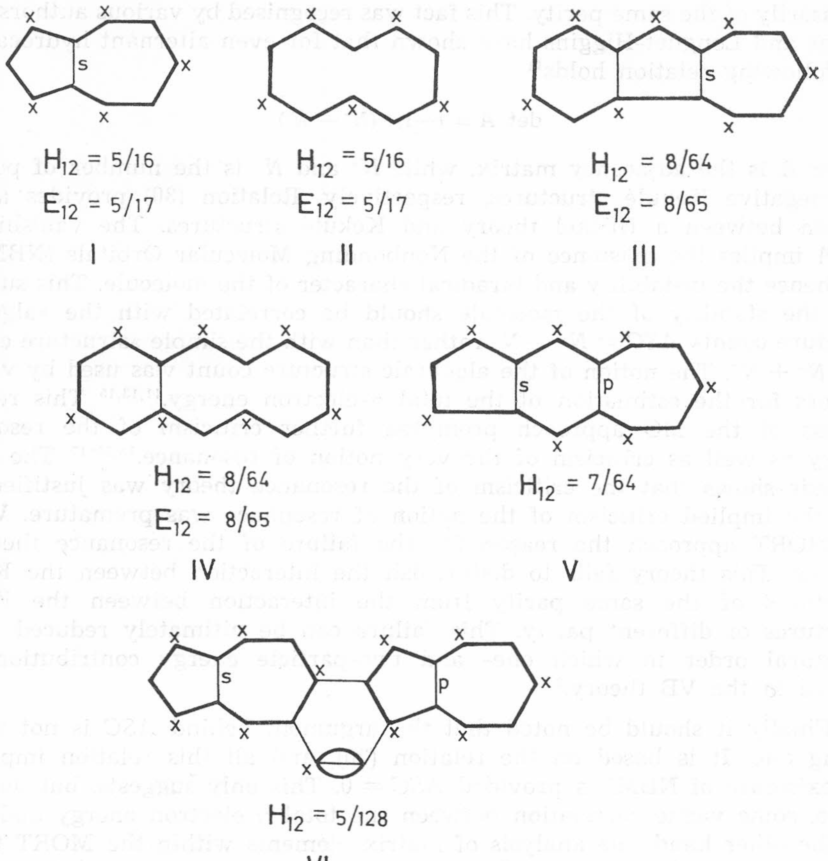
where A is the adjacency matrix, while N^+ and N^- is the number of positive and negative Kekulé structures, respectively. Relation (30) provides a connection between a Hückel theory and Kekulé structures. The vanishing of det A implies the existence of the Nonbonding Molecular Orbitals (NBMO-s), and hence the instability and biradical character of the molecule. This suggests that the stability of the molecule should be correlated with the »algebraic structure count« $ASC = N^+ - N^-$ rather than with the simple »structure cound« $N = N^+ + N^-$. The notion of the algebraic structure count was used by various authors for the estimation of the total π-electron energy.[11,13,15] This relative success of the MO approach prompted further criticism of the resonance theory as well as criticism of the very notion of resonance.[13,15–17] The above analysis shows that the criticism of the resonance theory was justified, but that the implied criticism of the notion of resonance was premature. Within the MORT approach the reason for the failure of the resonance theory is obvious. This theory fails to distinguish the interaction between the Kekulé structures of the same parity from the interaction between the Kekulé structures of different parity. This failure can be ultimately reduced to the unnatural order in which one- and two-particle energy contributions are treated in the VB theory.[2]

Finally it should be noted that the argument behind ASC is not a very strong one. It is based on the relation (30), and all this relation implies is the existence of NBMO-s provided $ASC = 0$. This only suggests, but does not prove, some vague correlation between the total π-electron energy and ASC. On the other hand, the analysis of matrix elements within the MORT theory presents a much more satisfactory approach. A posteriory, this analysis justifies the relative success of the ASC concept. Moreover, it restores the notion of the resonance showing that not this notion, but only the VB based resonance theory is in error.

The above splitting of the set $\mathbf{K}$ of all the MORT Kekulé structures into two mutually noninteracting subsets was derived here within the MORT-1 approximation. It can be however shown that this is only a special case of a splitting of a complete set of linearly independent NRS-s into two mutually noninteracting subsets.[18]

c) Nonalternant Hydrocarbons

Most results obtained for the case of alternant hydrocarbons remain valid in the nonalternant case. All the differences result from the trans-bridge contribution (21) which in the nonalternant case may be nonzero. If the superposition G_{ab} of the two Kekulé structures contains no passive cycle, this contribution is zero, and hence overlap S_{ab} and matrix element H_{ab} are the same as in the corresponding alternant case. Eqs. (26) and (28) hence remain valid. Some examples are shown in Figure 11. Thus the matrix element of the Hamiltonian H between the two Kekulé structures of azulene molecule



$H_{12} = 5/16$ $E_{12} = 5/17$ I

$H_{12} = 5/16$ $E_{12} = 5/17$ II

$H_{12} = 8/64$ $E_{12} = 8/65$ III

$H_{12} = 8/64$ $E_{12} = 8/65$ IV

$H_{12} = 7/64$ V

$H_{12} = 5/128$ VI

Figure 11. The superposition G_{ab} contains no passive cycle. Matrix element H_{ab} and resonance stabilisation E_{ab} does not depend on trans-bridges (*s*) and (*p*). Each normal bond contributes $S_{ab}/2$ to H_{ab}. Each cis- bridge bond contributes $(-1)^{n_s'+1}S_{ab}$ to H_{ab}. Overlap S_{ab} equals 2^{p-n}

(**I**) is the same as the corresponding matrix element for 10-annulene (**II**) Kekulé structures. Trans-bridge (*s*) in azulene does not contribute to H_{ab}. If however the superposition G_{ab} contains a passive cycle c_μ then

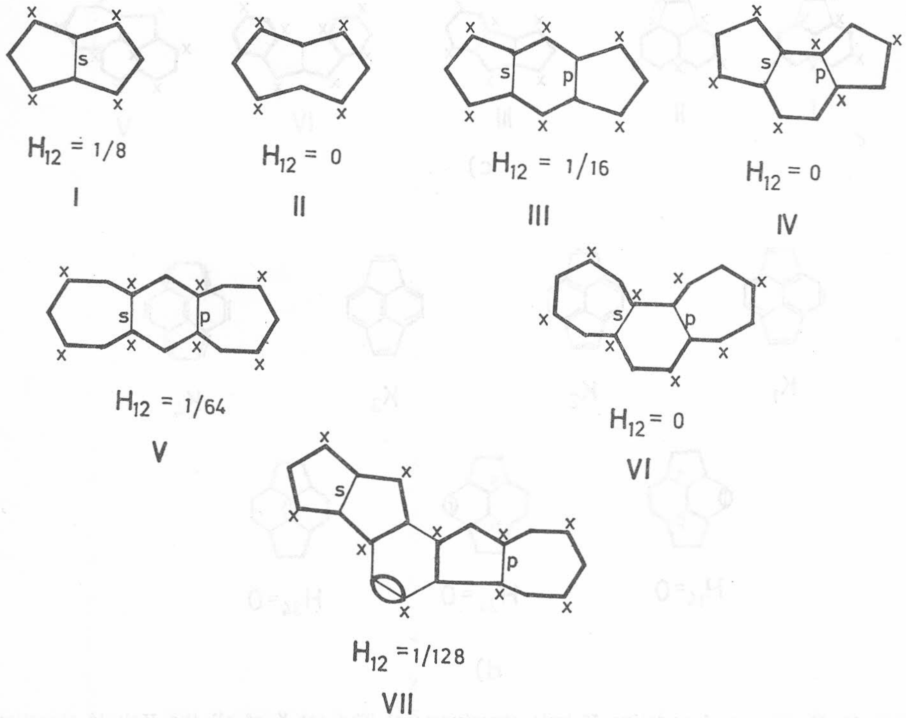
$$S_{ab} = 0$$

and

$$H_{ab} = \langle K_a \mid A_t \mid K_b \rangle = 2^{p-n} [\Sigma^0 (-1)^{n_s'} - \Sigma^* (-1)^{n_s'}] \tag{31}$$

where the summations Σ^0 and Σ^* refer to trans-bridges contained in the passive cycle. In this case $E_{ab} = |H_{ab}|$ and matrix element H_{ab} depends only on trans- bridges contained in c_μ. Some examples are shown in Figure 12. In the case of the pentalene molecule (**I**) the superposition G_{12} contains one passive cycle, and from eq. (31) it follows that $H_{12} = \langle K_1 \mid A_t \mid K_2 \rangle = 1/8$. The central nonalternant bond in pentalene is trans-bridge with respect to the superposition G_{12}, and the interaction between these two structures is due only to this bond. In the planar cyclooctatetraene (**II**), which is the corresponding alternant molecule, there is no interaction between the two structures. All other things being equal, planar cyclooctatetraene is predicted to be less stable than pentalene. From the two isomers of indacene, *s*-indacene (**III**) is predicted to be sligthy more stable than *as*-indacene (**IV**). Resonance stabilisation of *s*-indacene however does not amount to very much, $E_R = 2\,E_{12} = 1/8$ in negative β units. This isomer was synthesized, but it was found to be very reactive.[19] Similarly, compound (**V**) is predicted to be slightly more stable than compound (**VI**).

In an arbitrary nonalternant case one generally cannot partition the set $\mathbb{K}$ of all Kekulé structures into »positive« and »negative« subsets $\mathbb{K}^+$ and $\mathbb{K}^-$ (see Figure 13a). However, if the deletion of all essentially single bonds leads to some alternant graph G', then this partition is possible. In this case the graph G' can serve to partition the set of all vertices into sink and source subsets, and moreover this partition may coincide with the partition on starred and nonstarred vertices of a graph G'. Each nonalternant system with such a property will be called »semialternant«. For example, all nonalternant compounds in Figure 12 are semialternant. Some other examples of semialternant compounds are given in Figure 13c. In addition, even when the compound



$H_{12} = 1/8$
I

$H_{12} = 0$
II

$H_{12} = 1/16$
III

$H_{12} = 0$
IV

$H_{12} = 1/64$
V

$H_{12} = 0$
VI

$H_{12} = 1/128$
VII

Figure 12. The superposition G_{ab} contains one passive cycle. Matrix element H_{ab} depends only on the trans-bridges contained in this cycle. Trans-bridges (*s*) in pentalene (I) contributes 1/8 to H_{12}. In the 8-annulene (II) there is no trans-bridge, and hence $H_{12} = 0$. *s*-indacene (III) contains two trans-bridges, each contributing 1/32 to H_{12}. *as*-indacene (IV) contains also two trans-bridges, however in this case bridge (*s*) contributes 1/32 while bridge (*p*) contributes (—1/32) to H_{12}. Similarly for the two isomeric compounds (V) and (VI). Example (VII) illustrates the fact that only trans-bridges contained in the passive cycle contribute to H_{12}. Trans-bridge (*s*) contained in the passive cycle contributes 1/128 to H_{ab}, while trans-bridge (*p*) contained in the active cycle does not contribute to H_{ab}.

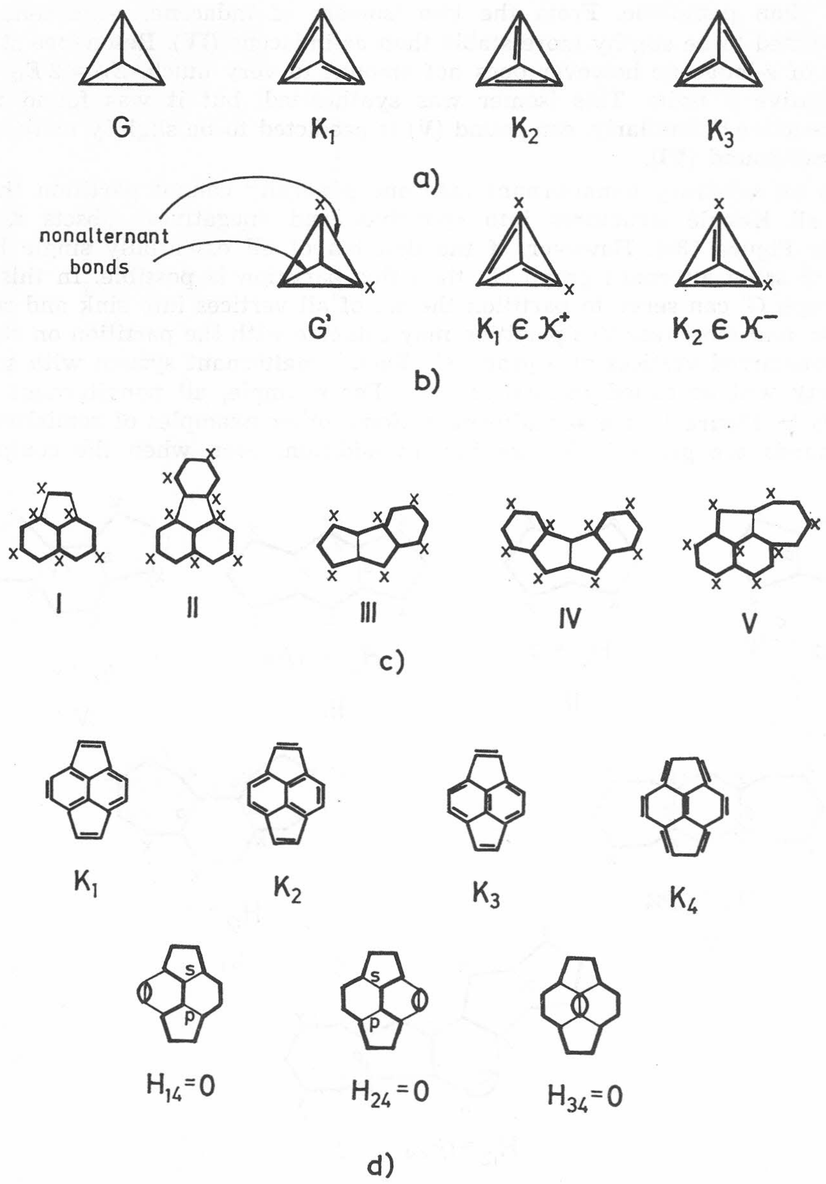


Figure 13. Positive and negative Kekulé structures: a) The set **K** of all the Kekulé structures corresponding to the graph *G* contains three Kekulé structures, and it can not be partitioned into positive and negative structures, b) Graph *G* can be visualised as being obtained from alternant subgraph *G'* by introduction of nonalternant bonds. The set **K'** of all the Kekulé structures corresponding to the subgraph *G'* can be partitioned into positive and negative subsets. The choice of the set **K'** depends on the alternant subgraph *G'* of the graph *G*, and hence it is not unique, c) Some semialternant compounds. Essentially single bonds are depicted with light lines, d) Kekulé structures of the pyracyclene molecule.

is not semialternant, it is still sometimes possible to partition the set $\mathbf{K}$ on subsets $\mathbf{K}^+$ and $\mathbf{K}^-$ (see Figure 13d). As shown above, in an alternant case there is no interaction between subsets $\mathbf{K}^+$ and $\mathbf{K}^-$. In the nonalternant case the interaction between these two subsets is accomplished through the trans-bridges. These bridges in a semialternant compound coincide with nonalternant bonds. Moreover, matrix element H_{ab} between Kekulé structures $K_a \in \mathbf{K}^+$ and $K_b \in \mathbf{K}^-$ depends only on those trans-bridges which are contained in the passive cycle $c_\mu \in G_{ab}$. The interaction (31) between structures of different parity is usually on an order of magnitude smaller than the interaction (28) between structures of the same parity, provided the corresponding superpositions G_{ab} in respective cases contain the same or a comparable number of cycles (and, of course, the same n). This follows from the fact that $f_{ab} \gg 1$. A pyracyclene molecule is an interesting example (Figure 13d). There are four Kekulé structures of pyracyclene, and it is not a semialternant compound. However, using the Dewar and Longuet-Higgins method one finds that these structures can be consistently partitioned into »positive« and »negative« structures. One obtains $K_1, K_2, K_3 \in \mathbf{K}^+$ and $K_4 \in \mathbf{K}^-$. Each of the superpositions G_{14}, G_{24} and G_{34} contains one passive cycle. With respect to the superposition G_{34} all trans-bridges are external, and hence $H_{34} = 0$. In the case of the superposition G_{14} trans-bridges (s) and (p) are internal. However, bridges (s) and (p) contribute respectively —1/32 and 1/32 to H_{14}. These contribution cancel out and hence $H_{14} = 0$. Analogously $H_{24} = 0$. Hence structure K_4 does not interact with any of the other three structures. The ground state is thus a linear combination of only the first three structures, and it is destabilised through the lack of resonance with structure K_4. The pyracyclene molecule is indeed found to be very unstable, and it could not be isolated from the solution.[20] The interaction between positive and negative structures in this example vanishes due to the cancellation of the contributions from different trans-bridges. Note however that the interaction per trans-bridge is 1/32. This should be compared with matrix elements $H_{12} = 3/8$, $H_{13} = 3/4$ and $H_{23} = 3/4$ representing interactions between Kekulé structures of the same parity.

Note finally that even when the partition of the set $\mathbf{K}$ into subsets $\mathbf{K}^+$ and $\mathbf{K}^-$ is not possible, one can still use the above approach. One can always obtain the system in question from some alternant subsystem by the introduction of nonalternant bonds. This alternant subsystem can then be used to partition the set of all vertices into sink and source subsets. This partition defines the set $\mathbf{K}'$ of MORT Kekulé structures, as well as the two subsets $\mathbf{K}^+$ and $\mathbf{K}^-$. In this case, however, the set $\mathbf{K}'$ does not contain all Kekulé structures, and it is not unique (see Figure 13b).

d) Generalised Hückel Rule

The results obtained so far can be looked upon from another point of view. Instead of concentrating on the resonance between the two Kekulé structures to see how strongly they interact, one can concentrate on a particular cycle $c_\mu \subseteq G$ which is a subgraph of the molecular graph G. Each such cycle is either contained in some superposition G_{ab} of Kekulé structures, or it is not contained in such a superposition. If there are Kekulé structures K_a and K_b such that the cycle $c_\mu \subseteq G$ is contained in G_{ab} then we will say that this cycle is »conjugated«.[22] Now, if a particular cycle $c_\mu \subset G$ is contained in some superposition G_{ab}, and if in addition matrix element $\langle K_a | \underline{H} | K_b \rangle$ is nonvanishing, then this cycle contributes to the resonance. From this observation and the results obtained so far one can formulate the following.

Lemma 8

1. Only conjugated cycles can contribute to a resonance. In particular, no odd cycle $c_\mu \subset G$ contributes to a resonance.

2. Each conjugated $(4m+2)$-type cycle contributes to a resonance. In addition.

a) Each proper cis-bridge (s) forming a $(4m+2)$-type cycle c_s' over c_μ contributes to the further stabilisation of a conjugated cycles c_μ.

b) Each proper cis-bridge (s) forming a $4m$-type cycle c_s' over c_μ contributes to the destabilisation of a conjugated cycle c_μ.

3. A $4m$-type conjugated cycle $c_\mu \subset G$ can contribute to resonance only if there is a trans-bridge (s) crossing this cycle. This contribution is much smaller than a contribution of a conjugated $(4m+2)$-type cycle of comparable size.

The above Lemma is recognised as the generalisation of the well known Hückel $(4m+2)$-rule. This rule was originally formulated for annulenes.[21] Attempts to generalise Hückel's rule in terms of the number of electrons were not successful. Thus pyrene is aromatic, though it contains $4x4 = 16$ electrons.[17] Applying the first-order perturbation MO (PMO) approximation Dewar derived the so called »extended Hückel rule«.[16,17] He reached the conclusion that in an even hydrocarbon odd rings are nonaromatic, $(4m+2)$-type rings are aromatic, while $4m$-type rings are antiaromatic. Using graph theory Gutman and Trinajstić concluded that every $(4m+2)$-type cycle has a positive contribution to the total π-electron energy E_π, while every $4m$-type cycle has a negative contribution to E_π.[26] Using SES structures Gründler derived Hückel $(4m+2)$-rule for monocyclic systems[5] and for some fused bicyclic systems.[5b,7,8] His conclusions are however essentially on the level of the original Hückel rule. Conclusions reached by PMO and graph theory are much more general, and in this respect they parallel Lemma 8. They are however not identical with this Lemma. In particular, a »fine structure« implied by points 2a, 2b and 3 is not recognised.

It should be appreciated that by using eqs. (28) and (31), a generalised Hückel rule, as expressed by Lemma 8, can be unambiguously formulated in a quantitative manner. Moreover, this rule can be shown to be valid with minor changes for much more sophisticated Hamiltonians and spaces.[18]

CONCLUSION

This paper deals with the further development of the Molecular Orbital Resonance Theory (MORT). In the first section o MORT resonance structure is defined as a determinant containing mutually disjunct bond orbitals (Definition 1). In particular, »normal« MORT resonance structures (NRS's) are defined. In the second section a full set of rules is given for the evalution of overlap and matrix elements of real one-particle operators between NRS-s. In the third section a simple MORT model called MORT-1 approximation is formulated. In this approximation only MORT Kekulé structures are retained and a Hückel Hamiltonian is assumed. Finally, in the fourth section some consequences of the MORT-1 approximation are derived. In particular, the following results are obtained:

1. If the superposition G_{ab} of Kekulé structures K_a and K_b contains no $4m$-type cycle, then matrix element H_{ab} of the Hamiltonian operator H between these structures equals $H_{ab} = f_{ab} \cdot S_{ab}$. Overlap S_{ab} equals $2^{\varrho - n}$ where ϱ is the number of cycles in the superposition G_{ab}, while n is the number of particles in a structure K_a (or K_b). The quantity f_{ab} contains only contributions from normal bonds and internal cis-bridge bonds. γ-cycles do not contribute to f_{ab}. Each normal bond (s) contained in some cycle $c_\mu \in G_{ab}$ which is not a γ-cycle, contributes $1/2$ to f_{ab}. Each internal cis-bridge bond (s) contributes 1 to f_{ab} if it forms a $(4m+2)$-type cycle c_s' over G_{ab}, and (-1) if it forms a $4m$-type cycle over G_{ab}.

2. If the superposition G_{ab} contains one $4m$-type cycle c_μ, then $S_{ab} = 0$ and moreover only trans-bridges internal to c_μ contribute to H_{ab}. In particular, in the alternant case Kekulé structures K_a and K_b do not interact with each other if their superposition G_{ab} contains one $4m$-type cycle. In the nonalternant case, the interaction between these two structures is due to trans-bridges, and it is given by eq. (31).

3. If the superposition G_{ab} contains more than one $4m$-type cycle, then $S_{ab} = 0$ and $H_{ab} = 0$. Accordingly, there is no interaction between the two Kekulé structures in this case.

4. In terms of positive and negative Kekulé structures one finds that structures of the same parity interact through normal and cis-bridge bonds, while structures of opposite parity interact only through trans-bridge bonds (nonalternant bonds). Hence in the alternant case there is no interaction between sets $\mathbf{K}^+$ and $\mathbf{K}^-$, and each eigenstate of the secular equation is a linear combination of either only positive or only negative Kekulé structures. In the nonalternant case the interaction between the two subsets is due to the nonalternant (trans-bridge) bonds. This interaction is on the average an order of magnitude smaller than the interaction between Kekulé structures of the same parity.

Among other things the above results express the generalisation of the well known Hückel $(4m+2)$-rule. It is encouraging that such a simple approximation as MORT-1 is able to produce these results. This approximation is essentially on the level of the VB based resonance theory, which is known to be incapable of producing anything like a Hückel rule. The MORT-1 approach retains the notion of a resonance, which has a strong intuitive appeal and which is still a very useful concept in organic chemistry. In spite of that, it produces results which are traditionally due to the MO approach. Moreover, not only qualitative but also quantitative estimates of the interaction between different structures and of the resonance stabilisation of different cycles were obtained. These results are formulated here for even conjugated hydrocarbon compounds. However they can be generalised to include odd conjugated systems as well as heteroconjugated compounds and ionic species.[18] But most important, all the results obtained here are based on the analysis of matrix elements H_{ab} of the Hamiltonian H between different Kekulé structures. Hence they directly reflect the properties of a secular equation, and this is a more »fundamental« approach than either perturbation or graph theory. This analysis can hence be extended to more realistic Hamiltonians and to larger spaces containing not only Kekulé structures.[18]

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SAŽETAK

Molekulsko-orbitalna rezonancijska teorija: jednostavan model i poopćeno Hückelovo pravilo

Tomislav P. Živković

U okviru pristupa MORT uvedena je jednostavna aproksimacija nazvana MORT-1. U toj aproksimaciji pretpostavljen je Hückelov hamiltonian i zadržane su samo Kekuléove strukture MORT-pristupa. Izvedeni su matrični elementi $H_{ab} = \langle K_a | \mathrm{H} | K_b \rangle$ Hamiltonova operatora H između Kekuléovih struktura K_a i K_b. Napose, dobiveno je poopćenje Hückelova ($4m+2$) pravila. Pokazano je da u slučaju alterantnih ugljikovodika s parnim brojem C-atoma MORT Kekuléove strukture međusobno djeluju ako i samo ako njihova superpozicija G_{ab} ne sadržava prsten $4m$-tipa. Skup $\mathbf{K}$ svih MORT Kekuléovih struktura dijeli se u dva podskupa $\mathbf{K}^+$ i $\mathbf{K}^-$ koji međusobno ne djeluju. Ova particija formalno odgovara Dewarovoj i Longuet-Higginsovoj podjeli na pozitivne i negativne Kekuléove strukture. U nonalternantnom slučaj interakcija između ta dva skupa postoji zbog (nonalternantnih) veza »cis-mosta«. Ta je interakcija, u prosjeku, za red veličine slabija od odgovarajuće interakcije Kekuléovih struktura iste parnosti.