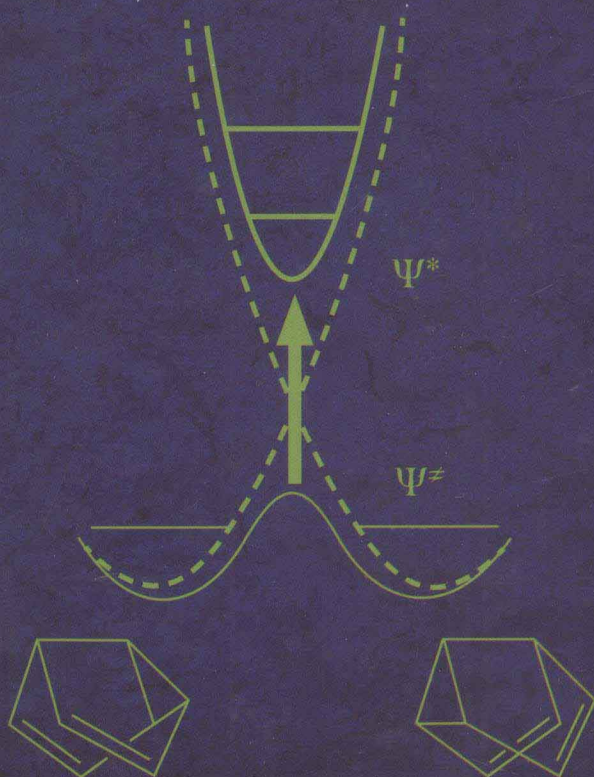


A CHEMIST'S GUIDE TO VALENCE BOND THEORY



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A CHEMIST'S GUIDE TO VALENCE BOND THEORY

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Lionel Salem,
and the late Edgar Heilbronner.*

PREFACE

This text was written to fill the missing niche of a textbook that teaches Valence Bond (VB) theory. The theory that once charted the mental map of chemists had been abandoned since the mid-1960s for reasons that are discussed in Chapter 1. Consequently, the knowledge of VB theory and its teaching became gradually more scarce, and was effectively eliminated from the teaching curriculum in much of the chemical community. Nevertheless, a few elements of the theory somehow survived as the *Lingua Franca* of chemists, mostly due to the use of the Lewis bonding paradigm and the post-Lewis concepts of hybridization and resonance. But there is much more to VB theory than these concepts and ideas. Since its revival in the 1980s, VB theory has been enjoying a renaissance that is characterized by the development of a growing number of *ab initio* methods that can be applied to chemical problems of bonding and reactivity. Alongside these methodology developments, there has been a surge of new post-Pauling models and concepts that have rendered VB theory useful again as a central theory in chemistry; especially productive concepts arose by importing insights from molecular orbital (MO) theory and making the VB approach more portable and easier to apply. Following a recent review article by us (1) and two essays on VB theory and its relation to MO theory (2,3), we felt that the time had come to write a textbook dedicated to VB theory, its applications, and special insights.

This text is aimed at a nonexpert audience and designed as a tutorial material for teachers and students who would like to teach and use VB theory, but who otherwise have basic knowledge of quantum chemistry. As such, the primary focus of this textbook is a qualitative insight of the theory and ways to apply this theory to the problems of bonding and reactivity in the ground and excited states of molecules. Almost every chapter contains problem sets followed by answers. These problems provide the teachers, students, and interested readers with an opportunity to practice the art of VB theory. We will be indebted to readers—teachers—students for comments and more suggestions, which can be incorporated into subsequent editions of this book that we hope, will follow.

Another features in this book is the description of the main methods and programs available today for *ab initio* VB calculations, and how actually one may plan and run VB calculations. In this sense, the book provides a snapshot of the current VB capabilities in 2007. Regrettably, much important work had to be left out. The readers interested in technical and theoretical development aspects of VB theory may wish to consult two other monographs (4,5).

The two authors owe a debt of gratitude to colleagues and friends who read the chapters and provided useful comments and insights. In particular, we acknowledge Dr. Benoît Braïda, Professor Narahary Sastry, Professor Hendrik Zipse, Professor François Volatron, and Dr. Hajime Hirao for the many comments and careful reading of earlier drafts. François Volatron actually solved all the problem sets and checked the equations of Chapter 3: The equations are in much better shape thanks to his careful screening. Hajime Hirao went over the entire book and its galley proofs in search for glitches. Sebastian Kozuch (S. Shaik's PhD student) helped in the design of the book cover. Needless to say, none of these gentlemen should be held responsible for the content of the book.

In addition, we are thankful to all our co-workers and students during the years of collaboration (1981—present). Especially intense collaborations with Professor Addy Pross and Professor Wei Wu are acknowledged. Professor Wei Wu and Professor Joop van Lenthe are especially thanked for making their programs (XMVB and TURTLE) available to us. In fact, Professor Wei Wu has been kind enough to give us unlimited access to his XMVB code during the work on this book. Dr. David Danovich is thanked for producing all the inputs and outputs in this book, for helping with the final proofing, and for keeping alive the VB computational know-how at the Hebrew University throughout the years from 1992 onward.

Finally, any readers, teachers, or students who wish to comment on aspects of the content, problems-, and/or answer-sets, as well as on errors, are welcome to do so by contacting the authors directly by e-mail (sason@yfaat.ch.huji.ac.il and philippe.hiberty@lcp.u-psud.fr).

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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).

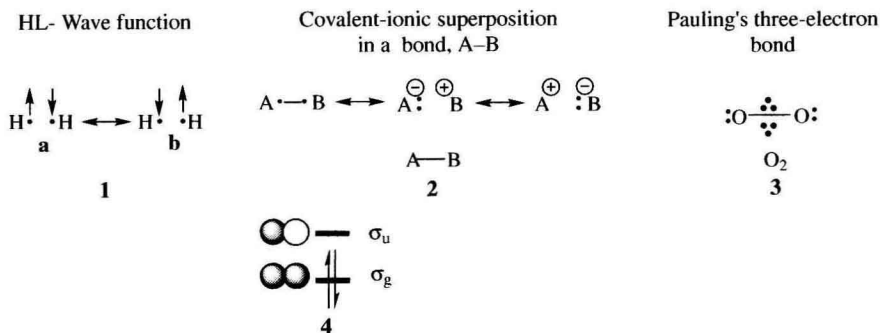
1.1 ROOTS OF VB THEORY

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.

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

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



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 $\sim 75\%$ 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