

*Dedicated to Avner Treinin, a Scientist and a Poet, on the occasion of his 73rd Birthday.

Abstract: The paper describes my own personal excursion into valence bond theory which has led eventually to the development of a general model of chemical reactivity based on valence bond diagrams.

I was always fascinated with chemical change. At first, these were color and consistency transformations which caught the eyes. I guess I am not unique in my attraction to the visual beauty that is occasionally associated with the chemical change. Later these visual pleasures were replaced by an intellectual satisfaction with the abstract expression of the change as is presented in the energy profile in Fig. 1

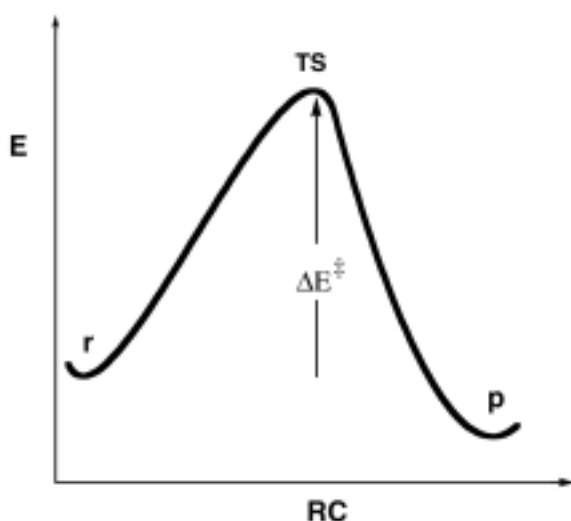


Fig. 1: A reaction profile.

Any chemical reaction starts with reactants (**r**) and ends with products (**p**). As the geometry of **r** changes along the reaction coordinate (**RC**) the energy rises, reaches a maximum which is called the transition state (**TS**), and thereafter it descends and becomes the product, **p**. In this general picture, the rate of the chemical change depends on the activation energy, or the energy barrier ΔE^\ddagger , that separates **r** and **p**. This

abstract picture held a lot of appeal for me as well as for many students of chemistry in my generation, and the elusive **TS** species added much allure and fascination. Understanding chemical reactivity promised a lot of fun and satisfaction. Even though, nowadays, it is possible to calculate by means of quantum chemical methods the barrier and **TS** geometry for most reactions and to do this with good accuracy, nothing has changed: *Understanding is still as important as it ever was, and the search for unifying models is an essential goal in chemistry.*

In my seminars on the topic I often show the cartoon (Fig. 2) of the bewildered student of reactivity facing the commandment tablets and asking: Which one do I obey?

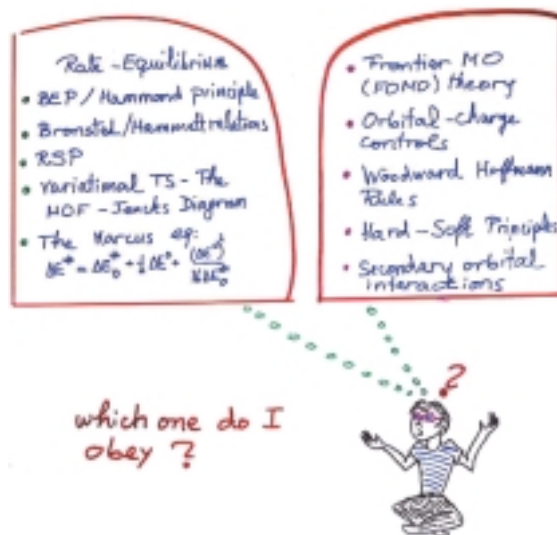


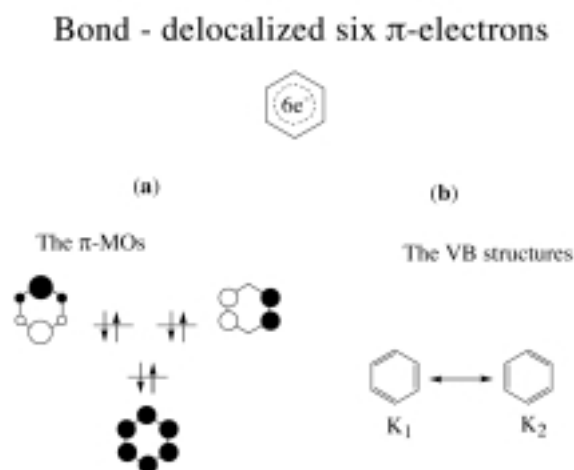
Fig. 2: A bewildered student of reactivity.

Indeed, while I was fascinated with the many principles which existed in interpreting reactivity, I at the same time, felt at a loss in deciding which one of the principles applies, more or less, in a given reactivity problem. As my expertise grew, I learned that the principles of reactivity originated from two different disciplines. Principles like the rate-equilibrium

relationship, or the reactivity-selectivity-principle, were formulated in physical organic chemistry, while others like the frontier molecular orbital theory, or the hard-soft principle, originated from emerging discipline of quantum chemistry. These sets of principles looked like two pieces truncated from a big jigsaw puzzle and separated by a rift. There was a need to unify and create bridges. But in order to do that, it was essential first to answer the fundamental question of reactivity: What is *the origin of the barrier in a chemical reaction, and what are the factors which govern its height*?

Answers to this question must be sought within quantum chemistry which contains theory, accepted by most chemists, that describes correctly chemical matter and its transformations. Quantum chemistry offers two conceptual tools called Molecular orbital (MO) and Valence Bond (VB) theories. A good example is the benzene molecule that possesses a delocalized π -system with six electrons. In MO theory the six π -electrons occupy six delocalized MOs as in Fig. 3a, while in VB theory the same information is conveyed through the combination or resonance of the two chemical structures, Fig. 3b, known as the Kekule structures of benzene.

In the early 1930's and for a decade or two later,



VB theory ruled chemical epistemology. There were a few good reasons for that. Firstly, VB theory relied on

Fig. 3: MO and VB Pictures of the π -electrons in benzene.

the concept of the Lewis electron-pair bond which was familiar to all chemists, and secondly, Pauling was able to package the complicated theory in terms of resonance structures which are the ones used regularly by chemists. In his monograph, *The Nature of the Chemical Bond*, Pauling treated virtually all known structural chemistry, at the time, using the VB-resonance concepts. This was a highly influential book that created a credibility nexus between a simple theory and experiment. However, as time passed, MO theory slowly took over, partly because it was more amenable to computer implementation, and partly because it used orbitals that possess symmetry. This latter property was easy to visualize and resulted in a decisive impact on chemical reactivity as was shown by the Woodward-Hoffmann Rules which relied on the principle of conservation of orbital symmetry. In the early 1970's, J.A. Pople and coworkers introduced the efficient computer program "GAUSSIAN 70" that was based on MO theory, and that enabled chemists to compute the properties of real molecules of contemporary interest to experimentalists. The victory of MO theory was decisive, and this dealt a fatal blow to VB theory that was completely abandoned.

Most theoreticians realize that at the limit of both theories they are entirely equivalent. In fact, any MO wave function can be expanded into a set of VB structures. For example, the MO wavefunction of the H_2 molecule is described by the doubly filled σ MO, Fig. 4(a). When this wavefunction is expanded it gives the three VB structures in Fig. 4(b). One is a covalent structure which pairs up the spins on the two H atoms, and the other two are the ionic structures which localize the two electrons on one of the atoms. Since the σ -MO is constrained to have the molecular symmetry, the covalent and ionic structures have identical weights in the MO-wavefunction. This identity is nonphysical since the electrons repel one another and would prefer to stay apart as in the covalent structure. Indeed, a correction of the MO wavefunction by a procedure

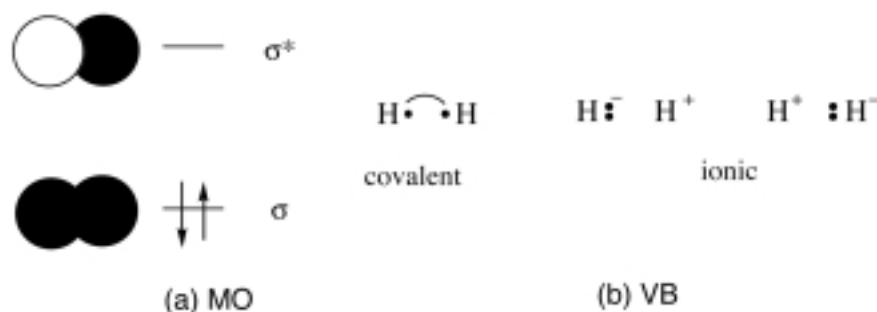


Fig. 4: MO and VB descriptions of the H-H bond.

called configuration interaction (CI) raises the weight of the covalent structure at the expense of the ionic structures (CI uses the wavefunction with σ^2 and σ^{*2} occupations). The corrected wavefunction of the H-H bond is then mostly the covalent structure with a small contribution from the two ionic fluctuations. VB theory, on the other hand, starts from the three structures and mixes them. This procedure leads to precisely the same wavefunction as from an MO followed by CI correction. Thus, in fact, VB theory is more precise than MO theory without the CI correction, but taken to the same level the two theories give precisely the same results. At no level are the two theories really different because the MO type wavefunction contains VB structures and can be expanded in terms of a linear combination of them (which might or might not have the physically meaningful weights, depending on the level of calculation). *The VB and MO wavefunctions for a given molecule (e.g., benzene) are two representations of the same physical picture; like two masks of the same person.* This is the beauty of the two theories; each mask reveals another face of reality and provides a different sort of insight into chemistry.

However, chemists like any other group of people with shared interests, tend to form camps and to side with one theory while strongly opposing the other. When I was a student in the mid to late 1970's, MO theory was in its hey days, while VB was in a low ebb. There were no efficient VB programs to calculate molecular properties and the theory seemed like a faint

primordial murmur from the past. It was considered to be a wrong theory or simply passe. I was of course of the same opinion and loved very much what I was doing in MO theory. However, this bad opinion concerning VB was destined to change completely, and as this change is connected with some special recollections, I would like to share them with the readers.

When I was a Ph.D. student at the University of Washington, R. Hoffmann visited to give a series of talks (I think this was the H. Dauben Series). As Hoffmann likes to do, he invited all the graduate students for beer in one of the local pubs. It was a great opportunity for all of us to sit in the company of this famous chemist, who by everybody's view was a future Nobel Laureate (which he became in 1981). In the relaxed atmosphere of the pub, I gathered enough courage to ask him what he thought will be the future of quantum chemistry. He answered in his typical thoughtful manner, and said many things I didn't understand. But one thing struck me the most: He was predicting that VB theory would make a come back! Considering the consensus on VB theory, what Hoffmann was saying sounded at best very strange, and I thought to myself: Doesn't he know that VB theory was a wrong theory? A few years passed, and I discovered VB theory on my own, and found what to me has become ever since a source of beauty and great lucidity. It was then that I could see *how VB theory provides the necessary insight into the fundamental questions of reactivity*, but that it also required the special insight of orbital symmetry which is typical to

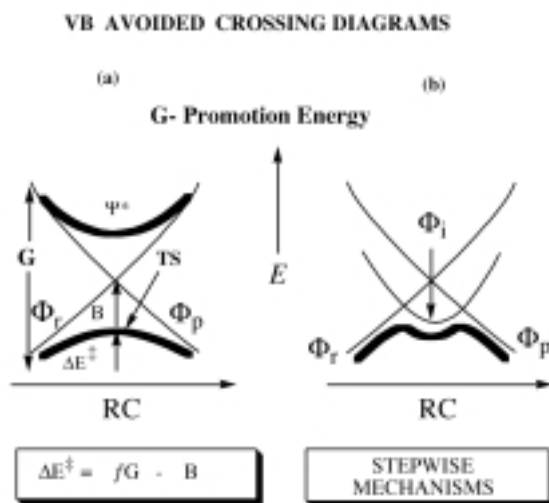
MO theory. *To comprehend reactivity, it was necessary to merge the two theories and to move to-and-fro between them.* This hybrid approach was achieved during my Post Doctoral year at Cornell and the model was published in a paper entitled *What Happens to Molecules as They React: A Valence Bond Approach to Reactivity*.^[1] In so doing a general model emerged which described the barrier formation in a unified manner for any chemical reaction.

In collaboration with Addy Pross from Ben-Gurion University, the model was articulated and applied to almost all the classical mechanisms of physical organic chemistry.^[2] Initially, the model was applied qualitatively. The reactivity parameters were derived from thermochemical data using a semiempirical approach.^[3] Subsequently, the Orsay group has developed a reasonable *ab initio* VB code, and together with Philippe Hiberty from Orsay we could show that the qualitative model can be faithfully computed. Many of the qualitative ideas were reproduced by the calculations, while others were modified. The model was further articulated and improved by the VB calculations.^[4] The advent of VB calculations was important because we could think and compute in precisely the same manner. Let me describe now the model very briefly. More details can be found in the original literature including in a few textbooks which incorporate elements of the model.^[5]

Fig. 5 shows the two VB diagrams which constitute the essence of the model. Reactivity turns out to be a simple outcome of the promotion energy, G , that prepares the molecules for the electronic reorganization inherent in the chemical transformation $\mathbf{r} \rightarrow \mathbf{p}$. The diagram on the left hand side (a) shows the mechanism of a barrier formation in an elementary chemical step. The barrier arises due to the behavior of the two VB states (the curves in the regular lines) along the reaction coordinate (\mathbf{RC}). In gross terms, these VB states, which are separated initially by the promotion energy, correspond to the electron pairing situations of \mathbf{r} and \mathbf{p} , and therefore they cross along \mathbf{RC} . The crossing mirrors the fact that the reactants

are transformed to products as a result of breaking old bonds and making new ones. The mixing of these VB situations leads to avoidance of the crossing and creates two new states which are drawn in heavy lines. The lower heavy-lined state is the reaction profile for the chemical reaction in the ground state. The top of this profile is the transition state (\mathbf{TS}) which is the resonating hybrid of the two VB situations. Thus the \mathbf{TS} is typified by bond-delocalization in analogy to benzene which is bond-delocalized due to the resonance of its two Kekule structures. The resonance of the VB structures endows the \mathbf{TS} with a resonance energy that is labeled as B . Since the \mathbf{TS} is a resonating hybrid of reactant-like and product-like bonding situations, it has a special status, as a transit point that includes equal weighted characters of the reactants and products. It is the 'egg' that contains all the information necessary to become \mathbf{r} or \mathbf{p} .

The diagram on the right hand (b) in Fig. 5 shows the origins of reaction intermediates and stepwise mechanisms, due to the involvement of a third VB-state in the avoided crossing. This intermediate state, Φ_i , involves electronic reorganization which is part-way between the reactant and product states. When Φ_i gets low enough, it crosses below the intersection



point of the two curves and mediates the transformation from \mathbf{r} to \mathbf{p} . In fact, the involvement of Φ_i offers a lower

Fig. 5: VB diagrams for an elementary step (a) and a stepwise mechanism (b).

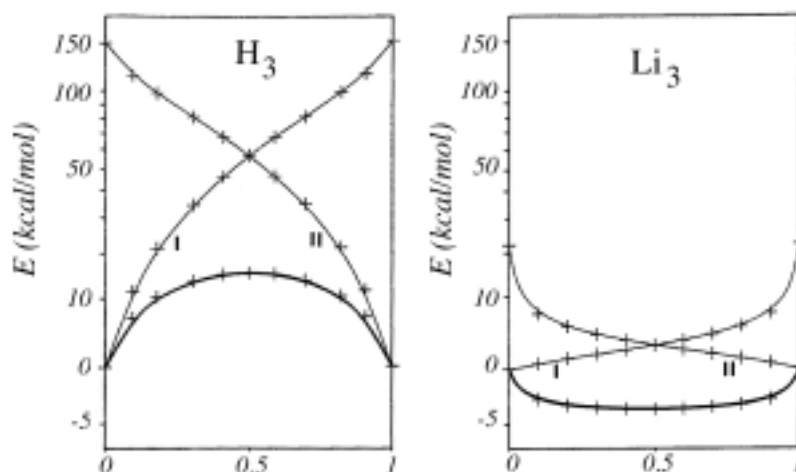
energy route for the $\mathbf{r} \rightarrow \mathbf{p}$ transformation and catalyzes it. For example, in C-H bond activation catalyzed by transition metal oxo cations (e.g., FeO^+) in the gas phase, the direct transformation $\mathbf{r} \rightarrow \mathbf{p}$ involves a high barrier and the reaction would have infinitely slow rate had this been the entire story. Fortunately however, an excited state of the catalyst, FeO^+ , is stabilized along the reaction coordinate and creates a low energy pathway for the transformation. This is one example of many mechanisms which have been discussed in a recent review.^[6] Even the most celebrated concerted reaction, called the Diels-Alder reaction, can be made stepwise by appropriate substitution (see, Sustmann et al in ref. 6). The proteolysis of the peptide and ester bonds follow *the same internal catalytic effect* via an intermediate state (here Φ_i is a π -charge transfer state. See ref. 6). As a matter of fact, *most transformations in Nature are stepwise, and molecules always find intermediate excited states which are low enough to mediate and catalyze the transformation.*

Let me turn back to the elementary processes described by Fig. 5(a). The barrier is expressed as a fraction (f) of the promotion energy (G) less the resonance energy gained in the **TS** by bond delocalization. The promotion energy gap, G , is the primary reactivity factor and its knowledge enables to make many predictions without the need to bother with

the other factors. Consider for example, the identity atom transfer reaction, $\text{X}\bullet + \text{X-X}' \rightarrow \text{X-X} + \text{X}'\bullet$ ($\text{X} = \text{X}'$). The promotion energy for this reaction is the singlet \rightarrow triplet unpairing ($\Delta E_{\text{ST}}(\text{X-X})$) of the electrons in the X-X bond which is broken during the process. When $\text{X} = \text{H}$ the $\Delta E_{\text{ST}}(\text{X-X})$ is huge, ca 250 kcal/mol, while when $\text{X} = \text{Li}$ or other metallic atoms $\Delta E_{\text{ST}}(\text{X-X})$ is very small, ca 30 kcal/mol. When the promotion gap varies in this manner, the outcome of the avoided crossing changes from a profile with a **TS** occupying the top of a barrier (in $\text{X} = \text{H}$) to one in which the bond-delocalized $\text{X}_3\bullet$ species is a stable cluster (in $\text{X} = \text{Li}$), as shown in the VB diagrams in Fig. 6 (from *JPC* 1990, 94, 4089). In fact, there are species of the two kinds for different X group, and there are even cases like $\text{X} = \text{I}$ where the profile is very flat. Based on this general trend, one could consider the $\Delta E_{\text{ST}}(\pi\pi^*)$ for a suspended π -bond which is 100 kcal/mol or more, and predict that the delocalized π -electrons of benzene and other bond-delocalized species are distortive **TS**-like species which are kept delocalized due to the constraints of the σ -frame that prefers a symmetric structure.^[7] There is a consensus now that the prediction is correct and would lead eventually to a paradigm change in the area.

This qualitative change in the nature of the bond-delocalized species, as in Fig. 6, is in fact the story of the division of the Periodic Table to nonmetals and metals. In nonmetallic elements, the excitation

Fig. 6: Quantitative VB diagrams showing the ground states for the atom transfer reactions $\text{X} + \text{XX}' \rightarrow \text{XX} + \text{X}'$ ($\text{X} = \text{X}' = \text{H}, \text{Li}$). Reproduced with permission of the ACS.



energies (which determined the value of G) are large. Therefore, these elements form discrete molecules which are stable, while the bond-delocalized clusters are transition states for transformations of the discrete molecules. On the other hand, in metallic atoms the excitation energies are small. Therefore these elements form bond-delocalized clusters and lattices which are more stable than the discrete molecules. Many more predictions and generalizations (e.g., How is it possible to reduce the barriers of forbidden reactions to almost zero? When do Zipper reactions become possible? Why do lanthanide positive ions activate the strongest bond (C-F) in an organic molecule? What are the reasons that the DNA repair mechanism requires an initial electron transfer step?, etc) can be made by considering only the promotion energy of the reaction.^[6] It is an awesome organizing quantity of reactivity.

The other two factors, B and f , are less obvious and need to be articulated for different reactions. In the case of S_N2 reactions, $X: + CH_3-X' \rightarrow X-CH_3 + X':$, a full articulation was achieved and the two factors are known quantitatively for these reactions.^[6] For example in the halide exchange reaction, f shows a small variation and is ca 0.25, while B is given as one quarter of the C-X bond energy. In cases where $X \neq X'$, the f factor is affected also by the reaction thermodynamics, and is reduced as the reaction becomes more exothermic.^[6] While much quantitative work still lies ahead to quantify B and f in a general case, the qualitative understanding of how these factors vary in a given chemical reaction exists. What is already apparent is that the three factors hold all the necessary information to account for other reactivity principles, to bridge between the disciplines of classical physical organic chemistry and quantum chemistry (see Fig. 2 above), and to suggest novel predictions. *In a nut shell, G gauges the size of the barrier for a given transformation, f scales the barrier for a given promotion energy, and B contains the stereochemical information of the reaction path.*

To appreciate the role of the resonance energy

of the **TS**, we can consider for example the S_N2 reaction, in which the **TS** has a collinear X-C-X arrangement. In this arrangement B is large, while in contrast, if the X-C-X arrangement is triangular B is close to zero. This is the reason why S_N2 reactions proceed with inversion of the chirality around the carbon atom (can be detected e.g., by using $CHH'H''X$, where $H' = D$, $H'' = T$). One can use B to derive orbital selection rules for a variety of reactions. This was achieved for radical processes, for nucleophilic cleavages of cation radicals, and for the competition of electron transfer and bond making reactions of ion radicals with nucleophiles and electrophiles.^[6] The selection rules have led to the concept of entangled mechanisms in which single **TS** serves two different mechanisms. In a recent publication (*JACS*, **2001**, 123, 130) classical trajectory calculations demonstrate that in the reactions of ketyl anion radicals $RR'CO(-^*)$ with alkyl halides CH_3X , a single **TS** with the C-C-X atom arrangement leads to both electron transfer and C-C bond-coupling reactions. This case of breakdown in microscopic reversibility may turn out to be more ubiquitous than we originally thought. If indeed so, a basic tenet of physical organic chemistry would have to change.

Another interesting concept that emerges from the VB model naturally is of the twin-states (*J. Chem. Soc. Faraday Trans.* **1994**, 90, 1631). As seen in Fig. 5(a) the avoided crossing generates two states; one is the **TS** and the other is the twin excited states, ψ^* . The twin state is a stable minimum on the excited state surface and can therefore be used in many different ways to communicate with the ground state.^[6] There are various mechanisms of communication and they can teach much about the nature of the **TS** (e.g., *Angew. Chem. Int. Edit. Engl.*, **1998**, 37, 1394). The VB model shows that the twin relationship is ubiquitous and every **TS** on the ground state has generally a twin minimum on the excited state. Moreover, in a stepwise mechanism as in Fig. 5(b) there are two **TS**'s and hence two twins, and the options for communication are therefore doubled. As the means of probing this

communication improve (e.g., the novel approach of coherent controlled excitation discussed by M. Shapiro in his ICS-Prize Lecture) so will chemical reactivity be enriched by more options and very importantly by more insight into the nature of the chemical change.

To conclude: The VB diagram approach is an art of piecing together reaction profiles from their building blocks. It creates order and unity, and makes new predictions in chemical reactivity and structure.

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