Myth and Reality in the Attitude toward Valence-Bond (VB) Theory: Are Its 'Failures' Real?

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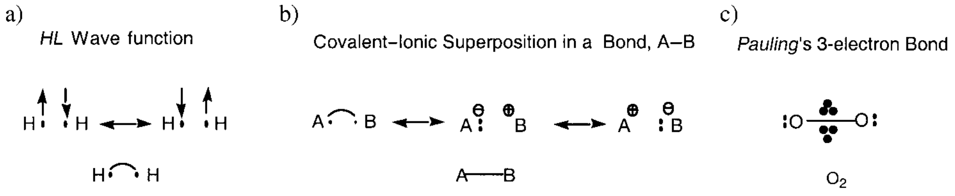
Dedicated to Professor *Jack D. Dunitz* on the occasion of his 80th birthday

According to common wisdom propagated in textbooks and papers, valence-bond (VB) theory fails and makes predictions in contradiction with experiment. Four iconic 'failures' are: *a*) the wrong prediction of the ground state of the O_2 molecule, *b*) the failure to predict the properties of cyclobutadiene (CBD) *viz.* those of benzene, *c*) the failure to predict the aromaticity/anti-aromaticity of molecular ions like $C_5H_5^+$ and $C_5H_5^-$, $C_3H_3^+$ and $C_3H_3^-$, $C_7H_7^+$ and $C_7H_7^-$, *etc*; and *d*) the failure to predict that, *e.g.*, CH_4 has two different ionization potentials. This paper analyzes the origins of these 'failures' and shows that two of them (stated in *a* and *d*) are myths of unclear origins, while the other two originate in misuse of an oversimplified version of VB theory, *i.e.*, simple resonance theory that merely enumerate resonance structures. It is demonstrated that, in each case, a properly used VB theory at a simple and portable level leads to correct predictions, as successful as those made by use of molecular-orbital (MO) theory. This notion of VB 'failure', which is traced back to the VB-MO rivalry, in the early days of quantum chemistry, should now be considered obsolete, unwarranted, and counterproductive. A modern chemist should know that there are two ways of describing electronic structure, which are not two contrasting theories, but rather two representations or two guises of the same reality. Their capabilities and insights into chemical problems are complementary, and the exclusion of any one of them undermines the intellectual heritage of chemistry.

1. Introduction. – The new quantum mechanics of the late 1920s has provided chemistry with two general theories, one called valence-bond (VB) theory and the other molecular-orbital (MO) theory. The two theories were developed at about the same time, but have quickly diverged into rival schools that have competed on charting the mental map and epistemology of chemistry. Even though the originators of both theories, and chiefly *Slater* [1], realized that the two were ultimately equivalent, and even though chemists, versed in quantum mechanics, have all along been aware of this equivalency, the rivalry has never subsided. In a nutshell, until the 1950s, VB theory had dominated chemistry, then MO theory gradually took over while VB theory fell into disrepute and was almost completely abandoned. The 1980s and onwards marked a comeback of VB theory, which has been ever since enjoying a renaissance in some respects. Despite this comeback, VB is still held by many chemists as an obsolete theory with fundamental 'flaws' – sort of a wrong theory. These 'flaws' or 'failures' are propagated through common wisdom, papers, talks, and textbooks, in some cases as definite statements, *e.g.*, that VB theory contradicts experimental findings [2]. Such attitudes towards VB theory undermine the intellectual achievements of chemistry and deprives chemists of the great merits of the theory. The question as to whether or not these 'flaws' are actually real is the focus of this paper. To this end, we analyze four iconic 'failures' of VB theory, discuss their origins, and ascertain their components of myth and truth.

2. Roots of VB and MO Theories and of the VB–MO Rivalry. – The roots of VB theory in chemistry can be traced to the famous paper of *Lewis*, '*The Atom and The Molecule*' [3], in which is introduced the notions of electron-pair bonding and the octet rule. This paper, which preceded the new quantum mechanics by 11 years, constitutes the first formulation of bonding in terms of the covalent–ionic classification. This classification has formed the basis for the subsequent construction and generalization of VB theory [4]. The origins of electron-pair bonding remained, however, unclear until 1927 when *Heitler* and *London* published their seminal paper, '*Interaction Between Neutral Atoms and Homopolar Binding*' [5], in which they showed that the bonding in H_2 can be accounted for by the wave function drawn in *Scheme 1, a*. This wave function, called also the *HL* wave function, is a superposition of two covalent situations that exchange the electron spins on the two atoms. Thus, the bonding in H_2 was found to originate in the quantum-mechanical 'resonance' between the spin arrangements that are required to form a singlet electron pair. This origin of the bonding was a remarkable feat of the new quantum theory, since, until then, it was not obvious how two neutral species could be at all bonded.

Scheme 1



In the winter of 1928, *London* extended the *HL* wave function and drew the general principles of the covalent or homopolar bonding [6]. In both treatments, *Heitler* and *London* did consider ionic structures, but discarded their mixing as being too small in homopolar cases. In essence, the *HL* theory was a quantum-mechanical version of the *Lewis* shared-pair theory. Thus, even though *Heitler* and *London* did their work independently and perhaps unknowingly of the *Lewis* model, still the *HL* wave function described precisely the shared pair of *Lewis*, as stressed later by *Pauling* [7]. The *HL* wave function formed the basis for the version of *HL*VB theory that became very popular later, and which was behind some of the failings that have been attributed to VB theory.

The success of the *HL* model and its relation to *Lewis*'s model prompted *Pauling* and *Slater* to construct a general quantum-chemical theory for polyatomic molecules. In the same year, 1931, they both published a few seminal papers in which they developed the notion of hybridization, the covalent–ionic superposition in a bond (*Scheme 1, b*), the resonating benzene picture, molecules like diborane, and one- and three-electron bonding as in H_2^+ and O_2 (*Scheme 1,c*), respectively [1][8–11]. *Pauling*'s series of papers enabled the description of any bond in any molecule, and culminated in the famous monograph in which all the structural chemistry of the time was treated in terms of the covalent–ionic superposition theory, resonance theory, and hybridization theory [12]. The book, published in 1938, is dedicated to *Lewis*, and the 1916 paper of *Lewis* [3] is the only reference cited in the preface to the first edition. In *Pauling*'s view, VB theory was a quantum-chemical version of *Lewis*'s theory of valence.

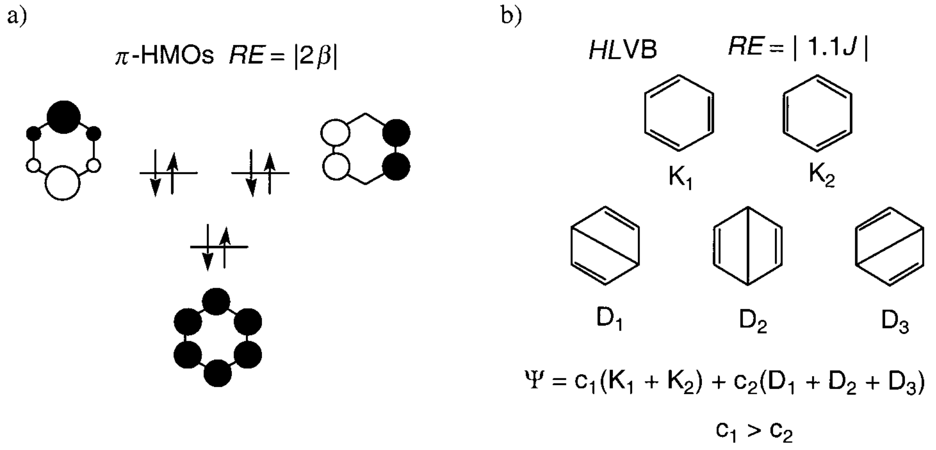
At the same time that *Slater* and *Pauling* created their VB theory, *Mulliken* [13] and *Hund* [14] were developing an alternative spectroscopy-based approach called molecular-orbital (MO) theory. According to *Brush* [15], the first to write a wave function for a molecular orbital was *Lennard-Jones* [16] in his 1929 treatment of the O_2 molecule. This treatment and an earlier paper by *Mulliken* [17] predicted correctly that the molecule should be paramagnetic. This property of O_2 became later, for some obscure reasons, associated with one of the 'fundamental failures' of VB theory.

The work of *Hückel* in the early 1930s converted MO theory into a widely applicable tool, albeit its impact was felt only later, in the 1950s [18]. In 1930, *Hückel* [19a] extended *Lennard-Jones*'s MO treatment to C=X (X = C, N, O) double bonds and suggested the σ-π separation. Based on his results, *Hückel* ascribed the restricted rotation in ethylene to the π-type orbital. Using this notion of σ-π separability, he turned, then, to solve the electronic structure of benzene using both *HL*VB theory and his new *Hückel*-MO (HMO) approach; the latter method gave better results and, hence, was preferred [19b]. In addition to its esthetic resolution of the experimental findings, which had led *Kekulé* to propose his oscillating scheme of two structures, the HMO picture offered a simple rationale for the special stability of benzene (*Scheme 2, a*). Thus, the molecule was shown to have a closed-shell π component, and its energy was found to be lower relative to three isolated π bonds in ethylene, by the quantity $2|\beta|$, which is the resonance energy (*RE*) due to cyclic delocalization. The treatment of the ion-molecules of C_5H_5 and C_7H_7, as well as the molecules C_4H_4 (CBD) and C_8H_8 (COT), in the same paper, enabled *Hückel* to understand why molecules with six π electrons have special stability, and why molecules like COT or CBD should not possess this stability (the term anti-aromaticity was coined much later). Already in this paper and in a subsequent one, *Hückel* [19c] laid the foundations for what became later known as the '*Hückel* Rule', regarding the special stability of 'aromatic" molecules with $4n+2$ π electrons [15].

Two years later, *Pauling* and *Wheland* [20] applied the *HL*VB theory to benzene, using the σ-π separability suggested by *Hückel*, but devising a more efficient computational approach compared with his *HL*VB treatment. They used all the five canonical structures, in *b* in *Scheme 2*, and approximated the matrix elements between the structures by retaining only close-neighbor resonance interactions. Their approach allowed them to extend the treatment to naphthalene and to a great variety of other species. Thus, in the *HL*VB approach, benzene is described as a 'resonance hybrid' of the two *Kekulé* structures ($K_{1,2}$) and the three *Dewar* structures (D_{1-3}). The pictorial representation of the wave function, the link to *Kekulé*'s oscillation hypothesis and to *Ingold*'s mesomerism, which were known to chemists, made the *HL*VB representation very popular.

With these two seemingly different treatments of benzene, the chemical community was faced with two alternative descriptions of one of its molecular icons, and this began

Scheme 2



the VB–MO rivalry that seems to accompany chemistry into the 21st Century. Interestingly, already back in the 1930s, *Slater* [1] and *van Vleck* and *Sherman* [21] stated that, since the two methods ultimately converge, it is senseless to argue on the issue of which one is the better theory. Unfortunately, however, this advice does not seem to have made much of an impression. The rivalry was in part personal (*e.g.*, *Pauling vs. Mulliken*, their disciples and supporters), and, in part, it reflected how the two theories were being conceived by a community of experimentalists, who were not necessarily conversant in theory, and who chose the theory that could have been applied instantly and still retain a useful predictive value [18].

In brief, until the end of World War II, *HL*VB and VB-resonance theories dominated the epistemology of chemists. But, perhaps due to this success, the conceptual evolution of VB theory seemed to have frozen at these simplistic levels. By the mid 1950s, VB theory started to be eclipsed by MO theory, which ultimately replaced VB theory in the paradigmatic practice of chemistry. What caused the shift was a combination of factors, of which the following two may have been decisive. First, these were the many successes of MO theory, *e.g.*, the experimental verification of *Hückel* rules, the construction of intuitive MO theories and their wide applicability for rationalization of structure and spectra, the highly successful predictive application of MO theory in chemical reactivity (the *Woodward–Hoffmann* rules [22] and *Fukui*'s [23] frontier-MO theory [23]), the instant rationalization of the bonding in exotic molecules like ferrocene [24], for which the VB theory description was cumbersome, and the development of MO *ab initio* computational techniques that made MO theory a daily tool available to all experimental chemists. On the other side, the conceptual arrest of VB theory in chemistry has crippled the predictive ability of the theory, and it started to accumulate 'failures'. Despite the fact that some of these 'failures' were not real, while others stemmed from the overly simplistic applications of VB theory, they were registered in the common wisdom as 'failures'. Even after modern VB theory has resolved all these problems, still these 'failures' stuck to the theory as such. It is deemed, therefore, necessary to try and understand these 'failures' and see them in the right perspective. Below, we focus on four most cited 'failures' of VB theory and analyze their origins and validity.

3. Often-Cited Failures of VB Theory. – *Brush* [25] discusses failures that are cited as a proof that VB theory is flawed. In our view, the main ones can be stated as follows:

a) VB Theory predicts that the O_2 molecule has a singlet ground state given by the *Lewis* structure O=O, as opposed to MO theory, which predicts correctly that the molecule is paramagnetic.

b) VB Theory wrongly predicts that CBD is stabilized by resonance much like benzene. By contrast, MO theory shows correctly that CBD has zero resonance energy and it should possess a rectangular shape, with unequal C−C bond lengths.

c) In contrast to MO theory, VB theory fails to predict the behavior of aromatic and anti-aromatic ions, such as $C_{4n+3}H_{4n+3}^{-,+}$ ($n = 0, 1$) and $C_5H_5^{-,+}$.

d) In contrast to MO theory, VB theory fails to predict that CH_4 exhibits two different ionization peaks in photoelectron spectroscopy.

4. Discussion. – All the so-called failures of VB theory are either due to misuse or to failures of very simplified versions of the theory. The hybridization–bond-pairing theory assumes that the most important energetic effect for a molecule is the electron pairing, and, hence, one should hybridize the atoms and make the maximum number of bonds – henceforth 'perfect-pairing'. The perfect-pairing approach will fail whenever other factors (see below) become equally or more important than bond pairing (*e.g.*, four-electron repulsion) [26][27]. *HL*VB theory is based on covalent structures only, and requires inclusion of ionic structures explicitly or implicitly (through delocalization tails of the atomic orbitals, as in the GVB method). In certain cases like anti-aromatic molecules, this deficiency of *HL*VB makes wrong predictions. Simple resonance theory enumerates structures without consideration of their interaction matrix elements (or overlaps). It will fail whenever the matrix element and its sign are important as in the case of aromatic *vs.* anti-aromatic molecular ions, *etc* [28]. Whereas these statements may be well recognized by many theorists, the goal here is to define the minimal level of upgrade that is needed to render these simple VB models predictive with a good degree of reliability. Such a level is an effective VB theory that is closely related to simple MO formulations [26][28][29] like the *Hückel* and extended *Hückel* theories. Elements of this effective VB theory, which will be handy in the following discussion, are presented below.

4.1. *Energetics of VB Structures.* Restricting ourselves to an effective Hamiltonian that is given as a sum of effective one-electron terms, $\mathbf{H}_{\mathrm{eff}} = \Sigma_i \boldsymbol{h}(\mathrm{i})$, much as in qualitative MO theory, we can express the binding and repulsive energies of a few archetypal situations.

Eqn. 1 gives the *HL* bond energy of two electrons in orbitals $\langle a|$ and $\langle b|$, which belong to the atomic centers A and B. The binding energy is defined relative to a nonbonded situation, the quasiclassical state, which is akin to the state of the separate atoms [26].

$$\mathrm{D_e}(\mathrm{A}^{\bullet}\!-\!{}^{\bullet}\mathrm{B}) = 2\beta S/(1 + S^2) \qquad (1)$$

Here, S is the orbital overlap $\langle a\,|\,b\rangle$, while β is the reduced-resonance integral defined in *Eqn. 2* in the same form used in qualitative MO theory:

$$\beta = h_{ab} - 0.5(h_{aa} + h_{bb})S;\ \beta < 0 \tag{2}$$

Similarly, one obtains the following expression for the repulsion energy of the triplet state (relative to the nonbonded state akin to separate atoms):

$$\Delta E_T(\mathrm{A}^{\bullet\bullet}\mathrm{B}) = -2\beta S/(1-S^2) \tag{3}$$

Thus, the triplet repulsion arises due to the *Pauli* exclusion rule and is often referred to as a *Pauli* repulsion.

For a situation where we have four electrons on the two centers, VB theory predicts a doubling of the *Pauli* repulsion, and the following expression is obtained by complete analogy to qualitative MO theory:

$$\Delta E(\mathrm{A}::\mathrm{B}) = -4\beta S/(1-S^2) \tag{4}$$

One can, in fact, generalize very simply the rules for *Pauli* repulsion. Thus, the electronic repulsion in an interacting system is equal to the quantity,

$$\Delta E_{\mathrm{rep}} = -n\beta S/(1-S2) \tag{5}$$

n being the number of electrons with identical spins on the centers A and B.

Consider now VB structures with three electrons on two centers, $(\mathrm{A}{:}^{\bullet}\mathrm{B})$ and $(\mathrm{A}^{\bullet}{:}\mathrm{B})$. The interaction energy of each one of these structures by itself is repulsive and, according to *Eqn. 5*, will be given by the *Pauli* repulsion term in *Eqn. 6:*

$$\Delta E((\mathrm{A}{:}^{\bullet}\mathrm{B}) \text{ and } (\mathrm{A}^{\bullet}{:}\mathrm{B})) = -2\beta S/(1-S2) \tag{6}$$

4.2. *Mixing Rules for VB Structures.* Whenever a wave function is written as a normalized resonance hybrid, *e.g.*, as in *Eqn. 7*, the energy of the hybrid is given by the normalized averaged self-energies of the constituent resonance structures and the interaction matrix element, H_{12}, between the structures in *Eqn. 8*.

$$\Psi = N\,[\Phi_1 + \Phi_2];\ N = 1/[2(1+S_{12})]^{1/2} \tag{7}$$

$$\mathrm{E}(\Psi) = N^2[E_1 + E_2] + 2N^2 H_{12};\ H_{12} = \langle \Phi_1\,|\,\mathbf{H}\,|\,\Phi_2\rangle \tag{8}$$

$$RE = H_{12}{}^{\mathrm{eff}} = \{H_{12} - 0.5[E_1 + E_2]S_{12}\}/(1+S_{12});\ S_{12} = \langle \Phi_1\,|\,\Phi_2\rangle \tag{9}$$

The resonance energies (RE; *Eqn. 9*) refer to the effective matrix element of many-electron wave functions, and, like in MO-based approaches, here, too, there exist rules for deriving matrix elements, called generalized *Slater–Condon* rules [30]. In terms of our effective VB theory, all the matrix elements can be related to the reduced resonance integral, β, defined above in *Eqn. 2*. However, in VB theory, these matrix elements are signed by the same sign as the overlap between the VB structures. A systematic derivation of these effective matrix elements was discussed before [28][29][31], while, for the purposes of the present paper, it suffices to focus on the following two situations:

Situation 1: This resonating situation involves two VB structures that can be generated from one another by transferring a single electron between two adjacent atomic centers, A and B. Such cases occur in resonance mixing between covalent and ionic structures and in cases of mixed valency (where the average number of electrons per orbital is noninteger) that involve single electrons hopping between centers [28][31], *e.g.*, from a doubly occupied orbital to a singly occupied one, or from a singly occupied orbital to a vacant one. In all these cases, the effective interaction matrix element is proportional to the reduced resonance integral, β_{ab} ($\beta_{ab} < 0$) of the orbitals, which are different in the two structures, as given by *Eqns. 10a* and *10b:*

$$H_{12}^{\mathrm{eff}}\ (\text{singlet spin}) = (-1)^{n-1}(-1)^{s}\,\beta_{ab};\ s = N_p - 1 \tag{10a}$$

$$H_{12}^{\mathrm{eff}}\ (\text{triplet spin})) = (-1)^{n}(-1)^{s}\,\beta_{ab};\ s = N_p - 1 \tag{10b}$$

However, these matrix elements are assigned signs that can be deduced systematically as described in detail before [28][31]. To avoid a lengthy digression, we have devised here a recipe to obtain the right sign for a given case. As seen in *Eqns. 10a* and *10b*, the sign of the matrix element is set by n, the occupancy of the orbital from which the electron is transferred, and by the number of electron pairs, N_p, that have to be reorganized as a result of the single-electron transfer, as well as by the spin state of the VB structures. For any given n and N_p, the singlet and triplet matrix elements have opposite signs, which arise from the different symmetries of the space parts of these spin states.

Eqns. 10a and *10b* are valid for even-electron systems, and two applications of this resonating situation are discussed later to predict the properties of anti-aromatic and aromatic cyclic ions. These expression apply also to radical species, if one uses a dummy radical at infinity, coupled to the real radical species in a singlet state that obeys *Eqn. 10a*. To exemplify this point, let us consider two odd-electron bonding situations: a one-electron bond ($A^{+}\ {}^{\bullet}B \leftrightarrow A^{\bullet}\ {}^{+}B$) and and a three-electron bond ($A^{\bullet}{:}B \leftrightarrow A{:}{}^{\bullet}B$). Coupling, in each case, the unpaired electron to a distant dummy center, $\bullet X$, as in *Scheme 3*, we get a positively signed β in the case of the one-electron-bonding ($N_p = 1$, $n = 1$) and a negatively signed β in the three-electron-bonding situation ($N_p = 1, n = 2$). Simple algebra shows that the overlap between the two VB structures is equal to S (the $\langle a\,|\,b\rangle$ orbital overlap) in each case, so that the resonance energy follows *Eqn. 11:*

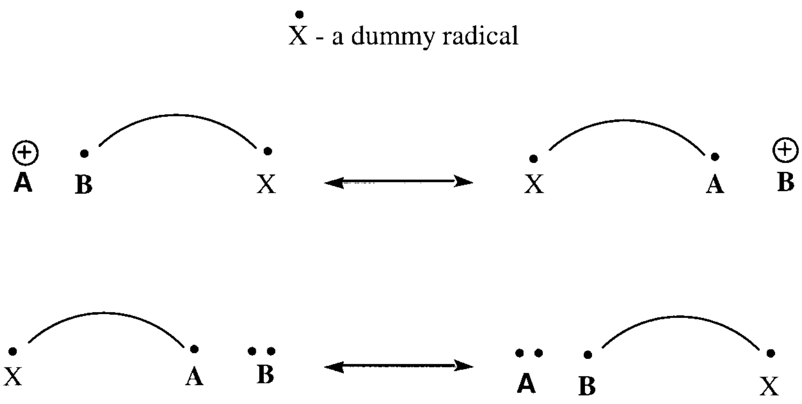
$$RE = \beta/(1+S) = D_e(A^{+}\ {}^{\bullet}B \leftrightarrow A^{\bullet}\ {}^{+}B) \tag{11}$$

Eqn. 11 also gives the bonding energy of a one-electron bond. Combining *Eqns. 11* and *6*, we get the bonding energy of the three-electron bond (*Eqn. 12*):

$$D_e(A^{\bullet}{:}B \leftrightarrow A{:}{}^{\bullet}B) = -2\beta S/(1-S^2) + \beta/(1+S) = \beta(1-3S)/(1-S^2) \tag{12}$$

Three-electron bonding will be discussed later in the case of the O_2 molecule.

Scheme 3



Situation 2: The resonating situation typifies all cases of monovalency (with one electron per orbital). In these situations, the VB structures can be obtained from one another by shifting electron pairs between adjacent bonds, as in benzene or CBD. For these cases, the interaction matrix element is proportional to $\beta_{ab}S_{ab}$ of the orbitals that constitute the electron-pair bond, as given by *Eqn. 13:*

$$H_{12} = C\,(-1)^s \beta_{ab} S_{ab};\; s = N_p - 1 \tag{13}$$

Here, C is a proportionality factor that depends on the minimal number of shifts that are needed to generate one VB structure from the other [29]. The sign of the matrix element depends, in turn, on the number of electron pairs, N_p, which are being shifted on going from one structure to the other [29]. For example, for CBD $N_p = 2$, and, hence, the matrix element is negatively signed, while for benzene $N_p = 3$ and the matrix element is positively signed.

With this minimal set of rules for the application of VB theory, we now proceed to consider the selected VB 'failures'.

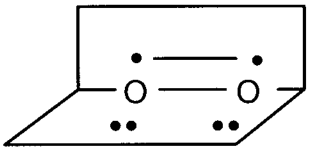
4.3. *The Ground State of the O_2 Molecule.* One of the major 'failures' is associated with the ground state of the dioxygen molecule, O_2. It is doubtful that this so-called failure can be attributed to *Pauling* himself, because, in his landmark paper, *Pauling* [10] described the molecule with two three-electron bonds (*c* in *Scheme 1*), and so did *Wheland* [32] on p. 39 of his book. Neither *Pauling* nor *Wheland* explained their choice for this type of bonding. By contrast, in a 1934 *Nature* paper, *Heitler* and *Pöschl* [33] considered the O_2 molecule with VB principles and argued lucidly in favor of a triplet ground state. They started with the coupling of two ^{3}P O-atoms in the *HL* manner into singlet and triplet states. Then, they considered the effect of mixing in of higher terms, the lowest of which is the ^{3}P,^{1}D coupling situation of the two atoms. Since this latter coupling has only a triplet situation, it will mix only into the triplet state, which is nascent from the ^{3}P,^{3}P coupling and stabilize it preferentially over the corresponding singlet state. Accordingly, they concluded, '*The* $^3\Sigma_g^-$ *term* [is the one] *giving the fundamental state of the molecule*'.

It is beyond us how the myth of this 'failure' grew and spread so widely to be accepted almost unanimously (see Footnote 112 in *Brush* [15]). It is true that a naïve application of hybridization followed by perfect pairing (simple *Lewis* pairing) would predict a $^1\Delta_g$ ground state, *i.e.*, the diamagnetic doubly bonded molecule O=O. This is likely the origin of the notion that VB theory makes a flawed prediction that contradicts experiment (see, *e.g.*, [2]). However, in all seriousness, this attitude is not particularly scientific, since, already in the early 1970s, *Goddard et al.* [34] performed GVB calculations and demonstrated that VB theory leads to a triplet $^3\Sigma_g^-$ ground state. This was followed by the same outcome in papers by *McWeeny* [35] and *Harcourt* [36]. In fact, any VB calculation, at whatever imagined level, would lead to the same result, so that the myth of 'failure' is definitely baseless.

Goddard et al. [34] and, subsequently, the present two authors [26] provided also a simple VB explanation for the choice of the ground state. Let us provide this explanation based on our qualitative VB theory, outlined above.

O_2 possesses six π electrons, which can be arranged in two distinct bonding situations shown in **1** and **2** (*Scheme 4*) where the two planes signify the π planes, and the line connecting the O-atoms corresponds to the σ bond (σ lone-pairs are omitted). Structure **1** is a perfect pairing configuration, in which the O-atoms maintain a double bond between them, and the remaining 4π electrons reside in the plane perpendicular to the π bond. Structure **2** is the diradical-bonding alternative, where the six π electrons are distributed in the two π planes and form two mutually perpendicular three-electron π bonds. Let us for a moment postpone the assignment of the spin states, and establish first the intrinsic energy factors of the two electronic distribution schemes in **1** *vs.* **2**; namely perfect pairing *vs.* diradical bonding.

Scheme 4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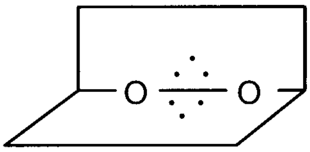
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Since the σ bond appears in both structures, we may disregard this bond and estimate only the difference in π-electronic contribution to bonding. Using the effective VB expression for the two-electron bond (*Eqn. 1*) and the four-electron expression (*Eqn. 4*), we can express the net bonding energy of the perfectly paired structure, **1**, by *Eqn. 14*. Similarly, since the diradical structure, **2**, possesses two three-electron bonds, its total bonding energy becomes twice the three-electron bond energy (*Eqn. 12*), as written in *Eqn. 15*. Finally, the energy difference of the two VB structures is given by *Eqn. 16*.

$$E(\mathbf{1}) = 2\beta S/(1+S^2) - 4\beta S/(1-S^2) \tag{14}$$

$$E(\mathbf{2}) = 2\beta\,(1-3S)/(1-S^2) \tag{15}$$

$$E(\mathbf{1}) - E(\mathbf{2}) = -2\beta\,(1-S)^2/(1-S^4) > 0 \tag{16}$$

It is seen that the energy of the perfect-pairing state, $E(\mathbf{1})$ in *Eqn. 14*, depends on the balance between the π bond and the 4-electron π repulsion in the perpendicular plane. On the other hand, the energy of the diradical alternative, $E(\mathbf{2})$ in *Eqn. 15*, is a sum of the two three-electron π bonds and will be stabilizing, as long as the p_π-p_π overlap does not exceed the critical value of 1/3, which is certainly true for the O–O case for which $S_{\pi\text{-}\pi} = 0.1454$ (with *Slater* orbitals). *Eqn. 16* refers to the energy difference between the two bonding options, and shows decisively that, since the reduced resonance integral is negative, the energy of the diradical bonding is lower than that of the perfect-pairing state for any value of atomic overlap. Therefore, the ground state of O_2 is predicted to be of diradical nature, in agreement with experiment.

Of course, our effective VB theory was chosen to disregard the bielectronic terms and, therefore, the theory, as such, will not tell us what is the lowest spin state in the O_2 diradical. This, however, is a simple matter, because further consideration can be made by calling into play *Hund*'s rule, which is precisely what qualitative MO theory has to do in order to predict the triplet nature of the O_2 ground state. Thus, among the two diradical states of the general type **2**, the triplet $^3\Sigma_g^-$ state is the lowest. The remaining excited states can be constructed from symmetry-adapted combinations of **1** and **1′** (the latter is analogous to structure **1** with inverted electron distribution in the two planes) by inclusion of electron-repulsion terms. This is, however, really out of context in the present paper, and the reader is referred to the explanations in the original literature.

What is more of interest, here, is to establish an ability to predict such diradical bonding in other cases. It is apparent from the above analysis that a major factor of the relatively high energy of the perfect-pairing situation, **1**, is the four-electron overlap repulsion. On the other hand, the resonating perpendicular three-electron bonds in **2** allow to get rid of the overlap repulsion and to replace it by net three-electron bonding. We may, therefore, say that O_2 adapts the diradical-bonding option to avoid the overlap repulsion in the perfect pairing alternative.

The application of this simple principle enables us to reason about ground-state bonding in more-complex situations than O_2, *e.g.*, in the iron oxide cation, FeO^+. The qualitative VB guideline shows that the perfect-pairing bonding between O(^{3}P; s^2p^4) and Fe^+ (^{6}D;s^1d^6) encounters overlap repulsion of the d_π-p_π type, and, consequently, FeO^+ should prefer the diradical-bonding option, in the high-spin $^6\Sigma^+$ state, over the lower spin states that maintain perfect pairing. Indeed, high-level *ab initio* calculations show that FeO^+ assumes a $^6\Sigma^+$ ground state, with a bonding block consisting of a σ bond and two mutually perpendicular three-electron π bonds [37]. In fact, the FeO bond of the active species of heme enzymes and their artificial analogs has an O_2-like bonding, which plays an interesting role in oxidation of organic compounds by these enzymes [38]. Furthermore, other metal oxide cations, NiO^+ and CoO^+, follow this prediction too and prefer, in their ground states, diradical bonding over perfect pairing [37].

4.4. *Benzene and Cyclobutadiene.* A second highly cited 'failure' of VB theory concerns the treatments of anti-aromatic molecules such as CBD and COT *vs.* benzene. Both CBD and COT can be expressed as resonance hybrids of their respective *Kekulé*-type structures. Indeed, *HL*VB calculations of CBD by *Wheland* [39] predicted the molecule to have resonance energy (*RE*) as large as or larger than that of benzene. Later, it became evident that, unlike benzene, which is stable and has a D_{6h} structure with uniform C–C bond lengths, CBD and COT are neither stable nor do they assume structures with uniform C–C distances. This conjecture about the properties of CBD and COT constitutes a failure of *HL*VB and of resonance theory. The failure gained added significance by comparison with the successful prediction of HMO for the same molecules. What is the true nature of this failure of *HL*VB and resonance theories?

In his 1934 and 1938 papers, *Wheland* [39] argued that the different descriptions of CBD by *HL*VB and HMO theories are due, in part, to the different accounting of ionic structures. Whereas *HL*VB neglects ionic structures completely, HMO incorporates them with significant weight. Indeed, 48 years later, *Voter* and *Goddard* [40] demonstrated that GVB calculations, which implicitly include ionic structures through the delocalization tails of the orbitals [41], predict correctly the properties of CBD. Subsequently, *Gerratt et al.* [42] showed that spin-coupled VB theory predicts correctly the geometries and ground states of CBD and COT. Recently, in 2001, the authors of the present manuscript and their co-workers used VB theory to demonstrate [43] that the standard *Dewar* resonance energy (*DRE*) of CBD is negative, in accord with the most sophisticated calculations [44] as well as with a recent experimental estimate [45]. Thus, properly applied VB theory needs to include ionic structures explicitly or implicitly, and when so done, it does not fail with CBD, COT, or with any other anti-aromatic species.

Does MO theory predict successfully the properties of CBD? *Wheland* [39b] analyzed this question and showed that the success of HMO is fortuitous. Subsequently, *Craig* [46] showed that neither HMO nor more sophisticated single-determinant MO treatments could reproduce correctly the fact that the ground state of CBD is the singlet $^1B_{1g}$, unless augmented by configuration interactions (CI). He further pointed out that, in contrast to MO theory, *HL*VB theory reproduces correctly the state ordering in CBD. Clearly, the story of CBD involves two aspects, revealing that simple MO and VB theories are both equally successful and fallible. These aspects are the geometry and stability (or resonance energy) of CBD, on the one hand, and the identity of the ground state, on the other. These two aspects require a separate treatment.

The *Table* [47] shows the distortion energies of CBD and benzene from D_{nh} to rectangular $D_{(n/2)h}$ geometry at the levels of *HL*VB and VB that include all the ionic structures. It is seen that, at the *HL*VB level, both species prefer the regular polygonal structure. However, once ionic structures are allowed to mix into the covalent wave function, CBD prefers the bond-alternating rectangular geometry, while benzene still prefers to be a regular hexagon. Clearly, therefore, ionic structures are required to predict correctly the geometry of CBD. So, the *HL*VB failure in predicting correctly the geometry is due to the lack of ionicity in the wave function. However, the *Table* shows

Table. *Distortion Energies* ΔE_{dis}[a])

Species	Basis set	ΔE_{dis}	
		*HL*VB	VB + ion
C_4H_4	STO-3G	2.2	–2.6
	6-31G	1.2	–2.6
C_6H_6	STO-3G	3.3	3.0
	6-31G	3.6	4.0

[a]) In kcal/mol. Calculated as the difference between the energy at the bond-alternating geometry and the uniform geometry, $\Delta E_{\text{dis}} = E(D_{(1/2)mh}) - E(D_{mh})$. The distortion is taken as $\Delta R = 0.05$ Å from the following uniform C–C distances: C_4H_4 (1.451 Å), C_6H_6 (1.388 Å).

that the *HL*VB failure is quantitatively small, of the order of 4 kcal/mol. How can VB theory rationalize this small error?

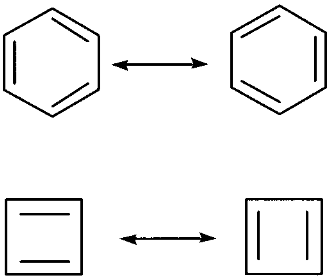
The VB diagram model that considers the crossing and resonance mixing of the *Kekulé* structures along a bond-alternating coordinate [43] shows that the geometry of a conjugated cyclic hydrocarbon is determined by a fine balance between the propensity of the σ frame to prefer equal C–C distances in a D_{nh} structure *vs.* the opposing tendency of the π system to distort to a $D_{(n/2)h}$ structure with alternating C–C bond length. In benzene, the σ frame wins over and forces delocalization of the π electrons in a regular D_{6h} geometry. In CBD, the π distortivity is slightly larger than the σ resistance [43], and the molecule distorts to a D_{2h} geometry. Indeed, we ascertained that this distortive propensity of the π electrons of CBD is present already at the *HL*VB level [47], but, relative to the full wave function where ionicity is included, the π-distortive propensity is by *ca.* 4 kcal/mol smaller. With this small change, the *HL*VB calculated π distortivity is insufficient to overcome the σ frame, and the CBD structure remains in D_{4h} symmetry.

This dependence of the π-distortive propensity on the ionicity of the wave function is predictable based on the same VB diagrammatic arguments, which revealed the π distortivity in the first place [43]. Thus, VB theory predicts that the π-distortive propensity will increase as the energy of the short π bond in the *Kekulé*-type structures increases [43]. Since inclusion of the ionic structures in CBD strengthens the short π-bonds in these *Kekulé*-type structures, the π distortivity increases by a small amount that is just sufficient to tip the balance in favor of the distortion. This fine balance is expressed very nicely in the geometry of anti-aromatic molecules like *s*-indacene, pentalene, and their derivatives, as shown by *Dunitz et al.* [48a], *Heilbronner* and *Yang* [48b], and *Heilbronner* and *Shaik* [48c].

Much like simple VB theory [43], HMO theory also predicts that the occupied π-MOs of CBD are stabilized by the $D_{4h} \rightarrow D_{2h}$ distortion, due to the pseudo-*Jahn–Teller* effect. However, a proper application of HMO theory, with a variable β parameter, reveals that the π energy of benzene has also an inherent preference to distort from the D_{6h} structure to D_{3h} [49]. It follows, therefore, that HMO theory can actually predict the rectangular distortion of CBD as opposed to the stable hexagonal geometry of benzene, only when the theory makes the tacit assumption that the σ frame of CBD yields to the distortive π propensity, whereas, in benzene, the σ frame overcomes this π distortivity. Does MO theory predict better than VB theory the geometry of CBD *vs.* benzene? In all honesty, based on the above analysis, the answer is no.

Let us turn now to discuss the resonance energy (*RE*) of CBD *vs.* benzene. As noted already, *HL*VB theory predicts similar *RE*s for the two molecules. However, *HL*VB uses an energy parameter (*J*, in *Scheme 2*), calibrated from the *RE* of benzene, to calculate the *RE* of CBD, and makes, thereby, a quantitative error. It was already pointed out by *Craig* [46] that the parameter used for CBD should be smaller than that of benzene. Be however the parameter what it may, VB theory predicts that CBD should have a nonzero *RE*. Indeed, the resonating GVB treatment of CBD by *Voter* and *Goddard* [40] reveals a significant *RE* of the order of 21 kcal/mol.

To understand this result, we must distinguish here between two different *RE* quantities, which are displayed in *Fig. 1* for CBD and benzene, based on our recent study [43]. One is the vertical *RE* (*VRE*), which is the *RE* between the two VB structures at the regular D_{nh} symmetry with identical C−C bonds. The other is the *Dewar RE* (*DRE*), which is the standard resonance energy used by organic chemists [44], by reference to an imaginary polyene with the same number of π-conjugative interactions as the polygon. It is seen from *Fig. 1* that CBD has a significant *VRE*, *ca.* 1/3 of the value for benzene. The *VRE* of benzene was estimated long ago by *Hornig* [50] from experimental data, and the correspondence of the VB-calculated and experimentally estimated quantities appears to be very good. The VB-computed *DRE* for benzene is smaller than the corresponding *VRE*, but still substantial, *ca.* 20.4 kcal/mol, and this is, again, in good agreement with an experimental estimate based on heats of formation [51], as well as with all best MO estimates [44]. In contrast, the *DRE* of CBD is highly negative, in accord with the recent experimental estimate of *Deniz et al.* [45]. However as they and we argued, much of this negative value originates in strain and π-π *Pauli* repulsion in the VB structure of CBD relative to the imaginary reference. Subtracting these effects, the net $DRE(\pi)$ for CBD can be estimated according to VB theory as *ca.* −13 kcal//mol, again, in line with accepted wisdom [51].



VRE/kcal/mol	*DRE*/kcal/mol
65 (exper. 65)	20.4 (exper. 21)
22	−70 (exper. − 87 ± 11)

Fig. 1. *Vertical resonance energies* (*VRE*) *and* Dewar *resonance energies* (*DRE*) *for benzene and cyclobutadiene*

What does MO theory predict for CBD? At the simplest level, HMO theory predicts a zero *RE*, as opposed to the substantial *RE* of 2β predicted for benzene. Only a more-advanced method devised by *Dewar* and *Gleicher* [52], and, certainly, sophisticated MO-CI methods led to the correct *DRE* prediction for CBD [44]. However, the early prediction of zero *RE* by HMO and the 'matching' experimental elusiveness of CBD created the everlasting impression that HMO theory truly makes a correct prediction.

In fact, in his 1938 paper, *Wheland* [39b] pointed out that HMO theory succeeds for the wrong reasons. To understand *Wheland*'s argument, consider the MOs of CBD in *Fig. 2*. With this set of orbitals, the lowest singlet state can be constructed from a linear combination of the closed-shell configurations, $\phi_1^2\phi_2^2$ and $\phi_1^2\phi_3^2$, *i.e.*:

$$\Psi_0\,(\mathrm{HMO}) = 2^{-1/2}[\phi_1^2\phi_2^2 - \phi_1^2\phi_3^2];\ E(\mathrm{HMO}) = 2\alpha + 2\beta \qquad (17)$$

Now, each one of these configurations has a *Hückel* energy of $2\alpha + 2\beta$, and, since HMO theory neglects bielectronic terms, the energy of the linear combination in *Eqn. 17*

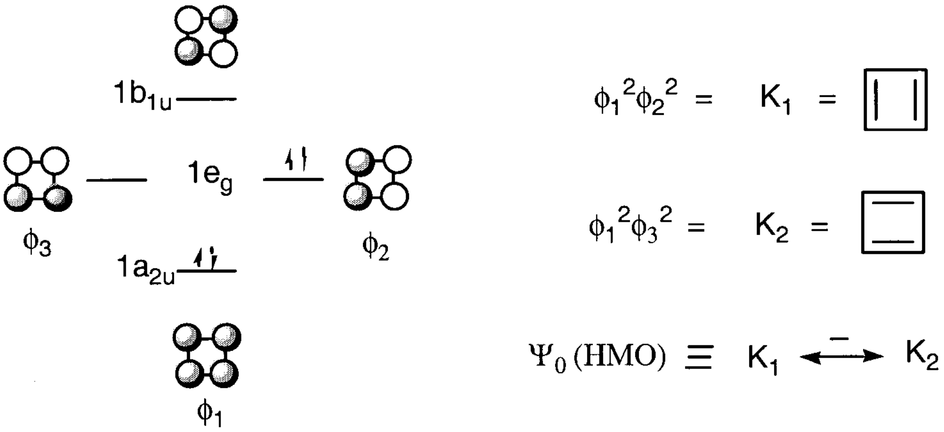


Fig. 2. *The two-configuration wave function of cycobutadiene in the MO framework, and its translation to VB forms*

remains of $2\alpha + 2\beta$. With this energy of the singlet state, HMO theory predicts a zero *RE*, which appears to be a successful prediction of the instability of this species.

The conclusion, however, is not so straightforward. To appreciate this point, the orbitals ϕ_i $(i = 1-3)$ can be re-expressed as sums and differences of the π orbitals of the isolated double bonds on the edges of CBD. With these orbital expressions, it is easily shown that $\phi_1^2\phi_2^2$ corresponds to one VB structure, while $\phi_1^2\phi_3^2$ to the other, as depicted on the right-hand side of *Fig. 2*. This means that the physically correct MO wave function in *Eqn. 17* is precisely the resonance hybrid of VB theory, albeit the isolated π bonds in the MO hybrid are described by doubly occupied π-MOs and not by VB bond-pairs. Despite this equivalence, *Hückel* theory predicts $RE = 0$ for this resonance hybrid, whereas *ab initio* calculations show that, for this particular hybrid, *RE* is significant [40].

Thus, the apparently successful HMO prediction of zero *RE* is fortuitous, and arises due to the inadequacy of HMO theory for treating CBD. In reality, both VB and MO theories predict that CBD has a significant *VRE* at the D_{4h} geometry.

Let us turn now to the second aspect, the identity of the ground state of CBD. *Craig* [46] already showed that *HL*VB theory assigns correctly the ground state of CBD, as the $^1B_{1g}$ state, in contrast to monodeterminental MO theory, which makes a wrong assignment of the ground state as the triplet $^3A_{2g}$ state. Indeed, at the *Hartree-Fock ab initio* level, the ground state is the triplet $^3A_{2g}$ state [40]. Only after configuration interaction (CI) does one get that the correct assignment for the ground state is the singlet $^1B_{1g}$ state [40][46]. This violation of *Hund*'s rule by CBD was explained by *Borden* [53] using the disjointed set of the $1e_g$ degenerate orbitals (*Fig. 3*), which can be made from linear combinations of ϕ_2 and ϕ_3 (shown in *Fig. 2*). With these orbitals, the advantage of the triplet $^3A_{2g}$ state over the singlet $^1B_{1g}$ due to exchange is very small (*ca.* 4 kcal/mol), and, since singlet configurations are more numerous, CI lowers the singlet $^1B_{1g}$ and violates *Hund*'s rule.

Rather simple arguments of VB theory can lead to the same conclusions as MO-CI theory. In *Fig. 3,b*, we show the argument used before by *Epiotis* [54], and by *Voter* and

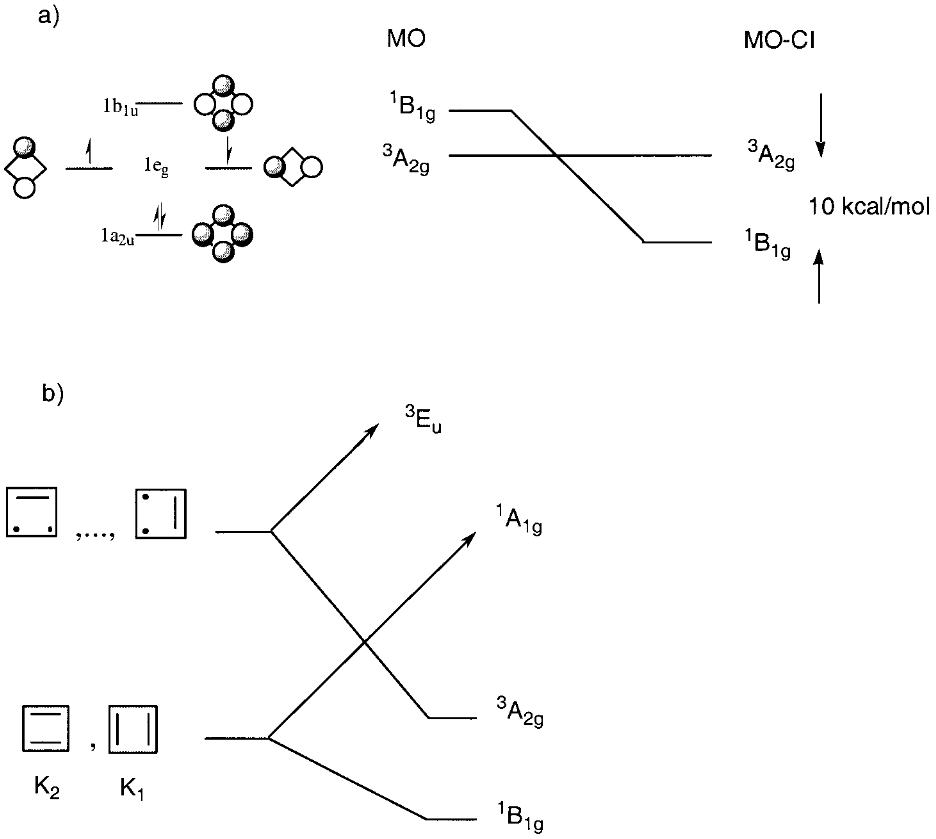


Fig. 3. *Singlet–triplet ordering in cyclobutadiene:* a) *in the MO framework;* b) *in the VB framework*

Goddard [40]. Thus, to create a triplet state, we must unpair the electrons in one of the double bonds of the singlet VB structure. This unpairing is costly (see *Eqns. 1* and *3*) since we replace a bond pair by a *Pauli* repulsion. The resonance mixing of the singlet and triplet VB structures conserves this initial excitation gap and generate a singlet ground state.

A related question is the symmetry of the ground state, which is not totally symmetric but rather the singlet $^1\mathrm{B}_{1g}$ state. This can be deduced quite easily from the mixing rule in *Situation 2* above. Thus, according to *Eqn. 10*, since the number of electron pairs in CBD is two, the interaction matrix element between the VB structures is negatively signed. Since β itself is a negative quantity, it follows that the interaction matrix element is positive. As such, the ground-state is the negative combination of the two structures, which, in this case, is the bonding combination. If we label these VB structures as K_1 and K_2, the normalized wave function becomes:

$$\Psi_0(\mathrm{CBD}) = N\,[\mathrm{K}_1 - \mathrm{K}_2]\ \Gamma(\Psi_0) = \mathrm{B}_{1g} \qquad (18)$$

The irreducible representation (*Γ*) of this combination is B_{1g}, while the positive combination gives rise to the $^1A_{1g}$ state that lies considerably higher in energy, *ca.* > 50 kcal/mol, which is more than twice the value of the *VRE* in *Fig. 1*, as expected for mixing of two overlapping structures [28].

VB Theory provides also an interesting rationale of the kinetic instability of CBD [43]. It shows that the very small barrier for dimerization of CBD arises not so much from the 'inherent instability' of the ground state, as much as from the fact that the triplet state of CBD is very stabilized and hence so low-lying (for its own intrinsic electronic factors).

Does VB theory really fail with CBD? And does MO theory really make better predictions than VB theory? Not really. The truth is that CBD, COT, and other neutral anti-aromatic compounds pose a tough problem for both theories at their simplest levels, and one needs to go to higher levels of calculations and higher modes of thinking to obtain correct answers.

4.5. *Anti-Aromatic and Aromatic Ions.* Simple resonance theory that merely enumerates resonance structures fails completely to predict the fundamental differences between, *e.g.*, $C_5H_5^+$ and $C_5H_5^-$, $C_3H_3^+$ and $C_3H_3^-$, and $C_7H_7^+$ and $C_7H_7^-$, *etc.* Hence, a decisive defeat was dealt to VB theory when, during the 1950s and 1960s, organic chemists were finally able to synthesize these transient molecules and establish their stability patterns. The results, which followed *Hückel* rules, convinced most of the organic chemists that *HL*VB and resonance theories were wrong. This era in organic chemistry marked a terminal demise of VB theory, because it showed that, at their simplest levels, one theory, VB, fails whereas the other, HMO, makes useful predictions. The question that we would like to pose here is: is it true actually that a simple VB theory is unable to distinguish aromatic and antiaromatic species?

In fact, in 1963 *Fischer* and *Murrell* [55] showed that the stability patterns of the above molecular ions follow naturally from resonance theory when one considers the sign of the matrix element between the resonanting VB structures. The same problem was treated subsequently by *Epiotis* [56] and by one of us [28]. Herein, we use the simple rules given by *Eqns. 10a* and *10b* to demonstrate the facility of VB theory in dealing with the problem of aromaticity/anti-aromaticity in molecular ions [28].

As an example, we compare the singlet and triplet states of the cyclopropenium molecular ions, $C_3H_3^+$ and $C_3H_3^-$, in (*Figs. 4* and *5*). The VB configurations needed to generate the singlet and triplet states of the equilateral triangle $C_3H_3^+$ are shown in *Fig. 4*. It is seen that the structures can be generated from one another by shifting single electrons from a singly occupied p_π orbital to a vacant one, and, in each case, a single pair of electrons has to switch position ($n = 1$ and $N_p = 1$ in *Eqns. 9a* and *9b*). Using *Eqns. 10a* and *10b*, we deduce that the matrix element between any pair of structures with singlet spins is $+\beta$, while, for any pair with triplet spin, the matrix element is $-\beta$. The corresponding configurations of $C_3H_3^-$ are shown in *Fig. 5*. In this case, since we now are shifting an electron from a doubly occupied orbital to a singly occupied one ($n = 2$ in *Eqns. 10a* and *10b*), the signs of the matrix elements are inverted compared with the case of the cyclopropenium cation, and are $-\beta$ for any pair of singlet VB structures, while $-\beta$ for any triplet pair of structures.

If we symbolize the VB configurations by heavy circles we can present these resonance interactions graphically, as shown in the mid-parts of *Figs. 4* and *5*. These

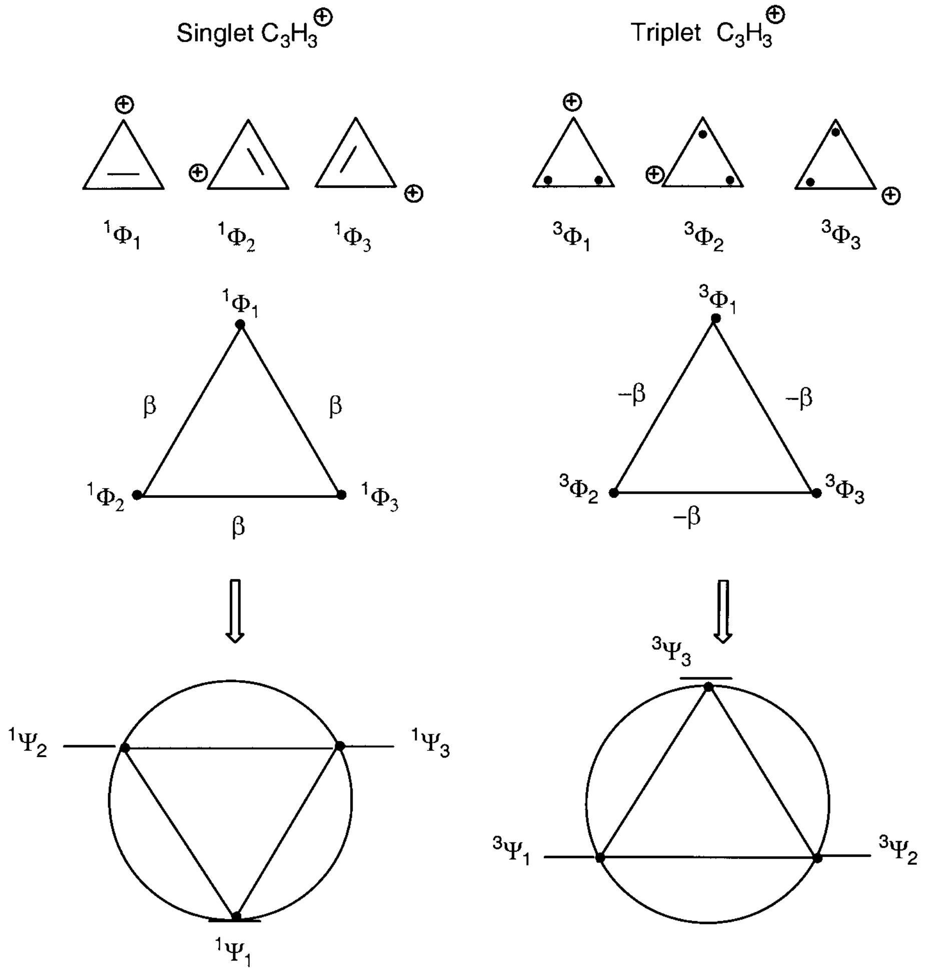


Fig. 4. *Singlet- and triplet-state energies for the $C_3H_3^+$ cation in the VB framework*

interaction graphs are all triangles and have the topology of corresponding *Hückel* and *Möbius* AO interactions [57]. Of course, we could go ahead to diagonalize the corresponding *Hückel–Möbius* matrices and obtain energy levels and wave functions. There is, however, a shortcut based on the well-known mnemonic of *Frost* and *Musulin* [58]. Thus, the triangle is inscribed within a circle having a radius $2\,|\beta\,|$, and the energy levels are obtained from the points where the vertices of the triangle touch the circle. As shown by this mnemonic for the VB mixing, the ground state of $C_3H_3^+$ is a singlet state, while the triplet state is higher-lying and doubly degenerate. In contrast, the ground state of $C_3H_3^-$ is a triplet state, while the singlet state is higher-lying, doubly degenerate, and hence *Jahn–Teller*-unstable. Thus, $C_3H_3^+$ is aromatic, while $C_3H_3^-$ is anti-aromatic [28].

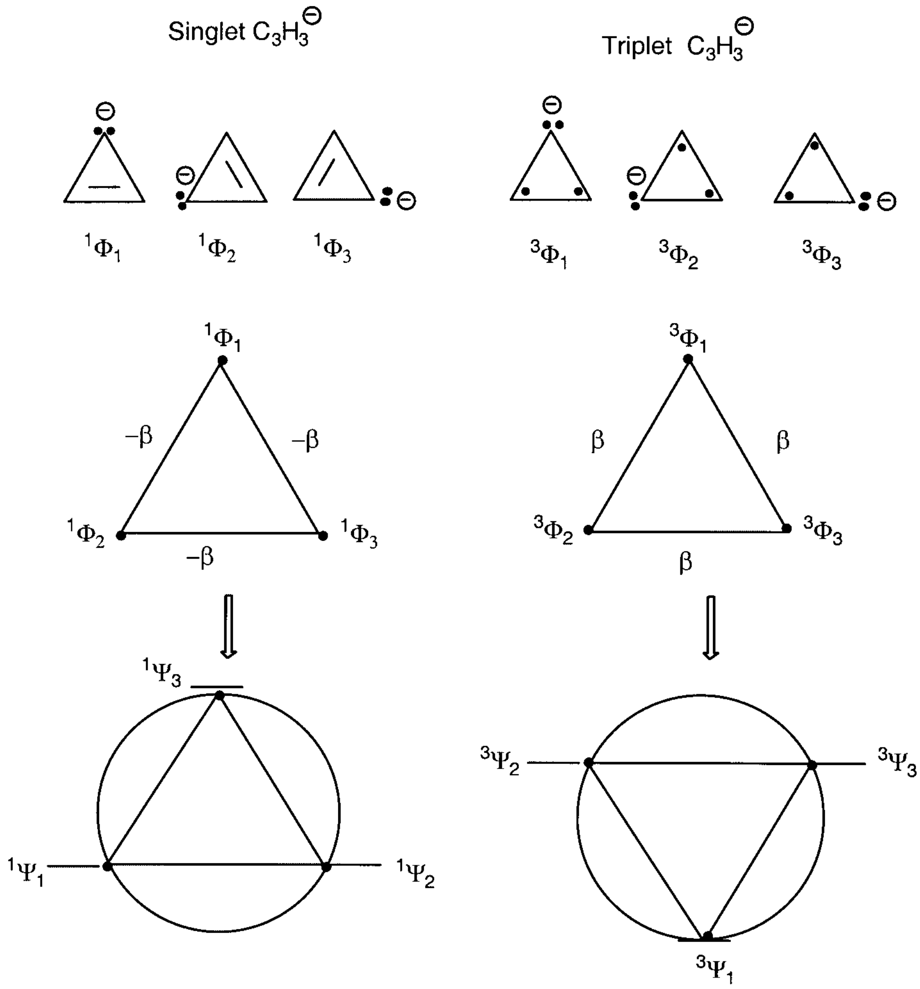


Fig. 5. *Singlet- and triplet-state energies for the $C_3H_3^-$ anion in the VB framework*

In a similar manner, the VB states for $C_5H_5^+$ and $C_5H_5^-$ can be constructed with *Eqns. 10a* and *10b* for the matrix elements and the corresponding VB-mnemonic. Restricting the treatment to the lowest energy structures, there remain five structures for each spin state, and the sign of the matrix elements will be inverted compared to the $C_3H_3^{+,-}$ cases. Now the cation will have $-\beta$ matrix elements for the singlet configurations and $+\beta$ for the triplets ($n = 1$ and $N_p = 2$ in *Eqns. 10a* and *10b*), while the anion will have precisely the opposite signs ($n = 1$ and $N_p = 2$ in *Eqns. 10a* and *10b*). The VB-mnemonics will show instantly that $C_5H_5^-$ possesses a singlet ground state, and, by contrast, $C_5H_5^+$ has a triplet ground-state whereas its singlet state is higher in energy and *Jahn–Teller*-unstable. Now, in the cyclopentadienyl ions the cation is anti-aromatic while the anion is aromatic. Moving, next, to the $C_7H_7^{+,-}$ species, the sign patterns of the matrix element will invert again and be as those in the corresponding $C_3H_3^{+,-}$ cases. As such, the VB-mnemonic will lead to similar conclusions, *i.e.*, the cation is aromatic, while the anion is anti-aromatic with a triplet ground state.

Clearly, a rather simple VB theory is required to reproduce the rules of aromaticity and anti-aromaticity of the molecular ions, and to provide the correct relative energy levels of the corresponding singlet and triplet states. This VB treatment is virtually as simple as HMO theory itself, with the exception of the need to know the sign of the matrix element. However, learning this feature of VB theory is not necessarily more complicated than has been the learning of HMO theory itself.

4.6. *The PES of Methane.* The development of photoelectron spectroscopy (PES) and its application to molecules in the 1970s showed that the spectra could be easily interpreted when one assumed that electrons occupy delocalized molecular orbitals [59][60]. In contrast, VB theory seems completely useless for interpretation of PES. All the more, since VB theory describes electron pairs that occupy localized bond orbitals, the PES results often serve to dismiss VB as a wrong theory that describes electronic structure in discord with experiment. An iconic example of this 'failure' of VB theory is the PES of methane, which displays two different ionization peaks. These peaks correspond to the a_1 and t_2 MOs, but not to the four equivalent C–H bond orbitals in *Pauling*'s hybridization theory.

It is remarkable that this 'failure' survives to this day (see a recent paper on a similar issue [61]) and discussed in books in this context, even when the conclusions in these books are rather favorable for VB theory [62][63]. The persistence is remarkable because it has been known since the 1930s that localized bond orbitals (LBOs) for methane or any molecule can be obtained by a unitary transformation of the delocalized MOs [64]. Thus, both MO and VB descriptions of methane can be cast in terms of LBOs, and, hence, both theories fail when we insist on using the naïve argument that four LBOs cannot yield two ionization peaks in PES.

In fact, the LBO picture is absolutely 'kosher' in both MO and VB theories. Thus, if one starts from the LBO picture of methane, the electron can come out of any one of the LBOs. A physically correct representation of the CH_4^{+} cation would be a linear combination of the four forms that ascribe electron ejection from each of the four bonds. As shown by *Honegger* and *Heilbronner* [60] in MO theory, the correct physical description can be achieved by combining the LBOs back to canonical MOs.

The corresponding VB picture is illustrated in *Fig. 6*, which enumerates the VB structures that involve localized one-electron-bond situations, and, for simplicity, the other bonds are described by doubly occupied LBOs. Since the structures can be generated from one another by single-electron transfers from a doubly occupied LBO to the singly occupied LBO, one can employ a singlet coupling of the unpaired electron in the one-electron bond to a distant dummy radical (*Scheme 3*), and use *Eqn. 10a*. It follows that the matrix element between the structures is negatively signed, *i.e.*, $-\beta$ ($n = 2$, $N_p = 1$ in *Eqn. 10a*). The interaction graph of the configurations is shown below them, and it corresponds to a tetrahedron where the resonance integrals are all $-\beta$. Thus, we can simply remove the sign, use instead $\beta > 0$, and solve the *Hückel* matrix with a *Hückel* program. The final states of CH_4^{+}, shown alongside the interaction graph, exhibit a three-below-one splitting of the cationic states, a low-lying $^2A_1$ state, and above it a triply degenerate $^2T_2$ state. Thus, simple VB theory predicts correctly that methane will have two ionization peaks, one at lower IP corresponding to transition to degenerate $^2T_2$ state and one at a higher IP corresponding to transition to the $^2A_1$ state. The facility of making this prediction and its correctness highlight once more that in this story too, the 'failure' of VB theory originates more in a myth that caught on due to the naivety of the initial argument.

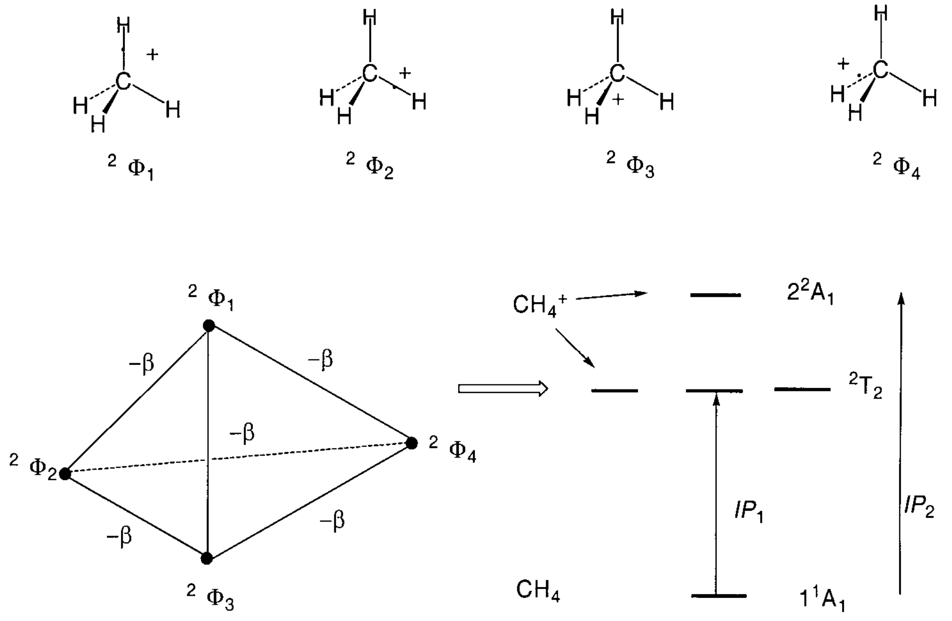


Fig. 6. *Electronic structure of the CH_4^+ radical cation in the VB framework, and corresponding ionization processes of CH_4*

5. Conclusions. – We considered in this paper four iconic 'failures' of VB theory [2][25][62]. Our treatments of these problems show that, in all cases, a rather simple level of VB theory is required to make correct predictions. Other 'failures' can be similarly discussed to reiterate the same conclusion that the basis for rejection of VB theory are not any flaws in the theory, but is part of the struggle of chemists to establish a working paradigm within the new quantum theory, and its MO and VB representations. The MO–VB rivalry may have been important once, when it was not still obvious that quantum theory contains much of chemistry, and when the rivalry sharpened the chemist's abilities to use quantum mechanics as a thinking tool in chemistry. However, what was understandable and maybe even necessary in the fifties is now obsolete, unwarranted, and counterproductive. With 70-odd years having passed since the nascence of the rivalry, today a theoretician and even an experimental chemist ought to know that there are two ways of describing electronic structure that are complementary rather than self exclusionary.

Our own philosophy has always been that the two theories are not really different. They are, rather, two representations or two guises of the same reality, which can be abridged by transforming one into the other [28][65–68]. Each pure representation has typical advantages; while MO theory is more portable in structural problems and in problems that require orbital-symmetry considerations, VB theory has an edge in questions of barrier heights and reaction mechanisms. Because of the transformability of the two representations, much of the portability of MO theory, *e.g.*, the role of orbital symmetry, can be incorporated into VB theory by rather simple means, *e.g.*, by constructing VB wave functions from fragment MOs [26][66][69]. Taken together, MO and VB theories constitute a valuable arsenal in the hands of the chemists. In fact, insistence to understand electronic structure without this complementary knowledge is crippling, and discarding any one of the two theories undermines the intellectual heritage of chemistry.

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