Theoret. Chim. Acta (Berl.) 62, 335–350 (1983)

THEORETICA CHIMICA ACTA

Molecular Orbital Resonance Theory: A New Approach to the Treatment of Quantum Chemical Problems

Tomislav P. Živković

Institute "Rudjer Bošković", Zagreb, Yugoslavia

An alternative approach to the treatment of the quantum chemical problems combining both, the MO and VB theory, is proposed. This approach retains the concept of resonance from the VB method, but it treats each particular bond in the MO sense. The method is illustrated with a few examples. Relative stabilities of benzene, pentalene and cyclobutadiene are derived. A Hückel $(4m+2)$ rule is derived for the annulenes. The charge polarisation in the case of the pentalene molecule is explained. A distortion of the pentalene molecule is considered and it is shown that within this approach the distortion depends on the charge polarisation.

Key words: Molecular orbital resonance theory – Hückel rule – Charge polarization – Double bond fixation.

1. Introduction

In the treatment of the quantum chemical problems of molecules there are two major ab initio and semiempirical approaches, namely the molecular orbital (MO) theory and the valence bond (VB) theory. The MO approach is more suited to the rigorous description of molecules and it serves as the basis for most semiempirical theories in use today. However, this approach lacks chemical intuition, and even in its simplest form, which is the Hückel theory, elaborate calculations have sometimes to be performed in order to obtain reasonable results. The VB approach which in its simplest form is the resonance theory (RT), is strongly supported by chemical intuition. However, the RT lacks mathematical rigour, it is only qualitative, and it gives sometimes completely

0040-5744/83/0062/0335/$03.20

erroneous results. For example, this theory is unable to reproduce the Hückel $(4m+2)$ rule and it predicts cyclobutadiene to be stable. In its full form the VB approach is mathematically well founded, but due to the enormous number of resonance structures it is quite impractical for the actual calculations which would yield results comparable to the results of MO approaches. In addition, the full VB theory loses all its intuitive appeal. The question remains: is it possible to combine the MO and VB approaches in such a way as to retain the advantages of both methods?

The MO and VB approaches follow physically completely different pictures. The basic physical picture behind the VB method is that the chemical bond results from the pairing of spins of the two electrons situated at the corresponding valence orbitals. The VB wavefunction describing the π-electron bond is given by [1]

$$\begin{aligned}\Psi_{\mathrm{VB}}(1,2) &= \frac{1}{\sqrt{2}}(|\chi_a\bar{\chi}_b| - |\bar{\chi}_a\chi_b| \\ &= \frac{1}{\sqrt{2(1+S^2)}}[w_a(1)w_b(2)+w_a(2)w_b(1)]\frac{1}{\sqrt{2}}[\alpha(1)\beta(2)-\beta(1)\alpha(2)]\end{aligned} \tag{1}$$

where $\chi = w\alpha$ and $\bar{\chi} = w\beta$ are spin orbitals with spins up and down, respectively, S is the overlap integral between atomic orbitals (AO's) w_a and w_b, and $|\chi_a\bar{\chi}_b|$ is the normalised Slater determinant. Numbers 1 and 2 refer to the coordinates of the first and second electron. The corresponding MO wavefunction is [2, 3]

$$\Psi_{\mathrm{MO}}(1,2) = |\phi\bar{\phi}| \tag{2}$$

where ϕ is a normalised molecular orbital (MO)

$$\phi = \frac{1}{\sqrt{2(1+S)}}(\chi_a + \chi_b).$$

Let the Hamiltonian of the system be $H = h + V$, where h is one-particle and V is a two-particle operator. The energy of the VB state (1) is [1]

$$E_{\mathrm{VB}} = (Q+K)/(1+S^2) \tag{3}$$

where

$$\begin{aligned}Q &= \int w_a(1)w_b(2)Hw_a(1)w_b(2)\,d1\,d2 \\ &= (aa|H|bb) = (a|h|a) + (b|h|b) + (aa|bb) \\ K &= (ab|H|ab) = (ab|ab) + 2S(a|h|b)\end{aligned} \tag{4}$$

and

$$(a|h|b) = \int w_a(1)hw_b(1)d1 \qquad S = \int w_a(1)w_b(1)\,d1$$

$$(ab|cd) = \int w_a(1)w_b(1)Vw_c(2)w_d(2)\,d1\,d2.$$

In Eq. (4) letters a and b stand for AO-s w_a and w_b. Q and K are known as the Coulomb and exchange integral, respectively. The energy of the MO state (2) is [4]

$$E_{\mathrm{MO}}=\frac{1}{1+S}[(a|h|a)+(b|h|b)+2(a|h|b)]$$

$$+\frac{1}{2(1+S)^2}[(aa|aa)+(aa|bb)+2(ab|ab)+4(aa|ab)]. \tag{5}$$

In the VB picture the bonding is attributed to the exchange integral K. The Coulomb integral Q leads only to the destabilization of the bond, and in order to produce bonding the exchange integral K should be negative. This integral contains a two-particle contribution $(ab|ab)$, which is positive, and a one-particle contribution $2S(a|h|b)$, which is negative. In order that the bonding can be consistently attributed to the exchange integral K, the overlap S must be nonvanishing, i.e. AO-s w_a and w_b should be nonorthogonal.

In the MO picture however, the bonding is due to the one-particle resonance integral $\beta=(a|h|b)$, which is negative, while all the two-particle integrals $(aa|aa)$, $(aa|bb)$ etc. in Eq. (5) are positive. This is in accord with intuition, since the mutual interaction of electrons should destabilize the molecule, while the stabilizing factor is the interaction of electrons with the nuclei. This latter interaction is represented by h, the one-particle part of the Hamiltonian H.

This simple feature is retained also in more complicated systems. In the VB picture the stabilizing factor is mainly the exchange integral K, while in the MO picture it is the one-particle resonance integral β. At this point there are two serious criticisms one can raise to the VB approach. First, in this method the bonding is due to the exchange integral K which contains both, two- and one-particle contributions. The real cause of bonding is thus obscured. Second, in the orthonormalized base $\{w_i\}$ of AO-s the exchange integral K is positive (since $S_{ij}=\delta_{ij}$), and hence at the lowest level of the approximation the VB approach can not explain any bonding. One way to avoid this problem is to parametrize K in the spirit of a semiempirical approach [5, 6]. One thus obtains a negative value of K, consistent with bonding. However, this negative semiempirical value of K is clearly inconsistent with the assumption of the orthogonality of AO-s w_i. Another solution to the problem is to introduce more and more VB structures to produce bonding in an ab initio approach. This is, however, not very appealing either. The real cause of bonding is quite obscured and the convergence is poor.

The MO approach does not suffer from these deficiencies. The bonding can be consistently attributed to the one-particle resonance integrals $\beta=(a|h|b)$, and the mechanism of bonding qualitatively does not depend on the orthogonality or nonorthogonality of the basic set w_i of AO-s. Already in the simplest Hückel theory there is bonding due to the resonance integral β. More sophisticated MO theories take into account two-particle interactions, but the main contribution to the bonding is still due to the one-particle terms. This hierarchy of approximations is implicitly contained in different MO theories. However, in the VB approach this order is inverted, i.e. two-particle interactions are first taken into account, and then one-particle interactions enter the theory. In our opinion this is the main reason for the poor convergence and the relative failure of the VB approach in practice.

In summary, the VB approach has a close connection with the familiar chemical concept of the bond, but it treats one- and two-particle energy contributions in an unnatural order. The MO approach treats those contributions correctly, but it has a poor connection with the chemical concept of a bond.

2. Molecular Orbital Resonance Theory (MORT)

In view of the respective advantages and disadvantages of the MO and VB approaches, one can combine the two methods in the following way [7, 8]:

Describe the wave function Ψ as a linear combination of different resonance structures of the type

$$\begin{aligned} S = |u_1, u_2, \ldots, u_n| &= \frac{1}{\sqrt{n!}} \sum_P (-1)^P u_1(P1) u_2(P2) \cdots u_n(Pn) \\ &= \frac{1}{\sqrt{n!}} \sum_P (-1)^P u_{P1}(1) u_{P2}(2) \cdots u_{Pn}(n) \end{aligned} \tag{6}$$

where u_s are excited or nonexcited bond orbitals

$$\begin{aligned} u_s &= u_{ij} = \frac{1}{\sqrt{2}}(\chi_i + \chi_j) \quad \text{nonexcited BO} \\ u_s^* &= u_{ij}^* = \frac{1}{\sqrt{2}}(\chi_i - \chi_j) \quad \text{excited BO.} \end{aligned} \tag{7}$$

Orbitals $\chi_i = w_i\eta$ are spin atomic orbitals where w_i are atomic orbitals while η represents either a spin-up or a spin-down state. The set $\{w_i\}$ is assumed to be orthonormalised. All BO-s u_s and u_s^* entering a given resonance structure (6) are assumed to be mutually disjunct, i.e. they have no spin AO χ_i in common. To emphasise both, the MO and the VB character of this approach, we will call it the Molecular orbital Resonance Theory (MORT).

It should be noted that the concept of localised bonds, such that each bond is described by the use of bond orbitals, is present in the so called PCILO method [9]. However, a PCILO approach is quite different from the MORT approach. In the PCILO approach BO-s are used to construct a determinant which serves as a zeroth order wave function. The lowest eigenvalue and eigenstate are then obtained by a Rayleigh–Schrödinger perturbation expansion. PCILO is hence a perturbation theory, while the MORT approach is not. Hence the PCILO method lacks the concept of resonance between different structures, which is one of the main features of the MORT approach.

3. MORT Model with the Hückel Hamiltonian

Let us illustrate the MORT approach in the case of even alternant hydrocarbon molecules. In the simplest variant of this approach we retain only MORT Kekulé structures and we use the Hückel Hamiltonian [7, 8]. In this approximation the spin separation is assumed, i.e. each eigenstate is of the form

$$\Psi = A\phi_a\bar{\phi}_b \tag{8}$$

where A is the antisymmetrization operator, while ϕ_a and $\bar{\phi}_b$ are spin-up and spin-down substates, respectively. Both, ϕ_a and ϕ_b are expressed as linear combinations of Kekulé structures

$$\phi_a = \Sigma_\mu c_\mu K_\mu \ \phi_b = \Sigma_\mu d_\mu K_\mu. \tag{9}$$

According to Eq. (6) each Kekulé structure is of the form

$$K = |\varphi_1, \varphi_2, \ldots, \varphi_n| = \frac{1}{\sqrt{n!}} \sum_P (-1)^P \varphi_{P1}(1)\varphi_{P2}(2) \cdots \varphi_{Pn}(n) \tag{10}$$

where all φ_s are bonding BO-s, $\varphi_s = \varphi_{ij} = 1/\sqrt{2}(w_i + w_j)$, such that corresponding AO-s w_i and w_j are adjacent to each other. We use the Hamiltonian operator

$$H = A - nI$$

where A is the adjacency operator and n is the number of particles in the state ϕ. The operator H is essentially the Hückel Hamiltonian. Eigenvalues of this operator express the energy in β-units. Since H is a one-particle spin independent operator, the eigenvalue equation splits into two equations, one for the spin-up state ϕ_a and one for the spin-down state ϕ_b. Assuming both states to contain the same number of electrons, the two equations are identical, and hence for the ground state $\phi_a = \phi_b$, i.e. $E_a = E_b$ and $\Psi = A\phi_a\bar{\phi}_a$. It is hence sufficient to perform all the calculations for the substate ϕ_a alone. Using Eq. (10) one easily finds

$$\begin{aligned}\langle K|K\rangle &= \int \varphi_1(1) \cdots \varphi_n(n) \sum_P (-1)^P \varphi_{P1}(1) \cdots \varphi_{P_n}(n)\, d1 \cdots dn \\ &= \sum_P (-1)^P \int \varphi_1(1)\varphi_{P1}(1)\, d1 \cdots \int \varphi_n(n)\varphi_{P_n}(n)\, dn. \end{aligned} \tag{11}$$

Since different BO-s φ_s contained in the Kekulé structure K are mutually disjunct, the only permutation in Eq. (11) leading to the nonvanishing term is the identity permutation and hence

$$\langle K|K\rangle = 1 \tag{12}$$

i.e. Kekulé structures (10) are normalised. Similarly one finds

$$\begin{aligned}\langle K|A|K\rangle &= \sum_P (-1)^P \sum_{s=1}^{n} \int \varphi_1(1)\varphi_{P1}(1)\,d1 \\ &\qquad \cdots \int \varphi_s(s)A\varphi_{Ps}(s)\,ds \cdots \int \varphi_n(n)\varphi_{Pn}(n)\,dn \\ &= \sum_{s=1}^{n} \int \varphi_s(s)A\varphi_s(s)\,ds = n.\end{aligned}$$

The last line follows from

$$\begin{aligned}\int \varphi_s A\varphi_s\,ds &= \tfrac{1}{2}\int (w_i+w_j)A(w_i+w_j)\,ds \\ &= \int w_i A w_j\,ds = 1.\end{aligned}$$

since A is the adjacency operator and AO-s w_i and w_j contained in the BO φ_s are adjacent to each other. Combining the above results one finds

$$\langle K|H|K\rangle = 0 \tag{13}$$

i.e. in this approximation all the Kekulé structures have zero energy. The eigenvalue of H expresses now how much a particular state ϕ (which represents both, a spin-up and a spin-down substate) is stabilised through the resonance between different Kekulé structures.

Let us now consider the following examples.

3.1. *Annulenes and the Hückel (4m+2) Rule*

Consider the cyclobutadiene molecule (Fig. 1). There are two Kekulé structures

$$\begin{aligned}K_1 &= |\varphi_{12}, \varphi_{34}| = \frac{1}{\sqrt{2}}[\varphi_{12}(1)\varphi_{34}(2) - \varphi_{34}(1)\varphi_{12}(2)] \\ K_2 &= |\varphi_{23}, \varphi_{41}| = \frac{1}{\sqrt{2}}[\varphi_{23}(1)\varphi_{41}(2) - \varphi_{41}(1)\varphi_{23}(2)].\end{aligned} \tag{14}$$

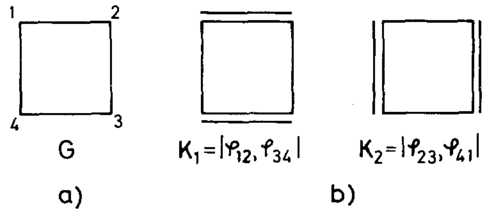


Fig. 1. **a** Graph G of the cyclobutadiene molecule. **b** MORT Kekulé structures of cyclobutadiene. $\varphi_{ij} = \frac{1}{2}(w_i + w_j)$ are bond orbitals

One easily finds

$$\langle K_1|K_2\rangle = \int \varphi_{12}(1)\varphi_{34}(2)[\varphi_{23}(1)\varphi_{41}(2) - \varphi_{41}(1)\varphi_{23}(2)]\,d1\,d2$$
$$= 1/4 - 1/4 = 0$$

and

$$\begin{aligned}\langle K_1|A|K_2\rangle = &\int \varphi_{12}(1)A\varphi_{23}(1)\,d1 \int \varphi_{34}(2)\varphi_{41}(2)\,d2\\ &+\int \varphi_{12}(1)\varphi_{23}(1)\,d1 \int \varphi_{34}(2)A\varphi_{41}(2)\,d2\\ &-\int \varphi_{12}(1)A\varphi_{41}(1)\,d1 \int \varphi_{34}(2)\varphi_{23}(2)\,d2\\ &-\int \varphi_{12}(1)\varphi_{41}(1)\,d1 \int \varphi_{34}(2)A\varphi_{23}(2)\,d2\\ = &\tfrac{1}{2}+\tfrac{1}{2}-\tfrac{1}{2}-\tfrac{1}{2}=0.\end{aligned}$$

Hence

$$\langle K_1|H|K_2\rangle = 0. \tag{15}$$

Within this picture the two Kekulé structures do not interact with each other, and there is no extra stabilization due to the resonance between them. The full ground state is four-fold degenerate

$$\begin{matrix}\Psi_1 = AK_1\bar{K}_1 & \Psi_2 = AK_1\bar{K}_2\\ \Psi_3 = AK_2\bar{K}_1 & \Psi_4 = AK_2\bar{K}_2\end{matrix} \tag{16}$$

with the energy $E = 0$.

Consider as another example the benzene molecule (Fig. 2). Using the same approach as above one obtains

$$\langle K_1|K_2\rangle = \tfrac{1}{4} \qquad \langle K_1|H|K_2\rangle = \tfrac{3}{4}.$$

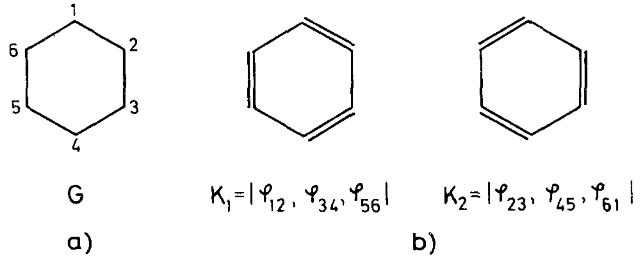


Fig. 2. **a** Graph G of the benzene molecule. **b** MORT Kekulé structures of benzene

The ground state is now

$$\Psi = A\phi\bar{\phi} \qquad \phi = K_1 + K_2 \tag{17}$$

with the eigenvalue $E = 1.2$.

Already at this simplest level of approximation this approach explains qualitatively the difference between the benzene and cyclobutadiene molecules. In the case of the cyclobutadiene molecule the two Kekulé structures do not interact with each other, i.e. there is no extra stabilization due to the resonance. In the case of the benzene molecule there is a resonance energy of 1.2β stabilizing the ground state. This result should be contrasted to the result of the VB approach on the comparable level of approximation. In the VB theory the matrix element between the two Kekulé structures is expressed in terms of two-particle exchange integrals which contributes to the stabilization in both cases. Accordingly, both molecules are predicted to be stable, contrary to experience.

The above approach can be generalized to include arbitrary annulene molecules (Fig. 3). After some straightforward algebra, which will be explained in a forthcoming paper [10], one finds

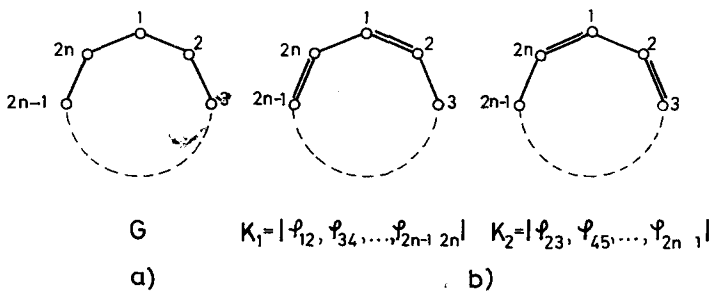
$$\begin{aligned} S_{12} &= \langle K_1 | K_2 \rangle = [1 + (-1)^{n+1}] 2^{-n} \\ H_{12} &= \langle K_1 | H | K_2 \rangle = n[1 + (-1)^{n+1}] 2^{-n} \end{aligned} \tag{18}$$

where $2n$ is the number of carbon atoms. In the case when n is even, $S_{12} = H_{12} = 0$, and the two Kekulé structures do not interact with each other. The ground state is degenerate both in the spin-up and spin-down subspaces, and there is no extra stabilization due to the resonance. A special case is the cyclobutadiene molecule, with $n = 2$. If, however, n is odd then $S_{12} = 2^{1-n}$, $H_{12} = n2^{1-n}$, and the full ground state is $\Psi = A\phi\bar{\phi}$ where $\phi = K_1 + K_2$ with the eigenvalue

$$E_n = 2n/(1 + 2^{n-1}) \tag{19}$$

(see Fig. 4).

We have derived here the well known Hückel rule, stating that conjugated hydrocarbon molecules containing $(4m + 2)$ π-electrons are stable, while conjugated hydrocarbon molecules containing $4m$ π-electrons are not. In the Hückel



a)

b)

Fig. 3. **a** Graph G of the annulene molecule. **b** MORT Kekulé structures of annulene

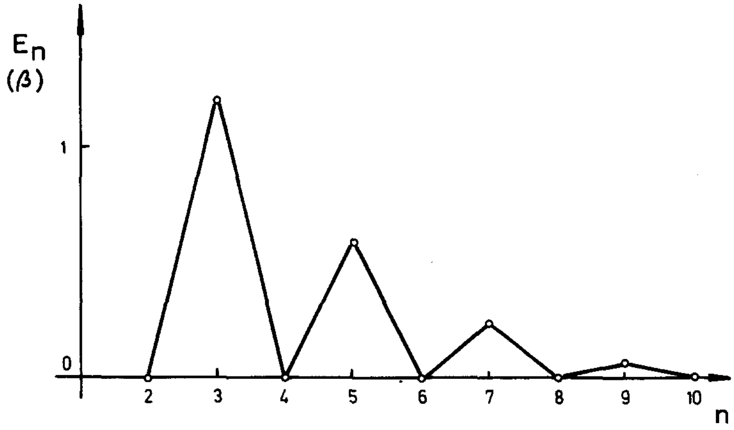


Fig. 4. MORT resonance energies of $2n$-annulenes in β units. In the case of $4m$-type anulenes (n even) there is no net stabilization due to the resonance between the two Kekulé structures. The resonance stabilization in the case of ($4m+2$)-annulenes (n odd) rapidly decreases with the increase of ring size

theory, which is an MO approach, this rule is derived for annulene molecules and the corresponding ions and then postulated for other hydrocarbon compounds [11]. In the VB approach this rule is untractable [11], at least at the simplest level of approximation where only Kekulé structures are taken into account. The MORT approach seems promising since it is able to produce such a simple qualitative result as the Hückel rule whilst retaining at the same time the intuitive appeal of the bond picture. This is particularly true since a generalization of this rule to all even π-electron hydrocarbons has been obtained [10].

3.3. Pentalene and Bond Length Alternation

As another example take the pentalene molecule (Fig. 5).

This molecule should be more stable than cyclobutadiene, but not as stable as benzene [12, 13]. There is a charge alternation along the perimeter of the molecule such that carbon atoms 1, 3, 4, 6, have a net positive charge, while carbon atoms 2, 5, 7, 8 have a net negative charge [12, 14, 15]. Pentalene is

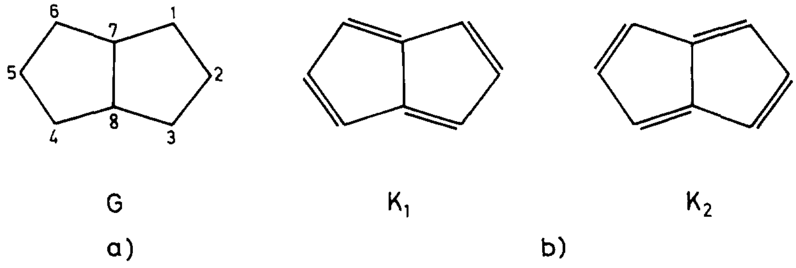


Fig. 5. a Graph G of the pentalene molecule. **b** MORT Kekulé structures of pentalene

further distinguished by a notable bond length alternation [15, 16, 17]. The bond length alternation can be explained neither in the Hückel [14] nor in the naive VB based resonance theory.

Let us now see how the MORT approach treats this molecule. In the case of pentalene there are again two MORT Kekulé structures:

$$\begin{aligned} K_1 &= |\varphi_{12}, \varphi_{38}, \varphi_{45}, \varphi_{67}| \\ K_2 &= |\varphi_{23}, \varphi_{84}, \varphi_{56}, \varphi_{17}|. \end{aligned} \tag{20}$$

After some algebra one finds

$$\langle K_1|K_2\rangle = 0 \quad \text{and} \quad \langle K_1|H|K_2\rangle = \tfrac{1}{8}.$$

The two Kekulé structures interact with each other, and the ground state equals $\Psi = A\phi\bar{\phi}$ where $\phi = K_1 + K_2$ with an energy of $\frac{1}{4}$ given in units of β. Pentalene molecule is stabilized through resonance between the two Kekulé structures, but the amount of stabilization ($\frac{1}{4}\beta$) is much smaller than for benzene (1.2β). This explains the relative stabilities of the cyclobutadiene, pentalene and benzene molecules.

In order to discuss the charge alternation let us introduce the one-particle charge operator Q^i. By definition $\int w_i Q^i w_i \, d\tau = 1$ while all other matrix elements of Q^i vanish. The expectation value

$$q_i = \langle Q^i \rangle_\Psi = \langle \Psi|Q^i|\Psi\rangle / \langle \Psi|\Psi\rangle$$

represents the charge of the state Ψ at the AO w_i. One easily finds

$$\langle K_1|Q^i|K_1\rangle = \langle K_2|Q^i|K_2\rangle = \tfrac{1}{2} \qquad (i = 1, \ldots, 8) \tag{21}$$

i.e. both Kekulé structures K_1 and K_2 represent a state with a uniform charge density distribution of $\frac{1}{2}$ over all AO-s w_i, as intuitively suggested. Concerning the diagonal matrix elements one finds

$$\langle K_1|Q^i|K_2\rangle = \begin{cases} \frac{1}{16} & i = 2, 5, 7, 8 \\ -\frac{1}{16} & i = 1, 3, 4, 6 \end{cases} \tag{22}$$

and hence

$$\langle Q^i \rangle_\Psi = \begin{cases} 1 + \frac{1}{8} & i = 2, 5, 7, 8 \\ 1 - \frac{1}{8} & i = 1, 3, 4, 6. \end{cases}$$

This charge alternation is qualitatively in complete agreement with other derivations.

Let us now consider the bond length alternation. Since the state $\phi = K_1 + K_2$ contains both Kekulé structures (20) with the same weight, and since these structures represent two alternant bonding distributions with interchanged single and double bonds, we would expect no bond alternation. This conclusion is correct and it can be formalised. Introduce the bond order operator $P^s = P^{ij}$. By definition this operator has a matrix element $\frac{1}{2}$ between AO-s w_i and w_j, while matrix elements of this operator between all other AO-s vanish, (the factor $\frac{1}{2}$ is needed in order to take into account the double counting of integrals $\int w_i P^{ij} w_j \, d\tau$ and $\int w_j P^{ij} w_i \, d\tau$). One easily finds e.g.

$$\langle K_1|P^{12}|K_1\rangle = \sum_P (-1)^P \sum_{s=1}^{4} \int \varphi_{12}(1)\varphi_{P12}(1)\, d1$$

$$\cdots \int \varphi_s(s) P^{12} \varphi_{Ps}(s)\, ds \cdots \int \varphi_{67}(4)\varphi_{P67}(4)\, d4$$

$$= \int \varphi_{12}(1) P^{12} \varphi_{12}(1)\, d1 \cdots \int \varphi_{67}(4)\varphi_{67}(4)\, d4 = \tfrac{1}{2}$$

and similarly $\langle K_1|P^{23}|K_1\rangle = 0$, as suggested by the intuitive interpretation of the Kekulé structure K_1 (see Fig. 5). MORT Kekulé structure K_1 represents a structure with a bond order $\frac{1}{2}$ between AO-s w_1 and w_2, and a vanishing bond order between AO-s w_2 and w_3. The bond order between AO-s w_1 and w_2 is only $\frac{1}{2}$ and not 1, since K_1 represents only "one half" (either spin-up or spin-down) of the total wavefunction. A similar meaning can be given to all other bond orders in structures K_1 and K_2. In order to find out bond orders represented by a state ϕ the off-diagonal matrix elements $\langle K_1|P^{ij}|K_2\rangle$ are also needed. After some algebra one finds

$$\langle K_1|P^{12}|K_2\rangle = \langle K_1|P^{23}|K_2\rangle = \cdots = \langle K_1|P^{71}|K_2\rangle = 0 \qquad (23)$$

for all the bond orders along the perimeter of the pentalene molecule. The only nonvanishing matrix element corresponds to the bond order between the AO-s w_7 and w_8 accross the bridge of the pentalene molecule

$$\langle K_1|P^{78}|K_2\rangle = \tfrac{1}{16}.$$

One hence finds

$$\langle P^{ij}\rangle_\phi = \tfrac{1}{4}$$

and accordingly

$$\langle P^{ij}\rangle_\Psi = \tfrac{1}{2}$$

for all bond orders along the perimeter of the pentalene molecule. Using the simple Coulson bond length–bond order relation one would thus predict equal bond length along the perimeter of the pentalene molecule. Here the MORT approach does not predict bond length alternation. But let us consider this problem in more detail.

Our Hamiltonian is a Hückel Hamiltonian $H = A - nI$ which takes into account only the one particle contribution due to the resonance integral β. The ground state $\Psi = A\phi\bar{\phi}$ however represents a state with separated charge densities, and this charge separation should lead through Coulomb interaction to destabilization. In the simplest approximation one can assume that this two-particle interaction is of the form

$$V = -\omega \sum_{i=1}^{n} (q_i - 1)^2 \tag{24}$$

where ω is a parameter in the β units and $(q_i - 1)$ is the net charge on the carbon atom (i). This assumption takes into account only the mutual repulsion of two electrons, one with the spin-up and the other with the spin-down, situated at the same atom (i). It is analogous to the ω-technique [18, 19, 20] and it introduces the two particle interactions at the simplest level possible. Assume now the state ϕ to be of the general form

$$\phi = \phi(\alpha) = K_1 \cos\alpha + K_2 \sin\alpha \tag{25}$$

where α is to be determined through the minimization of the energy. Using Eqs. (21)–(23) one obtains for a state $\Psi(\alpha) = A\phi(\alpha)\overline{\phi(\alpha)}$

$$\langle Q^i\rangle_{\Psi(\alpha)} = \begin{cases} 1 + \frac{1}{8}\sin 2\alpha & i = 2, 5, 7, 8 \\ 1 - \frac{1}{8}\sin 2\alpha & i = 1, 3, 4, 6 \end{cases}$$

and

$$\langle P^{ij}\rangle_{\Psi(\alpha)} = \begin{cases} \cos^2\alpha & (ij) = (12), (38), (4\ 5), (6\ 7) \\ \sin^2\alpha & (ij) = (23), (84), (56), (71) \end{cases}$$

$$\langle P^{78}\rangle_{\Psi(\alpha)} = \tfrac{1}{8}\sin 2\alpha.$$

The energy is

$$\langle H\rangle_{\Psi(\alpha)} = \tfrac{1}{4}\sin 2\alpha \quad \langle V\rangle_{\Psi(\alpha)} = -\frac{\omega}{8}\sin^2 2\alpha.$$

Hence

$$E(\alpha) = \langle H + V\rangle_{\Psi(\alpha)} = \frac{1}{4}\left(\sin 2\alpha - \frac{\omega}{2}\sin^2 2\alpha\right)$$

in the β units. If $|\omega| \leq 1$ the energy $E(\alpha)$ has two extreme values

$$\alpha_1 = \pi/4 \qquad E_1 = (1 - \omega/2)/4$$

$$\alpha_2 = 3\pi/4 \qquad E_2 = (-1 - \omega/2)/4.$$

If however $|\omega| > 1$, there are two additional extreme values

$$\alpha_3 = \tfrac{1}{2}\arcsin\left(\frac{1}{\omega}\right) \qquad \alpha_4 = \pi/2 - \alpha_3$$

$$E_3 = E_4 = 1/(8\omega).$$

In Fig. 6 $E(\alpha)$ is plotted as a function of α for three different values of the parameter ω. Provided $|\omega| \leq 1$ there is only one minimum. The corresponding eigenstate is the state $\Psi = A\phi\bar{\phi}$ where $\phi = K_1 + K_2$, and as shown above, there is no bond length alternation. If however $\omega > 1$ there are two minima, one for $\alpha = \alpha_3$ and another one for $\alpha = \alpha_4$. In both cases the two Kekulé structures K_1

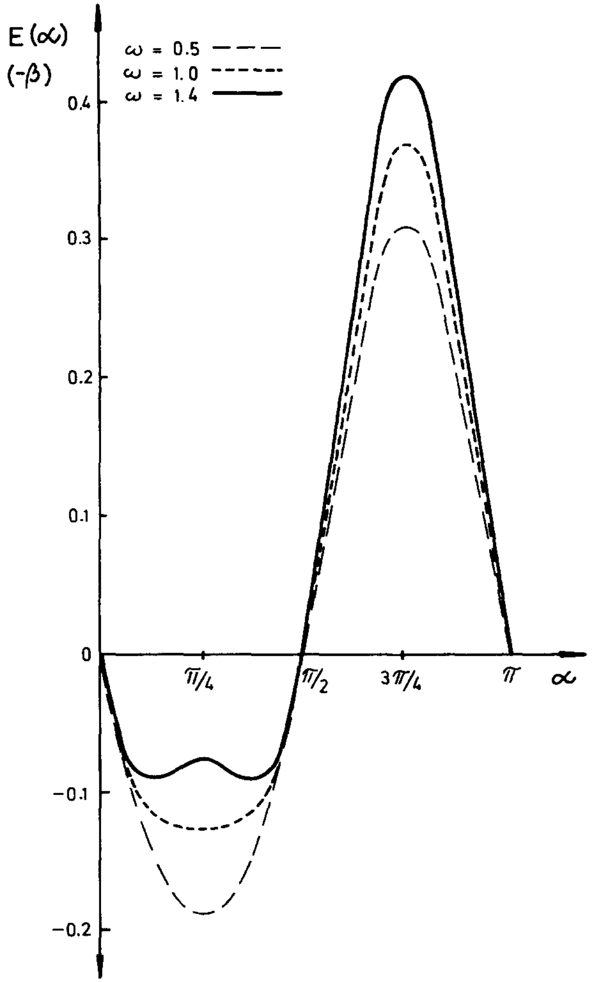


Fig. 6. Energy $E(\alpha)$ for three different values of a parameter ω in the case of a pentalene molecule. If $|\omega| \leq 1$ there is a stable minimum at $\alpha = \pi/4$ corresponding to the state $\phi = K_1 + K_2$. If $\omega > 1$ this state becomes unstable and the two minima develop corresponding to the two distorted structures of pentalene. Points $\alpha = 0$ and $\alpha = \pi$ correspond to the Kekulé structure K_1. Point $\alpha = \pi/2$ corresponds to the Kekulé structure K_2, while point $\alpha = 3\pi/4$ corresponds to the antibonding state $\phi' = K_1 - K_2$. The value $\omega = 1.4$ is an estimate given by Streitwieser [19, 20]

and K_2 do not enter the state $\phi(\alpha)$ with equal weights, one of those structures is dominant, and as a result there is a bond order alternation along the perimeter of the pentalene molecule. Using a bond length–bond order relationship one thus predicts bond length alternation. The resulting distortion changes the pentalene molecule from the symmetrical D_{2h} structure to an asymmetrical C_{2h} structure. The necessary and sufficient condition for the distortion to occur in this simple MORT picture is $\omega > 1$. Parameterizing the value of ω in the ω-technique approach Streitwieser estimates $\omega = 1.4$ [19, 20]. Though this value is obtained as the best fit within an MO approach, and hence can not be directly applied to the MORT picture, it still suggests that the analogous parameterization within the MORT approach is likely to produce a value $\omega > 1$.

One should notice the mechanism which is involved here. The Hückel interaction stabilizes the ground state through the resonance between the two Kekulé structures and this stabilization is the largest if those structures enter the ground state with the same weight. However, in this case there is a large polarization of the electron density causing the destabilization through the Coulomb interaction. Charge polarization, and hence Coulomb destabilization, vanishes if $\phi(\alpha)$ is represented by a single Kekulé structure. If this Coulomb interaction is strong enough, i.e. if in the case of pentalene $\omega > 1$, then the actual energy minima are obtained through a compromise between the stabilizing resonance effect, and the destabilizing Coulomb effect. The estimate ($\omega = 1.4$) suggests that this is actually the case. The result is bond length alternation and the lowering of the symmetry. The above approach can equally well be applied to the benzene and cyclobutadiene molecules. In the case of the benzene molecule one finds that the resonance between the two MORT Kekulé structures does not lead to a charge polarization, i.e. in this case $\langle Q^i \rangle_\Psi = 1$ ($i = 1, \ldots, 6$). There is no Coulomb destabilization, and the ground state is the state (17). Benzene is hence predicted to exhibit no bond length alternation. In the case of a cyclobutadiene molecule, the ground state is already without a potential (24) represented by a single Kekulé structure with manifest bond order alternation. One can easily show that the linear combination of the two Kekulé structures (14) leads to a charge separation and hence to a further destabilization of a molecule. The ground state is hence represented by either of the two MORT Kekulé structures.

In conclusion, the introduction of a two-particle interaction (24) leads to a correct prediction concerning bond length alternation, at least in the case of the benzene, pentalene and cyclobutadiene molecules. This approach can be further generalized to include more complicated systems [10].

In the literature there is an extensive treatment of distortions of this kind. Such double bond fixations are usually obtained within a framework of a much more elaborate theory. Thus Nakajima [15, 21] computes the total π-electron energy for a pre-selected type of bond alternation as a function of a parameter k, where k is defined by the ratio of the "single" to the "double" bond resonance integral. In his method the resonance integral is assumed to be an exponential function of interatomic distance, which is in turn a linear function of the bond order [15, 21]. Dewar et al. [22] treat this double bond fixation in the framework of an SCF MO model. They also assume an essentially exponential dependence of the resonance integral on interatomic distance. Binsch et al. [16, 23] present a theory which clearly distinguishes first and second order bond fixation. Only the second order bond fixation can lower the symmetry [16, 23]. Their method requires the diagonalization of the bond–bond polarizability matrix.

All these approaches are more complicated than the one presented here. It should be noted that Binsch et al. express the belief that the polarization of the electron density is not likely to be important in lowering the symmetry of a non-alternant, and they accordingly disregard the corresponding contributions [16, 23]. This is not in accord with the above MORT approach which attributes the distortion in a pentalene to a charge separation alone, without any further assumption.

4. Summary and Conclusion

The two major approaches to the treatment of quantum chemical problems, MO and VB, have both advantages and disadvantages. The VB approach retains a loose connection with the classical concept of the chemical bond. The MO approach treats correctly the one- and two-particle contributions to the energy leading to the stabilization of the molecule. A new approach is proposed combining the advantages of both theories. This method retains the resonance concept from the VB method, but it treats each particular bond in the MO sense. This approach has been called the Molecular Orbital Resonance Theory (MORT). The advantages of this method are illustrated with a few simple examples. It is shown how in this picture one can easily explain the relative stabilities of benzene, pentalene and cyclobutadiene molecules. A Hückel $(4m+2)$ rule is derived for the annulenes. The charge alternation in the case of the pentalene molecule is successfully explained. Extending the Hückel Hamiltonian to include a simple analogue of the ω-technique a bond length alternation in the pentalene molecule is explained.

All these results are obtained on a very simple level of approximation and they can be generalized. The generalization of the Hückel rule to include all the conjugated hydrocarbon molecules will be presented in a forthcoming paper. The rule thus obtained does not always coincide with the Hückel rule [10]. One can also generalize the charge alternation as well as bond length alternation. Using MORT one can derive many other simple regularities and rules [10]. This is the conceptual advantage of this approach since it offers a simple qualitative explanation for many regularities observed in conjugated systems. In this respect the MORT approach goes beyond the Hückel theory which can also give some simple rules. Most importantly, the MORT approach can be generalized to incclude more resonance structures and more sophisticated Hamiltonians. It can in fact be made equivalent to the full CI.

In the forthcoming papers a systematic generalization and presentation of this method will be given.

Acknowledgement. The author wishes to thank Dr. H. Monkhorst and Dr. Z. Meić for helpful discussions during the preparation of this paper. This work was supported in part by the National Science Foundation, Grant No. F 6 F 00 6Y.

References

1. Heitler, W., London, F.: Z. Phys. **44**, 455 (1927)
2. Hund, F.: Z. Phys. **40**, 742; **42**, 93 (1927)

3. Mulliken, R. S.: Phys. Rev. **32**, 186, 761 (1928); **33**, 730 (1929)
4. Ohno, K.: Advances in quantum chemistry **3**, 239 (1967)
5. McWeeny, R., Sutcliffe, B. T.: Methods of molecular quantum mechanics. London: Academic Press, 1969
6. Elements of quantum chemistry (by Zahradník and Polák). New York and London: Plenum Press, 1980. see also: Eyring, H., Kimball, G. E.: J. Chem. Phys. **1**, 239 (1933); Eyring, H., Walter, Kimball, G. E.: Quantum Chemistry (1960); Pauling, L.: J. Chem. Phys. **1**, 280 (1933)
7. Živković, T. P.: Theoret Chim. Acta (Berl.) **61**, 363 (1982)
8. Živković, T. P.: reported at the Fourth International Congress in Quantum Chemistry, Uppsala, Sweden, June 1982
9. Diner, S., Malrieu, J. P., Claverie, P.: Theoret. Chim. Acta (Berl.) **13**, 1 (1969); see also: Malrieu, J. P., Claverie, P., Diner, S.: Theoret. Chim. Acta (Berl.) **13**, 18 (1969); Diner, S., Malrieu, J. P., Jordan, F., Gilbert, M.: Theoret. Chim. Acta (Berl.) **13**, 101 (1969); Langlet, J., Gilbert, M., Malrieu, J. P.: Theoret. Chim. Acta (Berl.) **22**, 80 (1971)
10. Živković, T. P.: in preparation
11. Hückel, E.: Z. Phys. **70**, 204 (1931); **76**, 628 (1932); Z. Elektrochem. **43**, 752 (1937)
12. Dewar, M. J. S.: The molecular orbital theory of organic chemistry. New York: McGraw-Hill, 1969
13. Ginsburg, D.: Non-benzenoid aromatic compounds, Interscience Publishers, Inc., New York, Interscience Publishers, Ltd., London, 1959
14. Streitwieser, A., Baumann, J. I.: Supplemental tables of molecular orbital calculations, with a C. A. Coulson and A. Streitwieser, dictionary of π-electron calculations, Vol. II. Oxford, London, Edinburgh, New York, Paris, Frankfurt: Pergamon Press, 1965
15. Nakajima, T., Yaguchi, Y., Kaeriyoma, R., Nemoto, Y.: Bull. of Chem. Soc. of Japan **37**, 272 (1964)
16. Binsch, G., Heilbronner, E., Murrell, J. N.: Mol. Phys. **11**, 305 (1966)
17. Binsch, G., Heilbronner, E.: Tetrahedron **24**, 1215 (1968)
18. Wheland, G. W., Mann, D. E.: J. Chem. Phys. **17**, 264 (1949)
19. Streitwiser, A., Nair, P. M.: Tetrahedron **5**, 149 (1959)
20. Streitwieser, A.: J. Am. Chem. Soc. **82**, 4123 (1960)
21. Nakajima, T., Katagiri, S.: Mol. Phys. **7**, 149 (1963)
22. Chung, A. L. H., Dewar, M. J. S.: J. Chem. Phys. **42**, 756 (1965); Dewar, M. J. S., Gleicher, G. J.: J. Am. Chem. Soc. **87**, 685, 692, 4414 (1965); Dewar, M. J. S., Gleicher, G. J.: Tetrahedroon **21**, 1817, 3423 (1965)
23. Binsch, G., Heilbronner, E.: Structural chemistry and molecular biology, Rich, A., Davidron, N. Eds., p. 815. San Francisco: W. H. Freeman and Co., 1968

Received July 27/September 21, 1982

Note added in proof

Using the so called "significant electron structures" (SES), which are closed shell configurations identical to PCILO ground state structures [9], Gründler independently derived the Hückel $(4m+2)$-rule for annulenes (Gründler, W.: Z. Chem. **20**, 391 (1980)). The two SES structures stabilize benzene by $6/17\beta$ (ibid. **19**, 236 (1979)), which should be compared with the MORT-1 result of 1.2β. In general, MORT-1 function has significantly lower energy than the corresponding SES function, and hence it should represent better the "true" ground state.