1 A Brief Story of Valence Bond Theory, Its Rivalry with Molecular Orbital Theory, Its Demise, and Resurgence

The new quantum mechanics of Heisenberg and Schrödinger 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, sometimes fervently, on charting the mental map and epistemology of chemistry. In brief, until the mid-1950s VB theory had dominated chemistry, then MO theory took over while VB theory fell into disrepute and was almost completely abandoned. The more recent period from the 1980s onward marked a comeback of VB theory, which has since then been enjoying a renaissance both in the qualitative application of the theory and in the development of new methods for its computer implementation (1). One of the great merits of VB theory is its pictorially intuitive wave function that is expressed as a linear combination of chemically meaningful structures. It is this feature that has made VB theory so popular in the 1930s−1950s, and it is the same feature that underlies its temporary demise and ultimate resurgence. This monograph therefore constitutes an attempt to guide the chemist in the use of VB theory, to highlight its insight into chemical problems, and some of its state-of-the-art methodologies.

Since VB is considered, as an obsolete theory, we thought it would be instructive to begin with a short historical account of VB theory, its rivalry against the alternative MO theory, its downfall, and the reasons for the past victory of MO and the current resurgence of VB theory. Part of this review is based on material from the fascinating historical accounts of Servos (2) and Brush (3,4). Other parts are not official historical accounts, but rational analyses of historical events; in some sense, we are reconstructing history in a manner that reflects our own opinions and the comments we received from colleagues, as well as ideas formed during the writing of the recent ''conversation'' the two authors have published with Roald Hoffmann (5).
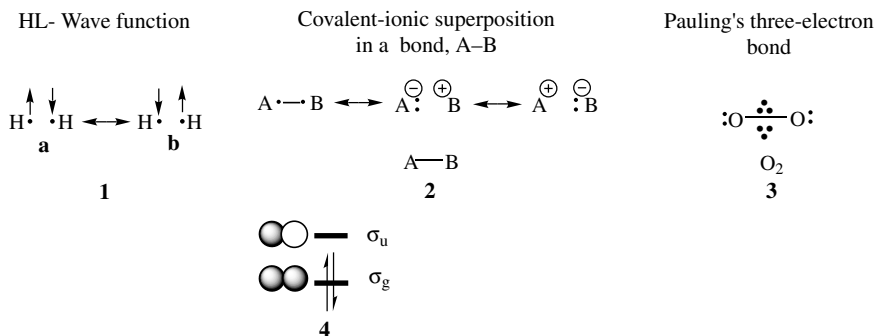
1.1 ROOTS OF VB THEORY

The roots of VB theory in chemistry can be traced back to the famous paper of Lewis *The Atom and The Molecule* (6), which introduces the notions of electron-pair bonding and the octet rule (initially called the rule of eight) (6). Lewis was seeking an understanding of weak and strong electrolytes in solution (2). This interest led him to formulate the concept of the chemical bond as an intrinsic property of the molecule that varies between the covalent (shared-pair) and ionic extremes. In this article, Lewis uses his recognition that almost all known stable compounds had an even number of electrons as the rationale that led him to the notion of electron pairing as a mechanism of bonding. This and the fact that helium was found by Mosely to possess only two electrons made it clear to Lewis that electron pairing was more fundamental than the octet rule; the latter rule was an upper bound for the number of electron pairs that can surround an atom (6). In the same paper, Lewis invents an ingenious symbol for electron pairing, the colon (e.g., H:H), which enabled him to draw electronic structures for a great variety of molecules involving single, double, and triple bonds. This article predated new quantum mechanics by 11 years and constitutes the first effective formulation of bonding in terms of the covalent−ionic classification, which is still taught today. This theory has formed the basis for the subsequent construction and generalization of VB theory. This work eventually had its greatest impact through the work of Langmuir, who articulated the Lewis model, applied it across the periodic table, and invented catchy terms like the octet rule and the covalent bond (7). From then onward, the notion of electron pairing as a mechanism of bonding became widespread and initiated the "electronic structure revolution" in chemistry (8).

   The overwhelming chemical support of Lewis's idea presented an exciting agenda for research directed at understanding the mechanism by which an electron pair could constitute a bond. This, however, remained a mystery until 1927 when Heitler and London went to Zurich to work with Schrödinger. In the summer of the same year, they published their seminal paper, *Interaction Between Neutral Atoms and Homopolar Binding* (9,10). Here they showed that the bonding in dihydrogen (H_2) originates in the quantum mechanical "resonance" interaction that is contributed as the two electrons are allowed to exchange their positions between the two atoms. This wave function and the notion of resonance were based on the work of Heisenberg (11), who showed earlier that, since electrons are indistinguishable particles, then for a two electron systems, with two quantum numbers n and m, there exist two wave functions that are linear combinations of the two possibilities of arranging these electrons, as shown Equation 1.1.

$$\Psi_A = (1/\sqrt{2})[\varphi_n(1)\varphi_m(2) + \varphi_n(2)\varphi_m(1)] \tag{1.1a}$$

$$\Psi_B = (1/\sqrt{2})[\varphi_n(1)\varphi_m(2) - \varphi_n(2)\varphi_m(1)] \tag{1.1b}$$

HL- Wave function

Covalent-ionic superposition
in a bond, A–B

Pauling's three-electron
bond

$$\text{H}\cdot \overset{\uparrow}{}\overset{\downarrow}{\cdot\text{H}} \longleftrightarrow \text{H}\cdot \overset{\downarrow}{}\overset{\uparrow}{\cdot\text{H}}$$
a   **b**

1

$$\text{A}\cdot\!\!-\!\!\text{B} \longleftrightarrow \text{A}\!:\!\overset{\ominus}{}\overset{\oplus}{\text{B}} \longleftrightarrow \overset{\oplus}{\text{A}}\,\overset{\ominus}{:}\!\text{B}$$

A—B

2

$$:\!\text{O}\!\cdots\!\text{O}\!:$$

O_2

3

σ_u

σ_g

4

Scheme 1.1

As demonstrated by Heisenberg, the mixing of $[\varphi_n(1)\varphi_m(2)]$ and $[\varphi_n(2)\varphi_m(1)]$ led to a new energy term that caused a splitting between the two wave functions Ψ_A and Ψ_B. He called this term "resonance" using a classical analogy of two oscillators that, by virtue of possessing the same frequency, form a resonating situation with characteristic exchange energy.

In modern terms, the bonding in H_2 can be accounted for by the wave function drawn in **1**, in Scheme 1.1. This wave function is a superposition of two covalent situations in which, in the first form (**a**) one electron has a spin-up (α spin), while the other has spin-down (β spin), and vice versa in the second form (**b**). Thus, the bonding in H_2 arises due to the quantum mechanical "resonance" interaction between the two patterns of spin arrangement that are required in order to form a singlet electron pair. This "resonance energy" accounted for ∼75% of the total bonding of the molecule, and thereby projected that the wave function in **1**, which is referred to henceforth as the HL-wave function, can describe the chemical bonding in a satisfactory manner. This "resonance 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.

In the winter of 1928, London extended the HL-wave function and drew the general principles of the covalent bonding in terms of the resonance interaction between the forms that allow interchange of the spin-paired electrons between the two atoms (10,12). In both treatments (9,12) the authors considered ionic structures for homopolar bonds, but discarded their mixing as being too small. In London's paper, there is also a consideration of ionic (so-called polar) bonding. In essence, the HL theory was a quantum mechanical version of Lewis's electron-pair theory. Thus, even though Heitler and London did their work independently and perhaps unaware of the Lewis model, the HL-wave function still precisely described the shared-pair bond of Lewis. In fact, in his letter to Lewis (8), and in his landmark paper (13), Pauling points out that the HL and London treatments are 'entirely equivalent to G.N. Lewis's successful theory of shared electron pair . . .''. Thus, although the final formulation of the

chemical bond has a physicists' dress, the origin is clearly the chemical theory of Lewis.
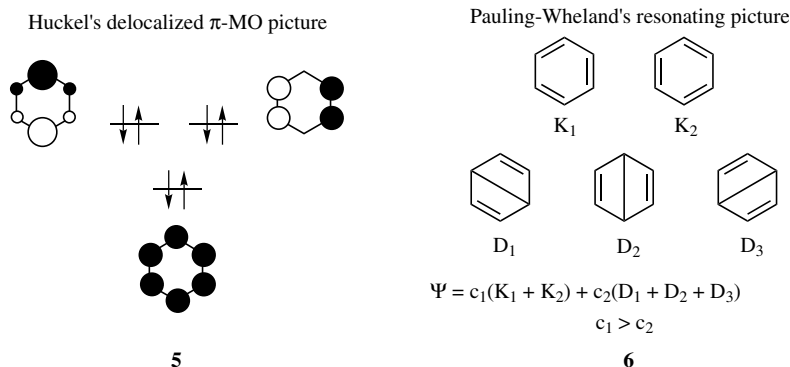
The HL-wave function formed the basis for the version of VB theory that later became very popular, and was behind some of the failings to be attributed to VB theory. In 1929, Slater presented his determinant-based method (14). In 1931, he generalized the HL model to *n*-electrons by expressing the total wave function as a product of *n*/2 bond wave functions of the HL type (15). In 1932, Rumer (16) showed how to write down all the possible bond pairing schemes for *n*-electrons and avoid linear dependencies among the forms in order to obtain canonical structures. We will refer hereafter to the kind of theory that considers only covalent structures as HLVB. Further refinements of the new theory of bonding (17) between 1928−1933 were mostly quantitative, focusing on improvement of the exponents of the atomic orbitals by Wang (18), and on the inclusion of polarization functions and ionic terms by Rosen and Weinbaum (19,20).

The success of the HL model and its relation to Lewis's model posed a wonderful opportunity for the young 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, and the resonating benzene picture (15,21–24). Especially effective were those Pauling's papers that linked the new theory to the chemical theory of Lewis, and rested on an encyclopedic command of chemical facts, much like the knowledge applied by Lewis to find his ingenious concept 15 years before (6). In the first paper (23), Pauling presented the electron-pair bond as a superposition of the covalent HL form and the two possible ionic forms of the bond, as shown in **2** in Scheme 1.1. He discussed the transition from covalent to ionic bonding. He then developed the notion of hybridization and discussed molecular geometries and bond angles in a variety of molecules, ranging from organic to transition metal compounds. For the latter compounds, he also discussed the magnetic moments in terms of the unpaired spins. In the following article (24), Pauling addressed bonding in molecules like diborane, and odd-electron bonds as in the ion molecule H_2^+, and in dioxygen, O_2, which Pauling represented as having two three-electron bonds, **3** in Scheme 1.1. These papers were followed by a stream of five papers, published from 1931 to 1933 in the *Journal of the American Chemical Society*, and entitled *The Nature of the Chemical Bond*. This 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, resonance, and hybridization theory (25). The book, which was published in 1939, is dedicated to G.N. Lewis, and the 1916 paper of Lewis is the only reference cited in the preface to the first edition. Valence bond theory in Pauling's view is a quantum chemical version of Lewis's theory of valence. In Pauling's work, the long sought for basis for the Allgemeine Chemie (unified chemistry) of Ostwald, the father of physical chemistry, was finally found (2).

1.2   ORIGINS OF MO THEORY AND THE ROOTS OF VB–MO RIVALRY

At the same time that Slater and Pauling were developing their VB theory (17), Mulliken (25–29) and Hund (30,31) were developing an alternative approach called MO theory that has a spectroscopic origin. The term MO theory appeared in 1932, but the roots of the method can be traced back to earlier papers from 1928 (26), in which both Hund and Mulliken made spectral and quantum number assignments of electrons in molecules, based on correlation diagrams tracing the energies from separated to united atoms. According to Brush (3), the first person to write a wave function for a MO was Lennard-Jones in 1929, in his treatment of diatomic molecules (32). In this paper, Lennard-Jones easily shows that the O_2 molecule is paramagnetic, and mentions that the HLVB method runs into difficulties with this molecule (32). This molecule would eventually become a symbol for the failings of VB theory, although as we wrote above there was no obvious reason for this branding, since VB theory always described this molecule as a diradical with two three-electron bonds **3**.

   In MO theory, the electrons in a molecule occupy delocalized orbitals made from linear combination of atomic orbitals. Drawing **4** (Scheme 1.1) shows the MOs of the H_2 molecule, and the delocalized σ_g MO can be contrasted with the localized HL description in **1**. Eventually, it would be the work of Hückel that would usher MO theory into the mainstream chemistry. The work of Hückel in the early 1930s initially had a chilly reception (33), but eventually it gave MO theory an impetus and formed a successful and widely applicable tool. In 1930, Hückel used Lennard-Jones's MO ideas on O_2, applied it to C=X (X=C, N, O) double bonds, and suggested the $\sigma-\pi$ separation (34). With this novel treatment, Hückel ascribed the restricted rotation in ethylene to the π-type orbital. Equipped with this facility of $\sigma-\pi$ separability, Hückel turned to solve the electronic structure of benzene using both HLVB theory and his new Hückel—MO (HMO) approach; the latter giving better "quantitative" results, and hence being preferred (35). The π-MO picture, **5** (Scheme 1.2), was quite unique in the sense that it viewed the molecule as a whole, with a σ-frame dressed by π-electrons that occupy three completely delocalized π-orbitals. The HMO picture also allowed Hückel to understand the special stability of benzene. Thus, the molecule was found to have a closed-shell π-component and its energy was calculated to be lower relative to that of three isolated π-bonds as in ethylene. In the same paper, Hückel treated 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). This treatment allowed him to understand why molecules with six π-electrons had special stability, and why molecules like COT or CBD either did not possess this stability (i.e., COT) or had not yet been made (i.e., CBD) at his time. In this and a subsequent paper (36), Hückel lays the foundations for what will become later known as the Hückel rule, regarding the special stability of aromatic molecules with $4n + 2$ π-electrons (3). This rule, its extension to

Huckel's delocalized π-MO picture

Pauling-Wheland's resonating picture

$$\Psi = c_1(K_1 + K_2) + c_2(D_1 + D_2 + D_3)$$
$$c_1 > c_2$$

5   **6**

Scheme 1.2

antiaromaticity, and its articulation by organic chemists in the 1950s−1970s will constitute a major cause for the acceptance of MO theory and the rejection of VB theory (4).

The description of benzene in terms of a superposition (resonance) of two Kekulé structures appeared for the first time in the work of Slater, as a case belonging to a class of species in which each atom possesses more neighbors than electrons it can share, much like in metals (21). Two years later, Pauling and Wheland (37) applied HLVB theory to benzene. They developed a less cumbersome computational approach, compared with Hückel's previous HLVB treatment, using the five canonical structures in **6**, 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 HLVB approach, benzene is described as a "resonance hybrid" of the two Kekulé structures and the three Dewar structures; the latter had already appeared before in Ingold's idea of mesomerism, which itself is rooted in Lewis's concept of electronic tautomerism (6). In his book, published for the first time in 1944, Wheland explains the resonance hybrid with the biological analogy of mule = donkey + horse (38). 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 HLVB representation very popular among practicing chemists.

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 the VB−MO rivalry that seems to accompany chemistry to the Twenty-first Century (5). This rivalry involved most of the prominent chemists of various periods (e.g., Mulliken, Hückel, J. Mayer, Robinson, Lapworth, Ingold, Sidgwick, Lucas, Bartlett, Dewar, Longuet-Higgins, Coulson, Roberts, Winstein, Brown). A detailed and interesting account of the nature of this rivalry and the major players can be found in the treatment of Brush (3,4). Interestingly, back in the 1930s, Slater (22) and van Vleck and

Sherman (39) stated that since the two methods ultimately converge, it is senseless to quibble on the issue of which one is better. Unfortunately, however, this rational attitude does not seem to have made much of an impression on this religious war-like rivalry.

1.3   ONE THEORY IS UP THE OTHER IS DOWN

By the end of World War II, Pauling's resonance theory was widely accepted, while most practicing chemists ignored HMO and MO theories. The reasons for this situation are analyzed by Brush (3). Mulliken suggested that the success of VB theory was due to Pauling's skill as a propagandist. According to Hager (a biographer of Pauling) VB won out in the 1930s because of Pauling's communication skills. However, the most important reason for this dominance is the direct lineage of VB-resonance theory to the structural concepts of chemistry dating from the days of Kekulé, Couper, and others through the electron-pair notion and electron-dot structures of Lewis. Pauling himself emphasized that his VB theory is a natural evolution of chemical experience, and that it emerges directly from the chemical conception of the chemical bond. This has made VB-resonance theory appear intuitive and chemically meaningful. Ingold was a great promoter of VB-resonance theory who saw in it a quantum chemical version of his own mesomerism concept (according to Brush, the terms resonance and mesomerism entered chemical vocabulary at the same time, due to Ingold's assimilation of VB-resonance theory; Reference 3, p. 57). Another very important reason is the facile qualitative application of this theory to all known structural chemistry of the time in Pauling's book (25), and to a variety of problems in organic chemistry in Wheland's book (38). The combination of an easily applicable general theory, and its ability to fit experiment so well, created a rare credibility nexus. In contrast, MO theory seemed alien to everything chemists had thought about the nature of the chemical bond. Even Mulliken admitted that MO theory departs from the chemical ideology (Reference 3, p. 51). To top it all, back at that period, MO theory offered no visual representation to compete with the resonance hybrid representation of VB-resonance theory with its direct lineage to the structure of molecules, the heartland of chemistry. At the end of World War II, VB-resonance theory dominated the epistemology of chemists.

By the mid-1950s, the tide had started shifting slowly in favor of MO theory, gaining momentum through the mid-1960s. What had caused the shift is a combination of factors, of which the following two may be decisive. First, there were many successes of MO theory, for example the experimental verification of the Hückel rules (33), the construction of intuitive MO theories, and their wide applicability for rationalization of structures (e.g., Walsh diagrams) and spectra [electronic and electron spin resonance (ESR)], the highly successful predictive application of MO theory in chemical reactivity, the instant rationalization of the bonding in newly discovered exotic molecules like

ferrocene (40), for which the VB theory description was cumbersome, and the development of widely applicable MO-based computational techniques (e.g., extended Hückel and semiempirical programs). Last, but not least, is the publication of influential books, which taught MO theory to chemists, like the books of Dewar and Coulson, on MO theory, and the books of Roberts and Streitwieser on Hückel theory and its usage (41–43). On the other side, VB theory, in chemistry, suffered a detrimental conceptual arrest that has crippled the predictive ability of the theory, which, in addition, has started to accumulate "failures". Unlike its fresh exciting beginning, in the period of 1950s−1960s VB theory ceased to guide experimental chemists to new experiments. This process ultimately ended in the complete victory of MO theory. However, the MO victory was over resonance theory and other simplified versions of VB theory, but not over VB theory itself. In fact, the true VB theory was hardly being practiced anymore in the mainstream chemical community.

1.4   MYTHICAL FAILURES OF VB THEORY: MORE GROUND IS GAINED BY MO THEORY

One of the major registered failures is associated with the dioxygen molecule. Application of the simple Pauling−Lewis recipe of hybridization and bond pairing to rationalize and predict the electronic structure of molecules fails to predict the paramagneticity of O_2. In contrast, using MO theory reveals this paramagneticity instantaneously (32). Even though VB theory does not really fail with O_2, and Pauling himself preferred, without reasoning why, to describe it in terms of three-electron bonds (**3**) in his early papers (24) [see also Wheland's description on p. 39 of his book (38)], this "failure" of Lewis's recipe sticks to VB theory and becomes a fixture of the common chemical wisdom (Reference 3, p. 49, footnote 112).

A second sore spot concerned the VB treatments of CBD and COT. Thus, using HLVB theory leads to a an incorrect prediction that the resonance energy of CBD should be as large or even larger than that of benzene. The facts that CBD had not yet been made and that COT exhibited no special stability were in favor of HMO theory. Another impressive success of HMO theory was the prediction that due to the degenerate set of singly occupied MOs, square CBD should distort to a rectangular structure, which made a connection to the ubiquitous phenomena of Jahn-Teller and pseudo-Jahn-Teller effects amply observed by the spectroscopic community. Wheland analyzed the CBD problem early on, and his analysis pointed out that inclusion of ionic structures would probably change the VB predictions and make them identical to MO (38,44,45). Craig showed that HLVB theory in fact correctly assigns the ground state of CBD, in contrast to HMO theory (46,47). Despite this demonstration and the fact that modern VB theory has subsequently demonstrated unique and novel insight into the problems of benzene, CBD, and their isoelectronic species, nevertheless the early stamp of the CBD story as a failure of VB theory still persists.

The increasing interest of chemists in large molecules, as of the late 1940s, has started making VB theory impractical, compared with the emerging semiempirical MO methods that allowed the treatment of larger and larger molecules. A great advantage of semiempirical MO calculations was the ability to calculate bond lengths and angles rather than assume them as in VB theory (4). Skillful communicators like Longuet-Higgins, Coulson, and Dewar, were among the leading MO proponents. They handled MO theory in a visualizable manner, which was sorely missing before. In 1951, Coulson addressed the Royal Society meeting and expressed his opinion that despite the great success of VB theory, it has no good theoretical basis; it is just a semiempirical method, of little use for more accurate calculations (48). In 1949, Dewar's monograph, *Electronic Theory of Organic Chemistry* (49), summarized the faults of resonance theory, as being cumbersome, inaccurate, and too loose ("it can be played happily by almost anyone without any knowledge of the underlying principles involved").

In 1952, Coulson published his book *Valence* (50) which did for MO theory, at least in part, what Pauling's book (25) had done much earlier for VB theory. It is interesting that the great pedagogy of Coulson relied on combined insights of MO and VB theory, and the creation of a portable MO theory (43), using localized bond orbitals instead of delocalized MOs. As analyzed by Park (43), the famous pictures for ethylene and benzene using the sp^2 hybridization and π-bonding were Coulson's and not Pauling's, who was still using the tetrahedral carbon to describe ethylene with two bent "banana" bonds. At the same time, Coulson stressed that this localized picture could be converted to the delocalized one (43). Thus, Coulson has provided a lucid qualitative account of the mathematics of quantum mechanical theories of valence and reoriented MO theory from spectroscopic concerns to chemical applications. Pauling strongly objected to Coulson's simpler pictures of, for example, ethylene, and chose to cling to his use of sp^3 hybridization to describe the bonding in ethylene. Only in 1960, in the third edition of his book (25), page 137 did Pauling give the two alternative descriptions with sp^3 and sp^2 hybridization; by that time VB theory was losing grounds, at least in part, because its founder was reluctant to change it and perhaps to infuse it with insights from MO theory. In 1960 Mulliken won the Nobel Prize and Platt wrote, "MO is now used far more widely, and simplified versions of it are being taught to college freshmen and even to high school students" (51). Indeed, many communities took to MO theory due to its proven portability and successful predictions.

A decisive victory was won by MO theory when organic chemists were finally able to synthesize transient molecules and establish the stability patterns of $C_8H_8^{2-}$, $C_5H_5^{-,+}$, $C_3H_3^{+,-}$, and $C_7H_7^{+,-}$ during the 1950s–1960s (3,4,33). The results, which followed the Hückel rules, convinced most of the organic chemists that MO theory was correct, while HLVB and resonance theories were wrong. During the 1960s–1978, C_4H_4 was made, and its structure and properties were determined by MO theory, which challenged initial experimental determination of a square structure (3,4). The syntheses of

nonbenzenoid aromatic compounds such as azulene, tropone, etc., further established the Hückel rules, and highlighted the failure of resonance theory (33). This era in organic chemistry marked a decisive downfall of VB theory.

By 1960, the 3rd edition of Pauling's book was published (25), and although it was still spellbinding for chemists, it contained errors and omissions. For example, the discussion of electron deficient boranes, where Pauling describes the molecule $B_{12}H_{12}$ instead of $B_{12}H_{12}^{2-}$ (Reference 25, p. 378), and a very cumbersome description of ferrocene and analogous compounds (on pp. 385–392), for which MO theory presented simple and appealing descriptions. These and other problems in the book, as well as the neglect of the then known species $C_5H_5^{-,+}$, $C_3H_3^{+,-}$, and $C_7H_7^{+,-}$, reflected the situation that unlike MO theory, VB theory did not have a useful Aufbau principle that could reliably predict the dependence of molecular stability on the number of electrons and project magic numbers as $4n/4n + 2$, and so on. As we have already pointed out, the conceptual development of VB theory was arrested since the 1950s, in part due to the insistence of Pauling himself that resonance theory was sufficient to deal with most problems (see, e.g., Reference 4, p. 283). Sadly, the creator himself contributed to the downfall of his own brainchild.

In 1952, Fukui published his Frontier MO Theory (52), which went initially unnoticed. In 1965, Woodward and Hoffmann published their principle of conservation of orbital symmetry, and applied it to all pericyclic chemical reactions. The immense success of these rules (53) renewed the interest in Fukui's approach and together they formed a new MO-based framework of thought for chemical reactivity (called, e.g., ''giant steps forward in chemical theory'' in Morrison and Boyd, pp. 934, 939, 1201, 1203). This success of MO theory resulted in its increased dissemination among chemists and in the effective decimation of the alternative VB theory. In this area, despite the early calculations of the Diels–Alder and $2 + 2$ cycloaddition reactions by Evans (54), VB theory did not make an impact, in part at least, because of the blind adherence of its practitioners to simple resonance theory (33). Further, the reluctance of its proponents to infuse it with insights from its rival MO theory and thereby to derive the dependence of reactivity phenomenon on magic numbers led to the further decline of VB theory. All the subsequent VB derivations of the rules (e.g., by Oosterhoff and by Goddard) were ''after the fact'' and failed to reestablish the status of VB theory. In Hoffmann, MO theory found another great teacher who, in 1965, started his long march of teaching MO theory by applying it to almost any branch of chemistry, and by demonstrating how portable MO ideas were and how useful they could be for chemists. One of his key contributions, the ''isolobal analogy'', in fact relied on the localized bond orbital picture, which created a bridge between organic and organometallic chemistries (55).

The development of photoelectron spectroscopy (PES) and its application to molecules in the 1970s, in the hands of Heilbronner, showed that the spectra could be easily interpreted if one assumes that electrons occupy

delocalized MO (56,57). This further strengthened the case for MO theory. Moreover, this has served to dismiss VB theory, because it describes electron pairs that occupy localized bond orbitals. A frequent example of this "failure" of VB theory is the photoelectron spectroscopy (PES) of methane, which shows two different ionization peaks. These peaks correspond to the a_1 and t_2 MOs, but not to the four C−H bond orbitals in Pauling's hybridization theory [see recent paper on a similar issue (58)]. With these and similar types of arguments, VB theory has eventually fell into a state of disrepute and became known, at least when the present authors were students, either as a "wrong theory" or simply as a "dead theory".

The late 1960s and early 1970s mark the era of mainframe computing. In contrast to VB theory, which is very difficult to implement computationally ("the $N!$ problem", which is a misnomer since no one really calculates $N!$ terms anymore), MO theory easily could be implemented (even GVB was implemented through an MO-based formalism—see later). In the early 1970s, Pople and co-workers developed the GAUSSIAN70 package that uses *ab initio* MO theory with no approximations other than the choice of basis set. Sometime later density functional theory made a spectacular entry into chemistry. Suddenly, it has become possible to calculate real molecules, and to probe their properties with increasing accuracy. The *lingua franca* of all these methods was MO theory, and even when density function theory (DFT) entered into chemistry it used Kohn−Sham orbitals that look almost identical to MOs. This theory further cemented the role of MO theory as the primary conceptual tool acceptable in chemistry.

The new and user-friendly tool created a subdiscipline of computational chemists who explored the molecular world with the GAUSSIAN series and many of the other packages, which sprouted alongside the dominant one. Today leading textbooks hardly include VB theory anymore, and when they do, the theory is misrepresented (59,60). Advanced quantum chemistry courses regularly teach MO theory, but books that teach VB theory are rare. This development of user-friendly *ab initio* MO-based software and the lack of similar VB software put the "last nail in the coffin of VB theory" and substantiated MO theory as the only legitimate chemical theory.

Nevertheless, despite this seemingly final judgment and the obituaries showered on VB theory in textbooks and in the public opinion of chemists, the theory never really died. Due to its close affinity to chemistry and its utmost clarity, it has remained an integral part of the thought process of many chemists, even among proponents of MO theory (see comment by Hoffmann on page 284 in Reference 4). Within the chemical dynamics community, the usage of the theory has never been arrested, and it lived in terms of computational methods called LEPS, BEBO, DIM, an so on, which were (and still are) used for generation of potential energy surfaces. Moreover, around the 1970s, but especially from 1980s onward, VB theory began to rise from the ashes, to dispel many myths about its "failures" and to offer a sound and attractive alternative to MO theory. Before some of these developments are

described, it is important to go over some of the mythical "failures" of VB theory and inspect them a bit more closely.

1.5   ARE THE FAILURES OF VB THEORY REAL?

All the so-called failures of VB theory are due to misuse and failures of very simplified versions of the theory. Simple resonance theory enumerates structures without proper consideration of their interaction matrix elements (or overlaps). It will fail whenever the matrix element is important, as in the case of aromatic viz. antiaromatic molecules, and so on (61,62). The hybridization-bond pairing theory (modern day Lewis theory) assumes that the most important energetic effect for a molecule is the bonding, 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 (62–64). The HLVB theory is based on covalent structures only, which become insufficient and require inclusion of ionic structures explicitly or implicitly (through delocalization tails of the atomic orbitals, as in the GVB method described later). In certain cases such as antiaromatic molecules, this deficiency of HLVB makes incorrect predictions (63,64). In the space below we consider four iconic "failures" and show that some of them stuck to VB in unexplained ways:

1.5.1   The O_2 Failure

It is doubtful whether this so-called failure can be attributed to Pauling himself, because in his landmark paper (23), Pauling was careful enough to state that the molecule does not possess a normal state, but rather one with two three-electron bonds (**3**), (also see Reference 38 where Wheland made the same statement on page 39). In 1934, Heitler and Pöschl (65) published a *Nature* paper describing the O_2 molecule with VB principles and concluded that "the $^3\Sigma_g^-$ term ... giving the fundamental state of the molecule". It is not clear how the myth of this "failure" grew, spread so widely, and was accepted so unanimously. Curiously, while Wheland acknowledged the prediction of MO theory by a proper citation of Lennard-Jones's paper (32), Pauling did not, at least not in his landmark papers (23,24), nor in his book (25). In these works, the Lennard-Jones paper is either not cited (24,25), or is mentioned only as a source of the state symbols (23) that Pauling used to characterize the states of CO, CN, and so on. One wonders what role the animosity between the MO and VB camps played in propagating the notion of the "failures"of VB to predict the ground state of O_2. Sadly, scientific history is determined also by human weaknesses. As we repeatedly stated, it is true that a naïve application of hybridization and perfect pairing approach (simple Lewis pairing) without consideration of the important effect played by the four-electron repulsion, would fail and predict a $^1\Delta_g$ ground state. As we will see later, in the case of O_2,

perfect pairing in the $^1\Delta_g$ state leads to four-electron repulsion, which more than cancels the π-bond. To avoid the repulsion, we can form two three-electron π-bonds, and by keeping the two odd-electrons in a high spin situation, the ground state becomes $^3\Sigma_g^-$, which is further lowered by exchange energy due to the two triplet electrons (62).

1.5.2 The C_4H_4 Failure

This finding is a failure of the HLVB approach that does not involve ionic structures. Their inclusion in an all-electron VB theory, either explicitly (64,66), or implicitly through delocalization tails of the atomic orbitals (67), correctly predicts the geometry and resonance energy. In fact, even HLVB theory makes a correct assignment of the ground state of CBD as the $^1B_{1g}$ state. In contrast, monodeterminantal MO theory makes an incorrect assignment of the ground state as the triplet $^3A_{2g}$ state (46,47). Moreover, HMO theory was successful for the wrong reason, since the Hückel MO determinant for the singlet state corresponds to a single Kekulé structure and for this reason, CBD exhibits zero resonance energy in HMO (44). This idea is of course incorrect, but is reinforced by the idea from experimental facts that the species is highly unstable.

1.5.3 The $C_5H_5^+$ Failure

This idea is a failure of simple resonance theory, not of VB theory. Taking into account the sign of the matrix element (overlap) between the five VB structures shows that singlet $C_5H_5^+$ is Jahn—Teller unstable, and the ground state is in fact the triplet state. As shown later in Chapter 5, this is generally the case for all of the antiaromatic ionic species having 4n electrons over $4n + 1$ or $4n - 1$ centers (61).

1.5.4 The Failure Associated with the Photoelectron Spectroscopy of CH_4

Starting from a naïve application of the VB picture of methane (CH_4), it follows that since methane has four equivalent localized bond orbitals (LBOs), ergo the molecule should exhibit only one ionization peak in PES. However, since the PES of methane shows two peaks, ergo VB theory "fails"! This argument is false for two reasons: first, as known since the 1930s, LBOs for methane or any molecule, can be obtained by a unitary transformation of the delocalized MOs (68). Thus, both MO and VB descriptions of methane can be cast in terms of LBOs. Second, 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 to each of the four bonds. One can achieve the correct physical description, either by combining the LBOs back to canonical MOs (57), or by taking a linear combination of the four VB configurations that correspond to one bond ionization (69,70). As seen later,

correct linear combinations are $^2A_1$ and $^2T_2$, the later in a triply degenerate VB state.

1.6   VALENCE BOND IS A LEGITIMATE THEORY ALONGSIDE MOLECULAR ORBITAL THEORY

Obviously, the rejection of VB theory cannot continue to invoke failures, because a properly executed VB theory does not fail, much as a properly executed MO-based calculation. 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 that 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. Indeed, theoretical chemists in the community of chemical dynamics continue to use VB theory and maintain an uninterrupted chain of VB usage from London, through Eyring, Polanyi, to Wyatt, Truhlar, and others today. Physicists also, continue to use VB theory, and one of the main proponents is the Nobel Laureate P.W. Anderson, who developed a resonating VB theory of superconductivity. In terms of the focus of this book, in mainstream chemistry too, VB theory begins to enjoy a slow but steady Renaissance in the form of modern VB theory.

1.7   MODERN VB THEORY: VALENCE BOND THEORY IS COMING OF AGE

The Renaissance of VB theory is marked by a surge in the following two-fold activity: (1) creation of general qualitative models based on VB theory; and (2) development of new methods and program packages that enable applications to moderate-sized molecules. Below we briefly mention some of these developments without pretence of creating exhaustive lists. We apologize for any omissions.

A few general qualitative models based on VB theory began to appear in the late 1970s and early 1980s. Among these models semiempirical approaches are also included based, for example, on the Heisenberg and Hubbard Hamiltonians (71–79), as well as Hückeloid VB methods (61,80–82), which can handle with clarity ground and excited states of molecules. Methods that map MO-based wave functions to VB wave functions offer a good deal of interpretative insight. Among these mapping procedures, we note the half-determinant method of Hiberty and Leforestier (83), and the CASVB methods of Thorsteinsson et al (84,85) and Hirao et al (86,87). General qualitative VB models for chemical bonding were proposed in the early 1980s and the late

1990s by Epiotis (88,89). A general model for the origins of barriers in chemical reactions was proposed in 1981 by one of the present authors, in a manner that incorporates the role of orbital symmetry (61,90). Subsequently, in collaboration with Pross (91,92) and Hiberty (93), the model has been generalized for a variety of reaction mechanisms (94), and used to shed new light on the problems of aromaticity and antiaromaticity in isoelectronic series (66). Following Linnett's reformulation of three-electron bonding in the 1960s (95), Harcourt (96,97) developed a VB model that describes electron-rich bonding in terms of increased valence structures, and showed its occurrence in bonds of main elements and transition metals.

Valence bond ideas also contributed to the revival of theories for photochemical reactivity. Early VB calculations by Oosterhoff et al (98,99). revealed a potentially general mechanism for the course of photochemical reactions. Michl (100,101) articulated this VB-based mechanism and highlighted the importance of "funnels" as the potential energy features that mediate the excited-state species back into the ground state. Subsequently, Robb and co-workers (102–105) showed that these "funnels" are conical intersections that can be predicted by simple VB arguments, and computed at a high level of sophistication. Similar applications of VB theory to deduce the structure of conical intersections in photoreactions were done by Shaik and Reddy (106) and recently by Haas and Zilberg (107).

Valence bond theory enables a very straightforward account of environmental effects, such as those imparted by solvents and/or protein pockets. A major contribution to the field was made by Warshel, who has created his empirical VB (EVB) method, and, by incorporating van der Waals and London interactions by molecular mechanical (MM) methods, created the QM(VB)/MM method for the study of enzymatic reaction mechanisms (108–110). His pioneering work ushered the now emerging QM/MM methodologies for studying enzymatic processes (111). Hynes et al. showed how to couple solvent models into VB and create a simple and powerful model for understanding and predicting chemical processes in solution (112–114). One of us has shown how solvent effect can be incorporated in an effective manner to the reactivity factors that are based on VB diagrams (115,116).

Generally, VB theory is seen to offer a widely applicable framework for thinking and predicting chemical trends. Some of these qualitative models and their predictions are discussed in the application sections of this book.

Sometime in the 1970s a stream of nonempirical VB methods began to appear and were followed by many applications of rather accurate calculations. All these programs divide the orbitals in a molecule into inactive and active subspaces, treating the former as a closed shell and the latter by some VB formalism. The programs optimize the orbitals, and the coefficients of the VB structures, but they differ in the manner by which the VB orbitals are defined. Goddard and co-workers developed the generalized VB (GVB) method (117–120) that uses semilocalized atomic orbitals (having small

delocalization tails), employed originally by Coulson and Fisher for the H_2 molecule (121). The GVB method is incorporated now in GAUSSIAN and in most other MO-based packages. Somewhat later, Gerratt and co-workers developed their VB method called the spin coupled (SC) theory and its follow-up by configuration interaction using the SCVB method (122–124). Both the GVB and SC theories do not employ covalent and ionic structures explicitly, but instead use semilocalized atomic orbitals that effectively incorporate all the ionic structures, and thereby enable one to express the electronic structures in compact forms based on formally covalent pairing schemes. Balint-Kurti and Karplus (125) developed a multistructure VB method that utilizes covalent and ionic structures with localized atomic orbitals. In a later development by van Lenthe and Balint-Kurti (126,127) and by Verbeek and van Lenthe (128,129), the multistructure method is being referred to as a VB self-consistent field (VBSCF) method. In a subsequent development, van Lenthe (130) and Verbeek et al. (131) generated the multipurpose VB program called TURTLE, which has recently been incorporated into the MO-based package of programs GAMESS-UK. Matsen (132,133), McWeeny (134), and Zhang and co-workers (135,136) developed their spin-free VB approaches based on symmetric group methods. Subsequently, Wu et al. extended the spin-free approach, and produced a general purpose VB program called the XIAMEN-99 package most recently named XMVB (137,138). Soon after, Li and McWeeny announced their VB2000 software, which is also a general purpose program, including a variety of methods (139). Another software of multiconfigurational VB (MCVB), called CRUNCH and based on the symmetric group methods of Young was written by Gallup and co-workers (140,141). During the early 1990s, Hiberty and co-workers developed the breathing orbital VB (BOVB) method, which also utilizes covalent and ionic structures, but additionally allows them to have their own unique set of orbitals (142–147). The method is now incorporated into the programs TURTLE and XMVB. Very recently, Wu et al. (148) developed a VBCI method that is akin to BOVB, but can be applied to larger systems. In a more recent work, the same authors coupled VB theory with the solvent model, PCM, and produced the VBPCM program that enables one to study reactions in solution (149). The recent biorthogonal VB method of McDouall has the potential to carry out VB calculations up to 60 electrons outside the closed shell (150). Finally, Truhlar and co-workers (151) developed the VB-based multiconfiguration molecular mechanics method (MCMM) to treat dynamic aspects of chemical reactions, while Landis and co-workers (152), introduced the VAL-BOND method that is capable of predicting structures of transition metal complexes using Pauling's ideas of orbital hybridization. A recent monograph by Landis and Weinhold makes use of VAL-BOND as well as of natural resonance theory to discuss a variety of problems in inorganic and organometallic chemistry (153). In the section dedicated to VB methods, we mention the main program packages and methods, which we used, and outline their features, capabilities, and limitations.

This plethora of acronyms of the VB programs starts to resemble a similar development that had accompanied the ascent of MO theory. While this may sound like good news, recall the biblical admonition, "let us go down, and there confound their language that they may not understand one another's speech" (*Genesis* 11, 7). Certainly, the situation is also a call for systematization much like what Pople and co-workers enforced on computational MO terminology. Nonetheless, at the moment the important point is that the advent of so many good VB programs has caused a surge in applications of VB theory, to problems ranging from bonding in main group elements to transition metals, conjugated systems, aromatic and antiaromatic species, all the way to excited states and full pathways of chemical reactions, with moderate-to-very good accuracies. For example, a recent calculation of the barrier for the identity hydrogen-exchange reaction, H + H−H' → H−H + H', by Song et al. (154) shows that it is possible to calculate the reaction barrier accurately with just eight classical VB structures! Thus, in many respects, VB theory is coming of age, with the development of faster, and more accurate *ab initio* VB methods (155,156), and with generation of new post-Pauling concepts. As these activities further flourish, so will the usage of VB theory spread among practicing chemists (157). This book aims to ease this goal and to serve as a source for teachers in advanced classes.

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